Supplementary Information

# Plasmonically sensitized metal-oxide electron extraction layers for organic solar cells

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**Figure S1** shows the statistical assessment of the AgNP formed upon thermal evaporation of a nominally 0.5-0.6 nm thick Ag layer (mass thickness according to quartz crystal microbalance) on top of a $TiO_x$ film. The particles are typically of semi-spherical shape. As can be seen, there are a few particles with a diameter of up to 60 nm. For automated particle counting and area assessment, we used the freely available software ImageJ (available from http://rsbweb.nih.gov/ij/). The SEM image seen in **Figure S1a** has first been thresholded to form a B/W image as seen in **Figure S1b**. An area coverage of roughly 6% is determined with a weighted average particle size of 11 nm. Even though most AgNPs are sizes less than 15 nm in diameter (Figure S1c), the relative contribution by the few larger sized particles to the total amount of Ag is significant. In a rough estimate, the amount of silver concentrated in the AgNP corresponds well to the 0.5-0.6 nm equivalent layer thickness as monitored by QCM. It has to be noted, that particles of less than 3 nm are below the resolution of our SEM equipment, therefore we excluded particles with a size of less than 3 nm from this analysis. Rutherford backscattering analysis (RBS) yielded a silver surface coverage of $3.4\text{-}4\times10^{15}$ atoms/cm$^2$. This corresponds to roughly 2.4-2.8 monolayers, as one monolayer of silver is equivalent to $1.4\times10^{15}$ atoms/cm$^2$. [1] The shape, size and distribution of Ag particles formed by thermal evaporation of Ag on $TiO_2$ single crystal surfaces have been studied by many authors.[2-8] For nominally two monolayers of Ag on $TiO_2$(110), Luo et al. have found Ag clusters with a typical size of 3-5 nm.[5] In the case of Ag deposited on slightly oxygen deficient $TiO_2$, substantial Ostwald ripening and cluster growth was encountered in the presence of Oxygen.[4] It is likely that a similar ripening process accounts for the formation of the larger Ag clusters seen in Fig. S1.

