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Visible-light-initiated one-pot clean synthesis of nitrone from nitrobenzene and benzyl alcohol over CdS photocatalyst

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ABSTRACT

The controlled visible-light mediated conversion of nitroaromatics to versatile nitrogen-containing intermediates is of great significance but still remains a challenge. Herein, we report for the first time a facile visible-light-initiated one-pot strategy for clean and efficient synthesis of nitrone from nitrobenzene and benzyl alcohol. It integrates the controlled photocatalytic reduction of nitrobenzene to phenylhydroxylamine by photogenerated electrons with the selective photocatalytic oxidation of benzyl alcohol to benzaldehyde by photoinduced holes over a low-cost CdS photocatalyst with a suitable reduction capability, followed by spontaneous condensation of the as-formed hydroxylamine and aldehyde at ambient pressure and room temperature. Furthermore, by modulating cocatalyst and illumination time, for the conversion of the same reactants, the other two useful nitrogen-containing compounds, imine and secondary amine, were also successfully synthesized. The reaction mechanisms for flexible synthesis of the three target products are proposed.

1. Introduction

The nitrogen-containing compounds including nitrones, imines and secondary amines, etc. are versatile organic building blocks for the synthesis of fine chemicals, pharmaceuticals and agricultural chemicals [1]. Nitrones can be used as radical spin-traps [2], antioxidants [3], and enzyme inhibitors [4] due to their spin-trapping ability. Many nitrogen-containing heterocycles, such as isoxazolidines and isoxazolines, can be obtained from nitrones through 1,3-dipolar cycloadditions [5]. These heterocycles can be transformed into amino-alcohols or β-lactams [6], which are used to produce many prescribed drugs. Therefore, the development of a facile and clean method for the synthesis of valuable nitrogen-containing compounds, especially nitrone, is very important.

Up to now, nitrones are commonly prepared by the following traditional synthetic routes (Fig. 1): (1) oxidation of imines [7] or secondary amines [8] (Route A); (2) condensation of hydroxylamines with carbonyl compounds (Route B) [9]; (3) N-alkylation of oximes (Route C) [10]; (4) a tandem process including a reduction of nitro compounds under higher H_2 pressure with a subsequent condensation with aldehyde (Route D). Routes A and B consist of multistep oxidation and reduction processes, consuming a great deal of chemical reagents. Moreover, a careful control of the reaction conditions is required to obtain high selectivity. Regarding Route C, the oxime anions as an intermediate is preliminarily synthesized by the stoichiometric reaction of aldehyde with hydroxylamine hydrochloride followed by reacting with sodium hydroxide, and then the nitrone is synthesized by N-alkylation [10]. The above multistep processes (Routes A-C) would lead to a high production cost and a heavy environmental pollution. In a direct and green approach, nitrone can be obtained by one-pot reaction from nitro compounds and aldehydes (Route D). Cisneros et al. [11] and Li et al. [12] successfully prepared nitrone from nitro compounds and aldehydes over Pt/C and Pt/MOF under 5–34 bar of high H_2 pressure, in which the tandem process circumvents the unstable hydroxylamine storage issues and also simplifies synthetic step. However, the noble metal Pt and harsh reaction conditions (high H_2 pressure) are required. The Pt/MOF system is only applicable for conversion of nitromethane [12]. Moreover, the deep reduction of reactants, intermediates and products depresses the selectivity to nitrone. Thus the large-scale industrial application is limited. Therefore, it is highly desirable to develop a facile and practical method to synthesize nitrone.

Heterogeneous photocatalysis has been considered as one of the most promising alternatives for selective synthesis of organic chemicals [13]. From references [14], alcohols can not only serve as substrate to be oxidized to aldehyde by photogenerated holes,

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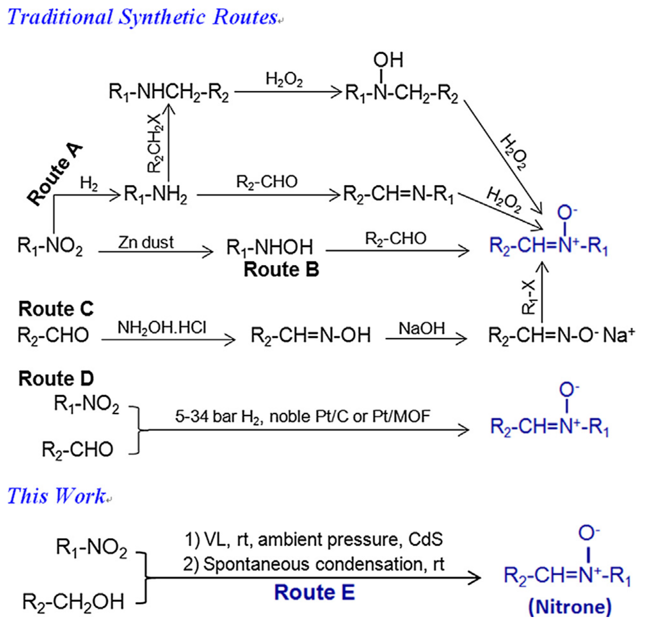

Fig. 1. Proposed synthetic routes of nitrones.

but also provide hydrogen for reduction reactions. Nitro compounds can be transformed into amines by photoinduced electrons through the intermediates including hydroxylamines and nitroso compounds [15]. If both photooxidation and photoreduction simultaneously take place in a same reaction system, the two half-reactions can be remarkably promoted each other owing to the efficient recombination inhibition of photoinduced charge carriers [16]. Moreover, from Route B, we know that nitrone can be prepared via condensation of hydroxylamine with aldehyde. Therefore, we envisaged the nitrone might be synthesized from nitro compound and alcohol through a facile visible-light-mediated one-pot strategy over low-cost CdS photocatalyst (Route E). The as-formed hydroxylamines from nitro compounds directly react with the as-produced aldehydes from alcohols to produce nitrones. The proposed approach not only takes over the merits of Route D, but also avoids the use of high H_2 pressure and noble metals that definitely required in Route D. In addition, benzyl alcohol is used to replace benzaldehyde, which further simplifies the reaction step and also reduces cost. More importantly, the proposed Route E can also overcome the shortcomings of Route D regarding the deep reduction of the reactants, intermediate and products under high H_2 pressure, which hopefully allows us to obtain high selectivity to nitrone. In order to realize the proposed Route E, to efficiently control reduction of nitrobenzene to hydroxylamine is the key for a facile, low-cost and sustainable production of nitrone. Till now, only amines and imines can been obtained by light-driven one-pot synthesis from nitrobenzene and benzyl alcohol because of the difficulty of precisely controlling reduction degree of nitrobenzene to hydroxylamine [17]. Unfortunately, to the best of our knowledge, there is no report regarding the photocatalytic synthesis of phenylhydroxylamine, not to mention one-pot synthesis of nitrones from nitro compound and alcohol. Furthermore, the relationship between selectivity of the production (imines or secondary amines) and the nature of catalyst remains unclear.

