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Letter

Preparation of transparent ordered mesoporous carbon/silica composites and their optical limiting properties

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ABSTRACT

Ordered mesoporous carbon/silica bulk composites were prepared via a simple sol–gel method and hot-pressing technique. Without removing the silica template, carbon particles were maintained in the form of ordered carbon wires and were dispersed homogeneously throughout the silica matrix. The linear transmittance of the composite with 0.3 wt% ordered mesoporous carbon reached ~81% near 1100 nm, larger than that of a carbon nanotubes/silica composite with less carbon content. The experimental results of *z*-scan indicated that the main optical limiting mechanism of the composites was nonlinear absorption, and that the optical limiting properties improved with increasing carbon content. Ordered mesoporous carbon/silica composites are more competitive materials for optical limiting compared to their carbon nanotube/silica counterparts.

1. Introduction

With the development of high-power laser sources, considerable attention has been paid to optical limiting materials owing to their applications in protecting the eyes and optical sensors from intense laser pulses. To date, a number of materials, such as organometallics [1], metallo-phthalocyanines [2], semiconductors [3], carbonaceous materials [4–6], and liquid crystals, have been investigated for their optical limiting properties. Among the widely investigated optical limiting materials, several carbonaceous materials have been proved to be competitive candidates for optical limiting. Carbon black suspensions undergo dramatic changes in transmittance because of nonlinear scattering [4,7]. Fullerenes and their derivatives are excellent reverse saturable absorbers due to their larger excited-state absorption cross-sections compared to ground state absorption cross-sections [5,8]. Carbon nanotubes (CNTs), which have many unique physical properties such as high electrical conductivity, high thermal conductivity and extraordinary mechanical performance, have also been considered as excellent broadband optical limiting materials [6,9–11]. Up to now, a great deal of effort has been made in searching for modified CNTs or CNT-based composites in an attempt to widen the real application of CNTs in optical limiting fields. CdS nanoparticles decorated multi-walled carbon nanotubes (MWCNTs) material showed enhanced optical limiting properties in comparison to the pristine MWCNTs [12]. A soluble MWCNTs hybrid material (MWCNT/POSS) functionalized by polyhedral oligomeric silsesquioxane (POSS), exhibited a remarkable optical limiting performance for nanosecond laser pulses at 532 nm [13]. The fabrication of a MWCNT/silica xerogel composite was reported by Zhan et al. and the material showed better optical limiting properties than those of a MWCNTs suspension [14]. However, the performance improvements or extensive applications of CNT-based composites were restricted due to the following reasons: firstly, CNTs tend to tangle together because of their large length-to-diameter ratio. Thus, it is hard to disperse CNTs homogeneously into a composite matrix. Secondly, so far there is no effective method for accurately controlling the diameter and length of CNTs. These are two of the most important factors that influence the optical limiting properties of CNTs and their composites.

In recent years, there has been growing interest in the synthesis of novel ordered mesoporous carbon (OMC) materials. OMC materials have many remarkable properties such as high specific surface areas, large pore volumes, chemical inertness, and good mechanical stability. For their unique nanostructures and good performance, they are important in many fields of modern science and technology, including water and air purification, gas separation, catalyst support, and energy storage [15–20]. Among the available mesoporous carbon materials, there is a particular type of OMC called CMK-3, which is normally synthesized by using ordered mesoporous silica (SBA-15) as a hard template [21]. CMK-3 possesses several special properties, such as good mechanical stability,

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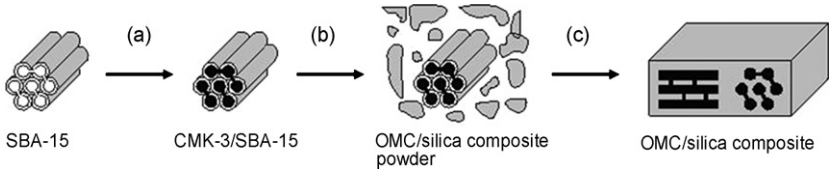

Scheme 1. Schematic illustration of the preparation of OMC/silica composites: (a) carbon filling and formation of CMK-3/SBA-15 composite powder. (b) added TEOS and absolute alcohol to prepare OMC/silica composite powders via sol–gel method. (c) OMC/silica composites with different carbon contents were prepared via hot-pressing.

unique electrical behavior, and special nanostructure composed of ordered nanowire arrays. Thanks to the existence of random interconnections in the pores of SBA-15 template, the ordered structure of the CMK-3 carbon can be exactly replicated without structural transformation during the removal of the silica template [21]. An additional advantage of CMK-3 is that it is easy to tailor the ordered pore size over a wide range by varying the SBA-15 pore wall thickness [22], which makes it more practical for real application. For example, a series of CMK-3/silica composites were synthesized and their electromagnetic (EM) wave-absorbing performance was found to be better than that of CNT-based composites [23].

