Electronic Supplementary Information

Amphiphilic Hollow Porous Shells Encapsulated Au@Pd Bimetal Nanoparticles for Aerobic Oxidation of Alcohols in Water

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Experimental Section

Chemicals. Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia ($NH_3 \cdot H_2O$, 28%), Sodium tetrachloropalladate(II) (Na_2PdCl_4, 98%) and Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.7%) were purchased from Sinopharm Chemical Reagent Co.Ltd. 1,4-bis(triethoxysilyl)benzene (BTEB, 96%) and L-Ascorbic Acid (99.9%) were obtained from Sigma–Aldrich. Cetyltrimethylammonium bromide (CTAB, 99.0 %) was obtained from Huishi Biochemical Reagent Company of China. All alcohols were purchased from Aladdin. All chemicals were used as received without any further purification.

Synthesis of monodisperse PVP-modified Au nanoparticles

Monodisperse Au nanoparticles were prepared according to the previous publications.[1,2] In a typical synthesis, 18.0 mg of $HAuCl_4 \cdot 3H_2O$ was dissolved in 30 mL water and heated to boil under vigorous stirring. 2.0 mL (3.0 wt%) of sodium citrate aqueous solution was injected quickly into above mixture and then refluxed for 30 min. After the solution was cooled down to room temperature, an aqueous solution of PVP10 (12.8 g/L, 0.235 mL) was added to the colloidal gold solution to modify the surface of gold nanoparticles to facilitate silica coating. The solution was stirred for 24 h at room temperature. The PVP-modified gold nanoparticles were collected by centrifugation and re-dispersed in 5.0 mL of water.

Synthesis of core-shell structured Au@SiO$_2$

For silica coating, the above PVP-modified Au nanoparticles aqueous solution was added into a mixture of ethanol (30 mL) and ammonium (1.0 mL). Then 1.72 mL of TEOS was added under vigorous stirring stirred for another 2 h. The resultants were collected by centrifuging and cleaned three times with water and ethanol. The obtained red precipitate was re-dispersed in 30 mL of ethanol.

Synthesis of yolk-shell structured Au@Ph-PMO

In a typical synthesis, 10 mL of above ethanol solution containing 100 mg of Au@SiO$_2$ was added into 22 mL of water, and the mixed solution was homogenized for 20 min to form a uniform dispersion by ultrasonication. After the addition of 0.12 g of CTAB and 2.0 mL of ammonium aqueous solution (25–28%), the resultant mixture was further stirred at room temperature for 30 min. And then, 0.27 mL of organosilane BTEB was slowly dropwise added. After completely hydrolysis of BTEB, the as-obtained mixture was transferred to a stainless steel autoclave with a Teflon container and hydrothermally treated at 100 ℃ for 24 h. After cooling down to room temperature, the red precipitate was collected by centrifugation and re-dispersed in 40 mL of water containing 2.272g of Na$_2$CO$_3$. And then, the obtained aqueous solution was treated at 80 ℃ for 3 h for presenting yolk-shell structured Au@Ph-PMO. Finally, the surfactant CTAB was removal by refluxing 0.5 g of as-made material in 100 mL of ethanol containing 1.5 g of concentrated HCl aqueous solution for 6 h.

Synthesis of catalytic active amphiphilic nanoreactor Au@Pd@Ph-PMO

The catalytically active amphiphilic nanoreactor Au@Pd@Ph-PMO was prepared through introducing palladium into Au@Ph-PMO via a simple seed growth process. In a typical synthesis, 200 mg of Au@Ph-PMO was dispersed in 40 mL of water containing 700 mg of AA by ultrasonication. 2.25 mL of Na_2PdCl_4 aqueous solution (35.5 mmol/L) was then added to the mixed suspension and stirred at room temperature for 8 h. The resulting solid Au@Pd@Ph-PMO were collected by centrifugation and washed with deionized water and then dried at room temperature under vacuum overnight.

