

Supporting Information for:

Nanostructures prepared via laser ablation of tin in water

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TEM images of samples

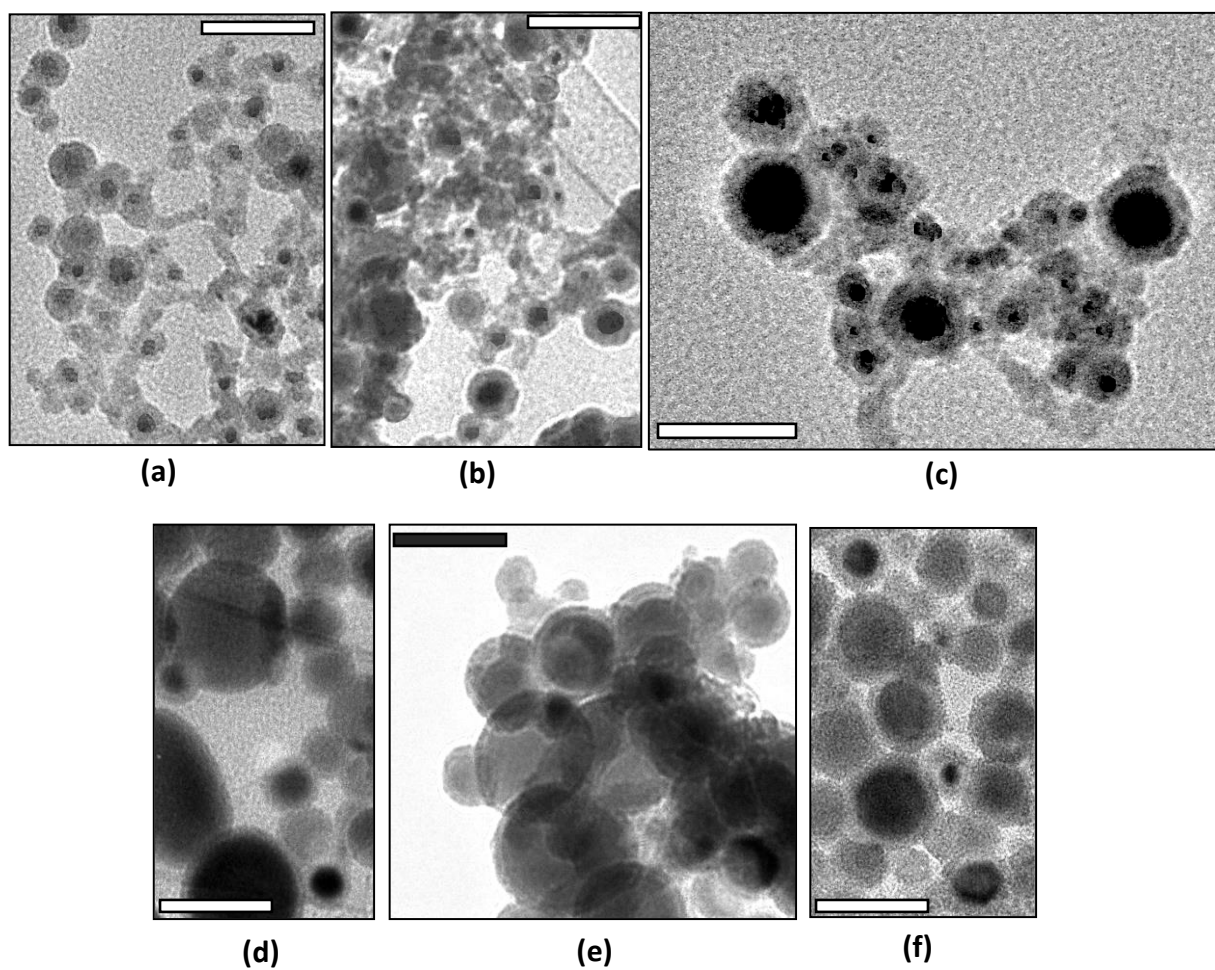


Figure S1. TEM images of samples prepared via laser ablation of Sn targets in water using nanosecond (a-c) and millisecond pulses (d-f). Scalebars indicate 10 nm (a-c) and 20 nm (d-f). Core@shell nanostructures are observed as dominating NPs in all images.

