Electronic Supplementary information (ESI) for

Ag Shell Thickness Effect of Au@Ag@SiO₂ Core-Shell Nanoparticles on Optoelectronic Performance for Dye Sensitized Solar Cells

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Experimental Section

Chemical Materials: All chemical reagents were used without further purification.

Chloroauric acid and silver nitrate was purchased from Sinopharm Chemical Reagent Co., Ltd. lithium iodide, I₂, tertbutylpyridine, 1-propyl-3-methylimidazolium iodide and dye sensitizercis-bis (isothicyanato) bis (2, 2'-bipyridyl-4, 4'-discarboxylato)-ruthenium (II)-bis-tetrabutylammonium, (coded as N719) were purchased from Sigma Aldrich. FTO glass was purchased from Wuhan Georgi & Education Equipment Co., Ltd.

Synthesis of Au@SiO₂ nanoparticles:

We chemically synthesized Au nanoparticles with diameters of about 50nm as cores using a standard sodium citrate reduction method ^[32]. 1.4 ml of trisodium citrate (1%) was added to 200 mL of a boiling aqueous solution containing HAuCl₄ (0.01%). The solution was boiled for 15 min and then cooled to room temperature. Then, 1 mM (3-Aminopropyl) trimethoxysilane (APS) was added to the Ag solution under vigorous magnetic stirring in 15 min. Then a 0.54 wt% sodium silicate solution was added to the solution, again under vigorous magnetic stirring under 100 °C. The resulting particles were centrifuged at 8000 rpm for 5 min.

Synthesis of Au@Ag@SiO2 core-double shells:

100 mM of L-ascorbic acid (180, 360, 540 and 900uL), 100 mM of AgNO₃ (45, 90, 135 and 225uL), and 100 mM of NaOH (225, 450, 675 and 1125uL) were added to a beaker containing 30mL of as-prepared Au NPs (~50 nm) at room temperature. A series of Au@Ag core-shell with the thickness of Ag shell (5, 10, 15 and 25nm) were obtained. Then, 1 mM (3-Aminopropyl) trimethoxysilane (APS) was added to the Au@Ag solution under vigorous magnetic stirring in 15 min. Then a 0.54 wt% sodium silicate solution was added to the solution, again under vigorous magnetic stirring under 100 °C. The resulting particles were centrifuged at 8000 rpm for 5 min. The Au@Ag@SiO₂ core-double shells nanomaterials were obtained.

Synthesis of Ag@SiO₂ nanoparticles:

Ag NPs were synthesized by the citrate reduction method ^[33]. AgNO₃ (45 mg) was dissolved in 200 mL of deionized water and the mixture heated to boiling. Then, 4mL of a 1% sodium citrate solution was added to the boiling solution, and boiling was maintained for 1 h. Then, 1 mM (3-Aminopropyl) trimethoxysilane (APS) was added to the Ag solution under vigorous magnetic stirring in 15 min. Then a 0.54 wt% sodium silicate solution was added to the solution, again under vigorous magnetic stirring under 100 °C. The resulting particles were centrifuged at 8000 rpm for 5 min.

Synthesis of anatase titanium dioxide nano-particles:

37 mL of titanium(IV) iso-propoxide (Aldrich) in 1 mL of iso-propanol was dripped slowly into a stirred mixture of 80 mL of glacial acetic acid and 250 mL of deionized water at 0 °C over 30 min, and the resulting solution was filtrated and heated to 80 °C for 8 h. After that, it was heated to 230 °C in Telflon autoclave for 12 h. Upon removal from the autoclave, the solution was sonicated for 30 min. The TiO₂ colloid solution was concentrated to TiO₂ 0.25 g/ml.

The preparation of electrodes:

The clean FTO glasses were immersed in 40 mM of a TiCl₄ aqueous solution at 70 °C for 30 min, followed by another heat treatment for 15 min at 450 °C. TiO₂ films were prepared by using the electro-spinning technique. The precursor solution was was composed of ethanol, poly (vinyl alcohol) (PVA, MW=22,000) water solution (33 wt %), TiO₂ colloid solution (0.25 g/mL), deionized water and the core-shell nanomaterials. A series of electrodes were fabricated, which defined as electrode 1, 2, 3, 4, 5, 6 and 7 with different core-shell nanomaterials (TiO₂, Au@SiO₂, Ag@SiO₂, Au@Ag (5nm) @SiO₂, Au@Ag (10nm) @SiO₂, Au@Ag (15nm) @SiO₂ and Au@Ag (25nm) @SiO₂). The precursor solution was sprayed onto the conducting FTO glass slides (the electrospinning method of which is described elsewhere ^{[411}). Then the samples were sprayed at an electric field of 2.3 kV/cm. Finally, the TiO₂ films on the conducting FTO glass slides were calcined at 450 °C for 50 min in air. The treated anodes were immersed in a dye N719 (1.68×10^4 M) for 24 h. The integral DSSCs were composed of a sensitized photoanode, an electrolyte, and a platinum counter electrode. The electrolyte was composed of 0.5 M LiI, 0.05 M I₂, 0.5 M tertbutylpyridine, and 0.6 M 1-propyl-3-methylimidazolium iodide in 3-methoxypropionitrile.

