Electronic Supplementary Information (ESI) for

Non-uniform spatial distribution of tin oxide (SnO_2) nanoparticles at the air-water interface

Inga Jordan,[a] Amaia Beloqui Redondo,[b] Matthew A. Brown,*[bc] Daniel Fodor,[b] Malwina Staniuk,[d] Armin Kleibert,[c] Hans Jakob Wörner,[a] Javier B. Giorgi,[e] and Jeroen A. van Bokhoven[bc]

a) Laboratory of Physical Chemistry, ETH Zürich
b) Institute for Chemical and Bioengineering, ETH Zürich
c) Paul Scherrer Institute
d) Department of Materials, ETH Zürich
e) Centre for Catalysis Research and Innovation and Department of Chemistry, University of Ottawa

E-mail: matthew.brown@chem.ethz.ch

Small angle X-ray scattering (SAXS): SAXS curve was recorded on an X'Pert PRO X-ray diffraction system (PANalytical B. V., Netherlands) with Cu K-alpha radiation (45 keV, 40 mA). The SAXS curve in the 2-Theta range 0.04–5.00° was recorded from a 7 wt % suspension of Nyacol SN15 (SnO_2) using 0.7 mm quartz capillaries (**Fig. ESI-1a**). The data were analyzed with the EasySAXS software. Prior to data analysis, the background arising from the capillary and solvent (50 mM KCl) was subtracted. The size distribution $D_v(R)$ was determined from the background corrected scattering curve (**Fig. ESI-1b**). The lower and upper limit for the scattering curve was set to 0.07 and 3 q^{-1}, respectively. The maximum radius was set at 20 nm. A Log-normal fit to Dv(R) yields a radius of 1.5 ± 0.8 nm. We report the NP diameters in the manuscript, 3.0 ± 1.6 nm.

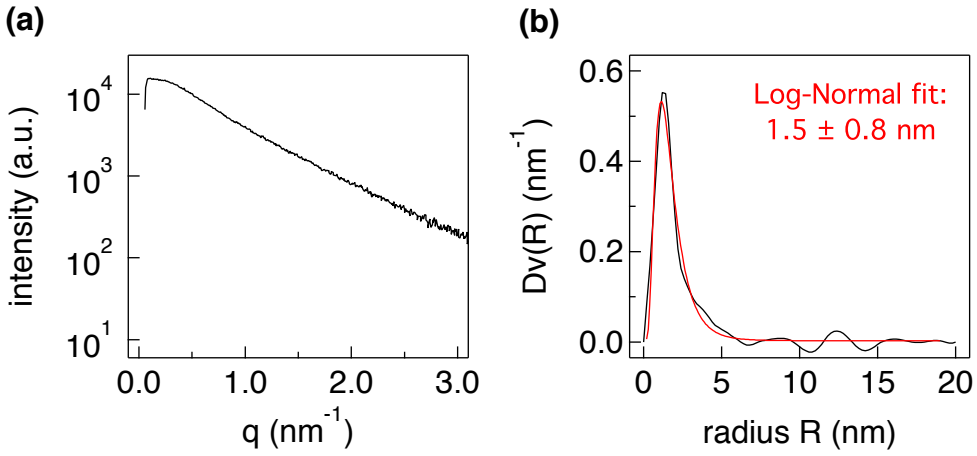

Figure ESI-1. (a) Background subtracted SAXS curve. (b) Size distributions $D_v(R)$ and log-normal fit showing the NP radius. The SnO_2 NPs have an average diameter of 3.0 ± 1.6 nm.

Transmission Electron Microscopy (TEM): As a complement to the in situ SAXS experiments measurements were performed using ex situ TEM. The stock 15 wt% SnO_2 suspension was diluted by a factor of 40 (0.375 wt%), and a small drop placed on a copper grid. The grid was dried in ambient air before being transferred to vacuum. The micrographs (for which **Fig. ESI-2** is representative of all collected) were measured with a FEI Tecnai G2 Spirit transmission electron microscope (120 kV). The micrographs show significant agglomeration of the particles that is not unexpected when drying a charge-stabilized NP suspension. From **Fig. ESI-2** it is clear that the large agglomerate consists of many smaller particles. At the edge of this large agglomeration several isolated particles can be seen. The inset shows one such particle that has a diameter of 3.1 nm, entirely consistent with the results of SAXS.

