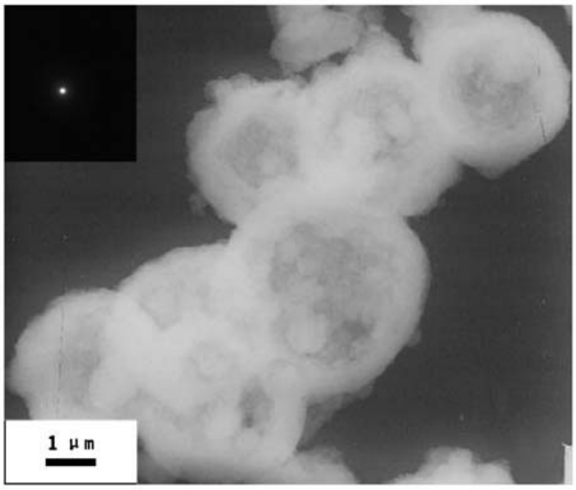
Summary: Hollow octahedrons or microspheres of polyaniline (PANI) were successfully prepared using cuprous oxide (Cu_2O) crystals as new templates in the presence of H_3PO_4 and ammonium peroxydisulfate as a dopant and an oxidant, respectively. Interestingly, the hollow octahedrons (in the reduced form with a conductivity of $<10^{-8}$ $S \cdot cm^{-1}$) could transform into conductive microspheres (in the emeraldine salt form with a conductivity of 10^{-2} $S \cdot cm^{-1}$) when the [APS]/[An] ratio was changed from 1:1 to 2:1. Compared with the common template reported, Cu_2O crystal is not only a new type of template in terms of both shape and quality, but also omits post-treatment due to soluble Cu^{2+} formed by the reaction of Cu_2O with APS during the polymerization process. The universality of Cu_2O as a template to prepare microstructured PANI was proved by changing the morphology of the Cu_2O crystal. It was found that the morphology, oxidation and protonation state of PANI microstructures prepared with octahedral Cu_2O as the template were affected by the [Cu_2O]/[An] and [APS]/[An] ratio due to the competitive reaction of aniline and Cu_2O with APS.



TEM images of PANI microspheres prepared using Cu_2O as a template in the presence of H_3PO_4 and APS as a dopant and an oxidant.

Hollow Microstructured Polyaniline Prepared Using Cuprous Oxide Crystals as Templates

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Introduction

Since the discovery that conjugated polymers can be made into conducting forms through doping,[1] a tremendous amount of research has been carried out in the field of conducting polymers.[2] Microstructured and nanostructured conducting polymers have recently attracted much attention in the field of nanomaterials and nanotechnology due to their unique properties and promising applications in material science and nanodevices.[3] To date, the template-synthesis method,[4] interfacial polymerization,[5] surfactant-assisted polymerization,[6] the "seeding" method,[7] the electrospinning technique[8] and the template-free method created by one of the authors[9] have been successfully used to prepare micro/nanostructured conducting polymers. Among those methods, the template synthesis method is an efficient, controllable and common route to prepare micro/nanostructured conducting polymers, especially oriented micro/nanostructured arrays. Usually, a post-treatment for removing the template is needed, which inevitably results in the disorder or destruction of the target micro/nanostructure. Polyaniline (PANI) is a unique conjugated polymer in that it can be tailored for specific applications through a non-redox acid/base doping process,[10] so much research has been focused on PANI micro/nanostructures.

Cuprous oxide (Cu_2O) is a p-type inorganic semiconductor[11] which has attracted attention for the conversion of solar energy into electrical or chemical energy,[12–14] and also use in catalysts[15] as well as in antifouling coatings.[16] Recently, Cu_2O as a template was successfully used to prepare hollow PANI octahedrons[17] and no removal of the template was needed. However, the resulting octahedrons were the reduced form of PANI with a poor conductivity ($<10^{-8}$ S · cm^{-1}), a potential drawback for their application. Thus, an improvement in the electrical properties of the octahedrons is required to match technological applications in the future. As a new template, moreover, it is necessary to prove the universality for preparing conducting polymer microstructures.