CMK-3 possesses a unique nanostructure of ordered carbon nanowire arrays with a large length-to-diameter ratio, which is similar with CNTs. Moreover, CMK-3 has a macroscopic structure of coarse particle, which makes it easier to be dispersed in the matrix than CNTs. Therefore, CMK-3 is a promising candidate to fabricate a composite for optical limiting material. The objective of this study is to synthesize OMC/silica composites for possible application as an optical limiting material.

2. Experimental procedures

2.1. Chemicals

Triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$, Sigma–Aldrich Inc., St. Louis, MO, USA), a kind of macromolecule with molecular weight of 5800, was used as a surfactant in the present study. Tetraethyl orthosilicate (TEOS, AR Grade, Shanghai Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) was used as the silica source. Sucrose (AR Grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as the carbon source. Cetyltrimethyl ammonium bromide (C_{16}TAB, AR Grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as a surfactant. Other chemicals used in the present study were also from Sinopharm Chemical Reagent Co., Ltd. All the above chemicals were used without further purification. Distilled water was used in all experiments.

2.2. Preparation

A schematic illustration of the preparation of OMC/silica composites are shown in Scheme 1.

Firstly, SBA-15 was synthesized following a previously reported method [22]. Typically, 1 g $EO_{20}PO_{70}EO_{20}$ was added into 36 ml of 2 M HCl. The mixture was stirred until the $EO_{20}PO_{70}EO_{20}$ was completely dissolved. 2.2 g TEOS was added into the mixture and then stirred at 38 °C for 24 h. The mixture was loaded into a hydrothermal reaction vessel and heat-treated at 110 °C for 48 h. In order to remove the surfactant, the as-obtained product was filtered, washed several times with distilled water, and calcined at 500 °C for 6 h.

Based on a previously reported method [21], CMK-3 was synthesized by using the obtained SBA-15 silica as the template and sucrose as the carbon source. Typically, 1 g SBA-15 was mixed with a solution obtained by dissolving 0.8 g of sucrose and 5 ml of 0.3 M sulfuric acid (H_2SO_4). The mixture was heated in a muffle furnace at 80 °C for 6 h to remove water, followed by a further heat-treatment at 160 °C for 6 h to guarantee the pre-carbonization of the sucrose. Afterwards, the silica template contained some carbonized sucrose in its channel, and the color of the product turned from white to dark brown. In order to obtain silica template with fully carbonized sucrose filled inside the channel, the sample was again heated at 80 °C and at 160 °C in muffle furnace after the addition of a solution (composed of 0.5 g sucrose and 5 ml of 0.2 M H_2SO_4). After heating at 900 °C for 4 h under vacuum, carbonization was completed, yielding a black CMK-3/SBA-15 composite powder.

OMC/silica composite powder was synthesized via sol–gel method. The obtained CMK-3/SBA-15 composite powder without removing the silica template was lightly ground and sieved through a 100 mesh screen. The sieved powder was added into a 1.2 mM aqueous solution of C_{16}TAB, ultrasonicated for 30 min, and then stirred for 2 h. TEOS and absolute alcohol (V_{TEOS}:V_{EtOH} = 2:1) were then slowly added into the solution and followed by a stirring for 4 h. In order to achieve complete hydrolysis of TEOS, the mixture was heated at 50 °C for 1 h with constant stirring. In order to initiate gelation, a 2 M NH_3 solution was then added into the mixture dropwise. The resultant gel was aged for 12 h and then broken up and washed with distilled water for several times so as to remove impurities or Br^- ions. After drying at 100 °C for 12 h and calcining at 400 °C for 1 h, the OMC/silica composite powder was obtained. Composite powders with various percentages of CMK-3 carbon (0.3, 0.5, and 0.7 wt%) were obtained by adjusting the ratio of CMK-3/SBA-15 composite powder and TEOS.

