Template Synthesis and Magnetic Response of Polyaniline/Fe_3O_4 Composite Microtubes

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ABSTRACT: Template synthesis technique was employed to prepare magnetic polyaniline (PANI)/Fe_3O_4 composite microtubes using anodic aluminum oxide (AAO) membrane as template. Magnetic microtubes were obtained through *in situ* polymerization of aniline in the presence of Fe_3O_4 nanoparticles in the microchannels of template. A tubular structure was formed once when aniline was preferentially adsorbed and polymerized on the surface of channels wall. Electron microscope images demonstrated that the shape and size of guest (PANI/Fe_3O_4 composite microtubes) were strictly depended on those of the host (template channels). Magnetic force microscopy images showed that the PANI/Fe_3O_4 composite microtubes possessed reasonable magnetism and the magnetism distribution of microtubes was regular as distribution of template channels. Moreover, the magnetic response and oriented arrangement of PANI/Fe_3O_4 microtubes were fulfilled in the magnetic field. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 963–969, 2009

Key words: polymer; ferriferous oxide; microtubes; magnetic response; template synthesis

INTRODUCTION

The composite materials of conducting polymer and magnetic nanoparticles integrate the magnetic, electrical, and optical properties. They possess potential applications in many fields, including directed target drug carrier,[1] cell separation,[2] fixed enzyme, electrical display, molecular device,[3] nonlinear optical materials,[4] sensors, electromagnetic shield,[5] absorbance of microwave, etc.[6] Butterwarth et al.[7,8] first prepared the magnetic and electrical composites using conventional chemical polymerization. Among conducting polymers, polyaniline (PANI) is a promising candidate for practical application because of its good environmental stability, ease of preparation, high temperature resistance, and tunable electrical conductivity from conductor to insulator with various kinds and concentration of dopant. Many works were developed based on PANI and magnetic oxide. Wan et al.[9] successfully synthesized γ-Fe_2O_3-PANI nanomembrane with high conductivity ($\sim$ 10 S/cm) and high saturated magnetization (Ms = 10–40 emu/g). Through wrapping magnetic fluid with PANI, Deng et al.[10] prepared PANI/Fe_3O_4 nanosphere with core-shell structure. Yang et al.[11] synthesized the composites of PANI doped by dodecylbenzenesulfonic acid (DBSA) with Fe_3O_4 magnetic nanoparticles in a neutral solution by a "modification and redoping" method. The results indicated that the composites of superpapramagnetic Fe_3O_4 nanoparticles and conductive polymer possessed a good electrical conductivity and magnetic susceptibility as well as high transmittance.

In addition, great efforts have been devoted to the preparation of one-dimensional nanomaterials, e.g., nanowires, nanotubes, and nanorods of metal, polymer, metal oxide, and alloy, etc.[12–15] It is expected that one-dimensional magnetic and conducting structure would have extensive application in the fields of electricity and magnetism because of its especial structure and function. Template synthesis is an efficient method for the preparation of one-dimensional materials. The ordered array of guest can be achieved via physical or chemical approach in the microchannels of template. A lot of materials with pore structure have been investigated, including mesoporous host MCM-41,[16] ion track-etch polycarbonate membrane,[17] and anodic aluminum oxide (AAO) membrane.[18] Many one-dimensional materials such as carbon nanotubes,[19] TiO_2 nanotubes, ZnO nanotubes,[20] etc. have been successfully prepared through template synthesis. In this article, we

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reported the preparation of PANI/Fe_3O_4 composite microtubes using AAO as template. The structure, morphology, and magnetic properties of PANI/Fe_3O_4 composite microtubes were investigated. Also, the ordered arrangement of PANI/Fe_3O_4 composite microtubes in magnetic field was realized.

