A versatile approach for coating oxidic surfaces with a range of nanoparticulate materials.

Supporting Information

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1) Calculation of the fractional coverage Φ_{NC}

The chemical equation for the anodic dissolution of PbS in aqueous media at neutral pH can be generalized to:

$$PbS \rightarrow \; Pb^{II} + S + 2e^{-}$$

where the Pb(II) species formed strongly depends on the nature of the electrolyte. The amount of oxidized PbS n_{ox} can be calculated from the charge Q determined by cyclic voltammetry using Faraday's law:

$$n_{ox} = \frac{Q}{zF}$$

where z is the stoichiometric number of charges transferred per ion (z = 2) and F is the Faraday constant.

The diameter d of the PbS NCs which were used in this study is 9 nm as determined by TEM. If a spherical geometry is assumed, then the amount of PbS present in one NC $n_{PbS,NC}$ is:

$$n_{PbS,NC} = 2\frac{V_{NC}}{V_{UC}} = \frac{\pi d^3}{3a^3 N_A}$$

where V_{NC} is the volume of one nanocrystal, V_{UC} is the volume of one unit cell of PbS (Fm3m, lattice constant a = 5,936 Å [1]) and N_A is the Avogadro constant. The factor 2 is introduced as PbS contains two formula units per unit cell.

The number of oxidized nanocrystals $N_{NC,ox}$ is the ratio of n_{ox} to $n_{PbS,NC}$:

$$N_{NC,ox} = \frac{n_{ox}}{n_{PbS,NC}}$$

and Φ_{NC} is defined as the ratio of the number of oxidized nanocrystals $N_{NC,ox}$ times their projected area A_{NC} and the active electrode area A_E (= 0.196 cm^2):

$$A_{NC} = \frac{\pi d^2}{4}$$

$$\Phi_{NC} = \frac{N_{NC,ox} \cdot A_{NC}}{A_E} = \frac{3}{8}\frac{Qa^3 N_A}{F d A_E}$$

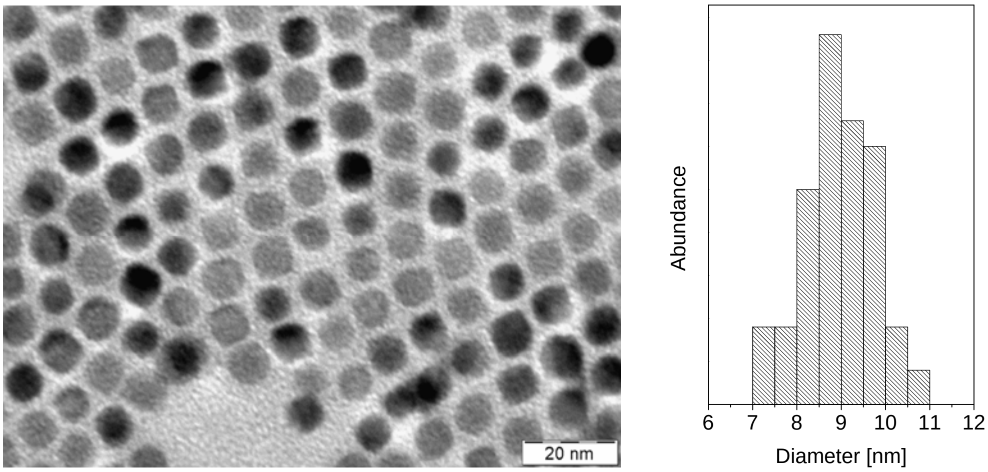

Figure S1: TEM image of the PbS nanocrystals used for the systematic comparison of the three different deposition methods and their size distribution histogram. The average particle diameter is 9 nm.

