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One-step synthesis of AgCl/polyaniline core–shell composites with enhanced electroactivity

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Abstract

Silver chloride/polyaniline (PANI) core–shell composites were synthesized through a facile one-step process in the presence of polyvinylpyrrolidone (PVP). PVP not only acted as an anchor agent leading to the formation of the core–shell structure but also prevented the aggregation of PANI efficiently. Transmission electron microscopy (TEM) images gave direct evidence of the core–shell structure. Fourier transform infrared (FTIR) confirmed the formation of PANI and x-ray diffraction (XRD) showed the presence of crystal AgCl. Cyclic voltammetric experiments indicated that this kind of material showed excellent redox ability in neutral solution. Based on the excellent electrochemical behaviour of the AgCl/PANI, it was applied to construct a H₂O₂ biosensor. The biosensor exhibited a fast amperometric response to H₂O₂ with the linear range 6×10^{-4} – 9×10^{-3} mol l⁻¹.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Polyaniline (PANI) is known as one of the most important conducting polymers due to its high conductivity, ease of preparation, good environmental stability, and a large variety of applications, especially in light-emitting and electronic devices [1], chemical sensors [2], separation membranes [3], and antistatic coatings [4]. PANI is unique among the family of conjugated polymers, since its doping level can be controlled through an acid doping/base dedoping process. However, PANI is redox-active only for acidic conditions, generally at pH < 4 [5, 6]; this greatly restricts its applications in bioelectrochemistry, which normally needs a neutral pH environment.

The inorganic/conducting PANI nanocomposites with different combinations of the two components have attracted significant academic and technological attention, since they have interesting physical properties and potential

applications [7]. Usually, controlling the shape, size, and morphology of the nanocomposites is very important for defining their properties [8, 9]. Recently, there has been increasing interest in the fabrication of core–shell nanomaterials because of their novel physical properties and potential applications [10]. Li *et al* reported PANI-capped silicon nanoparticles through the self-assembly method [11]. In their study, the photoluminescence spectrum and lifetime of silicon were not affected by the presence of PANI layers. Xia and Wang synthesized silica/PANI and titanium oxide/PANI core–shell nanocomposites through ultrasonic irradiation [12, 13]. Sarma and his coworkers have synthesized PANI-coated Au composite that has significantly higher electrical conductivity than PANI alone [14]. Qiu and Gao first presented the preparation of a new class of PANI/titanium nitride nanocomposites with enhanced electrical properties [15]. PANI/AgCl composites were synthesized in different reverse micelles that required large amounts of organic solvent [16, 17].

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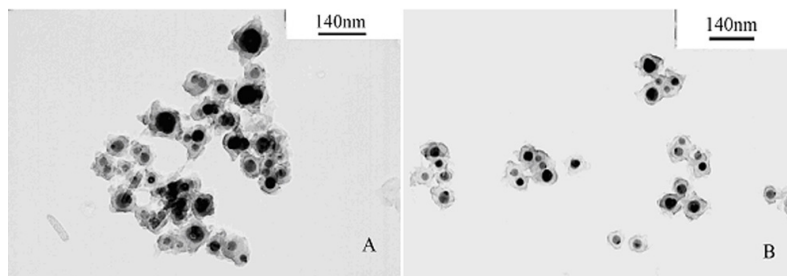


Figure 1. TEM images of AgCl/PANI core-shell composite synthesized in different concentration of PVP: (A) 2%; (B) 4%. Other synthesis conditions: AgNO_3 0.012 M; aniline 0.012 M; $[\text{An}]:[\text{APS}] = 1:1$; reaction time 24 h.

In the present study, we synthesized silver chloride/PANI core-shell composites through a facile one-step process in the presence of PVP. Herein, PVP could act as an anchor agent, resulting in the formation of PANI-coated AgCl nanocomposites. The obtained product showed excellent electrochemical behaviour and was applied to detect H_2O_2 at pH neutral environment. The core-shell structure was also characterized by TEM, XRD, FTIR, and TGA (thermogravimetric analysis).

2. Experimental section

2.1. Materials

Aniline, silver nitrate (AgNO_3), polyvinylpyrrolidone (PVP), hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS) were purchased from Shanghai Chemical Reagent Co. Aniline was distilled under reduced pressure and other reagents were used as received without further treatment.