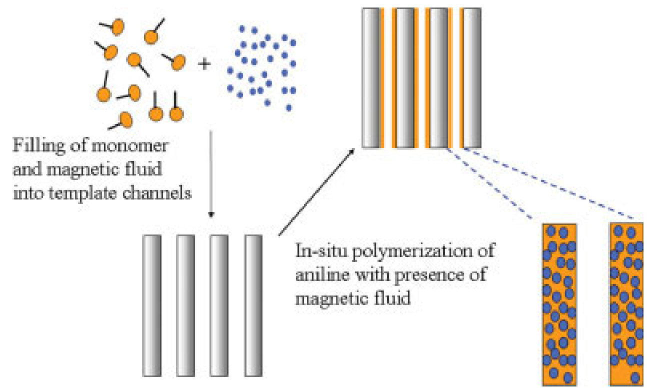
EXPERIMENTAL

Materials

Analytic reagent-grade aniline ($C_6H_5NH_2$), ammonium peroxydisulfate [$(NH_4)_2S_2O_8$, APS], and hydrochloric acid (HCl) were employed in the experiment. Aniline was distilled under reduced pressure and stored at low temperature before use. APS, HCl, sodium hydroxide (NaOH), and magnetic fluid (Fe_3O_4 nanoparticles with diameter of $\sim$ 10 nm) were used as received. AAO with pore diameter 200 nm was obtained from Whatman International (Kent, UK). The pore density of AAO is about 1.95×10^9 cm^{-2}.

Preparation of PANI/Fe_3O_4 composite microtubes

AAO membrane was treated with 0.5% (w/w) HCl aqueous solution to remove the impurity from the surface of template. It was then washed three times with distilled water, subsequently dried at 110°C for 1 h. Magnetic fluid (0.2 g) was dispersed in aniline monomer (1.86 g, 0.02 mol) by ultrasonic sound to form a brown color solution. The obtained solution was filled into template channels using homemade suction. The template with aniline monomer and Fe_3O_4 nanoparticles was immersed into the 150 mL of ammonium peroxydisulfate (1.0 mol/L) and hydrochloric acid (1.1 mol/L) solution immediately. The polymerization was lasted for 2 h with magnetic stirring in an ice water bath, and then the reaction was maintained for 24 h at ambient temperature. The sketch of preparation process of PANI/Fe_3O_4 composite microtubes was shown in Scheme 1.



Scheme 1 Preparation process of PANI/Fe_3O_4 composite microtubes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Characterization

The morphology and energy dispersive spectrometer (EDS) analysis of PANI/Fe_3O_4 composite microtubes were observed by JEM-100CX transmission electron microscope, SPA400 scanning probe microscopy (SPM), and JEOL JSM-5600L scanning electron microscope, respectively. The samples were prepared as follows: AAO membrane with PANI/Fe_3O_4 in its pores was glued to a piece of glass with epoxy resin. The surface of the template was polished carefully with fine grit sandpaper. Then the sample was treated with 10% (w/w) NaOH aqueous solution to partly dissolve the template. Ten nanometers of Au was sputtered on the surface of the sample for SEM observation. The SEM sample without Au sputtered was also used for AFM observation. The samples for TEM observation were prepared by fully removing the AAO template with 10% (w/w) NaOH solution. Then the solution was dialyzed until pH 7 using distilled water. Finally, the microtubes were dispersed with ultrasound to form a suspension. Before observation, the suspension was dropped on a copper grid. X-ray diffraction patterns of samples were taken by X'pert Pro MPD X-ray diffractometer, Cu Kα, wavelength 1.54 Å. The magnetic microtubes for XRD testing were obtained after template was removed with 10% (w/w) NaOH solution. The resultant suspension solution was filtered and washed with distilled water for five times. It was then dried at 50°C. The magnetic intensities of microtubes and magnetic fluid were measured by the Gouy magnetic balance at 80 and 100 mT magnetic field. The magnetic property of microtubes was tested with template. During the data analysis, the weight of template was subtracted. Magnetic forces microscopy (MFM) images of PANI/Fe_3O_4 composite microtubes were taken on SPA400 SPM with MFM model using magnetic probe with cobalt alloy coating tip side. The samples for oriented arrangement in magnetic field were prepared as follows: the suspended solution of PANI/Fe_3O_4 composite microtubes was dropped on a clear glass, and then two magnets were put on the two sides of glass. The suspended solution was evaporated at ambient temperature, and then the samples were sputtered with Au for SEM observation.

