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Electrochemical Reduction of Hexavalent Chromium on Two-step Electrosynthesized One-dimensional Polyaniline Nanowire

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In this work, polyaniline (PANI) film was synthesized by the two-step electrochemical polymerization method from sulfonic acid solution on the spectrographic pure graphite (SPG) surface. Scanning electron microscope (SEM) characterization shows that the resulting PANI film had porous morphology and loosely textured structure, which is composed of uniform 1D nanowires with an average diameter of about 100-200 nm. The electroreduction of Cr(VI) to the much less toxic trivalent state (Cr(III)) was then studied on the PANI/SPG electrode. The effects of various parameters such as cathode potential, solution pH, PANI film thickness and electrolyte temperature on the Cr(VI) removal rate were investigated in detail. It was found that the negative cathod potential, low solution pH and appropriate PANI film thickness are benefit for the removal of Cr(VI). While the electrolyte temperature had no evident effect on the Cr(VI) electroreduction reaction. The electrochemical stability of the PANI film after use in Cr(VI) reduction process was also investigated using cyclic voltammetry and Fourier transfer infrared spectroscopy technologies.

Keywords: Polyaniline; Hexavalent chromium; Electrochemical reduction; Spectrographic pure graphite; Film electrode

1. INTRODUCTION

Effluents from metal finishing, leather tanning, dyeing, electroplating and textile industries often contain elevated levels of hexavalent chromium (Cr(VI)), which is well-known to be highly toxic, carcinogenic, mutagenic to living organisms, and extremely mobile [1,2]. It is reported that compounds of Cr(III) are 10–100 times less toxic than those of Cr(VI) and easily precipitated or adsorbed on a variety of inorganic or organic substrates [3]. Thus, the reducing of Cr(VI) to Cr(III) seems to be a key efficient process for removing Cr(VI) from wastewater.

Many methods for treatment of Cr(VI)-containing sewage water have been proposed including adsorption, ion exchange, membrane separation and chemical reduction/precipitation methods [4,5]. Conventional processes for chemical reduction using chemicals such as sulfur dioxide or sodium metabisulfite are not entirely satisfactory and always accompanied with secondary pollutions and high volume of sludge products. Adsorption is another widely used method. The disadvantage of adsorption processes is that the adsorbent needs to be regenerated, which increase the cost of the process and is sometimes a very unconvinient procedure. Thus, on the basis of the consideration of practical application, an environment-friendly technology that can fast and effective remove Cr(VI) is desired.

In recent years, the electrochemical reduction of Cr(VI) has been widely studied and applied as an effective method for treating the Cr(VI)-contaminated wastewater. However, the direct electroreduction of Cr(VI) at carbon-based materials often suffers from poor electro transfer kinetics and selectivity problems [6]. Since the reduction of Cr(VI) on the electrosynthesized polypyrrole (PPy) films was reported for the first time in 1993 [3], conducting polymers for removing Cr(VI) have been intensively studied due to their excellent redox properties and high conductivities. The electroreduction process is based on the spontaneous electron transfer from the polymer chain to Cr(VI) present in acid solution. Among these conducting polymers, conducting polyaniline (PANI) has attracted most attention [7-16] and is considered to be potentially applied in industrial scale for treating Cr(VI)-contaminated wastewater due to its good environmental stability, low-cost and controllable electrical conductivity. The use of PANI proved to be more efficient than PPy for removing Cr(VI) with higher reaction rates and stability when the process is carried out under closed circuit conditions [11]. Ruotolo and Gubulin [10-16] used the reticulated vitreous carbon (RVC) electrodes covered with PANI film for reduction of Cr(VI), and important results concerning the polymer electrodeposition process, the effect of operational variables on the reaction rate and polymer stability have been investigated. It was found that an increase of electrode porosity could greatly improve the mass thansfer and reduction of Cr(VI) at PANI/RVC electrode, which could be attributed to the enlarged electrode surface [13].

It is well now known that many properties of conducting polymers, such as the degree of crosslinking, conductivity and morphology vary with the synthesis conditions such as the nature of solvent, the electrosynthesis method and the doping agent [17,18]. In the present work, PANI nanowire was electrodeposited under control on the spectrographic pure graphite (SPG) electrode surface by the cyclic voltammoetric mathod at 0 ^{0}C. The effects of electrode potential of PANI/SPG, solution pH, PANI film thickness and electrolyte temperature on the removal rate of Cr(VI) was studied in detail and the PANI film stability was also examined.