2.2. Synthesis of AgCl/PANI core-shell composites

AgNO_3 (0.012 M) and aniline (0.012 M) were added to 2% or 4% PVP aqueous solution. 5 ml of 1 M HCl aqueous solution of APS as oxidant was dropped into the above mixture under stirring at room temperature. The molar ratio of aniline to APS ($[\text{An}]:[\text{APS}]$) was 1:1. The reaction was allowed to proceed for 24 h. After that, the precipitate was centrifuged and washed several times with distilled water and ethanol. The final product was dried in vacuum at 40°C for 24 h.

2.3. Preparation of AgCl/PANI modified glassy carbon electrodes

The glassy carbon electrodes (GCE, 3 mm in diameter) were polished with 1.0, 0.3, and $0.05\ \mu\text{m}$ alumina slurry followed by a rinse with doubly distilled water and then allowed to dry at room temperature.

AgCl/PANI core-shell composites were dispersed in distilled water to form a $1.0\ \text{mg ml}^{-1}$ solution and ultrasonically treated for 30 min, then $5\ \mu\text{l}$ of colloidal solution was dropped onto the pre-treated GCE surface and allowed to dry under ambient conditions.

2.4. Characterization

The core-shell structure of AgCl/PANI was verified by transmission electron microscopy (TEM, JEOL JEM-200CX).

Powder x-ray diffraction patterns (XRD) were recorded on a Philip-X'Pert x-ray diffractometer with a $\text{Cu K}\alpha$ x-ray source. Fourier transform infrared (FTIR) spectroscopy measurements were performed on a Bruker Fourier transform spectrometer model VECTOR22 using KBr pressed discs. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument from room temperature to 800°C with a heating rate of $10^\circ\text{C min}^{-1}$ in air atmosphere. Electrochemical experiments were conducted using a CHI660B workstation (from Shanghai Chenhua, Shanghai) in a three-electrode system. All electrochemical experiments were performed in a cell containing 20.0 ml of phosphate buffer solution (PBS, 0.1 M) at room temperature and using a coiled platinum wire as the auxiliary, a saturated calomel electrode (SCE) as reference, and the AgCl/PANI modified glassy carbon electrode (GCE) as a working electrode. All experimental solutions were deaerated by bubbling highly pure nitrogen for 20 min, and a nitrogen atmosphere was kept over the solutions during measurements.

3. Result and discussion

PANI-coated AgCl nanocomposites were successfully synthesized through a facile one-step process in the presence of PVP. The core-shell structure can be confirmed directly by TEM, as shown in figure 1. The dark spots inside the nanoparticles correspond to AgCl that is surrounded by spherical PANI matrix. The effect of PVP concentration on the resultant core-shell composite has been studied. When the percentage content of PVP is 2%, the shell thickness and core diameter of the obtained particles is 20 and 20–70 nm (figure 1(A)), respectively. The diameter of the AgCl/PANI composite nanoparticles is between 40 and 90 nm. When the percentage content of PVP is increased from 2% to 4%, the prepared particles with a shell thickness of 20 nm and a core diameter of 20–50 nm are uniform in size and well dispersed (figure 1(B)). The diameter of the AgCl/PANI composite nanoparticles is between 40 and 70 nm. When the PVP concentration is increased from 2% to 4%, the degree of dispersion and the uniformity of resultant composite nanoparticles is improved. The PVP concentration has less effect on the PANI shell thickness, but has a strong effect on the AgCl core diameter due to the different reaction speeds and interaction mechanisms. During the process for the formation of AgCl/PANI core-shell nanoparticles, when HCl aqueous solution of ammonium persulfate is added dropwise to PVP solution containing AgNO_3 and aniline, a white AgCl precipitate appeared immediately and gradually turned

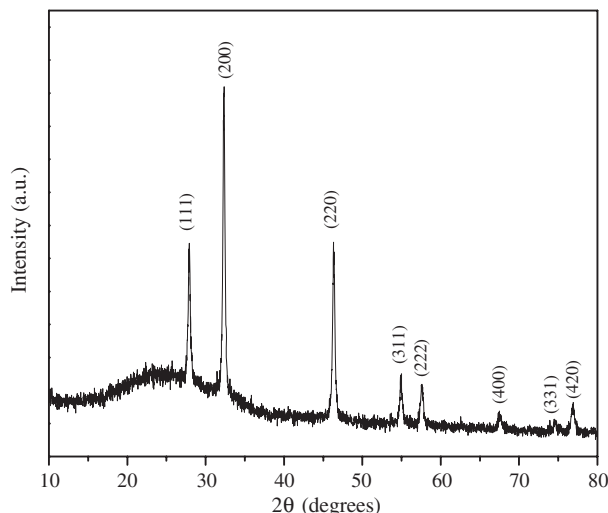


Figure 2. XRD pattern of AgCl/PANI core-shell composite. Synthesis conditions: AgNO₃ 0.012 M; aniline 0.012 M; [An]:[APS] = 1:1; PVP 4%; reaction time 24 h.