2) Estimation of the real surface area of bare ITO

Cyclic voltammetry was carried out in a standard three-electrode electrochemical cell using a clean ITO substrate as working electrode (exposed area 4 cm^{2}), a platinum sheet as counter electrode and a Ag/AgCl as reference electrode. A 1 M KOH solution was employed as electrolyte. All measurements were performed using a Reference 600 Potentiostat (Gamry Instruments) in surface mode to recover the capacitive currents, which are usually damped in a simple staircase voltammetry experiment. The roughness factor was calculated using a specific capacitance of 8 μF cm^{-2} according to Wu et. al..[2]

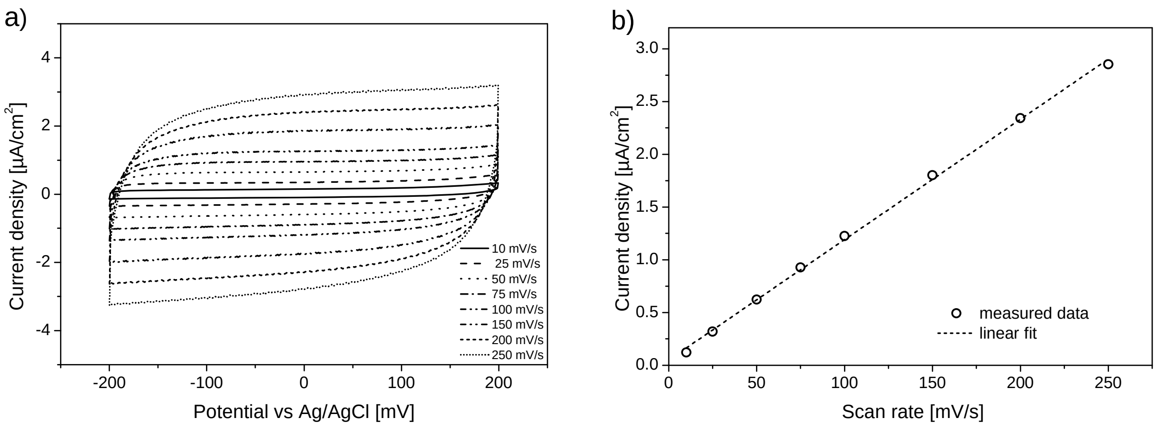

Figure S2: a) cyclic voltammograms of bare ITO in 1 M KOH at increasing scan rate ranging from 10 mV/s to 250 mV/s. b) Relationship of the current density and the scan rate at 0 mV vs Ag/AgCl.

The charging current densities have been measured by averaging the anodic and cathodic current densities at the midpoint of the CVs at 0 mV for several scan rates. Figure S2b shows the linear relationship between the current density and the scan rate, confirming the absence of faradic processes during the scans. The value of the specific double layer capacitance obtained from the slope is 11.4 μF cm^{-1}, resulting in a roughness factor of 1.42 for bare ITO.

AFM measurements were carried out on a Digital Instruments Dimension 3100 in tapping mode using a standard silicon probe (tip diameter: 10 nm). An area of 1 x 1 µm was scanned using a resolution of 1024 lines. A real surface area of 1.20 µm^2 was determined using the software “gwyddion”. The resulting roughness factor is 1.2.