Herein, for the first time, we report a facile visible-light-initiated one-pot strategy for efficient synthesis of nitrone with 91% selectivity at 77% conversion after only 25 min of illumination by visible light (89% selectivity at 91% conversion, 30 min) by using nitrobenzene and benzyl alcohol as starting reactants. This method integrates the controlled photocatalytic reduction of nitrobenzene to phenylhydroxylamine by photoinduced electrons over a low-cost CdS photocatalyst with a suitable reduction capability and the photocatalytic oxidation of benzyl alcohol to benzaldehyde by photogenerated holes, followed by a spontaneous condensation of the as-formed phenylhydroxylamine and benzaldehyde. Both photocatalyzed reduction and oxidation half-reactions can be efficiently promoted each other owing to the efficient recombination inhibition of photogenerated charge carriers. In addition, by tuning cocatalyst and illumination time, for the conversion of the same reactants, the other two versatile nitrogen-containing intermediates, imine and secondary amine, have been successfully synthesized. Finally, the tentative reaction mechanisms for flexible synthesis of the three target products by the developed visibly-light-initiated one-pot synthetic strategy are proposed. This work not only presents a novel and efficient method for a facile synthesis of nitrone, but also reveals the relationship between the properties of different CdS-based catalysts and the selectivity to nitrone, imine and secondary amine.

2. Experimental section

2.1. Chemicals

Cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$), nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), thioacetamide (CH_3CSNH_2), ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) and benzyl alcohol ($C_7H_8O$) were purchased from Tianjin Guangfu Fine Chemical Research Institute. Thiourea (CH_4N_2S) was gained from Tianjin Bodi Chemical Co. Ltd. Ethylene glycol ($C_2H_6O_2$) and acetonitrile (C_2H_3N) were gained from Tian in Fuyu Fine Chemical Co. Ltd. Nitrobenzene ($C_6H_5NO_2$) was purchased from Fuchen (Tianjin) Chemical reagent Co. Ltd. Phenylamine (C_7H_9N) was purchased from Tianjin Damao Chemical Reagent Factory. Trifluorotoluene ($C_7H_5F_3$) was gained from Aladdin. Benzaldehyde (C_6H_5CHO) was purchased from Xilong Chemical Co. Ltd. All the chemicals are analytical grade and directly used without further processing. Deionized water was used in all procedures and photocatalytic experiments were implemented under nitrogen atmosphere.

2.2. Preparation of CdS nanoparticles

The CdS NPs were prepared according to the previously reported literature with some modifications [18]. Briefly, 0.533 g cadmium acetate (2 mmol) and 0.451 g thioacetamide (6 mmol) were dissolved in 50 ml ethylene glycol and 5 ml H_2O mixed solution by ultrasonic processing. Above mixed solution was transferred into an 80 ml Teflon-lined autoclave and maintained at 160 °C for 18 h. Next, the autoclave was cooled to room temperature and the orange precipitates were washed three times with deionized water and once with absolute alcohol via centrifugation. The final product was dried at 65 °C in an oven and grinded by using the agate mortar.

2.3. Preparation of MoS_2/CdS

The MoS_2 was decorated on the CdS NPs by hydrothermal method [19]. In a typical process, 100 mg obtained CdS NPs were dispersed in 50 ml deionized water by ultrasonic processing, then, 39 mg of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and 12 mg thiourea were dissolved in the above mixture by stirring 10 min. The mixture was transferred into an 80 ml Teflon-lined autoclave and maintained at 160 °C for 18 h. Next, the autoclave was cooled to room temperature and the dark green precipitates were washed with deionized water and alcohol via centrifugation. The final product was dried at 65 °C in an oven. The theoretical loading ratio of MoS_2 on CdS

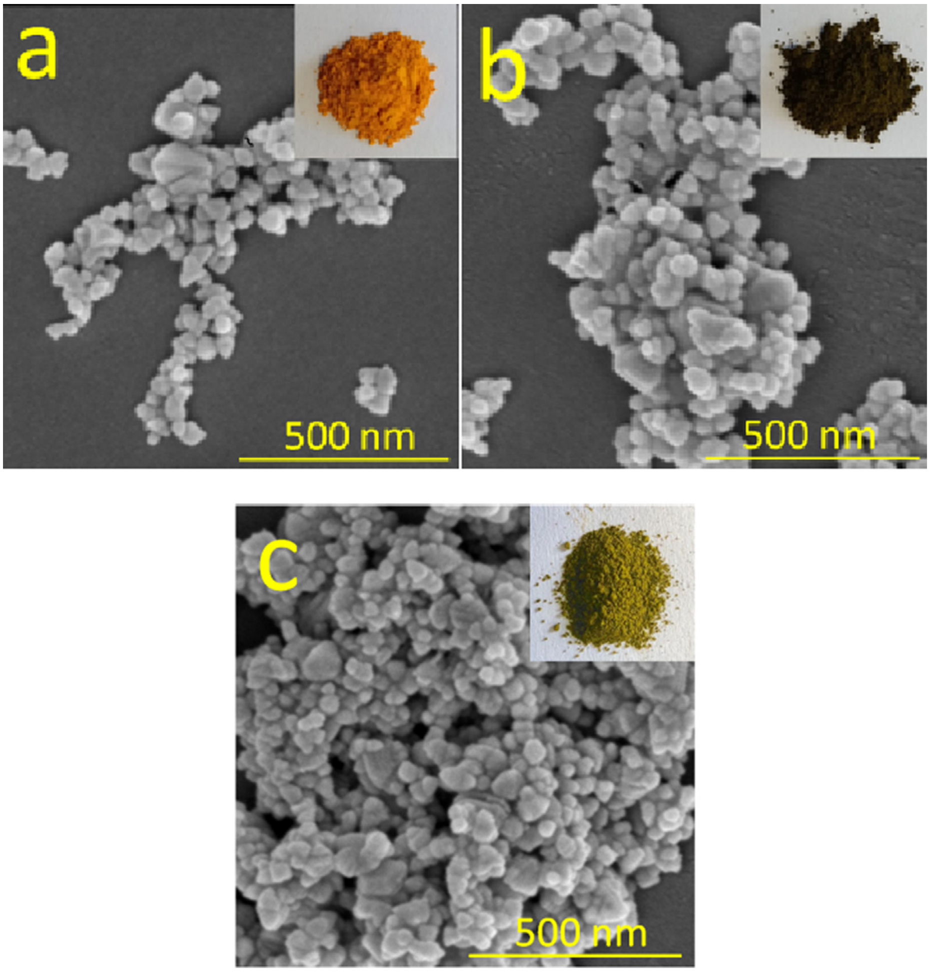

Fig. 2. SEM images of CdS (a), MoS_2/CdS (b), and Ni/CdS (c). The photographs of CdS (inset in a), MoS_2/CdS (inset in b), and Ni/CdS (inset in c).

