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Letter

Water-assisted self-assembly of polyaniline/Fe_3O_4 composite honeycomb structures film

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Abstract

4-dodecylbenzenesulfonic acid-doped polyaniline/Fe_3O_4 composite honeycomb structure film is obtained by water-assisted self-assembly method. The morphologies of this honeycomb structure film were studied by transmission electron microscopic and atomic force microscropy, while the Fourier transform infrared spectra were obtained to illustrate its composition. This as-prepared film with conducting polymers and magnetic inorganic compounds is proved to show superparamagnetic property. Fabrication of 3D ordered macro-porous structures with conducting polymers and magnetic inorganic compounds should lead to applications in electronic-magnetic materials.

Keywords: Composite; Honeycomb structures; Self-assembly; Magnetic properties

1. Introduction

Highly ordered porous films have attracted increased interest due to their potential applications in chemistry, biology, life science and material technology, and a lot of methods have been developed for fabricating various micro-porous film from different materials [1–3]. As reported, fabricating micro-porous film can be realized by using templates, which can provide physical confinement [1,4]. Micro-structured material can be prepared by down-sizing engineering techniques where micro-sized patterns are printed onto a material [5]. However, lithographic methods are complicated and expensive. Self-organization and self-assembly of functional materials have been widely focused with the view of bottom-up process for formation of functional interface, while micro-porous structures can also be fabricated by the self-organization technique [6–10]. Among many methods [11–18] for fabricating porous polymer films, breath figure formation is a simple and useful technique [19–21]. The honeycomb film can be fabricated using a star polymer, a block copolymer or protein [22] (which is able to form aggregates like micelles in the solution) on water surface or solid substrates under highly humid atmosphere. The porous structure bases on hexagonal packing of water microspheres formed by the condensation of gaseous water at the air-polymer solution interface as evaporation of the solvent. We have extended this method to the conductive polymer-polyaniline, and the electro-active honeycomb structure film was obtained by controlling the relative humidity in the atmosphere and concentration of the conducting polymer respectively [23]. Recently, the researches of the honeycomb structures are focused on the properties of the porous films, such as the light reflection property, superhydrophobicity and photocurrent generation [24–27].

The building and patterning of inorganic nanoparticles into two- and three-dimensional organized structures by manipulation of individual units is a potential route to chemical, optical, magnetic and electronic devices with useful properties [28–32]. Considering that the synthesis and assembly of magnetic nanoparticles is the current interesting issue, and the composites formed from magnetic nanoclusters and conducting polymers may possess unique application in such areas as battery, electro-

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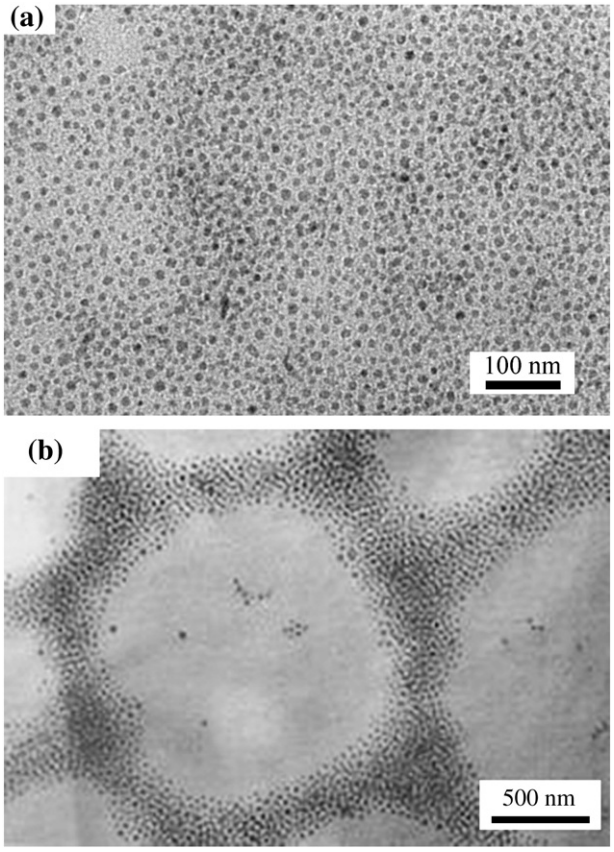


Fig. 1. (a) TEM image of 10 nm magnetite; (b) TEM images of as-prepared honeycomb structures of PANI-DBSA/Fe_3O_4 composite film. Inset is electronic diffraction pattern of PANI-DBSA/Fe_3O_4 composite. The content of Fe_3O_4 is 0.5 mg/mL in 0.002% PANI-DBSA chloroform solution (the mass ratio of Fe_3O_4 to PANI-DBSA is ca. 16:1).

display, molecular electronics, nonlinear optical materials, sensors, electromagnetic interference shielding, microwave absorption materials and electrochromic devices [33]. In this paper, water-assisted self-organization is adopted to fabricate polyaniline/Fe_3O_4 composite honeycomb structures and the morphology and composition are measured by atomic force microscropy (AFM), transmission electronic microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy, while the magnetic property of this composite is studied.

