

## 壳聚糖作用下一步法合成具有高电活性的 AgCl@ 聚苯胺核壳结构

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**摘要:** 在壳聚糖的作用下, 采用简单的一步法合成了具有星状结构的氯化银/聚苯胺核壳型复合材料。当壳聚糖的浓度为 1% 时, 所制备的氯化银/聚苯胺复合材料具有高度的分散性, 壳层厚度为 30~80 nm、核的直径在 25~60 nm 范围内。通过透射电镜、红外光谱和 X-射线衍射对样品的形态和组成进行了表征。循环伏安实验结果表明这种复合材料在中性条件下具有很好的电化学活性。

**关键词:** 氯化银; 聚苯胺; 核壳; 电化学活性

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## One Step Synthesis of AgCl@Polyaniline Core-shell Nanostructure with Enhanced Electrochemical Activity in the Presence of Chitosan

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**Abstract:** Silver chloride@polyaniline (PANI) core-shell composites with a star-like structure were synthesized through a facile one-step process in the presence of chitosan. When the chitosan concentration was 1%, highly dispersed AgCl@PANI core-shell nanostructure with a shell thickness of 30~80 nm and a core diameter of 25~60 nm could be obtained. The morphology and composition were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD). Cyclic voltammetric experiments indicated that this kind of material showed excellent electrochemical activity in neutral pH environment.

**Key words:** silver chloride; polyaniline; core-shell; electrochemical activity

## 0 Introduction

The synthesis of materials with controlled size and morphology is an important factor for defining properties such as the electronic band gap, conductivity and light emission efficiency<sup>[1]</sup>. Three-dimensional (3D) nanomaterials with core-shell structure, located in the transition region between atoms and bulk solids, are interesting in the fields of catalysis, biosensor, and light-emitting devices because of their large BET

surface area, particle size and quantum effect<sup>[2]</sup>.

Conducting polymer/inorganic nanocomposites with different combinations of the two components have attracted more and more attention, since they have interesting physical properties and many potential applications<sup>[3]</sup>. As one of the most important conducting polymers, polyaniline (PANI) has been intensively studied in recent years. This is mainly because it has many advantages such as easy synthesis and good environmental stability as well as electronic, biological,

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and optical properties<sup>[4-7]</sup>. The fabrication of nanocomposites containing PANI and a large variety of inorganic nanoparticles with core-shell structure have been reported<sup>[8-10]</sup>.

However, PANI is redox-active only at acidic conditions, generally at  $\text{pH} < 4$ <sup>[11]</sup>, this greatly restricts its applications in bioelectrochemistry, which normally needs a neutral pH environment. Many effective efforts have been directed towards enhancing the redox-active of PANI either by introducing acidic groups into the PANI chains or doping PANI with negatively charged polyelectrolytes<sup>[12,13]</sup>. Some of these materials have been successfully used to immobilize enzymes<sup>[14]</sup>.

We synthesized AgCl@PANI nanocomposites with core-shell structure in the presence of chitosan in this work. Herein, chitosan as an anchor agent promoted a strong interaction between AgCl particles and aniline monomer, leading to the formation of AgCl@PANI core-shell structure. The morphology and composition were characterized by transmission electron microscopy (TEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD). Cyclic voltammetric experiments indicated that this kind of material showed excellent electrochemical activity.

## 1 Experimental

### 1.1 Materials

Aniline, silver nitrate ( $\text{AgNO}_3$ ), hydrochloric acid (HCl) and ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , APS) were purchased from Shanghai Chemical Reagent Co. The deacetylation degree of chitosan (Nantong Shuanglin Biological Product Inc.) was about 95%. Aniline was distilled under reduced pressure and other reagents were used as received without further treatment.

### 1.2 Synthesis of AgCl@PANI core-shell composites

$\text{AgNO}_3$  (0.01 g) and aniline (0.05 mmol) were added to 20 mL of chitosan acetic acid solution. 5 mL of  $1 \text{ mol} \cdot \text{L}^{-1}$  HCl aqueous solution of APS as oxidant was added dropwise into the above mixture under stirring at room temperature. The molar ratio of aniline to APS ( $n_{\text{An}}:n_{\text{APS}}$ ) was 1:1. The reaction was allowed to proceed for 24 h to obtain the composites. After that, the pre-

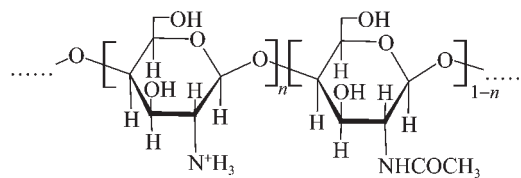
cipitate was centrifuged and washed several times with distilled water and ethanol. The final product was dried in vacuum at  $60^\circ\text{C}$  for 24 h.

