In_2S_3 nanoflakes-functionalized cotton cellulose electrospun nanofibers for visible light photocatalysis

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Abstract: We report a simple and effective route to fabricate ultrathin curved In_2S_3 nanoflakes-functionalized natural cotton cellulose nanofibers by combining electrospinning and hydrothermal growth technique. Cotton cellulose nanofibers(CCNFs) were obtained by electrospinning technique. Curved and interconnected In_2S_3 nanoflakes with 10-15nm in thickness were successfully grown on the surface of CCNFs via hydrothermal process. The as-prepared CCNFs/In_2S_3 nanocomposites were characterized by SEM, EDS, XRD and UV-vis spectrophotometry. It was found that In_2S_3 nanoflakes were uniform morphology with the cubic crystal structure, which band gap is responsed to visible light. The photocatalytic activity indicated that the CCNFs/In_2S_3 nanocomposites exhibited excellent photocatalytic activity for photodegradation of rhodamine B (RhB) solutions under the irradiation of visible light.

Introduction

Because of excessive consumption of fossil fuels and subsequent environmental concerns, it is urgent to develop sustainable and renewable energy that is environmentally friendly [1]. As one of the most abundant renewable natural resources and environment-friendly materials, cellulose has great potential industrial applications through modifying. In our previous work, we have fabricated functionalized cotton cellulose nanofibers (CCNFs). The CCNFs can be regarded as a good substrate to load inorganic functional nanomaterials duo to its large specific surface and a lot of hydroxyl groups on its surface. We have combined UV reduction and electrospinning techniques to produce CCNFs/Ag nanocomposites[2] and have prepared CeO_2 nanoparticles on the CCNFs by hydrothermal method, which has fine ultraviolet absorption performance[3].

Inorganic semiconductor materials could be loaded on the CCNFs to get nanocomposites with better performance than single semiconductor materials. Among the most widely used inorganic semiconductor materials, In_2S_3 has many potential applications for photocatalysis to decompose dye and solar cells due to its low toxicity, good stability, narrow band gap (2.0-2.3eV), and high carrier mobility[4]. In_2S_3 can exhibit three different structure forms: α-In_2S_3 (defect cubic), β-In_2S_3 (defect spinel), and γ-In_2S_3 (layered structure), among which β-In_2S_3 is an n-type semiconductor owning a defect spinel structure[5].

In this paper, we intend to synthesize the flake-like In_2S_3 on the CCNFs by a facile hydrothermal method and investigate the photocatalytic performance of CCNFs/In_2S_3 under visible light irradiation.

Experimental

Fabrication of CCNFs/In_2S_3 Nanocomposites: All chemical reagents are analytical grade and directly used without further purification. The preparation of CCNFs by electrospinning process is the same as our previous research[2]. In_2S_3 seed layer was loaded on the surface of CCNFs by using the successive ion layer adsorption and reaction (SILAR) method. In the SILAR process of In_2S_3 seeds layer deposition, the CCNFs were dipped sequentially in aqueous solutions of 0.1M $In(NO_3)_3 \cdot xH_2O$ and 0.05 M Na_2S (with pH equal to 8.0) for 1min. Between each dips, the samples were rinsed with deionized water for 1min. Such a cycle was repeated 20 times. Then, the In_2S_3 nanoflakes-functionalized CCNFs were prepared via a traditional hydrothermal process. For a typical reaction, 0.0625 mmol of $In(NO_3)_3 \cdot xH_2O$, 0.125 mmol of L-cysteine, and 0.125 mmol of urea were added to 20 ml deionized water and ultrasonicated for a five minutes. The resulting mixture was then transferred into a Teflon-lined stainless-steel autoclave (30 ml capacity) and 10mg CCNFs/In_2S_3 seeds were immersed into the solution. The autoclave was then sealed and maintained at 160℃ for 12 h. After the reactor was cooled down to room temperature, the as-obtained samples were washed with deionized water and absolute ethanol twice, respectively, and then were dried under 60℃ for relevant characterizations.

