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ORIGINAL CONTRIBUTION

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Synthesis of the composite material of polyaniline/NiO/sodium dodecylbenzenesulfonate in micelles

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Abstract The composite material of polyaniline/NiO/sodium dodecylbenzenesulfonate (SDBS) is synthesized in SDBS micelles. The composite material has satisfactory conductivity and thermostability, and the particle length, width, and thickness are about 200–500 µm, 3–5 µm, and 40–96 nm, respectively.

Keywords Composite material · Micelles · Polyaniline · NiO · SDBS

Polyaniline (PANi) was synthesized firstly from aniline (An) by Fritzsche in 1840. Since the beginning of late last century, PANi and its derivatives have been studied extensively and designated as one of the prospective conducting polymers [1–3]. Their performance on light, electricity, sound, and magnetism has changed remarkably after inorganic nanoparticle incorporation. The performance of PANi can be optimized and adjusted by doping PANi with various nanoparticles, such as organic acids [4], montmorillonite [5], inorganic oxides (ZnO, SiO_2, MnO_2, TiO_2, and Fe_3O_4) [6–8], and inorganic acids [9]. In the present paper, the composite materials of PANi/NiO/SDBS with particles of lengths about 200–500 µm, width about 3–5 µm, and the thickness about 40–96 nm have been synthesized in micelles, based on our former synthesis of PANi nanoparticles [10, 11] in micelles.

Experimental Section

Materials

Sodium dodecylbenzene sulfonate (SDBS, Fluka, A.R.), ammonium peroxydisulfate (APS, Aldrich, >99%), nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, Sigma, 98%), and urea (CH_4N_2O, Sigma, 99.5%) were used as received. Water used was distilled twice and An (Aldrich, >99%) was distilled under reduced pressure.

Synthesis of NiO nanoparticles and composite polyaniline nanomaterials

Preparation of NiO nanoparticles [12] The mixture of urea and $NiCl_2{\cdot}6H_2O$ with the molar ratio of 2:1 was dissolved in water and kept boiling for 80 min. The reaction was stopped by cooling with ice–water mixture. The precipitated $Ni(OH)_2$was cleaned with water until Cl^- could not be detected in the filtrate by $AgNO_3$. The precipitate was calcined at 500 °C for 2 h. NiO nanoparticles with dusky green color were obtained.

Synthesis of the PANi material The SDBS solution or water was added in a conical flask containing An. The initiator (APS aqueous solution) was added drop by drop under stirring at 30 ± 1 °C.

Synthesis of the composite material of PANi/NiO Adequate quantities of water, NiO nanoparticles, and

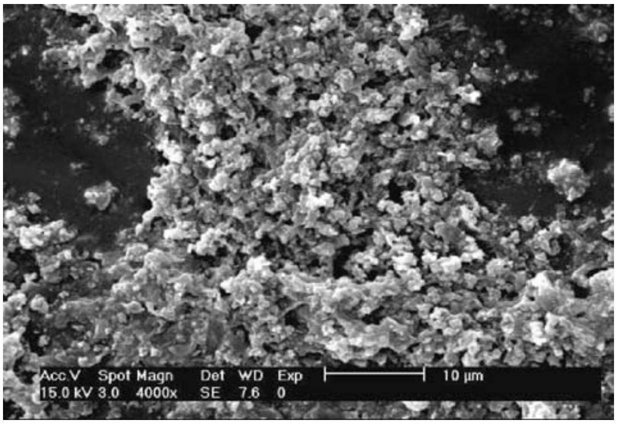


Fig. 1 Scanning electron microscopic picture of PANi prepared in water

An (molar ratios of NiO:An being 1:16) were added into a conical flask. The initiator (aqueous solution of APS) was added drop by drop under stirring at 30 ± 1 °C.

Synthesis of the composite material of PANi/NiO/SDBS Adequate quantities of water, NiO nanoparticles, An, and SDBS (molar ratios of NiO:An and SDBS:An being 1:16 and 5:1, respectively) were added into a conical flask. The initiator (aqueous solution of APS) was added drop by drop under stirring at 30 ± 1 °C.

