Encapsulation of polyaniline in 3-D interconnected mesopores of silica KIT-6

Yu-Qian Dou, Yunpu Zhai, Fanwu Zeng, Xiao-Xia Liu, Bo Tu, Dongyuan Zhao

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Composite material PANI/KIT-6, with polyaniline (PANI) chains encapsulated in the 3-D interconnected pore channels of mesoporous silica, KIT-6, has been synthesized via a gas-phase method. The composite formation and the presence of PANI inside the pore channels of KIT-6 were evidenced by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), small-angle X-ray scatter (SAXS), transmission electron microscopy (TEM), and N2 adsorption–desorption isotherms. The PANI/KIT-6 composite showed good electrical conductivity ($2.4 \times 10^{-3}$ S/cm) due to the formation of 3-D networks of PANI inside the 3-D interconnected channels of KIT-6. The resistance of PANI/KIT-6 composite at different relative humidities (RH) was investigated. An essentially linear relationship between the relative resistance of the composite and the relative humidity of the environment was found from 11.3% to 97.3% RH.

1. Introduction

Polyaniline (PANI), as one of the most important conducting polymers, has attracted considerable attention due to its potential applications in various fields such as energy storage, sensors, and electrochromic devices [1]. Recently, great effort has been devoted to the insertion of PANI chains into inorganic host materials. New materials can be obtained which showed enhanced mechanical and thermal stabilities. The chemical properties can be modified as well and thus make it suitable for applications in enlarged technological fields. Examples of those inorganic hosts are montmorillonites [2], layered metal oxides [3], zeolites [4], and mesoporous silicas [5–9]. Among them, ordered mesoporous silicas have been recognized as an ideal candidate because of its large surface area and uniform pore structure, especially the enlarged pore size [10]. A higher thermal stability in oxygen was obtained for PANI confined in the 3-nm-wide channels of mesoporous silica MCM-41 which has a two-dimensional (2-D) hexagonal (p6mm) structure [5]. The composite material, PANI/MCM-41, also showed enhanced electronegative properties due to the aligned PANI structures along the nanoscale channel of the MCM-41 host which resulted in superior electrical anisotropy to bulk PANI [7]. However, as PANI chains were isolated in channels of the insulating host, the electrical conductivity of PANI/MCM-41 was very low (around $10^{-9}$ S/cm), which restricted somewhat the free movement of electrons within PANI chains under an external electric field. Thus, the polarization within PANI/MCM-41 particles under an applied electric field would not be fast enough. The electrical conductivity of the composite of PANI and the mesoporous silica was increased several orders in magnitude to $10^{-3}$ S/cm using another kind of well-ordered mesoporous silica, SBA-15, as a host [8]. This may result from the larger pore size as well as the accompanied disordered smaller pores in the walls which provided interconnection of the encapsulated PANI chains in adjacent pore channels [11]. KIT-6 is cubic (Ia3d) mesoporous silica with large 3-D interconnected pore channels [12]. It is possible that the encapsulation of PANI chains inside the interpenetrated bicontinuous networks of KIT-6 channels will provide new composites with improved electrical conductivity by constructing 3-D connections of PANI.

Many applications of PANI rely on surface-related effects including humidity sensors, as the contact of water molecules with imine nitrogen centers are of paramount importance in sensitivity [13]. There are many advantages of PANI over other humidity-sensitive materials, such as metal oxides, alumina thin films, and ceramics. These include light weight, low cost, and being flexible, in addition to the room temperature operation [14,15]. Herein, we demonstrate the encapsulation of PANI in bicontinuous channels of mesoporous silica KIT-6. The electrical conductivity of the obtained composites was improved ($2.4 \times 10^{-3}$ S/cm) and showed a basically linear response to relative humidity (RH) from 11.3% to 97.3% at room temperature.

