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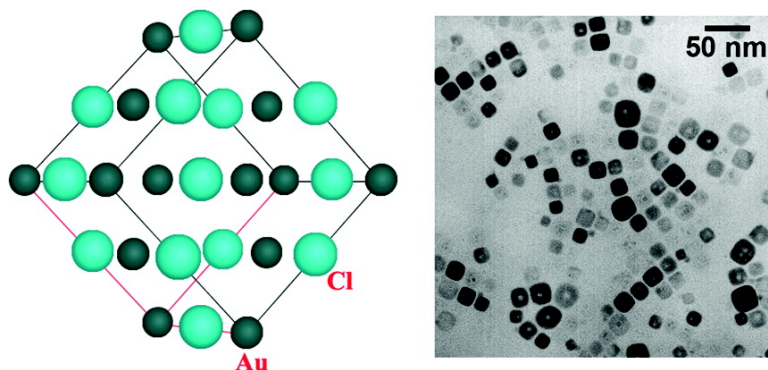
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## Directed Synthesis of Rocksalt AuCl Crystals

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We report the first-time experimental realization of rocksalt AuCl crystals. Our approach involves Au(III) complexing and reduction to Au(I) using an amine-terminated surfactant in a low dielectric permittivity solvent. The low charge screening in nonpolar solvents promotes crystallization of rocksalt AuCl, in which the bonding is predominantly ionic, in preference over tetragonal AuCl. The rocksalt AuCl crystals obtained here will facilitate studies to unveil the nexus between electronic structure and crystal structure in AuCl polymorphs, and provide insights on these relationships in other polymorphic crystal systems. Our approach provides a new means for crystallizing selective polymorphs of inorganic compounds by subtly influencing the cation electronic structure by varying the dielectric permittivity of the synthesis medium. In addition, the AuCl crystals can serve as inexpensive Au(I) precursors for forming a variety of Au nanostructures.

Au(I) halides are model systems for understanding the influence of cation electronic structure on the crystal structure of inorganic salts.<sup>1–3</sup> Theoretical calculations have predicted cubic as well as tetragonal AuCl<sup>1,2</sup> structures depending upon whether, or not, relativistic effects are included in describing the electronic structure of Au(I) ion. While tetragonal AuCl comprised of Au–Cl chains can be obtained by a variety of techniques including chlorination of metallic gold, the rocksalt AuCl has not been experimentally realized. The tendency for Au(I) to disproportionate in aqueous media is one of the major reasons for the difficulty in crystallizing Au(I) salts. However, recent work<sup>4</sup> has suggested that Au(I) ions can be stabilized during Au(III) reduction in a low dielectric permittivity medium. Here, we exploit this finding to obtain rocksalt AuCl crystals for the first time, showing that polymorph selection can be achieved by merely altering the synthesis medium. The nano/micro-scale rocksalt AuCl crystals obtained here would facilitate studies to unveil the nexus between electronic structure and crystal structure in AuCl polymorphs, and provide insights on these relationships in other polymorphic crystal systems.

### Experimental Section

**AuCl Synthesis.** A total of 30 mg of H<sub>2</sub>AuCl<sub>4</sub>·3H<sub>2</sub>O and 400  $\mu$ L of oleylamine were added to 50 mL of toluene and refluxed at 120 °C. Chloroauric acid is insoluble in toluene by itself but dissolves in the presence of the amine to form a yellow solution indicating the presence of the Au(III) oxidation state. The solution became colorless after a few minutes indicating chemical reduction to Au(I). We prepared microscopic crystals by lowering the temperature and/or lowering the amine concentration to facilitate detailed crystallographic analysis by tilting the crystal to different zone axes in the TEM. In order to vary

the cube size, the reactions were carried out at three different conditions by varying the amine concentration and reaction temperature. Larger cubes were seen to form at lower temperatures and for lower amine concentrations. The effect of solvent polarity on the formation of cubic AuCl was investigated by carrying out the reaction in 50% and 80% methanol/toluene mixtures or in chloroform at lower temperatures. Increasing solvent polarity increased the reaction rate. TEM investigations of the product indicated that the number density of the cubes on the TEM grid significantly decreased with increasing solvent polarity.

**Characterization.** The cube-shaped crystals were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). X-ray diffraction was carried out by drop-casting the solution on glass slides.

