Electronic Supplementary Information

Plasmon-enhanced dye-sensitized solar cells using SiO_2 spheres deco rated with tightly assembled silver nanoparticles

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1. Materials

Tetraethylorthosilicate (TEOS), 3-mercaptopropyl trimethoxysilane (MPTS), ethylene glycol (E G), poly(vinyl pyrrolidone) (PVP, MW ~40,000), silver nitrate ($AgNO_3$, 99.99+%), octylamine (OA), and all components of electrolyte were purchased from Sigma-Aldrich and used without fur ther purification. Ammonium hydroxide (NH_4OH, 27%) and ethanol (98%) were purchased from Daejung Chemical. N719 (cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)) dye was purchased from Solaronix.

2. Preparation of SiO_2 spheres decorated with tightly assembled silver nanoparticles

Tetraethylorthosilicate (TEOS, 1.6 mL) was dissolved in 40 mL of absolute ethanol, followed b y addition of a 3 mL portion of aqueous ammonium hydroxide (27%). The resulting mixture was vigorously stirred using magnetic bar for 20 h at 25 °C. The resulting silica spheres were centrifu

ged and then washed with ethanol five times to remove the excess reagents. These silica spheres were then functionalized with thiol group. Silica spheres (150 mg) were dispersed in 3 mL ethan ol containing 150 μL of MPTS and 30 μL of aqueous ammonium hydroxide (27 %). The mixture was stirred for 12 h at 25 °C. The resulting MPTS-treated silica spheres were centrifuged and wa shed with ethanol several times. In order to fabricate SiO_2 spheres decorated with tightly assembl ed silver nanoparticles (SiO_2-t-Ag), 25 mg portion of MPTS-treated silica spheres was thoroughl y dispersed in 100 mL of $AgNO_3$ solution (3.5 mM in ethylene glycol). An 82.7 μL of octylamin e (5 mM) was then rapidly added into the MPTS-treated silica spheres dispersion. The resulting mixture was stirred for 1 h at 25 °C. Afterwards, SiO_2 spheres decorated with tightly assembled s ilver nanoparticles were centrifuged and washed with ethanol five times for purification. In case of SiO_2 spheres decorated with sparsely assembled silver nanoparticles (SiO_2-s-Ag), 50 mg of M PTS-treated silica spheres was used in the same reaction condition except amount of SiO_2 sphere.

For silica coating to SiO_2 spheres decorated with tightly assembled silver nanoparticles, a 1 mL portion of MPTS solution (2 mM in ethanol) was added into 1 mg of silver nanoparticles-decorat ed silica spheres. The resulting dispersion was shaken for 1 h at 25 °C. The silver nanoparticles-d ecorated silica spheres were transferred to 50 mL of 2-propanol with 1 mg of PVP (MW ~40,000). A 2 ml of ammonium hydroxide was added to the reaction mixture under vigorous stirring, foll owed by the addition of 250 μL of TEOS solution (TEOS/2-propanol, 0.8 v/v %) in two separate portions with a time interval of 30 min. After adding the TEOS, the mixture was allowed to react for 12 h. Finally, the resulting silica coated SiO_2 spheres decorated with tightly assembled silver nanoparticles (SiO_2-t-Ag@SiO_2) were centrifuged and washed with ethanol five times.

3. Preparation of the photoanodes

F-doped SnO_2 (FTO) glass plates (8 Ω/cm^2, Pilkington TEC glass^{TM}) were cleaned in detergent s

olution using an ultrasonic bath for 20 min and washed with tap water and ethanol. The plates we re immersed in 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min and rinsed with DI water and ethanol. The photoanode pastes incorporating SiO_2-t-Ag@SiO_2 or SiO_2 were prepared by simple mixing. The SiO_2-t-Ag@SiO_2 or SiO_2 in ethanol solutions (SiO_2 to TiO_2 ratio = 1, 3 wt%) were mixed with commercial TiO_2 pastes (Dyesol, DSL 18NR-T), and they were stirred for 2 h and di spersed by ultrasonicator. Then ethanol was removed by rotary evaporator. The photoanode films were prepared by Doctor blade printing on $TiCl_4$-treated FTO plates, and annealed at 500 °C for 15 min. The thickness and the active area of photoanode films were controlled to 6 μm and 0.202 5 cm^2.

