Electronic Supplementary Information:

Generation of Reactive Oxygen Species and Charge Carriers in Plasmonic Photocatalytic Au@TiO_2 Nanostructures with Enhanced Activity

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Experimental section

Chemical and Materials. Chlorauric acid ($HAuCl_4 \cdot 3H_2O$), $TiCl_3$, Poly(Sodium 4-Styrenesulfonate) (PSS), L-ascorbic acid (AA), salicylic acid, cetyltrimethylammonium bromide (CTAB) are purchased from Alfa Aesar (Shanghai, China). The spin-trap 5-tert-butoxycarbonyl 5-methyl-1-pyrroline N-oxide (BMPO) was purchased from Applied Bioanalytical Labs (Sarasota, FL). 1-Hydroxy-3-carboxy-2,2,5,5-tetramethylpyrrolidine (CPH) and 2,2,6,6 -tetramethylpiperidine-1-oxyl (TEMPO) were purchased from Alexis, Enzo Life Sciences, Inc. (NY, USA). 2,2,6,6-tetramethylpiperidine (TEMP), NaN_3, DMSO and superoxide dismutase (SOD) were all purchased from Sigma-Aldrich (St. Louis, MO). Other chemicals are obtained from Sinopharm Chemical Reagent Co., Ltd. Milli-Q water (18 MΩ cm) was used for all the experimental preparations. All glassware and autoclave used in the following procedures were cleaned using an aqua regia solution ($HNO_3/HCl = 1:3$ v/v).

Synthesis of Au Nanospheres (NSs). Au NSs were prepared by a seed-mediated growth. First, CTAB-capped Au seeds were synthesized by chemical reduction of $HAuCl_4$ with $NaBH_4$: 7.5 ml 0.1 M CTAB aqueous solution was mixed with 250 μl 10 mM $HAuCl_4$ and diluted with water to 9.4 ml. Then, 0.6 mL ice-cold 10 mM $NaBH_4$ was added while stirring magnetically. After 3 min, the stirring was stopped and the seed solution was kept undisturbed at room temperature for 2 h prior to use. The seeds concentration is calculated to be 0.25 mM. The growth solution of the Au NS was prepared by mixing 100 mL 0.1 M CTAB, 2 ml 0.024 M $HAuCl_4$, 2 ml 0.5 M H_2SO_4, 0.1 ml 10 mM $AgNO_3$, and 550μl AA (0.1 M). 2.4 mL seed solution was added to the above growth solution to initiate the growth of the Au NS for 12 h. Then, 0.25 ml 0.1 M AA was added. After 2 hours, Au NSs were purified by centrifugation (11,000 rpm 7 min) once and the precipitates were re-dispersed in 100 ml water for PSS coating.

10 ml Au NSs suspension was mixed with 0.5 ml 20 mg/ml PSS solution (containing 60 mM NaCl). The suspension was placed in a 30 ºC water bath for at least 3 h. After that, one time centrifugation (10,000 rpm 5 min) was executed to remove the excessive PSS and the precipitate was re-dispersed in 200 μl water for further use.

Synthesis of Au@TiO$_2$ nanostructures. Typically, 6.0 ml H_2O, 200 ul $TiCl_3$ (17.1 wt%, containing 20-30 wt% HCl) were mixed in a glass bottle under vigorous stirring followed by the addition of 1.1 ml 1 M $NaHCO_3$. Then, 200 ul PSS-coated Au NSs suspension was immediately dropped into the mixture. After 30 min at room temperature, Au NSs coated with amorphous TiO_2 were obtained. The products were purified by centrifugation twice (10000 rpm 8 min) and re-dispersed in 5 ml water. The thermal treatment of the washed Au@TiO_2 nanostructures was carried out in a box furnace in air at 500, 700, 900 ºC for 2 h. Then, the Au@TiO_2 powders were re-dispersed in 5 ml water for further use. For clarity, we named the Au@TiO_2 before and after annealing at 500, 700 and 900 ºC as Au@TiO_2-as, Au@TiO_2-500, Au@TiO_2-700 and Au@TiO_2-900, respectively.

