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Article

Efficient visible light initiated hydrothiolations of alkenes/alkynes over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$: Role of Ir_2S_3

Xinglin Wang, Yuanyuan Li, Zhaohui Li *

Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, Fujian, China

ARTICLE INFO

Article history:

Received 19 May 2020

Accepted 25 June 2020

Published 5 March 2021

Keywords:

Photocatalysis

 $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$

Alkenes

Alkynes

Hydrothiolation

ABSTRACT

The hydrothiolations of alkynes/alkenes with thiols is an atom-economic and thus attractive method for the constructions of C–S bonds. Here $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites with varied Ir_2S_3 loadings were obtained by one-pot solvothermal method from ZnCl_2 , InCl_3 and thioacetamide with IrCl_3 . The loading of Ir_2S_3 on the surface of ZnIn_2S_4 promoted the hydrothiolations of alkenes and alkynes, with an optimum performance observed over 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite. Based on the studies on the performance of several other cocatalysts (MoS_2 , NiS and Pd) loaded ZnIn_2S_4 and the EIS analyses, it was proposed that the superior performance over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite can be ascribed to an improved efficiency on the photogeneration of the thiyl radicals by loading Ir_2S_3 as well as its inactivity for photocatalytic hydrogen evolution, a side reaction in the light initiated hydrothiolation reaction over ZnIn_2S_4 . This study not only demonstrates an efficient and green strategy to synthesize thiolated products under visible light based on semiconductor photocatalysis, but also provides some guidances for the design and development of photocatalytic systems for light induced organic syntheses.

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1. Introduction

The construction of C–S bonds is important in synthetic organic chemistry since a large amount of natural products and pharmaceuticals contain C–S bonds in their structures and sulfur-containing products are receiving increasing attention in polymer and material chemistry [1]. Among the various strategies developed, the hydrothiolations of unsaturated hydrocarbons with thiols is an atom-economic and thus attractive strategy for the construction of C–S bonds [2,3]. The metal-catalyzed hydrothiolations of unsaturated hydrocarbons with thiols can proceed with good to excellent regio- and stereoselectivity to sulfur containing molecules [4–6]. Recently, to

develop green and sustainable processes for chemical reaction, the use of solar energy to drive chemical transformations has attracted extensive research interest [7–10]. Semiconductors, in particular narrow-band-gap metal sulfides [11], have shown great potential in visible light induced organics transformations under mild conditions [12,13]. Specifically, the development of photoredox systems to realize the hydrothiolation reactions under visible light has also been demonstrated [14–16]. Homogeneous photocatalysts like Ru (II) complexes [17,18], dyes (Eosin Y) [19] as well as heterogeneous semiconducting TiO_2 [20] and ZnIn_2S_4 [21] have all been reported to realize the hydrothiolation reactions under visible light. In these photoredox systems, thiyls, the synthetically useful radicals generated in

* Corresponding author. Tel/Fax: +86-591-22865855; E-mail: haohuili1969@yahoo.com

This work was supported by the National Natural Science Foundation of China (21872031, U1705251) and the Award Program for Minjiang Scholar Professorship.

DOI: 10.1016/S1872-2067(20)63660-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 3, March 2021

the photoredox cycle, attack the unsaturated hydrocarbons (alkenes or alkynes) to generate the hydrothiolated products via a radical addition cycle. As compared with the direct addition of thiols to unsaturated hydrocarbons, in which the thiyls are generated by thermal/UV activation of a radical initiator or by direct irradiation with UV light [22,23], which usually requires harsh reaction conditions and leads to low selectivity with the possible formation of by-products as well as limited application to only simple systems [24–26], the hydrothiolations over these photoredox systems are more selective since the reactions can be carried out under mild conditions and no special UV equipments was required. In addition, these reactions protocols can be applied to expanded substrate scopes.