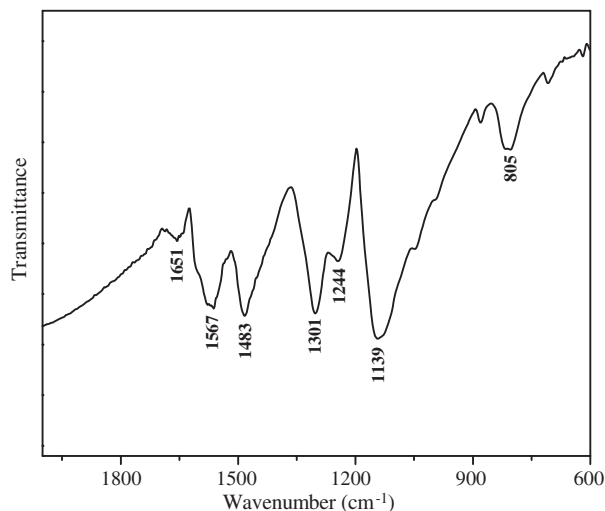


Figure 3. FTIR spectrum of AgCl/PANI core-shell composite. Synthesis conditions: AgNO₃ 0.012 M; aniline 0.012 M; [An]:[APS] = 1:1; PVP 4%; reaction time 24 h.

blue in 30 min. Herein, PVP as an anchor agent plays an important role. Without PVP, the core-shell structure could not be formed. It is well known that specific functional groups such as $-\text{CONH}-$, $-\text{SO}_4^-$, and $-\text{C}=\text{O}$ groups can be used to induce coating during the precipitation and surface reactions on the cores [18–21]. PVP is a useful steric agent to promote a strong interaction between AgCl particles and aniline monomer. For example, it has been used successfully in the preparation of uniform silica/polypyrrole core-shell particles [22]. The amphiphilic property of PVP would be beneficial for the adherence between the polymer shell and the inorganic core. Ag–O coordination could be formed through the pyrrolidone ring which was tilted on the surface of the silver [23]. PVP with its dipolar imide group carries a fractional negative charge on carbonyl oxygen [24]. Polycationic PANI can react with PVP by an electrostatic effect. The adsorbed PVP might provide active sites on the AgCl so as to induce the growing polycationic PANI chains to complete the coating of PANI layers. At the same time, PVP can prevent the aggregation of PANI efficiently [25, 26].

The powder x-ray diffraction (XRD) pattern confirms the presence of AgCl nanoparticles in the composites. As shown in figure 2, the broad band appearing at 2θ value of 25° is ascribed to the periodicity parallel to the polymer chains of PANI [27]. Another eight diffraction peaks above 25° correspond to Bragg's reflections from (111), (200), (220), (311), (222), (400), (331), and (420) planes of AgCl, and are in good agreement with the reported data (JCPDS File No. 06-0480), showing the existence of AgCl nanoparticles in the AgCl/PANI core-shell composite. Crystallite sizes were calculated from the AgCl(111) diffraction line using Scherrer's equation, $L = k\lambda/\beta \cos \theta$, where L is the mean dimension of the crystallites, β is the full width at half maximum of the diffraction peak, θ is the diffraction angle, λ is the wavelength of the Cu K α radiation (0.1540 nm), and K is equal to 0.89 [28]. The calculated average size of AgCl in the composite is about 40 nm, which is consistent with the result from TEM (figure 1(B)).

