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## ARTICLE

# Light-driving integration of reducing nitrobenzene to aniline and transforming glycerol into valuable chemicals in water

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Both effective utilization of glycerol and reduction of nitrobenzene to aniline are of great importance. It is very interesting to integrate these processes. This work reports the integration of efficient conversion of nitrobenzene to aniline and transformation of glycerol to valuable chemicals driven by UV-light using Pd/TiO<sub>2</sub> as the catalyst and water as the solvent at ambient temperature. In this integrated reaction process, glycerol acted as the hydrogen source for the reduction of nitrobenzene to aniline and the glycerol was converted into value-added chemicals simultaneously. At the optimized conditions, nitrobenzene could be converted completely with aniline selectivity of 95% with a nitrobenzene to glycerol mole ratio of 1:5. At the same time, glycerol was oxidized to form fine chemicals, including 1,3-dihydroxyacetone, glyceraldehyde, formic acid, and hydroxyacetic acid. This work opens a new and effective way for transformation of glycerol to fine chemicals and production of aniline from nitrobenzene.

## Introduction

Aniline is an important chemical and intermediate in the production of pharmaceuticals, dyes, pigments, and pesticides. Nowadays, the production of aniline is mainly by catalytic hydrogenation of nitrobenzene in vapor-phase or liquid-phase processes.<sup>1,2</sup> However, these processes suffer from some drawbacks, such as high reaction temperature, high pressure, low selectivity, and using organic solvents, etc. Moreover, hydrogen currently used for hydrogenation is mainly derived from fossil resources. Development of greener catalytic processes for aniline production from nitrobenzene using renewable hydrogen under mild reaction conditions is highly desirable.

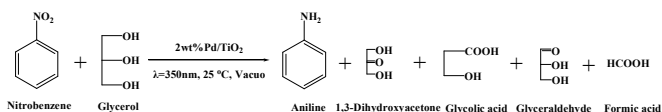
Glycerol, a well-known renewable chemical, has been identified as one of the top-12 building block chemicals by the U.S. Department of Energy. Currently, glycerol is worldwide oversupplied as the by-product of biodiesel production and its price is gradually reduced. The abundance of hydrogen and carbon makes it an attractive alternative of fossil reserves. It is no doubt that conversion of low-cost glycerol into more valuable chemicals is of great importance. In recent years, much effort has been made on efficient transformation of glycerol and various reaction routes have been developed, including hydrogenolysis,<sup>3</sup> oxidation,<sup>4</sup> and dehydration,<sup>5</sup> *etc.* So far, a variety of value-added chemicals have been obtained from glycerol, such as propanediols,<sup>6</sup> formic acid,<sup>7</sup> lactic acid,<sup>8</sup> dihydroxyacetone and acrolein,<sup>9</sup> *etc.* Furthermore, glycerol can be converted into hydrogen and syngas.<sup>10,11</sup> In addition,

glycerol can also be used as the hydrogen source in hydrogen transfer reaction.<sup>12,13</sup> Although much progress has been made, efficient conversion and utilization of glycerol under mild conditions is still an attractive and challenging topic.

Photocatalysis is considered to be excellent approach for chemical reactions under mild conditions. Many reactions can be conducted by photocatalysis, including water splitting,<sup>14,15</sup> pollutant degradation,<sup>16,17</sup> CO<sub>2</sub> reduction<sup>18</sup> and various organic reactions.<sup>19</sup> Particularly, photocatalytic reduction of organic compounds was reported by different researchers. For example, photocatalytic reduction of benzonitrile to benzylamine could be carried out in water in the presence of oxalic acid as a hydrogen source.<sup>20</sup> Photocatalytic hydrogenation of carbonyl compounds to hydroxyl compounds in the presence of appropriate sacrificial agents such as lactic acid and isopropanol was reported.<sup>21</sup> Photocatalytic reduction of organic compounds, including nitrobenzene, has been conducted using methanol, ethanol, and isopropanol as reducing agents and solvents.<sup>22-24</sup>

Use of glycerol as hydrogen resource, reduction of nitrobenzene to aniline, and transformations of glycerol into value-added chemicals are all important. Integration of these processes is more interesting. Herein, we report photocatalytic hydrogenation of nitrobenzene to aniline using glycerol as the hydrogen source under mild condition. In the reaction process, glycerol provided hydrogen for photoreduction of nitrobenzene and it was simultaneously converted into valuable chemicals, including formic acid, hydroxyacetic acid, glyceraldehyde, and 1,3-dihydroxyacetone (Scheme 1). As far as we know, this is

the first approach to integrate a hydrogenation reaction and conversion of glycerol into valuable chemicals.



