Electronic Supplementary Information

Facile Synthesis of Au@TiO_2 Core-Shell Hollow Spheres for Dye-Sensitized Solar Cells with Remarkably Improved Efficiency

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Experimental Section

Synthesis of Au nanoparticle: An aqueous solution of $HAuCl_4 \cdot 3H_2O$ (10 mM, 5 mL) was added to deionized water (190 mL) and stirred for 2 min, A sodium citrate solution (10 mM, 5 mL) was then added, and the resulting mixture was kept for 10 min under stirring. Finally, $NaBH_4$ (100 mM, 3mL) was added and the mixture was stirred for 12 h. The prepared Au nanoparticles had an average size of 5 nm (Fig. S3).

Synthesis of Au@TiO_2 hollow submicrospheres: The prepared Au nanoparticle solution (2 mL) was sequentially mixed with water (14 mL) and ethanol (14 mL), and the reaction mixture was stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 2 mL) was added, and the resulting mixture was kept for 30 min under stirring. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to 180 °C for 6 h. The resultant solid product was centrifuged, washed three times with distilled water, and dried in air at room temperature.

Synthesis of TiO_2 hollow submicrospheres: The sodium citrate solution (10 mM, 2 mL) was sequentially mixed with water (14 mL) and ethanol (14 mL), and the reaction mixture was stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 2 mL) was added, and the resulting mixture was kept for 30 min under stirring. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to 180 °C for 6 h. The resultant solid product was centrifuged, washed three times with distilled water, and dried in air at room temperature.

Synthesis of Au@TiO_2 hollow submicrospheres with thin shell in the presence of ethanol

The prepared Au nanoparticle solution (2 mL) was sequentially mixed with water (14 mL) and ethanol (14 mL), and the reaction mixture was stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 0.5 mL) was added, and the resulting mixture was kept for 30 min under stirring. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to 180 °C for 6 h. The resultant solid product was centrifuged, washed three times with distilled water, and dried in air at room temperature.

Synthesis of Au@TiO_2 hollow submicrospheres with thin shell in the absence of ethanol: The prepared Au nanoparticle solution (2 mL) was sequentially mixed with water (24 mL), and the reaction mixture was stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 0.5 mL) was added, and the resulting mixture was kept for 30 min under stirring. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to 180 °C for 6 h. The resultant solid product was centrifuged, washed three times with distilled water, and dried in air at room temperature.

Synthesis of Au@TiO_2 hollow submicrospheres with thin shell at different crystallization temperatures: The prepared Au nanoparticle solution (18 mL) was sequentially mixed with water (126 mL) and ethanol (126 mL), and the reaction mixture was stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 4.5 mL) was added, and the resulting mixture was kept for 30 min under stirring. Then, the resulting mixture was divided into nine parts. One of them was stirred 6 h at room temperature, and the other eight parts were transferred to Teflon-lined stainless steel autoclaves, in which the samples were heated at 50 °C, 60 °C, 75 °C, 100 °C, 120 °C, 140 °C, 160 °C and 180 °C for 6 h, respectively. The resultant solid products were centrifuged, washed three times with distilled water, and dried in air at room temperature.

Synthesis of Au@TiO_2 hollow submicrospheres with thin shell via shorter crystallization time: The prepared Au nanoparticle solution (4 mL) was sequentially mixed with water (28 mL) and ethanol (28 mL), and the reaction mixture was stirred for 10 min at room temperature. Subsequently, TiF_4 (40

mM, 1 mL) was added, and the resulting mixture was kept for 30 min under stirring. Then, the resulting mixture was divided into two parts. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves, which were heated at 1 min or 2 min at 180 °C, respectively. The resultant solid products were centrifuged, washed three times with distilled water, and dried in air at room temperature.

Synthesis of Au@TiO_2 hollow submicrospheres with double shells:

(1) Synthesis of Au@TiO_2 hollow submicrosphere seeds with single shell: The prepared Au nanoparticle solution (16 mL) was sequentially mixed with water (112 mL) and ethanol (112 mL), and the reaction mixture was then stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 16 mL) was added, and the resulting mixture was kept for 30 min under stirring. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to 180 °C for 6 h. The resultant solid product was centrifuged, washed three times with distilled water, and dried in air at room temperature. The solid product was dispersed into 15 ml deionized water.

