Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

Supporting Information

Synthesis of Au@ZIF-8 Single- or Multi-Core/Shell Structure for Photocatalysis

Liyong Chen,*[a] Yan Peng,[a] Hong Wang,[b] Zhizhi Gu[a] and Chunying Duan*[a]

EXPERIMENTAL SECTION

Materials and Characterization. All chemical reagents were used as purchased without further purification. Polyvinylpyrrolidone (PVP, M_w: 55000) was purchased from Sigma Aldrich, and all other chemicals were commercially available. Deionized water (resistance > 18.2 MΩ/cm) was used in all reactions. Copper specimen grids (300 mesh) with carbon film (referred to as TEM grids in the text) were purchased from Beijing XXBR Technology Co.

Transmission electron microscopy (TEM) images were collected on a Tecnai F30 operated at 300 kV. X-ray diffraction (XRD) was preformed with a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). FT-IR spectra were carried out on JASCO FT/IR-430. UV-vis spectra were recorded on TU-1900 UV-vis spectrophotometer.

Synthesis of Inorganic NPs. *Synthesis of Au NPs with a mean size of 15 nm*. Au NPs were prepared following a modified literature procedure by sodium citrate reduction of $HAuCl_4$.[1] Briefly, $HAuCl_4$ aqueous solution (100 mL, 0.01% w.t.) was added into a 250 mL flask, and was heated at 110 °C for 15 min under vigorously stirring. Subsequently, sodium citrate aqueous solution (3 mL, 1% w.t.) was induced to the solution one shot. After heating the solution for another 30 min, a deep-red citrate-stabilized Au NP (15 nm) colloidal solution was obtained.

Synthesis of Au NPs with a mean size of 50 nm. Au NPs were prepared by a seed-mediated growth method derived from the previous reports.[1] In a typical synthesis, H_2O (50 mL) was heated at 110 °C for 20 min, and $HAuCl_4$ aqueous solution (500 μL, 10 mg/mL) and sodium citrate (750 μL, 1% w.t.) aqueous solution were added quickly in turn under vigorously stirring. The mixture was heated another 30 min. After that, NaOH (100 μL, 6.6 mg/mL) aqueous solution was added dropwise, and then H_2O (hot, 50 mL), sodium citrate (500 μL, 1% w.t.) aqueous solution, and $HAuCl_4$ (500 μL, 10 mg/mL) aqueous solution were added in turn. The reaction solution continue to heat for 30 min. The second step was repeated eight times, and a dark-red citrate-stabilized Au NP (50 nm) colloidal solution was obtained.

Synthesis of Au NRs. Au NRs were prepared by a seed-mediated growth method derived from the previous reports.[2] Firstly, Au NP seeds were prepared by quickly adding $NaBH_4$ ice-cold aqueous solution (180 μL, 10 mM) to $HAuCl_4$ (3 mL, 0.25 mM) solution prepared in CTAB solution (0.1 M) under vigorously stirring for 10 min. The as-synthesized seed solution was left for another 1 h before being used. Next, CTAB solution (50 mL, 0.1M), $AgNO_3$ solution (500 μL, 10 mM) and $HAuCl_4$ solution (2.5 mL, 10 mM) were introduced into a conical flask. After that, ascorbic acid solution (275 μL, 0.1M) was added slowly and shaken gently to form uniform mixture. Finally, Au NP seeds (60 μL) were added. The resulting solution was kept at room temperature in the darkness for about 12 h without disturbing.

Synthesis of ZIF-8. In a 25 mL flask, Hmim (7.5 mM, 5 mL) and $Zn(NO_3)_2$ (7.5 mM, 5 mL) methanol solutions were mixed, and the mixture was heated at 50 °C for 2 h before cooled down to room temperature.

Synthesis of Au NP@ZIF-8 core/shell structures. *Preparation of PVP modified Au NPs*. PVP solution (400 μL, 25.5 mg/mL in H_2O) was added to 20 mL citrate-stabilized Au NPs (15 nm) solution, and the mixture was stirred for 24 h at room temperature. Citrate on Au NPs was exchanged by PVP molecules to form PVP-Au NPs.

Au NPs (50 nm) were modified with PVP molecules using the same procedure. Au NRs needed to centrifuge and remove the supernatants before adding to PVP solution.

Method A. A PVP-Au NPs (15 nm) solution (1mL) was concentrated to 5 μL by centrifugation at 16000 *g* for 15 min. The concentrated PVP-Au NPs were transferred to a 25 mL flask, and Hmim solution (5 mL, 7.5 mM in methanol) was added. After the solution was shaken several seconds by hand, $Zn(NO_3)_2$ solution (5 mL, 7.5 mM in methanol) was added one shot. The mixture was heated directly at 50 °C for 2 h without stirring and then cooled to room temperature in air. The transparent solution was gradually turned into cloudy within initial 5 min of reaction. Finally, the pale red cloudy product was collected by centrifugation at 7000 *g* for 10 min.

Other NPs, including PVP-Au NPs (50 nm), and PVP-Au NRs, were encapsulated with ZIF-8 using the same procedure.

