

Formation of colloidal copper indium sulfide nanosheets by two-dimensional self-organization

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Ultrathin 2-dimensional nanomaterials (nanosheets, NSs) are attracting increasing attention due to their unique physical, electronic and structural properties[1]. Colloidal semiconductor NSs are of particular interest, since they combine the extraordinary properties of 2D nanomaterials with versatility in terms of composition, size, shape and surface, and the prospects of solution processability. To date, colloidal NSs of a variety of binary compositions have been prepared (e.g. CdX with X = S, Se, Te; PbS; SnX, with X = S, Se; In₂S₃; Cu_{2-x}S; Cu_{2-x}Se; WS₂)[2], but reports on NSs of multinary semiconductors are scarce, despite the interesting properties of this class of materials. For instance, CuInS₂ (CIS) is a direct semiconductor with a bandgap of 1.45 eV and large absorption coefficients, which yields nanocrystals with photoluminescence tunable in the visible to NIR spectral range. In this work we developed a new two-stage method to synthesize colloidal CIS NSs, in which CIS nanocrystals (NCs) are used as building blocks.

In the first stage, 2.5 nm dodecanethiol-capped chalcopyrite CIS NCs with a tetrahedral shape are synthesized. These NCs are purified and subsequently resuspended in the reaction mixture and heated. This process yields ~3 nm thick NSs with triangular or hexagonal shapes and lateral dimensions ranging from 50 nm to ~1 μm (Figure 1A). The NSs are single crystalline and have the covellite crystal structure (Figure 1B). The stoichiometry of the NSs changes from CuInS₂ to Cu_xIn_yS_z (x/y = 1.5-3) during the reaction. The non-stoichiometry of the NSs is also reflected in the appearance of a broad absorption band in the NIR, which is assigned to a localized plasmon resonance involving excess charge carriers (Figure 1C).

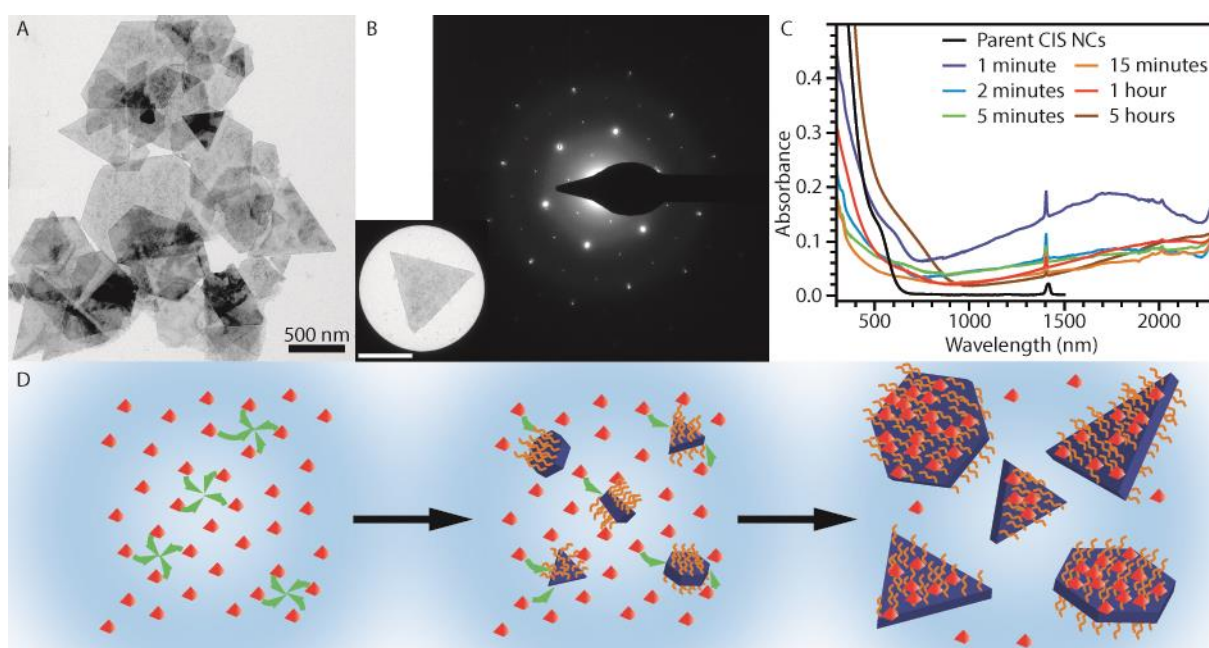


Fig. 1 A) TEM image of NSs. B) Electron diffraction pattern of single NS shown in the inset. C) Absorption spectra of NSs at different reaction times. D) Schematic representation of the proposed mechanism.

The mechanism we propose for the formation of the NSs is shown in Figure 1D. It consists of two-dimensional self-organization of the CIS seed NCs, followed by sintering and recrystallization from the original cubic chalcopyrite structure to the hexagonal covellite structure. The driving force for the self-organization is the extraction of cations (mostly indium) from the CIS seed NCs by H₂S, that forms *in situ*. The extraction of cations is assumed to create a transient charge imbalance that favors the attachment of the NCs. The formation of three-dimensional assemblies is prevented by the ligand coverage of the cation rich facets, which become the top and bottom facets of the NSs. This also constrains further growth of the NSs in thickness, allowing growth only in the lateral dimensions by attachment of NC building blocks.

- 1) Narita, A.; *et al. Nature Chem.*, **2014**, 6, 126-132.
- 2) van der Stam, W. *et al. Chem. Mater.*, **2015**, 27, 283-291.