In this article, the universality of the Cu_2O crystal as a template to prepare hollow microstructured PANI and the control of morphology and the oxidation and protonation state of the PANI microstructures were studied. Above all, the hollow PANI microstructures in the reduced form were successfully transformed to the emeraldine salt form, which can be tailored for specific applications through a non-redox acid/base doping process. Compared with conventional templates, the Cu_2O crystal is not only a new type of template in both shape and quality, but also omits the need for post-treatment after polymerization. The formation mechanism of the microstructures is also discussed.

Experimental Part

Materials

Aniline monomer (Beijing Chem. Co.) was distilled under reduced pressure. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS, Beijing Yili Chem. Co.), H_3PO_4 as the dopant and other reagents were purchased from Beijing Chem. Co. and used as received without further treatment. Octahedral and spherical cuprous oxide (Cu_2O) was prepared following a reported method.[18] A typical synthesis procedure to grow octahedral Cu_2O crystals was as follows. 50 ml of $CuSO_4 \cdot 5H_2O$ solution was mixed with 100 ml of NaOH and 0.1 g of hexadecyltrimethyl ammonium bromide (CTAB) and stirred at room temperature to form a uniform solution. 3 ml (1.0 M) of hydrazine hydrate was then added to the mixture with stirring at room temperature and the reaction was allowed to proceed for 1.0 h. The product was washed with deionized water several times and was finally dried under a vacuum at 60 °C for 24 h to obtain a blue-red Cu_2O crystal.

Spherical Cu_2O crystals were prepared according to the synthetic conditions and procedures above. However, before hydrazine hydrate was added, 54 ml of glucose (1 M) was used.

Polymerization

0.2 ml of aniline monomer, 3.3 mg of sodium (*p*-dodecylbenzene)sulfonate and a quantitative amount of Cu_2O were mixed with H_3PO_4 (0.06 ml) dissolved in 20 ml of deionized water under supersonic stirring for 10 min to form an emulsion of aniline/H_3PO_4 complex containing Cu_2O particles at ≈0 to 5 °C. The mixture was cooled in an ice bath and 10 ml of a pre-cooled aqueous solution of APS was added to the above mixture. The reaction was kept under magnetic stirring for 12 h in the ice bath. The resulting precipitate was washed with water, methanol and ether several times. Finally, the product was dried in a vacuum at room temperature for 24 h.

Characterization

The morphologies of the products were investigated with a JEOL JSM-6700F field emission scanning electron microscope (SEM) and a JEOL JEM-2010 transmission electron microscope (TEM), respectively. When the SEM investigation was carried out, the synchronous energy depressive X-ray analysis was recorded with a LINK ISIS300 instrument. Infrared spectra in the range 400–4 000 cm^{-1} of sample pellets made with KBr were measured by means of an infrared spectrophotometer (Bruker Tensor 27). The X-ray scatting of the products was carried out on an X-ray diffraction instrument (Micscience M-18XHF with Cu K_α radiation). A Keithley 196 System DMM Digital Multi-meter and an Advantest R1642 programmable dc voltage/current generator as the current source measured the electrical conductivity of compressed pellets at room temperature using a standard four probe method.

Results and Discussion

Universality of Cu_2O Crystals as Templates to Prepare Hollow PANI Microstructures

The octahedral or spherical Cu_2O crystals were used as a template, which were prepared by a reported method.[18] The typical morphology of the octahedral and spherical Cu_2O crystals is shown in Figure 1. As can be seen, uniform Cu_2O crystals with octahedral (0.6–1.3 μm in rhombic length) and spherical (1.2–2.5 μm in diameter) morphology were obtained. In particular, both octahedrons and microspheres of PANI were successfully prepared using octahedral and spherical Cu_2O as the template, respectively, as shown in Figure 2(a) and 2(b). The hollow structure of these microstructures was confirmed by TEM measurements as shown in Figure 2(c) and 2(d), indicating that Cu_2O is a universal template for preparing hollow PANI microstructures.

