

Electronic Supplementary Information

**Synthesis of Au@UiO-66(NH₂) Structures by Small
Molecule-Assisted Nucleation for Plasmon-Enhanced
Photocatalytic Activity**

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Experimental section

Materials and characterization methods

All chemical reagents were used as received. Polyvinylpyrrolidone (PVP, M_w : 55000) was purchased from Sigma Aldrich, and all other chemicals were commercially available. Copper specimen grids (300 mesh) were purchased from Beijing XXBR Technology Co.

Transmission electron microscopy (TEM) images were collected on a Tecnai F30 operated at 300 kV. Atomic force microscopy (AFM) was operated on Park systems XE-70. X-ray diffraction (XRD) was performed with a Rigaku D/Max 2400 automatic powder X-ray diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Electron spin resonance (ESR) spectra were conducted on Bruker A200 at room temperature. Nuclear magnetic resonance (NMR) spectra were collected on AVANCE II 400. Gas chromatography (GC) spectra were recorded with Agilent 5975C. UV-vis spectra were performed on HITACHI U-4100. N_2 sorption isotherm at 77 K was carried out Micromeritics 3Flex Surface Characterization Analyzer after being degassed in vacuum at 200 °C for 12 h. The content of Au was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 2000DV. The nanosecond transient absorption spectra were measured on an LP920 laser flash photolysis spectrometer (Edinburgh Instruments, U.K.).

Synthesis of UiO-66(NH₂) nanocrystals

UiO-66(NH₂) was synthesized with a modified method.¹⁸ In a typical procedure, ZrCl₄ (0.087 mmol) and 2-aminoterephthalate acid (ATA) (0.065 mmol) were dissolved in DMF (15 mL) in a glass vial with stirring for 10 min, and the resulting solution was transferred into a 20 mL Teflon-lined stainless steel autoclave and heated at 120 °C for 24 h. The final sample was cooled to room temperature naturally, collected by centrifugation at 4000 g for 10 min, washed several times with ethanol, and dried under vacuum at 120 °C for 12 h before it was subjected to characterization.

Synthesis of Au@UiO-66(NH₂) heterostructures

ATA (0.065 mmol) and acetic acid (1.2 mL) were mixed in a 20 mL Teflon-lined autoclave containing 7 mL of DMF and stirred for 30 min. Subsequently, ZrCl₄ (0.087 mmol) dissolved in DMF (7 mL) was introduced into the aforementioned mixture under magnetic stirring for another 5 min before different amount of PVP-Au NPs ($d_{Au} = 15 \text{ nm}$) were added to obtain Au@UiO-66(NH₂) nanocrystals with different contents of Au. After the resulting solution was bubbled carefully with Ar gas for 10 min to remove the air from the autoclave, it was heated at 120 °C for 24 h. The final sample was collected by centrifugation at 4000 g for 10 min and washed several times with ethanol after being cooled naturally. Finally, the powder product was dried under vacuum at 120 °C for 12 h before it was subjected to characterization.

In the preparation system, CO₂ instead of acetic acid and Ar was bubbled for 10 min to synthesize Au@UiO(NH₂) heterostructures under otherwise identical conditions.

Before encapsulation, PVP modified Au NPs were prepared first by introducing PVP aqueous solution (25.6 mg/mL, 2 mL) to pre-synthesized Au NPs colloid solution (100 mL) under magnetic stirring for 24 h. PVP-Au NPs were concentrated with centrifugation at 17000 g for 20 min and washed with DMF before being added to the synthetic system.

Synthesis of Au on UiO-66(NH₂) hybrids by a photodeposition method

UiO-66(NH₂) powder (20 mg) was suspended in a mixture solvent consisted of water (2 mL) and methanol (1 mL) in a quartz tube and an aqueous solution of HAuCl₄ (0.5 ml, 10 mg/mL) was injected into the tube. After Ar purging for 10 min, the photodeposition reaction system was sealed with Ar balloon, and irradiated by a white fluorescence lamp (40 W) for 12 h with magnetic stirring. The final pale red suspension was obtained, washed several times with ethanol, and dried under vacuum at 120 °C for 12 h before it was subjected to characterization and photocatalytic tests.

