HYDROTHERMAL SYNTHESIS OF SNO_2–ZNO AGGREGATES IN CELLULOSE AEROGELS FOR PHOTOCATALYTIC DEGRADATION OF RHODAMINE B

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Cellulose aerogels have been considered as ideal green matrices to support various nanoparticles due to their hierarchical porous nanostructures and an ocean of surface hydroxyl groups. Herein, an easily-operated low-energy hydrothermal method was implemented to synthesize SnO_2–ZnO aggregates in cellulose aerogels. The well-dispersed aggregates with the mean diameter of 45.4 nm are tightly adhered on the three-dimensional framework of the aerogels, due to the strong interactions between the hydroxyl groups of cellulose and the oxygen atoms of SnO_2 or ZnO. Furthermore, the tri-component composite shows good photocatalytic activity for degradation of rhodamine B under ultraviolet irradiation, which is possibly helpful to deal with dyestuff wastewater as a kind of low-pollution cost-effective photocatalyst.

Keywords: cellulose aerogels, nanocomposites, photocatalysts, hydrothermal method

INTRODUCTION

Aerogels are materials prepared by replacing the liquid solvent in a gel with air without substantially altering the network structure or the volume of the gel body.[1] The unique highly porous characteristic endows them with numerous extraordinary performances, such as low density, high specific surface area, and large open pores.[2] Nowadays, aerogels have been paid increasing attention and regarded as promising candidates for a variety of advanced applications, such as in biomedicine,[3] as oil absorbent,[4,5] for thermal and acoustic insulation,[6,7] and as molecular sensors.[8]

Aerogels based on cellulose (the most abundant natural polymer) have shown many advantages over traditional aerogels (such as inorganic and synthetic polymer-based aerogels), as they not only possess many of the above-mentioned merits, but also avoid the consumption of nonrenewable resources and thus have significant environmental advantages. Moreover, the features of cellulose aerogels, such as their hierarchical micro/nano-scale three-dimensional (3D) network and multitude of surface hydroxyls, make them suitable candidates as green matrices to support various nanoparticles, helping to reduce agglomeration and control particle growth.[9,10] Moreover, the generated composites create a multitude of new properties, such as photocatalysis, antibacterial activity, preferential adsorption, and energy conversion,[11] primarily dependent on the characteristics of inserted nanoparticles. Our previous studies[12-15] have confirmed that cellulose aerogels can serve as ideal hosts to support various nanostructures, such as γ-Fe_2O_3, $CoFe_2O_4$, rod-like ZnO, and anatase TiO_2. Therefore, it is interesting and meaningful to further develop this new class of composites and expand their functions.

In the present work, SnO_2–ZnO aggregates were synthesized and incorporated into the porous cellulose aerogels *via* a facile and cost-effective hydrothermal method. As an example of potential application, the tri-component hybrid, *i.e.*, SnO_2–ZnO@cellulose aerogel (coded as SZ@CA), was utilized as an eco-friendly photocatalyst for degradation of rhodamine B (RhB) under ultraviolet (UV) irradiation.

EXPERIMENTAL

Materials

All chemical reagents, including zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), cetyltrimethyl ammonium bromide (CTAB), sodium hydroxide (NaOH), absolute ethanol and tert-butyl alcohol, were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (China) and used without further purification.

Synthesis of SZ@CA

Wheat straw was collected from a wheat farmland, was ground and then screened through a 60-mesh sieve, and the resulting powder was subsequently collected and dried in a vacuum oven at 60 °C for 24 h before use. The resultant dried powder was subjected to a chemical treatment to isolate the cellulose. The isolated cellulose was dissolved in a NaOH/PEG solution and then regenerated in a HCl solution, and as a result a cellulose hydrogel (*i.e.*, the precursor of the cellulose aerogel) was formed. The detailed preparation process of the cellulose hydrogel can be found in previous works.[12,16]

