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The preparation and characterization of the cross-linked Ag–AgCl/polypyrrole nanocomposite

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ABSTRACT

The cross-linked Ag–AgCl/polypyrrole (PPy) nanocomposite was synthesized using silver nanowires as templates. In the process, $FeCl_3$ served not only as the oxidant for pyrrole monomer but also as the etching-agent for silver nanowires. The morphologies of the product were observed by transmission electron microscopy. The existence of silver chloride and silver in PPy matrix was confirmed by X-ray diffraction and X-ray photoelectron spectroscope technologies. A possible formation mechanism of the cross-linked Ag–AgCl/PPy nanocomposite was also discussed.

1. Introduction

In recent years, the fabrication of the inorganic/conducting polymer nanocomposite has attracted much attention. The as-produced nanocomposites exhibit some novel physical and chemical properties compared with individual inorganic materials or conducting polymers [1–4]. Of all conducting polymers, polypyrrole (PPy) is the most promising conducting polymer due to its adjustable conductivity, ease of synthesis, and good environmental stability [5,6]. To date, various inorganic/PPy nanocomposites, such as Ag/PPy [7–9], Au/PPy [10,11], SiO_2/PPy [12–14], Fe_3O_4/PPy [15] and Fe_2O_3/PPy [16] had been reported.

Among the inorganic/PPy nanocomposites, one-dimensional nanocomposites had drawn significant research interest [17,18]. Template-assisted method was probably the most effective and general strategy for fabricating 1D PPy matrix nanocomposite. Some research groups had devoted many efforts towards the research area. Xue et al. reported that the synthetic process of MWNT/PPy core–shell nanowires using multiwalled carbon nanotube (MWNT) as a template [19]. Hou fabricated polypyrrole/PB and PPy/Ag composite microtubes using self-degraded methyl orange (MO) as a template [20]. Using titanate nanowire as a template and cetyltrimethylammonium bromide (CTAB) as a structure-directing agent, Li and co-worker synthesized PPy/titanate composite nanofibers [21]. Ag nanowire was used as a template to synthesize Ag/PPy coaxial nanocable has also been reported [22,23]. However, very little attention has been directed towards the preparation of the cross-linked PPy matrix nanocomposite.

In this work, we reported the preparation of the cross-linked Ag–AgCl/PPy nanocomposite based on silver nanowires as templates. CTAB molecules were added into the system to form bilayer on the silver nanowire surfaces. Pyrrole monomers could be adsorbed in CTAB bilayer and were polymerized to PPy sheath after addition of $FeCl_3$. Meanwhile, the silver nanowires were also etched by the $FeCl_3$, which resulted in the formation of the cross-linked nanocomposite. The product was characterized by TEM, Raman, XRD, and XPS technologies. The possible formation mechanism of the cross-linked nanocomposite was also discussed.

2. Experimental

2.1. Materials

Ethylene glycol, silver nitrate, pyrrole, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and cetyltrimethylammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co., Ltd. Poly(vinyl pyrrolidone) (PVP, Mw = 550,000) was obtained from Aldrich. Pyrrole monomer was distilled under reduced pressure, and other reagents were used as received without further treatment.

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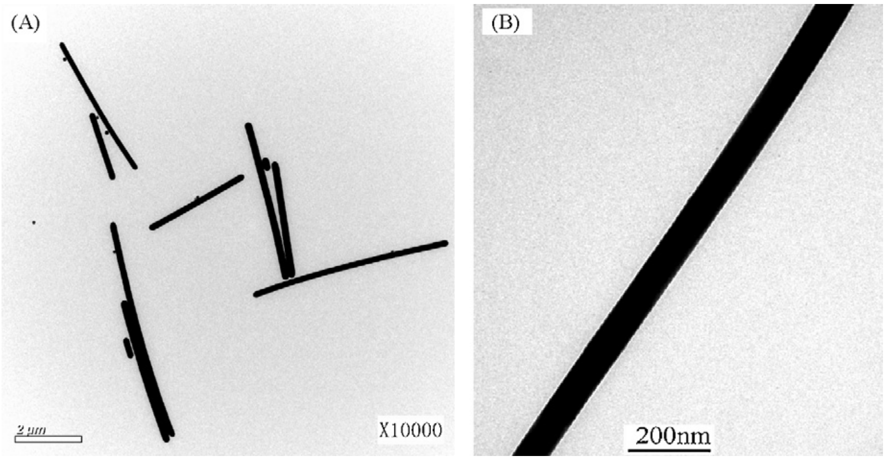


Fig. 1. TEM images of Ag nanowires with low resolution (A) and single Ag nanowire with higher resolution (B).

