

Supplementary Information

Photocatalytic Synthesis and Photovoltaic Application of Ag-TiO₂ Nanorod Composites

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Experimental Section

Chemicals

Tetrabutylorthotitanate (TBOT) was obtained from Fluka. Oleylamine, oleic acid, 1-hexadecanol and silver nitrate (AgNO₃, 99%) were purchased from Aldrich Chemical Co. Ethyl alcohol (denatured) and toluene (99.8%) were obtained from Fisher Scientific. All chemicals were used as received without further treatment.

Synthesis of TiO₂ nanorods

TiO₂ nanorods were synthesized using a high-temperature pyrolysis reaction¹. To an oleic acid (22 mL) solution pre-heated at 150 °C under vacuum for 1 hour and cooled down to room temperature, TBOT (3.5 mL) was injected under N₂ flow. The mixture was then heated to 270 °C and kept at this temperature for 3 hours. Ethanol (40 mL) was added after the solution was cooled down to 80 °C. The resulting white precipitate was collected by centrifugation and washed with a toluene/ethanol mixture

several times. The final product was re-dispersed in 20 mL of toluene to form a ~6 mg/mL dispersion.

Photocatalytic Synthesis of Ag-TiO₂ nanocomposites

A stock solution of the silver source was first prepared by mixing 0.60 mmol AgNO₃ with 1 mL of oleylamine under vigorous stirring at room temperature in air for 1 hour, and then with 2 mL toluene under stirring for another hour. In a typical photocatalytic synthesis, the total volume of the reaction solution is fixed at 3.00 mL, containing silver stock solution (1.5 mL), TiO₂ NRs (6 mg/mL, 500 μ L) and toluene (1.0 mL). When required, 1 mL 1-hexadecanol was added to the reaction, either at a low concentration of 0.1 mM or at a high concentration of 0.5 mM. The reaction vial was sealed by a Teflon faced rubber cap and the mixture was subsequently deaerated by gently purging with nitrogen for 15 min. Photochemical reduction was carried out by using a 6 W UV lamp (wavelength 365 nm, BLE-480B, Spectronics Corp.) positioned 10 cm from the reaction vial. Irradiation was typically performed for 30–300 min. The brown nanocomposites were collected by centrifugation and washed with a toluene/ethanol mixture several times. The final product was re-dispersed in 8 mL of toluene for device fabrication.

Device Fabrication:

The inverted OSCs were fabricated with the structure of glass/ ITO/ ETL/ PBDTTT-C:PC₇₁BM/ MoO₃/ Ag. The ITO glass substrates (15 Ω sq⁻¹) were cleaned stepwise in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each, and then dried by nitrogen flow. The pre-cleaned ITO substrate was transferred to a nitrogen-filled glove-box for the following process. The electron transport layer (ETL) was prepared by spin-coating (1500 rpm) a TiO₂ NRs or Ag-TiO₂ nanocomposites toluene solution on a pre-cleaned ITO substrate. After spin-coating, the ETL films were treated by ultraviolet light for 30 min, and annealed at 200 °C for 15 min on a hot plate in

nitrogen to degrade the organics. Subsequently, the photoactive layer (about 80 nm) was prepared by spin coating (1500 rpm) the 1,2-dichlorobenzene solution of PBDTTT-C and PC₇₁BM (1:1.5w/w, polymer concentration of 10 mg/mL) with 3% volume ratio of DIO additive on the ETL films. Finally, a 10 nm MoO₃ layer and 100 nm Ag layer were thermally deposited on the active layer under a vacuum of 2×10^{-4} Pa. The active area of the investigated devices was 4.5 mm².

Characterization:

The morphology of the TiO₂ nanorods and Ag nanoparticles were characterized using a Tecnai T12 transmission electron microscope (TEM). A probe-type Ocean Optics HR2000CG-UV-NIR spectrometer was used to measure the UV-vis spectra of the reaction system to obtain the real-time spectral changes during the formation of silver nanoparticles. The current density–voltage (*J*–*V*) characteristics were measured by using a Keithley 6430 Source Measure Unit. Solar cell performance was measured using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 mW/cm² (SAN-EI Electric XEC-301S solar simulator). The incident photon to current efficiency (IPCE) was measured with a Zolix Solar Cell Scan100.

