

SURFACE MODIFICATION OF CARBON MICROSPHERES WITH CHITOSAN

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Introduction

Carbon microspheres (CMSs) have attracted considerable attention in recent years as a result of their unique structure and potential applications [1]. However, because of their chemical stability and poor dispersion in water and organic solvents, their applications in photoelectric materials, biomedical, chemical industry and other fields were greatly restricted. Therefore, the surface modification of CMSs is required to improve their physical and chemical properties. Chitosan (CS), containing a large number of amino and hydroxyl and other active groups, is a common natural polymer, which has good biodegradability and biocompatibility. Combining the properties of CMSs and the versatility and biocompatibility of CS, CS surface-decorated CMSs could be used in biosensors and chemical sensors [2]. Besides, they can be applied to molecular recognition [3], waste water treatment [4], drug release [5] and so on.

In this paper, CMSs were first oxidized to introduce negative charges onto their surface. Then CS with positive charge was self-assembled onto the surface of CMSs to prepare CS/CMSs composite materials. The effects of CS addition on modification as well as dispersion in water and ethanol were discussed.

Experimental

Carbon microspheres (CMSs) were synthesized by chemical vapor deposition in Ar atmosphere using C_2H_2 as carbon source. The preparation was conducted for 2 h at $950^\circ C$ by introducing a mixture of C_2H_2/Ar into the reactor at the flow rate of $80/700\text{ ml}\cdot\text{min}^{-1}$. One gram of CMSs, 60 mL of concentrated HNO_3 and 60 mL of H_2O_2 were added in a flask. Then the suspension containing CMSs was refluxed at $110^\circ C$ for 2 h. After the reaction, the mixture was cooled to room temperature, filtered, washed with distilled water several times to close to neutral, then dried at $40^\circ C$ in air for 16 h to give the sample oxidized CMSs.

An appropriate amount of CS was dissolved in 100 mL of 1% acetic acid solution by sonication for 30 min. An aliquot of 0.2 g of CMSs was dispersed in 50 mL of distilled water, then the product was added in CS solution, and the mixture was magnetically stirred for 4 h. Finally, CS/CMSs were filtered, washed several times with acetic acid to completely remove free CS.

The samples were examined by field-emission scanning electron microscopy (FESEM), Fourier transformation infrared spectrometry (FTIR), and thermogravimetry (TG). TG measurements were conducted in Ar atmosphere from $100^\circ C$ to $700^\circ C$ at a heating rate of $10^\circ C/\text{min}$.

Results and Discussion

FESEM was used to investigate the morphologies and diameter distribution of the products (as shown in Fig. 1). Fig. 1 shows the FESEM images of as-synthesized CMSs, oxidized CMSs and CS/CMSs prepared with different CMSs-to-CS ratios. It can be obviously observed that CMSs with diameter of 370 nm were aggregated (Fig. 1a). However, the dispersion of CMSs oxidized by HNO_3/H_2O_2 (Fig. 1b) was improved and the diameter decreased to 360 nm, meanwhile, a high concentration of oxygen-containing functional groups was introduced on the surface of CMSs, as will be further discussed later. Fig. 1c, 1d and 1e show there is a cover coating on the surface of oxidized CMSs. At the same time, the diameter of the composite increased by 20 nm, indicating that CS was self-assembled on the surface of CMSs. When CMSs-to-CS ratios was 1:2 (Fig. 1d), CMSs with smooth surface, good dispersion and uniform size were obtained.

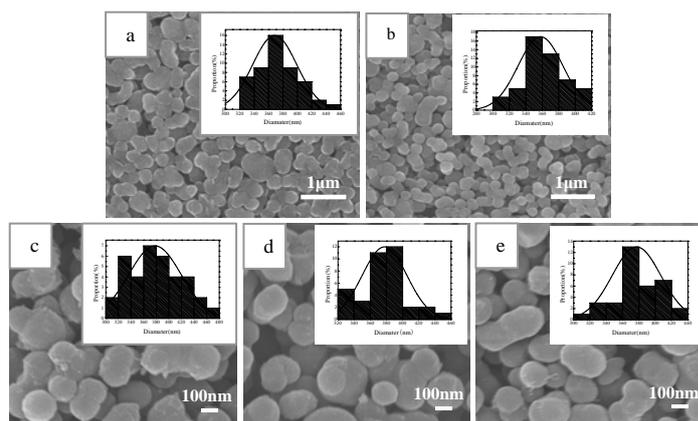


Fig. 1 FESEM images of as-synthesized CMSs (a), oxidized CMS (b), and CS/CMSs prepared with different CMSs-to-CS ratios of 1:1 (c), 1:2 (d), 1:3 (e)

FTIR spectroscopy was used to detect the surface functional groups of CMSs after modification, as shown in Fig. 2. After the oxidation treatment, several new bands present at 1103 , 1599 and 3440 cm^{-1} . The bands around 3440 cm^{-1} and 1103 cm^{-1} are attributed to the $-OH$ in oxidized CMSs. The peak appearing around 1599 cm^{-1} can be assigned to the $C=O$ stretching vibrations. It illustrates that oxygen-containing functional groups were introduced on the surface of oxidized CMSs after the oxidation treatment. From Fig. 2c, the absorption band at 1583 cm^{-1} attributed to the stretching vibration of $-NH$ structure can be observed. Another characteristic band at 3125 cm^{-1} can be assigned to the $-OH$ and $-NH$ stretching vibrations. Compared with CS, there are new characteristic occurring bands in the IR spectra of CS/CMSs (Fig. 2d, 2e and 2f). The band at 1652 cm^{-1} belongs to the $-NHCO$, which was formed

by the reaction between -NH_2 of CS and -COOH of oxidized CMS. Besides, owing to the -OH in CS, the band at 3426 cm^{-1} is enhanced in the composite CS/CMSs (Fig. 2e).

