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Polyaniline Coated Micro-capillaries for Continuous Flow Analysis of Aqueous Solutions

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Abstract: The inner walls of fused silica micro-capillaries were successfully coated with polyaniline nanofibres using the “grafting” approach. The optical response of polyaniline coatings was evaluated during the subsequent redoping–dedoping processes with hydrochloric acid and ammonia solutions, respectively, that were passed inside the micro-capillary in continuous flow. The optical absorbance of the polyaniline coatings was measured and analysed in the wavelength interval of [300–850 nm] to determine its optical sensitivity to different concentrations of ammonia. It was found that the optical properties of polyaniline coatings change in response to ammonia solutions in a wide concentration range from 0.2 ppm to 2000 ppm. The polyaniline coatings employed as a sensing material for the optical detection of aqueous ammonia have a fast response time and a fast regeneration time of less than 5 seconds at room temperature. The coating was fully characterised by Scanning Electron Microscopy, Raman Spectroscopy, absorbance measurements and kinetic studies. The response of the coatings showed very good reproducibility, demonstrating that this platform can be used for the development of micro-capillary integrated sensors based on the inherited sensing properties of polyaniline.

Keywords: polyaniline, continuous flow, sensor, ammonia, micro-capillary;

1. Introduction

Sensors providing continuous, direct and immediate analytical information are of great interest for many areas of research as such environmental monitoring [1-6]. In particular, some sectors of the water industry dealing with the detection and characterisation of chemical contaminants in surface water, predominantly rely on the batch sampling technique, where water samples are collected and analysed in the laboratory. This is mainly due to costs or legal constrains around certified methods[7]. Although this technique often offers accurate detection and possesses good sensitivity and limits of detection, it is time consuming, requires manpower and, most importantly, it fails to provide immediate or continuous information, which is of enormous interest when picking a sporadic, but fatal, event in the network. In this context, flow-through sensors have attracted a lot of attention for real time monitoring of water samples [8-12]. Flow-through sensors posses many advantages compared with classical probe-type sensors as such facile sample transport, sensor conditioning, maintenance and regeneration among others [13]. A subclass of flow-through sensors, accomplished through miniaturisation of the "flow-through" unit are micro-capillary integrated optical sensors, in which glass or plastic micro-capillaries are coated on their inner surface with a chemically sensitive layer that changes its optical properties (absorbance [14-17], reflectance [14], fluorescence [15, 16], swelling [16] and refractive index [15, 16]) in response to a particular analyte as it passes through the micro-capillary. Hence, in this type of systems, it is no longer the intrinsic optical properties of the sample as it passes through the detector that are being studied, but rather those of the inner micro-capillary coating, as they are modulated by the sample. Because the optical properties of the coating, instead of the sample itself, are being monitored, micro-capillary integrated optical sensors are virtually independent of the colour and turbidity of the sample, which may interfere with the chemical sensing process in a conventional optical sensor. Moreover, micro-capillary integrated optical sensors offer advantages in terms of size, electrical safety, costs and have no the need for a separate reference electrode, as is the case in electrochemical measurements [18]. In particular, several micro-capillary integrated optical sensors have been developed for the optical sensing of metal ions [14], solvent polarity [19], or carbon dioxide [18].

Exploring new means of developing micro-capillary integrated optical sensors capable of continuous flow analysis of water contaminants; we explored the optical properties of the semiconductive polymer polyaniline (PAni), [20-23] for the detection and quantification of aqueous ammonia. In fact, many recent articles describe electrical and optical sensors for ammonia detection with PAni as the sensitive layer, [24-28] or PAni composites [29, 30]. For the detection of aqueous ammonia, however, to our knowledge, only one recent study presents an optical sensor based on PAni. Castrellon-Uribe *et al.* [31] used a glass substrate covered with a film of polyaniline produced by the chemical bath method, for which transmittance is measured after immersing the glass slide in aqueous ammonia solutions and subsequently drying the slide. Although the sensor is reported to have good signal linearity over the concentration range 3–100 ppm of ammonia, the sensing method is disruptive, cannot provide immediate or continuous information, and it is not suitable for real-time measurements. Bearing these constraints in mind, we adopted a different approach to produce polyaniline modified sensing micro-capillaries that showed fast response and regeneration times providing with the possibility of working with a wide range of aqueous ammonia concentrations in a continuous flow mode.