2. Experimental section

Fe_3O_4 nanoparticles were prepared by thermal decomposition method as described elsewhere [34]. A 20 mL portion of phenyl ether solution containing 2.0 mmol Fe $(acac)_3$, 10 mmol 1,2-hexadecanediol, 6 mmol oleic acid and 6 mmol oleylamine was first purged with nitrogen to remove oxygen and then heated. The mixture was refluxed at 254 °C for 30 min. After cooled to room temperature, the mixture was precipitated with methanol. The resultant dark-brown precipitate was separated by centrifugation and then dispersed in chloroform as stock solution. The average diameter of as-synthesized Fe_3O_4 nanoparticles is ca. 10 nm (shown in Fig. 1a).

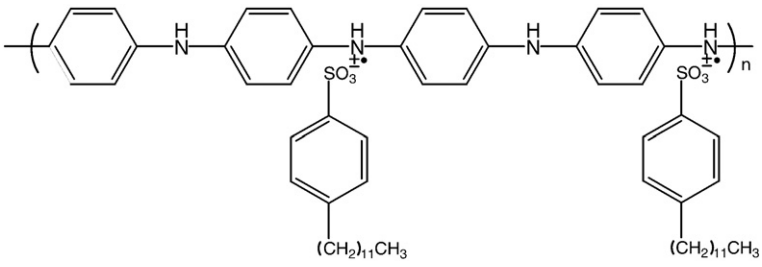
Then the as-prepared Fe_3O_4 is blended with 4-dodecylbenzenesulfonic acid (DBSA)-doped polyaniline (PANI) (0.002 wt.%) chloroform solution, whose chemical structure is shown in Scheme 1. 10 μL PANI-DBSA/Fe_3O_4 chloroform solution was cast on the hydrophilic treated substrates (glass or indium tin oxide glass) at room temperature in humid atmosphere with the relative humidity of 90%, and honeycomb-patterned films can be obtained.

Surface topographies of the as-prepared films were investigated by scanning probe microscopy (SPI3800N, Seiko Instruments Inc.) in the taping mode. A micro-fabricated silicon cantilever with a bending spring constant of 1.9 N/m and a resonance frequency of 25 kHz was used for imaging in the air with a 100 μm scanner in scan rate of 0.50 Hz. TEM images were obtained on a JEM-100CXII electron microscope operating at an acceleration voltage of 100 kV. FT-IR spectra was recorded by Perkin Elmer 2000 FT-IR spectroscopy.

The magnetic properties of the composite honeycomb structure film were investigated with a vibrating sample magnetometer (VSM).

3. Results and discussion

In order to understand the dispersion of Fe_3O_4 in PANI-DBSA honeycomb structure films, TEM images are given in Fig. 1b. The porous honeycomb structure can be observed with the aggregation of nanoparticles as the polygons' walls. Every Fe_3O_4 nanoparticle, with a size of ca. 10 nm, appears as a discrete entity in the walls of the hexagon, indicating the mono-dispersed nanoparticles in PANI-DBSA to form the walls in this honeycomb structure. Because PANI-DBSA may modify the surface of Fe_3O_4 nanoparticles well, the aggregation of Fe_3O_4 was prevented and the mono-dispersed nanoparticles in PANI-DBSA can be observed. The wall in the between of the porous structure was comprise of PANI-DBSA/Fe_3O_4, Cu grid with amorphous carbon supporting film was employed during TEM testing. The electronic diffraction pattern is shown in the inset of



Scheme 1. The chemical structure of PANI doped with DBSA.