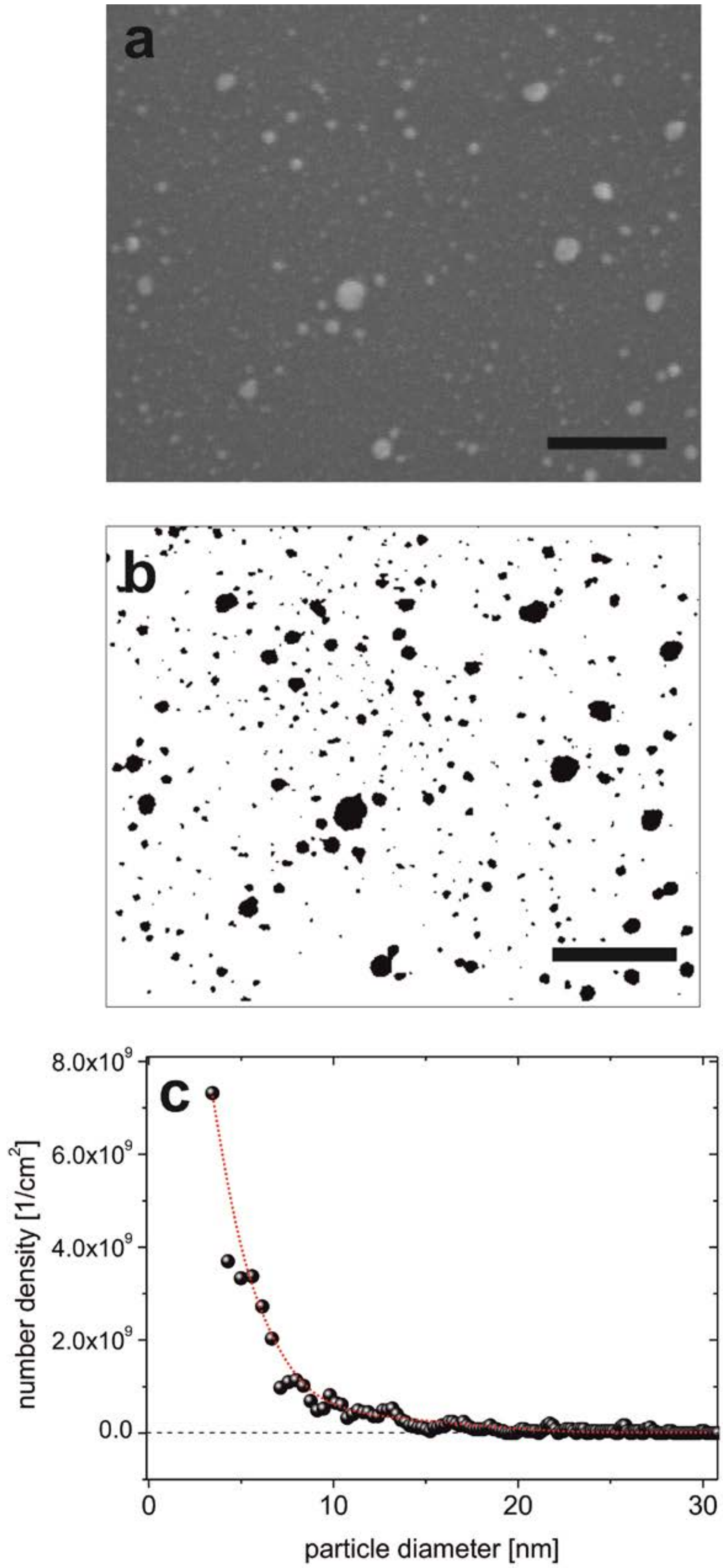


**Figure S1:** (a) Plan-view SEM image of AgNP on top of $TiO_x$. (b) Thresholded black and white image of (a). The scale bar is 200 nm. (c) Resulting number density of AgNP vs. particle diameter (assuming a spherical particle shape). The red line is guide to the eye.