2. Experimental

2.1. Materials and Methods

Aniline (BDH), hydrochloric acid (Fisher Scientific), ammonium persulfate (APS) (Aldrich), *N*-[3-(Trimethoxylsilyl)propyl]aniline (Aldrich), ammonium hydroxide solution (28.0-30.0 % NH_3 basis) (Aldrich) were used. The aniline monomer was purified by vacuum distillation before use. Other chemicals were used as received. Fused-silica micro-capillaries (100 μm ID, 375 μm OD) were purchased from Polymicro Technologies (Phoenix, AZ, USA).

Raman Spectroscopy was employed to study the chemical features of the polyaniline coatings inside the micro-capillary. Raman spectra were taken with a Perkin Elmer RamanStation at 2 cm^{-1} resolution, 3s per scan and 20 collections. A 785 nm laser line was used as it can detect both doped and dedoped features in polyaniline.

UV-Vis Spectroscopy was used to study the pH dependence of the polyaniline coatings. The absorbance spectra were recorded using 2 fiber-optic light guides connected to a Miniature Fiber Optic Spectrometer (USB4000 - Ocean Optics) and aligned using cross shaped cell (see Figure 4B). The light source used was DH-2000-

BAL UV-NIR deuterium tungsten halogen source (Ocean Optics). Data from the spectrometer was processed using Spectrasuite software provided by Ocean Optics Inc. For clarity, the absorbance spectra recorded were smoothed using Origin software using Savitzky-Golay algorithm.

2.2. Fused silica micro-capillaries coating protocol

The functionalisation of the inner walls of the micro-capillary with PAni nanofibres was achieved using chemical polymerisation. The protocol used to coat micro-capillaries with polyaniline nanofibres is described in Figure 1. Prior to functionalisation the inner micro-capillary surface was quickly washed with acetone and water, then flushed with a solution of NaOH 0.2 M for 30 min at a flow rate of 0.25 μL min^{-1} using a syringe pump and then, rinsed with deionised water. Next, the micro-capillary was flushed with a solution of HCl 0.2 M for 30 min at a flow rate of 0.25 μL min^{-1}, rinsed with water, and with ethanol. A 20 % wt solution of *N*-[3-(trimethoxysilyl)propyl]aniline in ethanol was then pumped through the micro-capillaries for 90 min at a flow rate of 0.25 μL min^{-1} (Fig. 1 – A). Later, the micro-capillaries were washed with ethanol, dried under nitrogen stream, and left at room temperature for 24h.

Fresh solutions of aniline and the oxidant (ammonium persulfate) in 1M HCl were prepared as follow: 82 μL aniline was added to 4 mL 1 M HCl solution; 0.050 g ammonium peroxydisulfate was dissolved in 4 mL 1M HCl solution. Equal volumes of the two solutions were rapidly mixed together in a micro-syringe and immediately used to fill the micro-capillary (Fig. 4 – B), which was after closed at both ends using rubber septa. After about 10 min the solution inside the micro-capillary turns slightly green which means that the polymerisation has started. The micro-capillary was left on the bench over night. The next day the micro-capillaries were thoroughly washed with water to remove any polyaniline nanofibres that were not attached to the inner walls and any physisorbed materials.

Figure 1. Coating protocol of the fused silica micro-capillaries with polyaniline.