### 1.3 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 taken on a Philip-X' Pert X-ray diffractometer with a  $\text{Cu K}\alpha$  X-ray source ( $\lambda = 0.15418 \text{ nm}$ ). Fourier-transform infrared (FTIR) spectroscopy measurements were performed on Bruker Fourier transform spectrometer model VECTOR22 using KBr pellets. Electrochemical experiments were conducted with a CHI660B workstation (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,  $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) at room temperature and using a coiled platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and the AgCl@PANI modified glassy carbon electrode (GCE) as the working electrode.

## 2 Results and discussion

Chitosan with excellent biodegradability, biocompatibility, and nontoxicity is an *N*-deacetylated derivative polyelectrolyte of chitin and the second-most abundant natural polysaccharide after cellulose<sup>[15-17]</sup>. In the molecular structure (Scheme 1) of chitosan, the hydroxyl and amino groups are regularly arranged at the equatorial positions in the  $\beta(1,4)$ -linked *D*-glucosamine repeating units. It can act as a stabilizer to promote the interaction between inorganic materials and PANI.



Scheme 1 Chemical structure of chitosan

AgCl@PANI core-shell nanocomposites were synthesized through a facile one-step process in the presence of chitosan. The core-shell structure can be confirmed by TEM as shown in Fig.1. The dark spots inside the nanoparticles correspond to AgCl that is

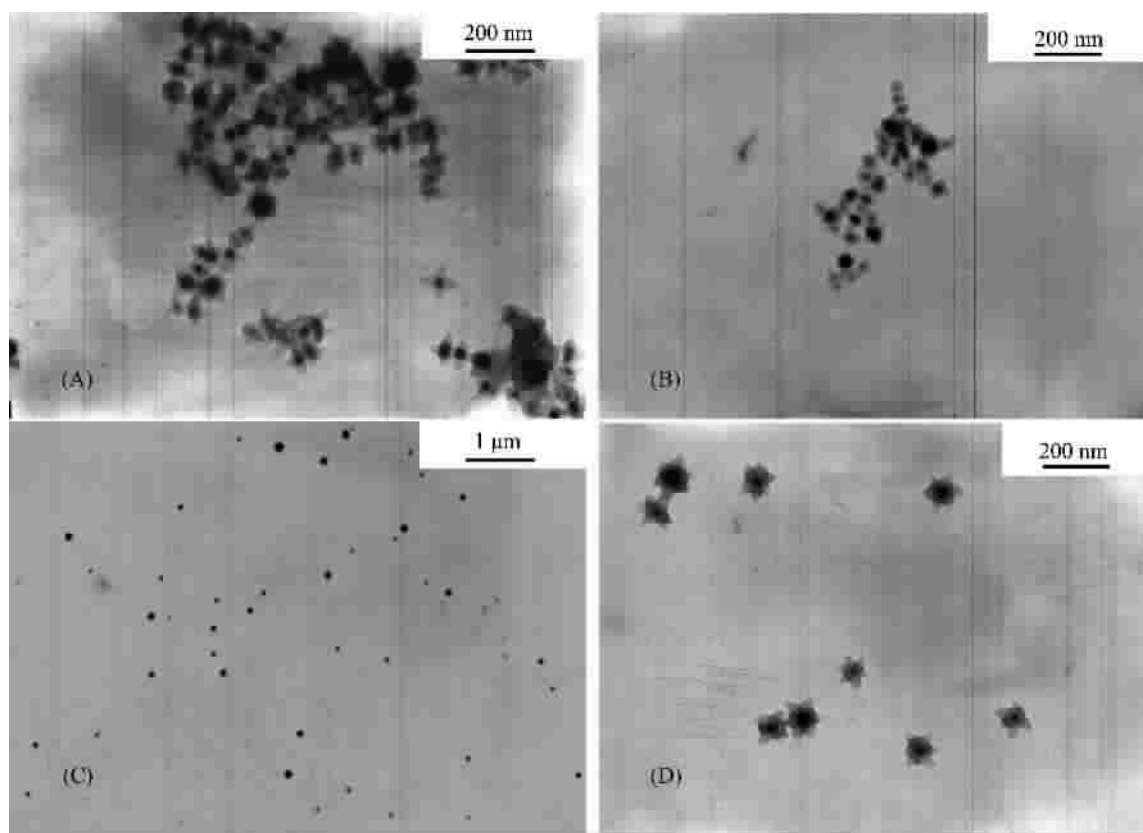


Fig.D is the TEM image with high magnification of (C)