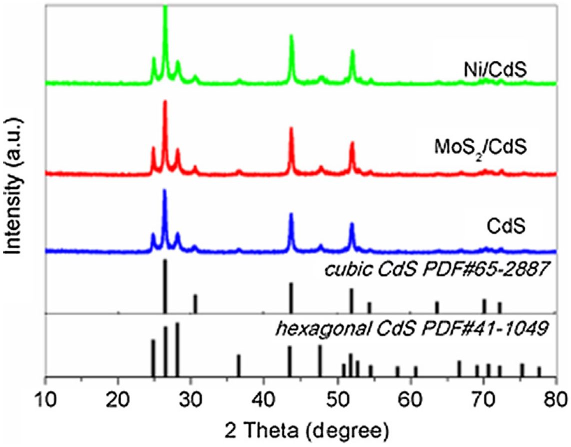

Fig. 3. XRD patterns of CdS, MoS_2/CdS and Ni/CdS.

is 5 wt%, and were referred to MoS_2/CdS-5 (abbreviated in MoS_2/CdS). Analogously, the resultant MoS_2-CdS composites with various amounts of MoS_2 were denoted as MoS_2/CdS-1, MoS_2/CdS-3, MoS_2/CdS-8 and MoS_2/CdS-10, respectively.

2.4. Preparation of Ni/CdS catalyst

According to Ref. [14a], 100 mg obtained CdS were dispersed in 20 ml CH_3CN by ultrasonic processing. Then 1430 μl $NiCl_2{\cdot}6H_2O$ aqueous (60 μ mol, 1 g/100 ml) was added above mixed solution. The mixed solution was sealed in a flask (100 ml) and thoroughly replaced the air by N_2 under stirring. Subsequently, the mixture was irradiated with a 300 W Xe lamp (PLSSXE300/300UV, Perfectlight) with a 420 nm cut-off filter for 5 min. The Ni/CdS was obtained via centrifugation and dried at 65 °C in an oven. The theoretical loading ratio of metallic nickel on CdS is 3.5 wt%, and were referred to Ni/CdS-3.5 (abbreviated in Ni/CdS). Analogously, the resultant Ni-CdS composites with various amounts of Ni were denoted as Ni/CdS-0.5, Ni/CdS-2, Ni/CdS-5 and Ni/CdS-6.5, respectively.

2.5. Characterization of materials

Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-5600LV SEM instrument. X-ray diffraction (XRD) was conducted on a D/Max 2400 diffractometer with monochromatic Cu Kα source. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 XPS system with a monochromatic Al Kα X-ray source. All the binding energies were referenced to the C 1s peak at 284.8 eV. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area, and the pore size distributions was calculated from an adsorption branch of the isotherm via the Barrett–Joyner–Halenda (BJH) model (3H-2000PS, BeiShiDe Instrument). The UV–vis diffuse reflectance spectra (DRS) were recorded on a JASCO V-550 UV–vis spectrometer. The Mott-Schottky plots measurements were performed on an electrochemical workstation (CHI660e) in 0.2 M Na_2SO_4 aqueous solution in a standard three electrode system with the as-prepared samples coated indium tin oxide (ITO) glass as the working electrode, Ag/AgCl as reference electrode, and the Pt wire as the counter electrode. The alternating current frequency is 1200 Hz.

2.6. Photocatalytic performance test

A flask (10 ml, Synthware) was used as the reaction container, and after 0.2 mmol nitrobenzene, 3 ml benzyl alcohol and 10 mg catalyst had been added, the flask was sealed and thoroughly replaced the air by N_2 under stirring. Subsequently, the mixture was illuminated by the Xe lamp for a certain time with continuous stirring. The reaction temperature was kept at 20 °C by a circulating bath during the experiment process. The generated H_2 was quantified by a gas chromatography (GC 9790 II, FuLi Instruments) equipped with a thermal conductive detector (TCD) and nitrogen as the carrier gas. The organic products were quantified by the GC and liquid chromatogram analysis (LC). The GC with a SE-54 capillary column (30 m × 0.32 mm × 0.50 μm), flame ionization detector (FID), argon as the carrier gas and trifluorotoluene as the internal standard. The LC was performed HP 1100 liquid chromatogram with a Nova – Pak C_{18} column and DAD detector, the mobile phase H_2O:methanol 3:7 and a flow rate of 1.0 ml/min. The qualitative analysis of the products was performed by gas chromatography-mass spectrometry (GC–MS, HP6890/5973MSD and 7000B, Agilent).

3. Results and discussion

3.1. Preparation and characterization of CdS based photocatalysts

CdS nanoparticles (NPs) were synthesized by a previously reported solvothermal method with some modifications [18]. The MoS_2 or Ni co-catalyst was deposited on the surface of CdS NPs to prepare MoS_2/CdS and Ni/CdS by hydrothermal and photodeposition methods, respectively [19,14a]. Scanning electron microscope (SEM) images of the CdS, MoS_2/CdS and Ni/CdS are shown in Fig. 2. The CdS features irregular nanoparticles with the size from 30 nm to 140 nm, and there is no significant effect on the morphology and size of CdS NPs when decorated MoS_2 and Ni. Moreover, the photographs (inset in Fig. 2) of CdS, MoS_2/CdS and Ni/CdS feature the orange color for CdS NPs, while the MoS_2/CdS and Ni/CdS show palm green[1] and yellow green nanoparticles, respectively. This indicates that the MoS_2 and Ni have been successfully decorated on CdS NPs. The X-ray diffraction (XRD) patterns (Fig. 3) confirm a mixture of cubic (PDF#65-2887) and hexagonal (PDF#41-1049) phases of CdS NPs. There is not visible diffraction peak towards molybdenum sulfide or Ni species on MoS_2/CdS and Ni/CdS to be resolved, ascribed to the low loading and/or small size. X-ray photoelectron spectroscopy (XPS) spectra of CdS, MoS_2/CdS and Ni/CdS are shown in Figs. 4–6. The Mo 3d spectrum can be fitted into two subsets of peaks at 228.2 and 231.7 eV attributed to Mo^{4+}, and at 232.7 and 235.4 eV ascribed to Mo^{6+}. The Mo^{4+} was found to be the dominant oxidation state, and the existed Mo^{6+} can be ascribed to exposure to air [20]). From Ni 2p spectrum in Fig. 6d, the peak appearing at 852.2 eV is assigned to metallic Ni, and at 856.0 eV ascribed to NiO. The existence of NiO originates from the oxidation of the deposited Ni while the catalyst is exposed to air [14a]. The surface area of CdS NPs, MoS_2/CdS and Ni/CdS are 16.1 $m^2\ g^{-1}$, 16.5 $m^2\ g^{-1}$ and 14.5 $m^2\ g^{-1}$, respectively (Fig. 7), further showing no obvious change in the CdS structure after loading MoS_2 or Ni cocatalysts.

