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Plasmonic Enhancement of the Optical Absorption and Catalytic Efficiency of $BiVO_4$ Photoanodes Decorated with $Ag@SiO_2$ Core-Shell Nanoparticles

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental section

BiVO$_4$ and Ag@SiO$_2$ decorated BiVO$_4$ photoanode

Dense thin films of BiVO$_4$ were prepared by spray pyrolysis, as reported in our previous publications.[1, 2] The substrates are FTO-coated glass (fluorine-doped tin dioxide, 15 Ω/□, TEC-15, Hartford Glass Co.), which were cleaned by three successive 15 min. ultrasonic rinsing treatments in a Triton® solution, acetone and ethanol. A total of 100 cycles were used to deposit the 100 nm-thick films. Prior to deposition of the BiVO$_4$, a SnO$_2$ interfacial layer (~80 nm) was deposited onto the FTO substrate to prevent recombination at the FTO/BiVO$_4$ interface.[2, 3] After deposition, the SnO$_2$/BiVO$_4$ samples were subjected to an additional 2-hour heat treatment in a tube furnace at 450^{o}C in air.

To prepare the Ag@SiO$_2$ decorated BiVO$_4$ photoanode (Ag@SiO$_2$/BiVO$_4$), Ag@SiO$_2$ core-shell nanoparticles were used as received (Silica shelled BioPureTM Silver, MilliQ water as the solvent, Nanocomposix). The diameter of the Ag core is ~50 nm and the thickness of the SiO$_2$ shell is ~10 nm. The nanoparticles-containing solution (1.4×10^{12} particles/mL) was then doctor-bladed on the surface of the spray-deposited BiVO$_4$ photoanode, and dried in atmospheric pressure at room temperature.

Characterization and measurements

Transmission electron micrograph was taken with Philips CM 12 Transmission Electron Microscope. Scanning electron micrograph was taken using JEOL JSM 6500F Scanning Electron Microscope at an accelerating voltage of 15 kV. Atomic force microscope image was taken with an NT-MDT NTEGRA Scanning Probe Microscope. The UV-Vis absorptions were measured with a Perkin Elmer Lambda 900 spectrometer.

Photoelectrochemical characterization was carried out in an aqueous 0.1 M potassium phosphate buffer (KPi, pH ~7) using a three-electrode configuration. The potential of the working electrode was controlled by a potentiostat (EG&G PAR 283). An Ag/AgCl electrode (XR300, saturated KCl+AgCl solution (KS120), Radiometer Analytical) and a coiled Pt wire were used as the reference and counter electrodes, respectively. The potentials vs Ag/AgCl were converted to the reversible hydrogen electrode (RHE) using the following relationship,

$$V_{RHE} = V_{Ag/AgCl} + V^0_{Ag/AgCl\ vs.\ NHE} + 0.059\,pH \tag{S1}$$

where $V^0_{Ag/AgCl\ vs.\ NHE}$ is 0.199 V at 25°C. White-light photocurrent measurements were performed under simulated AM1.5 solar illumination (100 mW/cm^2) with a Newport Sol3A Class AAA Solar Simulator (type 94023A-SR3). Monochromatic photocurrents were measured with a 300 W Xenon arc lamp (Oriel, model 6259) coupled into a grating monochromator (Acton SpectraPro 150i). An electronic shutter (Uniblitz LS6) was used, and a long-pass colored glass filter (Schott, 3 mm thick) was placed between the monochromator and the sample to remove second-order diffracted light. The shutter was actuated every 10 seconds, and the photocurrent was taken as the difference between the current when the shutter is opened and closed (3 seconds integration time and ~7 nm step size). The Incident Photon to Current Efficiency (IPCE, sometimes called the External Quantum Efficiency or EQE) is then calculated based on the following formula:

$$IPCE\ (\%) = \frac{1240 \times j_{ph}\ (\mathrm{mA/cm^2})}{P_{light}\ (\mathrm{mW/cm^2}) \times \lambda\ (\mathrm{nm})} \times 100\% \tag{S2}$$

where j_{ph} is the steady-state photocurrent density at a specific wavelength, and λ is the wavelength of the incident light. P_{light} is the light intensity for wavelength λ at the film surface. The illumination intensity from the Xenon source was measured with a calibrated photodiode (Ophir PD300-UV).

