

Decoration of silver nanoparticles on nitrogen-doped nanoporous carbon derived from zeolitic imidazole framework-8 (ZIF-8) via *in situ* auto-reduction

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Experimental section

Chemicals

2-Methylimidazole (2-MIM), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Silver nitrate (AgNO_3), sodium borohydride (NaBH_4) and methanol anhydrous were purchased from Sigma–Aldrich and were used without further purification. Polyvinylpyrrolidone (PVP) were purchased from TCI chemicals. 4-nitrophenol (4-NP) were purchased from Acros. Deionized water was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

Synthesis procedure for nitrogen-enriched nanoporous carbon (NC)

The nitrogen-enriched nanoporous carbon (NC) were synthesized from the previous literature.¹ Briefly, the polyvinylpyrrolidone (12 g) and 2-methylimidazole (4.2 g) was dissolved in 150 mL methanol solution and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.4 g) was dissolved in an another 150 mL methanol solution. The two solutions are magnetic stirrer for 10 min with separately. Subsequently, the zinc contains solution added into the 2-methylimidazole solution and stirring for another 1 h. After 24 h aging, the white sediment was centrifuged and washed with methanol solution. Finally, the white powder was dried in the vacuum at RT for 24 h. Furthermore, the ZIF-8 powder was carbonized by a tubular furnace at 900 °C for 8 h under N_2 atmosphere with a heating rate of 5 °C min^{-1} . The as-synthesized carbon samples were labelled as Zn@NC.

Synthesis of Ag NPs on the nanoporous carbon by auto-reduction method (Ag@NC)

For the synthesis of Ag@NC nanocomposites, 0.1 g of Zn@NC was dissolved in 30 mL of water. (notes: Zn@NC sample was used immediately after take out of the tubular to prevent the oxidation of Zn into ZnO). Further, the silver nitrate (2 mL; 0.1 M) solution directly added to above solution and stirred for 3 h at room temperature. After that, the black powder was washed by centrifugation using DI water and methanol solution. Finally, the sample was dried under vacuum for 1 day and labelled as Ag@NC.

By the same way, we also tried to the synthesis of Ag@NCW (NCW is nitrogen-doped carbon after washing by HCl), however, the Ag NPs could not form on the nanoporous carbon (**Fig. S2A**).

Synthesis of Ag/NC catalyst by impregnation method

The silver nitrate (2 mL; 0.1 M) solution was directly added to 30 mL solution containing NC sample (0.1 g) and stirred for 0.5 h at room temperature. After that, NaBH₄ (5 mL, 1 mmol) was dropped into the above solution, keep stirring in 1 h. The resulting solid was collected by centrifugation and washed with DI water and methanol solution. The obtained solid was dried under vacuum for 1 day and labelled as Ag/NC-SB, where SB is sodium borohydride.

Characterizations

The crystal structure of the samples was analyzed using powder X-ray diffraction (XRD - Rigaku-Ultima IV instrument) patterns. The morphology of the samples was monitored by scanning/transmission (SEM/TEM) electron microscopy (SEM, NovaTM NanoSEM 230; TEM, JEOL JEM-1200EX II). The internal surface area and pore size of the as-synthesized samples were determined using N₂-adsorption/desorption measurement (micromeritics ASAP 2020). The material compositions were recorded by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Theta Probe). The present weight percentage of material composition was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES).

Catalytic reaction of 4-NP

To investigate the catalytic ability and reusability of Ag@NC nanocomposite using for hydrogenation reaction of 4-NP. Typically, the 4-NP (1×10^{-4} M, 20 mL) and NaBH₄ (0.5 M, 5 mL) solutions were mixed together, then stir for 20 min to forming the 4-nitrophenolate ion. After that, Ag@NC catalyst (1 mg) was added to the above mixture, which was designated at a time (t_0) and stirrer in the room temperature. During these time periods, withdrawing 1.5 mL of the reaction mixture at every 2 min and monitored by using a UV-Vis spectroscopy (Jasco V-670 at a wavelength of 400 nm).