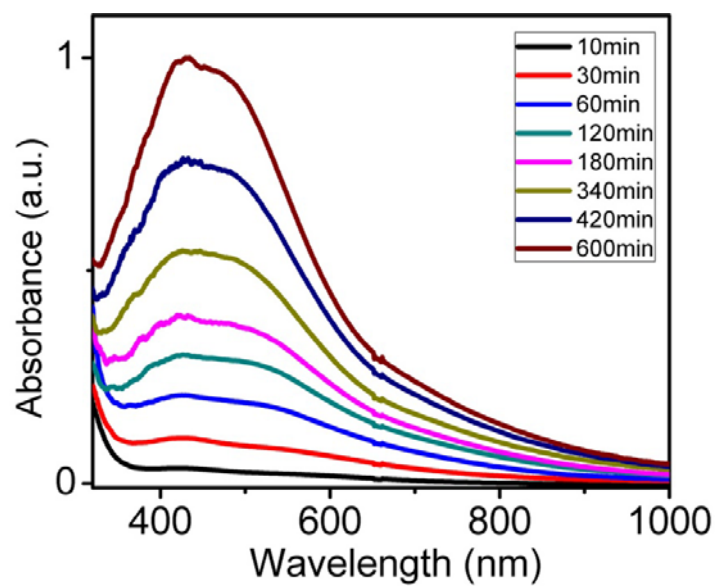


Figure S1. Absorption of Ag-TiO₂ nanocomposite solutions prepared with different irradiation time.

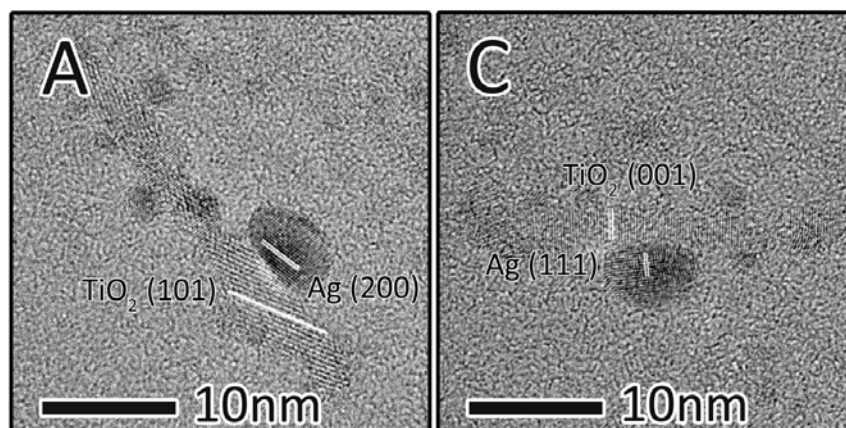


Figure S2. HRTEM image of the Ag-TiO₂ nanorod composites formed by UV irradiation for 300 min.

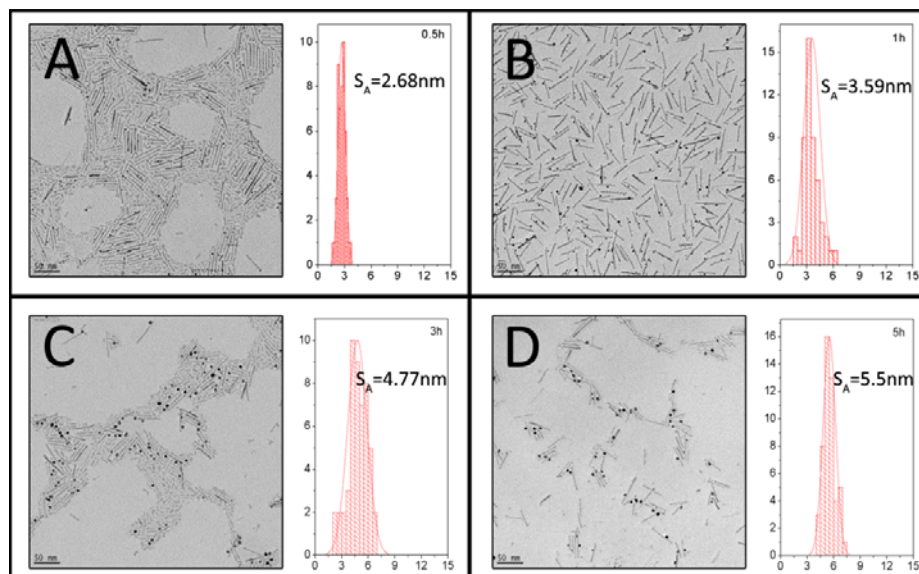


Figure S3. TEM images and particle size distribution histograms of Ag grown on TiO₂ nanorods without 16-OH under UV irradiation for (A) 30 min, (B) 60 min, (C) 180 min, and (D) 300 min.