**Scheme 1.** Photocatalytic reduction of nitrobenzene over Pd/TiO<sub>2</sub>.

## Results and discussion

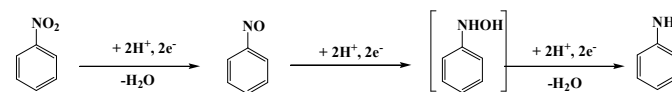
Catalytic activity of various catalysts was examined with a nitrobenzene to glycerol mole ratio of 1:5 and the results are shown in Table 1. Firstly, the photocatalytic reaction was catalyzed by different metal nanoparticles supported on TiO<sub>2</sub> (P-25). The typical transmission electron microscope (TEM) images of the catalysts are shown in Fig. S1. The size difference of the metal nanoparticles in the catalysts was not considerable. The results showed that Pd/TiO<sub>2</sub> exhibited the highest photocatalytic activity among the tested metallic catalysts (Entries 1-4, Table 1). It suggests that Pd supported on TiO<sub>2</sub> is unique for reducing nitrobenzene in the photocatalytic hydrogenation process. In addition, the supports of Pd nanoparticles affect the reaction efficiency significantly. Pd/C<sub>3</sub>N<sub>4</sub>, Pd/SiO<sub>2</sub>, and Pd/C did not show catalytic activity for nitrobenzene reduction under the same conditions (Entries 1 and 5-7, Table 1). These results indicate the existence of cooperative effect between Pd nanoparticles and TiO<sub>2</sub>. The main reasons are that the appropriate energy bandgap (3.2 eV) of TiO<sub>2</sub> results in electron-hole pairs separation under UV irradiation ( $\lambda=350$  nm). Meanwhile, Pd nanoparticles (PdNPs) can suppress the recombination of photoinduced electron-hole pairs and reverse reactions.<sup>25,26</sup> Moreover, PdNPs on the surface of TiO<sub>2</sub> offer active sites for forming H-PdNPs species and hydrogenation of nitrobenzene to aniline, in which H was from glycerol. Our control experiment indicated that the hydrogenation reaction could be prohibited by adding 50 mg 2,2',6,6'-tetramethylpiperidine N-oxyl (TEMPO) into the reaction system, which can abstract hydrogen atom from the metal surface to form hydroxylamine.<sup>27,28</sup> The result provides the evidence for the formation and function of the H-PdNPs species in the reaction process. In addition, no reaction took place over the Pd/TiO<sub>2</sub> in the absence of UV-irradiation. Therefore, it can be concluded that the light irradiation is the driving force of the reaction. In the following, we studied the reaction using Pd/TiO<sub>2</sub> as the catalyst in detail.

**Table 1.** Performance of photocatalytic reduction of nitrobenzene over various catalysts in glycerol aqueous solution.<sup>a</sup>

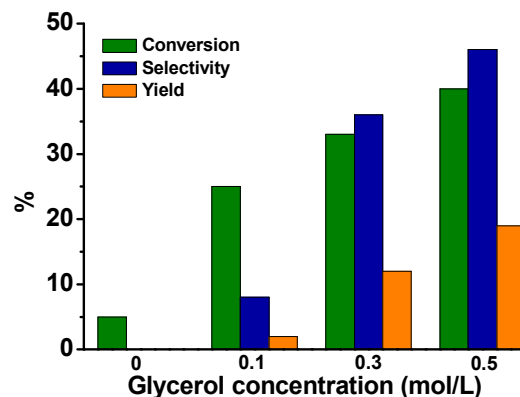
Entry	Catalysts	Nitrobenzene Conversion (%)	Aniline Selectivity (%)
1	Pd/TiO <sub>2</sub>	40	46
2	Pt/TiO <sub>2</sub>	35	20
3	Ru/TiO <sub>2</sub>	30	28
4	Rh/TiO <sub>2</sub>	32	22
5	Pd/C <sub>3</sub> N <sub>4</sub>	5	0
6	Pd/SiO <sub>2</sub>	3	0
7	Pd/C <sup>b</sup>	--	0

