

Supporting information

Facile fabrication of noble metal nanoparticles encapsulated in hollow silica with radial-oriented mesopores: multiple roles of N-lauroylsarcosine sodium surfactant

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Experimental

Synthesis

In a typical synthesis of Au@MSHS, 1.0 mmol N-lauroylsarcosine sodium (Sar-Na) was completely dissolved in 30.0 mL of deionized water under stirring, and 0.5 mL aqueous HAuCl₄ solution with desired concentration was then added to the aqueous solution under vigorous stirring for 1 h at 353 K, and the color of the solution became purple. Next, when the solution was cooled down to the room temperature. Next 2 g 0.1 M HCl was added to the solution under vigorous stirring for 10 min to adjust the pH value of the mixture to 6.0. Then the mixture of 1.50 mL TEOS and 0.10 mL 3-Aminopropyltrimethoxysilane (APMS) was added to the above solution under vigorous stirring. After ten minutes, the mixture was left static at room temperature for 2 h, and then was put in an 353 K oven for another 24 h. The purple product was centrifuged and washed with deionized water and dried at 333 K. The surfactants were removed by calcination at 823 K for 6 h. The obtained sample was denoted as Au@MSHS. The synthesis of Pd@MSHS was similar except that H₂PdCl₄ was used.

Characterization

The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-2500 diffractometer,

with CuK α Radiation at 40 kV and 100 mA. The XRD patterns were collected in the range of 5-80 degree in 2 θ / θ scanning mode with a 0.02 degree step and scanning speed of 12 degree/min. SEM images were obtained with a Shimadzu SS-550 instrument operating at 15 kV. The samples were coated with gold by sputtering before SEM observation. TEM observations were performed on a Philips Tecnai F20 microscope, working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on copper grids. N₂ adsorption measurements were performed on a BELSORP-mini II sorption analyzer. Before measurements, the samples were dried under dry N₂ flow at 350 °C for 5 h. The specific surface areas were calculated according to the standard Brunauer-Emmett-Teller (BET) method using adsorption data in the relative pressure (p/p_0) range from 0.06 to 0.25. The total pore volumes were evaluated by converting the volume adsorbed at p/p_0 of 0.95. The pore size distribution was calculated from the adsorption branch using BJH (Barett-Joyner-Halenda) method. Diffuse reflectance UV-vis spectra were measured on a Shimadzu 2450 spectrometer equipped with an integrating sphere for solid sample, and BaSO₄ was used as the background.

Catalytic reduction of 4-nitrophenol

The reduction of 4-NP by NaBH₄ was chosen as a model reaction to test the catalytic activity of the Au@MSHS nanocatalysts. Aqueous solution of 4-NP (0.25 mL, 0.01 M) and NaBH₄ (5mL 0.1 M) were added to deionized water (40 mL) in a colorimetric tube under magnetic stirring. After adding Au@MSHS catalyst particles (10 mg), the bright yellow solution gradually faded as the reaction proceeded. UV-Vis spectra were recorded at regular interval to monitor the progress of the reaction.

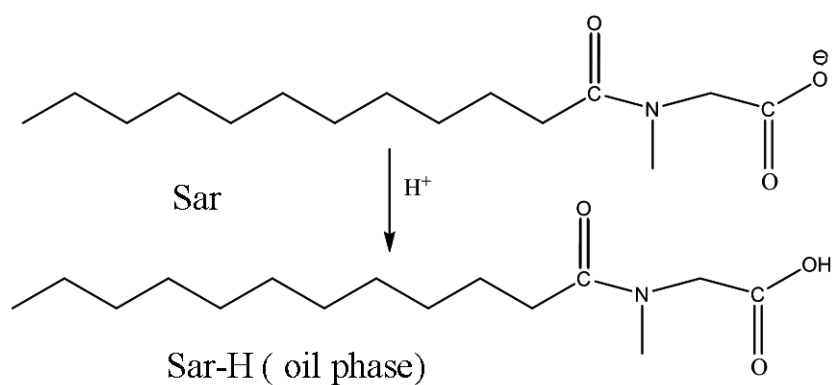


Fig. S1. Molecular Structure of N-lauroylsarcosine (Sar) and Sar-H.

