CuCl Nanoplatelets from an Ionic Liquid-Crystal Precursor**

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Research on ionic liquids (ILs) has focused on the synthesis of and organic chemistry in ILs. Recently, however, ILs have also received attention from the inorganic materials community. Ionic liquids can act as solvents for reactants and morphology templates for the products at the same time, which enables the synthesis of inorganic materials with novel or improved properties. In principle, the IL can be retrieved after synthesis and thus provides an ecologically friendly and economical approach to inorganic materials. While ILs are promising "all-in-one" solvent/templates for the synthesis of inorganic materials, only a few reports on this topic have appeared; they have mainly focused on ordered metal oxides[1–5] and metal nanoparticles.[6–8] For a recent review on the structural organization in ionic liquids, see also ref. [9]

Copper(I) chloride is extensively used as a desulfurizing agent in the petrochemical industry and as a catalyst for the denitration of cellulose;[10] there is thus considerable interest in improved CuCl systems. This paper introduces a novel

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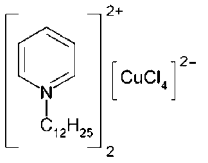
protocol for the controlled synthesis of CuCl nanoplatelets with a well-developed crystal habit and a tunable particle size and connectivity from the Cu-containing ionic liquid crystal **1** and 6-*O*-palmitoyl ascorbic acid (**2**). In a typical nanoparticle synthesis, equivalent weights of **1** and **2** were intimately mixed, and the mixture was heated to 85, 105, 125, or 145 °C, held at that temperature for 24 h, and quenched.



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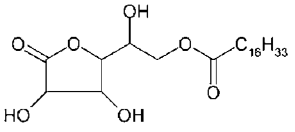

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Figure 1 shows that the mixture of **1** and **2** is liquid-crystalline at room temperature; it becomes isotropic at 90–92 °C. The author is currently investigating the structure of these liquid crystals in more detail, but as both pure **1** and pure **2** form lamellar self-assembled structures,[11,12] it is likely that mixtures of **1** and **2** are also layered. Compound **1** is essentially an IL (m.p. 66–70 °C), and **2** a guest molecule; this is thus another example showing that many ILs are ordered and have polar and nonpolar regions, similar to materials reported in refs. [8,13,14]

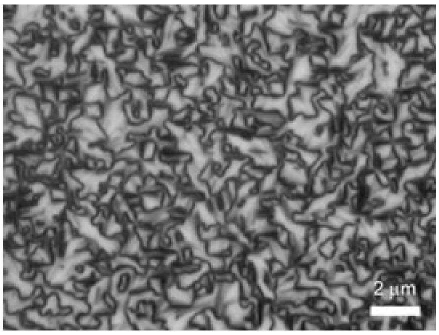

Figure 1. Optical micrograph (crossed polarizers) of a 1/1 (w/w) mixture of **1** and **2** at room temperature after rapid heating and quenching.

Figure 2 a shows a scanning electron micrograph of CuCl particles obtained at 85 °C. The particles are platelets with a relatively uniform thickness of about 220 to 260 nm and a large range of in-plane sizes, from about 5 to larger than 50 µm. Figure 2 b shows crystals obtained at 105 °C; the particles obtained at 125 and 145 °C are similar to these crystals. These particles are smaller but thicker than those in Figure 2 a, with typical in-plane dimensions 5–8 µm and thicknesses from (occasionally) 250 nm to (typically) about 1 to 1.2 µm.

Figure 3 shows that individual platelets in the samples precipitated at 85 °C are irreversibly connected at their junctions. This indicates that, during particle formation, individual platelets are in close contact for a long enough

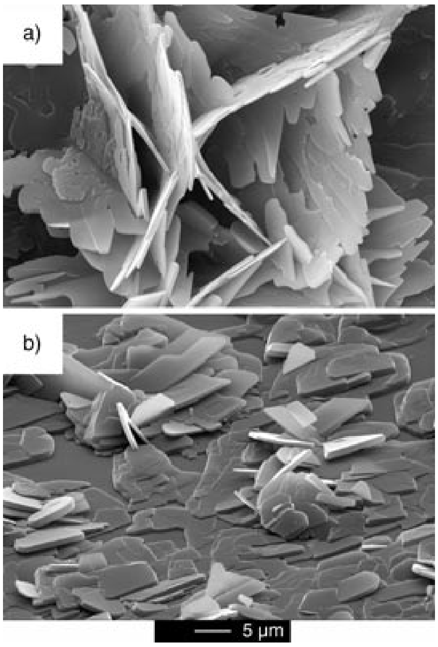

Figure 2. Scanning electron micrographs of CuCl nanoplatelets precipitated from a 1/1 (w/w) mixture of **1** and **2**. a) Relatively large and interconnected platelets typically obtained by reaction at 85 °C. b) Smaller platelets that are typical for reaction temperatures between 105 and 145 °C.

