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Efficient Chemoselective Hydrogenation of Nitrobenzene to Aniline, Azoxybenzene and Azobenzene over CQDs/$ZnIn_2S_4$ Nanocomposites under Visible Light

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Abstract

Efficient production of amino-, azo- and azoxy- aromatics is important in chemical industries. In this manuscript, we reported that controllable chemoselective hydrogenation of nitrobenzene to produce aniline, azoxybenzene and azobenzene was realized over CQDs/$ZnIn_2S_4$ nanocomposite under visible light via simply regulating the reaction medium including the alkalinity and the hydrogen source. An optimized production of aniline was obtained over 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite in a reaction medium of TEOA: MeOH (1:1), while a strong alkaline reaction medium promote N-N coupling to produce azoxybenzene and azobenzene. In addition, azoxybenzne is the intermediate to form azobenzene during the hydrogenation of nitrobenzene, in which a strong hydrogen source like TEOA is indispensable for the transformation. This study not only demonstrated a noble metal-free photocatalytic system for visible light induced efficient and controllable chemoselective hydrogenation of nitrobenzene to produce aniline, azobenzene and azoxybenzene, but also highlights the great potential of photocatalysis in organic syntheses.

Keywords: Chemoselective hydrogenation of nitrobenzene; Aniline; Azoxybenzene; Azobenzene; CQDs/ZnIn2S4 Nanocomposites

Introduction

With an aim to develop green and sustainable processes for organic syntheses, the use of visible light to initiate organic transformations have attracted extensive recent research interest.[1-7] Photoredox reactions can be carried out under mild conditions and therefore can be more selective, which avoid the generation of byproducts due to the presence of undesirable thermal side reactions.[8] During the past several years, photoredox catalysis has made great progress and is becoming more and more important in synthetic organic chemistry. A variety of organic transformations that used to be performed under harsh conditions have been realized under mild irradiations over both homogeneous and heterogeneous photocatalysts.[9-14]

Catalytic reduction of aromatic nitro compounds is a very useful reaction in chemical industry since the main reduction products, like aromatic amines, azo- and azoxy- aromatics are important intermediates in the syntheses of pharmaceuticals, agrochemicals, dyes and pigments.[15-21] Light initiated reduction of nitro aromatics has been demonstrated over a variety of photocatalytic systems including semiconductors, plasmonic metal nanoparticles as well as metal-free dyes and g-C_3N_4.[22-31] For example, nitrobenzene and different nitro aromatics were hydrogenated to aniline and corresponding functionalized amino aromatics over EY and CdS under visible light.[28, 17] The conversion of nitrobenzene to produce azoxybenzene was realized over a Rh loaded CdS photocatalyst (SiO_2/CdS/Rh) under visible light, but aniline and azobenzene was also obtained as the by-products and the activity is relatively low.[24] Under visible light irradiations, selective reduction of nitrobenzene to azobenzene can be realized over plasmonic Au/TiO_2 at room temperature or cheaper Cu/RGO at an elevated temperature.[25, 27] A recent study demonstrated a rare example of photocatalytic reduction of nitro aromatics to chemoselective syntheses of azo- and azoxy-aromatic compounds under either purple (410 nm) or blue light (450 nm) excitation over graphitic C_3N_4.[29] The high activity towards the production of azo- and azoxy-aromatics instead of amino aromatics is attributed to weakly bound photo-generated surface adsorbed H atoms, which are favorable for the N-N coupling. Even so, the development of an highly efficient yet inexpensive photocatalytic system to realize the controllable and chemoselective syntheses of aromatics amines, azoxy- and azo- aromatics via reduction of nitroaromatics under mild conditions is still very challenging.