4. Assembly of dye-sensitized solar cells

Cathodes were prepared by thermal deposition. A drop of 10 mM H_2PtCl_6 in 2-propanol was spr ead on FTO glass plate by spin coating followed by heating to 400 °C for 15 min. The prepared p hotoanode was assembled with Pt counter electrode (with drilled hole) into sandwich-type cell us ing thermal adhesive film (Surlyn: 30 μm, Dupont). The electrolyte solution was prepared by mix ing 0.60 M 1-butyl-3-methylimidazolium iodide, 0.03 M I_2, 0.10 M guanidinium thiocyanate and 4-*tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (v/v, 85:15). Before the measure ment of photovoltaic performance, a mask of 0.16 cm^2 was attached on the outside of FTO glass having the photoanode.

5. Instruments

UV-Vis absorption spectra of the particles in solutions were collected by a UV-Visible spectro

meter (Mecasys Co. Ltd., Optizen 2120 UV). UV-vis absorption and reflectance spectra of the ph otoanodes were collected by UV-vis spectrometer (Jasco, V-670) with integrated sphere. A TE M images were obtained using EF-TEM (Carl Zeiss, LIBRA 120). The photovoltaic performance was measured using a 500 W xenon lamp (XIL model 05A50KS source measure units and an A M 1.5 filter) at a power of 100 mW/cm^2. The incident photon-to-current efficiency was measured using solar cell quantum efficiency measurement system (QEX10, PV measurements, Inc.).

6. Individual silver nanoparticles and SiO_2 spheres decorated with sparsely assembled silve r nanoparticles (SiO_2-s-Ag)

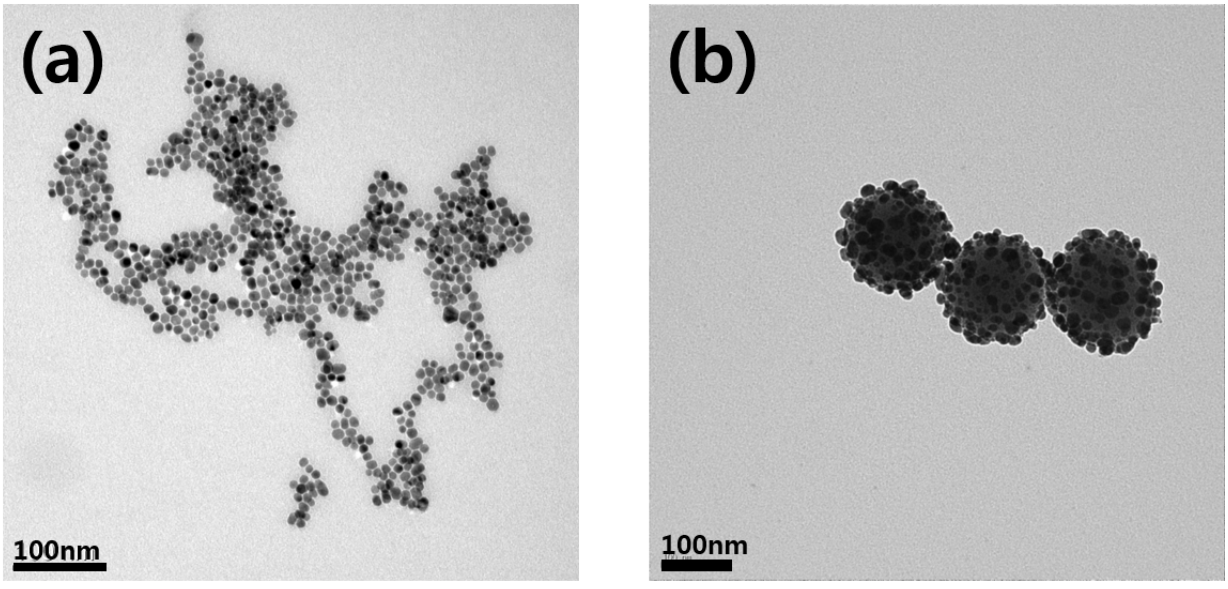

Fig. S1 TEM image of (a) individual Ag NPs and (b) SiO_2 spheres decorated with sparsely assembled silver nanopar ticles (SiO_2-s-Ag).

