Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Efficient Incorporating Diverse Components into Metal Organic Frameworks via Metal Phenolic Networks

EXPERIMENTAL SCECTION

Chemicals

Chloroauric acid tetrahydrate （$HAuCl_4 \cdot 4H_2O$），trisodium citrate dihydrate，silver nitrate （$AgNO_3$）， hydrochloric acid （HCl，36% ~ 38% wt.% in water）， ascorbic acid （AA）， sodium oleate（NaOL）， sodium borohydride （$NaBH_4$）, thiourea, N,N-dimethylmethanamide （DMF）, zinc nitrate hexahydrate （$Zn(NO_3)_2 \cdot 6H_2O$）, methanol，tannic acid （TA）, Ferric chloride anhydrous （$FeCl_3$）， ethylene glycol （EG）, diethylene glycol （DEG）, hexane and sodium acetate （CH_3COONa）were purchased from Sinopharm Chemical Reagent Co. Ltd., China. Cadmium acetate dihydrate （$Cd(CH_3COO)_2 \cdot 2H_2O$）, zirconium chloride （$ZrCl_4$）， terephthalic acid （$H_2BDC$）, 2-methylimidazole, sudan III and iron(III) chloride hexahydrate （$FeCl_3 \cdot 6H_2O$） were obtained from Aladdin Industrial Corporation, China. hexadecyl trimethylammonium bromide (CTAB) and tris(hydroxymethyl)aminomethane （Tris） were achieved from Sigma-Aldrich Co. Ltd. All these chemicals were used as received without further purification.

Characterizations

The scanning electron microscopy (SEM) measurement was conducted on a Zeiss Ultra 55 scanning electron microscope at 5.0 kV. Transmission electron microscopy （TEM） characterization was performed on Hitachi H-7000FA transmission electron microscope with an accelerating voltage of 100 kV and JEM-

2100 (HR) at 200 kV. The high-resolution TEM （HRTEM) images and elemental maps were obtained with FEI tecnai G2 F30 operating at 300 kV. Powder X-ray diffraction (XRD) patterns were recorded with a X'pert PRO diffractometer (PANalytical) using Cu Kα radiation (wavelength k =1.5406 Å). X-ray photoelectron spectroscopy （XPS） spectra was measured with a PHI Quantera II spectrometer equipped with a hemispherical analyzer. Fourier transform infrared (FT-IR) spectra were carried out on a NICOLET 5700 FTIR Spectrometer. Thermogravimetric analysis (TGA) was conducted on a TG/DTA7300 instrument under a nitrogen purge at a heating rate of 15 °C/min. Magnetic property characterization was carried out on a vibrating sample magnetometer (VSM) on a PPMS-9T physical property measurement system (Quantum Design) at 300K. N_2 adsorption and desorption studies were conducted using a Micromeritics ASAP 2020 adsorption apparatus at 77 K. The specific surface area was calculated utilizing Brunauer-Emmett-Teller （BET） method. The water contact angle (CA) measurements of different materials were recorded using a contact angle goniometer (USA KINO Industry CO.).

Synthesis of 50 nm Gold Nanoparticles (NPs)

Au NPs with a mean size of 50 nm were synthesized via a seed-mediated growth method.[1] In a typical synthesis, 10 nm citrate-stabilized Au seeds were prepared first. Briefly, a sodium citrate aqueous solution (150 mL, 2.2 mM) was injected into a 250 mL flask with a condenser, and heated for 15 min under vigorous stirring. After boiling, a $HAuCl_4$ aqueous solution (1 mL, 25 mM) was added one shot and the mixture was refluxed for another 10 min under vigorous stirring. A gradual color change from yellow to soft pink of the solution could be observed. The obtained gold seeds could be well dispersed in water. For the preparation of 50 nm Au NPs, the above 10 nm Au seeds solution in the same reaction vessel was cooled down until the temperature reached 90℃. Then, 1 mL of 25 mM $HAuCl_4$ was added under stirring, and the solution was heated for 30 min. This procedure was repeated twice. When reaction was finished, the solution was cooled down to room temperature. After that, 55 mL of the solution was extracted and diluted by adding 2 mL of 60 mM sodium citrate solution and 53 mL of deionized water. Finally, this mixture was used as seed solution, and the growth steps were repeated until dark-red 50 nm Au NPs solution was obtained.

Synthesis of Gold Nanostars (NSs)

Au NSs were synthesized by a seed-mediated growth method reported elsewhere with minor modification.[2] Briefly, 200 μL of a $HAuCl_4$ solution (25 mM), 20 μL of 1 M HCl and 200 μL of 10 nm citrate stabilized gold seeds were sequentially added into 15 mL deionized water under vigorous stirring. After about 2 min, 40 μL of 10 mM $AgNO_3$ was injected to the solution. The obtained mixture was stirred for another 2 min. Then, 100 μL of 100 mM AA was added one shot under stirring. The whole growth procedure was conducted at room temperature. Finally, 1 mL of 10 mM CTAB solution was added to increase the dispersity of obtained gold nanostars.