Method B. Hmim solution (5 mL, 7.5 mM in methanol) introduced to PVP-Au NPs (15 nm) in a 25 mL flask was shaken several seconds with hand, and $Zn(NO_3)_2$ solution (5 mL, 7.5 mM in methanol) was added to the flask in one shot. The mixture was incubated in room temperature for 2 min before heating at 50 °C for 2 h. The final product was collected by centrifugation at 2000 *g* for 10 min.

PVP-Au NPs (50 nm) were encapsulated with ZIF-8 to form multi-core structures using the same procedure.

Photocatalytic oxidation of benzyl alcohol. The Au@ZIF-8 powder (6 mg) was dried at 150 ^{o}C for overnight in vacuum oven, and dispersed into a 10 mL Pyrex glass reactor containing 1.5 mL of acetonitrile and 20 μL of benzyl alcohol. The reactor was sealed with a rubber septum after being bubbled with O_2. The mixture was irradiated using Xe lamp (500 W) for 24 h through a cutoff filter (λ > 400 nm) under magnetic stirring and water cooling. The final mixture after removing catalyst by centrifugation was analyzed by gas chromatography (GC7890II) with an FID detector, and conversion for benzyl alcohol was obtained from the peak area ratio of product and substrate.

Au/SiO_2 that was prepared by mixing citrate-stabilized Au NPs with NH_2-modified SiO_2 NPs was employed as photocatalysts to oxide benzyl alcohol using the similar procedure. Upon Au as catalytic centre, the amount of Au in Au/SiO_2 hybrids is equal to that in Au@ZIF-8.

REFERENCES

1. G. Frens, *Nat. Phys. Sci.*, 1973, **241**, 20.

2. A. Gole and C. J. Murphy, *Langmuir* 2008, **24**, 266.

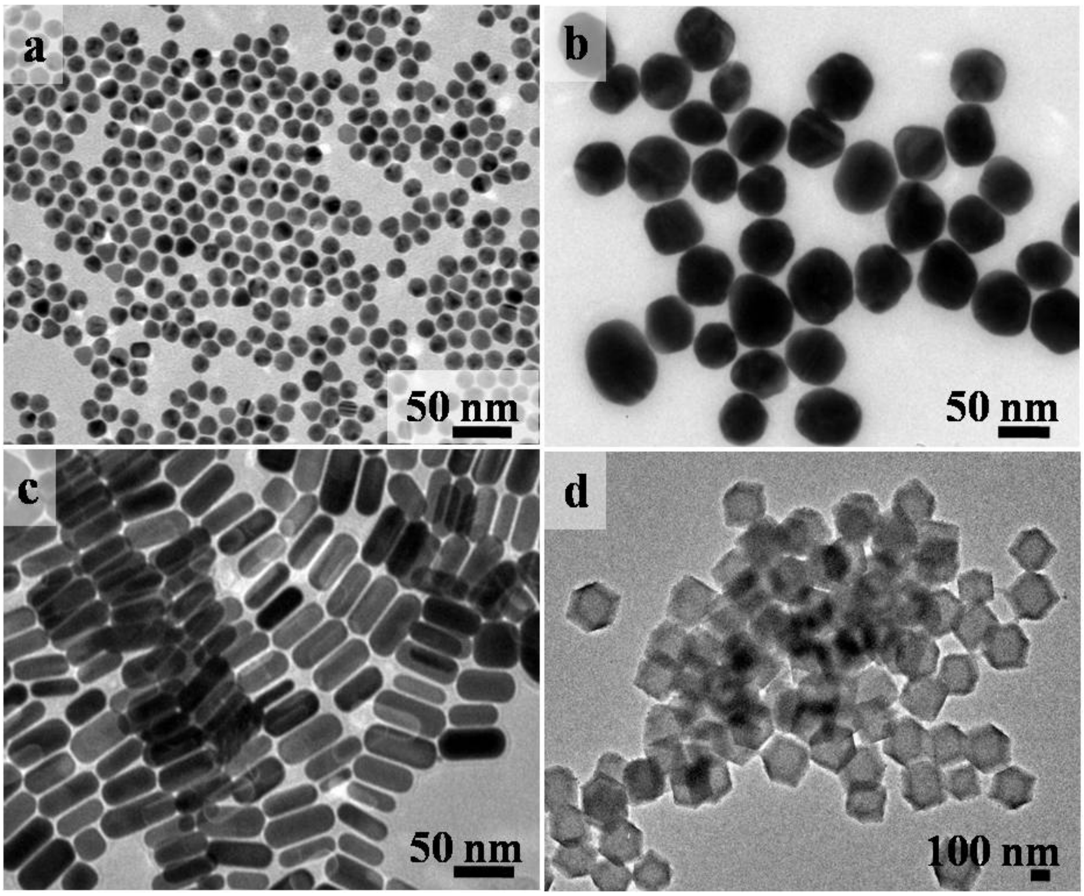


Fig. S1. TEM images of Au NPs with a mean size of 15 nm (a) and 50 nm (b), Au NRs (c), and ZIF-8 rhombic dodecahedral nanocrystals (d).

