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# Visible-light-driven chemoselective hydrogenation of nitroarenes to anilines in water via graphitic carbon nitride metal-free photocatalysis

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Abstract: Green and efficient procedures are highly required for the chemoselective hydrogenation of functionalized nitroarenes to industrially important anilines. Here, we show that visible-light-driven, chemoselective hydrogenation of functionalized nitroarenes bearing the sensitive groups to anilines can be achieved in good to excellent yields (82-100%) in water under relatively mild conditions, catalyzed by low-cost and recyclable graphitic carbon nitride. It is also applicable in gram-scale reaction with 86% yield of aniline. Mechanism study reveals that visible light induced electrons are responsible for the hydrogenation reactions and thermal energy can also promote the photocatalytic activity. Kinetics study shows that this reaction possibly occurs via one-step hydrogenation or stepwise condensation route. Wide applications can be expected using this green, efficient, and highly selective photocatalysis system in reduction reactions for fine chemical synthesis.

#### Introduction

As important intermediates for the manufacture of fine chemicals (agrochemicals, pharmaceuticals, dyes, and pigments) as well as bulk chemicals (polymers), functionalized amines represent an important type of feedstock in the chemical industry with over four million tons produced per year mainly by hydrogenation of the corresponding nitroarenes.[1-3] Non-catalytic methods using stoichiometric reducing agents such as Fe and S compounds can be used, but these processes will cause serious environmental problems by creating large amounts of toxic waste.<sup>[4]</sup> Catalytic hydrogenation of nitroarenes using noble metals (Pd, Pt, Rh, Ru, and Au) or more abundant transition metals (Fe, Co, and Ni) is the most widely used method for the production of anilines.<sup>[5,6]</sup> However, the use of large amounts of metal catalysts, harsh reaction conditions, organic medium, and expensive or harmful hydride source make these procedures not green.<sup>[5,6]</sup> Furthermore, the chemoselective hydrogenation of nitroarenes functionalized

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with other easily removed and reducible groups to produce several industrially important anilines remains challenging with limited success achieved.<sup>[1,2,6]</sup> It is highly desirable to develop a green procedure for the efficient and chemoselective hydrogenation of functionalized nitroarenes.

Visible-light-driven photocatalysis mediated by semiconductors and metal nanoparticles has caused increasing interests in utilizing abundant solar energy to perform diverse chemical reactions.<sup>[7-11]</sup> It is a sustainable and green procedure for fine chemicals synthesis.<sup>[12]</sup> It also provides new opportunities in fine chemical synthesis by manipulating the selectivity of chemical transformations and introducing novel reaction mechanisms.<sup>[13-15]</sup> Considering the non-renewability and potential environmental hazards of metals,<sup>[16]</sup> alternative photocatalysts based on metalfree materials,<sup>[17]</sup> especially graphitic carbon nitride (g- $C_3N_4$ ),<sup>[11,18,19]</sup> are under rapid development. This is because of their low-cost and non-toxic nature, and the convenience in modifying their composition, structure and properties using the well-established organic protocols.<sup>[20]</sup>

