

Electronic supplementary information for Article

" Ensemble modeling of very small ZnO nanoparticles"

Table 1 Resulting parameters of Rietveld refinements and ensemble modeling for all models presented in this article. For comparison the bulk values for ZnO are shown as well. ⁽¹⁾ For all polyhedra "height" means the size of the particle in the [001] direction (direction of layer stacking). ⁽²⁾ average size, for details see Table 2. ⁽³⁾ lateral diameter being identical in [100], [010] and [110] direction. ⁽⁴⁾ diameter in [100] / [010] direction, respectively. The size in [110] direction is identical to that in [010] direction, hence polyhedron II has 4 smaller and 2 bigger side-facets, see also inset of Fig. 2. ⁽⁵⁾ lateral diameter in [100] / [111] direction, respectively. Note that the [111]-direction is not a lateral direction (see inset of Fig. 2).

Method or model	R _{wp}	Number of parameters (structure + background)	Lateral diameter (in direction $\perp$ to side-facets) [Å]	Vertical size (height) [Å] ⁽¹⁾	Fraction (number- / volume- %)	Lattice parameters a [Å] c [Å]	z-position of O-atom [lattice units]	Atomic displacement parameter b [Å ²]	Shell thickness (lateral / vertical) [Å]	Max. lateral shift of Zn atoms [Å]	Max. lateral shift of O atoms [Å]	Max. vertical shift of Zn atoms [Å]	Max. vertical shift of O atoms [Å]
ZnO wurtzite bulk						3.250 5.207	0.382						
SIMREF Rietveld fit	5.7%	14+7	30 (Ø)			3.284 5.288	0.392	0.54					
FULLPROF Rietveld fit	3.7%	13+6	25 ⁽²⁾ (Ø)			3.279 5.263	0.373	0.50					
Polyhedron I + size distribution + surface strain	2.9%	13+7	30 ⁽³⁾	24	84.3% / 64.7%	3.258 5.215	0.380	1.72	1.71 / 3.49	0.360	0.030	0.734	0.062
			43 ⁽³⁾		3.8% / 5.7%				2.39 / 3.49	0.504	0.042		
			55 ⁽³⁾		11.9% / 29.6%				3.07 / 3.49	0.647	0.054		
Polyhedron I + surf. Strain	3.4%	10+7	35 ⁽³⁾	23		3.257 5.217	0.377	1.60	2.01 / 1.95	0.449	0.024	0.437	0.024
Polyhedron I + size distribution	4.9%	10+7	25 ⁽³⁾	21	93.2% / 77.1%	3.275 5.254	0.386	2.00					
			40 ⁽³⁾		1.4% / 3.1%								
			52 ⁽³⁾		5.4% / 19.8%								
Polyhedron I + stacking fault probability: 1.8%	5.4%	7+7	29 ⁽³⁾	21		3.275 5.253	0.385	1.95					
Polyhedron I	5.2%	6+7	28 ⁽³⁾	21		3.275 5.254	0.387	2.00					
Polyhedron II	5.5%	7+7	21 / 42 ⁽⁴⁾	18	35.3%	3.276 5.273	0.382	1.90					
Polyhedron III	5.8%	7+7	37 / 31 ⁽⁵⁾	20		3.266 5.282	0.383	1.87					
Sphere	7.4%	5+7	33 (Ø)			3.266 5.290	0.392	2.00					

Table 2 Details of the FULLPROF fit: Individual peak widths and the resulting “apparent particle sizes” in the corresponding crystallographic directions.

hkl	Apparent size [Å]	2 θ [°]	FWHM [°]
100	25.85	26.30	2.206
002	27.44	28.42	2.120
101	24.00	29.96	2.355
102	23.31	39.11	2.469
110	26.97	46.42	2.264
103	22.31	51.30	2.672
200	28.86	54.13	2.344
112	24.73	55.33	2.509
201	25.28	56.24	2.478
004	27.17	58.81	2.378
202	24.00	62.27	2.658
104	24.55	65.52	2.657
203	23.03	71.66	2.897
210	27.14	74.02	2.594
211	25.63	75.81	2.741
114	22.54	78.04	3.076
212	24.73	81.10	2.923
105	24.24	81.77	2.986
204	22.83	84.04	3.185
300	29.97	86.08	2.848
301	27.69	87.81	2.834
213	24.68	89.76	3.142
302	24.93	92.99	3.209
006	27.01	94.86	3.074
205	23.01	99.64	3.645