

Supporting Information

Macroporous TiO₂ Encapsulated Au@Pd Bimetal Nanoparticles for Photocatalytic Oxidation of Alcohols in Water under Visible-light

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Experimental Section

Chemicals. Tetraethylorthosilicate (TEOS, 98%), aqueous ammonia (NH₃·H₂O, 28%), titanium tetrakisobutanolate (TBOT, 98%), gold (III) chloride trihydrate (HAuCl₄·3H₂O, 99.7%) and sodium citrate (99%) were purchased from Sinopharm Chemical Reagent Co.Ltd. Sodium tetrachloropalladate(II) (Na₂PdCl₄, 98%) and all alcohols were purchased from Aladdin. L-Ascorbic Acid (AA, 99.9%) was obtained from Sigma–Aldrich. All chemicals were used as received without any further purification.

Synthesis of core-shell structured Au@SiO₂

Core-shell structured Au@SiO₂ was prepared according to a previous publication.¹ In a typical synthesis, 18.0 mg of HAuCl₄·3H₂O 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. 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 centrifugation and cleaned three times with water and ethanol. The obtained red precipitate was re-dispersed in 30 mL of ethanol.

Synthesis of Au@TiO₂ scaffold

In a typical synthesis, 15 mL of above ethanol solution containing 150 mg of Au@SiO₂ was added into 85 mL of ethanol, and the mixed solution was homogenized for 15 min to form a uniform dispersion by ultrasonication. After the addition of 0.4 mL of ammonium aqueous solution (25–28%), the resultant mixture was stirred at 45 °C for 30 min. And then, 1.0 mL of precursor TBOT was slowly dropwise added under stirring. The obtained mixture was further stirred at 45 °C for 24 h. After cooling down to room temperature, the red precipitate Au@SiO₂@TiO₂ was collected by centrifugation and cleaned three times with water and ethanol.

In order to obtain yolk/shell structured Au@TiO₂, the middle SiO₂ layer was selectively removed using 0.05 M NaOH aqueous. Typically, as-obtained Au@SiO₂@TiO₂ was added into 38 mL of H₂O, and the mixture was homogenized for 15 min to form a uniform dispersion by ultrasonication. After addition of 2 mL of 1 M NaOH aqueous, the mixture was stirred at 20 °C for 5 h. The red resultants were collected by centrifugation and cleaned several times with 0.1 M HCl aqueous and water. And then a process of calcination at 500 °C for 2 hours under air atmosphere was carried out to obtain crystalline Au@TiO₂ (anatase) scaffold.

Synthesis of catalytic active photocatalyst Au@Pd@TiO₂

The visible-light driven photocatalyst Au@Pd@TiO₂ was prepared through introducing palladium into Au@TiO₂ scaffold via a simple seed growth process.² In a typical

synthesis, 200 mg of Au@TiO₂ was dispersed in 40 mL of water containing 700 mg of AA by ultrasonication. 2.25 mL of Na₂PdCl₄ 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@TiO₂ were collected by centrifugation and washed with deionized water and then dried at room temperature under vacuum overnight.

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 G² 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 ($\lambda=1.5418$ °A). The optical absorption spectra of the samples were measured on a UV-Vis spectrophotometer (U-4100) detecting absorption over the range of 200-800 nm.

Catalytic Tests

In a typical oxidation, 0.5 mmol of alcohol, supported palladium catalysts (Pd loading 1.5 mol%), 0.5 mmol of K₂CO₃ (1 equi) and 4.0 mL of H₂O were mixed in a 25 mL round flask equipped with a reflux condenser and a magnetic stirrer. The reaction was performed at 40 °C in an oil bath with magnetic stirring (stirring rate: 1000 r.p.m.) under visible-light irradiation for a given time. A 300 W Xe lamp with a UV cutoff filter (\geq center wavelength 420 nm) was served as the visible-light source to trigger the photocatalytic reaction. When the reaction was finished, the reaction mixture was acidized with 36% HCl and extracted by CH₂Cl₂ 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°C, the heating rate was 5~30°C/min, and the final temperature was 280 °C, the temperature of FID detector was

250°C.

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.