Graphitic carbon nitride is the most stable allotrope of various carbon nitrides at ambient conditions and can be easily fabricated by a one-step thermal polymerization of abundant nitrogen-rich precursors such as cyanamide, dicyandiamide, melamine, urea, and thiourea.<sup>[21,22]</sup> It was first recognized as a heterogeneous catalyst in the pioneer works for the Friedel-Crafts acylation of benzene reported in 2006.<sup>[23,24]</sup> In 2009, Wang et al. discovered that g-C<sub>3</sub>N<sub>4</sub> acted as a metal-free conjugated semiconductor photocatalyst in visible-light-driven H<sub>2</sub> evolution from water splitting.<sup>[18]</sup> Since then, significant efforts have been made in g-C<sub>3</sub>N<sub>4</sub> mediated photocatalysis owing to its superior characteristics containing appropriate visible-light response, thermal stability up to 600 °C, chemical stability in acid, alkali, and organic solvents. high surface area, low cost, and the convenience towards tuning its properties.<sup>[18,19,25-27]</sup> It has hence found various applications in energy and environmental fields, especially in hydrogen evolution.<sup>[28]</sup> CO<sub>2</sub> reduction.<sup>[29]</sup> water and gas purification.<sup>[30]</sup> and organic synthesis.<sup>[15,31]</sup> Furthermore, as a heterogeneous catalyst, q-C<sub>3</sub>N<sub>4</sub> possesses multiple functionalities such as basic sites. Hbonding motif, and electronic properties.<sup>[32]</sup> These favorable features together with the proper band structure (+1.4 eV and -1.3 eV versus the normal hydrogen electrode) suggest that g-C<sub>3</sub>N<sub>4</sub> will find broader applications in promoting organic redox synthesis as a gentle metal-free photocatalyst.[33] Oxidation reactions catalyzed by g-C<sub>3</sub>N<sub>4</sub> have been well studied recently.<sup>[11,33-35]</sup> However, very few research on reduction reactions for fine chemical synthesis mediated by g-C<sub>3</sub>N<sub>4</sub> photocatalysis has been reported.<sup>[36]</sup> This motivated us to carry

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out the proof-of-concept study for  $g\text{-}C_3N_4$  in catalyzing the hydrogenation of functionalized nitroarenes.

Herein, we demonstrate that  $g-C_3N_4$  is an active, recyclable, lowcost, metal-free photocatalyst for the chemoselective hydrogenation of functionalized nitroarenes in water under relatively mild conditions and visible light irradiation. Hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), a green and safe reducing reagent only producing nitrogen gas as a byproduct,<sup>[37]</sup> was used as the hydride source as well as the hole scavenger. This green, efficient, and highly selective procedure is of high potential in the synthesis of various chemicals through hydrogenation using abundant solar energy.

#### **Results and Discussion**

Urea was selected as the precursor to synthesize the polymeric g-C<sub>3</sub>N<sub>4</sub> photocatalyst through the facile thermal condensation procedure. Urea has been recognized as an ideal precursor for the preparation of g-C<sub>3</sub>N<sub>4</sub> because it is a low-cost, large-scale industrial product and the gases generated during the condensation of urea will act as soft templates to help the formation of porous micro-structures.<sup>[38]</sup> TEM images (Figure S1) demonstrate the formation of the characteristic layered plateletlike morphology of g-C<sub>3</sub>N<sub>4</sub> with loose and porous structures. The Brunauer-Emmett-Teller (BET) specific surface area of 74.2 m<sup>2</sup>/g was determined by the N2 adsorption/desorption analysis (Figure S2). The XRD pattern (Figure S3) reveals a dominant (002) peak at 27.3° and a minor (100) peak at 13.0°, arising from the graphitic stacking of the conjugated aromatic C<sub>3</sub>N<sub>4</sub> units and the in-plane intervals of the periodic tri-s-triazine units.<sup>[18,31]</sup> XPS measurements (Figure S4) further prove the formation of sp<sup>2</sup> hybridized C-N coordination in g-C<sub>3</sub>N<sub>4</sub> and the elemental ratio of C:N:O is determined to be 0.77:1:0.17. The UV-vis-diffuse reflectance spectrum (Figure S5) exhibits the ability of the synthesized g-C<sub>3</sub>N<sub>4</sub> photocatalyst for utilizing solar energy in the visible light region with band gap estimated to be 2.80 eV. Thermogravimetric analysis (TGA, Figure S6) proves the thermal stability of g-C<sub>3</sub>N<sub>4</sub> in air up to 460 °C. ICP-OES analysis together with the two control experiments ruled out the possibility of the trace metal impurities affecting the instinct activity of g-C<sub>3</sub>N<sub>4</sub> photocatalyst (Table S1 and S2). The above characterization results prove the successful synthesis of g-C<sub>3</sub>N<sub>4</sub> photocatalyst with porous structures, visible light utilization ability, and excellent thermal stability.