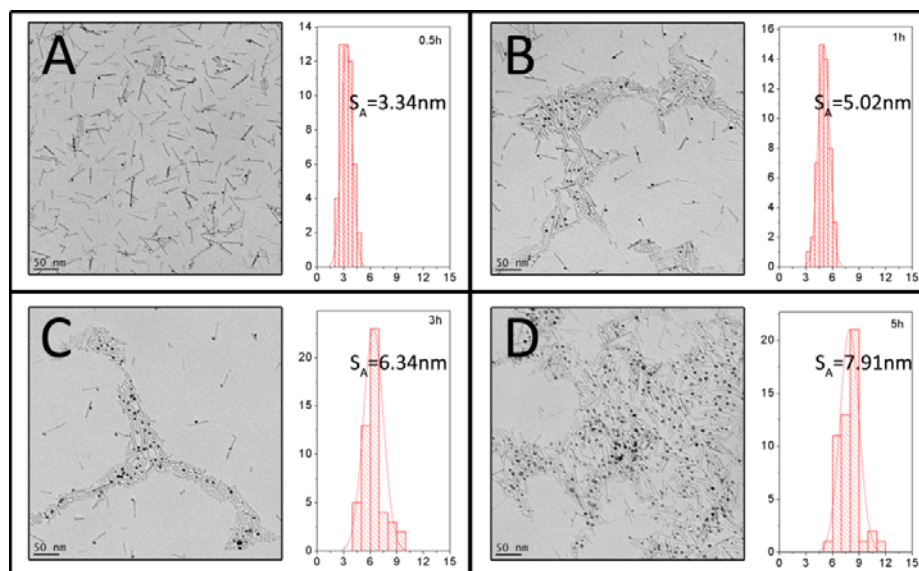


Figure S4. TEM images and particle size distribution histograms of Ag grown on TiO₂ nanorods using a low concentration (0.1 mM) of 16-OH under UV irradiation for (A) 30 min, (B) 60 min, (C) 180 min, and (D) 300 min.

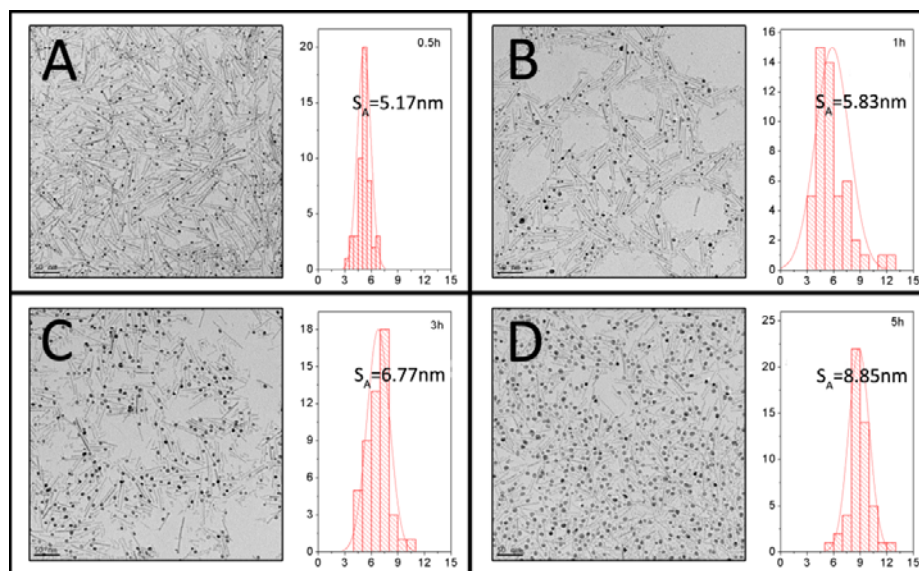


Figure S5. TEM images and particle size distribution histograms of Ag grown on TiO₂ nanorods using a high concentration (0.5 mM) of 16-OH under UV irradiation for (A) 30 min, (B) 60 min, (C) 180 min, and (D) 300 min.