(2) Synthesis of Au@TiO_2 hollow submicrospheres with double shells: The prepared Au@TiO_2 seeds (3 mL) were sequentially mixed with water (112 mL) and ethanol (112 mL), and the reaction mixture was then stirred for 10 min at room temperature. Subsequently, TiF_4 (40 mM, 16 mL) was added, and the resulting mixture was kept for 30 min under stirring. Finally, the mixture was transferred to Teflon-lined stainless steel autoclaves and heated to 180 °C for 6 h. The resultant solid product was centrifuged, washed three times with distilled water, and dried in air at room temperature.

Fabrication of different DSSC devices: To prepare the photoanode of Au@TiO_2 hollow submicrospheres, 3 g of poly(vinylalcohol) (PVA, MW 22000) water solution (30%) was firstly dissolved with the solvent containing 9 mL H_2O and 12.5 mL ethanol. Then, 1.62 g of Au@TiO_2 hollow submicrospheres were added to make the suspension of TiO_2. After the suspension was deposited on the fluorine-doped tin oxide (FTO) glass electrode, the thickness of Au@TiO_2 hollow submicrospheres was controlled by the doctor-blade technique. The thickness of all the different films was about 7.0 μm. The Au@TiO_2 hollow submicrospheres films were subsequently annealed at 450 °C for 60 min in air to improve the interconnection between the Au@TiO_2 composite spheres and the contact between the

composite film and the FTO substrate, as well as to remove any residual solvents or organic compounds. The annealed electrodes were sensitized by soaking in ethanol solution containing 3×10^{-4} M N719 dye, $Ru(dcbpy)_2(NCS)_2$ (N_3) (dcbpy=2,2'- bipyridine-4,4'-dicarboxylic acid) for 24 h. The DSSCs were composed of a sensitized photoanode, a platinum counter electrode, and an electrolyte. The electrolyte was composed of 0.5 M LiI, 0.05 M I_2, 0.5 M *tert*-butylpyridine, and 0.6 M 1-propyl-3-methylimidazolium iodide in 3-methoxypropionitrile.

Characterization: Powder X-ray diffraction (XRD) patterns were recorded on a Panaltical X'Pert-pro MPD X-ray power diffractometer, using Cu Kα radiation (λ = 1.54056 Å). SEM was performed on a Hitachi S-4800 electron microscope and TEM was performed on a FEI Tecnai G2 F20 electron microscope operated at 200 kV with the software package for automated electron tomography. The J-V characteristics of the cells were measured by an electrochemical analyzer (CHI630A, Chenhua Instruments Co., Shanghai) under solar simulator illumination (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) at room temperature. UV-vis spectra were recorded on a Hitachi Model U-4100 spectrophotometer, and the raw data was calculated by Kubelka-Munk model.

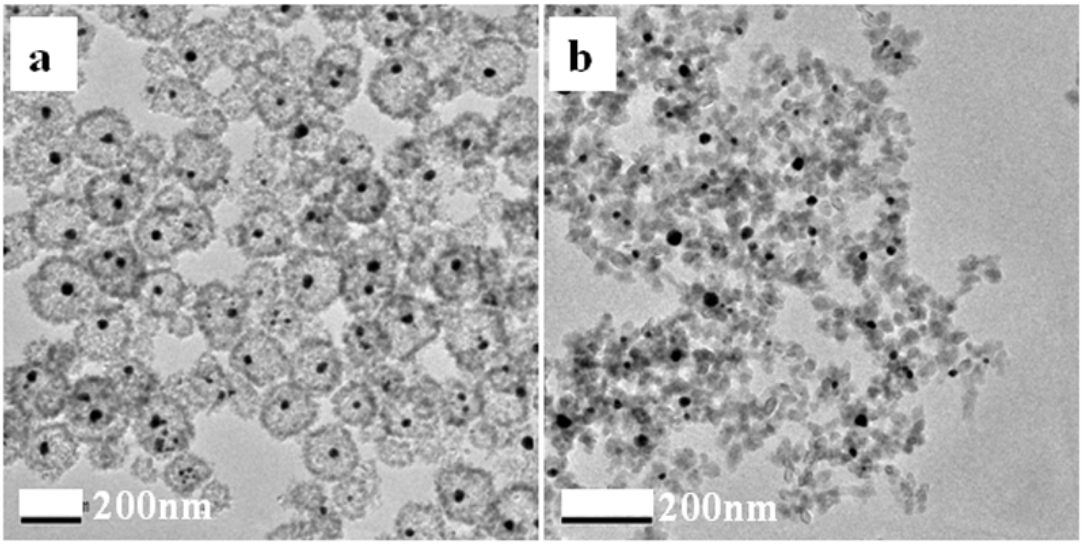

Fig. S1 TEM images of Au@TiO_2 hollow submicrospheres (thin shell), (a) with ethanol and (b) without ethanol.

