Tolerance in Superstructures Formed by High-Quality Colloidal ZnO Nanoparticles with Hexagonal Cross-Section

Sebastian Theiss, ^a Michael Voggel, ^a Moritz Schlötter, ^a Sebastian Sutter, ^a Martin Thomas Stöckl ^a and Sebastian Polarz^{a,*}

^{a.} University of Konstanz, Department of Chemistry, Functional Inorganic Materials Group, Universitätsstrasse 10, D-78457 Konstanz, Germany.

ELECTRONIC SUPPLEMENTARY INFORMATION



(a)



PXRD pattern - assignment.



PXRD patterns: Temperature-dependency of the intensity and the FWHM of the (002) reflex.



Correlation of the aspect ratio to synthesis temperature derived from particle-size analysis from TEM data.

S-2



Correlation of $D_{a,b}$ and D_c to synthesis temperature derived from particle-size analysis from TEM data.





DLS measurements of the ZnO nanoparticles with different morphologies in THF.

Fig. S2. Characterization of ZnO nanoplates prepared at $T = 45^{\circ}$ C.

(a)



TEM micrograph (scalebar = 100nm)



HRTEM (scalebar = 10 nm)





HRTEM (scalebar = 1 nm) and FFT.





TEM micrograph (scalebar = 30 nm). Original (left) and labelled image after application of the analysis tool. The Corners of the particles are marked by green points, the centroids by a red one. The numbers refer to the continuous indexing of particles per image.

In a first step, particle boundaries in a frequency band pass denoised image are identified by a laplacian filter and used to generate a binary particle map. For each particle two normalized circular profiles, the edge distance from the centroid (Maximum of the numerical derivative of the intensity profile starting from the centroid) and the intensity of the masked image (Average intensity of profiles from the centroid) with a data point for every degree of the circle were measured. These were summed in a weighted profile from which corner angles were identified as local maxima. Due to hexagon symmetry for each corner angle an opposite angle was introduced, if not present. For each of these angles the location of the edge was determined as the maximum of the numerical derivative of the corresponding intensity profile, yielding putative corner coordinates. From these coordinates the convex hull is calculated, removing corner points from the inside of the hexagon. In the next step, evaluating the angle formed by three adjacent putative corner points, coordinates on hexagon edges are removed. If less than six corners have been identified, iteratively the central region of the largest inner angle is probed for a local maximum of the intensity profile, indicating a missed corner.

If six corners have been identified, the area of the hexagon is calculated from the coordinates. To describe the shape of the hexagon, "Eccentricity" (E) and "Irregularity" (I) are used as parameters. To calculate E_{angle} from the angles, opposite inner angles of the hexagon are summed. E_{angle} is calculated as the ratio of minimum and maximum value. To calculate E_{edge} from the edge lengths, for the three pairs of opposite edges, the normalized ratio of the sum of the length of two opposite edges and the sum of the lengths of the remaining edges is formed. E_{edge} is the minimum of these ratios. To calculate I either inner angles (I_{angle}) or edge lengths (I_{edge}) are alternatingly divided into two groups. I is the ratio of the sums of these groups which is smaller than 1.

The ImageJ macro can be downloaded from: https://github.com/bic-kn/HexagonParameters

(b)

Excentricity (E_{angle})



 $\mathsf{E}_{\mathsf{angle}} = \mathsf{min}(\alpha,\beta,\gamma) \ / \ \mathsf{max}(\alpha,\beta,\gamma)$

Eccentricity is the ratio of the minimum sum of opposite angles divided by the maximum sum of opposite angles

Irregularity (I_{angle})



Irregularity is the ratio of the sums of alternating angles.

Irregularity is the ratio of the sum of length of alternating edges.

Schematic depiction of the geometrical terms used to evaluate and describe the spatial parameters of the hexagonal nanoplates.



 $E_{edge} = min(E_0, E_1, E_2)$

b

| = 1

Eccentricity is the minimum normalized ratio of the sum of the length of the remaining four edges and the length of two opposite edges.

(a+c+e)

(b+d+f)

| < 1



Fig. S4. Parameters influencing the size and polydispersity of the hexagonal ZnO nanoplate dispersions.

(a) Time-dependent correlation (left) of the position of the maximum and of the width according to the image analysis of the particle dispersion.



(b) Precursor concentration-dependent correlation (left) of the position of the maximum and of the width according to the image analysis of the particle dispersion.



