Electronic Supplementary Information:

Understanding the size effects on the electronic structure of ThO_2 nanoparticles.

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HRTEM characterization:

The microstructure of ThO_2 samples was determined using high-resolution transmission electron microscopy (HRTEM) technique (Libra 200 by Carl Zess and a Jeol-2100F). Images were taken in transmission mode at magnifications up to 1000K at an accelerating voltage of 200 kV. The electron diffraction (ED) patterns were collected from a selected region of the sample. The analysis of the interplanar distances from the electron diffraction patterns was performed by comparing with the gold standard, taken at the same length of the chamber. To estimate the average particle size and distribution from HRTEM images, sets of > 200 particles were used.

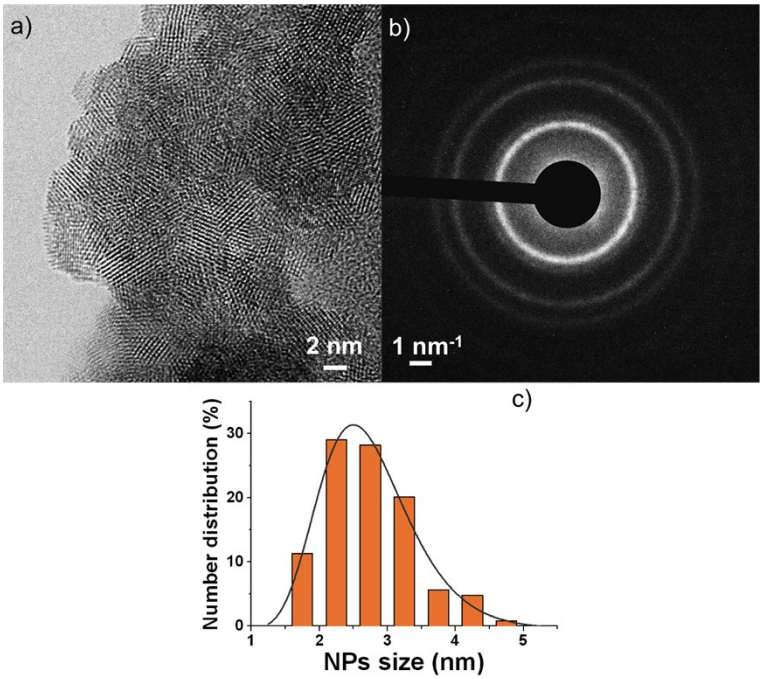

Figure S1: Sample "2.5 nm" a) HRTEM image and b) ED pattern for ThO_2 NPs obtained by precipitation from 0.1 M $Th(NO_3)_4 \cdot 5H_2O$ and 3M NaOH as precipitants with the subsequent drying at 40 °C on air; c) size distributions of ThO_2 NPs as obtained from HRTEM data.

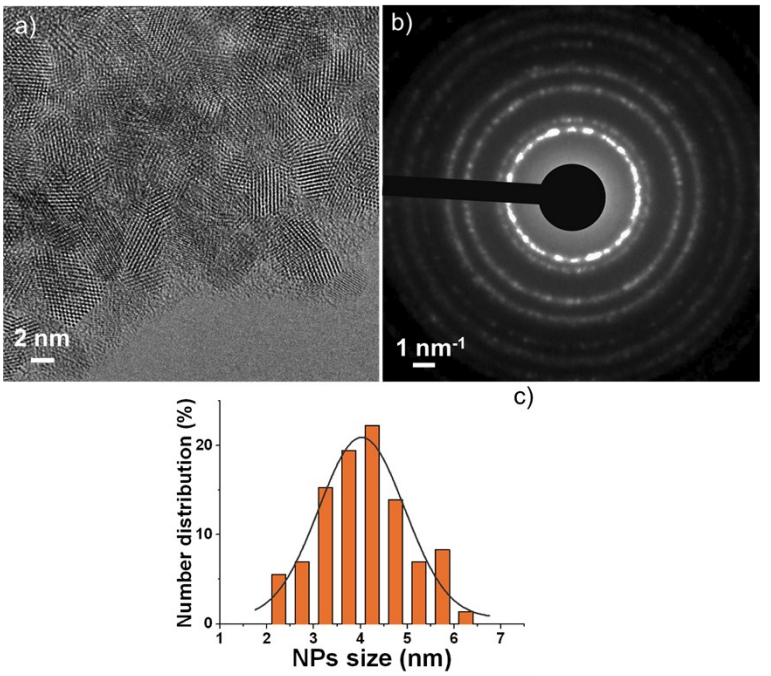

Figure S2: Sample "3.8 nm" a) HRTEM and b) ED data for ThO_2 NPs obtained by precipitation from 0.1 M $Th(NO_3)_4 \cdot 5H_2O$ and 3M NaOH as precipitants with the subsequent drying at 150 °C on air; c) size distributions of ThO_2 NPs as obtained from HRTEM data.

