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## Introduction

In recent years, nitrophenols and some other nitroaromatics are of great public concern because of their high pollution of water. In particular, the nitrophenolic compounds, resulting from the production processes of pesticides, herbicides, insecticides, and synthetic dyes, increase the pollution.<sup>1-7</sup> In contrast, the products of catalytic hydrogenation of nitroaromatics, such as aromatic amines, are potent intermediates in industrial synthesis of biologically active compounds, pharmaceuticals, rubber chemicals, photographic and agricultural chemicals.5-9 Thus, the reaction of catalytic hydrogenation of nitroaromatics to the corresponding amines has become academically as well as technologically important.<sup>1</sup> Traditionally, the hydrogenation of nitroaromatics employs noble metal (e.g. Au, Ag, Pd, and Pt) catalysts in the presence of excess amounts of reducing agents, such as NaBH<sub>4</sub> and  $H_{2,1}^{8,10-18}$  which has proven to be an effective approach. However, it is quite expensive to use these noble metals as catalysts for catalytic applications, and another major challenge is the aggregation of the metal nanoparticles during the catalytic reactions, which often leads to a rapid decay of their catalytic activity.19 Therefore, developing green, simple and effective routes for the hydrogenation of nitroaromatics is highly desirable.

# Synthesis of $In_2S_3$ -CNT nanocomposites for selective reduction under visible light

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 $In_2S_3$ -carbon nanotube ( $In_2S_3$ -CNT) nanocomposites have been prepared *via* a facile refluxing wet chemistry process. The as-synthesized  $In_2S_3$ -CNT nanocomposites can be used as selective and active visible-light-driven photocatalysts toward hydrogenation of nitroaromatics to amines in water. Photoirradiation ( $\lambda > 420$  nm) of  $In_2S_3$ -CNT photocatalysts suspended in water containing nitroaromatics produces the corresponding amines with high yields. The control experiments reveal that an inert atmosphere and the addition of a hole scavenger are both indispensable for the visible-light-driven photocatalytic hydrogenation of nitroaromatics over  $In_2S_3$ -CNT. In comparison with blank  $In_2S_3$ , the obviously enhanced photocatalytic performance of the  $In_2S_3$ -CNT photocatalyst is mainly ascribed to the unique physicochemical properties of CNTs, which enhances the adsorptivity of the substrate and performs as an electron reservoir to trap electrons, thereby hindering the recombination of photogenerated electron-hole pairs. It is hoped that the current work on the facile synthesis of semiconductor  $In_2S_3$ -CNT nanocomposites can broaden the applications of semiconductor-carbon based composite photocatalysts in the field of photocatalytic selective organic transformations under mild conditions.

Heterogeneous photocatalysis by semiconductor-based materials has been attracting tremendous research interest over the past decades, which is now considered as one of the most promising approaches to solve the energy and environmental issues toward sustainable processes.9,20-28 As a green technology, photocatalysis can be widely applied to environmental purification (non-selective process) and selective organic transformations to fine chemicals in both gas and liquid phases.<sup>25,29-38</sup> However, one of the fundamental issues limiting the applicability of semiconductor photocatalysis is that the photoinduced electron-hole pairs in the excited states are unstable and can easily recombine at or near the surface of semiconductors, resulting in a relatively low efficiency of semiconductor-based photocatalysis.9,39 Thus, the optimization and manipulation of a charge carrier transfer process on a semiconductor surface is a key and broad theme for improving the efficiency of such semiconductor-based photocatalysts toward target reactions.

In order to improve the photocatalytic performance of semiconductor-based photocatalysts, a variety of strategies have been developed. Thereinto, coupling semiconductors with carbonaceous nanomaterials has proven to be an effective approach for enhancing the photocatalytic activities of semiconductor photocatalysts.<sup>40-47</sup> Carbon nanotubes (CNTs), as a typical type of one-dimensional (1D) material in the carbon family, due to their superior physicochemical, mechanical, and electronic properties,<sup>48-50</sup> have received a lot of attention since their discovery in 1991.<sup>51</sup> The large specific surface area, hollow structure, and extraordinary mechanical and unique electronic properties of CNTs offer them various potential applications in

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energy conversion, electrocatalysts, sensors, environmental remediation, and catalysts.<sup>40,52,53</sup> In particular, the large electron-storage capacity and metallic conductivity of CNTs similar to metals suggest that they can perform as high performance candidates for photocatalyst carriers or promoters.<sup>54</sup>

Indium sulfide (In<sub>2</sub>S<sub>3</sub>), a typical III–VI group sulfide with a band gap of 2.0–2.3 eV, has attracted substantial attention as a potential semiconductor photocatalyst.<sup>32</sup> Due to its high photosensitivity and photoconductivity, stable chemical and physical characteristics and low toxicity,<sup>55,56</sup> many attempts have been made to make use of In<sub>2</sub>S<sub>3</sub> as a visible-light-driven photocatalyst for degradation of organic dyes and for water splitting to hydrogen.<sup>56</sup> However, the construction of In<sub>2</sub>S<sub>3</sub>–CNT nanocomposites toward photocatalytic selective organic synthesis has remained unavailable so far.