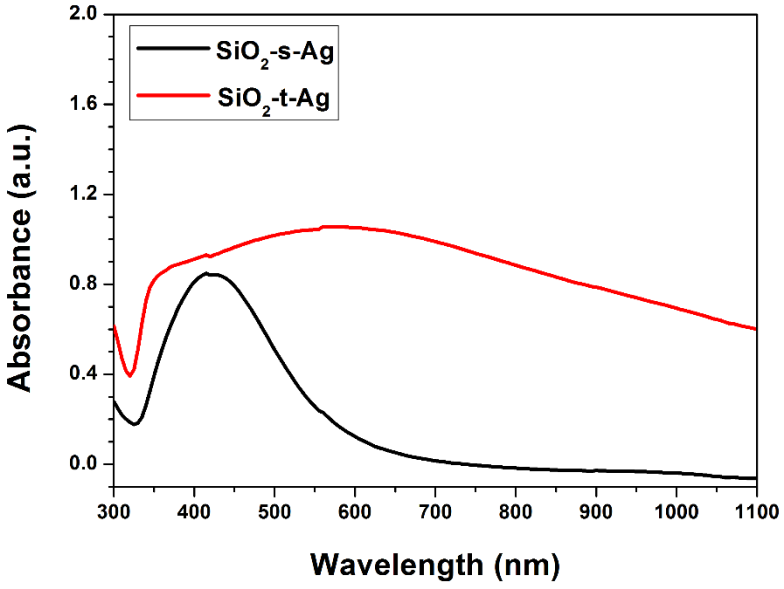

Fig. S2 UV-vis absorption spectra of SiO_2 spheres decorated with sparsely assembled silver nanoparticles (SiO_2-s-Ag) and SiO_2 spheres decorated with tightly assembled silver nanoparticles (SiO_2-t-Ag).

7. UV-vis absorption and diffused reflectance spectra of photoanodes before dye-adsorption

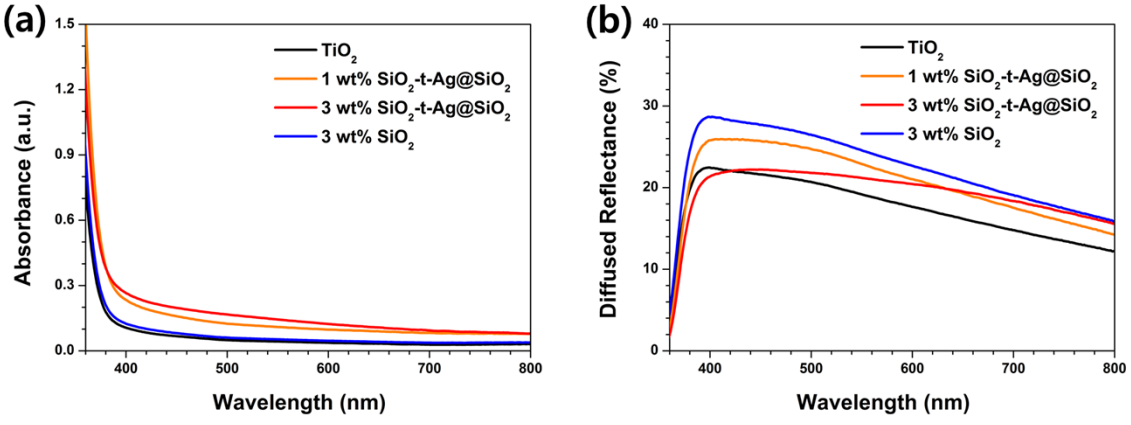

Fig. S3 (a) UV-vis absorption spectra of photoanodes before dye-adsorption (b) UV-vis diffused reflectance spectra of photoanodes before dye-adsorption.

8. Optical and photoelectrochemical properties of 5 wt% SiO_2-t-Ag@SiO_2 photoanode cell

To obtain an optimized performance, paste containing 5 wt% of SiO_2-t-Ag@SiO_2 was prepared. The photoanode containing 5 wt% of SiO_2-t-Ag@SiO_2 shows stronger UV-vis absorption because of higher concentration of SiO_2-t-Ag@SiO_2. (Fig. S4(a)) However, It exhibit lower photo-current and power conversion efficiency than 3 wt% cell. (Fig. S4(b,c)) It is mainly due to excessive light absorption by SiO_2-t-Ag@SiO_2, which isn`t delivered to the sensitizer completely.

