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SHORT COMMUNICATION

Growth of ramification-like ZnO rods in the presence of polyaniline

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Abstract To obtain new materials with synergetic or complementary behaviors, polyaniline composite filled with ZnO rods in ramification-like structure was prepared by a hydrothermal approach. Comparative experiments of ZnO preparation in the presence of some metal ions were also carried out. The results indicated that the morphology of ZnO was strongly affected by the preparation condition. The method to grow ZnO rods in the presence of polyaniline offers a simple approach to obtain polyaniline composite filled with linear ZnO structure. The results of X-ray photoelectron spectroscopy show that the strong interaction between ZnO and polyaniline possibly exists to cause the charge transfer.

Keywords ZnO rod · Polyaniline · Composite · Hydrothermal approach · Interaction

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Introduction

Recently, nanostructured materials and nano/microelectronic devices received considerable attention, which results in great progress [1–8]. Nanostructured material researches are mainly focusing on organic materials [5–12], inorganic materials [1–4], and organic–inorganic hybrid materials [13–20]. Among functional materials, organic–inorganic hybrid materials have been extensively investigated for many years to obtain new kind composite materials with synergetic or complementary behaviors for electronic or nanoelectronic devices [15–19].

ZnO is a typical n-type semiconductor as well as an important electronic and photonic material due to its wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV. So, it has many potential applications, such as field effect transistors, ultra-sensitive nano-sized gas sensors, nanoresonators, nanocantievers, UV detector, dye-sensitized photovoltaic cells, piezoelectronic materials, catalysts, hydrogen storage materials, chemical sensors, and biosensors [15–19, 21–26]. Polyaniline is one of the typical conductive polymers which are usually considered as p-type materials. Because it has good mechanical flexibility and environmental stability, and its conductivity can be controlled with acid/base (doping/undoping), polyaniline has potentials in many applications, such as lightweight battery electrode, electromagnetic shielding device, anti-corrosion coatings, and sensors [5, 6]. Consequently, it is hopeful to obtain new materials with complementary behaviors combining polyaniline and ZnO.

Although a large number of studies on organic–inorganic hybrid materials have been carried out, most researches are still focusing on the material preparation and morphology characterization [15, 27] such as size and shape of the oxide particles, degree of the dispersion, kind of interaction and

interface between the organic and inorganic phase, and so on. Schnitzler et al. [15] prepared the polyaniline–TiO_2 (SnO_2) hybrid materials and characterized them by thermal analysis, X-ray diffractometry, Raman, UV-Vis, FTIR spectroscopy, transmission electron microscopy, cyclic voltammetry, and conductivity measurements to obtain some valuable information. We prepared polyaniline–TiO_2 composite film and polyaniline/zeolite film which showed improved gas sensitivity and thermal stability [14, 28]. These research results inspire us to study further to develop other composite systems.

To obtain well-dispersed organic–inorganic hybrid materials, in situ polymerization was usually employed in the presence of inorganic materials. However, it is difficult to obtain polyaniline–ZnO composite using conventional in situ polymerization method, especially ZnO rods, because the aniline polymerization requires strong acid medium and ZnO belongs to amphiprotic compound. Different from conventional methods to prepare ZnO, including thermal evaporation, metalorganic chemical vapor deposition, solution-phase approach and oxidation of ZnS, we report the growth of ramification-like ZnO rods in the presence of polyaniline suspension and investigate the interaction mechanism between ZnO and polyaniline.

Experimental section

Materials

Aniline (AR) was freshly distilled in vacuum before use; ammonium peroxydisulfate (AR), hydrochloride (AR), zinc acetate (AR), ethanol (AR), ammonia (25% CP), and triethanolamine (AR) were commercially available.

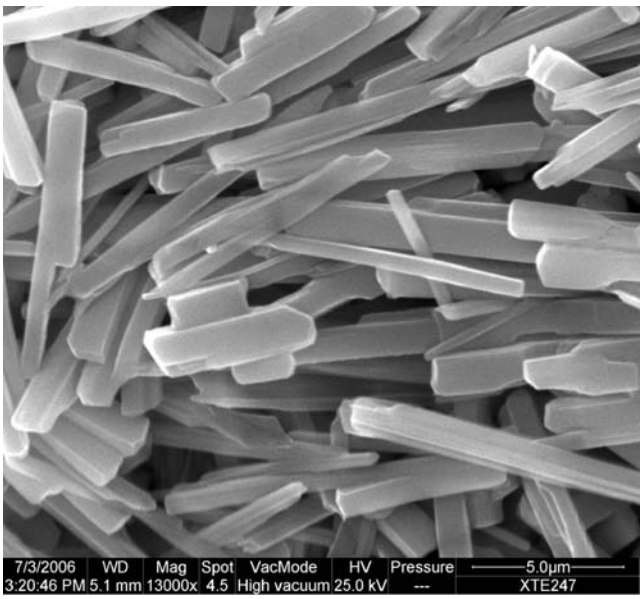


Fig. 1 SEM image of ZnO nanobelts obtained under conventional hydrothermal condition

