

Efficient visible light initiated hydrothiolations of alkenes/alkynes over Ir₂S₃/ZnIn₂S₄: Role of Ir₂S₃

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ABSTRACT

The hydrothiolations of alkynes/alkenes with thiols is an atom-economic and thus attractive method for the constructions of C–S bonds. Here $Ir_2S_3/ZnIn_2S_4$ 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% $Ir_2S_3/ZnIn_2S_4$ 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 $Ir_2S_3/ZnIn_2S_4$ 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 TiO₂ [20] and ZnIn₂S₄[21] have all been reported to realize the hydrothiolation reactions under visible light. In these photoredox systems, thiyls, the synthetically useful radicals generated in

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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 addtion, these reactions protocols can be applied to expaned substrate scopes.

Among the already reported photoredox systems for light initiated hydrothiolation reactions, ZnIn₂S₄, a promising semiconductor which has been widely used in a variety of photocatalytic applications [27-29], is in particular appealing since the hydrothiolations over ZnIn₂S₄ 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, ZnIn₂S₄ is cheap and non-toxic [30,31]. However, the light initiated hydrothiolation reactions for some bulky substrates over bare ZnIn₂S₄ are still not so high. Considering that the light initiated hydrothiolation reactions over ZnIn₂S₄ 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 ZnIn₂S₄ for light initiated hydrothiolation, Ir₂S₃ was loaded on the surface of ZnIn₂S₄ via a one-step solvothermal method and the as-obtained Ir₂S₃/ZnIn₂S₄ nanocomposites was used in the visible light initiated thiol-ene and thiol-yne coupling reactions. It was found that loading of Ir₂S₃ on the surface of ZnIn₂S₄ did promote the hydrothiolations of alkenes and alkynes, with an optimum performance observed over 0.5 mol% Ir₂S₃/ZnIn₂S₄ nanocomposite. The superior performance over Ir₂S₃/ZnIn₂S₄ nanocomposites can be ascribed to an improved efficiency on the photogeneration of the thiyl radicals by loading Ir₂S₃ as well as its inactivity for photocatalytic hydrogen evolution, a side reaction in the light initiated hydrothiolations over ZnIn₂S₄. 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 $Ir_2S_3/ZnIn_2S_4$, different amounts of IrCl₃ was dispersed in a mixed solution containing 30 mL of *N*,*N*-dimethylformamide (DMF) and 30 mL of ethylene glycol (EG). ZnCl₂ (0.136 g, 1mmol), InCl₃·4H₂O (0.586 g, 2mmol) 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 Ir₂S₃/ZnIn₂S₄ nanocomposites with different amount of Ir₂S₃ were denoted as *x* mol% Ir₂S₃/ZnIn₂S₄. Bare ZnIn₂S₄ was synthesized similarly in a reaction without the introduction of IrCl₃.

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 N₂ to remove any dissolved O₂. 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 μ m 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 ZnIn₂S₄ [27,44], Ir₂S₃/ZnIn₂S₄ nanocomposites with different loading amount of Ir₂S₃ were obtained by one-pot solvothermal method from ZnCl₂, InCl₃ and TAA in a mixed solvent of DMF and EG, with the presence of different amounts of IrCl₃. 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 ZnIn₂S₄ phase (JCPDS 65-2023) [31], indicating that the introduction of Ir species does not influence the formation of hexagonal ZnIn₂S₄ (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 4f7/2 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) ZnIn₂S₄; (b) 0.5 mol% Ir₂S₃/ZnIn₂S₄; (c) 1 mol% Ir₂S₃/ZnIn₂S₄; (d) 2 mol% Ir₂S₃/ZnIn₂S₄.