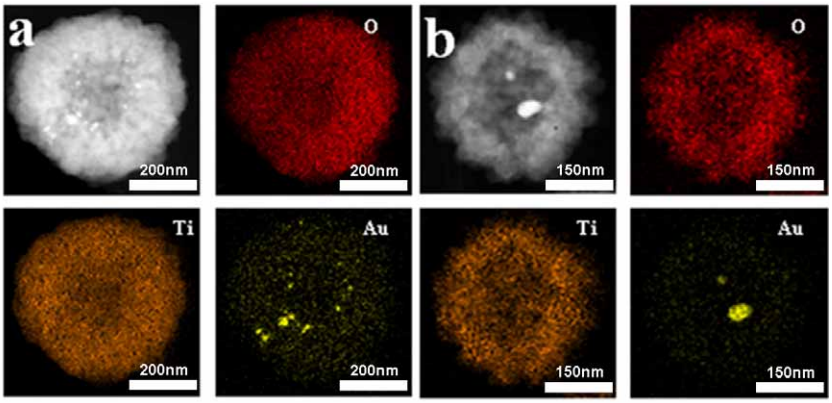

Fig. S2 HAADF-STEM image and HAADF-STEM-EDS mapping images of Au@TiO_2 hollow submicrospheres with a) thick shell and b) medium-thickness shell.

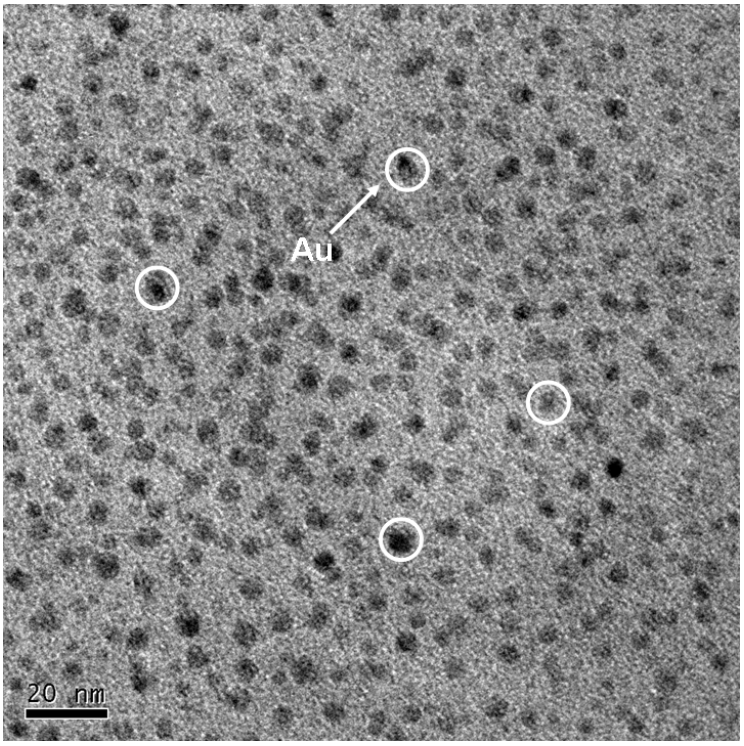

Fig. S3 TEM image of Au NPs for preparation of Au@TiO_2 hollow submicrospheres.