<sup>a</sup>Reaction conditions: nitrobenzene 100  $\mu$ mol; water 1 mL; glycerol 500  $\mu$ mol; 25 mg catalysts with 2 wt% metal loading; temperature 25 °C; reaction time 3 h. <sup>b</sup>25 mg Pd/C with 5 wt% Pd.

The effect of the initial concentration of glycerol on the photocatalytic reduction of nitrobenzene to aniline is shown in Fig. 1. It can be seen that aniline could not be formed in pure water although little amount of nitrobenzene was converted. The conversion, selectivity, and yield increased with increasing concentration of glycerol. At glycerol concentration of 0.5 mol/L, 40% of nitrobenzene was converted towards aniline with a selectivity of 46% and the others were the intermediates such as nitrosobenzene, which were confirmed by HPLC and GC-MS. The intermediates could be converted to aniline with prolonged reaction time (Scheme 2), which was confirmed by the fact that the yield of aniline could approach nearly 100% by prolonging the reaction time to 18 hours as will be discussed in the following sections. From these results, it can be confirmed that glycerol is the hydrogen source for nitrobenzene hydrogenation. Meanwhile, glycerol also acted as the hole scavenger to inhibit the recombination of the photoinduced electron-hole pairs on TiO<sub>2</sub> because the hydroxyl groups in glycerol can capture the photoinduced holes, which is similar to the effect of hydroxyl group in methanol.<sup>23</sup> In the reaction system, high glycerol concentration favors fast consumption of photoexcited holes and the rapid formation of H-PdNPs species, resulting in high efficiency of the photocatalytic reaction.



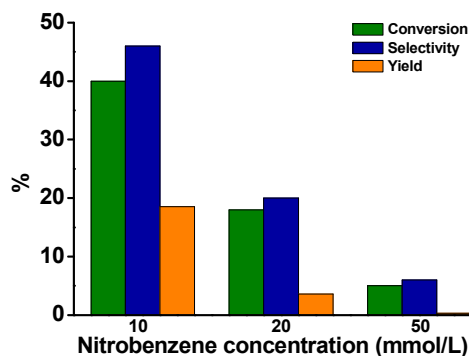
**Scheme 2.** Photocatalytic reduction of nitrobenzene over Pd/TiO<sub>2</sub>.



**Fig. 1.** Effect of the initial glycerol concentration on the photocatalytic hydrogenation of nitrobenzene to aniline. Reaction conditions: nitrobenzene 100  $\mu$ mol; water 1 mL; 25 mg Pd/TiO<sub>2</sub> (P-25) with 2 wt% Pd; temperature 25 °C; reaction time 3 hours.

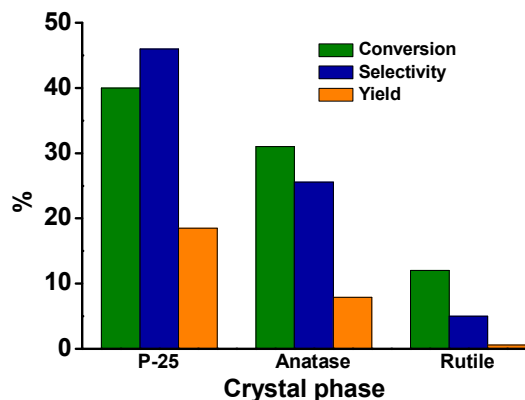
We also investigated the effect of the initial concentration of nitrobenzene on the photocatalytic reduction. As shown in Fig. 2, the conversion, selectivity, and yield decreased sharply when the initial concentration of nitrobenzene increased from 10 mmol/L to 50 mmol/L. It is well known that the photoreduction occurs only when photons are absorbed by the semiconductor.<sup>22</sup> Increasing concentration of nitrobenzene led to that photons were predominantly adsorbed by nitrobenzene

and thus suppressed charges separation of TiO<sub>2</sub> induced by UV-light irradiation.<sup>22</sup> Thus, the efficiency of the reaction decreased.