RESULTS AND DISCUSSION

Template synthesis of PANI/Fe_3O_4 composite microtubes

Through *in situ* polymerization of aniline in the presence of magnetic fluid in the template channels, the shape and size of resultant PANI/Fe_3O_4

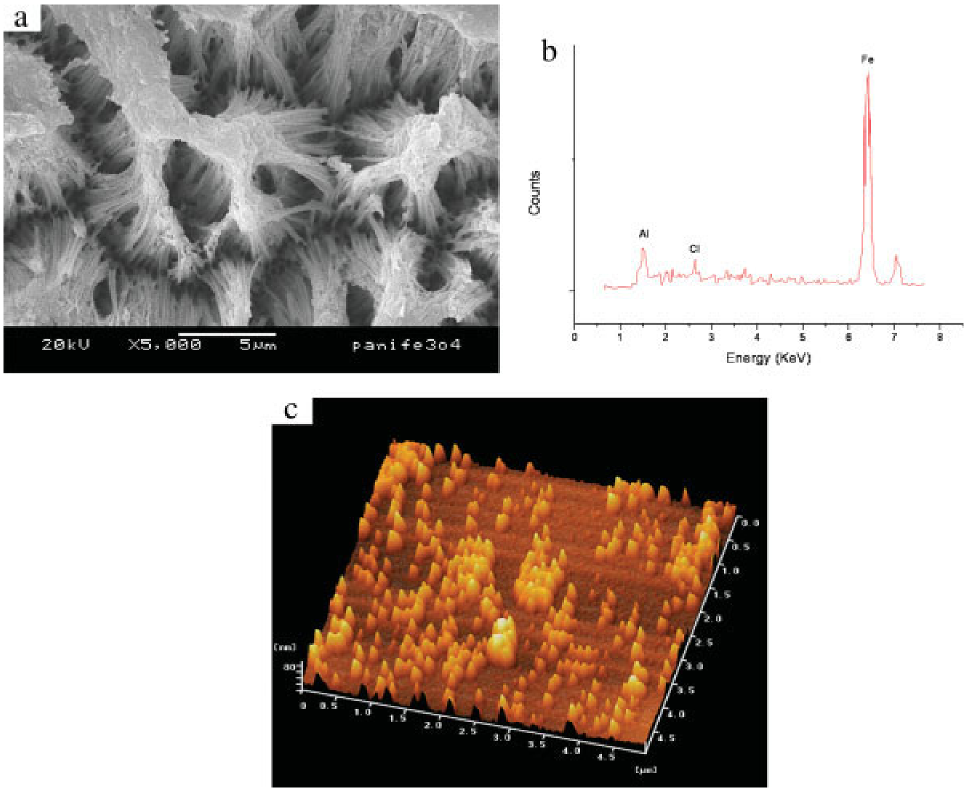


Figure 1 Morphologies and element analysis of PANI/Fe_3O_4 microtubes. (a) The microtubes exposed from the pores of template after the template was removed partially. Without support of template, the microtubes arrays were collapsed. (b) Element analysis of SEM samples. (c) Top view of AFM image of microtubes array. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

composite microtubes are similar to those of the template channels, most of the microtubes are open structure and the arrangement of microtubes is the same as that of template channels (Fig. 1). After the template is partially removed, the microtubes are exposed from the pores of template [Fig. 1(a)]. Because of the damage during the SEM samples preparation process, some of the microtubes are splitted into two parts from the root of microtubes. The element analysis of selected area [Fig. 1(b)] verifies that Al, Cl, and Fe elements exist in microtubes, attributing to residual template, dopant agent of HCl and Fe_3O_4, respectively. Also, the AFM image [Fig. 1(c)] shows an ordered array with diameter of 200 nm, which supports the results of SEM observation. Combining with the preparation process, it confirms that the PANI/Fe_3O_4 composite microtubes are prepared successfully.

The TEM image [Fig. 2(a)] shows that the magnetic fluid consisted of nanoparticles of Fe_3O_4 with diameter of 10 nm and the distribution of particles size is narrow. TEM image [Fig. 2(b)] of PANI/Fe_3O_4 composite microtubes shows that the diameter of the microtubes ($\sim$ 200 nm) is similar to that of the