Against this background, we herein construct the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites via a facile wet chemistry process, aiming at a synergetic combination of their intrinsic outstanding properties and, thus, enhanced photocatalytic performance to meet new requirements imposed by specific applications in green-chemistry-oriented organic synthesis in water under visible light.33,34 The as-synthesized In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites have been successfully applied for visible-light-driven photocatalytic hydrogenation of nitrophenols and other substituted nitroaromatics to the corresponding amines in water. In comparison with blank In<sub>2</sub>S<sub>3</sub>, the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposite exhibits an obviously enhanced photocatalytic performance, which is caused by the enhanced adsorption of the substrate and the electron accepting and transport properties of CNTs, thereby providing a convenient way to boost the transport and separation of photogenerated charge carriers and thus improving the photocatalytic performance toward hydrogenation of nitroaromatics in water under mild conditions.

## **Experimental section**

#### **Catalyst preparation**

Materials. Indium chloride tetrahydrate (InCl<sub>3</sub>·4H<sub>2</sub>O), thioacetamide (C<sub>2</sub>H<sub>5</sub>NS, TAA), ammonium formate (HCOONH<sub>4</sub>), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), nitric acid (HNO<sub>3</sub>, 65%), 4-nitrophenol (C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>), 3-nitrophenol (C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>), 2-nitrophenol (C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>), 4-nitroaniline (C<sub>6</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>), 3-nitroaniline  $(C_6H_6N_2O_2),$ 2-nitroaniline  $(C_6H_6N_2O_2),$ 4-nitrotoluene (C<sub>7</sub>H<sub>7</sub>NO<sub>2</sub>), 4-nitroanisole (C<sub>7</sub>H<sub>7</sub>NO<sub>3</sub>), 1-bromo-4-nitrobenzene (C<sub>6</sub>H<sub>4</sub>BrNO<sub>2</sub>) and 1-chloro-4-nitrobenzene (C<sub>6</sub>H<sub>4</sub>ClNO<sub>2</sub>) were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the materials were used as received without further purification. The multiwalled carbon nanotubes were purchased from Shenzhen Nanotech Port Co., Ltd., China, with 60–100 nm in diameter, 5–15  $\mu$ m in length and  $\geq$ 95% purity. The product catalog number of the purchased CNTs was L.MWCNTs-60100. The deionized water for solution preparation was from local sources.

**Synthesis.** *Acid treatment of carbon nanotubes (CNTs).* The purification and surface functionalization of CNTs were carried out before being used for preparing nanocomposites. Typically, a 500 mg portion of raw CNTs was refluxed in 150 mL of

concentrated nitric acid at 140 °C for 8 h. Then, the treated CNTs were collected by centrifugation at 8000 rpm for 15 min and washed with DI water several times until pH = 7. After that, the product was dried at 60 °C in an oven.

Fabrication of In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites. The In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites were fabricated by a facile one-step refluxing method. The preparation process is illustrated in Scheme 1. The weight addition ratios of CNTs were selected as 1%, 2%, 3%, and 5%. In detail, a certain amount of acid treated CNTs was dispersed into 100 mL distilled water by ultrasonication to obtain a homogeneous CNT dispersion. After that, 0.25 g of indium chloride tetrahydrate (InCl<sub>3</sub>·4H<sub>2</sub>O) was added into the above CNT suspension. After stirring for 30 min, 0.12 g of thioacetamide (TAA) was dissolved in the above mixed solution and stirred for another 30 min. The obtained solution was refluxed at 95 °C for 5 h. After cooling, the resulting composite was recovered by centrifugation at 8000 rpm for 15 min, washed with water, and fully dried at 60 °C in an oven to obtain the final In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites with different weight addition ratios of CNTs. The blank  $\beta$ -In<sub>2</sub>S<sub>3</sub> was obtained in the absence of CNTs.

#### Catalyst characterization

The crystal phase properties of the samples were analyzed with a Bruker D8 Advance X-ray diffractometer (XRD) using Nifiltered Cu K $\alpha$  radiation at 40 kV and 40 mA in the 2 $\theta$  range from  $5^\circ$  to  $80^\circ$  with a scan rate of  $0.02^\circ$  per second. UV-vis diffuse reflectance spectra (DRS) were recorded on a Cary-500 UV-vis-NIR spectrometer in which BaSO<sub>4</sub> powder was used as the internal standard to obtain the optical properties of the samples over a wavelength range of 200-800 nm. The morphology of the samples was determined by field-emission scanning electron microscopy (FE-SEM) using an FEI Nova NANOSEM 230 spectrophotometer. Transmission electron microscopy (TEM) images were collected using a JEOL model JEM 2010 EX microscope at an accelerating voltage of 200 kV. The photoluminescence (PL) spectra were obtained using an Edinburgh Analytical Instrument PLS920 system with an excitation wavelength of 420 nm. Raman spectroscopy was performed on a Renishaw inVia Raman System 1000 with a 532 nm Nd:YAG excitation source at room temperature.