Results

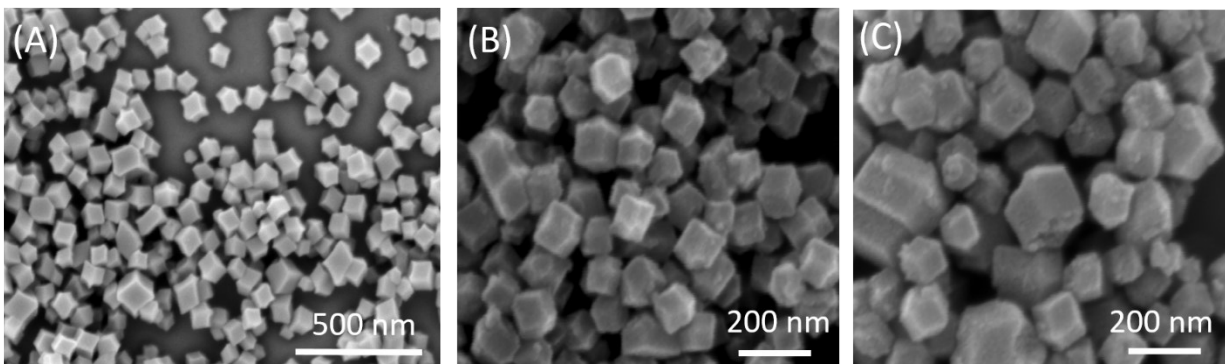


Fig. S1 SEM images of ZIF-8 (A), Zn@NC (B) and Ag@NC (C) samples.

Table S1: Metal content in synthesized samples results

Sample	Ag (wt.%)	Zn (wt.%)
Zn@NC	-	33.6
Ag@NC	8.46	10.5
NCW	-	8.2
Ag@NCW	-	6.3

NCW: nitrogen-doped carbon after washed by HCl concentrate

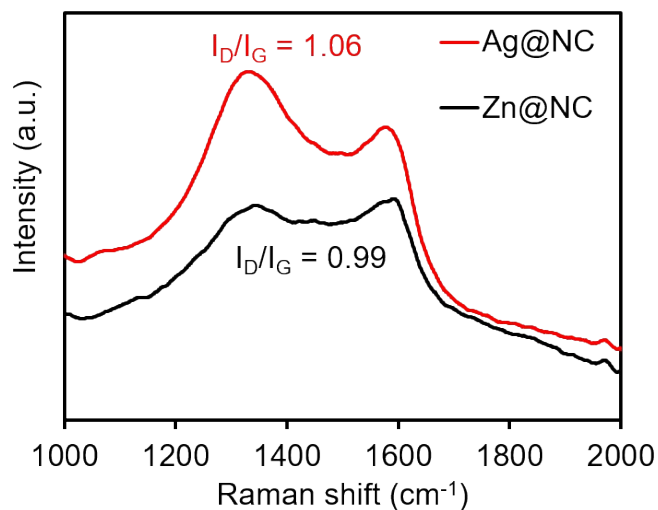


Fig. S2: Raman spectra of the synthesized samples

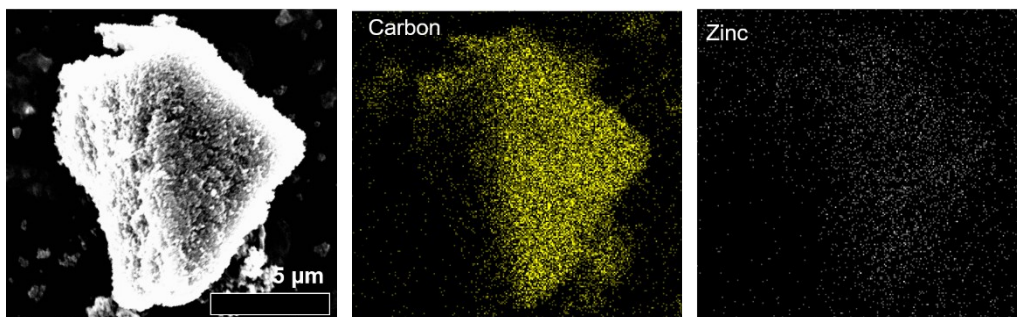


Fig. S3: SEM mapping of Zn@NC revealed the distribution of Zn in the NC.

