

## Electronic Supporting Information

### **Antimony Dope Tin Oxide (ATO) nanoparticle formation from H<sub>2</sub>O<sub>2</sub> solutions: a new generic film coating from basic solutions**

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## Contents

- A. Experimental Section
- B. SEM and TEM studies of ATO coated minerals
- C. XRD studies of ATO coated mica

### A. Experimental section

**Materials.** Tin (IV) chloride, antimony (V) chloride, tetramethyl ammonium hydroxide (25% aq. solution) and hydrogen peroxide (30%) and calcite were purchased from Sigma-Aldrich (Rehovot, Israel). Ammonium hydroxide and ethanol (abs.) were purchased from Biolab (Jerusalem, Israel). Muscovite mica (Mica-M) was purchased from Merck (Darmstadt, Germany) and was cleaned before use by reflux in 2.6M nitric acid and annealing at 600°C for 2hrs. Other clay minerals were treated by the same procedure. LiNbO<sub>3</sub> was donated by Professor M. Rott from the Hebrew University. Silica nanoparticles were prepared by the microemulsion technique.<sup>1</sup>

**Hydroxostannate solution preparation.** 10 ml of SnCl<sub>4</sub> (0.086 mol) was dissolved in few ml of water and neutralized with ammonia until pH 7. The precipitate was washed several times with water and dissolved in 31 ml of 25% tetramethylammonium hydroxide (0.086mol) under moderate heating (the dissolution process takes approximately 30 min). After full dissolution, water was added to achieve 1.4M tin concentration.

**Hydroxoantimonate solution preparation.** 10 ml of SbCl<sub>5</sub> (0.078 mol) was dissolved in a few ml water and neutralized with ammonia until pH 7. The precipitate was washed several times with water and dissolved in 28.5 ml of 25% tetramethylammonium hydroxide (0.078mol) under moderate heating (dissolution process takes approximately 4h). After full dissolution, water was added to achieve 1.4M antimony concentration.

**Peroxy precursor preparation.** 1.9 mL of hydroxostannate and 5 mL of hydroxoantimonate solutions were mixed together in 15 mL of hydrogen peroxide (30%) with addition of 8 mL of

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<sup>1</sup> Abarkan, I.; Doussineau, T.; Smaïhi *Polyhedron* **2006**, 25, 1763-1770.

water (final hydrogen peroxide concentration was 15% according to perganatometric titration). Excess of hydroxoantimonate is taken because of its partial solubility in ethanol. This ratio of tin and antimony seems to be close to optimal for conductive coating preparation.

**Coating procedure.** Typically 600 mg of clay was dispersed in 15 mL of the precursor solution by sonication, and after additional 10 min of stirring, precipitation of particles onto the clay surface was accomplished by addition of 120 mL of ethanol. Coated clay was washed with ethanol, dried, and calcined at 800°C for 3h.

**HR TEM** imaging was performed at 200 kV using the FEI Technai F20 G2 (Eindhoven, Holland) High Resolution Transmission Electron Microscope (HR TEM) . A drop of the suspension of the sample in ethanol was deposited onto 400 mesh copper grids covered with thin amorphous carbon films.

**SEM** imaging was performed using the FEI Sirion High Resolution Scanning Electron Microscope (HR SEM, Eindhoven, Holland). Accelerating voltage was set at 5-15 kV, working distance 5 mm, using Ultra-High resolution mode with Through-the-Lens Detector. The dried samples were either placed directly onto carbon conductive film, or immersed in ethanol, placed in an ultrasonic bath for 10 min, and the suspension was then dropped on a glass surface and dried out. Samples were coated by Au/Pd for conductivity.

**$^{119}\text{Sn}$  NMR** spectra were collected on a Bruker Avance-500 (11.7T) spectrometer at resonance frequency 186.4 MHz. The measurements were performed using a single pulse sequence with rf pulse duration of 10  $\mu\text{s}$  and recycling time 30 s.

**XPS measurements** were performed on a Kratos Axis Ultra X-ray photoelectron spectrometer (Manchester, UK). High resolution spectra were acquired with monochromated Mg K $\alpha$  (1253.6 eV) X-ray source with 0° takeoff angle. The pressure in the test chamber was maintained at 1.7  $10^{-9}$  Torr during the acquisition process. Data analysis was performed with Vision processing data reduction software (Kratos Analytical Ltd.) and CasaXPS (Casa Software Ltd.).