Synthesis of hydrophilic nanoreactor Au@Pd@SiO$_2$

Firstly, the yolk-shell structured Au@SiO$_2$ was obtained after calcination of as-made yolk-shell structured Au@Ph-PMOs at 550 ℃ for 6 hours. And then the same seed growth process led to the formation of hydrophilic nanoreactor Au@Pd@SiO$_2$ (Fig.S10).

Synthesis of hydrophobic nanoreactor Au@Pd@C

Hydrophobic nanoreactor Au@Pd@C was prepared according to the previous publications.[1,2]

Synthesis of conventional hydrophilic catalyst Pd-MCM-41

The synthesis of conventional hydrophilic Pd-based catalyst Pd-MCM-41 was according to a literature method.[3] The Pd-MCM-41 catalyst was made through an immersion and reduction method as follows: 40 mg of MCM-41 material was immersed into 10 mL of ethanol solution containing 0.45 mL of Na_2PdCl_4 aqueous solution (35.5 mmol/L). After ultrasonic treatment for 20 min, the solution was stirred for 12 h at room temperature. Ethanol was then removed by rotation evaporation at room temperature. The obtained solids were reduced using $NaBH_4$ solution, leading to the formation of Pd-MCM-41 catalyst.

Synthesis of amphiphilic Ph-PMO hollow shell supported Pd nanoparticle catalyst (Pd@Ph-PMO)

The amphiphilic Ph-PMO hollow shell was prepared by replacing Au@SiO$_2$ nanosphere with SiO$_2$ nanosphere. The Pd@Ph-PMO catalyst was made through an identical immersion and reduction method with Pd-MCM-41 catalyst.

Materials Characterization

Scanning electron microscope (SEM) images was performed on a JEOL JSM-6700F field-emission electron microscope. Transmission electron microscope (TEM) images were obtained on an FEI Tecnai G^2 F20s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200kV. Powder XRD patterns were obtained by using a Rigaku 2550 diffractometer with Cu Ka radiation (λ=1.5418 °A). N_2 adsorption-desorption isotherms were obtained at -196 ℃ on a Micromeritics ASAP 2010 sorptometer. Samples were degassed at 120 ℃ for a minimum of 12 h prior to analysis. Brunauer–Emmett–Teller (BET) surface areas were calculated from the linear part of the BET plot. Pore size distribution was estimated from the adsorption branch of the isotherm by the BJH method. The total pore volume was estimated from the adsorbed amount at P/P_0 = 0.995. ^{29}Si CP-MAS NMR measurements were performed on a Bruker AVANCE III 400 WB spectrometer. The spinning rate was 12 kHz and a total number of 20 000 scans were recorded with 6 s recycle delay for each sample. ^{13}C-MAS NMR measurements were performed on Varian Infinity Plus 400 NMR spectrometer. The spinning rate was 4 kHz and a total number of 800 scans were recorded with 4 s recycle delay for each sample.

Absorption of Hydrophobic 4-Methoxybenzyl Alcohol in Water

62 μL of 4-methoxybenzyl alcohol was added to 4 mL of water containing 20 mg of Au@Ph-PMO or MCM-41. The absorption was carried out in a sealed glass vial by stirring the mixture for 3 h on a magnetic stirring apparatus. After sorption, the sorbent Au@Ph-PMO was collected by centrifugation, and the aqueous phase was extracted by CH_2Cl_2 for 3 times. The amount of 4-methoxybenzyl alcohol in water was identified by GC-MS, and dodecane was used as an internal standard.

Catalytic Tests

In a typical oxidation, 0.5 mmol of alcohol, supported palladium catalysts (Pd loading 1.5 mol%), 0.5 mmol of K_2CO_3 (1 equi) and 4.0 mL of H_2O were mixed in a 25 mL round flask equipped with a reflux condenser and a magnetic stirrer. The reaction was performed at 80 ℃ in an oil bath with magnetic stirring (stirring rate: 1000 r.p.m.) for a given time. When the reaction was finished, the reaction mixture was acidized with 36% HCl and extracted by CH_2Cl_2 for 3 times. The liquid phase was subsequently analyzed by gas chromatography-mass spectrum Shimadzu GCMS-QP2010 Plus with a flame ionization detector (FID), and dodecane was used as an internal standard. The column was GsBP-1ms (30 m); the initial temperature was 50 ℃, the heating rate was 5～30 ℃/min, and the final temperature was 280 ℃, the temperature of FID detector was 250 ℃.