Among the already reported photoredox systems for light initiated hydrothiolation reactions, ZnIn_2S_4 , a promising semiconductor which has been widely used in a variety of photocatalytic applications [27–29], is in particular appealing since the hydrothiolations over ZnIn_2S_4 can be carried out in a green solvent (methanol), with only stoichiometric thiols required and applicable to a broad substrate scope, which makes it a green, sustainable and cost-effectively strategy for the synthesis of thiolated products [21]. In addition, ZnIn_2S_4 is cheap and non-toxic [30,31]. However, the light initiated hydrothiolation reactions for some bulky substrates over bare ZnIn_2S_4 are still not so high. Considering that the light initiated hydrothiolation reactions over ZnIn_2S_4 is a coupling of the photoredox generation of the thiyl radicals and the successive radical addition to produce the desired hydrothiolated products [21], it is therefore proposed that an improved efficiency in the photogeneration of the thiyl radicals would be beneficial to the whole hydrothiolation reactions [32,33]. Cocatalysts have been widely used in photocatalysis to promote a variety of photocatalytic reactions since they can improve the separation of the photogenerated charge carriers and promote their transportation [34–43].

In this manuscript, to improve the performance of ZnIn_2S_4 for light initiated hydrothiolation, Ir_2S_3 was loaded on the surface of ZnIn_2S_4 via a one-step solvothermal method and the as-obtained $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites was used in the visible light initiated thiol-ene and thiol-yne coupling reactions. It was found that loading of Ir_2S_3 on the surface of ZnIn_2S_4 did promote the hydrothiolations of alkenes and alkynes, with an optimum performance observed over 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite. The superior performance over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites can be ascribed to an improved efficiency on the photogeneration of the thiyl radicals by loading Ir_2S_3 as well as its inactivity for photocatalytic hydrogen evolution, a side reaction in the light initiated hydrothiolations over ZnIn_2S_4 . This work provides an efficient and green strategy to synthesize thiolated products based on semiconductor photocatalysis.

2. Experimental

2.1. Preparation

All the reagents were commercially available and used without further purifications. For the synthesis of $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, different amounts of IrCl_3 was dispersed in a mixed solution containing 30 mL of *N,N*-dimethylformamide (DMF) and 30 mL of ethylene glycol (EG). ZnCl_2 (0.136 g, 1 mmol), $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (0.586 g, 2 mmol) and thioacetamide (TAA) (0.3 g, 4 mmol) were added under vigorous stirring. The resultant suspension was transferred to a 100 mL Teflon liner, sealed and heated at 180 °C for 18 h. After the reaction, the autoclave was cooled, and the product was collected and washed with deionized water and ethanol for several times and dried overnight at 60 °C. The $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites with different amount of Ir_2S_3 were denoted as *x* mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$. Bare ZnIn_2S_4 was synthesized similarly in a reaction without the introduction of IrCl_3 .

2.2. Catalytic reactions

The visible light induced hydrothiolation reactions were carried out in a sealed reaction tube irradiated with an LED lamp (Beijing Perfect Light, PCX50B). The catalyst (10 mg), thiol (0.1 mmol) and alkynes/styrene (0.12 mmol) were suspended in a Schlenk tube containing methanol (4 mL). Before the reaction, the suspension was degassed and saturated with N_2 to remove any dissolved O_2 . The reaction was performed under irradiation for 15 h with an LED lamp (65 mW cm^{-2}) irradiated from bottom, with the reaction suspension continuously stirring during the whole reaction. A photograph of the experimental set-up has been provided in Supporting Fig. S5. After reaction, the mixture was filtered through a porous membrane (20 μm in diameter) and the filtrate was analyzed by GC-MS and GC-FID (Shimadzu GC-2014) equipped with an HP-5 capillary column.

3. Results and discussion

Similar to that for the preparation of bare ZnIn_2S_4 [27,44], $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites with different loading amount of Ir_2S_3 were obtained by one-pot solvothermal method from ZnCl_2 , InCl_3 and TAA in a mixed solvent of DMF and EG, with the presence of different amounts of IrCl_3 . The XRD patterns of the products show 2θ peaks at values of 14.3°, 21.2°, 27.7°, 30.4°, 39.3°, 47.5°, 52.1°, 55.8° and 76.4°, which can be assigned to (004), (006), (102), (104), (108), (110), (116), (022) and (123) crystallographic planes of hexagonal ZnIn_2S_4 phase (JCPDS 65-2023) [31], indicating that the introduction of Ir species does not influence the formation of hexagonal ZnIn_2S_4 (Fig. 1). No diffraction peak corresponding to either metallic Ir or Ir-containing compound was observed in the XRD patterns, probably due to the low amount of Ir introduced in the products. However, the presence of Ir in the as-obtained products was evidenced from the XPS. As shown in Fig. 2(a), the XPS spectrum of the product with 0.5 mol% Ir loaded in Ir 4f region shows peaks at binding energy of 61.68 eV for Ir 4f_{7/2} and 64.91 eV for Ir 4f_{5/2} respectively, suggesting that Ir exists as Ir³⁺ [45]. The XPS spectrum in S 2p region can be deconvoluted into two sets of peaks, indicating that S exists in two different chemical

