Electronic Supplementary Information

The synthesis and catalytic activity of bimetallic CuAg nanoparticles and their magnetic hybrid composite materials

Ruifeng Xie,[a†] Te Wei,[b†] Shuang Bai,[b] Zhida Wang[b], Fang Chai[bc*], Lihua Chen[c*] and Shuying Zang[a*]

a Heilongjiang Province Key Laboratory of Geographical Environment Monitoring and Spatial Information Service in Cold Regions, Harbin Normal University, Harbin, 150025, PR China. zsy6311@163.com

b Key Laboratory of Photochemical Biomaterials and Energy Storage Materials Heilongjiang Province; Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, College of Chemistry and Chemical Engineering, Harbin Normal University, Harbin, 150025, PR China. fangchai@gmail.com.

c Shandong Key Laboratory of Biochemical Analysis, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China Lihuachen@qust.edu.cn

The process of catalysis

Catalytic Reduction of 4-NP

The catalytic property of CuAg NPs in the reduction reaction of 4-NP to 4-AP was monitored by periodical UV-Vis spectra taken from the reaction mixture using a Rigaku DMax-2600 PC instrument with super pure water as reference.

The detailed description of using CuAg NPs and Fe_3O_4-CuAg NPs as the catalyst to reduce nitrophenols and potassium ferricyanide(III) by $NaBH_4$ is as follows.

The catalytic experiments were performed according to a previously reported process. For the catalytic reduction of 4-NP, 0.03 mL anhydrous solution of 4-NP (0.01 M) and a solution of CuAg NPs (50 μL) were added to 2.5 mL of water in a quartz cuvette. Then, 200 μL of a freshly prepared solution of $NaBH_4$ (0.5 M) in ice-cold water was rapidly injected into the above mixed solution. Meanwhile, the reaction process was monitored by UV-vis spectroscopy. Similarly, the reduction reactions of other nitrophenols were carried out by changing the corresponding concentrations of the reactants with the same amounts of CuAg NPs as the catalyst. The volumes of 2-NP and 3-NP in the reduction reactions are displayed in Table S1.

When the Fe_3O_4-CuAg NPs were used as catalyst, the other conditions were still remained just introduce 25 μL of 2.8 $mg \cdot mL^{-1}$ Fe_3O_4-CuAg NPs suspension instead the 50 μL of CuAg NPs. The reaction was monitored by acquiring absorption spectra. The reusability was investigated by separating the used catalysts from the solution with a magnet for the next cycle of the catalytic reaction after the reduction process

was complete. To ensure the quantity of catalyst was su□cient to reuse in the recycling process, 100 μL of a 2.8 mg·mL^{-1} solution of catalyst was added to the reaction solution. The similar process of reaction was recycled five times in this experiment.

Catalytic Reduction of 2-NP and 3-NP

For catalytically reducing 2-NP, 0.09 mL of 2-NP (0.01 M) aqueous solution and 0.6 mL fresh $NaBH_4$ (0.5 M) aqueous solution were added into a quartz colorimetric dish containing 2 mL ultra-pure water. And in the procedure of reducing 3-NP, 50 μL of suspension of CuAg NPs was added as substitution. Then 2 mL ultra-pure water was injected in a quartz cuvette. 0.15 mL 3-NP (0.01M) aqueous solution and 1 mL $NaBH_4$ (0.5 M) aqueous solution equipped newly were put in subsequently. Finally, 50 μL of suspension of CuAg NPs was added into above solution as catalyst. The other steps of reduction reaction are consistent with catalytic reduction of 4-NP.

Table S1 The amount of reactants used in reduction of nitrophenols catalyzed by CuAg NPs

Nitrophenols	Amount of nitrophenols		Amount of $NaBH_4$	Rate constant (K)
2-nitrophenol (2-NP)	0.01 M,	90 uL	0.5 M , 600 μL	24. 81×10^{-3} s^{-1}
3-nitrophenol (3-NP)	0.01 M,	150 uL	0.5 M, 1 mL	22. 54×10^{-3} s^{-1}
4-nitrophenol (4-NP)	0.01 M,	30 uL	0.5 M, 200 μL	19. 30×10^{-3} s^{-1}

Catalytic Reduction of $K_3(Fe(CN)_6)$

To catalytically reduce the $K_3(Fe(CN)_6)$, 1.2 mL of ultrapure water was added into the quartz dish, followed by the addition of 0.4 mL of $K_3(Fe(CN)_6)$ (8×10^{-3} M) aqueous solution and 0.8 mL of a freshly equipped $NaBH_4$ (0.04 M) aqueous solution. Finally, 0.03 mL of a CuAg NPs suspension (2 mg/mL) was added to the above solution. The reaction was monitored by UV-visible spectroscopy without any agitation.

