[Ru-POM] PHOTO-ELECTROCATALYSIS

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School of Chemical Science Dublin City University June 2011 I hereby certify that this material, which I now submit for assessment on the program of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to extent that such work has been cited and acknowledged within the text of my work.

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This thesis is dedicated to my beloved grandmother, FengMei Yang, who sadly left us on 2nd of Jan, 2011.

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-Tony Blair

Abbreviation

- [Ru-POW]: ruthenium polypyridyl:polyoxotunsten adduct
- [Ru-POM]: ruthenium metallopolymer:polyoxomolydate adduct
- [Ru-PVP:POM]: ruthenium polyvinylpyridyl:polyoxomolydate adduct

[Ru-Co-P:POM]: ruthenium co-polymer:polyoxomolydate adduct

[Ru-PVP-AuNP:POM] ruthenium polyvinylpyridyl-gold nanoparticle:polyoxomolydate adduct

TBABF₄: tetrabutylammonium tetrafluoroborate

Abstract

In the past years, photo-sensitation of polyoxometalate anions with Ruthenium polypyridyl cations has received intensive investigation as the excellent photoluminescence properties and stability of Ruthenium polypyridyl complexes in multiple redox states can be coupled to the POM in order to extend the absorbance crosssection of the resulting complex into the visible region. In this thesis, remediation of organic solvent, such as benzyl alcohol and toluene, and a number of key processes that influence the overall output from photocatalytic thin films were optimized. These steps included; (1) the extent to which the catalyst and sensitizer interact electronically, (2) the film structure since this can influence the substrate access to the catalytic centres and (3) their rate of regeneration.

Thin an electrostatically associated adduct formed between the layers of polyoxomolybdate, and the ruthenium polypyridyl complex or metallopolymers have been deposited onto electrodes using alternate immersion layer-by-layer assembly. Photocatalytic properties of the ruthenium polypyridyl:polyoxometalate adduct (Ru:POM) in electrolyte-free media was firstly studied. Although slow electron transfer process occurs for Ru:POM in electrolyte-free acetonitrile, the overall photocurrent was optimized at 59±0.02 µA through a number of key steps, i.e., electrolyte, potential, etc. This photocurrent is substantially lower than those found for ruthenium dye sensitized TiO₂. However, it is important to note that Gr□tzel type cells use iodine as the sacrificial donor and are not usually capable of photocurrent generation with donors such as benzyl alcohol or toluene that are challenging to oxidize. In common with Ru:POM films, Raman spectroscopy reveals that the Ru-PVP:POM films exhibit an additional vibrational mode at 900 cm⁻¹ that is not present in either of the components suggesting significant electronic communication between the ruthenium centres and the polyoxomolybdate. Despite the similarity of their redox and photonic properties, this optical transition is

absent in the Ru-Co-P:POM layers. Significantly, the Ru-PVP:POM films generate a higher photocurrent $(38\pm1 \text{ nA cm}^{-2})$ than the Ru-Co-P:POM films $(8.9\pm0.8 \text{ nA cm}^{-2})$ or $[S_2Mo_{18}O_{62}]^{4-}$ films $(9.7\pm1.1 \text{ nA cm}^{-2})$. These results suggest that the catalytic efficiency is strongly influenced by subtle differences in the physical structure of the metallopolymer, e.g., bulkiness of peripheral ligands, even when their redox and photophysical properties are indistinguishable.

The overall photocurrent for Ru-PVP:POM was optimized further. For example, increasing the thickness of the film yielded average photocurrents for the [Ru-PVP:POM] films following two, three, five and seven layers of 46 ± 0.8 , 70 ± 0.3 , 60 ± 1.1 and 48 ± 1.7 nA, respectively. Combining these optimization steps the experiment involved three dip coating cycles to create the Ru-PVP:POM film in the presence of benzyl alcohol (100% V/V) in 0.1 M TBATBF₄ held at a potential of +0.8 V. The optimized system produced more photocurrent (183.6±17.6 nA) than those found in the previous Ru-PVP:POM study.

Finally, photo-electrocatalysis using thin films of polyoxomolybdates sensitised with ruthenium metallopolymers/gold nanoparticles using visible irradiation was described. Significantly, the efficiency of the photocatalysis depends markedly on the structure of the [RuPVP-AuNP:POM] even when photonic properties are very similar. Specifically, electrostatic thin films of [RuPVP-AuNP:POM] prepared by drop cast and dip coated methods have been achieved. Strikingly, despite their similar photonic properties, an additional optical transition at approximately 927 cm⁻¹ is observed in the Raman spectra of pre-assembled drop cast [RuPVP-AuNP:POM] films, which was not seen in dip coated [RuPVP-AuNP:POM] films. Importantly, this electronic communication enhances the photocatalytic oxidation of benzyl alcohol by a factor of more than four. While there is clear evidence for photosensitisation in the drop cast not present for the dip coated systems, the magnitude of the photocurrent, i.e., 82.2±6.6 nAcm⁻² for pre-assembled drop cast [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1, is twice as large as those found in [Ru-PVP:POM] films with corresponding conditions.

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CHAPTER ONE

LITERATURE REVIEW

1 Introduction

A major driving force in solar cell research is the development of dye sensitized solar cell (DSSC) due to their relatively inexpensive building blocks compared to single crystal silicon-based solar cells.[1] The recent development using polyoxometalates (POMs) in DSSCs has been drawn significant attention thanks to polyoxometalate's photocatalytic ability and low cost. Ruthenium polypyridyl complexes have been studied and recognized for their applications in solar energy conversion due to their strong absorption in the visible and emission region around 450 nm. In dye sensitized solar cells, TiO₂ is commonly used to accept an electron from the photoexcited ruthenium complex. However, other classes of materials, e.g., polyoxometalates, offer the possibility of fine tuning the energy of the acceptor states, more efficient electron transfer and easier fabrication. Much of the work in this thesis focuses on finding ways to identify and improve photo-sensitization between the components, i.e., ruthenium polypyridyl complexes and polyoxometalates. Resonance Raman spectroscopy has been employed to probe electronic communication between the ruthenium and the polyoxometalate. A steady state quenching study of ruthenium polypyridyl on addition of POM has shown that the [POM-Ru] ion cluster is bound by purely electrostatic forces and adding electrolyte can disrupt the ion-pairing. Therefore, platinum micro-electrode was used to avoid the use of electrolyte.

1.1 Brief History of Dye-Sensitised Solar Cell

A solar cell is defined as a device that converts sunlight into electricity by photovoltaic and photocatalytic means.[1] There are many types of solar cells but the dye-sensitized solar cell (DSSC), first developed in 1991 by Grätzel and co-workers and shown in Figure 1.1, is an important example.[1] In this section, the structural properties of the dye sensitized solar cell as well as its recent developments to achieve high conversion efficiency are reviewed. With good understanding of how a DSSC works and how to achieve high conversion efficiency, we can then develop a suitable, efficient dyesensitized solar cell based on those previous studies.

Structural properties:

The structure of a dye sensitized solar cell is composed of three essential elements. Firstly, the transparent anode coated with fluorine-doped tin oxide or indium-doped tin oxide. Secondly, a thin porous layer of nanocrystalline titanium dioxide, TiO_2 , is deposited on the conductive surface. The porous TiO_2 is immersed in a solution of a photosensitising dye and the dye binds covalently to the metal oxide. The back part of the assembly consists of a conductive sheet, usually platinum and has a solution of iodide/tri-iodide on the top in which an electron is transferred to triiodide to yield iodide.

Figure 1.2 shows how the dye-sensitised solar cell converts sunlight into electricity by photovoltaic means. When the sunlight strikes the dye, enough energy is provided to create the excited state of the dye and electrons from this state are then pumped into conduction band of TiO_2 . From there, the electrons move by diffusion to the anode. The counter electrode, usually a platinum metal plate and electrolyte, i.e., a solution of iodide/tri-iodide, is used to recycle electrons in the solar cell and the first reduction replenishes the oxidised dye molecules.



Figure 1.1 Schematic construction diagram of dye-sensitised solar cell (DSSC). Reproduced from Solaronix, Retrieved 2007-05-22.[2]



Figure 1.2 A schematic diagram of how a DSSC works. Reproduced from Solaronix, Retrieved 2007-05-22.[2]

Recent developments:

General approaches to achieve high conversion efficiency of the solar cell require three key elements, namely, dye sensitizers, photocatalyst and electrolyte.

Most dyes incorporated into a DSSC are based on ruthenium polypyridyl complexes as they fulfill the key requirements for an efficient sensitizer as outlined by Grätzel et al [1]: (*i*) the excited state should have enough thermodynamic driving force for the injection of electrons into the conduction band of TiO₂ in order to produce a photocurrent. This is achieved when the dye LUMO is both matched in energy and strongly coupled to the semiconductor. (*ii*) The oxidized sensitizer should be stable in order to facilitate replenishment of the dye and (*iii*) the dye MLCT absorption should overlap strongly with the solar emission spectrum in order to achieve maximum power conversion. For example, A. Grabulosa et al. reported that a film (Figure 1.3) was formed on Pt and ITO glass slides by repeated scan oxidation of a Ru complex containing pyrrolostyryl bipyridine ligands.[3] The UV-vis spectrum and voltammogram of the Ru-based polymer film showed blue-shifts of the MLCT absorption bands and increased oxidation potentials indicating conjugation in the π -extended system.[3]

There are two fundamental limitations to be addressed for the ruthenium polypyridyl complex; the first drawback is spectral coverage. A lot of photons are available in the 750-900 nm region of the solar spectrum that are not absorbed by conventional ruthenium polypyridyl complexes.[4-5] Another limitation is their molar absorptivity, they require large geometric area so that a monolayer of the dye can collect 90% of the light at the most strongly absorbed wavelength.[6] In order to extend a dye's absorption into the near infrared, one needs to either lower the energy of the LUMO or raise the energy of the HOMO.[7] Figure 1.4 shows one of the most efficient dyes applied to the DSSC to date, N_3 .[8] The ruthenium polypyridyl, N_3 complex has a wide spectral absorbance and the incident photon to current efficiency is approximately 80% (<650 nm) and tails off at longer wavelengths. [9]

Attempts have been made to increase the spectral coverage and absorptivity by replacing ruthenium dyes with organic dyes.[6] Organic dyes can incorporate both donor and acceptor moieties that can effectively produce photoinduced charge-separated states and have strong and broad light absorbance in the visible and near infared.[6] The best performing organic dye to date is indoline shown in Figure 1.5. It contains an arylamine moiety that acts as an electron donor and a carboxylic moiety that acts as an electron acceptor and an archoring group to attach to the dye to the nanocrystalline TiO₂. The extinction coefficient for indoline is five times higher than that of the ruthenium N₃ complex. In addition, it shows an incident photon to current efficiency, IPCE value exceeding 80% throughout the range of 400 and 670 nm.[10] However, many organic dyes are problematic due to aggregation and poor energy matching of the LUMO level when paired with tri-iodide electrolyte.[11-12]



Figure 1.3 The structure of the ruthenium complex containing pyrrolostyryl bipyridine ligand. Reproduced from A. Grabulosa, M. Beley, P. C. Gros, Inorg. Chi. Acta., 363 (2010) 1404.[3]



Figure 1.4 The structure of the ruthenium polypyridyl complex, N₃. Reproduced from M.K. Nazeeruddin, P. Pechy, T. Renouard, S.M. Zakeeruddin, R. Humphry Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 123 (2001) 1613.[9]



Figure 1.5 Molecular structure of Indoline. Reproduced from T. Horiuchi, H. Miura, S. Uchida, Chem. Commun., 26 (2003) 3036.[10]

Recent developments to address the spectral coverage and absorptivity issues have included quantum dots. In 1998, Nozik et al. found that quantum dots (QDs) of InP adsorb strongly onto transparent, porous, nanocrystalline TiO₂ electrodes prepared by sintering 200-250 Å diameter TiO₂ colloidal particles. The key feature of this system is the use of nanocrystalline TiO₂ films that have an extremely large surface-to-volume ratio. This allows for greatly increased dye coverage in the TiO₂ film and produces very high quantum yields for photon-to-electron conversion.[13]

A second approach to optimizing the conversion efficiency is to replace the liquid electrolyte with an inorganic p-type conductor.[14] The liquid electrolyte in the solar cell leads to several problems such as seal imperfection, degradation, and most importantly dye desorption.[15] One type of electrolyte system that could resolve these problems is copper iodide bound to 1-ethyl-3-methylimidazolium thiocyanate (EMISCN). CuI alone acts as p-type conductor and is not stable in acetonitrile solution. EMISCN helps fill the TiO₂ pores and greatly improves the performance of the cell and acts as a CuI crystal growth inhibitor. Figure 1.6 shows that the particle size of CuI is reduced dramatically with larger amount of EMISCN present. Other electrolytes that have been employed in optimising the system are copper thiocyanate (CuSCN)[9] and an n-butyl complex of copper bromide (CuBr).[16-17]

Other approaches to optimizing the power conversion efficiency in DSSC are (1) to dope metal into the TiO₂, this is mainly to overcome the large band gap of titanium dioxide which makes it sensitive only to the UV light. Choi et al. reported that doping Fe, Mo, Ru, Os, Re, V, Rh into TiO₂ can enhance the power production,[18] (2) to combine titania nanoparticles as cations and sodium sulfonated polystyrene (PSS) as polyanions.[19] This combination blocks the physical contact between ITO or FTO and electrolyte and in turn enhances performance. (3) To combine titanium dioxide with polyoxometallate.[20] The powerful oxdizing properties of these polyoxometalates, mainly of molybdenum and tungsten, are capable of excitating near visible and UV light. The properties of polyoxometalates will be discussed in Section 1.2



(a)

(b)

Figure 1.6 SEM image of CuI film with (a) 1.98 mol% and (b) 4.44 mol% of EMISCN deposited onto nanoporous TiO_2 electrode. Reproduced from A. Konno, T. Kitagawa, K. Tennakone., Current Applied Physics 15 (2005) 149.[16]

Finally, in this thesis an approach to optimize the power conversion efficiency by exciting the polyoxometalate with a ruthenium sensitizer is reported. Previous evidence suggests that ruthenium polypyridyl complexes can photosensitize the powerful photocatalyst polyoxometalates and it was hoped that this approach would prove useful.

1.2 Polyoxomatallate : Photocatalytic properties

A polyoxometallate is an anionic cluster that is composed of three or more transition metal oxyanions connected by shared oxygen atoms. The metal atoms that are commonly seen in polyoxometallate structures are vanadium (V), niobium (V), tantalum (V), molybdenum (VI), and tungsten (VI). Their electronic configuration therefore is either d^0 or d^1 . Since the discovery of the first example made in 1826, two classes have been distinguished; namely, the Keggin and Dawson structures.[21] Most recent POMs have been used in the area of photocatalysis, where their excellent catalytic properties have been found to be further enhanced by photo-excitation, which makes electron transfer to and from the POM species more facile. In this section, the structural and photocatalytic properties of POMs relative to this project are reviewed.

The Keggin ion has the general molecular formula of $XM_{12}O_{40}^{n-}$, where X is the heteroatom and M is the metal which commonly is molybdenum or tungsten. The Keggin ion usually consists of a tetrahedral central ions, XO₄ⁿ⁻⁸, surrounded by twelve MO₆ octahedral units. Figure 1.7 shows the structure of classical Keggin ion structure and a recently developed Keggin structure with vanadium substituted Keggin-type polyoxomolybdophosphates and Cd/Zn complex fragments.[22] The general formula for the Dawson polyoxometallate is $[M_{18}O_{54}(XO_4)_2]^{m}$, where M is the addenda-atom and X is the heteroatom, this structural type was first synthesised in 1953 [23]. Like the Keggin ion, the heteroatom in the conventional Dawson type is 4-coordinated but the central tetrahedra are limited to only main group elements, mainly sulfur, phosphorus and arsenic as shown in Figure 1.8. Significantly, the creation of such complex molecules in only one synthetic step has made a wide variety of these compounds possible. This is mainly possible because the POM structure that self-assemble depend on solution pH. Another characteristic is that the negatively charged oxygen atoms are polarized towards the positive transition metal, such as tungsten, on the interior of the structure. Therefore, the oxygen atoms are relatively inert, making them resistant to acidic or basic decomposition. In recent years, Baffert et al. synthesized several compounds including several unconventional Dawson structure types such as $[Mo_{18}O_{54}(SO_3)_2]^{4-}$, $[W_{18}O_{54}(SO_3)_2]^{4-}$ as shown in Figure 1.9 [24] where in this structure the heteroatoms are no longer 4-coordinated.





Figure 1.7 The images of (a) a classical structure of Keggin ion and (b) 2D Crystal data structure of newly developed Keggin structure with vanadium substituted Keggin-type polyoxomolybdophosphates and Cd/Zn complex fragments. Adapted from R. Murugesan, P. Sami, T. Jeyabalan, A. Shunmugasundaram, Transition Met. Chem. 23 (1998) 583.[22]

The countercations of a POM can be exchanged by a metathesis reaction, a molecular process involving the exchange of the bonds between the two reacting chemical species. This salt metathesis allows for the preparation of both inorganic and organic salts and makes POMs attractive target for homo- and heterogeneous catalysis. The selection of the countercation can make the POM soluble in either aqueous or organic phases.[25] Typically, tetrabutylammonium (TBA) is chosen as the countercation for organic phase reactions, and Na⁺ or K⁺ is chosen for the aqueous phase reactions. The ability to create anions is also useful because the POM can then be attached to positively charged material, thus changing a homogeneous catalyst to a heterogeneous catalyst.[26] For example, [MnMo₆-O₁₈{(OCH₂)₃CNHCO(4-C₅H₄N)}₂](NBu₄)₃ (Figure 1.10) is a sandwich POM covalently bound to organic ligands which then acts as a photocatalyst to reduce AgSO₄ under visible irradiation in air in the presence of propanol at the interface between water and the copolymeric film (Figure 1.10). [27].

$$[S_{2}M_{18}O_{62}]^{4-} \xleftarrow{e^{-}} [S_{2}M_{18}O_{62}]^{5-} \xleftarrow{e^{-}} [S_{2}M_{18}O_{62}]^{6-}$$

$$1.3$$

$$[S_{2}M_{18}O_{62}]^{6-} \xleftarrow{e^{-}} [S_{2}M_{18}O_{62}]^{7-} \xleftarrow{e^{-}} [S_{2}M_{18}O_{62}]^{8-}$$

Where M=W or Mo

In addition to their structural robustness, POMs possess important electronic characteristics. The incorporation of transition metals provides a source of weakly attached electrons which can be transferred to other compounds (reduction), making polyoxometallates (POMs) powerful electron acceptors and also active electrocatalysts for hydrogen and oxygen evolution due to their rich redox properties. Equation 1.3 demonstrates the extent of POM redox process and these redox properties can lead to interesting and potentially useful catalysis and photochemistry.[29-31] For example hydrocracking is possible, which is the process to break down complex organic molecules into simpler molecules. Razo et al reported one vanadium-substituted Dawson

type phosphotungstates, $K_2P_2W_{18}O_{62}$ can be employed to hydrocrack alkylaromatics, such as tetralin, which has a formula of $C_{10}H_{12}$, to aliphatic hydrocarbon.[31]

POMs have also found applications in analytical chemistry due to the blue reduction products of many POMs, these blue reduced POMs can be monitored using visible spectroscopy. POMs also have been long used in medicinal application, such as anti-HIV and anti-tumoral drugs etc.[32] However, it is beyond the scope of this literature review to discuss them.



Figure 1.8 A representation of the structures of the sulfite-based Dawson clusters: (a) α - $[Mo_{16}O_{54}(SO_3)_2]^{6-}$, (b) β - $[Mo_{18}O_{54}(SO_3)_2]^{4-}$, and (c) a comparison with the conventional a-type sulfate-based Dawson anion $[Mo_{18}O_{54}(SO_4)_2]^{4-}$. Adapted from C. Baffert, A. M. Bond, D. L. Long and L. Cronin., Chem.- Euro. J, 33 (2006) 8472.[24]



Figure 1.9 A representation of (a) 3-D and (b) ORTEP structure of $[Mo_{18}O_{54}(VO_4)_2]^{6-}$. Reproduced from C. Baffert, A. M. Bond, D. L. Long and L. Cronin., Chem.- Euro. J, 33 (2006) 8472.[24]



Figure 1.10 Representations of (a) $[MnMo_6-O_{18}{(OCH_2)_3CNHCO(4-C_5H_4N)}_2](NBu_4)_3$ and (b) copolymer obtained with zinc-dipyridinium-octaethylporphyrin Hexafluorophosphate (ZnOEP) in the presence of $[MnMo_6-O_{18}{(OCH_2)_3CNHCO(4-C_5H_4N)}_2](NBu_4)_3$. This new coordination polymer used as a photocatalyst to reduce AgSO₄ under visible irradiation in air in the presence of propanol at the interface between water and the copolymeric film. Reproduced from D. Schaming, C. Allain, B. Hasenknof an L. Ruhlmann. Languire. 26 (2010) 5101.[27]

The photooxidative behaviour of POM has received less attention than semiconductor photocatalysis.[33] In fact, many POMs share very similar photochemical characteristics to semiconductor photocatalysts, and most importantly neither POMs nor those semiconductor photocatalysts normally absorb visible light (λ >330 nm). Most studies on the photooxidative behaviours of POMs have been on homogeneous systems. For example, Rüther *et al.* demonstrated voltammetrically that benzyl alcohol in CH₃CN is photo-oxidized to benzaldehyde. [34]

$$C_{6}H_{5}CH_{2}OH + [S_{2}W_{18}O_{62}]^{4-} \xrightarrow{hv((\pi 330nm))} C_{6}H_{5}CHO + [S_{2}W_{18}O_{60}(OH)_{2}]^{4-} 1.4$$

Equation 1.4 describes the two-electron oxidation of benzyl alcohol to benzaldehyde.

$$\left[S_2 W_{18} O_{60} (OH)_2\right]^{4-} \rightarrow \left[S_2 W_{18} O_{62}\right]^{4-} + H_2$$
 1.5

Equation 1.5 shows that the POM can be regenerated to produce hydrogen and $[S_2M_{18}O_{62}]^{4-}$ and is multiply reduced when triphenylphosphine or many other organic compounds are present and the POM is irradiated. As mentioned earlier, the polyoxometallates do not absorb visible light (λ > 330 nm). Therefore, the requirement for UV irradiation restricts their application in solar conversion and increases the cost if they are to be used for industrial photocatalytic applications.[35-36]

1.3 Ruthenium Polypyridyl Complexes and Metallopolymers

Ruthenium polypyridyl complexes have played a key role in the study of photoactivated electron-transfer reactions since they were discovered in 1959 [37]. These complexes have been studied widely because of their potential applications such as in solar energy conversion [38], luminescent and electroluminescent sensors [39] which is mainly owe to their strong absorption in the visible and emission region around 450 and 610 nm, respectively [40]. In this section, the photophysical properties of the ruthenium polypyridyl complex relevant to this project are reviewed.

