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Supporting Information

Mesoporous Anatase TiO_2 Nanocups with Plasmonic Metal Decoration for Highly Active Visible-light Photocatalysis

Jianwei Lu, Peng Zhang, Ang Li, Fengli Su, Tuo Wang, Yuan Liu, and Jinlong Gong*

Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

*Corresponding author: jlgong@tju.edu.cn

Preparation of TiO_2 nanocup photocatalysts: Tetraethyl orthosilicate (TEOS, 28%,Tianjin Chemical Reagent No 1 Plant, 0.96 mL), deionized water (4.3 mL), dehydrated ethanol (99.8%, Tianjin Guangfu Fine Chemical Institute, 23 mL) and ammonia solution (26%, Tianjin Guangfu Fine Chemical Institute, 0.62 mL) were mixed and stirred for 4 h at room temperature. Then the precipitated silica nanoparticles were separated from the mixture by centrifugation and washed with ethanol several times followed by re-dispersion in 5 mL of ethanol. The products were dispersed in a mixture of hydroxypropyl cellulose (HPC, Tokyo Chemical Industry Co., Ltd, 0.1 g), ethanol (20 mL), and deionized water (0.1 mL). Stirring for 40 min, titanium tert-butoxide (TBOT, 98%, Tianjin Chemical Reagent No 1 Plant, 1 mL) dispersed in 5 mL ethanol was injected into the mixture at a rate of 0.5 $mL \cdot min^{-1}$. After injection, the temperature was increased to 85 ºC and kept stirring at 900 rpm under refluxing condition for 100 min. The final product was isolated using centrifugation, washed with ethanol, and kept in 5 mL of ethanol to form $SiO_2@TiO_2$ nanocomposites. The $SiO_2@TiO_2$ was calcined in air at 500 ºC for 2 h to remove all organic compounds and crystallize the amorphous TiO_2 (2 ºC/min). Then the calcined samples were dispersed in 20 mL water under sonication and heated to the desired temperature (50 ºC) and then aqueous NaOH solution (2.5 M, Tianjin Guangfu Fine Chemical Institute, 1 mL) was added. When it was heated to 70 ºC, adding another aqueous NaOH solution (2.5 M, 1 ml) for 6 h to remove the SiO_2 layers and produce TiO_2 nanocup.

Preparation of Au-TiO_2 photocatalysts: TiO_2 nanocup photocatalyst (0.1 g) and sodium citrate (1%, Tianjin Chemical Reagent, 5 ml) was dispersed into 50 ml $HAuCl_4 \cdot 3H_2O$ aqueous solution (4×10^{-4} M) under sonication and then heated to 95 ºC. After 5 min, the mixture became burgundy and continued to heat for 15 min with vigorous stirring. The same procedures are operated for TiO_2 HSs and P25. Finally, the product was isolated using centrifugation method, washed with deionized water and dried for 10h at 100 ºC

Photocatalytic Activities Measurements: Photocatalytic activity of each sample was evaluated by photodegradation of methylene blue (MB, 98%, Tianjin Damao Chemical Co., Ltd) dyes. The photocatalyst (50 mg) was first added into a 100 mL quartz photoreactor containing 100 mL of 12 m mol L^{-1} MB solution. Before irradiation under a visible light source ($780\ nm \geq \lambda \geq 400\ nm$), the mixture was ultrasonicated for 2 min and magnetically stirred for 30 min in the dark in order to ensure good dispersion of the photocatalysts in solution and reached the adsorption-desorption equilibrium between, MB molecules and the surface of the photocatalysts. The reaction was kept and cooled with flowing water in a quartz cylindrical jacket around the lamp, and ambient temperature was maintained during the photocatalytic reaction. At the given time intervals (30 min/time), 2 ml analytical suspensions were sampled from the mixture solution and immediately centrifuged at 5000 rpm for 10 min to purified the samples. The treated sample is obtained with a pipette (1 ml) to analyze the concentration of solution. The concentration of the filtrate was analyzed by checking the by recording the maximum absorption peak (664 nm for MB) using a UV-vis spectrophotometer.

Characterization: BET surface area and pore structure of the catalysts were measured using a Micromeritics Tristar3000 analyzer by nitrogen adsorption at 77 K. The specific surface areas were calculated from the isotherms using the BET method, and the pore distribution and the cumulative volumes of pores were obtained by the BJH method from the desorption branches of the adsorption isotherms. X-ray diffraction patterns were recorded with a Bruker D8 Focus operating at 40 kV and 40 mA equipped with a nickel-filtered Cu Kα radiation (λ = 1.54056 Å) and operating in a 2θ range of 10 – 85° (and 5 – 65º) at a scanning rate of 0.02°/step and 0.15 s/step. TEM images were obtained on a FEI Tecnai G2 F20 transmission electron microscope at 100 kV. The sample powder was dispersed in ethanol by sonification; drops of the suspension were applied onto a copper grid-supported transparent carbon foil and dried in air. Surface morphology was seen and analyzed by SEM images using JEM-2100F. The Diffuse Reflectance Spectra (DRS) of the photocatalysts were obtained using a SHIMADZU UV-2550 spectrophotometer equipped with a 60 nm diameter integrating sphere using $BaSO_4$ as the reflectance sample.