Characterization. Transmission electron microscopy (TEM) images were captured on a Tecnai G^2 F20 U-TWIN electron microscope with an accelerating voltage of 200 kV. That same microscope was used to perform high-resolution TEM (HRTEM), selected-area electron diffraction and energy dispersive X-ray spectrometry. X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with monochromatized Cu Kα radiation (λ = 1.5418 Å) was used to characterize the crystal structure of Au@TiO_2 nanostructures. UV-visible absorption spectra were obtained by a UV-VIS-NIR Spectrometer (Varian Cary 5000). The photocatalytic activities of Au@TiO_2 were evaluated by measuring the degradation of salicylic acid (SA) in aqueous solution and hydrogen production in 20% methanol aqueous solutions. A 300 W Xe-lamp with or without filter pass was used as light source. 0.5 mg/ml of TiO_2 or Au@TiO_2 photocatalyst was dispersed in a 20 mL aqueous solution containing 0.4 mM salicylic acid (SA). The solution was continuously stirred in the dark for about 1 h to establish an adsorption-desorption equilibrium between the photocatalyst and dyes. Then, the suspension was irradiated using a 300 W Xenon lamp or filtered to deliver light with wavelength above 420 nm. During irradiation, the solution was stirred to maintain a suspension. After 3 hours, aliquots of suspension were removed and centrifuged. The residual concentration of SA was monitored using a Varian Cary 5000 spectrometer. The photocatalytic production is similar to degradation of SA unless that the reaction was performed in a reactor containing 20 ml water, 5 ml methanol and 25 mg Au@TiO_2 nanostructures, then the suspension was thoroughly degassed to remove air, and the reactor was irradiated from the top with light. Photocatalytic H_2 evolution rate was analyzed with an online gas chromatograph.

All the ESR measurements were carried out using a Bruker EMX ESR spectrometer (Billerica, MA) at ambient temperature. A solar simulator consisting of a 450 W Xenon lamp filtered to provide simulated sunlight was used in ESR studies. Fifty microliter aliquots of control or sample solutions were put into quartz capillary tubes with internal diameters of 0.9 mm and sealed. The capillary tubes were inserted in the ESR cavity, and the spectra were recorded during irradiation at selected times. All ESR measurements were carried out using the following settings for detection of the spin adducts: 20 mW microwave power, 100 G scan range and 1 G field modulation.

The spin trap BMPO was used to verify the formation of superoxide (•OOH) and hydroxyl radicals (•OH) during exposure of TiO_2 and Au@ TiO_2 nanostructures to simulated sunlight. TEMP was used to demonstrate the generation of singlet oxygen during irradiation of samples. CPH and TEMPO were used as spin labels for studying the holes and electrons generated during photoexcitation of Au@TiO_2 hybrid nanostructures. In these experiments, the intensity of the ESR signal was measured as the peak-to-peak height of the second line of ESR spectrum. ESR spectra were recorded from the sample mixture, containing spin probes (BMPO, TEMP, CPH or TEMPO) and nanoparticles, after exposure to light for selected times. For comparison, the controls either without catalysts or without irradiation were also recorded.