Fig. 1. XRD patterns of different samples. (a) ZnIn_2S_4 ; (b) 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$; (c) 1 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$; (d) 2 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$.

environments (Fig. 2(b)). Considering that Ir exists as Ir^{3+} and by comparison with the XPS of bare ZnIn_2S_4 , the peaks with binding energy at 161.38 and 162.62 eV can be assigned to $\text{S } 2p_{3/2}$ and $\text{S } 2p_{1/2}$ in ZnIn_2S_4 , while the other two peaks with binding energy at 161.77 and 162.89 eV can be attributed to $\text{S } 2p_{3/2}$ and $\text{S } 2p_{1/2}$ in Ir_2S_3 , respectively. The formation of Ir_2S_3 on the surface of hexagonal ZnIn_2S_4 is not unexpected since previous studies also demonstrated that the surface deposited PtS was obtained via a photoreduction of PtCl_6^{2-} over ZnIn_2S_4 [46]. Both Zn $2p$, with binding energies located at 1021.52 and 1044.55 eV for Zn $2p_{3/2}$ and $2p_{1/2}$, and In $3d$, located at 444.83

and 452.34 eV, in the as-obtained $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, slightly shift to higher binding energies as compared with those in bare ZnIn_2S_4 , indicating the existence of the interaction between the surface of deposited Ir_2S_3 and ZnIn_2S_4 (Figs. 2(c), (d)). The SEM image of 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ shows that it consists of flower-like microspheres with dimension of ca. 2–3 μm (Fig. 3(a)). The TEM image shows that each microsphere is assembled by very thin nanosheets (Fig. 3(b)). As compared with bare ZnIn_2S_4 , it is obvious that the deposition of Ir_2S_3 on the surface of ZnIn_2S_4 does not change its morphology. The HRTEM image shows that Ir_2S_3 nanoparticles of ca. 6 nm, were deposited on the nanosheet of ZnIn_2S_4 . Clear lattice fringes of 0.291 nm, corresponding to (102) crystallographic plane of Ir_2S_3 , can be observed. In addition, lattice fringes of 0.322 nm, which belongs to (102) crystallographic plane of hexagonal ZnIn_2S_4 , are also observed, which again confirms the deposition of Ir_2S_3 in hexagonal ZnIn_2S_4 . The EDX mapping of 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite also confirms the presence of Ir and its even distribution on the surface of ZnIn_2S_4 (Fig. S1).

The UV-vis DRS of $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites with different amount of Ir_2S_3 were displayed in Fig. 4. All the $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites show light absorption in the visible light region, with an absorption edge extending to 550 nm, in accordance with their yellow color. As compared with bare ZnIn_2S_4 , the deposition of Ir_2S_3 on the surface of ZnIn_2S_4 does not influence its light absorption.

To study the performance of $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ for visible light initiated hydrothiolation reactions, the reaction between phenylacetylene (**1a**) and benzyl mercaptan (**2a**) was first selected as the model reaction. The reaction was initially

Fig. 2. XPS spectra of 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite. (a) Ir 4f; (b) S 2p; (c) Zn 2p; (d) In 3d.

Fig. 3. SEM (a), TEM (b) and HRTEM (c) image 0.5 mol% Ir₂S₃/ZnIn₂S₄ nanocomposite.