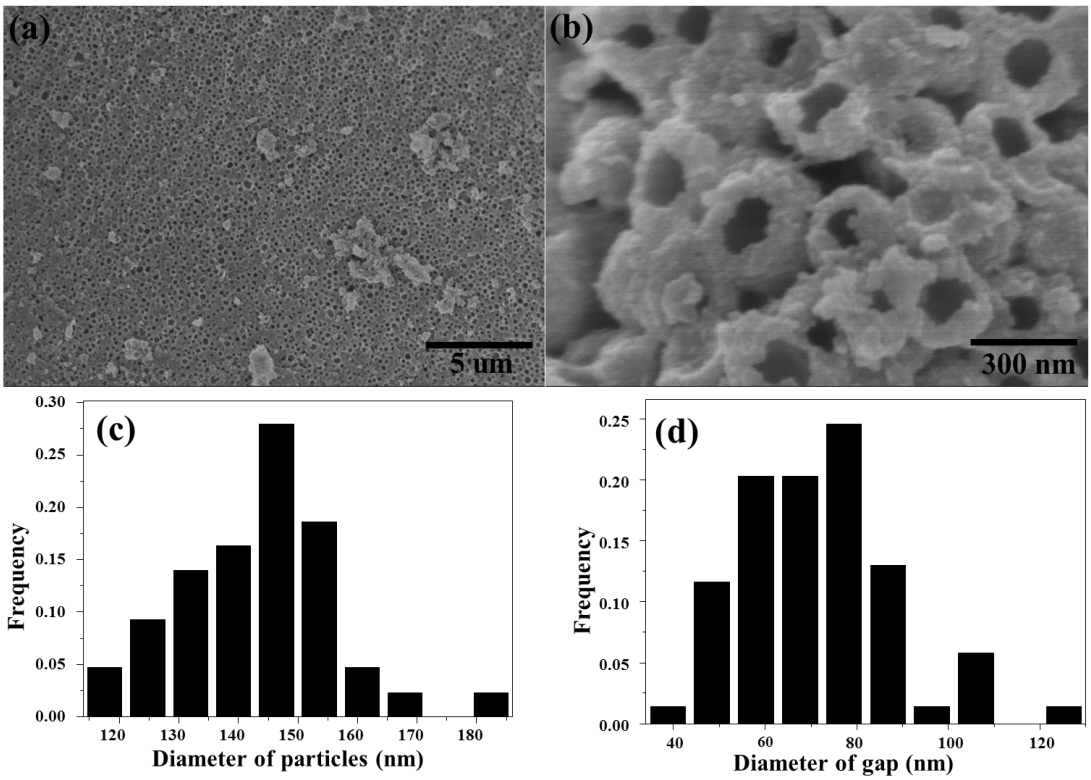

Fig. S1. *(a), (b) SEM images of TiO_2 nanocups in different magnification, (c), (d) distribution of diameter and round opening of nanocup particles.*

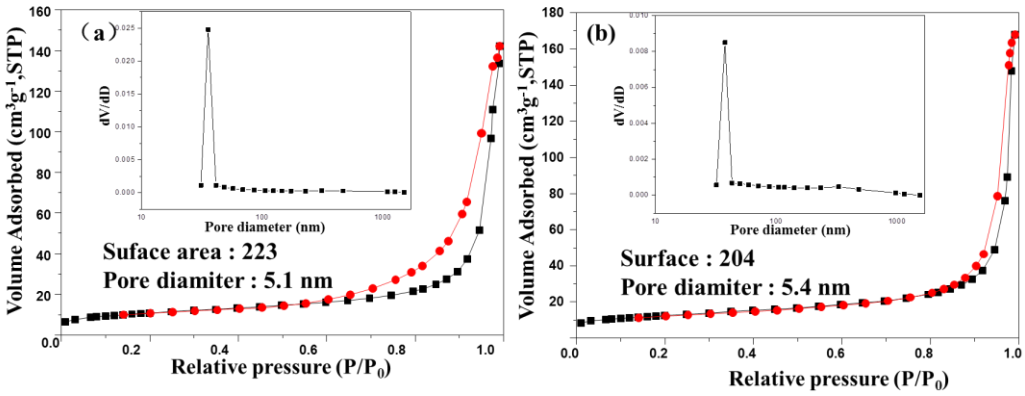

Fig. S2. *Nitrogen adsorption isotherm and pore size distribution: (a) TiO_2 hollow sphere structure, (b) as-prepared TiO_2 nanocup structure.*

