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Self assembly of SiO_2-encapsulated carbon microsphere composites

Yongzhen Yang[a,b], Jingjing Song[a,c], Yanxing Han[a,d], Xingmei Guo[d], Xuguang Liu[a,d,*], Bingshe Xu[a,b]

[a] Key Laboratory of Interface Science and Engineering in Advanced Materials (Taiyuan University of Technology), Ministry of Education, Taiyuan 030024, China
[b] Research Center on Advanced Materials Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China
[c] College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China
[d] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

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ABSTRACT

SiO_2 was firstly coated onto the surface of carbon microspheres (CMSs) using tetraethyl orthosilicate (TEOS) as precursor by Stöber method. Then SiO_2-encapsulated CMS (CMS@SiO_2) composites were self-assembled by vertical deposition, in which the effects of deposition temperature and suspension concentration on the quality of self-assembling film were investigated. Morphologies and structures of the samples were characterized by field emission scanning electron microscopy, Fourier transformation infrared spectrometry, X-ray diffraction and thermogravimetry. The results show that uniform CMS@SiO_2 composites with good mono-dispersion were prepared by Stőber method with 0.5 g of CMSs, 2 mL of TEOS, 30 mL of ammonia and 12 h of reaction time, the CMSs-based films with ordered and denser structure were prepared by vertical deposition using CMS@SiO_2 composites as monodipersion spheres under suspension concentration of 1 wt% and deposition temperature of 50 °C. The ultraviolet-visible absorption measurement shows that the absorbance of CMS@SiO_2 composite films grew steadily with increasing suspension concentration.

1. Introduction

Carbon films, with excellent physical and chemical properties, are a kind of advanced materials having good development and application prospect in optical devices, magnetic memory devices, high temperature semiconductor materials, machine tools, protective coating on medical orthopedic parts and so on [1]. At present, preparation of carbon films mainly includes physical vapor deposition (PVD) [2] and chemical vapor deposition (CVD) [3]. Compared with carbon films prepared by traditional methods, carbon films prepared by self-assembly have high order degree, high packing density, low defects and good structural stability, which make them have broad application prospects in nonlinear optics, molecular devices, microelectronics, sensors and other fields [4]. Carbon microspheres (CMSs), which have good chemical, mechanical and thermal stabilities, and thermal and electrical conductivity [5], are promising for materials of carbon films. However, as-synthesized CMSs exist in aggregated state because of intensive Van der Vaals attractive force, and have non-polar nature and inert surface [6]. So CMSs should be effectively modified to improve hydrophilicity and dispersibility to meet the requirement of preparing carbon films [5,7,8]. The surface modification of CMSs with SiO_2 coating (CMS@SiO_2) not only can improve their hydrophilicity and dispersibility, but also is beneficial to environment, because SiO_2, as a kind of non-toxic and non-polluting material, contains abundant hydroxyl functional groups [9,10]. Here, SiO_2 was firstly coated onto the surface of CMSs using tetraethyl orthosilicate (TEOS) as precursor by Stöber method [10]. Then CMS@SiO_2 composites were self-assembled by vertical deposition, in which the effects of deposition temperature and suspension concentration on the quality of self-assembling film were investigated.

2. Experimental

For preparation of CMS@SiO_2 composites by Stöber method, 0.5 g of CMSs was added into 250 mL flask with 8 mL of distilled water and 40 mL of anhydrous ethanol under ultrasonic vibration. Then surfactant cetyltrimethyl ammonium bromide (CTAB) was added into the suspension under ultrasonic vibration, then appropriate amount of ammonia was added to adjust pH value to 10. The suspension was stirred at 60 °C for 12 h after adding 2 mL of TEOS. Finally, the mixture was filtered, washed several times with distilled water and ethanol, and dried at 40 °C in air to obtain CMS@SiO_2 composites.

For self-assembly of CMS@SiO_2 composites by vertical deposition, a certain amount of CMS@SiO_2 composites were dispersed in 20 mL of anhydrous ethanol by sonication for 30 min to obtain

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* Corresponding author. College of Chemistry and Chemical Engineering, Taiyuan University of Technology, 79, West Yingze Street, Taiyuan 030024, China.
Tel.: +86 0351 6014138; fax: +86 0351 6014138.
E-mail address: liuxuguang@tyut.edu.cn (X. Liu).

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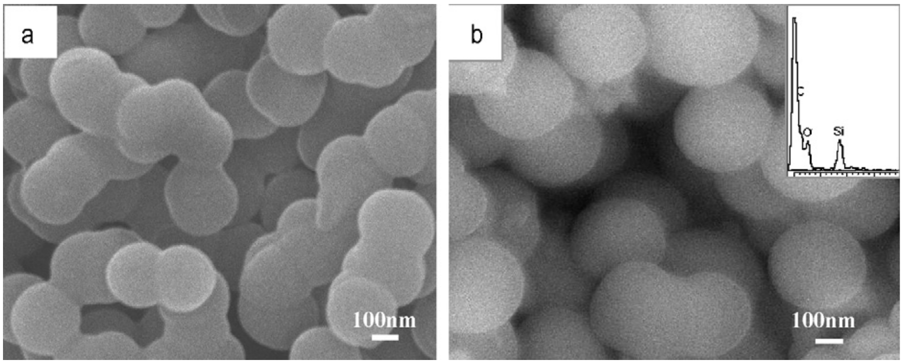

Fig. 1. FESEM images of (a) parent CMSs and (b) CMS@SiO_2 composites. (Insert is EDS spectra).

suspension with concentration of 2 wt%. The cleaned glass slides (20 mm × 20 mm × 2.5 mm) were placed vertically in the vial containing the above-mentioned suspension. The entire apparatus was placed in an isotemp oven at 20, 50 and 80 °C, respectively. As a result, CMS@SiO_2 composites were self-assembled on the substrate. In addition, the effect of suspension concentration (0.5, 1, 2 wt%) on the composite film was also investigated at deposition temperature of 50 °C.

