

Electronic Supplementary Information

Selective reduction of nitroaromatics to azoxycompounds on supported Ag-Cu alloy nanoparticles through visible light irradiation

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LEGENDS

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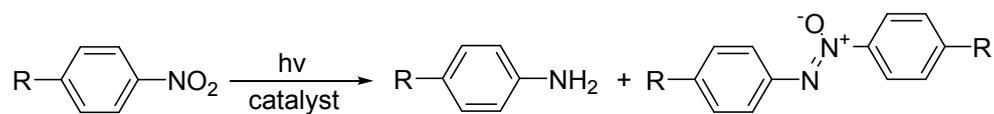
Figure S4. Transmission electron microscopy (TEM) analysis of the Ag NPs

Table S1. The quantified composition of Ag and Cu for catalysts with different ratios

Entry	Mole ratio of Ag to Cu		Weight ratio of Ag to Cu	
	Experimental design	TEM ^[a]	Experimental design	SEM ^[b]
1	4-1	4.3-1.0	2.6-0.4	2.65-0.35
2	1-1	1.4-1.0	1.9-1.1	1.97-1.03
3	1-4	1.0-4.4	0.9-2.1	1.05-1.95

[a] Determined from EDX spectrum and element mapping from TEM analysis in Figure 2e and Figure S2.

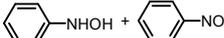
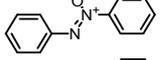
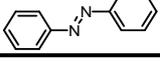
[b] Determined from EDX spectrum and elemental mapping from SEM analysis in Figure S3.

Table S2. Performance of Ag-Cu (4-1)@ZrO₂ for reduction of nitrobenzene with different substituent groups:

Entry	R	Conv. (%) (dark)	Select. (%)	
			Aniline	Azoxy
1	Cl	80 (46)	11	89
2	Br	70 (25)	29	71
3	MeO	50 (3)	29	71
4	H	96 (16)	14	86

Reaction condition: photocatalyst 50 mg, reactant 0.5 mmol, 3 mL isopropyl alcohol (IPA) as solvent, 0.15 mmol KOH as base, 1 atm argon atmosphere, reaction temperature 60°C, reaction time 16 h and the light intensity was 0.8 W/cm². The conversions and selectivity were analysed by gas chromatography (GC).

Table S3. Photocatalytic performance of pure Ag@ZrO₂ using various intermediates as reactant

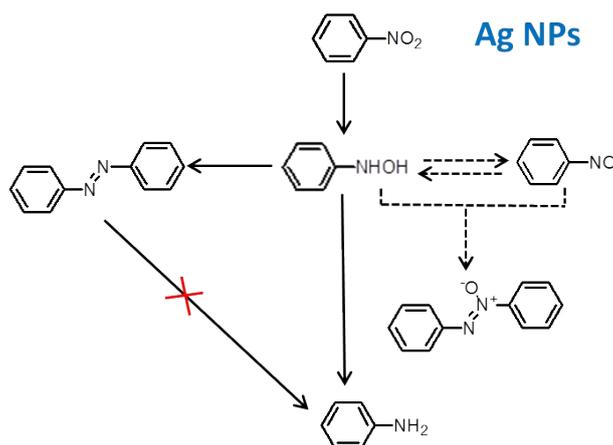
Entry	Substrate	Conv. (%)	Select. (%)		
			Aniline	Azo	Azoxy
1		90	17	83	0
2 ^[a]		100	4	4	92
3 ^[a]		100	6	71	23
4 ^[a]		100	3	13	84
5		16	0	100	0
6		0	-	-	-

Reaction condition: photocatalyst 50 mg, reactant 0.5 mmol, 3 mL IPA as solvent, 1 atm argon atmosphere, environment temperature 60°C, reaction time 16 h and the light intensity was 0.8 W/cm². The conversions and selectivity were analysed by gas chromatography (GC). [a] reaction time 5 h.

Table S4. The amount of Ag and Cu in the supernatant liquid after in the recycle of catalyst as detected by ICP-AES analysis