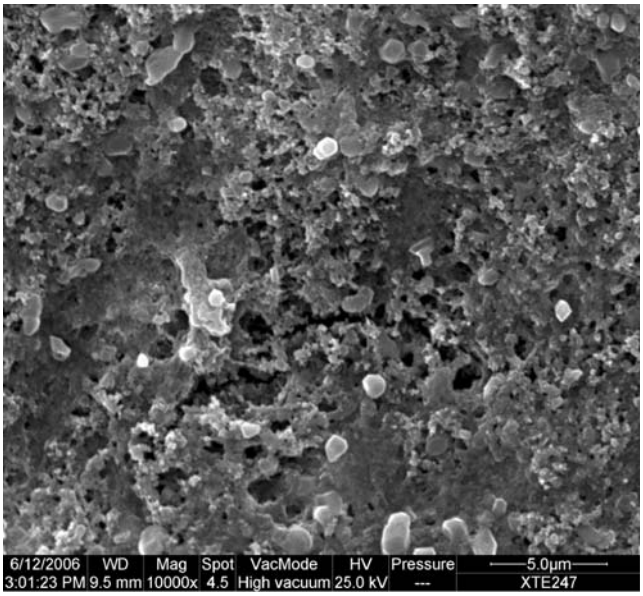


Fig. 2 SEM image of polyaniline

Preparation of ZnO sol

The mixture was prepared by adding zinc acetate (2.195 g) and 50 ml ethanol then stirred at 50 °C for 3 h. Afterward, a small amount of triethanolamine was added to obtain transparent ZnO sol.

Preparation of ZnO sol–gel

The ZnO sol–gel was obtained by adding 100 ml deionized water in the aforementioned 100 ml ZnO sol.

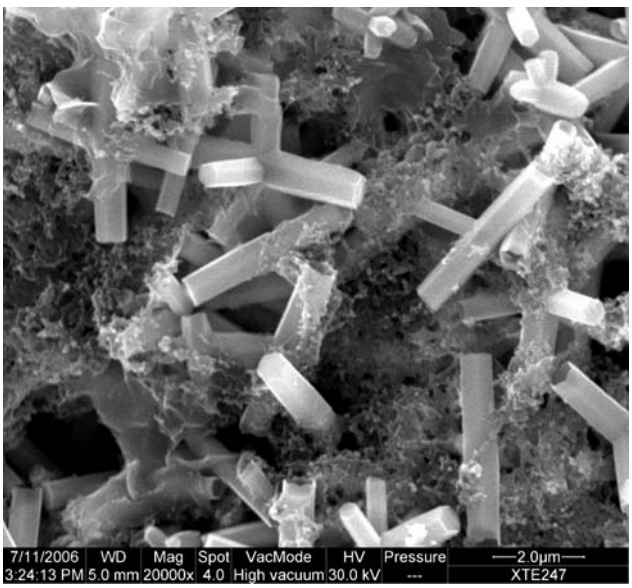
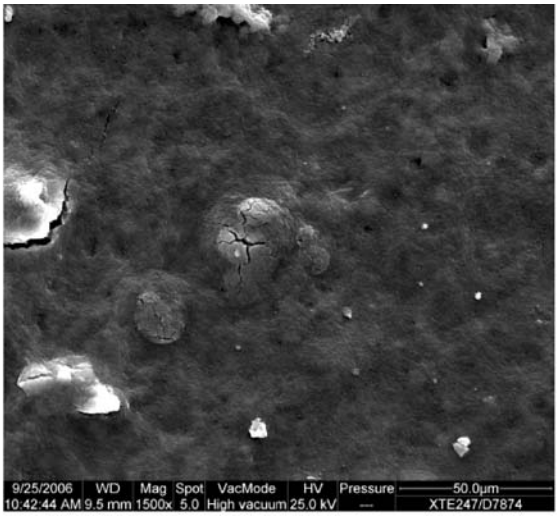
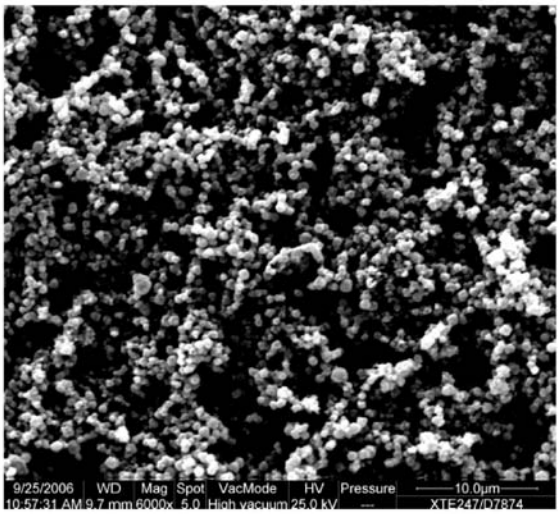


