

Electronic Supplementary Information for

Controlled Synthesis of Novel Au@MIL-100(Fe) Core–Shell Nanoparticles with Enhanced Catalytic Performance

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Materials and Instrumentation

Benzene-1,3,5-tricarboxylic acid (H₃btc) was purchased from Aldrich. Tetrachloroauric acid tetrahydrate (HAuCl₄·4H₂O), Ferric trichloride hexahydrate (FeCl₃·6H₂O), Mercaptoacetic acid (HSCH₂COOH) were purchased from Shanghai Chemical Reagent Co., Ltd., China. All other chemicals used in this work were of analytical grade and used without further purification unless of otherwise noted.

The powder X-ray diffraction (PXRD) patterns of the samples were collected using an X-ray diffractometer with Cu target (36 kV, 25 mA) from 2 to 70°. The size and morphology of the samples were conducted by a JSM-6700F field emission scanning electron microscope (FE-SEM) and a JEOL JEM 2100 transmission electron microscope at 200 kV. The UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. TGA measurements were carried out between 30 and 700 °C under air atmosphere, using a Pyris1 TGA-1. Nitrogen sorption-desorption isotherms were obtained at 77 K on a Micromeritics Tristar II 3020 M analyzer.

Experimental

Synthesis of Au nanoparticles:

Au nanoparticles were synthesized as reported previously.¹ Typically, 50 mg of potassium carbonate (K₂CO₃) was dissolved in 200 mL of distilled water, followed by the addition of 3 mL of Tetrachloroauric acid tetrahydrate (HAuCl₄·4H₂O) (25 mM). The mixture was aged in the dark for 12 h, and then 1.334 mL of formaldehyde solution (HCHO) was dropped under vigorous magnetic stirring. A brick red colloidal suspension began to form after ~15 min, and kept stirring for 30 min. Finally, the obtained Au nanoparticles were collected from reaction mixture by centrifugation (13000 r min⁻¹) and thoroughly washed with polyvinylpyrrolidone (PVP) aqueous solution (20 g L⁻¹) and ethanol, and then re-dispersed in ethanol.

Synthesis of mercaptoacetic acid (MAA)-functionalized Au nanoparticles:

Mercaptoacetic acid (MAA)-functionalized Au nanoparticles were prepared according to the following process. 0.01 g Au was added to 10 mL of ethanol solution of mercaptoacetic acid (0.029 M) under shaking for 24 h. The product was recovered by centrifugation (13000 r min⁻¹) and washed several times with ethanol, then re-dispersed in ethanol.

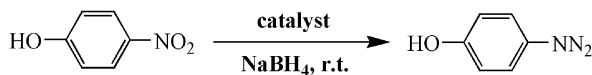
Synthesis of core-shell Au@MIL-100(Fe) nanoparticles:

0.01 g MAA-functionalized Au core synthesized as described above was dispersed in 4 mL of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ethanol solution (2 mM) for 15 minutes and then in 4 mL of benzenetricarboxylic acid (H_3btc) ethanol solution (2 mM) for 30 minutes at 70 °C. Between each step the nanoparticles were separated by centrifugation (13000 r min^{-1}) and washed with ethanol. After a given number of cycles the samples were washed with ethanol, and dried under vacuum at 60 °C.

Catalytic reaction of reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) :

The reduction of 4-NP to 4-AP by NaBH_4 was chosen as a model reaction for testing and comparing the efficiency of the catalysts with the pure Au. Typically, 162.3 mg of NaBH_4 was dissolved in 11.3 mL deionized water and then mixed with 15 mL of 0.18 mM 4-NP. The mixture was stirred for 20 min, and then 3.4 mg of catalyst (Au or Au-MAA or MIL-100(Fe) or Au@MIL-100(Fe)) was added. After introducing the catalyst, the bright yellow solution gradually faded as the reaction progressed. UV-vis spectra of the solution were recorded during the course of the reaction.