environments (Fig. 2(b)). Considering that Ir exists as Ir³⁺ and by comparison with the XPS of bare ZnIn₂S₄, the peaks with binding energy at 161.38 and 162.62 eV can be assigned to S $2p_{3/2}$ and S $2p_{1/2}$ in ZnIn₂S₄, while the other two peaks with binding energy at 161.77 and 162.89 eV can be attributed to S $2p_{3/2}$ and S $2p_{1/2}$ in Ir₂S₃, respectively. The formation of Ir₂S₃ on the surface of hexagonal ZnIn₂S₄ is not unexpected since previous studies also demonstrated that the surface deposited PtS was obtained via a photoreduction of PtCl₆^{2–} over ZnIn₂S₄ [46]. Both Zn 2*p*, with binding energies located at 1021.52 and 1044.55 eV for Zn 2*p*_{3/2} and 2*p*_{1/2}, and In 3*d*, located at 444.83 and 452.34 eV, in the as-obtained Ir₂S₃/ZnIn₂S₄, slightly shift to higher binding energies as compared with those in bare ZnIn₂S₄, indicating the existence of the interaction between the surface of deposited Ir₂S₃ and ZnIn₂S₄ (Figs. 2(c), (d)). The SEM image of 0.5 mol% Ir₂S₃/ZnIn₂S₄ shows that it consists of flower-like microspheres with dimension of ca. $2-3 \mu m$ (Fig. 3(a)). The TEM image shows that each microsphere is assembled by very thin nanosheets (Fig. 3(b)). As compared with bare ZnIn₂S₄, it is obvious that the deposition of Ir₂S₃ on the surface of ZnIn₂S₄ does not change its morphology. The HRTEM image shows that Ir₂S₃ nanoparticles of ca. 6 nm, were deposited on the nanosheet of ZnIn₂S₄. Clear lattice fringes of 0.291 nm, corresponding to (102) crystallographic plane of Ir₂S₃, can be observed. In addition, lattice fringes of 0.322 nm, which belongs to (102) crystallographic plane of hexagonal ZnIn₂S₄, are also observed, which again confirms the deposition of Ir₂S₃ in hexagonal ZnIn₂S₄. The EDX mapping of 0.5 mol% Ir₂S₃/ZnIn₂S₄ nanocomposite also confirms the presence of Ir and its even distribution on the surface of ZnIn₂S₄ (Fig. S1).

The UV-vis DRS of $Ir_2S_3/ZnIn_2S_4$ nanocomposites with different amount of Ir_2S_3 were displayed in Fig. 4. All the $Ir_2S_3/ZnIn_2S_4$ 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 $Ir_2S_3/ZnIn_2S_4$ 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% Ir₂S₃/ZnIn₂S₄ 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% $Ir_2S_3/ZnIn_2S_4$ 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 $ZnIn_2S_4$, 0.5 mol% $Ir_2S_3/ZnIn_2S_4$, 1 mol% $Ir_2S_3/ZnIn_2S_4$, 2 mol% $Ir_2S_3/ZnIn_2S_4$.

Table 1

Light initiated hydrothiolation between benzyl mercaptane and phenylacetylene over $Ir_2S_3/ZnIn_2S_4$ under different conditions.



Reaction conditions: **1a** (0.12 mmol), **2a** (0.1 mmol), cat. (10 mg), CH₃OH (4 ml), visible light irradiation for 15 h. ^aCalculated based on **2a**. ^bBased on GC analyses. ^cNo catalyst. ^dWithout light. ^fTEMPO 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 $0.5 \text{ mol}\% \text{ Ir}_2\text{S}_3/\text{ZnIn}_2\text{S}_4$.



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 Ir₂S₃/ZnIn₂S₄ under visible light irradiation; (b) XRD patterns of (a) used Ir₂S₃/ZnIn₂S₄ after three cycling reactions (1) and fresh Ir₂S₃/ZnIn₂S₄ (2).

thiol-yne reactions, the introduction of Ir₂S₃ also promoted all the investigated thiol-ene reactions. 0.5 mol% Ir₂S₃/ZnIn₂S₄ showed superior performance for all the light initiated hyrothiolation 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 ZnIn₂S₄ (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 ordodecyl mercaptan gave yields of 74% and 69% to the desired products (4c and 4f) over Ir2S3/ZnIn2S4, as compared with 55% and 50% respectively over bare ZnIn₂S₄. It is obvious that the loading of Ir₂S₃ as a cocatalyst can promote the light initiated hydrothiolation reactions between unsaturated hydrocarbons with different thiols over ZnIn₂S₄. Ir₂S₃/ZnIn₂S₄ 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 ZnIn₂S₄ 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 ZnIn₂S₄ to generate the thiyl radicals. To investigate whether radicals are also involved in the hydrothiolation reactions over Ir₂S₃/ZnIn₂S₄, 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 Ir₂S₃/ZnIn₂S₄ nanocomposites. It is therefore proposed that the promoting effect on the light initiated hydrothiolation reaction by loading Ir₂S₃ on ZnIn₂S₄ should be ascribed to an improved efficiency in the photogeneration of the thiyl radicals, due to the introduction of Ir₂S₃ 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 $Ir_2S_3/ZnIn_2S_4$ nanocomposite shows a smaller radius as compared with that of bare ZnIn₂S₄, indicating that the loading of Ir_2S_3 enhances the charge separation and transportation in ZnIn₂S₄.