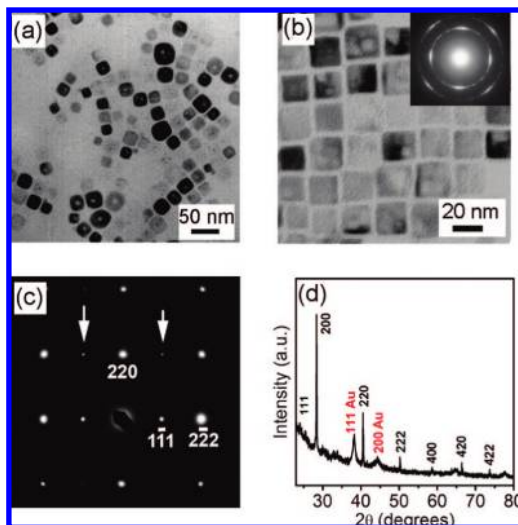
In a typical synthesis, H<sub>2</sub>AuCl<sub>4</sub> was refluxed in toluene in the presence of oleylamine, leading to the formation of a yellow solution characteristic of Au(III) ions. The yellow color fades upon heating at 120 °C for about 10 min, indicating Au(III) reduction, and yields cube-shaped nanostructures with average edge length of  $\sim$ 20 nm (see Figure 1a). High magnification micrographs (e.g., see Figure 1b) reveal that the cubes self-assemble in a face-to-face configuration during drying. The nearest neighbor intercubal spacing is consistently  $\sim$ 3.6 nm, which corresponds to about twice the oleylamine length, suggesting that oleylamine caps the crystals and serves as a spacer. The crystal size is sensitive to oleylamine concentration and temperature, and can be adjusted from  $\sim$ 10 nm to  $\sim$ 5  $\mu$ m (see the Supporting Information), confirming that the crystals are formed in solution rather than during postprocessing steps.

Electron diffraction analyses show that the nanocubes and their microscopic counterparts are single crystals that can be specified by a cubic-F Bravais lattice. The lattice parameter is 0.632 nm, close to the theoretical value predicted for rocksalt AuCl. The low intensity of the “all-odd” reflections, e.g., (111)

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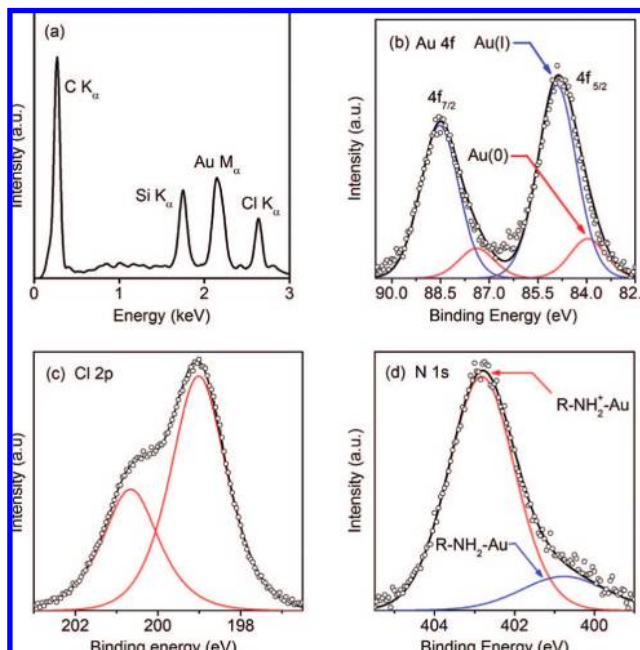


**Figure 1.** (a and b) Bright-field TEM images of cube-shaped AuCl crystals along with an electron diffraction pattern (inset) acquired from an area including several cubes. (c) A [112] zone axis pattern with arrows pointing to faint “all odd” reflections characteristic of the rocksalt structure. (d) X-ray diffractogram from a powder comprised of larger (>100 nm average size) AuCl cubes.

spots in [112] zone axis patterns from the crystals (Figure 1c) is uncharacteristic of cubic crystals with a one atom basis, and is consistent with the rocksalt structure. X-ray diffractograms (see Figure 1d) also show a low-intensity (111) peak, confirming the rocksalt structure. The strong out-of-plane (200) texture arises due to the tendency of the cubic crystals to assemble with their (001) faces aligned to the glass slide substrate surface. The low-angle Bragg peaks observed correspond to AuCl-amine strands<sup>5–7</sup> formed by aurophilic complexation (see the Supporting Information). The faint Au(111) peaks indicate the presence of residual metallic Au, with characteristic dimensions <~10 nm as estimated using the Scherrer formula.

