

Short Communication

Visible-light-induced photocatalytic hydrogenation of 4-nitroaniline over In_2S_3 photocatalyst in water

Weiming Wu, Rui Lin, Lijuan Shen, Ruowen Liang, Rusheng Yuan, Ling Wu*

State Key Laboratory Breeding Base of Photocatalysis, Research Institute of Photocatalysis, Fuzhou University, Fuzhou 350002, PR China

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ABSTRACT

Photocatalytic hydrogenation of 4-nitroaniline over the In_2S_3 photocatalyst was investigated in water under visible light irradiation ($\lambda \geq 420$ nm). After 90 min of visible light irradiation, 100% of 4-nitroaniline could be reduced to *p*-phenylenediamine over the In_2S_3 photocatalyst in the presence of triethanolamine as a hole scavenger. Moreover, the photoreduction activity of the In_2S_3 photocatalyst could keep at ~ 100% in the 5th cycle of testing. On the basis of the results of electron spin resonance, photoinduced electrons of the In_2S_3 photocatalyst were identified as the active species for the photocatalytic hydrogenation of 4-nitroaniline.

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1. Introduction

Hydrogenation of 4-nitroaniline (4-NA) is an important reaction in the field of chemical industry, since the produced *p*-phenylenediamine (PPD) is a useful component to many industrial chemicals (e.g., rubber antioxidants, textile fibers and thermoplastics) [1–3]. Generally, the hydrogenation of 4-NA is achieved by using noble metals under H_2 atmosphere [3].

Recently, photocatalysis provides a new feasible approach for the hydrogenation of 4-NA via utilizing sunlight in water [4–7]. Imamura et al. have reported that TiO_2 shows catalytic activity for the photocatalytic hydrogenation of 4-NA under UV light irradiation in the presence of hole scavengers under deaerated conditions [4]. $\text{SrBi}_2\text{Nb}_2\text{O}_9$ has also been found as an efficient UV-light-induced photocatalyst for the photocatalytic hydrogenation of 4-NA [5]. In order to efficiently utilize the sunlight, we have developed $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS visible-light-induced photocatalysts for the hydrogenation of 4-NA [6,7]. However, it is noted that these catalysts contain toxic metal ions (Pb^{2+} and Cd^{2+}), which may limit their industrial applications. Therefore, developing non-toxic and efficient visible-light-induced photocatalysts for the hydrogenation of 4-NA is required.

Indium sulfide (In_2S_3), which has a band gap of ~ 2.0 eV, is an attractive material as a candidate of non-toxic and efficient visible-light-induced photocatalysts [8–14]. He et al. have found that it shows high catalytic activity for the decoloration of methyl orange under visible light irradiation [8]. Subsequently, some researchers have investigated the effect of the morphology of In_2S_3 on its

photocatalytic activity [9,10]. Moreover, it is reported that In_2S_3 can photocatalytic split water to produce H_2 in the presence of SO_3^{2-} and S^{2-} as hole scavengers under visible light irradiation, when a noble metal (Pd, Pt, Ru or Au) is used as a co-catalyst or it is combined with other materials to construct the heterojunction photocatalysts (such as $\text{In}_2\text{S}_3/\text{TiO}_2$ and $\text{In}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$) [11–13]. Very recently, An et al. have revealed that the photocatalytic activity of the In_2S_3 photocatalyst can be enhanced by the modification of graphene [14]. However, as far as we known, the study on the photocatalytic hydrogenation reactions over the In_2S_3 photocatalyst has not been reported.

Herein, the photocatalytic hydrogenation of 4-NA over the In_2S_3 photocatalyst was investigated in detail under visible light irradiation ($\lambda \geq 420$ nm) upon purging with N_2 , including the effects of the addition of hole scavengers and the stability of the catalyst. Moreover, on the basis of the results of electron spin resonance, a mechanism for the photocatalytic hydrogenation of 4-NA over the In_2S_3 photocatalyst was proposed. Our results might allow us to provide an instructive guidance for developing non-toxic and efficient visible-light-induced photocatalysts to the photocatalytic hydrogenation of 4-NA.