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 MoS₂, NiS and Pd NPs, were also deposited on ZnIn₂S₄ and was denoted as MoS₂/ZnIn₂S₄, NiS/ZnIn₂S₄ and Pd/ZnIn₂S₄ and Pd/ZnIn₂S₄ and Pd/ZnIn₂S₄ 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 ZnIn₂S₄ 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 ZnIn₂S₄ also improves the separation of photogenerated charge carriers



Fig. 6. Nyquist plots of experimental impedance data for bare $ZnIn_2S_4$, $Ir_2S_3/ZnIn_2S_4$, $MoS_2/ZnIn_2S_4$, $NiS/ZnIn_2S_4$ and $Pd/ZnIn_2S_4$ in the frequency range of $0.1-1.0 \times 10^5$ Hz using an ac bias of 0 V vs Ag/AgCl without visible light irradiations in an aqueous solution containing K_3 [Fe(CN)₆] (1 mmol/L), K_4 [Fe(CN)₆] (1 mmol/L) and KCl (0.1 mol/L).

Table 3

	+ CH ₃ (CH ₂) ₁₁ SH -	cat.	\bigcirc	∕ ^S ∕ _{(CH₂)₁₁CH₃}
Entry	Catalyst	Conversion ^a	Yield b (%)	H ₂ (µmol)
1	0.5 mol% Ir ₂ S ₃ /ZnIn ₂ S ₄	79	76	0.7
2	0.5 mol% MoS ₂ /ZnIn ₂ S ₄	55	54	13.2
3	0.5 mol% Pd/ZnIn ₂ S ₄	60	59	1.9
4	0.5 mol% NiS/ZnIn ₂ 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), CH₃OH (4 mL), visible light irradiation for 15 h; ^a Conversion was calculated based on phenylacetylene. ^bThe 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 ZnIn₂S₄, although NiS is not as efficient as the other three cocatalysts (Ir₂S₃, MoS₂ and Pd) (Fig. 6). However, all the three cocatalysts (MoS₂, Pd and NiS) loaded do not promote the hydrothiolation reaction between phenylacetylene and 1-dodecanethiol. Among them, MoS₂/ZnIn₂S₄ and Pd/ZnIn₂S₄ show comparable performance as that over bare ZnIn₂S₄, 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 ZnIn₂S₄ nanocomposites.

In the light initiated hydrothiolation reactions over these cocatalysts loaded ZnIn₂S₄ nanocomposites, we also notice that varied amount of hydrogen were generated, although no detectable hydrogen evolved over bare ZnIn₂S₄, indicating that the loading of all the cocatalysts also promotes the hydrogen evolution. In addition, the amount of hydrogen evolved follows an order of MoS₂/ZnIn₂S₄> NiS/ZnIn₂S₄> Pd/ZnIn₂S₄> Ir₂S₃/ZnIn₂S₄, a result not unexpected since both MoS₂ and NiS have been previously demonstrated to be good cocatalysts for photocatalytic hydrogen evolution over ZnIn₂S₄. As previously



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

proposed in the light initiated hydrothiolation reactions over ZnIn₂S₄, 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 ZnIn₂S₄ 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 photogenrated 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 ZnIn₂S₄ should be able to improve the separation and transportation of the photogenerated charge carriers in ZnIn₂S₄, but itself cannot act as the active sites for hydrogen evolution, as that observed over Ir₂S₃, as shown in Scheme 1.

3. Conclusions

In conclusion, the loading of Ir₂S₃ on the surface of ZnIn₂S₄ was found to promote the light initiated thiol-ene and thiol-yne reactions. The superior performance of Ir₂S₃/ZnIn₂S₄ nanocomposite for the light initiated hydrothiolation reactions can be ascribed to an improved efficiency on the photogeneration of the thiyl radicals by loading of Ir₂S₃ as well as its inactivity for photocatalytic hydrogen evolution, a side reaction to the light initiated hydrothiolation reaction over ZnIn₂S₄. 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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$Ir_2S_3/ZnIn_2S_4$ 催化下可见光诱导发生的烯烃/炔烃的高效硫氢化反应: Ir_2S_3 的作用

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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相同,以Ir₂S₃/ZnIn₂S₄复合材料催化的硫氢化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;硫化铱/ZnIn₂S₄;烯烃;炔烃;硫氢化反应

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