The visible-light-driven hydrogenation of nitrobenzene to aniline was chosen as the representative reaction for the proof-ofconcept experiments. The reaction was conducted in water under relatively mild conditions (from room temperature to 100 °C, visible light) using the synthesized g-C<sub>3</sub>N<sub>4</sub> as the metal-free photocatalyst and hydrazine hydrate as a green hydride source and hole scavenger. After 20 hours (80 °C), we observed the formation of aniline with excellent yield (> 99%) as expected. Dark reaction yielded less than 5% of aniline and the control experiment without the addition of g-C<sub>3</sub>N<sub>4</sub> yielded no aniline.

We moreover compared the present procedure with previously reported results on heterogeneous catalysis using noble metals, transition metals, and metal-based photocatalysts (Table S3). For noble metals and metal-based photocatalysts, although the hydrogenation of nitrobenzene to aniline can be achieved under very mild conditions, the use of precious or hazardous catalysts restricts the applications. Low cost catalysts based on Co or Fe have also been used for this reaction, but high H<sub>2</sub> pressure was needed. The present study demonstrate that an excellent aniline yield can be achieved through a green and low-cost procedure at very low reaction temperatures.

Light is a key factor influencing the photocatalytic reactions. The study on the effect of light intensity and wavelength on the photocatalytic activity will provide guidelines for manipulating the reaction process alternatively by controlling the incident light.<sup>[10,39,40]</sup> More importantly, it will offer insights into the light induced mechanism.<sup>[10,39,40]</sup> A positive dependence of the photocatalytic activity on the incident light intensity has been observed for both semiconductors and metal nanoparticles photocatalytic processes and is considered as an experimental signature of light induced processes mediated by energetic charge carriers (hot electrons and holes).[13,39-41] This relationship was also observed for the g-C<sub>3</sub>N<sub>4</sub> photocatalytic hydrogenation of nitrobenzene to aniline with an almost linear dependence ( $R^2$  = 0.991, Figure 1). When the incident photons are absorbed by g-C<sub>3</sub>N<sub>4</sub>, transient electron/hole pairs are generated on its surface. The resulting hot electrons are transferred to the adsorbed nitrobenzene molecules on the basic sites of g-C<sub>3</sub>N<sub>4</sub>. The hot holes can be effectively scavenged by hydrazine which is a strong reducing agent, thus strengthening the separation of the charge carriers and the following reactions. Under a higher light intensity, more photons are introduced into the photocatalyst to excite more energetic charge carriers which will facilitate the hot electron induced hydrogenation reaction of nitrobenzene to aniline.

Another possible mechanism for the observed higher activity at higher light intensity is the photothermal effect, where the wavelength of the incident light has a negligible effect on the photocatalytic activity when the intensity remains identical.<sup>[42]</sup> The



Figure 1. Dependence of aniline yield on the incident light intensity. See Table S4 for detailed conditions and results for the reactions under different light intensities.

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Figure 2. Action spectrum for the photocatalytic hydrogenation of nitrobenzene to aniline using the  $g-C_3N_4$  photocatalyst. See Table S5 for detailed conditions and results for the reactions under different light wavelengths.

photocatalytic action spectrum presents one-to-one mapping between the wavelength dependent apparent quantum yield (AQY) and the light absorption spectrum of the photocatalyst. It is a useful tool to distinguish whether the observed chemical reaction occurs via a photo-induced process.<sup>[43]</sup> As shown in Figure 2, higher AQY can be observed at shorter wavelength where the g-C<sub>3</sub>N<sub>4</sub> photocatalyst absorbs more light. The good match between AQY and the photocatalyst's light absorption spectrum suggests that this reaction proceeds via a light induced process.<sup>[44]</sup>

As demonstrated above, the hydrogenation of nitrobenzene to aniline catalyzed by  $g-C_3N_4$  is proven to be driven by a light induced mechanism (Scheme 1). The population of hot electrons generated via light excited charge separation is the key factor influencing the observed photocatalytic activity. This helps us to better understand the light induced mechanism for photocatalytic reactions mediated by  $g-C_3N_4$  as well as other semiconductors. Furthermore, it provides us an extra tool to tune the chemical reactions by appropriately adapting the incident light.



