

Electronic Supplementary Information

H₂O₂ induced formation of graded composition sodium - doped tin dioxide and template - free synthesis of yolk - shell SnO₂ particles and their sensing application

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Fig. S2 Pictures of the test vials 1 h and 3 days after preparation

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Thermodynamic data used for preparation of the pC-pH diagram of tetrahydroxostannate

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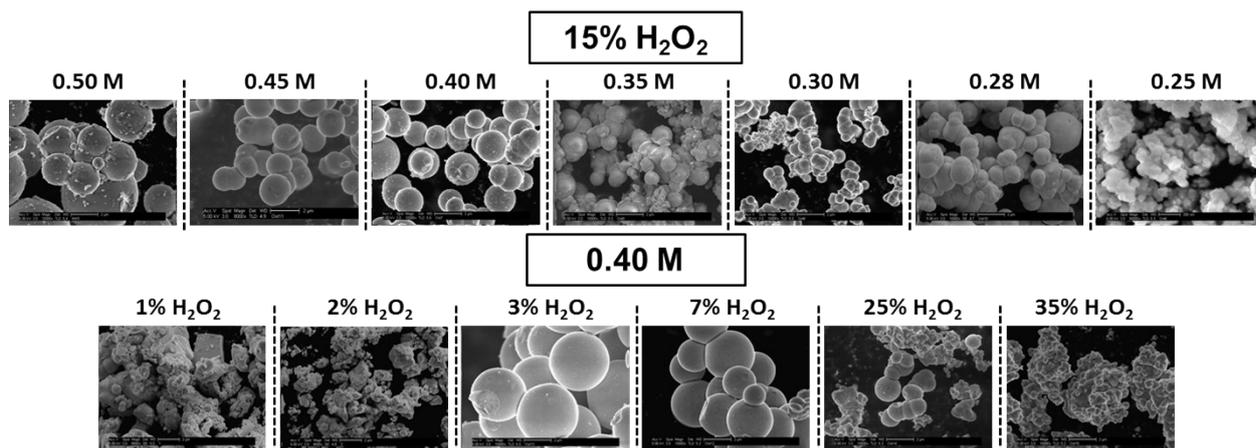


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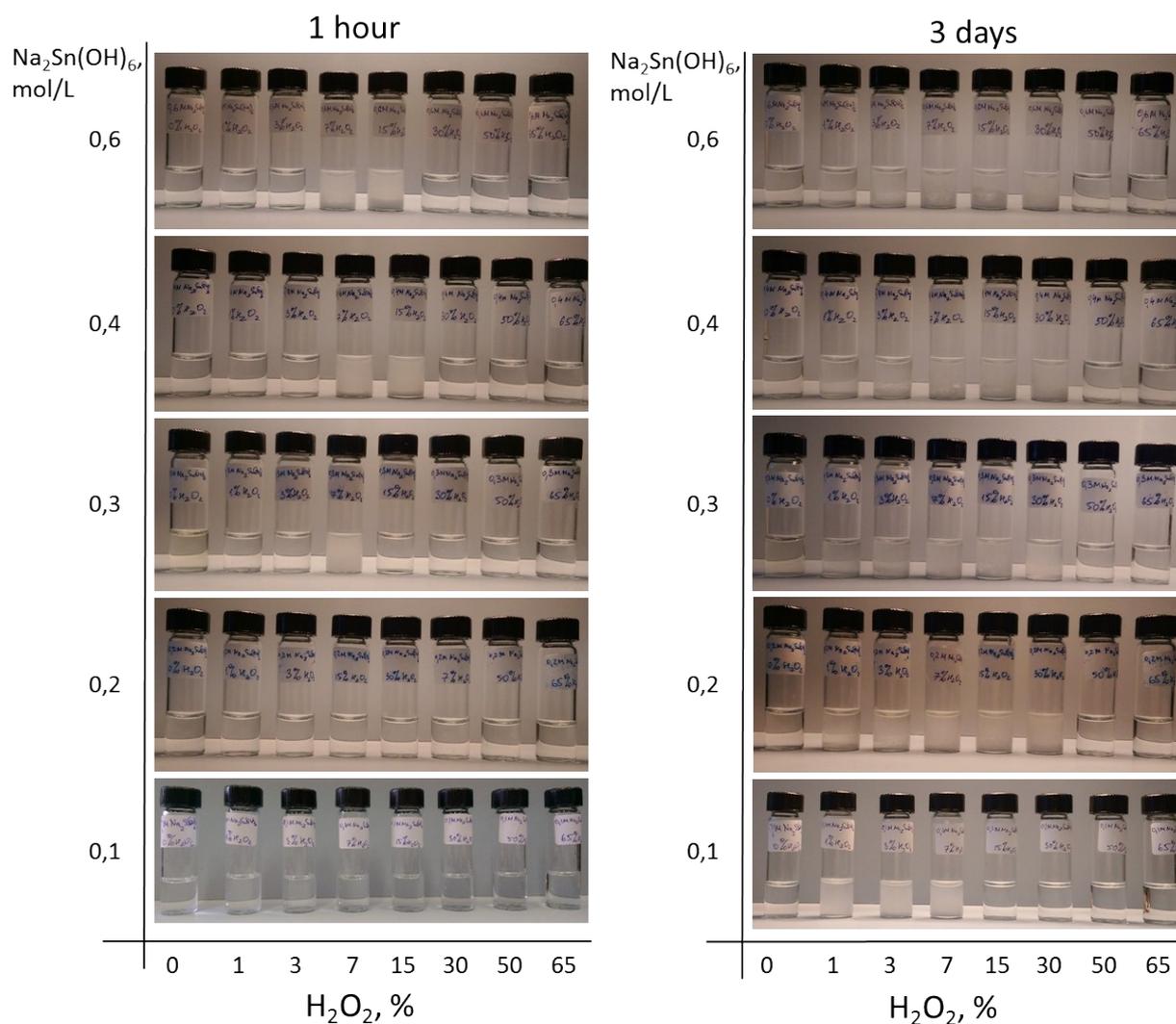


