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Fabrication of Polypyrrole/Ag Composite Nanotubes via In Situ Reduction of $AgNO_3$ on Polypyrrole Nanotubes

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Nanostructured conducting polymer/metal composites have attracted much attention due to their unique properties. Polypyrrole (PPy) nanotubes were first synthesized via a self-degraded template and then used as supports for in situ reduction of Ag^+ ions. Ag nanoparticles could be uniformly assembled onto the PPy nanotube surface to get PPy/Ag composite nanotubes. The formation mechanism, morphology and structure of the nanocomposites were studied by transmission electron microscopy, thermogravimetric analysis, and X-ray diffraction. The one-dimensional hollow nanocomposites showed improved properties.

Over the decades, there has been growing interest in the fabrication of nanostructural materials with desired morphologies and properties. Among the various morphologies of nanostructures, one-dimensional nanostructures with hollow interiors are receiving intense attention not only for scientific research but also for practical applications.[1,2] Besides conventional hard-template synthesis methods,[3] soft template or template-free approaches such as liquid crystalline phases, reverse microemulsion, surfactant gel, and micelles have been reported and used to prepare one-dimensional conducting polymer nanomaterials.[4,5] Polypyrrole (PPy)/Ag coaxial nanocables were prepared through the redox reaction of silver nitrate and pyrrole with the aid of assistant agent.[6] Yang prepared polyaniline/Au composite nanofibers exhibiting bistability of the nonvolatile memory.[7] Polyaniline/Au composites can be used as a catalyst for the electrochemical oxidation of ascorbic acid.[8] However, it still remains a challenge to design and fabricate functional nanomaterials with particular shape and morphology. Among various types of conducting polymers, PPy stands out because of environmental stability, electronic conductivity, ion exchange capacity, and biocompatibility. Up to now, most reports have focused on the preparation of PPy/Ag nanocomposites from the reaction between pyrrole monomers and $AgNO_3$ in different reaction systems,[6,9] and there are few reports of one-dimensional PPy/silver nanocomposites.[9]

In this study, we report a facile approach to synthesize conducting PPy nanotubes decorated with uniformly dispersed Ag nanoparticles. PPy nanotubes were prepared by a self-degraded template of a fibrillar complex of $Fe(NO_3)_3$ and Methyl Orange (MO), and then Ag nanoparticles were deposited in situ by the reduction of $AgNO_3$ in the presence of poly(vinylpyrrolidone) (PVP). The electrical conductivity of the composites was improved compared with that of the pure PPy nanotubes. The formation mechanism and structural characteristics of the obtained PPy/Ag composite nanotubes were studied.

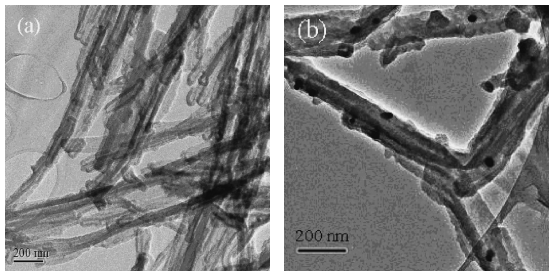

Figure 1. TEM images of (a) PPy nanotube and (b) PPy/Ag composite nanotube.

PPy nanotubes with diameter of 100–150 nm and length of several micrometers, as shown in Figure 1a, were first prepared by a self-degraded template. Then after the addition of an $AgNO_3$ solution, Ag nanoparticles were deposited on the PPy nanotubes in situ by the reduction of $AgNO_3$. The dark spots in Figure 1b are Ag nanoparticles. It can be seen from Figure 1b that Ag nanoparticles with sizes in the range of 30–40 nm are dispersed onto the PPy nanotubes without aggregation. The existence of Ag in the nanocomposites can be further proven in the following observations. During the formation of PPy/Ag composite nanotubes, MO and PVP play an important role. The tubular nanostructure of PPy cannot be formed without MO. As is commonly known, MO with a planar hydrophobic section and hydrophilic edge group ($-SO_3^-$) is water-soluble and has anionic characteristic in aqueous solution. On the other hand, complexation can be achieved between organic dye compounds and metal ions such as Al^{3+} or Fe^{3+}.[10] As shown in Figure 2, Fe^{3+} of $Fe(NO_3)_3$ could be complexed with MO and form a one-dimensional fibrillar template. Pyrrole would be oxidized and polymerized just on the surface of the fibrillar templates. Meanwhile, the template itself degraded automatically due to the reduction of oxidizing cations[11] to result in the formation of PPy tubes. If PVP was absent during the addition of $AgNO_3$, TEM image of the obtained composite nanotubes revealed the aggregation of metal nanoparticles (not shown here). It is well known that amphiphilic PVP is beneficial for the adherence between the polymer and the inorganic material. It could be concluded that PVP promotes the nucleation of inorganic species and prevents the aggregation of nanoparticles efficiently.[12]