 $[Ru(bpy)_3]^{2^+}$ is a coordination complex as shown in Figure 1.11. The complex has an octahedral D₃ symmetry. It has been resolved into its enantiomers, which are kinetically stable. When $[Ru(bpy)_3]^{2^+}$ is excited under visible irradition, an electron is promoted from the metal based ground state to a π^* orbital of the 2,2-bipyriyl ligand. In solution, fast and efficient intersystem crossing occurs from the singlet-excited state to the triplet MLCT state as shown in Figure 1.12. The tripet excited state is both a better oxidant and a reductant than the associated ground state of the complex. This situation arises because the excited state can be described as a Ru³⁺ complex containing a bpy⁻ ligand. Several deactivation processes can occur from the triplet state, i,e. either radiative decay the excess energy is dissipated by the interaction with solvent or via electron or by energy transfer to another molecule as shown in Equation 1.6.

Oxidative electron transfer
$$Ru^{2+*} + Q \rightarrow Ru^{3+} + Q^{-}$$
1.6Reductive electron transfer $Ru^{2+*} + Q \rightarrow Ru^{+} + Q^{+}$ Energy transfer $Ru^{2+*} + Q \rightarrow Ru^{2+} + Q^{*}$



Figure 1.11 Structure of [Ru(bpy)₃]²⁺. Reproduced from V. Balzani, A. Juris., Coord. Chem. Rev. 211 (2001) 97-115.[37]



Figure 1.12 Diagram of relative energy levels following photo-excitation of $[Ru(bpy)_3]^{2+}$.

 $[Ru(bpy)_3]^{2+}$ derivatives have been recognized and examined as possible photosensitisers for both the oxidation and reduction of water.[41] Visible-light absorption by $[Ru(bpy)_3]^{2+}$ produces a metal-to ligand charge transfer (MLCT). The $[Ru(bpy)_3]^{2+*}$ species acts as a potent reductant which is capable of transferring an electron, located on one of the bpy ligands, to a sacrificial oxidant such as persulfate $(S_2O_8^{2-})$. The resulting $[Ru(bpy)_3]^{3+}$ is a powerful oxidant and can oxidize water into O₂ and protons at a metal oxide catalyst.[42] Alternatively, the reducing power of $[Ru(bpy)_3]^{2+*}$ can harnessed to reduce methyl viologen, a recyclable carrier of electrons, which in turn reduces protons at a platinum catalyst. For this process to be catalytic, a sacrificial reductant, such as EDTA⁴⁻ or triethanolamine is provided to return the Ru(III) back to Ru(II). The excited state of the $[Ru(bpy)_3]^{2+}$ complexes can be altered by using different ligands which can be substituted in order to achieve varying excited energy level.[43]

As mentioned previously, ruthenium bipyridyl complexes are of interest due to their use in areas such as solar energy conversion, photosynthesis, the development of high speed display devices and DNA sensors.[44] Recently, ruthenium containing metallopolymers such as $[Ru(bpy)_2(PVP)_{10}]^{2+}$, where PVP is poly-4-vinyl pyridine, has been shown to exhibit electrochemiluminescence from the reaction of $[Ru(bpy)_2(PVP)_{10}]^{2+}$ with the DNA base guanine.[45]

1.4 Photophysical, Electrochemical and Photoelectrochemical properties of [Ru-POM] Ion Cluster

As mentioned in Section 1.2, polyoxometallate anions alone do not absorb visible light. One way in which this limitation can be overcome is to couple the POM to $[Ru(bpy)_3]^{2+}$, as a molecular sensitizer to extend the absorbance into the visible spectral region. Thereby, photoexcited states created by $[Ru(bpy)_3]^{2+}$ provide enough driving force to trigger photocatalysis without the need for UV excitation. For example, McCormac *et al* synthsised the ionic complex, $[Ru(bpy)_3]_3[P_2W_{18}O_{62}]$, which was formed by addition of $[Ru(bpy)_3][Cl_2]$ to $K_6P_2W_{18}O_{62}.15H_2O$ in aqueous solution.[46] Figure 1.13 shows a cyclic voltammogram for a $[Ru(bpy)_3]_3[P_2W_{18}O_{62}]$ solid deposit immobilized on a carbon electrode. It was found that changing the electrolyte concentration in the aqueous phase influenced the voltammetric response for the $[Ru(bpy)_3]_3[P_2W_{18}O_{62}]$ solid deposit immobilized on the carbon electrode, suggesting there was an ionic interactions within the solid.[46] Furthermore, investigation by Keyes et al. indicate that there is effective electronic communication between the two ions within the clusters which can lead to photosensitization.[36] Therefore, in this section examples of photo-sensitization of POMs and related ruthenium polypyridyl complex as are reviewed.

Figure 1.14 shows a steady state quenching study of $[Ru(bpy)_3]^{2+}$ by addition of $[S_2W_{18}O_{62}]^{4-}$ in dry acetonitrile. Addition of $[S_2W_{18}O_{62}]^{4-}$ resulted in significant quenching of the $[Ru(bpy)_3]^{2+}$ luminescence intensity. To ensure the $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ ion cluster is formed by purely electrostatic means, the impact of adding LiClO₄ to a solution of this ion cluster was probed. Figure 1.15 shows that with increasing concentrations of LiClO₄, the luminescence intensity increased until the luminescence intensity became identical to that of free $[Ru(bpy)_3]^{2+}$. These experiments suggest that the perchlorate ion paired with the $[Ru(bpy)_3]^{2+}$ dissociating Ru-POM association and suggests that the binding was electrostatic.[20]



Figure 1.13 Repetitive cyclic voltammograms for a $[Ru(bpy)_3]_3[P_2W_{18}O_{62}]$ solid deposit immobilized on a carbon electrode (A = 0.0707 cm²) in 1.0 M HCLO₄. Scan rate = 100 mV s⁻¹. Reproduced from N. Fay, E. Dempsey, A. Kennedy, T. McCormac, J. Electroanal. Chem., 556 (2003) 63.[46]



Figure 1.14 Luminescence spectrum (uncorrected) of $[Ru(bpy)_3]^{2+}$ (5 × 10⁻⁶ M) on addition of $[S_2W_{18}O_{62}]^{4-}$; excitation wavelength 450 nm. The solvent is dry acetonitrile. Reproduced from N. Fay, V. M. Hultgren, A. G. Wedd, T. E. Keyes, D. Leane, A. M. Bond, Dalton Trans, (2006) 4218.[20]

Electronic spectroscopy was employed to probe for new optical transitions between the Ru moiety and the POM that would indicate significant orbital mixing or electronic communication.[37] Two key features observed were that cluster formation made the Ru complex photostable and secondly that the cluster itself seemed to be weakly luminescent with a λ_{max} which was shifted compared with $[Ru(bpy)_3]^{2+}$ alone. Figure 1.16 shows the presence of a new charge-transfer transition centered at 474 nm which indicates strong electronic communication between the $[Ru(bpy)_3]^{2+}$ and $[S_2W_{18}O_{62}]^{4-}$. This new absorption band is not observed in either $[Ru(bpy)_3]^{2+}$ or $[S_2W_{18}O_{62}]^{4-}$.

This strong communication between the $[Ru(bpy)_3]^{2+}$ and $[S_2W_{18}O_{62}]^{4-}$ was further confirmed using the Resonance Raman Spectroscopy. Figure 1.17 shows the solid state Raman Spectra of $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$, $[Ru(bpy)_3]Cl_2$ and $[Hex_4N]_4[S_2W_{18}O_{62}]$. The $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ salt exhibited modes at 1460, 1570 and 1590 cm⁻¹ which were assigned to the bipyridyl modes, and in addition it also possesses a broad feature at 1093 cm⁻¹. The broadness of the band at 1093 cm⁻¹ is attributed to hydrogen bond between Mo-O and hydrogen of pyridyl complex of $[Ru(bpy)_3]^{2+}$. In addition, this new resonantly enhanced feature is not seen in either $[Ru(bpy)_3]Cl_2$ or $[Hex_4N]_4[S_2W_{18}O_{62}]$ suggesting that the new optical transition found in $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ salt is resonant with 458 irradiation indicating that strong chemical communication between $[Ru(bpy)_3]Cl_2$ and $[Hex_4N]_4[S_2W_{18}O_{62}]$.



Figure 1.15 Influence of increasing solution ionic strength on quenching of $[Ru(bpy)_3]^{2+}$ by $[S_2W_{18}O_{62}]^{4-}$ in acetonitrile. Adapted from M. Seery, N. Fay, T. McCormac, E Dempsey, R. Forster and T. Keyes, Phys. Chem. Chem. Phys., 7 (2005) 3426.[36]



Figure 1.16 Difference electronic spectra for titration of $[S_2W_{18}O_{62}]^{4-}$ into $[Ru(bpy)_3]^{2+}$ in acetonitrile. The spectra were generated by subtracting the spectra of the separate solutions from the experimental spectrum of the mixture. The process was carried out as a function of increasing concentration of $[S_2W_{18}O_{62}]^{4-}$. Reproduced from M. Seery, N. Fay, T. McCormac, E Dempsey, R. Forster and T. Keyes, Phys. Chem. Chem. Phys., 7 (2005) 3426.[36]



Figure 1.17 Resonance Raman spectroscopy of $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$, 5% dispersed in KBr, excited at 457.9 nm. (a) $[Ru(bpy)_3](PF_6)_2$; (b) $[Hex_4N]_4[S_2W_{18}O_{62}]$; (c) $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$. Reproduced from M. Seery, N. Fay, T. McCormac, E Dempsey, R. Forster and T. Keyes, Phys. Chem. Chem. Phys., 7 (2005) 3426.[37]



Figure 1.18 Cyclic voltammogram for solid $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ adhered to a glassy carbon electrode immersed in acetonitrile (0.1 M Bu₄NPF₆) (d = 3 mm; m = 100 mV s–1). Adapted from N. Fay, V. M. Hultgren, A. G. Wedd, T. E. Keyes, D. Leane, A. M. Bond, Dalton Trans, (2006) 4218.[21]


Figure 1.19 Photocurrent-time curves at a glassy carbon electrode (d = 3 mm) for (a) $[\text{Hx}_4\text{N}]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ (0.1 mM) alone or (b) with $[\text{Ru}(\text{biq})_2(\text{box})]^+$ (0.4mM) in DMF (0.1M Bu₄NPF₆) irradiated by white light. The potential was held at +0.4 V (*vs.* Fc/Fc⁺). Adapted from N. Fay, V. M. Hultgren, A. G. Wedd, T. E. Keyes, D. Leane, A. M. Bond, Dalton Trans, (2006) 4218.[20]

Bond et al. used cyclic voltammetry to explore the electrochemical properties of the $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ salt. Figure 1.18 and 1.19 show the cyclic voltammogram and photocurrent for [Ru-POM] salt. Well defined redox peaks for $[Ru(bpy)_3]^{2+/3+}$, $[S_2W_{18}O_{62}]^{4-/5-}$ and $[S_2W_{18}O_{62}]^{5-/6-}$ were confirmed and the formal potential for the $[Ru(bpy)_3]^{2+/3+}$ oxidation process obtained from the surface-confined solid is similar to that of the free ion in solution.[20]

A higher quantum yield for sensitization of $[S_2Mo_{18}O_{62}]^{4-}$ by $[Ru(bpy)_3]^{2+}$ was found in the presence of DMF suggesting that photocurrents for DMF oxidation would be enhanced by the presence of ruthenium cations although studies of Ru-POW and POM at electrode interface have not been studied to date. In that work all films were formed by drop casting.

There are many advantages for employing a layer-by-layer assembly technique compared to drop casting such as increased structural and thickness control.[47-52] For example, by using a layer-by-layer assembly method, Wang et al. fabricated an organic and inorganic hybrid thin film based on $[P_2W_{18}O_{62}]^{6-}$ and $[Ru(bpy)_3]^{2+}$ on ITO.[53] The luminescence from this thin film is quenched when a reducing potential is applied in order to investigate the reversibility of the film.[53] Many [POM-Ru] films were formed on FDTO or ITO electrode as these are optically transparent and therefore more useful for spectroscopic study and solar cells due to their transparency.[54-57] For example, Figure 1.20 shows a uniform photoluminescent multilayer film based on the Keggin-type polyoxometalate, $[PMo_{12}O_{40}]^{3-}$ and $[Ru(bpy)_3]^{2+}$ films prepared on an ITO electrode by using a layer-by-layer assembly method.[57]



Figure 1.20 The Schematic illustration of (a) $[Ru(bpy)_3]^{2+}$, (b) PMo_{12} and (c) the {PSS/PEI/PMo_{12}/Ru(bpy)_3} multilayer film. PSS is poly(styrenesulfonate) and PEI is poly(ethylenimine). Reproduced from H. Ma, J. Peng, Y. Chen, Y. Feng, E. Wang, J. Solid State. Chem, 177 (2004) 3333.[57]

1.5 Electrochemical Techniques: Cyclic Voltammetry

A key requirement for successful photocurrent generation from a [Ru-POM] film is to achieve an appropriate thermodynamic driving force based on the redox potential of the compound. Cyclic voltammetry is an electrochemical technique that produces current-voltage curves.[58-61] This highly versatile technique can rapidly provide thermodynamic and kinetic information about redox systems both in solution and on an electrode surface.[59] In this section, the analysis of CVs to yield various information relevant to this project is discussed. If a redox system remains in equilibrium throughout the potential scan, the redox process is said to be reversible. This reversibility requires that the surface concentrations of oxidizing and reducing species are maintained at the values required by the Nernst equation shown in Equation 1.7.

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{C_o}{C_R}$$
 1.7

Solution Phase:

The peak current, i_p , is given by Equation 1.8, which is known as the Randles-Sevcik equation and this equation predicts that for a reversible system in the solution phase the peak current is proportional to the square root of the sweep rate:

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2}$$
 1.8

Where n is the number of electrons, A is the area of the electrode (cm²), D is the diffusion coefficient (cm² s⁻¹) and C is the concentration of the redox species (mol cm⁻³). Another important diagnostic for characterizing the electrode reaction is the value of the peak potential, E_p . When the rate of electron transfer is fast, the E_p value will be independent of the scan rate; indicating a reversible electrode reaction. Then the difference, ΔE_p , between the anodic peak potential, E_{pa} and the cathodic, E_{pc} value, will be equal to 57 mV/n and can be described by Equation 1.9 The thermodynamically reversible potential,

 E° , is the average of two peak potentials. This value should also be independent of the scan rate.

$$\Delta E_p = E_{p,a} - E_{p,c} = \frac{57}{n} mV$$
 at 298K 1.9

Significantly, reversibility depends on the relative values of the standard heterogeneous electron transfer rate constant, k_s , and the scan rate, v. Therefore, varying the scan rate can yield information about kinetics of the electron transfer. For example, increasing the scan rate makes the ratio of k_s/v small so that Nernstian concentrations cannot be maintained. This process is then called quasi-reversible and can be characterized by $\Delta E_p > 57 \text{ mV/n}.$

However, increasing ΔE_p with increasing scan rate can also be due to uncompensated solution resistance (ohmic) between the working and reference electrode. This resistance occurs when the background electrolyte concentration is low or the tip of the reference electrode is far from the surface of the working electrode. In that case, the peak potentials depends on the resistance (R) of the electrochemical cell and the current (i) passing through the cell by Ohm's Law. This results in a potential drop that acts to weaken the applied potential by an amount iR, described by Equation 1.10. Therefore, it is best to minimize the *i*R drop by using a high background electrolyte concentration (ions that carry the current in the solution) and/or by placing the tip of the reference electrode close to (but not touching) the surface of the working electrode.

$$E = E_{applied} - iR$$
 1.10

The current response is defined as a voltammogram, and consists of a plot of current versus potential. Figure 1.21 shows a typical cyclic voltammogram recorded for a reversible single electron transfer reaction involving a solution phase reactant. This figure also shows that the scan begins from the left hand side of the current/voltage plot where a oxidizing species is ready to be reduced. As the voltage is swept further to the right a current reaches a peak where reduction occurs before decreasing. After the sharp response, which is a result of the logarithmic characteristic of the Nernst equation, the current falls as to the depletion layer containing the reduced species grows and the flux of un-reacted species to the electrode surface falls which results in current decreasing. Therefore, from the forward sweep the oxidizing species is consumed at the electrode and a reductive current is observed and from the reverse sweep oxidizing species is regenerated by oxidation of reducing species and an oxidative current is seen.



Figure 1.21 A typical cyclic voltammogram for reversible solution phase electrochemistry. Oxidation and therefore anodic current occur at the reverse half, and reduction and so cathodic current occurs at the forward scan half. Reproduced from A. J. Bard, L. R. Faulkner, Eds., Electrochemical Methods: Fundamentals and Applications, 2^{nd} ed., John Wiley and Sons: New York, 2001.[58]

Surface confined:

Species adsorbed onto an electrode surface exhibit a distinct voltammetric response to those in solution. The peak current varies linearly with scan rate for an adsorbed species, which is characteristic of finite diffusion and the current is described by Equation 1.11.

$$i_p = \frac{n^2 F^2}{4RT} A \Gamma V \tag{1.11}$$

The surface coverage can be determined by measuring the Faradaic charge (coulomb), Q, which is passed at slow scan rates and determined by graphical integration of background corrected cyclic voltammograms, according to Equation 1.12:

$$\Gamma = \frac{Q}{nFA}$$
 1.12

Under Nernstian conditions, Equation 1.13 applies for the cyclic voltammetry of surfaceconfined species, assuming that lateral interactions of the adsorbates are not present, where FWHM is the full width at half maximum of the peak of the cathodic or anodic wave) and $E_{pc}=E_{pa}$.

$$FWHM = 3.53 \frac{RT}{nF} = \frac{90.6}{n} mV$$
 1.13

1.6 Metal Working Electrodes

In general, metal electrodes show fast electron-transfer kinetics for many redox systems and have a relatively wide anodic potential window. The cathodic window for platinum is more limited than that for semi-conductors such as ITO due to hydrogen evolution. [62]

1.6.1 Platinum microelectrodes

The adduct $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ is formed by electrostatic association and an electrolyte such as lithium perchlorate can disrupt this composite film due to strong electrostatic interaction between perchlorate anion and ruthenium cation. Therefore, to maintain Ru and POM association, electrochemical experiments were carried out in the absence of deliberately added electrolyte using a microelectrode so as to minimize ohmic drop.

A microelectrode is an electrode with dimensions on the micrometer scale [63-64]. When faradaic and charging currents flow through a solution, they generate a potential that acts to weaken the applied potential by an amount, iR, which is described in Equation 1.9.[65] The electrolysis current generated by micro-electrode is small, i.e., it produces current that typically lies in the range of pA to nA, virtually eliminating ohmic effects that are observed for macroelectrodes. Equation 1.14 below indicates that the cell resistance increases with decreasing electrode radius. Thus, the ohmic drop is reduced at microelectrode due to the relatively small current generated not due to a lower resistance. This characteristic feature ensures that electrochemical experiment at a microelectrode can be carried in the absence of deliberately added electrolyte [66].

$$R = \frac{i}{4kr_0}$$
 1.14

(where k is constant, *i* is the total current, *R* is the cell resistance and r_0 is the electrode radius.)

The second unique property of microelectrode is that two different diffusion fields can be observed at an experimentally accessible time scale [67-69]. Figure 1.22 shows that at short times, the thickness of the diffusion layer is much smaller than, or similar to the electrode radius, and the diffusion layer becomes planar and response is described by planar diffusion. At relatively long times, the diffusion layer thickness becomes much larger than the electrode radius. The diffusion field becomes hemispherical and mass transport process is dominated by radial diffusion shown in Figure 1.23. Figure 1.24a illustrates an example of radial diffusion control, where the sigmodial-shaped responses corresponding to a steady-state mass transfer in slow scan rate cyclic voltammetry. Figure 1.24b shows the response obtained under linear diffusion conditions, the current response is similar to those observed at conventional macroelectrode.[70]



Figure 1.22 Linear diffusion observed for a microelectrode at fast scan rates.



Figure 1.23 Radical (convergent) diffusion observed for a microelectrode at fast scan rates.



Figure 1.24 Effect of scan rate on the cyclic voltammetry of 1.0 mM ferrocene at 6.5- μ m gold microdisk where the supporting electrolyte is 0.1 M tetrabutylammonium perchlorate in acetonitrile. (a) Scan rate is 0.1 V sec⁻¹; (b) scan rate is 10 V sec⁻¹. Adapted from J. O. Howell and R. M. Wightman. Anal. Chem, 56 (1984) 524.[70]

1.7 Conclusions

It is clear from this literature review that dye sensitized solar cells offer an excellent opportunity for sustainable energy due to their relatively inexpensive building blocks compared to single crystal silicon-based solar cells. However, many drawbacks have been recognized, for example, in the areas of energy conversion efficiency. Polyoxometallate (POM) anions offer a promising opportunity to be used as an additional material for a Grätzel type solar cell. Efficient electronic communication was evident between $[S_2W_{18}O_{62}]^{4-}$ and $[Ru(bpy)_3]^{2+}$ within the cluster but additional electrolyte disrupt the ion-pairing. Therefore, to maintain ruthenium and POM association, electrochemical experiments can be carried out in the absence of deliberately added electrolyte using a microelectrode so as to minimize ohmic drop. Finally, the use of ruthenium metallopolymers as sensitizers is an area of much promise, which up until now has not been fully explored. These metallpolymers offer an opportunity to enhance the processablity and stability of the dyes used in Grätzel dye sensitized solar cell.