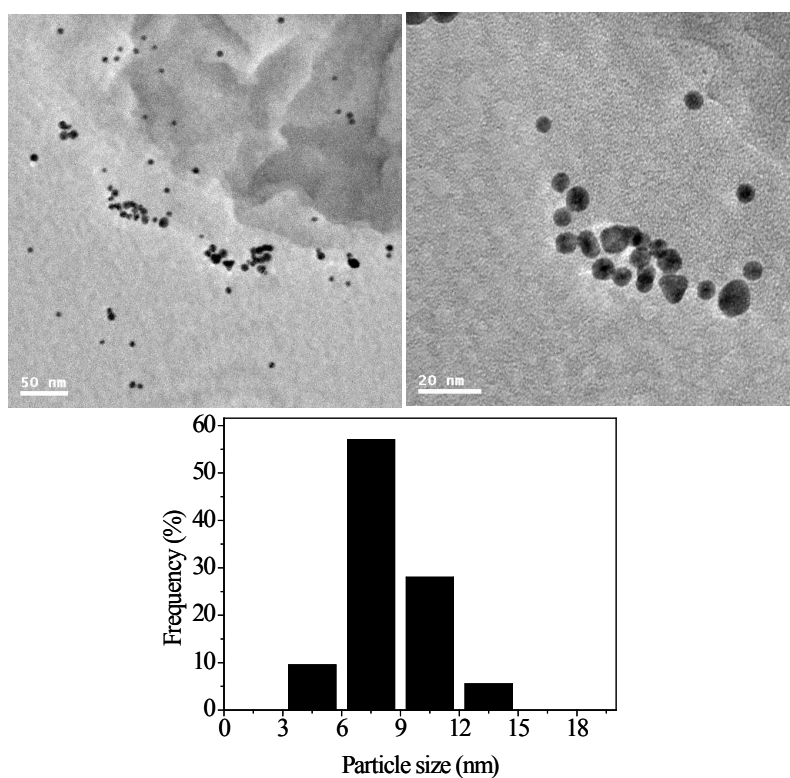


Fig. S2. TEM images and histogram of particle size distribution of Au nanoparticles. The average size was 7.9 nm and the standard deviation of the particle size was calculated to be 2.6 nm.

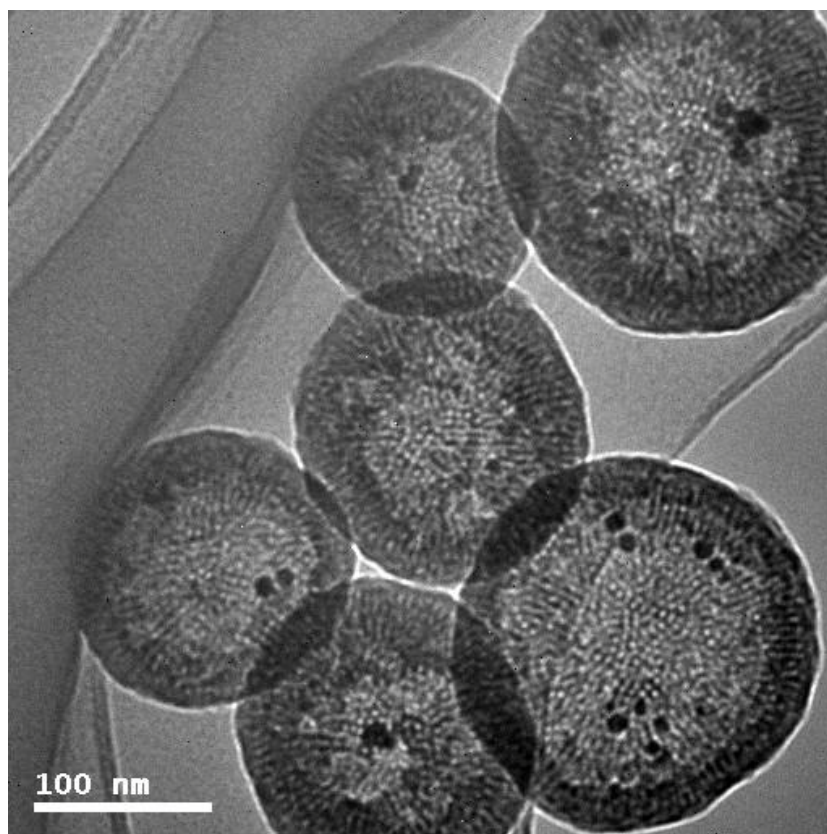


Fig. S3. TEM image of Au@MSHS.