Photoelectrochemical measurements were performed in a homemade three electrode quartz cell with a PAR VMP3 Multi Potentiostat apparatus. A Pt plate was used as the counter electrode, and Ag/AgCl electrode was used as the reference electrode, while the working electrode was prepared on fluoride tin oxide (FTO) conductor glass. Typically, the sample powder



 $\mbox{Scheme 1}$  The schematic flowchart for preparation of  $\mbox{In}_2\mbox{S}_3\mbox{-CNT}$  nanocomposites.

(5 mg) was ultrasonicated in 0.3 mL of N,N-dimethylformamide (DMF, supplied by Sinopharm Chemical Reagent Co., Ltd.) to disperse it evenly to obtain a slurry. The slurry was spread onto FTO glass, whose side part was previously protected using Scotch tape. The working electrode was dried overnight under ambient conditions. A copper wire was connected to the side part of the working electrode using conductive tape. Uncoated parts of the electrode were isolated with epoxy resin. The photocurrent measurement was carried out on a BAS Epsilon workstation without bias and the electrolyte was 0.2 M aqueous  $Na_2SO_4$  solution (pH = 6.8) without an additive. The electrochemical impedance spectroscopy (EIS) measurements were carried out using an EIS spectrometer (CHI-660D workstation, CH Instrument) in the three electrode cell in the presence of 0.5 M KCl solution containing 5.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] by applying an AC voltage with a 5 mV amplitude in the frequency range from 1 Hz to 100 kHz under open circuit potential conditions. The cyclic voltammograms were measured in the same solution in the three electrode cell as that of the EIS measurement. The visible light irradiation source ( $\lambda > 420$  nm) was a 300 W Xe arc lamp system.

#### Catalytic activity

Photocatalytic hydrogenation of nitroaromatics. The photocatalytic hydrogenation of nitroaromatic compounds was performed at ambient temperature in an inert atmosphere. In a typical reaction, 40 mg of the samples and 40 mg of ammonium formate were added into 40 mL of nitroaromatic compound solution (10 ppm) in a quartz vial. A 300 W Xe arc lamp (PLS-SXE 300C, Beijing Perfectlight Co., Ltd.) equipped with a filter to cut off light of wavelength below 420 nm was used as the irradiation source to trigger the photocatalytic reaction. After the reaction, the mixture was centrifuged at 12 000 rpm for 10 min to remove the catalyst completely. After that, the solution was analyzed using a Varian ultraviolet-visible light (UV-vis) spectrophotometer (Cary-50, Varian Co.).8 The identification of reactants and products was also confirmed by the high performance liquid chromatography (HPLC) analysis (Shimadzu HPLC-LC20AT equipped with a C18 column and SPD-M20A photodiode array detector). The whole experimental process was conducted under N<sub>2</sub> bubbling at a flow rate of 80 mL min<sup>-1</sup>.

## **Results and discussion**

Fig. 1a displays the XRD patterns of CNTs before and after the acid treatment. The observed diffraction peaks at 26.4, 42.2, 54.5, and 77.2° can be attributed to the hexagonal graphite structures (002), (100), (004), and (110).<sup>57</sup> Similar XRD patterns of the two samples indicate that the acid treatment has not destroyed the graphitic structure of the CNTs. However, after the acid treatment, the dispersibility of CNTs in water is significantly enhanced in comparison with the pristine CNTs. This is due to the fact that the acid treatment introduces a lot of functional groups (*e.g.* carboxylic groups) on the surface of CNTs, which has been well demonstrated by previous studies.<sup>58-61</sup> The grafting of functional groups on the CNT



Fig. 1 X-ray diffraction patterns of the samples of CNTs before and after acid treatment (a), and the samples of blank  $In_2S_3$  and  $In_2S_3$ -CNT nanocomposites with different weight addition ratios of CNTs (b).

surface is beneficial for improving its hydrophilicity and provides the possibility of preparing CNT-based nano-composites *via* a wet chemistry process.

