

<Supporting Information>

Hierarchically Porous Ternary Au/ZnO@ZIF-8 Nanocomposite: Spatial In-situ Au encapsulation and Catalytic Activity for The Reduction of *p*-Nitrophenol

Xiaokai Song,^a Hongzhao Sun,^a Xin Cao,^a Zhixian Wang,^a Dejian Zhao,^a Jianhua Sun,^{*a}
Haojie Zhang^b and Xiaopeng Li^{*b}

^a School of Chemical & Environmental Engineering, Jiangsu University of Technology,
Changzhou 213001, China.

^b CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai
Advanced Research Institute (SARI), Chinese Academy of Sciences (CAS), Shanghai
201210, China.

E-mail: sunjh@jsut.edu.cn, lixp@sari.ac.cn.

General procedures

All reagents and solvents were purchased and used without further purification. Deionized (DI) water with resistivity higher than 18 M Ω cm was used during the experiments. The morphology of the samples was characterized using a Hitachi S3400N scanning electron microscope (SEM) at an accelerating voltage of 15 kV. Transmission electron microscope (TEM) was measured by a JEM-1200EX operated at 200 kV. Powder X-ray diffraction (PXRD) patterns were recorded in a PANalytical diffractometer Model PW3040/60 X'pert PRO using monochromated Cu K α radiation (40 kV, 40 mA) at a scanning rate of 2 $^{\circ}$ ·min $^{-1}$. Au content was analyzed using a Varian 720-ES inductively coupled plasma atomic emission spectrometer (ICP-AES). UV–vis absorption spectra were recorded in quartz cells of 1 cm path length using a TU-1800 SPC spectrophotometer at room temperature. Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2020 system at 77 K.

Experimental section

Preparation of Au/ZnO

Au/ZnO nanoflowers containing different contents of Au NPs were prepared via a one-step hydrothermal reaction that was slightly modified from the reported synthetic procedure.^{S1} Typically, a solid mixture of Zn(CH₃COO)₂·2H₂O (0.071 g, 0.46 mmol) and

NaOH (0.400 g, 10 mmol) were dissolved in 39.7 mL DI water. After stirring for 20 min, 0.3 mL of $\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$ ($0.02 \text{ g} \cdot \text{mL}^{-1}$) aqueous solution was introduced to the above mixture, and this solution was transferred into a 50 mL Teflon lined stainless steel autoclave. Then, it was sealed and heated at $180 \text{ }^\circ\text{C}$ for 2 h, and cooled to room temperature naturally to obtain Au(7.5%)/ZnO. The product was separated by centrifugation and washed thoroughly with DI water and ethanol, and finally dried at $60 \text{ }^\circ\text{C}$ for 12 h. The Au/ZnO powder was further activated at $500 \text{ }^\circ\text{C}$ in muffle furnace for 2 h prior to use. 5%, 10% and 12.5% Au/ZnO was synthesized using 0.2, 0.4, and 0.5 mL $\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$ solution, respectively.

Preparation of Au/ZnO@ZIF-8

The Au/ZnO@ZIF-8 nanocomposite was prepared via solvothermal reaction that is slightly modified from the reported synthetic procedure.^{S2} Typically, 2-methylimidazole (0.330 g, 4.0 mmol) and Au/ZnO nanoflowers (0.040 g) were added in sequence to a glass vial (40 mL) containing a mixed solvent of DMF/ H_2O (32 mL, 3:1 of v/v). After sonication for 5 min, the mixture was reacted at $50 \text{ }^\circ\text{C}$ for 6 h, and cooled to room temperature naturally to obtain Au/ZnO@ZIF-8. The product was collected by centrifugation and washed with DI water and ethanol, and finally dried at $60 \text{ }^\circ\text{C}$ in vacuum for 12 h.