2. EXPERIMENTAL

2.1 Reagents and chemicals

Aniline (Aldrich) was purified by vacuum distillation and stored in the dark under nitrogen atmosphere before used. Other reagents were A.R. and used as received. Doubly distilled water was used throughout the experiments. All electrolyte and monomer solution were purged with nitrogen before and during the polymerization experiments.

2.2 Electrode preparation

The electrochemical oxidation synthesis of PANI film was performed in a standard three-electrode electrolysis cell. A spectrographic pure graphite (SPG) rod with a cross sectional area of 0.785 cm^2 was used as the working electrode, a Pt foil with a surface area of 4 cm^2 and a saturated calomel electrode (SCE) acted as the counter and reference electrodes, respectively. The working electrode was polished to a mirror with 1.0 and 0.3 μm alumina slurries and subsequently sonicated in 1:1 HNO_3, 1:1 ethanol and pure water for 3 min successively. Then, the SPG electrode was electrochemically activated by cycling the potential three times between −0.5 and 1.0 V in a 0.5 M H_2SO_4 aqueous solution. Finally, it was rinsed with doubly distilled water before use.

The PANI film modified SPG electrode was synthesized in a N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution containing 0.1 mol L^{-1} aniline monomer and monitored using a potentionstat/galvanostat Model 263A electrochemical station. First, the polymerization solution was cooled in an ice-water bath. Second, the electropolymerization was carried out by cycling the potential two cycles between −0.2 and 0.9 V at a scan rate of 8 mV s^{-1}, and then cycling the potential between −0.2 and 0.7 V until the first anodic peak current grows up to ca. 4 mA cm^{-2}. Finally, the resulting PANI/SPG electrode was rinsed with distilled water and dried at 60 °C for 2 h in vacuum drying oven to get a firmly modified electrode. Before the electroreduction of the Cr(VI), the PANI/SPG modified electrode was maintained at −0.2 V in 0.1 mol L^{-1} H_2SO_4 for 30 min.

The electrochemical reduction of Cr(VI) was carried out in a one compartment electrolysis cell with the same three-electrode system as above mentioned. The potentiostatic reduction of Cr(VI) was performed with REX DJS-292 potentiostat/galvanostat (Shanghai Cany Precision Instrument Co., Ltd) in 0.1 mol L^{-1} H_2SO_4 solution containing 10.0 mg L^{-1} Cr(VI) under different experiment conditions. A 0.01 mol L^{-1} NaOH was used to adjust the solution pH. The concentration of Cr(VI) after 135 min electrolysis was measured with a spectrophotometer (SHIMADZU, Japan) using the standard method of the diphenylcarbazide.

The morphology of the PANI/SPG electrode was characterized using an environmental scanning electron microscope (ESEM; Quanta 200 FEG) with an accelerating voltage of 30 kV. The chemical structures of the PANI film before and after use in the electrochemical reduction of Cr(VI) were investigated with KBr-pellets using Fourier transfer infrared (FT-IR) spectrometer (Thermo Nicolet Nexus, USA) in the spectral range from 4000 to 400 cm^{-1} at room temperature.

2.3 Determination of PANI film thichkess

In this study, the PANI films were grown to different thickness, the peak current of the leucoemeraldine/emeraldine (LE/EM^{2+}) redox transition recorded in an aniline-free 0.1 mol L^{-1} H_2SO_4

solution was taken as an approximate measure of the thickness of the polymers. The PANI film thickness (*d*) can be calculated by Eq. (1) [19]:

$$d = \frac{QM_w}{nAF\rho} \qquad (1)$$

where Q is the charge from the area under the PANI switch from LE to EM^{2+} peak corrected by the baseline at a low scan rate of 8 mV s^{-1}, A is the electrode area, and F the Faraday constant (96,485 C mol^{-1}); $n = 0.5$ is the charge number of aniline unit in polymer chains; M_w is the molecule weight of aniline (93.13); ρ is the aniline density (1.02 g cm^{-3}).

