Early Growth Stages of Hierarchically Organized Chiral Structures

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Biomineralization in nature often involves multiple organic-inorganic components undergoing complex interactions to form geometrically intricate structures such as coccoliths, sea-shells, corals etc. Chiral amino acids are a common organic component in biomineralization with the ability to transfer their chirality over multiple length scales under "appropriate conditions". Deciphering these "appropriate conditions" in nature is not straightforward, therefore biomimicry in laboratory settings, provides a simple tool to understand complex interactions [1-2]. Herein, we introduce gold (Au), chiral cysteine (L- or D-cys) complexes which self-assemble to form hierarchical stacks of twisted sheets (Fig 1a). We study the early stages of this self-assembly to unravel the different intermolecular and interparticle interactions defining the "appropriate conditions" that guide the formation of such complex Au-cys structures.

Early stages of Au-Cys structures were studied using AFM, SEM, TEM and XRD with a focus on electron microscopy to image nanoscale arrangement of Au-cys particles. Scanning electron microscopy (SEM) was performed on FEI Helios with an accelerating voltage of 1.5 kV (landing energy 500 V, stage bias 1000 V). BF-TEM imaging and electron were obtained using a JEOL 2010F analytical electron microscope, operating at 300 kV under reduced electron dose to minimize beam damage.

Following an incubation period, gold nanoparticles emerged as ~ 5 nm ellipsoidal platelets with thickness of ~ 1.5 nm (Fig 1c). Atomistic simulations confirm that interaction between chiral cysteine and gold introduces an intrinsic twist in these platelets (Fig 1b). These twisted nanoplatelets further attach in-plane in an oriented manner (Fig 1d) to form twisted sheets on the micron scale with out of plane stacking governed by the interlamellar interactions. The self-assembly is induced in presence of a surfactant (CTAB), which forms layered micelles (Fig 1c) possibly providing the soft scaffold for twisted sheets to stack together. Focusing on Au, Cys and CTAB, we will discuss in further detail the atomic structure of nanoplatelets, and the morphological evolution using high-resolution TEM and electron diffraction. [3]

References

- [1] S.H. Yu et al, Nat. Mater. 4, (2005), 51-55.
- [2] Y.Wang et al, Nano. lett. 4, (2004), 225-231.
- [3] The central part of this work was supported by the NSF project "Energy- and Cost-Efficient Manufacturing Employing Nanoparticles" NSF 1463474 and NSF 1566460 "Nanospiked Particles for Photocatalysis". All the authors thank the Michigan Center for Materials Characterization (MC)2 for its assistance with electron microscopy, and for the NSF grant #DMR-9871177 for funding the JEOL 2010F analytical electron microscope used in this work.



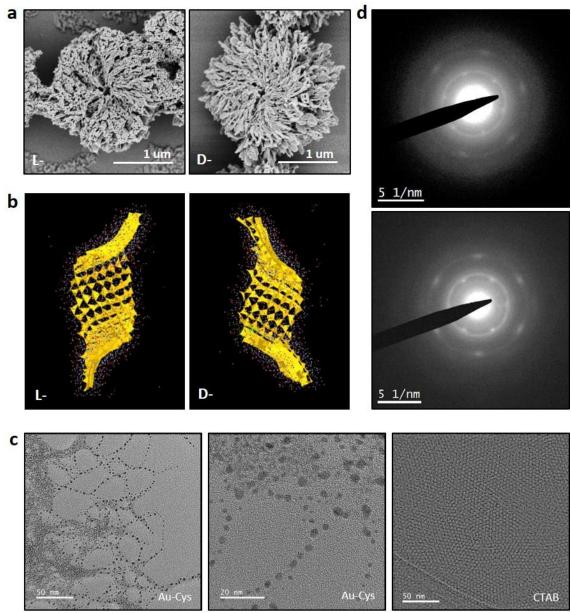


Figure 1. Morphology and early stages of gold-cysteine structures. a) Internal arrangement of twisted gold-cysteine sheets in an anticlockwise (L-) and clockwise (D-) manner for fully formed superstructures. b) atomistic simulation snapshots for a relaxed platelet of ~ 5 nm size. Platelets arising from L/D-Cys, gold atom interactions show twisting in directions guided by the chirality of amino acid involved. c) Early stage evidences of particle-particle attachment between gold nanoparticles (left and middle) possibly supported by the CTAB micelles (right). d) Ordering of atomic planes as seen from diffraction patterns acquired from ~ 100 nm x 100 nm area, indicating oriented particle-particle attachment.