Based on the generally accepted pathways for catalytic reduction of nitrobenzene proposed by Haber (shown in Scheme 1),[32] nitrosobenzene (NBS) and N-phenylhydroxylamine (NPH), the initially formed hydrogenated products of nitrobenzene, can be directly reduced to aniline (Pathway I) or via a condensation pathway to produce azoxybenzene (Pathway II), which can be further hydrogenated in a series of consecutive steps to azobenzene, hydrazobenzene, and finally to aniline (Pathway III). Since the hydrogenation of nitrobenzene to produce aniline, azoxybenzene and azobenzene involves proton-coupled multi-electron reduction processes, its performance can be influenced not only by the catalytic system, but also by the reaction medium. However, to the best of our knowledge, to realize an efficient and controllable syntheses of aniline, azoxybenzene and azobenzene via simply regulating the reaction medium in photocatalytic reduction of nitrobenzene has not been reported previously.

In this manuscript, we reported that controllable and efficient chemoselective hydrogenation of nitrobenzene to aniline, azobenzene and azoxybenzene can be realized over CQDs/$ZnIn_2S_4$ nanocomposites under visible light via simply regulating the reaction medium. $ZnIn_2S_4$, with a suitable band gap of 2.4 eV, has been widely used in a variety of photocatalytic reactions.[33-38] Particularly, the conduction band of $ZnIn_2S_4$ locates at -1.03 V vs NHE, which is more negative than the reduction potential of nitrobenzene to form aniline (ca. -0.48 V vs NHE), azoxybenzene (ca. -0.78 V vs NHE) and azobenzene (ca. -0.80 V vs NHE).[39, 40] Therefore, it is possible that the photocatalytic reduction of nitrobenzene to produce aniline, azoxybenzene and azobenzene can be realized over $ZnIn_2S_4$. The self-assembly of $ZnIn_2S_4$ in the presence of preformed carbon quantum dots (CQDs) led to the formation of CQDs/$ZnIn_2S_4$

nanocomposites. The photocatalytic reduction of nitrobenzene over CQDs/$ZnIn_2S_4$ nanocomposites not only was influenced by the incorporated CQDs, but also depended on the reaction medium including the alkalinity and the strength of the hydrogen source. This study not only demonstrated a noble metal-free photocatalytic system for controllable and efficient chemoselective hydrogenation of nitrobenzene to produce aniline, azobenzene and azoxybenzene under visible light, but also highlights the great potential of photocatalysis in organic syntheses.

Experimental

Preparations

All the reagents were commercial available and used without further purifications. Carbon Quantum Dots (CQDs) were prepared by thermalizing citric acid according to literature.[41] CQDs/$ZnIn_2S_4$ nanocomposite was prepared following a previously reported solvothermal method by self-assembly of $ZnIn_2S_4$ microspheres in the presence of preformed CQDs.[42] CQDs/$ZnIn_2S_4$ nanocomposites with different amount of CQDs were denoted as x wt% CQDs/$ZnIn_2S_4$ (x = 1.0, 3.0 and 5.0). Bare $ZnIn_2S_4$ was synthesized similarly without the introduction of preformed CQDs.

Characterizations

The X-ray diffraction (XRD) patterns of the as-obtained products were carried out on a D8 Advance X-ray diffractometer (Bruker, Germany) using Cu K_α (λ= 1.5406 Å) radiation at a voltage of 40 kV and 40 mA. XRD patterns were scanned over the angular range of 10-60° (2θ) with a step size of 0.02°. The FT-IR analyses were carried out on a Nicolet IS50 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA) with a monochromatic Al K_a source and a charge neutralizer. All the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. The scanning electron microscopy (SEM) was obtained on JSM-6700F. The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were measured by

JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. UV-visible diffraction spectra (UV-vis DRS) of the powders were obtained for the dry pressed disk samples using a UV-visible spectrophotometer (Cary 7000 Scan Spectrophotometers, Varian). $BaSO_4$ was used as a reflectance standard.

Photocatalytic reactions

The photocatalytic reactions were carried out in a sealed reaction tube irradiated with a 5 W LED lamp (Light-emitting diodes, PCX50A, multichannel optical catalytic reaction system). The catalyst (10 mg) and nitrobenzene (0.2 mmol) were suspended in a solvent containing different hydrogen sources (2 mL). Before the reaction, the suspension was degassed and saturated with N_2 to remove any dissolved O_2. After the reaction, the resultant suspension 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.

