Electronic Supplementary Information

In situ chemoresistive sensing in the environmental TEM: probing functional devices and their nanoscale morphology

Stephan Steinhauer,[a] *Jerome Vernieres,*[a] *Johanna Krainer,*[b] *Anton Köck,*[b]

Panagiotis Grammatikopoulos[a] *and Mukhles Sowwan*[*a]

[a] Nanoparticles by Design Unit, Okinawa Institute of Science and Technology (OIST) Graduate University, 1919-1 Tancha, Onna-Son, Okinawa 904-0495, Japan

[b] Materials Center Leoben Forschung GmbH, 8700 Leoben, Austria

Corresponding author: Mukhles Sowwan (mukhles@oist.jp)

Materials & Methods

SnO_2 nanowire growth and device fabrication

Growth of SnO_2 nanowires was achieved in a constant Ar gas flow (1000sccm) at 900ºC for 1h using SnO_2 thin films (500nm) deposited by spray pyrolysis as source material. The nanowires were mechanically transferred to commercial membrane-based TEM heating chips (Protochips Inc.) with two W electrodes for simultaneous heating and electrical biasing. Electron beam-induced deposition of Pt at the SnO_2-W contacts was performed with a FEI Helios G3 UC FIB-SEM at an electron acceleration voltage of 1kV. In order to minimize Pt contamination due to precursor gas molecules, samples were subsequently treated in an O_2/Ar plasma using a Gatan Solarus plasma cleaning system. Before electrical characterization in the environmental TEM, SnO_2 nanowire devices were annealed *in situ* at 400ºC in vacuum.

Deposition of Fe-Pd nanoparticles by magnetron sputtering inert-gas condensation

Nanoparticles were prepared using a magnetron sputtering inert gas condensation system equipped with a NanoGen cluster source (Mantis Deposition Ltd UK). Before deposition the main chamber base pressure was in the low 10^{-8}mbar range, whereas pressures during deposition were in the 10^{-4}mbar and 10^{-1}mbar range for the deposition chamber and the aggregation zone, respectively. Fe-Pd nanoparticles were deposited by co-sputtering of two separate 1″ Fe targets (purity 99.9%; individually operated at 20W magnetron power) and one 1″ Pd target (purity 99.95%; 5W magnetron power) at a constant Ar flow of 61sccm.

(Environmental) transmission electron microscopy

Experiments were performed using an FEI Titan Environmental TEM equipped with a spherical aberration image corrector at an operation voltage of 300kV. Fe-Pd nanoparticles were characterized by manually analyzing the size and shape of around 420 nanoparticles from 15 low-magnification TEM images (130k magnification), which resulted in a log-normal size distribution centered at around 9nm and a high probability of cuboid morphology (83%). Scanning TEM images were recorded using a high angle annular dark field detector, whereas electron energy loss spectroscopy was performed using a Gatan GIF Quantum spectrometer and a collection semi-angle of around 13mrad. *In situ* heating and biasing were achieved by means of the Protochips Aduro^{TM} 500 TEM holder platform and membrane-based heating chips with closed loop temperature control. The corresponding software package and a Keithley 2636 SourceMeter were used for operating the membrane-based heating chips and for nanowire device characterization in two-point configuration. Constant voltage bias was applied for the electrical resistance measurements, which were in some cases processed by an adjacent-averaging algorithm.