Synchronous energy depressive X-ray (EDX) analysis was used to check the true features of the hollow octahedrons. As shown in Figure 3, the hollow octahedrons were mainly composed of C, Na and O, but a little Cu was detected, indicating that the observed octahedron was PANI instead of an octahedral Cu_2O crystal. Moreover, electronic diffraction measurements [inset of Figure 2(c)] and XRD (Figure 4) showed that the hollow octahedrons were

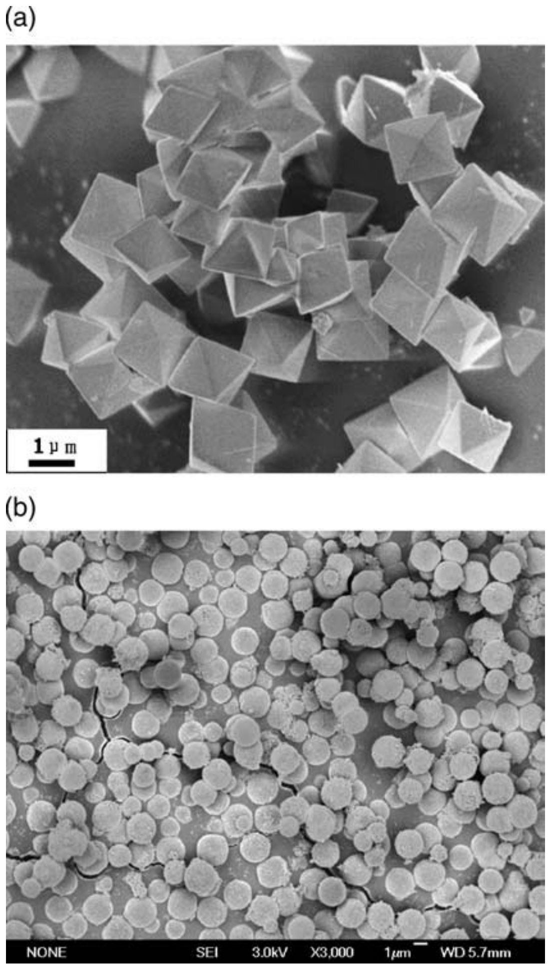

Figure 1. SEM images of octahedral (a) and spherical (b) Cu_2O crystals used as templates.

amorphous instead of Cu_2O crystals, further proving that the observed octahedrons were real PANI. However, FT-IR and conductivity measurements using a four probe method showed that the octahedral PANI prepared with Cu_2O/An at 1:2 is a reduced form of PANI,[19] which was proved by the fact that the band at 1 590 cm^{-1} assigned as a quinoid ring was very weak and the conductivity was poor ($<10^{-8}$ S $\cdot$ cm^{-1}). These results showed that unusual hollow octahedral PANI could be obtained using octahedral Cu_2O as the template. However, it belongs to the reduced form of PANI with a poor conductivity. Fortunately, the insulating hollow octahedrons could be changed to conductive hollow microspheres, accompanied by an enhancement in conductivity of more than 10^6 times when the molar ratio of APS to aniline was increased from 1:1 to 1.6:1 or 2:1. Compared with the conventional template, obviously, the Cu_2O crystal is not only a new template in terms of shape and quality, but also omits the need for post-treatment after polymerization, which will be discussed in a later section in detail.