The crystallographic structure and phase purity of the assynthesized  $In_2S_3$  and  $In_2S_3$ -CNT nanocomposites are shown in Fig. 1b. It can be seen that the samples of  $In_2S_3$ -CNT with different weight addition ratios of CNTs show similar XRD patterns to blank  $In_2S_3$ . The peaks located at *ca.* 14.2, 23.3, 27.4, 28.7, 33.2, 43.6, 47.7, 56.6, 59.4, 66.6 and 69.8° are distinctly indexed to the (111), (220), (311), (222), (400), (511), (440), (622), (444), (731) and (800) crystal planes of the cubic  $In_2S_3$  phase ( $\beta$ -In\_2S\_3) (JCPDS no. 65-0459), respectively. Notably, no diffraction peaks for CNTs can be observed in the  $In_2S_3$ -CNT nanocomposites. One possible reason might be due to the low amount of CNTs in the  $In_2S_3$ -CNT nanocomposites, and the other is probably due to the overlapping of the main characteristic peak of CNTs at 26.6° with the (311) peak at 27.4° of cubic  $In_2S_3$ .

Table 1 summarizes the average crystallite sizes of blank  $In_2S_3$ , and the samples of  $In_2S_3$ -CNT with different addition ratios of CNTs. For all the samples, the average crystallite sizes of  $In_2S_3$  particles are calculated from the (440) peak of the XRD patterns by the Scherrer formula:  $D = 0.89\lambda/\beta \cos \theta$ , where *D* is the average crystallite size,  $\lambda$  is the Cu K $\alpha$  wavelength (0.15406 nm),  $\beta$  is the half-width of the peak in radians, and  $\theta$  is the corresponding diffraction angle.<sup>8</sup> The average crystallite sizes of  $In_2S_3$  particles in blank  $In_2S_3$  and  $In_2S_3$ -CNT

Table 1 Summary of the average crystallite size of blank  $In_2S_3$  and  $In_2S_3\text{-}CNT$  nanocomposites with different weight addition ratios of CNTs

Samples	Average crystallite size (nm)				
Blank In <sub>2</sub> S <sub>3</sub>	18.7				
In <sub>2</sub> S <sub>3</sub> -1%CNT	19.2				
In <sub>2</sub> S <sub>3</sub> -2%CNT	19.1				
In <sub>2</sub> S <sub>3</sub> -3%CNT	18.6				
$In_2S_3-5\%CNT$	18.9				

nanocomposites are close to each other, implying that the introduction of CNTs into the matrix of  $In_2S_3$  has no obvious influence on the crystallite sizes of  $In_2S_3$  particles.

Raman spectroscopy as a valuable tool to characterize the nanostructures of carbon based nanomaterials has also been carried out. Fig. 2 shows the typical Raman spectra of the blank  $In_2S_3$  and  $In_2S_3$ -CNT (here, taking  $In_2S_3$ -3%CNT as an example) under the excitation of a 532 nm laser at room temperature. It can be seen that there are four predominant bands located at 114, 266, 306 and 368 cm<sup>-1</sup> for blank In<sub>2</sub>S<sub>3</sub>, which correspond to the typical vibration modes of  $\beta$ -In<sub>2</sub>S<sub>3</sub>.<sup>62</sup> As for the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposite, it is notable that besides the typical peaks of  $\beta$ -In<sub>2</sub>S<sub>3</sub> at the low wavenumber, there are two additional characteristic bands of CNTs at 1345 cm<sup>-1</sup> and 1580 cm<sup>-1</sup>. The structure around 1345 cm<sup>-1</sup> is called the "D band" and is related to scattering from local defects or disorders present in the CNT sample.<sup>58,59</sup> The peak at 1580 cm<sup>-1</sup> is referred to as the "G band" and it originates from the in-plane tangential stretching of the C-C bonds in the graphitic structure.58,59 The Raman characterization confirms the presence of In<sub>2</sub>S<sub>3</sub> and CNT components in the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposite.

The UV-vis diffuse reflectance spectra (DRS) measurement has been performed to determine the optical properties of the samples. Fig. 3 displays the DRS of blank  $In_2S_3$  and  $In_2S_3$ -CNT nanocomposites with different weight addition ratios of CNTs.



Fig. 2 Raman spectra of the blank  ${\sf In}_2{\sf S}_3$  and  ${\sf In}_2{\sf S}_3\text{--}3\%{\sf CNT}$  nanocomposite.

It can be seen that the presence of different amounts of CNTs has a significant influence on the optical properties of light absorption for the  $In_2S_3$ -CNT nanocomposites. The sample of blank  $In_2S_3$  exhibits a wide range light absorption with an absorption edge onset at 610 nm, corresponding to the band gap ( $E_g$ ) of about 2.0 eV. The addition of CNTs induces the increased light absorption intensity in the visible light region ranging from 610 to 800 nm as compared to blank  $In_2S_3$ , which can be ascribed to the broad background absorption of CNTs in the visible light region. This is in accordance with the color change of the samples (Fig. 3, bottom).