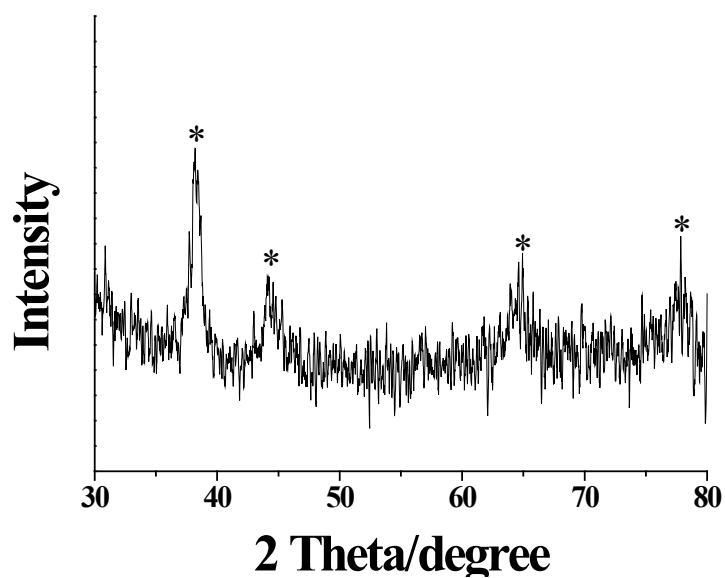


Fig. S4. XRD patterns of Au@MSHS, * indicate Au diffraction peaks (JCPDS No. 4-784).

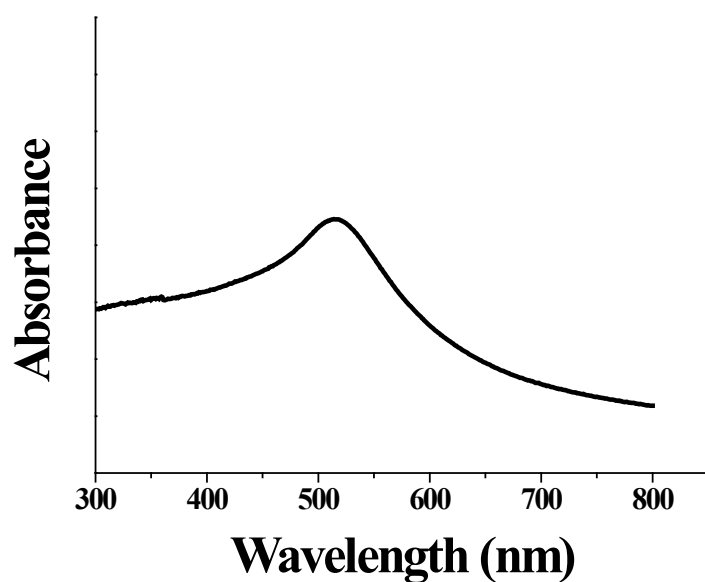


Fig. S5. UV-vis spectrum of Au@MSHS.