The characterization of composite nanomaterials

The morphology was observed using scanning electron microscopy (SEM, XL-30E Philips, The Netherlands) and transmission electron microscopy (TEM, TECHNAI-12 Philips, The Netherlands). The amounts of C, H and O were measured by elemental analysis (Elementa Vario EL III America Vario). The infrared absorption spectra of the samples were recorded by a Fourier transform infrared spectrometer (FT-IR) (Nicolet-740, America). The X-ray diffraction patterns of the particles were recorded in an X-ray diffractometer (XRD, Mo3XHF22 Japan MAC Co.), Cu K_α. The thermostability of the composite materials was determined using differential scanning calorimetry (DSC, DSC-131 France SETARAM Co.) and the specific conductivity was measured at 25 ± 1 °C using the four-point probe techniques.

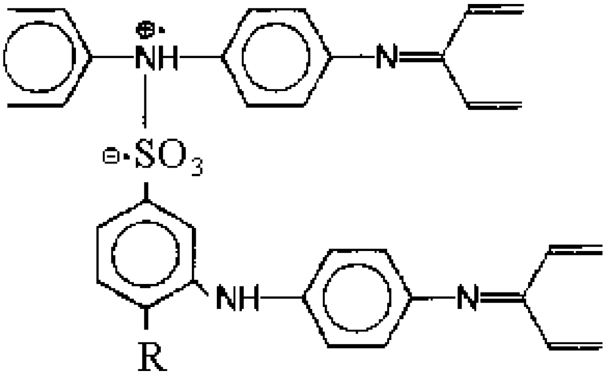
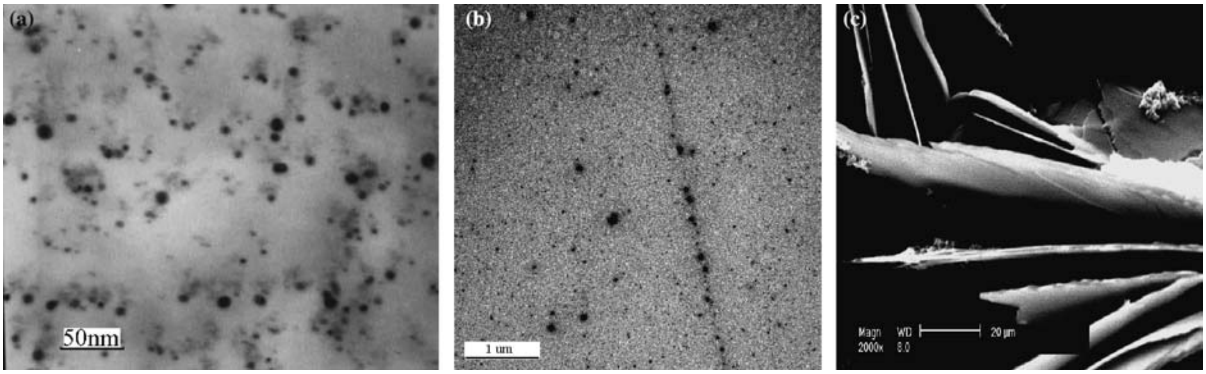


Fig. 3 Illustration for the structure of the block polymers

Results and discussion

Figure 1 shows the aggregates of PANi prepared without SDBS. The PANi nanoparticles synthesized in SDBS/An/H_2O micelles, self-assembled to form nano-lines after 3 days and nano-rods after a week are shown in Fig. 2. In the SDBS micelles, An exists in the oil core and the palisade layer of the micelles, which can limit the size of the PANi particles. PANi particles prepared in the micelles vary in size from several nanometers to decades of nanometers (Fig. 2a). Due to the electrostatic interaction between the sulfonyl groups of SDBS, the

Fig. 2 Transmission electron microscopic and SEM pictures of PANi prepared in SDBS/An/H_2O micelles. **a** TEM picture after reaction; **b** TEM picture after 3 days; **c** SEM picture after a week



