

Supporting Information

Correlating the excited state relaxation dynamics as measured by photoluminescence and transient absorption with the photocatalytic activity of Au@TiO₂ core-shell nanostructures

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1. Preparation of Au@TiO₂ yolk-shell samples

a. Au nanoparticle synthesis:

An aqueous solution of HAuCl₄·3H₂O (2.54 M, 18 μL) was added to deionized water (30 mL) and heated to boiling point (100°C). A sodium citrate solution (3 wt%, 1 mL) was added, and the resulting mixture was kept for 30 min under stirring. Upon cooling down to room temperature, an aqueous PVP solution (Mw, 40,000, 12.8 mg/mL, 0.235 mL) was added and the solution was kept overnight under stirring to allow for the adsorption of PVP on the Au surface. The Au nanoparticles were separated from the solution by centrifugation, and re-dispersed in water (5 mL).

b. Au@SiO₂ synthesis:

The above-mentioned PVP treated Au solution (1 mL) was sequentially mixed with water (3.3 ml), ethanol (23 mL), Tetraethyl orthosilicate (TEOS, 0.86 mL) and an aqueous solution of ammonia (28%, 0.62 mL). The reaction mixture was stirred for 4 h at room temperature, and then the resulting Au@SiO₂ particles were separated by centrifuging and washed three times with ethanol. Finally, the particles were re-dispersed in ethanol (20 ml) under sonication.

c. Au@SiO₂@TiO₂ synthesis:

The above-mentioned Au@SiO₂ solution (20 ml) was dispersed in a mixture containing hydroxypropyl cellulose (HPC 400 mg), ethanol (80 mL) and water (0.48 mL). After reaction mixture had been stirred for 30 min, a solution of tetrabutyl titanate (TBOT, 4 ml) dissolved in ethanol (18 mL) was slowly added to the above solution using a syringe pump (0.5 mL/min). After injection, the temperature was increased to 85 °C while the reaction mixture was stirred for

90 min under reflux conditions. The precipitate which contained Au@SiO₂@TiO₂ nanocomposites, was collected using centrifugation, washed with ethanol and re-dispersed in the deionized water (40 mL). PVP (M_w, 40,000, 0.8 g) was added into the solution and it was kept overnight under stirring to allow for the adsorption of PVP on the TiO₂ surface. The Au@SiO₂@TiO₂ particles were separated using centrifugation, washed and re-dispersed in ethanol (20 mL).

d. Au@SiO₂@TiO₂@SiO₂ synthesis and calcination:

The above-mentioned PVP treated Au@SiO₂@TiO₂ solution (20 mL) was sequentially mixed with water (17.2 ml), ethanol (72 mL), Tetraethyl orthosilicate (TEOS, 3.44 mL) and an aqueous solution of ammonia (28%, 2.48 mL). The reaction mixture was stirred for 4 h at room temperature, and then the resulting Au@SiO₂@TiO₂@SiO₂ particles were separated by centrifuging, washed three times with ethanol and dried under vacuum. The sample is finally calcined in air at 800°C for 4 h to crystallize the amorphous TiO₂ to small anatase TiO₂ grains. Both of inner and outer silica layers were completely etched out by using NaOH solution at 90°C (Ref. Adv. Funct. Mater., 2012, 22, 166-174) and the Au@TiO₂ sample (sample A) was obtained after centrifuging and washing step.

c. Partial etching and recalcination for controlling TiO₂ crystallinity

The above calcined Au@SiO₂@TiO₂@SiO₂ particles (170 mg) were dispersed in 30 mL of water under ultrasonication and etched with NaOH solution (typically, 0.5 mL, 2.5 M) at 90 °C for 1 h. During the etching process, the silica layers were dissolved out preferentially near or inside the TiO₂ layer and it produce a small gap between SiO₂ and TiO₂ layers which allows space for the TiO₂ to further grow into large crystal grain (Ref., Energy Environ. Sci., 2012, 5, 6321-6327). The partially etched Au@SiO₂@TiO₂@SiO₂ particles were then isolated by centrifugation, washed with de-ionized water and ethanol, dried under vacuum, re-calcined in air at the desired temperature for a certain period (e. g. 4 or 16 h) to enhance the crystallinity of the TiO₂. Sample B was re-calcined at 700°C for 4 h, Sample C was re-calcined at 800°C for 4h, and Sample D was re-calcined at 800°C for 16 h. The samples were then finally etched in a mixture of water (30 mL) and NaOH (2 mL, 2.5 M) at 90° C for 2 h to completely remove the silica. The samples isolated by centrifugation, washed with de-ionized water and ethanol, and dried.

