Electronic supplementary information

From evaporation-induced self-assembly to shear-induced alignment

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Evolution of the ZnO nanorod aspect ratio (AR) with synthesis time

Due to the wurtzite crystal structure ZnO promotes the shape-anisotropic growth of nanorods. The obtained particles are thus ideal candidates for self-assembly to liquid crystalline phases in solution and thin films. The nanorod length (L) and aspect ratio (AR, length/diameter) is varied by the synthesis time ranging from 1 day to 14 days. The mean diameter (D) of the nanorods stays almost constant at about 20 nm \pm 5 nm.



S1. Aspect ratio (AR) plotted versus the length (L) of the synthesized ZnO nanorods. The deviation in AR and L is increasing with increasing synthesis time.

The mean AR can be tuned between 2 and 8 and the mean L between 30 and 190 nm. The deviation in AR and L is steadily increasing with synthesis time as depicted in S1.



S2. Intensity versus the scattering vector for a) ZnO nanorods with AR > 5 and 3.4 vol.-%, b) ZnO nanorods with AR < 5 and 3.4 vol.-%, c) ZnO nanorods with AR > 5 and 36 vol.-% and d) ZnO nanorods with AR < 5 and 36 vol.-%. Original suspensions are given by the black slopes; the red slopes are corresponding dilutions (about 0.042 vol.-%). The resulting structure factor is given by the green slopes.

The intensity versus the scattering vector of ZnO nanorod dispersions with AR > 5 and AR < 5 at 3.4 vol.-% and 36 vol.-% and appropriate dilutions with concentrations of about 0.042 vol.-% (red curves) are shown in S2. To determine the S(Q) (green line) we simply dived the scattering pattern of the concentrated samples (black) with the pattern of the corresponding diluted sample (red). Only the structure factors of the concentrated samples show at least one peak due to the high concentration of the nanorods.

Evaporation-induced self-assembly (EISA)

When high volume concentrations are used highly unordered and rather thick films are formed by EISA. Although the substrate is not withdrawn convective flows reorganize the nanorod ensembles near the substrate. Near the solvent-air interface the nanorods are oriented parallel to the contact line as depicted in S3.



S3. ZnO nanorods with high AR > 5 processed solely by evaporation using a suspension with high volume concentration of 3.4 vol.-%. As can be seen in the image EISA forms highly unordered films at high volume fractions.

Surface coverage of ZnO nanorods with AR > 5 and AR < 5

Thin films formed by EISA comprised of nanorods with an AR > 5 are compact. Films obtained from EISA of AR < 5 nanorods are striped whereby the individual stripes are sparsely interconnected. Microscope images of both films are depicted in S4. Both films are formed at the same conditions (see figure caption).



S4. Light microscope images of evaporation-induced thin films of ZnO nanorods. Nanorods with AR >5 form dense compact films (left). Low AR nanorods (AR < 5) form stripes, which are sparsely connected (right). Both films were processed at 20 °C from a dispersion containing 0.142 vol.-% of ZnO nanorods.

Reorientation and domain like alignment at AR > 5 and 5.7 vol.-%

The SEM image given in S5 depicts the reorientation of nanorod ensembles by convective flows in the wet film. The nanorod ensembles form domains prior to drying. This leads to reduced BO and SO.



S5. Domains of nematically aligned ZnO nanorods at AR > 5 and 5.7 vol.-%

Rheology measurements

In S6 the shear responses in the shear rate ($\dot{\gamma}$) range 10 s⁻¹ to 1000 s⁻¹ are depicted for low (< 5) and high (> 5) AR nanorods. At low AR all ZnO dispersions show Newtonian flow behaviour over the whole concentration range (see S6, left). The viscosity is increasing with the volume fraction. At high volume fractions (exceeding 25 vol.-%) shear thinning is observed for ZnO nanorods with AR >5 due to structure formation in the suspension (see S6, right).



S6. Rheology measurements performed for different concentrations of ZnO nanorod dispersions containing low AR < 5 (left) and high AR > 5 (right) nanorods.