2. Materials and methods

2.1. Chemicals

Triblock poly(ethylene oxide)-poly(propylene oxide)-poly-(ethylene oxide) copolymer Pluronic P123 (MW = 5800,
EO_{20}-PO_{70}-EO_{20}) was purchased from Acros Corp. Other chemicals were purchased from Shanghai Chemical Corp. Aniline was distilled under reduced pressure before use. Other chemicals were used as received without any further purification. Millipore water was used in all experiments.

2.2. Synthesis of mesoporous silica KIT-6

Bicontinuous cubic (Ia3d) mesoporous silica KIT-6 was obtained following the method reported by Kleitz et al. [12]. Hydrothermal treatment was operated at 130 °C in order to obtain large mesopore diameters. Briefly, 1.0 g of triblock copolymer Pluronic P123 was dissolved in 35 g of 0.60 mol/L HCl under vigorous stirring. After complete dissolution, 1.0 g of butanol was added. The mixture was left stirring at 35 °C for 1 h. Then 2.08 g of tetraethyl orthosilicate (TEOS) was added to the homogeneous clear solution. This mixture was left stirring at 35 °C for 24 h, followed by aging at 130 °C for 24 h under a static condition. The solid product was filtered without washing, dried, and subsequently calcined at 550 °C to remove the surfactant.

2.3. Synthesis of PANI/KIT-6 composite

Before the synthesis, the sample of KIT-6 was vacuum-dried at 100 °C to remove absorbed water and air in the mesochannels and then contacted with aniline gas at 40 °C for 24 h. The obtained sample containing aniline in the channels of KIT-6 was then immersed in 0.20 mol/L HCl. Then the oxidant initiator, ammonium persulfate, was added to the reaction system with stirring. The polymerization was continued at room temperature for 24 h. The obtained PANI/KIT-6 composite was washed for several times with aqueous solutions of LiCl (for relative humidity of 11.3%), CH₃COOK (22.5%), MgCl₂ (32.8%), K₂CO₃ (43.2%), Mg(NO₃)₂ (52.8%), KI (68.8%), NaCl (75.2%), KCl (84.3%), and K₂SO₄ (97.3%).

3. Results and discussion

Similar to mesoporous silica MCM-48, KIT-6 has a cubic Ia3d structure [16]. The encapsulation of PANI chains in the 3-D interconnected pore channels of KIT-6 can be explained by Fig. 1.
Aniline vapor was adsorbed into the dehydrated channels of the host, KIT-6, followed by reaction with ammonium persulfate, and then PANI/KIT-6 composite with PANI chains encapsulated in the channels of KIT-6 was obtained. Because of the predominant 3-D pore structure of the KIT-6 host, the encapsulated PANI chains formed 3-D networks in the channels.

Fig. 2 presents the FTIR spectra of KIT-6 (a), similarly prepared bulk PANI (b), and PANI/KIT-6 composite (c). Similar to mesoporous silica KIT-6 (Fig. 2a), PANI/KIT-6 composite shows the typical vibrations of antisymmetric and symmetric stretching, as well as the rocking of Si–O–Si at 1094, 802, and 465 cm\(^{-1}\) (Fig. 2c) [17,18]. The band at 967 cm\(^{-1}\) is related to Si–OH vibrations of the surface silanols (Fig. 2a) [19], which is characteristic of mesoporous silica. The existence of PANI in the composite is evidenced by the appearance of typical PANI vibrations on the FTIR spectrum. The characteristic band of the conducting emeraldine salt form assigned to B–NH\(^+\) stretching is overlapped with that of the antisymmetric Si–O–Si stretching vibration of KIT-6 (Fig. 2c) [20,21]. However, the bands attributed to C=C stretching vibrations of the quinonoid and benzenoid rings of PANI blue-shift from 1565 and 1478 to 1583 and 1489 cm\(^{-1}\), respectively, on composition, and C=N\(^+\) stretching vibration also blue-shifts from 1294 to 1304 cm\(^{-1}\) (Fig. 2b and c). These results suggested that the PANI peaks shift to higher wavenumbers. These phenomena may result from diffusion restriction of the insertion polymer in the channels [22].

