Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information for

Visible light driven selective hydrogenation of unsaturated aromatics in aqueous solution by direct photocatalysis of Au nanoparticle

Yiming Huang,[a] Zhe Liu,[a] Guoping Gao,[b] Qi Xiao,[c] Wayde Martens,[a] Aijun Du,[a] Sarina Sarina,* [a] Cheng Guo,[d] and Huaiyong Zhu[a]

[a] School of Chemistry, Physics and Mechanical, Faculty of Science and Technology, Queensland University of Technology, Brisbane, Queensland 4001, Australia

[b] Materials Sciences, Lawrence Berkeley National Lab, Berkeley CA 94720, United States

[c] Ian Wark Laboratory, Commonwealth Scientific and Industrial Research Organisatio, Bayview Ave, Clayton, Victoria 3168, Australia

[d] College of Science, Nanjing University of Technology, Nanjing, Jiangsu 211800, China

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1. Apparent activation energy of light irradiated and dark hydrogenation reaction

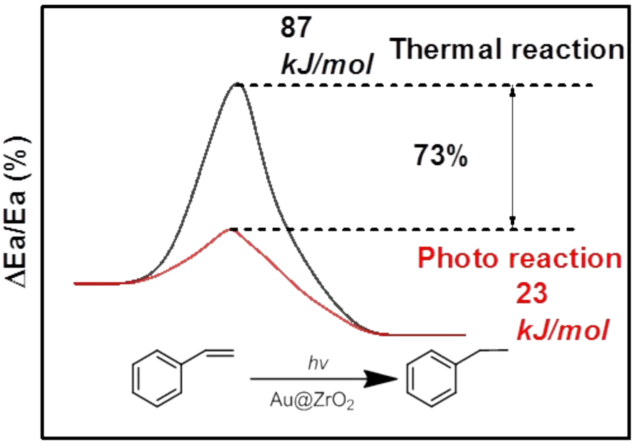


Figure S1-1. Apparent activation energy of styrene hydrogenation. 50 mg Au@ZrO_2 photocatalyst, 1 mmol nitrobenzene as reactant, 2 ml formic acid mixed with 2 ml H_2O as solvent, 0.5 W/cm^2 irradiance, 1 atm argon gas and 16 h. The apparent activation energy of catalytic styrene hydrogenation was estimated by using the Arrhenius equation and kinetic data at different temperatures: 40 °C, 50 °C, 60 °C and 70 °C.

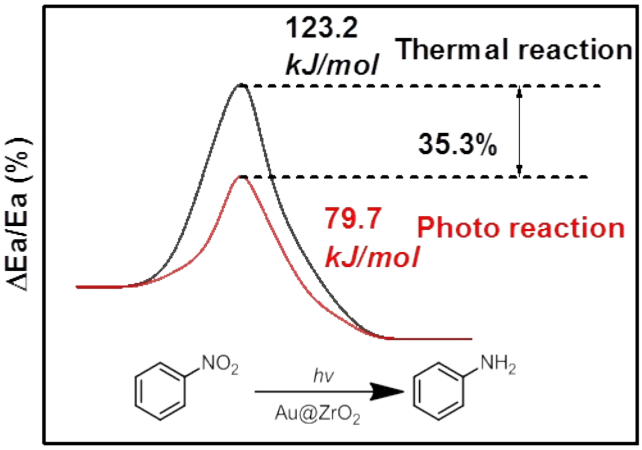


Figure S1-2. Apparent activation energy of nitrobenzene hydrogenation. 50 mg Au@ZrO_2 photocatalyst, 1 mmol nitrobenzene as reactant, 2 ml formic acid mixed with 2 ml H_2O as solvent, 0.5 W/cm^2 irradiance, 1 atm argon gas and 14 h. The apparent activation energy of catalytic styrene hydrogenation was estimated by using the Arrhenius equation and kinetic data at different temperatures: 30 °C, 40 °C, 50 °C and 60 °C.

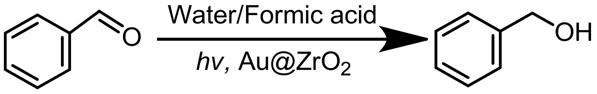
2 Reductive potential of relevant substrate

Table S1 Reductive potential of relevant substrates

Entry	Substrate	Reduction potential (eV)
1[1]	Acetaldehyde	-1.7
2[1]	Benzaldehyde	-1.36
3[2]	Styrene	-2.65
4[3]	Nitrobenzene	-0.356

3 Impact of water/formic acid ratio on photocatalytic performance

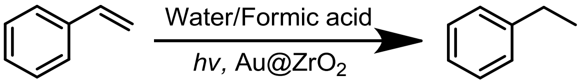
Table S2-1. Impact of water/formic acid ratio on the photocatalytic performance of benzaldehyde hydrogenation.



Entry	H_2O:Formic Acid* Volume ratio	Conversion %
1	1.5:8.5	8
2	3.5:6.5	11
3	6:4	28
4	8:2	42
5	10:0	0

Reaction condition: 50 mg Au@ZrO_2 photocatalyst, 1 mmol benzaldehyde as reactant, formic acid mixed with H_2O as solvent, 0.5 W/cm^2 irradiance, 70 ℃, 1 atm argon gas and 16 h.

