**In$_2$S$_3$ nanoflakes-functionalized cotton cellulose electrospun nanofibers for visible light photocatalysis**

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**Keywords:** Electrospinning; Cellulose; In$_2$S$_3$; Photocatalysis

**Abstract:** We report a simple and effective route to fabricate ultrathin curved In$_2$S$_3$ 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$_2$S$_3$ nanoflakes with 10-15nm in thickness were successfully grown on the surface of CCNFs via hydrothermal process. The as-prepared CCNFs/In$_2$S$_3$ nanocomposites were characterized by SEM, EDS, XRD and UV-vis spectrophotometry. It was found that In$_2$S$_3$ nanoflakes were uniform morphology with the cubic crystal structure, which band gap is responded to visible light. The photocatalytic activity indicated that the CCNFs/In$_2$S$_3$ 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 due 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$_2$S$_3$ 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$_2$S$_3$ can exhibit three different structure forms: $\alpha$-In$_2$S$_3$ (defect cubic), $\beta$-In$_2$S$_3$ (defect spinel), and $\gamma$-In$_2$S$_3$ (layered structure), among which $\beta$-In$_2$S$_3$ is an n-type semiconductor owning a defect spinel structure[5].
In this paper, we intend to synthesize the flake-like In$_2$S$_3$ on the CCNFs by a facile hydrothermal method and investigate the photocatalytic performance of CCNFs/In$_2$S$_3$ under visible light irradiation.

**Experimental**

**Fabrication of CCNFs/In$_2$S$_3$ 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$_2$S$_3$ 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$_2$S$_3$ seeds layer deposition, the CCNFs were dipped sequentially in aqueous solutions of 0.1M In(NO$_3$)$_3$•xH$_2$O and 0.05 M Na$_2$S (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$_2$S$_3$ nanoflakes-functionalized CCNFs were prepared via a traditional hydrothermal process. For a typical reaction, 0.0625 mmol of In(NO$_3$)$_3$•xH$_2$O, 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$_2$S$_3$ seeds were immersed into the solution. The autoclave was then sealed and maintained at 160°C 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°C 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$_2$S$_3$ 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$_2$S$_3$ nanocomposites were added into 50 ml 1x10$^{-5}$mol/L RhB solutions under the irradiation of visible light (PHILIPS, 500W, λ≥420nm) 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$_2$S$_3$ seeds, and CCNFs/In$_2$S$_3$ 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$_2$S$_3$ seed layer was successfully growth on CCNFs. As can be seen from Fig.1c, In$_2$S$_3$ 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$_2$S$_3$ nanoflakes, which can increase the specific surface area of CCNFs/In$_2$S$_3$ and the adsorption ability for dye. Energy-dispersive X-ray(EDS) spectrum (Fig.1d) further confirmed that the CCNFs/In$_2$S$_3$ 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$_2$S$_3$ seeds, and (c) CCNFs/In$_2$S$_3$ nanocomposites, (d) EDS spectrum of the CCNFs/In$_2$S$_3$ 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$_2$S$_3$ seeds due to the less mount of In$_2$S$_3$. All the diffraction peaks of the final CCNFs/In$_2$S$_3$ nanocomposite can be indexed to the cubic crystal structure of β-In$_2$S$_3$ (JCPDS card#32-0456).

Fig.2 The XRD patterns of CCNFs, CCNFs/In$_2$S$_3$ seeds, and CCNFs/In$_2$S$_3$ 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$_2$S$_3$ as photocatalyst during different exposure time under the light irradiation. Fig.3b gives the results of RhB photodegradation for CCNFs and CCNFs/In$_2$S$_3$ nanocomposites. It is found that RhB have been degraded ca.97.86% by CCNFs/In$_2$S$_3$ after 60min of irradiation, however, the CCNFs only can adsorb some dyes. The CCNFs/In$_2$S$_3$ have exhibited excellent photocatalytic activity due to the narrow band gap (2.0-2.3eV) and the high carrier mobility of In$_2$S$_3$. In addition, CCNFs substrate well dispersed In$_2$S$_3$ to increase the contact area of In$_2$S$_3$ and dye.
The CCNFs/In$_2$S$_3$ nanocomposites also have favorable cycle performance, which has been demonstrated by three successive recycling tests. As shown in Fig.3c, during three cycles of photoactivity test for RhB under visible light irradiation, the CCNFs/In$_2$S$_3$ nanocomposites shows almost no deactivation. Therefore, the as-prepared CCNFs/In$_2$S$_3$ can perform as a stable visible light driven photocatalyst for the degradation of organic dyes.

Conclusions

In summary, we have synthesized curved and interconnected ultrathin In$_2$S$_3$ nanoflakes on the CCNFs via an efficient and easily hydrothermal method. For the CCNFs/In$_2$S$_3$ functional nanocomposites, In$_2$S$_3$ 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$_2$S$_3$ has excellent photocatalytic efficiency for RhB solution under visible light irradiation.

Acknowledgements

This work was supported by Natural Science Foundation of China (Nos. 51172209 and 91122022), and by the Program for Changjiang Scholars and Innovative Research Team in University.

References