Preparation of Au/ZIF-8

Au/ZIF-8 was prepared via a simple aqueous synthesis using $\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$ as gold precursor and NaBH_4 as reducing agent. The as-prepared ZIF-8 was dispersed in 30 mL DI water and was sonicated for 10 min to obtain a well-dispersed ZIF-8 aqueous solution. An aqueous stock solution (3 mL, 10^{-2} M) of $\text{HAuCl}_4 \cdot 6\text{H}_2\text{O}$ was slowly added to the ZIF-8 solution under stirring. The resulting mixture was sonicated again for 10 min and stirred for 1 day at room temperature. The Au^{3+} /ZIF-8 sample was hardly be separated by centrifugation, so 0.3 mL NaBH_4 aqueous solution (0.5 M) was added quickly into the above solution with agitated stirring to obtain Au/ZIF-8. After additional 10 min stirring, the Au/ZIF-8 was separated by centrifugation and washed with water (60 mL, 2 times), and finally dried at 60 °C in vacuum for 12 h. The Au loaded on the sample was 6.8 wt% based on inductively coupled plasma mass spectrometry (ICP-MS) analysis.

Reduction of *p*-nitrophenol

In a typical process, the aqueous solutions of *p*-nitrophenol (7.4 mM) and NaBH_4 (2.4 M) were freshly prepared. 15 μL of *p*-nitrophenol solution was added to a quartz cuvette. Its color changed from colorless to yellow immediately when 15 μL NaBH_4 solution was added. Then, 2 mL aqueous solution containing the Au NPs loaded catalysts (30 $\mu\text{g}/\text{mL}$)

was injected into the cuvette to start the reaction. The change in the intensity of the absorbance at 400 nm was monitored by UV-vis spectroscopy.

References

S1 X.-Y. Xue, Z.-H. Chen, L.-L. Xing, C.-H. Ma, Y.-J. Chen and T.-H. Wang, *J.*

Phys. Chem. C, 2010, **114**, 18607.

S2 W. W. Zhang, Q. Kuang, J. Z. Zhou, X. J. Kong, Z. X. Xie and L. S. Zheng, *J. Am.*

Chem. Soc., 2013, **135**, 1926.

