

Water-dispersible copper sulfide nanocrystals for photocatalytic applications

C.H.M. van Oversteeg,^{a,b} P.E. de Jongh,^b C. de Mello Donegá^a

^a Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, Utrecht University, the Netherlands

^b Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, the Netherlands

Colloidal copper sulfide nanocrystals (NCs) have attracted increasing attention over the last decade due to their low toxicity, relatively low cost and wide size, shape and composition tunability [1]. Furthermore, copper sulfides have a wide stability window in aqueous solutions [2]. These factors make copper sulfide NCs promising materials for various applications, including photocatalysis [1,3,4]. In this study the synthesis of water-dispersible colloidal copper sulfide NCs, and their application in photocatalysis are investigated.

The NCs are synthesized using two different colloidal synthesis methods [5,6]. These methods allow for precise control over size, shape and composition of the NCs, but also leave the NCs capped with long organic ligands. One method yields 12 nm diameter Cu₂S NCs coated with 1-dodecanethiol (DDT) [5], whereas the other produces 7 nm diameter Cu_{1.94}S NCs coated with oleylamine (OLAM) [6]. The presence of neutral organic ligands at the surface of the NCs renders them hydrophobic, preventing their dispersion in water. Furthermore, the ligands may influence the catalytic performance of the NCs by blocking the catalytic sites. Consequently, we investigated several ligand exchange strategies to phase transfer the NCs to water. We found that both the NCs capped with DDT and OLAM can be transferred to water using Na₂S to exchange the native ligands by S²⁻, but aggregate after phase-transfer to water. This aggregation is more severe for the OLAM coated NCs. Ligand exchange using 11-mercaptoundecanoic acid at high pHs (>9) successfully transfers OLAM capped NCs to water, but fails for DDT capped NCs. The different behaviors of the DDT-capped and OLAM-capped NCs with respect to the ligand exchange procedures can be ascribed to the different binding modes of the ligands: the S-donor atom of DDT is effectively incorporated in the NC (i.e. crystal-bound ligand), while the N-donor atom of OLAM is only dynamically bound to the NC surface (surface-bound ligand) [7].

The production of water-dispersible copper chalcogenide NCs via colloidal synthesis allows for a high degree of control over the NC size, shape and composition, making it possible to investigate the influence of these variables on the photocatalytic performance of the NCs. The photocatalytic degradation of Rhodamine B will be used as a model reaction, since it can be easily followed by optical spectroscopy.

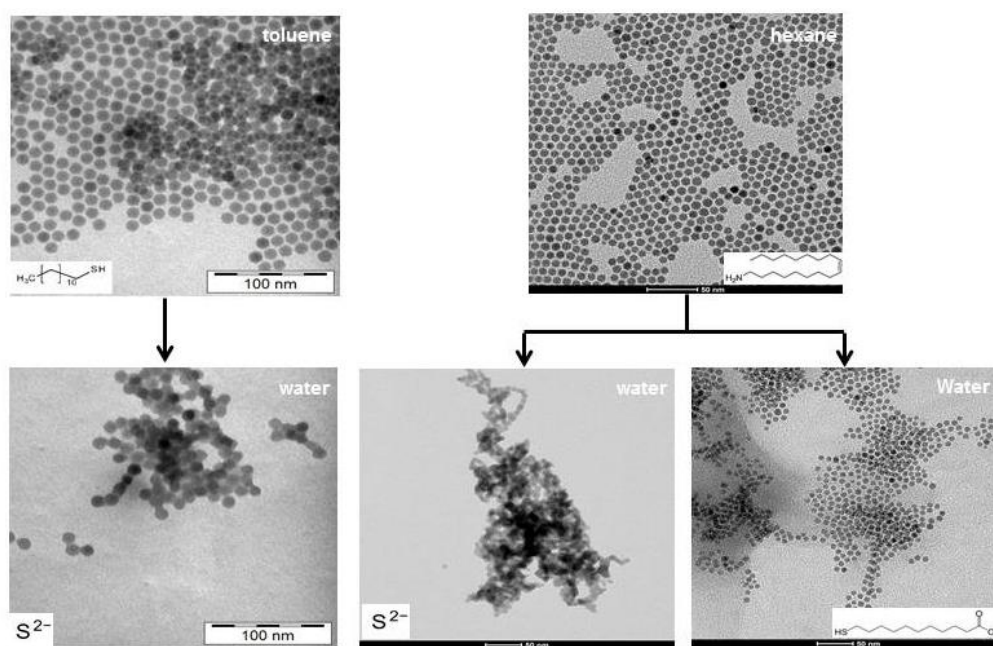


Fig. 1 Transmission electron microscopy images of Cu_{2-x}S nanocrystals as synthesized in apolar solvents (top) and after phase-transfer to water (bottom).

- 1) W. van der Stam et al., *ChemPhysChem*, **2016**, *17*, 559-581
- 2) Woods et al., *Int. J. Miner. Process.*, **1987**, *20*, 109-120
- 3) Basu et al., *Environ. Sci. Technol.*, **2010**, *44*, 6313-6318
- 4) Wang et al., *In submission*
- 5) W. van der Stam et al., *Chem. Mater.*, **2015**, *27*, 621-628
- 6) C.B. Williamson et al., *JACS*, **2015**, *137*, 15843
- 7) Turo et al., *ACS Nano*, **2014**, *8*, 10205-10213