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CHAPTER TWO

Photocatalytic Properties of Ruthenium Polypyridyl: Polyoxometalate Adducts in electrolyte-free media

2.1 Introduction

In Chapter one, the capacity for polyoxometalates to undergo multiple photoinduced electron and proton transfer processes in the presence of electron and proton donors under ultraviolet light irradiation was described.[1-19] In this chapter, a ruthenium polypridyl transition metal complex, $[Ru(bpy)_3]^{2+}$ (Figure 1.11) where bpy is 2,2'-bipyridyl was employed to overcome the limitation of having to use UV excitation. Based on previous studies,[1] the intention is that the ruthenium complex would allow photoexcited states to be produced with enough driving force to drive photocatalysis with visible irradiation. Studies of polyoxometalate anions, such as $[S_2W_{18}O_{62}]^{4-}$ have been reported with redox-active and / or photo-active cations and convincing evidence of effective electronic communication between the two ions within the clusters has been descirbed.[1] Dissociation of the $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ complex in solution in the presence of LiClO₄ suggested that the binding between these cations and anions is dominated by electrostatic forces.

A layer-by-layer assembly method was employed to build [Ru-POW] films from the $[Ru(bpy)_3]^{2+}$ and $[S_2W_{18}O_{62}]^{4-}$ anions. Since the binding nature of the polyoxometalate anion and ruthenium cation is electrostatic, these films dissociate in the presence of electrolytes such as LiClO₄.[13] Therefore, platinum microelectrodes were used to permit measurements without deliberately added electrolyte so as to avoid dissociation of the film. As discussed in literature review, the problems associated with high resistance in the absence of electrolyte can be minimized using microelectrodes. The general electrochemical, Raman spectroscopic and morphological properties of [Ru-POW] films are also reported.

This chapter also reports on the use of benzyl alcohol as an electron donor for the photooxidation with the [Ru-POW] film. Scheme 2.1 shows the proposed overall

photocatalyic reaction that occurs at a [Ru-POW] film adsorbed on a platinum microelectrode surface could occur. The key steps anticipated in this photooxidation process are photoexcitation, photocatalysis and reoxidation such that at the end [Ru-POW] will be regenerated. During the photoexcitation process, the [Ru-POW] complex is excited by incident light to become [Ru-POW]^{*}. This excited [Ru-POW]^{*} complex can oxidise benzyl alcohol to form benzaldehyde in the photocatalysis step. Therefore, this process not only involves oxidation but also deprotonation of benzyl alcohol. The [Ru-POW]^{*} complex becomes reduced and finally [Ru-POW⁴] is reformed in an oxidation process at the electrode.

There are several processes that could ultimately limit the overall photocurrent (i_{photo}) observed; (1) the rate at which mediated sites are regenerated (the charge transport diffusion coefficient, D_{CT}), (2) transport of the electron donors, e.g., benzyl alcohol through the film and (3) the rate at which heterogeneous electron transfer occurs at the electrode. Here, we report on the capacity of a layer by layer assembled film on a platinum microelectrode to photocatalyse the oxidation of benzyl alcohol and examine the role that these factors play in limiting the performance of the film.



Scheme 2.1 A schematic diagram of [Ru-POW] film photo-oxidize benzyl alcohol to form benzaldehyde. In the (1) photoexcitation step, the [Ru-POW] complex is excited by incident light to become [Ru-POW]^{*}.]^{*}. This excited [Ru-POW]^{*} complex can oxidize benzyl alcohol to form benzaldehyde in the (2) photocatalysis step.

2.2 Experimental

2.2.1 Materials

Acetonitrile (CH₃CN; LabScan) was of HPLC or spectroscopic grade. Recrystalised tetrabutyl ammonium tetrafluoroborate (TBATBF₄; Fluka) was used as the supporting electrolyte in the electrochemical studies. { $[Ru(bpy)_3](Cl)_2$ } (Sigma-Adrich) was used as purchased and $[Hx_4N]_4[S_2W_{18}O_{62}]$ was prepared according to the literature procedures.[14]

2.2.2 Preparation of Films of [Bu₄N]₄[S₂W₁₈O₆₂] and [Ru(bpy)₃](PF₆)₂ by the Layer By Layer (LBL) Method

The method by which the [Ru-POW] film was formed is shown in Scheme 2.2; the first step is immersion of the platinum microelectrode (d=25 μ m) into the [S₂W₁₈O₆₂]⁴⁻ solution (1 mM) for 20 minutes, followed by washing with acetonitrile. This POM modified electrode was then immersed in a [Ru(bpy)₃][PF₆] solution (1 mM) for 20 minutes, followed by washing with acetonitrile. The above dip coating cycles were repeated to produce different surface coverages of [Ru-POW].



Scheme 2.2 Schematic diagram of [Ru-POM] film formation using a layer by layer self-assembly method

2.2.3 Instrumentation and Procedure

Cyclic voltammetry was performed in a conventional three-electrode cell using a CH Instruments Model 660a electrochemical workstation. All solutions were deoxygenated with N_2 . The working electrode, reference electrode and counter electrode were as follows; Pt microelectrode as the working electrode, Ag/AgCl as the reference electrode and the counter electrode was a platinum counter electrode. The surface coverages of the film were determined by graphical integration of the background corrected cyclic voltammograms and films were scanned first until stable.

For cyclic voltammetry determination of charge transfer diffusion coefficients, D_{CT} , scan rates between 50 and 5 mVs⁻¹ were used to obtain linear plots of the peak current versus the square root of scan rate. Relatively short experimental time-scales were used to ensure that the response is dominated by semi-infinite diffusion making it possible to analyse the behaviour using the Randles–Sevcik equation.

The morphology of the layer-by-layer self-assembled POM-Ru was investigated using a Hitachi S-3000N scanning electron microscope. Image analysis was completed using Image J version 1.47d image analysis software and the layer thicknesses were directly obtained from SEM cross-sections. AFM images of these [Ru-POW] layers were recorded with a Digital Instruments Nanoscope II in contact mode using commercial silicon nitride cantilever tips. These tips are pyramidal in shape with spring constants between 12-103 N/m and the tip size of the tips was $3.6 \,\mu$ m.

Amperometric i-t measurements were used to measure the photocurrent using the following set up illustrated in Scheme 2.3; A quartz cuvette was used to accommodate an ITO electrode, a platinum flag and a non-aqueous reference electrode (Ag/AgCl). The solution consisted of different concentrations of benzyl alcohol in acetonitrile. Electrolyte added or not was used as described in text. The white light source was a 350 W Oriel 68811 arc lamp and the potential was held at 0.5 V and the distance between the working electrode surface and the light source was 15 cm. A filter was put in place to cut

off light below 400 nm to ensure irradiation of the samples with visible light (> 400 nm) was achieved.



Scheme 2.3 A schematic diagram for cells employed for measurements of photocurrent.

2.3 Results and Discussion

2.3.1 General electrochemical and photo-electrochemical properties

This section reports the electrochemistry of the [POW-Ru] films and their potential for use in a photo-electrochemical cell. In the layer by layer method, the platinum microelectrode was first immersed into a $[S_2W_{18}O_{62}]^4$ solution (1 mM) for 20 minutes and then removed, washed with acetonitrile and dried. In order to ascertain if $[S_2W_{18}O_{62}]^4$ had been adsorbed onto the Pt microelectrode, the electrochemistry of the resulting $[S_2W_{18}O_{62}]^4$ in electrolyte-free acetonitrile was characterised.

Figure 2.1b illustrates the voltammetric behavior of the $[S_2W_{18}O_{62}]^{4-1}$ layer adsorbed on a Pt microelectrode at a slow scan rate (10 mVs⁻¹), where there is no supporting electrolyte. In comparison with Figure 2.1a, the POW^{4./5-} couple was identified and the formal potential was determined as -0.37 V. The apparent irreversibility of the POM process is attributed to two possible reasons;(1) structure, irreversibility is commonly accepted for polyoxometallate redox since different numbers of terminal oxygen atoms affect the rate and reversibility of the electron transfer [20] and (2) electrolyte-free media, in such system, more energy is required to oxidize or reduce. The next stage was to immerse the POW-modified Pt microelectrode (d = 25 μ m) into a [Ru(bpy)₃]²⁺ solution (1 mM) for 20 minutes followed by washing and drying. Figure 2.2 shows the cyclic voltammograms of the [Ru-POW] film formed on a Pt microelectrode in electrolyte-free acetonitrile. The formal potential and a ΔE_p value of $Ru^{2+/3+}\, of$ this film was measured from CV and determined to be approximately +1.1 V and 72 mV, respectively. In comparision with [Ru-POW] in DMF with 0.1M Bu₄NPF₆, a relative broader peak shape (higher ΔE_p) for Ru^{2+/3+} of this film is observed and this is attributed to the slow electron transfer process.[1]



Figure 2.1 Cyclic voltammograms of (a) a bare Pt microelectrode (d = 50 μ m)(A=250 μ m²) and (b) [S₂W₁₈O₆₂]⁴⁻ film using one dip coating cycle on Pt microelectrode (d = 50 μ m)(A=250 μ m²) in electrolyte-free acetronitrile. The scan rate for both CVs was 10 mVs⁻¹.

Figure 2.3a-b illustrate the scan rate dependence of the [Ru-POW] film following a single dip coating cycle formed on a Pt microelectrode in electrolyte-free acetonitrile. In the absence of added supporting electrolyte, the peak current increases nonlinearly with the square root of scan rate, $v^{1/2}$ as shown in Figure 2.3b. This finding is consistent with the results described by Alan Bond's group in which a nonlinear response for peak current versus $v^{1/2}$ was reported in scan rate dependence in a study of $[(C_6H_{13})_4N]_4[S_2Mo_{18}O_{62}]$ in electrolyte-free acetonitrile.[21] This nonlinear behavior is attributed to the scan rate, with relatively slower scan rates lessening the effect of IR drop. The surface coverage was measured at the slowest scan rate in order to minimize IR effects. Although it is difficult to measure the surface coverages for the POW^{4-/5-} process because of IR drop, the surface coverage for the $Ru^{2+/3+}$ oxidation at a scan rate of 5 mV s⁻¹ is 1.03×10^{-10} mol cm^{-2} for $Ru^{2+/3+}$. Another interesting finding from Figure 2.3 is that there is a shift in peak potential with increasing scan rate. This peak shift with scan rates is again attributed to Ohmic drop (120 mV) and high resistance $(1 \times 10^7 \Omega)$ measured by cyclic voltammetry in the absence of electrolyte as well as slow ion diffusion though the layer.

As mentioned previously, a plot of peak current vs square root of scan rate is nonlinear for a process that is influenced by IR drop and the slope from this plot cannot therefore, be used to obtain the charge transport diffusion coefficient (D_{CT}) . Nonetheless, initial studies indicate that an electroactive film can be formed from $[Ru(bpy)_3]^{2+}$ and $[S_2W_{18}O_{62}]^{4-}$ and as mentioned in the introduction, Keyes et al. reported a new optical transition appearing in this cluster in the Resonance Raman spectroscopy. The presence of this transition in the film may be used to indicate the same kind of interaction between two components is occurring here, indicating that sensitized oxidative photocurrent generation in the process of electron transfer at the electrode, the potential of the electrode needs to be chosen such that it is sufficiently positive to oxidize the [Ru-POW⁵⁻] back to the starting oxidation state. A potential of +0.4 V (vs Ag/Ag⁺) was used initially so as to be in agreement with previous work.[1] Equation 2.1 shows the proposed photooxidation reaction for benzyl alcohol by the [POW-Ru] layer by layer assemblied film. On the basis of Equation 2.1, the reaction at the electrode driving the photocatalytic cycle is expected to be the [Ru-POW] oxidation, therefore an oxidative current is anticipated. Figure 2.4 shows a photocurrent experiment for a [Ru-POW] film using a 400 nm cut-off filter. Sufficient time was allowed for the current to equilibrate to its baseline level before the photo-excitation. The light was then switched on and the current started to rise indicating that the photo-oxidation of benzyl alcohol was taking place. Two hundred seconds later, the current reached a maximum. Once the light source had been switched off the current reverted to its baseline level. The current recorded was oxidative, as expected according to Equation 2.1. The average magnitude of the current was measured as $0.12 \pm 0.008 \,\mu A \, cm^{-2}$.

In order for the photo-catalytic oxidation of benzyl alcohol to proceed, all of the steps in the photocatalytic cycle must be present, i.e. $[S_2W_{18}O_{62}]^{4-}$, Pt electrode and $[Ru(bpy)_3]^{2+}$. Removal of $[S_2W_{18}O_{62}]^{4-}$ from the layer or benzyl alcohol from the solution should prevent the reaction from proceeding, and no appreciable current would be recorded. Therefore, control experiments were carried out sequentially removing these components from the system. As shown in Figure 2.5 in the absence of $[S_2W_{18}O_{62}]^{4-}$ no photocurrent was observed. The absence of current also rules out the possibility that photocurrent is generated by the process of $[Ru(bpy)_3]^{2+*}$ oxidation to $[Ru(bpy)_3]^{3+}$, followed by reduction at the electrode back to $[Ru(bpy)_3]^{2+}$. Figure 2.6 illustrates that in the absence of irradiation, no current was recorded for a $[Bu_4N]_4[S_2W_{18}O_{62}]$ thin film in benzyl alcohol (20% V/V) at 0.4 V. Under white light irradiation, the $[Bu_4N]_4[S_2W_{18}O_{62}]$ thin film produced a photocurrent, but the [Ru-POW] film generated current was almost three times higher than that of the $[Bu_4N]_4[S_2W_{18}O_{62}]$ alone. This is an important observation and suggests that $[Ru(bpy)_3]^{2+}$ sensitizes photocurrent generation.

Although the above results show that the [Ru-POW] film produced higher photocurrent

than $[Bu_4N]_4[S_2W_{18}O_{62}]$ alone, the assembled film still yielded lower photocurrents than reported for ruthenium dye sensitized TiO₂[22]. There are two processes that may limit the overall photocurrent (i_{photo}); namely, ion diffusion and the rate of heterogenous electron transfer at the electrode. The former issue can normally be addressed by adding electrolyte to the solution and the latter by applying higher voltage. The next section investigates these issues in an attempt to optimize the photocurrent and identify the key limitations for photo-oxidation of benzyl alcohol using the [Ru-POW] films. However, a significant barrier is that [Ru-POW] film can be dissociated in the presence of electrolyte. Also we investigate if an increase in the surface coverage of [Ru-POW] on the electrode makes an impact on the overall photocurrent.

PHOTOEXCITATION: $[Ru-POW^{4-}] \rightarrow [Ru_2-POW^{4-}]^*$ (2.1) PHOTOCATALYSIS: $[Ru-POW^{4-}]^* + C_6H_5CH_2OH \rightarrow [Ru_2-POW^{5-}] + C_6H_5CHO + H_2$ REOXIDATION: $[Ru-POW^{5-}] - e^- \rightarrow [Ru_2-POW^{4-}]$



Figure 2.2 Cyclic Voltammogram of one layered [Ru-POW] film on a Pt microelectrode $(d = 50\mu m)$ in the absence of electrolyte in acetonitrile. The scan rate was 10 mV s⁻¹. Anodic (oxidative) currents are positive. The initial potential of of the fifth segment is - 0.7 V. The surface coverage, estimated from the charge passed for the reduction of Ru³⁺ at a scan rate of 10 mV s⁻¹, and is 1.03×10^{-10} mol cm⁻².



Figure 2.3(a) Cyclic voltammograms of one layered [Ru-POW] film formed on a Pt microelectrode (d = 50μ m) in the absence of electrolyte in acetonitrile. The scan rates are 50, 25, 10, 5 and 1 mV s⁻¹ from top to bottom. Anodic (oxidative) currents are positive.

Figure 2.3(b) Plot of i_{pa} vs square root of scan rate for the $[Ru(bpy)_3]^{2+/3+}$ redox process.



Figure 2.4 Photocurrent-time curves of one layered [Ru-POW] film with a ruthenium surface coverage of 1.03×10^{-10} mol cm⁻² formed on a platium flag ($A \approx 1 \text{ cm}^2$) in a solution of benzyl alcohol (20% V/V) and electrolyte-free acetonitrile irradiated by white light. The potential was held at 0.4 V.



Figure 2.5 Photocurrent-time curves of (a) Bare platinum electrode (A = 1 cm²) and (b) $[Ru(bpy)_3]^{2+}$ using a platinum flag ($A \approx 1 \text{ cm}^2$) in a solution of benzyl alcohol (20% V/V) and electrolyte-free acetonitrile irradiated by white light. The potential was held at 0.4 V.



Figure 2.6 Photocurrent-time curves of $[S_2W_{18}O_{62}]^{4-}$ thin film formed on a Platium flag $(A \approx 1 \text{ cm}^2)$ in solution of benzyl alcohol (20% V/V) and electrolyte-free acetonitrile irradiated by white light. The potential was held at 0.4 V.

2.3.2 Ion diffusion and charge transport diffusion coefficient (D_{CT})

As discussed in the last section, a [Ru-POW] film using one depositing cycle produced a low photocurrent compared to those found in ruthenium dye sensitised TiO_2 (approximately 5 mA cm⁻²) and the general electrochemical properties of the film suggest an IR drop issue and this was attributed to the absence of electrolyte. Therefore, in this section an attempt was made to solve this problem by adding an electrolyte into the solution. Previous studies have shown LiClO₄ readily disrupts the adduct therefore an organic salt was chosen to minimise the disruption problem. We also kept the electrolyte at relatively low concentrations to avoid layer disruption.

Figure 2.7 shows the cyclic voltammogram of a [Ru-POW] film following one depositing cycle on a Pt microelectrode in acetonitrile containing 1 mM TBATBF₄ as the supporting electrolyte. The Ru^{2+/3+} redox couple is evident in the CV and the formal potential of the Ru^{2+/3+} and POW^{4-/5-} processes measured from the voltammogram were approximately 1.21 V and -0.23 V, respectively. In contrast to the high resistance and IR drop evident in electrolyte-free media, the resistance in electrolyte-contained media was relatively low and was recorded as $1 \times 10^6 \Omega$ and IR drop was calculated as 0.3 mV compared with $1 \times 10^7 \Omega$ and 120 mV, in electrolyte-free media. The surface coverages for the Ru^{2+/3+} and POW^{4+/5-} were measured from the CV in electrolyte-containing media as 3.2×10^{-10} mol cm⁻² and 1.4×10^{-10} mol cm⁻² respectively. Although these surface coverage values were lower compared to the corresponding values obtained in electrolyte-free solution, the assembled film adsorbed on Pt electrodes showed good stability towards voltammetric cycling and the surface coverage decreased by less than 10% over a 1-hour period.

Figure 2.8a-b shows the cyclic voltammetry of the [Ru-POW] film using one depositing cycle on a Pt microelectrode in 1 mM TBATBF₄ in acetonitrile at various scan rates and

the inset shows the peak current dependence on the square root of scan rate. This figure does not exhibit the shift in peak potential with increasing scan rates observed in electrolyte-free media which suggests that the ohmic resistance is reduced in the presence of electrolyte. However, a nonlinear relationship is found in Figure 2.8b indicating the rate of electron transfer is still slow.

In general, the current through the film is limited by concentrations of the electroactive species within the film and the rate of charge transport. Therefore, it is vitally important to optimize concentrations of the electroactive species within film on the electrode to enhance the overall photocurrent. Since the [Ru-POW] film was constructed by a layer by layer method, we can simply increase the surface coverage of the [Ru-POW] film on a Pt microelectrode by repeating the dip-wash-dip cycle several times. The electrochemical and photo-electrochemical properties of the resulting [Ru-POW] films were then investigated.



Figure 2.7 The cyclic voltammograms of one layered [Ru-POW] film formed on the Pt microelectrode (d = $25 \ \mu m$) in TBATBF₄ (1 mM)-contained acetonitrile. The scan rate was 50 mVs⁻¹. The initial potential of the fifth segment is -0.7 V.



Figure 2.8a Cyclic voltammetry of one layered [Ru-POW] film with ruthenium's surface coverage of 3.203×10^{-10} mol cm⁻² formed on a Pt microelectrode (d = 25 µm) in TBATBF₄ (1 mM)-contained acetonitrile. The scan rates were 50, 25, 10, 5 and 1 mVs⁻¹ from top to bottom.

Figure 2.8b Plot of i_{pa} vs square root of scan rate.
2.3.3 Film thickness

To attempt to optimize the surface coverage of the electroactive centres on the electrode surface so as to enhance the overall photocurrent, thicker films of the [Ru-POW] were assembled on Pt. Firstly, as mentioned in the previous section, the surface coverage of the [Ru-POW] film was increased by repeating the dip-wash-dip cycle. Cyclic voltammetry was then employed not only to confirm that the assembled film had formed onto the substrate but also to measure the surface coverage. Figure 2.9 illustrates the voltammograms of three layered [Ru-POW] films on a Pt microelectrode in electrolyte-free acetonitrile, i.e. dipped into each solution 3 times. Distinctly different electrochemical behaviours for the POM and Ru centres are observed for the three layers compared with those found in Figure 2.7.

It can be seen from Figure 2.10a-b that the peak to peak separation changed significantly with increasing scan rates, this is attributed to the increasing resistance which was meausured as $4.0\pm0.5\times10^7 \Omega$ for three layers. These values of resistance for 3 layers are slightly higher compared with the one layered [Ru-POW] film $(1.0\times10^7 \Omega)$. Given the high IR drop, it can be concluded from the scan rate dependence studies that charge transport diffusion coefficient could not be obtained.

The purpose of this section was to investigate whether the increased thickness of the film on the electrode would enhance the overall photocurrent. According to Equation 2.1, the [Ru-POW] film is excited photonically in Step 1 and increasing the film thickness of the [Ru-POW] on the electrode would directly enhance the amount of available [Ru-POW]^{*} on the electrode surface. Figure 2.11 shows the photocurrent produced from three dip coated [Ru-POW] films and Table 2.1 summarizes the magnitude of photocurrent produced from films with different depositing cycles. The table shows that photocurrent *decreases* with *increasing* number of depositing cycles of [Ru-POW] at Pt electrodes.

This behaviour is likely to be due to ion diffusion limitations, although a charge transport diffusion coefficient could not be measured. In addition, the fact that ion diffusion slows with increasing film thickness is unsurprising given that the available ion will have greater distance to travel through the film to the underlying electrode.

The next section reports on the optimization of the applied potentials to promote photocurrent generation. However, potentials must be chosen so as not be positive enough to trigger excitation of Ru^{2+} to form Ru^{3+} .