Absorption Spectroscopy Measurements

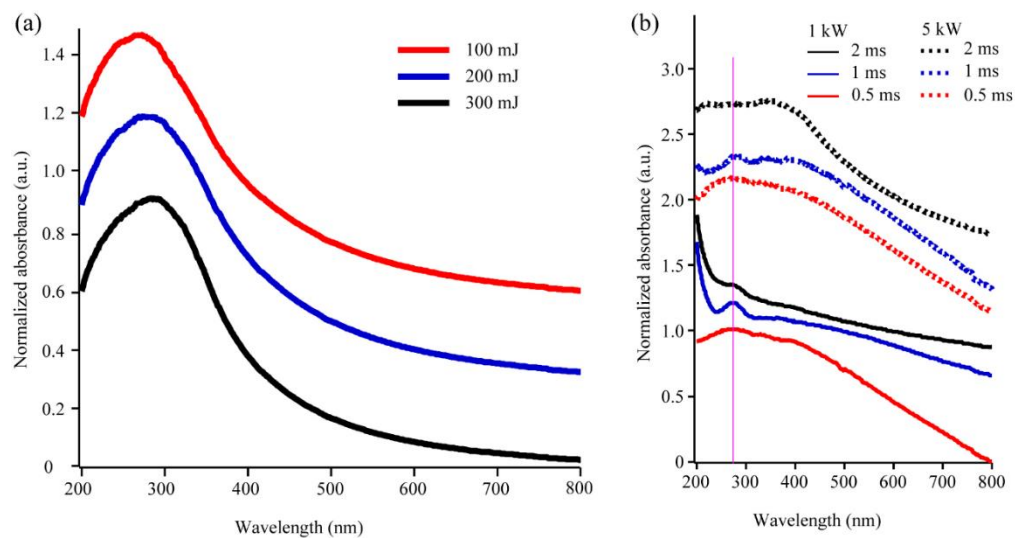


Figure S2. Absorption spectra of as-prepared nanomaterials produced with ns- long (a) and ms- long pulses (b). In panel (a), red, blue and black lines indicate 100, 200 and 300 mJ/pulse. In panel (b), solid and dotted lines denote different peak powers, 1 and 5 kW, while red, blue and black colors correspond to pulse widths, 0.5, 1 and 2 ms, respectively. Vertical pink line in panel (b) indicates metallic phase peak position.

XPS Measurements of Samples after Sputtering

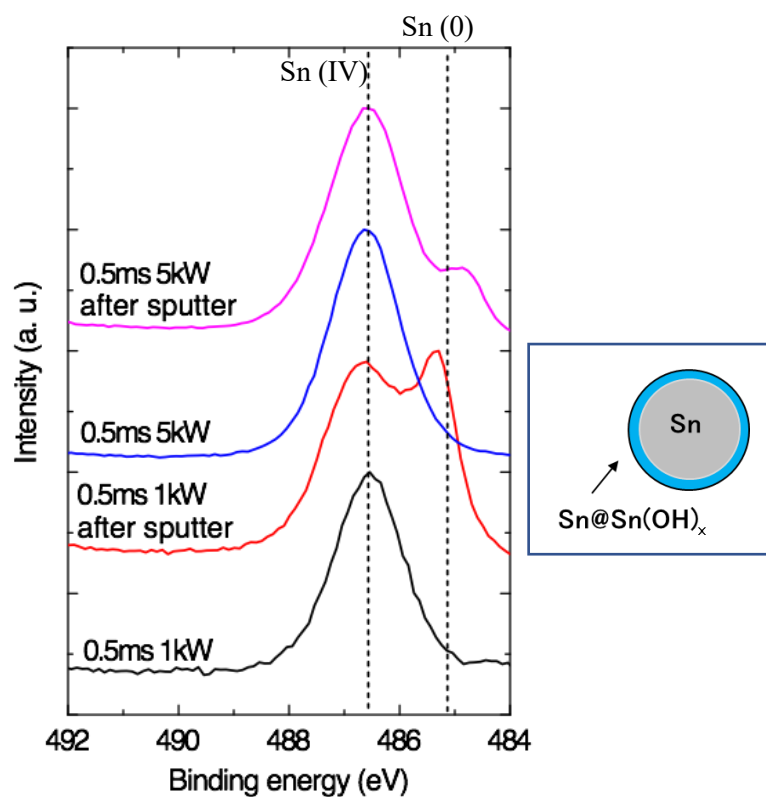


Figure S3. XPS Sn3d spectra of two samples measured on as-deposited (blue and black lines) and on sputtered (1.4 min with Ar ions, pink and red lines) samples. The latter samples were prepared by means of ms-laser using 0.5 ms-long pulses and 1 kW (black and red spectra) or 5 kW as pulse peak power (blue and pink spectra). Upon sputtering, it is seen that the nanoparticle cores in both samples are metallic Sn, while their shells are based on hydrated Sn(IV) oxide.

Gas Sensing Experiments

To evaluate gas sensing potential of prepared nanomaterials, the sample prepared by ns-laser (100 mJ/pulse) was chosen. The Sn@SiO₂ nanoparticles were drop-cast on a commercial interdigitated electrode (with gap 5 μm, from DropSens, Spain). Ten layers (each resulting from a 30 μL drop) were subsequently drop-cast and dried at 50 °C to provide a thick nanomaterial-based layer. The prepared sample was tested with 50, 100, 250, and 500 ppm of ethanol vapor mixed into the ambient atmosphere at room temperature. Gas sensing performance toward ethanol was studied using an acrylic chamber (5.4 L) equipped with a fan and electrometer (8846A model from Fluke). Figure 6 (see the main text) exhibits a response curve of the sample to 100 ppm of ethanol, where the response and recovery times are seen to be about 96 and 86 s, respectively.