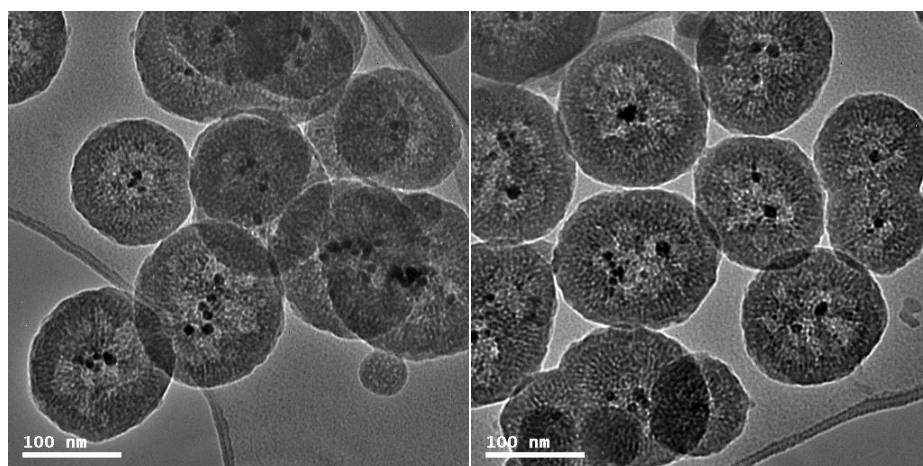


Fig. S6. TEM images of sample synthesized at pH value of 6.9 before addition of APMS/TEOS.

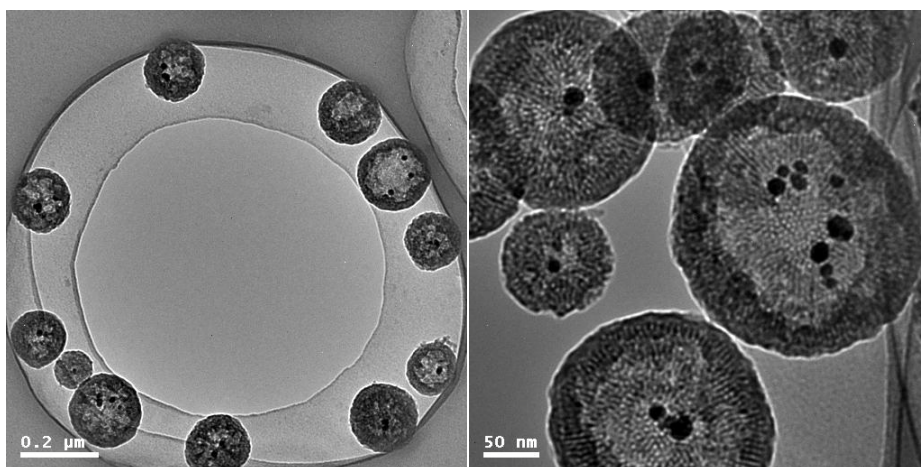


Fig. S7. TEM images of sample synthesized at pH value of 6.4 before addition of APMS/TEOS.

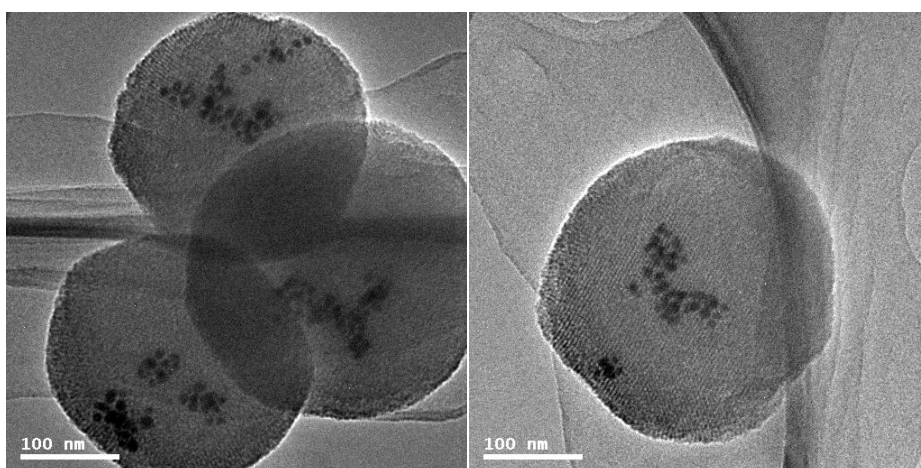


Fig. S8. TEM images of sample synthesized at pH value of 5.3 before addition of APMS/TEOS.

Due to more acid the size of Sar-H oil droplets increased. Meanwhile, at lower pH value the hydrolysis rate of silica precursors increased and this would induce fast penetration of the APMS/TEOS precursors into the whole oil droplets. There was no oil phase left as the core and the solid spheres were formed. The gold nanoparticles were still embedded inside the mesoporous solid spheres.