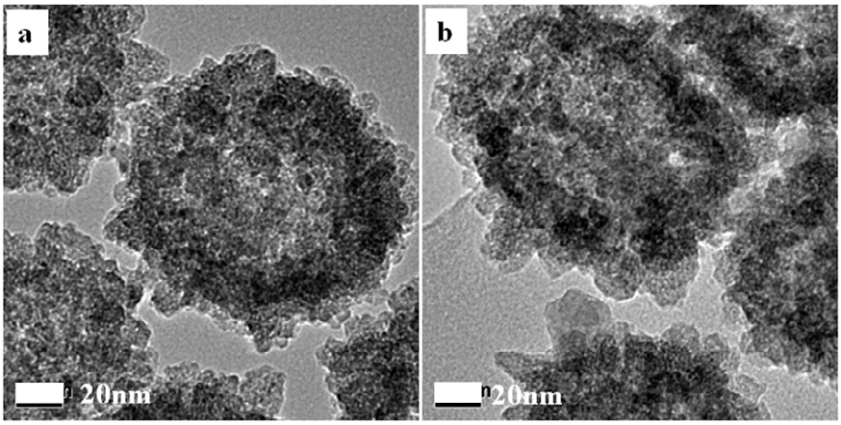

Fig. S4 TEM images of Au@TiO_2 hollow submicrospheres with thin shell at 180 ^oC via different crystallization times: a) 1 min or b) 2 min.

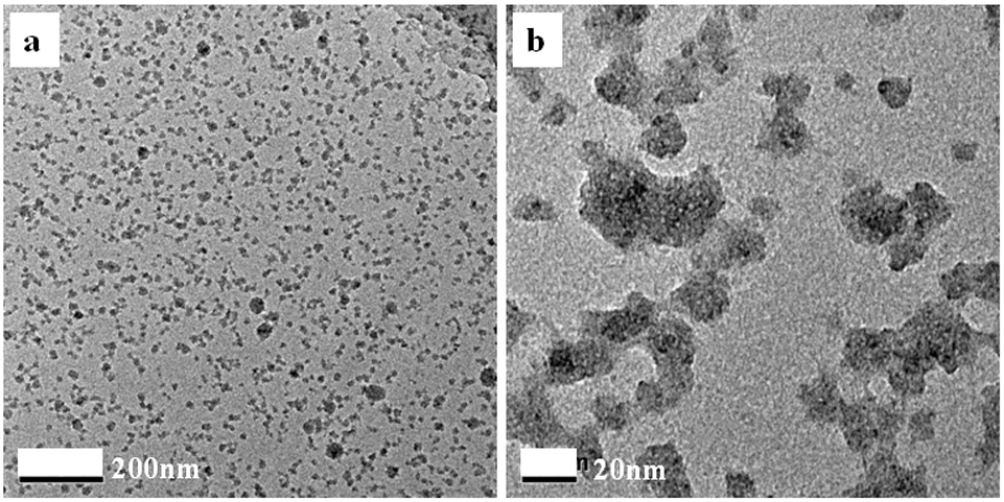

Fig. S5 TEM image of a) the product synthesized at room temperature for 6 h, b) is corresponding enlarged TEM image.

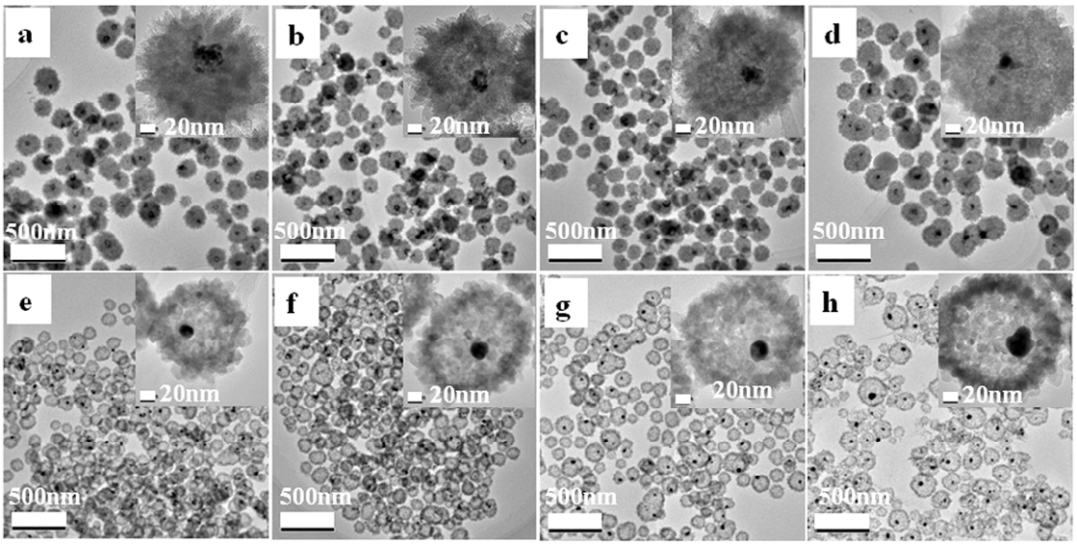

Fig. S6 TEM images of Au@TiO_2 hollow submicrospheres with thin shell at different crystallization temperatures : a) 50 °C, b) 60 °C, c) 75 °C, d) 100 °C, e) 120 °C, f) 140 °C, g) 160 °C and h) 180 °C for 6 h. Insets in a) – h) are corresponding enlarged TEM images.