**Fig. 2.** Effect of the initial concentration of nitrobenzene. Reaction conditions: glycerol 500  $\mu$ mol; water 1 mL; 25 mg Pd/TiO<sub>2</sub> with 2 wt% Pd; temperature 25  $^{\circ}$ C; reaction time 3 hours.

The photocatalytic performance of TiO<sub>2</sub> supports with different crystal phases was studied, and the results are presented in Fig. 3. The XRD patterns of the rutile, anatase, and P-25 (with anatase/rutile mixed crystal phase) are given in Fig. S3 (Supporting information). The results indicate that the TiO<sub>2</sub> (P-25) was more effective for the reaction than the pure rutile or anatase, and the conversion and selectivity followed the order of P-25 > anatase > rutile. The reason is that the difference in the energy levels of anatase and rutile conduction bands in P-25 enhances the photoexcited electron-hole separation, thus improving the photocatalytic efficiency for efficient oxidation and reduction processes.<sup>29</sup> In contrast, electrons and holes produced in pure anatase phase or rutile phase suffer from relative short lifetime and fast recombination, which was not favorable to the photoreaction process. Therefore, mixed crystal phase is preferable to achieve good photocatalytic activity.



**Fig. 3.** Photocatalytic performance of TiO<sub>2</sub> with different crystal phases. Reaction conditions: nitrobenzene 100  $\mu$ mol; water 1 mL; glycerol 500  $\mu$ mol; 25 mg Pd/TiO<sub>2</sub> with 2 wt% Pd; temperature 25  $^{\circ}$ C; reaction time 3 hours.

The various alcohols were used as the hydrogen source for the reaction. The results are given in Table 2. Glycerol had superior performance compared with methanol, ethanol and isopropanol under the same alcohol concentration (1 mol/L) or the same concentration of hydroxyl groups (3 mol/L). The main reason for this interesting phenomenon may be that the different molecular structures of the alcohols resulted in different adsorbing behavior on the catalyst. Glycerol has three hydroxyl groups and can be adsorbed more strongly, which is favorable to the reaction. We designed and carried out the control experiment to find evidence to support this argument. In the experiment we used a mixture of glycerol (0.5 mol/L) and isopropanol (0.5 mol/L), and the results are illustrated in Fig. S2. Glycerol was predominantly consumed. In contrast, photooxidation of isopropanol did not occur obviously. This suggests that glycerol has stronger adsorption on the catalyst than isopropanol, which prevents the adsorption of isopropanol, and therefore it could not be oxidized in the presence of glycerol. Furthermore, polyhydroxy structures favored efficient transferring of photogenerated holes in TiO<sub>2</sub> to the adsorbed glycerol, which could suppress the charge carriers recombination and promotes the formation of active hydrogen.<sup>30,31</sup> This also enhanced the reaction.

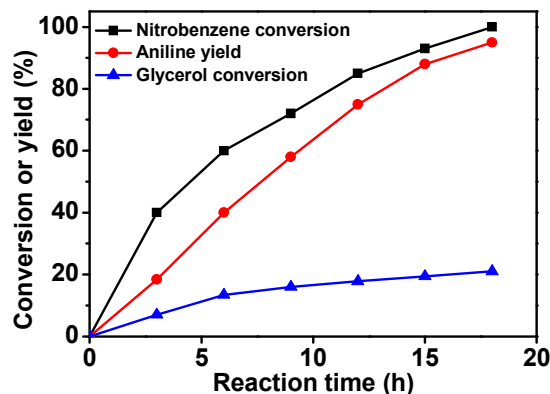
**Table 2.** Effect of concentration and type of scavengers on the reaction.<sup>a</sup>

Entry	Hydrogen source	Concentration (mol/L)	Nitrobenzene Conv(%)	Aniline Sel (%)
1	Glycerol	1	47	58
2	Methanol	1	17	17
3	Methanol	3	20	31
4	Ethanol	1	15	11
5	Ethanol	3	21	27
6	Isopropanol	1	18	11
7	Isopropanol	3	21	15