Fig. S2 Pictures of the test vials 1 h and 3 days after preparation

Preparation of the gas sensor and the gas sensing setup.

For manufacturing of the gas sensor alumina substrates, composed of inter-digitated Pt electrodes on the topside and Pt heater on the backside (Figure S3) was used. The gas-sensor characterization was performed in a continuous flow test chamber (chamber volume: 3.5 cm³). Dry air and 1000 ppm H₂ in the air were delivered to the chamber at a constant rate of 400 mL/min, controlled by a system of mass flow controllers. Special Bronkhorst and Fluke software was used to control and record the sensor signals during the experiment. By applying different voltages to the heater, the temperature of the sensors was adjusted to the desired value. Thus, the sensors were tested at 50 °C operating temperatures.

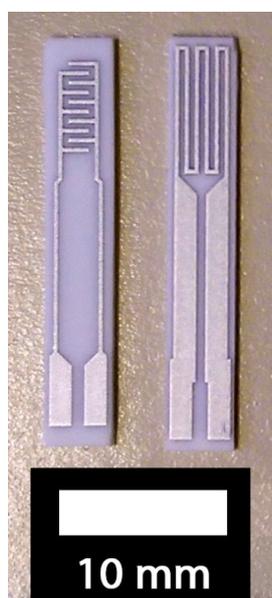


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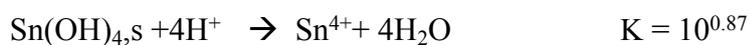
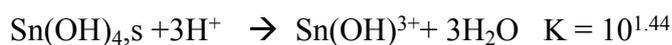
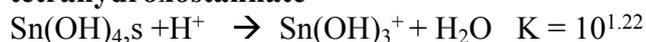


Table S1 Composition of the solutions used to construct the solubility diagram. 1.5 M solution of $\text{Na}_2\text{Sn}(\text{OH})_6$ in DIW is denoted as Sn; DIW is denoted as W; and aqueous hydrogen peroxide is denoted as O. The wt% of H_2O_2 is presented in parentheses.

