

Cu₂ZnSnS₄ nanocrystal dispersions in polar liquids†

Cite this: *Chem. Commun.*, 2013, **49**, 3549

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Received 16th January 2013,
Accepted 13th March 2013

DOI: 10.1039/c3cc40388b

www.rsc.org/chemcomm

Cu₂ZnSnS₄ (CZTS) nanocrystals sterically stabilized with oleic acid and oleylamine ligands and dispersed in nonpolar organic liquids have been extracted into, and electrostatically stabilized in, polar liquids by covering their surfaces with S²⁻.

Rapid development of thin-film copper zinc tin sulfide (Cu₂ZnSnS₄ or CZTS) and selenide (Cu₂ZnSnSe₄ or CZTSe) solar cells with power conversion efficiencies in the 7–10% range attests to the remarkable potential of this material as a light absorber comprised of earth-abundant and nontoxic elements.^{1–3} Thin CZTS films can be synthesized in many different ways including coevaporation from elemental sources in vacuum^{4,5} or high-temperature sulfidation of metal precursors deposited on substrates by evaporation or sputtering.^{6–8} While most methods rely on traditional vacuum thin-film deposition, coating from colloidal nanocrystal dispersions (inks) have also received attention because they have the potential to be less expensive than vacuum processing.^{9,10} Recently, several approaches for synthesizing CZTS nanocrystal dispersions have been reported^{11–14} and solar cells made from these dispersions have achieved efficiencies exceeding 7%.¹⁵ However, all methods produce nanocrystal dispersions in organic nonpolar liquids where the nanocrystals are sterically stabilized by long alkyl ligands adsorbed on their surfaces. Deposition of thin films by coating and drying from nanocrystal dispersions necessitates the handling of large volumes of organic liquids such as toluene, undermining the presumed cost advantage of making solar cells from nanocrystal inks. Aqueous dispersions of CZTS are preferred.¹⁶ Herein, we describe a method for extracting CZTS nanocrystals from organic non-polar liquids into polar liquids and ultimately forming aqueous dispersions.

CZTS nanocrystals used in this work were synthesized from copper, zinc and tin dithiocarbamate complexes in presence of oleic acid and oleylamine as described by Khare *et al.*¹⁴ The as-synthesized CZTS nanocrystals are stabilized in organic nonpolar liquids such as

toluene by oleic acid and oleylamine adsorbed on their surfaces. To make nanocrystals dispersions in polar liquids, these long alkyl-chains must be at least partially removed and replaced. Inspired by recent reports of replacing organic ligands on III–V and II–VI nanocrystals (CdSe, InP, ZnSe, *etc.*) with inorganic ions,¹⁷ we extracted the nanocrystals from toluene into formamide, containing K₂S in at room temperature and eventually dispersed them in water.

In a typical extraction, CZTS nanocrystals dispersed in toluene are added to a mixture of formamide and K₂S solution in deionized (DI) water and the resulting two-phase mixture is stirred vigorously for a period ranging from 20 minutes to 16 hours. The detailed experimental procedures are given in the ESI.† The extent of extraction can be monitored through the color changes in the nonpolar toluene and polar formamide phases (Fig. 1 inset). Initially, CZTS containing toluene phase appears black and the formamide phase is clear and colorless. The formamide phase turns orange with the addition of K₂S. As S²⁻ adsorb on the CZTS surface, the nanocrystals are electrostatically stabilized and extracted to the formamide phase. While the formamide phase begins to get darker after stirring for 20 minutes, a thick emulsion still remains visible between the polar formamide and nonpolar toluene phases. Stirring longer gradually thins the emulsion and the formamide phase gets darker.

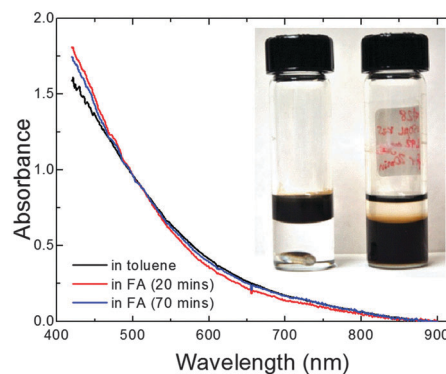


Fig. 1 Optical absorption spectra of ~5 nm diameter CZTS nanocrystal dispersions in toluene before extraction and in formamide (FA) after extraction. The 20 and 70 minutes refer to the duration of the extraction. The inset shows the as-synthesized CZTS nanocrystals in toluene before extraction (left) and in formamide after extraction (right).