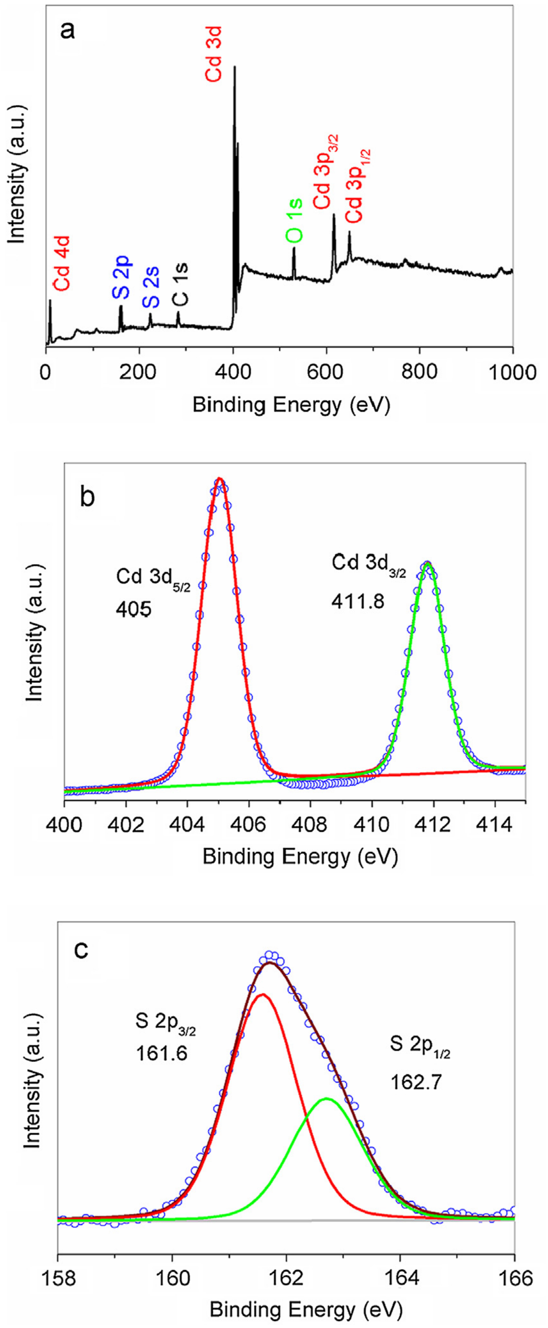

Fig. 4. XPS spectra of CdS: (a) full spectrum, (b) Cd 3d, (c) S 2p.

The photocatalysis is strongly dependent on light absorption capacity and the charge-carriers separation efficiency, mainly affected by the energy band structure of photocatalyst. Furthermore, the position of valence band (VB) and conduction band (CB) of a photocatalyst determines its oxidation and reduction capability, which is crucial to the product distribution of photocatalytic organic reactions. The band gap and the positions of VB and CB were determined by combining UV–Vis diffuse reflectance spectroscopy and VB-XPS (Fig. 8). The UV–Vis diffuse reflectance spectra (Fig. 8a) indicate the increased visible light absorption with a wide absorption tail if MoS_2 or Ni (NiO_x) is loaded on CdS NPs. The corresponding Tauc plots coming from the UV–Vis diffuse reflectance spectra are shown in Fig. 8a (inset), and the band gaps

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[1] For interpretation of color in Fig. 2, the reader is referred to the web version of this article.

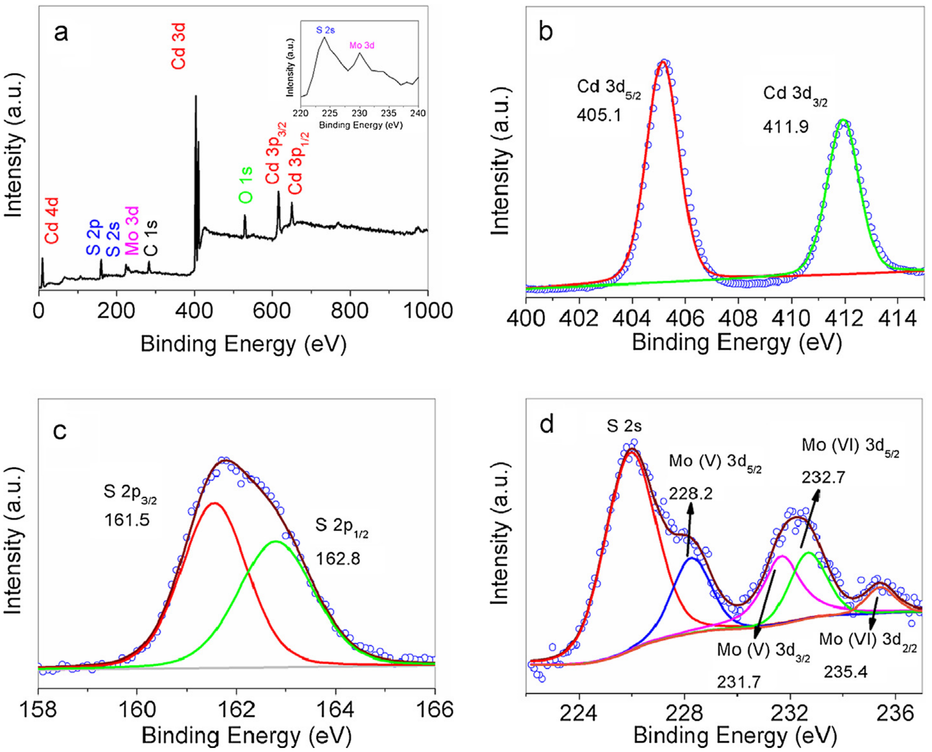


Fig. 5. XPS spectra of MoS_2/CdS: (a) full spectrum, (b) Cd 3d, (c) S 2p, (d) Mo 3d.