Supplementary Figures

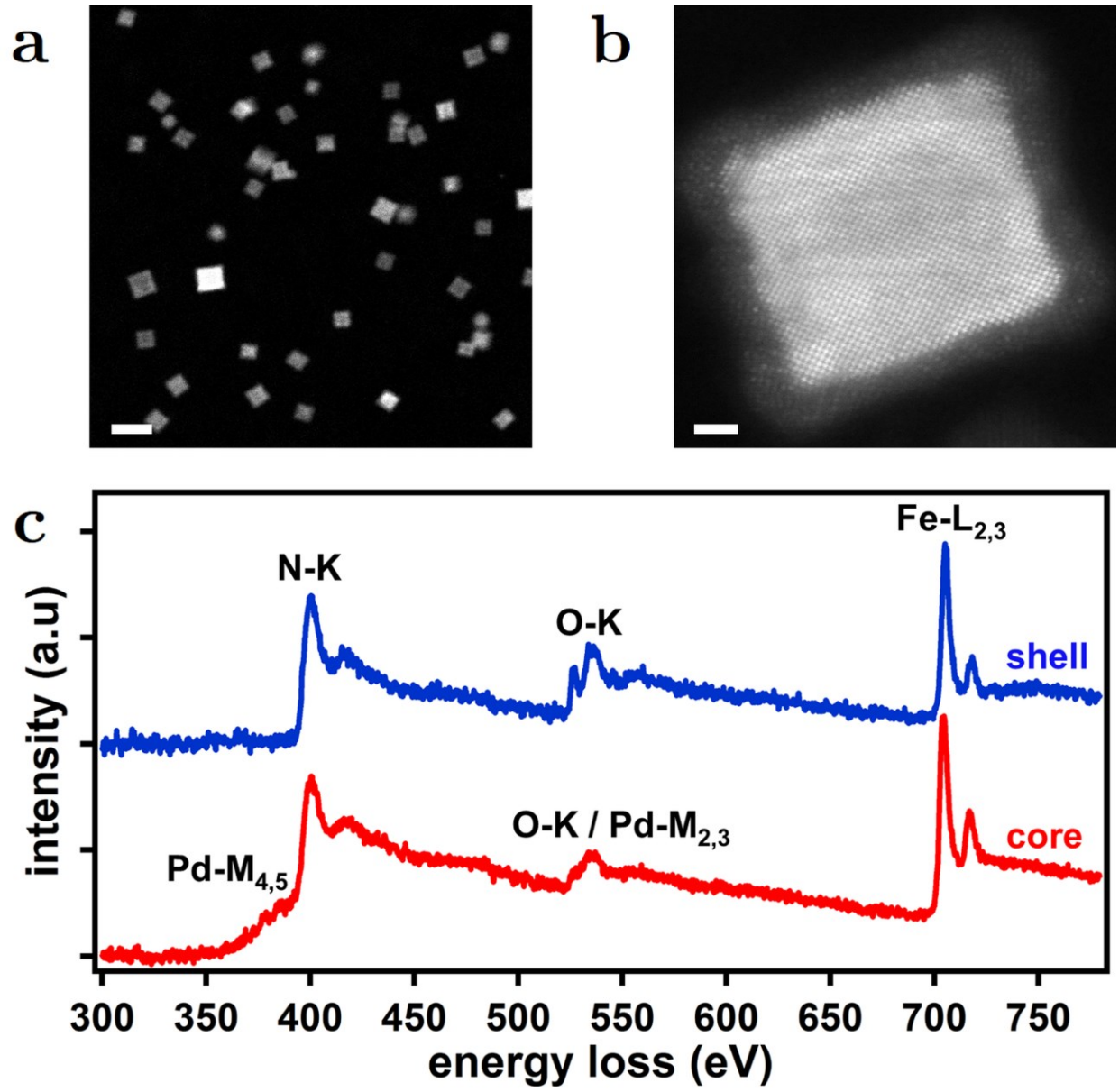

Fig. S1. Scanning TEM micrographs of Fe-Pd nanocubes at a) low (scale bar 20nm) and b) high (scale bar 2nm) magnification. c) Electron energy loss spectroscopy (EELS) confirmed the bi-metallic nature of the nanocube core and the formation of an Fe oxide shell.