3. RESULTS AND DISCUSSION

3.1 Electropolymerization of PANI film on SPG

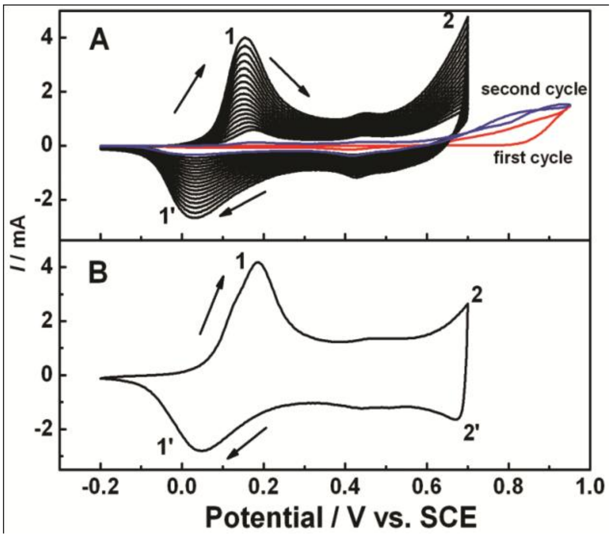


Figure 1. (A) Potentiodynamic polymerization of aniline in N_2-saturated 0.5 mol L^{-1} H_2SO_4 + 0.1 mol L^{-1} aniline monomer solution at 8 mV s^{-1} (first two cycles: –0.2 to 0.7 V, other cycles: –0.2 to 0.9 V). **(B)** Stable cyclic voltammogram of the PANI film right after electropolymerization recorded in N_2-saturated aniline-free 0.5 mol L^{-1} H_2SO_4 at scan rate of 8 mV s^{-1}.

Cyclic voltammograms (CVs) for the electrochemical polymerization of aniline is shown in Fig. 1A. It can be seen that the current sharply increases from 0.75 V in the first positive sweep, which indicates the aniline oxidation and consequent cation radical formation to initiate the polymeric growth. Two initiation cycles were necessary to attain the formation of higher number of aniline radicals and necessary to initiate the oligomeric formation. Andrade et al. [20] reported that the polymerization rate of only the first or the first two cycles is an important factor in controlling PANI morphology and its electrochemical behavior. After the first two cycles, two pairs of redox peaks labeled as 1/1′-2/2′ and a distinct irreversible anodic current peak at about 0.92 V were observed. The oxidation current peak 1/1′ at 0.2 V is due to the transformation of PANI from LE state to EM^{2+}state. The pair of current peaks 2/2′ centred at about 0.45 V is contributed to the redox behavior of the reaction intermediates of aniline oxidation, which are trapped within the PANI matrix. The formation of benzoquinone (BQ) as hydrolysis product has been indentified by CV, rotating ring disk electrode (RRDE) and UV visible spectroscopy in literature [21]. The assignment for these redox peaks were verified earlier by *in situ* electro spin resonance and spectroelectrochemical studies [22,23]. On the other hand, the formation of BQ during polymerization was generally avoided by using an appropriate upper potential limit below 0.8 V [24,25]. From the third cycle, the highest polymerization potential is controlled at 0.7 V and the first redox peak current increase with time, suggesting the formation and growth of conducting PANI film on the SPG electrode surface.

The stable CVs of the EM^{2+} form of PANI in N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution after dried for 2 h is shown in Fig. 1B. It can be seen that the polymer have good redox reversibility.

3.2 SEM characterization

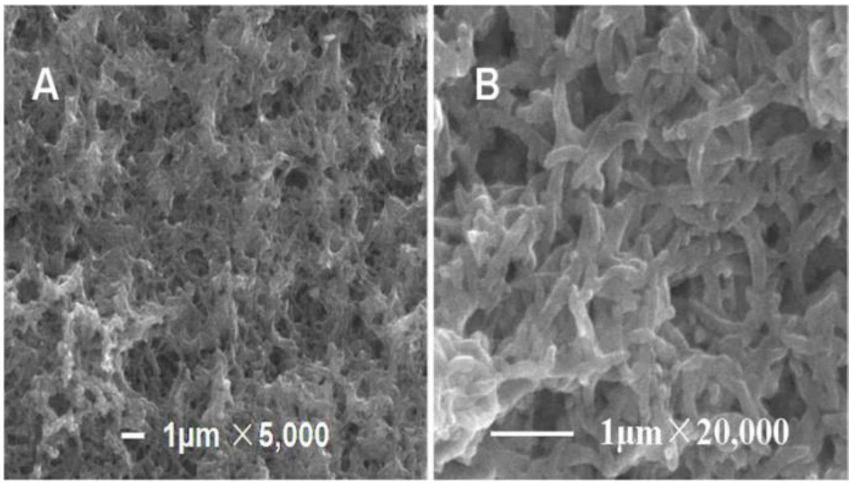


Figure 2. SEM micrographs of the as-prepared PANI film at different magnification times: **(A)** × 5,000 and **(B)** × 20,000.