The hydrogenation of nitrobenzene to produce azobenzene was investigated over 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite with the presence of different amount of bases, while the hydrogenation of nitrobenzene to produce azoxybenzene was carried out in a reaction medium in absence of TEOA. After irradiated with the LED lamp, the resultant suspension was filtered through a porous membrane (20 μm in diameter). The filtrate was extracted with CH_2Cl_2 and the subnatant was analyzed by GC.

Results and discussion

$ZnIn_2S_4$ and CQDs/$ZnIn_2S_4$ nanocomposites were prepared following previously reported method.[40] CQDs with dimension of ca. 5 nm were synthesized via thermolysis of citric acid, which was used for the assembly of CQDs/$ZnIn_2S_4$ nanocomposites (Supporting Fig. S1). The as-obtained CQDs/$ZnIn_2S_4$ nanocomposites (take 3.0 wt% CQDs/$ZnIn_2S_4$ for example), show similar XRD patterns as that of bare $ZnIn_2S_4$ (Supporting Fig. S2).[43] The SEM image of the CQDs/$ZnIn_2S_4$ nanocomposite shows microspheres of ca. 2.5 μm, which are consists of numerous interwoven ultrathin nanosheets (Supporting Fig. S3). Although the diffraction peaks corresponding to CQDs are not observed in the XRD patterns, the successful incorporation of CQDs in the as-obtained CQDs/$ZnIn_2S_4$ nanocomposite can be confirmed by its TEM, FT-IR and XPS (Supporting Fig. S4-S6).[44] As compared with bare $ZnIn_2S_4$, the morphology of CQDs/$ZnIn_2S_4$ nanocomposite does not change obviously, indicating that the existence of CQDs do not influence the self-assembly of $ZnIn_2S_4$ microspheres (Supporting Fig. S3 and S4). The UV-vis DRS of CQDs/$ZnIn_2S_4$ nanocomposite shows absorption edge extended to 520 nm, in accordance with the band gap of $ZnIn_2S_4$ (ca. 2.4 eV). Although the incorporation of CQDs in $ZnIn_2S_4$ does not change the band gap of $ZnIn_2S_4$, CQDs/$ZnIn_2S_4$ nanocomposite shows a slightly enhanced absorption beyond 500 nm, ascribable to the absorption of CQDs (Supporting Fig. S7).

The performance of CQDs/$ZnIn_2S_4$ nanocomposites for the reduction of nitrobenzene under visible light was investigated. The reaction was initially carried out in MeOH over 1.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite, with triethanolamine (TEOA) as the hydrogen source. It was found that 51% of nitrobenzene was converted after irradiated for 12 h, with the only detectable product to be aniline in a reaction medium containing TEOA: MeOH (1:1) (Table 1, entry 1). No conversion of nitrobenzene was observed in dark or in absence of 1.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite, indicating that reduction of nitrobenzene to aniline is truly induced by photocatalysis over CQDs/$ZnIn_2S_4$ nanocomposite (Table 1, entries 2-3). Bare $ZnIn_2S_4$ showed inferior performance, with only 23% of nitrobenzene converted and a yield of 19% to aniline under otherwise similar condition (Table 1, entry 4), suggesting that CQDs promotes the photocatalytic reduction of nitrobenzene to aniline over $ZnIn_2S_4$. In addition, the amount of CQDs in the CQDs/$ZnIn_2S_4$ nanocomposites influenced the performance. The conversion of the nitrobenzene improved with the amount of CQDs in the nanocomposites and then decreased (Table 1, entries 1, 5-6), with an optimized performance observed over 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite, in which 79% of nitrobenzene was converted, with a yield of 76% to aniline in 12 h (Table 1, entry 5).