Photocatalytic oxidation of alcohol tests

UiO-66(NH₂) and Au@UiO-66(NH₂) powders were incubated in ethanol for 24 h to remove residual DMF and other ions adsorbing on internal pores following drying under vacuum at 120 °C for 12 h before both were used as photocatalysts for oxidation reactions. The photocatalyst powder (8 mg) was dispersed into a 20 mL quartz glass reactor containing 2 mL of acetonitrile-d₃ and 50 μM of alcohol. The reactor was sealed with a rubber septum after being bubbled carefully with O₂ for 10 min, The mixture was irradiated using a white fluorescence lamp (40 W) for 24 h under magnetic stirring. The final mixture after removing catalyst by centrifugation was analyzed by NMR and GC, and conversion of alcohol over different photocatalysts was obtained from the peak area ratio of product and substrate.

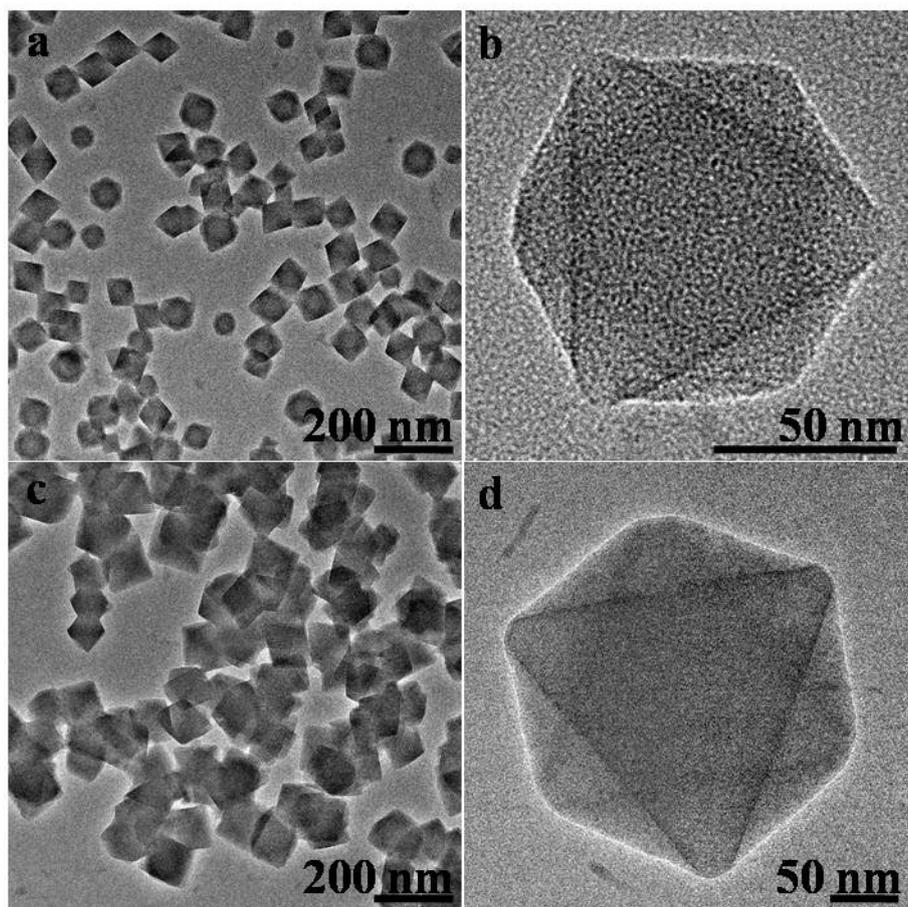


Fig. S1. TEM images of UiO-66(NH₂) (a) and (b) with introducing HAc, and (c) and (d) without introducing HAc in synthesis process, respectively.