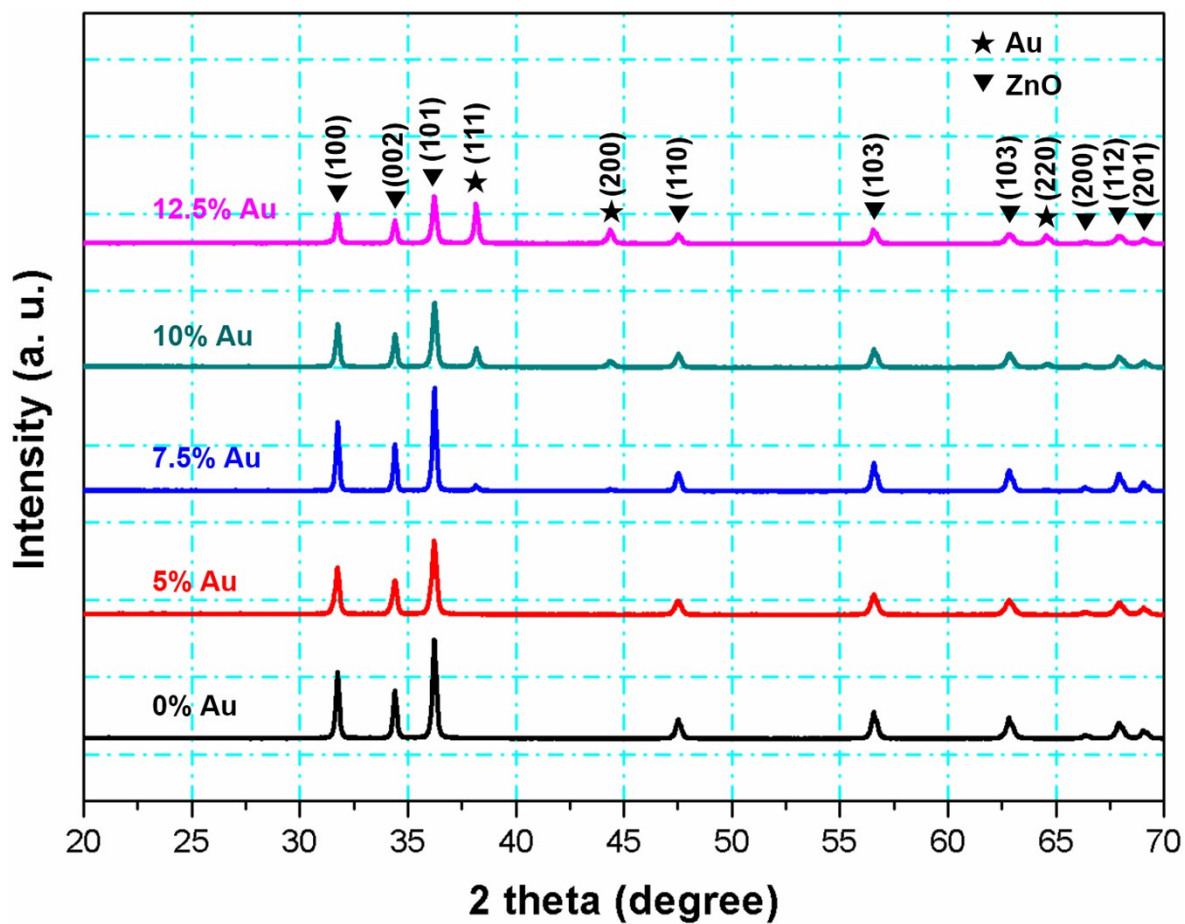


Figure S1. PXRD patterns of Au/ZnO samples with different Au decoration.