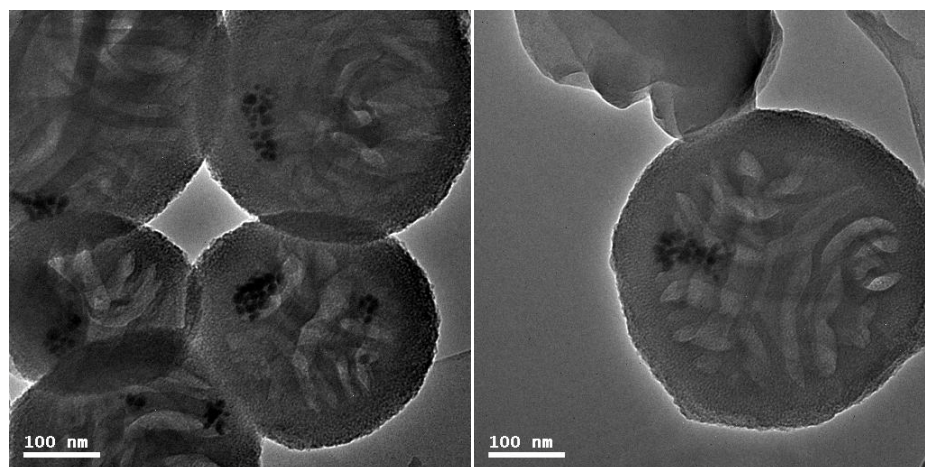


Fig. S9. TEM images of sample synthesized at pH value of 3.8 before addition of APMS/TEOS.

Further increasing of the acid would induce some extra Sar-H oil phase during the co-assembly with APMS/TEOS precursors and would lead to lamellar phase formation.¹

¹. W. Wang, J. Wang, P. Sun, D. Ding, T. Chen, *J. Colloid Interface Sci.*, 2009, **331**, 156.

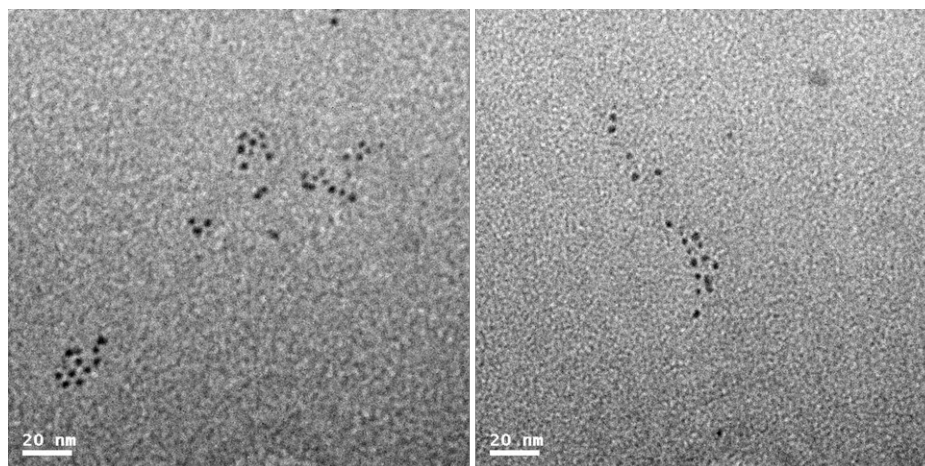


Fig. S10. TEM images of Pd nanoparticles.

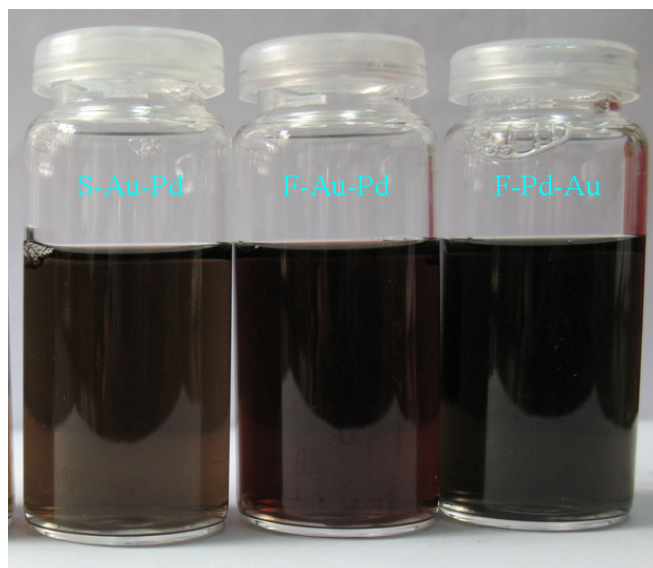


Fig. S11. Photographs of alloy nanoparticles in Sar-solution.