Scheme 1. Light induced mechanism for the photocatalytic hydrogenation of nitrobenzene to aniline catalyzed by  $g-C_3N_4$ .

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Figure 3. Dependence of aniline yield on the reaction temperature. See Table S6 for detailed conditions and results for the reactions under different reaction temperatures.

The photocatalytic reaction catalyzed by  $g-C_3N_4$  can also utilize thermal energy to promote the photocatalytic activity, supported by the fact that higher aniline yields were obtained at elevated reaction temperatures (Figure 3). This conclusion can also be supported by several reported works, although none have recognized this important phenomenon at that time.<sup>[11,33,34]</sup> One reason responsible for this is that the relative population of adsorbate excited vibrational states increases at higher reaction temperatures according to the Bose-Einstein distribution, so less energy from the hot electrons is required for the reactant molecules to overcome the activation barrier.<sup>[39,40,42]</sup>

Although a similar phenomenon has also been observed for plasmonic metal nanostructures mediated photocatalysis, the underlying mechanism should be different because of the different band structures. Recent studies have demonstrated a signature of plasmonic metal nanostructures distinguished with semiconductor photocatalysts that they can effectively couple thermal and light to drive chemical transformations due to the continuum of metal electron energy levels.<sup>[39,40,42]</sup> Semiconductors possess discontinuous energy levels and their photocatalytic activities are always lower at higher temperatures because the charge carriers can more readily recombine.[39] However, in the present reaction system, a strong reducing agent, hydrazine was used as an effective hole scavenger, thus the recombination of the charge carriers could be highly restricted. As the activation of the adsorbed reactant molecules is much easier at higher temperatures, the light induced hot electrons are expected to activate more nitrobenzene molecules, thus higher aniline yields will be observed.

Another interesting feature observed for the reactions at different temperatures is that under dark condition, the hydrogenation of nitrobenzene to aniline did not happen below 90 °C. Only 5 % of aniline yield was obtained when the reaction temperature was as high as 100 °C under dark (Figure 3). This result proves that the photothermal effect dose not play an important role in the present light-induced reaction which is consistent with the conclusion obtained from the study on light intensity and wavelength.

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**Figure 4.** Kinetic profile of the visible-light-driven hydrogenation of nitrobenzene via g-C<sub>3</sub>N<sub>4</sub> metal-free photocatalysis. Reaction conditions: g-C<sub>3</sub>N<sub>4</sub> (20 mg), nitrobenzene (0.2 mmol), hydrazine hydrate (1 mmol, 5 equiv.), H<sub>2</sub>O as solvent (2 mL),  $I = 0.5 \text{ W} \cdot \text{cm}^{-2}$ , T = 80 °C.

Kinetics study was carried out by recording the conversion of nitrobenzene and formation of the products during the reaction. The kinetic profile of the reaction (Figure 4) demonstrates that nitrobenzene was smoothly converted into aniline with an unobvious formation of other products. And during the initial four hours, aniline formed as the sole product. This clearly illustrates that a highly selective way of direct hydrogenation of nitrobenzene to aniline should exist in the visible-light-driven hydrogenation of nitrobenzene.<sup>[45]</sup> According to the previous studies, two stepwise routes are generally accepted to be responsible for the hydrogenation of nitrobenzene to aniline: one is the direct route which proceeds via nitrosobenzene and N-phenylhydroxylamine intermediates, and the other one is the condensation route with azoxybenzene, azobenzene, and hydrazobenzene as the intermediates.<sup>[4,46]</sup> Small amount of azoxybenzene and azobenzene were detected during the reaction, suggesting that the condensation route also exists in this reaction.