***X-ray powder diffraction*** measurements were performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Sollers slits and 0.2 mm receiving slit. The powder samples were carefully filled into low background quartz sample holders. The specimen weight amounted to approximately 0.5 g. XRD patterns from 5° to 60° 2 $\theta$  were recorded at room temperature using CuK $\alpha$  radiation ( $k = 1.5418 \text{ \AA}$ ) under the following measurement conditions: Tube voltage of 40 kV, tube current of 40 mA, step scan mode with a step size 0.02° 2 $\theta$  and counting time of 1 s/step. XRD patterns were processed using Diffrac Plus software.

***Resistivity of ATO coated mica samples.*** Triply coated mica powder was placed in a home made hand press device, pressed by  $2 \times 10^6 \text{ Pa}$  and then the conductivity was measured.

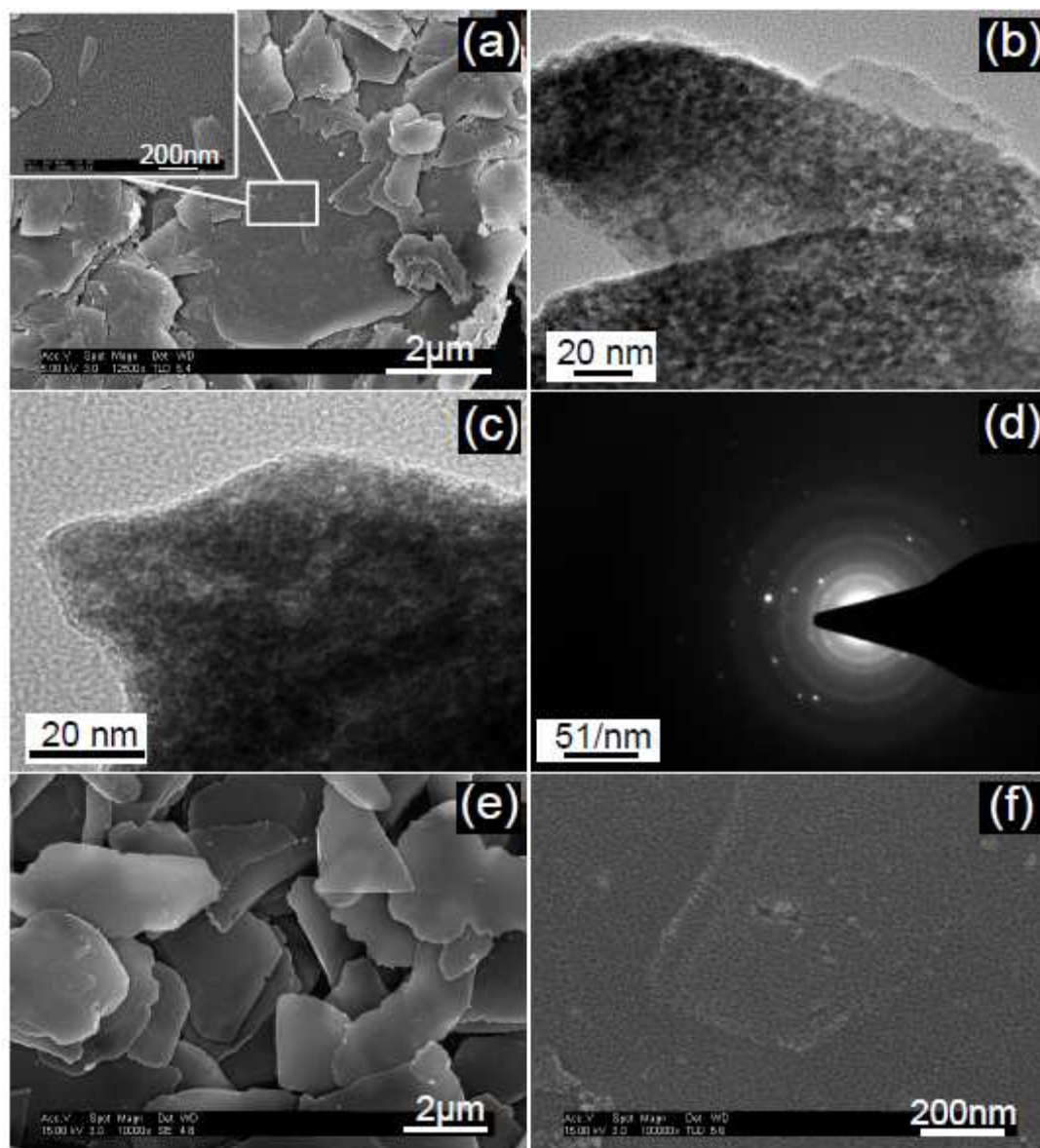
## **B. SEM and TEM studies of ATO coated minerals**

The TEM and SEM micrographs of coated and heat treated kaolin mineral (Fig. S1) show that the ATO is exclusively attached to the clay and it is not agglomerated elsewhere. The relevant TEM micrograph, taken at the edge of the platelets, shows approximately 5 nm crystalline ATO particles almost uniform in size, as for all other coated clays and minerals. The TEM micrograph of lithium niobate, LiNbO<sub>3</sub>, shows that the coating takes place exclusively on the mineral and the size of the crystallite is again around 5 nm. Figure (d) shows the local diffraction pattern of the ATO coated LiNbO<sub>3</sub>. The single crystal diffraction dots of the lithium niobate and the multicrystalline diffraction rings of the ATO nanocrystals are apparent. These crystalline rings are, of course, apparent in all other heat treated coated samples, though they are not shown here.