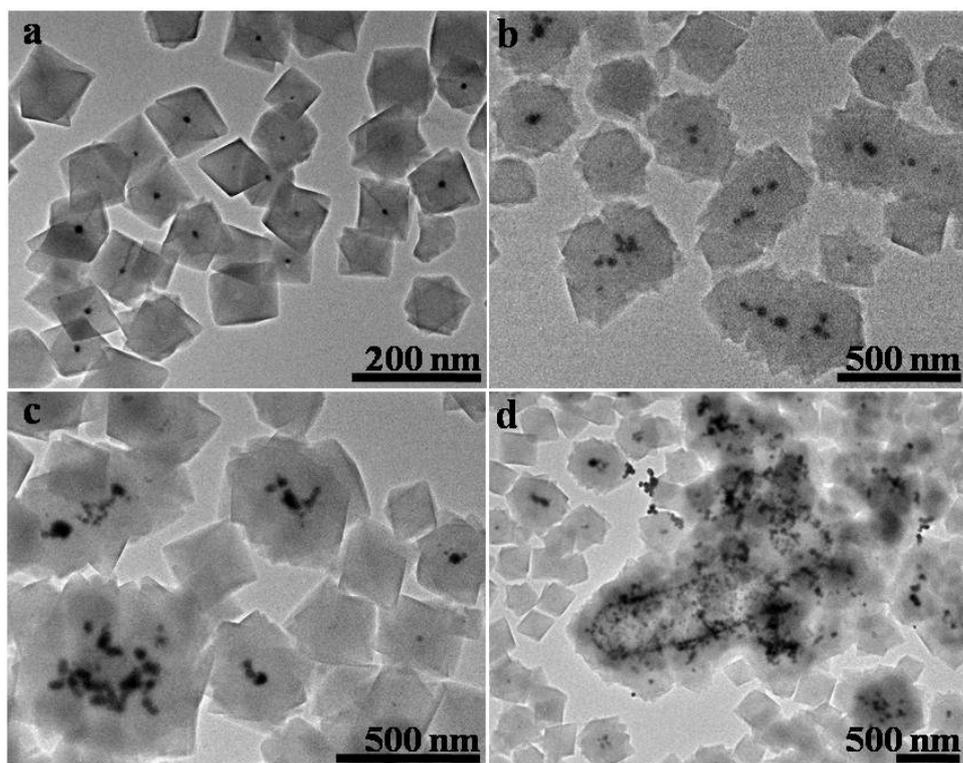


Fig. S2. TEM images of samples obtained with different amount of Au NP solutions: (a) 8 mL, (b) 20 mL, (c) 26 mL, and (d) 32 mL. Corresponding to the Au content by ICP-AES is about 1.3 wt%, 3.5 wt%, 4.7 wt%, and 5.6 wt%, respectively.

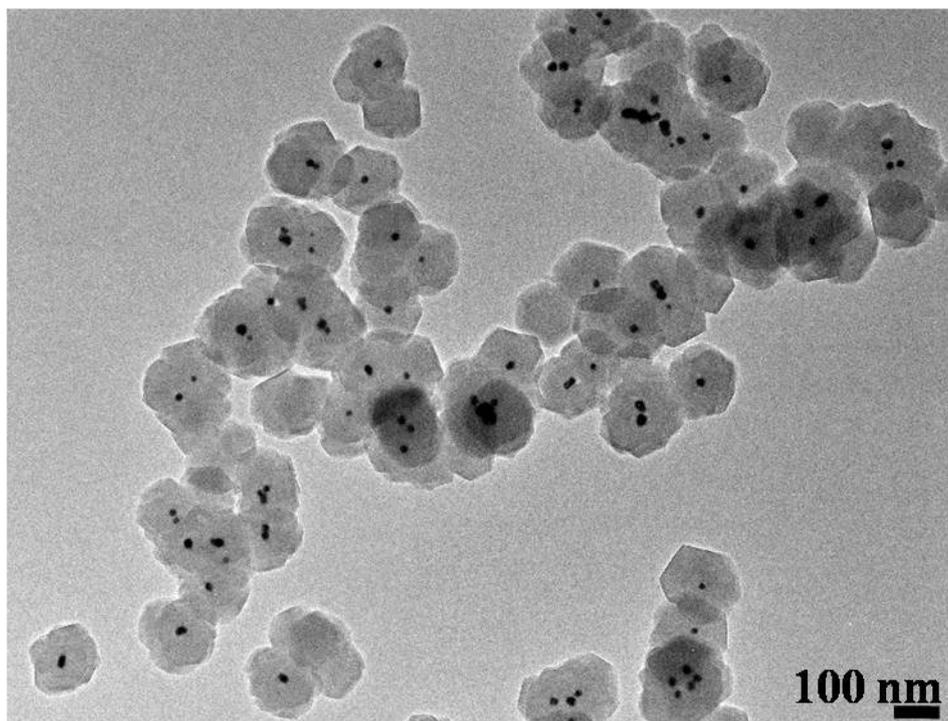


Fig. S3. TEM images of encapsulation of Au NPs in UiO-66(NH₂) while CO₂ instead of acetic acid and Ar was bubbled into the preparation system.