For the recycling test, the catalyst was collected by centrifugation after reaction. The residual catalyst was washed with water and ethanol for several times and used directly for the next catalytic reaction.

Supplementary Figures and Legends

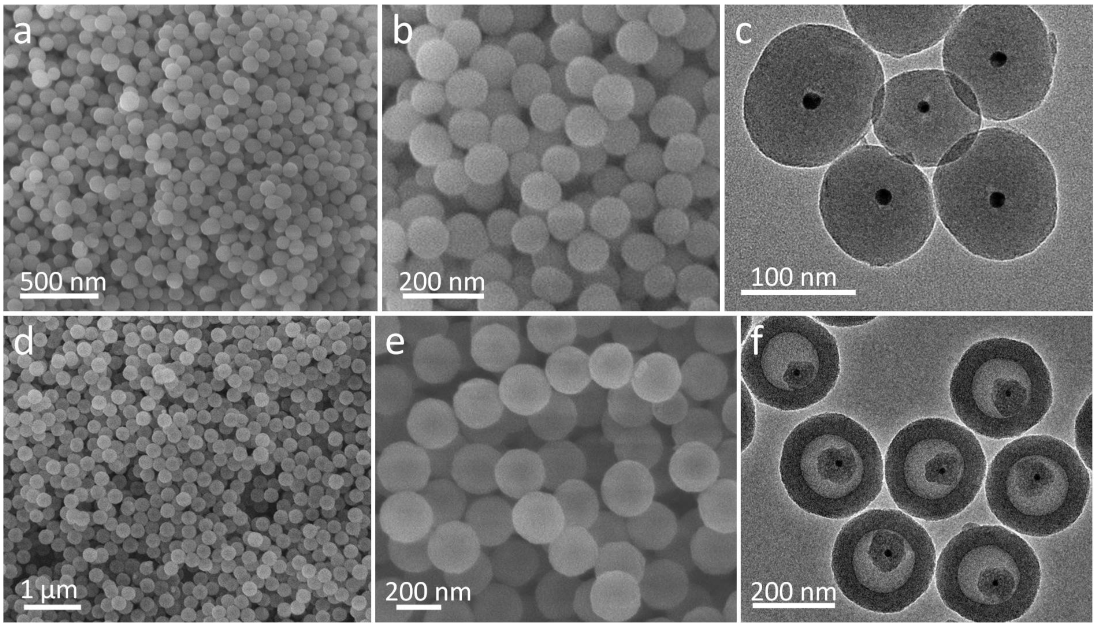


Figure S1. SEM and TEM images of core-shell structured $Au@SiO_2$ (a, b, c) and yolk-shell structured $Au@SiO_2@Ph\text{-}PMO$ (d, e, f).