The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, JSM-6700F) with X-ray energy dispersive spectroscopy (EDS), atomic force microscopy (AFM, SPI3800N), Fourier transformation infrared spectroscopy (FTIR, FTS-165), X-ray diffraction (XRD, D/Max-3C, Cu-Kα radiation, $\lambda = 1.54018$ Å) and thermogravimetry (Netzsch TG 209F3) operating in air atmosphere from 40 °C to 900 °C at a heating rate of 10 °C/min. The assembling process was monitored by an ultraviolet-visible (UV–vis) spectrophotometer (VARIAN Cary 300) at room temperature.

3. Results and discussion

3.1. Preparation of CMS@SiO_2 composites

Fig. 1 shows the FESEM images of parent CMSs and CMS@SiO_2 composites. It can be seen from Fig. 1(b) that CMS@SiO_2 composites with uniform size of ~380 nm have better monodispersion than parent CMSs (Fig. 1(a)). EDS spectra inserted in Fig. 1(b) shows the existance of Si and O, implying that the cover coating is a kind of silica oxide.

Fig. 2 shows FTIR spectra of parent and modified CMSs. The band at about 3450 cm^{-1} is attributed to –OH stretching vibration. Compared with parent CMSs (Fig. 2(a)), CMS@SiO_2 composites show several new bands at 470, 793, 950 and 1097 cm^{-1} (Fig. 2(b)). The bands at 470 and 793 cm^{-1} are assigned to Si–O–Si bending and stretching vibration, respectively. Other bands at 950 and 1097 cm^{-1} are attributed to the asymmetric stretching vibrations of the Si–OH and Si–O–Si bonds from the silica shells [11]. This result illustrates the formation of SiO_2 on the surface of CMSs.

The products were further characterized by XRD (Fig. 3). Fig. 3(a) shows the XRD patterns of parent CMSs. The peak at $2\theta = 24.3°$ can be attributed to the (0 0 2) reflection of graphite, indicating that CMSs had a structure of stacked graphitic fragments, which was between amorphous carbon and concentric graphitic shells. The peaks at $2\theta = 43.1°$ can be ascribed to the (1 0 0) reflection of graphite. Fig. 3(b) shows the XRD patterns of CMS@SiO_2 composites. The peak at 23.8°, which is attributed to amorphous SiO_2, indicates that the covering layer outside the CMSs was SiO_2. The overlapping peaks were observed because of the nearness of the diffraction peaks of amorphous SiO_2 (23.8°) and carbon (24.3°).

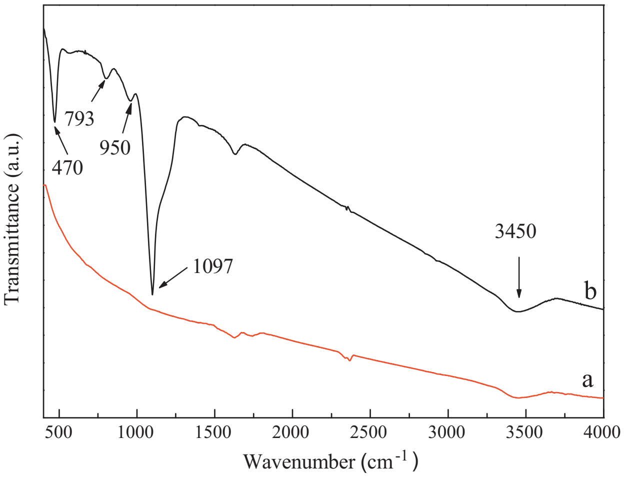

Fig. 2. FTIR spectra of (a) parent CMSs, and (b) CMS@SiO_2 composites.

Fig. 4 shows TG curves of parent CMSs and CMS@SiO_2. As can be seen in Fig. 4(a), as-synthesized CMSs exhibited ~100 wt% weight loss, suggesting CMSs were completely oxidized in air. CMS@SiO_2 composites (Fig. 4(b)) showed 49.8 wt% weight loss, indicating that the loading of SiO_2 was ~50.2 wt%. Moreover, the initial degradation temperature of CMS@SiO_2 composites (~550 °C) was higher than that of CMSs (~450 °C), suggesting that CMS@SiO_2 composites had higher thermal stability, which lays the

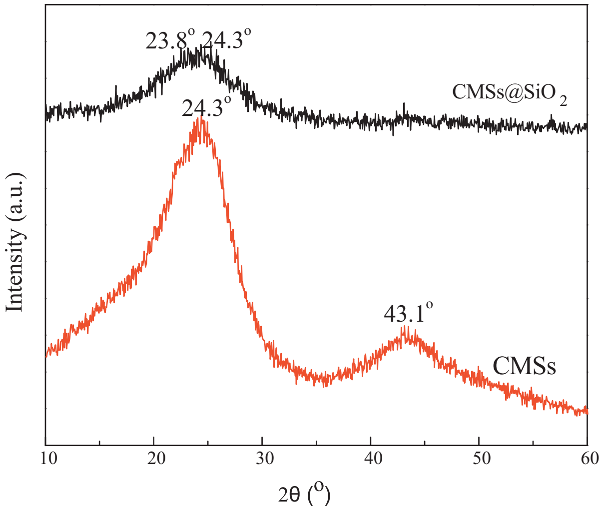

Fig. 3. XRD spectra of parent CMSs and CMS@SiO_2 composites.