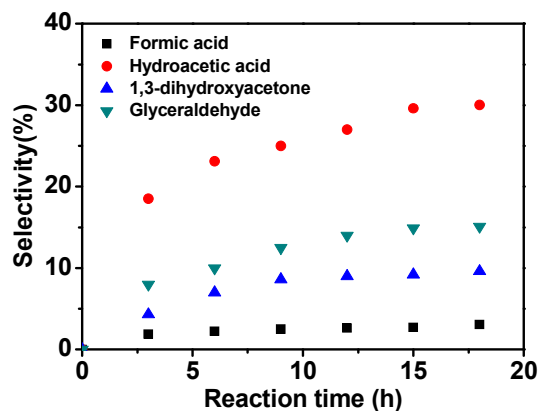
<sup>a</sup>Reaction conditions: nitrobenzene 50  $\mu$ mol; water 5 mL; 25 mg Pd/TiO<sub>2</sub> (P-25) with 2 wt% Pd; temperature 25  $^{\circ}$ C; reaction time 1 hour.

The dependence of the conversions of nitrobenzene and glycerol and the selectivity to aniline on time was examined at a nitrobenzene to glycerol mole ratio of 1:5 and the results are illustrated in Fig. 4. The conversions and the selectivity increased with reaction time within 18 hours. The selectivity of aniline increased with time because aniline was formed via intermediates as discussed above (Scheme 2). The nitrobenzene could be entirely converted with an aniline selectivity of 95% at a reaction time of 18 hours. We also examined the oxidation products of glycerol, including glyceraldehyde, 1,3-dihydroxyacetone, hydroxyacetic acid, and formic acid (shown in Scheme 1) by HPLC with a refractive detector (Shimadzu RID-10A) and a UV-Vis detector (Shimadzu SPD-20A), and the results are shown in Fig. 5. It indicated that glycerol could be converted into value-added products simultaneously when nitrobenzene was transformed into aniline. Under photoirradiation, glycerol was firstly dehydrogenated to glyceraldehyde and 1,3-dihydroxyacetone when electron and H<sup>+</sup> were released at the same time. In sequence, glyceraldehyde and 1,3-dihydroxyacetone were further oxidized by photoexcited holes with water to hydroacetic acid and formic acid through C-C bond cleavage, releasing another hydrogen ions. Formic acid obtained from glycerol oxidation could be further utilized for nitrobenzene hydrogenation. Thus, the selectivity of formic acid is lower than that of hydroacetic acid. The amount of the

products from glycerol increased with the increasing reaction time because glycerol was continually oxidized as the reaction proceeded.



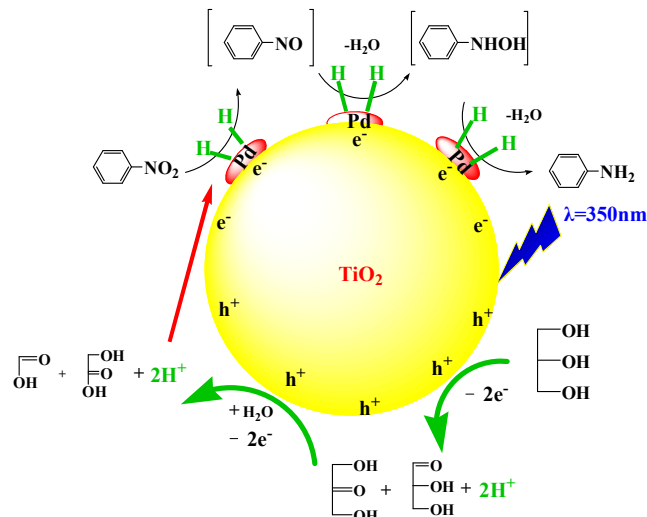
**Fig. 4.** Dependence of the conversion and yield on reaction time. Reaction conditions: nitrobenzene 100  $\mu\text{mol}$ ; water 1 mL; glycerol 500  $\mu\text{mol}$ ; 25 mg Pd/TiO<sub>2</sub> (P-25) with 2 wt% Pd; temperature 25 °C.