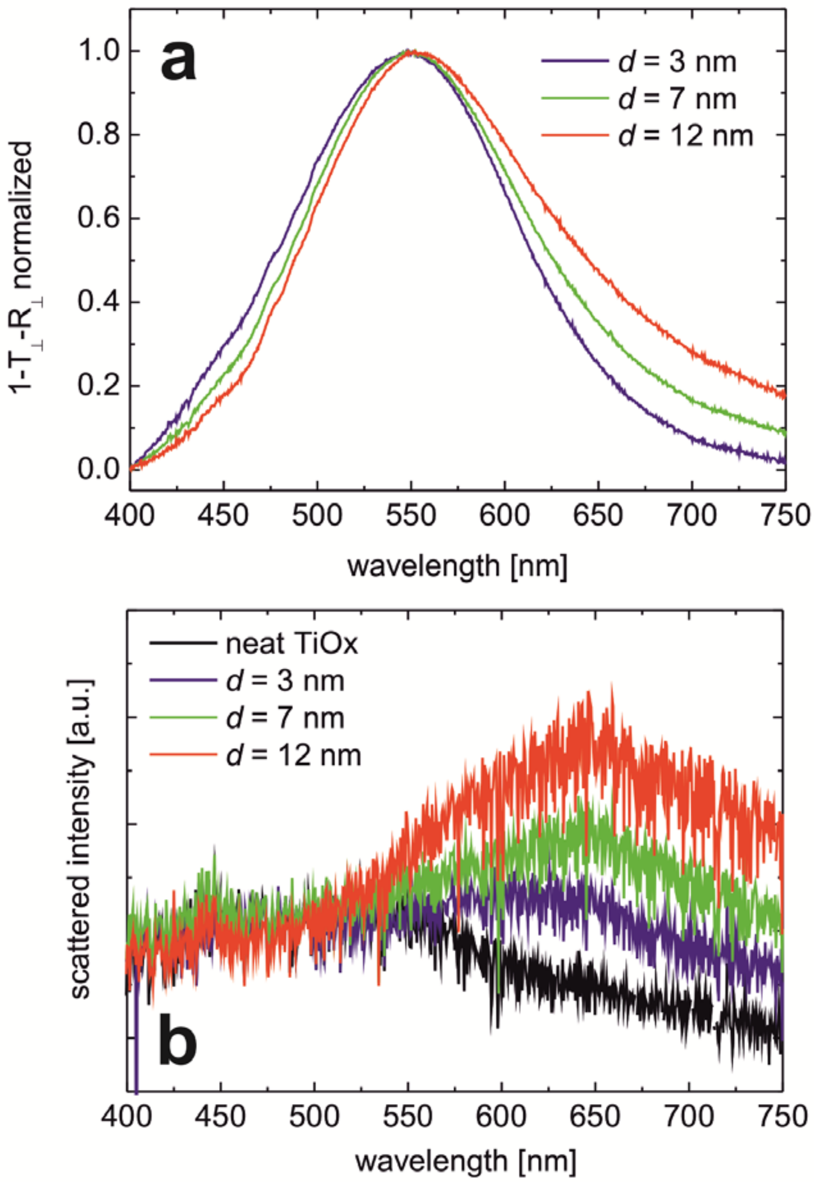


**Figure S2:** (a) Optical spectra of (1-$T_{\perp}$-$R_{\perp}$ , normalized) for $TiO_x$/AgNP/$TiO_x$ (*d* nm) shown in the region of the plasmon resonance. The overall layer thickness is 100 nm. $T_{\perp}$ and $R_{\perp}$ denote the transmission and reflection measured normal to the sample surface (see experimental). (b) Scattered transmission measured under an angle of 45°.