The SEM images of the PANI/SPG are shown in Fig. 2, it is observed that the as-prepared PANI film had porous morphology and loosely textured structure. The PANI film is composed of uniform 1D nanowires with an average diameter of about 100-200 nm and the fibers interconnected together to form a three dimensional network structure, which is quite different from that of PANI film synthesized by the chemical or direct electrochemical oxidation polymerization method [18]. The as-prepared PANI nanowire provides good in-out channels and would be an ideal candidate as electrode material for electrocatalysis since they possess three-dimensional reaction zone with higher surface area and more available active sites, which would enhance the energy efficiency and the electron transfer rate of redox reactions.

3.3 Electrochemical reduction of Cr(VI) by PANI/SPG

3.3.1 Influence of electrode potential

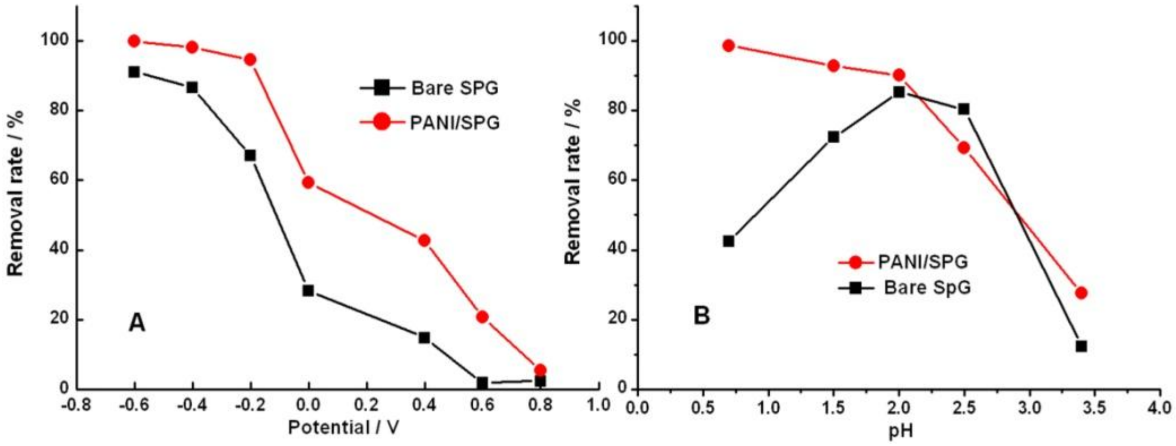
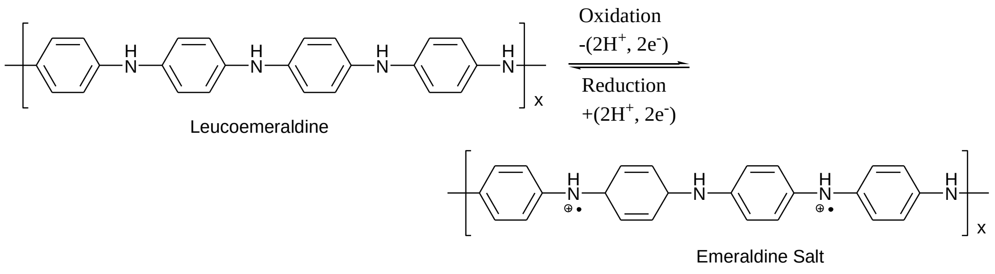


Figure 3. The effects of **(A)** cathode potential and **(B)** electrolyte pH on the removal rate of Cr(VI) at the PANI/SPG and the bare SPG electrodes. The other conditions in (A): 0.1 M H_2SO_4, PANI film thickness of 2.2 μm, 25 ^{0}C and electrolyte stirring speed of 200 rpm; in (B): cathode potential at –0.2 V, PANI film thickness of 2.2 μm, 25 ^{0}C and electrolyte stirring speed of 200 rpm.