**Fig. 5.** Dependence of the selectivities (based on the glycerol converted) of products from glycerol on time. Reaction conditions: nitrobenzene 100  $\mu\text{mol}$ ; water 1 mL; glycerol 500  $\mu\text{mol}$ ; 25 mg Pd/TiO<sub>2</sub> (P-25) with 2 wt% Pd; temperature 25 °C. The conversion of glycerol was given in Fig. 4.

Based on the results above and the knowledge in the literature, we propose the possible mechanism for the integration of the photocatalytic hydrogenation of nitrobenzene to aniline and conversion of glycerol into valuable chemicals catalyzed by Pd/TiO<sub>2</sub> (Scheme 3). Firstly, electrons of TiO<sub>2</sub> are excited from valence band to conduction band by UV irradiation. The photoinduced electrons are trapped by Pd nanoparticles. The glycerol is then directly dehydrogenated to 1,3-dihydroxyacetone and glyceraldehyde, releasing two H<sup>+</sup>. Subsequently, 1,3-dihydroxyacetone and glyceraldehyde were further oxidized by the holes with water to form formic acid and hydroxyacetic acid originated from C-C cleavage, releasing another two H<sup>+</sup>. The H<sup>+</sup> is reduced by electrons on Pd nanoparticles to form H-PdNPs. Finally, nitrobenzene is successively hydrogenated to aniline at the reducing sites

(PdNPs) by H-PdNPs. In the catalytic cycle, Pd nanoparticles not only serve as electron sinks, but also offer active sites for the formation of H-PdNPs species from glycerol for the reduction of nitrobenzene. Photoinduced holes of TiO<sub>2</sub> are crucial for photooxidation of glycerol to chemicals. The cooperative effect between Pd nanoparticles and TiO<sub>2</sub> plays a significant role in photocatalytic hydrogenation of nitrobenzene.



**Scheme 3.** Plausible mechanism for the integration of the photocatalytic hydrogenation of nitrobenzene to aniline and conversion of glycerol into valuable chemicals Pd/TiO<sub>2</sub>.

## Conclusions

In conclusion, it has been discovered that photoreduction of nitrobenzene to aniline can be integrated with photooxidation of glycerol under UV irradiation in aqueous solution catalyzed by Pd/TiO<sub>2</sub>. The yield of aniline can reach 95% with a nitrobenzene to glycerol mole ratio of 1:5, and glycerol is converted into several value-added chemicals at the same time. Glycerol is more effective for the reactions than methanol, ethanol and isopropanol. The high efficiency of the reactions results mainly from the cooperative effect of PdNPs, TiO<sub>2</sub>, and glycerol. In the reactions, TiO<sub>2</sub> with mixing crystal phases results in efficient separation of electron-hole pairs under UV irradiation. The PdNPs can suppress the recombination of photoinduced electron-hole pairs and also offer active sites for forming H-PdNPs species and hydrogenation of nitrobenzene to aniline. Glycerol provides hydrogen for the nitrobenzene hydrogenation. The polyhydroxy structure of glycerol leads to efficiently transfer of photoexcited holes to glycerol adsorbed on the catalyst. This work provides a new, sustainable, and effective protocol for production of aniline from nitrobenzene and fine chemicals from glycerol. The strategy can also be used to integrate some other hydrogenation reactions with transformation of glycerol.

## Experimental Section

### Materials

H<sub>2</sub>PtCl<sub>6</sub> aqueous solution (20%Pt), NaBH<sub>4</sub> (98%) and nitrobenzene (99%) were purchased from Alfa Aesar.

RhCl<sub>3</sub>·nH<sub>2</sub>O (98%) was provided by Accela. PdCl<sub>2</sub> (99.5%) was obtained from Jinke Chemical Reagent Shenyang Co., Ltd, China. Glycerol (99%), formic acid (99%), and RuCl<sub>3</sub>·nH<sub>2</sub>O (99.9%) were provided by J&K Scientific Co., Ltd. Hydroxyacetic acid (95%) and 1,3-dihydroxyacetone (95%) were obtained from Ark. Glyceraldehyde (90%) was offered by Sigma-Aldrich. Aniline (A. R. Grade) and TiO<sub>2</sub> (anatase) were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. TiO<sub>2</sub> (P-25) was obtained from Acros. The rutile of TiO<sub>2</sub> was prepared by calcining anatase at 800 °C for 4 hours. The catalyst Pd/C was purchased from Baoji Rock Pharmachem Co., Ltd, China (5 wt% Pd, Product No. D5L3). All chemicals were used without further purification. Double distilled water was used throughout the experiments.