2. Experimental section

2.1. Photocatalytic hydrogenation of 4-NA

For the photocatalytic hydrogenation of 4-NA, an ozone-free 300 W Xe lamp (PLS-SXE300C, Perfectlight Co., Beijing, intensity: 0.96 W/cm^2 at $\lambda = 420$ nm) with a cutoff filter of 420 nm and an infrared filter was used as the light source ($\lambda \geq 420$ nm). Prior to

* Corresponding author. Tel.: +86 591 83779362; fax: +86 591 83779105.
E-mail address: wuling@fzu.edu.cn (L. Wu).

the catalytic test, 80 mg of In_2S_3 powders (99.98%, Alfa Aesar Co.) was suspended in 80 mL of 4-NA (98%, Alfa Aesar Co.) aqueous solution (20 mg/L) in a reactor (100 mL). After adding 50 μL of triethanolamine (TEOA, A.R., Sinopharm Chemical Reagent Co.), the suspension was stirred in the dark for 30 min to ensure eliminate oxygen in the system by purging with nitrogen (>99.95%). As the reaction proceeded, 4 mL of the suspension was taken at a certain interval and was filtrated. The change of the 4-NA concentration during the reaction was analyzed by measuring the absorbance at 380 nm with a Cary 50 UV-vis spectrophotometer (Varian Co.). The whole photocatalytic process was carried out under N_2 bubbling with a flow rate of 60 mL/min.

2.2. Characterization

Experimental details for the electron spin resonance (ESR), X-Ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP-AES) and GC-MS analysis were described in detail in Supplementary data.

3. Results and discussion

3.1. Photocatalytic hydrogenation of 4-NA

Fig. 1 shows UV-vis spectral changes of the 4-NA aqueous solution over the In_2S_3 photocatalyst as a function of irradiation time in the presence of TEOA under visible light irradiation ($\lambda \geq 420$ nm). A decrease in the absorption of 4-NA at 380 nm along with simultaneous appearance of two peaks at 238 and 305 nm has been observed in this work. The peaks observed at 238 and 305 nm can attribute to the characteristic peaks of PPD. After 90 min of visible light irradiation, 100% of 4-NA can be converted to PPD over the In_2S_3 photocatalyst. GC-MS analysis results (see Fig. S1 and S2) indicate that 4-NA is completely reduced to PPD and no other products is detected in the present system. Furthermore, the control experiment (4-NA and TEOA without the In_2S_3 photocatalyst) exhibits negligible photocatalytic hydrogenation of 4-NA (see Fig. S3), indicating the photolysis of 4-NA can be ignored under visible light irradiation in the presence of TEOA. These results reveal that the In_2S_3 photocatalyst shows the catalytic activity for the photocatalytic hydrogenation of 4-NA under visible light irradiation in the presence of TEOA as the hole scavenger upon purging with N_2 .

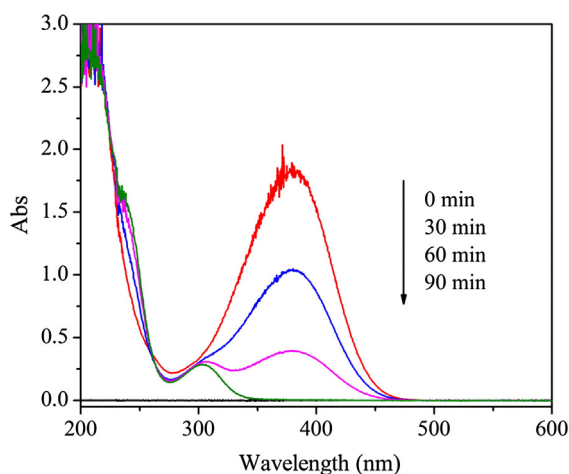


Fig. 1. UV-vis spectral changes of the 4-NA aqueous solution over the In_2S_3 photocatalyst as a function of irradiation time in the presence of TEOA under visible light irradiation ($\lambda \geq 420$ nm).