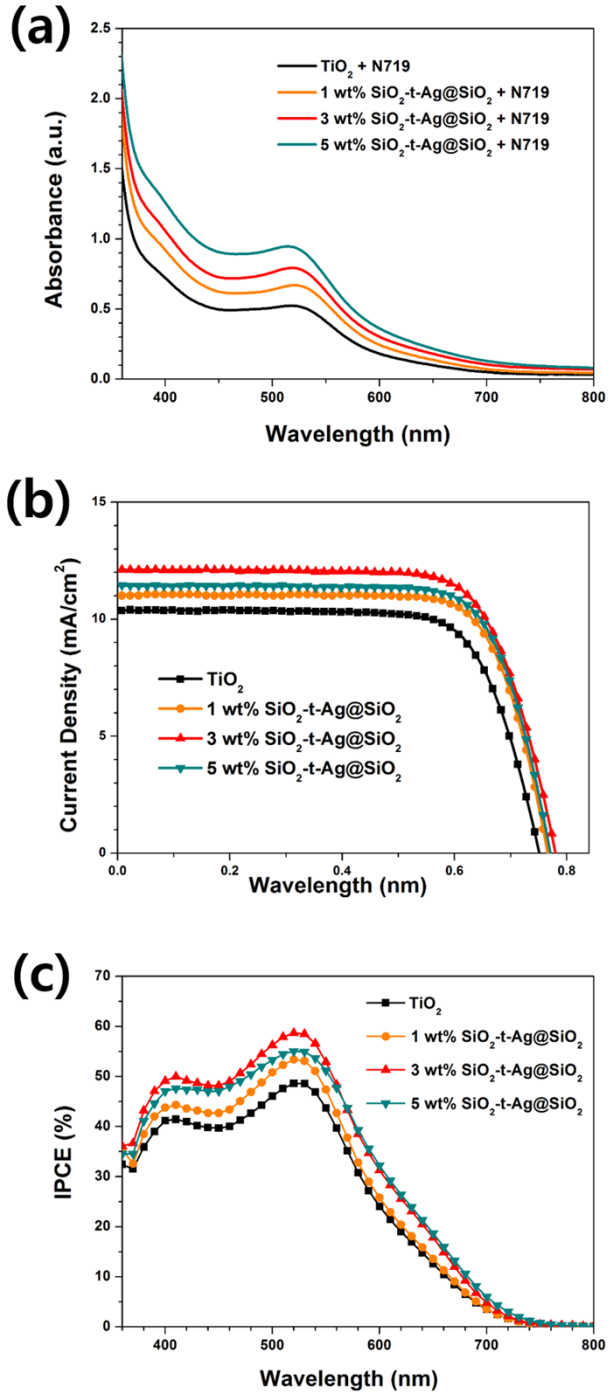

Fig. S4 (a) UV-vis absorption spectra of photoanodes, (b) *J-V* curves of DSSCs, (c) IPCE spectra of DSSCs.

9. Discrete Dipole Approximation (DDA) simulations

To further study the origin of the increased short-circuit current, we simulated the electric filed distribution around the light-illuminated SiO_2 sphere decorated with silver nanoparticles by using the DDSCAT 7.1 package [1]. In our simulation, isotropic dipoles are evenly placed in silver nan oparticles at dipole–dipole distances of 2 nm. These silver nanoparticles were 20 nm in diameter, and the distance between each silver nanoparticle is about 2 nm, and silica core was 160 nm in di ameter. From this DDA simulation results, a strong electric field at the surface of silver was obse rved. Also, the enhanced field was confirmed outside of the SiO_2 shell. The enhanced electric fiel d around silver nanoparticle increases the absorption of N719 dye adsorbed on adjacent TiO_2.

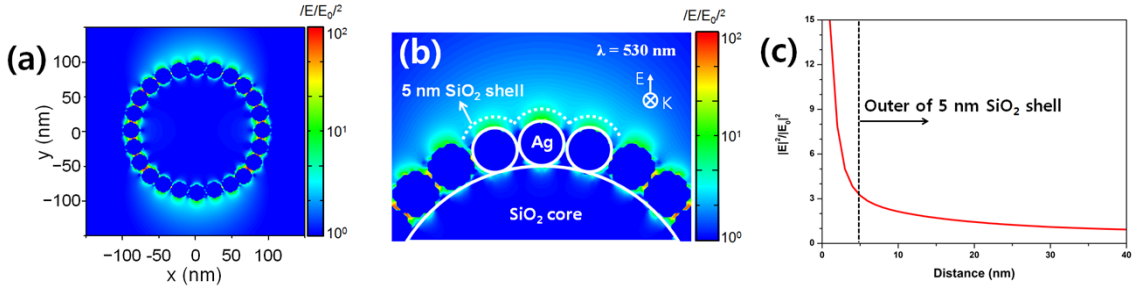

Fig. S5 (a) Electric field intensity distribution in SiO_2 sphere decorated with silver nanoparticles, (b) showing a clos e up silver nanoparticle surface, (c) Intensity of electric fields with respect to the distance from silver nanoparticle.