proceeded in methanol over 1.0 mol% Ir₂S₃/ZnIn₂S₄ since previous study revealed that methanol was the best solvent for the light initiated hydrothiolation reaction over ZnIn₂S₄. Similar to bare ZnIn₂S₄, 1.0 mol% Ir₂S₃/ZnIn₂S₄ is also active for the reaction between phenylacetylene (**1a**) and benzyl mercaptan (**2a**) to produce benzyl styryl sulfide (**3a**). 99 % of benzyl mercaptane was converted after irradiated for 15 h, with a yield of 94% to benzyl styryl sulfide (**3a**), a performance superior to that over bare ZnIn₂S₄ (Table 1, entry 1). The amount of Ir₂S₃ loaded influences the performance of Ir₂S₃/ZnIn₂S₄ (Table 1, entries 2 and 3). Among the three Ir₂S₃/ZnIn₂S₄ nanocomposites (0.5, 1.0 and 2.0 mol%) investigated, Ir₂S₃/ZnIn₂S₄ nanocomposite with 0.5 mol% Ir₂S₃ loaded exhibited an optimum performance, with 97% of phenylacetylene converted and a yield of 95% to the desired product benzyl styryl sulfide (**3a**). Therefore, the following investigations were carried out over 0.5 mol% Ir₂S₃/ZnIn₂S₄ nanocomposite.

Similar to the reactions over bare ZnIn₂S₄, the visible light initiated thiol-yne reactions over 0.5 mol% Ir₂S₃/ZnIn₂S₄ nanocomposite can also be applied to a wide range of substrate scopes (Table 2). The hydrothiolation reactions between phenylacetylenes with different substituents and different thiols, including both aliphatic and aromatic thiols as well as thiophenols, led to desirable thiolated products with yields ranged in 70%–96%. As compared with bare ZnIn₂S₄, 0.5 mol% Ir₂S₃/ZnIn₂S₄ nanocomposite showed superior performance for all the thiol-yne reactions (Table 2, **3b–3l**). In particular, obvious improvement in the activity was observed over those bulky substrates. For example, the reactions of **1a** and 4-tert-butylbenzylthiol, **1a** and dodecyl mercaptan as well as **1a** and 2-naphthyl mercaptans gave yields of 89%, 76% and

Fig. 4. UV-visible diffuse reflectance spectra of ZnIn₂S₄, 0.5 mol% Ir₂S₃/ZnIn₂S₄, 1 mol% Ir₂S₃/ZnIn₂S₄, 2 mol% Ir₂S₃/ZnIn₂S₄.

Table 1

Light initiated hydrothiolation between benzyl mercaptane and phenylacetylene over Ir₂S₃/ZnIn₂S₄ under different conditions.

Entry	Catalyst	Conv ^a (%)	Yield of 3a ^b (%)
1	1 mol% Ir ₂ S ₃ /ZnIn ₂ S ₄	99	94
2	2 mol% Ir ₂ S ₃ /ZnIn ₂ S ₄	91	85
3	0.5 mol% Ir ₂ S ₃ /ZnIn ₂ S ₄	97	95
4	ZnIn ₂ S ₄	94	90
5 ^c	—	0	0
6 ^d	0.5 mol% Ir ₂ S ₃ /ZnIn ₂ S ₄	trace	trace
7 ^e	0.5 mol% Ir ₂ S ₃ /ZnIn ₂ S ₄	5	5

Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), cat. (10 mg), CH₃OH (4 mL), visible light irradiation for 15 h. ^a Calculated based on **2a**. ^b Based on GC analyses. ^c No catalyst. ^d Without light. ^e TEMPO was added in the reaction.

70% respectively to desirable hydrothiolated products **3f**, **3h** and **3j** over Ir₂S₃/ZnIn₂S₄, as compared with yields of 61%, 56% and 51% respectively over bare ZnIn₂S₄. In addition to the

Table 2

Investigations of the substrate scope of visible-light-initiated hydrothiolations of alkynes and alkenes over 0.5 mol% Ir₂S₃/ZnIn₂S₄.

$R^1\text{---}\equiv + R^2\text{---}HS \xrightarrow[\text{CH}_3\text{OH, rt}]{\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4} R^1\text{---}\text{CH=CH---S---}R^2$		
3		
$\text{or } R^3\text{---}\text{CH=CH} + R^2\text{---}HS \xrightarrow[\text{CH}_3\text{OH, rt}]{\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4} R^3\text{---}\text{CH}_2\text{---CH}_2\text{---S---}R^2$		
4		
$R^1 \text{ or } R^3 = \text{Aryl, Alkyl} \quad R^2 = \text{Aryl, Alkyl}$		

Reaction conditions: alkynes or styrene (0.12 mmol), thiols (0.1 mmol), Ir₂S₃/ZnIn₂S₄ (10 mg), CH₃OH (4 mL), visible light irradiation for 15 h. Conversion was calculated based on thiols; The amount of the products was calculated based on GC and GC-MS; The content in parentheses was the yields of the reaction over bare ZnIn₂S₄ according to Ref. [21].