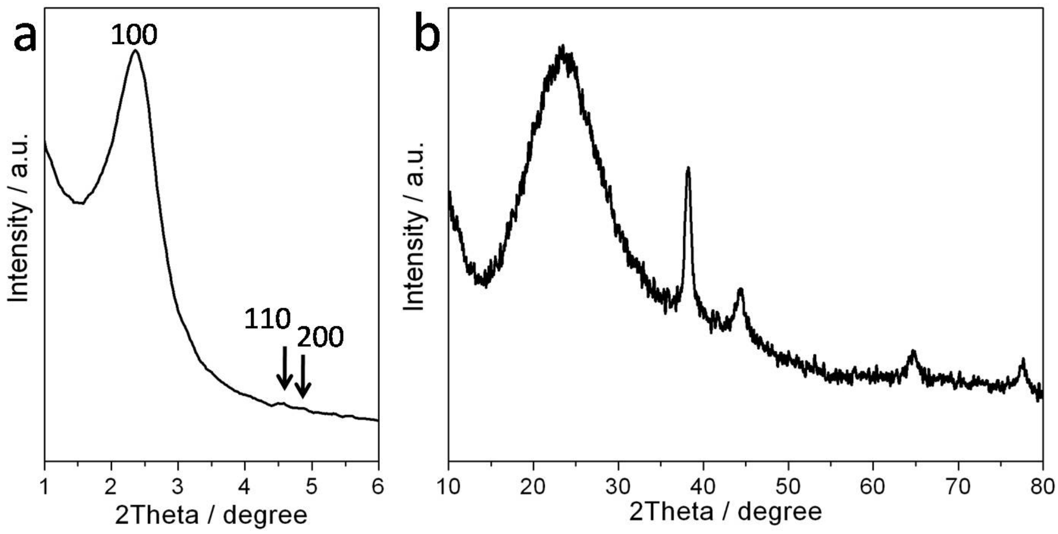


Figure S2. Small- and wide-angle XRD patterns of yolk-shell structured Au@Ph-PMO. The diffraction peaks at 2θ values of approximately 38.2, 44.3, 64.7 and 77.6 degrees in the wide-angle XRD pattern (b) are attributed to the Au nanoparticles.

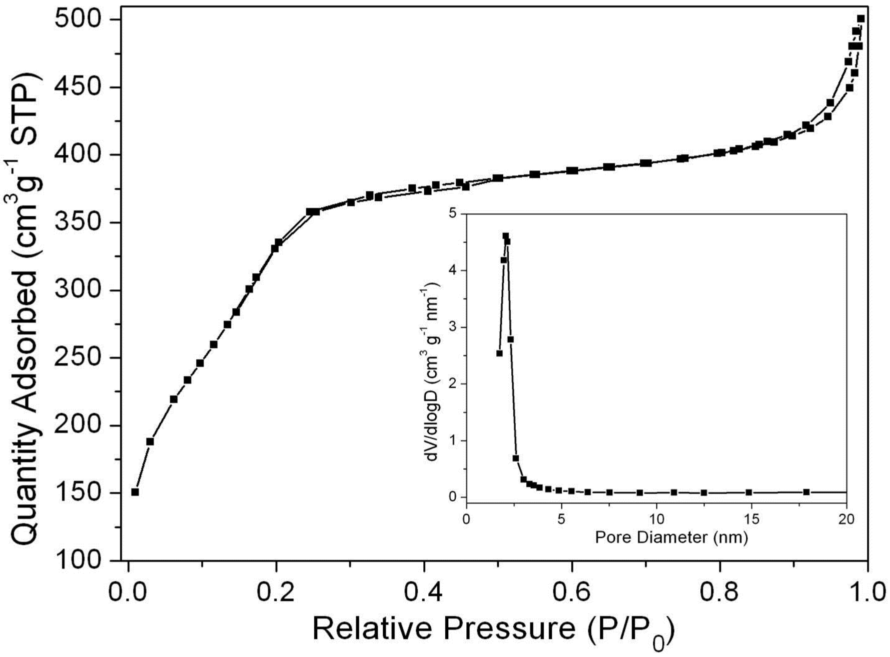
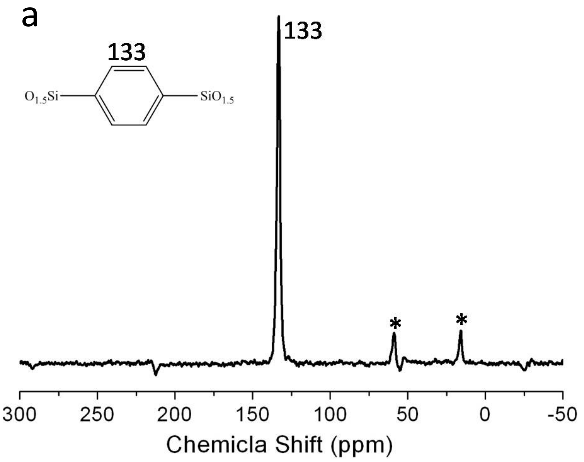


Figure S3. Nitrogen sorption isotherm and BJH pore size distribution curve (the inset) of yolk-shell structured Au@Ph-PMO.