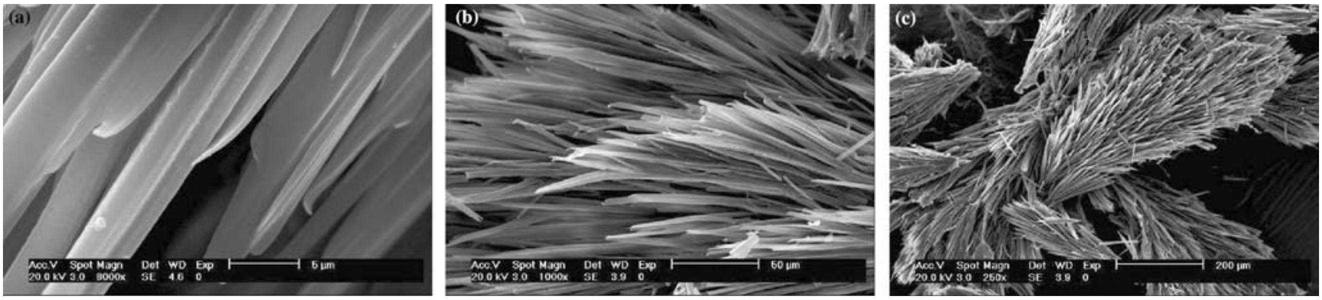


Fig. 4 Scanning electron microscopic pictures of high degree composite materials of PANi/NiO/SDBS

protruded amino group of An and PANi [13] in the An combine with each other to form a co-polymer (Fig. 3). As a result, nano-rods are formed.

When NiO nanoparticles are added to the SDBS/An/H_2O system, it is surprising that the structure of the PANi takes on a high order (Fig. 4). It is possible that An may polymerize and grow along the coordination bond formed between N (aniline) and Ni. Hence PANi nanoparticles grow up in one-dimensional direction and form nano-rods with thickness about 40–96 nm (Fig. 4b). The elemental analysis and the electron spectrum indicate that the molar ratio of An:SDBS is 4:1 in the nano-rods. Since the molar ratio of the reactants of An:SDBS is 5:1 (the molar ratio of NiO:An being 1:16), the conversion of An is about 80%.

Figure 5a shows the FT-IR spectrum of composite PANi/NiO nanomaterials. The bands at 3,300–3,450 cm^{-1} (Fig. 5a) are assigned to the secondary aromatic amine. The benzene ring skeletal vibration is seen at 1,600 cm^{-1}. The band at 1,485–1,496 cm^{-1} is attributable to the N–Q–N quinone stretching vibration. Since this peak is very weak, the main isomer of the product shows benzene structure. The aromatic C–N stretching vibration is at 1,130–1,150 cm^{-1}. NiO nanoparticles show a characteristic peak at 458 cm^{-1}(Fig. 5c).

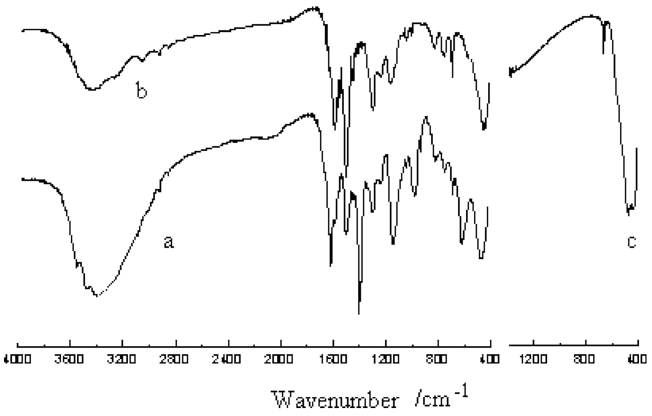


Fig. 5 The IR spectra of the different materials. **a** PANi/NiO; **b** PANi/SDBS/NiO; **c** NiO