Fig. 3. SEM images of mesoporous silica KIT-6 (a) and PANI/KIT-6 composite (b).

The morphologies of the KIT-6 host and PANI/KIT-6 are shown in Fig. 3. (The images in low magnification are in Fig. S3 of the supporting information.) KIT-6 host (Fig. 3a) and PANI/KIT-6 (Fig. 3b) are agglomerations of small irregular particles. Virtually no difference in particle surface morphology between the KIT-6 host and the PANI/KIT-6 composite is observed, which indicates that the polymerization takes place in the channels rather than on the outer surface [7].

Fig. 4 shows the SAXS patterns of silica KIT-6 (a) and PANI/KIT-6 composite (b). Both of them exhibit three identical diffraction peaks which can be indexed as 211, 220, 332 reflections of cubic mesostructure with la3d symmetry [23]. This indicates that the highly ordered cubic bicontinuous structure is well retained after the encapsulation of PANI chains in the channels. Compared with the host KIT-6, a bit of a decrease in diffraction intensities is observed on filling pores with PANI, which can be attributed to relative low scattering contrast between the pores and the walls of mesoporous silica resulting from the formation of PANI chains in the channels. This can be further demonstrated by TEM images, as shown in Fig. 5. Although the images are smeared and dark after the encapsulation of PANI chains inside the mesochannels (Fig. 5c), the ordered cubic la3d symmetric mesostructure of KIT-6 is retained.

N\(_2\) adsorption–desorption isotherms and pore size distribution curves of the host KIT-6 and PANI/KIT-6 composite are shown in Fig. 6, while the physical–chemical properties are summarized in Table 1. Both samples show isotherms of type IV with a sharp capillary condensation step at high relative pressures and H1 hystetic loop, indicative of large channel-like mesopores with a narrow pore size distribution. Compared with these two pore size distribution curves, it can be seen clearly that the pore size
distribution is narrowed after the insertion of polymer, which indicates that the polymer distributes uniformly in the channels. It can be clearly seen from Table 1 that compared to the host KIT-6, the specific surface area ($S_{\text{BET}}$), pore volume ($V_t$), and pore size ($D$) of the PANI/KIT-6 composite decrease obviously, while the wall thickness ($h$) increases at the same time. It can be estimated that about 80 m$^2$/g reduction in specific surface area is generated owing to insertion of PANI in the mesochannels of KIT-6. This evidence supports the fact that aniline polymerization occurred inside the mesopore channels of the host KIT-6.

TGA and DTG curves of bulk PANI and PANI/KIT-6 composite are presented in Fig. 7. Bulk PANI (Fig. 7a) and PANI/KIT-6 composite (Fig. 7b) demonstrate a three-step weight loss process with three peaks in the DTG curves [24]. At temperatures below 120 °C, the weight loss mainly corresponds to the removal of adsorbed water. The weight loss between 130 and 240 °C is due to elimination of dopant (HCl). The decomposition of the bulk PANI and the polymer in the composite occurs at ca. 216 and 235 °C, respectively. It is worth noting that bulk PANI decomposes completely before 570 °C, while the temperature for complete decomposition of the encapsulated PANI is 623 °C. The weight loss of PANI/KIT-6 between 235 and 630 °C is ca. 36%, which is accordant with the elemental analysis. It has been reported that the higher decomposition temperature for polyaniline/mesoporous silica composite implies that the thermal stability of PANI chains is enhanced by encapsulation in the mesochannels. In order to verify this, the temperature of the composite is kept at 570 °C for 120 min in the heating process. The corresponding TGA curve is presented in Fig. 8. It can be seen that the polymer can be completely decomposed at this temperature. Therefore, the measured higher decomposition temperature for PANI in the mesochannels of KIT-6 is not a result of the enhanced thermal stability of the polymer, but may be caused by slower diffusion of decomposition products from the silica pores.