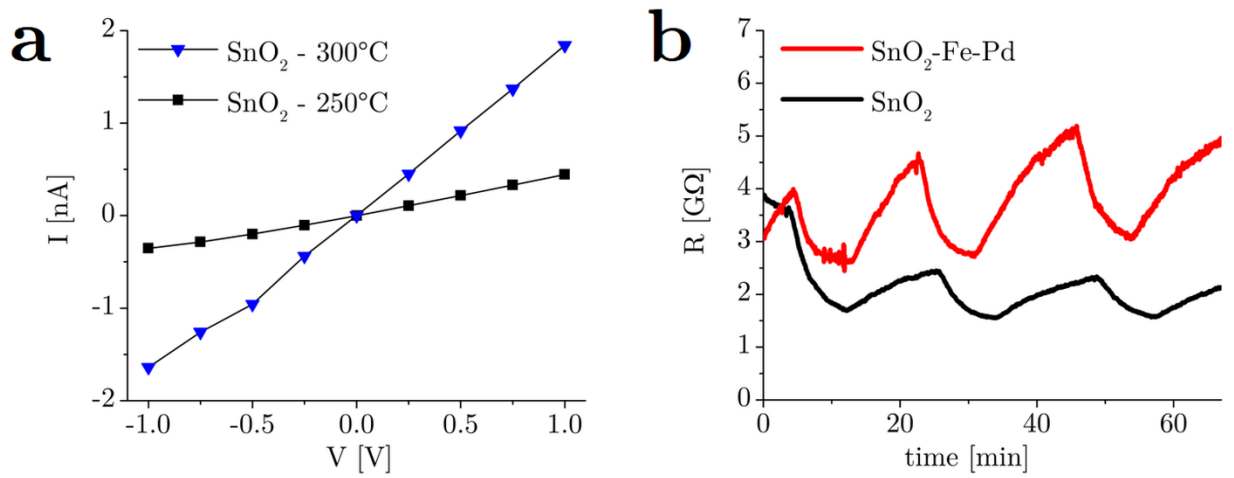

Fig. S2. a) Comparison of SnO_2 nanowire electrical resistance at 300°C and 250°C (20mbar O_2 pressure), exhibiting a considerably larger temperature coefficient compared to vacuum (shown in main article). Note that the absolute resistance value at 300°C is larger compared to the one reported in the main article due to a long-term resistance drift during prolonged *in situ* measurements, which is attributed to the compensation of bulk oxygen vacancies through ion diffusion from the surface [1]. b) Electrical resistance of pristine and Fe-Pd nanoparticle-decorated SnO_2 nanowire at 250°C and 20mbar O_2 pressure during exposure to three pulses of 100ppm CO. Sensor responses were calculated as 39.0±0.5% (SnO_2-Fe-Pd) and 33.6±2.3% (SnO_2) according to $(R_{O2} - R_{CO}) / R_{O2}$. The corresponding mean values and standard deviations were estimated using only the last two CO pulses in order to minimize systematic errors due to resistance drifts at the beginning of the measurements.

