Facile direct synthesis of ZnO nanoparticles within lyotropic liquid crystals: towards organized hybrid materials

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Supplementary Information

1. Experimental

1.1. Characterization techniques and Materials

Small-angle X-ray scattering experiments were performed at the BM02 experimental station of the European Synchrotron Radiation facility at Grenoble, France. The sample-to-detection distance was 0.365 m and the wave length was $\lambda = 0.1159$ nm. The data were recorded using a CCD Peltier-cooled camera (SCX90-1300, Princeton Instruments) of 1340×1330 pixels. Data processing (dark current subtraction, flat-field correction, and normalization) was performed using homemade software. The accessible range of scattering vector modulus q ($q = (4\pi\sin\theta)/\lambda$, where 2θ is the scattering angle) was $0.25 < q < 5$ nm^{-1}. Further characterization of liquid crystal phases was performed on a hot stage FP 82HT from Mettler Toledo under a polarized optical microscope BX50 from Olympus. TEM samples were prepared by slow evaporation of droplets of colloidal solution deposited on carbon-supported copper grids. Micrographs were taken using a JEOL 120 kV electron microscope. The nanoparticle size-distribution histograms were determined by using magnified TEM images. The size distribution of the particles was determined by measuring a minimum of 200 particles for each sample. The size distributions observed were analyzed in terms of Gaussian statistics (w_c (σ)).

Unless otherwise stated, the chemicals have been used as provided from the suppliers and water content was systematically measured by Karl Fischer coulometric titration on a Metrohm instrument. Sensitive substances and reactions were handled in an MBraun Inert Gas System or under an argon atmosphere in carefully heated glassware, using the standard Schlenk techniques. Zinc precursor was purchased from NANOMEPS.

1.2. Synthetic Procedures

Several mixtures have been prepared for the formation of LLC phases based on the phase diagram.[1] These mixtures consisted of $PEO_{37}PPO_{58}PEO_{37}$ and formamide together with heptane. The quantity of heptane used varied between 0 % for binary mixtures up to a maximum of 10 % for ternary ones. The synthesis was achieved by mixing the desired components in a sealable vial and homogenized at room temperature in an ultrasound bath for 1 hour. The samples were then left to stand for several days in order to ensure homogenization. The mixtures obtained at equilibrium were transparent and homogeneous. In the microemulsion phase, the samples consisted of low-viscosity fluids while clear stiff gels were obtained for samples with higher pluronic content.

2. Characterization of the undoped LLCs

2.1. SAXS

Mixtures in the region between the hexagonal phase and microemulsions show phases in which micelles crystallize in cubic lattices. Samples within this lyotropic cubic phase boundaries were also analyzed by SAXS. Figure S1 shows the typical x-ray scattering pattern of a sample in the micellar cubic phase.
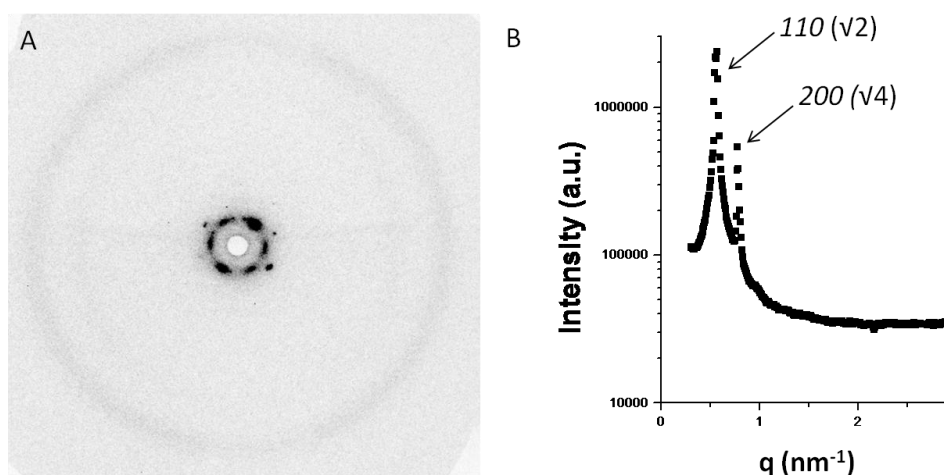

Figure S1: SAXS diffraction pattern for a lyotropic pluronic-based mixture in the cubic phase (A) and its corresponding diffraction intensity profile (B). First two *hkl* indices are shown; *110* and *200* in ratios √2:√4.