In order to characterize the morphology of the samples and analyze the effect of CNTs on the microscopic structure of the  $In_2S_3$ -CNT nanocomposites, scanning electron microscopy (SEM) analysis has been performed. Fig. 4a displays the typical SEM images of blank  $In_2S_3$ , from which it can be seen that the sample is composed of a large quantity of aggregated small nanoparticles. When CNTs are added during the synthesis of  $In_2S_3$ -CNT nanocomposites, as can be observed from Fig. 4b, CNTs are surrounded by  $In_2S_3$  nanoparticles and some of the



Fig. 3 Top: UV-vis diffuse reflectance spectra (DRS) of blank  $In_2S_3$  and the samples of  $In_2S_3$ -CNT with different weight addition ratios of CNTs. Bottom: photographs of blank  $In_2S_3$  and the samples of  $In_2S_3$ -CNT.



Fig. 4 Typical SEM images of blank  $In_2S_3$  (a) and the sample of  $In_2S_3{-}3\% CNT$  (b).

 $\rm In_2S_3$  particles are bound onto the CNT surface. Furthermore, it can also be observed that the morphology of the  $\rm In_2S_3$  component in  $\rm In_2S_3-3\%CNT$  is not significantly different compared to that of blank  $\rm In_2S_3$ .

The microscopic morphology and structure information of the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposite have been further investigated by the transmission electron microscopy (TEM) analysis. It can be seen from Fig. 5a-c that there is good contact between the CNTs and the In<sub>2</sub>S<sub>3</sub> particles and the nanosized In<sub>2</sub>S<sub>3</sub> particles formed along the side wall of the CNTs can be clearly observed (Fig. 5b). Fig. 5d shows the HR-TEM image of the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposite, displaying distinct lattice fringes with a lattice spacing of 0.621 nm, which can be ascribed to the (111) face of cubic In<sub>2</sub>S<sub>3</sub>. In addition, the SAED pattern in Fig. 5c indicates that In<sub>2</sub>S<sub>3</sub>-CNT possesses a polycrystalline structure, which is in accordance with the result of XRD analysis. The joint SEM and TEM characterization indicates the good interfacial contact between CNTs and In<sub>2</sub>S<sub>3</sub> nanoparticles. Since the separation and transfer of photogenerated charge carriers in CNT-semiconductor nanocomposites is intimately associated with the interfacial interaction between the CNT and the semiconductor, it should be expected that such a good interfacial contact for the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposite would favor the charge carrier transfer process across the interface, thereby contributing to the photoactivity improvement.

The photocatalytic activity of the as-prepared blank  $In_2S_3$ and  $In_2S_3$ -CNT nanocomposites is initially examined by selective hydrogenation of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) in water under visible light irradiation, as displayed in Fig. 6. It can be seen that the combination of CNTs with  $In_2S_3$ has an important influence on its photocatalytic activity. When a small amount weight ratio of 1%CNT is added, the conversion of 4-NP is obviously enhanced, and the optimal photocatalytic performance is obtained while the weight ratio of CNTs is increased to 3%, for which the conversion of 4-NP reaches ca. 96% under visible light irradiation for 1 h. However, further increase of the weight addition ratio of CNTs in the In2S3-CNT nanocomposites leads to a rapid decrease of the photocatalytic activity, which is also observed in other carbon-semiconductor nanocomposite photocatalysts.<sup>29,31,40,63</sup> This is understandable because the relatively high weight ratio of carbon materials in carbon-semiconductor nanocomposites would increase the opacity and shield light from samples, lowering the contact surface of semiconductor nanoparticles with the light illumination and thus leading to a decreased photocatalytic activity.40,64 The result indicates that proper control of the loading amount of CNTs is crucial for optimizing the synergistic interaction between semiconductor In2S3 and CNTs, thus improving the photocatalytic activity of In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites efficiently. In addition, a control experiment over blank CNTs shows that it does not display visible light photocatalytic activity and no apparent conversion of 4-NP has been observed, confirming that the primary photoactive ingredient is semiconductor In<sub>2</sub>S<sub>3</sub> in the In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites.

Based on the above results, it is clear that, among the  $In_2S_3$ -CNT nanocomposites with different addition ratios of CNTs, the  $In_2S_3$ -3%CNT nanocomposite shows the best photocatalytic performance. Therefore, it is chosen as the testing candidate to evaluate the photocatalytic activity for selective hydrogenation of other nitroaromatics with different substituent groups. As shown in Table 2, in comparison with blank  $In_2S_3$ , the  $In_2S_3$ -3% CNT nanocomposite displays higher photocatalytic activities for all testing reactions. The result demonstrates that  $In_2S_3$ -CNT is able to perform as an efficient visible-light-driven photocatalyst for selective hydrogenation of nitroaromatics to their corresponding amines, and the improvement of the photocatalytic activity over the  $In_2S_3$ -3%CNT nanocomposite should be ascribed to the introduction of the CNT material. To understand the origin of CNTs in improving the photoactivity of



Fig. 5 Typical TEM images (a–c) and high-resolution TEM (HR-TEM) image (d) of the sample of  $In_2S_3-3\%$ CNT; the inset of panel (c) is the corresponding SAED pattern.