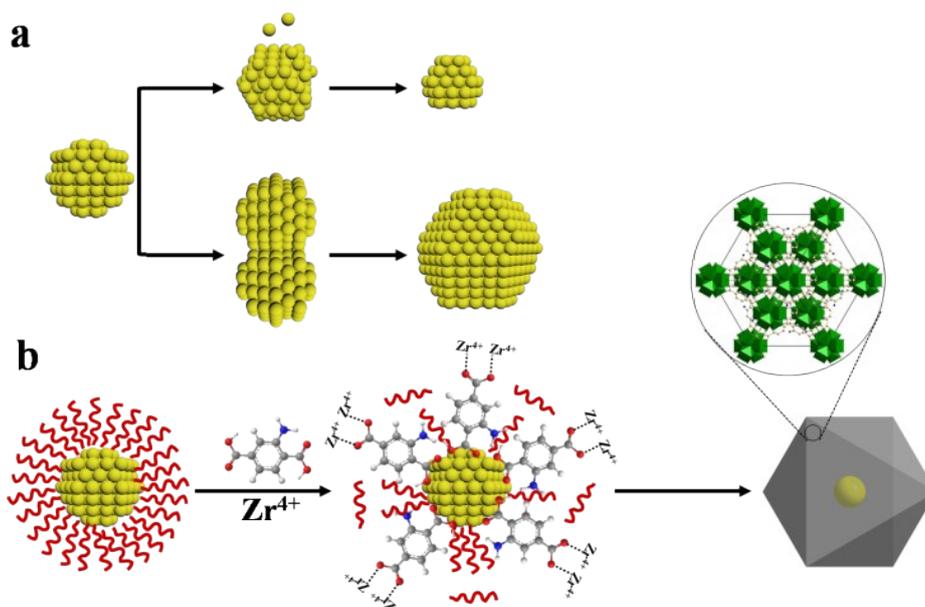


Fig. S4. Schematic illustrating of (a) the size evolution of Au NPs, and (b) the encapsulation of PVP-Au NPs into UiO-66(NH₂) process.

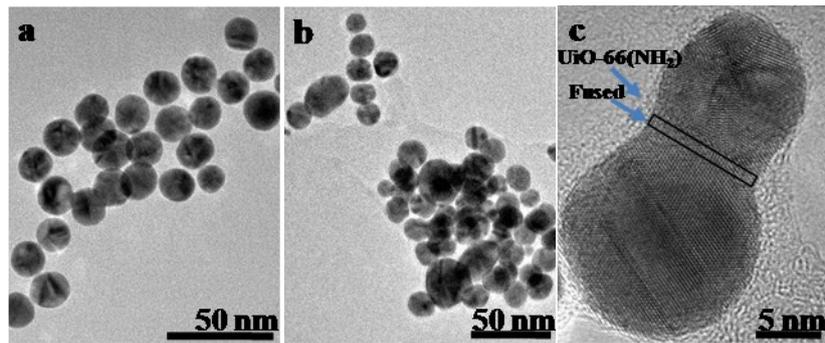


Fig. S5. TEM images of (a) pre-synthesized Au NPs ($d_{\text{Au}} = 15$ nm), and (b) and (c) intermediate captured heating for 1 h in synthesis process of Au@UiO-66(NH₂) with different magnification, respectively.