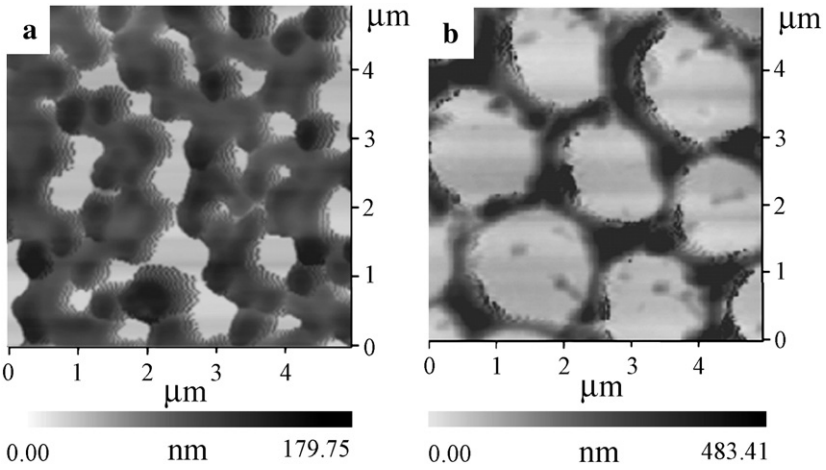


Fig. 2. The AFM images of as-prepared honeycomb structures of PANI-DBSA/Fe_3O_4 composite films with different concentration of Fe_3O_4 in PANI-DBSA. (a) top-view, the content of Fe_3O_4 is 1 mg/mL in 0.002% PANI-DBSA chloroform solution (the mass ratio of Fe_3O_4 to PANI-DBSA is ca. 32:1); (b) top-view, the content of Fe_3O_4 is 0.5 mg/mL in 0.002% PANI-DBSA chloroform solution (the mass ratio of Fe_3O_4 to PANI-DBSA is ca. 16:1).

Fig. 1b. The diffraction rings are very clear, indicating the polycrystallization of Fe_3O_4 in the composite film of PANI-DBSA/Fe_3O_4, and thus further proves the existence of Fe_3O_4 in PANI-DBSA.

Fig. 2 shows the AFM images of as-prepared honeycomb structures of PANI-DBSA/Fe_3O_4 composite films with different concentrations of Fe_3O_4 in PANI-DBSA chloroform solution. Fig. 2a and b are the images of the honeycomb patterns formed with the contents of Fe_3O_4 as 1 mg/mL and 0.5 mg/mL in 0.002% PANI-DBSA chloroform solution, respectively. Discontinuous porous structures are formed with the average pore diameter of 640 nm and the wall thickness of 110 nm when the content of magnetic nanoparticles is high. However, honeycomb structures clearly formed with the average pore diameter of 1.4 μm and the wall thickness of 215 nm when the concentration of Fe_3O_4 decreases to the half of the original value.

The mechanism for the formation of the honeycomb structures of PANI-DBSA/Fe_3O_4 can be well-understood, which has been proposed elsewhere [35,36]. It is well known that several key sections are included in this fabrication procedure, *i. e.* formation of breath figures, which needs to control the relative humidity; polymer precipitation on the water/organic solution interface and form a solid polymer envelope around the isolated water droplet so that to prevent the coalescence; evaporation of solvent and water [37]. This film formation mechanism tells us that the precipitation of the polymer on the interface is the key step to the formation of highly ordered honeycomb structures. And it has been pointed out that a spherical-shaped polymer such as star polymer or a block copolymer, which can form aggregates like micelles in the solution, is essential to obtain high regularity. While it is hard to use inorganic compounds as raw materials for the self-organization of the regular honeycomb structures by this method. In this case, PANI-DBSA is adopted not only as a conductive polymer, but also a film formation material for dispersion of inorganic nanoparticles as well. The content of Fe_3O_4 influences the morphology of the PANI-DBSA/Fe_3O_4 composite honeycomb structure obviously, because the addition

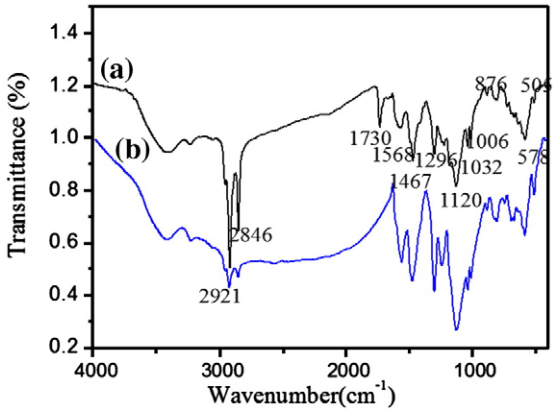


Fig. 3. The FT-IR spectra of (a) PANI-DBSA and (b) PANI-DBSA/Fe_3O_4 composite compounds.