Having set the novel procedure for the hydrogenation of nitrobenzene, the substrate scope, which is an important criterion to evaluate its application potential,<sup>[47]</sup> was further studied using several functionalized nitroarenes (Table 1). For all the substrates, the expected functionalized anilines were obtained in good to excellent yields (82-100%) under visible light irradiation and optimized conditions (no reaction observed under dark). For example, both electron-rich (methyl-, Table 1, Entry 1) and electron-deficient (trifluoromethyl-, Table 1, Entry 2) substituents were not interfering. For halogen bearing nitroarenes, dehalogenation is always a competitive process of the hydrogenation reaction, leading to the formation of undesired aniline.<sup>[45]</sup> However, using the present visible-light-driven procedure, the dehalogenation was well suppressed with halogen containing anilines obtained in good yields (Table 1, Entry 3 & 4). Furthermore, dinitrobenzene which bears two nitro groups could also be hydrogenated to form phenylenediamine with good yield although higher temperature and longer time were needed (Table 1, Entry 5).





[a] Reaction conditions:  $g-C_3N_4$  (20 mg), substituted nitroarenes (0.2 mmol), hydrazine hydrate (1 mmol, 5 equiv.),  $H_2O$  as solvent (2 mL), I = 0.5 W·cm<sup>2</sup>. [b] T = 90 °C, t = 32 h. [c] T = 70 °C, t = 24 h. [d] T = 70 °C, t = 32 h. [e] T = 90 °C, t = 18 h. [f] T = 90 °C, t = 32 h. [g] T = 70 °C, t = 36 h. [h] T = 70 °C, t = 24 h.

The nitroarenes bearing other easily reducible moieties are the most challenging substrates to be chemoselectively hydrogenated.<sup>[2,45]</sup> In this respect, we were pleased to find that 3-nitrobenzoic acid could be hydrogenated into 3-aminobenzoic acid quantitatively and selectively without affecting the easily reducible carboxyl group (Table 1, Entry 6). However, nitrile, isonitrile, and aldehyde groups cannot be preserved in this reaction (see Table S7 and detailed discussion in Supporting Information). Moreover, a nitroheteroarene substrate, 8-nitroquinoline, was chemoselectively and quantitatively converted to 8-aminoquinoline which is one of the industrially valuable heteroaromatic amines, while its heterocyclic rings were kept unaffected (Table 1, Entry 7).

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For further evaluate the application potential of the present visible-light-driven procedure, the reusability of the synthesized metal-free photocatalyst,  $g-C_3N_4$ , was tested for four successive cycles. To our delight, although we did not use the complex regeneration processes, this metal-free photocatalyst could maintain its activity and selectivity for aniline yield during the four successive cycles (Table S8).

Finally, we performed a gram-scale reaction for the hydrogenation of nitrobenzene (10 mmol, 1.23 g) using a 300 W Xenon lamp as the simulated sunlight resource. We were pleased to find that a good aniline yield (86%) was achieved at 80 °C after 20 h, which further demonstrated the applicability of the present procedure for the production of anilines.

#### Conclusions

In summary, we have developed a novel, green, efficient, and visible-light-driven procedure for the chemoselective hydrogenation of functionalized nitroarenes in water using lowcost g-C<sub>3</sub>N<sub>4</sub> as a metal-free photocatalyst, and hydrazine hydrate as the green reducing agent as well as hole scavenger. Visible light acts as a critical factor in activating this reaction by inducing charge separation in the photocatalyst to generate hot electrons. Thermal energy can also be utilized to promote the photocatalytic activity which facilitates the full utilization of abundant solar energy. Kinetics study reveals that both a highly selective route of one-step hydrogenation and the stepwise condensation route are possibly responsible for this reaction. Several functionalized nitroarenes bearing the sensitive groups were converted smoothly into the corresponding anilines in good to excellent yields (82-100%). The multiple-cycle use of the photocatalyst and the applicability of this procedure in gram-scale reaction (86% yield of aniline) further demonstrate the application significance of this procedure. The general scope of this procedure will be elaborated in the near future to extend the results of the present report on g-C<sub>3</sub>N<sub>4</sub> metal-free photocatalysis for the reduction reactions for fine chemical synthesis.