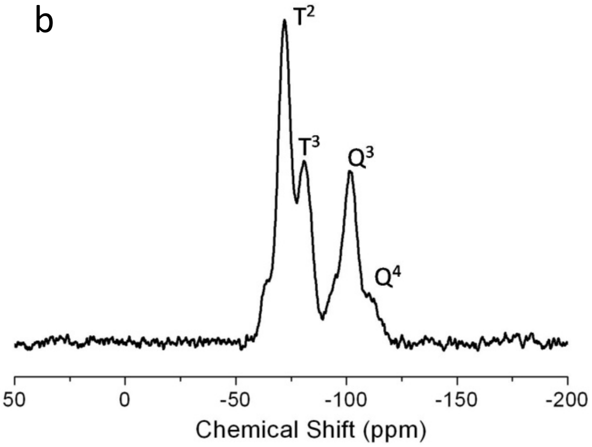


Figure S4. Solid-state ^{13}C NMR (a) and ^{29}Si NMR (b) spectroscopy of yolk-shell structured Au@Ph-PMO.

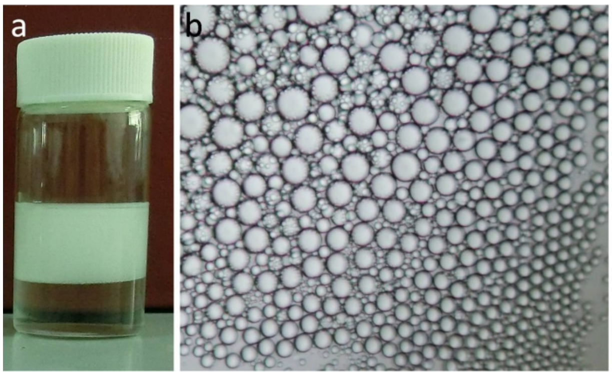


Figure S5. (a) Digital photograph of water in oil emulsion in toluene-water system obtained using surfactant CTAB as emulsifier. (b) Microphotograph of the water in oil emulsion in (a).

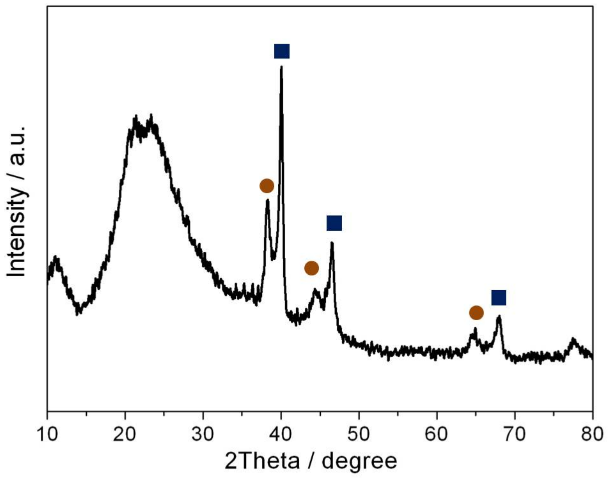


Figure S6. Wide-angle XRD pattern of amphiphilic nanoreactor Au@Pd@Ph-PMO. The diffraction peaks at 2θ values of approximately 40.0, 46.5 and 67.9 degrees (directed by ■) in the wide-angle XRD pattern are attributed to the crystalline Pd nanoparticles.