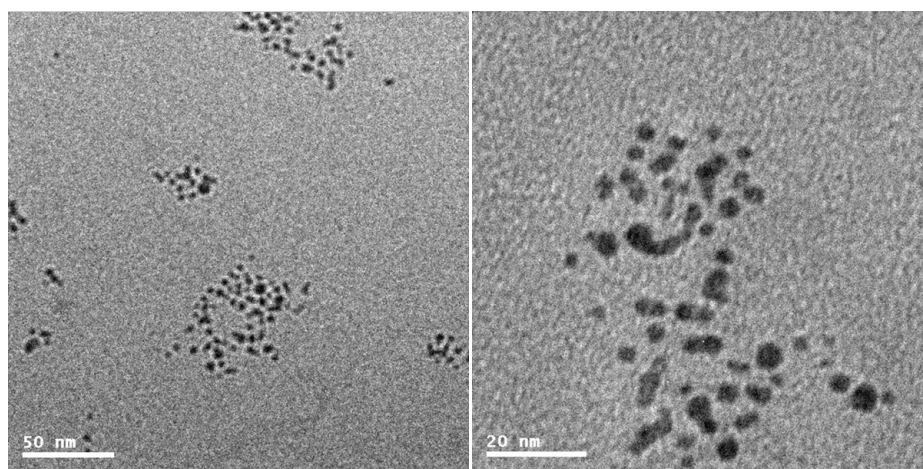


Fig. S12. TEM images of S-Pd-Au nanoparticles

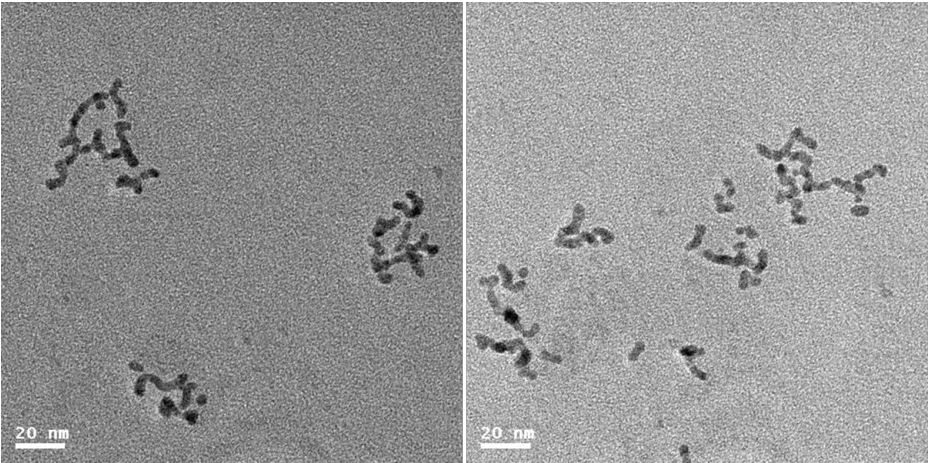


Fig. S13. TEM images of F-Pd-Au nanoparticles

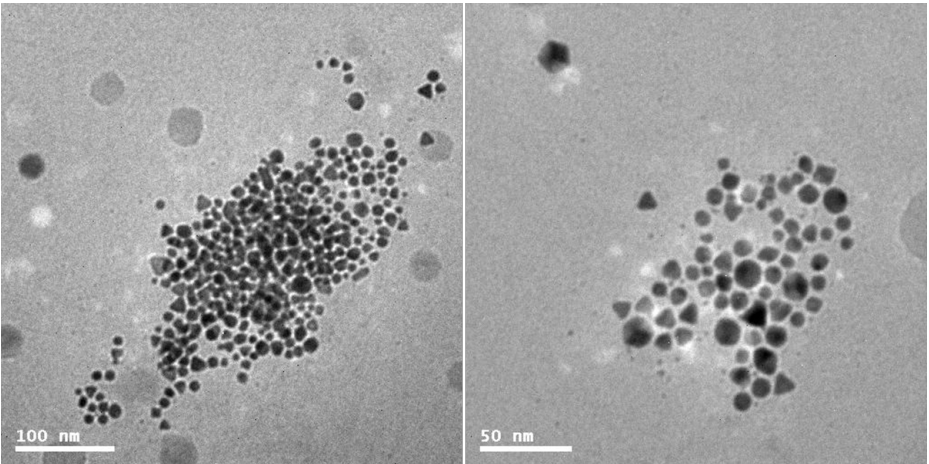


Fig. S14. TEM images of F-Au-Pd nanoparticles