2. Additional TEM images

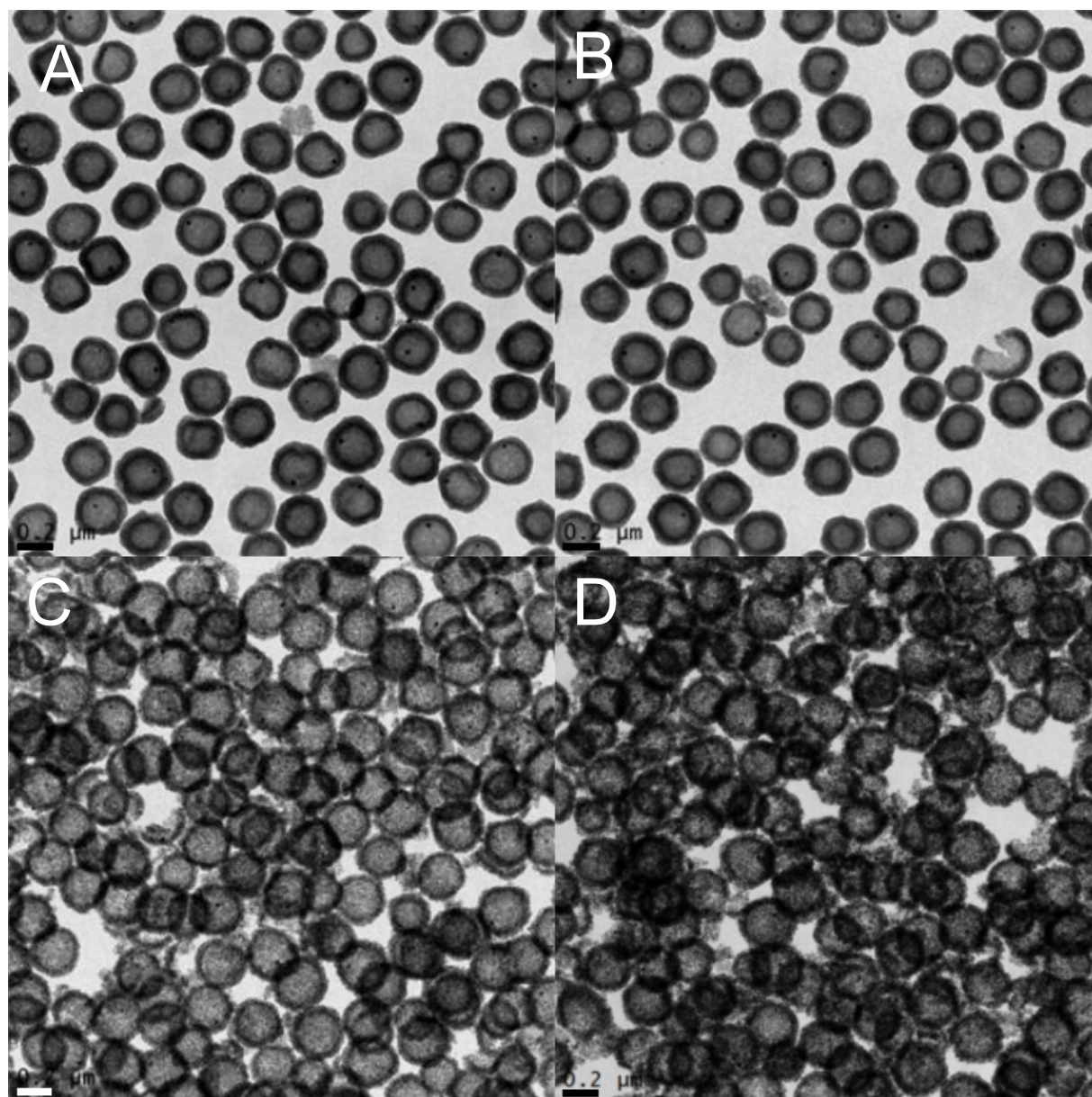


Figure S1: Zoomed out TEM of the Au@TiO₂ samples A-D. The scale bar is 0.2 μm.