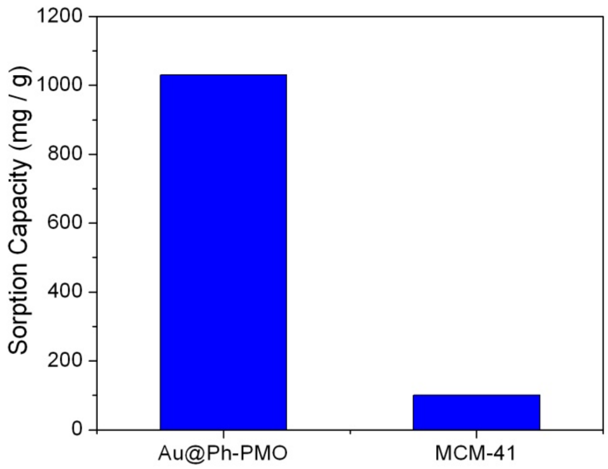


Figure S7. The absorbencies of amphiphilic Au@Ph-PMO and hydrophilic MCM-41 for 4-methoxybenzyl alcohol in water.

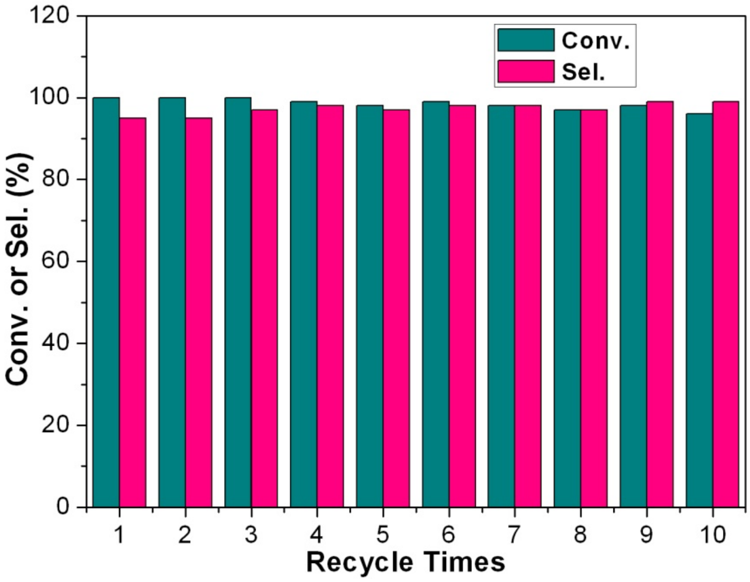


Figure S8. Recycling runs for the aerobic oxidation of 4-methoxybenzyl alcohol by Au@Pd@Ph-PMO catalyst. Reaction condition: 4-methoxybenzyl alcohol (0.5 mmol), K_2CO_3 (0.5 mmol, 1 equi), 4 mL of H_2O, catalyst (Pd 1.5 mol%), open air, 5 h.