Finally, the OMC/silica composite powders were hot-pressed to prepare OMC/silica composites. Composite powders with various percentages of CMK-3 carbon were loaded into a graphite die and then hot-pressed at 1250 °C under a pressure of 30 MPa for 0.5 h in nitrogen atmosphere. The sintered samples were machined into 30 mm × 20 mm × 1 mm cubes, and both sides of the samples were polished for the transmittance and optical limiting properties analysis.

2.3. Characterization

Transmission electron microscopy (TEM) (JEOL JEM 2100F FETEM, Tokyo, Japan) was employed to observe the internal structure of the OMC powder. Thermogravimetric and differential thermal analysis (TG–DTA) of the OMC powder was carried out on a thermal analyzer (Netzsch STA-449c, Selb, Germany) at a heating rate of 10 °C/min under a constant air flow. The transmittance test was carried out on a Model U-2800 Spectrophotometer (Hitachi, Tokyo, Japan). The *z*-scan experimental setup was based on a Spectra-Physics mode-locked Ti:sapphire laser, which produced laser pulses with a duration of about 100 fs and an 82 MHz repetition rate at a wavelength of 800 nm. The measurements were performed by using transmission *z*-scan (TZ-scan) techniques with an objective lens of 10 cm focal-length [24,25].

3. Results and discussion

Fig. 1(a) shows typical transmission electron micrograph (TEM) image of CMK-3/SBA-15, which is viewed along and perpendicular to the direction of the hexagonal pore arrangement. Mesoporous carbon particles are incorporated into the SBA-15 silica template, and no residual carbon particles can be found beyond the template, which can be assigned to the reduced sucrose mass used in our experiments compared to that used in a previous study [21]. The diameter of the carbon nanorods in CMK-3 is about 6 nm. Fig. 1(b) shows TEM observation of the ordered mesoporous structure OMC/silica composite powder, which indicates that the gelation procedure does not destroy the ordered structure of CMK-3.

The carbon content of the CMK-3/SBA-15 composite powder was estimated by the thermal decomposition of carbon performed in a TG–DTA study. Fig. 2 shows two main weight loss events. A weight loss of about 28.4% of the initial weight, which occurred between 400 and 700 °C, could be assigned to the combustion of carbon in air. At the temperature of 800 °C, the residual mass was about 65% of the initial weight, which matched the mass percentage of SBA-15 silica within the CMK-3/SBA-15 composite powder.

The optical transmission spectra of the composites with various percentages of CMK-3 carbon or CNTs at the wavelength range of 200–1100 nm are compared in Fig. 3. The transmittance of the sample with 0.3 wt% OMC reached ~81% near 1100 nm and maintained at a high level in the visible region, which was even higher than that of CNTs/silica composites with less carbon content (0.02 wt%) employed in a previous work [26]. Although the transmittance of the CNTs/silica composite reached ~76% near 1100 nm, it decreased to ~64% at 400 nm. Thus, the OMC/silica composites with higher linear optical transmittance should be more promising optical limiter, which can ensure the quality of observation.