Table S1 Results of the reduction of 4-NP at room temperature catalyzed by Au, Au-MAA, MIL-100(Fe), and Au@MIL-100(Fe) core-shell NPs.



Catalyst	Au/MIL-100(Fe) molar ratio	k [min^{-1}]
Au	–	0.016
Au-MAA	–	0.011
MIL-100(Fe)	–	0.032
Au@MIL-100(Fe) (5 cycles)	64.25:1	0.29
Au@MIL-100(Fe) (20 cycles)	3.48:1	0.33

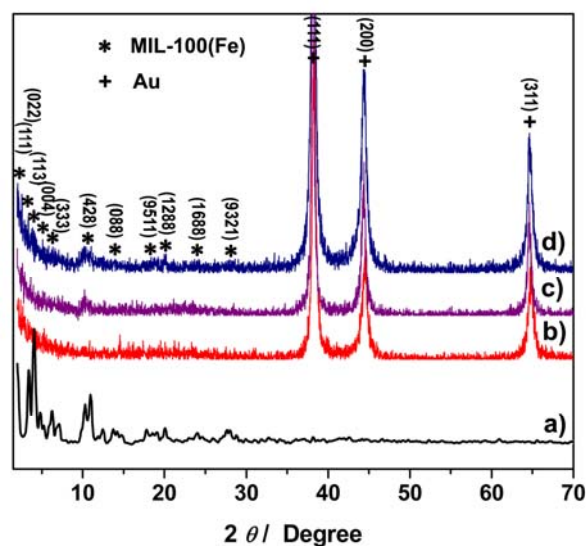


Fig. S1 PXR D patterns simulated from the crystallographic data of (a) MIL-100(Fe) and Au@MIL-100(Fe) core-shell NPs after 5 (b) and 20 assembly cycles before (d) and after (c) catalytic reaction, respectively.

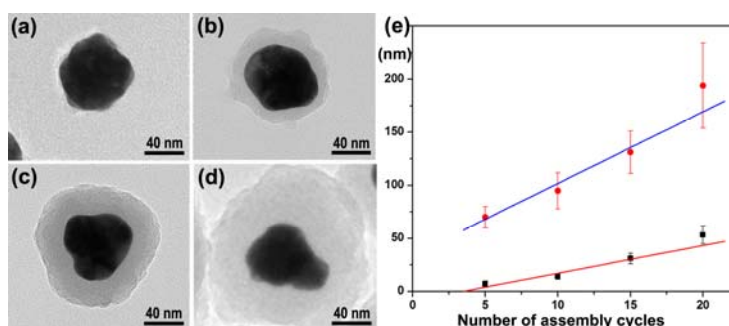


Fig. S2 TEM images of individual Au@MIL-100(Fe) core-shell nanocatalyst after (a) 5, (b) 10, (c) 15, and (d) 20 assembly cycles. (e) The correlations between the assembly cycles and the resulting diameter and shell thickness, obtained from the TEM investigations by averaging over 20 NPs.

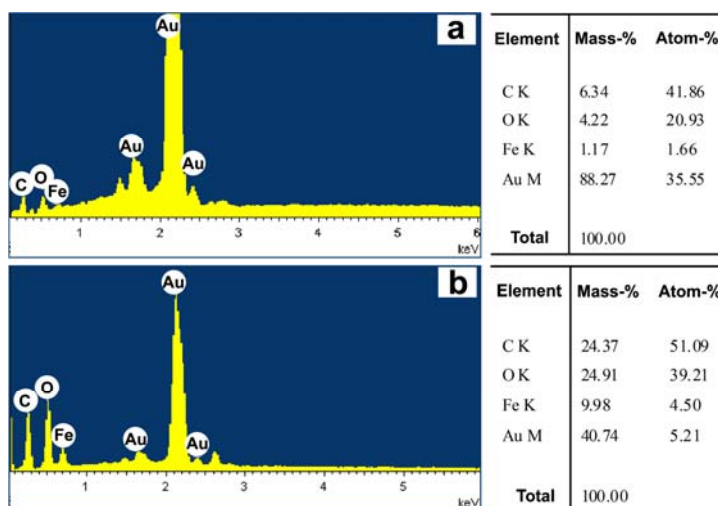


Fig. S3 EDX spectra of the Au@MIL100(Fe) core-shell NPs after 5 (a) and 20 assembly cycles (b).