Table S2-2. Impact of water/formic acid ratio on the photocatalytic performance of styrene hydrogenation.



Entry	H_2O/Formic Acid* Volume ratio	Conversion %
1	1.5:8.5	10
2	3.5:6.5	30
3	6:4	44
4	8:2	41
5	10:0	0

Reaction condition: 50 mg Au@ZrO_2 photocatalyst, 1 mmol styrene as reactant, formic acid mixed with H_2O as solvent, 0.5 W/cm^2 irradiance, 50 ℃, 1 atm argon gas and 5 h.

4 Scheme of Haber's mechanism

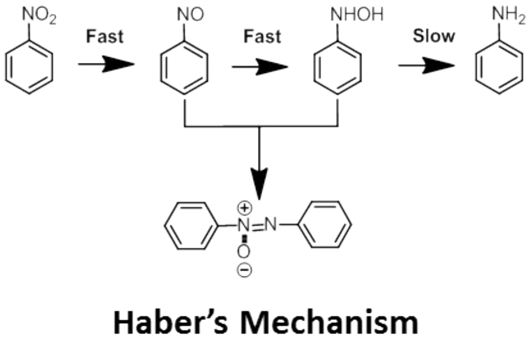


Figure S2. Haber's mechanism for nitrobenzene reduction

According to Haber's mechanism,[4] the nitro group is reduced stepwise first to nitrosobenzene and then the hydroxylamine. Hydroxylamine can easily react with nitrosobenzene yielding azoxybenzene, which is further reduce to azobenzene and eventually aniline.

5 Time resolved evolution of hydroxylamine and azobenzene hydrogenation

Table S3. Time resolved performance of the hydrogenation using hydroxylamine and azobenzene.

Reactant	Time	Conv. %	Select. %	
			Aniline	Azobenzene
Hydroxylamine	1h	100	54	46
	2h	100	50	50
	4h	100	52	48
Azobenzene	1h	68	100	-
	2h	100	100	-
	4h	100	100	-

Reaction condition: 50 mg Au@ZrO_2 dispersed into a solution of 4 mL of 85% formic acid and 15 mL deionised water, light intensity 0.5 W/cm^2, 40 °C, 1 atm argon, reaction time 4 h, 1 mL specimen was taken every hour and analysed by MS (identifying the species) and GC (determining the concentration of the species).

6 Mechanism for the photocatalytic hydrogenation of nitrobenzene

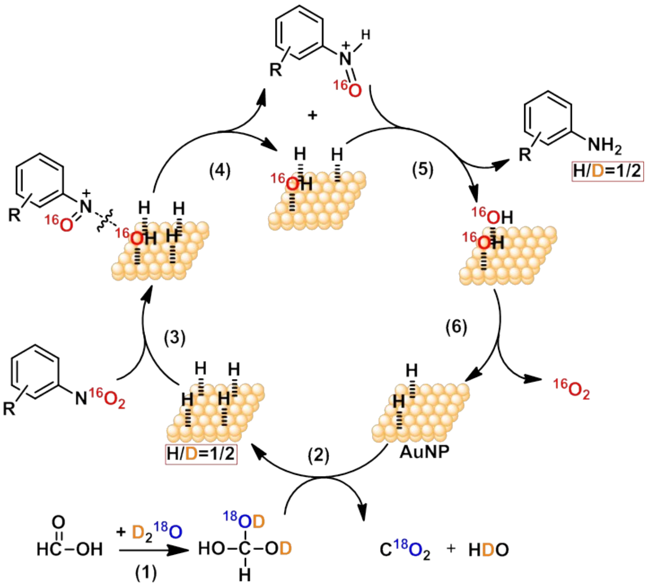


Figure S3. Mechanism for the photocatalytic hydrogenation of nitrobenzene.

The first step is that orthoformic acid forms via the hydration of formic acid (step 1), which can provide hydrogen to yield H-Au species (step 2). This step should appear in all the reactions in the present study. These H-Au surface species are capable of interacting with the oxygen atom of the N-O bonds (step 3), yielding OH-Au species on the surface of AuNPs meanwhile a hydrogen atom from another H-Au species is added to the nitrogen atom forming a N-H bond (step 4). Further reaction of the intermediate with H-Au surface species could yield aniline and HO-Au surface species (step 5)

In the previously reported photocatalytic system of AuNP catalyst and KOH in isopropanol,[5] which has weaker reduction power, the one N-O bond in the -NO$_2$ group of nitrobenzene react with the H-Au surface species yielding nitrosobenzene. The subsequent conversion of nitrosobenzene to azoxybenzene, and azoxybenzene to azobenzene are much easier than that from azobenzene to aniline, and azoxybenzene was observed. As we did not observed the Ph-(HNO) and other intermediates in the present study, we cannot exclude that the two N-O bonds in -NO$_2$ group react simultaneously with the H-Au surface species. In a difference from the hydrogenation of styrene, this reduction of a nitrobenzene molecule consumes 4 H-Au species and produces two OH-Au species on the surface of AuNPs. The two OH-Au species release an oxygen molecule (oxygen gas was detected in the reaction system) and yield two H-Au species in the subsequent process (step 6). As expected, the addition of TEMPO also stopped this reaction, further supporting the role of H-Au species in the catalytic cycle.

Reference

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