## **C. XRD studies of ATO coated mica**

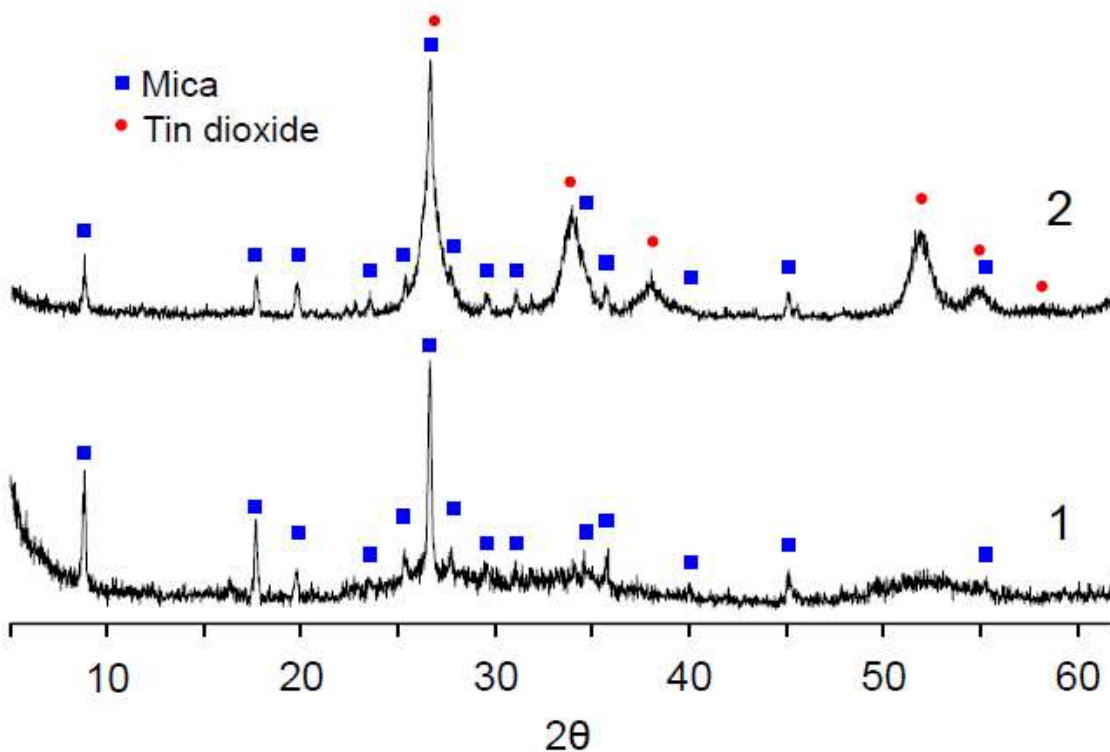
XRD studies of 800°C - calcined and room temperature prepared ATO-coated-mica are depicted in Figure S2. The room temperature coated mica shows some broad shallow peaks at 2 $\theta$  = 50-55 and at 25-35 degrees corresponding to amorphous tin oxide. Heat treatment resulted in formation of tin-oxide phase as observed by the crystalline x-ray diffraction (denoted by circles). The

crystalline size by Scherrer equation <sup>2</sup> is 9 nm, which is somewhat larger compared to the uniform 5 nm size obtained in the TEM studies.



**Figure S1.** SEM and TEM micrographs of kaolin (a,b), and TEM picture of Li niobate (c). The electron diffraction pattern of ATO coated single crystal lithium niobate is given in frame (d). Frames (e) and (f) present micrographs of uncoated Muscovite (e) and of ATO coated Muscovite (f).

<sup>2</sup> Patterson, A. *Phys. Rev.* **1939**, 56, 978–982.



**Figure S2.** XRD patterns of (1) mica coated peroxostannate & peroxoantimonate (as prepared) and (2) ATO coated mica annealed at 800°C. Square symbols denote mica diffraction peaks and the tin oxide peaks are denoted by full circles (in red).