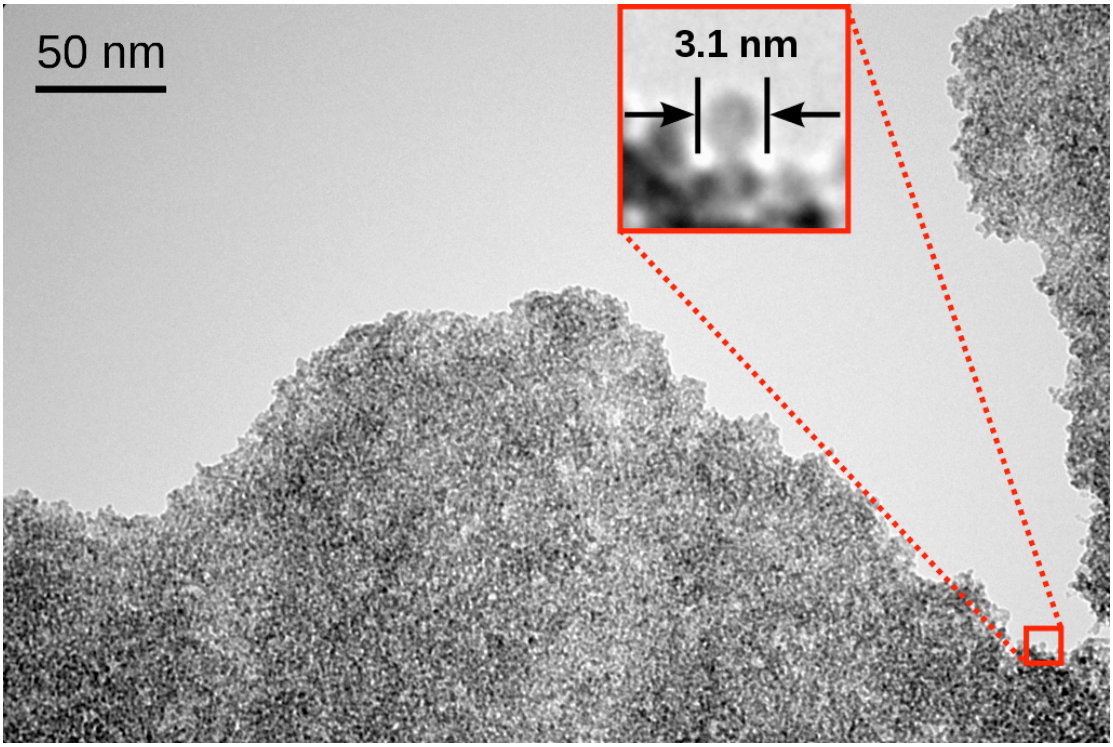

Figure ESI-2. TEM micrograph from a 0.375 wt% suspension of SnO_2. The inset shows an isolated particle at the edge of the large agglomerate with diameter of 3.1 nm.

X-ray Photoelectron Spectroscopy (XPS) peak fits: The Sn $3d_{5/2}$ spectra are fit using a single Gaussian function following a linear background subtraction. Representative fits for photoelectron kinetic energies of 209 and 809 eV are shown in **Fig. ESI-3**. The integrated peak area is normalized to photon flux, photoionization cross section, and the the transmission function of the NAPP hemispherical analyzer.

