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BiOCI NANOPARTICLES SYNTHESIZED IN LYOTROPIC LIQUID CRYSTAL NANOREACTORS

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Introduction

The synthesis of nanoparticles of controlled size and shape has attracted much recent interest (1–6). One promising route to nanostructured materials involves synthesis in lyotropic liquid crystals (7–10) formed by mixing a solvent, usually water, and an amphiphile, typically either an ionic or non-ionic surfactant. These amphiphilic molecules typically consist of covalently bound hydrophobic and hydrophilic segments. When such amphiphilic molecules are mixed with water, the resulting amphiphile-water systems self organize into structured periodic lattices consisting of nanometer sized hydrophobic and hydrophilic domains in order to minimize free energy (11). Lyotropic liquid crystals are of exceptional interest because the size, shape, symmetry, and connectivity of these self organized nanoreactors can be predetermined through appropriate selection or design of the liquid crystal phase. Important for scale-up, these nanoreactors are easily reproducible, and can be generated in large volume. When these nanoreactors are used for materials synthesis, it is the subtle interplay of the “soft” nanoreactors with the growing inorganic phase that determines the final size, shape, and crystallographic orientation of the resulting nanomaterials. Liquid crystal nanoreactors are exceptionally versatile for materials synthesis, because there are many chemistries that can be designed to operate exclusively within either the hydrophilic or hydrophobic domains of the liquid crystal. The nanomorphology of the resulting inorganic product is thus greatly influenced by the geometric properties of the nanoreactors it was associated with.

Here, we explore the effect of two liquid crystalline phases on the synthesis of BiOCl, the first being a three-dimensionally percolated hexagonal liquid crystal, and the second, a two dimensionally percolated lamellar liquid crystal. Both systems were chemically similar, the only difference being the relative ratio of amphiphile to water, the two components that made up the liquid crystal. We compare these results with synthesis in an isotropic fluid. The size and shape of the BiOCl product correlated directly with the connectivity and confinement effects of the two liquid crystals. The three dimensionally interconnected hexagonal phase yields fairly monodisperse 250 nm long arrowhead shaped particles, while the two dimensionally connected lamellar, phase yields roughly spherical 5 nm particles. Particles synthesized in the absence of the liquid crystal had a completely different shape, and were highly polydisperse in size, consisting of disks ranging from 50 to 250 nm in diameter.

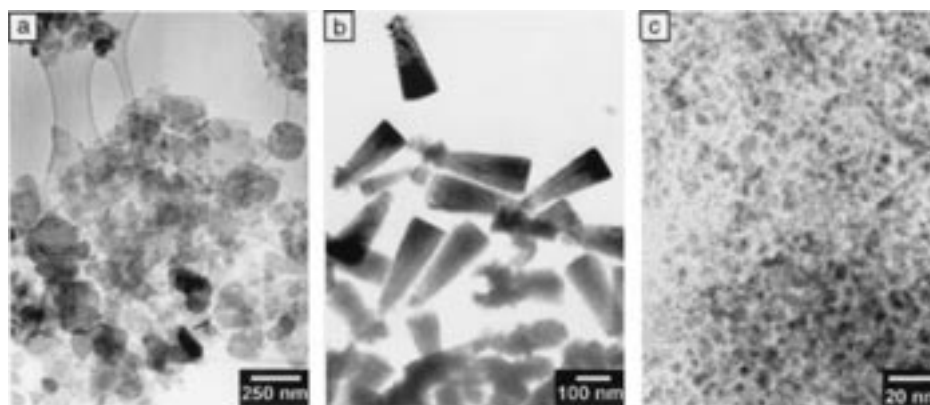


Figure 1. TEM micrographs of BiOCl produced (a) in free solution, (b) in the hexagonal liquid crystal, and (c) in the lamellar liquid crystal.

Experimental

A saturated solution of BiCl_3 was made by adding an excess of BiCl_3 (Aldrich) to de-ionized water and slowly adding HCl until the solution went clear, yielding a solution of approximately 0.025 M BiCl_3 with a pH less than 1. Hexagonal phase lyotropic liquid crystals were created by heating a mixture of 50 wt% oligo(ethylene oxide)₁₀ oleyl ether ((EO)₁₀oleyl ether) (ICI International) and 50 wt% aqueous BiCl_3 solution up to $\sim 90^\circ\text{C}$ while stirring, and then allowing the mixture cool to room temperature. Lamellar liquid crystals were created in the same manner with a composition of 78 wt% (EO)₁₀oleyl ether and 22% aqueous BiCl_3 solution. After cooling to room temperature, the liquid crystals were then placed in a chamber containing NH_4OH . Ammonia released from the aqueous NH_4OH solution diffused into the liquid crystals, raising the pH inside the nanoreactors, resulting in the precipitation of BiOCl. BiOCl was also precipitated in a sample of aqueous solution containing no (EO)₁₀oleyl ether as a control experiment, done in the same manner as the liquid crystal samples.