Figure 2.9 Cyclic voltammogram of three layered [Ru-POW] film modified on a Pt microelectrode (d = $25 \ \mu$ m) in electrolyte-free acetonitrile. The scan rate for above voltammogram was 10 mVs⁻¹. The initial potential of the fifth segment is -0.7 V.



Figure 2.10a Cyclic voltammogram of three layered [Ru-POW] film formed on a Pt microelectrode (d = 25μ m) in electrolyte-free acetonitrile. The scan rates were 50, 25, 10, 5 and 1 mV s⁻¹ from top to bottom.

Figure 2.10a Plot of i_{pa} vs square root of scan rate.



Figure 2.11 Current-time curves for the photooxidation of benzyl alcochol in acetonitrile (20% V/V) by three layered [Ru-POW] film formed on a Pt flag ($A \approx 1 \text{ cm}^2$) in electrolyte-free acetonitrile at 0.4 V with T = 298 K. A filter was used to cut off light below 400 nm.

No. of layer by layer cycles [Ru- POM]	Redox process	Photocurrent density (µA/cm²)
	Ru ^{2+/3+}	
4	1.34V	0.08 ± 0.017
3	1.32V	0.09 ± 0.01
1	1.21V	0.12±0.018

Table 2.1 Summary of voltammetric data for [Ru-POW] film with different depositing cycles modified on pt microelectrode and photocurrent-time curves for photooxidation of benzyl alcohol (20% V/V) by [Ru-POW] film formed on Pt flag ($A \approx 1 \text{ cm}^2$) using +400 nm light filter. All experiments were performed in the electrolyte-free acetonitrile.

2.3.4 Potential Dependence of Polyoxometalate Reoxidation

In general, the rate constant for heterogeneous electron transfer can be influenced by changing the overpotential. For the POW oxidation, if the applied potential is shifted to a more positive value, the free energy for the electron transfer, will become more negative. Therefore, in this section on the effect of increasing the overpotential for POW oxidation on the photocurrent is reported.

Initially, photocurrent experiments at various potentials were carried out with one layered [Ru-POW] film on a Pt flag in electrolyte-free acetonitrile. Potentials from 0.4 up to 1.0 V were applied to increase the overall photocurrent without triggering the oxidation of the Ru centre. Figure 2.12 shows a photocurrent-time graph for a one layered [Ru-POW] film on Pt at different potentials in benzyl alcohol (20% v/v) in acetonitrile (electrolyte-free). This figure shows the magnitude of photocurrent generated from [Ru-POW] self assembled film at 1.0 V which is measured to be approximately $6.85\pm0.02 \mu$ A which is more than fifty times higher than the value obtained at 0.4 V (0.12μ A). Nonetheless, this indicates that the magnitude of the photocurrent increases with overpotential, which is consistent with the increased free energy for the oxidation process.

At the more positive potentials an important control experiment is whether $[Ru(bpy)_3]^{2+}$ can produce a photocurrent, i.e. can drive the photooxidation of benzyl alcohol. Figure 2.13 shows photocurrent-time graph of a $[Ru(bpy)_3]^{2+}$ (1mM) dissolved in electrolyte-free acetonitrile using a Pt flag as working electrode in benzyl alcohol (20% v/v) at +1.0V. This indicates that there was no photocurrent produced. Therefore, it can be concluded that the overall photocurrent increase for the [Ru-POW] at 1.0 V originates from the multilayer film itself and not from the Ru component alone.

In order to determine the transfer coefficient and other kinetic parameters, a Tafel Plot of log *i* versus η , where η is the overpotential was obtained. In Section 2.3.1 the photocurrent experiment for a [Ru-POW] film was performed by holding the potential at +0.4 V. Therefore, in this section $E_{equilibrium}$, was set to 0.089 V, i.e., 0.089 V is the formal potential for the POW^{4-/5-} and the value of η is determined using Equation 2.2 below.

$$\eta = E - E_{equilibrium} \qquad 2.2$$

The rate of the electron transfer partly depends on the transfer coefficient, α , known as a measure of the symmetry of the energy barrier. Figure 2.14 illustrates that if the transfer coefficient is greater than 0.5, the oxidation process is likely to be favoured and it also shows the Tafel Plot for the oxidation of [Ru-POW⁵⁻] to [Ru-POW⁴⁻] at 298 K. The slope can be used to determine the transfer coefficient, α , and the current at E_{equilibrium}, i_0 by using Equation 2.3.

$$\log \frac{i}{1 - e^{nf\eta}} = \log i_0 - \frac{\alpha n F\eta}{2.3RT}$$
 2.3

These values are calculated approximately as 0.92 for α and 0.09µA for i_0 from this plot. As mentioned previously the E_{equilibrium} was set as 0.089 V and the photocurrent measured from the [Ru-POW] film at 0.089 V was 0.12 µA. This value is consistent with the calculation from the Tafel Plot which shows the current at E_{equilibrium}, i_0 is 0.09µA.

Figure 2.14 shows the current-overpotential curve for $[Ru-POW^{5-}] \rightarrow [Ru-POW^{4-}] + e^{-1}$ and it can be seen from the plot that the current density grows exponentially with overpotential and this behaviour can be explained by the Butler-Volmer Equation (Equation 2.4) which relates the current density at the electrode surface due to the electrode reaction to the overpotential.

$$j = j_0 \{ \exp(-\alpha n F \eta / RT) - \exp[(1 - \alpha) n F \eta / RT] \}$$
 2.4

The transfer coefficient is regarded as an indicator of the symmetry of the barrier to reaction and therefore, the transfer coefficient of 0.92±0.01 obtained from Figure 2.14, indicates that the symmetry barrier for reoxidation process of [POW-Ru] photocatalytic cycle is low and the photocatalytic mechanism at the electrode surface is favoured at more positive potentials. Therefore, the effect of various concentrations of benzyl alcohol in solution on the photocurrent was studied.



Figure 2.12 Current vs time curves for the photooxidation of benzyl alcochol (20% V/V) at one layered [Ru-POW] film on Pt flag (A= 1 cm²) in electrolyte-free acetonitrile at a potential of (a) 0.6, (b) 0.7, (c) 0.8, (d) 0.9 and (e) 1.0 V with T = 298 K. A filter cut off light below 400 nm.



Figure 2.13 Current-time curve shows there is no photooxidation of benzyl alcochol (20% V/V) by $[\text{Ru(bpy)}_3]^{2+}(1\text{ mM})$ dissolved in electrolyte-free acetonitrile using Pt flag as working electrode (A= 1 cm²) at 1.0 V with T = 298 K. A filter cut off light below 400 nm.



Figure 2.14a The current-overpotential curve for the conversion of [Ru-POW⁵⁻] to [Ru-POW⁴⁻] in the presence of benzyl alcohol (20% V/V) in electrolyte-free acetonitrile with $\alpha = 0.92$.

Figure 2.14b The Tafel plot for the oxidation of $[Ru-POW^{5-}]$ to $[Ru-POW^{4-}]$ on Pt flag (A=1 cm²) in the presence of benzyl alcohol (20% V/V) in electrolyte-free acetonitrile at 298 K.

2.3.5 The Effect of The Benzyl Alcohol Concentration

Since the potential dependence study shows that the [Ru-POW] film can photooxidize benzyl alcohol at potentials between 0.4-1.0V, the potential chosen to carry out these experiments in this study was 0.8V. Figure 2.15 illustrates the effect of different concentrations of benzyl alcohol in solution at a [Ru-POW] film on the measured photocurrents. It also shows that in the absence of benzyl alcohol, a [Ru-POW] film produces a photocurrent of $0.3\pm0.01 \,\mu$ A, this being possibly due to the presence of small traces of water in the acetonitrile. The photocurrent observed rises with concentrations of benzyl alcohol exceeds about 20% V/V in acetonitrile. This is because when the concentration of the electron donor gets larger there is insufficient [Ru-POW]^{*} to interact with the benzyl alcohol, which results in no increase in the photocurrent.



Figure 2.15 Photocurrent generation from a one layered [Ru-POW] film on Pt flag (A= 1 cm^2) in electrolyte-free acetonitrile at potential of 0.8 V with T = 298 K using following benzyl alcohol concentration (a) 0, (b) 10, (c) 20, (d) 40, (e) 50 and (d) 60 % (V/V). The filter was used to cut off light below 400 nm.



Benzyl Alcohol Concentration (%, V/V)

Figure 2.16 Dependence of the photocurrent on the concentration of benzyl alcohol for a one layered [Ru-POW] film formed on Pt flag ($A= 1 \text{ cm}^2$) in electrolyte-free acetonitrile at 0.8 V. A filter was used to cut off light below 400 nm.

2.3.6 Optimized system

So far the electrochemical and photo-electrochemical properties of the [Ru-POW] films on Pt electrodes in the electrolyte-free media have been studied. Good evidence was provided for sensitization of the POM photochemistry by ruthenium polypyridyl complex but low photocurrent values were found compared to ruthenium dye sensitized TiO_2 . In order to optimize the system we have further investigated the following steps essential for photo-oxidation of benzyl alcohol; (1) electrolyte studies, i.e., low concentration (1 mM) of TBATBF₄ enhanced and facilitated ion diffusion across the [Ru-POW] film on Pt in the electrolyte-free media, (2) potential dependence studies, i.e., photo-electrochemical experiment held at 1 V provided best overall current, (3) at 20% (V/V) benzyl alcohol the film generated best photocurrent and (4) film thickness, i.e., single bilayer gave the best photocurrent generation in the electrolyte-free media. Therefore, having optimized these parameters individually the performance of the optimized system was investigated.

Figure 2.17 shows the current-time curve for photo-oxidation of benzyl alcohol using a one layered [Ru-POW] film at +1.0 V. The optimized system produced more photocurrent (59±0.02 μ A) than those found in other systems. A control experiment was carried out to observe the photocurrent generation by $[S_2W_{18}O_{62}]^{4-}$ alone using the optimized conditions described above. Figure 2.18 shows that $[S_2W_{18}O_{62}]^{4-}$ alone in the presence of benzyl alcohol (20% V/V) in electrolyte-free acetonitrile at +1 V which produced a photocurrent of 0.65±0.004 μ A. Therefore, under optimized conditions, a single bilayer of the [Ru-POW] film in the presence of benzyl alcohol (20% V/V) in electrolyte-free acetonitrile at 1 V produced a photocurrent which is approximately two orders of magnitude greater than $[S_2W_{18}O_{62}]^{4-}$ alone.



Figure 2.17 Current-time curves for the photooxidation of benzyl alcohol (20% V/V) by one layered [Ru-POW] film modified on a Pt flag ($A=1 \text{ cm}^2$) in acetonitrile containing 1 mM TBATBF₄ as supporting electrolyte. The potential was held at 1.0 V.



Figure 2.18 Current-time curves for the photooxidation of benzyl alcohol (20% V/V) by $[S_2W_{18}O_{62}]^{4-}$ self assembled film alone on a Pt flag (A= 1 cm²) in acetonitrile containing 1 mM TBATBF₄ as supporting electrolyte. The potential was held at 1 V.

2.3.6 Surface Topography of [Ru-POW] films

This section reports on [Ru-POW] films formed on ITO electrode using the same procedure employed previously for Pt. Control experiments of $[Hex_4N]_4[S_2W_{18}O_{62}]$ and $[Ru(bpy)_3](PF_6)_2$ deposited separately on ITO electrode were carried out to compare with the [Ru-POW] film and SEM and AFM were employed to probe the structure of these films. These figures has shown that the behavior of the 'layer by layer' structure is reminiscent of behavior of the composite, formed in solution

Figure 2.19 shows the AFM images of (a) a bare ITO electrode with (b) thin film of $[Hex_4N]_4[S_2W_{18}O_{62}]$ and (c) one layer of $[Ru(bpy)_3](Cl)_2$ on an ITO electrode, respectively. These AFM images clearly show that $[Hex_4N]_4[S_2W_{18}O_{62}]$ forms clusters rather than thin layers on the ITO electrode which was observed for the $[Ru(bpy)_3](Cl)_2$. It also can be seen from Figure 2.19 that the $[Hex_4N]_4[S_2W_{18}O_{62}]$ possesses larger crystallites (with the diameter of approx. 200 nm) than are found for the $[Ru(bpy)_3](Cl)_2$ (with the diameter of approx. 15 nm)



Figure 2.19 AFM images for (a) bare ITO electrode alone and thin film of (b) $[Hex_4N]_4[S_2W_{18}O_{62}]$ and (c) $[Ru(bpy)_3](Cl)_2$ formed on ITO electrode using layer by layer method.



Figure 2.20 AFM images of [Ru-POW] layer by layer film formed on ITO electrode with scan size of (a) 1 μ m and (b) 3 μ m. Figure 21 (a) is the close-up of the same structure in Figure 21 (b).



(a)

(b)

Figure 2.21 SEM images obtained from three layered [Ru-POW] film and formed on ITO electrode using three layers and the red line indicates the distance which marked as 20 μ m in (a) and 400nm in (b). Figure 22 (b) is the close-up of the same structure in Figure 22 (a).

Figure 2.20 shows an AFM image of an [Ru-POW] film on an ITO electrode. This figure was clearly distinguishable from both the $[Hex_4N]_4[S_2W_{18}O_{62}]$ and $[Ru(bpy)_3](Cl)_2$ on the ITO electrode and exhibits a nanoporous structure. It seems that the additional layer of $[Ru(bpy)_3]^{2+}$ assembled on the $[S_2W_{18}O_{62}]^{4-}$ drives the formation of this nanoporous structure. Figure 2.21 shows SEM images of three layered [Ru-POW] film on the ITO electrode. Figure 2.21b is consistent with the observation in Figure 2.21 that the layer consists of a self-organized nanoporous crystalline structure with a pore diameter of approximately 200 nm. Interestingly, this porous structure is similar to the SEM images of mesoscopic TiO₂ used in the dye-sensitised solar cell. This suggests that the film has attractive features including a high surface area and a porous structure that allows solvent and ions to move easily through the film.

1.4 Conclusion

This chapter reports investigations into the optimization of the photocurrent from thin films composed of assembled ruthenium polypyridyl polyoxometalate clusters. In the first part of this work, the electrochemical and photoelectrochemical properties of the [Ru-POW] films are explored. The [Ru-POW] film was successfully adsorbed onto a Pt microelectrode and its electrochemical properties were probed using CV. In electrolyte-free acetonitrile, scan rate dependence studies showed that a slow electron transfer is present which can be attributed to the absence of electrolyte. Low photocurrent produced in comparison with ruthenium dye sensitized TiO_2 system.

In the second part, the overall photocurrent was optimized by identifying key limiting factors; (1) electrolyte; adding low concentrations of electrolyte (1 mM TBATBF₄) resulted in an increased charge transport diffusion coefficient but higher concentrations of electrolyte decomposed the layer, (2) film thickness; increasing the thickness of [Ru-POW] film on Pt. However, the overall photocurrent decreased with increasing film thickness of the adduct. This is attributed to poor ion diffusion through the thicker layer and possibly blocking of the exciting radiation, (3) applied potentials; increasing the applied potential to speed up the heterogeneous electron transfer process at the electrode surface. The magnitude of the photocurrent increased with increasing overpotential, indicating that the photooxidation of the benzyl alcohol by the [Ru-POW] film is at least partly controlled by the rate of heterogeneous electron transfer. (4) Donor concentrations; increasing the concentration of benzyl alcohol in the solution increased the photocurrent for concentrations up to 20% V/V.

Finally, the topography of the [Ru-POW] film has been investigated. These [Ru-POW] films consist of a nanoporous crystalline structure with pore diameters of approximately 200nm. Interestingly, this porous structure is similar to that found in mesoscopic TiO_2 used in the dye-sensitised solar cell. This suggests that the film has attractive features including a high surface area and a porous structure that allows solvent and ions to move

easily through the film, and may explain why good photocurrent yields are achieved.

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CHAPTER THREE

Photocatalytic Properties of Thin Films of Ruthenium Metallopolymers: Polyoxometalate Composites Using Visible Excitation

3.1 Introduction

In their reduced states, polyoxometallates (POMs) such as the Dawson anion α -[S₂ Mo₁₈O₆₂]⁴⁻ (POM, Scheme 1) are powerful electron acceptors and are active electrocatalysts for hydrogen and oxygen evolution.[1-2] In addition, the redox and photophysical properties of polyoxometalates (POM) make them useful for (photo)catalysis. However, polyoxometalates can undergo multiple photoinduced electron and proton transfer processes in the presence of electron/proton donors *only* under ultraviolet light ($\lambda < 330$ nm) irradiation. [3]

As mentioned above, polyoxometalate anions do not absorb visible light. One way in which this limitation can be overcome is to couple them to a ruthenium polypridyl transition metal complex such as $[Ru(bpy)_3]^{2+}$. For example, the steady state quenching study of $[Ru(bpy)_3]^{2+}$ on addition of $[S_2W_{18}O_{62}]^{4-}$ in dry acetonitrile shows it resulted in significant quenching of the $[Ru(bpy)_3]^{2+}$ luminescence intensity [4] and strong communication between the $[Ru(bpy)_3]^{2+}$ and $[S_2W_{18}O_{62}]^{4-}$ was further confirmed using Resonance Raman Spectroscopy.

Thus, polyoxomolydates sensitized with ruthenium metal complexes maybe attractive for photocatalysis, but the influence of the metal complex structure, as well as the redox and photonic properties on the photocatalytic process needs further elucidation.[5-6] Based on the rather poor photocurrent experiment results for the $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ layer by layer film,[4] it is important to create thin films of the photocatalysts in which the overall performance, e.g., the rate of sacrificial co-reactant ingress, the rate of charge transport through the films and the rate of electron transfer, are optimised.

This chapter reports on the extent of electronic communication between ruthenium metallopolymers and polyoxomelatates and probes the possibility of translating their properties into a photoelectrochemical cell. In order to achieve this objective, a thin film of α - [S₂Mo₁₈O₆₂]⁴⁻ sensitized with ruthenium containing metallopolymers has been created using alternate immersion layer-by-layer assembly.[7-13] The polycationic

metallopolymers, $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ and $[Copolymer(7)-CH_2NHCO-Ru](PF_6)_2$, have been used; PVP is poly(4-vinylpyridine), bpy is 2,2'-bipyridyl, CO-P is the copolymer which is derived from two or more monomeric species and PIC is 2-(4carboxyphenyl) imidazo [4,5-f][1,10] phenanthroline (Scheme 3.1). These complexes were chosen because they possess great processablity and stability towards layer formation and in addition, they display strong absorbance (400-500 nm) and emission (650 nm) in the visible region. The films exhibit well-defined, almost ideal electrochemical responses over a wide range of voltammetric scan rates. Moreover, the $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ and $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ metallopolymers both have nitrogen atoms on the backbones making it likely that they will bind strongly to indium tin oxide (ITO) or metallic substrates.

The electronic communication between the ruthenium metallopolymer cations and polyoxometalate anions within the film was investigated using UV-vis spectroscopy and Resonance Raman microscopy. Cyclic voltammetry was employed to study the electrochemical properties of the films and the photocatalytic current was measured using benzyl alcohol as the substrate using visible irradiation. The surface topology of Ru-PVP:POM and Ru-CO-P:POM films was investigated by employing atomic force microscopy.



(a)



Scheme 3.1 Structure of (a) α -[S₂Mo₁₈O₆₂]⁴⁻, (b) [Ru(bpy)₂(CO-P PIC)₇]²⁺ and (c) [Ru(bpy)₂(PVP)₁₀]²⁺.

3.2 Experimental

3.2.1 Materials

Acetonitrile (CH₃CN; LabScan) was of HPLC or spectroscopic grade. Recrystallised tetrabutylammonium tetrafluoroborate (TBATBF₄; Fluka) was used as supporting electrolyte in the electrochemical and photo-electrochemical studies. $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ and $\{[Hx_4N]_4[S_2Mo_{18}O_{62}]\}$ were prepared according to literature procedures and $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ was synthesised using a novel procedure.[14-16]

3.2.2 Preparation of Films of [POM-Ru]

Thin films of the [POM-Ru] composite were created using layer by layer self assembly as similarly illustrated in Scheme 2.2. First, ITO electrodes (Delta Technologies Ltd., Stillwater, MN, USA were immersed in a 1 mM solution of $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ in ethanol or $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ in acetonitrile for 20 minutes. This modified electrode was then immersed in a 1mM aqueous solution of $[S_2Mo_{18}O_{62}]^{4-}$ for 20 minutes. After each emersion, the electrode was repeatedly washed with CH₃CN to remove any un-bound material.

3.2.3 Instrumentation and Procedure.

Cyclic voltammetry was performed in a conventional three-electrode cell with a CH Instruments Model 660a electrochemical workstation. All measurements were performed at 25 ± 2 °C and all solutions were deoxygenated with N₂ before each measurement. The reference electrode was Ag/AgCl and the counter electrode was a large area platinum wire coil. The surface coverages were determined by graphical integration of background corrected cyclic voltammograms and films were scanned first until stable.

The substrate for photocatalytic oxidation was pure benzyl alcohol containing 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) as supporting electrolyte. The white light source was an Oriel 68811 arc lamp employing a 350 W Xe bulb which was focused onto the film (1 cm^2) . The potential was held at +0.4 V so as to re-oxidise the reduced POM following benzyl alcohol oxidation. A filter was used to cut off light below 488 nm so as to preferentially excite into the metallopolymer metal-to-ligand charge transfer, MLCT.

UV-vis spectra of these self assembled films on ITO were recorded using a Jasco V-670 UV/Vis/NIR spectrophotometer.

Resonance Raman microscopy was performed on a confocal HR micro-Raman instrument (HR800, Jobin-Yvon, Horiba) with an 1800 groves/mm grating to give a spectral resolution of 0.1 cm⁻¹. The 514, 488 and 450 nm lines of an argon ion laser (Coherent, Innova) were employed for excitation and the scattered light was collected in an 180° alignment. The acquisition time was typically 20s.

AFM images were recorded always with a Digital Instruments Nanoscope II in the contact mode using commercial silicon nitride cantilever tips. These tips are pyramidal in shape with spring constant between 12-103 N/m and the size of the tips was $3.6 \,\mu$ m.