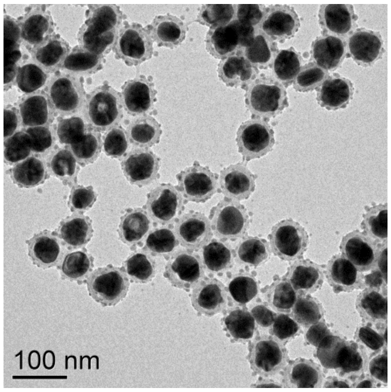

Figure S1. Transmission electron micrograph of the Ag@SiO$_2$ core-shell nanoparticles.

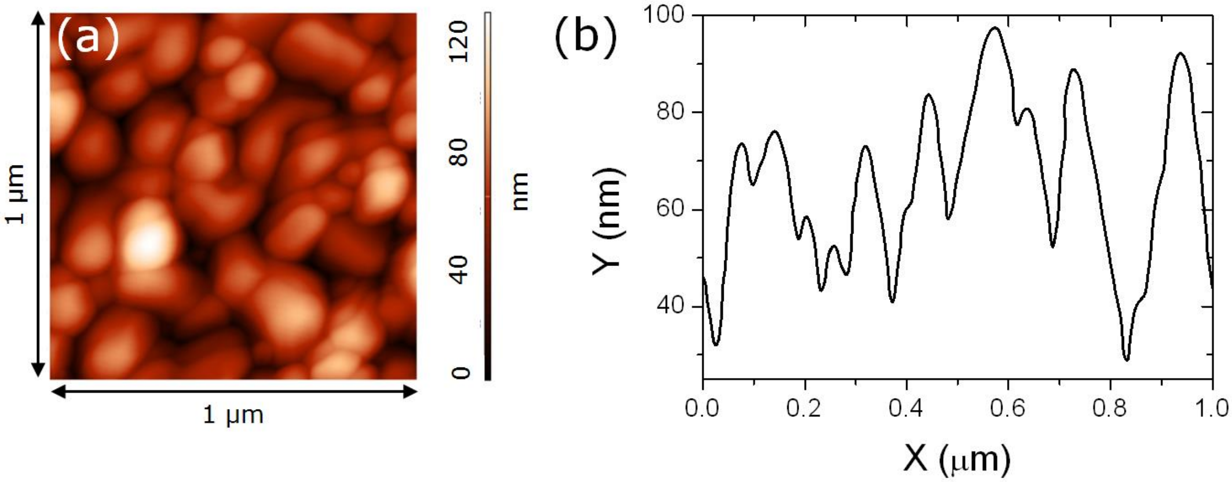

Figure S2. (a) Atomic force microscope (AFM) image of the surface of 100 nm-thick, spray deposited BiVO$_4$ photoanode. A representative surface profile is shown in **(b)**.

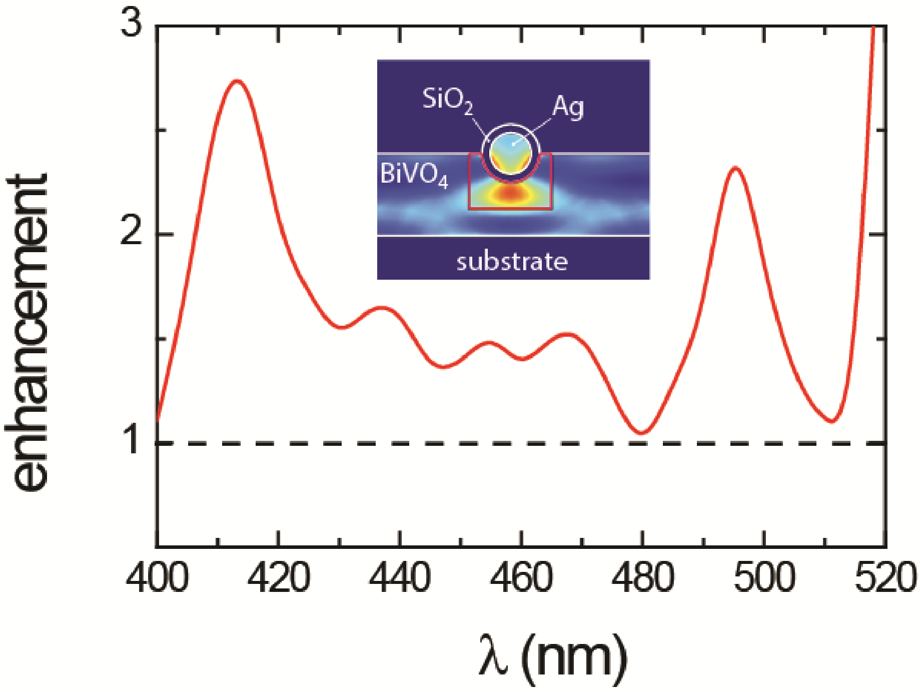

Figure S3. Calculated enhancement of Ag@SiO$_2$ on BiVO$_4$, considering only the small area confined by the red lines shown in the inset. Inset also shows simplified geometry of the sample and the colorplot of the full-field electromagnetic simulated enhancement for excitation of 415 nm.