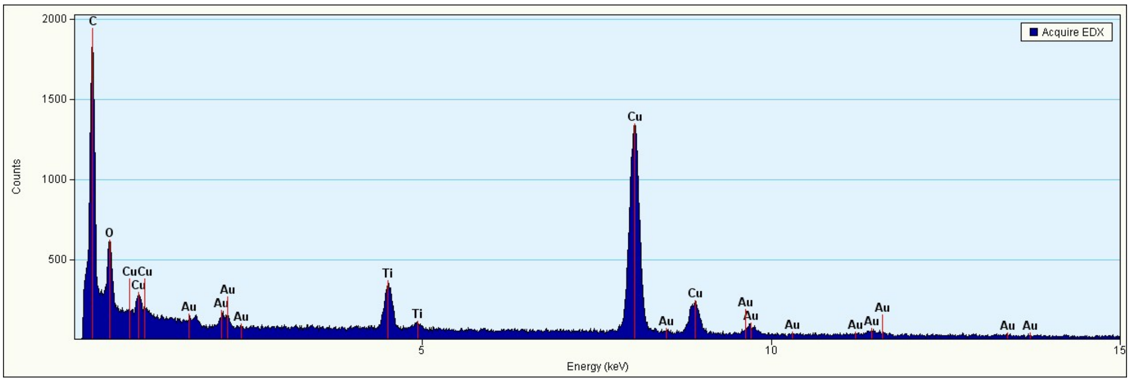

Figure S1. Energy dispersive X-ray (EDX) spectra of Au@TiO_2 nanostructures.

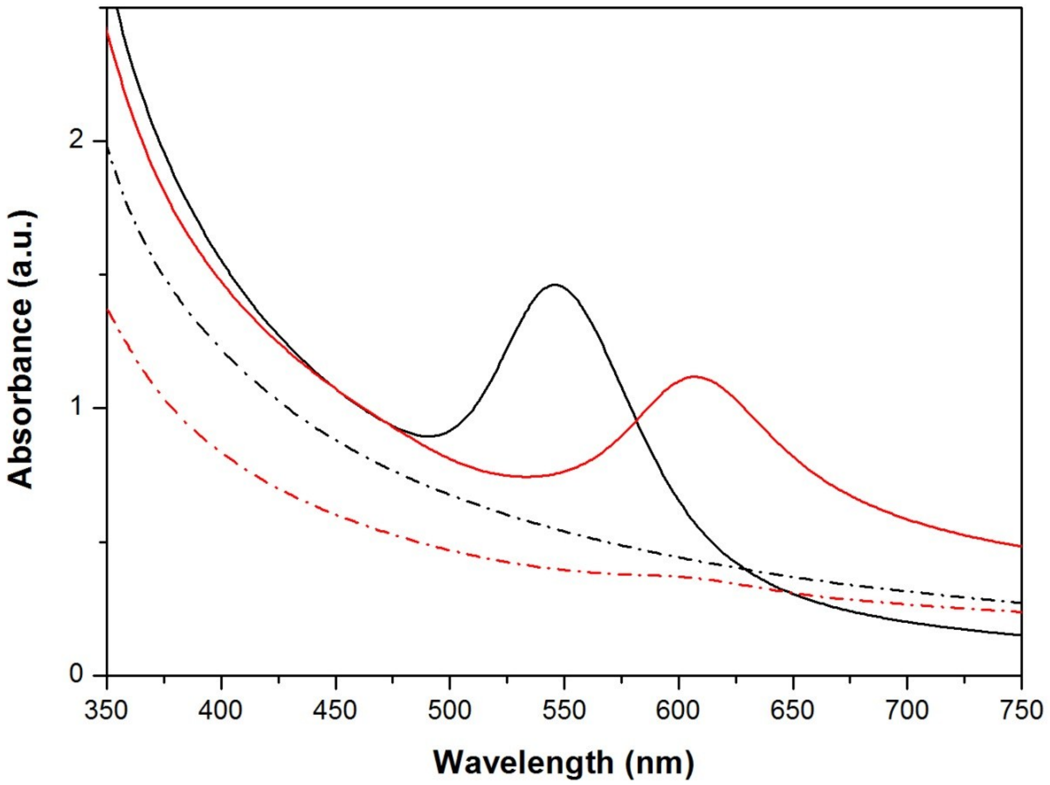

Figure S2. UV-Vis spectra of Au@TiO_2-as (solid black) and Au@TiO_2-500 (solid red) before and after etching by I_2/KI solutions.