3.3 Results and Discussion

3.3.1 UV-vis characterisation

As mentioned in Section 3.1, polyoxometalates sensitized with ruthenium metal complexes are attractive for photocatalysis. A strong electronic interaction between the catalyst and the sensitiser is essential to perform photocatalysis. Keyes et al. reported a new optical transition at 485 nm in a $[Ru(bpy)_3]_2[S_2Mo_{18}O_{62}]$ ion cluster. Evidence for the presence of this optical transition within a ruthenium metallopolymer and polyoxometalate cluster was investigated using UV-vis spectroscopy and Raman spectroscopy.

Figure 3.1(a-b) shows the absorption spectra for $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ and Ru-PVP:POM on the ITO electrode, respectively. An MLCT absorption band is observed at approximately 455 nm for the ruthenium metallopolymers in Figure 3.1a. However, interestingly, Figure 3.1b shows differences following addition of $[S_2Mo_{18}O_{62}]^{4-}$ into the film. The absorption band present at 455 nm in Figure 3.1a is shifted to approximately 480 nm as shown in Figure 1b. In addition, a long tail into the IR (approximately 700 nm) is observed. These features are suggestive of the new transition existing within the [Ru-PVP:POM] film. This phenomenon is also observed in the case of $[Ru(bpy)_3]^{2+}$ and $[S_2Mo_{18}O_{62}]^{4-}$ but the tail was not as pronounced in this case.[4-5]

Significantly, a long tail into the NIR and new transition centred at approximately 480 nm are not observed for the Ru-CO-P:POM film. Figure 3.2a and 3.2b show the absorption spectra for $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ and Ru-CO-P:POM. The absorption spectra for $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ shows the signature ruthenium MLCT band at approximately 460 nm whereas this absorption band at 460 nm is shifted approximately 10 nm in the Ru-CO-P:POM spectra. However, a long tail into the IR and new transition centred at approximately 480 nm apparent in the PVP based film is not observed in the

absorption spectra of CO-P based system. Therefore, these absorption spectra suggest that there is a new optical transition in the PVP but not the CO-P PIC system.

Difference spectra were performed over a range of Ru-PVP and POM ratios.[17] They reveal the presence of a new optical transition that grows in with increasing POM concentration. This new feature tails quite far into the red to approximately 700 nm. Resonance Raman spectroscopy was then employed to probe the features of this new optical transition.



Figure 3.1 UV-vis spectra of (a) $[Ru(bpy)_2(PVP)_{10}]^{2+}$ film and (b) Ru-PVP:POM film on an ITO electrode. The surface coverages for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and the Ru-PVP:POM film are $6.9 \pm 0.1 \times 10^{-10}$ molcm⁻², and $1.5 \pm 0.34 \times 10^{-10}$ molcm⁻², respectively.



Figure 3.2 UV-vis spectra of (a) $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ film and (b) Ru-CO-P:POM film on an ITO electrode. The surface coverages for $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ and Ru-CO-P:POM film are $2.4 \pm 0.08 \times 10^{-10}$ molcm⁻², and $9.1 \pm 0.02 \times 10^{-11}$ molcm⁻², respectively.


Figure 3.3 UV-vis spectra of $[Hx_4N]_4[S_2Mo_{18}O_{62}]$ film on ITO electrode.

3.3.2 Resonance Raman Spectroscopy

Resonance Raman spectroscopy was employed to characterise the electronic communication between the ruthenium metallopolymer cations and polyoxometalate anions within the film. When a strong interaction exists between $[Ru(bpy)_3]^{2+}$ and $[S_2W_{18}O_{62}]^{4-}$ a new mode was observed in the resonance Raman spectroscopy at approximately 1093 cm⁻¹ as previously described.[4] Here, excitation wavelengths of 450, 488 and 514 nm were used to investigate the nature of the optical changes for the [POM-Ru] self assembled films.

Figure 3.4 a-c and Figure 3.4e show the Raman spectra, with an excitation wavelength of 514 nm, for a bare ITO electrode, thin films of $[Hx_4N]_4[S_2Mo_{18}O_{62}]$, [Ru(bpy)₂(PVP)₁₀](ClO₄)₂ and Ru-PVP:POM formed by the layer by layer method, respectively. This excitation wavelength is expected to be post-resonant with the ruthenium metallopolymer MLCT at 450 nm. In common with 450 and 488nm excitation, bands associated with Mo-O stretching modes are observed at 986 and 815 The vibration at 991 cm⁻¹ is attributed to the $[Hx_4N]^+$ counterion. cm^{-1} . $[Ru(bpy)_2(PVP)_{10}]^{2+}$ exhibits seven signature bipyridyl vibration modes at 1606, 1564, 1484, 1326, 1270, 1173 and 670 cm⁻¹ typical of resonance with Ru (d π) to bpy (π^*) MLCT and the Ru-N mode is also present at 370 cm⁻¹. Figure 3.4e shows that Ru-PVP:POM contains the signature bipyridyl mode but, in addition, a new broad feature apparent at 900 cm⁻¹ that is not present in either $[Ru(bpy)_2(PVP)_{10}]^{2+}$ or $[S_2Mo_{18}O_{62}]^{4-}$ spectrum is observed. The broadness of the band at 900 cm⁻¹ is attributed to two reasons: (1) H bond, hydrogen bond between Mo-O of $[S_2Mo_{18}O_{62}]^{4-}$ and hydrogen of pyridyl complex of $[Ru(bpy)_2(PVP)_{10}]^{2+}$ is responsible for the band at 900 cm⁻¹. The broadness, however, is attributed to (2) the chromophore, the energy of the incoming laser coincide with an electronic transition of the molecule which associats with the chromophore. In such case, the charge transfer transitions of the metal complex enhance metal-ligand stretching mode. The intensity of this transition was dramatically lower compared to those found in 514 nm when using an excitation at 450 or 488 nm. This indicates that the new transition is centred further into the red (post resonant) than the Ru MLCT and is also consistent with UV-vis spectroscopic studies which demonstrated that the new transition exhibits a long tail into the NIR (approximately 700 nm).

Figure 3.4d and f show the Raman spectra, with an excitation wavelength of 514 nm, for $[Ru(bpy)_2(CO-PPIC)_7]_2[S_2Mo_{18}O_{62}]$ and $[Ru(bpy)_2(CO-PPIC)_7](PF_6)_2$, respectively. Raman spectra for $[Ru(bpy)_2(CO-PPIC)_7]_2[S_2Mo_{18}O_{62}]$, and $[Ru(bpy)_2(CO-PPIC)_7](PF_6)_2$ both show signature bipyridyl modes observed at 1611, 1558, 1486, 1326, 1175, 1040 and 664 cm⁻¹. In addition, two relatively weak features at 1469 and 1421 cm⁻¹, which are not attributed to bpy, are visible. This is most likely due to the heteroligand-based optical transition observed at 330 nm.[18] However, the new broad feature appearing at 900 cm⁻¹ for PVP based film is not observed in the Raman spectrum of CO-P based system. Nevertheless, Figure 4f exhibits features at 996 and 973 cm⁻¹ which were assigned to the polyoxomolybdate anion.[18]

These Raman spectra, together with absorption spectra, suggest that there is a new optical transition in the PVP but not the CO-P PIC system. This observation is significant and suggests that the extent of electronic interaction between the polymeric ruthenium complex and the POM depends on subtle differences in the optical, electrochemical or structural properties of the metallopolymer. Therefore, in the coming sections, electrochemical and structural properties of [Ru-PVP:POM] and [Ru-CO-P:POM] are investigated.



Figure 3.4 Resonance Raman spectra of one dip coat cycled films excited at 514 nm: (a) a bare ITO electrode, (b) $[Hx_4N]_4[S_2Mo_{18}O_{62}]$, (c) $[Ru(bpy)_2(PVP)_{10}]^{2+}$, (d) $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, (e) Ru-PVP:POM and (f) Ru-CO-P:POM. The laser power for all experiments was held at 50 mW. The surface coverages for $[Ru(bpy)_2(PVP)_{10}]^{2+}$, $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, Ru-PVP:POM and Ru-CO-P:POM are followed as $6.9 \pm 0.1 \times 10^{-10} \text{ molcm}^{-2}$, $2.4 \pm 0.08 \times 10^{-10} \text{ molcm}^{-2}$, $1.5 \pm 0.34 \times 10^{-10} \text{ molcm}^{-2}$, and $9.1 \pm 0.02 \times 10^{-11} \text{ molcm}^{-2}$, respectively.

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Figure 3.5 Resonance Raman spectra of one dip coat cycled films excited at 488 nm: (a) a bare ITO electrode, (b) $[Hx_4N]_4[S_2Mo_{18}O_{62}]$, (c) $[Ru(bpy)_2(PVP)_{10}]^{2+}$, (d) $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, (e) Ru-PVP:POM and (f) Ru-CO-P:POM. The laser powers for all experiments were held at 50 mW. The surface coverages for $[Ru(bpy)_2(PVP)_{10}]^{2+}$, $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, Ru-PVP:POM and Ru-CO-P:POM are followed as $6.9 \pm 0.1 \times 10^{-10} \text{ molcm}^{-2}$, $2.4 \pm 0.08 \times 10^{-10} \text{ molcm}^{-2}$, $1.5 \pm 0.34 \times 10^{-10} \text{ molcm}^{-2}$, and $9.1 \pm 0.02 \times 10^{-11} \text{ molcm}^{-2}$, respectively



Figure 3.6 Resonance Raman spectra of one dip coat cycled films excited at 458 nm: (a) a bare ITO electrode, (b) $[Hx_4N]_4[S_2Mo_{18}O_{62}]$, (c) $[Ru(bpy)_2(PVP)_{10}]^{2+}$, (d) $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, (e) Ru-PVP:POM and (f) Ru-CO-P:POM. The laser power for all experiments were held at 50 mW. The surface coverages for $[Ru(bpy)_2(PVP)_{10}]^{2+}$, $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, Ru-PVP:POM and Ru-CO-P:POM are followed as $6.9 \pm 0.1 \times 10^{-10} \text{ molcm}^{-2}$, $2.4 \pm 0.08 \times 10^{-10} \text{ molcm}^{-2}$, $1.5 \pm 0.34 \times 10^{-10} \text{ molcm}^{-2}$, and $9.1 \pm 0.02 \times 10^{-11} \text{ molcm}^{-2}$, respectively.

2.3.3 Electrochemistry

Section 2.3.3 suggested that subtle differences in the optical, electrochemical or structural properties of the metallopolymer play important roles in the extent of electronic interaction. Therefore, it is essential to investigate the influence of the ruthenium metallopolymeric cations on the electrochemical behaviour of $[S_2Mo_{18}O_{62}]^{4-}$ within the films. The redox properties of the films were probed by cyclic voltammetry and comparative voltammetric data for $[Ru(bpy)_2(PVP)_{10}]^{2+}$, $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ and $[S_2Mo_{18}O_{62}]^{4-}$ were acquired under the same conditions.

Figure 3.7 illustrates the solution phase cyclic voltammogram for $[S_2Mo_{18}O_{62}]^{4-}$ in CH₃CN where the scan rate is 50 mVs⁻¹ and the supporting electrolyte is 0.1 M TBATBF₄. The electrochemistry of the $[S_2Mo_{18}O_{62}]^{4-}$ in CH₃CN has been previously reported, [6,19-20] and the initial two reduction steps are summarized in Equation 3.1:

$$[S_2Mo_{18}O_{62}]^{4-} + e^{-} \leftrightarrow [S_2Mo_{18}O_{62}]^{5-} + e^{-} \leftrightarrow [S_2Mo_{18}O_{62}]^{6-}$$
(3.1)

The difference in the anodic and cathodic peak potentials, ΔE_p , is 336±5 mV and 372±11 mV for the $[S_2Mo_{18}O_{62}]^{4./5-}$ and $[S_2Mo_{18}O_{62}]^{5./6-}$ couples, respectively. In addition, the $[S_2Mo_{18}O_{62}]^{4./5-}$ and $[S_2Mo_{18}O_{62}]^{5./6-}$ couples exhibited cathodic shifts of approximately 80±2 mV in CH₃CN (0.1 M TBATBF₄) compared with these found in DMF (0.1 M Bu₄NPF₆).[6] This cathodic shift seen in the TBATBF₄ system suggests that $[S_2Mo_{18}O_{62}]^{4./5-}$ is harder to reduce.

Figures 3.8 and 3.9 illustrate voltammograms for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ thin films adsorbed on ITO electrodes. The formal potentials, $E^{\circ'}$, and the difference in the anodic and cathodic peak potentials, ΔE_p , for the $[S_2Mo_{18}O_{62}]^{4-}$ anion, $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ cations are presented in Table 3.1. In CH₃CN (0.1 M TBATBF₄), $E^{\circ'}$ values of 0.995 and 1.03 V

were obtained for the $\operatorname{Ru}^{2+/3+}$ redox process in $[\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{PVP})_{10}]^{2+}$ and $[\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{CO-P}\operatorname{PIC})_7]^{2+}$ PIC)₇]²⁺ thin films. These formal potential values suggest that $[\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{CO-P}\operatorname{PIC})_7]^{2+}$ is harder to oxidize and reduce compared to $[\operatorname{Ru}(\operatorname{bpy})_2(\operatorname{PVP})_{10}]^{2+}$. Investigating the voltammetric behaviour of Ru:PVP:POM and Ru-CO-P:POM films is facilitated by their limited solubility in CH₃CN. The films showed good stability towards voltammetric cycling and the surface coverage decreased by less than 10% over a 1-hour period of continuous cycling.

	*Redox process (POM=[S ₂ Mo ₁₈ O ₆₂])		
	Ru ^{2+/3+}	POM4-/5-	POM ^{5-/6-}
$[Hx_4N]_4[S_2Mo_{18}O_{62}]$	-	0.189 (0.336)	0.157 (0.372)
$[Ru(bpy)_2(PVP)_{10}](ClO4)_2$	0.995 (0.168)	-	-
$[Ru(bpy)_2(PVP)_{10}]_2[S_2Mo_{18}O_{62}]$	0.929 (0.142)	0.163 (0.124)	-0.156 (0.154)
$[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$	1.03 (0.043)	-	-
$[Ru(bpy)_2(CO-PIC)_7]_2[S_2Mo_{18}O_{62}]$	0.978 (0.065)	0.223 (0.194)	-0.197 (0.175)

Table 3.1 Formal potentials, E°', and peak-to-peak separations, ΔE_P , for metallopolymer and composite layers formed on ITO electrodes in contact with 0.1 M TBATBF₄ dissolved in acetonitrile as supporting electrolyte. *All values are in volts (vs Ag/AgCl) and ΔE_P values are in brackets.

The voltammograms for Ru-PVP:POM and Ru-CO-P:POM films of one layer are shown in Figure 3.10 and Figure 3.11. These composite films show clearly defined redox waves associated with both the ruthenium and POM components. The formal potential for the $Ru^{2+/3+}$ process in both the PVP and CO-P systems shifts in a positive potential direction by approximately 60 mV when associated with the POM suggesting a lower electron density on the ruthenium centres. It is more difficult to precisely determine the formal potentials of the POM^{4-/5-} couple. However, association with the Ru-PVP and Ru-CO-P metallopolymers causes E°' to shift in a positive potential direction, i.e., E°' for the POM⁴⁻ ⁷⁵⁻ couple shifts by approximately +120 mV and +100 mV for the Ru-PVP:POM and Ru-CO-P:POM adducts, respectively. These shifts suggest that the POM electron density may be somewhat increased by association with the ruthenium metallopolymers. Similar shifts in E°' were also observed when $[Ru(bpy)_3]^{2+}$ associates with $[S_2Mo_{18}O_{62}]^{4-}$.[4] In addition, Figure 3.10 shows an additional reduction process is observed at -0.489 V for the Ru-PVP:POM adducts which is consistent with a POM^{6-/7-} couple. This process is observed for the adduct because POM reduction becomes more facile in the adduct relative to the parent polyoxometalate.

The surface coverage for both the ruthenium and POM centres was obtained by measuring the charge passed under each wave in the background corrected cyclic voltammogram recorded at a series of slow scan rates, typically less than 10 mVs⁻¹, where the charge passed is independent of the scan rate, i.e., the films were exhaustively electrolysed. The Ru:POM ratio obtained was 4.5 ± 0.2 :1 where $\Gamma_{POM}=3.02\pm0.3\times10^{-11}$ and $1.97\pm0.1\times10^{-11}$ molcm⁻² for Ru-PVP:POM and Ru-CO-P:POM, respectively. The Ru:POM ratio of 4.5 ± 0.2 :1 is consistent with results obtained from Stern-Volmer plots and suggests these films contain more ruthenium centres than is required to charge balance the POM⁴⁻ centres. This behaviour may arise because the cation is polymeric, i.e., ruthenium metallopolymer was firstly formed on the ITO and subsequent POM would have penetrate layer.

Figures 3.12-15 show that the peak current for both the ruthenium and POM centres varies linearly with the square root of scan rate for scan rates between 50 and 10 mVs⁻¹, suggesting that semi-infinite linear diffusion controls the rate of charge transport through these films. Equation 1.7 was employed to determine the homogenous charge transport diffusion coefficients, D_{CT} for $[Ru(bpy)_2(PVP)_{10}]^{2+}$, $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$, Ru-PVP:POM and Ru-CO-P:POM. The effective redox site concentrations were determined from the film thickness as measured using atomic force microscopy and the surface coverage determined using slow scan rate cyclic voltammetry. The difference in

thickness, reported in Section 3.3.5 and surface coverages yielded the ruthenium concentration within the pure PVP and CO-P metallopolymers was 0.73 ± 0.08 M and 0.54 ± 0.08 M, respectively, while the Ru-PVP:POM and Ru-Co-P:POM yielded concentrations of 0.34 ± 0.02 M and 0.16 ± 0.01 M, respectively.

Using the effective redox site concentrations, the slope of inset plots from Figure 3.12-15 yielded diffusion coefficients for charge transport through the ruthenium centres of $2.49 \pm 0.92 \times 10^{-10}$ cm⁻²s⁻¹, $5.62 \pm 0.8 \times 10^{-10}$ cm⁻²s⁻¹, $1.26 \pm 0.43 \times 10^{-11}$ cm⁻²s⁻¹ and $9.84 \pm 0.64 \times 10^{-11}$ cm⁻²s⁻¹ for the pure PVP and CO-P polymers, the PVP:POM and CO-P:POM systems, respectively. Significantly, the D_{CT} values for both the metallopolymer:POM composites are more than five times lower than those found for the parent suggesting that ion diffusion through the composite is impeded most likely by crosslinking or compaction of the film by the POM. This result is important since the rate of charge transport directly influences the number of catalytic centres generated per unit time.



Figure 3.7 Cyclic voltammogram for solution phase $[Hx_4N]_4[S_2Mo_{18}O_{62}]$ (1 mM) in CH₃CN at an ITO electrode (A = 1 cm²). The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 50 mVs⁻¹, respectively. The initial potential of the fifth segment is - 0.8 V.



Figure 3.8 Cyclic voltammograms for a one layered $[Ru(bpy)_2(PVP)_{10}]^{2+}$ film formed on an ITO electrode (A = 1 cm²) immersed in CH₃CN. The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 50 mVs⁻¹, respectively. The initial potential of the fifth segment is -0.7 V.



Figure 3.9 Cyclic voltammograms for a one layered $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ film formed on an ITO electrode (A = 1 cm²) immersed in CH₃CN. The initial potential of of the fifth segment is -0.7 V. The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 50 mVs⁻¹, respectively



Figure 3.10 Cyclic voltammograms for a one layered Ru-PVP:POM film formed on an ITO electrode ($A = 1 \text{ cm}^2$) immersed in CH₃CN. The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 50 mVs⁻¹, respectively. The initial potential of the fifth segment is -0.7 V.



Figure 3.11 Cyclic voltammograms for a one layered Ru-CO-P:POM film formed on an ITO electrode ($A = 1 \text{ cm}^2$) immersed in CH₃CN. The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 50 mVs⁻¹, respectively. The initial potential of the fifth segment is -0.7 V.



Figure 3.12a Cyclic voltammograms for a $[Ru(bpy)_2(PVP)_{10}]^{2+}$ film formed on ITO electrode (A = 1 cm²) immersed in CH₃CN. The supporting electrolyte is 0.1 M TBATBF₄. Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic currents are positive. The surface coverage for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ formed on ITO electrode is $6.9 \pm 0.1 \times 10^{-10}$ molcm⁻².

Figure 3.12b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$.



Figure 3.13a Cyclic voltammograms for a film of $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ formed on ITO electrode (A = 1 cm²) immersed in CH₃CN. The supporting electrolyte is 0.1 M TBATBF₄. Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive. The surface coverage for $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ formed on ITO electrode is $2.4 \pm 0.08 \times 10^{-10}$ molcm⁻².

Figure 3.13b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$.



Figure 3.14a Cyclic voltammograms for a Ru-PVP:POM film of one depositing cycle formed on ITO electrode (A = 1 cm²) immersed in CH₃CN. The supporting electrolyte is 0.1 M TBATBF₄. Scan rates (top to bottom) were 50, 40, 30, 20 and 10 V s⁻¹. Anodic (oxidative) currents are positive. The ratio of surface coverage between Ru^{2+/3+} and $[S_2Mo_{18}O_{62}]^{4/5-}$ is 4.5±0.2:1 where Γ_{POM} = 3.02±0.3×10⁻¹¹ molcm⁻².

Figure 3.14b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+/3+}$ (blue) and $[S_2Mo_{18}O_{62}]^{4-/5-}$ (pink).



Figure 3.15a Cyclic voltammograms for a Ru-CO-P:POM film of one depositing cycle formed on ITO electrode (A = 1 cm²) immersed in CH₃CN. The supporting electrolyte is 0.1 M TBATBF₄. Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive. The ratio of surface coverage between Ru^{2+/3+} and $[S_2Mo_{18}O_{62}]^{4-/5-}$ is 4.5±0.2:1 where Γ_{POM} = 1.97±0.1×10⁻¹¹ molcm⁻².

Figure 3.15b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(CO-P PIC)_7]^{2+/3+}$ (blue) and $[S_2Mo_{18}O_{62}]^{4-/5-}$ (pink).

