Supporting Information

Electrospun Antimony-doped Tin Oxide (ATO) Nanofibers as Versatile Conducting Matrix

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Experimental details

Nanoparticle synthesis
A precursor solution is prepared from 0.2 mL conc. HCl, 980 mg SnCl\textsubscript{4} and 65 mg SbCl\textsubscript{3} (7.5 at\%) in 12 g EtOH. This solution is added dropwise to 2.5 g of an aqueous solution of NH\textsubscript{3} (20 wt\%) under vigorous stirring. A white slurry containing preformed ATO nanoparticles is obtained, from which the nanoparticles can be separated by repeated centrifugation and washing with H\textsubscript{2}O until some nanoparticles remain in the solution. The remaining particles can be redispersed in 600 mg H\textsubscript{2}O and 150 mg Et\textsubscript{2}N, giving a final concentration of 20 wt\%. According to the literature\textsuperscript{1}, such nanoparticles can also be produced with stabilizing ligands, such as the amino acid alanine and then subjected to hydrothermal crystallization (by heating at 120-150 °C for 2.5 h). However, tin oxide-based nanoparticles are dispersible in basic aqueous solutions without any ligands and we found that a solution of 20 wt\% of diethylamine in water was most suitable for yielding clear yellow dispersions with 20 wt\% ATO (determined from the residue after calcination at 550°C for 20 min). After hydrothermal treatment addition of TMAH (Tetramethylammonium hydroxide) was necessary to obtain highly concentrated ATO dispersion that possess a brownish color, due to the higher crystallinity of the ATO particles. However, using ATO nanoparticles of different crystallinity, it was found that the conductivity of the resulting nanofibers was best without any hydrothermal treatment. This finding shows that the composition was already fixed during the precipitation step and later hydrothermal only affected the degree of crystallinity of the particles. Figure S1 shows the XRD pattern of the nanoparticles as-prepared, after hydrothermal treatment and calcination that show increasing crystallinity. [Actually, even the clear nanoparticle dispersion turned crystalline, i.e. from yellow to brownish, upon solvothermal treatment]

The nanoparticles were further characterized by TEM and analytical ultracentrifugation, revealing their diameter to be 4-7 nm (see Fig. S2)

Electrospinning
For electrospinning a solution was prepared from 1 g ATO (antimony-doped tin oxide) nanoparticles dispersion (20 wt\% of ATO in 4:1 mixture of H\textsubscript{2}O and diethylamine) to which 250 mg ethanol and 1.25 g of a solution of 12 wt\% Poly(vinylpyrrolidone) (PVP, M\textsubscript{w} ≈ 1,300,000) in methanol was added.
In a typical electrospinning experiment, this solution was fed through a metallic needle by a syringe pump (KDS scientific) at the rate of 0.4 ml/h. The needle was placed at a distance of 5 cm from the aluminum foil that serves as collector and a voltage of 5 kV (Spellman CZE1000R high-voltage power supply) was applied to produce a non-woven mat. The nanofiber mats were then cut and calcined at 550°C for 10 min.

To increase the packing density of the fibers, the mat is soaked with hexane and dried at room temperature, before calcination in air at 550°C for 10 min.

**Electrodeposition**

TiO$_2$ can be anodically deposited from acid TiCl$_3$ solution as proposed by O’Regan and Graetzel and the addition of surfactants like SDS (sodium dodecylsulfate) or BTB (bromothymol blue) affords the generation of porous titania. In a typical experiment, 9.5 g of H$_2$O are thoroughly degassed with Ar, before adding 500 mg of 15% TiCl$_3$ in 10% HCl and 80 mg Na$_2$CO$_3$, raising the pH to 2.5. Ultrasonic agitation is used for the dissolution and the solution is slowly stirred under Ar during the electrodeposition. The nanofibrous electrode or an FTO-coated glass is used as working electrode, a Pt wire as counter electrode and an Ag wire as pseudo-reference. TiO$_2$ is deposited potentiostatically with +150 mV vs. Ag for up to 60 min. During the first 5 min no surfactant is present in the electrolyte, so that a compact TiO$_2$ blocking layer is deposited. To obtain highly porous deposits, 8 mg of BTB in 500 mg degassed H$_2$O are injected after 5 min.