2.2. Fabrication of silver nanowires

Silver nanowires were synthesized according to the literature [24]. 3 ml ethylene glycol of silver nitrate (0.1 M) and 3 ml ethylene glycol of PVP (0.6 M) were injected simultaneously into 5 ml of ethylene glycol. The above solution was refluxed at 160 °C for 60 min. Then the product was centrifuged and washed with acetone several times.

2.3. Synthesis of Ag–AgCl/PPy nanocomposites

About 0.015 g silver nanowires was dispersed in 30 mM CTAB aqueous solution (10 ml) by ultrasound. Subsequently, 15 μL pyrrole was added and the mixed solution was stirred for 2 h at room temperature. The polymerization was initiated by addition of $FeCl_3$ (the mole ratio of monomer to oxidizing agent was kept at 1:4) at room temperature. After 24 h, the product was centrifuged and washed with deionized water several times. Finally, the product was dried at 50 °C under vacuum for 12 h.

2.4. Characterization and measurements

Transmission electron microscope (TEM, H-7650) was used to observe the morphologies of the nanocomposites. Raman spectra (HR800), X-ray diffraction (XRD, RigakuD/max-1200), and X-ray photoelectron spectroscope (XPS, Axis Utltradld) were used to characterize the nanocomposite. Thermogravimetric analysis was determined with a Perkin-Elmer thermogravimetric analyzer (TG-DTA; model SSC-5200) at a heating rate of 10 °C/min in N_2.

3. Results and discussion

3.1. Formation mechanism and morphology

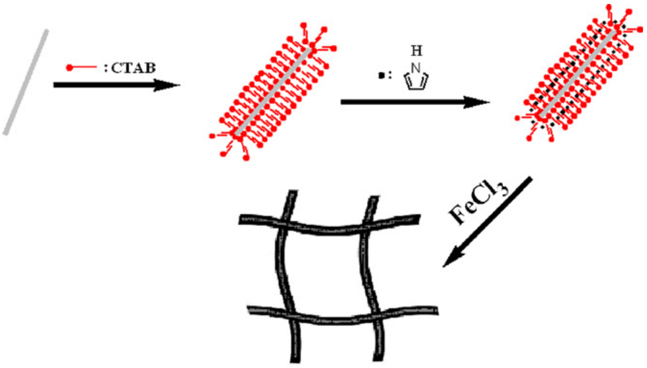
The possible formation mechanism of the cross-linked Ag–AgCl/PPy nanocomposite was represented in Scheme 1. When CTAB was added into the aqueous solution containing silver nanowires, CTAB molecules could assemble on the surfaces of silver nanowires to form bilayer structures [25]. Pyrrole monomers easily inserted themselves into the CTAB bilayers and were oxidized to PPy by the oxidant [26]. Because the standard reduction potential of Fe^{3+}/Fe^{2+} pair (0.771 V) was higher than that of AgCl/Ag pair (0.221 V), silver nanowires could be oxidized by $FeCl_3$ through the following replacement reaction:

$$Fe^{3+} + Cl^- + Ag = Fe^{2+} + AgCl$$

The etching of silver and the polymerization of pyrrole monomer occurred simultaneously. Consequently, the silver was converted into AgCl and the resultant cross-linked nanocomposites were formed. Theoretically, the silver could be consumed completely. However, in our studies, it was found that a small amount of silver was still present in the final product, which could be attributed to the probability: in the above replacement reaction, few silver nanowires could be closely wrapped by the silver chloride, which prevented the silver nanowires from being etched further.

Fig. 1 shows the TEM images of silver nanowires synthesized through polyol process. We could observe that the length of silver nanowires varied from hundreds nanometers to tens micrometers (Fig. 1A), and the diameter of single Ag nanowire was about 80 nm (Fig. 1B).

When the concentration of CTAB was kept constant, and the morphologies of the product with different amount of pyrrole monomer were shown in Fig. 2. The distinct contrast between the dark center and light edge was observed, which was confirmed the core–sheath nanostructures. The diameter of as-produced nanocable was about 200–300 nm. In addition, we noted that the core–sheath nanofibers were curved and interconnected. The formation of the cross-linked network based on the interlink of the core materials due to the etching of silver rather than on physical entanglement of the nanofibers. From Fig. 2, we also found that nanostructures of some internal cores were kept relatively complete, and those of other cores were incomplete and were even disappeared (as shown by the arrows in Fig. 2a, b, and c, respectively). The results could be explained that a portion of silver chloride produced from the replacement reaction could duplicate



Scheme 1. The possible fabrication mechanism of the cross-linked Ag–AgCl/PPy nanocomposite.