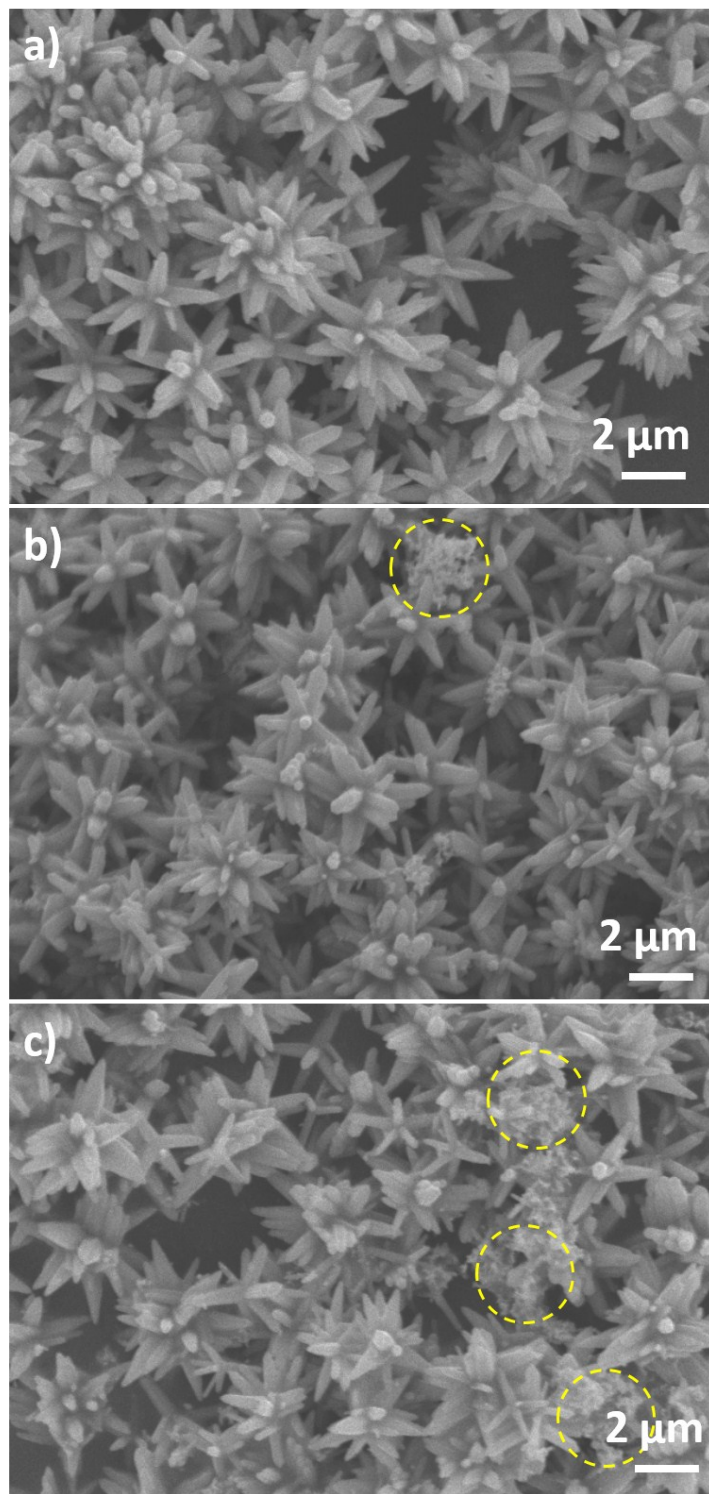


Figure S2. SEM images of Au/ZnO nanoflowers with Au contents of 5% (a), 10% (b) and 12.5% (c), respectively. The scale bars are 2 μm .

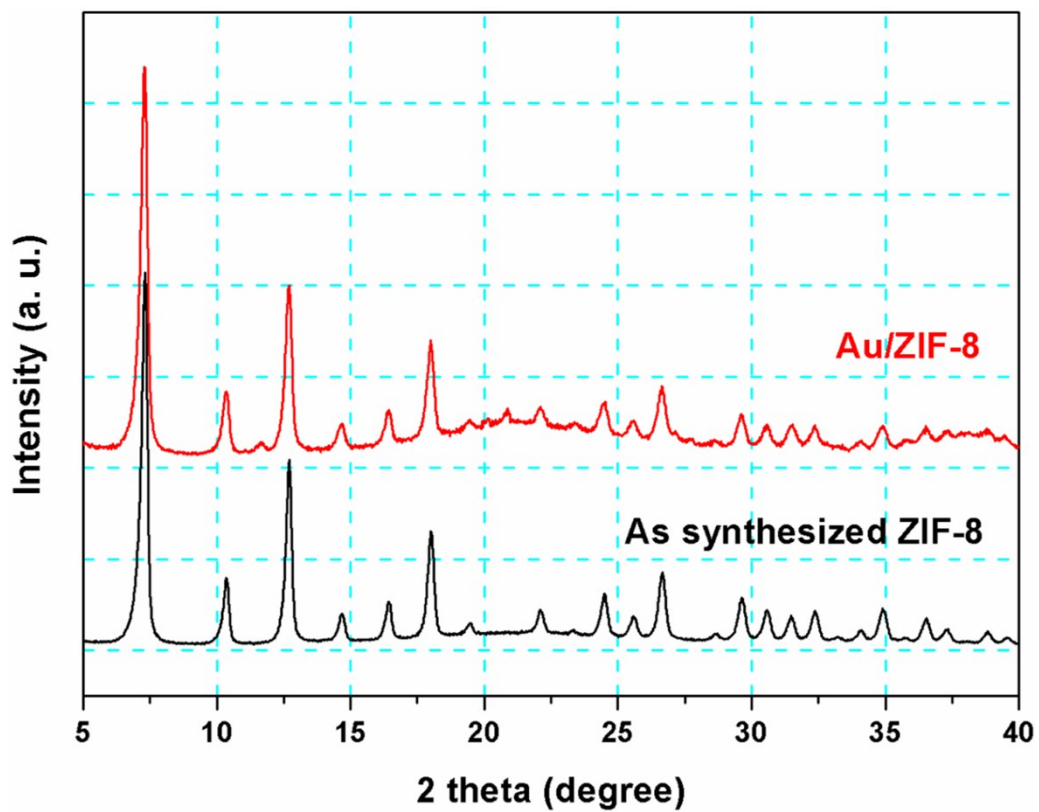


Figure S3. PXRD patterns of as synthesized ZIF-8 (black) and Au/ ZIF-8 (red), respectively.