Characterization Methods: The surface morphology and structure of the samples were investigated using Field-emission scanning electron microscope (FESEM, Hitachi S-4800) equipped with an Energy-dispersive X-ray spectroscopy (EDS). The phase structures of the CCNFs/In_2S_3 nanocomposites were studied by X-ray diffraction (XRD, Bruker AXS D8-discover). The UV-visible spectroscopy measurement and RhB UV absorbance were investigated by UV-vis absorption (Hitachi U-3900). In this experiment, 20 mg CCNFs/In_2S_3 nanocomposites were added into 50 ml $1x10^{-5}$mol/L RhB solutions under the irradiation of visible light (PHILIPS, 500W, $\lambda \geq 420$nm) for photocatalytic examination under magnetic stirring. The UV-vis absorbance spectra of RhB solution were collected every 10 min.

Results and Discussion

The SEM images of CCNFs, CCNFs/In_2S_3 seeds, and CCNFs/In_2S_3 nanocomposites were shown in Fig.1. As shown in Fig.1a, CCNFs have uniform and smooth surfaces, with a diameter of about 100-200nm. Fig.1b reveals that dense and uniform In_2S_3 seed layer was successfully growth on CCNFs. As can be seen from Fig.1c, In_2S_3 nanoflakes with 10-15 nm in thickness were successfully grown on the surface of CCNFs. Furthermore, it appears that there are many highly porous structures were composed of curved and interconnected In_2S_3 nanoflakes, which can increase the specific surface area of CCNFs/In_2S_3 and the adsorption ability for dye. Energy-dispersive X-ray(EDS) spectrum (Fig.1d) further confirmed that the CCNFs/In_2S_3 nanocomposites were successfully fabricated, as only the C, In, and S elements existed in the sample and the atom ratio of In and S very close to 2:3.

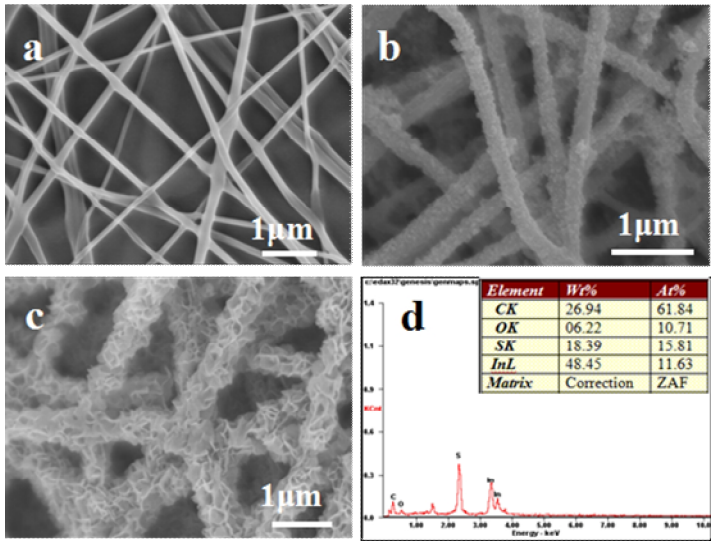

Fig.1 The SEM images of (a) CCNFs, (b) CCNFs/In_2S_3 seeds, and (c) CCNFs/In_2S_3 nanocomposites,
(d)EDS spectrum of the CCNFs/In_2S_3 nanocomposites.

Fig.2 shows the XRD patterns of as-prepared samples. As can be seen there are broad diffraction peaks of the CCNFs in the range of 15–25°, which can be ascribed to amorphous cellulose structure. Meanwhile, there are hardly distinguishable characteristic diffraction peaks of CCNFs/In_2S_3 seeds duo to the less mount of In_2S_3. All the diffraction peaks of the final CCNFs/In_2S_3 nanocomposite can be indexed to the cubic crystal structure of β-In_2S_3 (JCPDS card#32-0456).

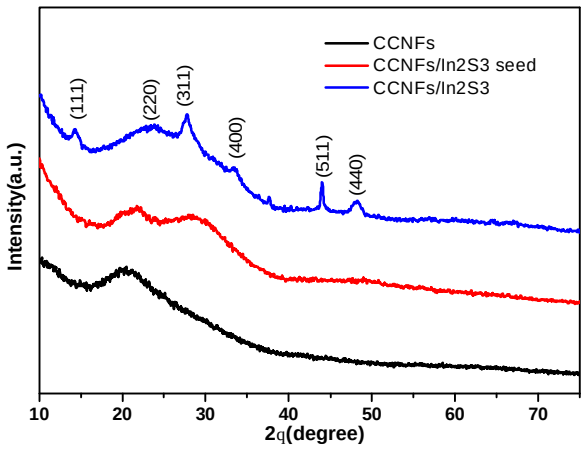

Fig.2 The XRD patterns of CCNFs, CCNFs/In_2S_3 seeds, and CCNFs/In_2S_3 nanocomposites.