3.3.4 Photo-electrochemistry

Clear evidence of a new transition between $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and $[S_2Mo_{18}O_{62}]^{4-}$ within the Ru-PVP:POM film was observed in the UV-vis and confirmed in the Raman spectra. The influence of this new mode on the photocurrent intensity compared to Ru-CO-P:POM and $[S_2Mo_{18}O_{62}]^{4-}$ layers was determined using a 488 nm cut-off filter. The photo-electrochemistry of the Ru-PVP:POM film was measured using benzyl alcohol as both the contacting solvent and electron donor where TBATBF₄ (0.1 M) was used as supporting electrolyte. Comparative photocurrent experiments for Ru-CO-P:POM and $[S_2Mo_{18}O_{62}]^{4-}$ were acquired under identical conditions. The potential of the electrode was held at +0.4 V. If the reduced form of [POM-Ru] was generated in the presence of light, a current corresponding to oxidation of the [POM-Ru] adduct would be observed. The surface coverages, Γ , for the [Ru-POM] films were obtained where Γ for $[S_2Mo_{18}O_{62}]^{4-}$ within the adduct were measured as $3.0\pm0.3 \times 10^{-11}$ and $1.9\pm0.1 \times 10^{-11}$ molcm⁻² for Ru-PVP:POM and Ru-CO-P:POM, respectively.

The reaction sequence for the photo-oxidation of benzyl alcohol by the [POM-Ru] films is shown in Equation 3.1:

PHOTOEXCITATION: $[Ru-POM^{4-}] \rightarrow [Ru-POM^{4-}]^*$ (3.1) PHOTOCATALYSIS: $2[Ru-POM^{4-}]^* + C_6H_5CH_2OH \rightarrow 2[Ru-POM^{5-}] + C_6H_5CHO$ REOXIDATION: $[Ru-POM^{5-}] - e^- \rightarrow [Ru_2-POM^{4-}]$

Given the new vibrational mode at 900 cm⁻¹ and a long tail into the IR for Ru-PVP:POM found in the Raman spectrum and UV-vis spectroscopy, respectively. It might be anticipated that the photocurrent for benzyl alcohol oxidation by Ru-PVP:POM would be enhanced compared to that for Ru-CO-P:POM and $[S_2Mo_{18}O_{62}]^{4-}$ alone. Figure 3.16 confirms this expectation. No current was evident for any film at +0.4 V in the absence

of irradiation. White light, that was cut off below 488 nm, was used to irradiate these films and they produced currents of 38 ± 1 , 8.9 ± 0.8 and 9.7 ± 1.1 nAcm⁻², for the Ru-PVP:POM, Ru-CO-P:POM and $[S_2Mo_{18}O_{62}]^{4-}$, respectively. This photocurrent is substantially lower than those found for ruthenium dye sensitized TiO₂. [21] However, it is important to note that Grätzel type cells use iodine as the sacrificial donor and are not usually capable of photocurrent generation with donors such as benzyl alcohol or toluene that are challenging to oxidise. Poor photocurrents for all three films suggested slow ion diffusion through the film. In addition, the photocurrents increase slowly for illumination for times of the order of 100 seconds. The slow rate at which steady-state photocurrent through the layer. For example, taking the D_{CT} value for the Ru-PVP:POM adduct of $1.3\pm0.4\times10^{-11}$ cm²s⁻¹, it will take approximately 150 s to fully oxidise the film. Other factors that limit the overall photocurrent will be discussed in the next chapter.

Although relatively low intensity photocurrents were found for all three films, the Ru-PVP:POM film produced higher photocurrents than those found in Ru-Co-P:POM or [S₂Mo₁₈O₆₂]⁴⁻ alone. Therefore, these photocurrent experiments are consistent with photo-sensitization within Ru-PVP:POM films and this photo-sensitization is associated with the new charge-transfer transition. This result is significant since Raman spectroscopy and UV-vis spectroscopy reveal that this new optical transition, indicative of strong electronic communication, is only observed for the Ru-PVP:POM system. The observation that the catalytic efficiency of the Ru-PVP system is significantly greater than that of Ru-CO-P is important given that the redox and photophysical properties of the Ru-PVP and Ru-CO-P systems are indistinguishable. The most likely explanation lies with the counter ligands, i.e., the PIC ligands are bulkier than bipyridyl leading to a larger Ru-POM separation despite similar electronic communication between the PIC ligand and $[S_2Mo_{18}O_{62}]^{4-}$ compared to the PVP ligand as shown in UV and CV. In such circumstances, [Ru(bpy)₂(CO-P PIC)₇]²⁺ complex would possibly act as a filter to light reaching the polyoxometalate anion, thereby reducing the observed photocurrent relative to those found in the Ru-PVP:POM.



Figure 3.16 Photocurrent vs. time curves for thin films of Ru-PVP:POM (solid line), Ru-Co-P:POM (open circles) and $[Hx_4N]_4[S_2Mo_{18}O_{62}]$ (*) formed on ITO electrodes in contact with pure benzyl alcohol containing 1 mM TBATBF₄ as supporting electrolyte. The modified ITO electrodes were irradiated by an arc lamp source with a cut off filter below 488 nm that was initiated at t=0 and turned off at 100 s for the PVP-POM and POM films. The potential was continuously poised at 0.4 V.

3.3.5 Surface Topography

As described previously, the extent of electronic interaction between the polymeric ruthenium complex and the POM depends on subtle differences in the structural properties of the metallopolymer. According to the layer by layer method, the ITO electrode was firstly immersed in a 1 mM solution of $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ in ethanol or $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ in acetonitrile for 20 minutes. Following washing, this modified electrode was then immersed in a 1mM aqueous solution of $[S_2Mo_{18}O_{62}]^{4-}$ for 20 minutes. In this section, the structural properties of the films on an ITO electrode as determined using AFM for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ film are reported.

Figure 3.17-19 show the AFM images for bare ITO electrode, dip coated $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and the layer by layer Ru-PVP:POM, respectively. Figure 3.17 and 3.18 clearly demonstrate that the $[Ru(bpy)_2(PVP)_{10}]^{2+}$ film on the ITO electrode is non-continuous and that it possesses crystallites (with the diameter of approx. 95 nm). As mentioned previously in Scetion 2.3.6, the addition of $[Ru(bpy)_3]^{2+}$ triggers a major structural change in the film leading to the formation of a nanoporous crystalline film when $[S_2W_{18}O_{62}]^{4-}$ is present. This was not observed for Ru-PVP:POM as shown in Figure 3.19. Instead, Ru-PVP:POM forms a non-continuous film in the air. The thickness, however, for Ru-PVP:POM (approx. 350 nm measured from AFM) is dramatically thinner than for $[Ru(bpy)_3]_2[S_2W_{18}O_{62}]$ (approx. 3.5 µm measured from SEM).

Figure 3.20-21 show the AFM images of self assembled layers for $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ and Ru-CO-P:POM, respectively. Figure 3.17 and 3.20 clearly demonstrate that a uniform thin layer is observed for $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ on the ITO electrode. This thin layer of $[Ru(bpy)_2(CO-P PIC)_7](PF_6)_2$ possesses crystallines (with

the diameter of approx. 100 nm). However, like Ru-PVP:POM, a structural change is not observed for the Ru-CO-P:POM as shown in Figure 3.21 compared to Figure 3.20. The thickness, for Ru-CO-P:POM (approx. 520 nm) is thicker than for Ru-PVP:POM (approx. 350 nm). Therefore, it can be concluded that the subtle differences in the optical, electrochemical or structural properties of the metallopolymer play important roles in the extent of electronic interaction.



(a)

(b)



Figure 3.17 AFM images of a bare ITO electrode with scan size of (a) 1 μ m, (b) 5 μ m and (c) 10 μ m. Figure 17a-b is the close-up of the same area shown in Figure 3.17c.



(a)

(b)



Figure 3.18 AFM images of $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2]$ self assembled film formed on ITO electrode with scan size of (a) 1 µm, (b) 5 µm and (c) 10 µm. Figure 3.18a-b is the close-up of the same area shown in Figure 3.18c.







(b)



Figure 3.19 AFM images of Ru-PVP:POM film following one layer formed on an ITO electrode with scan size of (a) 1 μ m, (b) 5 μ m and (c) 10 μ m. Figure 3.19a-b is the close-up of the same area shown in Figure 3.19c.





(a)

(b)



Figure 3.20 AFM images of $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ self assembled film formed on an ITO electrode with scan size of (a) 1 µm, (b) 5 µm and (c) 10 µm. Figure 3.20a-b is the close-up of the same area shown in Figure 3.20c.





(b)



Figure 3.21 AFM images of Ru-CO-P:POM film following one dip coating cycle formed on an ITO electrode with scan size of (a) 1 μ m, (b) 5 μ m and (c) 10 μ m. Figure 3.21a-b is the close-up of the same area shown in Figure 3.21c.

2.4 CONCLUSION

In this chapter, photocatalysis using thin films of polyoxomolybdates sensitised with ruthenium containing metallopolymers using visible irradiation was described. Significantly, the efficiency of the photocatalysis depends markedly on the coordination sphere of the ruthenium centres even when their redox and photonic properties are very similar. Specifically, electrostatic thin films of Ru-PVP:POM and Ru-CO-P:POM have been investigated. Strikingly, despite their similar redox and photonic properties, an additional optical transition is observed in the Raman spectra of the Ru-PVP:POM film, which was not seen in the Ru-CO-P:POM film. Importantly, this electronic communication enhances the photocatalytic oxidation of benzaldehyde by a factor of more than three. While there is clear evidence for photosensitisation in the PVP polymers which is not present for the CO-P systems, the magnitude of the photocurrent, i.e., $38\pm1nAcm^{-2}$ for Ru-PVP:POM, is not as large as that expected for a system that is controlled by either benzyl alcohol diffusion or the kinetics of the reaction between the photocatalyst and benzyl alcohol. The magnitude of the photocurrent is consistent with the slow rate at which the catalytic centres are generated within the film (as described by the homogeneous charge transport diffusion coefficient, D_{CT}) and suggests that substantially higher photocurrents could be achieved by enhancing D_{CT}, e.g., by incorporating metal nanoparticles.[22-23]

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groups containing $[Ru(bpy)_2(CAIP)](ClO_4)_2$, where bpy is 2,2'-bipyridyl and CAIP is 2-(4-carboxyphenyl)imidazo[4,5-f] [1,10]phenanthroline. This manuscript is in preparation.

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CHAPTER FOUR

Optimization of Photocurrent Generation from Thin Films of Ruthenium Metallopolymer: Polyoxometalate Composites Using Visible Excitation

4.1 Introduction

In Chapter three, the properties of thin layers of an electrostatically associated adduct formed between the polyoxomolybdate, $[S_2Mo_{18}O_{62}]^{4-}$, and the metallopolymers $[Ru(bpy)_2(PVP)_{10}]^{2+}$ or $[Ru(bpy)_2(CO-P PIC)_7]^{2+}$ have been deposited onto electrodes using the layer-by-layer technique were described, where PVP is poly(4-vinylpyridine), bpy is 2,2 -bipyridyl, CO-P is poly[(4-(aminomethyl)styrene)1 (4-vinylpyridine)₆] and PIC is 2-(4-carboxyphenyl) imidazo [4,5-f][1,10] phenanthroline. Raman spectroscopy reveals that the RuPVP:POM films exhibit an additional vibrational mode at 900 cm⁻¹ that is not present in either of the components suggesting significant electronic communication between the ruthenium centres and the polyoxomolybdate. Despite the similarity of their redox and photonic properties, this optical transition is absent in the Ru-Co-P:POM layers. Significantly, the Ru-PVP:POM films (8.9±0.8 nA cm⁻²) or $[S_2Mo_{18}O_{62}]^{4-}$ films (9.7±1.1 nA cm⁻²).[1]

However, this photocurrent is approximately four orders of magnitude lower than those found for ruthenium dye sensitized TiO_2 .[2] A number of key issues and barriers that limit the photocurrent generated by Ru-PVP:POM are addressed in this chapter. These issues are firstly, the rate at which mediated sites are regenerated as controlled by the charge transport diffusion coefficient, D_{CT} . Secondly, the surface coverages of the film on the electrode. Thirdly, the rate at which electron transfer occurs at the electrode/film interface. Fourthly, transport of electron donors across the film:sample interface.

Three approaches are made to overcome these limitations; they are (1) to increase the surface coverages of the film on the electrode. According to Equation 2.3, the current through the film is limited by the total number of moles of the photocatalyst deposited and the rate of charge transport. This limitation can be overcome by using a higher

concentration of electrolyte and increasing the surface coverage of the adduct on the electrode surface. A number of different surface coverages of the film can be produced by repeated diping during film formation. However, the choices for electrolytes and their concentrations could be problematic since the film formation is based on electrostatic attractive force, where high concentrations of electrolyte disrupt the ion pairing within the film and loss of material from the electrode surface. Therefore, the effects of electrolyte concentration on film properties were not studied. The second approach is to increase the rate constant for heterogeneous electron transfer at the electrode. The substantially lower photocurrent generation for the Ru-PVP:POM film is partly due to the slow electron transfer process at the electrode which can be optimized by applying a large driving force. Thirdly, the efficiency of the Ru-PVP:POM film can be enhanced by optimizing concentrations of substrate such as benzyl alcohol on the film. This is important since the diffusion of benzyl alcohol can influence the photocatalysis step in which [Ru-POM⁵⁻] is generated from [Ru-POM⁴⁻]^{*}.

4.2 **Results and Discussion**

4.2.1 Film thickness

The performance of dye-sensitized POM-based photovoltaic devices depends on the quantity of photocatalyst present on the electrode surface.[3] Four different surface coverages of the Ru-PVP:POM film were prepared by alternate layer deposition. The electrochemical behavior of these four different surface coverages of the film has been probed using cyclic voltammetry. Amperometric *i*-*t* measurement was used to record the generated photocurrent by these four different films.

In order to probe the influence of the surface coverage on the performance of Ru-PVP:POM films, the electrochemical properties of films using two, three, five and seven deposting cylces were investigated. Figure 4.1 illustrates the voltammetric behaviours of Ru-PVP:POM films for one, two, three, five and seven dip coated cycles on ITO electrodes at a scan rate of 50 mV s⁻¹ with 0.1 M TBATBF₄ as the supporting electrolyte. For all films, Figure 4.1 shows that well defined redox waves are present for both the Ru^{2+/3+} and POM^{4-/5-} redox processes. The formal potential and surface coverages for various dip coated cycled [POM-Ru] films are shown in Table 4.1.
No. of layers	Surface coverage (Γ, mol cm ⁻²)		Formal potential (E ⁰ / v)	
	Ru ^{2+/3+}	POM4-/5-	Ru ^{2+/3+}	POM4-/5-
1	$1.3 \pm 0.06 \times 10^{-10}$	$3.0 \pm 0.02 \times 10^{-11}$	0.929	0.163
2	$2.4 \pm 0.07 \times 10^{-10}$	$6.3 \pm 0.04 imes 10^{-11}$	0.946	0.214
3	$3.1 \pm 0.04 \times 10^{-10}$	$7.2 \pm 0.08 \times 10^{-11}$	0.957	0.23
5	$5.3 \pm 0.06 imes 10^{-10}$	$7.5 \pm 0.02 \times 10^{-11}$	0.937	0.253
7	$7.7 \pm 0.07 \times 10^{-10}$	$7.4 \pm 0.01 \times 10^{-11}$	0.925	0.26

Table 4.1 $E^{o'}$ (V vs. Ag/Ag⁺) and associated surface coverage (Γ , mol cm⁻²) for [Ru-PVP:POM] films with different numbers of layers formed on ITO electrodes. The solvent and supporting electrolyte are CH₃CN (0.1 M TBATBF₄)(A=1 cm²). The surface coverages for all film were recorded at the scan rate of 10 mVs⁻¹.

It is noticed that $E^{0'}$ of the $Ru^{2+/3+}$ process was essentially unaffected by the number of layers while the $E^{0'}$ for the POM^{4-/5-} process exhibited a slightly positive shift as the number of dip cycles increased. The peak current versus number of depositing cycles for the $Ru^{2+/3+}$ and POM^{4-/5-} redox processes are plotted in Figure 4.2. The peak currents for the $Ru^{2+/3+}$ process rose linearly with layer number indicating effective deposition. In contrast, the peak current for the POM^{4-/5-} process increases more gradually with an increasing layer number until n=5, n is number of depositing cycles, when the current shows deviation from a normal linear relationship. This nonlinearity is attributed to the electron transfer through the film becoming slower with increasing depositing cycles and distance from the electroactive site to the surface of electrode increases, which were illustrated by Wang.[4]

The surface coverage for both the ruthenium and POM centers was measured by recording the charge passed under each wave in the background corrected cyclic voltammogram recorded at 10 mVs⁻¹. The Ru:POM ratio for one dip coating cycle was reported in Chapter three as 4.5 ± 0.2 :1 [1] and this ratio of 4.5 ± 0.2 :1 is expected to remain constant with increasing the layer number. However, Figure 4.3 shows that the

Ru:POM ratio obtained from the cyclic voltammograms for two, three, five and seven dip coating cycle were $4.5\pm0.2:1$, $4.3\pm0.3:1$, $4.0\pm0.1:1$, $7.1\pm0.4:1$ and $10.0\pm0.3:1$, respectively. These changing ratios may be due to the structure of $[S_2Mo_{18}O_{62}]^{4-}$ and a similar observation was reported by Dong, in which less SiW₁₂ in each film after 8 deposition was observed in CoTMPyP:SiW₁₂, where CoTPPyP is [tetrakis(Nmethylpyridyl)porphyrinato] Cobalt (Scheme 4.1) but was not observed in CoTMPyP:PW₁₈. [5] Figures 4.4-4.8 show that the peak current for both the ruthenium and POM centres varies linearly with the square root of scan rate for scan rates between 10 and 50 mVs⁻¹, suggesting that semi-infinite linear diffusion controls the rate of charge transport through these films. In addition, Figure 4.4c shows the plot of i_{pa} vs log of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and indicates that solution behavior dominates the rate of charge transport through these films.

The influence of the surface coverages on the photocurrent generated for Ru-PVP:POM film with two, three, five and seven layers in the presence of benzyl alcohol was determined. The potential of the electrode was held at +0.4 V (vs. Ag/Ag⁺) to re-oxidize the POM⁵⁻ generated by the photo-oxidation of benzyl alcohol. Figures 4.9-4.11 show photocurrent-time curves for the photooxidation of benzyl alcohol (100% V/V) by two, three and five dip coated cycled Ru-PVP:POM on ITO in acetonitrile (0.1 M TBATBF₄) at a potential of 0.4 V (vs. Ag/Ag⁺) with T = 298 K. The average photocurrents generated for the Ru-PVP:POM films with two, three, five and seven dip coated cycles using a 488 nm cut-off filter are 46±4.8, 70±2.3, 60±3.1 and 48±2.7 nA, respectively. Although the total surface coverages for Ru is increasing with layer number, the photocurrent produced by Ru-PVP:POM is partly limited by the thickness of the film, i.e., as the number of deposition increase over n=3, there is less POM than Ru in each film than in the preceding film. The photocurrent is lower for n>3 compared to those found for n=1 or 2.



Scheme 4.1 Structure of CoTMPyP.



Figure 4.1 Cyclic voltammograms for (a) one, (b) two, (c) three, (d) four and (e) seven layered Ru-PVP:POM films on ITO electrodes immersed in CH_3CN (0.1 M TBATBF₄)(A=1 cm²; v=30 mVs⁻¹).



Figure 4.2 Plots of peak current vs number of layers for (a) $[Ru-PVP]^{2+/3+}$ and (b) $[POM]^{4-/5-}$ processes of Ru-PVP:POM films on ITO electrodes (A=1 cm²) immersed in CH₃CN. The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 10 mVs⁻¹, respectively.



Figure 4.3 Plots of surface coverage vs number of layers for (a) $[Ru-PVP]^{2+/3+}$ and (b) $[POM]^{4-/5-}$ processes of Ru-PVP:POM films on ITO electrodes (A=1 cm²) immersed in CH₃CN. The supporting electrolyte and scan rate are 0.1 M TBATBF₄ and 10 mVs⁻¹, respectively.



Figure 4.4a Cyclic voltammograms for a one layered Ru-PVP:POM film on an ITO electrode immersed in CH₃CN (0.1 M TBATBF₄)(A=1 cm²). Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive.

Figure 4.4b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ (top) and $[S_2Mo_{18}O_{62}]^{4-}$ (bottom).



Figure 4.4c Plot of i_{pa} vs log of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$.



Figure 4.5a Cyclic voltammograms for a two layered Ru-PVP:POM film on an ITO electrode immersed in CH₃CN (0.1 M TBATBF₄)(A=1 cm²). Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive.

Figure 4.5b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ (top) and $[S_2Mo_{18}O_{62}]^{4-}$ (bottom).



Figure 4.6a Cyclic voltammograms for a three layered Ru-PVP:POM on an ITO electrode immersed in CH₃CN (0.1 M TBATBF₄)(A=1 cm²). Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive.

Figure 4.6b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ (top) and $[S_2Mo_{18}O_{62}]^{4-}$ (bottom).



Figure 4.7a Cyclic voltammograms for a five layered Ru-PVP:POM films on an ITO electrode immersed in CH₃CN (0.1 M TBATBF₄)(A=1 cm²). Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive.

Figure 4.7b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ (top) and $[S_2Mo_{18}O_{62}]^{4-}$ (bottom).



Figure 4.8a Cyclic voltammograms for a seven layered Ru-PVP:POM film on an ITO electrode immersed in CH₃CN (0.1 M TBATBF₄)(A=1 cm²). Scan rates (top to bottom) were 50, 40, 30, 20 and 10 mV s⁻¹. Anodic (oxidative) currents are positive.

Figure 4.8b Plot of i_{pa} vs square root of scan rate for $[Ru(bpy)_2(PVP)_{10}]^{2+}$ (top) and $[S_2Mo_{18}O_{62}]^{4-}$ (bottom).



Figure 4.9 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a two layered [Ru-PVP:POM] film on an ITO electrode in acetonitrile (0.1 M TBATBF₄) at a potential of +0.4 V (vs. Ag/Ag⁺). A filter cut off light below 488 nm.



Figure 4.10 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a three layered [Ru-PVP:POM] film on an ITO electrode in acetonitrile (0.1 M TBATBF₄) at a potential of +0.4 V (vs. Ag/Ag^+) with T = 298 K. A filter cut off light below 488 nm.



Figure 4.11 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a five layered [Ru-PVP:POM] film on an ITO electrode in acetonitrile (0.1 M TBATBF₄) at a potential of +0.4 V (vs. Ag/Ag^+) with T = 298 K. A filter cut off light below 488 nm.