Synthesis of Gold Nanorods (NRs)

Au NRs were synthesized via a binary surfactant protocol.[3] A gold seeds solution was prepared first. Typically, 5 mL of 0.2 M CATB solution was added into a 25 mL flask, followed by the addition of 5 mL of 0.5 mM $HAuCl_4$. Then, 600 μL of freshly prepared ice-cold $NaBH_4$ solution was injected, and the mixture was vigorously stirred for 2 min. With addition of $NaBH_4$, a color change from yellow to brownish yellow could be observed. The obtained seed solution was left for 30 min at room temperature before use. To synthesize gold nanorods, 4.5 g of CTAB and 0.617 g of NaOL were dissolved in 125 mL deionized water in a 500 mL flask. Then, 12.0 mL of 4 mM $AgNO_3$ solution was added. 15 min later, 125 mL of 1 mM $HAuCl_4$ solution was added, and the mixture was stirred for 90 min at 700 rpm, a color change to colorless could be observed. Then, 0.75 mL of 37 wt.% HCl was injected to adjust the pH. After another 15 min, 0.625 mL of 64 mM AA and 0.1 mL of Au seeds were added sequentially, and the resultant mixture was kept undisturbed for 12 h to complete the growth.

Synthesis of Fe_3O_4 Nanospheres

The magnetic Fe_3O_4 nanospheres were prepared by a one-pot solvothermal approach.[4] 1.62 g of $FeCl_3$ and 1.00 g of trisodium citrate dihydrate were first dissolved in a mixture of ethylene glycol (10 mL) and diethylene glycol (70 mL) at 120°C for 30 min. Then, 4.10 g of CH_3COONa was added. The mixture was stirred vigorously until all the reactants were fully dissolved. The solution was then sealed in a Teflon-lined stainless-steel autoclave and heated at 200°C for 10 h. After the reaction，the autoclave was cooled to room temperature naturally. Finally, the resulting Fe_3O_4 nanospheres were magnetically collected and washed with ethanol and deioned water for several times， and then dried under vacuum for 12 h.

Synthesis of CdS spherical Nanoparticles

In a typical synthetic procedure, 2.21 g $Cd（CH_3COO)_2\cdot 2H_2O$ was added into 240 mL water at room temperature, followed by the addition of 7.308 g thiourea. The solution was stirred for 30 min to fully dissolve the reactant. The mixture was then transferred into a 100 mL Teflon-lined autoclave, and heated at 200℃ for 5 h. After the reaction，the autoclave was cooled to room temperature naturally, and the product was collected by centrifugation. Finally, the obtained product was washed several times with water and freeze dried for 12 h.

Synthesis of UiO-66 Nanocrystals

UiO-66 nanocrystals were obtained by a reported protocol with minor modifications.[5] Typically, 0.8 mmol of $ZrCl_4$ and 0.8 mmol of terephthalic acid (H_2BDC) were dissolved in 86.22 mL DMF solution with magnetic stirring for 30 min at 70℃. Then 13.78 mL of acetic acid was added and the resulting mixture was transferred into a Teflon-lined stainless steel autoclave. The autoclave was heated in 120℃ oil bath for 24 hours. After cooling down to room temperature naturally, the final sample was collected by centrifugation, washed with DMF , and then purified with methanol for several times to eliminate DMF molecules. Finally, the obtained

UiO-66 nanocrystals were dried under vacuum for 12 h at 100°C.

Synthesis of Core Shell Au@TA-Fe^{3+} Nanoparticles

A TA-Fe^{3+} (Tannic acid-iron) network could be formed on Au particles (Au NPs, Au NSs, and Au NRs) via the following procedure. Typically, a predetermined amount of Au particles was redispersed in 4 mL of deionized water. 25 μL of 10 mg/mL of $FeCl_3·6H_2O$ (100 μL of 20 mg/mL of TA was added first for Au NPs) solution was added into the above solution, followed by vigorously mixing by a vortex mixer for 20s. Next, 50 μL of 20 mg/mL of TA solution (50 μL of 10 mg/mL of $FeCl_3·6H_2O$ for Au NPs) was injected with another 20s mixing. Subsequently, the pH of the solution was raised by adding 4 mL of Tris-HCl buffer solution (pH=8.5) followed by vortexing. Afterwards, the Au@TA-Fe^{3+} nanoparticles were collected by centrifugation and washed with water to remove the excess TA-Fe^{3+} complexes. Finally, the obtained Au@TA-Fe^{3+} was redispersed in methanol for further use.

Synthesis of Core Shell X@TA-Fe^{3+} Nanoparticles (X = Fe_3O_4, CdS and UiO-66)

In a typical synthesis, a predetermined amount of X was dispersed in 10 mL of deionized water under sonication. 100 μL of 10 mg/mL of $FeCl_3·6H_2O$ solution was added into the above solution, followed by vigorously mixing by a vortex mixer for 20s. Next, 200 μL of 20 mg/mL of TA solution was injected with another 20s mixing. Subsequently, the pH of the solution was raised by adding 10 mL of Tris-HCl buffer solution (pH=8.5) followed by vortexing. Afterwards, the X@TA-Fe^{3+} nanoparticles were collected by centrifugation and washed with water to remove the excess TA-Fe^{3+}

complexes. Finally, the obtained X@TA-Fe^{3+} was redispersed in methanol for further use.