Figure 3 shows the XRD patterns of the prepared composite nanotubes prepared at different times. In the case of 15 min, a very small peak at $2\theta = 38.2°$ could be observed and there were no other peaks corresponding to Bragg's reflections from Ag. However, when the reaction time was increased to 1 h, five strong diffraction peaks appeared with the maximum intensity at 2θ values of 38.2, 44.4, 64.5, 77.3, and 81.5°, which represented

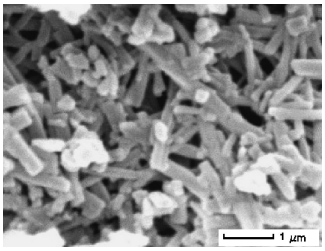

Figure 2. SEM image of the complex of $Fe(NO_3)_3$ and MO.

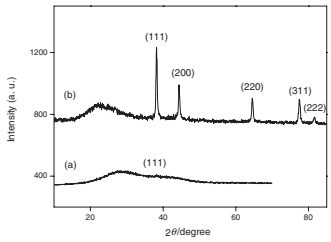

Figure 3. XRD patterns of PPy/Ag composite nanotubes prepared for (a) 15 min and (b) 1 h.

Bragg's reflections from the crystal planes of Ag. Crystallite sizes were calculated from the Ag(111) diffraction line according to Scherrer's equation,

$$L = k\lambda/\beta\cos\theta \quad (1)$$

in which 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 Kα radiation, and K is equal to 0.89. The average size of Ag nanoparticles in the nanocomposites was calculated to be about 35 nm, which was consistent with the result of TEM. In a previous report, the prepared PPy nanotubes were doped with MO and Cl^-, together.[11] When $AgNO_3$ solution was added to the above PPy nanotubes, Ag^+ ions immediately reacted with the dopant Cl^- in PPy nanotubes, which leaded to the formation of AgCl nanoparticles but not Ag nanoparticles. But the dopants of PPy nanotubes prepared by our method were MO and NO_3^-. Only Ag nanoparticles could deposit in situ by the redox of PPy and $AgNO_3$. As a consequence, the TEM and XRD observations strongly demonstrated that the PPy/Ag composite nanotubes were successfully prepared.

Since silver is a good conductor, it is expected that when PPy is combined with silver, the conductivity of the composites could be enhanced. The conductivity of PPy/Ag composite prepared for 15 min was similar to that of PPy. However, the conductivity of PPy/Ag composite nanotubes prepared for 1 h was 67 S cm^{-1}, which was much higher than that of PPy. This phenomenon was different with that of PPy/Au nanocomposites prepared by the reaction of PPy and $HAuCl_4$.[13] It could be ascribed to the difference of oxidation ability between $HAuCl_4$ and $AgNO_3$. Although metallic Au nanoparticles were evenly distributed on the conducting PPy nanotubes, the overoxidation of PPy and the decrease in the conjugation degree of PPy resulted in the obvious decrease in the conductivity of the PPy/Au nanocomposites compared with that of the PPy nanotubes.[13]

The thermal stabilities of PPy nanotubes and PPy/Ag composite nanotubes were studied by TGA. As shown in Figure 4, all TGA curves showed a two-step weight loss. The weight loss in the first step was attributed to the loss of residual water. The second step that started from about 250 °C corresponded to the degradation of polymer and the departure of dopant. It could be observed that the beginning temperature of the second step for PPy/Ag composite nanotube is increased by about 20 °C over that of PPy nanotubes. The total weight loss of PPy nanotubes was 100% under the experimental conditions. Because Ag is not lost under the experimental conditions, the residual weight percentage can be referenced to the content of Ag. The residual weight percentage of PPy/Ag composite nanotube was about 15.5%.

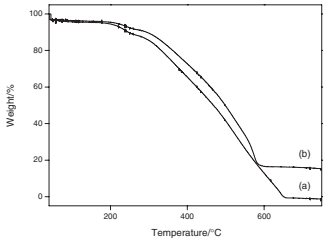

Figure 4. TGA curves of (a) PPy nanotube and (b) PPy/Ag composite nanotube.

In conclusion, PPy/Ag composite nanotubes have been successfully prepared. PPy nanotubes were assembled on the reactive self-degraded template of a fibrillar complex of $Fe(NO_3)_3$ and MO. By introducing PPy nanotubes into $AgNO_3$ solution, Ag nanoparticles could be decorated onto the PPy nanotube surface without aggregation. The thermal stability and electrical conductivity of the as-prepared composites was improved compared with that of the pure PPy nanotubes. The applications of conducting polymer nanotubes decorated with uniform dispersed metal nanoparticles in the fields of vapor sensors and electrocatalysis are now under investigation.

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