Characterization:

The electrodes were characterized using an X-ray diffractometer (XRD) using Cu K_a radiation, and the scanning speed was 2 °min⁻¹. SEM images were obtained using a JEOL JSM-6700F scanning electron microscope at 3.0 kV. UV-vis spectra were recorded on a Hitachi Model U-4100 spectrophotometer. I-V characteristics of the cell were measured by an electrochemical analyzer (CHI 660D, Chenhua Instruments Co., Shanghai) under solar simulator illumination (CMH-250, Aodite Photoelectronic Technology Ltd., Beijing) at room temperature. The IPCE was measured by illumination with monochromatic light, which was obtained by a series of light filters with different wavelengths.



Figure S1. Images of real electrode: (a) electrode 1 (TiO₂); (b) electrode 6 (Au@Ag(15nm)@SiO₂).



Figure S2. UV-vis absorption of different electrodes (1, 2, 3, 4, 5, 6 and 7) with TiO₂,

Au@SiO₂, Ag@SiO₂, Au@Ag(5nm)@SiO₂, Au@Ag(10nm)@SiO₂,

Au@Ag(15nm)@SiO2 and Au@Ag(25nm)@SiO2.



Figure S3. Typical I-V curve of electrodes 1, 2, 3, 4, 5, 6 and 7 under light (100

 mW/cm^2). (The sensitizer is N719. The cell active area is 0.15 cm²)



Figure S4. Photoluminescence spectra of pure TiO₂ films and TiO₂/Au@Ag@SiO₂ films with different the thickness of Ag shell.

We measured the photoluminescence spectra of different films with a series of core-shell structure nanoparticles. As shown in figure S4, the photoluminescence (PL) spectra of pure TiO₂ films and TiO₂/Au@Ag@SiO₂ films with different thickness of Ag shell from 5nm to 25nm are given under an excitation of the 330 nm line of a Xe lamp. Figure S4 shown the effect of the Ag shell thickness on the photoluminescence intensity of TiO₂ films. The emission spectrum excited at 330 nm exhibited two peaks at 402 and 465 nm, which were corresponding to the reported TiO₂ PL spectra before ^[1]. As shown in figure S4, the PL intensity of TiO₂ increased with the increment of the Ag shell thickness of Au@Ag@SiO₂. When the Ag shell thickness reached 15 nm, the PL intensity of TiO₂ obtained the maximum value. It was attribute to the LSPR effect of plasmon nanoparticles (Au@Ag@SiO₂) to enhance the fluorescence ^[2] and the outer SiO₂ layer of Au@Ag@SiO₂ core shell structure efficiently avoided the fluorescence quenching ^[3]. Therefore, the electrode 6 (Au@Ag(15nm)@SiO₂) under an excitation of the 330 nm obtained a lot of excited electrons comparing with others, which was benefit to improve the photocurrent for DSSCs.



Figure S5. IPCE spectra of electrodes 1, 2, 3, 4, 5, 6 and 7.



Figure S6. (a) EIS: Nyquist plots and (b) Tendency of charge transfer resistance of

the electrodes 1, 2, 3, 4, 5, 6 and 7 under illumination conditions.

Electrodes			J _{sc} (mA/cm ²)	V _{oc} (V)	ff (%)	The averages of values η (%)	Adsorbed dye amount (10 ⁻⁷ mol cm ⁻²)
		1	13.89±0.11	0.679 ± 0.010	68.82±0.16	6.49±0.06	1.978
Light (100 mW/cm ²)		2	14.34±0.11	0.666 ± 0.010	69.71±0.16	6.66±0.05	1.657
		3	15.12±0.78	0.690 ± 0.005	68.56±0.24	7.15±0.07	1.702
		4	15.17±0.13	0.685 ± 0.004	67.89±0.23	7.06±0.06	1.601
		5	15.34±0.13	0.685 ± 0.004	68.94±0.30	7.24±0.13	1.530
		6	16.67±0.09	0.676 ± 0.002	68.16±0.11	7.68±0.04	1.461
		7	14.40±0.25	0.675 ± 0.006	68.37±0.50	6.64±0.05	1.353
monochromatic illumination (10 mW/cm ²)	486nm	1	3.59±0.05	0.604±0.003	67.51±0.12	14.64±0.06	-
		6	5.16 ± 0.05	0.648 ± 0.004	70.02±0.10	23.42±0.07	-
	532nm	1	3.36±0.06	0.593±0.005	67.47±0.17	13.44±0.07	-
		6	4.54±0.03	0.640 ± 0.005	70.65±0.12	20.55±0.08	-

Table S1 Parameters for DSSCs based on the different electrodes [a].

[a] The active area of the photo electrodes for DSSC is kept at 0.15 cm^2 .

References:

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