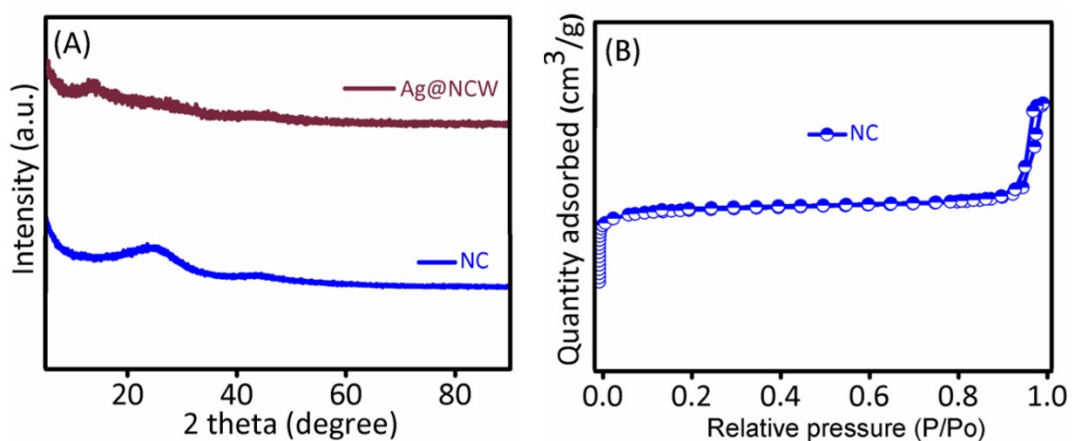


Fig. S4: (A) XRD pattern for ZIF-8-derived NC and Ag@NCW (NCW: nitrogen-doped carbon was washed by HCl to remove Zn residual), (B) N₂ adsorption/desorption analysis for NC samples.

Table S2. Pore characteristics of ZIF-8 and its composite materials.

Sample	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Pore size (nm)
ZIF-8	1398.9	0.92	1.5
NC	807.9	1.1	0.9
Zn@NC	792.5	0.91	0.8
Ag@NC	534.9	0.57	0.8

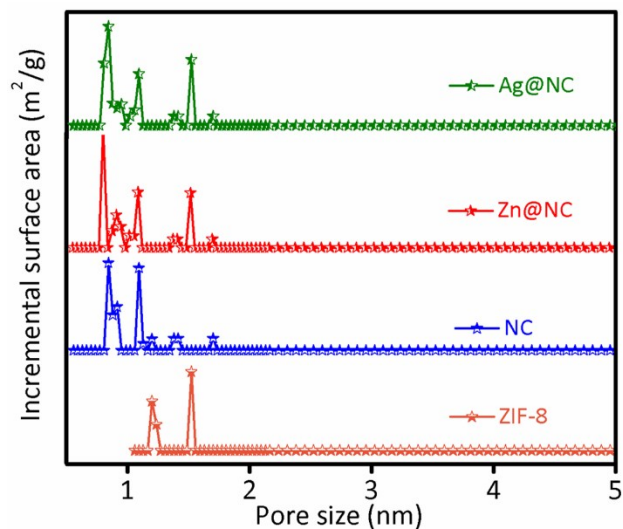


Fig. S5: Pore-size distribution of ZIF-8, NC, Zn@NC and Ag@NC samples. Notes: Porosity distributions were calculated by Density Functional Theory using Non-Negative Regularization methods.

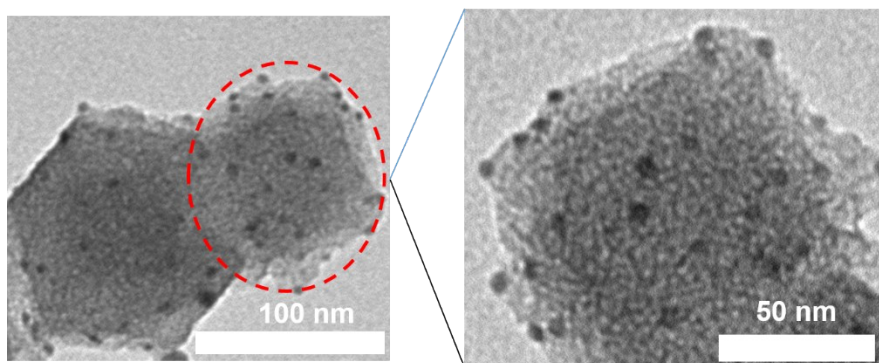


Fig. S6: High resolution TEM of Ag@NC revealed that the Ag NPs confined inside the NC.

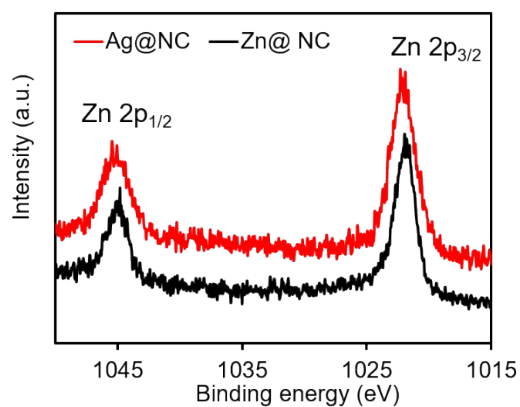


Figure S7: XPS spectrum of Zn in the samples.

