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SHORT COMMUNICATION

Polypyrrole–multi-walled carbon nanotube nanocomposites synthesized in oil–water microemulsion

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Abstract An oil–water microemulsion system, having been successfully used for synthesizing polypyrrole (PPy) nanoparticles, is introduced for preparing PPy–multi-walled carbon nanotube (MWCNT) nanocomposites via in situ chemical oxidative polymerization. The structures and the physical properties of the PPy–MWCNT nanocomposites are also investigated. The studies show that PPy can coat MWCNTs to form core–shell structure. The backbone structure of PPy is not damaged by the introduction of MWCNTs, and the PPy in the PPy–MWCNT nanocomposites is still amorphous as pure PPy. The conductivities of PPy–MWCNT nanocomposites are higher than that of pure PPy and are enhanced with the increase in the MWCNT–monomer mass ratio. Furthermore, a model is supposed to be used for illustrating the mechanism for PPy–MWCNT nanocomposite formation via in situ microemulsion synthesis.

Keywords Polypyrrole · Nanocomposite · Microemulsion

Introduction

Since the discovery of carbon nanotubes (CNTs) with one-dimensional (1-D) nanostructure by Iijima, CNTs have attracted special attention owing to their especially more excellent properties [1], such as unique structure, big specific surface area, and high thermal and chemical stability. Recently, many studies have been directed towards the polymer–CNT nanocomposites because the introduction of CNTs into a polymer matrix can improve the electrical conductivity as well as the mechanical properties of the original polymer matrix [2–4].Among these polymer–CNT composites, many reports have focused on the combination of CNT and intrinsic conducting polymers (ICPs), for CNTs can play a role as hard templates for ICPs to attain the materials with 1-D core–shell nanostructures, and these materials have many promising potential applications, such as photovoltaic cells [5] and supercapacitor [6]. Incidentally, ICPs are a kind of polymer with conjugated π-bonds, and CNTs are also with conjugated π-bonds so as to be able to be also considered as a kind of ICP composed solely of carbon [7]. The well-known reason for the CNTs being able to play a role as hard templates for ICPs is as follows [8–13]: Each carbon atom of CNTs has a surplus p-orbit, and the electrons in these surplus p-orbits form highly delocalized big π-bonds. These delocalized π electrons can bond with the π electrons of ICPs to form π–π noncovalent bonds, so that the energy of this system can be reduced to form a new stable system. Thus, the ICPs bond with the sidewalls of CNTs in the form of π–π noncovalent bonds and the ICP–CNT nanocomposites with core–shell structure are obtained.

So far, several methods for preparing polymer–CNT nanocomposites have been developed. They mainly include dissolving polymer into the MWNT suspension of organic solvents, melt mixing, grafting macromolecules to the CNT, in situ polymerization, and so on [14]. Because ICPs are not easy to molten in nature and generally insoluble in common solvent [15, 16], it is difficult to prepare homogeneous and stable ICP–CNT nanocomposites by conventional blending or mixing in solution or melt form. So the most advisable method to obtain ICP–CNT nanocomposites is to polymerize monomer in situ in the presence of CNTs; thus, the even polymerization of monomer and the well dispersion of CNTs become particularly important factors.

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Among various ICPs, PPy has been much extensively studied owing to its unique properties [17–20], such as high conductivity, good environmental stability, and easy preparation, which have made it become a promising candidate for preparing ICP–CNT nanocomposites. Generally, PPy can be easily synthesized in aqueous solution with chemical method. In recent years, several other chemical methods have been developed to prepare the PPy with nanostructure; for example, Liu and Wan [21] used a template-free method to synthesize microtubules of PPy. Furthermore, microemulsion system, which is a thermodynamically stable and isotropic transparent solution, has also been employed to prepare superfine particles. Yan et al. [22] have prepared PPy nanoparticles with the size of 20–50 nm in oil–water microemulsion. Their studies confirm that, compared with the aqueous solution and conventional emulsion polymerization, the microemulsion polymerization of PPy increases the yield of the resultant PPy, the extent of the p-conjugation along the polymer backbone, and the ordered arrangement of the macromolecule chains. In addition, during the microemulsion polymerization, the reaction system is quite stable without any evident precipitation, which is especially favorable for the preparation of the PPy–CNT nanocomposites when using in situ polymerization in the presence of CNTs. Because the microemulsion polymerization of PPy has so many excellences, we may use this microemulsion polymerization system to synthesize PPy–CNT nanocomposite in situ. Therefore, in this paper, we describe a route for preparation of PPy–CNT nanocomposites in the above-mentioned microemulsion, and these PPy–CNT nanocomposites are also investigated with high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) analysis, and Fourier transform infrared (FT-IR) spectrometry, etc.