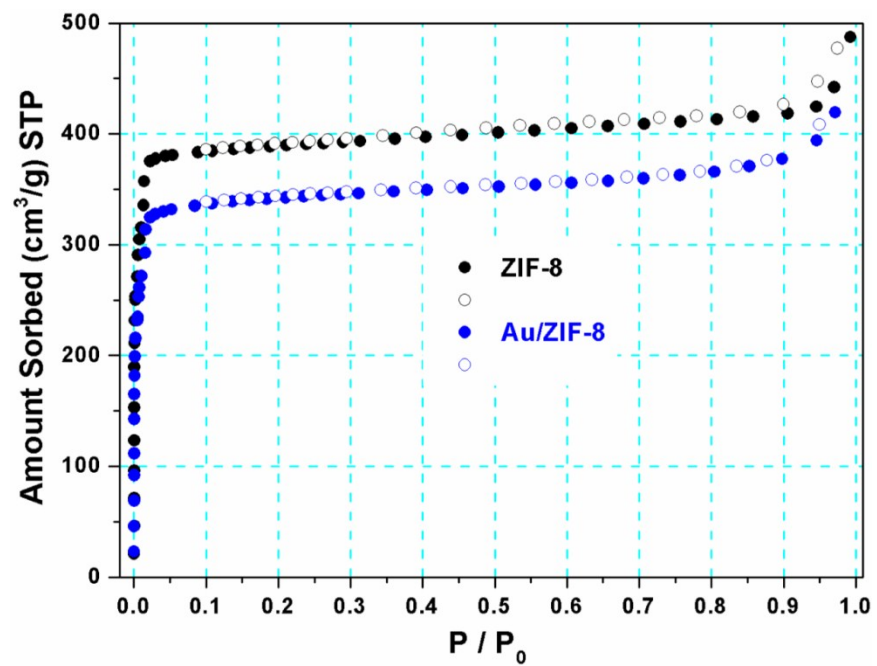


Figure S4. N₂ sorption isotherms of ZIF-8 (black) and Au/ ZIF-8 (blue) at 77 K, respectively.