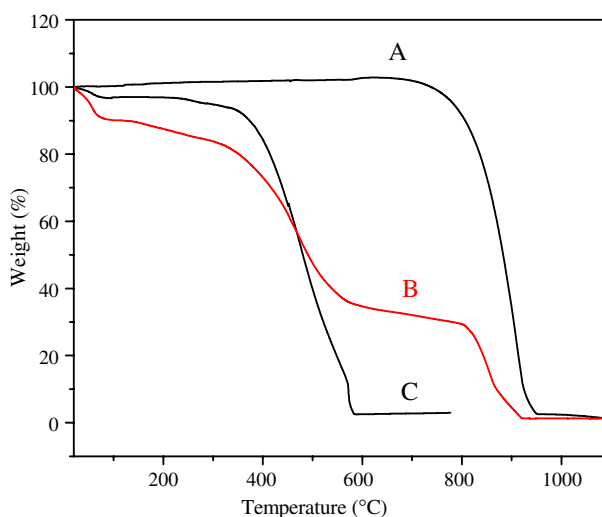


Figure 4. TGA curves for (A) AgCl, (B) AgCl/PANI core-shell composite, and (C) intrinsic PANI. Synthesis conditions: AgNO₃ 0.012 M; aniline 0.012 M; [An]:[APS] = 1:1; PVP 4%; reaction time 24 h.

The molecular structure of the AgCl/PANI is characterized by FTIR spectroscopy as shown in figure 3. The characteristic peaks at 1567 and 1483 cm^{-1} correspond to the $\text{C}=\text{C}$ stretching of quinoid and benzenoid rings [29], 1301 and 1244 cm^{-1} are related to the $\text{C}-\text{N}$ and $\text{C}=\text{N}$ stretching modes [30], 1139 cm^{-1} is assigned to the in-plane bending of $\text{C}-\text{H}$, [31] and 805 cm^{-1} is attributed to the out-of-plane bending of $\text{C}-\text{H}$ [32]. The absorption band assignable to $\text{C}=\text{O}$ is observed at 1651 cm^{-1} , which indicated the presence of PVP.

The core-shell AgCl/PANI was also characterized by the thermogravimetric studies. Figure 4 summarizes the results of the thermo-gravimetric studies on AgCl, AgCl/PANI core-shell composite, and intrinsic PANI. The TGA curve of intrinsic PANI shows a two-step weight loss. The weight loss in the first step is attributed to the loss of residual water.

The second step starting at around 300 °C corresponds to polymer degradation [33]. The total weight loss of intrinsic PANI is 100% in this experimental conditions. In the case of AgCl/PANI core-shell composite, TGA curves show a four-step weight loss. The first weight loss is consistent with the intrinsic PANI. The second weight loss ranging from 200 to 300 °C is believed to be due to the departure of a proportion of acid dopant, and the third weight loss step is attributed to the decomposition of PANI and PVP chains and the departure of residual acid dopant [23]. The fourth step, starting at around 800 °C, is due to the decomposition of AgCl that is consistent with pure AgCl.

Cyclic voltammetric experiments were performed to test the electroactivity of the composite. The bare GCE was previously tested in different pH phosphate buffer solutions (PBS) before the AgCl/PANI composite was drop-coated onto it. It presents no redox process in the potential range studied. To assure diffusion of the solution into the interlayer space and to permit better ionic exchange, the working electrode coated with the composite is immersed in the electrolyte solution for 30 min prior to the measurement. Figure 5 gives the cyclic voltammograms of AgCl/PANI modified GCE measured in different pH PBS at a scan rate of 100 mV s⁻¹. A broad redox peak is observed in pH 4 PBS buffer solution for the sample with the redox potential at around 0.17 V. This redox peak is the overlap of two redox processes normally found for the PANI system in acidic conditions [34, 35], as confirmed by the redox behaviour of the composites measured in different pH buffer solutions. PANI shows two separate redox peaks in pH 1 PBS; however, these two redox peaks move closer as the pH of the solution is increased to 3, and finally they merge to show only one broad redox peak when the pH is 4. It is well known that PANI exists in three well-defined oxidation states: leucoemeraldine, emeraldine and pernigraniline. In the leucoemeraldine state, all the nitrogen atoms are amines, whereas in the pernigraniline state the nitrogen atoms are imines. The amine/imine ratio in emeraldine is ~1. Moreover, emeraldine can be in its base or salt form, depending on the pH value. The first oxidation wave is assigned to the transition of leucoemeraldine to emeraldine salt and the second oxidation wave is due to the transition from emeraldine salt to pernigraniline state [36]. This electrochemical behaviour of AgCl/PANI is also similar to that of PANI/carbon nanotube multilayer films prepared via the layer-by-layer method [37].

Figure 5(B) gives the effect of the potential scan rate (v) on the peak current for the AgCl/PANI modified electrode in the range of 20–500 mV s⁻¹. With the increase in scan rate, the anodic peak potential shifts to a more positive direction and the cathodic peak potential shifts toward the more negative direction. The anodic peak currents for PANI increase linearly with the square root of the scan rate ($v^{1/2}$), indicating that the peak current is diffusion controlled [38].