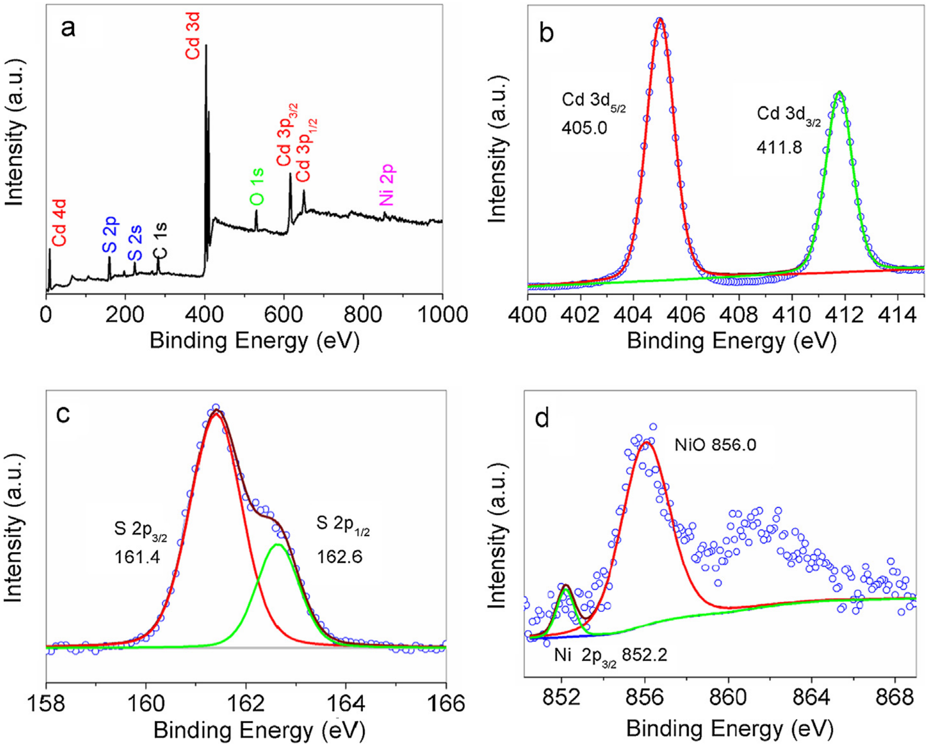


Fig. 6. XPS spectra of Ni/CdS: (a) full spectrum, (b) Cd 3d, (c) S 2p, (d) Ni 2p.

of CdS, MoS_2/CdS and Ni/CdS are 2.28, 2.23 and 2.26 eV, respectively. Based on XPS valence band spectra (Fig. 8b), the top of VB of CdS, MoS_2/CdS and Ni/CdS are 1.35, 1.06 and 1.10 eV vs. E_F (the potential of the Fermi level), respectively. The Fermi levels of CdS, MoS_2/CdS and Ni/CdS are obtained from Mott-Schottky plots (Fig. S1) are −0.44, −0.48 and −0.57 V vs. RHE (reversible hydrogen electrode), respectively. The top of VB of CdS, MoS_2/CdS and Ni/CdS are calculated to be 1.79, 1.51 and 1.67 eV vs. RHE [21]. Fig. 8c displays the electronic band structure of CdS, MoS_2/CdS and Ni/CdS. The CB of CdS is −0.49 eV. MoS_2/CdS and Ni/CdS

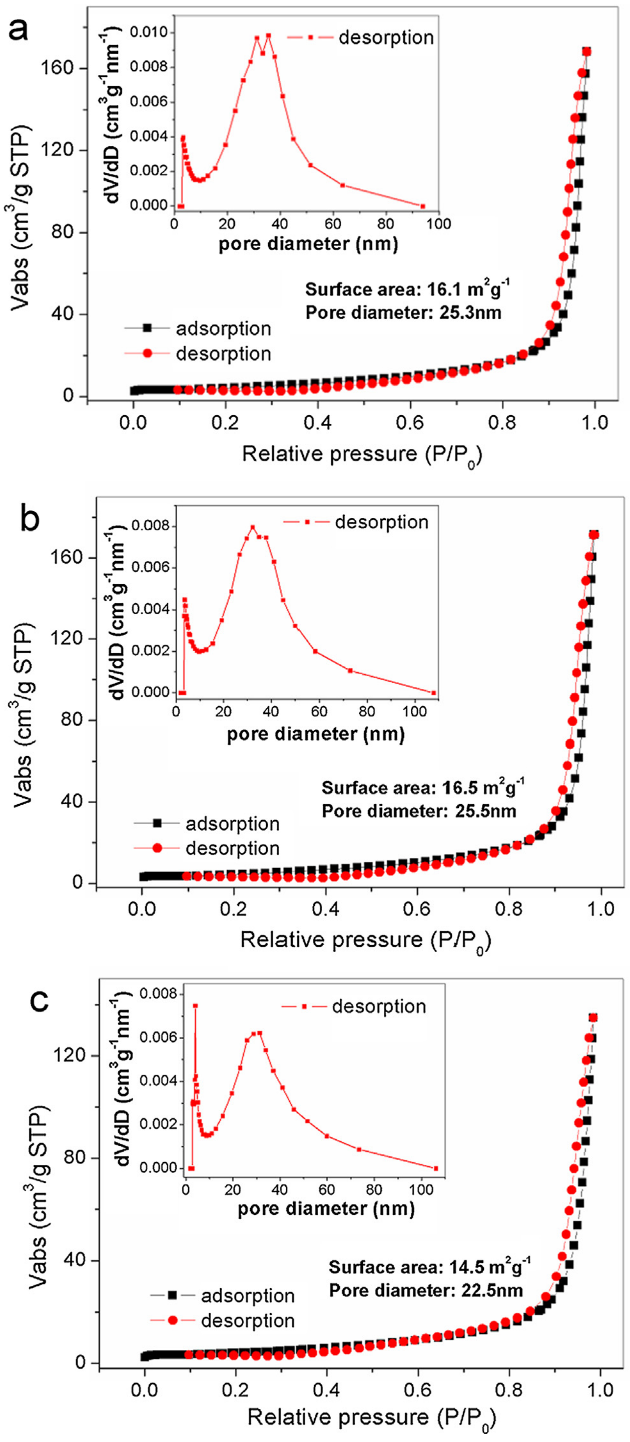


Fig. 7. N_2 sorption isotherms and BET surface area of CdS (a), MoS_2/CdS (b) and Ni/CdS (c). Inset: pore size distribution.

indicate a more negative CB by 0.2 eV and 0.1 eV than that of CdS, respectively. This implies that CdS has a relatively low reduction capability [19]. On the other hand, CdS shows higher VB than MoS_2/CdS and Ni/CdS by 0.25 and 0.12 eV, respectively, which endows CdS with higher oxidation capability than the other two photocatalysts. The relatively low reduction capability makes it possible for CdS to controllably reduce nitrobenzene to phenylhydroxylamine by photogenerated electrons. As a result, the proposed visible-light-initiated one-pot method (Route E in Fig. 1) can be realized.

3.2. Photocatalytic properties for nitrone clean synthesis

Based on the results of controlled experiments, both imine and nitrone can be formed by the spontaneous condensation of benzaldehyde with aniline (Fig. S2) and phenylhydroxylamine (Figs. S3 and S4) at ambient pressure and room temperature, respectively. However, nitrosobenzene cannot react with benzaldehyde (Fig. S5). Therefore, to controllably obtain phenylhydroxylamine without further reduction to aniline is a key for the synthesis of nitrone with high selectivity. With respect to the proposed Route E for nitrone synthesis, we design a one-pot two-stage process: one is photocatalytic stage containing the controlled reduction of nitrobenzene to phenylhydroxylamine and the selective oxidation of benzyl alcohol to benzaldehyde; the other is the spontaneous condensation between the as-formed phenylhydroxylamine and benzaldehyde. Fig. S6 further confirms that the designed one-pot two-stage process works well, and the as-formed phenylhydroxylamine at the 1st stage gradually decreases while the desired nitrone gradually increases when the reaction mixture stands for 2 h.