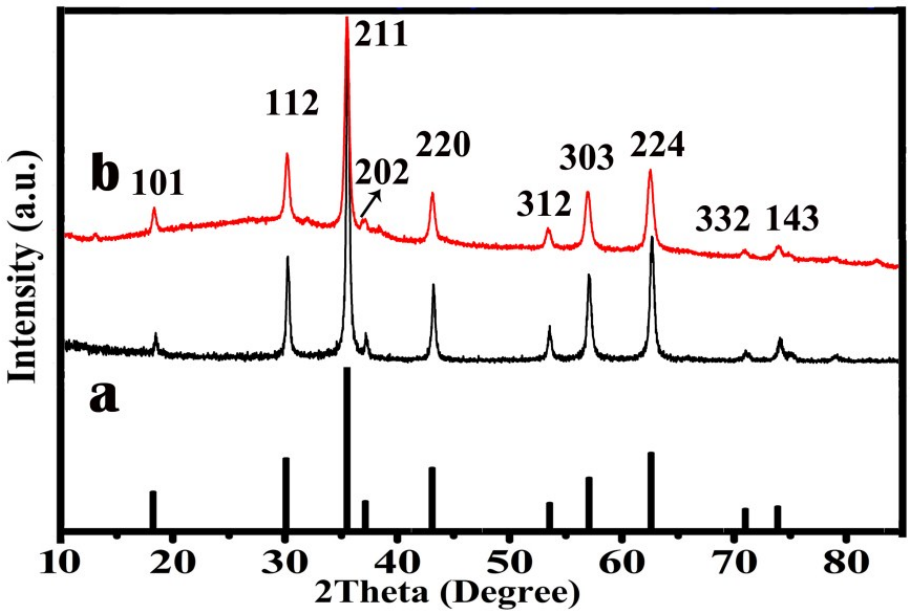

Fig. S1 The XRD of (a) Fe_3O_4 spheres and (b) Fe_3O_4-CuAg NPs

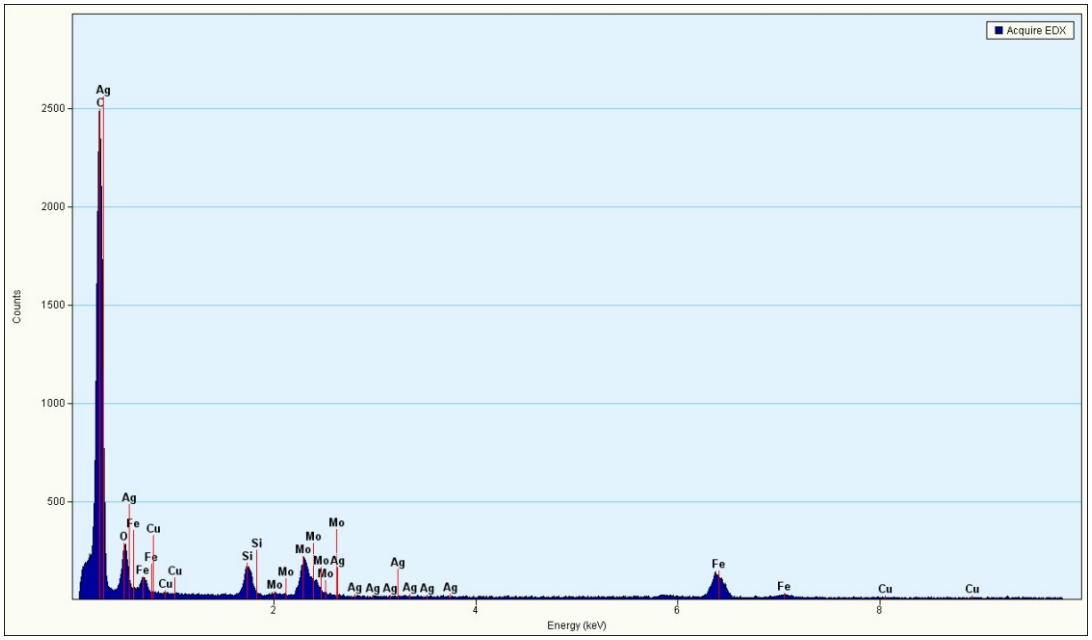

Fig. S2 The TEM EDS of Fe_3O_4-CuAg NPs with a Mo supporting carbon membrane.

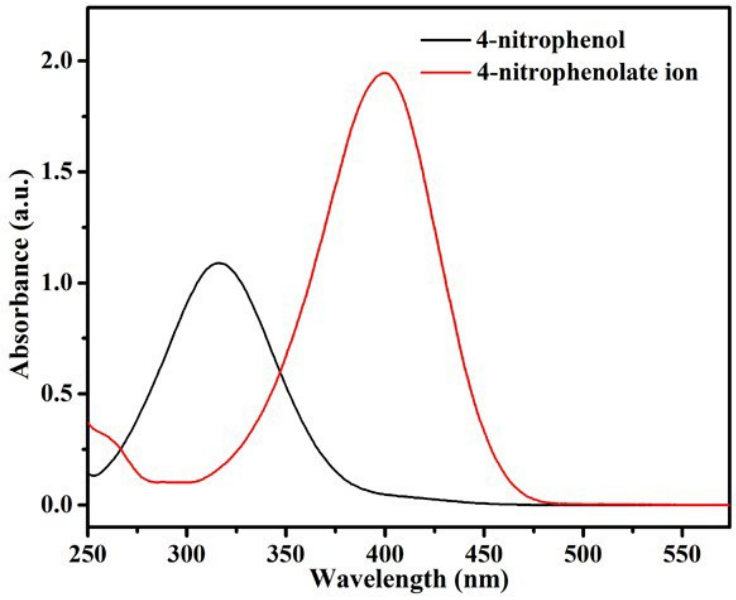

Fig. S3. The UV-vis characteristic peaks of freshly prepared 4-nitrophenol and 4-nitrophenolate ion aqueous solution at 317 and 400 nm, respectively.