Other synthesis conditions:  $\text{AgNO}_3$  0.01 g; aniline 0.05 mmol;  $n_{\text{An}}:n_{\text{AP}} = 1:1$ ; reaction time 24 h

Fig.1 TEM images of AgCl@PANI core-shell nanocomposites synthesized in different concentrations of chitosan: (A) 0.2%; (B) 0.5%; (C) and (D) 1%

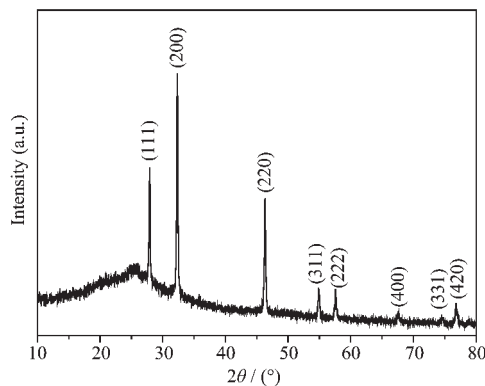
surrounded by a layer of PANI matrix. When the chitosan concentrations were 0.2% and 0.5%, the obtained AgCl@PANI nanocomposite with a diameter in the range of 40~120 nm was conglomerated. When the chitosan concentration increased from 0.5% to 1%, highly dispersed AgCl@PANI core-shell nanostructure with a shell thickness of 30~80 nm and a core diameter of 25~60 nm could be obtained. It should be noted that most of the as-prepared nanocomposites had a star-like structure. During the process for the formation of AgCl@PANI core-shell nanoparticles, after HCl aqueous solution of ammonium persulfate was added dropwise to chitosan solution containing  $\text{AgNO}_3$  and aniline, a white AgCl precipitate appeared immediately and gradually turned blue. In the experiment, chitosan as an anchor agent plays an important role. Without chitosan, the core-shell structure could not be formed. Chitosan is a useful stabilizer that can promote a strong

interaction between AgCl particles and aniline monomer. For example, it has been used successfully in the preparation of uniform AgCl/polypyrrole core-shell particles<sup>[18]</sup>.

The XRD pattern confirms the presence of AgCl nanoparticles in the composites, as shown in Fig.2. The broad diffraction peak appeared at  $2\theta$  value of  $25^\circ$  is ascribed to the periodicity parallel to the polymer chains of PANI<sup>[19]</sup>. Another eight diffraction peaks above  $25^\circ$  ( $2\theta$ ) correspond to Bragg's reflections from (111), (200), (220), (311), (222), (400), (331), and (420) planes of AgCl. They are in good agreement with the reported data (PDF No.06-0480), showing the existence of AgCl nanoparticles in the AgCl@PANI core-shell composites.

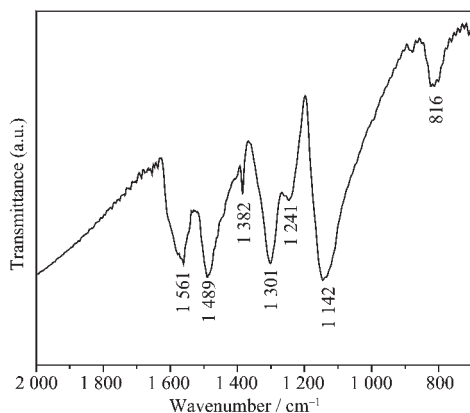
The FTIR spectrum of the AgCl@PANI is shown in Fig.3. The characteristic peaks at  $1561\text{ cm}^{-1}$  and  $1489\text{ cm}^{-1}$  correspond to the C=C stretching of quinoid and benzenoid rings<sup>[20]</sup>,  $1301\text{ cm}^{-1}$  and  $1241\text{ cm}^{-1}$  are

related to the C-N and C=N stretching modes<sup>[21]</sup>, 1 142  $\text{cm}^{-1}$  is assigned to the in-plane bending of C-H<sup>[22]</sup>, and 816  $\text{cm}^{-1}$  is attributed to the out-of-plane bending of C-H<sup>[23]</sup>. Furthermore, an absorption band assignable to  $\text{NO}_3^-$  is observed at 1 382  $\text{cm}^{-1}$ . This suggests that the obtained PANI in the composite was doped by  $\text{NO}_3^-$ .