3. Powder x-ray diffraction vs. crystallinity

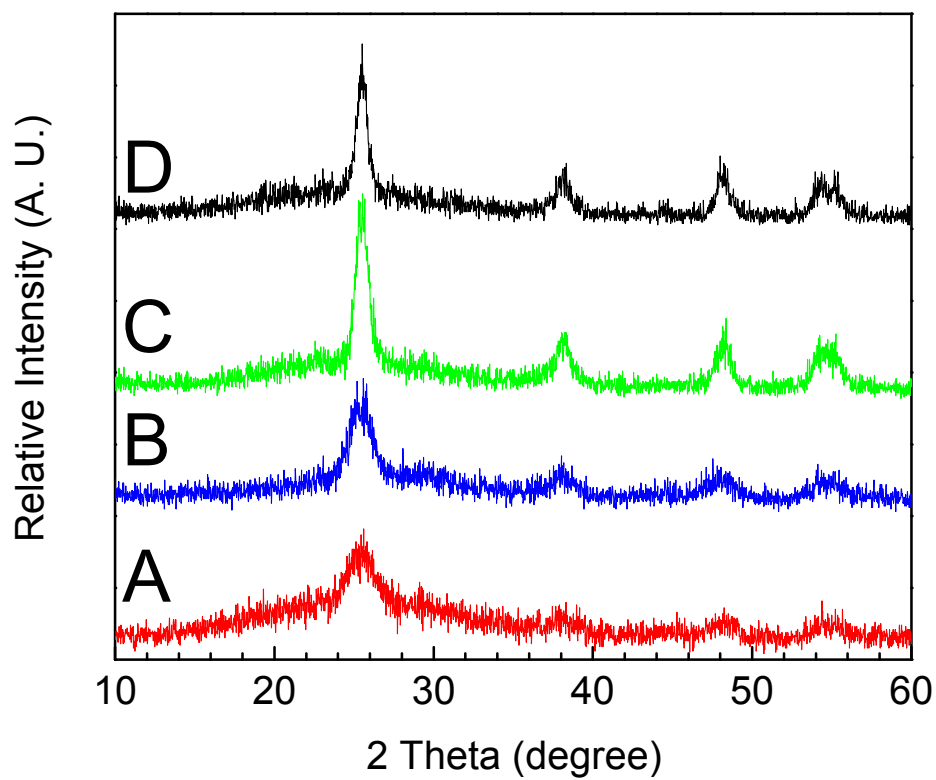


Figure S2: The powder x-ray diffraction spectra for each sample. The crystallinity increases from A to D, with a powder pattern indicative of anatase TiO₂.