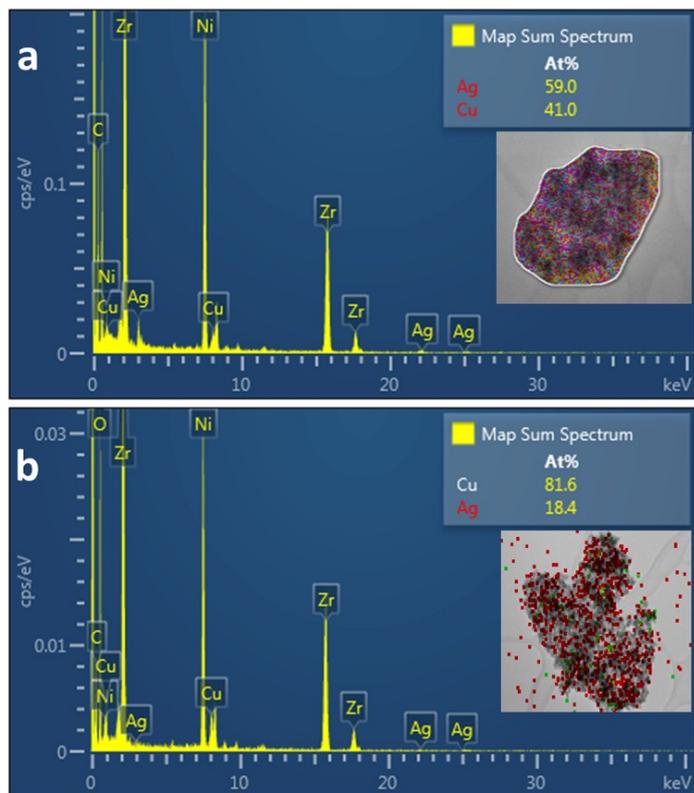
Entry	Runs	Amount of Ag (ppm)	Amount of Cu (ppm)
1	1	0.067	8.004
2	2	0.587	4.569
3	5	0.017	1.238
4	10	0.008	0.181

Scheme S1. Possible reaction pathways for the reduction of nitrobenzene with pure Ag NPs.



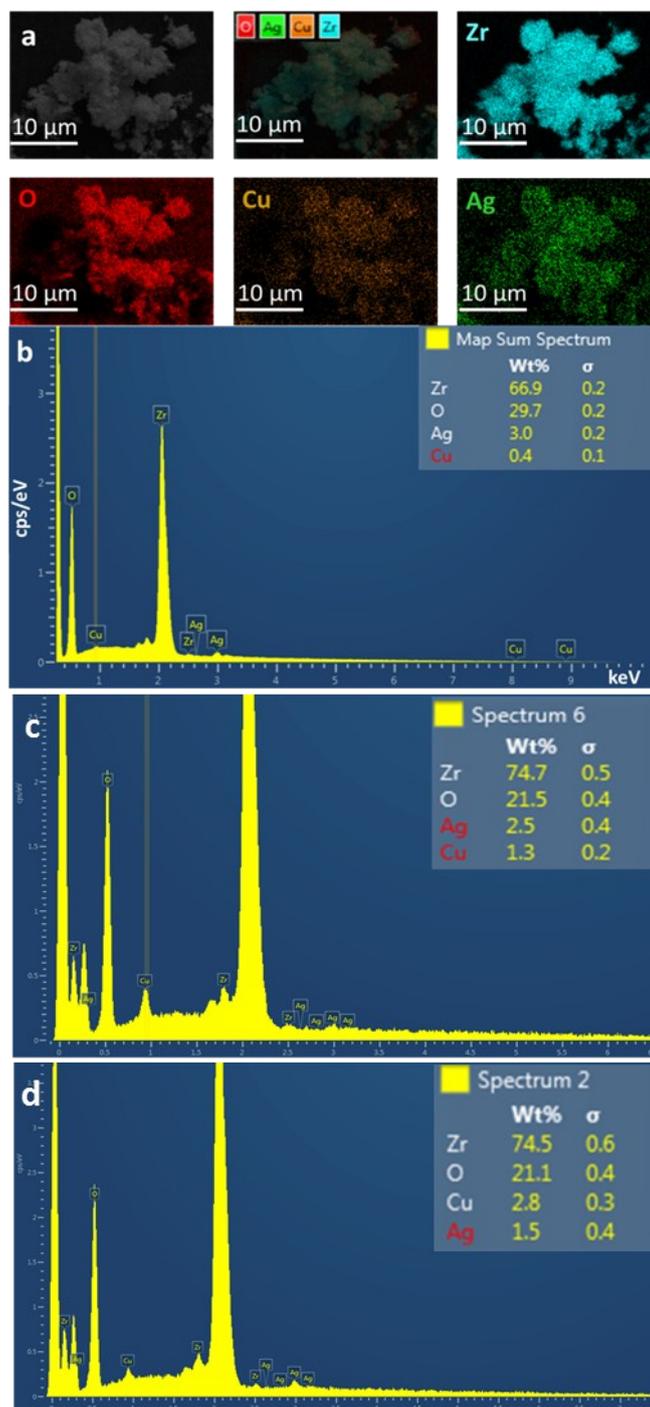
In the Ag NPs catalyst's case, we observed the same result as Ag-Cu NPs catalyst that azoxybenzene cannot be further reduced to aniline, it leads to same conclusion of formation of aniline and azoxybenzene are parallel reactions (entry 6, Table S2). It was demonstrated Ag NPs cannot efficiently convert azoxybenzene into azobenzene (entry 5, Table S2), this phenomenon implies that in the reduction of nitrobenzene the great amount of azoxybenzene was not transferred from azoxybenzene but follows another pathway. On the other hand, when both nitrosobenzene and hydroxylamine was introduced into the reaction, we observed 84% yield of azoxybenzene (entry 4, Table S2). The reduction of nitrobenzene over Ag NPs catalyst cannot produce both nitrosobenzene and hydroxylamine otherwise azoxybenzene instead of azobenzene would have been observed. We separately investigated the reduction of nitrosobenzene and hydroxylamine and found reduction of hydroxylamine gives similar selectivity as the reduction of nitrobenzene only with faster reaction rate (entries 1 and 3, Table S2), however adverse selectivity was observed with nitrosobenzene (entry 2, Table S2). It illustrates the absence of nitrosobenzene as an intermediates in the reduction of nitrobenzene because if it exists stably in reaction system, azoxybenzene can be obtained as main product of coupling. Therefore, the complete reaction route of nitrobenzene reduction over Ag NPs catalyst is illuminated in Scheme S1.