The synthesis of SZ@CA was performed by a hydrothermal method.[17] Firstly, in the preparation of ZnO rods, 50 mL of an aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.13 M) was mixed with 50 mL of an aqueous solution of NaOH (1.3 M) under magnetic stirring for 30 min. The mixture was heated in a water bath at 50 °C for 90 min. After the heating, the mixed solution was allowed to naturally cool to room temperature, and the product was separated by centrifugation and then rinsed with a large amount of absolute ethanol and finally dried at 60 °C for 24 h under vacuum. The resulting ZnO rods were used as the starting zinc source. Secondly, for the hydrothermal treatment, CTAB (2.19 g), $SnCl_4 \cdot 5H_2O$ (1.58 g), ZnO rods (0.1 g), and a NaOH aqueous solution (1.8 g, 70 mL) were mixed with magnetic stirring for 30 min. Thereafter, the mixed solution and the cellulose hydrogel were transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 12 h. Thirdly, the resulting SZ@CA was repeatedly rinsed with distilled water and tert-butyl alcohol in sequence for the removal of residual impurities. After that, the hybrid was subjected to a freeze drying process at -35 °C for 48 h in an approximate vacuum (25 Pa) to remove most of the liquid.

Characterizations

Transmission electron microscopy (TEM) observations and selected area electron diffraction (SAED) were performed with a FEI, Tecnai G2 F20 TEM equipped with an energy dispersive X-ray (EDX) detector for elemental analysis. The samples were suspended in ethanol and were prepared by being drop-cast onto a carbon-coated 200-mesh copper grid and subsequently dried at room temperature.

Photocatalytic activity measurements

The SZ@CA sample (0.2 g) was ground into powder and added to an aqueous RhB solution (20 mg L^{-1}, 50 mL), and the mixture was magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption–desorption equilibrium on the catalyst surface. Thereafter, a dish containing the mixture was placed in a closed chamber with a UV source (mercury lamp, 300 W). The dish was exposed to the mercury lamp for 2 h. The RhB solution was collected at regular time intervals. The mixed solution was centrifuged at 8000 rpm for 5 min to remove the catalyst, and the supernatant was collected. The concentration of RhB was tested by a UV-vis-NIR spectrophotometer (U-4100, Hitachi) at its maximum absorption wavelength of 554 nm.

RESULTS AND DISCUSSION

Figure 1a shows the TEM image of SZ@CA. Obviously, these SnO_2–ZnO aggregates were uniformly adhered on the cellulose aerogels matrices, and no free aggregates separated from the matrices were observed, which confirm that the cellulose aerogels can act as ideal host materials. Increasing the magnification of TEM image, it can be seen in Figure 1b that the aggregates are approximately spherical and composed of several smaller particles. The good interface combination between the cellulose aerogels and the SnO_2–ZnO aggregates can be clearly seen (Fig. 1c). The aggregates are inserted and tightly immobilized in the 3D framework of the aerogels, possibly due to the interactions between the hydroxyl groups of cellulose and the oxygen atoms of SnO_2 or ZnO.

Randomly collecting the aggregates in Figure 1b and accurately measuring their diameters using Adobe Photoshop CS5 software, the diameter distribution was plotted in Figure 1d. We can see that the diameter histogram exhibits Gaussian-like distribution, and the diameters of the aggregates range from 26 to 68 nm. The mean diameter (d) and standard deviation (σ) were calculated to be around 45.4 and 8.56 nm, respectively.

The EDX spectrum in Figure 2a displays the existence of C, O, Sn and Zn elements, which are derived from the cellulose aerogels and SnO_2–ZnO aggregates. The signals of Cu and partial C are

generated from the sample holder. According to the EDX analysis, the content of the Zn element is about 3.2 wt%, and the content of the Sn element is approximately 19.4 wt%. Therefore, the content of the metal aggregates (*i.e.*, SnO_2–ZnO aggregates) was calculated to be 28.6 wt%.