3.2. Reusability of In_2S_3 photocatalyst

Generally, the stability of a catalyst is a very important factor for its practical applications. As shown in Fig. 2, the photoreduction activity of the In_2S_3 photocatalyst does not obviously decrease in the recycling experiments (Experimental details see Supplementary data). Its catalytic activity can keep at $\sim 100\%$ in the 5th cycle of testing. XRD patterns (see Fig. 3) indicate that the crystal structure of the In_2S_3 photocatalyst is intact after the reaction. The XRD patterns of the catalyst can be well indexed to tetragonal In_2S_3 (JCPDS card no. 051-1160). Moreover, the In^{3+} concentration changes in aqueous solution have been measured by ICP-AES. The In^{3+} concentrations before and after the reaction are 0.33 and 0.36 ppm, respectively. The slight change in the In^{3+} concentrations before and after the reaction can be ignored due to the instrumental detection limit (0.04 ppm for the In element). These results confirm that the In_2S_3 photocatalyst has high stability for the photocatalytic hydrogenation of 4-NA under visible light irradiation.

3.3. Effect of hole scavengers

As mentioned in our previous work, the addition of a hole scavenger is proved to be an efficient way to enhance the photocatalytic activity of the In_2S_3 photocatalyst for the photocatalytic hydrogenation of 4-NA [5–7]. Therefore, other hole scavengers (CH_3OH , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, HCO_2NH_4 and Na_2SO_3) have been used to investigate the photocatalytic hydrogenation of 4-NA over the In_2S_3 photocatalyst upon purging with N_2 . As shown in Table S1, only $\sim 30\%$ of 4-NA is converted to PPD over the In_2S_3 photocatalyst in the presence of CH_3OH , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, HCO_2NH_4 or Na_2SO_3 as the hole scavenger after 90 min of visible light irradiation. However, the photoreduction activity of the In_2S_3 photocatalyst is dramatically increased when TEOA is used as the hole scavenger. These results reveal that TEOA is a efficient hole scavenger for the photoreduction reactions over the In_2S_3 photocatalyst.

3.4. ESR analysis

5, 5-Dimethyl-1-pyrroline *N*-oxide (DMPO) spin-trapping ESR technique has been introduced to investigate the photocatalytic hydrogenation of 4-NA over the In_2S_3 photocatalyst. Fig. 4 shows DMPO spin-trapping ESR spectra of the In_2S_3 photocatalyst in dark and under visible light irradiation ($\lambda \geq 420$ nm). Sextet characteristic peaks of the $\text{DMPO} \cdot \text{O}_2^-$ adduct are observed in the In_2S_3 photocatalyst methanol suspension under visible light irradiation. This confirms that the In_2S_3 photocatalyst can produce photoinduced electrons under visible light irradiation. It has been reported that the redox potential of the conduction band (CB) of the In_2S_3 photocatalyst

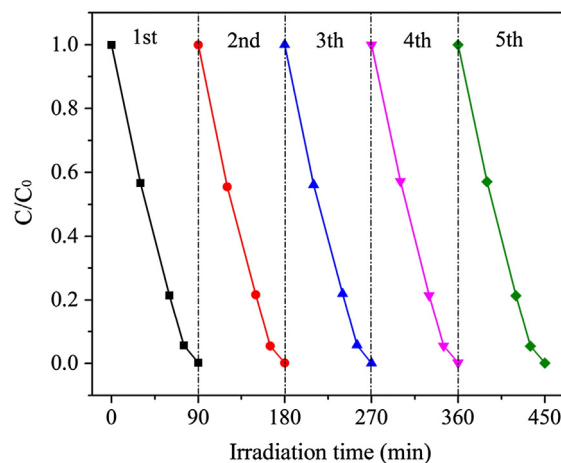


Fig. 2. Reusability of the In_2S_3 photocatalyst for the photocatalytic hydrogenation of 4-NA.