2.3. Polyaniline coatings imaging protocol

The polyaniline coatings inside the micro-capillary were imaged using scanning electron microscopy (SEM) performed on a Carl Zeiss EVOLS 15 system at an accelerating voltage of 3.87 kV. The micro-capillaries were cut using a SGT capillary column cutter with rotating diamond blade (SHORTIX, Nederland) to create a smooth cut of the micro-capillary wall. Then they were placed in vertical position in a custom made metallic capillary holder that has holes of internal diameters equal to the external diameter of the micro-capillary (375 µm). This set-up allows the micro-capillaries to be kept in vertical position. During the imaging process, the stage was tilted of an angle between 0 – 15° for better imaging of the inner wall of the micro-capillary (Figure 2A).

For imaging purposes, a flat silicon wafer was coated with polyaniline nanofibres using the same procedure as the one employed for the coating of micro-capillaries. For this, a polydimethylsiloxane (PDMS) layer containing a micro-fluidic channel (100 µm x 50 µm x 2 cm) incorporating one inlet and one outlet was placed on top of a silicon wafer. The obtained micro-channel (PDMS/silicon wafer) was coated with polyaniline following the procedure described above. Prior imaging, the PDMS layer was removed and the silicon wafer containing the polyaniline film was coated with 10 nm Au layer. The imaging was performed on a Carl Zeiss EVOLS 15 system at an accelerating voltage of 5.75 kV (Figure 2B).

3. Results and Discussion

3.1. Polyaniline coatings

3.1.1. Morphological Analysis

Fused silica micro-capillaries were covalently functionalised with polyaniline as described in the experimental section. Scanning electron microscope (SEM) images showed that using the described polymerisation technique, a 3D arrangement of polyaniline isles, homogeneously distributed along the micro-capillary walls were obtained, in which polyaniline is covalently attached to the inner walls of the micro-capillary (Figure 2A). For a better visualisation of the morphology of polyaniline coatings, a flat silicon wafer surface was coated (Figure 2B and C) using the same procedure (see Experimental Section 3.3). Figure 2C shows that the method employed produces nanofibres that are around 200 nm in diameter and up to several microns in length. The great advantage of nanofiber structured films (*versus* bulk polyaniline) is the high surface area that is exposed to the target molecules and the very short diffusional path lengths[1, 22] which, coupled with rather thick films, produces enhanced sensitivity and fast response times[32-34]. The covalent attachment of the nanofibres ensures good mechanical stability of the coating, moreover no leaching has been observed over a period of three months of use for lab experiments.

Figure 2. SEM images of the polyaniline coated micro-capillary (A) and silicon wafer (B and C).

3.1.2. Structural Analysis

Raman spectroscopy was used to characterise the chemical structure of the polyaniline since this technique allows non-invasive, *in situ* analysis of the polyaniline coating inside the micro-capillary. Raman spectroscopy showed that the polyaniline coating is obtained in its half-oxidised emeraldine state[35]. In addition, Raman spectroscopy was also employed to study the changes in the bonding structure of the coatings upon doping-dedoping, as very distinct signature bands appear for the quinoid and benzenoid rings, respectively [36, 37]. Figure 3A presents the Raman spectra of the polyaniline coatings in the region of interest (1000-1800 cm^{-1}) after a solution of hydrochloric acid (HCl) 10^{-2} M and aqueous solution of ammonia (200 ppm), respectively, are passed inside the micro-capillary.

When a solution of 10^{-2} M HCl is passed through the micro-capillary, polyaniline exists in the doped state, emeraldine salt (ES). Passing a solution of 200 ppm aqueous ammonia inside the micro-capillary causes changes in the bonding structure of the material (Figure 3B) reflecting the adoption of the dedoped– emeraldine base (EB) state. Signature bands between 1300 and 1400 cm^{-1} appear for the doped material (Fig. 3A – in green). After dedoping of the polymer with ammonia, these bands are less significant, and strong bands between 1400 and 1500 cm^{-1} reflect the dedoped state (Fig. 3A – in blue). Complete characterisation and assignments are listed in Table 1.