10. Photovoltaic characteristics of DSSCs with 12 µm photoanodes (TiO_2 and 3 wt% SiO_2-t-Ag@SiO_2)

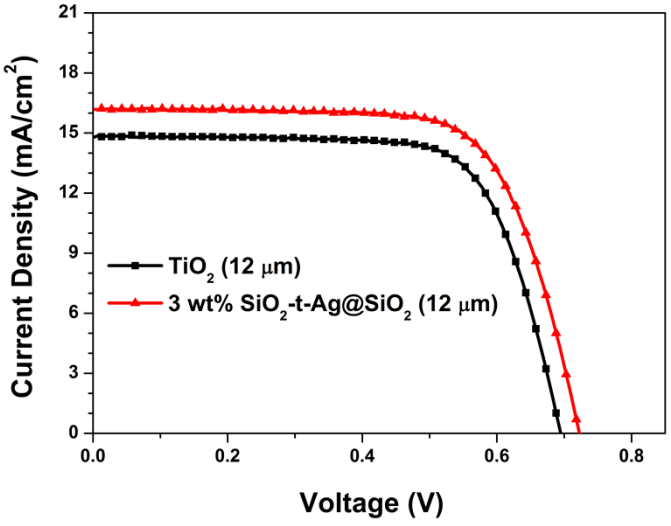

Fig. S6 *J-V* curves of DSSCs with 12 μm photoanodes.

Table S1 Photovoltaic parameters of DSSCs with 12 μm photoanodes

Photoanode	J_{SC} (mA/cm^2)	V_{OC} (V)	*ff*	η (%)
TiO_2 (12 μm)	14.84	0.703	0.71	7.44
3 wt% SiO_2-t-Ag@SiO_2 (12 μm)	16.18	0.731	0.70	8.31

11. Absorbed photon-to-current conversion efficiency (APCE)

The absorbed photon-to-current conversion efficiency (APCE) was calculated by dividing measured incident photon-to-current conversion efficiency (IPCE) by light harvesting efficiency (LHE = 1 - 10^{-A}, with A being the absorbance of the film). APCE spectra of samples are similar because the plasmonic particle does not affect the quantum yield for the electron injection or efficiency of transporting injected electrons, whereas total amount of absorbed photons is affected. At wavelength above 550 nm, APCE of 3 wt% SiO_2-t-Ag@SiO_2 is lower than that of TiO_2, because SiO_2-t-Ag@SiO_2 absorbs too many photons that do not participate in charge

generation.

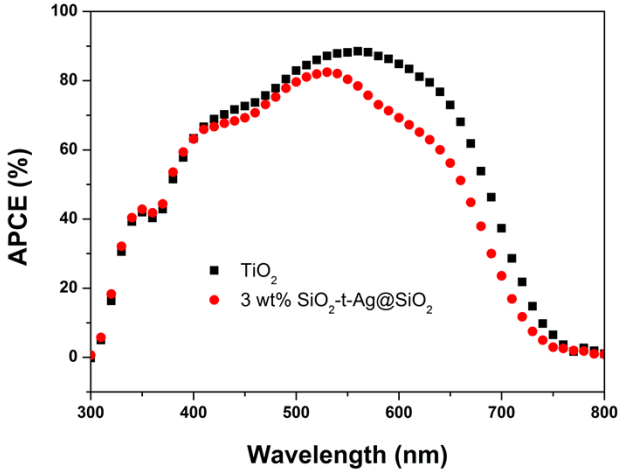

Fig. S7 Absorbed photon-to-current conversion efficiency

References

[1] B. T. Draine, P. J. Flatau, **2010**, "User Guide to the Discrete Dipole Approximation Code DD SCAT 7.1", http:// http://arxiv.org/abs/1002.1505