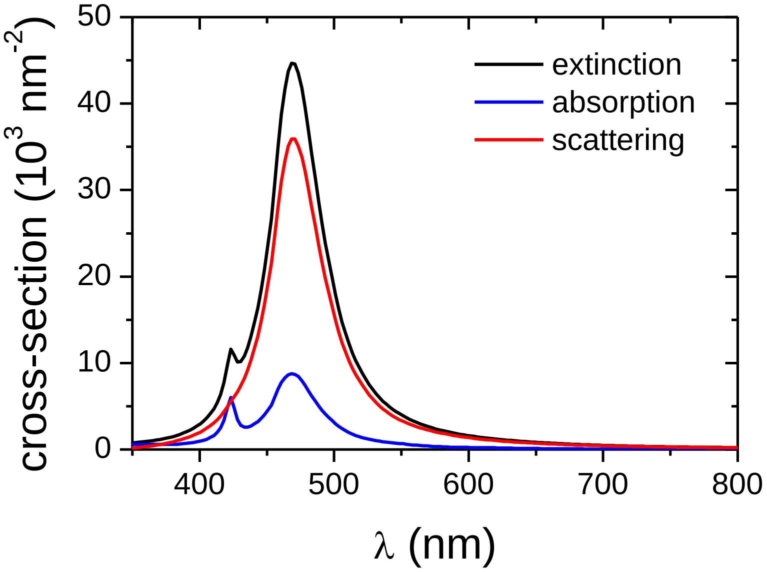

Figure S4. Calculated total extinction (black), absorption (blue), and scattering (red) cross-section for a single Ag@SiO$_2$ core-shell nanoparticle. The surrounding medium is water. The diameter of the Ag core is 50 nm and the thickness of the SiO$_2$ shell is 10 nm. Data obtained by using a web-applet for Mie light scattering by a single coated sphere (http://garciadeabajos-group.icfo.es/widgets/index.html) following web-applet. Calculation method and examples are shown in the literature.[4, 5]

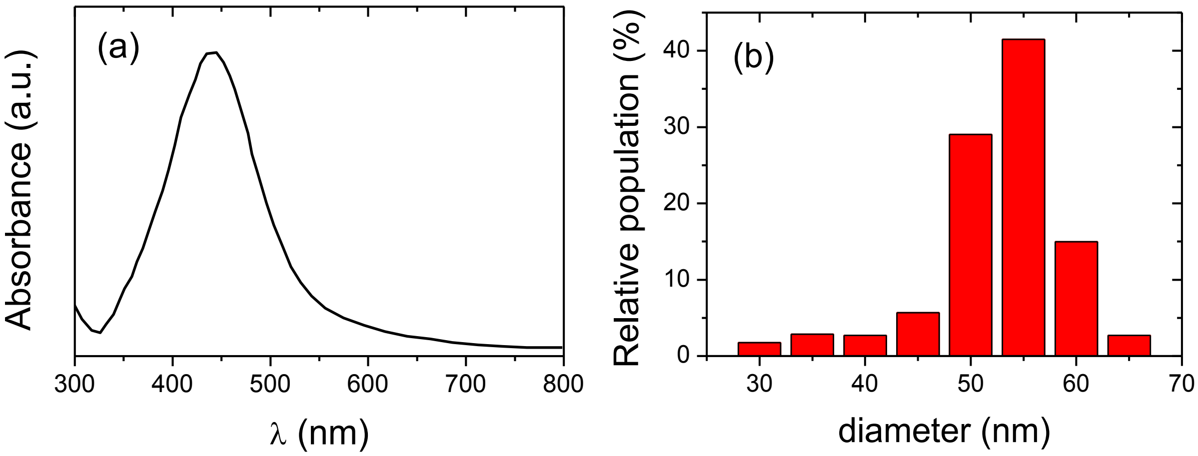

Figure S5. (a) Measured absorbance and **(b)** particle size distribution of the Ag@SiO_2 nanoparticles used in this work.