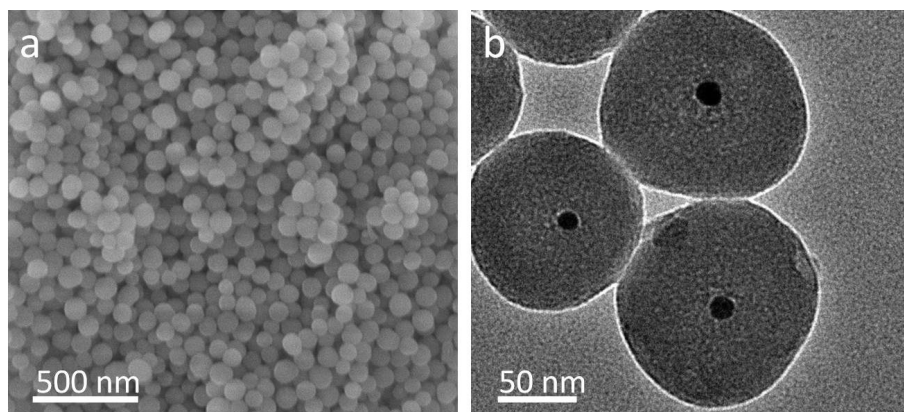


Figure S1. SEM (a) and TEM images of core/shell structured Au@SiO₂ nanospheres with a diameter of 130 nm.

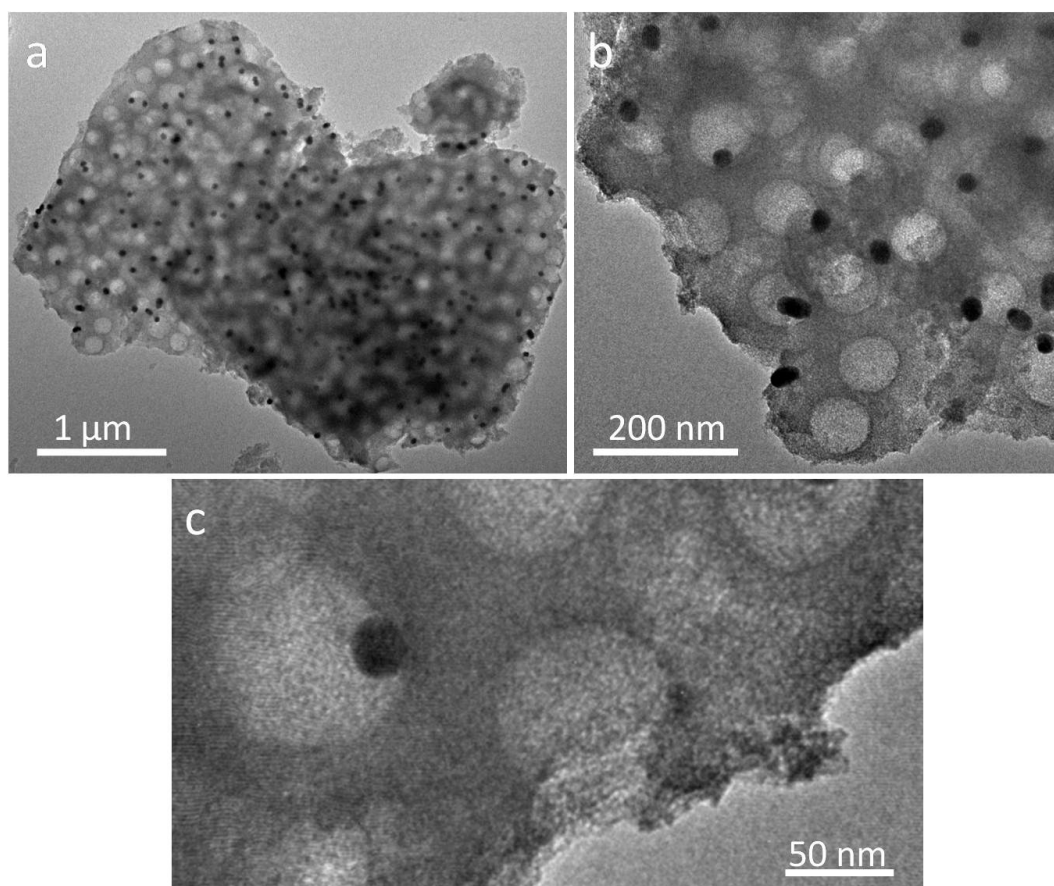


Figure S2. TEM images of macroporous Au@TiO₂ scaffold with amorphous frameworks. From the high-magnification TEM image in Fig.S2c, the amorphous framework of TiO₂ could be clearly

identified.

References

- (1) H. B. Zou, R. W. Wang, X. X. Li, X. Wang, S. J. Zeng, S. Ding, L. Li, Z. T. Zhang and S. L. Qiu, *J. Mater. Chem. A*, 2014, **2**, 12403-12412.
- (2) H. B. Zou, R. W. Wang, J. Y. Dai, Y. Wang, X. Wang, Z. T. Zhang and S. L. Qiu, *Chem. Commun.*, 2015, **51**, 14601-14604.