Fig. 5. (a) Cycling of the hydrothiolation reaction between phenylacetylene and benzyl mercaptane over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ under visible light irradiation; (b) XRD patterns of (a) used $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ after three cycling reactions (1) and fresh $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ (2).

thiol-yne reactions, the introduction of Ir_2S_3 also promoted all the investigated thiol-ene reactions. 0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ showed superior performance for all the light initiated hydrothiolation reactions between styrene and different thiols, with better yields of 42%–82% to the desirable products, as compared with yields of 49%–63% over bare ZnIn_2S_4 (Table 2, 4a–4h). Similar to that observed over the thiol-yne reactions, the degree of improvement on the performance of thiol-ene reactions is more obvious in those bulky thiols. For example, the reactions between styrene and 4-*tert*-butylbenzylthiol or dodecyl mercaptan gave yields of 74% and 69% to the desired products (4c and 4f) over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, as compared with 55% and 50% respectively over bare ZnIn_2S_4 . It is obvious that the loading of Ir_2S_3 as a cocatalyst can promote the light initiated hydrothiolation reactions between unsaturated hydrocarbons with different thiols over ZnIn_2S_4 . $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ also shows high stability during the reactions. No obvious loss of the activity was observed after three cycling tests (Fig. 5(A)) and the catalyst after three runs showed almost unchanged XRD patterns (Fig. 5(B)).

Light initiated hydrothiolation reactions over ZnIn_2S_4 has been proposed to be a coupling of a photoredox cycle and a radical addition cycle, in which the first step involves the attack on the thiols by the photogenerated holes on ZnIn_2S_4 to generate the thiyl radicals. To investigate whether radicals are also involved in the hydrothiolation reactions over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, controlled experiment was carried out by addition of TEMPO, a radical trapping agent, into the reaction system. It was found that the introduction of TEMPO led to an almost complete quench of the hydrothiolation reaction, with the yield to the benzyl styryl sulfide significantly decreased to 5% under otherwise similar conditions (Table 1), indicating that radicals are also involved in the light initiated hydrothiolation reactions over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites. It is therefore proposed that the promoting effect on the light initiated hydrothiolation reaction by loading Ir_2S_3 on ZnIn_2S_4 should be ascribed to an improved efficiency in the photogeneration of the thiyl radicals, due to the introduction of Ir_2S_3 as a cocatalyst to improve the separation and transportation of the photogenerated charge

carriers. This assumption was confirmed by the EIS results. As shown in Figs. 6(a) and 6(e), EIS Nyquist plot of $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite shows a smaller radius as compared with that of bare ZnIn_2S_4 , indicating that the loading of Ir_2S_3 enhances the charge separation and transportation in ZnIn_2S_4 .

Since cocatalysts have been widely used to promote the separation and transportation of the photogenerated charge carriers in photocatalysis, several other generally used cocatalysts, including MoS_2 , NiS and Pd NPs, were also deposited on ZnIn_2S_4 and was denoted as $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$, $\text{NiS}/\text{ZnIn}_2\text{S}_4$ and $\text{Pd}/\text{ZnIn}_2\text{S}_4$, respectively. The preparations of $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$, $\text{NiS}/\text{ZnIn}_2\text{S}_4$ and $\text{Pd}/\text{ZnIn}_2\text{S}_4$ followed the procedures reported previously [27,31,37], with their XRD patterns showed in the supporting information Figs. S2–S4. The performance of the as-obtained ZnIn_2S_4 nanocomposites for light initiated hydrothiolation reaction was investigated. As shown in Figs. 6(b), 6(c) and 6(d), the loading of all three cocatalysts on ZnIn_2S_4 also improves the separation of photogenerated charge carriers

Fig. 6. Nyquist plots of experimental impedance data for bare ZnIn_2S_4 , $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$, $\text{NiS}/\text{ZnIn}_2\text{S}_4$ and $\text{Pd}/\text{ZnIn}_2\text{S}_4$ in the frequency range of 0.1–1.0×10⁵ Hz using an ac bias of 0 V vs Ag/AgCl without visible light irradiations in an aqueous solution containing $\text{K}_3[\text{Fe}(\text{CN})_6]$ (1 mmol/L), $\text{K}_4[\text{Fe}(\text{CN})_6]$ (1 mmol/L) and KCl (0.1 mol/L).