4. H₂ production vs. crystallinity

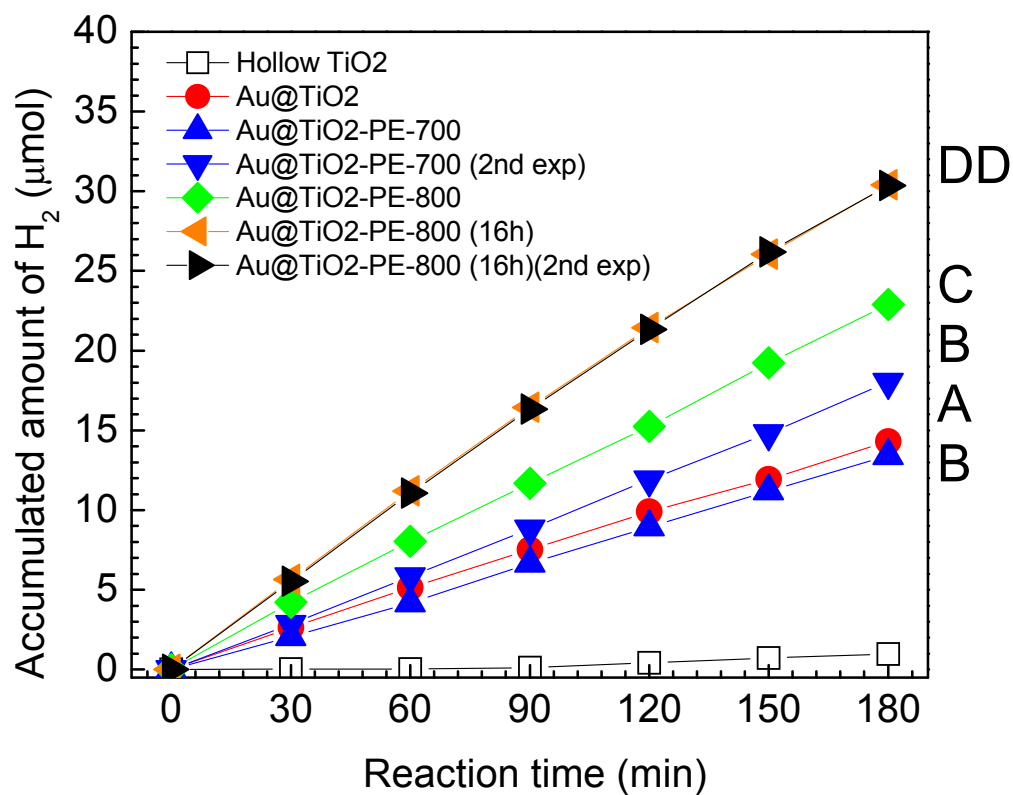


Figure S3: The accumulated hydrogen over time for each sample as well as comparison to TiO₂ without any gold. Some experiments were performed twice.

5. Hg Lamp Spectrum

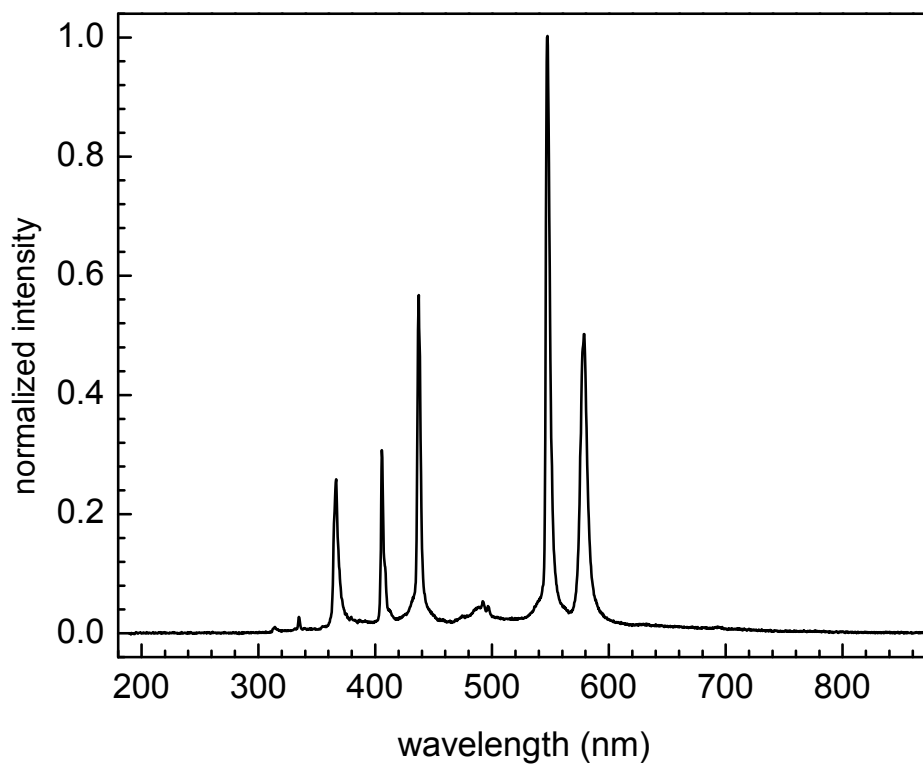


Figure S4: The spectrum of the Hg lamp used for the photocatalysis measurements. The lamp power was 2.26 mW/mm^2 .