Figure 3. (**A**) Raman Spectra of PAni functionalised micro-capillary after being filled with a HCl solution 10^{-2} M (green) and with NH_3 aqueous solution 200 ppm (blue).

(**B**) Scheme showing the differences in the chemical structure of polyaniline (two different states: Emeraldine Salt (ES) and Emeraldine Base (EB).

In particular, in the case of EB, an important peak can be observed at 1456 cm^{-1} and is characteristic to C=N stretching vibration of the quinoid units[35, 37-40]. Other bands at 1592 cm^{-1} and 1162 cm^{-1}, are assigned to C-C stretching[35, 39] and C-H bending modes[35, 38], respectively, centered on the quinoid ring. Another new peak at 1220 cm^{-1} appears in the spectra of polyaniline upon dedoping and is assigned to C–N stretching vibrations of the benzenoid units [35, 39] (the EB form consists of both C=N and C-N bonds). In the case of ES, the most important band appears at 1346 cm^{-1} and can be assigned to a C-N• + polaron stretch [35, 39, 41, 42] while the band at 1170 cm^{-1} is characteristic to the C–H in-plane bending of the benzenoid ring [35, 40]. These studies have been repeated on the same micro-capillary in similar conditions after a period of two months. Raman spectroscopy indicated no noticeable changes in the chemical structure of polyaniline (ES and EB).

Table 1. Assignment of the vibrational bands (cm^{-1}) observed between 1800 and 1000 cm^{-1} in the Raman spectra (λ_{ex} = 785 nm) of PAni functionalised micro-capillary after being filled with a HCl solution 10^{-2} M (doped) and PAni functionalised micro-capillary after being filled with NH_3 aqua solution 200 ppm (dedoped).

3.1.3. Optical properties of the coating

To evaluate the optical response of the PAni coatings, hydrochloric acid (10^{-2} M) and aqueous ammonia solution (200 ppm) were alternatively pumped through the micro-capillary at a flow rate of 5 μL min^{-1} and the absorbance of the coating was monitored transversally across the micro-capillary over the wavelength interval [350–1100nm] (Figure 4A) using the configuration described in Figure 3B. When hydrochloric acid is passed through the micro-capillary, the polyaniline coating presents a green colour (ES) as depicted in Figure 4A. When the ammonia solution reaches the surface of the coating, the micro-capillary rapidly changes its colour – from green to blue (Figure 4A - photos). This is due to the fact that when the emeraldine salt form of polyaniline is exposed to a basic solution, such as ammonia, it undergoes deprotonation and it is converted to the emeraldine base (EB) state which presents a blue color. The process occurs on the imine nitrogen atoms as shown in Figure 3B. More specifically, the doped state – emeraldine salt – has a characteristic absorption band at around 360 nm associated to π-π* transition of the conjugated ring system [23] and an absorption band at ~420 nm together with an extended tail at 850 nm assigned to polaron band transition [23]. Dedoping the polymer with ammonia leads to a shift in the absorption lambda maxima of PAni from ~360 nm (ES) to ~320 nm (EB). The band at 610 nm is ascribed to the exciton formation in the quinonoid rings and this absorption gives rise to the blue colour of the PAni coatings [23]. The UV-Vis spectra of the polyaniline coatings obtained using the setup shown in Figure 4B is similar to the absorbance spectra of polyaniline presented in the literature, in the case when polyaniline can be found in the form of dispersions in aqueous solutions [20, 23, 43, 44]. Moreover, the UV-Vis spectra can also provide useful information about the electronic structure of the polymer and its geometric structure such as polymer chain conformation [23]. A number of theoretical studies have examined the influence of PAni chain conformation, in particular the effect of the phenyl and phenyl/quinoid torsional angles along the chain on the electronic structure of polyaniline (and consequently their absorbance spectra) [23, 45, 46]. It was found that the position of the absorption bands of PAni is sensitive to the conformation adopted by the polymer chains as well as the conjugation length. In the case of polyaniline coatings, having the polaron band centered at around 827 nm, suggests that the PAni chains are adopting a “compact coil” conformation compared with an “extended coil” conformation that is characterised by a red shift in the λ_{max} to 1500-2500 nm [23].