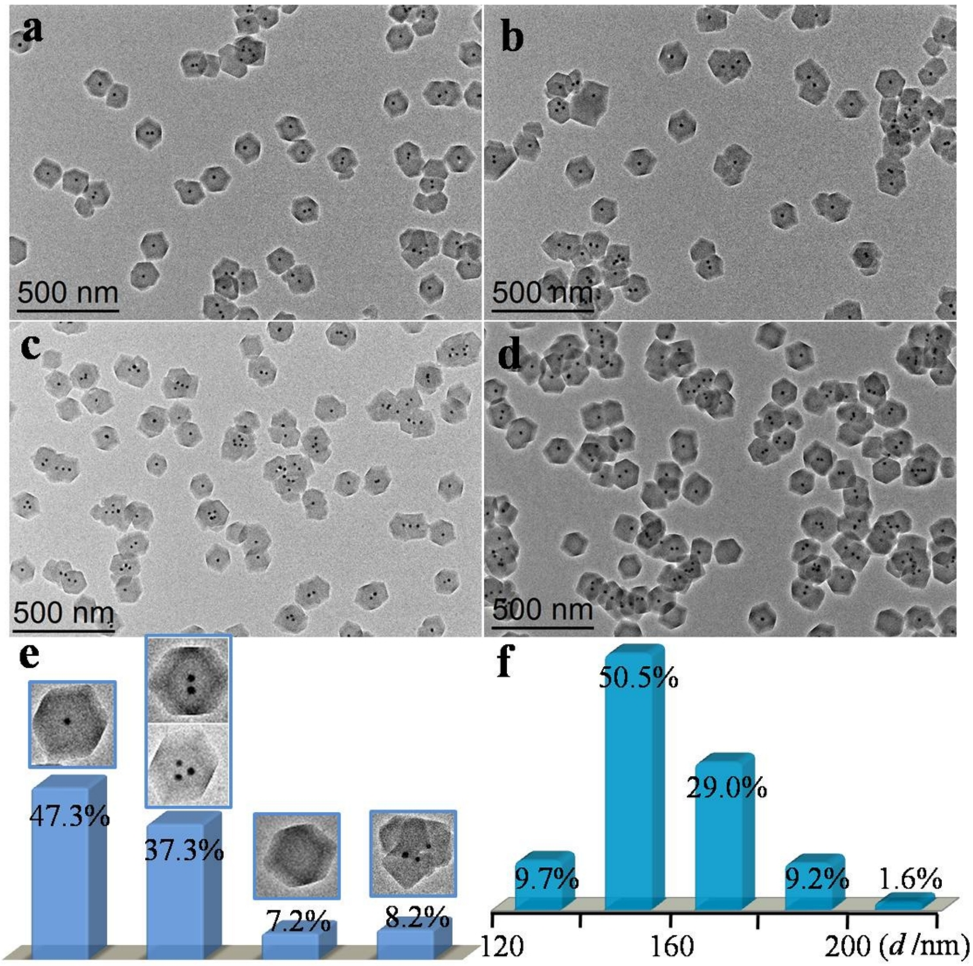


Fig. S2. (a-d) Typical panoramic TEM images of Au@ZIF-8 (d_{Au} = 15 nm) core/shell structures prepared by method A. (e) Histogram of single-, dual- and triple-core structures of Au@ZIF-8 (d_{Au} = 15 nm), and core-free ZIF-8. (f) Histogram shows size distribution of each Au@ZIF-8 based on these TEM images.

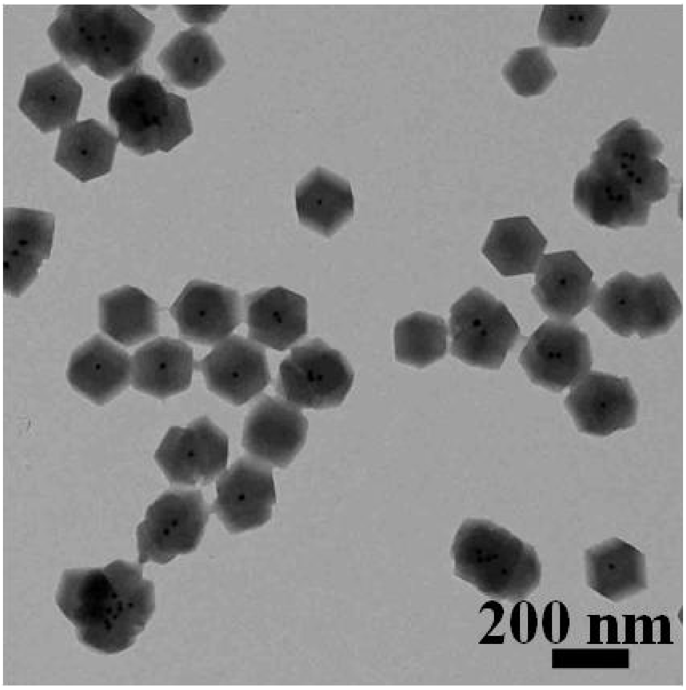
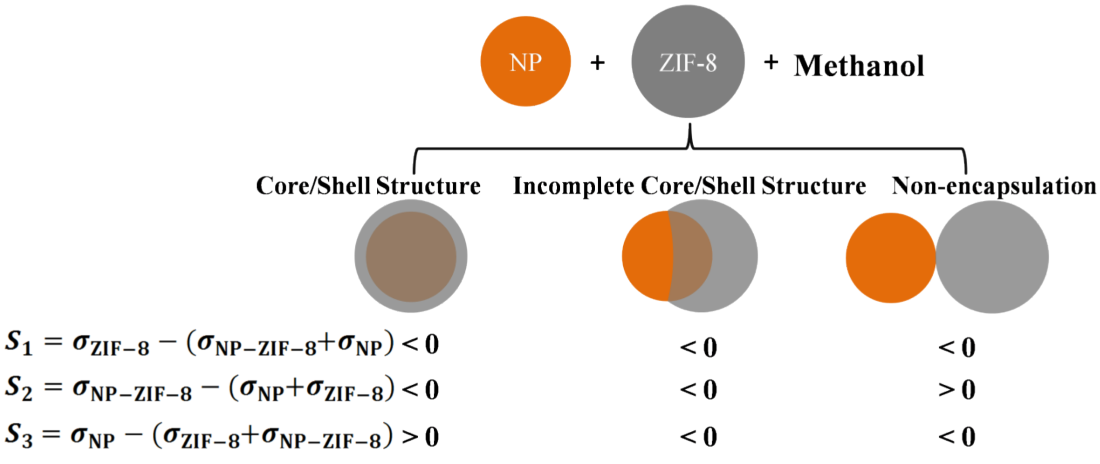