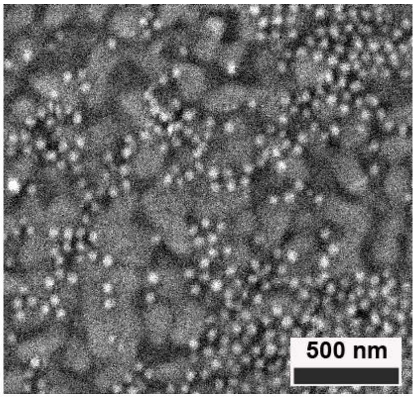

Figure S6. Scanning electron micrograph of the surface of $BiVO_4$ photoanode decorated with Ag@SiO_2 core-shell nanoparticles.

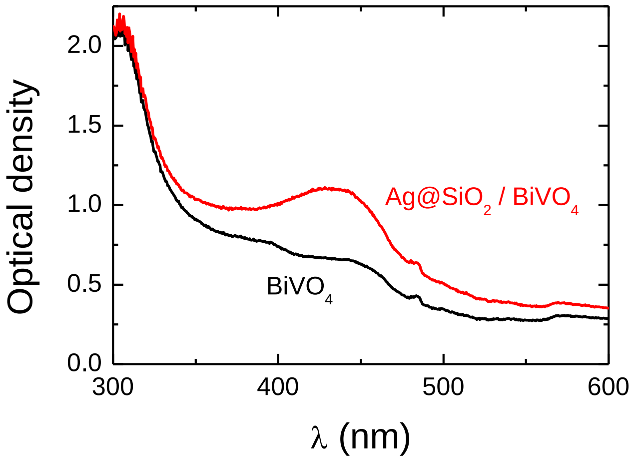

Figure S7. Optical density of bare $BiVO_4$ (black) and $Ag@SiO_2/BiVO_4$ (red) photoanode.

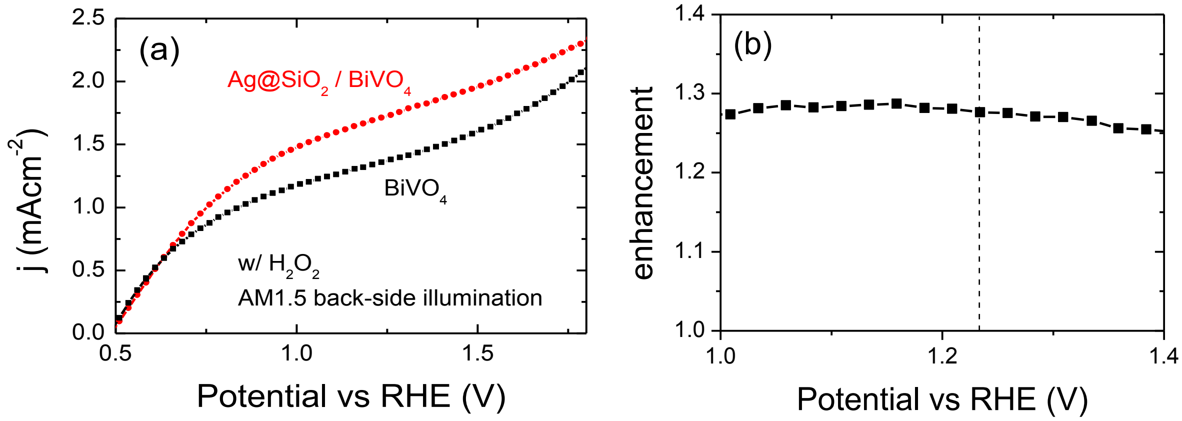

Figure S8. (a) AM1.5 photocurrent vs voltage (J-V) curve of bare $BiVO_4$ (black) and $Ag@SiO_2/BiVO_4$ (red) photoanode under backside illumination in the presence of H_2O_2 in the electrolyte. The scan rate is 50 mV/s. **(b)** The enhancement of $Ag@SiO_2/BiVO_4$ in H_2O_2 (i.e., the normalization of the red curve to the black curve in Fig. S5a).