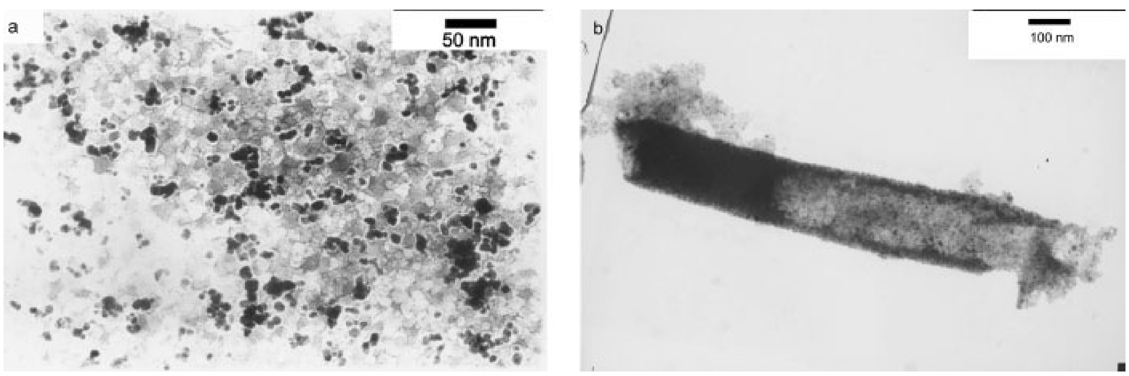


Figure 2 TEM images of magnetic fluid (a) and PANI/Fe_3O_4 microtubes (b), the microtube is half broken, the black dots on the tube well attribute to Fe_3O_4 particles.

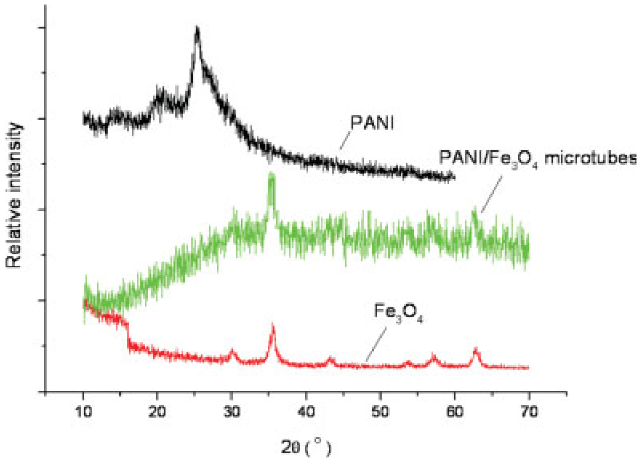


Figure 3 WAXD patterns of PANI, Fe_3O_4, and PANI/Fe_3O_4 microtubes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

template channels, and some dark dots (Fe_3O_4) with diameter of ~ 10 nm are well dispersed in PANI matrix. The hollow structure of PANI/Fe_3O_4 composite microtubes is observed after the microtube is broken. The thickness of microtubes wall is about 30 nm. Some Fe_3O_4 particles are observed in the wall of microtubes. It is evident that the highly ordered PANI/Fe_3O_4 composite microtubes are successfully synthesized through template synthesis technique. The formation mechanism of tubular structure can be explained as follows: when aniline is filled into the channels, it can be preferentially adsorbed and nucleated on the channel walls due to the electrostatic interaction between aniline and channel walls[21] and high surface energy of channel walls. In addition, after the suction is removed, partially aniline can get out from template channel and diffuse into the aqueous system. Then only channel well is totally wetted by monomer. After the aniline is polymerized, the tubular structure is fixed.

The XRD patterns of PANI, magnetic fluid, and PANI/Fe_3O_4 composite microtubes are shown in Figure 3. According to the indexation of characteristic peaks, the crystal form of PANI is pseudo-orthorhombic, and magnetic fluid is a typical spinel crystal form of Fe_3O_4. Because of the relativistically weak crystalline, no crystal peak of PANI appears in microtube sample. The characteristic peaks (2θ) of Fe_3O_4 at 30.18° (220), 35.86° (311), 57.00° (511), and 62.43° (440) appeared in PANI/Fe_3O_4 composite microtubes. The crystalline domain size (L) of Fe_3O_4 nanoparticle can be estimated using the Scherrer formula as follows:

$$L = \frac{k\lambda}{\Delta(2\theta)\cos\theta}$$

where λ is the X-ray wavelength, k is the shape factor, and Δ (2θ) is the width of the peak at half height of the maximum. When the shape is unknown, k is often assigned a value of 0.89. When the diffraction peak at $2\theta = 35.86°$ is chosen to calculate, the particle size of the Fe_3O_4 is 9.28 nm, consistent with the result of TEM image.