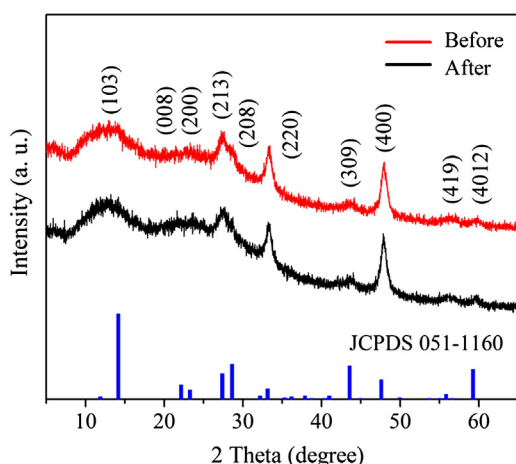


Fig. 3. XRD patterns for the In_2S_3 photocatalyst before and after the catalytic test.

is -0.7 V vs. RHE [15]. Therefore, the photoinduced electrons of the In_2S_3 photocatalyst can take part in the photocatalytic hydrogenation of 4-NA ($E(4\text{-NA}/\text{PPD}) = -0.3$ V vs. RHE [16]). It is noted that there are no obvious signals of DMPO- $\cdot\text{OH}$ adduct over the In_2S_3 photocatalyst under visible light irradiation. The result indicates that In_2S_3 can't produce $\cdot\text{OH}$ radicals due to the low redox potential of the valence band (VB) ($E_{\text{VB}}(\text{In}_2\text{S}_3) = 1.3$ V [15] and $E(\cdot\text{OH}/\text{H}_2\text{O}) = 2.7$ V [17] vs. RHE). As a result, CH_3OH , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, HCO_2NH_4 , Na_2SO_3 and TEOA are used as the hole scavengers.

In our previous work, the photocatalytic hydrogenation of 4-NA can be achieved by using photocatalysis in the presence of CH_3OH due to the production of methanol radicals ($\cdot\text{CH}_2\text{OH}$ radicals, $E(\cdot\text{CH}_2\text{OH}/\text{CH}_2\text{O}) = -0.5$ V vs. RHE) [18,19]. However, as mentioned above, photoinduced holes rather than $\cdot\text{OH}$ radicals are detected over the In_2S_3 photocatalyst. Therefore, $\cdot\text{CH}_2\text{OH}$ radicals can't be produced in the present system (see Fig. 5) [18]. This can explain that the In_2S_3 photocatalyst shows low catalytic activity for the hydrogenation of 4-NA in the presence of CH_3OH . Similar situation has been observed when $(\text{NH}_4)_2\text{C}_2\text{O}_4$ or HCO_2NH_4 as the hole scavenger, because carbon dioxide radicals ($\cdot\text{CO}_2^-$ radicals, $E(\cdot\text{CO}_2^-/\text{CO}_2) = -1.8$ V vs. RHE [6,7,20]) do not exist in the present system (see Fig. 5). The absence of the $\cdot\text{CO}_2^-$ radicals can attribute to the low redox potential of the VB for In_2S_3 . Although $\cdot\text{SO}_3^-$ radicals can be detected over the In_2S_3 photocatalyst in the presence of Na_2SO_3 (see Fig. 5), these radicals do not participate in the photocatalytic hydrogenation of 4-NA due to the disproportionation or/and dimerization of the $\cdot\text{SO}_3^-$ radicals [7,21]. As a result, the conversion rate of 4-NA over the In_2S_3