Synthesis of CdS@TA-Fe^{3+}@Au and UiO-66@TA-Fe^{3+}@Au Nanoparticles

In a typical preparation of CdS@TA-Fe^{3+}@Au, CdS nanoparticles were dispersed in 8 mL of Tris-HCl buffer solution (pH=8.5) under sonication followed by vigorously magnetic stirring at 85°C. Then, 30 uL of 50 mM of $HAuCl_4$ was injected into the solution, and the mixture was vigorously stirred for 15 min. After cooling down the room temperature naturally, the product was purified by centrifugation/redispersion circles. Similar protocol was applied to obtain UiO-66@TA-Fe^{3+}@Au nanoparticles.

Synthesis of ZIF-8 Polyhedral Nanocrystals

In a typical synthesis of ZIF-8 nanocrystals, 4 g of 2-methylimidazole and 1.68 mg of zinc nitrate hexahydrate were each dissolved in 60 mL and 20 mL of methanol, respectively. Then, methanolic solution of zinc nitrate hexahydrate was poured into the methanolic solution of 2-methylimidazole followed by stirring for 1 h. The mixture was incubated at room temperature for 24 h. The white powder of ZIF-8 nanocrystals was isolated by centrifugation and washed several times by methanol, and finally vacuum-dried for further use.

Synthesis of Core Double Shell X@TA-Fe^{3+}@ZIF-8 Nanoparticles (X = Au NPs, Au NSs, Au NRs, Fe_3O_4, CdS, UiO-66)

For synthesis of X@TA-Fe^{3+}@ZIF-8 nanostructure, 3 mL of methanolic solution of X@TA-Fe^{3+} was mixed with 2.5 mL of methanolic solution of zinc nitrate hexahydrate (2.5 mM), and then the mixed solution was sonicated for 3 min. Next, 2.5 mL of methanolic solution of 2-methylimidazole (5 mM) was added. The mixture was then incubated at room temperature for 12 h (2 h for Fe_3O_4@TA-Fe^{3+} and CdS@TA-Fe^{3+}) to grow ZIF-8 shell. Finally, the obtained products were isolated by centrifugation and washed several times with methanol. The above described method was also used to encapsulate CdS@TA-Fe^{3+}@Au into ZIF-8, except that, X@TA-Fe^{3+} was replaced by CdS@TA-Fe^{3+}@Au. (**In order to achieve a better absorbing performance for n-hexane, a higher precursor concentration (20 mM of $Zn(NO_3)_2$ and 40 mM of 2-HIM) was used during the syntheses of Fe_3O_4@TA-Fe^{3+}@ZIF-8, because higher ZIF-8 loading would both increase the hydrophobicity, thermal stability and the surface area of the product.**)

Absorption of n-Hexane Measurements

The organic solvent-absorbent capacity of the Fe_3O_4@TA-Fe^{3+}@ZIF-8 was determined following a reported literature procedure.[6] The Fe_3O_4@TA-Fe^{3+}@ZIF-8 nanoparticles were immersed into n-Hexane for an hour to allow the absorption process. Then, excess solvent was removed by magnetic separation and the absorbents were gently wiped to remove extra solvents on the surface. Then, the solvent absorbed Fe_3O_4@TA-Fe^{3+}@ZIF-8 wet mixture was quickly measured by an electronic balance to avoid the evaporation of solvents. The weights of absorbents before and after absorbance were referred as W_0 and W_1, respectively. The relative absorption capacity of Fe_3O_4@TA-Fe^{3+}@ZIF-8 was calculated following the equation below:

$$\text{Absorbency} = (W_1 - W_0)/W_0 \times 100\,\%$$

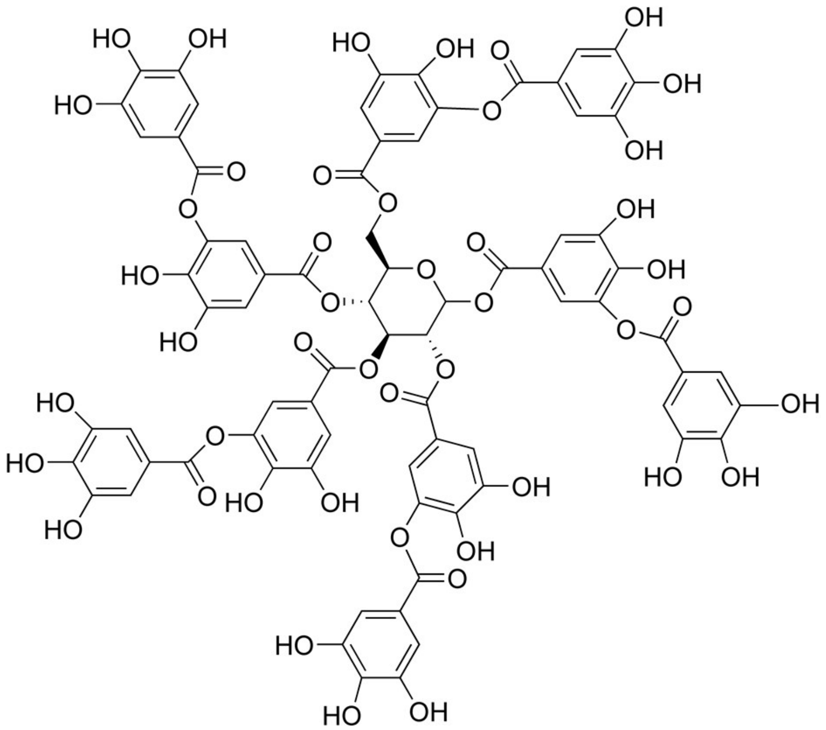

Figure S1. Molecular structure of tannic acid (TA).

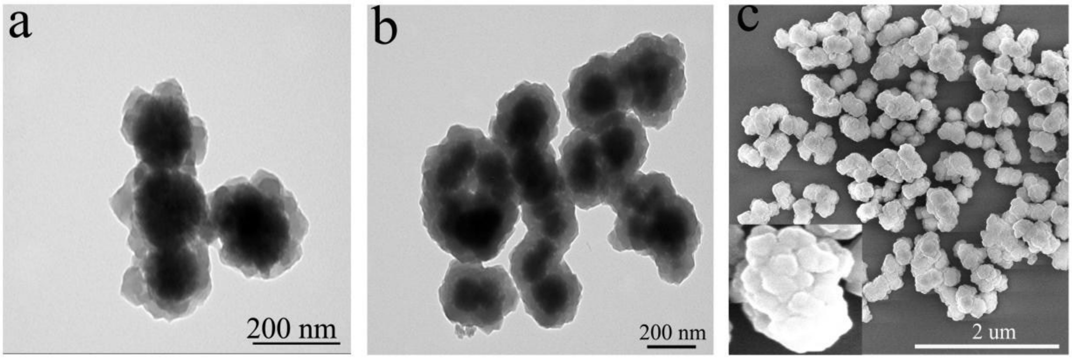

Figure S2. TEM images of Fe_3O_4@TA-Fe^{3+}@ZIF-8 with different thickness of ZIF-8 shell when added precursor concentration of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-HIM were 5 mM and 10 mM (a), 10 mM and 20 mM (b), respectively. (c) SEM image of Fe_3O_4@TA-Fe^{3+}@ZIF-8 and the inset shows the surface morphology of an enlarged particle.

The thickness of ZIF-8 shell on core particles was tailorable by judiciously choosing the precursor concentration of ZIF-8 introduced to the reaction system while other parameters were remained, and a thicker coating layer could be obtained by increasing the added concentration of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-HIM.