Figure S4 shows the dynamic-response curve of the sample toward different ethanol concentrations (at room temperature). The sample resistance shows a stable resistance in the ambient atmosphere, while it is seen to decrease when ethanol is added. The observed increase in resistance when the sample is exposed to the ambient atmosphere supports its sensing characteristics. The cyclic sensing response to different concentrations exhibits the detection limit of at least as little as 50 ppm (or even lower).

The change in resistance can be calculated as sensing response using the formula $S = R_a/R_g$, where R_a and R_g are the resistance of the sample at ambient atmosphere and in presence of ethanol vapor [1]. The surface-adsorbed oxygen (O₂) turns to O₂⁻ form via trapping electrons and thereby leads to increase in surface resistance and formation of depletion layer [1-4]. Because of its reducing nature, ethanol molecules reduce oxygen chemisorbed on the SnO₂ surface, which increases the electron concentration, thus decreasing the surface resistance and depletion layer.

Thus, for gas sensing, the device uses the chemical interaction of ethanol vapor and oxygen molecules chemisorbed on the sample surface [2,3]. Normally, such adsorption and desorption of chemical molecules requires high thermal activation energy. However, the sample prepared using LAL possesses high density of surface defects that are favorable for gas sorption even at room temperature [4]. The observed long recovery time (see Fig.6 and Fig.S4, the response toward 100 ppm) confirms the importance of thermal activation energy. Further systematic studies are necessary to understand the gas sensing mechanisms of the material, for which surface properties such as grain resistance, grain boundary resistance, surface area, and so on should be first evaluated.

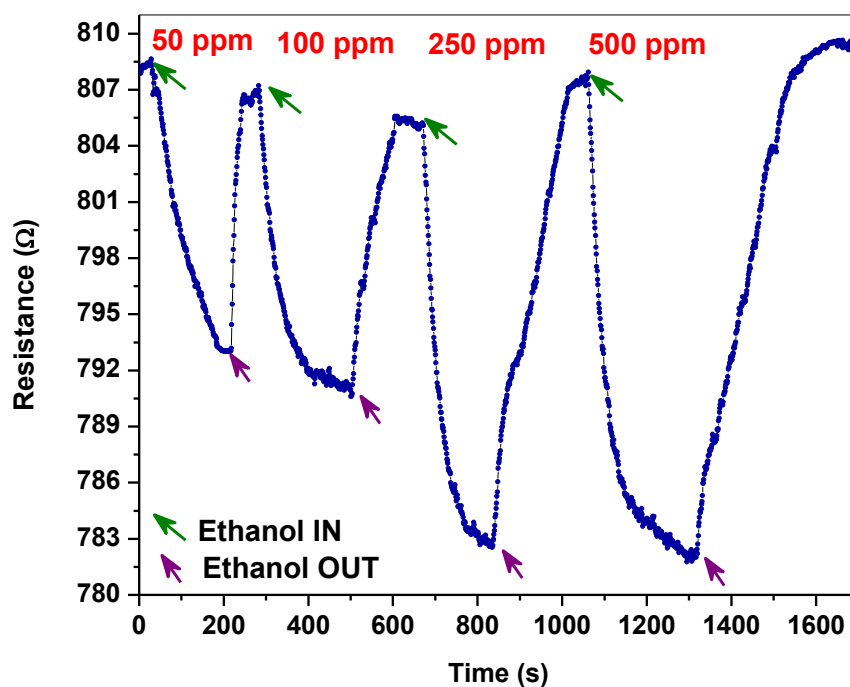


Figure S4. Dynamic response curve recorded for Sn@SnO₂ nanomaterial deposited onto an interdigitated electrode and tested as gas sensor toward ethanol at room temperature. As little as 50 ppm or ethanol could be detected by the device.

References

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- [2] J. Tao, M. Batzill, Surface Science Studies of Metal Oxide Gas Sensing Materials, in: M.A. Carpenter, S. Mathur, A. Kolmakov (Eds.), *Met. Oxide Nanomater. Chem. Sensors*, Springer New York, New York, NY, 2013: pp. 35–68.
- [3] M. Batzill, Surface Science Studies of Gas Sensing Materials: SnO₂, *Sensors* 2006, 6, 1345–1366.
- [4] Z. Song, Z. Wei, B. Wang, Z. Luo, S. Xu, W. Zhang, et al., Sensitive Room-Temperature H₂S Gas Sensors Employing SnO₂ Quantum Wire/Reduced Graphene Oxide Nanocomposites, *Chem. Mater.* 2016, 28, 1205–1212.