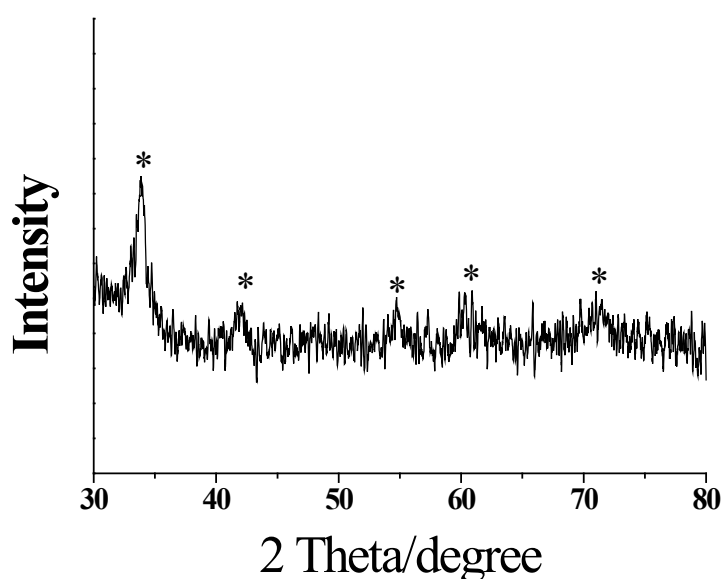


Fig. S15. XRD patterns of Pd@MSHS, * indicate diffraction peaks of PdO (JCPDS No. 6-515).

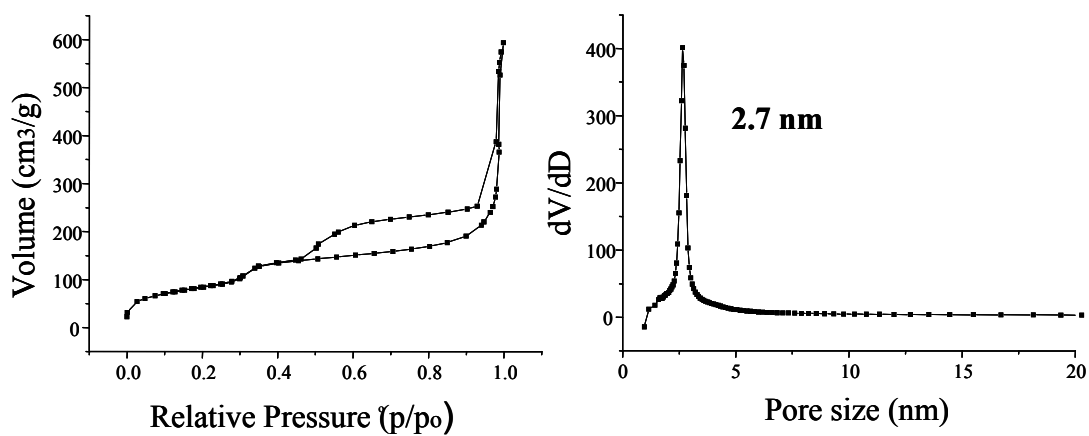


Fig. S16. Nitrogen adsorption-desorption isotherms and the pore size distribution of Pd@MSHS.