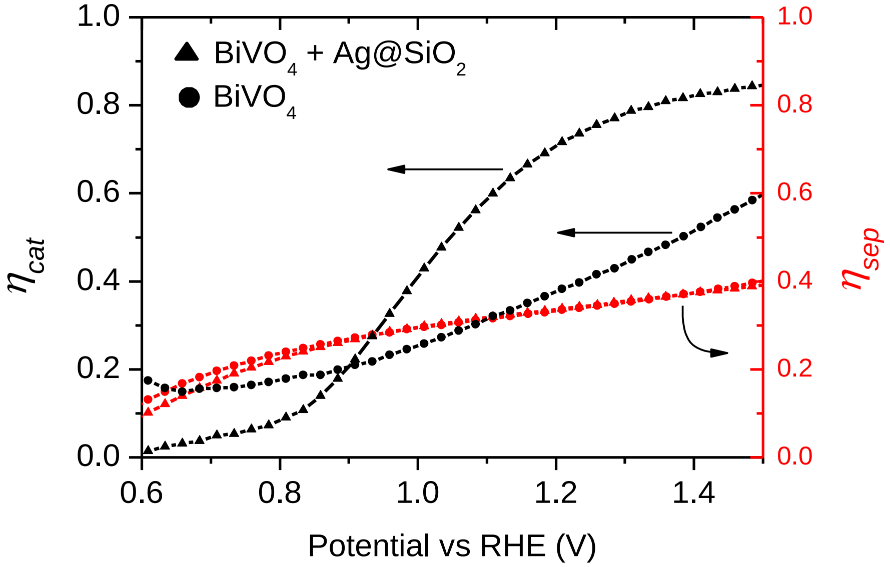

Figure S9. Catalytic (η_{cat}) and carrier separation (η_{sep}) efficiencies of bare (circle) and Ag@SiO$_2$ decorated BiVO$_4$ photoanode (triangle). These efficiencies are calculated according to the following equations: $\eta_{cat} = \frac{J_{H_2O}}{J_{H_2O_2}}$ and $\eta_{sep} = \frac{J_{H_2O_2}}{J_{abs}}$. J_{H_2O} and $J_{H_2O_2}$ are the photocurrents in electrolyte without and with H$_2$O$_2$, respectively, and J_{abs} is the photon-absorption rate expressed as current density.

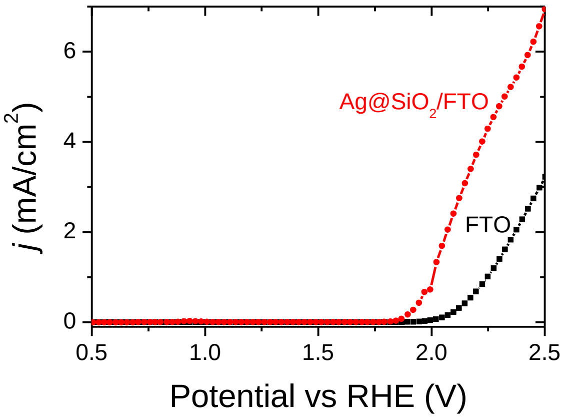

Figure S10. Dark current vs voltage (J-V) curve of bare FTO substrate (black) and Ag@SiO$_2$ decorated FTO (red) in 0.1 M phosphate electrolyte (pH 7). The cathodic shift in the onset potential of Ag@SiO$_2$ decorated FTO illustrates the catalytic activity of Ag@SiO$_2$ nanoparticles.

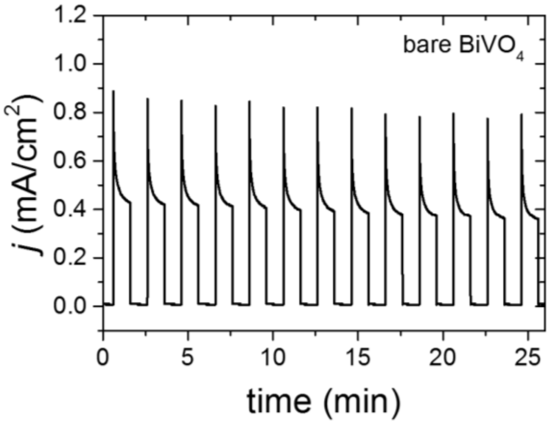

Figure S11. Chronoamperometry plot of bare BiVO$_4$ under back-side chopped AM1.5 illumination at 1.23 V vs RHE.

REFERENCES

1. F. F. Abdi, N. Firet and R. van de Krol, *ChemCatChem*, 2013, **5**, 490-496.
2. F. F. Abdi and R. van de Krol, *J. Phys. Chem. C*, 2012, **116**, 9398-9404.
3. Y. Q. Liang, T. Tsubota, L. P. A. Mooij and R. van de Krol, *J. Phys. Chem. C*, 2011, **115**, 17594-17598.
4. F. J. García de Abajo, *Physical Review B*, 1999, **60**, 6086-6102.
5. V. Myroshnychenko, J. Rodriguez-Fernandez, I. Pastoriza-Santos, A. M. Funston, C. Novo, P. Mulvaney, L. M. Liz-Marzan and F. J. Garcia de Abajo, *Chem. Soc. Rev.*, 2008, **37**, 1792-1805.