Solvents and hydrogen sources also influenced the performance of the reduction of nitrobenzene to produce aniline. The change of the solvent from MeOH to either EtOH, MeCN or H_2O led to lowering of the conversion of nitrobenzene, with 48%, 72% and 38% of nitrobenzene converted for the reactions carried out in EtOH, MeCN and H_2O respectively (Supporting Table 1, entries 1-3). Although the reduction of nitrobenzene to aniline occurred when either ammonium formate or formic acid was used as the hydrogen source, the conversion of nitrobenzene over these two systems was low, with only 38% and 41% of nitrobenzene converted under otherwise similar conditions (Supporting Table 1, entries 4-5). Alcohols are even worse hydrogen sources for this reaction, with only 11% of nitrobenzene converted for reaction carried out in the presence of benzyl alcohol and no aniline was detected when isoproponal was used (Supporting Table 1, entries 6-7). Therefore, among the investigated systems, an optimized performance for photocatalytic reduction of nitrobenzene to produce aniline was obtained in mixed MeOH/TEOA (1:1) over 3.0 wt% CQDs/$ZnIn_2S_4$.

The time-dependent reduction of nitrobenzene in a mixed TEOA/MeOH (1:1) over 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite showed that the amount of aniline increased with the irradiation time, accompanied by the gradual consumption of nitrobenzene (Fig. 1). No other products were detected during the whole investigated process although NBS and NPI were assumed to be the intermediates during the hydrogenation of nitrobenzene to produce aniline, based on the well-known pathways proposed by Haber. It is either because that the hydrogenation of NBS and NPI are much faster than the reduction of nitrobenzene to produce NBS, or nitrobenzene can be hydrogenated to produce aniline directly over CQDs/$ZnIn_2S_4$ nanocomposite, a phenomenon previously reported over Au/TiO_2.[15] In such a reaction system, a full conversion of nitrobenzene can be realized after irradiation for 16 h (Table 1, entry 7). In addition, it was found that no obvious decrease of the activity of 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite was observed after three cycling tests (Fig. S8).

When base like NaOH was introduced into the above reaction system, in addition to aniline, azoxybenzene and azobenzene were also obtained. Not only the conversion of nitrobenzene, but also the distribution of the products varied with the amount of NaOH introduced. When 2 mmol of NaOH was added, 52% of nitrobenzene was converted after irradiated for 12 h, with the yield to aniline, azobenzene and azoxybenzene to be 9%, 5% and 36% respectively, indicating that the alkaline condition promotes the condensation pathway to produce azoxybenzene and azobenzene (Table 1, entry 8). The increase of the amount of NaOH to 4 mmol led to enhanced conversion of nitrobenzene (80%), with the products obtained to be aniline (37%), azobenzene (31%) and azoxybenzene (11%) (Table 1, entry 9), suggesting that enhanced alkalinity promoted the conversion of nitrobenzene as well as the hydrogenation of azoxybenzene to produce azobenzene over CQDs/$ZnIn_2S_4$. The further increase of the amount of NaOH to 6 mmol, by simultaneous addition of water to dissolve the base, led to a full conversion of nitrobenzene, with a significantly improved yield to azobenzene (73%), although a small amount of azoxybenzene (9%) and aniline (18%) was still present after irradiated for 12 h (Table 1, entry 10). Prolonging the irradiation time to 13 h, all the azoxybenzene was converted, with a yield of 84% to azobenzene. However, aniline was still present as a minor product (16%) in the system. Time-dependent reactions in a reaction medium of TEOA/MeOH/H_2O (2:1:1) in the presence of 6 mmol of NaOH revealed that the amount of nitrobenzene decreased with the irradiation time, with a full conversion of nitrobenzene achieved after irradiated for 7 h (Fig. 2). The amount of azoxybenzene increased in the first 7 h, and then decreased with the concomitant increase of azobenzene, with a maximum yield to azoxybenzene in the system to be 82% after irradiated for 7 h, suggesting that azoxybenzene is the intermediate during the transformation of nitrobenzene to azobenzene. After an optimum yield of 84% to azobenzene was obtained after irradiated for 13 h, the further irradiation led to a decrease of the yield to azobenzene, together with an slightly improved yield to aniline, indicating that the further hydrogenation of azobenzene led to the production of aniline, although no intermediates like hydrazobenzne was observed in this process.