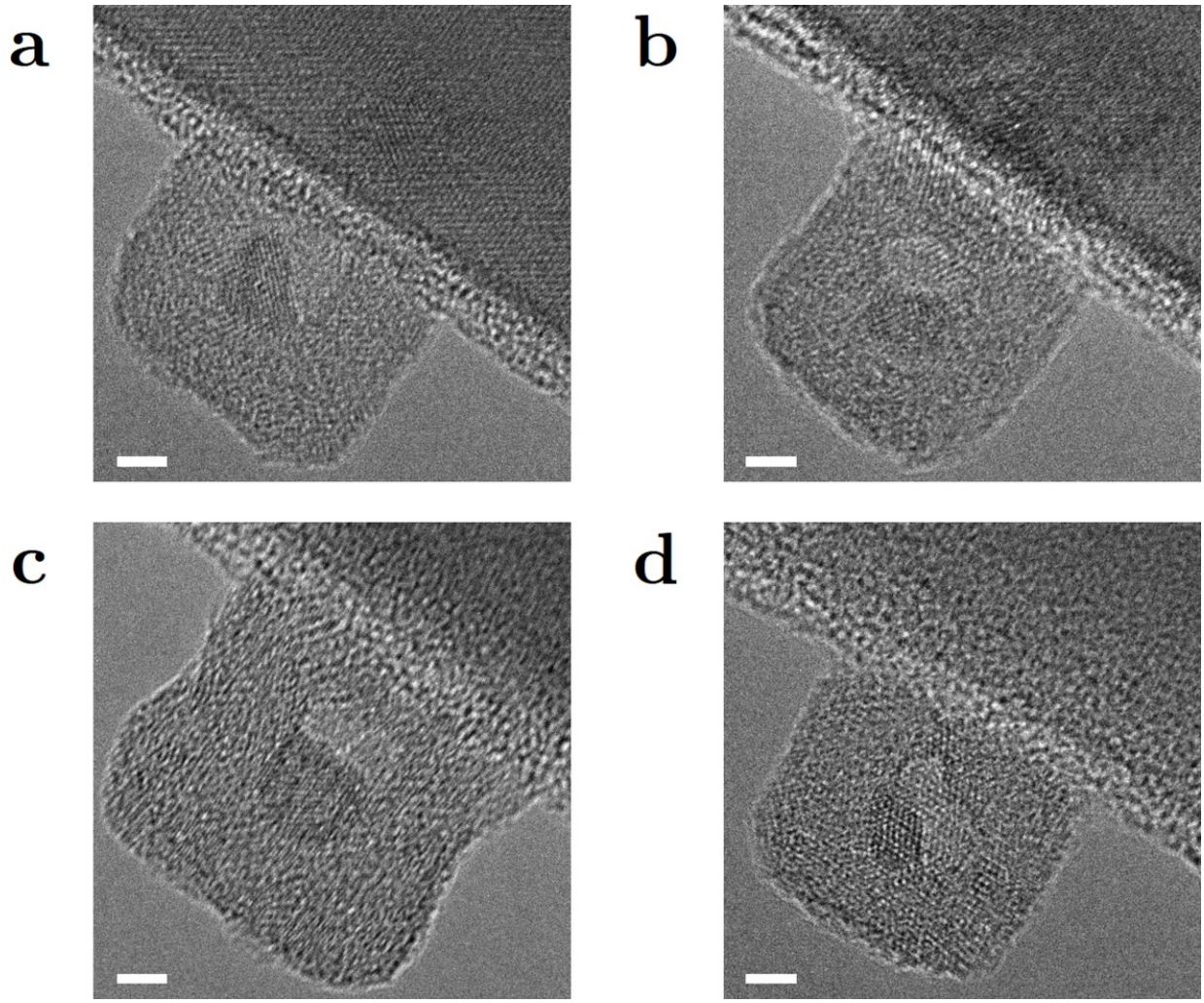

Fig. S3. a) – d) Exemplary Fe-Pd nanocubes supported on SnO_2 nanowire exhibiting specific Pd-rich core/void/shell structure after *in situ* chemoresitive sensing (scale bars 2nm). Visual inspection of multiple TEM images indicated that at least 75% of the 60 Fe-Pd nanocubes considered in the analysis showed noticeable void formation.