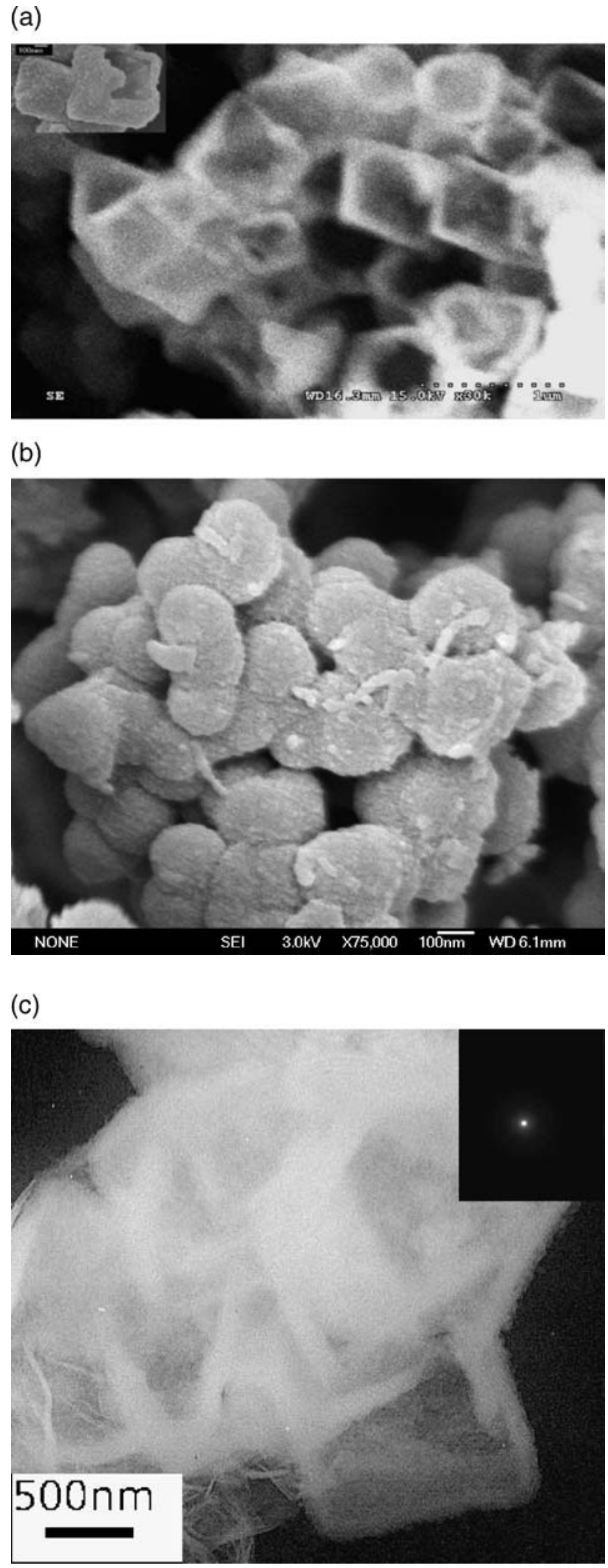

Figure 2. Typical SEM and TEM images of hollow octahedrons (a, c) and microspheres (b, d) of PANI prepared using Cu_2O crystal as the template in the presence of H_3PO_4 and APS as a dopant and an oxidant respectively (inset of c and d is the electronic diffraction pattern).

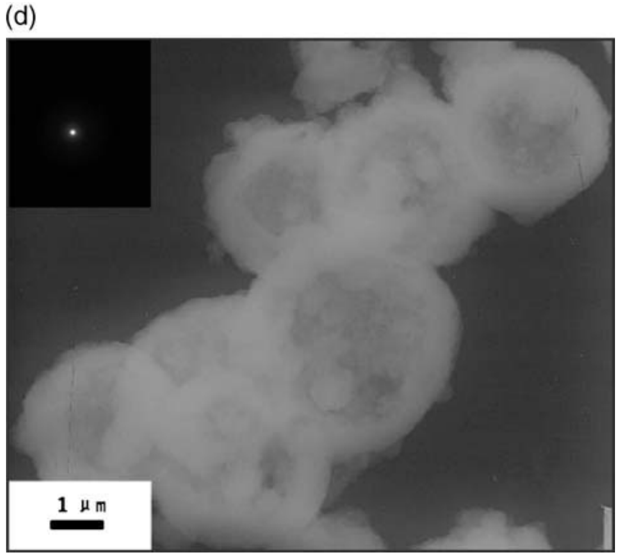

Figure 2. (*Continued*)

Controllability of Morphology, Oxidation and Protonation State of the PANI Microstructures