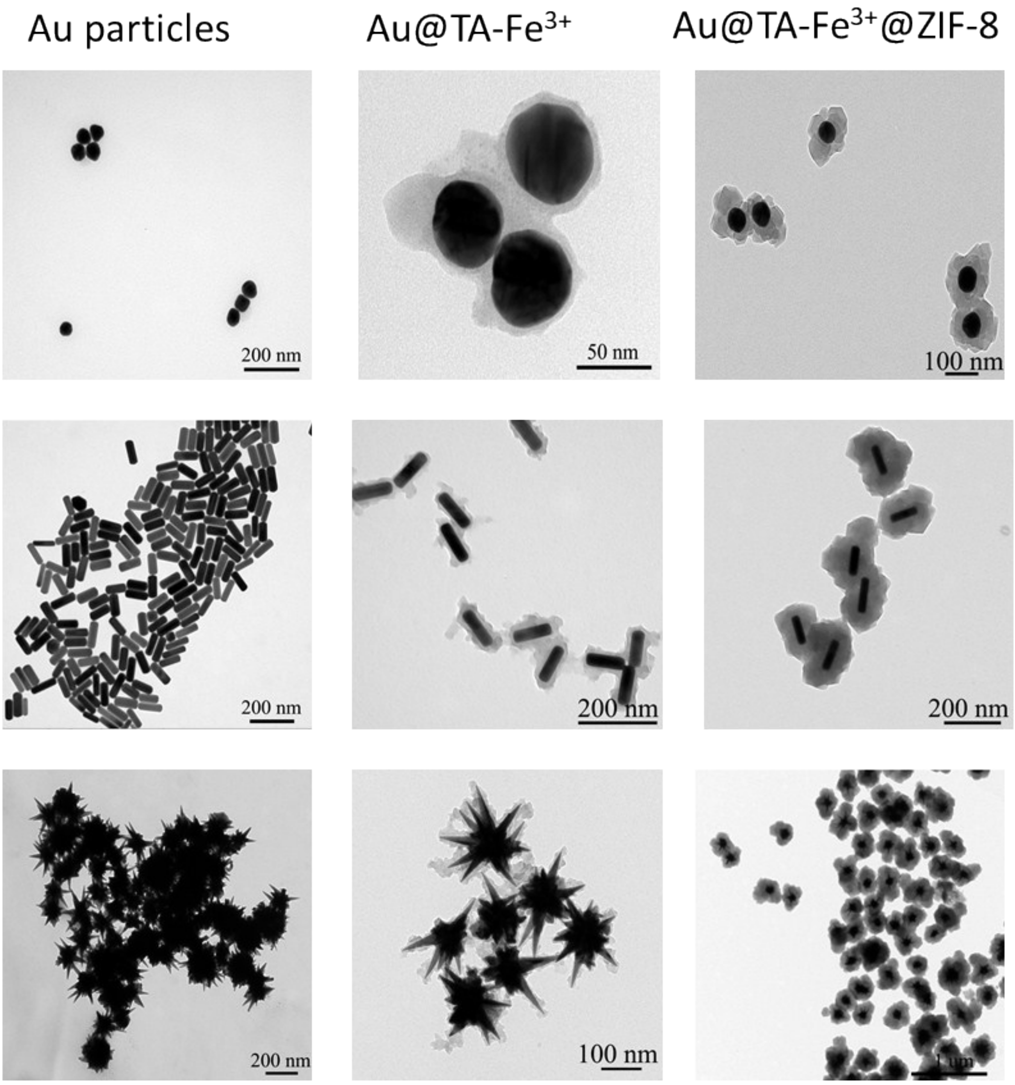

Figure S3 Enlarged TEM images of bare Au particles, Au@TA-Fe^{3+} and Au@TA-Fe^{3+}@ZIF-8.

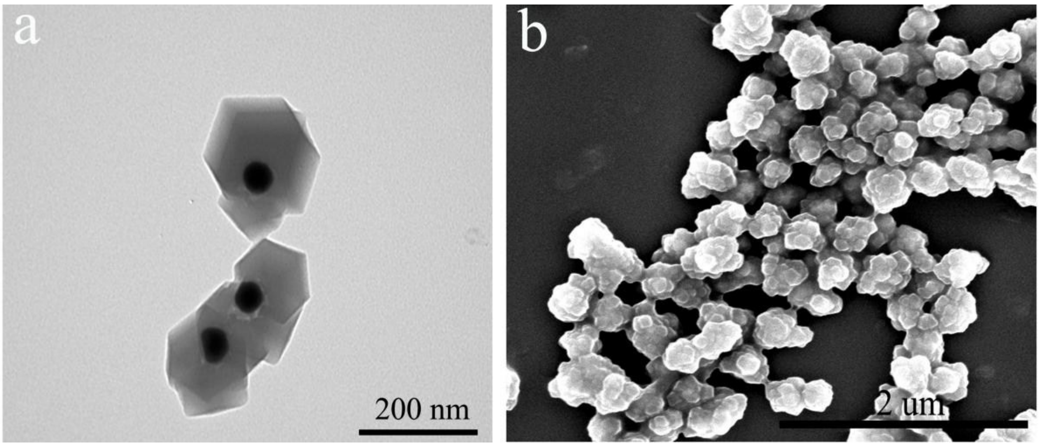

Figure S4 (a) TEM image of Au NPs@TA-Fe^{3+}@ZIF-8 when added precursor concentration of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-HIM were 10 mM and 20 mM, respectively. (b) SEM image of Au NSs@TA-Fe^{3+}@ZIF-8.

When the precursor concentration introduced to the reaction doubled (10 mM of $Zn(NO_3)_2$ and 20 mM of 2-HIM), two concentric layers on Au nanoparticles were observed. It should be mentioned here that the robust coating of TA-Fe^{3+} thin film not only facilitate the coating of ZIF-8 layer, but also imparted citrate-stabilized Au nanoparticles with excellent colloidal stability while bare Au nanoparticles suffered from serve aggregation and quickly precipitated in the methanolic solution of ZIF-8 precursor.