Table 3

Light initiated hydrothiolation between phenylacetylene and 1-dodecanethiol over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$, $\text{Pd}/\text{ZnIn}_2\text{S}_4$, $\text{NiS}/\text{ZnIn}_2\text{S}_4$ and bare ZnIn_2S_4 .

Entry	Catalyst	Conversion ^a	Yield ^b (%)	H ₂ (μmol)
1	0.5 mol% $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$	79	76	0.7
2	0.5 mol% $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$	55	54	13.2
3	0.5 mol% $\text{Pd}/\text{ZnIn}_2\text{S}_4$	60	59	1.9
4	0.5 mol% $\text{NiS}/\text{ZnIn}_2\text{S}_4$	41	39	3.9
5	ZnIn_2S_4	58	56	—

Reaction conditions: phenylacetylene (0.12 mmol), 1-dodecanethiol (0.1 mmol), cat. (10 mg), CH_3OH (4 mL), visible light irradiation for 15 h;

^a Conversion was calculated based on phenylacetylene. ^b The amount of the products was calculated based on GC and GC-MS analyses.

as evidenced from the smaller radius on their EIS Nyquist plots as compared with bare ZnIn_2S_4 , although NiS is not as efficient as the other three cocatalysts (Ir_2S_3 , MoS_2 and Pd) (Fig. 6). However, all the three cocatalysts (MoS_2 , Pd and NiS) loaded do not promote the hydrothiolation reaction between phenylacetylene and 1-dodecanethiol. Among them, $\text{MoS}_2/\text{ZnIn}_2\text{S}_4$ and $\text{Pd}/\text{ZnIn}_2\text{S}_4$ show comparable performance as that over bare ZnIn_2S_4 , while the loading of NiS even lower the activity for light initiated hydrothiolation reaction (Table 3). The obvious inconsistent between the catalytic performance and the results from the EIS Nyquist plots clearly indicated that, in addition to the improved efficiency in the generation of thiyl radicals, there is other factors influencing the performance of light initiated hydrothiolation reaction over these cocatalysts loaded ZnIn_2S_4 nanocomposites.

In the light initiated hydrothiolation reactions over these cocatalysts loaded ZnIn_2S_4 nanocomposites, we also notice that varied amount of hydrogen were generated, although no detectable hydrogen evolved over bare ZnIn_2S_4 , indicating that the loading of all the cocatalysts also promotes the hydrogen evolution. In addition, the amount of hydrogen evolved follows an order of $\text{MoS}_2/\text{ZnIn}_2\text{S}_4 > \text{NiS}/\text{ZnIn}_2\text{S}_4 > \text{Pd}/\text{ZnIn}_2\text{S}_4 > \text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$, a result not unexpected since both MoS_2 and NiS have been previously demonstrated to be good cocatalysts for photocatalytic hydrogen evolution over ZnIn_2S_4 . As previously

proposed in the light initiated hydrothiolation reactions over ZnIn_2S_4 , the reduction of the protons by the photogenerated electrons to produce the hydrogen consumes the protons [47,48], which is a detrimental side reaction to the light initiated hydrothiolation reactions and should be suppressed. Therefore, the loading of the cocatalysts on the surface ZnIn_2S_4 have dual functions. First, the loading of the cocatalyst can improve the efficiency on the photogeneration of the thiyl radicals, due to enhanced separation and transportation of the photogenerated charge carriers, which is beneficial for the light initiated hydrothiolation reaction. On the contrary, the loading of the the cocatalyst also promotes the photocatalytic hydrogen evolution, which is detrimental to the light initiated hydrothiolation reaction. Therefore, a suitable cocatalyst to promote the light initiated hydrothiolations over ZnIn_2S_4 should be able to improve the separation and transportation of the photogenerated charge carriers in ZnIn_2S_4 , but itself cannot act as the active sites for hydrogen evolution, as that observed over Ir_2S_3 , as shown in Scheme 1.