(c) Capping agent concentration-dependent correlation (left) of the position of the maximum and of the width according to the image analysis of the particle dispersion.

Fig. S5. Colloidal stability of ZnO of the hexagonal ZnO nanoplate dispersions.



(a) Time-dependency of UV-VIS absorption spectra (left), the blue line (λ = 355 nm) corresponds to the graph shown on the right side indicating a constant absorption intensity over time.



(b) Time-dependency of particle size distributions derived from DLS.

Fig. S6. Liquid-air assembly of ZnO nanoparticles.



Photographic images of a nanoparticle film prepared at the DEG/air interface. For better visibility, the bottom image shows the edges of the film. Diameter of Petri-dishes equals to 4 cm.

Fig. S7. Ligand exchange processes; hexagonal ZnO nanoplates.



(a) ¹H-NMR of free GlyOL (grey), OL (black) as a references, the synthesized OL-stabilized ZnO nanoplates (red) and after ligand exchange with GlyOL (blue).

¹**H NMR OL.** (400 MHz, THF) δ (ppm) = 0.89 (t, 3H, CH₃), 1.31 (m, 20H, -CH₂-), 1.57 (t, 2H, -CH₂-), 2.04 (q, 2H, -CH₂C=), 2.2 (t, 2H, -CH₂-), 5.3 (dt, 2H, -CH=CH-)

¹H NMR GlyOl. (400 MHz, CDCl₃) δ (ppm) = 0.88 (t, 3H, -CH₃), 1.27 (m, 20H, -CH₂-), 1.63 (t, 2H, -CH₂-), 2.02 (m, 4H, -CH₂C=), 2.35 (t, 2H, -CH₂-), 3.6 (dd, 1H, -CHH´-), 3.7 (dd, 1H, -CHH´-), 3.93 (pq, 1H, -CHO-) 4.15 (dd, 1H, -CHH´-), 4.21 (dd, 1H, -CHH´-)



(b) FT-IR spectra (fingerprint region) of free GlyOL as a reference (grey), the synthesized OL-stabilized ZnO nanoplates (black) and after ligand exchange with GlyOL (blue).

1744 cm⁻¹: carbonyl stretching of GlyOl, C=O
1562 cm⁻¹: shifted carbonyl stretching due to deprotonation of OL
1450 cm⁻¹: asymmetric C-H bending
1300-1000 cm⁻¹: aliphatic C-O ester stretching of Monoolein

Fig. S8. Interface-aided 2-D assembly of hexagonal ZnO nanoplates

(a) OL-stabilized particles



TEM micrograph scalebar = 300nm

(b) GlyOL-stabilized particles



TEM micrograph scalebar = 1000nm



TEM micrograph scalebar = 300nm



TEM micrograph scalebar = 200nm



TEM micrographs of ZnO nanoplate superstructures. The white bars mark straight lines of continuously ordered ZnO nanoplates. The long range order spans about 600-70 nm, correlating to 50-60 nanoplates.

Fig. S9. Purification effects due to self-assembly by the DEG-based process.









FT-IR spectra (trans, KBr) of the synthesized OL-stabilized ZnO nanorods (black) and after ligand exchange with GlyOL (blue).

3400 cm⁻¹: residual H₂O from KBr matrix
300-2800 cm⁻¹: aliphatic C-H stretching
300 cm⁻¹: C=C stretching
1744 cm⁻¹: carbonyl stretching of GlyOl, C=O
1562 cm⁻¹: shifted carbonyl stretching due to deprotonation of OL
1450 cm⁻¹: asymmetric C-H bending
1300-1000 cm⁻¹: aliphatic C-O ester stretching of Monoolein

(b) Interface-aided 2-D assembly of hexagonal ZnO nanorods; OL-stabilized particles.



TEM micrograph scalebar = 500nm



TEM micrograph scalebar = 100nm

(c) Interface-aided 2-D assembly of hexagonal ZnO nanorods; GlyOL-stabilized particles.



TEM micrograph scalebar = 500nm



TEM micrograph scalebar = 200nm

Figure S11. Bond order correlation analysis.



References

1 C. Lizandara-Pueyo, S. Siroky, M. R. Wagner, A. Hoffmann, J. S. Reparaz, M. Lehmann and S. Polarz, *Adv. Funct. Mater.*, 2011, **21**, 295-304.