Fig. S3. TEM image of sample prepared using method A while initial volume of PVP-Au NPs (d_{Au} = 15 nm) is 3 mL.



	Core/Shell Structure	Incomplete Core/Shell Structure	Non-encapsulation
$S_1 = \sigma_{ZIF-8} - (\sigma_{NP-ZIF-8} + \sigma_{NP})$	< 0	< 0	< 0
$S_2 = \sigma_{NP-ZIF-8} - (\sigma_{NP} + \sigma_{ZIF-8})$	< 0	< 0	> 0
$S_3 = \sigma_{NP} - (\sigma_{ZIF-8} + \sigma_{NP-ZIF-8})$	> 0	< 0	< 0

Fig. S4. Equilibrium configurations for NP and ZIF-8 in methanol.

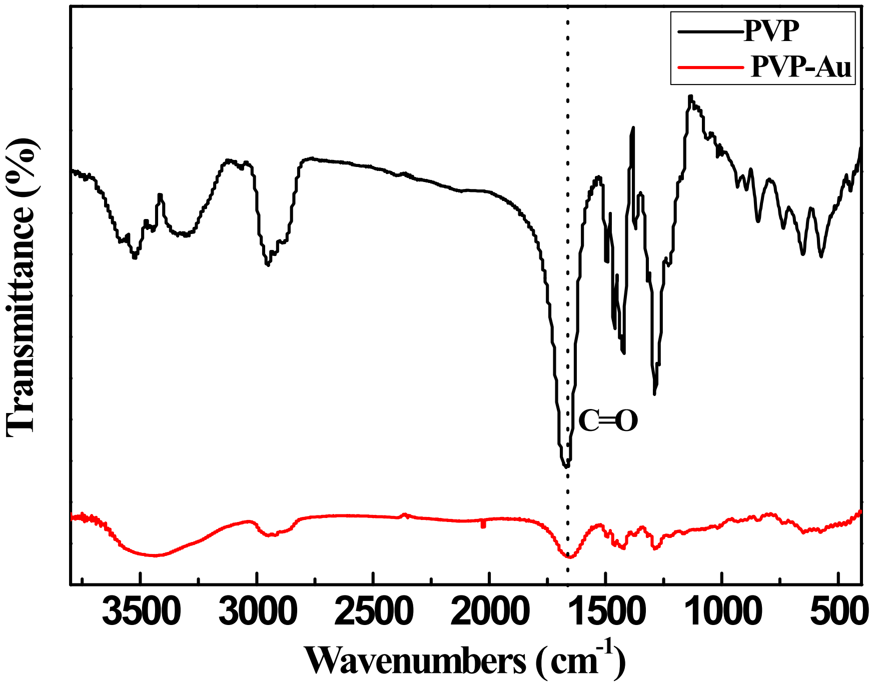


Fig. S5. FTIR spectra of PVP and PVP-Au (d_{Au} = 15 nm).