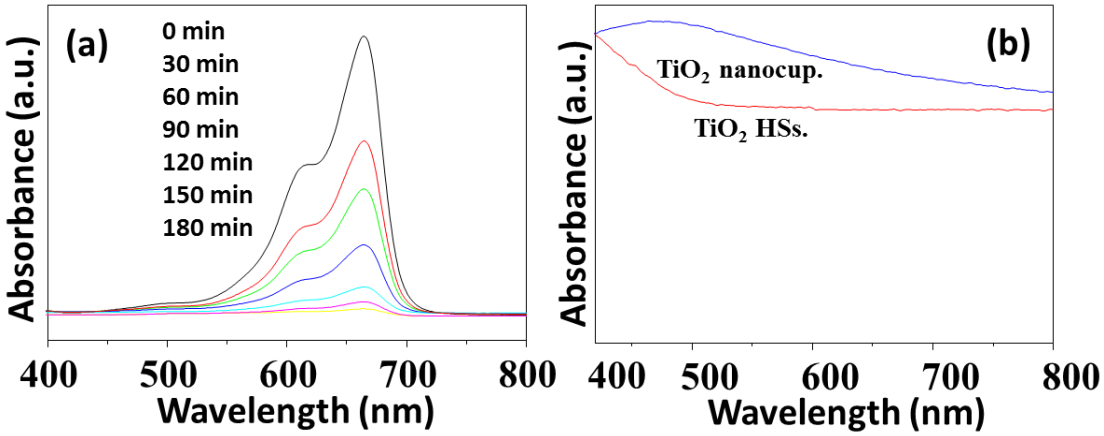

Fig. S3. *(a) UV-vis adsorption spectra showing photodegradation of MB using Au-nanocup TiO_2 photocatalyst. (b) Diffused reflectance spectra of the TiO_2 HSs and TiO_2 nanocup.*

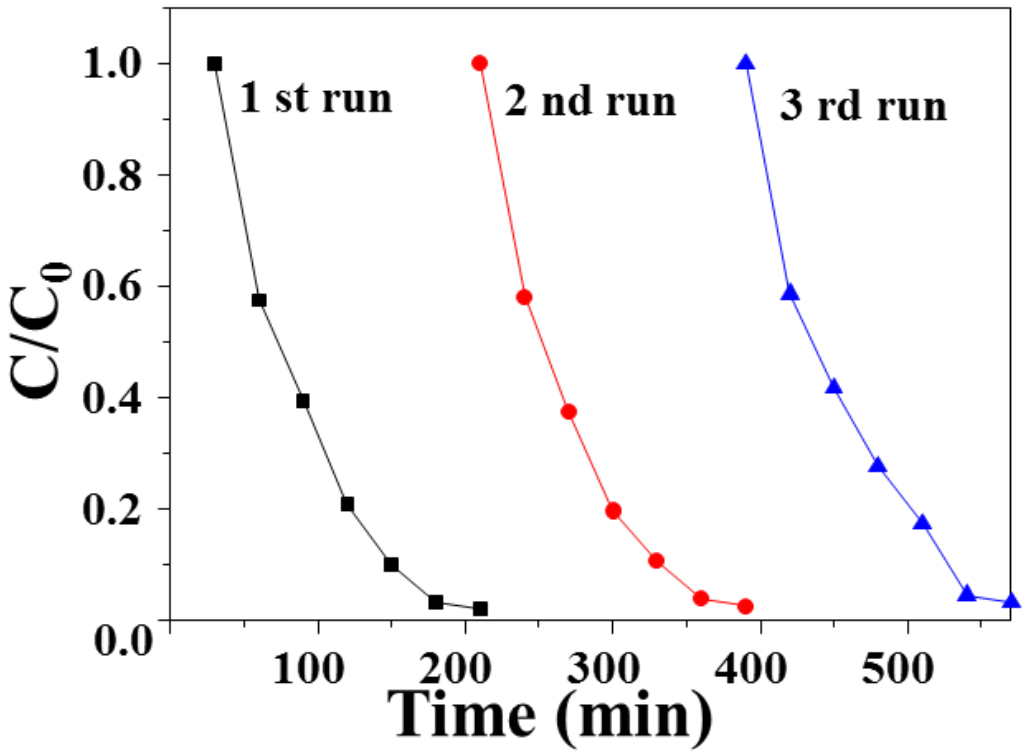

Fig. S4. *Recyclability of the photocatalytic degradation of MB aqueous solution using Au-TiO_2 nanocups.*

Samples	S_{BET} /m^2 g^{-1}
Hollow sphere	223
Au-Hollow sphere	195
Nanocup	204
Au-Nanocup	181
Au-P25	36

Table. 1 *BET surface area results of TiO_2 hollow sphere, Au-TiO_2 hollow sphere, TiO_2 Nanocup, Au-TiO_2 Nanocup, and Au-P25, respectively.*