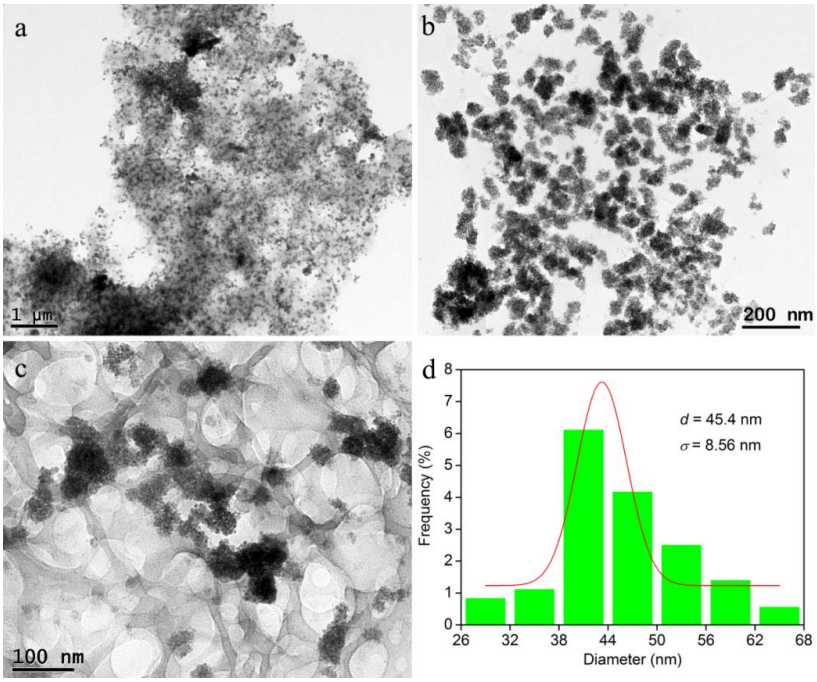

Figure 1: (a-c) TEM images of SZ@CA at different levels of magnification; (d) Diameter distribution of SnO_2–ZnO aggregates in SZ@CA

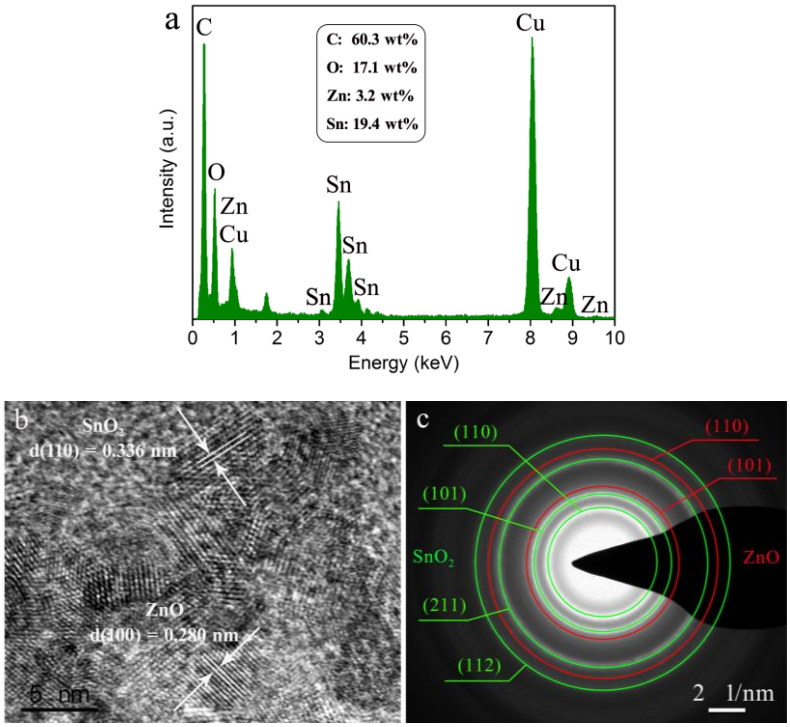

Figure 2: (a) EDX spectrum, (b) HRTEM image, and (c) SAED pattern of SZ@CA, respectively