Many effective efforts have been directed toward enhancing the electroactivity of PANI, either by introducing acidic groups into the PANI chains [39] or doping PANI with negatively charged polyelectrolytes [40, 41]. Some of these materials have been successfully utilized to immobilize enzymes [42]. In the capacitance–voltage (CV) curves, it is clear that the AgCl/PANI core-shell composites show very good redox activity at neutral pH environment in PBS. It

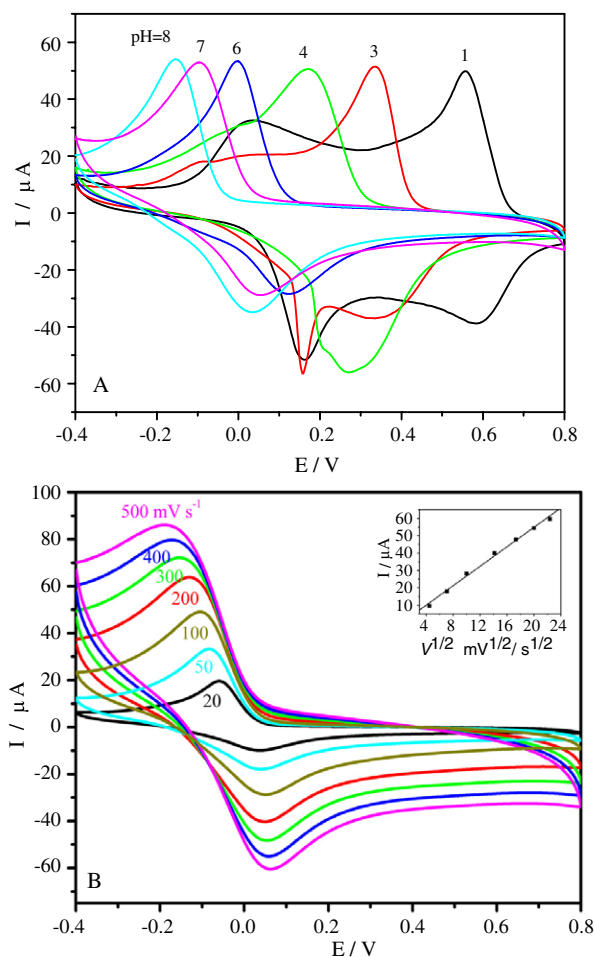


Figure 5. Cyclic voltammograms of (A) AgCl/PANI core-shell composites modified GCE measured in different pH PBS buffer at a scan rate of 100 mV s⁻¹ and (B) AgCl/PANI modified GCE in PBS (pH = 7.0) at different scan rates: from inner to outside 20, 50, 100, 200, 300, 400, 500 mV s⁻¹. Insets show calibration plots between the anodic peak current and the square root of the scan rate. Synthesis conditions: AgNO₃ 0.012 M; aniline 0.012 M; [An]:[APS] = 1:1; PVP 4%; reaction time 24 h.

is well known that silver halides are one type of important semiconductor. Although AgCl particles do not make a continuous electron path, the incorporated conducting AgCl generates more active sites for the charge transfer through the interface inside the electrode by making good contacts with the PANI matrix, thus PANI particles located far from the electrode surface can effectively take part in the redox reaction [43]. The existence of a small amount of stabilizer, PVP, may have an effect on the electroactivity of PANI. At the same time, we believe that more studies are needed to investigate the exact mechanism for the enhancement in electroactivity.

Based on the excellent electrochemical behaviour of AgCl/PANI composite, it was immobilized on the surface of glassy carbon electrode and applied to construct a H₂O₂ sensor. In the potential range of 0.8 and -0.4 V, the cyclic voltammograms of AgCl/PANI modified electrode in PBS before and after the addition of H₂O₂ are shown in figures 6(A) and (B), respectively. Both the reduction and oxidation current for the AgCl/PANI modified GCE are increased after the