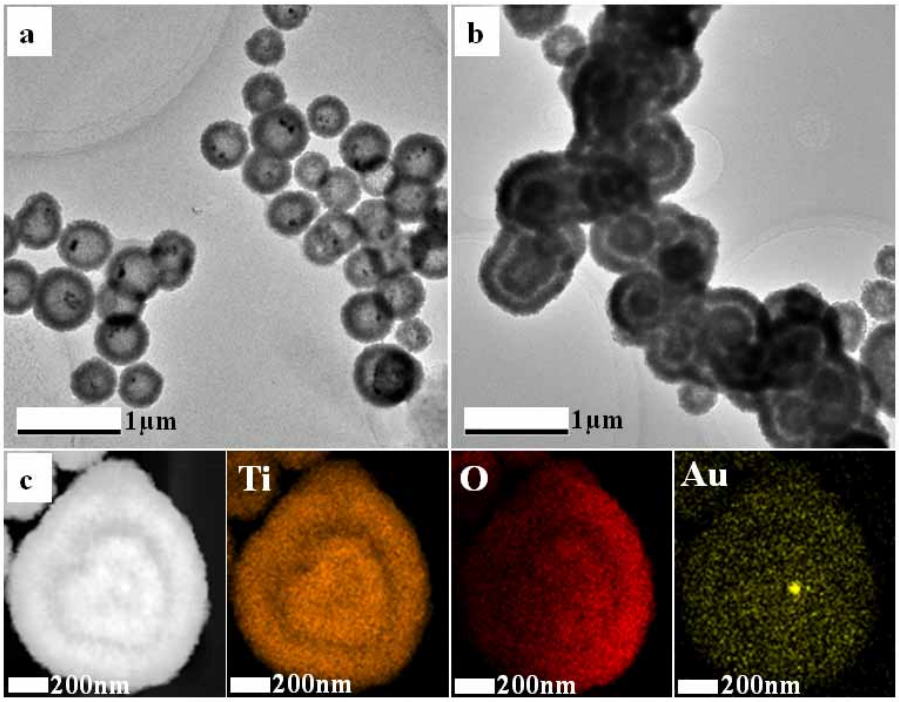

Fig. S7 TEM images of Au@TiO_2 hollow submicrospheres, a) Au@TiO_2 submicrospheres with single shell, b) Au@TiO_2 submicrospheres with double shells, c) is the HAADF-STEM image and HAADF-STEM-EDS mapping images of b).

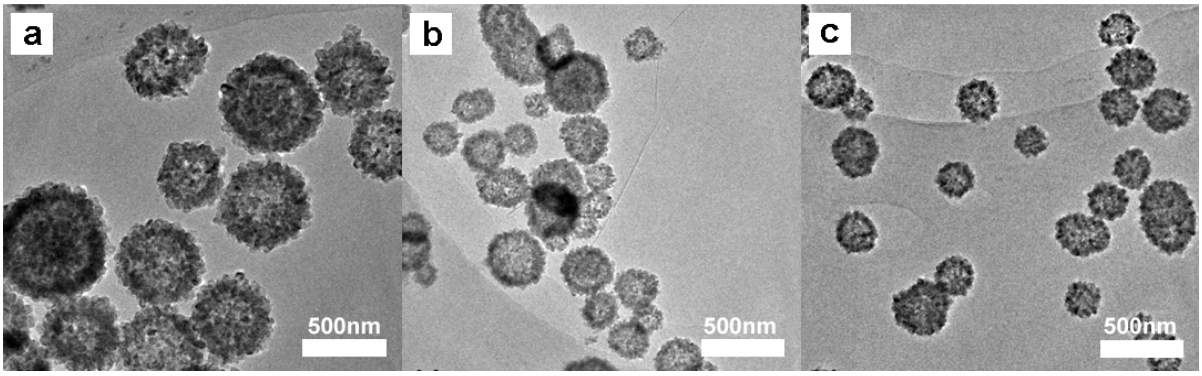

Fig. S8 TEM images of TiO_2 hollow submicrospheres with a) thick shell, b) medium-thickness shell and c) thin shell.