To improve the crystallinity the electrodes were heated to 550°C with a ramp of 5°C/min.

**Sensitization and solar cell measurements**

N3 (Ru(dcbpy)$_2$)(NCS)$_2$, dcbpy = 2,2’-bipyridine-4,4’-dicarboxylic acid) was adsorbed to the TiO$_2$ layer on the fibrous and flat electrode from a 50 µmol L$^{-1}$ solution in ethanol at 80 °C for 60 minutes. For solar cell measurements, the dye-sensitized TiO$_2$ film was used as working electrode in an unsealed liquid cell in a three electrode setup with a Pt wire as counter electrode and with a Ag/AgNO$_3$ reference electrode in acetonitrile as internal solvent. The electrolyte was composed of acetonitrile and ethylene carbonate (1 : 4 by volume) with 0.5 mol L$^{-1}$ tetra-n-butylammonium iodide (TBAI) and 0.05 mol L$^{-1}$ iodine. The illumination was performed by a 1000 W Xenon arc lamp (LOT Oriel) equipped with water and UV filters. The light intensity was adjusted by neutral density filters to 100 mW cm$^{-2}$. Other deposition techniques like atomic layer deposition or deposition of other metal oxides like zinc oxide might prove more suitable for the cell performance, as solar cells based on nanofibers and nanorods of both TiO$_2$ and ZnO have already been demonstrated.

**Polymer films**

The free-standing ATO nanofibers mats were deposited on or sandwiched between poly(styrene) and poly(vinylpyrrolidone) films and manually hot pressed between teflon blocks. The temperature and pressing time were approx. 150°C and 60 s.

**Raytracing (3D schemes)**
The free raytracing software POV-Ray version 3.62 has been used to produce the 3D schemes (figures 1 & S5). The code files of the images are available upon request from the authors.

**Additional results**

![Graph showing X-ray diffraction (XRD) of nanoparticles as-prepared (25°C), after hydrothermal treatment (125°C for 3h) and thermal treatment (550°C for 30min). The vertical bars represent the positions of Bragg peaks of tin dioxide (cassiterite) for comparison.]

**Fig. S1** X-ray diffraction (XRD) of nanoparticles as-prepared (25°C), after hydrothermal treatment (125°C for 3h) and thermal treatment (550°C for 30min). The vertical bars represent the positions of Bragg peaks of tin dioxide (cassiterite) for comparison.

![Graph showing particle size distribution from AUC.]

**Fig. S2** Analytical ultracentrifugation (left) and
Fig. S3 Left: High-Resolution Transmission Electron Microscopy image of crystalline ATO nanoparticles. The inset shows a single nanoparticle with lattice fringes, proving that the nanoparticles are highly crystalline. Right: Selected Area Diffraction, the ring positions corresponding to the cassiterite structure.

<table>
<thead>
<tr>
<th>Spinning time</th>
<th>Resistance Ω / cm</th>
<th>Thickness / µm</th>
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<tbody>
<tr>
<td>30 s</td>
<td>8500</td>
<td>1-2</td>
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<tr>
<td>60 s</td>
<td>2000</td>
<td>3-4</td>
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<tr>
<td>90 s</td>
<td>700</td>
<td>6-7</td>
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<tr>
<td>120 s</td>
<td>400</td>
<td>8-9</td>
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Fig. S4 Left: Table with resistivities for ATO nanofiber mats after calcination at 550°C for different spinning times. Right: The resistivity measurement was performed on 2 stripes of conducting silver (1 cm in length and 1 cm in distance apart)
**Fig. S5** Cyclic voltammogram of Prussian Blue deposited on ATO fibers and on compact FTO electrode.

**Fig. S6** SEM image of TiO$_2$ deposited on flat FTO coated glass: beyond 500 nm cracks appear.
Fig. S7  a) Scheme and SEM of ATO nanofibers before and after electrodeposition of TiO$_2$ from TiCl$_3$

b) EDX analysis of the composition and TEM image of ATO fibers covered with TiO$_2$
Fig. S8 TiO$_2$ deposited on ATO nanofibers: measurement of dye-sensitized solar cell (left) and SEM image

References