### Preparation of Pd/TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, Ru/TiO<sub>2</sub> and Rh/TiO<sub>2</sub>

These supported catalysts were synthesized by photoreduction method, which was similar to that reported in the literature.<sup>32</sup> We describe the preparation of Pd/TiO<sub>2</sub> because the procedures for preparing other catalysts were nearly the same, and the main difference was that the corresponding metal precursors were used. In a typical experiment, 5 mL of water, 0.046 g of glycerol, 0.025 g of TiO<sub>2</sub>, desired amounts of PdCl<sub>2</sub> were added into a stainless-steel reactor of 10 mL with a top-irradiation quartz window. The Pd/TiO<sub>2</sub> was obtained after photocatalytic reduction of the Pd(II) by UV irradiation ( $\lambda = 350$  nm, 450 W Xenon lamp) for 1 h.

### Preparation of Pd/C<sub>3</sub>N<sub>4</sub> and Pd/SiO<sub>2</sub>

C<sub>3</sub>N<sub>4</sub> was firstly prepared according to the procedures used previously.<sup>33</sup> In the experiment, 2.0 g of urea was put into an alumina crucible with a cover. It was heated to 550 °C in a muffle furnace with a heating rate of 3.0 °Cmin<sup>-1</sup> and maintained at this temperature for 2 h. The resultant yellow powder was collected for use. In a typical experiment to prepare the C<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub> (obtained from Alfa Aesar) supported catalysts, 0.0083 g of PdCl<sub>2</sub> and 0.25 g support (C<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub>) were dispersed in 50 mL water. After stirred for 2 h, 10 mL aqueous solution of NaBH<sub>4</sub> with 0.0364 g NaBH<sub>4</sub> was added into the dispersion dropwise with a time of 1h. Then, the mixture was continually stirred for another 1 h. Finally, the catalyst was collected by centrifugation and washed by water and ethanol, and then was dried at 60 °C for 12 h under vacuum.

### Characterization of the catalysts

The transmission electron microscopy (TEM) images were obtained using a TEM JEOL-1011 with an accelerating voltage of 120 kV. The sample was dispersed in ethanol with the aid of sonication and dropped on an amorphous carbon film supported on a copper grid for the TEM analysis. The contents of metals in the catalysts were determined by ICP-AES method (VISTA-MPX). Powder XRD patterns of the crystal phases of TiO<sub>2</sub> were recorded on Rigaku D/max-2500 X-ray diffractometer using Cu-K $\alpha$  radiation ( $\lambda=0.15406$  nm) at a scanning rate of 5 degree min<sup>-1</sup>. The tube voltage was 40 kV and the current was 200 mA.

### Photocatalytic Reactions

The photocatalytic reaction was carried out in a cylindrical stainless-steel reactor of 8 mL. There was a quartz window at the top of the reactor for the UV irradiation. In an experiment, desired amounts of water, catalyst, glycerol (or other alcohols),

and nitrobenzene were added into the reactor. After degassing, the reactor was irradiated by a 450 W Xenon lamp equipped with an optical filter ( $\lambda = 350$  nm) for a desired reaction time at 25 °C. The reaction mixture was analyzed by HPLC with Shimadzu LC-15C pump, Shimadzu UV-Vis SPD-15C detector at 295 nm, and a Hypersil ODS2 column at 35 °C. Methanol/water solution (60/40 V/V) was used as the mobile phase at a flow rate of 1.0 mL/min. The chemicals in the reaction mixture were identified by GC-MS (QP-2010) as well as by comparing retention times to the respective standards in HPLC traces.

### Acknowledgements

The authors thank the National Natural Science Foundation of China (21133009, 21373230, U1232203, 21321063) and the Chinese Academy of Sciences (KJCX2.YW.H30).

### Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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