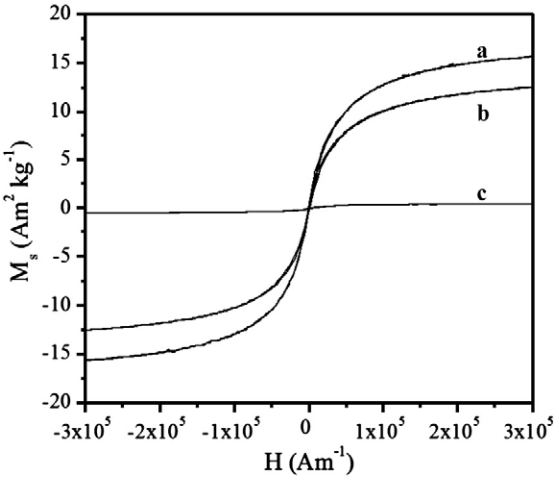


Fig. 4. The saturation magnetization (Ms) curves of the as-prepared compounds with different mass ratio of Fe_3O_4 to PANI-DBSA characterized by VSM. (a) pure iron oxide nanoparticles; (b) the mass ratio of Fe_3O_4 to PANI-DBSA is 10:1; (c) mass ratio of Fe_3O_4 to PANI is 1: 20.

of Fe_3O_4 decreases the precipitation of PANI-DBSA at the water/solution interface. When the concentration of Fe_3O_4 is as high as 1 mg/mL, the water droplet coalescence happens during the formation procedure so that the pores are discontinuous as shown in Fig. 2a.

Fig. 3 shows the FT-IR spectra of PANI-DBSA (line a) and PANI-DBSA/Fe_3O_4 composite (line b), respectively. Compared with line a, there are characteristic peaks of PANI-DBSA at 1568, 1467, 1296, 1239, 1120 cm^{-1} in line b, while the peaks at 1568, 1467 and 1296 cm^{-1} are corresponding to the strech vibration of C=C in quinoid, benzene rings and C–N in the bone of PANI, respectively, where the peaks at 1239, 1120 cm^{-1} correspond to the typical absorption of the doped PANI, *i.e.* the absorpiton peak of proton, indicating the existence of the main chain structure of the conductive doped PANI in this composite [38]. In particular, the band at 505 cm^{-1} –SO_3H group [39]. The new peak at 578 cm^{-1} in line b is attributed to the vibration of Fe–O lattice in Fe_3O_4. And the new peak appearing at 1730 cm^{-1} is the vibration of C=O in the modifier of monocarboxyl-terminated poly (ethylene glycol)(MPEG-COOH). The peaks at 2921, 2846 cm^{-1} correspond to the increase of the C–H vibration in the long chain, because there are C–H bonds provided by the modifier of poly(ethylene glyol) and MPEG–COOH in Fe_3O_4 [34] besides the existence of DBSA in this system.

The magnetic properties of these composite compounds with different mass ratio of PANI-DBSA to Fe_3O_4 were investigated with VSM. Fig. 4 shows the room-temperature magnetization of these composites. All of these compounds exhibit the super-paramagnetic properties due to the existence of magnetic nanoparticles. However, the saturation magnetization (Ms) decreases with the decreasing of the content of Fe_3O_4. As to the pure iron oxide nanoparticles, its Ms is 15.8 $A{\cdot}m^2{\cdot}kg^{-1}$. When PANI-DBSA is added for the formation of honeycomb structure with the mass ratio of Fe_3O_4 to PANI-DBSA as 10:1, the Ms decreases a little to 12.6 $A{\cdot}m^2{\cdot}kg^{-1}$ because of the addition of the organic compound. When the content of PANI-DBSA increases to the certain amount for the mass ratio of Fe_3O_4 to PANI as 1: 20, the Ms reduces significantly to 0.5 $A{\cdot}m^2{\cdot}kg^{-1}$. Therefore, the honeycomb structure of PANI-DBSA/Fe_3O_4 with magnetic property can be obtained at the certain composition of the organic/inorganic composite compounds.

In summary, water-assisted self-assembly of PANI-DBSA/Fe_3O_4 honeycomb structure is obtained. The inorganic compound is directly adopted by using conductive polymer as film formation materials to fabricate porous honeycomb structure with this approach. Additionally, the as-prepared film shows the super-paramagnetic property in the appropriate composition of PANI-DBSA/Fe_3O_4. The ability to make 3D ordered macro-porous structures with conducting polymers and magnetic inorganic compounds should lead to applications in electronic-magnetic materials.

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