Magnetic properties of PANI/Fe_3O_4 composite microtubes

The magnetic properties of magnetic fluid and PANI/Fe_3O_4 microtubes were recorded by Gouy magnetic balance. The magnetic intensities of samples at 80 and 100 mT magnetic fields were measured and listed in Table I. The magnetic intension of pure magnetic fluid and microtubes were amended as 55.98 and 4.20 emu/g, respectively, in consideration of influence of template and additive of magnetic fluid. By comparison with magnetic fluid, the magnetic intension of microtubes is very weak because of the low content of Fe_3O_4 particle in microtubes. Nevertheless, the magnetic response of PANI/Fe_3O_4 microtubes in horizontal magnetic field is very obvious (Fig. 4). The PANI/Fe_3O_4 microtubes can be equably distributed in the water for a long time without magnetic field. After a horizontal magnetic field is introduced, the PANI/Fe_3O_4 composite microtubes are attracted by magnet and separated quickly from water. The whole process is accomplished in 30 s, which confirms that the speed of magnetic response of PANI/Fe_3O_4 composite microtubes is very fast. This characteristic is very useful for its application in the field of separation and target-direct carrier. Moreover, the hollow structure of microtubes is convenient for loading of carried materials.

Also, MFM was utilized for characterization of the magnetic property and magnetic distribution of PANI/Fe_3O_4 composite microtubes. The MFM images were obtained through measuring the interaction forces between PANI/Fe_3O_4 composite microtubes and magnetic probe of SPM. Figure 5 shows MFM images of PANI/Fe_3O_4 composite microtubes. The magnetic forces distribution image of microtubes [Fig. 5(a)] indicates that the magnetic domain size is very small because of the small particle size of Fe_3O_4. According to the analysis of MFM image [Fig. 5(b)], the magnetic force signal is even

TABLE I
Magnetic Intensities of Magnetic Fluid and Microtubes

Samples	Intensity of magnetic field 80 mT	100 mT	Average value (emu/g)
Magnetic fluid	9.42	8.13	8.78
Magnetic microtubes	1.11	1.40	1.26

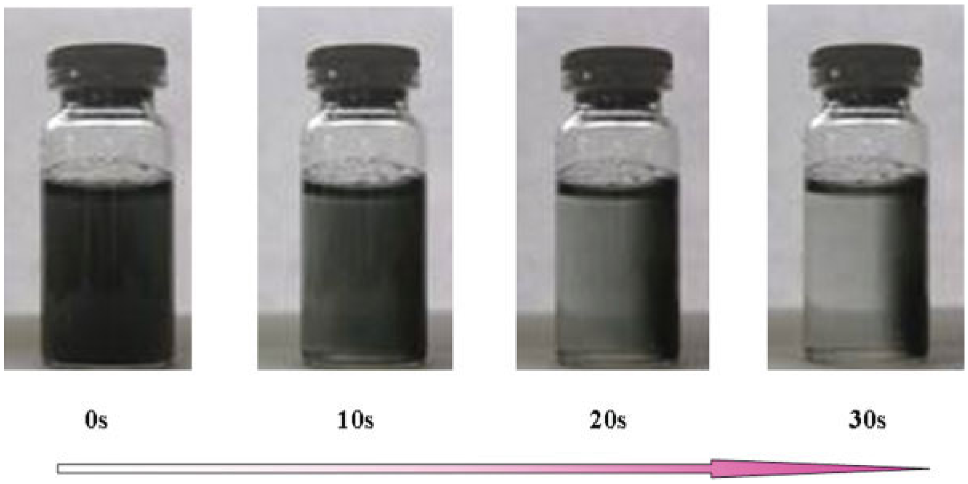


Figure 4 Magnetic responses of PANI/Fe_3O_4 microtubes, with a horizontal magnetic field, the microtubes separate entirely from water in 30 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

distributed, and the least size of magnetic force signal is about 36 nm, larger than the particle size of Fe_3O_4 due to the aggregation of Fe_3O_4 nanoparticles and the resolution limit of MFM. In addition, the cycle of distribution of magnetic signal is about 200 nm, which is similar to the cycle of distribution