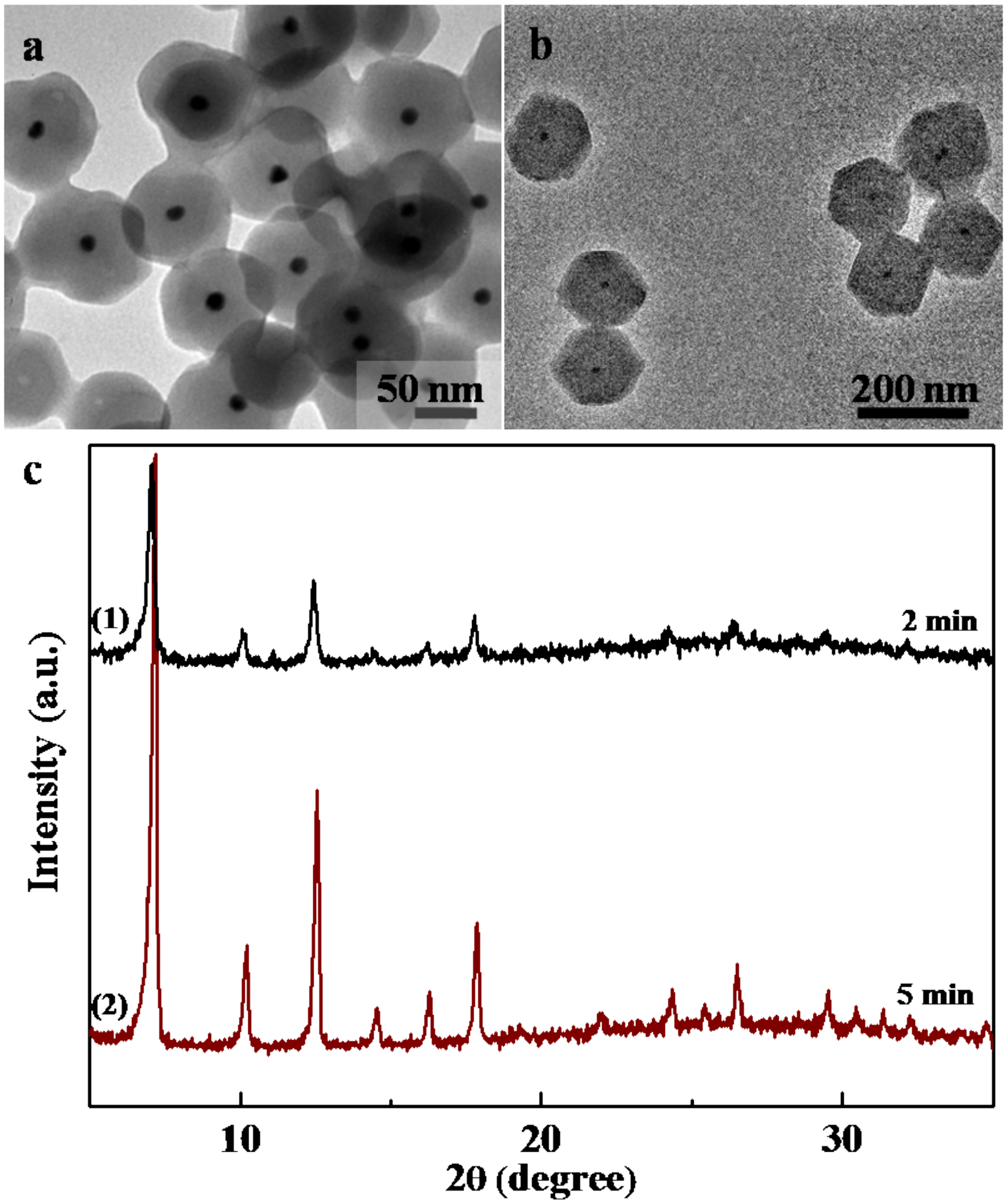


Fig. S6. TEM images of intermediates captured after heating at 50 °C for (a) 2 min and (b) 5 min in method A; (c) XRD patterns of these intermediates: (1) 2 min and (2) 5 min, respectively.

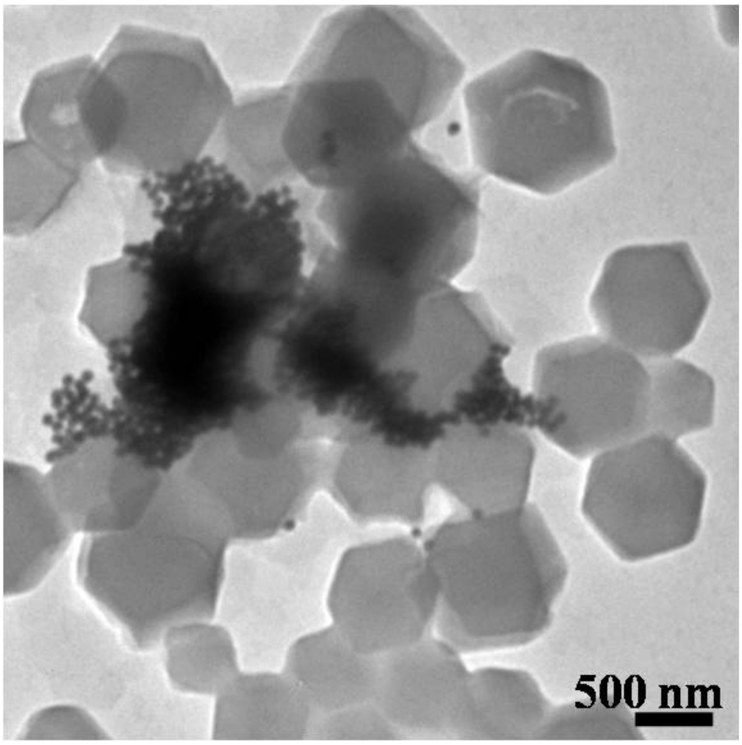


Fig. S7. TEM image of sample prepared using citrate-stabilized Au NPs (d_{Au} = 15 nm) as seeds in method A.