Experimental

Materials

Pyrrole monomer was distilled twice under reduced pressure before use. CNTs were kindly provided by Tsinghua University, and these CNTs were MWCNTs and produced by the catalytic pyrolysis of C_2H_2 with Fe as the catalyst. The sodium dodecylbenzenesulfonate (SDBS) was dried at 80 °C for 24 h. Other reagents, such as butanol and $FeCl_3$, were used without further purification.

Synthesis of PPy–MWCNT nanocomposites

The chemical composition of the microemulsion system we used followed that of the aforementioned microemulsion system used by Yan et al. [22]. They used the microemulsion system to synthesize PPy nanoparticles, and we used it to synthesize PPy–MWCNT nanocomposites. The microemulsion system they used contained 0.49 g $FeCl_3$, 10-mL distilled water, 4 g SDBS, 0.9 mL butanol and 6 mL hexane. But we increased the quantity of every constituent in the same proportion to magnify the microemulsion system, in case the system got unstable by the addition of MWCNTs. The PPy–MWCNT nanocomposites were synthesized via in situ microemulsion polymerization. The synthetic route was as follows: MWCNTs were dispersed into the microemulsion system containing monomer by sonication; and then on constant stirring, the reaction initiator $FeCl_3$ was added slowly to initiate the polymerization of pyrrole monomer. After that, the reaction was carried out at room temperature for another 24 h. During the polymerization, the reaction system was quite stable without any evident precipitation. Finally, the reaction mixture was filtrated and rinsed with acetone and water repeatedly, and then the obtained black powder was dried in vacuum at 40 °C for 24 h.

Characterization of PPy–MWCNT nanocomposites

HRTEM images were obtained by JEM-2010 transmission electron microscopy. FT-IR spectra were recorded on a PerkinElmer Fourier transform infrared spectrometer. XRD analysis was conducted on a powder Philips PW1830 diffractometer with CuKα radiation. The electrical conductivity was determined with the four-probe method on a Keithley 196 system digital multimeter and an Advantest R6142 programmable direct current voltage–current generator as the current source.

Results and discussion

For comparison, we also synthesize PPy–MWCNT nanocomposites in $FeCl_3$ aqueous solution with the same $FeCl_3$ to monomer molar ratio and $FeCl_{3\ (mass)}$ to water $_{(volume)}$ ratio as in microemulsion. As a result, we find that the PPy−MWCNT nanocomposites synthesized in $FeCl_3$ aqueous solution, such as the PPy–MWCNT nanocomposite prepared with the monomer to CNT mass ratio of 100:10, are hard to be dispersed in water or ethanol, and there are still many bulky grains that can be seen by eyes after a long time sonication. However, the PPy–MWCNT nanocomposites synthesized in microemulsion system are very easy to be dispersed. When the PPy–MWCNT nanocomposites are sonicated, they are dispersed well at once. The above phenomena shows that the PPy–MWCNT nanocomposites synthesized in microemulsion system are with smaller microcosmic size.

The HRTEM images of MWCNTs and the PPy–MWCNT nanocomposites are shown in Figs. 1 and 2, respectively. It

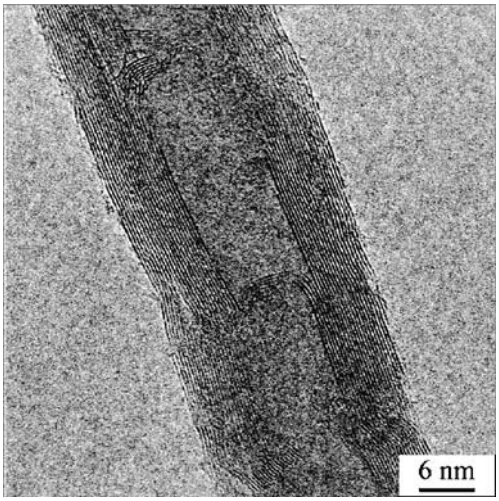

Fig. 1 HRTEM image of MWCNTs

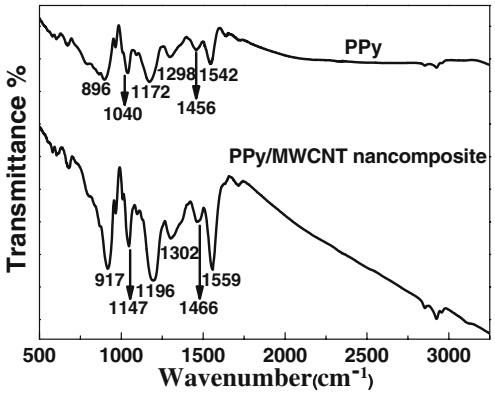

Fig. 3 FT-IR spectra of PPy and PPy–MWCNT nanocomposite

can be seen distinctly that PPy can coat the MWCNTs to form core–shell structure. PPy forms the outer shells and MWCNTs form the inner cores. The shell surface of the nanowire is accidented. The multilayer sidewalls of the MWCNTs are easy to be seen in Fig. 1, but they are hard to be seen in Fig. 2 because of the coating of MWCNT by PPy.