The conductivity of PANI/KIT-6 composite is measured according to the standard four-point probe technique to be 2.4 × 10$^{-3}$ S/cm, which is two orders higher in magnitude than that of...
the reported PANI/SBA-15 composite [8]. It was reported that the conductivity of PANI depends on the transport of charge carriers both along the polymer backbone and between the polymer chains [25]. The encapsulation of PANI in the bicontinuous mesostructural networks of the KIT-6 host facilitates the hopping of the charge carriers between polymer chains and thus the composite shows enhanced conductivity because of 3-D interconnected pore channels of the bicontinuous cubic mesostructure.

Fig. 9 shows the relative resistance \( S \) of films of bulk PANI (a) and PANI/KIT-6 composite (b) on exposure to environments of different relative humidities. The relative resistance is defined as \( S = (R_d/R_h) \times 100 \), where \( R_d \) and \( R_h \) are the resistance of the films in a dry environment and at specified relative humidity, respectively. The relative resistance of both films decreased significantly on exposure to the environment with the relative humidity as low as 11.3%, while the conductivity of composite of PANI/SBA-15 with PANI inside the mesopore channels of SBA-15 did not change significantly until the relative humidity increased to 54% due to its high resistance [26]. Note that the relative resistance of PANI/KIT-6 decreases linearly along with humidity increase up to 97.3% (Fig. 9b). However, the relative resistance of the bulk PANI only shows a linear dropping up to 43.2% RH (Fig. 9a). Afterward the relative resistance of PANI film decreases slowly along with relative humidity increase. The unique feature of change in conductivity in wet environment involves two main processes: the adsorbed water molecules dissociate at imine nitrogen centers and a positive charge migrates through the polymer. Generally, most of the imine units in bulk PANI are enveloped in the polymeric networks, and only those on the surface have a chance of coming into contact with water which affects its sensitivity to humidity. As the specific surface area of bulk PANI is very small (18 \( \text{m}^2/\text{g} \)), the ratio of imine units which are on the surface is very low, too. Thus adsorption of water molecule is gradually saturated with the increase of relative humidity. For the composite of PANI/KIT-6, PANI chains are dispersed in the interconnected helical mesochannels of KIT-6 host; thus the composite possesses high specific surface area (230 \( \text{m}^2/\text{g} \)). Hence, the probability of the interaction between the imine units and the molecules of water in the PANI/KIT-6 composite is greater than that in bulk PANI, especially at high relative humidity.

4. Summary

A composite material of PANI/KIT-6 was obtained by encapsulating PANI into the 3-D interconnected pore channels of

<table>
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<th>Table 1</th>
<th>Physical–chemical properties of mesoporous silica KIT-6 host and PANI/KIT-6 composite.</th>
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<tr>
<td>( a_0 ) (nm)</td>
<td>( D ) (nm)</td>
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<tr>
<td>KIT-6</td>
<td>23.9</td>
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<tr>
<td>PANI/KIT-6</td>
<td>24.0</td>
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Fig. 7. TGA (under air with a heating rate of 1 °C/min) and DTG (insert) curves of bulk PANI (a) and PANI/KIT-6 composite (b).

Fig. 8. TGA curve of PANI/KIT-6 composite with isothermal process obtained under air with a heating rate of 1 °C/min, but kept for 120 min at 570 °C before continuing to 700 °C.

Fig. 9. Relative resistance of bulk PANI (a) and PANI/KIT-6 composite (b) at different relative humidities.
mesoporous silica, KIT-6. The well-ordered cubic bicontinuous structure was retained in the composite. The electrical conductivity of the composite is as high as $2.4 \times 10^{-3}$ S/cm due to the 3-D distribution of the polymer in the host. The relative resistance of PANI/KIT-6 composite was sensitive to humidity linearly from 11.3% to 97.3% RH as the result of high surface area originated from the uniform distribution of PANI in channels of KIT-6. Thus, the composite shows potential applications in humidity sensors.

Acknowledgments

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Appendix A. Supplementary material


References