Figure 4. (A) Absorbance spectra and photos of PAni functionalised micro-capillary after being filled with a HCl solution 10^{-2} M (green) and PAni functionalised micro-capillary after being filled with ammonia aqueous solution (blue). (B) Picture of the UV-Vis flow cell set-up used for UV-Vis characterisation.

The change in colour and absorbance spectra of the coating in response to hydrochloric acid and ammonia solution, respectively, shows the potential of this type of coatings for building micro-capillary integrated micro-sensors capable of working in continuous flow.

To further investigate the reversibility of color change of the micro-capillary sensor during the protonation/deprotonation processes, the absorbance at fixed wavelengths was monitored while pumping HCl 10^{-2} M and aqueous ammonia 200 ppm solutions respectively, through the micro-capillary at a flow rate of 5 μL min^{-1}. The two wavelengths monitored correspond to typical absorbance of emeraldine salt (827nm – polaron strech) and emeraldine base (600nm – exciton formation in the quinoid ring). An absorbance reading was taken every 100 ms and no smoothing algorithms were applied for the acquired data (Figure 5).

Firstly, a solution of hydrochloric acid is passed through the micro-capillary and the absorbance at 827 nm (Figure 5 - in green) and 600 nm (Figure 5 – in blue) is recorded in real time. After approximately three to four minutes, aqueous ammonia solution is injected inside the micro-capillary, replacing the previous solution and causing a change in colour of the micro-capillary. The absorbance is continuously monitored, recording the moment when the micro-capillary changes from green to blue (decrease in the absorbance at 827 and increase in the absorbance at 600 nm). The absorbance value stabilises rapidly and after another 3 to 4 minutes the 10^{-2} M hydrochloric acid is injected inside the micro-capillary. The sequence of doping/dedoping/ followed by dedoping/doping process is repeated seven times in total. The results showed excellent reproducibility, with no visible loss in the coating sensitivity. The response time and the recovery time of the PAni coating exposed to aqueous ammonia and hydrochloric acid solutions, respectively, were less than 5 s at room temperature when the solutions are pumped through the micro-capillary at 5 μL $\min^{-1}$ flow rate (Figure 5 – Inset A and B). The response of the PAni coatings, when exposed to aqueous ammonia, is depicted in Figure 5 by a decrease in the absorbance at 827 nm and an increase in the absorbance at 600nm. The absorbance values become stable after less than 5 seconds (4.43 ± 0.13, n = 4) and remain stable as long as the solution and the flow passing through the micro-capillary is not modified. In order to ensure a good coating regeneration (doped state), a solution of HCl 10^{-2} M is pumped through the modified micro-capillary. The regeneration of the coating occurs in less than 4 seconds (3.34 ± 0.16, n = 3) and it is characterised by an increase in the absorbance at 827 nm and a simultaneous decrease of the absorbance at 600 nm to their original values (doped state). These results showed that the modified micro-capillary sensor exhibits very rapid response times towards ammonia and HCl solutions with excellent reproducibility.

Figure 5. Continuous monitoring of the absorbance at 827 nm and 600 nm of the PAni coatings while HCl 10^{-2} M and ammonia (200 ppm) solutions are passed through the PAni coated micro-capillary in continuous flow (5 μL min^{-1}). The inset A and B show the response and recovery times of the PAni coatings.