It was found that the morphology of PANI prepared using octahedral Cu_2O as the template was strongly affected by the mass ratio of Cu_2O to aniline (represented by Cu_2O/An) and the molar ratio of APS to aniline (represented by APS/An). For a given APS/An ratio (e.g., 1:1), for example, inhomogeneous PANI nanotubes were formed on the surface of the Cu_2O template at the Cu_2O/An ratio of 2:1, as shown in Figure 5(a). On decreasing the ratio of Cu_2O/An, octahedrons started to form, especially uniform octahedral PANI was observed at a Cu_2O/An ratio of 1:2 [Figure 2(a)]. When the Cu_2O/An ratio was further reduced to 1:5, however, the yield of the octahedral PANI significantly reduced, and short PANI nanotubes were mainly observed [Figure 5(b)]. At an optimal Cu_2O/An of 1:2 and an APS/An ratio of 1:1 for forming octahedrons, interestingly, the octahedrons disappeared and the hollow microspheres were obtained when the APS/An ratio increased from 1:1 to 1.6:1, 1.8:1 and 2:1 (Figure 6). FT-IR showed that the hollow microspheres were the emeraldine salt form, as shown in Figure 7. As shown in Figure 8, the conductivity increased with increasing APS/An ratio, and a maximum conductivity of $\approx 10^{-2}$ $S \cdot cm^{-1}$ was achieved. The above results indicate that the morphology, oxidation and protonation state of the microstructures prepared using octahedral Cu_2O as the template could be adjusted by changing the APS/An ratio, showing that the method employed in this paper is controllable.

Formation Mechanism of the PANI Microstructures

As mentioned before, a significant advantage of the Cu_2O crystal as a template is the ability to omit post-treatment of the template compared with common templates. We propose that Cu_2O is able to react with APS to form soluble Cu^{2+} salt during the polymerization via the following reaction:

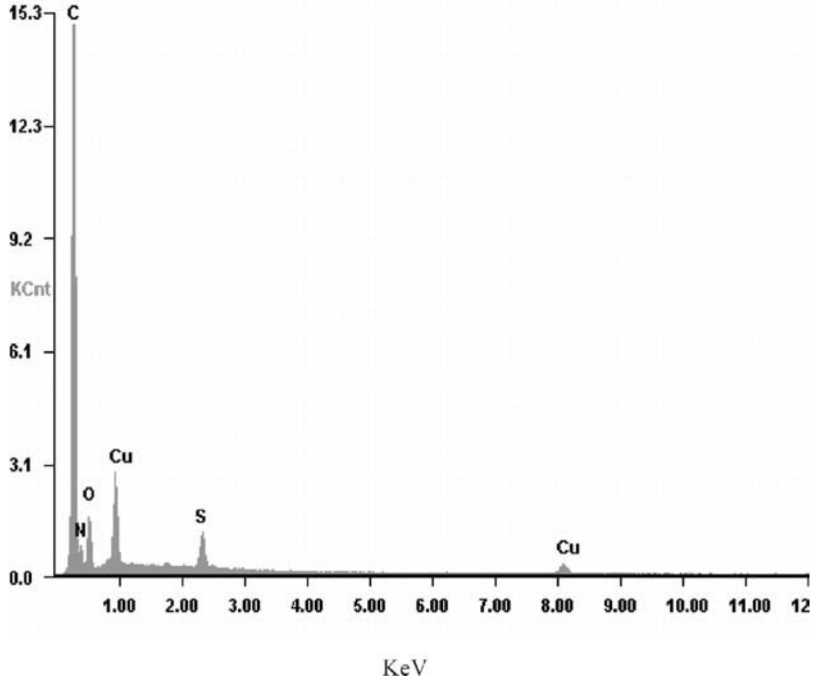

Figure 3. EDX analysis of the octahedrons of PANI prepared with octahedral Cu_2O as the template at [APS]/[An] = 1:1 and $[Cu_2O]$/[An] = 1:2.