Figure S1. The EDX spectrum from TEM



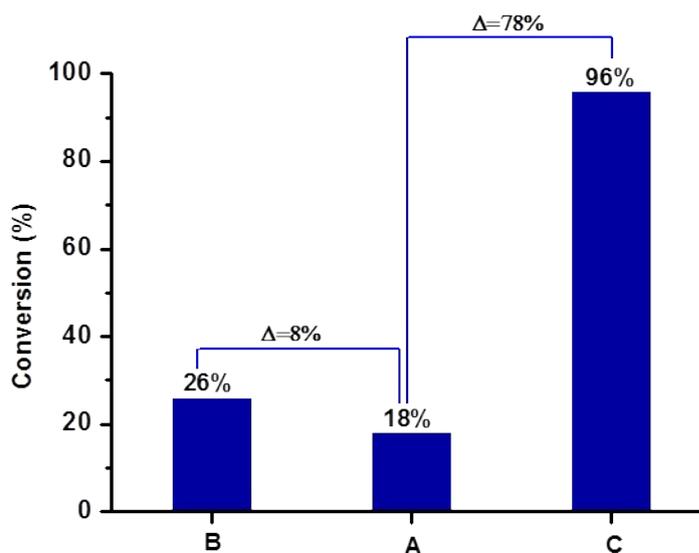
(a) EDX spectrum from TEM for Ag-Cu (1-1)@ZrO₂ samples. (b) EDX spectrum from TEM for Ag-Cu (1-4)@ZrO₂ samples

Figure S2. Scanning electron microscopy (SEM) analysis of the catalysts



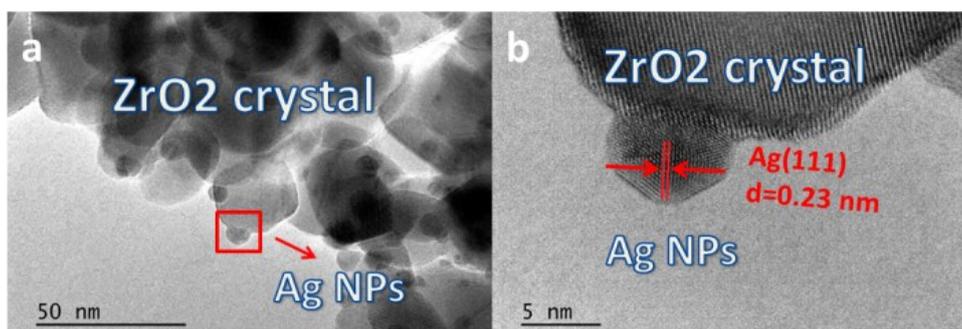
(a) SEM image of Ag-Cu (4-1) @ZrO₂ sample and the corresponding mapping of Zr, O, Cu and Ag elements. (b) EDX spectrum from SEM for Ag-Cu (4-1) @ZrO₂ sample. (c) EDX spectrum from SEM for Ag-Cu (1-1) @ZrO₂ sample. (d) EDX spectrum from SEM for Ag-Cu (4-1) @ZrO₂ sample.

Figure S3. The results of the hot filtration test



The reaction was interrupted at 1.0 h, and the catalyst was removed by filtration, the solution was labelled as A, 0.5 mL sample was collected for GC test. The rest solution without catalyst was re-irradiated as typical procedure, and after the reaction, sample was collected for GC test (labelled as B). After moving catalyst, the conversion for B increased by 8 % (from 18 % from 26 %). The conversion of typical reaction with catalyst (labelled C) was 96 %, which increased by 78 % from the first hour. It can be seen that the reaction did not proceed too much for the solution B, which means that the NPs peeled off from catalyst has little effect to the reaction. Moreover, from the reusability of Ag-Cu alloy NPs (Figure 9 in main text), we can also confirm that the catalytic activity doesn't lose too much during the reaction. Overall the main contribution of the activity results from the photocatalytic response of heterogeneous Ag-Cu alloy NPs.

Figure S4. Transmission electron microscopy (TEM) analysis of the Ag NPs



(a) TEM image of the Ag@ZrO₂ samples. (b) HR-TEM image of Ag particle indicated in part a (red square).