Figure S2 shows a typical SAXS pattern of a sample in the hexagonal phase and its corresponding diffraction intensity profile recorded at room temperature. The relative positions of the four diffraction peaks observed are in ratios $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ known for the 2D symmetry hexagonal phase and correspond to the *10*, *11*, *20* and *21* Bragg reflections. The structure of the system comes from the self-assembly of cylindrical domains arranged in a hexagonal lattice. The nearest neighbour distance is 109 Å which corresponds to the distance between two adjacent cylindrical structures.
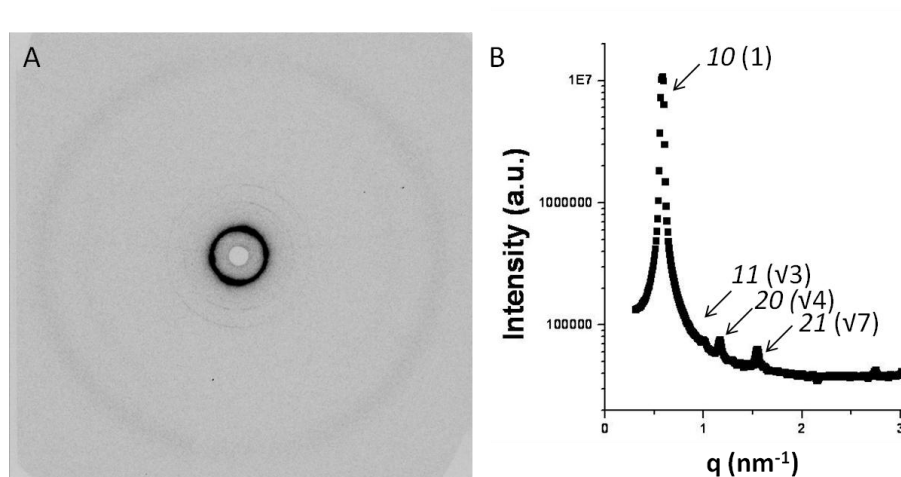

Figure S2: SAXS diffraction pattern for a lyotropic pluronic-based mixture in the hexagonal phase (A) and its corresponding diffraction intensity profile (B).

2.2. POM

Figure S3. Birefringent texture for a hexagonal phase mixture consisting of 55% $PEO_{37}PPO_{58}PEO_{37}$, 40% formamide and 5% heptane under ambient conditions.