The removal rate of Cr(VI) at cathode potentials ranging from –0.6 to 0.8 V are shown in Fig. 3A. It can be seen that the reduction rate is very slow at 0.6 V and practically did not occur at 0.8 V, which agrees well with the fact that PANI degradation takes place at high anodic potentials (above 0.6 V) [14], resulting in the low reaction rate of Cr(VI) reduction. At the potential of −0.6 V, the Cr(VI) removal rate reached ca. 98.65% on PANI/SPG electrode, but only 85.32% is achieved on the bare SPG electrode, indicating that the more negative cathode potential will facilitate the reduction of PANI to the fully reduced LE state, which exhibited the favorable advantage of PANI/SPG electrode with extremely higher removal percentage for Cr(VI) over the bare SPG electrode. This phenomenon is in agreement well with the early results reported by Farrell and Breslin [7], which suggests that much higher rates of Cr(VI) electroreduction were obtained on the oxidation of PANI from the LE to EM^{2+} state. This change in the redox state of the PANI can be viewed as a two-electron exchange reaction, as shown in Eq. (2):



(2)

At more cathodic potentials the process is limited by the low current efficiencies resulting from the parallel reaction of hydrogen evolution. Additionally, the Cr(VI) removal rate of PANI/SPG electrode is always higher than the bare SPG electrode in different potential during the same times due to the enlarged specific surface area of PANI.

3.3.2 Influence of solution pH

The effects of pH on the removal rate of Cr(VI) are shown in Fig. 3B. As seen, the pH has a strong influence on the activity of bare SPG electrode in the pH range of 0.7-3.4, but was not as important on the PANI/SPG electrode in the pH range of 0.7-2.0. In the pH range of 0.7-3.4, the PANI is considered to be conductive and spontaneous electron transfer from the polymer to Cr(VI), i.e. the PANI film acts as the reaction intermediate. When pH is greater than 2.0, the removal rates of Cr(VI) decrease dramaticlly for both electrodes, and for pH larger than 4.0 there is no longer any reaction. The absence of Cr(VI) electroreduction reaction for PANI/SPG electrode in high pH medium (especially in alkaline media) was expected since at these conditions the PANI film becomes non-conducting [26]. In addition, this phenomenon can also be explained on the basis of the fact that at higher pH values, i.e. neutral to alkaline conditions, chromium species occur in chromic form. At higher pH, the following reaction takes place and chromium may also form hydroxide in the form of $Cr(OH)_3$ [27]. Therefore under neutral to alkaline conditions the hydrated Cr^{3+} ion hydrolyses or precipitates as $Cr(OH)_3$ as shown in Eq. (3).

$$\mathrm{Cr^{3+}_{aq}} + 3\mathrm{OH^{-}_{aq}} \rightarrow \mathrm{Cr(OH)_3} \downarrow \qquad (3)$$

At pH lower than 2.0, most Cr(VI) exists as dichromate and it can be easily reduced to trivalent state, while when pH is higher than 4, Cr(VI) exists as chromate [28] and it is quite difficult to be reduced to Cr(III). Therefore, it was concluded that acid medium facilitates the kinetic of Cr(VI) reduction on conducting PANI film. In fact, the Cr(VI) oxidizes the PANI and the EM^{2+} state is immediately reduced by the electrons supplied by the current source.

3.3.3 Influence of film thickness

To investigate the effect of electrochemically synthesized PANI film thickness on the Cr(VI) reduction efficiency, the PANI film with different thickness (0.216~3.18 μm) were prepared. Fig. 4A shows the electroreduction efficience of Cr(VI) for different polymer thickness. It can be seen that the removal efficiency of Cr(VI) increase with the polymer film thickening. When the film thickness is 0.216 μm the removal efficiency of Cr(VI) is 82.32%, while the removal efficiency of Cr(VI) is up to 97.82% with the film thickness grow to 3.18 μm. The reason for this phenomenon is that the PANI film have a porous morphology and loose textured structure, the thicker film had more specific surface area. The PANI films interdigitated together and coated on the electrode, allows more interaction between solution molecule and the polymers. The Cr(VI) molecules penetrate through the entire film and interact with all the nanowires. In other word, the PANI as the reaction intermediate plays an important role on electron transfer. On the other hand, the thicker PANI film contained more reduced units, which reduced more Cr(VI) with a faster rate as reported by Farrell and Breslin [7].