### **Experimental Section**

**Materials.** All the chemicals were purchased commercially and used without further purification. Deionized water was used throughout all the experiments. Detailed information of the chemicals is provided in Supporting Information.

**Synthesis and characterization of g-C<sub>3</sub>N<sub>4</sub>.** The polymeric g-C<sub>3</sub>N<sub>4</sub> photocatalyst was prepared by a facile thermal condensation method: 10 g of urea crystal was put into an alumina crucible with a cover, and then heated to 550 °C for 4 h at a ramp of 10 °C-min<sup>-1</sup> in a muffle furnace under air. The resultant yellow powder (~0.5 g) was collected as the photocatalyst without further treatment. To prepare Fe doped g-C<sub>3</sub>N<sub>4</sub>, 10 g of urea crystal and 4.2 mg of FeCl<sub>3</sub> were well mixed and the mixture was treated using the same method. The characterization of the synthesized g-C<sub>3</sub>N<sub>4</sub> photocatalyst was carried out using several advanced technics such as TEM, XRD, XPS, TGA, etc. with the detailed description given in Supporting Information.

General procedure for photocatalytic hydrogenation of nitroarenes. A 10 mL borosilicate glass tube ( $\phi$ 16×100 mm, ASONE) was employed as

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the reaction container. Typically, after being charged with g-C<sub>3</sub>N<sub>4</sub> photocatalyst (20 mg), the substrate (0.2 mmol), hydrazine hydrate (1 mmol), the solvent (2 mL H<sub>2</sub>O), the tube was sealed with a polypropylene screw cap with silicone gasket. Then the photocatalytic reactions were carried out with magnetic stirring at a certain temperature (well controlled by an oil bath) under visible light irradiation using a LED lamp as the light source (spectral output in the range of 400-800 nm as shown in our previous work<sup>[48]</sup>). After certain times, 0.5 mL of the reaction solution were collected and then filtered through a Millipore filter (0.45 µm) to remove the solid photocatalyst particulates. After mixed with 1 mL of absolute ethanol, the products were analyzed quantitatively using an Thermo Trace 1300 gas chromatography (GC) with HP-5 column using external standard method. A Shimadzu GCMS-QP2010 was used to identify the products. All the reactions were performed at least twice to obtain the reproducible results. Experimental details for dark reactions, action spectrum experiments, photocatalyst recycling experiments, and gram scale reaction are given in Supporting Information.

#### Acknowledgements

The authors express their thanks for the supports from the National Natural Science Foundation of China (21525625), the National Basic Research Program (973 Program) of China (2014CB745100), the (863) High Technology Project of China (2013AA020302), the Chinese Universities Scientific Fund (JD1417), the project funded by China Postdoctoral Science Foundation (2017M610038), and the Fundamental Research Funds for the Central Universities (ZY1712, XK1701).

**Keywords:**  $g-C_3N_4 \cdot photocatalysis \cdot visible light \cdot green chemistry \cdot nitroarenes$ 

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Visible-light-driven chemoselective hydrogenation of functionalized nitroarenes to produce industrially important anilines can be achieved in water using  $g-C_3N_4$  as low-cost and recyclable metal-free photocatalyst. Abundant solar energy provides light and heat to promote the reactions. Wide applications in reduction reactions for fine chemical synthesis are expected using this green, efficient, and highly selective photocatalysis system.



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Visible-light-driven chemoselective hydrogenation of nitroarenes to anilines in water via graphitic carbon nitride metal-free photocatalysis