Controlled experiment using azoxybenzene as the substrate revealed that azoxybenzene was totally converted to azobenzene in a similar reaction medium over 3.0 wt% CQDs/$ZnIn_2S_4$ after irradiated for 13 h (Table 1, entry 11), although such a transformation did not occur over CQDs/$ZnIn_2S_4$ nanocomposites without light irradiations (Table 1, entry 12), indicating that the hydrogenation of azoxybenzene to produce azobenzene is really induced by photocatalysis over CQDs/$ZnIn_2S_4$ nanocomposite. In addition, the transformation of azoxybenzene to azobenzene did not occur over bare $ZnIn_2S_4$, suggesting that CQDs in the nanocomposites is indispensable for the hydrogenation of azoxybenzene (Table 1, entry 13). The promoting of the hydrogenation of azoxybenzene to produce azobenzene by introduction of CQDs is not unexpected since our previous studies have also revealed that electron-rich CQDs can promote the hydrogenation of imines to amines due to the presence of Frustrated Lewis acid-base Pairs (FLPs)-like separated positive and negative charge centers in their structure.[42]

In addition, the hydrogenation of nitrobenzene carried out in a reaction medium of MeOH/H_2O (1:1) in the presence of 6 mmol of base (NaOH), i.e., a TEOA-free reaction medium, led to a full conversion of nitrobenzene to yield azoxybenzene after irradiated for 12 h (Table 1, entry 14). An increase of the reaction time to 16 h did not lead to the transformation of azoxybenzene to azobenzene, indicating that the hydrogenation of azoxybenzene to produce azobenzene can only be realized using a strong hydrogen source like TEOA. This is not difficult to understand since TEOA, with a pKa value of ca. 7.77, is a much stronger hydrogen source as compared with MeOH, with a pKa value of 15.49. [45, 46]

Based on what Haber has proposed, the hydrogenation of nitrobenzene follows different pathways as shown in Scheme 1, leading to the formation of different products. In the direct pathway (Pathway I in Scheme 1), nitrobenzene is first reduced to NBS and then to corresponding NPH, which can be further hydrogenated to produce aniline. Meanwhile, the alkaline-promoted condensation between NBS and NPH also occurs to give azoxybenzene (Pathway II in Scheme 1). The azoxybenzene can further be hydrogenated in a series of consecutive steps to produce azobenzene, hydrazobenzene and finally to aniline (Pathway III in Scheme 1). Therefore, in addition to the catalyst, the modifications on the reaction medium as well as the hydrogen source can also tune the rate of the different steps during the hydrogenation of nitrobenzene, which can ensure a highly chemoselective hydrogenation of nitrobenzene to produce aniline, azoxybenzene and azobenzene.

With regard to the current CQDs/$ZnIn_2S_4$ nanocomposite, the chemoselective hydrogenation of nitrobenzene to produce aniline, azoxybenzene and azobenzene can be rationalized as following (shown in Scheme 2, Path 1). $ZnIn_2S_4$ is a visible light responsive semiconductor. When irradiated with visible light, $ZnIn_2S_4$ is excited to generate electrons and holes. Coupled with a strong hydrogen source like TEOA, the photogenerated electrons can hydrogenate nitrobenzene to produce aniline, probably through NBS and NPH as the intermediates, even though these two compounds were not detected during the time-dependent reactions. However, the reactions carried out using either NBS and NPH instead of nitrobenzene occurs quickly to produce aniline, implying that the absence of NBS and NPH during the hydrogenation of nitrobenzene may be due to their fast hydrogenation to produce aniline as compared with their production from nitrobenzene. TEOA also acts as the electron donor to react with the photogenerated holes in $ZnIn_2S_4$ and complete the whole photocatalytic cycle. When CQDs are deposited on the surface of $ZnIn_2S_4$, the electrons photogenerated in $ZnIn_2S_4$ can transfer to CQDs to form electron-rich CQDs, due to a more negative conduction band of $ZnIn_2S_4$ as compared with that of CQDs. With the assistance of TEOA as a hydrogen source, the electron-rich CQDs can act like FLPs to promote the stepwise hydrogenation of nitrobenzene to NBS, NPH and finally to aniline, resulting in an improved yield to aniline over CQDs/$ZnIn_2S_4$ nanocomposite as compared with that over bare $ZnIn_2S_4$.