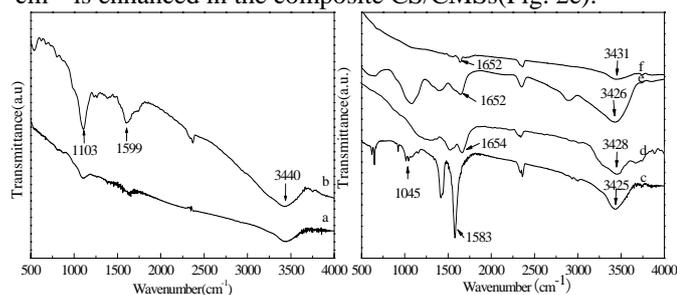


Fig.2 FTIR spectra of as-synthesized CMSs (a), oxidized CMS (b), CS (c) and CS/CMSs prepared with different CMSs-to-CS ratios of 1:1 (d), 1:2 (e), 1:3 (f)

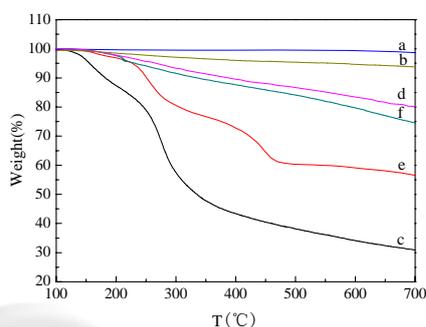


Fig.3 TG curves of as-synthesized CMSs (a), oxidized CMSs (b), CS (c), and CS/CMSs prepared with different CMSs-to-CS ratios of 1:1 (d), 1:2 (e), 1:3 (f)

The synthesized products were further investigated by TG. Fig. 3 shows TG curves of as-synthesized CMSs, oxidized CMSs, CS and CS/CMSs. As can be seen in Fig. 3a, as-synthesized CMSs had no weight loss. Oxidized CMSs exhibiting about 7 wt% weight loss (Fig. 3b) was attributed to the thermal degradation of the unstable functional groups such as carboxylic and hydroxyl groups that formed on the CMSs surface. The TG curve of CS (Fig. 3c) was divided into two stages, the weight loss in the temperature range of $130\sim 230^\circ\text{C}$ was mainly caused by $\text{C}_1\text{-O-C}_4$ bond breaking, the main chain degradation and dehydration of CS, the weight loss after 230°C might be associated with the thermal degradation of polysaccharide ring. It was found that the initial degradation temperature of CS/CMSs was higher than CS and the weight loss was about 45 wt% (Fig. 3e). When CMSs-to-CS ratio was 1:1 (Fig. 3d) and 1:3 (Fig. 3f), CS/CMSs showed 20 wt% and 26 wt% weight loss, respectively. So the maximum CS grafting on the CMSs was obtained when CMSs-to-CS ratio was 1:2. It is clear that coating volume gradually increased with increasing CS content, but when the amount of CS exceeded a certain value, coating volume decreased. It illustrates that excessive use of CS resulted in polymerization of CS in solution to form colloidal solution, which was difficult to combine with the CMSs.

Fig. 4 shows the dispersion of as-synthesized CMSs, oxidized CMSs and CS/CMSs in water and ethanol. The as-synthesized CMSs were completely insoluble in water, floating on the water, and precipitated at the bottom in

ethanol. After the oxidation modification, the dispersion of CMSs was improved, but precipitated after two days. Whereas the CS/CMSs remained soluble in water and ethanol without precipitation for two days. It indicates that CS/CMSs have good hydrophilicity and dispersibility in solution, which can be used to further liquid phase reaction.

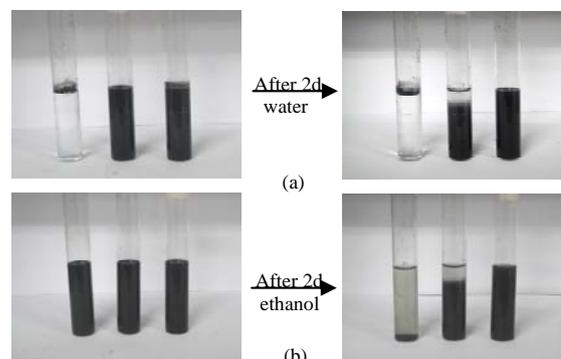


Fig. 4 The dispersion of CMSs (left), oxidized CMSs (middle) and CS/CMSs (right) (CMSs-to-CS ratios is 1:2) in water (a) and ethanol (b)

Conclusions

CMSs were synthesized by chemical vapor deposition in Ar atmosphere using acetylene as carbon source. Concentrated HNO_3 and H_2O_2 aqueous solution was used to oxidized CMSs to introduce oxygen-containing functional groups onto the surface of CMSs. CS was self-assembled on the surface of oxidized CMSs by electrostatic interaction. When the mass ratio of CMSs to CS was 1:2, CS/CMSs with narrow particle size distribution and good monodispersity were gained and the dispersion in water and ethanol was obviously improved, which lays the foundation for the preparation of functional materials.

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