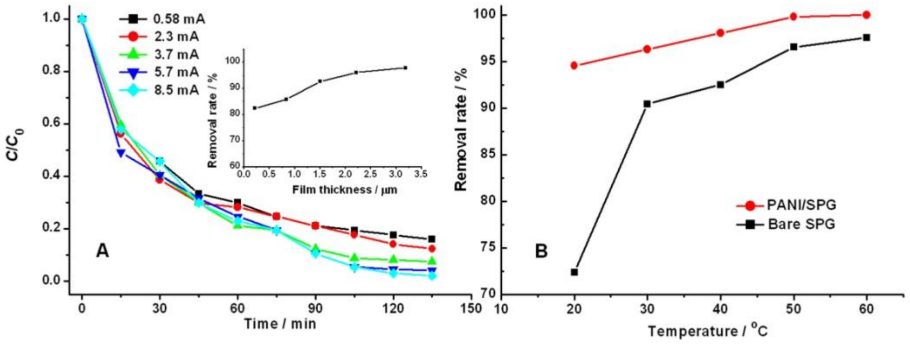


Figure 4. The effects of **(A)** PANI film thivkness and **(B)** temperature on the removal rate of Cr(VI) at the PANI/SPG and the bare SPG electrodes. The other conditions in (A): cathode potential at –0.2 V, 0.1 M H_2SO_4, 25 ^{0}C and electrolyte stirring speed of 200 rpm; in (B): cathode potential at –0.2 V, 0.1 M H_2SO_4, PANI film thickness of 2.2 μm and electrolyte stirring speed of 200 rpm.

3.3.4 Influence of temperature

The removal rate of Cr(VI) as a function of solution temperature is plotted in Fig. 4B. The temperature is chosen from 20~60 ºC, because it has been shown that the electroactivity of PANI starts to decrease when the temperature exceeds 70 ºC [29]. When the heated temperature is lower than 70ºC, the PANI only loss of water or solvent [30] and is still stable. In solution containing Cr(VI) at 20ºC, the removal rate is about 94.57%. With the increase of temperature, the removal efficiency goes up to ca. 100% when the temperature is 60 ºC. These date show that the temperature has no evident effect on the Cr(VI) reduction on PANI/SPG. As for the bare SPG electrode, the removal efficiency is about 70% at 20 ^{0}C. With the increase in temperature, the removal efficiency goes up to more than 95%, indicating that the redcttion rate of Cr(VI) with bare SPG electrode is accelerated by the increase of temperature. So the higher temperature is beneficial for the electroreduction of Cr(VI) on the bare SPG electrode.

3.4 Mechanism and Kinetics of Cr(VI) electroreduction on PANI/SPG

A possible explanation for the electroreduction behavior of Cr(VI) on the PANI/SPG electrode can be given by the redox chemistry of PANI. The reduction of Cr(VI) by PANI film has previously been described by Eq. (2). During the electroreduction reaction, PANI is transformed from the fully reduced form, LE to the partially oxidized EM^{2+} form. The reduction of Cr(VI) at the PANI/SPG electrode can be described by Eq. (4). PANI film coated on the SPG electrode not only increases the electrode area but also accelerates the electron transfer from the polymer chain to the Cr(VI) present in solution.

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 3PANI^0\ (LE) \longrightarrow 2Cr^{3+} + 3PANI^{2+}(EM) + 7H_2O} \tag{4}$$

where $PANI^0$ refers to PANI in the LE state and $PANI^{2+}$ refers to PANI in the EM^{2+} state. The large amounts of reduced Cr(III) is released into the solution phase, although some may be trapped within the polymer. Indeed, it was possible to detect the Cr(III) complex by adjusting the solution pH with sodium hydroxide. A white precipitate was observed to generate, which indicates the presence of Cr(III) and the formation of the $Cr(OH)_3$ precipitation product as described in Eq. (3).