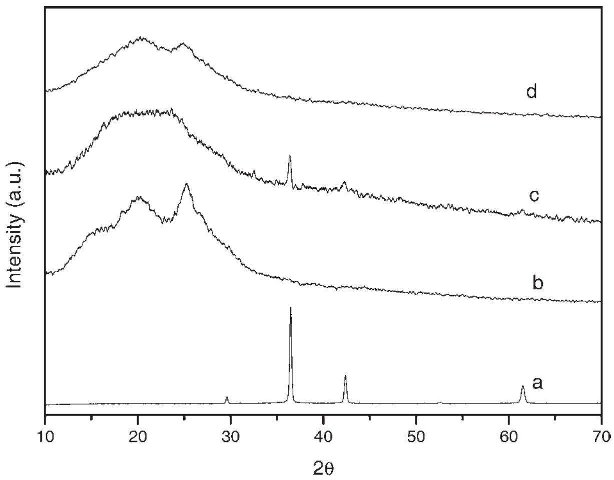

Figure 4. X-ray diffraction of the Cu_2O crystal (a), the PANI-H_3PO_4 nanotubes (b), the octahedral PANI prepared at [APS]/[An] = 1:1 and [Cu_2O]/[An] = 1:2 (c) and the spherical PANI prepared at [APS]/[An] = 1.6:1 and [Cu_2O]/[An] = 1:2 (d).

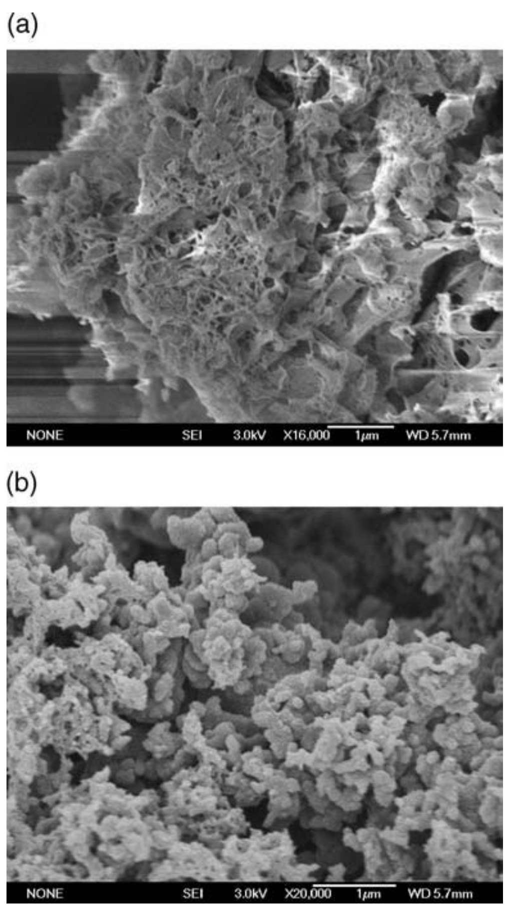

Figure 5. Effect of the [Cu_2O]/[An] mass ratios on the morphology of the PANI prepared with octahedral Cu_2O as a template at [APS]/[An] = 1:1 (a) [Cu_2O]/[An] = 2:1; (b) [Cu_2O]/[An] = 1:5.