By using nitrobenzene and benzyl alcohol as reactants, the reaction properties of CdS, MoS_2/CdS and Ni/CdS photocatalysts for nitrone synthesis via one-pot two-stage approach were tested. Table S1 summarizes the photocatalytic results for diverse illumination times, and the results for the combined photocatalytic process and subsequent condensation is presented in Table 1. Fig. S7 shows the time-dependent change in the amounts of products and no visible change in products distribution if the standing time reaches up to 8 h. In order to make sure the complete condensation, we stand the photocatalytic reaction mixture more than 12 h. To our delight, the results verify the flexible synthesis of nitrone, imine, and secondary amine from nitrobenzene and benzyl alcohol over the low-cost CdS-based photocatalysts by tuning cocatalyst and illumination time. The blank experiments (Table S1 and 1, entry 5,6,11,12,18,19) reveal only negligible transformation of nitrobenzene and benzyl alcohol. Interestingly, in combination of the photocatalytic process over bare CdS NPs and the subsequently spontaneous condensation process, nitrone is successfully synthesized. However, only trace nitrone is obtained in the absence of subsequent condensation process (entry 1,2 in Table S1). The extension of illumination time heightens the conversion of nitrobenzene and benzyl alcohol, but it depresses the selectivity to nitrone (Table 1, entry 1–4). Thanks to the suitable reduction capability of CdS photocatalyst and the efficient inhibition of recombination of photogenerated charge carriers by the integrating effect of the simultaneous photoreduction of nitrobenzene and photooxidation of benzyl alcohol half-reactions, the 91% selectivity to nitrone at 77% conversion (89% selectivity at 91% conversion) is obtained after only 25–30 min of illumination by visible light (Table 1, entry 1,2). In a word, we develop a facile visible-light-initiated one-pot strategy for efficient synthesis of nitrone at ambient pressure and room temperature. To the best of our knowledge, this is the first report on efficient synthesis of nitrone from nitrobenzene and benzyl alcohol. This discovery presents a practical method for the industrial production of nitrone, a versatile intermediate. In order to obtain functionalized nitrones, the substituted nitrobenzenes were used as reaction substrates to replace the nitrobenzene, and the results are listed in Table S2. It can be found that the developed strategy regarding nitrone synthesis can be extended to the substituted nitrobenzenes with diverse methyl, chloro, and methoxyl groups. However, if the hydroxyl and carboxyl groups substituted nitrobenzenes as substrates, only the corresponding imines can be obtained, owing to the amines being formed but not hydroxylamine. It was established that the submitted benzyl alcohols could be easily oxidized to benzaldehydes. Therefore, it can be safely say that a series of submitted nitrones

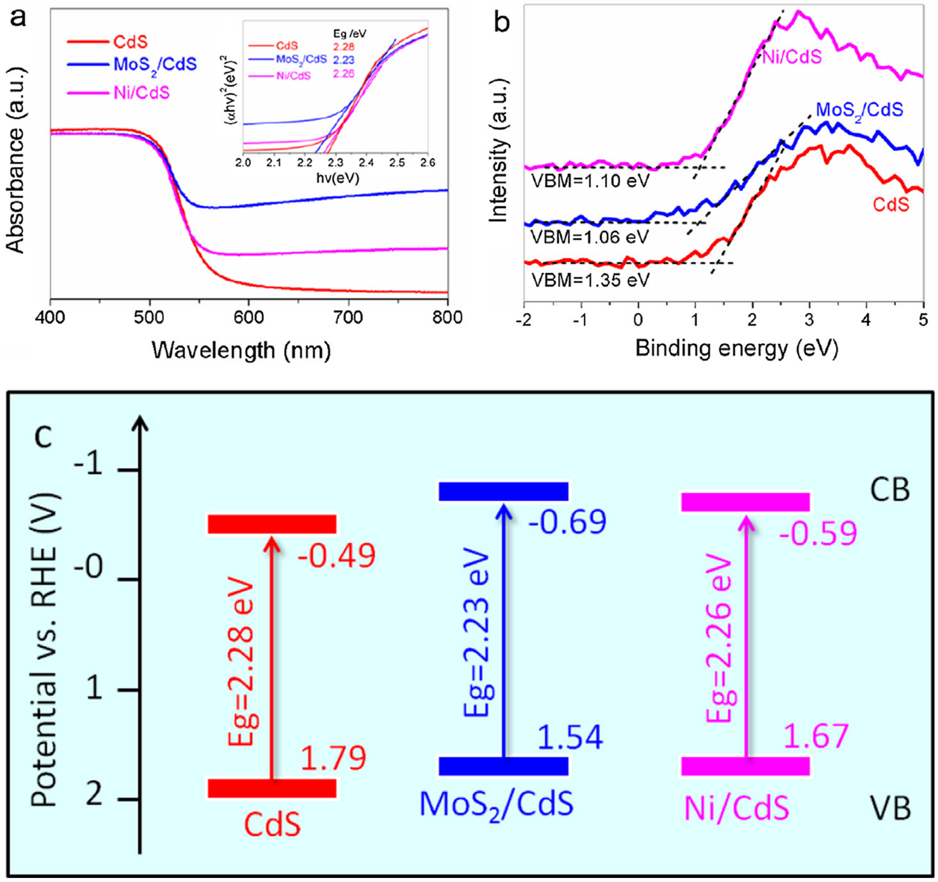


Fig. 8. UV–Vis diffuse reflectance spectra (a) XPS valence band spectra (b), and electronic band structures (c) of the CdS, MoS_2/CdS and Ni/CdS catalysts. Inset in a: Tauc plots.

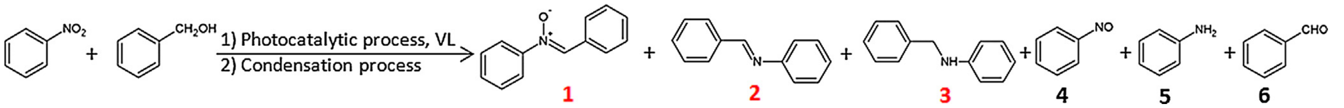
can be obtained by our developed strategy by using the selected substituted nitrobenzenes with diverse substituted benzyl alcohols as starting materials. It is of great significance to elucidate the reaction mechanism behind the developed visible-light-initiated one-pot strategy for efficient synthesis of nitrone. On the basis of the aforementioned controlled experiments (Fig. S3-6) and the reactions results (entry 1–6 in Tables 1 and S1), a tentative mechanism is proposed as depicted in Fig. 9. Upon illumination, the photoinduced electrons in VB migrate to CB, which leaves the equal photoinduced holes in VB. Then, benzyl alcohol is oxidized to form benzaldehyde and to release H^+ by the holes. At the same time, nitrobenzene is reduced to nitrosobenzene by the photogenerated electrons, and then further hydrogenated to phenylhydroxylamine by the electrons and H^+. Finally, nitrone can be obtained by the spontaneous condensation reaction (no light, no catalyst) of the as-formed phenylhydroxylamine with benzaldehyde at ambient pressure and room temperature (Fig. S3,4,6) [9]. The controlled reduction of nitrobenzene to phenylhydroxylamine but not to aniline by combining suitable reduction capability of CdS and illumination time is crucial to the selective synthesis of nitrone.