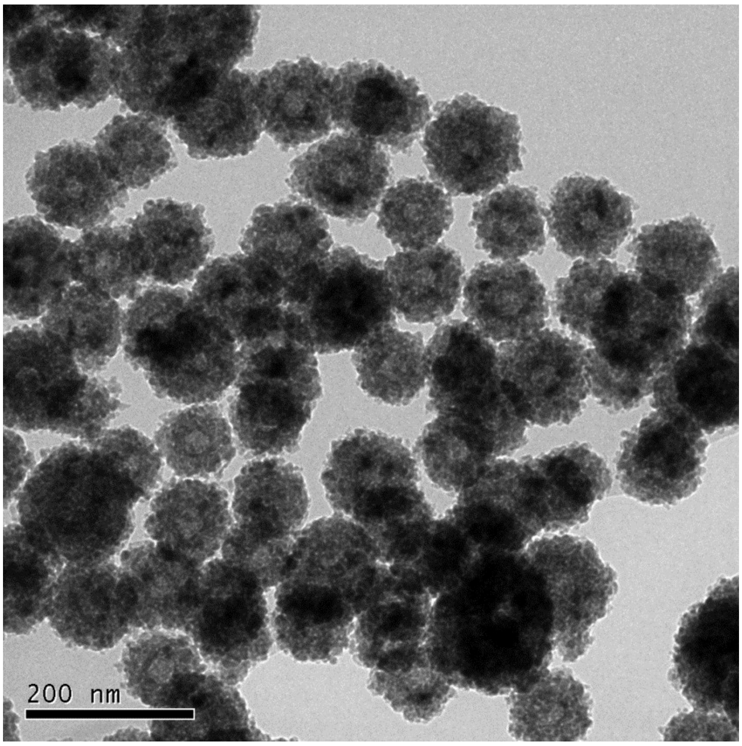

Figure S3. TEM images of TiO_2 hollow structures derived from Au@TiO_2 by etching Au nanoparticles.

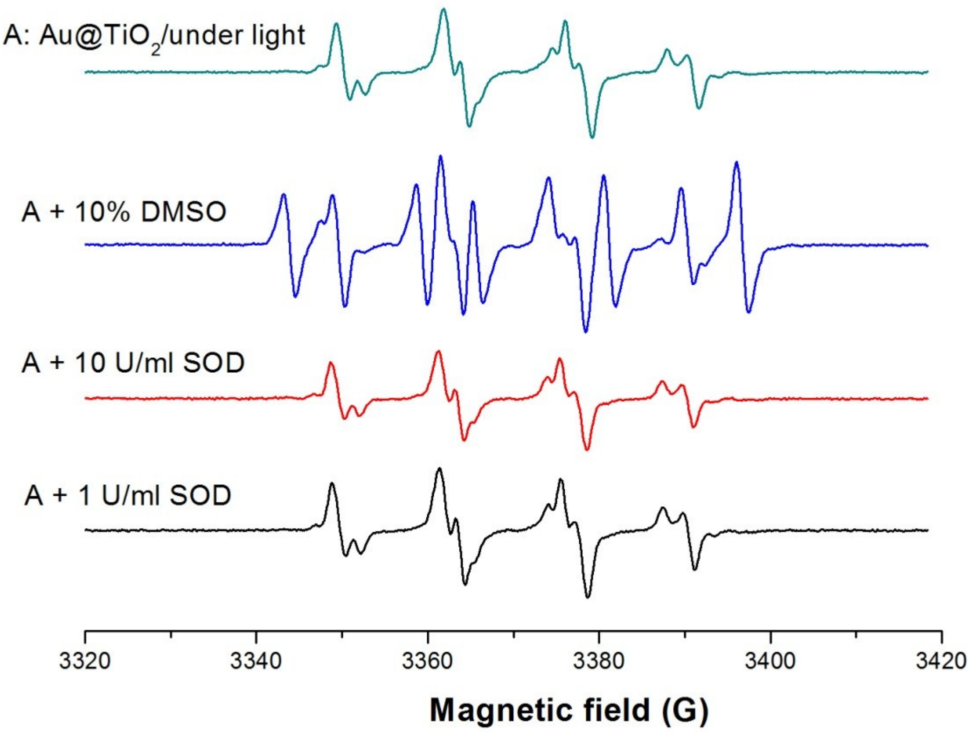

Figure S4. Effect of DMSO and SOD on the ESR signal generated from Au@TiO_2 nanostructures under simulated sunlight.