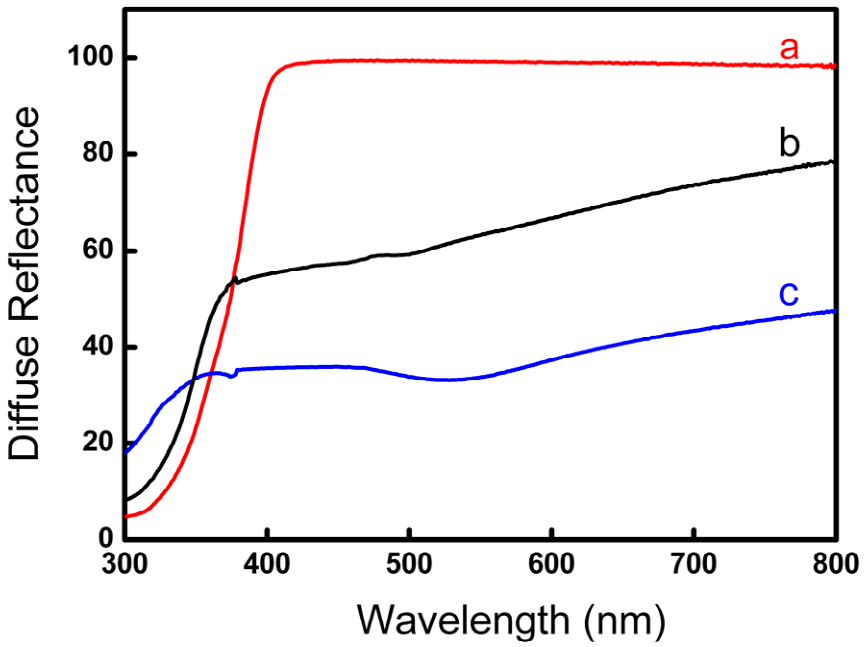

Fig. S9 Diffuse reflectance of a) P25, b) TiO_2 hollow submicrospheres with thin shell, and c) Au@TiO_2 hollow submicrospheres with thin shell

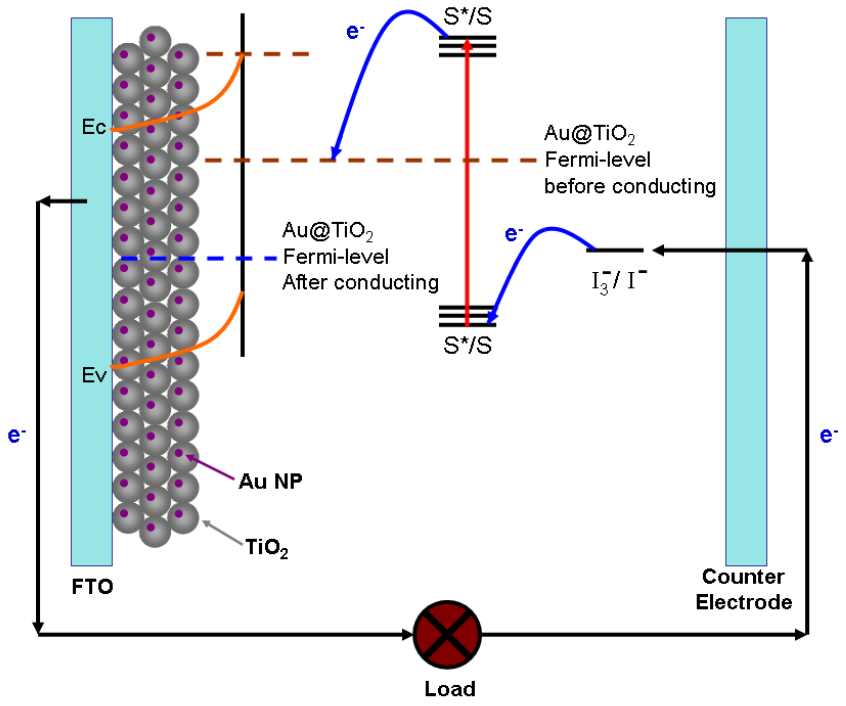

Fig. S10 Scheme of the charge separation process in the DSSCs with the photoanode of Au@TiO_2 hollow submicrospheres.