After allowing the reaction to proceed for 24 hours, BiOCl was removed from the liquid crystal by dissolving it with ethanol, followed by centrifugation. The resulting white powder was washed an additional two times with ethanol through centrifugation. Nanoparticle solutions were then ultrasonically dispersed in ethanol and deposited onto holey carbon grids for transmission electron microscopy (TEM) in a Phillips CM-12 electron microscope and onto glass slides for x-ray diffraction (XRD) with a Rigaku D-MAX x-ray diffractometer.

Results and Discussion

Mineral growth in liquid crystalline media resulted in dramatic structural changes compared to growth in an isotropic solution. Furthermore, the nanomorphologies of the BiOCl synthesized in the liquid crystals can not be obtained by any other route. TEM imaging of the BiOCl produced in free solution (no (EO)₁₀oleyl ether) reveals polydisperse, polycrystalline plate shaped particles ranging from 50 nm to 250 nm across, and ~ 20 nm thick (Fig. 1a). Moiré patterns are also visible, indicating particles stacked on top of each other. Particles produced in the three-dimensionally connected hexagonal phase are fairly monodisperse, with a very interesting arrowhead morphology (Fig. 1b). They are 100 nm wide and 250 nm long. Dark field imaging shows them to be primarily single crystals. A drastic morpho-

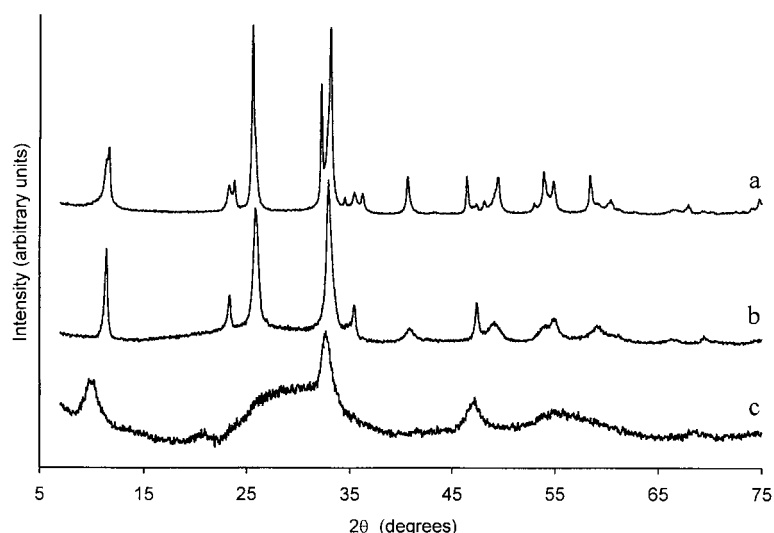


Figure 2. XRD scans of BiOCl produced (a) in free solution, (b) in the hexagonal liquid crystal, and (c) in the lamellar liquid crystal.

logical change is seen in the nanocrystals produced in the lamellar phase; they are roughly spherical and are only 5 nm in diameter (Fig. 1c).

These distinct morphologies are also evidenced by the results of the XRD (Fig. 2). The 001 peak (~ 11 degrees 2θ) in the diffractogram acquired from the nanoparticles produced in the lamellar liquid crystal has a full width at half max (FWHM) of 1.16 degrees, which, through the Scherrer formula (12) corresponds to a grain size 7 nm, in agreement with the TEM observations. The BiOCl produced in both the hexagonal liquid crystal and aqueous solution result in much narrower XRD peaks, indicating a larger grain size, which is again in agreement with our TEM observations.