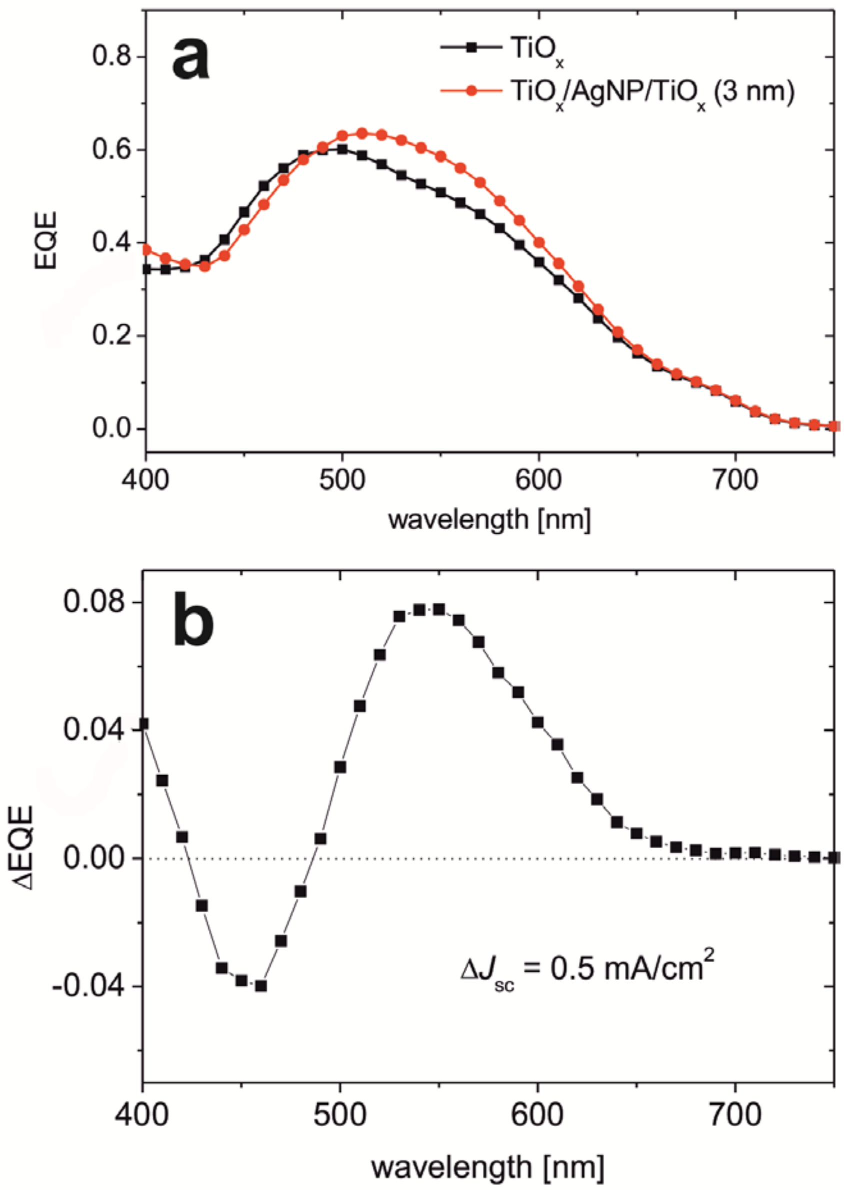


**Figure S3:** (a) EQE spectra of inverted OSCs using plasmonically sensitized $TiO_x$ /AgNP/ $TiO_x$ (3 nm) and non-sensitized $TiO_x$ as electron extraction layer. (b) Difference of EQE spectra ($\Delta$EQE = EQE ($TiO_x$/AgNP/$TiO_x$ (3 nm)) - EQE ($TiO_x$). The difference in EQE results in a difference of $J_{sc}$ of about 0.5 mA/cm$^2$.

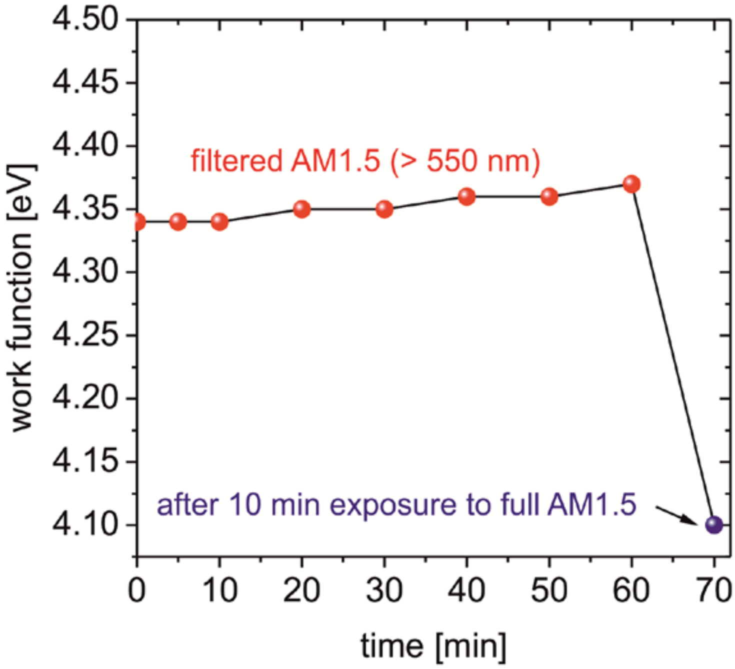


**Figure S4:** WF of a $TiO_x$ layer upon illumination for 1 h with filtered AM1.5 solar light ($\lambda$ > 550 nm) and after an additional 10 min illumination with full (unfiltered) AM1.5 solar light.