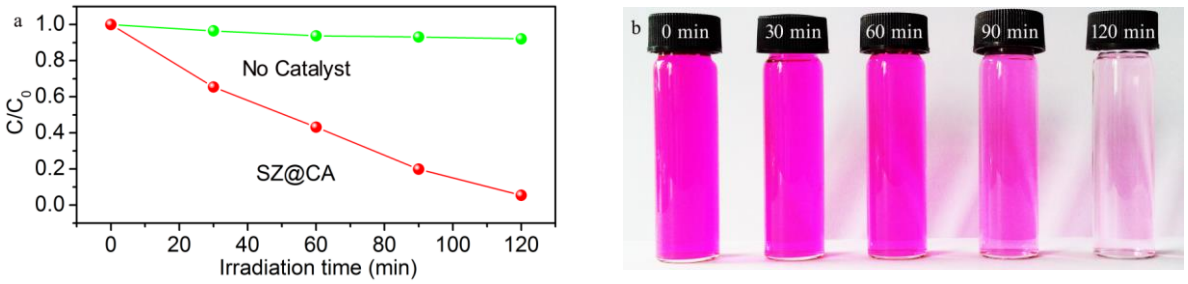

Figure 3: (a) Photocatalytic degradation rates of RhB under UV irradiation by no catalyst and SZ@CA; (b) Color changes of RhB solution during the photocatalytic degradation process

In Figure 2b, the high resolution TEM (HRTEM) image reveals the simultaneous presence of crystalline ZnO and SnO_2 phases. The measured two lattice fringes with lattice spacings of 0.336 and 0.280 nm agree well with the *d*-spacings of the (110) plane of the tetragonal rutile SnO_2 and the (100) plane of the hexagonal wurtzite ZnO,[18] respectively.

The corresponding SAED pattern in Figure 2c shows several concentric rings, indicating that the aggregates have a polycrystalline structure. These concentric rings can be assigned to diffraction from (110) and (101) planes of ZnO and (110), (101), (211) and (112) planes of SnO_2.[19] Therefore, these aforementioned characterizations confirm that the secondary particles (namely, the aggregates) consist of ZnO and SnO_2.

As an example of potential applications, SZ@CA was used as a green biodegradable photocatalyst for the degradation of RhB under UV irradiation. Figure 3a shows the degradation rates of RhB over no catalyst and SZ@CA (C_0 and C are the equilibrium concentration of RhB before and after UV irradiation, respectively). The negligible noncatalytic degradation of RhB shown by the blank test was detected after the exposure to UV light for 2 h. By contrast, under identical conditions with exposure to UV light, SZ@CA displays good photocatalytic activity. The RhB molecules were gradually degraded into colorless organic compounds or small molecules (*e.g.*, CO_2), leading to color changes of the RhB solution from purple to approximately transparent and colorless (Fig. 3b). Previously published studies have verified that the cellulose composition has no obvious photocatalytic activity for the degradation of dye molecules.[20] Thus, these results reveal that the SnO_2–ZnO aggregates play important roles in the photocatalytic activity of the hybrid. The unique porous nanostructures of the aerogel matrices help to maintain good dispersion of the aggregates, which is crucial for the photocatalytic property.

CONCLUSION

A mild, simple and low-cost hydrothermal method was employed to synthesize SnO_2–ZnO aggregates in porous cellulose aerogels. The obtained approximately spherical aggregates have the mean diameter of 45.4 nm and display favorable dispersion in the aerogel matrices without significant agglomeration. Moreover, the composite displays good photocatalytic activity for the degradation of RhB under UV irradiation, which is possibly useful as a kind of novel environmentally friendly photocatalyst for the treatment of dyestuff wastewater.

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