2.3. Characterisation of NP-embedded LLCs

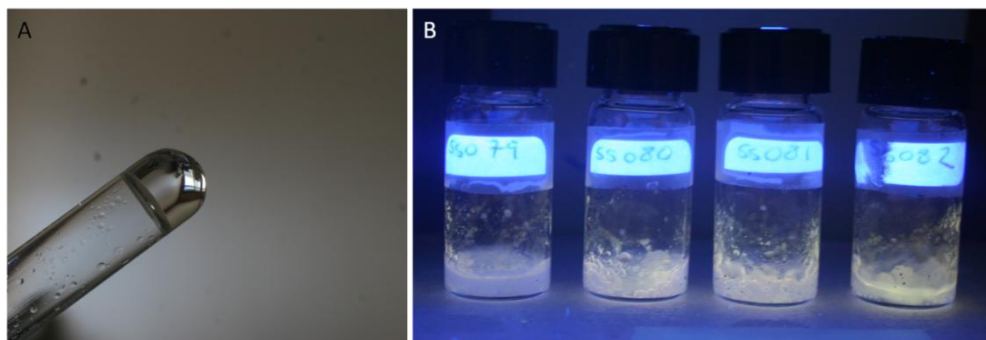**Figure S4:** (A) a $PEO_{37}PPO_{58}PEO_{37}$-formamide-heptane gel and (B) a series of gels which are luminescent under a UV lamp due to the ZnO NPs grown within.
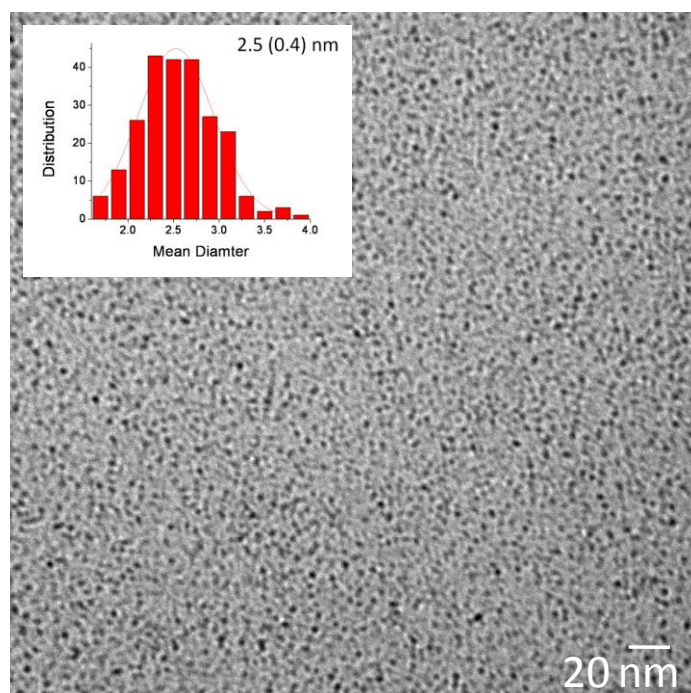

Figure S5: TEM micrograph for patterned ZnO NPs of 2.5(0.4) nm formed inside the hexagonal phase of a 55% $PEO_{37}PPO_{58}PEO_{37}$-40% formamide-5% heptane mixture (Hex-2).
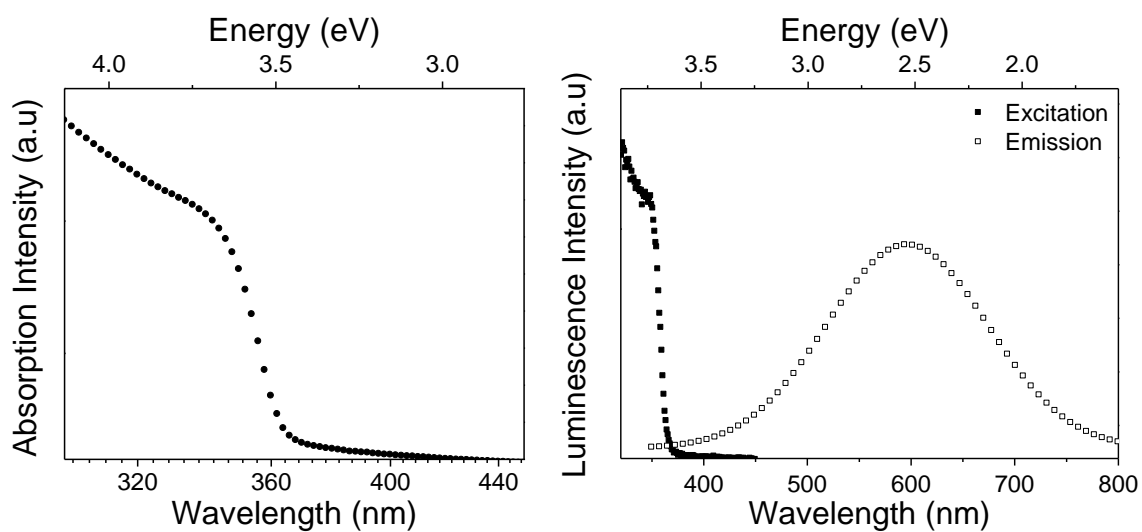
Figure S6: (left) Absorption spectra, (right) emission (λ_{exc}=340 nm) and excitation spectra (for an emission of 600 nm) of ZnO NPs formed in the hexagonal phase Hex-2, [Hex-2] ~ 10 mg/mL in heptane. Similar spectra were obtained in the cubic region.

(1) Karanikolos, G. N.; Alexandridis, P.; Mallory, R.; Petrou, A.; Mountziaris, T. J. *Nanotechnology* **2005**, *16*, 2372.