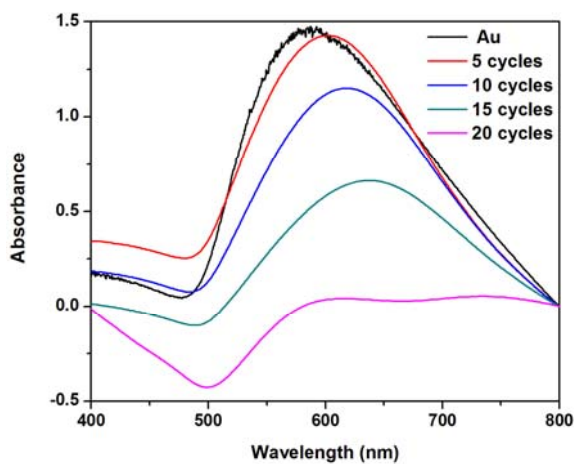


Fig. S4 UV-vis spectra of the ethanol solution of pure Au and Au@MIL-100(Fe) core-shell NPs after 5, 10, 15, and (d) 20 assembly cycles.

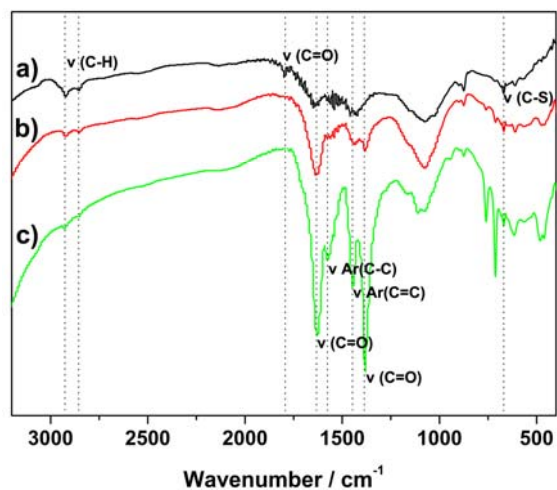


Fig. S5 Infrared spectra of the Au-MAA (a), and Au@MIL100(Fe) core-shell NPs after 5 (b) and 20 assembly cycles (c).

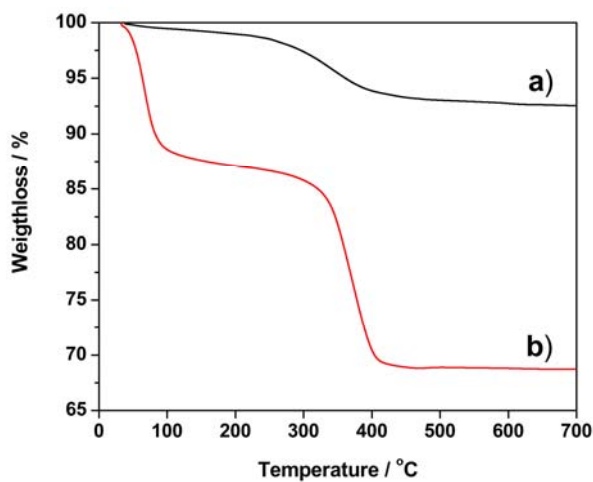


Fig. S6 TGA under air of the Au@MIL100(Fe) core-shell NPs after 5 (a) and 20 assembly cycles (b).