Figure 3 shows the FT-IR spectra of PPy and PPy–MWCNT nanocomposite. All the main characteristic peaks of PPy [23–27] can be observed in the PPy spectrum, and they are corresponding to the =C–H out-of-plane deformation vibrations at 896 cm^{-1}, the =C–H in-plane deformation vibrations at 1,172 and 1,040 cm^{-1}, the C–N stretching vibrations at 1,298 cm^{-1}, and the asymmetric and symmetric ring stretching modes of pyrrole rings at 1,542 and 1,456 cm^{-1}, respectively. The above characteristic peaks of PPy are all reflected in the spectrum of the PPy–MWCNT nanocomposite, but they all have some shift; so it can be proved that the backbone structure of PPy is not damaged by the introduction of MWCNTs, and there are interactions (probably π–π noncovalent bonds) between PPy and MWCNTs.

However, the amorphous state of PPy is not changed much by the introduction of MWCNTs. The XRD patterns of PPy, MWCNTs, and PPy–MWCNT nanocomposite are shown in Fig. 4. The only broad characteristic peak [21] at about 2θ=22° of PPy exhibits that pure PPy is amorphous. The XRD patterns of PPy–MWCNT nanocomposite are very similar to those of pure PPy, showing that the PPy in the PPy–MWCNT nanocomposite is amorphous all the same.

The putative mechanism for PPy–MWCNT nanocomposite formation by in situ microemulsion synthesis is illustrated in Fig. 5. In oil–water microemulsion, nanometer-sized oil droplets disperse in water phase, which provide a vast interfacial area; because of different polarities, the hydrophobic groups of SDBS dissolve in oil droplets and the hydrophilic head groups of SDBS are solvated in the water phase, so that the nanometer-sized oil droplets can be stabilized. The pyrrole monomer dissolves in nanometer-

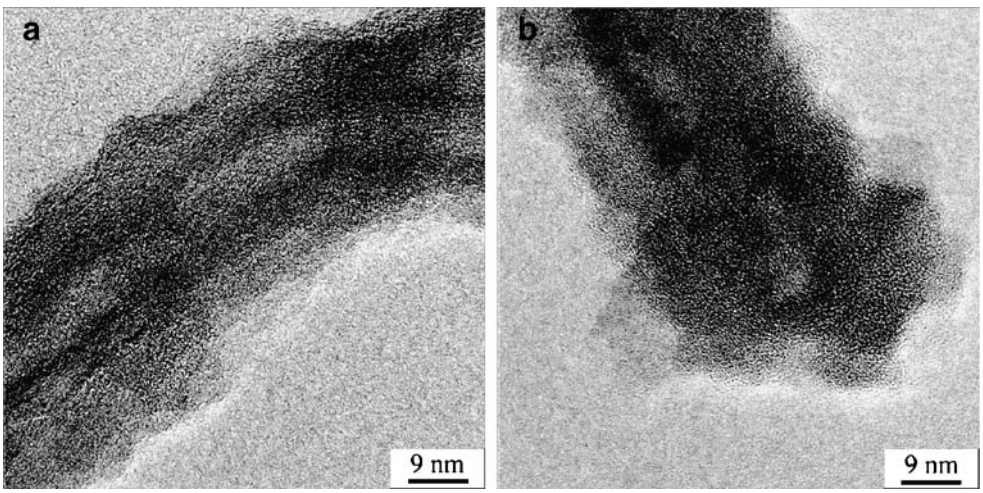

Fig. 2 HRTEM images of PPy–MWCNT nanocomposites **a** in the middle of the MWCNT; **b** in the end of the MWCNT