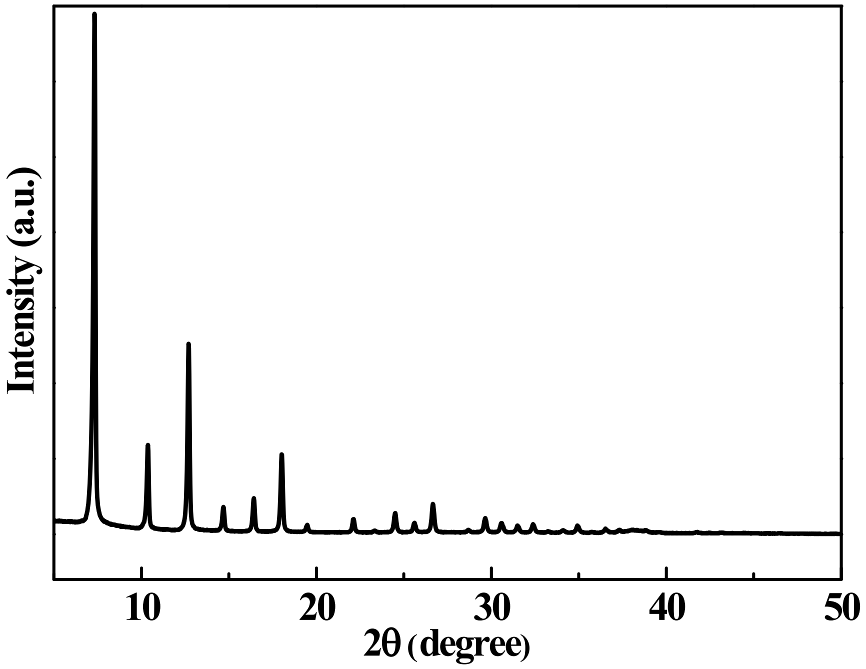


Fig. S8. XRD pattern of as-synthesized Au@ZIF-8 (d_{Au} = 15 nm) using method B.

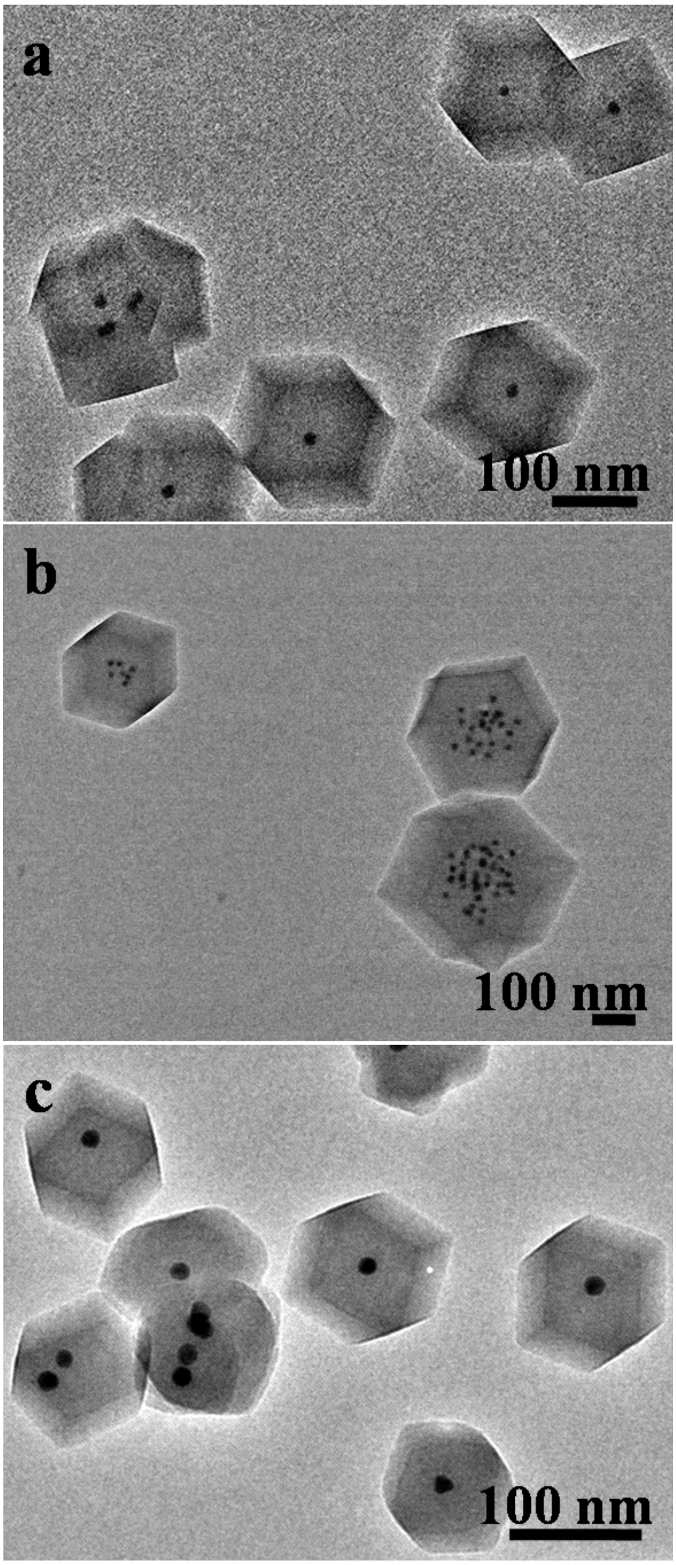


Fig. S9. TEM images of samples prepared using method B: (a) incubation time *t* = 1 min at room temperature, (b) *t* = 2 min at 30 °C, and (c) *t* = 2 min at 40 °C before heating at 50 °C for 2 h.