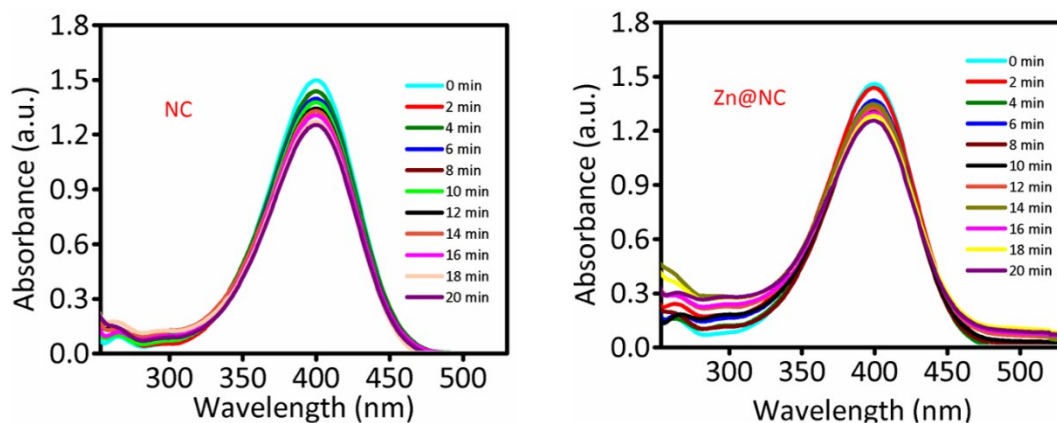


Fig. S8 (A and B) UV-vis spectra of 4-nitrophenol reduction recorded in every 2 min using NC and Zn@NC catalyst, respectively.

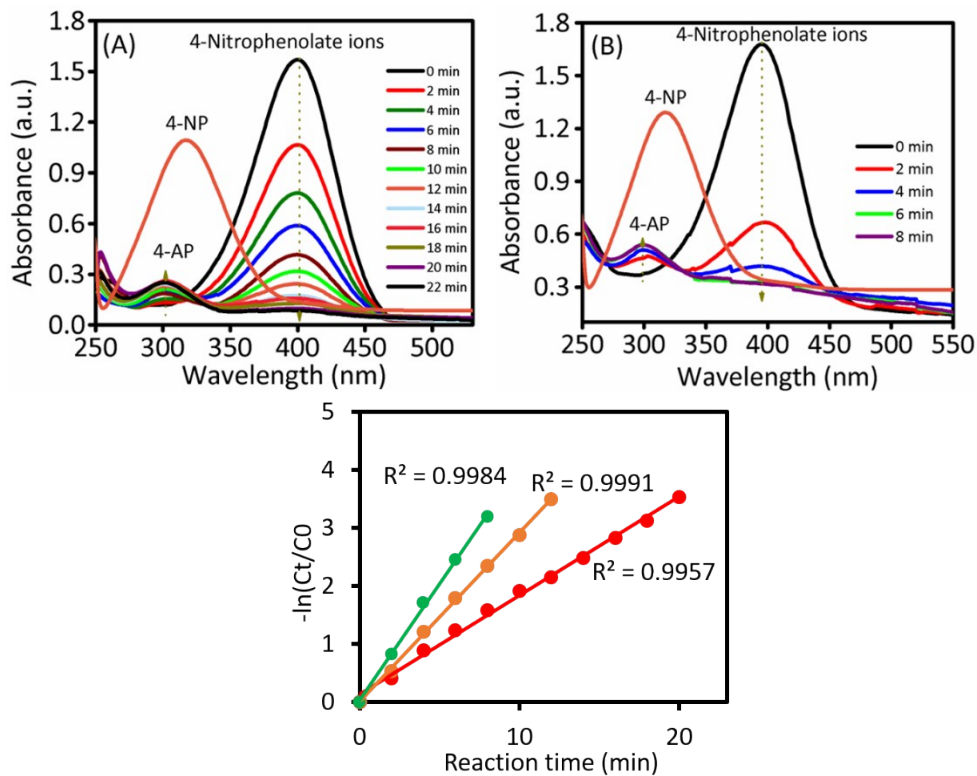


Fig. S9 (A and B) UV-vis spectra of 4-nitrophenol reduction recorded at every 2 min using different amount Ag@NC (0.5 mg) and Ag@NC (1.5 mg) catalyst respectively. (C) The relationship of $\ln(C_t/C_0)$ versus reaction time for the reduction of 4-NP from 4-NP using Ag@NC (0.5, 1.0 and 1.5 mg) catalyst.