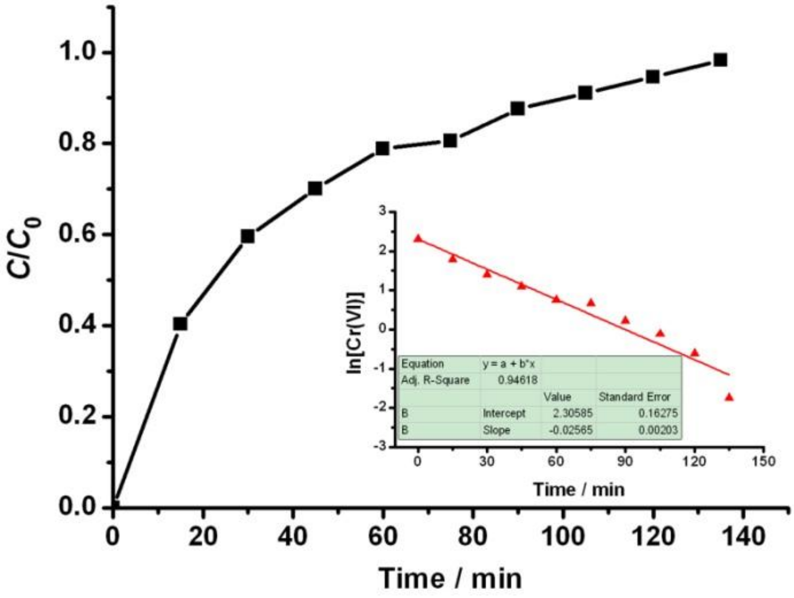


Figure 5. Normalized Cr(VI) concentration depletion as a function of time under the optimal conditions of cathode potential at –0.2 V, solution pH of 1.5, PANI film thickness of 3.4 µm, 25 ^{0}C and electrolyte stirring speed of 200 rpm. The inset shows a typical pseudo-first-order plot showing the logarithm of the Cr(VI) concentration as a function of time.

The electroreduction process of Cr(VI) on the PANI/SPG electrode was found to obey pseudo-first-order kinetics. This is in agreement with reports in the literature, in which Cr(VI) has been reduced at a PPy-coated carbon substrate [31,32] and by iron [33]. The rate law for the Cr(VI) reduction reaction at PANI film may be expressed as Eq. (5).

$$R = k[\mathrm{Cr(VI)}]^1[\mathrm{PANI}^0]^m[\mathrm{H}^+]^p \tag{5}$$

However, since the acid is in excess and assuming that the concentration of $PANI^0$(LE) remains high and is invariant relative to the levels of Cr(VI), then Eq. (5) may be reduced to Eq. (6) where k^0 represents a pseudo-first-order rate constant.

$$R = k^0[\mathrm{Cr(VI)}]^1 \qquad (6)$$

Normalized concentration depletion as a function of time under the optimal conditions (–0.2 V, pH 1.5, film thickness: 3.4 μm, 25 ^{0}C and electrolyte stirring rate: 200 rpm) and a typical pseudo-first-order plot showing the logarithm of the Cr(VI) concentration as a function of time are shown in Fig. 5. This reasonable adherence to pseudo-first-order kinetics indicates that the concentration of PANI^0 remains essentially constant throughout the duration of the experiments. The pseudo-first-order rate constant (k^0) was found to be 2.57 × 10^{-2} min^{-1}. Although this low value is indicative of a slow reaction, it is partly related also with the low surface area of the polymer exposed to the solution (0.785 cm^2), as the reduction of Cr(VI) is a surface phenomenon.

3.5 Electrochemical reproducibility and stability of PANI

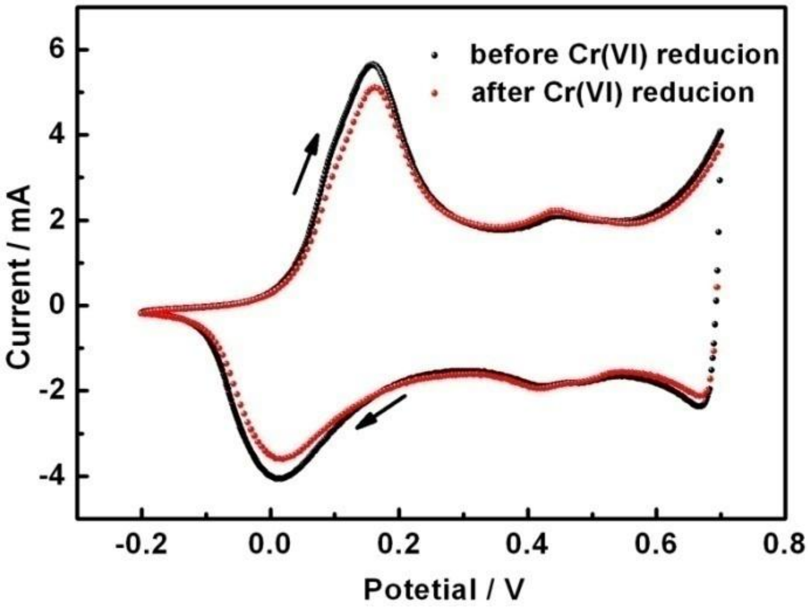


Figure 6. Cyclic voltammograms of the PANI/SPG electrode before and after used in Cr(VI) electroreduction process recorded in N_2-saturated 0.5 mol L^{-1} H_2SO_4 solution at scan rate of 10 mV s^{-1}.