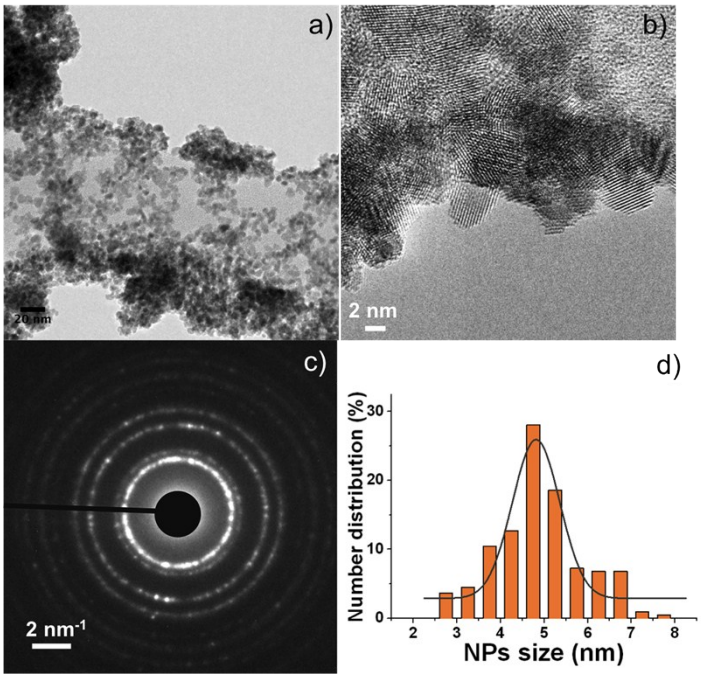

Figure S3: Sample "5.8 nm" a) b) HRTEM and d) ED data for ThO_2 sample obtained by annealing thoria NPs at 400°C for 4 hours; d) size distributions of ThO_2 NPs as obtained from HRTEM data.

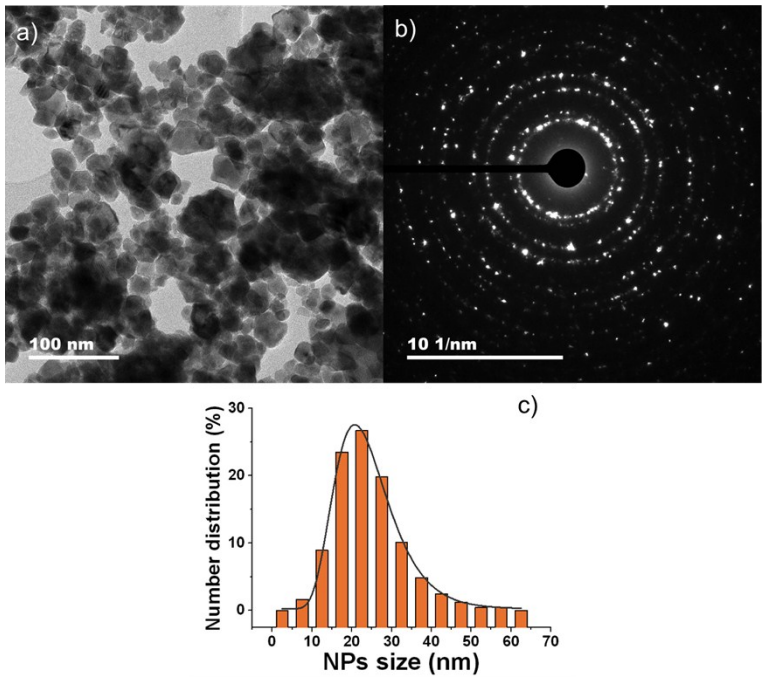

Figure S4: Sample "33.8 nm" a) HRTEM and b) ED data for ThO_2 sample obtained by annealing thoria NPs at 800°C for 4 hours; d) size distributions of ThO_2 NPs as obtained from HRTEM data.

Table S1. Experimental and theoretical interplanar distances in Å for ThO_2 NPs, studied in the present work.

Database PCPDF for ThO_2 [1]	Sample "2.5 nm"	Sample "3.8 nm"	Sample "5.8 nm"	Sample "33.8 nm"
3.23	3.15	3.56	3.32	3.17
2.79	2.71	3.09	2.91	2.75
1.98	1.93	2.15	2.04	1.93
1.61	1.63	1.84	1.73	1.65
1.39		1.49	1.45	1.36
1.28		1.24	1.32	1.26
1.25			1.22	1.21

1. Holzer, J. & McCarthy, G. *ICDD Grant-in-Aid*, (North Dakota State University, Fargo, North Dakota, USA, 1991).