Photocatalytic activities of the samples were evaluated by measuring the degradation of RhB in aqueous solution under visible light irradiation. Fig.3a shows the UV-vis absorption spectrum of RhB aqueous solution with CCNFs/ In_2S_3 as photocatalyst during different exposure time under the light irradiation. Fig.3b gives the results of RhB photodegradation for CCNFs and CCNFs/In_2S_3 nanocomposites. It is found that RhB have been degraded ca.97.86% by CCNFs/In_2S_3 after 60min of irradiation, however, the CCNFs only can adsorb some dyes. The CCNFs/In_2S_3 have exhibited excellent photocatalytic activity duo to the narrow band gap (2.0-2.3eV) and the high carrier mobility of In_2S_3. In addition, CCNFs substrate well dispersed In_2S_3 to increase the contact area of In_2S_3 and dye.

The CCNFs/In_2S_3 nanocomposites also have favorable cycle performance, which has been demonstrated by three successive recycling tests. As shown in Fig.3c, during three recycles of photoactivity test for RhB under visible light irradiation, the CCNFs/In_2S_3 nanocomposites shows almost no deactivation. Therefore, the as-prepared CCNFs/In_2S_3 can perform as a stable visible light driven photocatalyst for the degradation of organic dyes.

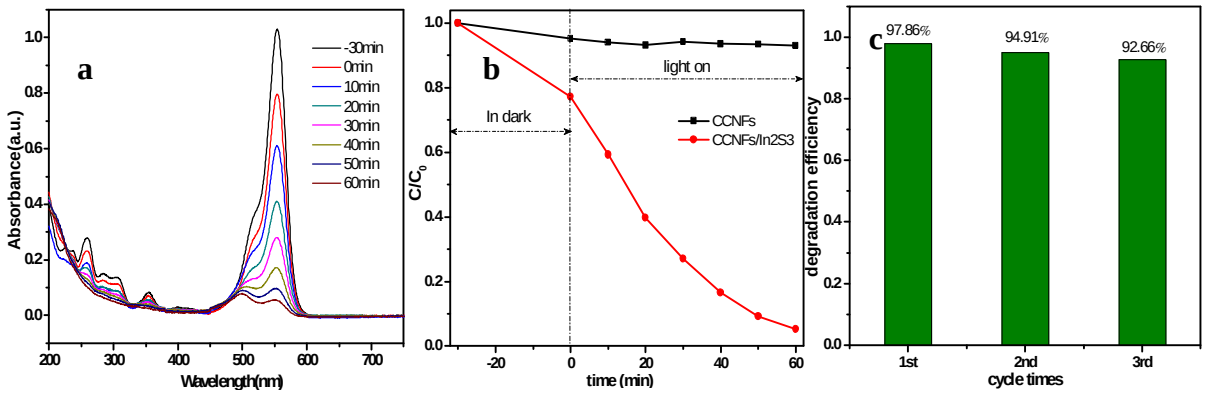

Fig.3 (a)UV-vis absorption spectra for degradation of RhB by using CCNFs/In_2S_3 as photocatalyst. (b) Curves of photocatalytic degradation on RhB with CCNFs and CCNFs/In_2S_3, (c) Cyclic photo degradation curves of RhB with CCNFs/In_2S_3.

Conclusions

In summary, we have synthesized curved and interconnected ultrathin In_2S_3 nanoflakes on the CCNFs via an efficient and easily hydrothermal method. For the CCNFs/In_2S_3 functional nanocomposites, In_2S_3 has a good light responsiveness in the visible region. CCNFs play an important role in the recycling of the photocatalyst as the substrate material. The result indicates CCNFs/In_2S_3 has excellent photocatalytic efficiency for RhB solution under visible light irradiation.

Acknowledgements

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