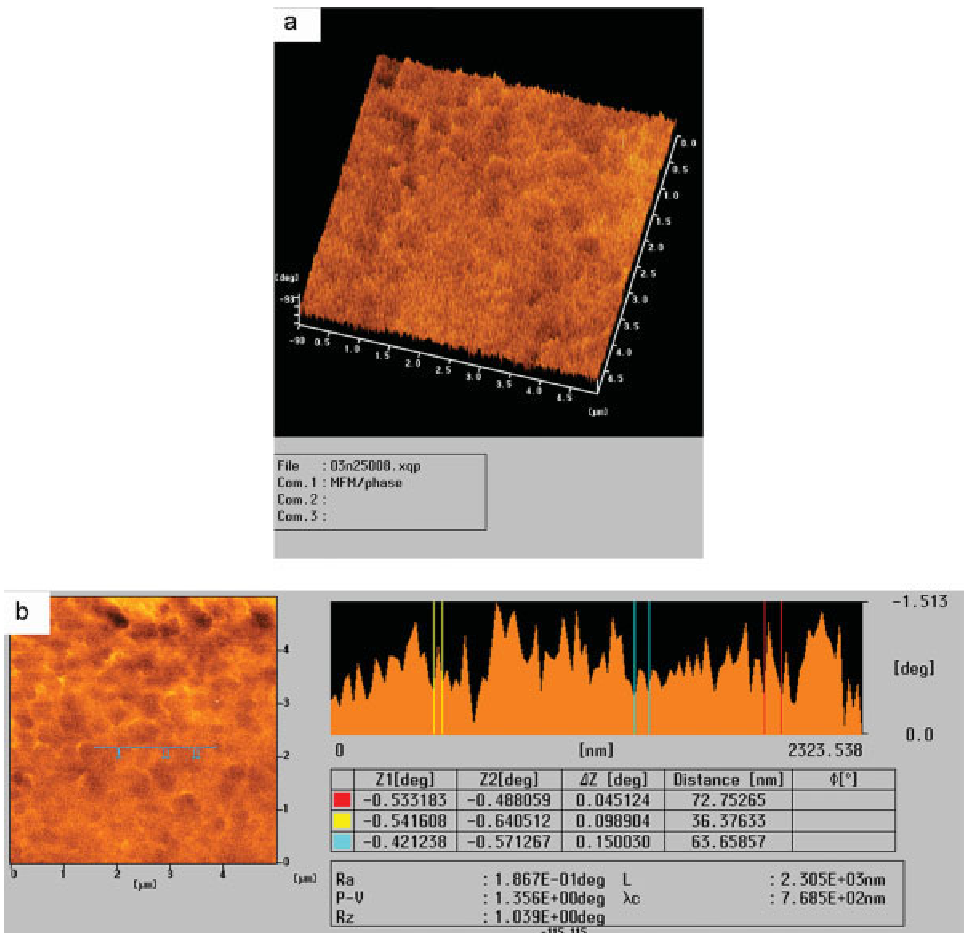


Figure 5 MFM images of PANI/Fe_3O_4 microtubes. (a) MFM of PANI/Fe_3O_4 microtubes and (b) magnetic distribution of PANI/Fe_3O_4 microtubes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