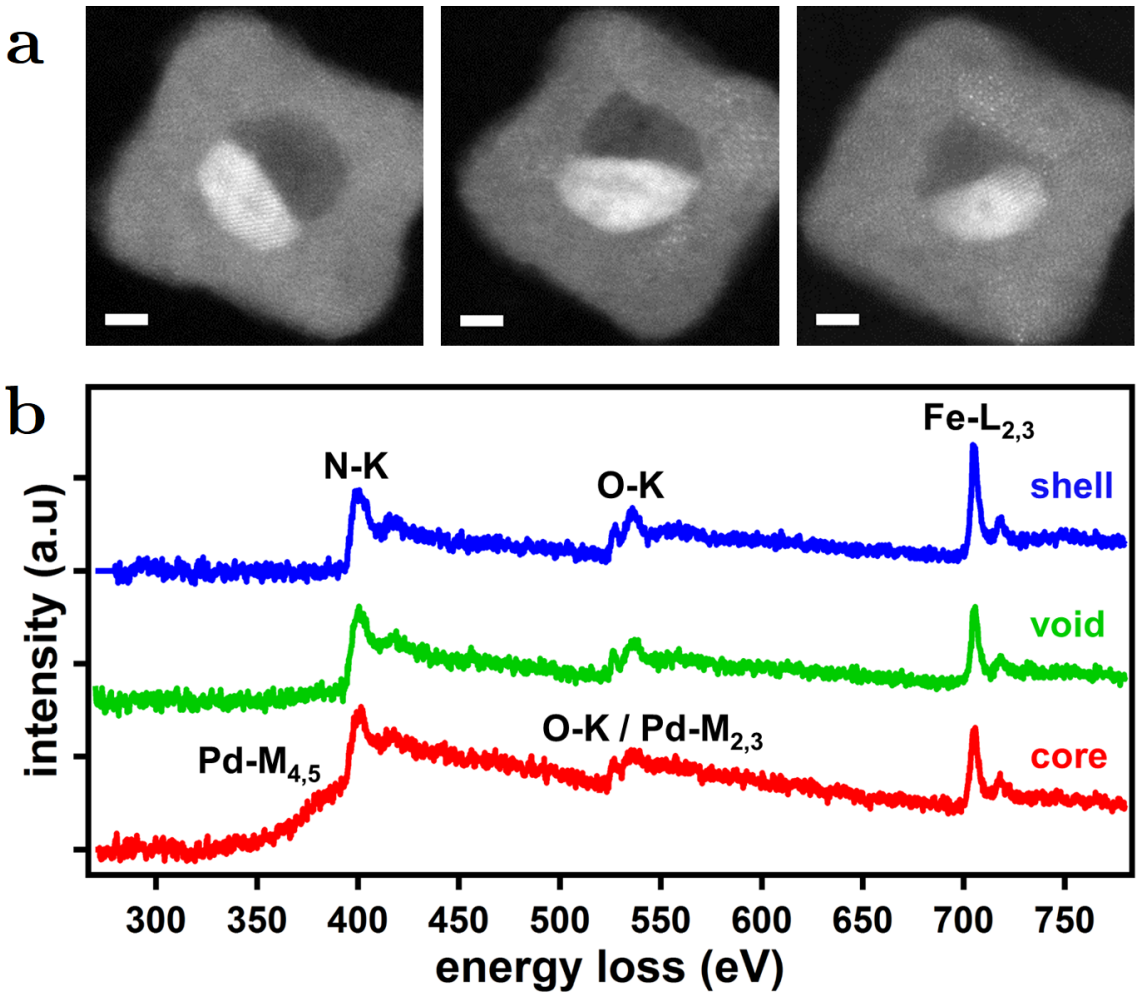

Fig. S4. Morphology of Fe-Pd nanocubes after *ex situ* thermal oxidation. a) Fe-Pd nanocubes deposited on a SiN TEM grid showed similar morphological changes compared to the *in situ* gas sensing experiment after *ex situ* thermal oxidation (250ºC, 90min, ambient air; scale bars 2nm). b) Electron energy loss spectra at different nanocube positions confirmed the formation of Pd-rich regions. The N-K peak can be attributed to the substrate.

References

1 F. Hernandez-Ramirez, J. D. Prades, A. Tarancon, S. Barth, O. Casals, R. Jimenez-Diaz, E. Pellicer, J. Rodriguez, J. R. Morante, M. A. Juli, S. Mathur, A. Romano-Rodriguez, *Adv. Funct. Mater.*, 2008, **18**, 2990.