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Conducting polypyrrole confined in ordered mesoporous silica SBA-15 channels: Preparation and its electrorheology

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Abstract

A new nanocomposite with conducting polypyrrole (PPy) confined in ordered mesoporous silica SBA-15 channels has been synthesized by an in situ polymerization technique. The resulting material was characterized by X-ray diffraction (XRD), N_2 adsorption/desorption, high-resolution transmission electron microscopy (HRTEM), Fourier-transform infrared spectra (FT-IR) and thermogravimetric analysis (TGA). The results show that PPy is formed in the channels instead of coating the outer surface of SBA-15 and nanocomposite possesses well-ordered hexagonal structure. Further, nanocomposite particles were used as dispersed phase in silicone oil for electrorheological (ER) investigation. Suspension of PPy–SBA-15 displays notable ER characteristics under external electric fields.

Keywords: Conducting polymer; Polypyrrole; Mesoporous materials; SBA-15; Electrorheology

1. Introduction

In recent years, there has been increasing interest in the development of mesoporous silica-supported nanocomposites due to their potential applications in catalysis, as well as miniaturized electronic and optical devices [1–3]. Mesoporous silica materials exhibit uniform pore structure and large surface area, which makes them an ideal host for the preparation of new nanostructured composite materials. A number of studies have reported on the encapsulation of guest materials, such as semiconductors [4,5], metals [6,7] and polymer [8–12] into mesoporous silica hosts. The resultant nanocomposites exhibit unique properties which differ from the properties of bulk materials. Meanwhile, there has been particular interest in the materials where conducting polymer is confined in the channels of mesoporous host to produce novel structures, even on the molecular level. Encapsulation of conducting polymer can improve the mechanical, thermal, and chemical stabilities of the assemblies, and possibly allowing individual molecular wires to be addressed [13]. For example, polyaniline filaments confined in MCM-41 channels can be used in nanometer electronic devices [14,15]. Choi et al. [16,17] reported on polyaniline encapsulated in the channels of mesoporous host and investigated its electrorheological behavior. Other recent studies on polyaniline/SBA-15 and polyaniline/Na-AlMCM-41 composites with respect to their proton conductivities and semiconductor behavior were published by Balkus et al. [18] and Anunziata et al. [19], respectively. The above mentioned work clearly reveals that electronic properties of the guest material can be influenced by the confinement effect induced by mesoporous hosts.

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Polypyrrole (PPy), as a promising conducting polymer, has been widely studied because of its high polarizability, superior conductivity [20,21] and electrorheological properties [22–24]. It exhibits different properties in comparison with polyaniline and other conducting polymers. Therefore, incorporation of PPy inside the channels of mesoporous hosts may provide material with different electric characteristics. Although some papers on polyaniline/mesoporous silica have been published, few studies dealing with polypyrrole confined in channels of mesoporous silica hosts have been reported [25,26].

PPy can also be used as the dispersed phase for ER fluids. In general, ER fluids are one of the most promising class of smart materials and have been regarded as a great potential in engineering applications [27,28]. A typical ER response can make a rapid and reversible change of rheological properties (such as yield stress, shear viscosity, etc.) under external electric field [29,30]. Recently, interesting ER behavior induced by mesoporous silica-based suspension [31,32] has also been reported.

In this work, the synthesis and ER behavior of PPy–SBA-15 nanocomposite are described for the first time. SBA-15 was used as a template for nanocomposite because of its larger mesopores and thicker wall (large unit-cell constant) than MCM-41 [33]. The pyrrole monomer was introduced into the dehydrated and evacuated hosts from the vapor phase to avoid the formation of PPy layers on the outer surface. Polymerization took place in the channels to form PPy–SBA-15 nanocomposites. The nanocomposite formation and confinement effect were confirmed by means of XRD, HRTEM, N_2 adsorption/desorption, FT-IR and TGA. ER properties of nanocomposite particle dispersed in silicone oil were then investigated. This mesoporous material is a novel anhydrous system for ER materials, in which semiconducting PPy confined in insulating SBA-15 channels brings new properties compared to other core/shell conducting composites [34,35]. So a major motivation of this work is to present a possible approach to the design of new ER materials.

2. Experimental

2.1. Chemicals

Pluronic 123 (P123, $EO_{20}PO_{70}EO_{20}$, $M_w = 5800$), tetraethylorthosilicate (TEOS, 98%), and pyrrole (98%, distilled twice under reduced pressure before use) were obtained from Aldrich. Other highly pure chemicals were purchased from Shanghai Chemical Reagent Co.

2.2. Synthesis of materials

SBA-15 materials were synthesized according to the literature, using tri-block copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123) as a template in acid conditions [36]. To obtain PPy/SBA-15 nanocomposites, the calcined SBA-15 was dried under vacuum at 250 °C for 6 h to remove air and water from the channels. Then the host was suspended above the pyrrole monomer in a flask under vacuum at room temperature for 24 h (pyrrole is driven into the pores by capillary effects [9]). The SBA-15-containing pyrrole was immersed in a 0.25 M aqueous solution of $FeCl_3 \cdot 6H_2O$ with stirring at room temperature for 24 h. Finally, the products were washed several times with water and acetone, and then dried at room temperature under reduced pressure. In addition, pure PPy was also prepared under the same conditions for comparison.

2.3. Characterization of materials

Small-angle and wide-angle X-ray diffraction (SAXRD, WAXRD) patterns were determined with Rigaku D/MAX 2550 V diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). N_2 adsorption/desorption isotherms at about −195.6 °C were measured using Micromeritics ASAP 2010 system. The specific surface area and the pore size distribution were calculated by the Barrett–Emmett–Teller (BET) and Barrett–Joyner–Halanda (BJH) methods using the branch of the isotherms. FT-IR spectra were obtained on Nicolet Magna-550 spectrometer. Thermogravimetric analysis was carried out with a TGA/SDTA 851^e at a heating rate of 10 °C/min under a purging atmosphere of N_2. Finally, high-resolution transmission electron micrographs (HRTEM) were taken on a JEM 2100 F electron microscope operating at 200 kV. The DC electrical conductivity of the nanocomposite was performed with Keithley 6517A electrometer/high resistance meter using the standard four-probe method.

2.4. Electrorheological measurements

Dried SBA-15, PPy and PPy/SBA-15 particles were dispersed in silicone oil (Fluid 200, Dow Corning, UK; viscosity $\eta_c = 108$ MPa s, density $d_c = 0.965$ g cm^{-3}) in the concentration of 10% (w/w). Measurements of rheological properties were carried out under both controlled shear-stress (CSS) and controlled shear-rate (CSR) modes using a coaxial cylinder viscometer (Bohlin Instruments, UK). The suspensions were placed in the Couette cell with a rotating inner cylinder of 14 mm diameter and the outer cylinder separated by a 0.7 mm gap. They were connected to a DC power supply producing a field strength $E = 0.5$–3 kV mm^{-1}. An electric field was applied for 3 min to get an equilibrium structure before applying the shear. The flow curves were obtained in the CSR mode and static yield stress was measured in the CSS mode. All experiments were performed at 25 °C.

3. Results and discussion

3.1. Mesoporous PPy–SBA-15 materials synthesis and characterization

To prove that PPy chains were incorporated in the channels instead of growth on the surface of SBA-15, the