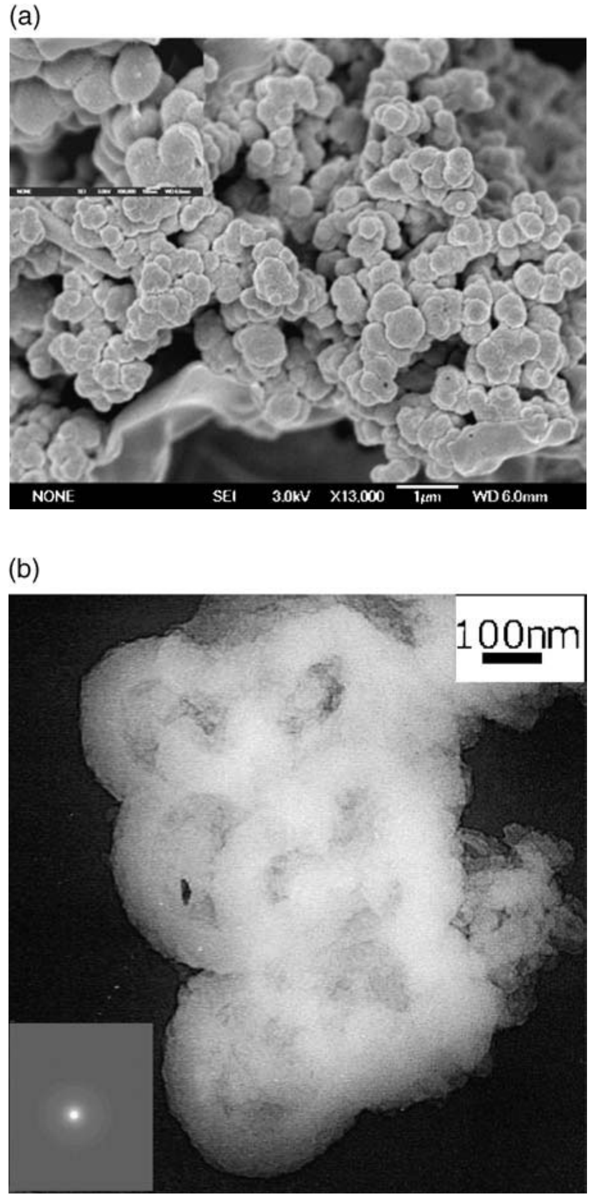

Figure 6. SEM (a) and TEM (b) images of PANI prepared at [Cu_2O]/[An] = 1:2 and [APS]/[An] = 1.6:1 with octahedral Cu_2O as a template (inset of b is the electronic diffraction pattern).

$$Cu_2O + S_2O_8^{2-} + 2H^+ \rightarrow 2Cu^{2+} + 2SO_4^{2-} + H_2O \qquad (1)$$

In order to prove the above reaction, a desired amount of Cu_2O was dispersed into 10 ml (0.11 M) of H_3PO_4 solution with stirring at room temperature and 10 ml of APS was then added with stirring at 0–5 °C for 15 min. The color of the solution became blue, indicating that a soluble Cu^{2+} salt was formed. The above result suggests that Cu_2O in an acidic solution could be oxidized by APS to form a soluble Cu^{2+} salt in the absence of aniline. This is a reason why

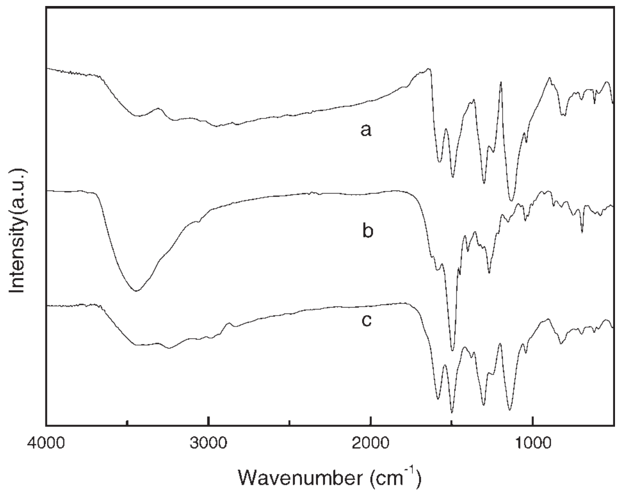

Figure 7. FT-IR spectra of the PANI-H_3PO_4 nanotubes (a), the octahedral PANI (b) prepared at [APS]/[An] = 1:1 and [Cu_2O]/[An] = 1:2 and the spherical PANI (c) prepared at [APS]/[An] = 1.6:1 and [Cu_2O]/[An] = 1:2.

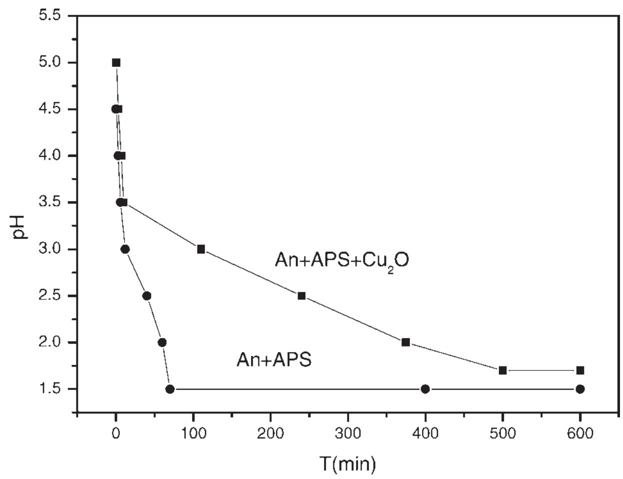

Figure 9. Variation of pH value with polymerization time: (a) in absence of Cu_2O; (b) in the presence of Cu_2O. [An]/[H_3PO_4] = 2:1, [Cu_2O]/[An] = 1:2, [An]/[APS] = 1.6:1 and $T = 0-5$ °C.