3.2. Ammonia Sensing

Different concentrations of aqueous ammonia (from 0.2 ppm - 2000 ppm) were passed through the modified micro-capillary in continuous flow (5 μL min^{-1}). The absorbance of the coating was recorded in the interval 300 – 850 nm, using the same methodology presented above, to determine the sensitivity of the PAni coatings to ammonia. Before conducting the experiments, 10^{-2} M hydrochloric acid was passed through the PAni modified micro-capillary to assure the complete doping of the coating. As observed in Figure 6, the absorbance intensity of the two absorption bands (350 nm, 600 nm) increases with ammonia concentration. Complete dedoping of the polymeric coating is achieved at 20 ppm ammonia solution, and can be depicted from Figure 6 by the disappearance of the absorbance band centered at 420 nm. Moreover, the λ_{max} of the absorbance band, due to the exciton formation in the quinoid rings, shows a gradual shift towards lower wavelength with increasing ammonia concentrations. To further characterise the performance of the polyaniline based micro-capillary sensor towards aqueous ammonia, three sets of aqueous ammonia solutions (from 0 ppm - 2000 ppm) were passed through the modified micro-capillary in continuous flow (5 μL min^{-1}) and this time the absorbance at 600 nm was recorded continuously. The integration time in the Ocean Optics software was set to 1 second and an absorbance reading was recorded every five seconds for three minutes for each of the solutions (see Table S1 – Supplementary data). A plot of the absorbance at 600 nm versus concentration of aqueous ammonia is shown in Figure 6 - Inset B showing the logarithmic calibration curve. This type of logarithmic response is commonly depicted in the case of ammonia sensors based on polyaniline [28, 31]. However, to further simplify the calibration curve, often in cases of ammonia concentration over a wide range, logarithm of concentration is plotted [28]. In the case of the micro-platform presented here, this approach offers a linear calibration curve ($R^2 = 0.991$) between absorbance at 600 nm and log[conc] (Figure 6 – Inset B) making the sensor more practical. The limit of detection and limit of quantification were found to be 0.0067 ppm and 0.041 ppm, respectively. The relative standard deviation of the sensor's response lies typically in the range 1-3% over the calibration range. The results indicate that the PAni modified micro-capillary integrated optical sensors could be used for sensing aqueous ammonia over wide concentration range (0.2 – 2000 ppm).

Figure 6. Absorbance spectra of the polyaniline coatings exposed to different concentrations of aqueous ammonia. Inset A shows the logarithmic dependency of the

absorbance at 600 nm *versus* ammonia concentration. Inset B shows the linear dependency of the absorbance at 600 nm *versus* logarithm of ammonia concentration.

4. Conclusions

A micro-capillary integrated optical sensor suitable for the detection of aqueous ammonia has been realised by coating the inner walls of a fused-silica micro-capillary with polyaniline nanofibres. In this approach, the ammonia solution does not need to be pretreated prior entering the micro-capillary, for the incoming optical analysis, as the polymer coating itself acts as the indicator dye. The ability to form nanostructures together with its intrinsically pH-sensitive property makes polyaniline an excellent candidate for the fabrication of optical sensors in the visible-near IR regions, capable for real time continuous-flow measurements of aqueous ammonia. The performance of the PAni modified optical sensor when aqueous ammonia solutions are passed through the micro-capillary in continuous flow, showed that the polyaniline modified micro-capillary optical sensors can operate in a wide range (0.2 – 2000 ppm) of ammonia concentrations. The high surface area of the polymer offers good permeability for the analyte. Very fast response times of less than 5 seconds are achieved. Another distinguishing feature of the PAni-modified micro-capillary optical sensor is the possibility of a fast regeneration process of less than 4 seconds by just pumping hydrochloric acid solutions through the modified micro-capillary. Good reproducibility of the signal was obtained when cycling ammonia and hydrochloric acid solutions, respectively, showing the stability of the polyaniline coating through at least 7 cycles. It was determined that by monitoring the absorbance at 600 nm, the concentration of ammonia can be determined with good linearity. Therefore, we have shown the feasibility of employing polyaniline to develop micro-capillary integrated optical sensors capable of operating in continuous flow mode for the optical detection of aqueous ammonia.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/

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