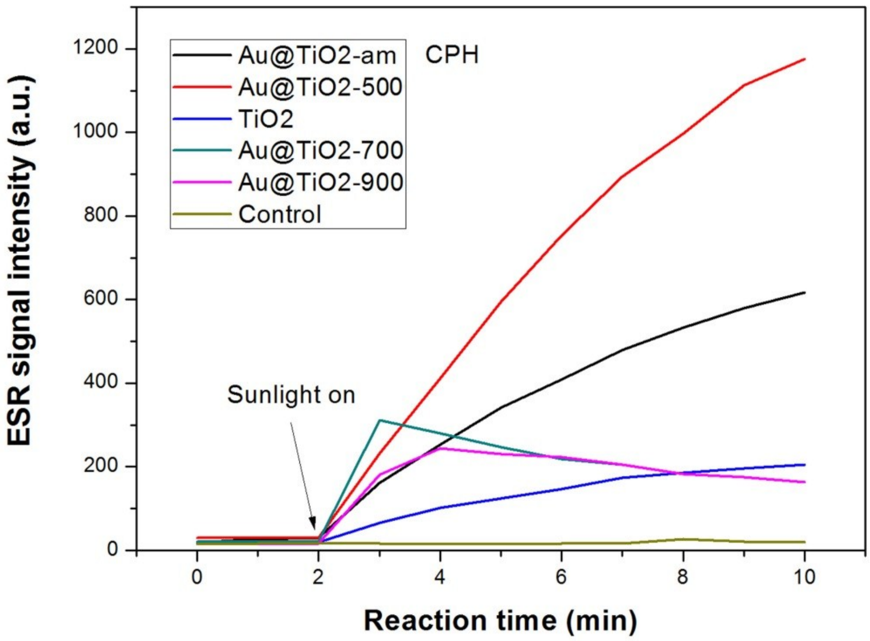

Figure S5. The evolution ESR signal intensity from CPH as a function of time before and after irradiation with sunlight in the presence of TiO2 and different Au@TiO2 nanostructures.

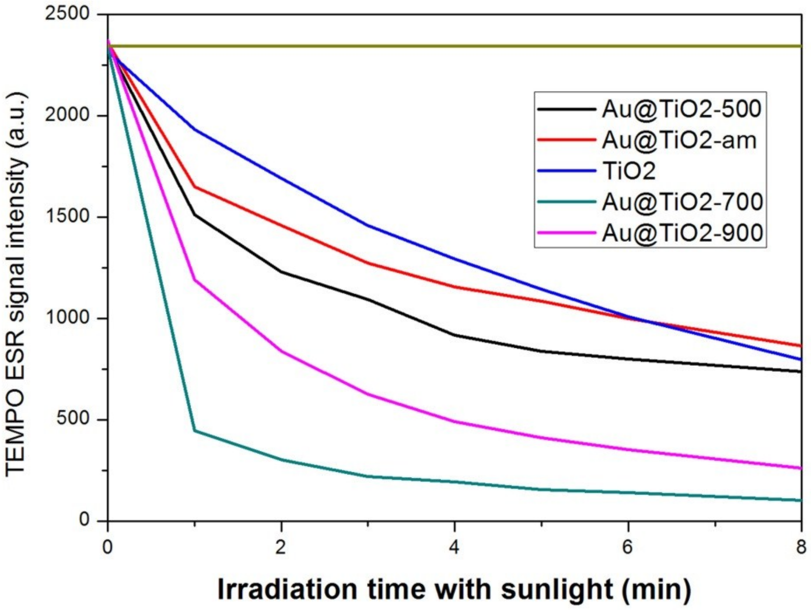

Figure S6. The evolution ESR signal intensity from TEMPO as a function of time before and after irradiation with sunlight in the presence of TiO_2 and different Au@TiO_2 nanostructures.