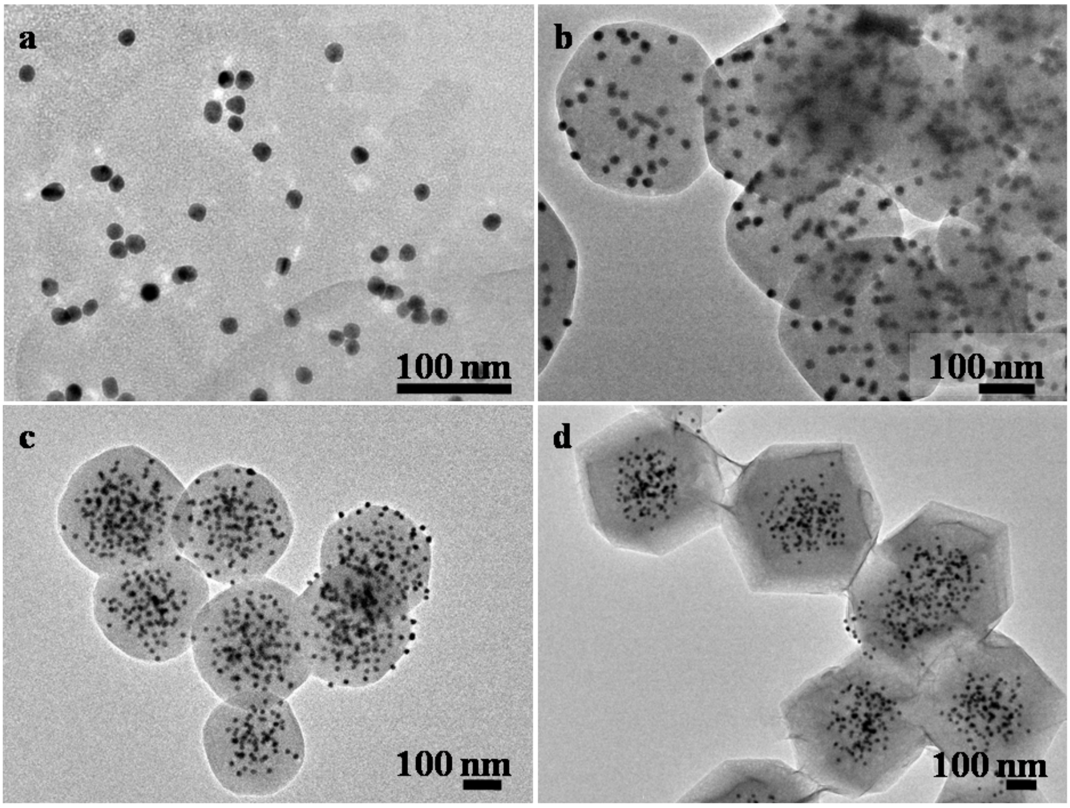


Fig. S10. TEM images of intermediates captured in method B: (a) incubation at room temperature for 2 min, and heating at 50 °C for (b) 2 min, (c) 5 min, and (d) 15 min after incubation.