The introduction of the base like NaOH to the reaction system promotes the condensation between NBS and NPH to produce azoxybenzene over CQDs/$ZnIn_2S_4$ nanocomposite (shown in Scheme 2, Path 2).[47] Although azoxybenzene can be further hydrogenated to produce azobenzene over CQDs/$ZnIn_2S_4$ nanocomposite, such a transformation is completely inhibited over CQDs-free bare $ZnIn_2S_4$ or a reaction medium without TEOA, indicating that only a strong enough catalyst for hydrogenation (CQDs) and a strong hydrogen source (TEOA) can realize the hydrogenation of azoxybenzene to produce azobenzene. As mentioned above, electron-rich CQDs can act as a catalyst for hydrogenation due to the presence of FLPs-like separated positive and negative charge centers. Based on Scheme 2, it is therefore possible to realize a controllable and an efficient chemoselective hydrogenation of nitrobenze to produce aniline, azoxybenzene and azobenzene over CQDs/$ZnIn_2S_4$ nanocomposite.

Conclusion

In summary, the self-assembly of $ZnIn_2S_4$ in the presence of preformed CQDs led to the formation of CQDs/$ZnIn_2S_4$ nanocomposites, which can be used for visible light induced hydrogenation of nitrobenzene. A controllable and efficient chemoselective hydrogenation of nitrobenzene to produce aniline, azobenzene and azoxybenzene can be realized over 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite under visible light via simply regulating the reaction medium including the alkalinity and the hydrogen source. This study not only demonstrated a noble metal-free photocatalytic system for efficient visible light initiated chemoselective hydrogenation of nitrobenzene to produce aniline, azobenzene and azoxybenzene, but also highlights the great potential of photocatalysis in organic syntheses.

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Captions for Figures

Fig. 1 Time-dependent changes in the amounts of nitrobenzene and aniline during hydrogenation of nitrobenzene in a mixed solvent of TEOA/MeOH (1:1) over irradiated 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite.

Fig. 2 Time-dependent changes in the amounts of nitrobenzene and the products during hydrogenation of nitrobenzene in a reaction medium of TEOA/MeOH/H_2O (2:1:1) and 6 mmol of NaOH over irradiated 3.0 wt% CQDs/$ZnIn_2S_4$ nanocomposite.

Caption for Table

Table 1 Hydrogenation of nitrobenzene under different conditions.

Captions for Schemes

Scheme 1 Generally accepted pathways for catalytic hydrogenation of nitrobenzene proposed by Haber.

Scheme 2 Proposed mechanism for chemoselective hydrogenation of nitrobenzene to produce different products over CQDs/$ZnIn_2S_4$ nanocomposite.