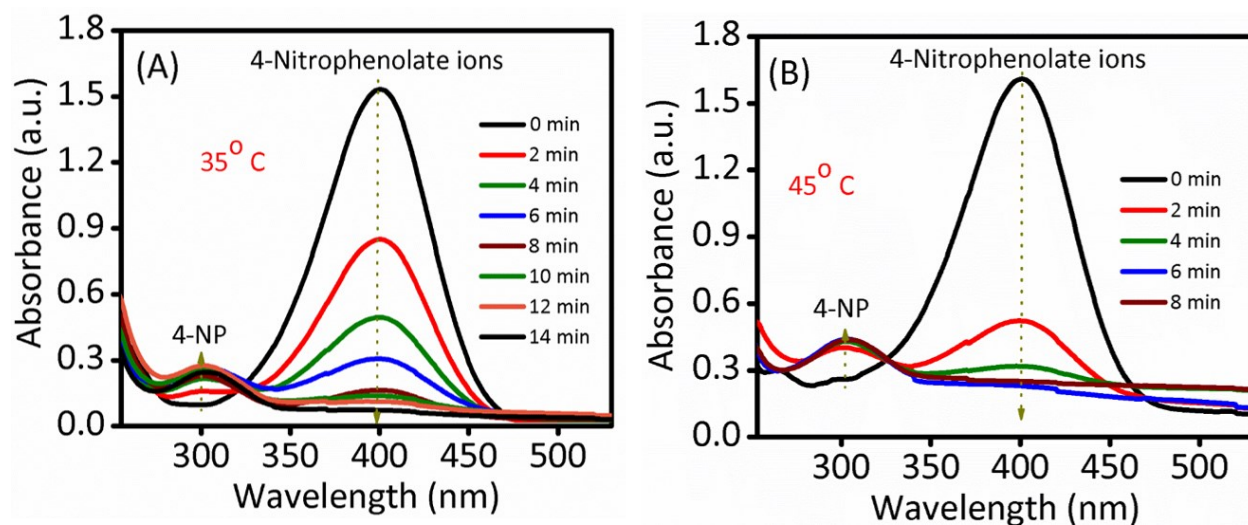


Fig. S10 UV-vis spectra of 4-nitrophenol reduction recorded in every 2 min using Ag@NC (1.0 mg) catalyst at 35°C (A), and 45°C (B) temperatures.

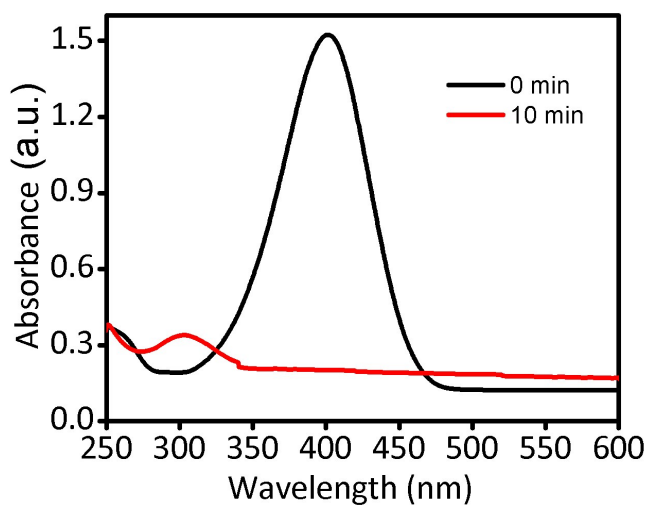


Fig. S11 UV-vis spectra of 4-nitrophenol reduction recorded using Ag@NC-SB (1.5 mg).