Fig. 6 Photocatalytic selective hydrogenation of 4-NP over blank  $In_2S_3$  and  $In_2S_3$ -CNT nanocomposites under visible light irradiation for 1 h in water with the addition of ammonium formate as a hole scavenger and  $N_2$  purge at room temperature.

**Table 2** Photocatalytic selective hydrogenation of different nitroaromatics to the corresponding amines over blank  $In_2S_3$  and  $In_2S_3$ -3%CNT under the irradiation of visible light ( $\lambda$  > 420 nm) for 1 h with the addition of ammonium formate as a quencher for photogenerated holes and  $N_2$  purge at room temperature

			Blank In <sub>2</sub> S <sub>3</sub>			In <sub>2</sub> S <sub>3</sub> -3%CNT		
Entry	Substrate	Product	Conversion (%)	Yield (%)	Selectivity (%)	Conversion (%)	Yield (%)	Selectivity (%)
1	OH OH	OH OH	44	44	100	75	74	98
2	NO <sub>2</sub>	NH <sub>2</sub>	18	18	100	30	29	97
3	NO <sub>2</sub>	NH <sub>2</sub>	20	19	97	45	45	100
4	NO <sub>2</sub> NH <sub>2</sub>	NH <sub>2</sub> NH <sub>2</sub>	12	12	100	23	22	96
5	NO <sub>2</sub>	NH2 NH2	22	21	95	40	39	98
6	NO <sub>2</sub>	NH <sub>2</sub>	60	59	98	78	76	97
7	NO <sub>2</sub> Br	NH <sub>2</sub> Br	53	52	98	71	70	98
8	CH <sub>3</sub>	NH <sub>2</sub> CH <sub>3</sub>	62	62	100	79	78	99
9	NO <sub>2</sub> OCH <sub>3</sub>	NH <sub>2</sub> OCH <sub>3</sub>	50	49	98	81	80	99

semiconductor  $In_2S_3$ , we have then comparatively characterized the optimal sample of  $In_2S_3$ -3%CNT and blank  $In_2S_3$ .

Photoelectrochemical experiments have been performed to investigate the electronic interaction between  $In_2S_3$  and CNTs. Fig. 7 displays a comparison of the photocurrent-time (*I-t*) curves for blank  $In_2S_3$  and  $In_2S_3$ -3%CNT electrodes that are recorded over on-off cycles of intermittent visible light irradiation ( $\lambda > 420$  nm). It is clear to observe the fast photocurrent response for each switch-on and switch-off event in both

electrodes. Notably, it can be seen that the photocurrent density obtained on  $In_2S_3$ -3%CNT under visible light illumination is obviously enhanced as compared to that of blank  $In_2S_3$ . Due to that the photocurrent is mainly formed by the diffusion of the photogenerated electrons to the back contact, and meanwhile the photoinduced holes are taken up by the hole acceptor in the electrolyte,<sup>65</sup> the enhanced photocurrent over  $In_2S_3$ -3%CNT indicates the more efficient separation and longer lifetime of photogenerated charge carriers over it than that of blank  $In_2S_3$ ,



Fig. 7 Transient photocurrent–time (*I*–*t*) curves of blank  $In_2S_3$  and the  $In_2S_3-3\%$ CNT nanocomposite in 0.2 M  $Na_2SO_4$  (pH = 6.8) aqueous solution *versus* Ag/AgCl electrode.

suggesting that the life span of photogenerated charge carriers can be remarkably boosted by the strategy of combining  $In_2S_3$  with CNTs in an appropriate manner.

In addition, electrochemical impedance spectra (EIS) analysis as a powerful tool in studying the charge transfer process occurring in the three electrode system has also been performed. As displayed in Fig. 8, the Nyquist plots of blank  $In_2S_3$ and  $In_2S_3$ -3%CNT electrode materials cycled in 0.5 M KCl solution containing 5.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] all show semicircles at high frequencies. It is known that the highfrequency arc corresponds to the charge transfer limiting process and can be attributed to the charge transfer resistance at the contact interface between the electrode and the electrolyte solution.<sup>32,64</sup> The smaller arc radius of the EIS Nyquist plot corresponds to the lower electric charge transfer resistance. Consequently, in comparison with blank  $In_2S_3$ , the smaller arc radius of  $In_2S_3$ -3%CNT implies that it has faster interfacial electron transfer than that of blank  $In_2S_3$ .



Fig. 8 Electrochemical impedance spectroscopy (EIS) Nyquist plots of blank  $In_2S_3$  and  $In_2S_3$ -3%CNT nanocomposite in 0.5 M KCl solution containing 5.0 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>].