3.3. Imine and secondary amine from nitrobenzene and benzyl alcohol

It can be clearly observed that the main product is imine but not nitrone over MoS_2/CdS photocatalyst even at a low conversion of nitrobenzene (Table 1, entry 7,8), ascribed to the deep reduction of nitrobenzene to aniline owing to more negative CB potential of MoS_2/CdS than that of CdS that comes from the introduction of MoS_2. The selectivity to imine increases gradually with the extension of illumination time, and up to 95% at 100% of nitrobenzene conversion after 6 h of illumination by visible light (Table 1, entry 10). The 6 h for photocatalytic process is long enough for the subsequent condensation of the as-formed aniline with benzaldehyde, confirmed by the similar results with and without subsequent standing period after photocatalytic reaction (entry 10 in Tables 1 and S1). The developed process for imine synthesis in this work eliminates the required non-polar solvent like toluene and cyclohexane in the previous reports [17a,b], since benzyl alcohol serves as both reactant and solvent. The influence of amount of MoS_2 decorated on CdS on the selectivity of imine (shown in Fig. S8) was also studied, and the highest selectivity was obtained when the optimized theoretical weight ratio of MoS_2 was 5 wt%. The proposed mechanism for imine evolution over MoS_2/CdS is illustrated in Fig. 10, similar to the previously reported process over different photocatalysts [17a,b]. Upon illumination, the photo-excited electrons in VB move to CB and leave the equal amount of photo-excited holes. Then, benzyl alcohol is oxidized to benzaldehyde and release H^+ by the holes. Simultaneously, nitrobenzene is reduced to nitrosobenzene and phenylhydroxylamine, and ultimately hydrogenated to amine by the electrons and H^+. Finally, imine can be obtained by condensation amine and benzaldehyde. The as-formed nitrone can be photoreduced to imine under visible light irradiation.

Distinct from CdS and MoS_2/CdS, using Ni/CdS as photocatalyst, the photocatalytic reaction mixture mainly consists of condensation products including nitrone, imine, and secondary amine. No obvious change in the reaction results for the process including the subsequent condensation or not can be observed Ni/CdS photocatalyst while illumination time is not less than 1 h (Table S1 and 1, entry 13–17), suggesting the complete condensation in the photocatalytic reaction process. With the increase in the illumination time, nitrone gradually decreases and then disappears after 3 h of

Table 1
Photocatalytic performance of various catalysts under different visible-light irradiation times.[a]



Entry	Catalyst	Time (min/h)	Conv.[b] (%)	Benzaldehyde 6 (μmol)	H_2 (μmol)	Sel.[c] (%)				
						Nitrone 1	Imine 2	Amine 3	Nitrosobenzene 4	Aniline 5
1	CdS	25 min	77	138	–	91	5	–	4	–
2	CdS	30 min	91	184	–	89	9	–	2	–
3	CdS	35 min	100	205	–	79	18		3	–
4	CdS	1 h	100	320	0.08	52	45	–	2	1
5[d]	–	25 min	–	–	–	–	–	–	–	–
6[e]	CdS	25 min	–	–	–	–	–	–	–	–
7	MoS_2/CdS	30 min	31	100	–	20	70	–	5	5
8	MoS_2/CdS	1 h	63	172	–	37	59	–	2	2
9	MoS_2/CdS	3 h	100	312	0.05	6	89	–	2	3
10	MoS_2/CdS	6 h	100	462	0.08	0	95	–	2	3
11[d]	–	6 h	–	–	–	–	–	–	–	–
12[e]	MoS_2/CdS	6 h	–	–	–	–	–	–	–	–
13	Ni/CdS	30 min	66	145	0.1	36	59	–	2	3
14	Ni/CdS	1 h	95	321	0.4	20	75	1	1	3
15	Ni/CdS	3 h	100	452	2.3	–	58	39	–	3
16	Ni/CdS	4 h	100	649	18.3	–	34	57	–	3
17[f]	Ni/CdS	5 h	100	1151	28.6	–	25	56	–	3
18[d]	–	4 h	–	–	–	–	–	–	–	–
19[e]	Ni/CdS	4 h	–	–	–	–	–	–	–	–

[a] Reaction condition unless otherwise noted: 0.2 mmol nitrobenzene, 3 ml benzyl alcohol, 10 mg catalyst, N_2 1 atm, $\lambda > 420$ nm, 20 °C. After photocatalytic reaction, the mixture was detected after a period (more than 12 h) of spontaneous condensation process without catalyst in dark.

[b] Determined by GC with trifluorotoluene as an internal standard.

[c] Determined by GC–MS.

[d] No catalyst.

[e] Without light irradiation.

[f] The by-product is 2-hydroxy-N-benzylideneaniline (9%) and N-benzyl-4-hydroxyaniline (10%). Balance corresponds to small amount of unidentified products.

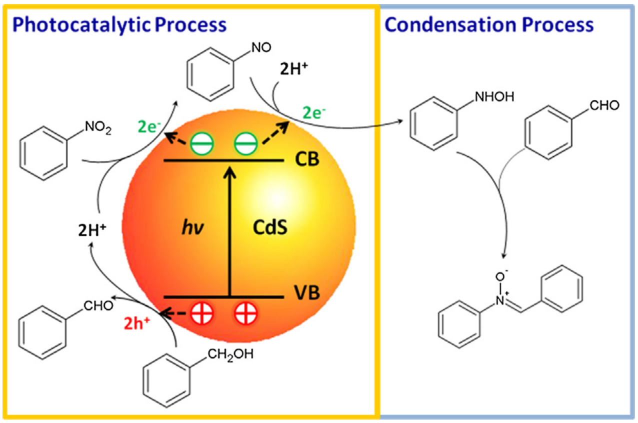


Fig. 9. Proposed mechanism for visible-light-initiated one-pot synthesis of nitrone.