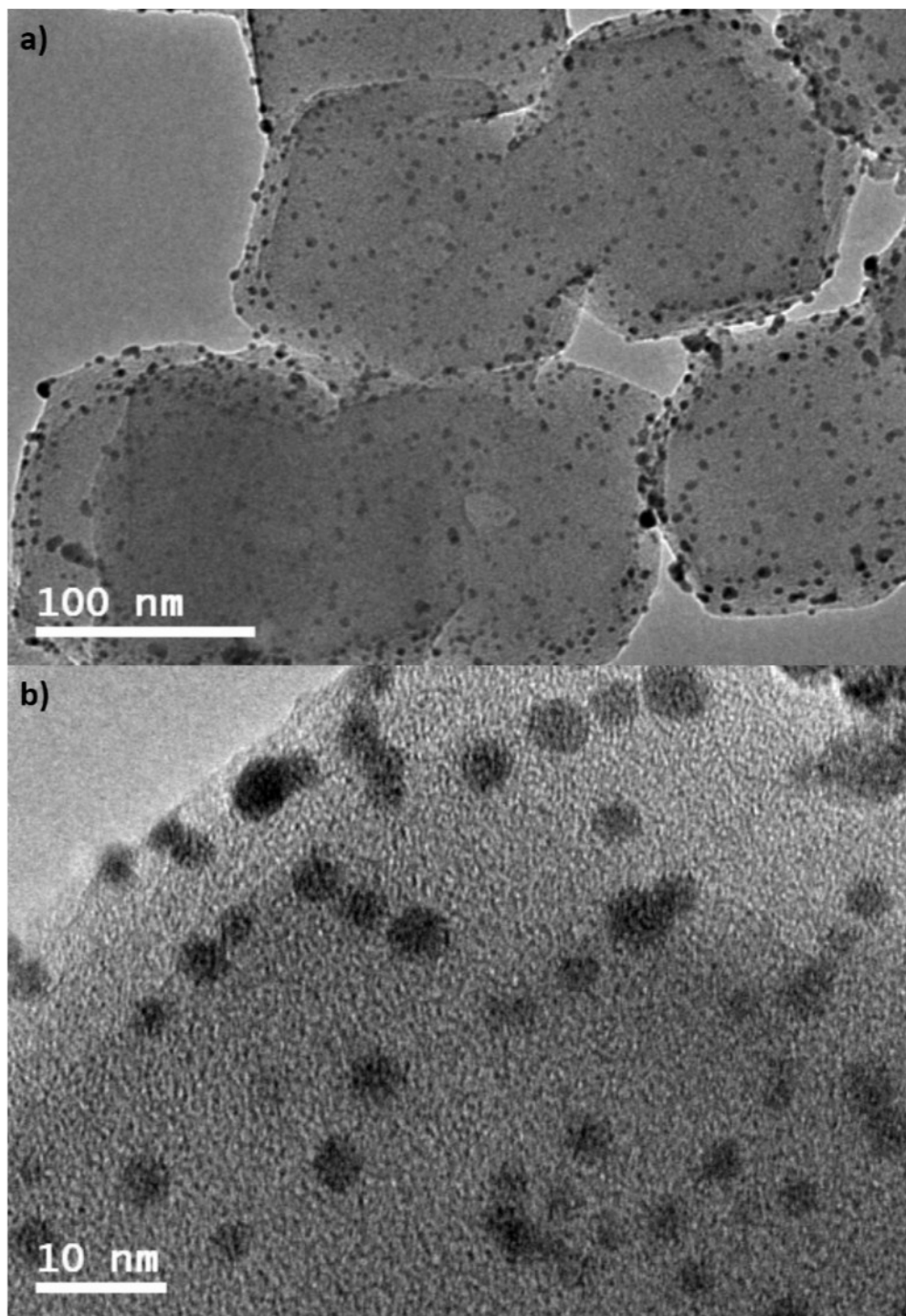


Figure S5. TEM images (a, b) of Au/ZIF-8.

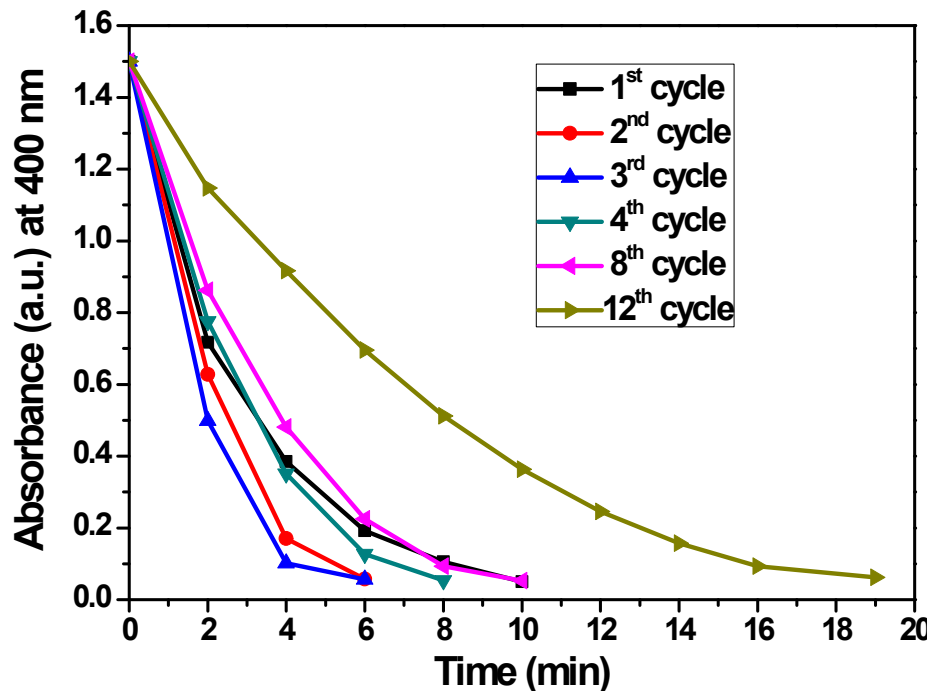


Figure S6. Durability test for the reduction of *p*-nitrophenol catalyzed by Au(7.5%)/ZnO@ZIF-8 through successive recycling reactions.