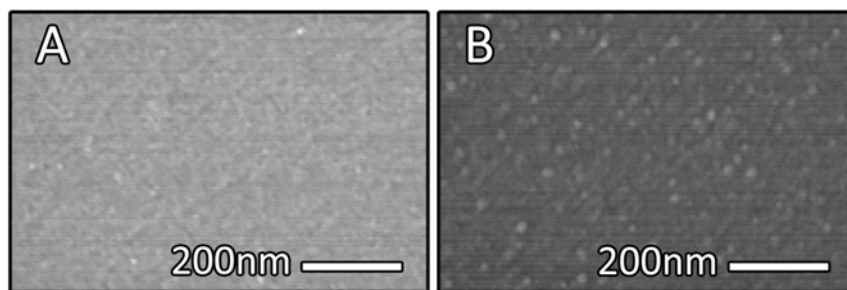


Figure S6. (A) SEM image of the TiO_2 nanorods spin-coated on an ITO substrate. (B) SEM image of Ag- TiO_2 nanorod composites spin-coated on ITO substrate. To clean up the organic ligands on surface, UV irradiation was applied to the sample for 300 min.

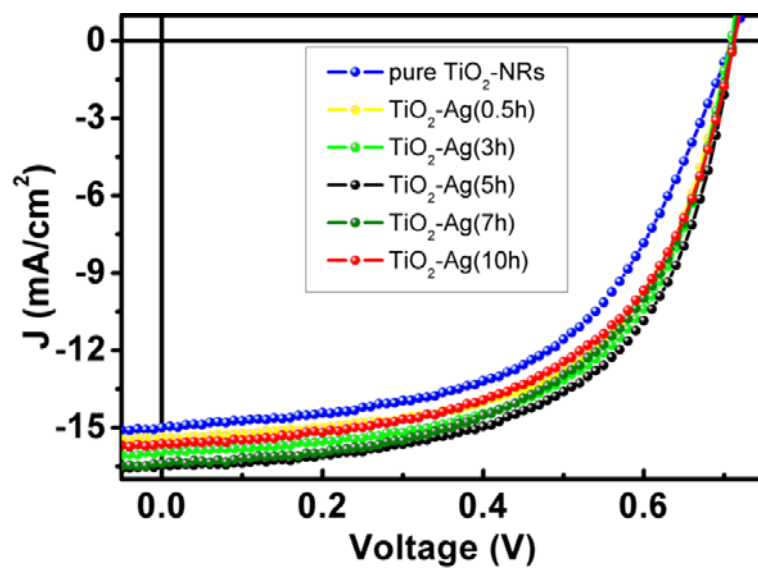


Figure S7. The current density versus voltage (J - V) characteristics of the devices with various electron transport layers taken under Air Mass 1.5 Global (AM 1.5 G) solar simulator illumination.

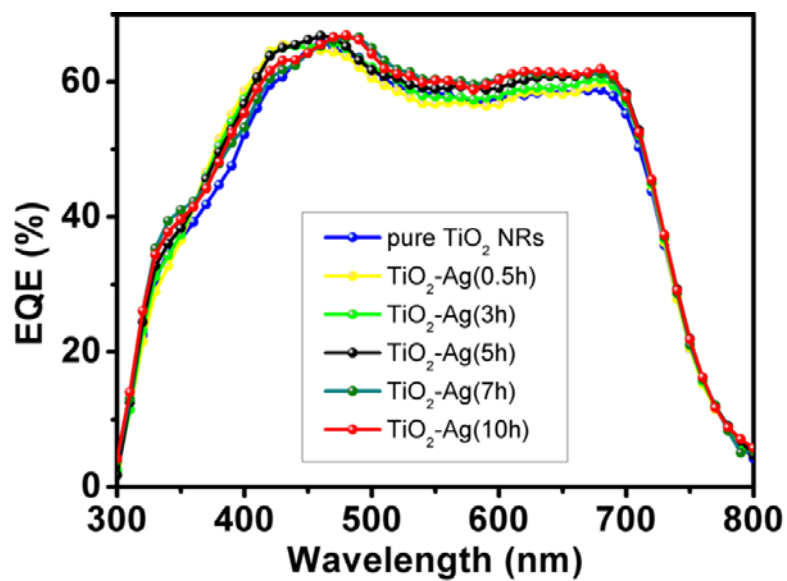


Figure S8. External quantum efficiency (EQE) of the devices with different electron transport layers.

Reference:

1. J. Joo, S. G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon and T. Hyeon, *J. Phys. Chem. B*, 2005, **109**, 15297-15302.