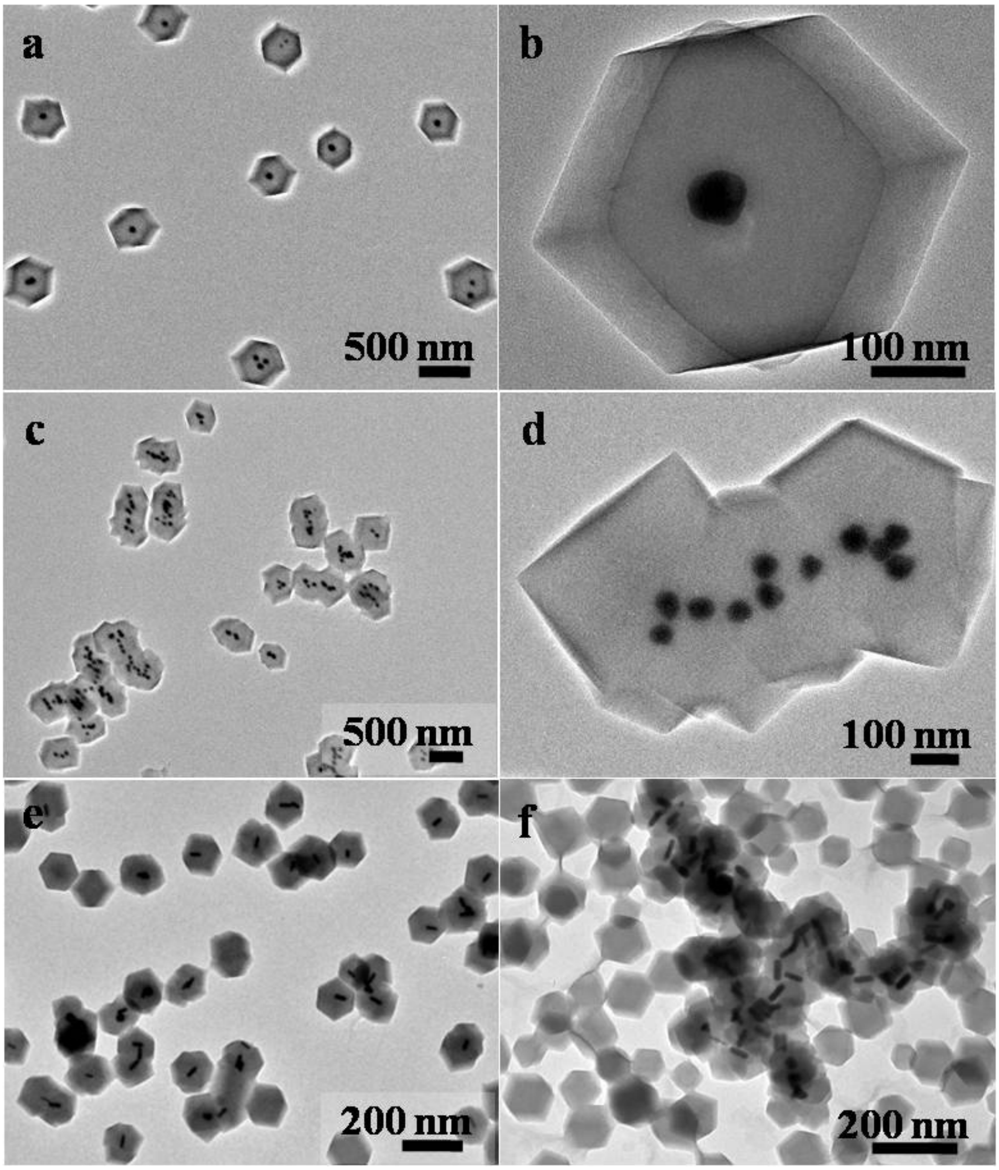


Fig. S11. TEM images of as-synthesized (a, b) Au@ZIF-8 (d_{Au} = 50 nm) structures with different magnification using method A, respectively, (c, d) multi-core Au@ZIF-8 (d_{Au} = 50 nm) structures with different magnification using method B, respectively, and samples of ZIF-8 encapsulating (e) PVP-Au NRs and (f) CTAB- Au NRs using method A.

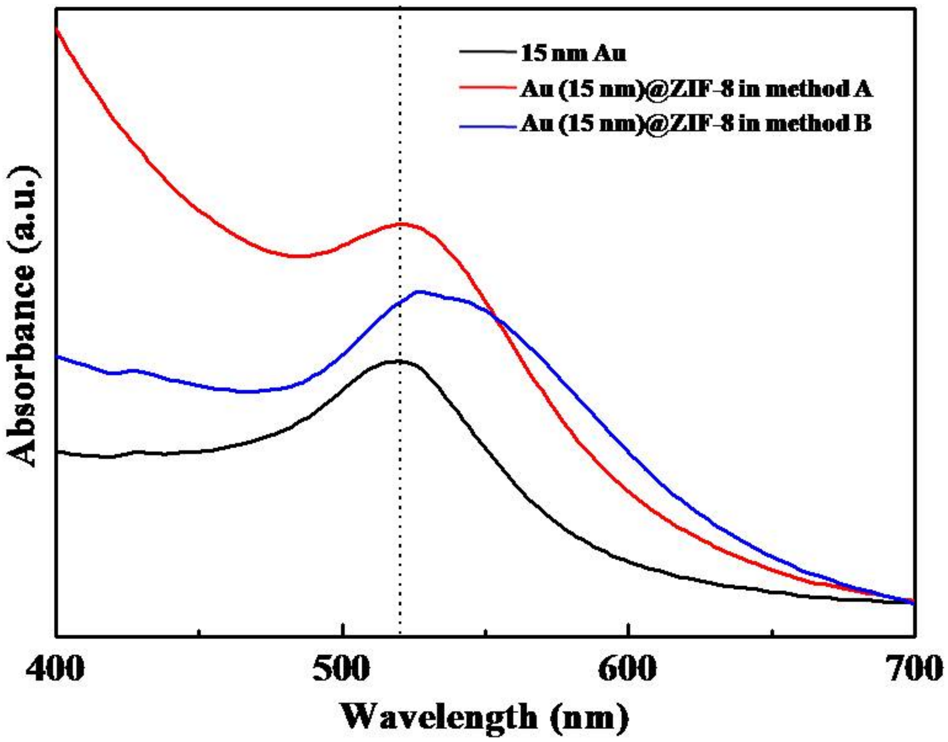
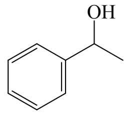
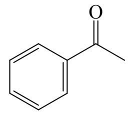


Fig. S12. UV absorption spectra of Au NPs (d_{Au} =15 nm), and Au@ZIF-8 (d_{Au} =15 nm) prepared in method A and B, respectively.

Table S1. Oxidation of benzyl alcohol in acetonitrile suspensions of Au/SiO_2, single-core and multi-core Au@ZIF-8 samples under irradiation by Xe light ($\lambda > 400$ nm) in the presence of O_2.

Photocatalyst	Substrate	Product	Solvent	Time / h	Conversion / %	Selectivity / %
Au/SiO_2			Acetonitrile	12[a]	56.9%	>99%
single-core Au@ZIF-8				24	25.8%	>99%
multi-core Au@ZIF-8					51.6%	>99%

a: The photocatalytic time of Au/SiO_2 reduced to 12 h is due to occurrence of Au aggregation.