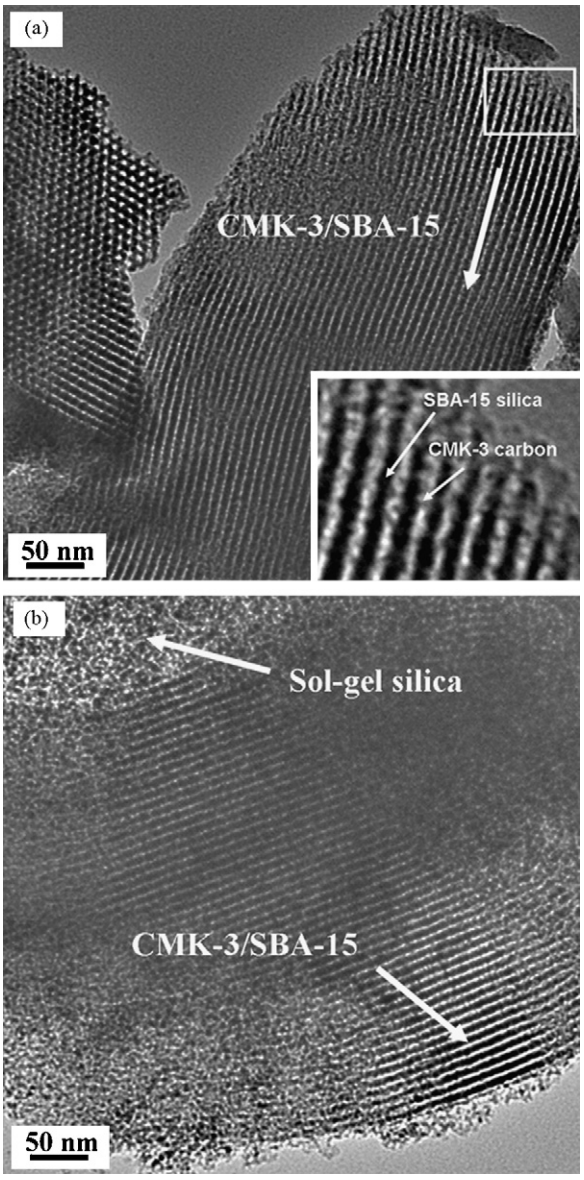

Fig. 1. Typical TEM images of (a) CMK-3/SBA-15 composite powder and (b) OMC/silica composite powder.

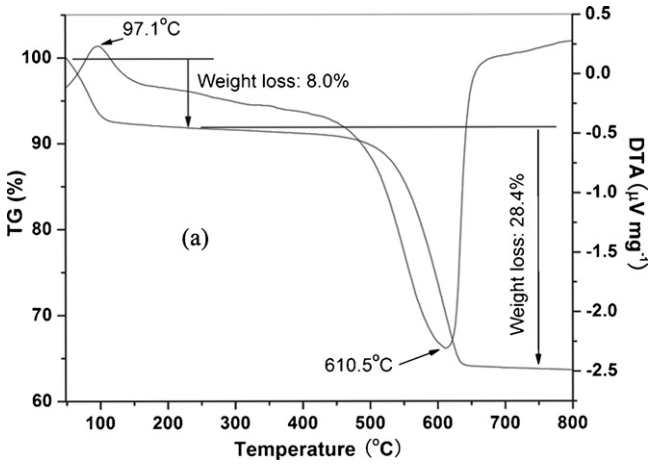

Fig. 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curve of CMK-3/SBA-15 composite powder.

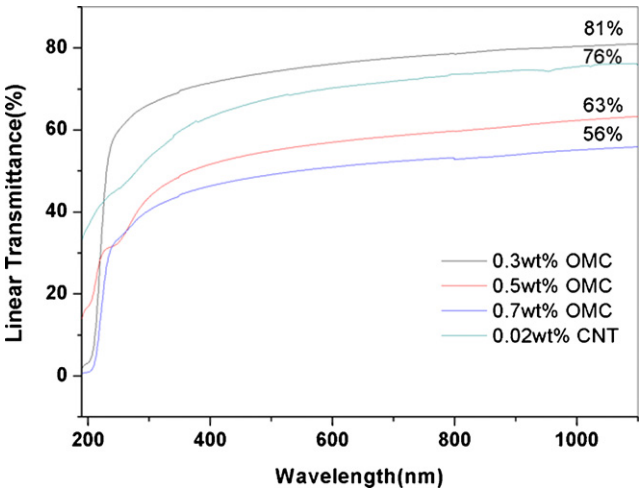

Fig. 3. Optical transmission spectra of OMC/SiO_2 composites and CNTs/SiO_2 composite.

As shown in Fig. 4(a), a *z*-scan experiment was performed to determine the optical limiting properties of the sample. The *z*-scan technique is a kind of sensitive and simple characterization method used to determine the intensity-dependent optical properties of materials. When measurement begins, a sample is moved along the axis of propagation (*z*) of a focused Gaussian beam through its focal plane. The input and output energies are simultaneously measured by two highly sensitive detectors (D1 and D2) for each *z* position. When all the transmitted light is detected, open-aperture and closed-aperture *z*-scans provide information about the nonlinear absorption and nonlinear refraction of the sample, respectively.