Fig. 3 Ramification-like ZnO rods grown in the presence of polyaniline suspension



a ZnO grown in the presence of small amount of Mg^{2+}.



b ZnO grown in the presence of small amount of Cd^{2+}.

Fig. 4 ZnO grown in the presence of small amounts of doping agents. **a** ZnO grown in the presence of small amount of Mg^{2+}. **b** ZnO grown in the presence of small amount of Cd^{2+}

Preparation of polyaniline suspension

Equal mole aniline (about 0.03 M) in hydrochloride solution and ammonium peroxydisulfate in hydrochloride solution was mixed in 100-ml vessel with ultrasonic. After standing 24 h at room temperature (25–30 °C), the resulting product was washed with deionized water repeatedly.

Growth of ramification-like ZnO rods

The aforementioned polyaniline suspension 30 ml was mixed with 30 ml ZnO sol–gel then was transferred into a Telon-lined stainless steel autoclave. Then, the autoclave was sealed tightly and hydrothermally treated at 90–100 °C for 3 h.

Table 1 The XPS results of polyaniline and the polyaniline composite filled with linear ZnO rods

	Polyaniline	Polyaniline composite filled with ZnO rods
C_{1S}	288.41 eV	290.68 eV
N_{1s}	402.80 eV	404.94 eV

Morphology observations with SEM

The scanning electron microscopic (SEM) observations were performed with FEI Quanta 200 (FEI Company). The samples obtained were washed with deionized water repeatedly, deposited on the glass substrate, dried at room temperature, and then sputtered with a thin layer of gold on the surface for SEM observation.

XPS and EDAX characterization

The X-ray photoelectron spectroscopy (XPS) were recorded on PHI-5300 (USA) working at 12.5 kV, and the energy dispersive X-ray analysis (EDAX) was measured with INCAX-sight (Oxford Instruments) working at 40 kV. The sample obtained was washed with deionized water repeatedly, deposited on the glass substrate, dried at room temperature, and sputtered with a thin layer of carbon on the surface for EDAX observation.

Results and discussion

Typical SEM image of ZnO nanobelts obtained under conventional hydrothermal condition is shown in Fig. 1. The morphology of ZnO is in the nanobelt structure. This may be the results of the presence of small amount of triethanolamine, which acts as a soft template. These nanobelts are generally in random and not uniform, very similar to those described in the previous report [22].

Table 2 Details of the XPS results of polyaniline and the polyaniline composite filled with linear ZnO rods

Amount of nitrogen in polyaniline (%)	Polyaniline	Polyaniline composite filled with linear ZnO rods
Amine	19.03	21.30
Imine	60.84	55.06
charged nitrogen	20.14	23.64

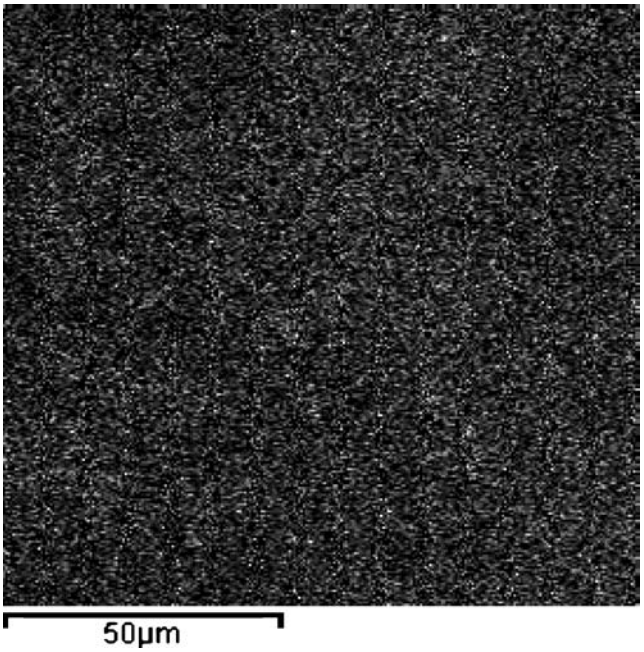


Fig. 5 Distribution of zinc ion in polyaniline

The SEM image of polyaniline is shown in Fig. 2, and the SEM image of polyaniline–ZnO composite is shown in Fig. 3.