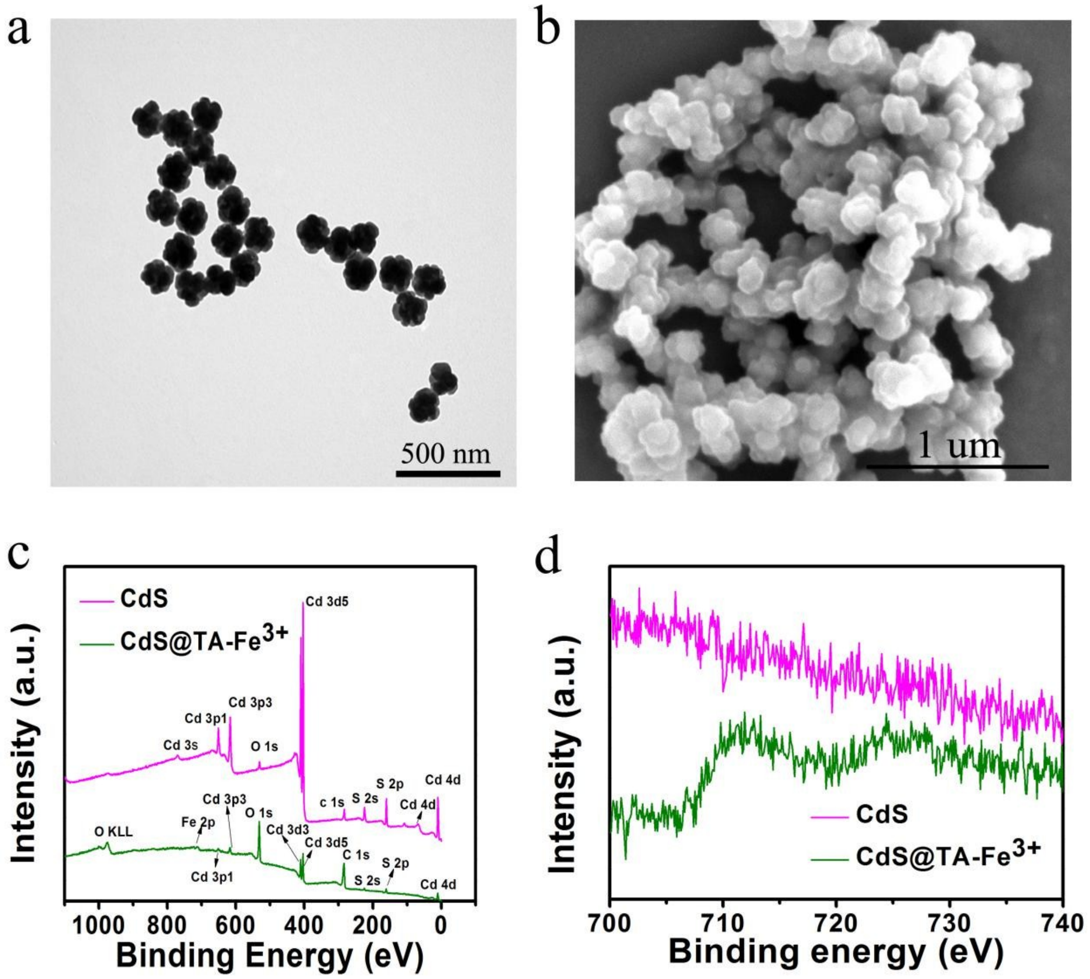

Figure S5. (a) TEM image of bare CdS nanoparticles. (b) SEM image of CdS@TA-Fe^{3+}@ZIF-8. (c) Survey XPS spectra of CdS and CdS@TA-Fe^{3+}. (d) High-resolution Fe 2p XPS data of CdS and CdS@TA-Fe^{3+}.

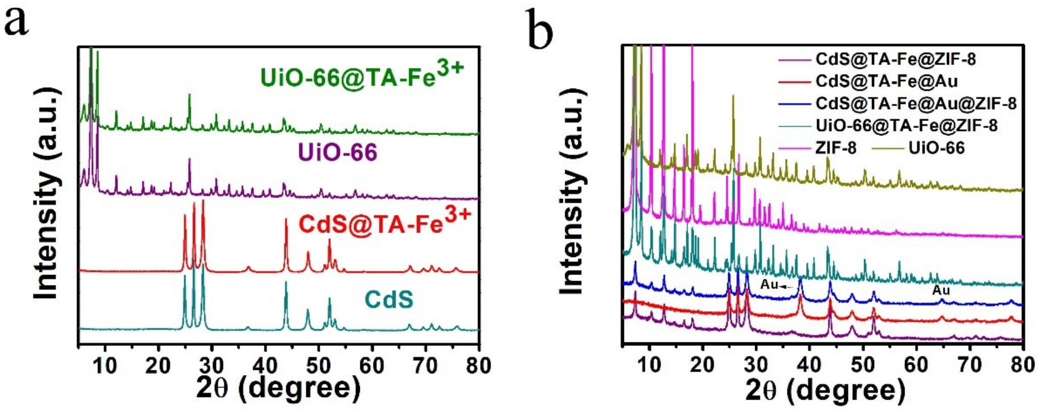

Figure S6. Crystalline structure characterizations of (a) CdS, CdS@TA-Fe^{3+}, UiO-66, and UiO-66@TA-Fe^{3+}, (b) ZIF-8, UiO-66，CdS@TA-Fe^{3+}@Au, CdS@TA-Fe^{3+}@ ZIF-8 , CdS@ TA-Fe^{3+}@Au@ZIF-8 and UiO-66@TA-Fe^{3+}@ZIF-8.