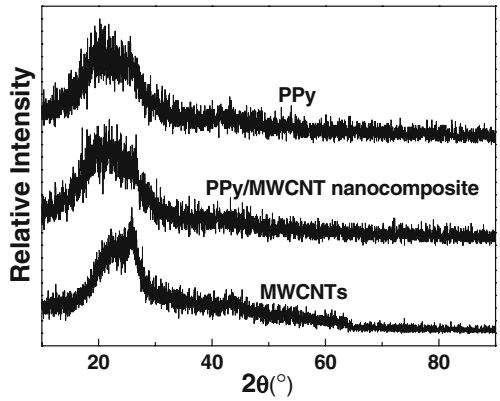

Fig. 4 XRD patterns of PPy, MWCNTs and PPy–MWCNT nanocomposite

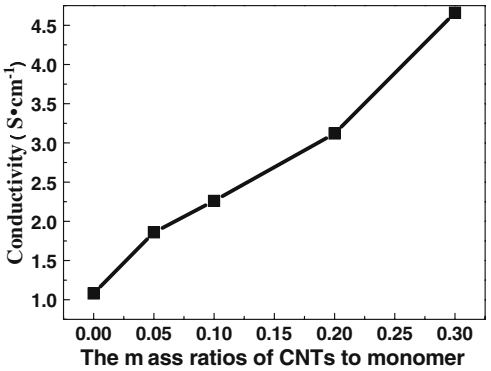

Fig. 6 Conductivities dependent on the mass ratio of MWCNTs to monomer

sized oil droplets and the initiator $FeCl_3$ dissolves in water phase. Thus, the polymerization occurs at the interfaces between nanometer-sized oil droplets and water phase, and subsequently the generated PPy nanoparticles confined in nanometer-sized oil droplets diffuse continuously to the surface of the MWCNT to coat the MWCNT due to the π–π interaction [8–13] between PPy particles and MWCNT. Finally, the MWCNT is coated completely by PPy to form the PPy–MWCNT nanocomposite with core–shell structure as the polymerization goes on. The resulting PPy–MWCNT nanocomposite with core–shell structure is then stabilized by the surfactant SDBS.

The electrical conductivities of PPy and PPy–MWCNT nanocomposites are shown in Fig. 6. It can be found that the electrical conductivities of PPy–MWCNT nanocomposites are higher than that of pure PPy and enhanced with the increase in the mass ratio of MWCNTs to monomer, which is similar to the results reported by other groups with other synthetic methods [12]. The increase of electrical conductivity may be mainly owed to the charge transfer from PPy to MWCNTs and the improvement of the compactness of PPy by MWCNTs [28, 29].

Conclusions

In summary, an oil–water microemulsion system, which can be used for synthesizing PPy nanoparticles, has been successfully introduced for preparing PPy–MWCNT nanocomposites. The PPy can coat the MWCNTs to form core–shell structure. The backbone structure of PPy is not damaged by the introduction of MWCNTs, and the PPy in the PPy–MWCNT nanocomposites is still amorphous as pure PPy. The conductivities of PPy–MWCNT nanocomposites depend on the mass ratio of MWCNTs to monomer, and they are higher than that of pure PPy. Thus the article provides a new route for synthesizing PPy–MWCNT nanocomposites.

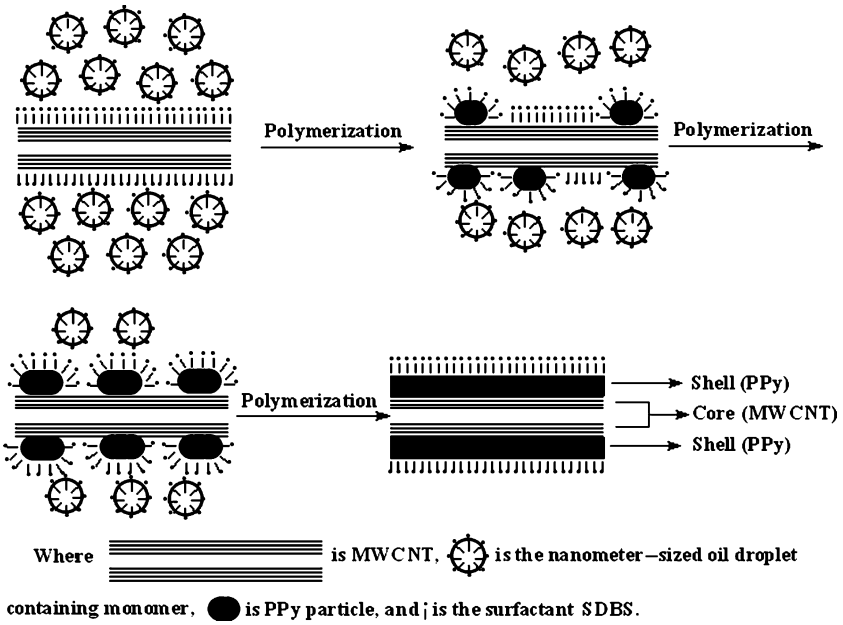

Fig. 5 Schematic diagram of the formation of PPy–MWCNT nanocomposite

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