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Self-assembled hierarchical Sn_3O_4-multi-wall carbon nanotubes: Facile fabrication, promoted charge separation, and enhanced photocatalytic performances

Meng Sun[a,*], Tao Yan[a], Tingting Wu[a], Yunhui He[c], Yu Shao[c], Dong Wei[b], Bin Du[a,b,**]

[a] School of Resources and Environment, University of Jinan, Jinan 250022, PR China
[b] Key Laboratory of Interfacial Reaction & Sensing Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, PR China
[c] State Key Laboratory of Photocatalysis on Energy and Environment, Research Institute of Photocatalysis, Fuzhou University, Fuzhou 350016, PR China

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ABSTRACT

Controlled assembling of Sn_3O_4 nanoflakes over multi-wall carbon nanotubes (CNTs) was achieved for the first time by using a facile hydrothermal method. The SEM and TEM images showed that numerous Sn_3O_4 nanoflakes were widely assembled over the surface of CNTs. In these hybrids, the CNTs served as dispersing-template could reduce the agglomeration of Sn_3O_4 nanoflakes, as well as facilitate the interfacial charge transfer because of its high electrical conductivity. The Sn_3O_4-CNTs photocatalysts have exhibited remarkably promoted performances in decomposing organic contaminant under visible or solar light. The Sn_3O_4-CNTs hybrid with CNTs mass ratio of 4.37% exhibited the best activity under visible light, while that with CNTs mass ratio of 1.41% was more efficient when irradiated by solar light, the activity of which was about 3.47 times higher than that of pristine Sn_3O_4 under identical conditions. Controlled experiments proved that $\cdot O_2^-$ and h^+ played the chief role in decomposing organic pollutants.

1. Introduction

Along with the rapid development of industry, more and more oil, coal and other energy have been consumed, resulting in the depletion of fossil fuel reserves and serious environmental pollution [1–4]. Thus, the exploration of renewable clean energy and remediation of environmental pollution have become the most pressing issues in the past many years. Semiconductor photocatalysis, as a promising technology for environmental remediation as well as hydrogen energy production, has attracted enormous attention in the whole world [5–9]. For the practical application of photocatalysis, one of the key issues is to explore novel photocatalyst with superior activity. So far, numerous photocatalytic materials have been developed and used to decompose organic pollutants or split water, among which titanium dioxide (TiO_2) was the most popular one because of its intrinsic advantages [10–14]. Unfortunately, the wide band gap (3.2 eV for anatase TiO_2) has severely restricted its application because it can hardly absorb visible light, which accounted for 54% of the whole solar spectrum [15,16]. So, great efforts have been devoted to exploring visible light-responsive materials in order to take advantage of the clean and permanent solar energy.

In recent years, tin-based photocatalytic materials have been reported and deeply researched, such as β-$SnWO_4$ [17], Sn–SnO_2 [18], $SnNb_2O_6$ [19], SnS_2 [20,21], SnO_2 [22,23], SnS [24], Sn_3O_4 [25,26], $Sn(MoO_4)_2$ [27], and $Sn_6O_4(OH)_4$ [28]. Zhang et al. reported the fabrication of SnS_2 nanocrystals and the reduction of aqueous Cr(VI) under visible light [29]. He and co-workers fabricated Sn_3O_4 photocatalyst with hierarchical 3D nanostructures and investigated its visible light-responsive performance toward methyl orange (MO) [30]. However, just as discussed in our previous papers, all these single-phase semiconductor photocatalysts commonly suffer from low quantum efficiency because of the rapid recombination of photo-induced electron/hole pairs, leading to a poor photocatalytic activity. In order to depress the recombination of photo-induced carriers over Sn_3O_4, several methods have been tried by researchers, among which the constructing of hybrid photocatalyst was proved to be more effective. For example, Chen et al. reported the constructing of Sn_3O_4/TiO_2 composites with enhanced visible light activity [31]. Yu and co-workers reported hierarchical Sn_3O_4/N-TiO_2 hybrid nanostructures with promoted photocatalytic activity toward MO [32]. However, except for these work, Sn_3O_4 has rarely been reported.

* Corresponding author.
** Corresponding author at: School of Resources and Environment, University of Jinan, Jinan 250022, PR China.
E-mail addresses: stu_sunm@ujn.edu.cn (M. Sun), dubin61@gmail.com (D. Bin).

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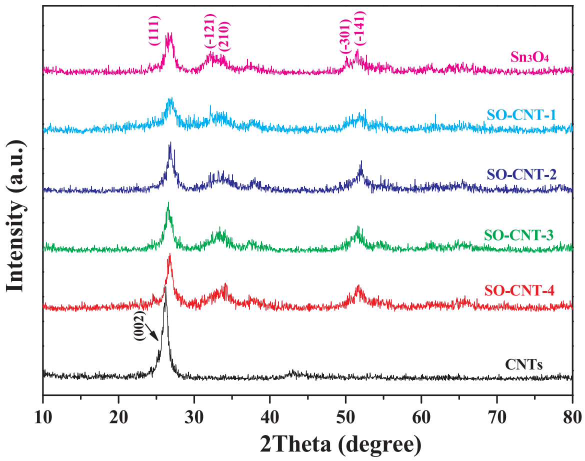

Fig. 1. XRD patterns of the obtained pristine Sn_3O_4, Sn_3O_4-CNTs hybrids, and purified CNTs.