Fig. 1

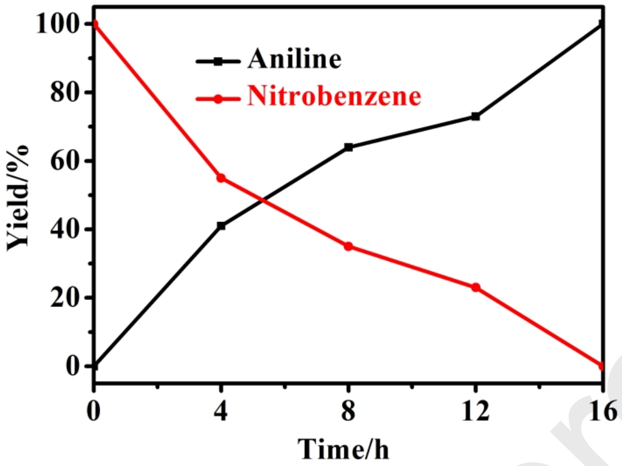


Fig.2

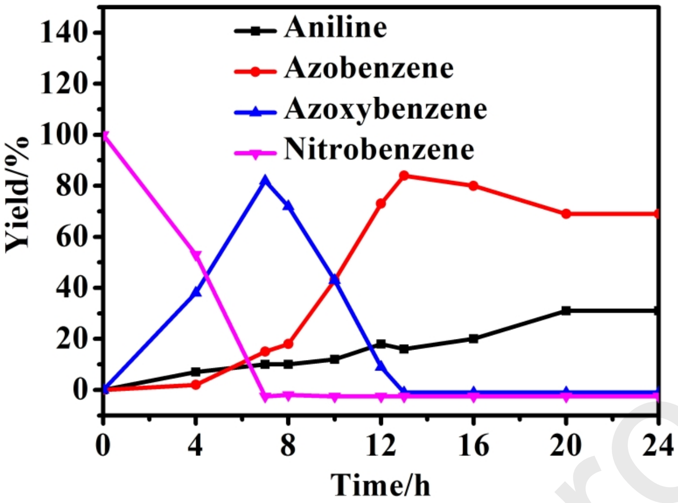
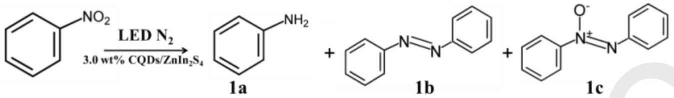

Aniline
Azobenzene
Azoxybenzene
Nitrobenzene
Yield/%
140
120
100
80
60
40
20
0
0
4
8
12
16
20
24
Time/h