Fig. 9 shows the cyclic voltammograms of blank  $In_2S_3$  and  $In_2S_3$ -3%CNT nanocomposite, which display obvious anodic and cathodic peaks for both samples. The peak at positive potentials on the anodic (forward) sweep represents the oxidation of ferrocyanide to ferricyanide with the loss of one electron.<sup>66</sup> The sample of  $In_2S_3$ -3%CNT presents a large anodic current density as compared to that of blank  $In_2S_3$ , indicating a significantly enhanced electron transfer rate of the  $In_2S_3$ -3% CNT nanocomposite due to the incorporation of CNTs with high electrical conductivity.

The improved efficiency in prolonging the lifetime of photogenerated charge carriers of  $In_2S_3$  by coupling with CNTs is further supported by the photoluminescence (PL) spectra measurement. The PL spectra can give information about the photoexcited energy/electron transfer and recombination processes, and it has been used to study the optoelectronic properties and charge transfer efficiency of the photocatalyst successfully.<sup>32,67</sup> Fig. 10 shows the PL spectra of  $In_2S_3$  and  $In_2S_3$ -3%CNT powder samples. It is easy to observe that at an



Fig. 9 Cyclic voltammograms of the as-synthesized thin films on FTO glass with blank  $In_2S_3$  and  $In_2S_3$ -3%CNT nanocomposite.



Fig. 10 Photoluminescence (PL) spectra of blank  $In_2S_3$  and  $In_2S_3-3\%$  CNT nanocomposite.

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excitation wavelength of 420 nm, the addition of CNTs will lead to the PL quenching due to the preferential segregation of energetic electrons onto CNTs, indicating that the recombination of photogenerated electron-hole pairs is efficiently inhibited after the combination of  $In_2S_3$  with CNTs in the sample of  $In_2S_3$ -3%CNT. The result is in good accordance with the photoelectrochemical analysis and also in line with its higher photocatalytic activities of  $In_2S_3$ -3%CNT than blank  $In_2S_3$ .

In addition, the adsorption experiment in the dark for 4-NP over the blank  $In_2S_3$  and  $In_2S_3$ -CNT nanocomposite photocatalysts has also been performed, as displayed in Fig. 11. Apparently, the result suggests that the adsorption of the substrate over the samples can be significantly increased with the introduction of CNTs into the matrix of  $In_2S_3$ . The increased adsorptivity of  $In_2S_3$ -CNT can be attributed to the addition of CNTs, which is also observed in other semiconductor-CNT nanocomposites toward different photocatalytic applications.<sup>29,68</sup> Because semiconductor-based heterogeneous photocatalysis is a surface-based process, the increased adsorptivity of 4-NP on the surface of the  $In_2S_3$ -CNT nanocomposite is believed to be beneficial for improving the photocatalytic performance under the visible light irradiation.

In order to explore the influence of reaction conditions on the photocatalytic hydrogenation of nitroaromatics over  $In_2S_3$ -CNT nanocomposites, additional control experiments have been performed. As shown in Fig. 12b, the control experiment without the  $In_2S_3$ -CNT photocatalyst exhibits no conversion of 4-NP, which ensures that the reaction is really driven by a photocatalytic process. When a radical scavenger for photogenerated electrons  $K_2S_2O_8$  is added into the reaction system (Fig. 12c),<sup>69,70</sup> no obvious conversion of 4-NP can be observed, clearly demonstrating that the photogenerated electrons play a decisive role in driving the photocatalytic hydrogenation of nitroaromatics. In addition, it can be seen that the



Fig. 11 Remaining fraction of 4-NP after the adsorption–desorption equilibrium is achieved over blank  $In_2S_3$  and  $In_2S_3$ –CNT nanocomposites.



Fig. 12 Control experiments for photocatalytic hydrogenation of 4-nitrophenol over the  $In_2S_3$ -3%CNT nanocomposite under visible light irradiation ( $\lambda$  > 420 nm); the reaction with the addition of ammonium formate in a N<sub>2</sub> atmosphere (a), reaction without a photocatalyst (b), reaction with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as a scavenger for electrons (c), reaction without ammonium formate (d) and reaction without the purge of N<sub>2</sub> (e).

photocatalytic conversion of 4-NP over the optimal  $In_2S_3-3\%$  CNT nanocomposite is strongly inhibited in the absence of  $N_2$  (Fig. 12d) and HCOONH<sub>4</sub> (Fig. 12e), indicating that the inert atmosphere and the addition of HCOONH<sub>4</sub> as a hole scavenger are both indispensable for the photocatalytic hydrogenation of 4-NP over the  $In_2S_3$ -CNT nanocomposites. These also suggest that photocatalytic selective reduction of nitroaromatics over  $In_2S_3$ -CNT requires the appropriate control of reaction conditions, ensuring that the photoreduction process driven by photogenerated electrons proceeds efficiently.