4.2.2 Potential dependence study of [Ru-POM⁴⁻] reoxidation

As discussed previously, it is clear that the photocurrent produced for the Ru-PVP:POM films was lower compared to ruthenium dye sensitized TiO₂.[2] A possible explanation is the slow electron transfer at the electrode. This is important since the photocurrent generation for the [POM-Ru] film in the presence of benzyl alcohol will be influenced by the rate of heterogeneous electron transfer, i.e., the rate of the [Ru-POM⁵⁻] oxidation process. Notably, according to Equation 4.2, the rate constant for heterogeneous electron transfer depends on the potential and the larger the overpotential the faster the electron transfer process will be. Therefore, the rate of the [Ru-POM⁵⁻] oxidation process can then be optimized by changing the applied potential:

$$k = k^{0} \exp \left[(1 - \alpha) f(E - E^{0'}) \right]$$
(4.2)

where k (s⁻¹) is the heterogeneous electron transfer rate, k⁰ is the standard heterogeneous electron transfer rate constant at equilibrium, α is the transfer coefficient, f is F/RT, E is applied potential and E⁰ is the formal potential at equilibrium.

Figures 4.12-4.16 illustrate the photocurrent-time curves for the Ru-PVP:POM film following one dip coating cycle on an ITO electrode where benzyl alcohol acts as both the electron donor and the solvent for the supporting electrolyte, TBATBF₄ (0.1 M). The potential was systematically varied from +0.4, 0.5, 0.6, 0.7 and 0.8 V and the resulting photocurrent was measured. Irradiation of the film in the presence of benzyl alcohol with white light that is cut off below 488 nm at these potentials yielded photocurrents, which are listed in Table 2. It is obvious that the Ru-PVP:POM film produced significantly more current at +0.8 V than those found at lower potentials. These current-time curves indicate that the magnitude of the overall photocurrent increases with increasing overpotential, indicating that the rate of heterogeneous electron transfer clearly influences the magnitude of the photocurrent.

As mentioned previously, thermodynamic information about the electron transfer process can be obtained from these photocurrent data. The photocurrent produced from the experiments was normalized to unit area to provide current density. The overpotential was determined using the formal potential, $E^{0'}$, for POM^{4-/5-} redox process of 0.163 V.

Potential	Photocurrent generated by [POM-Ru]
(V)	(nA)
0.4	30±1.9
0.5	43±1
0.6	56.7±1.5
0.7	72.7±2.3
0.8	100.0±6.6

Table 4.2 The impact of different applied potentials on photocurrent generation at a Ru-PVP:POM film following one dip coating cycle on an ITO electrode in acetonitrile (0.1 M TBATBF₄). A filter was used to cut off light below 488 nm.

Figure 4.17 shows the current density-overpotential curves for the reoxidation of [POM⁵⁻-Ru] to [POM⁴⁻ Ru]. Significantly, the current density increases exponentially with increasing overpotential which is consistent with the Butler-Volmer Equation (2.4). The inset graph is a plot of log i versus overpotential, i.e., Tafel Plot, for the reoxidation of [Ru-POM⁵⁻] to [Ru-POM⁴⁻] The Tafel slope was employed to determine the transfer coefficient and current at $E_{equilibrium}$, i₀ using Equation 2.3, which are 0.92±0.01 and 0.015 μ A, respectively. As mentioned previously, the transfer coefficient is regarded as an indicator of the symmetry of the barrier to reaction and therefore, the transfer coefficient of 0.92±0.01 obtained from the Tafel Plot indicates that the barrier is unusually asymmetric making the activation energy for the forward (oxidation) process significantly lower than that for the backward (reduction) process



Figure 4.12 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a one layered [Ru-PVP:POM] film onto an ITO electrode with 0.1 M TBATBF₄ as supporting electrolyte at a potential of +0.4 (vs. Ag/Ag⁺). A filter cut off light below 488 nm.



Figure 4.13 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a one layered [Ru-PVP:POM] film onto an ITO electrode with 0.1 M TBATBF₄ as supporting electrolyte at a potential of +0.5 (vs. Ag/Ag⁺). A filter cut off light below 488 nm.



Figure 4.14 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a one layered [Ru-PVP:POM] film onto an ITO electrode with 0.1 M TBATBF₄ as supporting electrolyte at a potential of +0.6 (vs. Ag/Ag⁺). A filter cut off light below 488 nm.



Figure 4.15 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a one layered [Ru-PVP:POM] film onto an ITO electrode with 0.1 M TBATBF₄ as supporting electrolyte at a potential of +0.7 (vs. Ag/Ag⁺). A filter cut off light below 488 nm.



Figure 4.16 Photocurrent-time curves for the photooxidation of benzyl alcochol (100% V/V) by a one layered [Ru-PVP:POM] film onto an ITO electrode with 0.1 M TBATBF₄ as supporting electrolyte at a potential of +0.8 (vs. Ag/Ag^+). A filter cut off light below 488 nm.



Figure 4.17 The current-overpotential curve for the conversion of [Ru-POM⁵⁻] to [Ru-POM⁴⁻] on an ITO electrode in benzyl alcohol (0.1 M TBATBF₄) with $\alpha = 0.92\pm0.01$. The graph is a plot of log *i* versus η for the oxidation of [Ru-POM⁵⁻] to [Ru-POM⁴⁻] on ITO.

4.2.3 Optimized system

As described previously, the optimum overpotential and numbers of layers have been identified. Therefore, having identified the optimum potential as +0.8 V and the number of layers as three, the performance of a modified surface under these conditions, was investigated in benzyl alcohol (100% V/V) where the supporting electrolyte is 0.1 M TBATBF₄.

Figure 4.18 shows the current-time curve for the photo-oxidation of benzyl alcohol by using a three layered Ru-PVP:POM film on ITO at +0.8 V. The optimized system produced a greater photocurrent (183.6 ± 17.6 nA) than those found in other systems.



Figure 4.18 Photocurrent-time curves for the photooxidation of benzyl alcohol (100% V/V) by a three layered [Ru-PVP:POM] film on an ITO electrode in acetonitrile (0.1 M TBATBF₄) at a potential of +0.8 V (vs. Ag/Ag⁺). A filter cut off light below 488 nm.

4.2.4 Concentration of Benzyl Alcohol

Figure 4.19 shows the effect of various concentrations of benzyl alcohol on the cyclic voltammetry of bare ITO and one layered [Ru-PVP:POM] film in the absence of light. All the electrochemical experiments were performed at a scan rate of 50 mV s⁻¹ with TBATBF₄ (0.1 M) as the supporting electrolyte. The relevant voltammtric data are summarized in Table 4.3. Clearly defined redox waves associated with both the POM and the ruthenium centre were present both in the absence and presence of benzyl alcohol. The formal potential for Ru^{2+/3+} process is unaffected by varying the benzyl alcohol concentration. In contrast, Figure 4.19 reveals that the formal potential of the POM moiety shifts by approximately 50±3 mV from benzyl alcohol concentration of 0 % (V/V) to 100 % (V/V). These shifts found indicate dielectric and environmental effects influence the POM E^{0°}. Notably, there was no obvious increase in current apparent in either Ru^{2+/3+} or POM^{4-/5-} redox processes in the absence of light, confirming that there is no ground state catalysis.



Figure 4.19 Cyclic voltammograms for a one layered [Ru-PVP:POM] films formed on an ITO electrode immersed in CH₃CN (0.1 M TBATBF₄)(A=1 cm²; v=50 mVs⁻¹) in various concentration of benzyl alcohol. The benzyl alcohol concentrations from (a) to (f) are 0, 20, 40, 60, 80 and 100 % (V/V).

Benzyl alcohol concentration %(V/V)	Redox process (P=[S2M018O62]
	Ru ^{2+/3+} (V)	P ^{4-/5-} (V)
0	0.929	0.163
20	0.931	0.194
40	0.936	0.199
60	0.940	0.202
80	0.951	0.211
100	0.952	0.214

Table 4.3 The impact of different concentrations of benzyl alcohol on $E^{0^{\circ}}$ (V vs. Ag/Ag⁺) values for a one layered [Ru-PVP:POM] film on an ITO electrode in CH₃CN (0.1 M TBATBF₄)(A=1 cm²; v=50 mVs⁻¹).

4.4 CONCLUSIONS

This chapter describes the overall photocurrent obtained at a [Ru-PVP:POM] film that was optimized by identifying key limiting factors; (1) increasing the applied potential speeds up the heterogeneous electron transfer at the electrode. The magnitude of photocurrent increased with increasing potential, indicating that the photo-oxidation of the benzyl alcohol by the [Ru-PVP:POM] film is at least partly kinetically limited. (2) Increasing the surface coverages of the [Ru-PVP:POM] film on ITO increases the magnitude of the photocurrent produced, i.e., three layered [Ru-PVP:POM] film produces the most photocurrent at a Ru:POM ratio of $4.0\pm0.1:1$. Finally, the conclusive experiment involving three dip coated cycled [Ru(bpy)₂(PVP)₁₀]₂[S₂Mo₁₈O₆₂] self assembled film in the presence of benzyl alcohol (100% V/V) in 0.1 M TBATBF₄ with potential held at +0.8 V was carried out. The optimized system produced more photocurrent (183.6±17.6 nA) than those found in other systems.

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CHAPTER FIVE

Photocatalytic Properties of Thin Films of Ruthenium Metallopolymers / Gold Nanoparticle: Polyoxometalate Composites Using Visible Excitation

5.1 Introduction

As mentioned previously in Chapter three, the relatively low photocurrents are consistent with catalytic centres which are regenerated within the film (as described by the homogeneous charge transport diffusion coefficient, D_{CT}) at a slow rate and suggests that substantially higher photocurrents could be achieved by enhancing the D_{CT} , e.g., by incorporating metal nanoparticles.[1-2] Metal nanoparticles are a subject of great interest due to their many advantages compared to those of the bulk metal. There are two primary features of metal nanoparticles that are relevant to this work, i.e., the presence of a localized surface plasmon band may modulate the excited state properties and adding them to the metallopolymers may increase the films overall conductivity.

Metallic surfaces strongly influence the emission characteristics of luminophores. In part, the rate of radiative decay of the luminophore controls the sensitivity in fluorescence and this rate can be changed by placing the luminophore in a suitable distance from a metal nanoparticle. Depending on the distance, d, that separates a luminophore from the metal surface, either quenching (d<10 nm) or metal-enhanced emission (20<d<50 nm) are possible.[3] For example, gold nanoparticles (AuNP) have been shown to quench the photoluminescence of the ruthenium metallopolymer by a static quenching mechanism.[1]

Localized surface plasmons involve the collective oscillation of electrons within a metal film or particle.[4] When electromagnetic radiation at the appropriate wavelength is incident on such metal nanoparticles, the electromagnetic field of the incoming light increases the amplitude of the plasmon field oscillations. These localized surface plasmons result in two important effects: Firstly, the localized surface plasmon absorption. This localized surface plasmon absorption is attributed to the frequency of incident light being resonant with the frequency of oscillation of the electrons of the nanoparticles. Secondly, localized surface plasmons result in a substantial increase in the intensity of Raman scatter and fluorescent intensity, which is a major contributor towards

the enhancement of the intensity observed in surface enhanced Raman scattering and metal enhanced fluorescence.[5-10]

The conductivity of thin films of ruthenium metallopolymers can be improved by incorporating metal nanoparticles.[1] When close-packed, the metal nanoparticles promote fast electron hopping and could therefore, increase the catalytic rate. Devadoss *et al* reported that the homogeneous charge transport diffusion coefficient, D_{CT} value for the nanocomposites containing gold nanoparticles and a ruthenum metallopolymer is approximately seven times larger at the optimum loading than that observed for the pure metallopolymer.[1] A similar improvement in the rate of charge transport was also described by Brennan,[11] in which the D_{CT} value increased two orders of magnitude for nanocomposite polymer films in neutral electrolyte.

As mentioned previously, the slow rate at which the catalytic centres are generated within the RuPVP:POM film influences the photocatalytic current. Therefore, the objective of this chapter was to incorporate gold nanoparticles into ruthenium metallopolymer-POM film and determine if there was a significant increase in photocatalysis. In order to achieve this objective, a solution of the ruthenium metallopolymers and gold nanoparticles were mixed at different molar ratios of ruthenium centres to nanoparticles. Then, a RuPVP-AuNP:POM film was formed using the layer-by-layer technique. The polycationic metallopolymer (Scheme 3.1) and the DMAP-protected gold nanoparticle,(Scheme 5.1) [Ru(bpy)₂(PVP)₁₀](ClO₄)₂ have been used; PVP is poly(4vinylpyridine), bpy is 2,2'-bipyridyl, DMAP is 4-dimethylaminopyridine.

The electronic communication between the nanocomposite and the polyoxometalate anions within the film was investigated using UV-vis spectroscopy and Resonance Raman microscopy. Cyclic voltammetry was employed to study the electrochemical properties of the films and the photocatalytic current was measured using benzyl alcohol as the substrate under visible irradiation. The structure of the Ru-PVP-AuNP:POM film was investigated using scanning electron microscopy.



Scheme 5.1 Structure of the DMAP protected gold nanoparticles.

5.2 Experimental

5.2.1 Materials

Acetonitrile (CH₃CN; LabScan) was of HPLC or spectroscopic grade. Recrystallised tetrabutylammonium tetrafluoroborate (TBATBF₄; Fluka) was used as the supporting electrolyte in electrochemical and photo-electrochemical studies. $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$, { $[Hx_4N]_4[S_2Mo_{18}O_{62}]$ } and DMAP-protected Au nanoparticle (AuNP) were synthesised using a literature procedures.[1-2]

5.2.2 Preparation of Nanocomposite solution of [RuPVP-AuNP]

A composite solution of [RuPVP-AuNP] was made by mixing the $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ and DMAP-protected AuNP together. The molar concentration of the Au nanoparticle was maintained constant at 12 µM and the required volume of the aqueous conc. solution of $[Ru(bpy)_2(PVP)_{10}](ClO_4)_2$ was then added to give the required mole ratio of 48 to 1 Ru:AuNP and 6 to 1.

5.2.3 Preparation of films of [RuPVP-AuNP:POM]

Two types of the films were deposited. Firstly, thin films of the [RuPVP-AuNP:POM] were created using layer by layer as illustrated in Scheme 3.2. Indium tin oxide, ITO, electrodes (Delta Technologies Ltd., Stillwater, MN, USA were immersed in a composite solution of [RuPVP-AuNP] of mole ratio 48:1 to 6:1 for 20 minutes. This modified electrode was then immersed in a solution of [S₂Mo₁₈O₆₂]⁴⁻ (576 and 72 μ M for 48:1 and 6:1, respectively) for 20 minutes. After each immersion, the electrode was repeatedly washed with CH₃CN to remove any un-bound material. Secondly, drop-cast composite films of [RuPVP-AuNP:POM] at the required nanoparticle mole ratio were made by drop-casting pre-mixed solutions of [RuPVP-AuNP:POM] onto the ITO electrode (A = 1 cm²). These pre-mixed solutions of [RuPVP-AuNP:POM] were made by mixing solutions of [RuPVP-AuNP] and [S₂Mo₁₈O₆₂]⁴⁻ solution at mole ratio of 1:1.

5.2.4 Instrumentation and Procedure.

Cyclic voltammetry was performed in a conventional three-electrode cell with a CH Instruments Model 660a electrochemical workstation. All measurements were performed at 25 ± 2 °C and all solutions were deoxygenated with N₂. The reference electrode was Ag/AgCl and the counter electrode was a large area platinum wire coil. The surface coverages were determined by graphical integration of background corrected cyclic voltammograms and films were scanned first until stable.

The photocurrent was measured using the cell as illustrated in Scheme 3.3. The substrate for photocatalytic oxidation was pure benzyl alcohol containing 0.1 mM tetrabutylammonium tetrafluoroborate (TBABF₄) as the supporting electrolyte. The white light source was an Oriel 68811 arc lamp employing a 350 W Xe bulb which was focused onto the film (1 cm^2) . A filter was used to cut off light below 488 nm so as to preferentially excite into the metallopolymer metal-to-ligand charge transfer, MLCT. The potential was held at +0.4 V so as to re-oxidise the reduced POM following benzyl alcohol oxidation.

UV-vis spectra of the films on ITO were recorded using a Jasco V-670 UV/Vis/NIR spectrophotometer.

Resonance Raman microscopy was performed on a confocal HR micro-Raman setup (HR800, Jobin-Yvon, Horiba) with an 1800 groves/mm grating. The 514, 488 and 450 nm lines of an argon ion laser (Coherent, Innova) were employed for excitation and the scattered light was collected in an 180° alignment. The acquisition time was typically 20s.

Scanning Electron Microscopy was performed on a Hitachi S5500 FeSEM.

5.3 Results and Discussion

5.3.1 UV-vis characterisation

As mentioned in Section 5.1, when electromagnetic radiation at the appropriate wavelength is incident on metal nanoparticles, the electromagnetic field of the incoming light increases the amplitude of the plasmon field oscillations. These localized surface plasmons result in a localized surface plasmon absorption, which is found in the UV-vis region of the spectrum. Furthermore, strong electronic communication was found between ruthenium metallopolymer and polyoxometallate within [RuPVP:POM] film as described in Chapter three. Therefore, the objective of this section was to determine whether there is a broad surface plasmon absorption band present for the [RuPVP-AuNP:POM] films and if any changes arise for the nanocomposite compared to the pure [RuPVP:POM] film by using UV-vis spectroscopy.

An intense broad absorption peak is expected around 500-550 nm for Au nanoparticles arising from the surface plasmon resonance (SPR).[12-13] The plasmon band is sensitive to the surrounding environment, e.g., dielectric changes and surface binding. For example, the TOAB-protected Au nanoparticles exhibit a plasmon absorption band at 531 nm in toluene, whereas DMAP-Au NPs exhibit a plasmon absorption band at 524 nm. Figure 5.1(a-b) shows the absorption spectra for dip coated thin films of [RuPVP-AuNP] of ruthenium to Au nanoparticle mole ratio of 6:1 and 48:1, respectively. Significantly, broad surface plasmon absorption bands are observed at approximately 597 and 558 nm for the [RuPVP-AuNP] film at ratios of 6:1 and 48:1 in Figure 5.1 which are not seen in the pure metallopolymer. The absorption band present at 597 nm in Figure 5.1a is shifted to approximately 558 nm in Figure 5.1b, which is consistent with finding that the plasmon band is sensitive to the surrounding environment, i.e., it is assumed that the shift in the wavelength of the plasmon absorption is attributed to more ruthenium centres surrounding Au nanoparticles.
However, a long tail into the IR region unapparent in the layer by layer (LBL) film is observed in the absorption spectra of pre-assembled drop-cast composite systems as shown in Figure 5.3. Figure 5.3a-b show the absorption spectra for drop cast [RuPVP-AuNP:POM] pre-assembled composite film at 6:1 and 48:1 ratios. The plasmon absorption bands are both present in Figure 5.3a and Figure 5.3b. Therefore, these absorption spectra suggest that there is a new optical transition in the composite but not in the LBL films. This finding is significant and Resonance Raman spectroscopy was employed to assign the features of the new optical transition matched in the absorption spectra.



Figure 5.1 UV-vis spectra for dip coated thin films of [RuPVP-AuNP] at an ruthenium to Au nanoparticle molar ratios of (**a**) 6:1 and (**b**) 48:1, respectively on an ITO electrode. The Γ_{Ru} for thin films of [RuPVP-AuNP] of ruthenium to Au nanoparticle molar ratios of (**a**) 6:1 and (**b**) 48:1 on ITO electrodes are $0.8 \pm 0.12 \times 10^{-11}$ molcm⁻² and $7.9 \pm 0.32 \times 10^{-11}$ molcm⁻², respectively.



Figure 5.2 UV-vis spectra for dip coated thin films of [RuPVP-AuNP:POM] at an ruthenium to Au nanoparticle molar ratios of (**a**) 6:1 and (**b**) 48:1, respectively on an ITO electrode. The surface coverages of [RuPVP-AuNP]^{2+/3+} and POM^{4-/5-} for [RuPVP-AuNP:POM] at ruthenium to Au nanoparticle molar ratios of (**a**) 6:1 and (**b**) 48:1 are $1.51\pm0.24\times10^{-11}$ molcm⁻² and $5.12\pm0.45\times10^{-12}$ molcm⁻², $8.13\pm0.15\times10^{-11}$ molcm⁻² and $1.32\pm0.21\times10^{-12}$ molcm⁻², respectively.



Figure 5.3 UV-vis spectra for drop cast composite films of [RuPVP-AuNP:POM] where the ruthenium to Au nanoparticle molar ratios are (**a**) 6:1 and (**b**) 48:1 on an ITO electrode. The surface coverages of [RuPVP-AuNP]^{2+/3+} and POM^{4-/5-} for [RuPVP-AuNP:POM] at ruthenium to Au nanoparticle molar ratios of (a) 6:1 and (b) 48:1 are $5.9 \pm 0.21 \times 10^{-11}$ molcm⁻² and $1.3 \pm 0.21 \times 10^{-11}$ molcm⁻², $2.4 \pm 0.19 \times 10^{-10}$ molcm⁻² and $4.0 \pm 0.23 \times 10^{-11}$ molcm⁻², respectively.

5.3.2 Resonance Raman Spectroscopy

As mentioned in Chapter three, there is significant electronic interaction between the ruthenium metallopolymer and the polyoxometalate as evidenced by the presence of an additional mode in the Raman spectrum of the film at 900 cm⁻¹.[2] Therefore, Resonance Raman spectroscopy was employed to characterise the electronic communication between the ruthenium metallopolymer nanocomposite and polyoxometalate anions within the film. Here, an excitation wavelength of 514 nm was used which is post-resonant with the ruthenium MLCT transition. However, but 514 nm excitation was also used to directly excite the NP plasmon.