As shown in Fig. 3, the morphology of ZnO is clearly different from that of Fig. 1. The ZnO is in rod structure surrounded by polyaniline. The diameter of ZnO rods is about 500 nm, and the length is about 10 μm. The overall morphology exhibits the polymer composite filled with rod structure materials. Most rods are in ramification-like structures. This morphology is very interesting and would be meaningful to prepare composite filled with fillers. This structure not only has some advantages of linear ZnO structure but also can avoid the disadvantages of anisotropic materials.

Among so many ZnO modification approaches, organic–inorganic hybrid composite is one of the most important methods. To tailor the band gap of ZnO, modification of ZnO with several doping agents, such as Mg^{2+} and Cd^{2+}, is widely employed. Considering the morphology of ZnO strongly depending on preparation medium and doping agent, we carried out the comparative experiments by adding small amount of doping agents under similar condition.

The results are shown in Fig. 4, which illustrates the prominent effects of small amounts of doping agents on the morphology of ZnO. The presence of small amounts of Cd^{2+} or Mg^{2+} heavily affects the growth of ZnO crystal and its structure, while the effect of polyaniline is very little. Due to the simple procedure and low cost, this method to prepare polyaniline composite filled with ZnO rods has meaningful potentials on device applications.

ZnO is one of the typical of n-type semiconductor, while polyaniline is usually considered as p-type material. Therefore, the strong interaction of charge between ZnO and polyaniline must exist. It may improve the functional properties of the device with polyaniline–ZnO composite. Based on these aforementioned considerations, the XPS examinations were carried out, and the results are shown in Table 1 and Table 2.

Due to the hybrid composite effects of polyaniline and ZnO, the changes of binding energy of C_{1S} and N_{1s} are about 2.27 and 2.14 eV, respectively (as shown in Table 1). Table 2 shows that the presence of ZnO led to the variation of the amount of nitrogen (mine, imine, and charged nitrogen) in polyaniline. This illustrates that the charge transfer possibly occurred between ZnO and polyaniline, which is the reason why polyaniline contains conjugation benzyl ring long chain. The strong interaction between ZnO and polyaniline is important for developing some devices with outstanding properties, such as ultra-sensitive nano-sized gas sensors, dye-sensitized photovoltaic cells, and so on.

To obtain good organic–inorganic hybrid materials, the dispersion effect of inorganic oxide in polymer matrix, which is another key property of ZnO–polyaniline composite, was also examined. The dispersion effects of inorganic oxide in polymer matrix can be seen in Fig. 3, and the results of distribution of zinc element in polyaniline are shown in Figs. 5 and 6. Figures 3 and 5 show that the ZnO was well dispersed in the polyaniline.

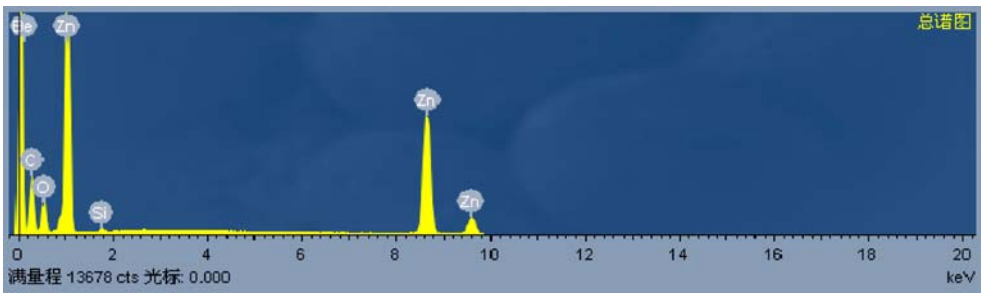


Fig. 6 Energy-dispersive X-ray analysis of polyaniline composite filled with ramification-like ZnO rods

Conclusion

Ramification-like ZnO rods were obtained in the presence of polyaniline suspension via a hydrothermal approach, which offers a simple method to prepare polyaniline–ZnO composite. This is meaningful to manufacture devices based on organic–inorganic hybrid materials.

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