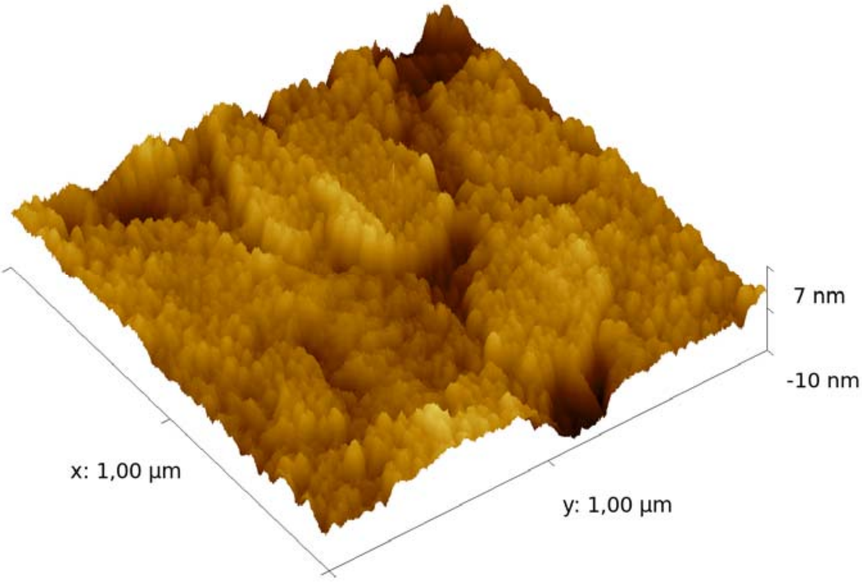

Figure S3: 3-D view of a bare ITO surface.

3) Preparation and coating of ZnO films

Electrochemical deposition of ZnO nanorod (ZnO NR) films was conducted in a conventional thermo-jacketed three-electrode electrochemical cell.[3] FTO substrates (Solaronix, 15 Ω/□) were cleaned by wiping with isopropanol and sonication in alkaline detergent (Extran, Merck, 10x diluted) for 15 min, followed by sonication in deionized water for an additional 15 min. The clean substrates were then dried carefully in a stream of nitrogen.

The cleaned FTO substrates were subsequently used as working electrodes. A zinc sheet was employed as counter electrode and a standard calomel electrode (SCE) as reference electrode. The electrolyte contained 2 mM zinc acetate dihydrate (purum, AppliChem GmbH) and 0.1 M sodium acetate (p. A., Grüssing GmbH) to reduce the solution resistance. Electrodeposition was carried out potentiostatically at −1.0 V versus SCE at 70 °C for 1 h. After deposition the films were rinsed thoroughly with deioized water and finally dried in air.

For coating with PbS NCs, 10 μL MPTMS were added to 200 μL of the PbS (3.5 μM with respect to PbS NCs) sol in a micro test tube. The tube was shaken for a few seconds and the particles then precipitated by the addition of 500 μL of n-hexane and separated by centrifugation. Excess ligands were removed by washing with a second 500 μL volume of n-hexane and finally the particles were redispersed in 8 ml of dry dichloromethane. Subsequently the ZnO NR coated FTO substrates was placed into the resulting solution and shaken for 24 h. Excess particles were removed by rinsing with toluene.

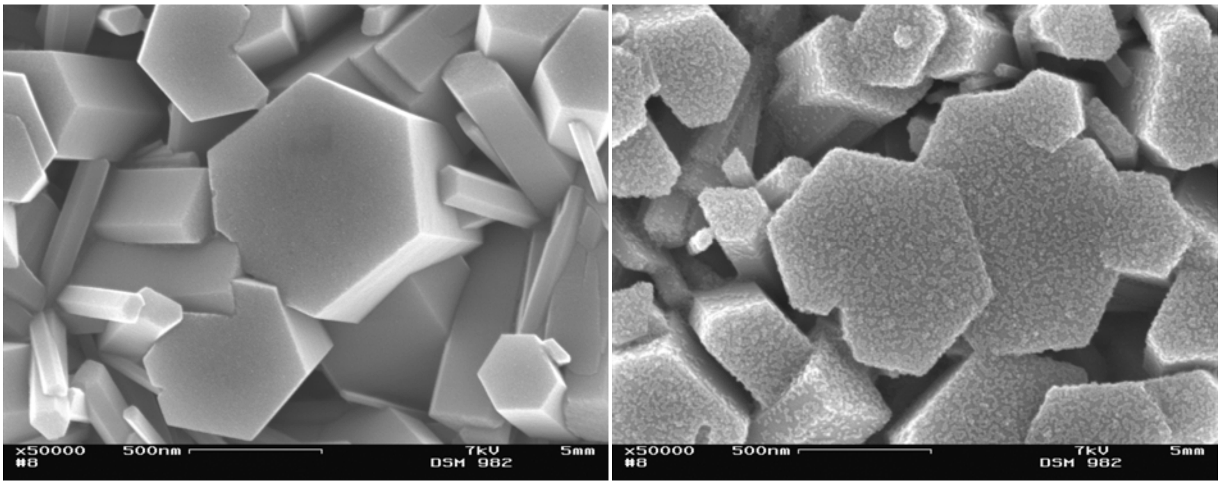

Figure S5: SEM images of a zinc oxide nanorods a) before and b) after coating with MPTMS stabilized PbS NCs.