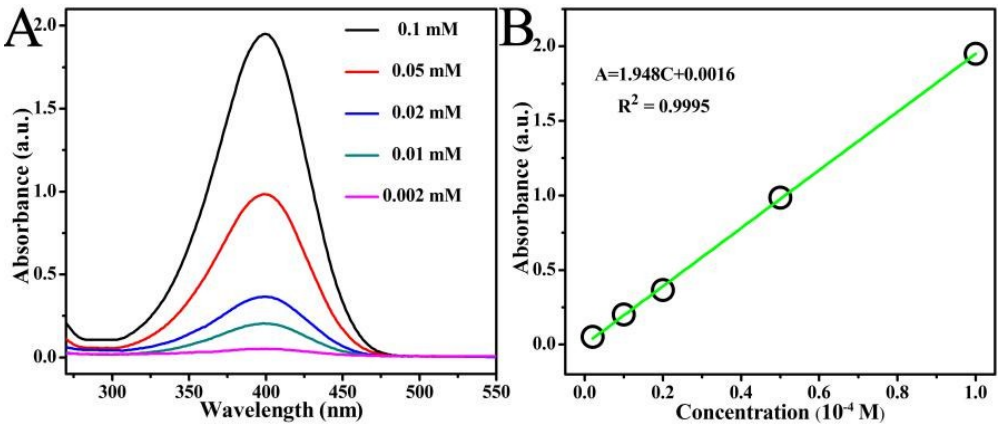

Fig. S4. Absorption spectra of aqueous mixture solutions of 4-NP and $NaBH_4$ at different concentrations of 4-NP. (b) Plot of the peak absorbance against the concentration of 4-NP.

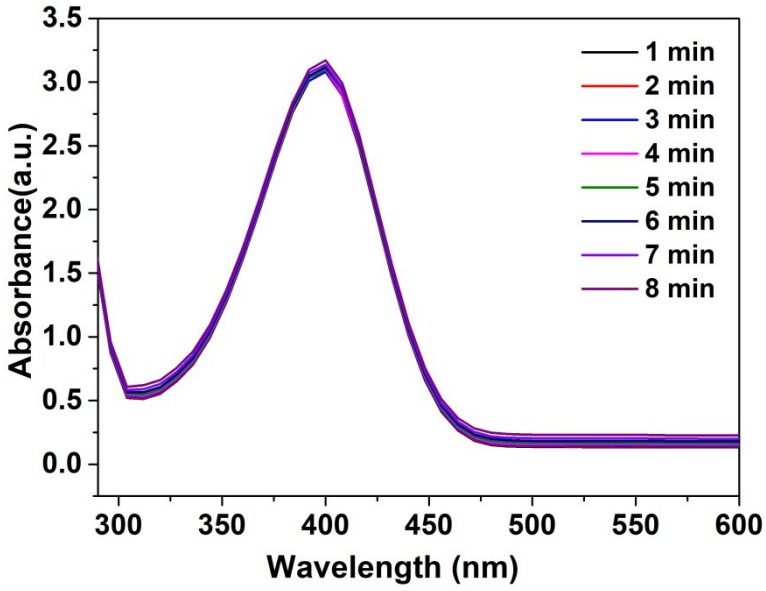

Fig. S5. the UV-vis absorbance mornitoring of the reaction of hydrogenation of 4-NP by using Fe_3O_4 template as catalyst.

Table S2 first order rate constants of several catalysts catalyzed $NaBH_4$ to reduce the 4-NP, 2-NP, 3-NP and $K_3Fe(CN)_6$

Materials	UA-Ag NPs[25]	CuAg NPs	Fe_3O_4-CuAg NPs
4-NP	17. 60×10^{-3} s^{-1}	20. 02×10^{-3} s^{-1}	20. 19×10^{-3} s^{-1}
2-NP	11. 76×10^{-3} s^{-1}	24. 81×10^{-3} s^{-1}	26. 49×10^{-3} s^{-1}
3-NP	25.66×10^{-3} s^{-1}	22. 54×10^{-3} s^{-1}	27. 39×10^{-3} s^{-1}
$K_3Fe(CN)_6$	9.52×10^{-3} s^{-1}	19. 30×$10^{-3}$$s^{-1}$	12. 96×10^{-3} s^{-1}