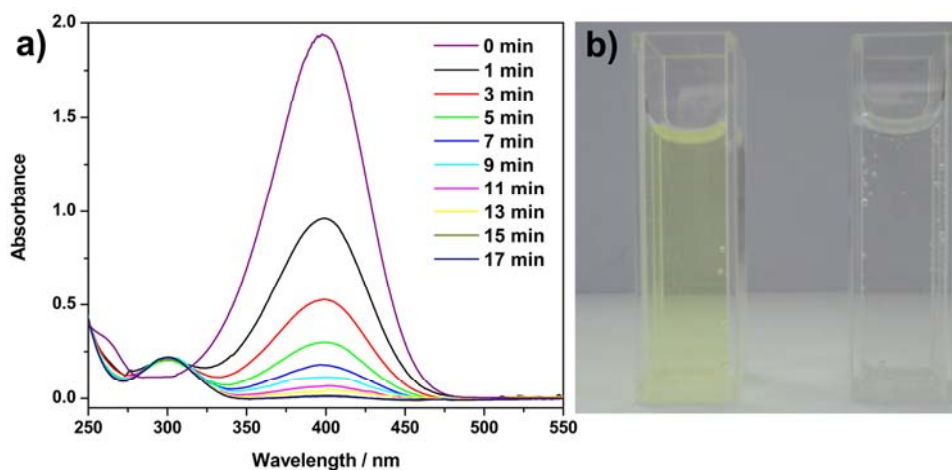


Fig. S7 (a) UV-vis spectra showing gradual reduction of 4-NP over Au@MIL-100(Fe) core-shell NPs after 5 assembly cycles, and (b) photographs of the color changes for 4-NP solution before (left) and after (right) catalytic reaction.

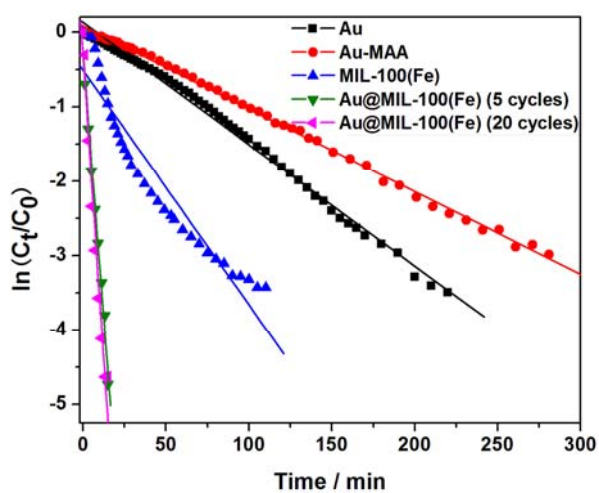


Fig. S8 Relationship of $\ln(C_t/C_0)$ and reaction time t for the reduction of 4-NP over Au, Au-MAA, MIL-100(Fe), and Au@MIL-100(Fe) core-shell NPs with 5 and 20 assembly cycles, respectively.

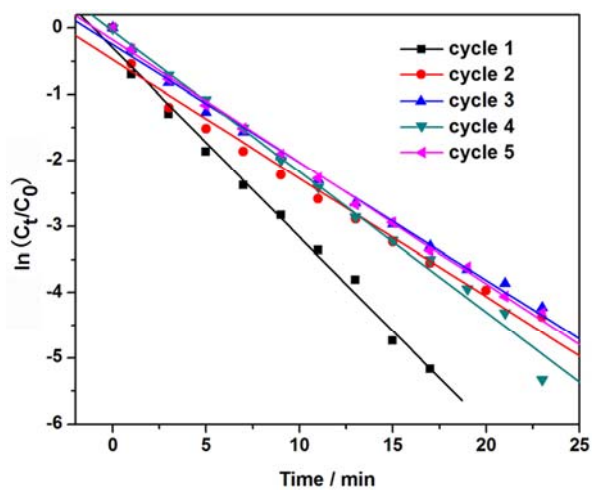


Fig. S9 Relationship of $\ln(C_t/C_0)$ and reaction time t for 5 cycles of 4-NP reduction under the same reaction conditions over the Au@MIL-100(Fe) core-shell nanocatalysts. The catalysts were synthesized with five assembly cycles.

1. L. Zhang, D. A. Blom and H. Wang, *Chem. Mater.*, 2011, **23**, 4587.