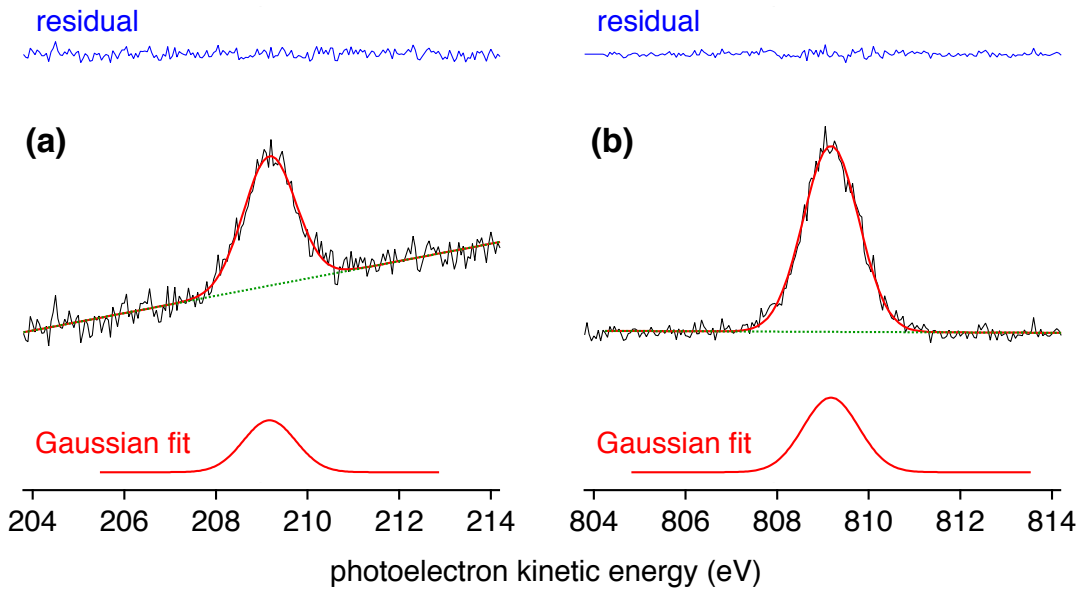

Figure ESI-3. Representative peak fits for the Sn $3d_{5/2}$ component at (a) 209 eV and (b) 809 eV photoelectron kinetic energy. Fitting involves a linear background and a Gaussian peak. The integrated peak area was normalized to photon flux, photoionization cross section, and NAPP analyzer transmission function. The residual to the fits are shown.

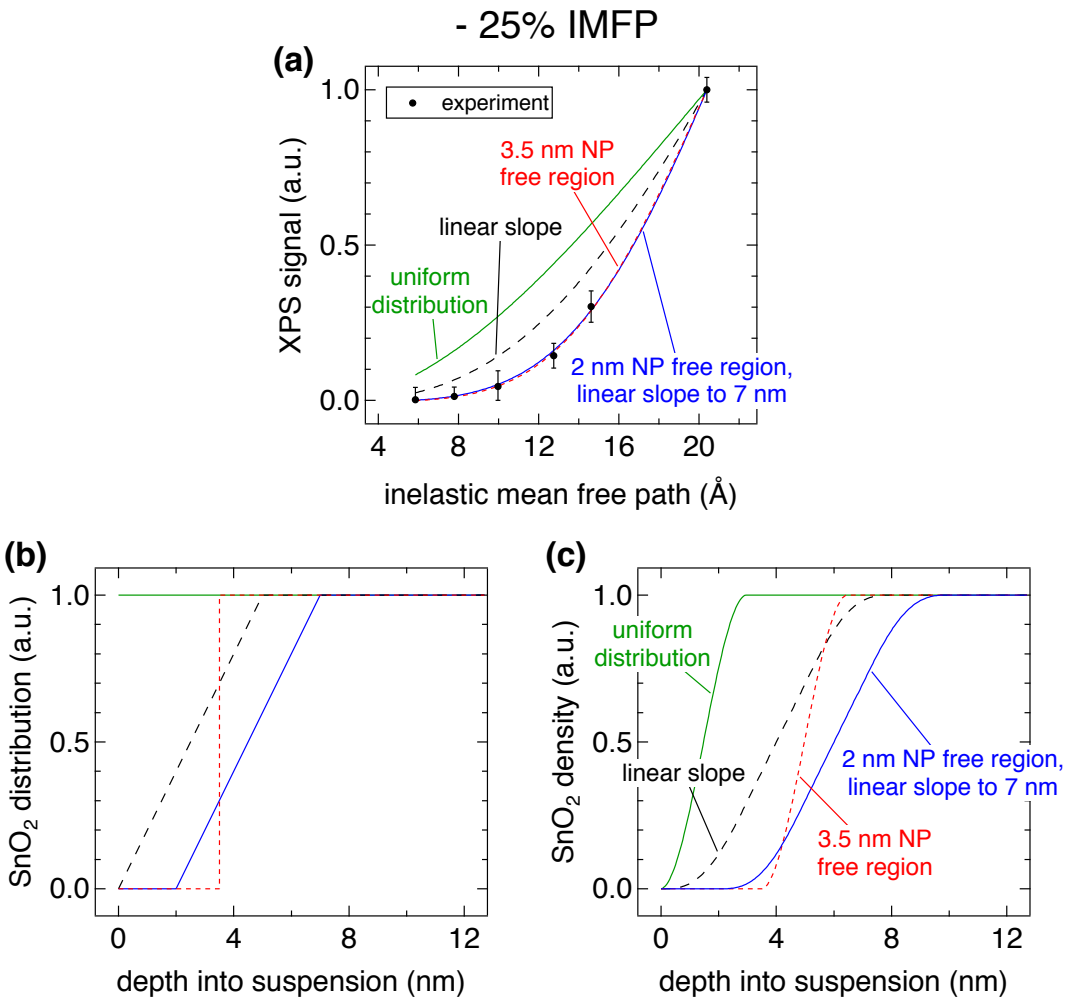

Figure ESI-4. Results for −25% inelastic mean free path. (a) Measured (markers) and calculated (lines) signal intensities as a function of inelastic mean free path. (b) Four different NP spatial distribution models and (c) their corresponding density profiles. The air-water interface is at a depth of 0 nm in (b) and (c). Results are consistent with a NP free region at the air-water interface of 2-3.5 nm.