Cu_2O as a template does not need removing after polymerization. It also indicates that the reaction of aniline or Cu_2O with APS in the reaction solution is competitive. Therefore, the pH value of the reaction solution with reaction time was measured, as shown in Figure 9. As can be seen, the pH value decreased with increasing polymerization time due to the H_2SO_4 produced during polymerization.[20] It is clearly shown that the variation of pH value with reaction time in the presence of the Cu_2O template is smoother compared with that in the absence of the Cu_2O template. This suggests that aniline monomer was oxidized by APS more easily than Cu_2O, which results in either maintaining the template or dissolving the Cu_2O crystal at the same time. Based on the above assumption, it is easy to explain all the observed results. For a given APS/An ratio (e.g., 1:1), for example, the Cu_2O/An ratio would affect the aggregated morphology

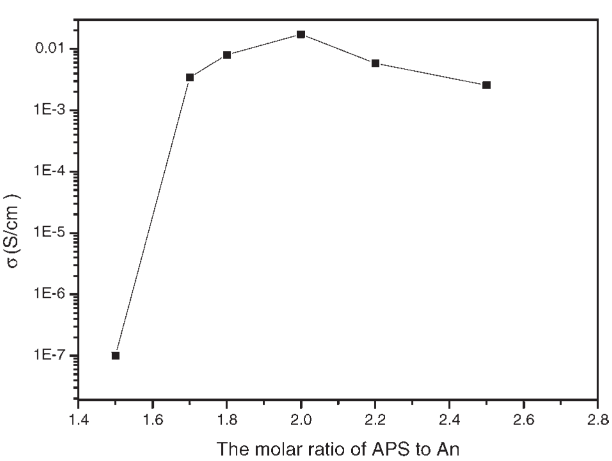

Figure 8. Effect of the [APS]/[An] ratio on the conductivity of the PANI microstructures prepared at [Cu_2O]/[An] = 1: 2 with octahedral Cu_2O as a template.

of PANI due to the competitive reaction of Cu_2O and aniline with APS, which is consistent with our observations shown in Figure 5. At the optimal Cu_2O/An ratio for forming octahedrons (e.g., 1:2), on the other hand, the APS/An ratio would play an important role in controlling the morphology, oxidation and protonation state of the PANI microstructures. The octahedrons were transformed to microspheres, for instance, when the APS/An ratio increased from 1:1 to about 1.6:1 to 2:1 even though octahedral Cu_2O crystal was used as the template. Moreover, it is also accepted that the oxidation state and protonation state of the PANI micro/nanostructures was affected by the APS/An ratio, for example, the octahedrons are the reduced form with an insulating property, while the microspheres are the emeraldine salt form with a conductivity of $\approx 10^{-2}$ $S \cdot cm^{-1}$. Therefore the above results suggested that the ability to omit post-treatment of the template is due to soluble Cu^{2+} formed by the reaction of Cu_2O with APS during the polymerization, while the competitive reaction of aniline and Cu_2O with APS results in the morphology, oxidation and protonation state of the PANI micro/nanostructures being affected by the Cu_2O/An and APS/An ratio when Cu_2O was used as a template to prepare microstructures.

Conclusion

Hollow octahedrons or microspheres of PANI were successfully prepared using Cu_2O crystal as the template in the presence of H_3PO_4 and APS as the dopant and the oxidant respectively. The universality of Cu_2O crystal as a template to prepare PANI microstructures was proved by changing the morphology of Cu_2O crystal. The morphology, oxidation and protonation state of the PANI microstructures prepared using the octahedral Cu_2O template was affected by the Cu_2O/An and APS/An ratio due to a competitive reaction between aniline and Cu_2O crystal with APS. Compared with the common template reported, Cu_2O crystal is not only a new type of template in both shape and quality, but also omits the need for post-treatment due to the soluble Cu^{2+} formed by the reaction of Cu_2O with APS during the polymerization process.

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