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† Electronic supplementary information (ESI) available: Details of experimental procedure. See DOI: 10.1039/c3cc40388b

We surmise that the nanocrystals covered with both alkyl ligands and S^{2-} act as a surfactant and stabilize the emulsion at the toluene–formamide interface. When the nanocrystals are mostly covered with S^{2-} they are transferred to the formamide phase and the emulsion breaks up. Following stirring, the toluene phase is removed from the top and the nanocrystals are separated from formamide by adding acetonitrile and centrifuging the resulting mixture to precipitate them out of dispersion. The nanocrystals are cleaned by washing with formamide and redispersed in fresh formamide by vortexing and sonicating. Typically, washing and redispersion in formamide is repeated several times (3 to 6). Repeating the cleaning step removes excess K_2S but also decreases the stability of the dispersion. When washed once, the S^{2-} capped particles ($\sim 1 \text{ mg ml}^{-1}$) are stable for more than a week in formamide but only a few days if the washing step is repeated several times. The dispersion stability depends on the K_2S concentration and can also be improved by addition of K_2S . For making aqueous dispersions, water is added to the CZTS nanocrystals after the last cleaning step.

The CZTS nanocrystals were characterized using optical absorption spectroscopy, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy and attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy before and after extraction into formamide (see ESI†).

The extraction of CZTS nanocrystals into formamide does not change their structure, size and optical properties. Fig. 1 compares the optical absorption of CZTS nanocrystals when they are dispersed in toluene and, after extraction, when they are dispersed in formamide. The optical absorption begins to rise at $\sim 850 \text{ nm}$ corresponding to the band gap of bulk CZTS (1.45 eV). The average diameter of these particles were too large ($\sim 5 \text{ nm}$) to show quantum confinement.¹⁴

Fig. 2 shows the XRD from CZTS nanocrystals that were drop cast and dried on a silicon substrate from toluene, formamide and aqueous dispersions. All three diffraction patterns match with the expected CZTS powder diffraction pattern (JCPDS 26-0575). The average crystallite size extracted from the width of the (112) diffraction peak (28.5°) using Debye–Scherrer analysis was 5 nm for all CZTS nanocrystals regardless of the liquid they were dispersed in. This average size agreed well with the nanocrystal diameters measured from HRTEM images (Fig. 3), which showed nanocrystal with diameters between 4 and 6 nm in ensembles cast from both toluene and formamide.

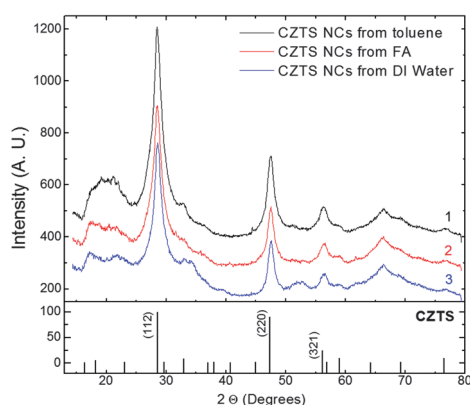


Fig. 2 XRD from CZTS nanocrystals (NCs) drop cast and dried on silicon(100) substrates from toluene, formamide (FA) and water.

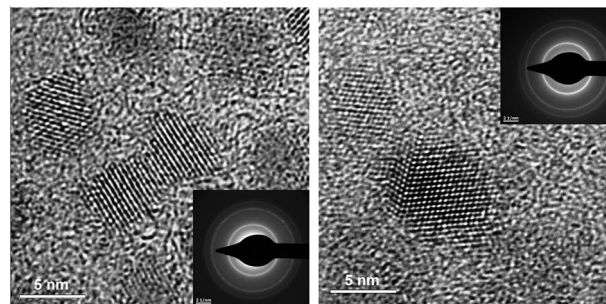


Fig. 3 HRTEM images of as synthesized CZTS nanocrystals drop cast onto TEM grids from toluene (left) and S^{2-} capped CZTS nanocrystals drop cast onto TEM grids from formamide (right). The insets are diffraction patterns recorded from samples.

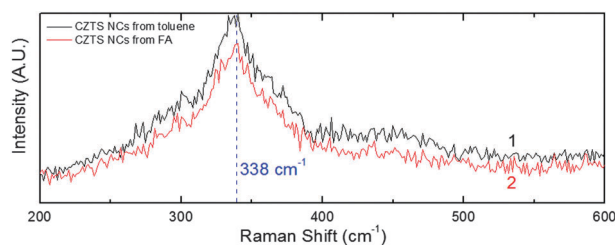


Fig. 4 Raman spectra of (1) as synthesized CZTS nanocrystals drop cast from toluene and (2) S^{2-} capped CZTS nanocrystals drop cast from formamide (FA).