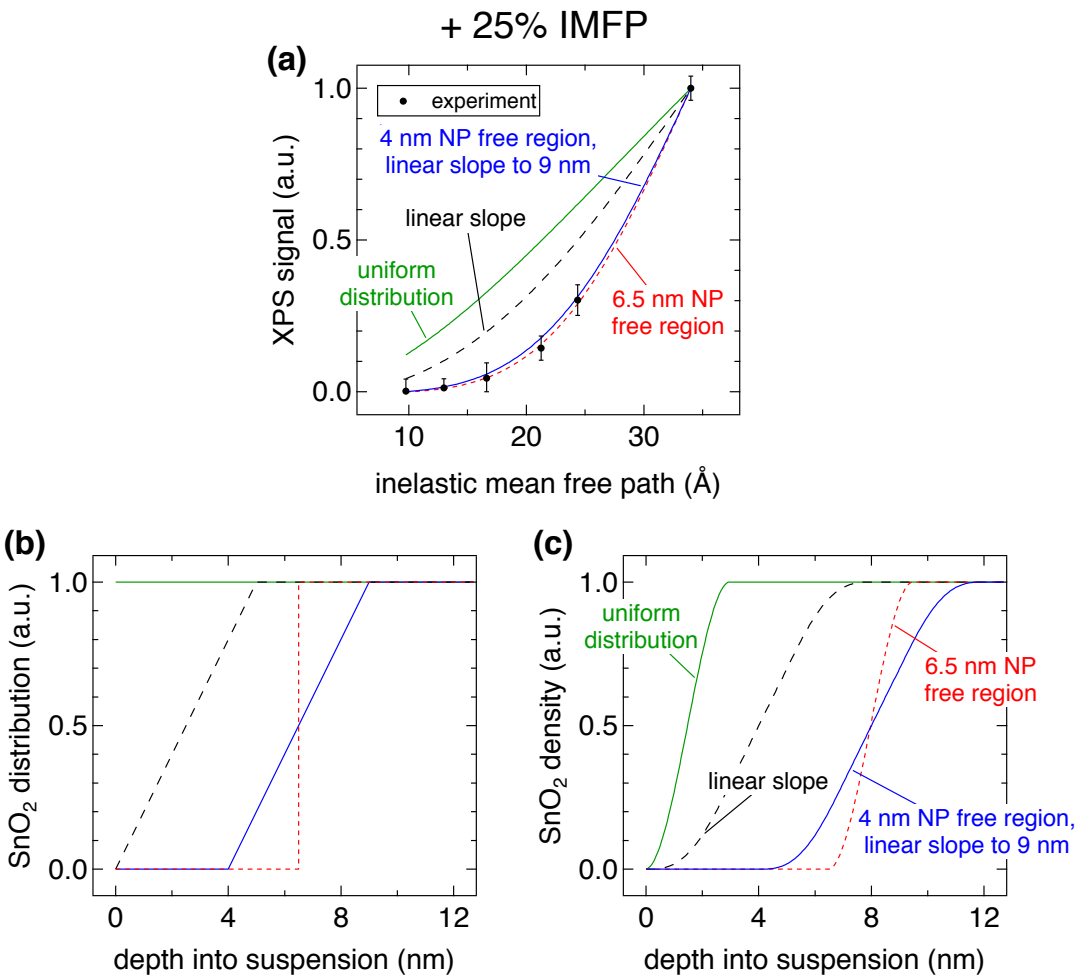

Figure ESI-5. Results for +25% inelastic mean free path. (a) Measured (markers) and calculated (lines) signal intensities as a function of inelastic mean free path. (b) Four different NP spatial distribution models and (c) their corresponding density profiles. The air-water interface is at a depth of 0 nm in (b) and (c). Results are consistent with a NP free region at the air-water interface of 4-6.5 nm.