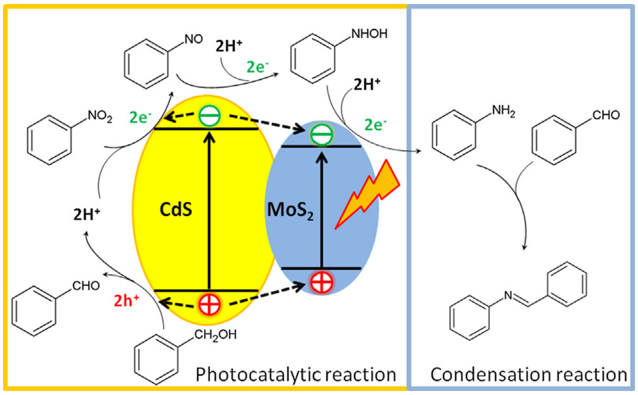


Fig. 10. Plausible reaction mechanism for the visible-light-initiated one-pot synthesis of imine.

illumination time, while imine increases and reaches the maximum at 1 h of illumination time and then decreases along with an increase in secondary amine. The 57% selectivity to secondary amine (the left is mainly imine) at 100% nitrobenzene conversion can be obtained after 4 h of illumination time (Table 1, entry 15). We also studied the influence of amount of Ni decorated on CdS on the selectivity of secondary amine (shown in Fig. S9), and the highest selectivity was obtained when the optimized theoretical weight ratio of Ni was 3.5 wt%. This approach for visible-light photocatalytic secondary amine production over Ni/CdS shows its advantages in contrast to the previously reported methods regarding the elimination of the required noble metals and UV light [17c, d]. The further hydrogenation of imine to secondary amine over Ni/CdS cannot be ascribed to the higher reduction capability owing to its lower reduction capability than that of MoS_2/CdS. Controlled experiments were performed to understand the origin of the promoted formation of secondary amine over Ni/CdS photocatalyst. Besides the comparable catalytic performance for the reduction of imine to secondary amine can be obtained in the absence and presence of the added H_2 (Table S3, entry 2,3), we can find that the yield of secondary amine over Ni/CdS is much higher than that over MoS_2/CdS or CdS under either H_2 atmosphere (Table S3, entry 2,6) or nitrogen atmosphere (Table S3, entry 3,7). This implies that the reduction of imine to secondary amine over Ni/CdS doesn't result from the released H_2 from benzyl alcohol. Even if extra H_2 was introduced, imine still cannot be converted into secondary amine while acetonitrile acted as solvent to replace benzyl alcohol, suggesting the further reduction of imine to secondary amine by

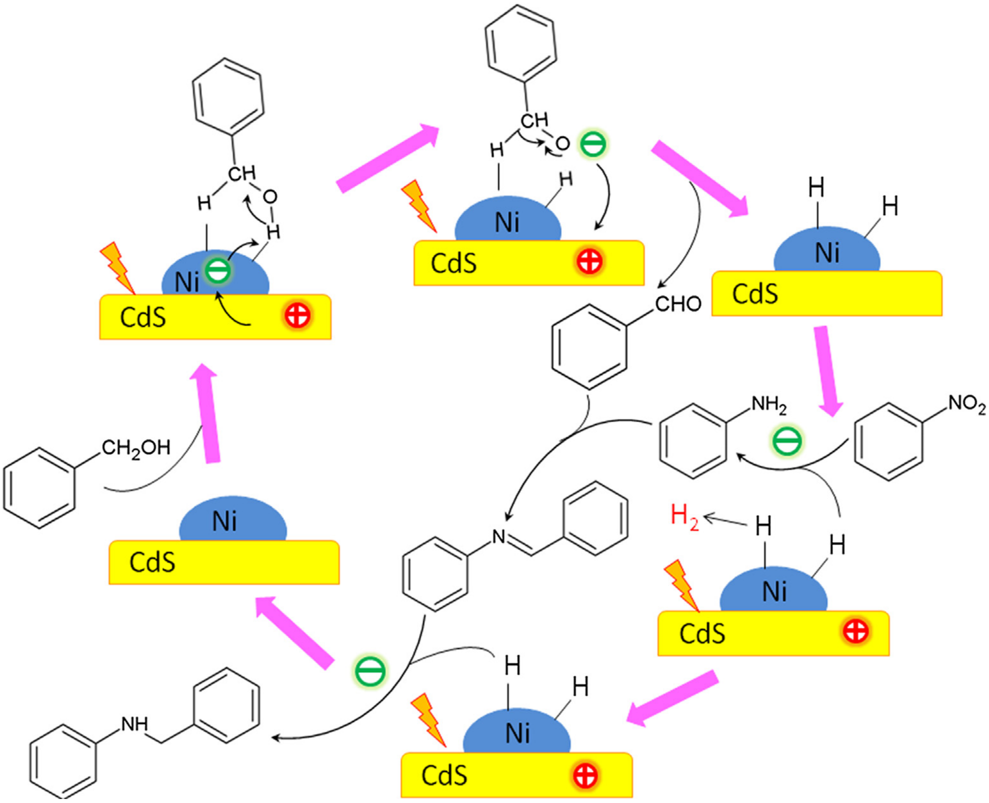


Fig. 11. Plausible reaction mechanism for the visible-light-initiated one-pot synthesis of secondary amine.

the Ni-H hydrids that comes from the reduction of the adsorbed alcohol on the Ni species by photogenerated electrons. Based on the above controlled experiments, a tentative mechanism is proposed as presented in Fig. 11. Initially, benzyl alcohol can be absorbed on the surface of Ni particles. When CdS is illuminated, the photo-excited electrons in VB will move to CB and leave equal amount of holes, and the electron is localized from CdS to the deposited Ni NPs. A proton from benzyl alcohol absorbed on Ni surface is reduced by electron, resulting in a Ni-H hydrid and an alkoxide anion. Subsequently, this alkoxide anion is oxidized by the hole, and the Ni-assisted homolytic cleavage of α-C-H occurs, affording another Ni-H hydrids and the corresponding aldehyde [17c,d]. A part of Ni-H hydrids and electrons are used to reduce nitrobenzene to aniline and reduce imine to secondary amine and the left Ni-H hydrides are used to release H_2.

4. Conclusions

In summary, we for the first time realize the visible-light- initiated one-pot synthesis of nitrone from nitrobenzene and benzyl alcohol under ambient pressure and room temperature conditions. Thanks to the suitable reduction capability of CdS photocatalyst and efficient inhibition of recombination of photogenerated charge carriers by the integrating effect of the spontaneous photoreduction of nitrobenzene and photooxidation of benzyl alcohol half-reactions, 91% selectivity to nitrone at 77% conversion (89% selectivity at 91% conversion) has been achieved after only 25–30 min of illumination by visible light. Furthermore, by tuning cocatalyst and illumination time, for the conversion of the same reactants, the other two useful nitrogen-containing compounds including imine and secondary amine have been successfully synthesized. The tentative reaction mechanisms for flexible synthesis of the three target products are proposed. In addition, the relationship between the properties of different CdS-based catalysts and the selectivity of nitrone, imine and secondary amine has been revealed. This work not only presents a new and efficient method for the synthesis of nitrone, but also opens a new avenue for a facile one-pot synthesis of the other chemicals.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2018.12.011.

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