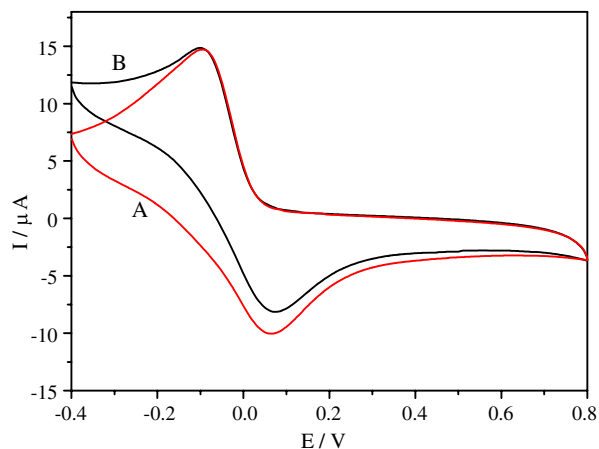


Figure 6. Cyclic voltammograms of AgCl/PANI core-shell composites modified in GCE immersed in pH 7 PBS without (A) and with (B) 0.25 mM H_2O_2 at 100 mV s^{-1} . Synthetic conditions: AgNO_3 0.012 M; aniline 0.012 M; $[\text{An}]:[\text{APS}] = 1:1$; PVP 4%; reaction time 24 h.

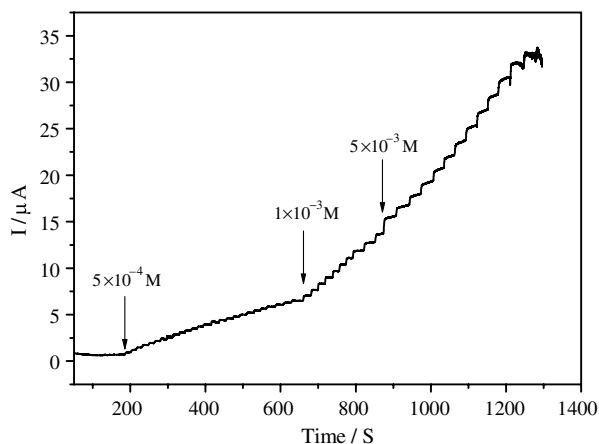


Figure 7. Typical steady-state response of AgCl/PANI modified GCE on successive injection of different concentration of H_2O_2 into 0.1 M PBS (pH = 7.0) while stirring with an applied potential of -0.4 V . Synthetic conditions: AgNO_3 0.012 M; aniline 0.012 M; $[\text{An}]:[\text{APS}] = 1:1$; PVP 4%; reaction time 24 h.

addition of H_2O_2 . However, no electrocatalytic current can be obtained at bare GEC in the potential range scanned, indicating that the AgCl/PANI composite can act as a catalyst for the reduction of H_2O_2 .

The current–time curve is recorded under the conditions of continuous stirring of the solution and successive step changes of H_2O_2 concentration at -400 mV (as shown in figure 7). When an aliquot of H_2O_2 is added into 20 ml of PBS, the reductive current rises steeply to reach a stable value. The time to reach 95% of the maximum current is within 6 s, which indicates a fast response process. The AgCl/PANI modified GCE display increasing amperometric responses to H_2O_2 with linear ranges from 6×10^{-4} to $9 \times 10^{-3} \text{ mol l}^{-1}$, and the detection limit was $2 \times 10^{-4} \text{ mol l}^{-1}$ based on $\text{S/N} = 3$.

Additional experiments were done to test the reproducibility and stability. It was found that the peak current retained 99% of its initial response for AgCl/PANI modified GCE after 100 cycles at a H_2O_2 concentration of 2 mM (scan rate

100 mV s^{-1}). Besides, no obvious change was found after the modified electrodes were immersed in PBS and stored in the refrigerator at 4°C for 20 h and when the biosensor was stored in a dry state at 4°C for 20 days. The relative standard deviation of the peak current (RSD) in six successive determinations at a H_2O_2 concentration of 2 mM was 0.6% for AgCl/PANI modified GCE. Furthermore, five AgCl/PANI modified GCEs were fabricated independently. The corresponding RSD value determined at a H_2O_2 concentration of 2 mM was 4.5%.

4. Conclusion

We have demonstrated the one-step synthesis of AgCl/PANI core-shell nanocomposites in the presence of PVP. When the percentage content of PVP was 4%, the obtained particles with shell thickness of 20 nm and core diameter of 20–50 nm were uniform in size and well dispersed. The core-shell structure was characterized by TEM, XRD, FTIR, TGA and CV. In the CV measurements, it was found that the AgCl/PANI nanocomposites showed one well-defined pair of redox peaks in neutral pH environment. This material with excellent electrochemical behaviour was exploited to develop a H_2O_2 biosensor.

Acknowledgments

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