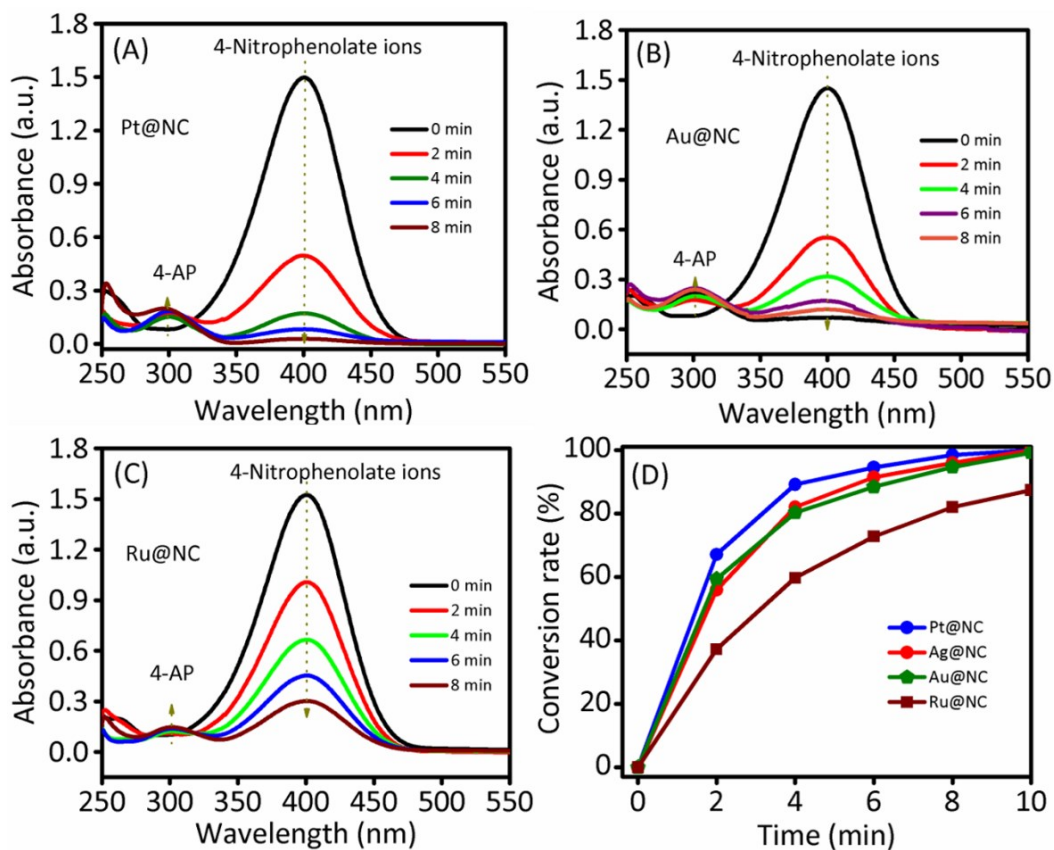


Fig. S12 (A-C) UV-vis spectra of 4-nitrophenol reduction recorded in every 2 min using Pt@NC (1.5 mg), Au@NC (1.5 mg), and Ru@NC (1.5 mg) catalyst. (D) Catalytic conversion of 4-AP from 4-NP at different catalysts.

Table S3: Comparison of catalytic activity of various nanostructured catalysts

Catalysts	Reaction rate constants *10 ⁻³ (s ⁻¹)	Ref.
Ag@NC	4.2	This work
Ag/r-GO	0.45	2
Ag/Carbon sphere	1.69	3
Ag-1/CMK-3	5.33	4
Ag/CNF	6.2	5

Au/C	0.3	6
Au/NC	3.5	6
Pt-SPB	4.4	7

Reference

1. C. Van Nguyen, Y.-T. Liao, T.-C. Kang, J. E. Chen, T. Yoshikawa, Y. Nakasaka, T. Masuda and K. C.-W. Wu, *Green Chem.*, 2016, **18**, 5957-5961.
2. T. V. Thu, P. J. Ko, N. H. H. Phuc and A. Sandhu, *Journal of nanoparticle research*, 2013, **15**, 1975.
3. S. Tang, S. Vongehr and X. Meng, *J. Phys. Chem. C*, 2010, **114**, 977-982.
4. Y. Chi, L. Zhao, Q. Yuan, X. Yan, Y. Li, N. Li and X. Li, *J. Mater. Chem. A*, 2012, **22**, 13571-13577.
5. P. Zhang, C. Shao, Z. Zhang, M. Zhang, J. Mu, Z. Guo and Y. Liu, *Nanoscale*, 2011, **3**, 3357-3363.
6. Y. T. Liao, J. E. Chen, Y. Isida, T. Yonezawa, W. C. Chang, S. M. Alshehri, Y. Yamauchi and K. C. W. Wu, *ChemCatChem*, 2016, **8**, 502-509.
7. Y. Mei, Y. Lu, F. Polzer, M. Ballauff and M. Drechsler, *Chem. Mater.*, 2007, **19**, 1062-1069.