The electrochemical behaviors of the PANI film before and after use in Cr(VI) reduction at the optimal conditions were investigated in N_2-saturated 0.5 M H_2SO_4 solutions (Fig. 6). The redox peaks change slightly indicating that the PANI film had good stability. In order to further clarify this conclusion, the FT-IR spectra of the PANI film before and after use in Cr(VI) reduction process were also measured and the results are shown in Fig. 7.

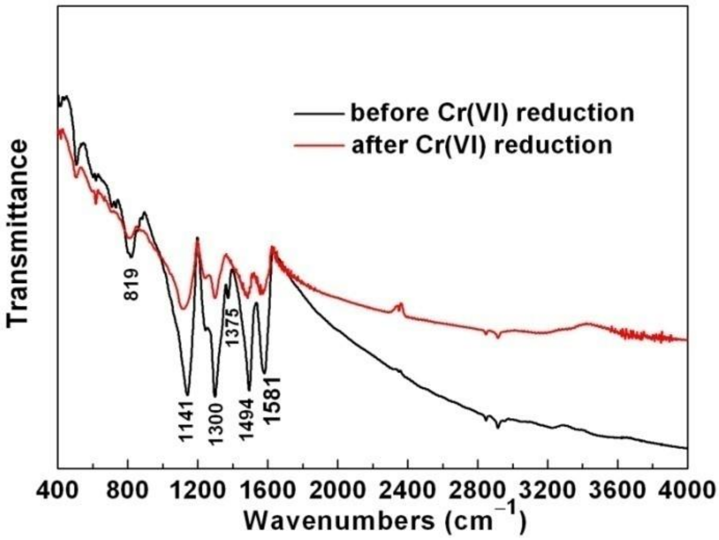


Figure 7. FT-IR spectra of the PANI films before and after used in Cr(VI) electroreduction process.

As seen, the peaks at 1581, 1494, 1300 and 819 cm^{-1} in the FT-IR spectra of before used PANI are attributed to the EM^{2+} form of PANI, while the bands corresponding to stretching vibration of N-B-N and N=Q=N structures appeared at 1494 and 1581 cm^{-1}, respectively, where -B- and =Q= stands for benzenoid and quinoid moieties in the polymer. The bands corresponding to stretching mode of C-N bond located at ca. 1300 cm^{-1}. The C-H in-plane and out-plane bending vibration of p-disubstituted benzene ring appeared around 1141 and 819 cm^{-1}, respectively [34]. The bonds in FT-IR spectra of the after used PANI film show that the peak intensities become lower than that of the before used PANI. The intensity of the broad band at wavenumbers above 2000 cm^{-1} is the characteristic of the conducting form of PANI. It decreases after the PANI was used in Cr(VI) electrochcemical reduction, reflecting the decrease in the conductivity of PANI. The band at 1375 cm^{-1} attributed to C-N stretching in the neighbourhood of a quinonoid ring, and it is typical for the spectrum of the PANI base. This band disappeared after Cr(VI) reduction indicating the convertion of PANI from EM^{2+} to LE form. The spectrum of PANI is red-shifted after used in Cr(VI) reduction, suggesting that the PANI film are more protonated after Cr(VI) reduction than the fresh one. Above results suggested that a slight change in PANI structure occurred after used in Cr(VI) reduction.

4. CONCLUSION

PANI nanowire developed on SPG electrode surface was achieved by the two-step electrochemical oxidation polymerization method. SEM shows that the PANI films on SPG have porous morphology and loose textured structure, it have a large amount of thin and long fibers with diameters of 100-200 nm. Compared to the bare SPG electrode, the PANI/SPG electrode has obvious advantages on Cr(VI) electroreduction reaction. The negative potential, low pH, the appropriate electrolyte temperature and PANI film thickness facilitated the removal of Cr(VI). The electroreduction of Cr(VI) on the PANI modified SPG electrode proceeds by pseudo-first-order kinetics. The CV and FT-IR results demonstrate that PANI modified electrode may be a promising alternative for heavy matel electroreduction.

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