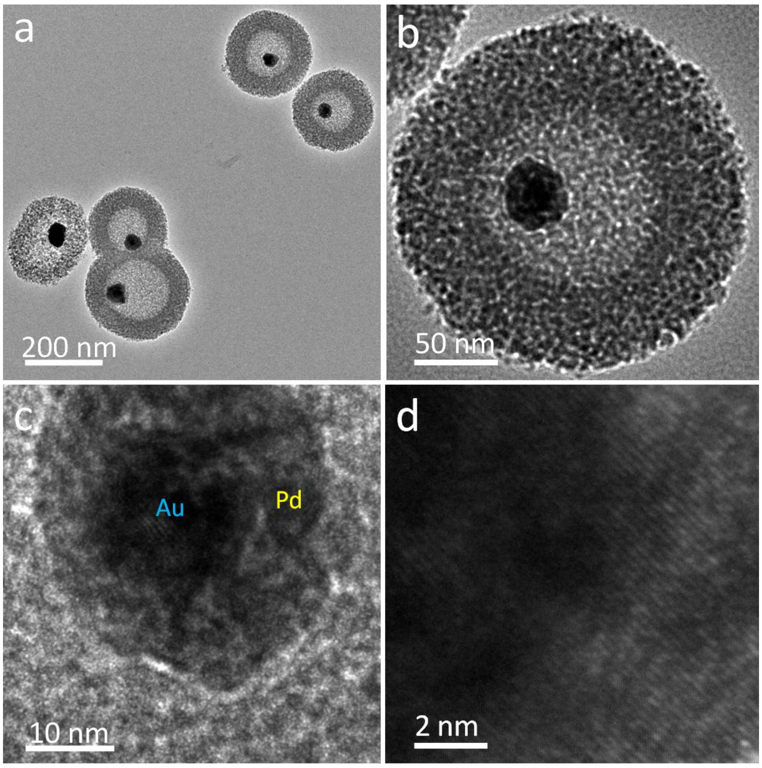


Figure S9. Low-magnification and high-magnification TEM images of amphiphilic nanoreactor Au@Pd@Ph-PMO recovered after successive recycling ten times for oxidation of 4-methoxybenzyl alcohol.

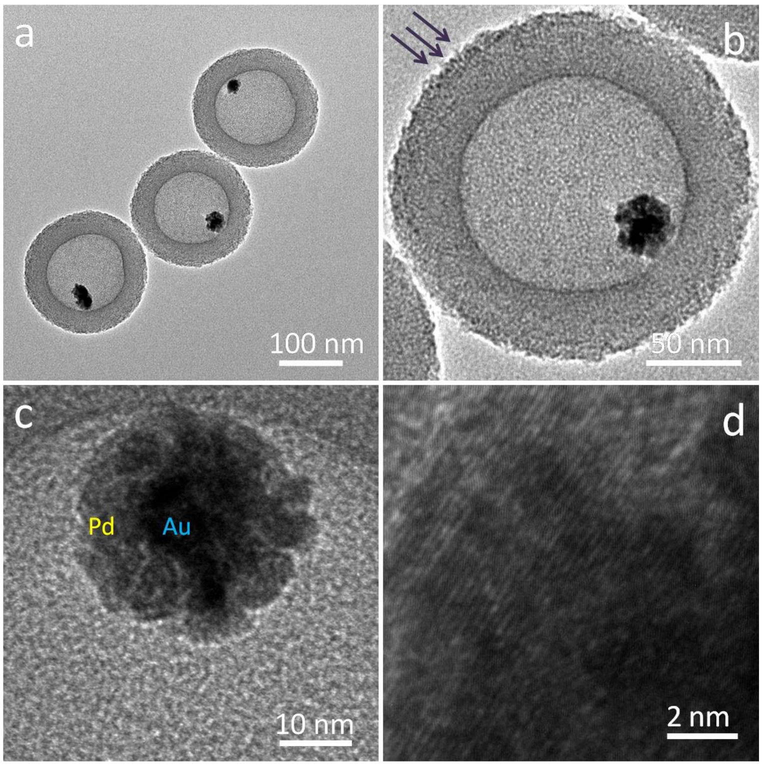


Figure S10. Low-magnification and high-magnification TEM images of hydrophilic nanoreactor Au@Pd@SiO_2. These images indicate that this hydrophilic nanoreactor Au@Pd@SiO_2 has the identical structural property including the unique yolk-shell nanostructure, the oriented mesochannels in external shell and the catalytically active Au@Pd bimetal structure with the amphiphilic nanoreactor Au@Pd@Ph-PMO.

References

(1) X. Fang, Z. Liu, M. Hsieh, M. Chen, P. Liu, C. Chen, N. Zheng, *ACS Nano* 2012, **6**, 4434.

(2) B. Y. Guan, X. Wang, Y. Xiao, Y. L. Liu, Q. S. Huo, *Nanoscale* 2013, **5**, 2469.

(3) Y. Yang, M. Ambrogi, H. Kirmse, Y. Men, M. Antonietti, J. Yuan, *Chem. Mater.* 2015, **27,** 127.