Quantitative energy-dispersive X-ray analysis of the microscopic cubes in a scanning electron microscope reveals that the rocksalt crystals are comprised of stoichiometric AuCl (Figure 2a). X-ray photoelectron spectra show strong Au 4f<sub>7/2</sub> and Cl 2p<sub>3/2</sub> bands at 84.9 and 199 eV (Figure 2, panels b and c), respectively, confirming that Au(I) and Cl(I) are the predominant oxidation states<sup>8</sup> in the crystals. The small Au 4f<sub>7/2</sub> sub-band at 83.95 eV corroborates the presence of metallic Au(0) revealed by X-ray diffraction. The presence of two core-level N 1s sub-bands at 400 and 402.8 eV, typical of nonionized and ionized ligated amines respectively,<sup>9–11</sup> indicate that amines are attached to the AuCl surface (Figure 2d), consistent with the intercubal spacing seen in the TEM images.

Baseline experiments show that the presence of an amine and a nonpolar solvent are necessary conditions for obtaining rocksalt AuCl by our synthesis route. In the absence of oleylamine, HAuCl<sub>4</sub> remains insoluble in toluene. Synthesis with different chain length amines yields AuCl crystals with different sizes, but with no detectable lattice parameter changes, indicating that the amine-terminated surfactants are not incorporated into the AuCl crystal. Adding oleic acid along with an amine produces AuCl crystals in a shorter time, suggesting that cosurfactants could be used to manipulate AuCl growth kinetics. Our results point to amine-facilitated crystallization through Au(III)–amine complex formation and reduction, consistent with earlier works,<sup>4</sup> followed by the amines serving as capping agents. Replacing toluene with polar media such as water or chloroform in our synthesis promotes AuCl–oleylamine strand



**Figure 2.** (a) Energy dispersive X-ray spectrum from a micron-sized cube indicating stoichiometric AuCl. Core-level XPS spectra from the rocksalt AuCl cubes in the vicinity of (b) Au 4f, (c) Cl 2p, and (d) N 1s bands.

formation at the expense of AuCl crystallization (see the Supporting Information), underscoring the importance of low solvent polarity for rocksalt AuCl formation.

Based upon our experimental results presented above, rocksalt AuCl formation can be understood as follows. Oleylamine complexes with chloroauric acid leading to Au(III)–amine complex formation in toluene, thereby circumventing the difficulty of low solubility of ionic species in organic solvents. The amines also subsequently reduce the Au(III) to Au(I),<sup>5,7</sup> to form organized AuCl–oleylamine strands and rocksalt AuCl, as described by our diffraction analysis. Nonpolar solvents, such as toluene used in our synthesis, favor aggregation and crystallization of neutral ionogens<sup>12,13</sup> due to strong Coulombic interactions. This tendency is mitigated with increasing solvent polarity due to increased charge screening, which in turn is conducive for retaining the molecularly ligated complexes, leading to the formation AuCl-amine strands.<sup>5,7</sup> Such strands have also been reported to form by solubilizing tetragonal AuCl,<sup>6</sup> pointing to a nexus between the two structures. The presence of the strands as well the rocksalt phase in our synthesis suggests that Au-amine complexation is a common step in the formation pathways for both tetragonal and cubic polymorphs of AuCl. The low dielectric permittivity medium tilts the balance in favor of rocksalt AuCl, where the bonding has a greater ionicity.<sup>2</sup>

Our method of using Au(III) salts for in situ generation of Au(I) ions provides a new cost-effective alternative for synthesizing polymorphs inaccessible by other methods, and realizing the shape and size control offered by the Au(I) precursors.<sup>6</sup> Such in situ cation formation during synthesis is also conducive for forming larger dimensional structures, e.g., single-crystal nanowires.<sup>14</sup>

In summary, we have synthesized the rocksalt form of AuCl for the first time from Au(III) salt by surfactant complexing and reduction in a low dielectric permittivity medium. Amine-terminated molecular surfactants enable complexing and reduction of Au(III) to Au(I). The low charge screening in low permittivity solvents promotes crystallization of rocksalt AuCl

in preference to the AuCl-amine strands or the equilibrium tetragonal AuCl because of the stronger ionic character in the rocksalt structure. Thus, our approach provides a means for crystallizing selective polymorphs of inorganic compounds by subtly tuning the cation electronic structure through appropriate choice of synthesis medium and surfactant. Besides serving as a model system for studies of crystal chemistry and properties, the rocksalt AuCl nanocubes could also be used as building blocks that can be conveniently manipulated in solution for forming hybrid structures.

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**Supporting Information Available:** Additional figures and tables as well as discussion on particle size tuning. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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