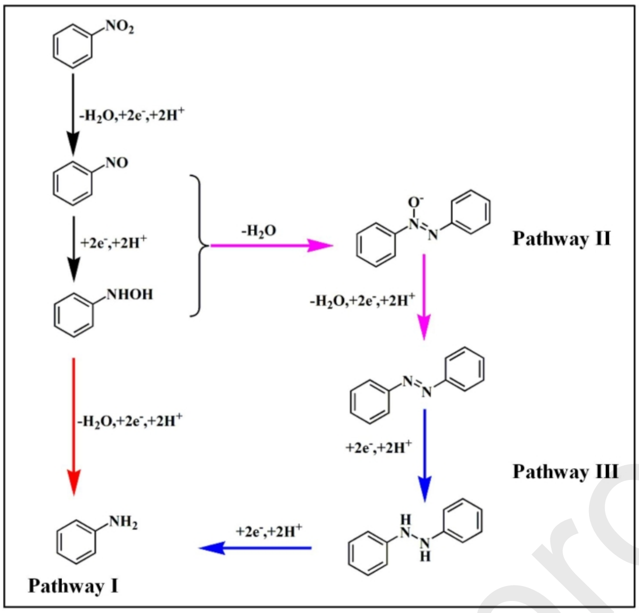
Table 1



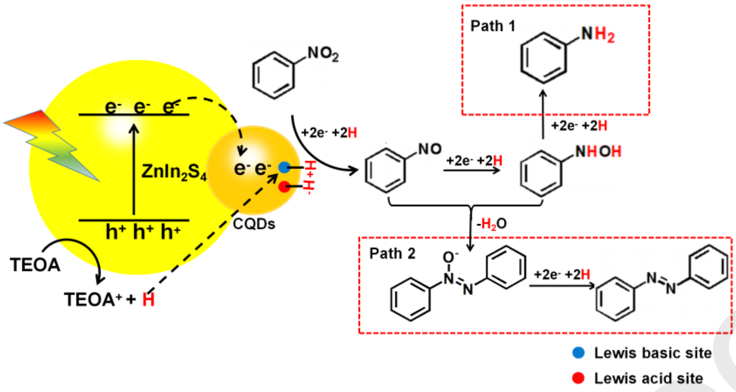
Entry	Catalyst	Solvent	Base	Light	Time/h	Conv./%	Yield/%		
							1a	1b	1c
1	1.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	-	ON	12	51	50	-	-
2	1.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	-	OFF	12	-	-	-	-
3	-	TEOA/MeOH (1:1)	-	ON	12	-	-	-	-
4	$ZnIn_2S_4$	TEOA/MeOH (1:1)	-	ON	12	23	19	-	-
5	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	-	ON	12	79	76	-	-
6	5.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	-	ON	12	56	53	-	-
7	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	-	ON	16	>99	>99	-	-
8	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	2 mmol NaOH	ON	12	52	9	5	36
9	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH (1:1)	4 mmol NaOH	ON	12	80	37	31	11
10	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH/H_2O (2:1:1)	6 mmol NaOH	ON	12	>99	18	73	9
11[a]	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH/H_2O (2:1:1)	6 mmol NaOH	ON	13	>99	-	>99	-
12[a]	3.0 wt% CQDs/$ZnIn_2S_4$	TEOA/MeOH/H_2O (2:1:1)	6 mmol NaOH	OFF	13	-	-	-	-
13[a]	$ZnIn_2S_4$	TEOA/MeOH/H_2O (2:1:1)	6 mmol NaOH	ON	13	-	-	-	-
14	3.0 wt% CQDs/$ZnIn_2S_4$	MeOH/H_2O (1:1)	6 mmol NaOH	ON	12	>99	-	-	>99

Reaction conditions: 0.2 mmol nitrobenzene, 10 mg catalyst, 2 mL solvent, N_2, LED irradiation.[a] azoxybenzene as substrate.

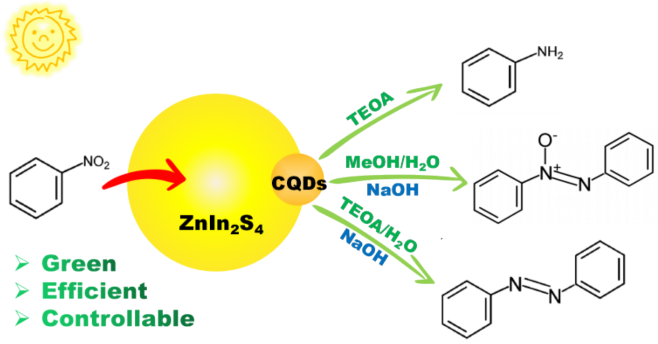
Scheme 1


NO2
-H2O,+2e-,+2H+
NO
+2e-,+2H+
NHOH
-H2O
Pathway II
-H2O,+2e-,+2H+
-H2O,+2e-,+2H+
+2e-,+2H+
Pathway III
NH2
+2e-,+2H+
Pathway I

Scheme 2


ZnIn2S4
e- e- e-
h+ h+ h+
TEOA
TEOA+ + H
CQDs
e- e-
H+
NO2
+2e- +2H
NO
+2e- +2H
NHOH
Path 1
NH2
+2e- +2H
-H2O
Path 2
O-
N
N
+2e- +2H
N
N
● Lewis basic site
● Lewis acid site

Graphical abstract



The authors declared that they have no conflicts of interest to this work.

Highlights

- Efficient hydrogenation of nitrobenzene over CQDs/$ZnIn_2S_4$ under visible light
- Chemoselective production of aniline, azoxybenzene and azobenzene over CQDs/$ZnIn_2S_4$ under visible light
- Chemoselectivity can be tuned via regulating the reaction medium including alkalinity and the hydrogen source