As shown in Fig. S6, the catalytic activity of Au(7.5%)/ZnO@ZIF-8 was even slightly enhanced after the first cycle reaction, suggesting the full initiation of Au NPs. After eight successive runs, the activity drop was observed, suggesting its great recyclability and durability. The recycling results were well explained by TEM observations (Fig. S7), which showed that Au NPs incorporated into ZIF-8 crystal matrix have well remained sizes after 8 runs.

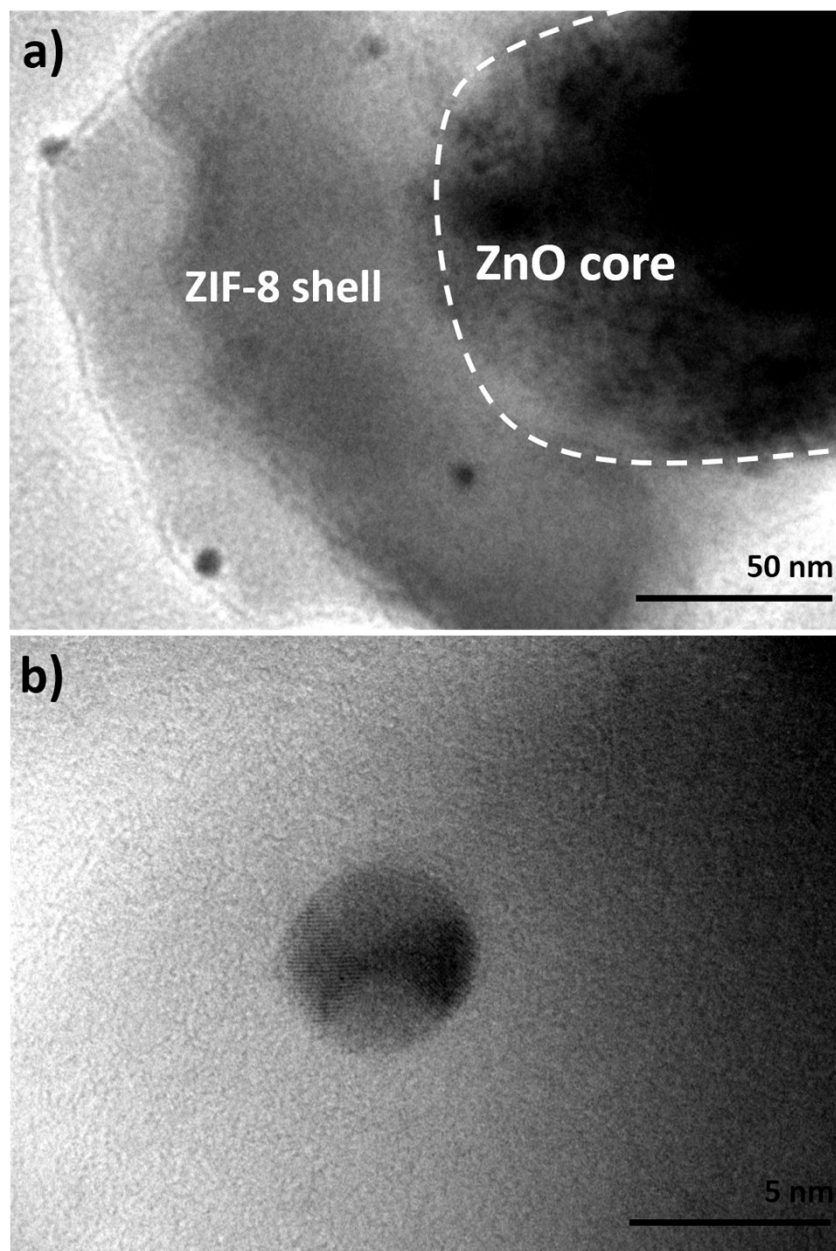


Figure S7. Corresponding TEM images (a, b) of Au(7.5%)/ZnO@ZIF-8 after the 8th successive recycling reaction.