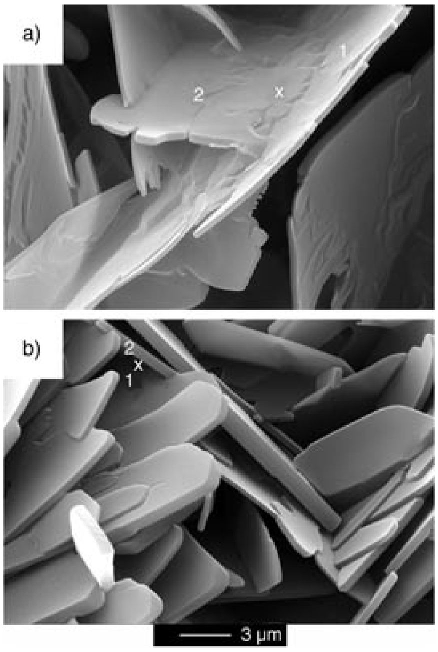

Figure 3. Scanning electron micrographs of CuCl nanoplatelet junctions. a) Thin particles with a rough surface typically obtained at 85 °C. The junction × between platelets 1 and 2 is covered with additional CuCl, thereby providing a permanent connection between the platelets. b) Thicker particles with a smooth surface typical for reaction temperatures between 105 and 145 °C. The junction × between particles 1 and 2 is not covered with CuCl, and most particles are simply touching one another.

time to enable crystal growth at the junction. In contrast, the junctions of the platelets obtained at or above 105 °C are not covered and stabilized by additional CuCl. Unlike the above particles, these platelets just touch one another; only in rare cases does a permanent linkage appear to be present.

As platelets are not typically observed for CuCl, the organic matrix must act as a template; the alkyl pyridinium ion is part of the solvent and a structure-directing agent for the crystallization; similarly, **2** probably acts as both a structure-directing agent and as an agent for reducing Cu^{2+} to Cu^{+}. However, the platelets are too thick to be the product of direct phase replication as observed ,for example, for SiO_2 grown in ILs.[2–4] Hence, one can argue that the system is always ordered, even above the LC–isotropic transition; an "ordered liquid" similar to those reported in refs. [9,13,15] could impose a platelet morphology on the particles, but also be responsible for the rather subtle changes in particle morphologies.

In conclusion, this paper presents a novel procedure for the synthesis of CuCl nanoparticles and (macro)porous structures. It is possible to tune the particle size, thickness, and connectivity by varying the reaction temperature. This approach thus provides a simple and—as the IL is not consumed and can be recycled—green method to tune the properties of CuCl nanocrystals and assemblies for applications in, for example, catalysis. Furthermore, the data give some empirical insight into the structure of ILs, which is of general interest to the chemistry, physics, and biotechnology communities.

Finally, the versatility of the system is a major asset: First, ligand exchange can change the symmetry of the LC template;[11] second, imidazolium ligands can replace pyridinium ligands;[16] third, Pd^{2+} can replace Cu^{2+};[16] and finally, preliminary experiments by the author have shown that also Co^{2+}, Fe^{2+}, Ni^{2+}, and Zn^{2+} can replace Cu^{2+}, and didodecyldimethylammonium bromide and tetraoctylammonium bromide can replace alkylpyridinium salts. Thus, exchange of the ligand, metal cation, anion, and/or reducing agent should offer a universal pathway towards metal halide and metal (alloy) nanostructures with tunable chemistry and morphology. The synthesis and properties of such materials, as well as the kinetics and reaction mechanisms of the system presented here, are currently under investigation.

Experimental Section

Chemicals (Fluka, Siegfried) were used as received. 2 equiv of dodecylpyridinium chloride and 1 equiv of $CuCl_2 \cdot 2H_2O$ were heated to 140 °C for 10 min to afford dark red, soft **1** after cooling. Equivalent weights of **1** and **2** were intimately mixed to form a dark red, soft material; this mixture was heated in a Perkin Elmer DSC6 (50 °C min^{-1}) to 85, 105, 125, or 145 °C, held at that temperature for 24 h, and then quenched at 50 °C min^{-1} to −5 °C to give CuCl nanoparticles.

X-ray diffraction experiments for determination of crystal phase (data not shown) were performed on a Siemens D5000 with $Cu_{K\alpha}$ radiation. SEM images were recorded on a Philips XL30 ESEM with a Noran energy-dispersive X-ray spectrometer; samples were sputtered with gold prior to imaging. Energy dispersive X-ray spectroscopy was used to confirm the absence of organic material from the precipitate; as only a trace of C and no N or O were detected, the organic material is not incorporated in the crystals, and the IL can thus be recovered and reutilized. Optical microscopy was carried out on a Leica DM-RP with a hotstage and cryostat.

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