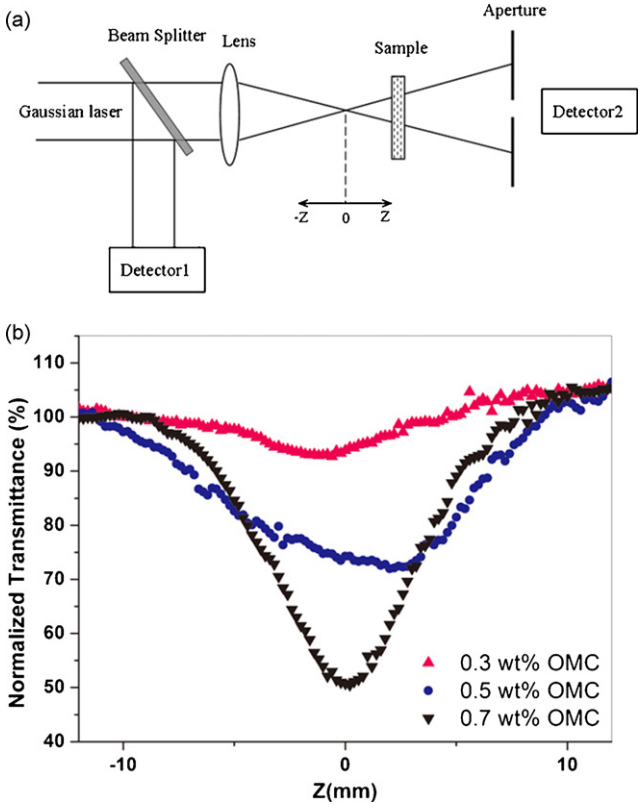

Fig. 4. (a) The *z*-scan experimental apparatus in which the ratio D2/D1 is recorded as a function of the sample position *z*. (b) Open-aperture *z*-scan measurements (100 fs laser pulse at 800 nm) of the OMC/silica composites with different carbon contents.

Fig. 4(b) shows the open-aperture *z*-scan results of OMC/silica composites with various carbon contents. The incident power used in the measurement was 50 mW for all the samples. Accordingly, the incident laser intensity at the focus was about 1.47 GW/cm^2. At the *z* position far away from the focus ($z = 0$), that is at low input energy, all the samples exhibited linear optical behaviors. The normalized transmittance was about 100%. When the samples moved towards the focus, the incident laser intensity increased remarkably. However, the normalized transmittances of OMC/silica composites decreased to 92.7%, 72.0% and 50.5%, respectively, indicated an exceptional optical limiting performance of the composites. The symmetrical valleys of different samples with respect to the focus indicated the presence of nonlinear absorption in the composites. Moreover, the normalized transmittances of the laser beam decreased with increasing OMC content, indicating a stronger nonlinear effect of the samples with higher OMC carbon content. We also performed a closed-aperture *z*-scan experiment, which was sensitive to the nonlinear refraction. However, no pronounced signals could be found from the closed-aperture *z*-scan experiments. Therefore, nonlinear refraction results were excluded from this study. Actually, it had been previously reported that optical limiting behavior of a MWCNT suspension can be attributed to the nonlinear scattering arising from expanding microplasmas, similar to the observation with carbon black suspension [27]. In the nonlinear scattering process, the laser-induced heat can lead to vaporization and ionization of carbon nanotubes, and then form rapidly expanding of microplasmas, which can strongly scatter the laser beam. Contributions from other mechanisms, such as self-defocusing and the thermal lensing effect, have also been suggested [11]. When the laser beam passes through the sample and the absorbed energy is converted into heat, changing the refraction index of the sample and the path of the laser beam. According to our work, it seems that the main optical limiting mechanism of OMC in solids proceeds via a nonlinear absorption. When the incident laser beam passes through the OMC/silica composites, some of them are absorbed by the carbon nanowires and the remaining beam are reflected and scattered for many times between the ordered nanowire arrays until they are completely absorbed. Besides, reflection and scattering of the laser beam will increase with the increasing carbon content, resulting in a higher absorption. The above experiment results and discussion improves that OMC/silica composites possessing good optical limiting properties are suitable for optical limiting application.

4. Conclusions

In summary, a series of transparent OMC/silica composites were prepared via a simple sol–gel method followed by a hot-pressing technique. The OMC particles were maintained in the form of ordered CMK-3 in the composites. *Z*-scan measurements on the OMC/silica composites revealed good optical limiting properties with increasing CMK-3 content. The ordered carbon nanowire arrays showed the advantage of an easier dispersion throughout the matrix and corresponding higher linear transmittance of the obtained OMC/silica composite than that of CNTs/silica. OMC/silica composites are promising candidates for future optical limiting applications.

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