Synthesis conditions:  $\text{AgNO}_3$  0.01 g; aniline 0.05 mmol;  $n_{\text{An}}:n_{\text{APS}} = 1:1$ ; chitosan concentration 1%; reaction time 24 h

Fig.2 XRD pattern of AgCl@PANI core-shell nanocomposite

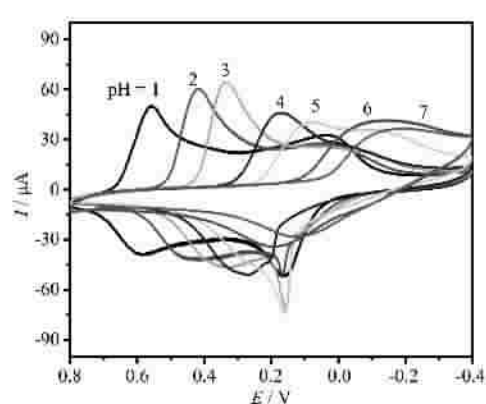


Synthesis conditions:  $\text{AgNO}_3$  0.01 g; aniline 0.05 mmol;  $n_{\text{An}}:n_{\text{APS}} = 1:1$ ; chitosan concentration 1%; reaction time 24 h

Fig.3 FTIR spectrum of AgCl@PANI core-shell nanocomposite

The bare GCE was tested by cyclic voltammetric (CV) in different pH values of phosphate buffer solutions (PBS) before it was drop-coated by AgCl@PANI composite. It presents no redox process in the potential range studied. The working electrode coated with the composite was immersed in the electrolyte solution for 30 min prior to the measurement to assure diffusion of the solution into the interlayer space and permit a better ionic exchange. Fig.4 gives the cyclic voltammograms of AgCl@PANI modified GCE measured in different pH PBS at a scan rate of

100  $\text{mV} \cdot \text{s}^{-1}$ .



Synthesis conditions:  $\text{AgNO}_3$  0.01 g; aniline 0.05 mmol;  $n_{\text{An}}:n_{\text{APS}} = 1:1$ ; chitosan concentration 1%; reaction time 24 h

Fig.4 Cyclic voltammograms of AgCl@PANI core-shell nanocomposite modified GCE measured in different PBS pH buffers at a scan rate of 100  $\text{mV} \cdot \text{s}^{-1}$

PANI shows two separate redox peaks at pH value of 1 PBS. However, these two redox peaks move closer as the pH value of the solution is increased, and finally they merge to show only one broad redox peak when the pH value 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, but in pernigraniline the nitrogen atoms are imines. The amine/imine ratio in emeraldine is  $\sim 1$ . Furthermore, 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<sup>[24]</sup>. The broad redox peak is observed at pH value of 4 in PBS for the sample with the redox potential around 0.2 V. This redox peak is the overlap of two redox processes normally found for the PANI system in acidic conditions<sup>[25]</sup>, as confirmed by the redox behavior of the composites measured in different PBS pH values. This electrochemical behavior of AgCl/PANI is also similar to that of PANI/carbon nanotube multilayer films prepared by the layer-by-layer method<sup>[26]</sup>.

In the CV curves, it is clear that the AgCl/PANI core-shell composites show good redox activity not only

at acidic solution but also at neutral pH environment in PBS. It is well known that silver halides are one type of important semiconductors. Although AgCl particles do not make a continuous electron path, the incorporated conducting AgCl provides more active sites for the charge transfer through the interface inside the electrode by making good contacts with the PANI matrix. Therefore, PANI particles located far from the electrode surface can effectively take part in the redox reaction. Meanwhile, we believe that more studies are needed to investigate the exact mechanism for the enhancement in electroactivity. The AgCl@PANI core-shell composites with good electrochemical activity have the potential application in the area of biosensor.

### 3 Conclusion

We have demonstrated the one-step synthesis of AgCl@PANI core-shell nanostructures in the presence of chitosan. Chitosan as a useful anchor agent promote a strong interaction between AgCl particles and aniline monomer leading to the formation of AgCl@PANI core-shell structure. The core-shell structure was characterized by TEM, XRD, FTIR 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.

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