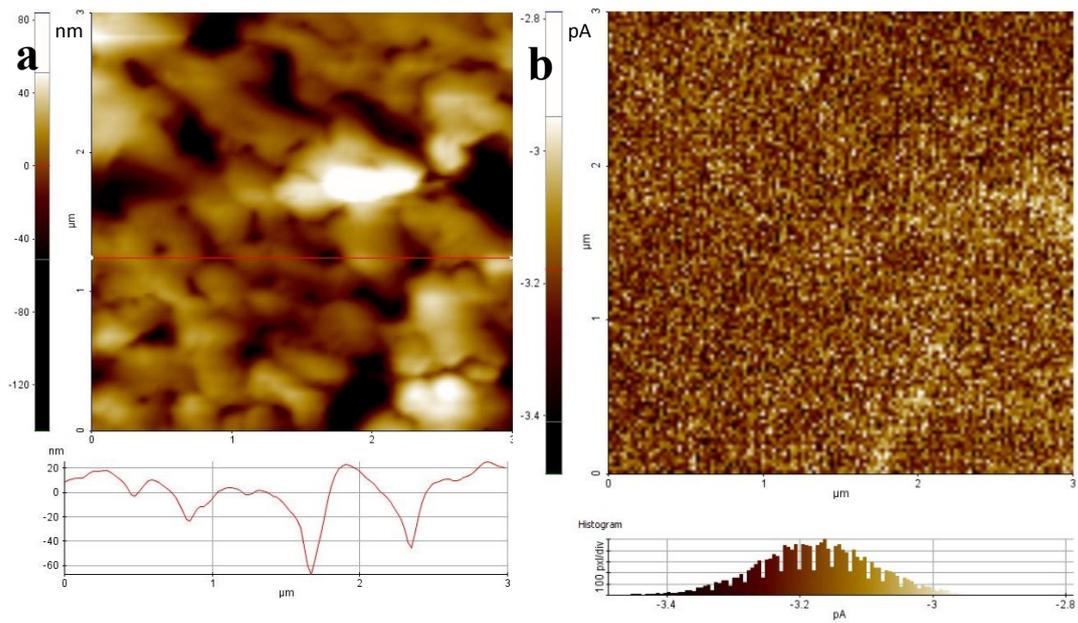


Fig. S6. (a) AFM image of UiO-66(NH₂) film and (b) corresponding current distribution image examined by using C-AFM..

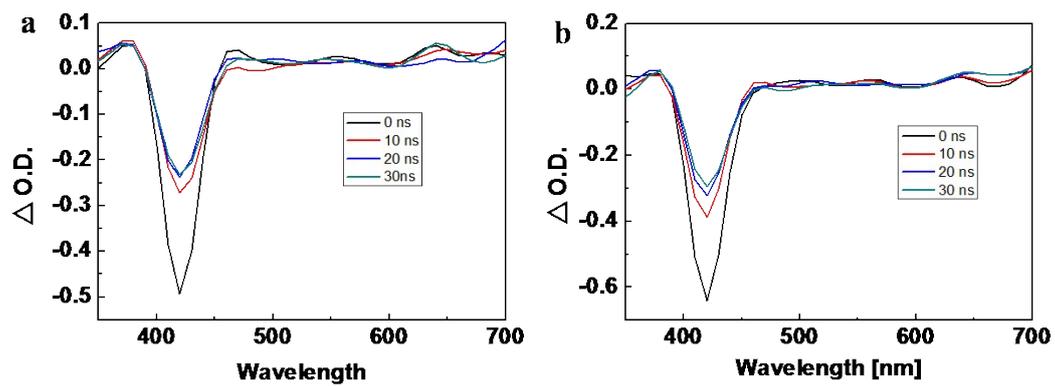


Fig. S7. Nanosecond transient absorption of (a) UiO-66(NH₂) and (b) Au@UiO-66(NH₂) excitation with a pulsed nanosecond laser at 355 nm. The solvent was water during transient absorption tests.