	0.05 M Sn	0.1 M Sn	0.2 M Sn	0.4 M Sn	0.6 M Sn
0% H_2O_2	Sn-0,084 mL O -0 mL W-2,416 mL	Sn -0,167 O-0 W-2.333	Sn-0,333 O-0 W-2.167	Sn-0,667 O-0 W-1.831	Sn-1,001 O-0 W-1.499
0.02% H_2O_2	Sn-0,084 O-0.003 (15) W-2.413	Sn -0,167 O-0.0032(15) W-2.330	Sn-0,333 O-0.0033(15) W-2.164	Sn-0,667 O-0.002(30) W-1.831	Sn-1,001 O-0.002(30) W-1.497
0.1% H_2O_2	Sn-0,084 O -0.0071(30) W-2.409	Sn -0,167 O-0.072(30) W-2.261	Sn-0,333 O-0.0073(30) W-2.163	Sn-0,667 O-0.008(30) W-1.825	Sn-1,001 O-0.008(30) W-1.491
1% H_2O_2	Sn-0,084 O-0.071(30) W-2.345	Sn -0,167 O-0.072(30) W-2.261	Sn-0,333 O-0.073(30) W-2.094	Sn-0,667 O-0.076(30) W-1.757	Sn-1,001 O-0.079(30) W-1.420
3% H_2O_2	Sn-0,084 O-0.214(30) W-2.202	Sn -0,167 O-0.216(30) W-2.117	Sn-0,333 O-0.221(30) W-1.946	Sn-0,667 O-0.230(30) W-1.603	Sn-1,001 O-0.239 (30) W-1.260
7% H_2O_2	Sn-0,084 O-0.299(50) W-2.177	Sn -0,167 O-0.302(50) W-2.031	Sn-0,333 O-0.308(50) W-1.859	Sn-0,667 O-0.321(50) W-1.512	Sn-1,001 O-0.334(50) W-1.165
15% H_2O_2	Sn-0,084 O-0.661(50) W-1.755	Sn -0,167 O-0.688(50) W-1.665	Sn-0,333 O-0.682(50) W-1.485	Sn-0,667 O-0.709(50) W-1.124	Sn-1,001 O-0.737(50) W-0.762
20% H_2O_2					Sn-1.001 O-0.999 (30) W-0.499
30% H_2O_2	Sn-0,084 O-0.713(86) W-1.703	Sn -0,167 O-0.721(86) W-1.612	Sn-0,333 O-0.736(86) W-1.431	Sn-0,667 O-0.766(86) W-1.067	Sn-1,001 O-0.796(86) W-0.703
40% H_2O_2					Sn-1.001 O-1.094 (86) W-0.405
50% H_2O_2	Sn-0,084 O-1.273(86) W-1.143	Sn -0,167 O-1.286(86) W-1.047	Sn-0,333 O-1.312(86) W-0.855	Sn-0,667 O-1.366(86) W-0.467	Sn-1,001 O-1.419(86) W-0.080
65% H_2O_2	Sn-0,084 O-1.747(86) W-0.699	Sn -0,167 O-1.765(86) W-0.568	Sn-0,333 O-1.801(86) W-0.366	Sn-0,667 O-1.876(86) W-0	
	0.3 M Sn	0.9 M Sn	1.3 M Sn	1.5 M Sn	
55% H_2O_2			0.3706 gr $\text{Na}_2\text{Sn}(\text{OH})_6$ 1 mL 70% H_2O_2		
74% H_2O_2		0.2488 gr $\text{Na}_2\text{Sn}(\text{OH})_6$ 1 mL 86.5% H_2O_2			
94% H_2O_2	0.0724 gr $\text{Na}_2\text{Sn}(\text{OH})_6$ 1 mL 98.5% H_2O_2				
H_2O				0.5200 gr $\text{Na}_2\text{Sn}(\text{OH})_6$ 1 mL H_2O_2	

Material and Solution Characterizations.

High Resolution Scanning Electron Microscope. 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 with 5 mm working distance. Imaging was conducted using high resolution mode with a Through-the-Lens Detector. The specimen was prepared by dispersion of dried samples in ethanol in an ultrasonic bath, and the suspension was then dropped on a silicon wafer to dry.

Scanning Transmission Electron Microscope. STEM imaging was performed at 20 kV using the FEI Extra High Resolution Scanning Electron Microscope, MagellanTM 400L (Eindhoven, Holland). The specimen was prepared by dispersion of dried samples in ethanol in an ultrasonic bath, and the suspension was then dropped on a silicon wafer to dry.

The Helios PFIB DualBeam. SEM imaging of cross section of particles was performed using the Helios PFIB DualBeam. Microscope (DB FIB, Hillsboro, USA). Accelerating voltage was set at 5-15 kV with 5 mm working distance. The specimen was prepared by placing of dried samples on a carbon tape.

X-ray powder diffraction. XRD measurements were performed on a D8 Advance Diffractometer (Bruker AXS, Karlsruhe, Germany). The powder samples were carefully filled into low background quartz sample holders. The specimen weight was approximately 0.5 g. XRD patterns from 10° to 75° 2 θ were recorded at room temperature using CuK α 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 θ and counting time of 1 s/step. XRD patterns were processed using Diffrac Plus software.

Determination of the size distribution profile of particles was performed using the Multi-angle dynamic and static light scattering instrument Photocor Complex (Photocor Instruments, Tallinn, Estonia).

Determination of the surface area. The specific surface area of samples was performed using ATX-06 ("Katakon", Novosibirsc). As an adsorbate gas was used nitrogen and as a carrier gas was used helium. Definitions conducted by BET method. Sample characteristics measurements were occurred automatically in the adsorption-desorption mode using "Sorbometr M" program. Relative measurement error did not exceed 6%.

¹¹⁹Sn 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 μs and recycling time 30 s.

pH measurements were performed using HI-2210-02 Bench Top pH Meter (HANNA Instruments Deutschland GmbH, Germany).