3. Conclusions

In conclusion, the loading of Ir_2S_3 on the surface of ZnIn_2S_4 was found to promote the light initiated thiol-ene and thiol-yne reactions. The superior performance of $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposite for the light initiated hydrothiolation reactions can be ascribed to an improved efficiency on the photogeneration of the thiyl radicals by loading of Ir_2S_3 as well as its inactivity for photocatalytic hydrogen evolution, a side reaction to the light initiated hydrothiolation reaction over ZnIn_2S_4 . This study provides an efficient and green strategy to synthesize thiolated products via the hydrothiolation of unsaturated hydrocarbons (alkenes and alkynes) with thiols over a semiconductor-based photocatalyst under visible light. This study also provides some guidances for the design and development of photocatalytic systems for light induced organic syntheses.

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Scheme 1. Promoting mechanism by loading Ir_2S_3 for visible-light-initiated hydrothiolations over ZnIn_2S_4 .

Graphical Abstract

Chin. J. Catal., 2021, 42: 409–416 doi: 10.1016/S1872-2067(20)63660-9

Efficient visible light initiated hydrothiolations of alkenes/alkynes over $\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$: Role of Ir_2S_3 Xinglin Wang, Yuanyuan Li, Zhaohui Li *
Fuzhou University

$\text{Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$ nanocomposites were obtained by one-pot solvothermal method, and the loading of Ir_2S_3 on the surface of ZnIn_2S_4 was found to promote the light initiated thiol-ene and thiol-yne reactions.

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Ir₂S₃/ZnIn₂S₄催化下可见光诱导发生的烯烃/炔烃的高效硫氢化反应: Ir₂S₃的作用

王星林, 李媛媛, 李朝晖*

福州大学化学学院, 能源与环境光催化国家重点实验室光催化研究室, 福建福州350116

摘要: C–S键的构建在化学中具有非常重要的意义. 利用硫醇和烯烃/炔烃的硫氢化反应来构建C–S键是一种绿色、可持续和低成本的方法. 本文以ZnCl₂, InCl₃, 硫代乙酰胺为前驱体, 在微量IrCl₃存在条件下, 通过一步溶剂热法制备得到了含有不同Ir摩尔比(0.5 mol%, 1 mol%和2 mol%)的Ir₂S₃/ZnIn₂S₄纳米复合材料, 并考察了它在可见光下诱导烯烃/炔烃的硫氢化反应中的催化性能. 以苄基硫醇和苯乙炔的硫氢化反应为模型反应, 发现在ZnIn₂S₄中引入微量的Ir₂S₃可明显提升其性能, 其中以0.5 mol% Ir₂S₃/ZnIn₂S₄为催化剂时反应性能最佳; 反应15 h后苄基硫醇的转化率为97%, 苄基苯乙烯基硫醚的产率为95%, 明显高于以未修饰的ZnIn₂S₄为催化剂时的转化率和产率. 在反应中加入自由基捕获剂TEMPO之后可淬灭该反应, 表明与未修饰的ZnIn₂S₄相同, 以Ir₂S₃/ZnIn₂S₄复合材料催化的硫氢化反应同样是由硫醇自由基诱发的反应. 这种微量Ir₂S₃对ZnIn₂S₄上光诱导硫氢化反应的提升作用在所考察的多个系列底物的反应中都有不同程度的体现, 尤其对于一些空间体积较大的底物, 其提升作用尤为明显, 表明微量Ir₂S₃的存在对ZnIn₂S₄上光诱导硫醇和烯烃/炔烃硫氢化反应的提升作用具有普适性. 通过研究负载不同助催化剂(MoS₂, NiS和Pd)的ZnIn₂S₄纳米复合材料在烯烃/炔烃硫氢化反应中的性能及其电化学交流阻抗, 我们发现, Ir₂S₃的存在可促进ZnIn₂S₄上光生电子空穴的分离, 从而有利于巯基自由基的生成, 同时还抑制了副物氢气的产生, 因此, 烯烃/炔烃的硫氢化反应性能显著提高. 该文提出了一种在可见光下利用半导体光催化来构建C–S键的绿色途径, 对于理解和设计新的光催化有机合成反应体系具有一定的指导意义.

关键词: 光催化; 硫化铟/ZnIn₂S₄; 烯烃; 炔烃; 硫氢化反应

收稿日期: 2020-05-19. 接受日期: 2020-06-25. 出版日期: 2021-03-05.

*通讯联系人. 电话/传真: (0591)22865855; 电子信箱: zhaohuili1969@yahoo.com

基金来源: 国家自然科学基金(21872031, U1705251); 闽江学者特聘教授科研启动基金.

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).