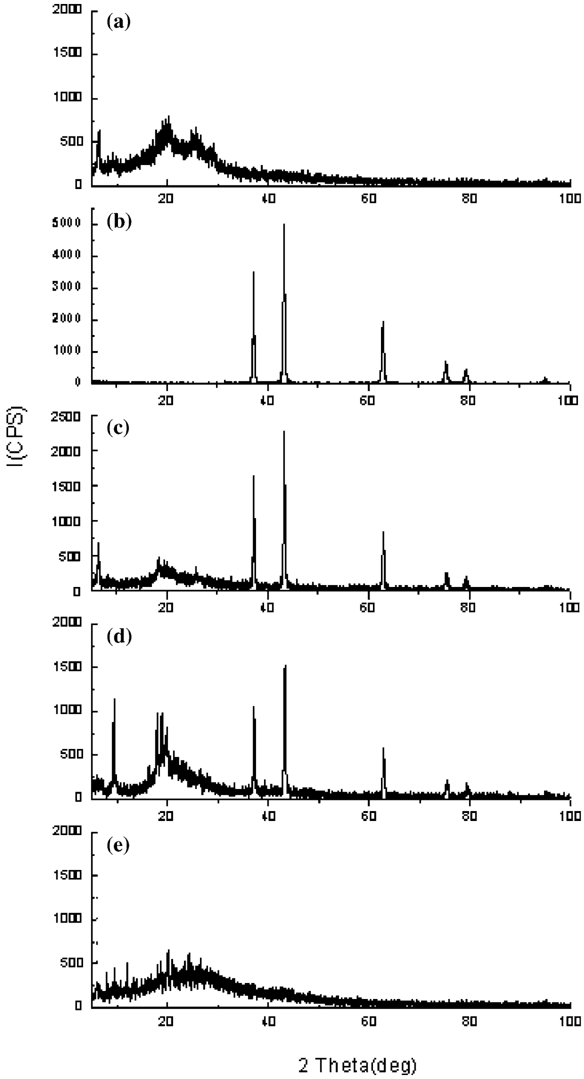


Fig. 6 The XRD spectra of the different materials. **a** PANi; **b** NiO; **c** PANi/NiO; **d** PANi/NiO/SDBS; **e** PANi/SDBS

Figure 5b depicts the FT-IR spectrum of PANi/SDBS/NiO composite particles. Compared to Fig. 5a, Fig. 5b still contains the characteristic peak of the

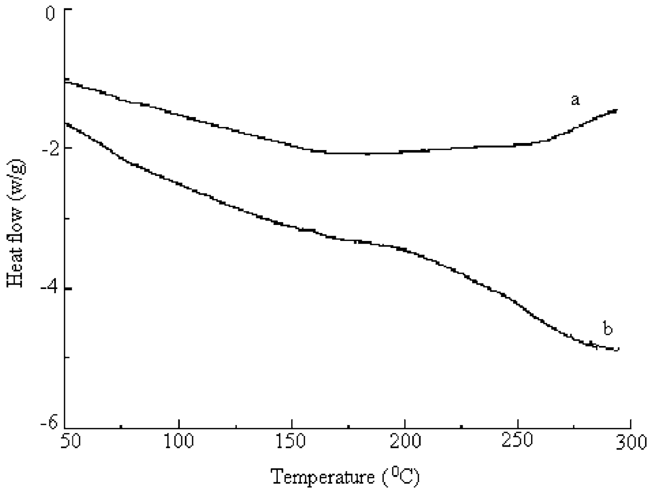


Fig. 7 The DSC spectra of the composite materials. **a** PANi/NiO/SDBS; **b** PANi/SDBS

secondary aromatic amine at 3,300–3,450 cm^{-1}. The higher intensity of the bands at 1,485–1,496 cm^{-1} indicates a higher content of quinone curds in PANi/SDBS/NiO than in PANi/NiO particles, as a consequence of the increased tertiary amine and decreased secondary amine content. The absorption peaks at 1,576–1,586 cm^{-1}, assigned to the stretching vibration of N–B–N of benzene, shows the vibrating structures of benzene and quinone to coexist in this composite material. The peaks at 1,100–1,150 cm^{-1} and 693 cm^{-1} are assigned to the characteristic S = O and S–O stretching vibrations, respectively. The peaks at 1,160–1,180 cm^{-1} indicate the interaction between sulfonyl groups and N atoms, showing that SDBS actually takes part in the polymerization of An. The peaks at 790–840 cm^{-1} render the existence of 1, 4-bisubstituted benzene in PANi/NiO/SDBS and the characteristic peak at 472 cm^{-1} proves that PANi/NiO/SDBS also contains NiO nanoparticles [14, 15].

A broad diffractive peak centered at an angle of 20.5° in Fig 6a indicates the usual PANi to be amorphous, whereas Fig. 6d shows a higher degree of crystalline PANi in the presence of the crystalline NiO and SDBS micelles.

In the DSC thermograms of PANi/NiO/SDBS and PANi/SDBS (Fig. 7) the decomposition temperature of PANi increases distinctly to show that the NiO particles enhance the heat-resistance.

The conductivity is 1.05×10^{-4} S·cm^{-1} for usual PANi, but 2.2×10^{-3} S·cm^{-1} for PANi/NiO/SDBS with the molar ratio of NiO:An being 1:16.

Conclusions

Polyaniline particles doped with SDBS and NiO can form nanorods. They show satisfactory conductivity, thermostability, and a suitable length for microelectronic equipment. The method of preparing PANi/NiO/SDBS composites in micelles has great potential in preparing other metal oxide nanoparticles and may open the path to a wide variety of advanced application of PANi.

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