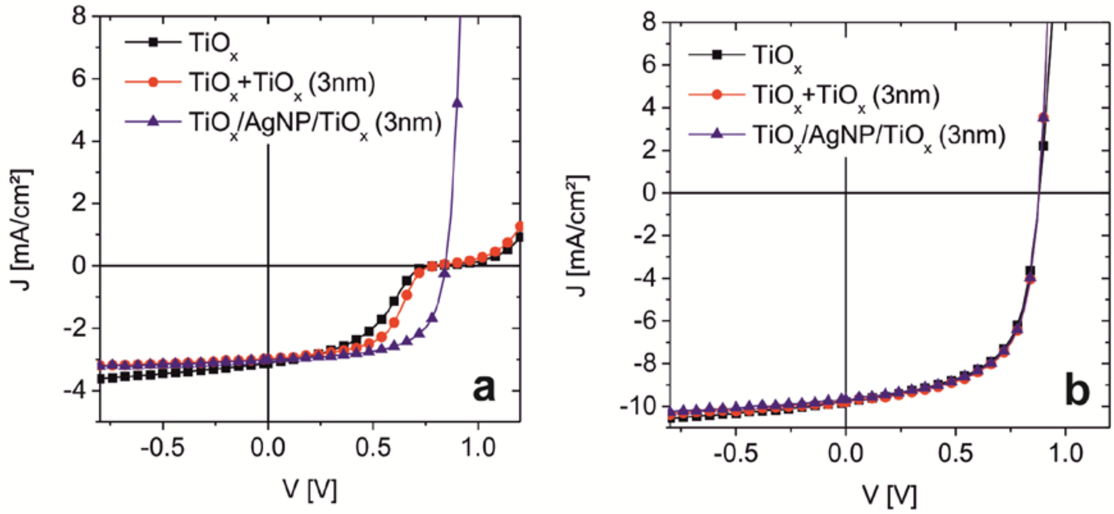


**Figure S5:** (a) *J/V* characteristics of inverted OSCs using non-sensitized and sensitized $TiO_x$ as EEL. In a control device the AgNP have been omitted but the 3 nm thick $TiO_x$ cap has been deposited on top of the $TiO_x$ layers using ALD ($TiO_x$ + $TiO_x$ (3 nm)) . For illumination a filtered ($\lambda$ > 550 nm) AM1.5 solar spectrum has been used. (b) The *J/V* characteristics of the same devices upon illumination with full (unfiltered) AM1.5 simulated solar light. Devices are based on PCDTBT:$PC_{70}BM$.

**Table S1.** Characteristics of the OSCs with various cathode interlayers as discussed in the manuscript, upon illumination with the full AM1.5 solar spectrum.

| BHJ | Cathode interlayer | PCE [%] | $V_{oc}$ [V] | $J_{sc}$ [mA/cm²] | FF [%] |
|---|---|---|---|---|---|
| P3HT/$PC_{60}$BM | $TiO_x$ | 2.8 | 0.56 | 9.1 | 54 |
| | $TiO_x$/AgNP/$TiO_x$ (3 nm) | 3.3 | 0.57 | 10.8 | 54 |
| | ZnO | 3.1 | 0.57 | 10.1 | 53 |
| | ZnO/AgNP/ZnO (3 nm) | 3.1 | 0.57 | 10.2 | 53 |
| PCDTBT/$PC_{70}$BM | $TiO_x$ | 5.3 | 0.90 | 9.5 | 62 |
| | $TiO_x$/AgNP/$TiO_x$ (3 nm) | 5.5 | 0.90 | 9.9 | 62 |
| | $TiO_x$/AgNP/$TiO_x$ (5 nm) | 5.4 | 0.90 | 9.8 | 61 |
| | $TiO_x$/AgNP/$TiO_x$ (7 nm) | 5.4 | 0.90 | 9.7 | 62 |
| | $TiO_x$/AgNP/$TiO_x$ (10 nm) | 5.4 | 0.90 | 9.7 | 61 |
| | $TiO_x$/AgNP/$TiO_x$ (12 nm) | 5.3 | 0.90 | 9.4 | 63 |
| | $TiO_x$/AgNP/$TiO_x$ (20 nm) | 5.3 | 0.90 | 9.6 | 61 |


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