Figure 5.4a-c and Figure 5.5a-c show the Raman spectra, with an excitation wavelength of 514 nm, for drop cast and LBL deposited thin films of [RuPVP-AuNP:POM] for ruthenium to Au nanoparticle molar ratios of 6:1 and 48:1, respectively. The 514 nm excitation wavelength is post-resonant with the ruthenium metallopolymer MLCT at 450 nm, and as described previously in Chapter three, the spectra produced from 514 nm excitation wavelength exhibits enhanced features compared to those recorded using excitation wavelengths of 450 or 488 nm. Significantly, a new broad feature apparent at 900 cm⁻¹ in the [RuPVP:POM] film is not observed in the [RuPVP-AuNP:POM] film formed by layer by layer film but is present in the drop cast composite system. In common with the [RuPVP-AuNP] films with a mole ratio of 48:1, films based on a [RuPVP-AuNP] of 6:1, exhibit six signature bipyridyl vibration modes at 1604, 1558, 1488, 1418, 1320 and 1189 cm⁻¹ from the Ru ($d\pi$) to bpy (π^*) MLCT and the Ru-N mode is also present at 370 cm⁻¹. Figure 5.4a and Figure 5.5a show that the [RuPVP-AuNP:POM] composite films with ratios of 6:1 and 48:1 contain the signature bipyridyl mode but, in addition, a new broad feature apparent at approximate 920 cm⁻¹ that is not present in either the [RuPVP-AuNP] or $[S_2Mo_{18}O_{62}]^{4-}$ spectra. This indicates that the new transition is present in [RuPVP-AuNP:POM] composite films and is centred at higher wavelength than the [Ru-PVP:POM] films formed by the LBL technique.

Therefore, these Raman spectra, together with absorption spectra, suggest that there is a new optical transition in the pre-assembled composite. This observation is significant and suggests that the extent of electronic interaction between the gold nanoparticle, the polymeric ruthenium metallopolymer and the POM depends on subtle differences in the structural properties of the film. The surface topography of the layer by layer and composite films of [RuPVP-AuNP:POM] was probed by using scanning electron microscopy.

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Figure 5.4 Resonance Raman spectra, with an excitation wavelength of 514nm for (a) 6:1 [RuPVP-AuNP:POM] drop cast pre-assembled composite film on an ITO slide, (b) 6:1 [RuPVP-AuNP] dip coating layer by layer film on an ITO slide, (c) 6:1 [RuPVP-AuNP:POM] dip coated layer by layer film on an ITO slide, (d) blank ITO slide. The Γ_{Ru} for (a), (b) and (c) are 5.9×10^{-11} molcm⁻², 0.8×10^{-11} molcm⁻² and 1.5×10^{-11} molcm⁻², respectively.



Figure 5.5 Resonance Raman spectra, with an excitation wavelength of 514nm for (a) 48:1 [RuPVP-AuNP:POM] drop cast pre-assembled composite film on an ITO slide, (b) 48:1 [RuPVP-AuNP] dip coating layer by layer film on an ITO slide, (c) 48:1 [RuPVP-AuNP:POM] dip coated layer by layer film on an ITO slide, (d) blank ITO slide. The surface coverage for (a), (b) and (c) are 2.4×10^{-10} molcm⁻², 7.9×10^{-11} molcm⁻² and 8.1×10^{-11} molcm⁻², respectively.

5.3.3 Scanning Electron Microscopy

The surface topography of the layer by layer and composite films of [RuPVP-AuNP:POM] was probed using scanning electron microscopy. It was anticipated that differences in structure, which in turn affect catalytic efficiency of the films, would be evident. Figures 5.6-5.7 show SEM images for the dip coated films of [RuPVP-AuNP] at ruthenium to Au nanoparticle molar ratios of 6:1 and 48:1, respectively. These images show features associated with the underlying ITO and suggest that continuous films were not formed at both molar ratios. Figures 5.8-5.9 show SEM images for dip coated films of [RuPVP-AuNP:POM] for ruthenium to Au nanoparticle molar ratios of 6:1 and 48:1, respectively. In common with the dip coated films, these films are rather inhomogeneous in nature and are not continuous across the whole ITO surface.

Significantly, [RuPVP-AuNP:POM] films produced by the drop-casting method appear to be considerably more homogeneous. Figures 5.10-5.11 show SEM images for drop cast composite films of [RuPVP-AuNP:POM] at ruthenium to Au nanoparticle molar ratios of 6:1 and 48:1, respectively. It is obvious that the 48:1 [RuPVP-AuNP:POM] drop-cast film formed a highly porous layer. A similar structure is shown in Figure 2.21b. This film structure suggests that the 48:1 [RuPVP-AuNP:POM] drop-cast film would better facilitate ion diffusion. In contrast to the 48:1 [RuPVP-AuNP:POM] drop-cast film, the 6:1 [RuPVP-AuNP:POM] drop-cast film possesses crystallites with diameters of the order of 3.5 μ m. These SEM images confirm that the two different deposition methods produced films with different structural properties and that this is the most likely explanation for the differences in electronic interaction observed.



Figure 5.6 SEM images for a dip coated film of [RuPVP-AuNP] at a ruthenium to Au nanoparticle mole ratio of 6:1 on an ITO electrode. The accelerating voltage is 20 kV.



Figure 5.7 SEM images for a dip coated film of [RuPVP-AuNP] at a ruthenium to Au nanoparticle mole ratio of 48:1 on an ITO electrode. The accelerating voltage is 20 kV.



Figure 5.8 SEM images for a dip coated film of [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 6:1 on an ITO electrode. The accelerating voltage is 20 kV.



Figure 5.9 SEM images for a dip coated film of [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1 on an ITO electrode. The accelerating voltage is 20 kV.



Figure 5.10 SEM images for a drop cast composite film of [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 6:1 on ITO electrode. The accelerating voltage is 20 kV.



Figure 5.11 SEM images for a drop cast composite film of [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1 on ITO electrode. The accelerating voltage is 20 kV.

5.3.4 Electrochemistry

Section 5.3.3 suggested that the two different deposition methods produced films with different structural properties. A key objective in the incorporation of metallic nanoparticles within the metallopolymer film is to increase the rate at which the oxidation state of the ruthenium centers can be regenerated. Therefore, it is essential to investigate the influence of the Au nanoparticles on the electrochemical behaviour of $[Ru(bpy)_2(PVP)_{10}]^{2+}$ within the [RuPVP-AuNP:POM] films prepared by the two deposition methods. The redox properties of the films were hence probed using cyclic voltammetry.

Figures 5.12b and 5.13a illustrate voltammograms for [Ru-PVP:AuNP] at a ruthenium to Au nanoparticle molar ratios of 48:1 and 6:1 on ITO electrodes. The formal potentials, $E^{o'}$, and the difference in the anodic and cathodic peak potentials, ΔE_p , for the [Ru-PVP:AuNP] at ruthenium to Au nanoparticle molar ratios of 48:1 and 6:1 are presented in Table 5.1. In CH₃CN (0.1 mM TBATBF₄), reversible $E^{o'}$ of 0.761 and 0.783 V were obtained for the Ru^{2+/3+} redox process in [Ru-PVP:AuNP] at a ruthenium to Au nanoparticle mole ratios of 48:1 and 6:1 on ITO electrodes. These formal potential values suggest that these [Ru-PVP:AuNP] are easier to oxidize and reduce compared to [Ru(bpy)₂(PVP)₁₀]²⁺. Investigating the voltammetric behaviour of the [RuPVP-AuNP:POM] films at different molar ratios prepared by the layer by layer method is facilitated by their limited solubility in CH₃CN. The films showed good stability towards voltammetric cycling and the surface coverage decreased by less than 10% over a 1-hour period of continuous cycling. The relevant voltammetric data are summarized in Table 5.1.

The voltammograms for dip coated [RuPVP-AuNP:POM] films of one layer at a ruthenium to Au nanoparticle mole ratios of 48:1 and 6:1 on ITO electrodes are shown in

Figure 5.12a and Figure 5.13b. These composite films show clearly defined redox waves associated with both the ruthenium and POM components. In common with the Ru-PVP:POM film, the formal potential for the $Ru^{2+/3+}$ process in both the 48:1 and 6:1 systems shifted in a positive potential direction by approximately +80 mV when associated with POM suggesting a lower electron density on the ruthenium centres. It is more difficult to precisely determine the formal potentials of the POM^{4-/5-} couple. However, association with the [RuPVP-AuNP:POM] causes E° to shift in a positive potential direction, i.e., E° for the POM^{4-/5-} couple shifts by approximately +50 mV and +120 mV for the 48:1 and 6:1 adducts, respectively. These shifts suggest that the POM electron density may be somewhat increased by association with the ruthenium metallopolymers. Similar shifts in E° were also observed when [Ru(bpy)₂(PVP)₁₀]²⁺ associates with [S₂Mo₁₈O₆₂]⁴.[14]

The surface coverage for both the ruthenium and POM centres was measured by recording the charge passed under each wave in the background corrected cyclic voltammogram recorded at a series of slow scan rates, typically less than 10 mVs⁻¹, where the charge passed is independent of the scan rate, i.e., the films were exhaustively electrolysed. The Ru:POM ratio obtained was 3.5 ± 0.2 :1 where Γ =1.8±0.1×10⁻¹¹ and $7.1\pm0.9\times10^{-12}$ molcm⁻² for 48:1 and 6:1, respectively. The Ru:POM ratio of 3.5 ± 0.2 :1 is consistent with results obtained from [Ru-PVP:POM] film and suggests these films contain more ruthenium centres than is required to charge balance the POM⁴ centres.

As shown in Section 5.3.3, SEM shows rather inhomogeneous and discontinuous films across the whole ITO surface for the dip coated [RuPVP-AuNP:POM]. Therefore, it is not appropriate to calculate these charge transport diffusion coefficients. In contrast to dip coated films, drop cast pre-assembled composites possess homogeneous films. To investigate the stability of the layers both the 6:1 and 48:1 [RuPVP-AuNP:POM] composite films were scanned at $100mVs^{-1}$ in a potential window -0.7-1.3V using a supporting electrolyte of 0.1mM TBATBF₄. The conditions were identical to those used

to scan the layer by layer films however a stable film failed to form even using smaller potential windows.



Figure 5.12 Cyclic voltammograms for dip coated (a) [RuPVP-AuNP:POM] and (b) [Ru-PVP:AuNP] films at a ruthenium to Au nanoparticle mole ratio of 6:1 formed by layer by layer deposition on an ITO electrode immersed in CH₃CN (0.1 mM TBATBF₄)(A=1 cm²; v=100 mVs⁻¹).



Figure 5.13 Cyclic voltammograms for dip coated (a) [Ru-PVP:AuNP] and (b) [RuPVP-AuNP:POM] films at a ruthenium to Au nanoparticle mole ratio of 48:1 formed by layer by layer deposition on an ITO electrode immersed in CH₃CN (0.1 mM TBATBF₄)(A=1 cm²; v=100 mVs⁻¹).

	Ru ^{2+/3+}	POM4-/5-
6 :1 [Ru-PVP:AuNP]	0.783 (0.081)	-
6:1 [RuPVP-AuNP:POM]	0.86 (0.079)	0.218 (0.065)
48 :1 [Ru-PVP:AuNP]	0.761 (0.312)	-
48:1 [RuPVP-AuNP:POM]	0.84 (0.209)	0.314 (0.096)

Table 5.1 Formal potentials, E° , and peak-to-peak separations, ΔE_{P} , for dip coated metallopolymer and composite layers formed on an ITO electrode in contact with 0.1 mM TBATBF₄ dissolved in acetonitrile as supporting electrolyte. *All values are in volts (vs Ag/AgCl) and ΔE_{P} values are in brackets.

5.3.5 Photo-electrochemistry

Clear evidence of a new transition between [Ru-PVP:AuNP] and $[S_2Mo_{18}O_{62}]^4$ within the [RuPVP-AuNP:POM] pre-assembled drop cast films were observed in the UV-vis and confirmed in the Raman spectra. The influence of this new mode on the photocurrent intensity compared to [RuPVP-AuNP:POM] dip coated films were determined using a 488 nm cut-off filter. The photo-electrochemistry of [RuPVP-AuNP:POM] preassembled drop cast films were measured using benzyl alcohol as both the contacting solvent and electron donor where TBATBF₄ (0.1 mM) was used as supporting electrolyte. Comparative photocurrent experiments for [RuPVP-AuNP:POM] dip coated films and AuNP were acquired under identical conditions, i.e., solvent, electrolyte. The potential of the electrode was held at +0.4 V. If the reduced form of [RuPVP-AuNP:POM] was generated in the presence of light, a current corresponding to oxidation of the [RuPVP-AuNP:POM] adduct would be observed.

The reaction sequence for the photo-oxidation of benzyl alcohol by the [RuPVP-AuNP:POM] film is shown in Equation 3.1. Given the new vibrational mode at approximately 927 cm⁻¹ and a long tail into the IR for [RuPVP-AuNP:POM] pre-assembled film found in the Raman spectrum and UV-vis spectroscopy, respectively, it might be anticipated that the photocurrent for the benzyl alcohol oxidation by [RuPVP-AuNP:POM] pre-assembled film would be enhanced compared to that for [RuPVP-AuNP:POM] dip coated films and AuNp. Figure 5.14-5.16 confirm this expectation. No current was evident for any film at +0.4 V in the absence of irradiation. In white light that was cut off below 488 nm, irradiation of these films produced currents for the AuNP, [RuPVP-AuNP:POM] dip coated and drop cast films and are shown in Table 5.2.

Film	Photocurrent generated (nA)	
AuNP	2±0.4	
6:1 [Ru-PVP:AuNP]	6±1.9	
48:1 [Ru-PVP:AuNP]	8±1.4	
Dip coated 6:1 [RuPVP-AuNP:POM]	5.2±1	
Dip coated 48:1 [RuPVP-AuNP:POM]	17±1.5	
Drop cast 6:1 [RuPVP-AuNP:POM]	25±2.3	
Drop cast 48:1 [RuPVP-AuNP:POM]	82.2±6.6	

Table 5.2 Photocurrent generation by AuNP, [Ru-PVP:AuNP] and [RuPVP-AuNP:POM] following different deposition methods on ITO in acetonitrile (0.1 M TBATBF₄). A filter was used to cut off light below 488 nm.

Significantly, [RuPVP-AuNP:POM] pre-assembled films produce higher photocurrent than those of [RuPVP-AuNP:POM] dip coated films and AuNP. These photocurrent experiments are consistent with photo-sensitization within [RuPVP-AuNP:POM] pre-assembled films and this photo-sensitization is associated with the new charge-transfer transition. This result is significant since Raman spectroscopy and UV-vis spectroscopy reveal that this new optical transition, indicative of strong electronic communication, is only observed for the [RuPVP-AuNP:POM] pre-assembled drop cast system. The observation that the catalytic efficiency of the pre-assembled drop cast system is significantly greater than that of dip coated film is important given that the photophysical properties of the drop cast and dip coated system are indistinguishable. The most likely explanation lies with their structure, i.e., the dip coated films are less homogeneous in nature than drop cast pre-assembled films leading to a larger Ru-POM separation despite similar electronic communication between the [Ru-PVP:AuNP] and $[S_2Mo_{18}O_{62}]^4$ - moieties.



Figure 5.14 Photocurrent vs. time curves for thin films of AuNP formed on ITO electrodes in contact with pure benzyl alcohol containing 0.1 mM TBATBF₄ as supporting electrolyte. The modified ITO electrodes were irradiated by an arc lamp source with a cut off filter below 488 nm that was initiated at t=1700 and turned off at 100 s. The potential was continuously poised at 0.4 V.



Figure 5.15 Photocurrent vs. time curves for thin films of dip coated [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1 formed on ITO electrodes in contact with pure benzyl alcohol containing 0.1 mM TBATBF₄ as supporting electrolyte. The modified ITO electrodes were irradiated by an arc lamp source with a cut off filter below 488 nm that was initiated at t=1600 and turned off at 100 s. The potential was continuously poised at 0.4 V.



Figure 5.16 Photocurrent vs. time curves for thin films of drop cast pre-assembled [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1 formed on ITO electrodes in contact with pure benzyl alcohol containing 0.1 mM TBATBF₄ as supporting electrolyte. The modified ITO electrodes were irradiated by an arc lamp source with a cut off filter below 488 nm that was initiated at t=1000 and turned off at 100 s. The potential was continuously poised at 0.4 V.

5.4 Conclusion

In this chapter, photocatalysis using thin films of polyoxomolybdates sensitised with ruthenium metallopolymers/gold nanoparticles using visible irradiation was described. Significantly, the efficiency of the photocatalysis depends markedly on the structure of the [RuPVP-AuNP:POM] even when photonic properties are very similar. Specifically, electrostatic thin films of [RuPVP-AuNP:POM] prepared by drop cast and dip coated methods have been achieved. Strikingly, despite their similar photonic properties, an additional optical transition is observed in the Raman spectra of pre-assembled drop cast [RuPVP-AuNP:POM], which was not seen in dip coated [RuPVP-AuNP:POM]. Importantly, this electronic communication enhances the photocatalytic oxidation of benzaldehyde by a factor of more than four. While there is clear evidence for photosensitisation in the drop cast film that is not present for the dip coated systems, the magnitude of the photocurrent, i.e., 82.2±6.6 nAcm⁻² for pre-assembled drop cast [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1, is twice as large as that those found in [Ru-PVP:POM] film.

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CHAPTER SIX

CONCLUSION

This thesis involves the photocatalysis by ruthenium complexes and polyoxometallate.

Investigations into the optimization of the photocurrent from novel thin films of assembled ruthenium polypyridyl polyoxometalate cluster, [Ru-POW] are described in Chapter two. In the first part of this work, the electrochemical and photoelectrochemical properties of the [Ru-POW] film were explored. The films were successfully adsorbed onto Pt microelectrodes and their electrochemical properties were probed using cyclic voltammetry. In electrolyte-free acetonitrile, scan rate dependence studies showed that a slow electron transfer occurs for the [Ru-POW] films in this media. This is attributed to the lack of ions for charge compensation in the solution and a low photocurrent is produced compared to previously studied ruthenium dye sensitized TiO_2 in the literature.

In the second part, the overall photocurrent was optimized by identifying several key limiting factors; (1) presence of electrolyte; adding low concentrations electrolyte (1 mM TBATBF₄) resulted in an increased charge transport diffusion coefficient but higher concentrations of electrolyte decomposed the layer, (2) film thickness; increasing the thickness of the [Ru-POW] films, i.e., increasing the photocurrent up to a limiting thickness. This can be attributed to poor ion diffusion through the thicker films and possibly blocking of the exciting radiation, (3) applied potentials; increasing the applied potential to speed up the heterogeneous electron transfer process at the electrode. The magnitude of the photocurrent increased with increasing potential, indicating that the photooxidation of benzyl alcohol by the [Ru-POW] films is at least partly controlled by the rate of heterogeneous electron transfer. (4) Donor concentrations; increasing the concentrations up to 20% (V/V) of benzyl alcohol.

Finally, the topography of the [Ru-POW] films has been investigated. These films were found to consist of a nanoporous crystalline structure with pore diameters of approximately 200nm. Interestingly, this porous structure is similar to that found in mesoscopic TiO_2 used in the dye-sensitised solar cell. This suggests that the film has attractive features including a high surface area and porous structure that allows solvent

and ions to move easily through the film, and may explain why good photocurrent yields from TiO_2 are achieved with low ion concentrations.

Photocatalysis using thin films of polyoxomolybdates sensitised with ruthenium containing metallopolymers using visible irradiation was described in Chapter three. Significantly, the efficiency of the photocatalysis depends markedly on the coordination sphere of the ruthenium centres even when their redox and photonic properties are indistinguishable. Specifically, electrostatic thin films of Ru-PVP:POM and Ru-CO-P:POM have been successfully surface immobilized. Strikingly, despite their similar redox and photonic properties, an additional optical transition is observed in the Raman spectra of Ru-PVP:POM, which was not seen in the Ru-CO-P:POM film. Importantly, this electronic communication between the polymer and POM enhances the photocatalytic oxidation of benzaldehyde by a factor of more than three. While there is clear evidence for photosensitisation in the PVP system, which is not present in the CO-P films, the magnitude of the resulting photocurrents, i.e., 38±1 nAcm⁻² for Ru-PVP:POM, are not significant (what would be) as expected for a system that is controlled by either benzyl alcohol diffusion or the reaction kinetics between the photocatalyst and benzyl alcohol. Optimization of the system was performed to increase the overall resulting photocurrent by again identifying the key limiting factors as described in Chapter four; (1) increasing the applied potential speeds up the heterogeneous electron transfer at the The magnitude of the photocurrent increased with increasing potential, electrode. indicating that the photooxidation of benzyl alcohol by the [Ru-PVP:POM] film is at least partly kinetically controlled. (2) Increasing the surface coverages of the [Ru-PVP:POM] film increased the magnitude of the photocurrent produced, i.e., three layered [Ru-PVP:POM] film produced the most photocurrent at a Ru:POM molar ratio of 4.0±0.1:1. Finally, the conclusive experiment involving three layered [[Ru-PVP:POM] self assembled film in the presence of benzyl alcohol (60% V/V) in 0.1 M TBATBF4 with potential held at +0.8 V was carried out. The optimized system produced more photocurrent (183.6±17.6 nA) than those found in other systems. The magnitude of the photocurrent is consistent with the slow rate at which the catalytic centres are regenerated

within the film (as described by the homogeneous charge transport diffusion coefficient, D_{CT}) and suggests that substantially higher photocurrents could be achieved by enhancing the D_{CT} , e.g., by incorporating metal nanoparticles.

Therefore, photocatalysis using thin films of polyoxomolybdates sensitised with ruthenium metallopolymers/gold nanoparticles using visible irradiation was described in Chapter five. The efficiency of the photocatalysis depends markedly on the structure of the [RuPVP-AuNP:POM] even when the photonic properties are very similar. Specifically, electrostatic thin films of [RuPVP-AuNP:POM] prepared by drop cast and dip coated methods have been achieved. Strikingly, despite their similar photonic properties, an additional optical transition is observed in the Raman spectra of pre-assembled drop cast [RuPVP-AuNP:POM] films, which was not seen in dip coated [RuPVP-AuNP:POM] films. Importantly, this electronic communication enhances the photocatalytic oxidation of the benzyl alcohol by a factor of more than four. While there is clear evidence for photosensitisation in the drop cast films which is not present for the dip coated systems, the magnitude of the photocurrent, i.e., 82.2±6.6 nAcm⁻² for pre-assembled drop cast [RuPVP-AuNP:POM] at a ruthenium to Au nanoparticle mole ratio of 48:1, is twice as large as that those found in [Ru-PVP:POM] film.

APPENDIX

PUBLICATION