In present manuscript, we reported the controlled assembling of Sn_3O_4 nanoflakes over multi-wall carbon nanotubes (CNTs) to construct 3D hierarchical Sn_3O_4-CNTs hybrid nanostructures. For these Sn_3O_4-CNTs hybrids, CNTs with good chemical stability and tubular structure not only served as dispersing template to reduce the agglomeration of Sn_3O_4, but also accelerated the interfacial charge migration and separation process because of its high conductivity [33–36]. Accordingly, the obtained Sn_3O_4-CNTs photocatalysts have exhibited remarkably enhanced visible- and solar-light-responsive performances in decomposing MO. The depressed charge recombination and expanded visible light absorption should be responsible for the activity enhancement.

2. Experimental section

2.1. Synthesis of Sn_3O_4-CNTs hybrid photocatalysts

Sn_3O_4-CNTs hybrids were fabricated by a one-pot hydrothermal method. Firstly, the raw commercial CNTs (purchased from Nan Jing JI Cang Nano Technology Co. Ltd, China) were purified before usage. Briefly, a certain amount of CNTs was firstly calcined in a muffle furnace at 500 °C for 2 h, which was then treated with 6.0 M HCl solution at 95 °C for 6 h to remove amorphous carbon particles and other impurities [37]. The acid-treated CNTs were washed with distilled water and absolute ethanol for several times and then dried in vacuum at 60 °C overnight. In the later fabrication process for Sn_3O_4-CNTs hybrids, 2.5 mmol $SnCl_2{\cdot}2H_2O$ and 6.25 mmol $Na_3C_6H_5O_7{\cdot}2H_2O$ were dissolved into 50 mL distilled water to form a transparent solution, to which 5 mg of purified CNTs was introduced and dispersed by ultrasonic for 30 min.

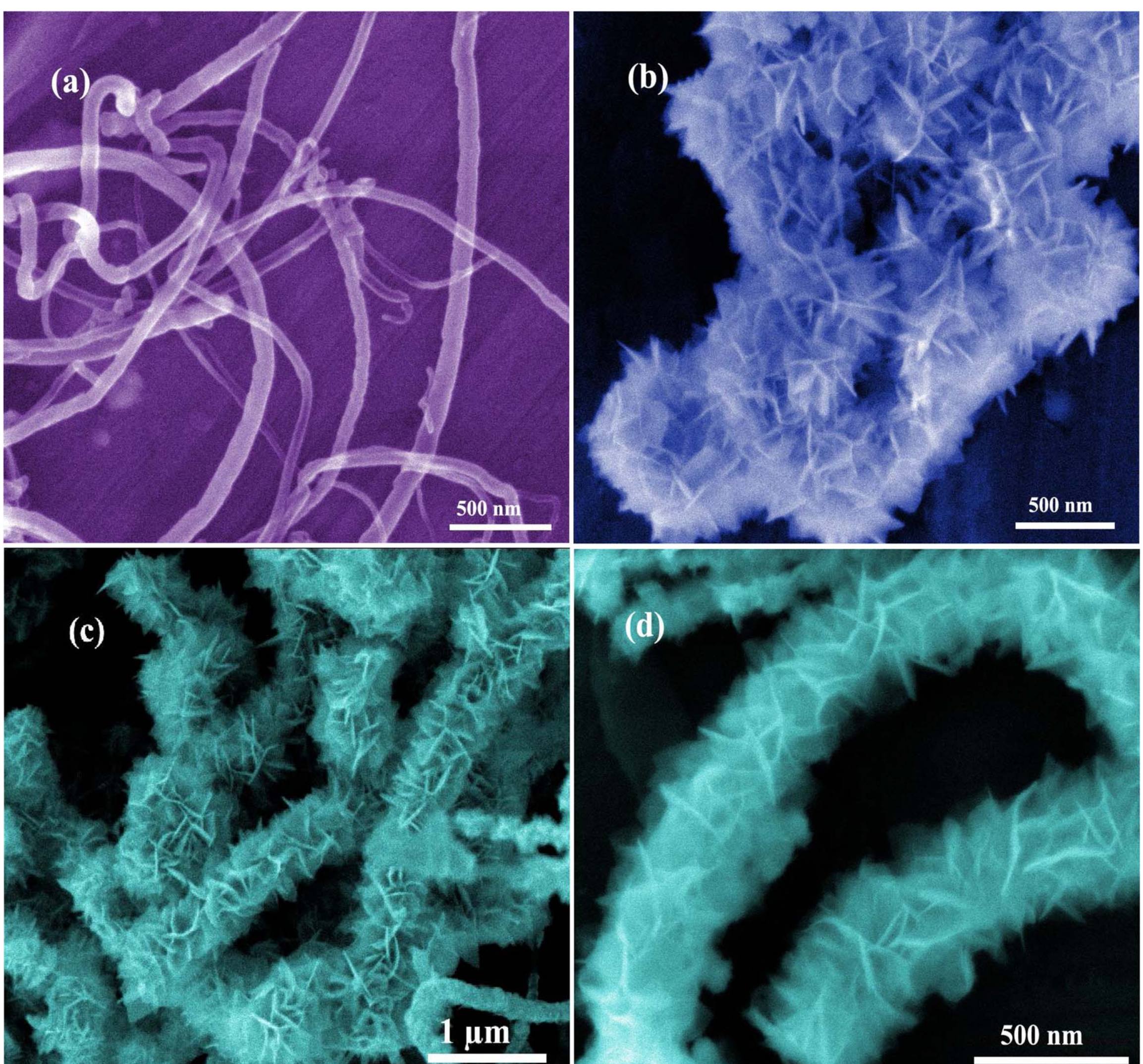

Fig. 2. SEM images of purified CNTs (a), pristine Sn_3O_4 (b), and SO-CNT-4 hybrid (c–d).