It is clear that it is the nanoreactor morphology that determines the nanostructure of the inorganic product. Aqueous based lyotropic liquid crystals can behave as nanoreactors due to the extreme chemical differences between their hydrophilic and hydrophobic domains (11). The hexagonal lyotropic liquid crystal consists of parallel hydrophobic rods 3 nm in diameter, arranged on a hexagonal lattice with a lattice constant of 8 nm (8). The hydrophobic rods are surrounded by a continuous hydrophilic phase containing both water and the oligoethylene oxide segment of the amphiphile. The lamellar liquid crystal consists of alternating sheets of hydrophobic and hydrophilic regions, with a period of 5.5 nm (8). A schematic showing the morphologies of the two liquid crystal phases is presented in Fig. 3. The solvated BiCl_3 and HCl ions are exclusively restricted to the nanometer scale hydrophilic regions of the liquid crystals, thus BiOCl is formed only in the hydrophilic region of the liquid crystals. This confinement, and the characteristic structure and connectivity of the liquid crystal, determines the morphology of the mineral product. The nanodomains within the liquid crystal physically limit mineral growth, and the characteristic connectivity of hydrophilic nanodomains of the liquid crystal highly influences diffusion. The regulation of diffusion by the liquid crystal is especially dramatic in the lamellar phase, where the hydrophilic region is only two dimensionally continuous. The unique arrowhead morphology of the product generated within the hexagonal phase is thought to be a result of the three dimensional structure of the hydrophilic domain.

The diffusion of NH_3 into the liquid crystal and later dissolution of the liquid crystal in ethanol are thought to have little effect on the structure of the BiOCl. The amount of NH_3 required to raise the pH

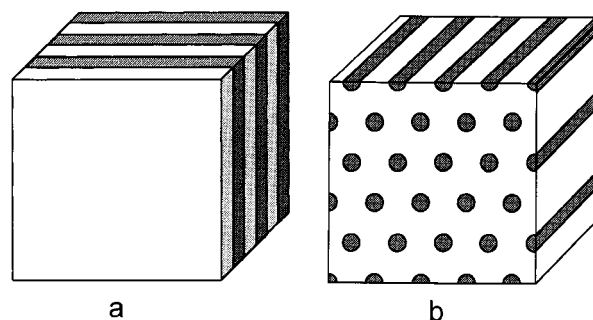


Figure 3. Schematic representation of (a) the lamellar liquid crystal and (b) the hexagonal liquid crystal. The white regions represent the hydrophilic domains (water and oligoethylene oxide), and the shaded regions represent the hydrophobic domains (oleyl).

to the point where BiOCl precipitates is small, and disruption of the liquid crystalline phases by addition of NH_3 has not been observed except at concentrations much higher than required to precipitate BiOCl. Thus, the BiOCl is formed within the liquid crystal and not in a destabilized phase. The removal of the BiOCl precipitates by dissolution of the liquid crystal in ethanol is unlikely to affect the structure of the precipitated BiOCl because BiOCl is highly insoluble in ethanol. Any unreacted BiCl_3 is soluble in the ethanol and thus is washed away with the $(\text{EO})_{10}$ oleyl ether. Furthermore, BiOCl is insoluble in water, so the morphology of the nanoparticles most likely does not change after initial formation in the liquid crystal. Since the BiOCl was formed inside a highly viscous liquid crystal, it was pinned in place and could not aggregate during the synthesis. Growing nanoparticles were thus kept at a fixed distance from each other during growth, which we believe results in a more monodisperse product.

The characteristic dimension of the BiOCl particles produced within the lamellar phase, and the characteristic dimension of the lamellar phase are both 5 nm. However, the BiOCl formed in the hexagonal phase did not adopt the characteristic length scale of the liquid crystal, instead forming particles more than ten times larger than the lattice spacing of the hexagonal phase. It is not clear from the micrographs whether the BiOCl has grown around the hydrophobic regions, incorporating them and thus producing an internal microstructure, as was seen in our previous work (7–9), or whether the growing BiOCl distorts the liquid crystal, pushing it aside as the inorganic phase grows. Regardless, the arrowhead morphology is a unique result of growth in the hexagonal phase, and has not been observed previously.

The TEM micrographs and XRD data demonstrate the morphological control that the liquid crystals exerted on the formation of the inorganic materials. The nanometer size of the product synthesized in the lamellar liquid crystal and the morphologically unique structure of the product synthesized in the hexagonal liquid crystal, along with the monodispersity in size of both systems attest to the efficacy of utilizing liquid crystal nanoreactors for nanomaterials synthesis.

Conclusions

Synthesis of inorganic materials in the confined nanoreactors formed by self organized lyotropic liquid crystals has been shown to direct the formation of BiOCl nanoparticles, yielding morphologies previously not obtainable. Liquid crystal based synthetic methodologies are very flexible, and can be generalized for a wide range of inorganic materials, offering opportunities to create a diversity of structures.

Acknowledgments

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