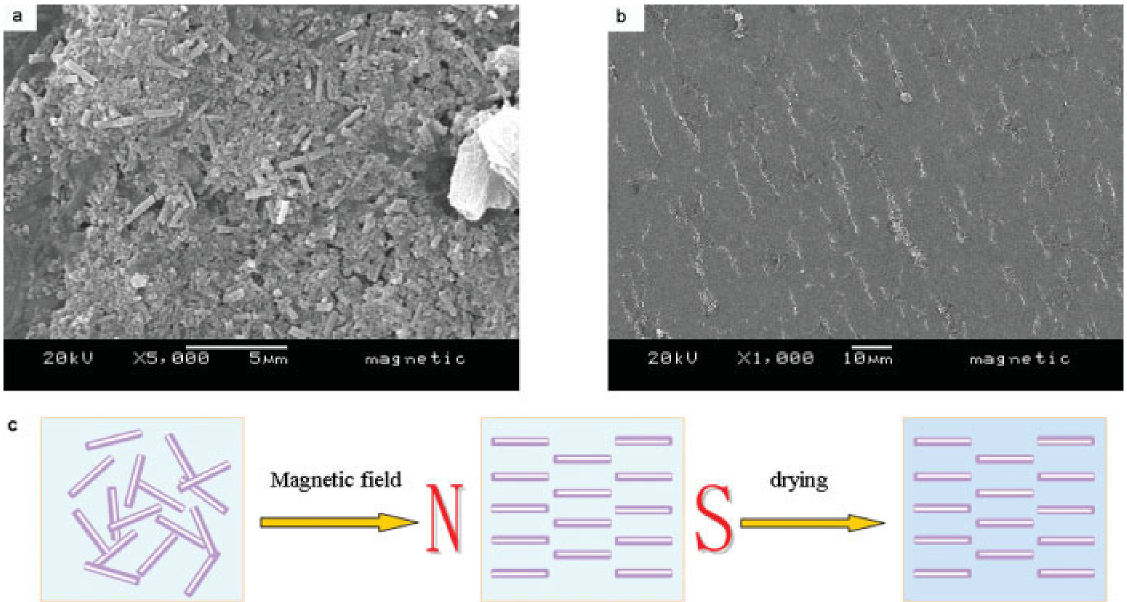


Figure 6 Assembly of PANI/Fe_3O_4 microtubes in magnetic field. (a) Without magnetic field, the microtubes were distributed disorderedly. (b) With magnetic field, the microtubes were arranged to magnetic field direction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of template pores. Accordingly, it can be concluded that the PANI/Fe_3O_4 composite microtubes possess magnetism, and the distribution of magnetic force is the same as template pores. Based on the data of Figure 5(b), the maximum phase difference ($P - V$) is 1.356° and average phase difference (Ra) is 0.187°. It indicates that the difference of magnetic force is small and the magnetic force is moderate due to the Fe_3O_4 nanoparticles packed by PANI matrix.

Oriented arrangement of PANI/Fe_3O_4 composite microtubes in magnetic field

PANI/Fe_3O_4 composite microtubes possess magnetic and electrical properties and hollow structure, which would have wide application in drug delivery or directed target drug carrier. In addition, the oriented arrangement of microtubes is very useful for the assembly and manipulation of one-dimensional nanomaterials. So, it is very interesting to study the oriented behavior and magnetic response of PANI/Fe_3O_4 microtubes in magnetic field. Through introducing the PANI/Fe_3O_4 microtubes suspension into a magnetic field, an oriented arrangement is realized. It can be seen that without magnetic field [Fig. 6(a)], PANI/Fe_3O_4 microtubes are out of order and the microtubes are aggregated. Many disordered microtubes with length of several micrometer and particles are mixed together due to high surface energy of microtubes. With magnetic field [Fig. 6(b)], the PANI/Fe_3O_4 composite microtubes form many lines parallel with each other, along with the direction of magnetic field. The arrangement consisted of many short tubes, probably because the intensity of magnetic field is not strong enough to move the long one. The mechanism of arrangement is that the magnetic PANI/Fe_3O_4 composite microtubes are magnetized in magnetic field. Each microtube could be viewed as a small magnet and arrange along with the magnetic field direction. After water is vaporized, the oriented arrangement is fixed. It can be imaged that if the drug or other materials which need be carried is filled into magnetic microtube, it can be delivered to target position in patent body with assistance of magnetic field.

CONCLUSIONS

Magnetic PANI/Fe_3O_4 composite microtubes with diameter of 200 nm and length of several micrometers were successfully synthesized with template synthesis method. TEM images confirmed that the microtubes were hollow structure and the Fe_3O_4 nanoparticles were even dispersed in the wall of microtubes. MFM images showed that the magnetic force distribution of samples was regular and the magnetic intensity was moderate due to the fact that the Fe_3O_4 nanoparticles were packed by PANI matrix. In magnetic field, the manipulation and arrangement of PANI/Fe_3O_4 composite microtubes were accomplished. The PANI/Fe_3O_4 composite microtubes possessing conductive property, magnetic response in magnetic field, and hollow structure should have potential application in various fields, i.e., directed target drug carrier, etc.

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