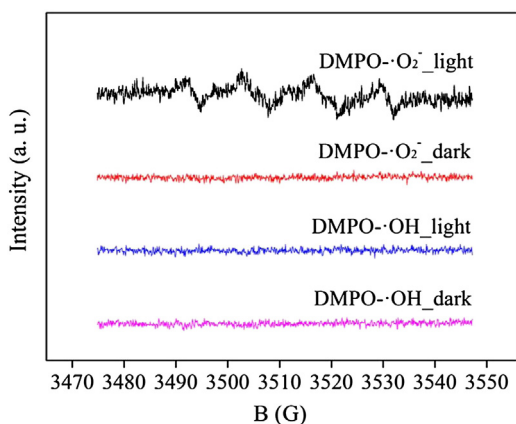


Fig. 4. DMPO spin-trapping ESR spectra of the In_2S_3 photocatalyst in dark and under visible light irradiation ($\lambda \geq 420$ nm).

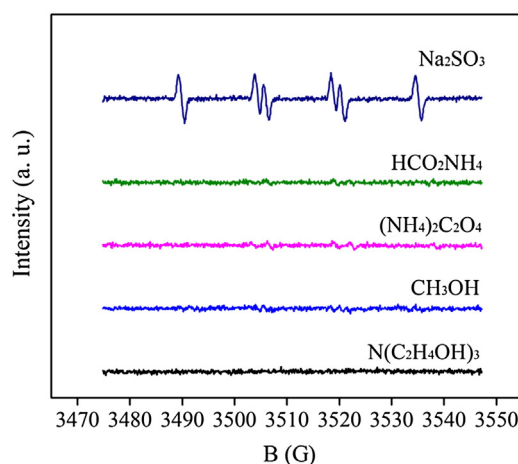


Fig. 5. DMPO spin-trapping ESR spectra of the In_2S_3 photocatalyst under visible light irradiation ($\lambda \geq 420$ nm) in the presence of various hole scavengers.

photocatalyst in the presence of Na_2SO_3 is only $\sim 30\%$ after 90 min of visible light irradiation.

As shown in Fig. 5, there are no obvious ESR signals of the adducts over the In_2S_3 photocatalyst when TEOA is used as the hole scavenger. However, it is reported that the oxidation potential of TEOA is 1.1 V vs. RHE [22]. Different from other hole scavengers (CH_3OH , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, HCO_2NH_4 and Na_2SO_3), TEOA can be easily oxidized to TEOA^+ by the photoinduced holes of the In_2S_3 photocatalyst ($E_{\text{VB}}(\text{In}_2\text{S}_3) = 1.3$ V vs. RHE [15]). As a result, the photoinduced electrons of the In_2S_3 photocatalyst can escape from the pair recombination, and are available to reduce 4-NA to PPD. This can explain that the In_2S_3 photocatalyst shows the catalytic activity for the photocatalytic hydrogenation of 4-NA in the presence of TEOA as the hole scavenger. Therefore, the photoinduced electrons of the In_2S_3 photocatalyst are the active species responsible for the photocatalytic hydrogenation of 4-NA.

4. Conclusions

The In_2S_3 photocatalyst showed the catalytic activity for the photocatalytic hydrogenation of 4-NA under visible light irradiation ($\lambda \geq 420$ nm) in the presence of the hole scavenger (CH_3OH , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, HCO_2NH_4 , Na_2SO_3 or TEOA) upon purging with N_2 . As compared to other hole scavengers, TEOA was found as the most effective hole scavenger for the In_2S_3 photocatalyst. 100% of 4-NA could be converted to PPD over the In_2S_3 photocatalyst in the presence of TEOA as the hole scavenger after 90 min of visible light irradiation. The photocatalytic activity of the In_2S_3 photocatalyst could keep at $\sim 100\%$ in the 5th cycle of testing. DMPO-spin trapping ESR analysis results revealed that photoinduced electrons were the active species responsible for the photocatalytic hydrogenation of 4-NA over the In_2S_3 photocatalyst.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.catcom.2013.05.016>.

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