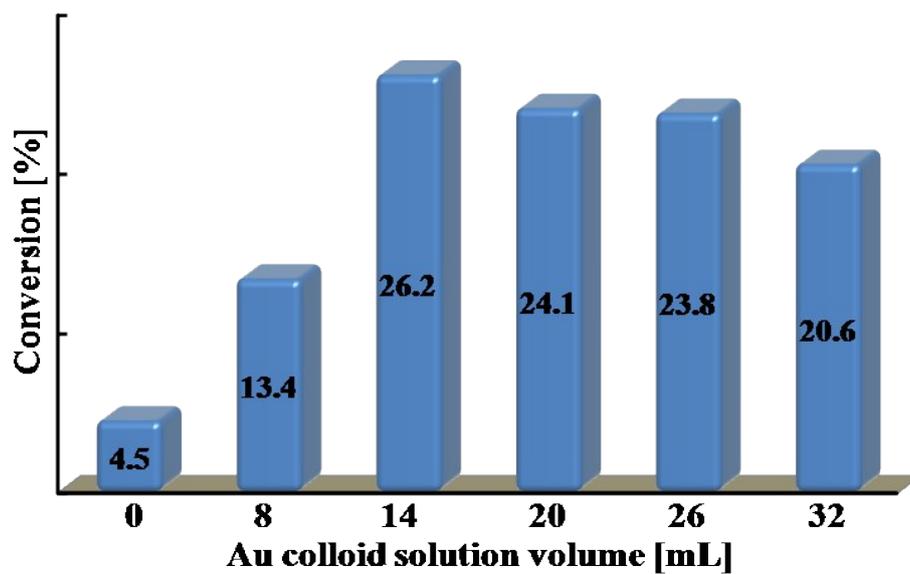


Fig. 8. The conversion of photocatalytic oxidation of benzyl alcohol over pure UiO-66(NH₂) nanocrystals and Au@UiO-66(NH₂) heterostructures.

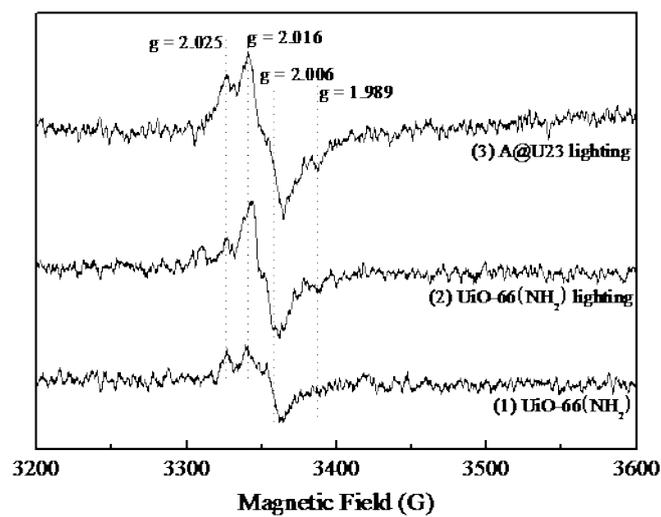


Fig. S9. ESR spectra of (1) UiO-66(NH₂), and (2) UiO-66(NH₂) and (3) A@U23 under visible-light irradiation.

The signal at $g = 1.989$ could be attributed to Zr^{3+} , and the three signals at g value of 2.006, 2.016 and 2.025 could be originated from superoxide radicals.

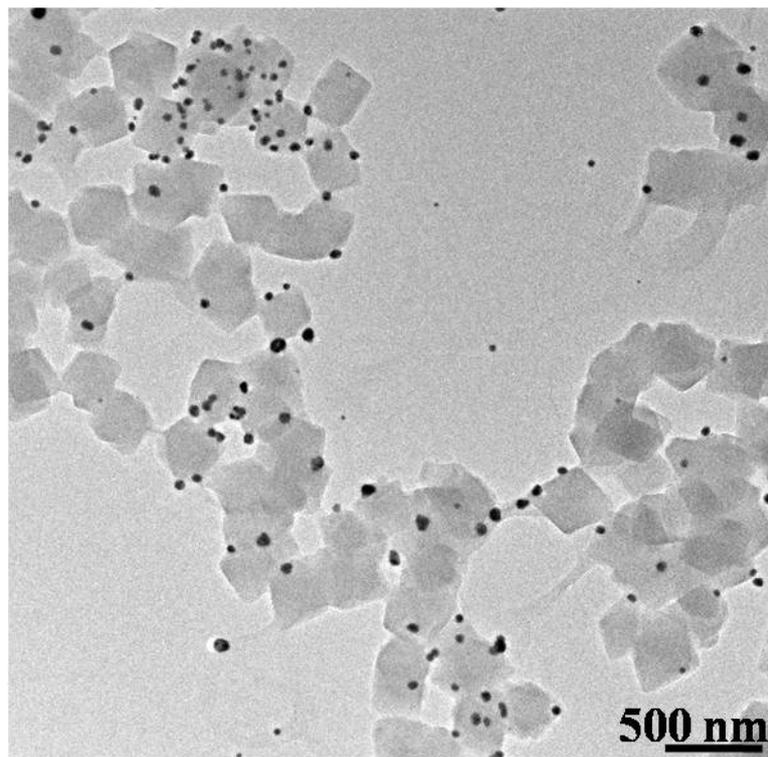


Fig. S10. TEM image of Au on UiO-66(NH₂) hybrids by a photo-deposition process.