4) Preparation and coating of TiO_2 films

Single-crystaline TiO_2 nanorod (TiO_2 NR) films were synthesized using a modified protocol published by Liu et al.[4] In a 150 mL-Erlenmeyer flask 500 µL of titanium isopropoxide (97% Sigma Aldrich) were added slowly to a stirred solution of 15 mL concentrated hydrochloric acid (37% by weight) in 15 mL deionized water. This mixture was stirred for another 5 minutes and then a clean FTO substrate is placed into the solution. After 24 h of refluxing a thin white film of TiO2 has formed on the conductive site of the FTO substrate.

For the coating with PbS NCs, the same procedure as for the ZnO NRs was used.

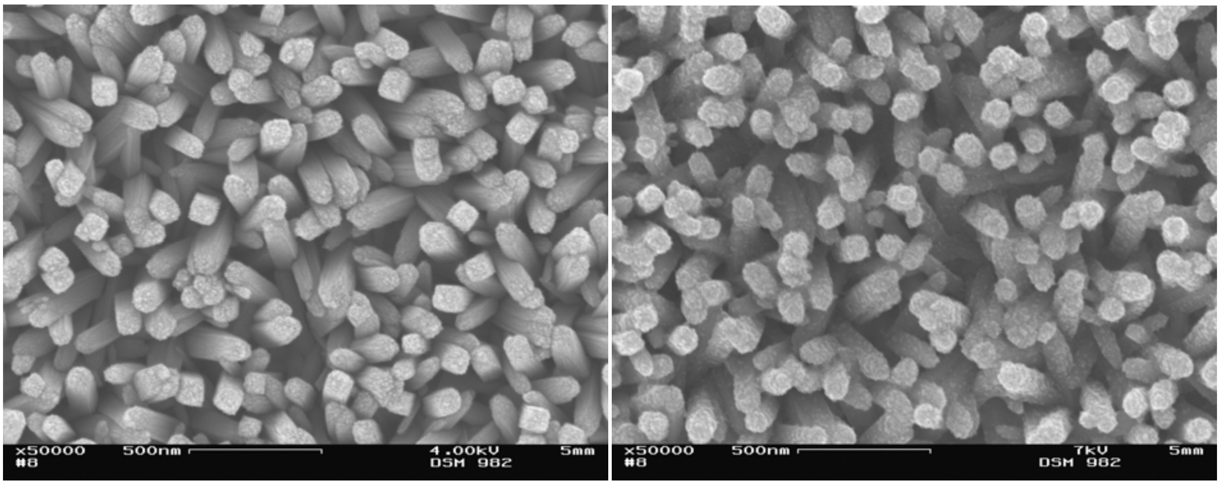

Figure S4: SEM images of a single crystalline titania nanorod array a) before and b) after coating with MPTMS stabilized PbS NCs.

[1] Madelung, *Semiconductors Data Handbook*, 3 ed., Springer, Berlin, **2004**.

[2] N. L. Wu, J. Y. Hwang, P. Y. Liu, C. Y. Han, S. L. Kuo, K. H. Liao, M. H. Lee, S. Y. Wang, *Journal of The Electrochemical Society* **2001**, *148*, A550.

[3] G. Guerguerian, F. Elhordoy, C. J. Pereyra, R. E. Marotti, F. Martín, D. Leinen, J. R. Ramos-Barrado, E. a. Dalchiele, *Nanotechnology*, *22*, 505401.

[4] B. Liu, E. S. Aydil, *Journal of the American Chemical Society* **2009**, *131*, 3985.