On the basis of the above discussion, it can be concluded that the enhanced photocatalytic performance over In2S3-CNT is attributed to the contribution of CNTs, which enhances the adsorptivity of the substrate, and they act as electron acceptors and transfer channels for enhancing the charge separation efficiency. Accordingly, a probable reaction mechanism has been proposed and illustrated in Fig. 13. Under the visible light irradiation ( $\lambda > 420$  nm), the electrons are photoexcited from the valence band (VB) to the conduction band (CB) of In<sub>2</sub>S<sub>3</sub> in the framework of In<sub>2</sub>S<sub>3</sub>-CNT, by which holes in the VB are created. The photogenerated electrons tend to transfer to CNTs due to the large electron-storage capacity, metallic conductivity and lower potential of CNTs,29,54 which can efficiently facilitate the separation of photoexcited charge carriers and lengthen the lifetime of electron-hole pairs. Since the reduction of nitroaromatics is a multi-electron driven process, the efficient separation and transfer of electrons are beneficial for boosting the reduction of nitroaromatics. On the other hand, the large specific surface area of CNTs has also proven to improve the adsorption of the substrate on the surface of In2S3-CNT, leading to the fact that a high concentration of substrate nitroaromatic compounds can be accumulated over the In2S3-CNT photocatalysts, thereby contributing to the photoactivity



Fig. 13 Illustration of the proposed reaction mechanism for photocatalytic selective reduction of nitroaromatics over  $In_2S_3-CNT$  nanocomposites.

enhancement. Besides, the photogenerated holes in the VB of  $In_2S_3$  are trapped by the hole quencher of ammonium formate in a  $N_2$  atmosphere, which efficiently restrains the occurrence of the oxidation process for nitroaromatics and thus guarantees that the selective photoreduction proceeds efficiently. The whole photocatalytic reduction of nitroaromatics can be expressed by the following formula (Scheme 2).

Finally, the  $In_2S_3$ -CNT nanocomposite also has the excellent recycle photocatalytic performance for selective hydrogenation

$$R \xrightarrow{\text{NO}_2 + 6 \text{ H}^+ + 6 \text{ e} - \frac{\text{In}_2 \text{S}_3 - \text{CNT}}{\lambda > 420 \text{ nm}}} R \xrightarrow{\text{NH}_2 + 2 \text{ H}_2 \text{O}}$$

Scheme 2 Photocatalytic reduction of nitroaromatics to amines in water with the addition of ammonium formate ( $HCOONH_4$ ) for guenching photogenerated holes in a N<sub>2</sub> atmosphere.



Fig. 14 The recycle experiment of photocatalytic reduction of 4-NP over the  $In_2S_3-3\%$ CNT nanocomposite under visible light irradiation ( $\lambda > 420$  nm) with the addition of ammonium formate as a quencher for photogenerated holes in a  $N_2$  atmosphere.

of nitroaromatics under visible light irradiation with the addition of ammonium formate as a quencher for photogenerated holes in a N<sub>2</sub> atmosphere. The stability of the samples has been proven by the successive recycle test for photocatalytic hydrogenation of 4-NP over the optimal sample of In<sub>2</sub>S<sub>3</sub>–3%CNT. As displayed in Fig. 14, during the five times recycle test for photocatalytic reduction of 4-NP under 1 h visible light irradiation, the In<sub>2</sub>S<sub>3</sub>–3%CNT nanocomposite shows almost no deactivation. The conversion of 4-NP is nearly constant (*ca.* 96%) for each run of the recycle photoactivity test. Therefore, In<sub>2</sub>S<sub>3</sub>–3% CNT can perform as a stable visible-light-driven photocatalyst toward selective photoreduction of nitroaromatics under the current photocatalytic reaction conditions.

## Conclusion

In summary, we have synthesized a series of In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites via an efficient and easily accessible low-temperature refluxing method. The In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites have been successfully applied to photocatalyze the hydrogenation of nitroaromatics to the corresponding amines in water under ambient conditions. The hydrogenation rate of In<sub>2</sub>S<sub>3</sub> under visible light irradiation ( $\lambda > 420$  nm) is obviously enhanced by loading a suitable amount of CNTs, which improves the adsorption of the substrate, facilitates the electron transfer, and boosts the separation of photogenerated charge carriers. As a result, the photocatalytic performance of In2S3-CNT is remarkably enhanced. The optimal synergistic interaction between In<sub>2</sub>S<sub>3</sub> and CNTs is achieved when the content of CNTs is ca. 3 wt%. The In<sub>2</sub>S<sub>3</sub>-CNT nanocomposites display good photostability and recycle performance for photocatalytic reduction of nitroaromatics under visible light. We hope this study can enrich the applications of semiconductor-CNT nanocomposite photocatalysts with improved photoactivity for targeting applications in the field of photocatalytic selective organic synthesis.

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