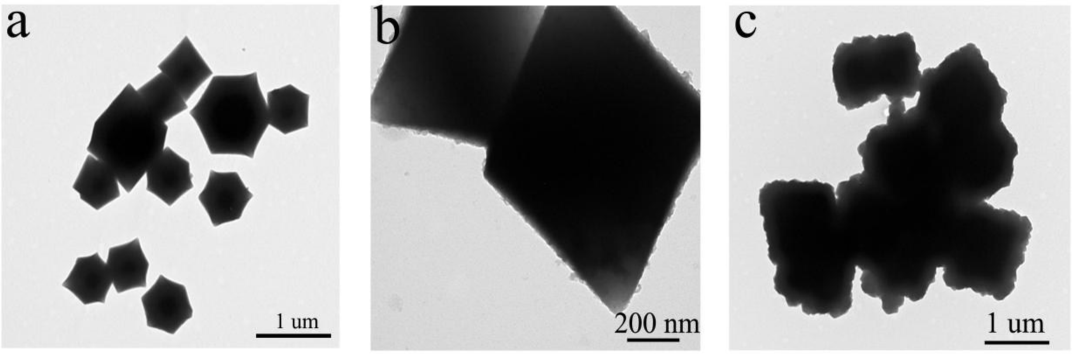

Figure S7. TEM images of (a) UiO-66, (b) UiO-66@TA-Fe^{3+} and (c) UiO-66@TA-Fe^{3+}@ZIF-8.

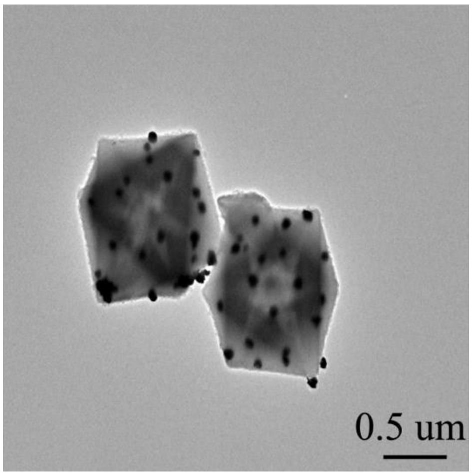

Figure S8. TEM image of UiO-66@TA-Fe^{3+}@Au.

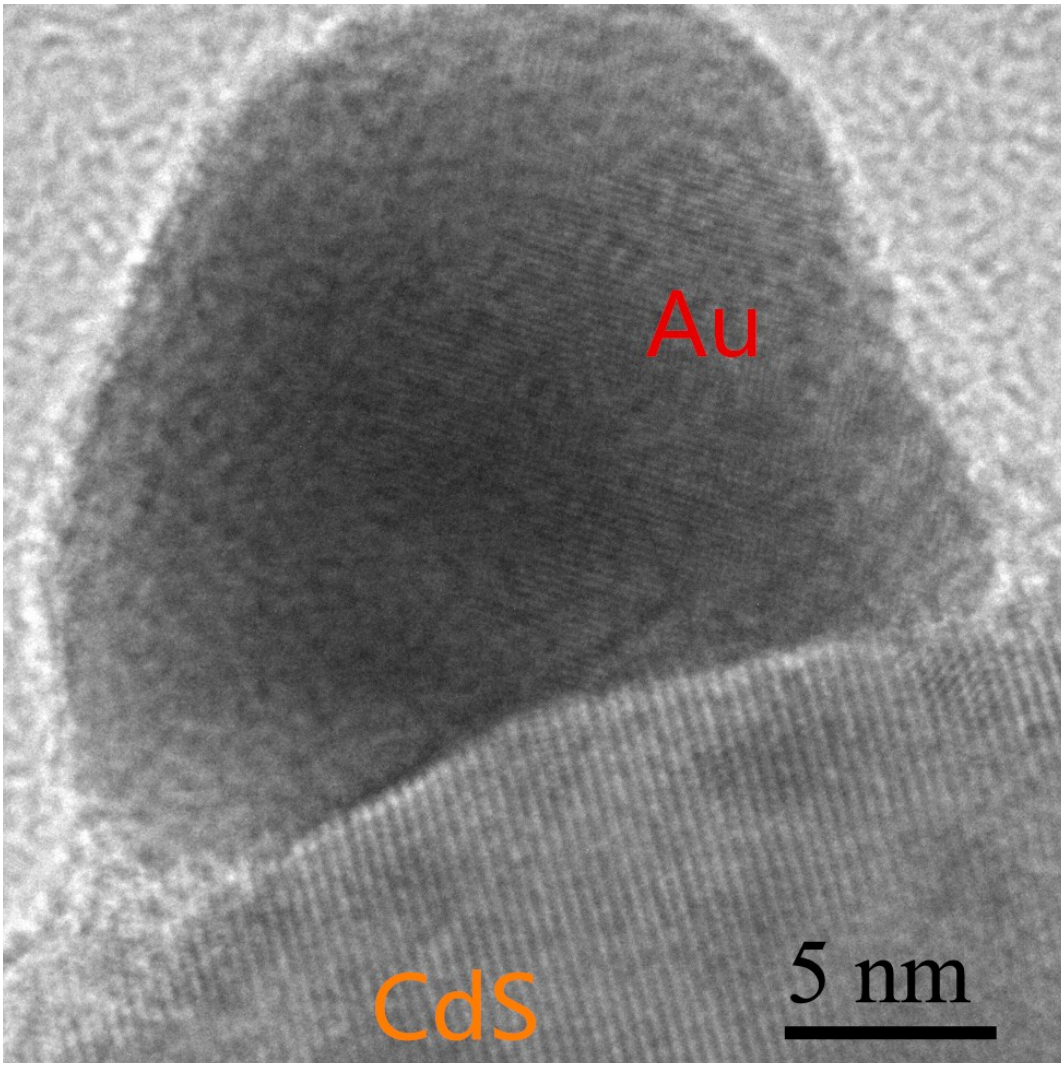

Figure S9. HRTEM image of CdS@TA-Fe^{3+}@Au.

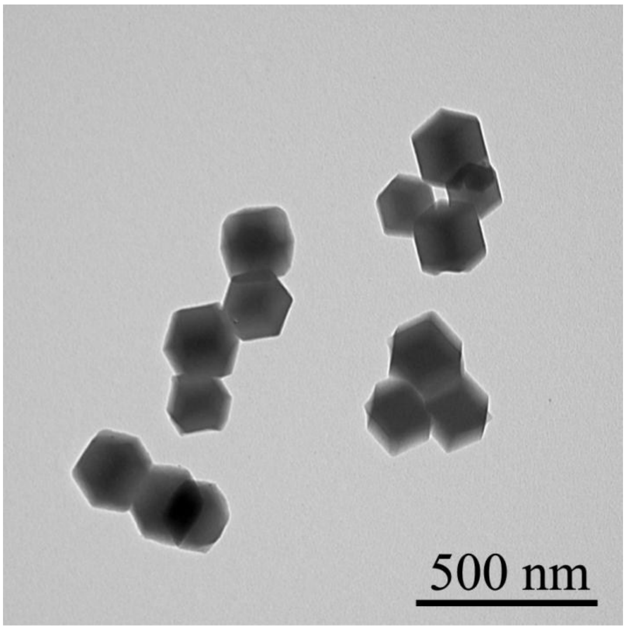

Figure S10. TEM image of ZIF-8.

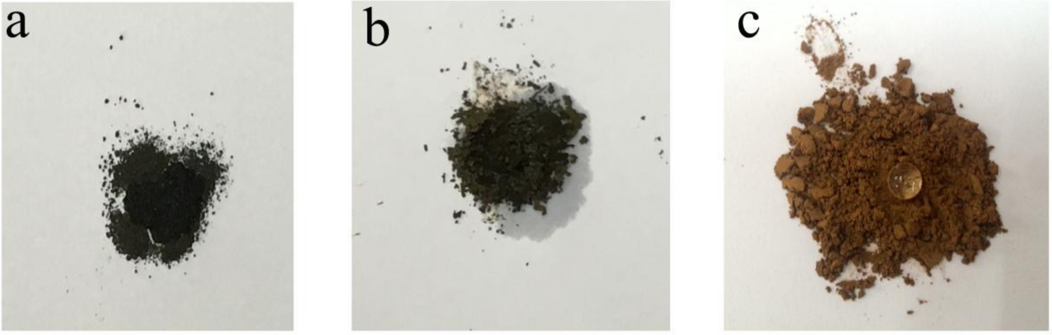

Figure S11. Photographs of a water droplet on (a) Fe_3O_4, (b) Fe_3O_4@TA-Fe^{3+} and (c) Fe_3O_4@TA-Fe^{3+}@ZIF-8.

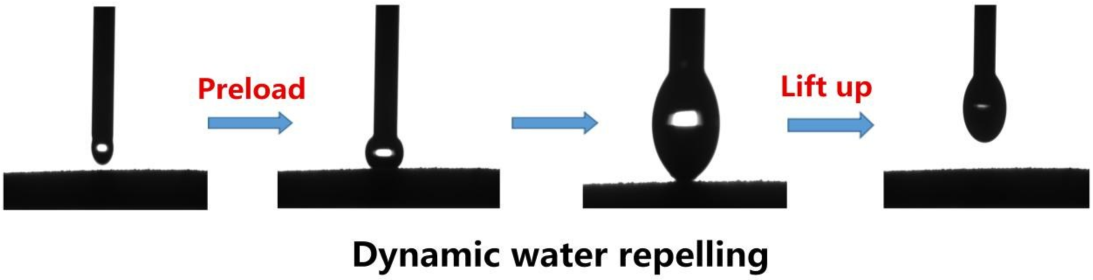

Figure S12. Photographs of dynamic measurement of water adhesion on the surface of Fe_3O_4@TA-Fe^{3+}@ZIF-8 powder, the volume of water droplet was 0.5 μL.

References:

[1] N. G. Bastús, J. Comenge, V. Puntes, *Langmuir* **2011**, 27, 11098-11105.

[2] H. Yuan, C. G. Khoury, H. Hwang, C. M. Wilson, G. A. Grant, T. Vo-Dinh, *Nanotechnology* **2012**, 23, 75102.

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[6] Z. Abbai, E. Shamsaei, X.-Y. Fang, B. Ladewig, H. Wang, *J. Colloid. Interf. Sci.* **2017**, 493, 150-161.