Raman spectra of nanocrystal films cast from dispersions in toluene and formamide were identical and showed a single scattering peak centered at 338 cm^{-1} consistent with CZTS (Fig. 4).

Clearly, the bulk of the CZTS nanocrystals remain unaltered during the extraction but their surfaces must be different to change their interactions with polar and nonpolar liquids. To investigate these changes on the nanocrystal surface we employed ATR-FTIR. Fig. 5 shows the ATR-FTIR spectra of nanocrystal films cast onto a Ge ATR crystal from toluene and from water, before and after extraction, respectively. The as-synthesized nanocrystals in toluene exhibit IR absorption at 2852 cm^{-1} and 2925 cm^{-1} corresponding to the vibrations of C–H bonds in oleylamine and oleic acid adsorbed onto the nanocrystal surfaces. Fig. 5 shows that, surprisingly, even the nanocrystals extracted into polar liquids have residual oleylamine and oleic acid on their surfaces and not all organic ligands

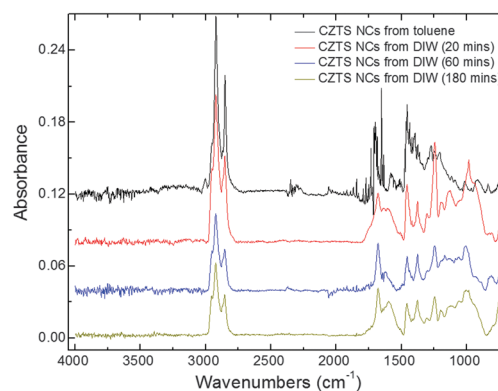


Fig. 5 ATR-FTIR spectra of the CZTS nanocrystals drop cast from toluene, before extraction, and drop cast from DI water, after extraction. Spectra for different extraction times are shown. The blue, red and black spectra baselines were shifted for clarity.

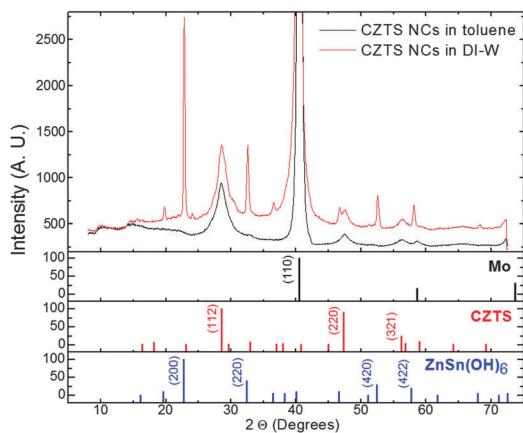


Fig. 6 XRD from CZTS nanocrystals drop cast and dried from toluene and from aqueous dispersions after extraction. The CZTS NCs were cleaned only once after extraction before dispersing them in DI water. The bottom panels show reference powder XRD patterns for Kesterite CZTS (JCPDS 26-0575) and cubic ZnSn(OH)_6 (JCPDS 20-1455). The particles were drop cast on Mo coated Si(100) substrates.

are removed during extraction. Despite these remaining organic ligands, the CZTS nanocrystals are extracted into and dispersed in formamide and water. We could rationalize this surprising result only after quantifying the absolute coverage of the organic ligands on the CZTS nanocrystal surface (see ESI† for details). Quantification of the ligand coverage on the CZTS nanocrystals revealed that the magnitude of the C–H stretching absorbance corresponds to $\sim 9 \times 10^{13}$ ligand molecules per cm^2 . This is only $\sim 13\%$ of the available sulfur (or metal) sites ($\sim 6.8 \times 10^{14} \text{ cm}^{-2}$) on the $\{001\}$ surfaces of the CZTS nanocrystals. Approximately 50–60% of these ligands are removed during extraction so that the ligand coverage decreases to $\sim 3.5 \times 10^{13}$ ligand molecules per cm^2 or about $\sim 5\%$ of the available sites. Thus, we conclude that the extraction into the polar liquid is achieved by covering the remaining surface sites with S^{2-} ions in formamide and the small amount of remaining alkyl ligands are inconsequential to their dispersion in polar solvents. Likely, the residual alkyl ligands left on the surface take on more compact configurations when the nanocrystals are in water or formamide and do not extend into the polar solvent. Moreover, dynamic light scattering (DLS) experiments show some degree of agglomeration with an average agglomerate size of ~ 93 nm in the formamide phase and ~ 220 nm in the toluene phase (see ESI†). Thus, the ligands remaining on the surfaces may be those that are trapped within these small agglomerates.

In water, K_2S hydrolyzes rapidly to KOH and KSH so that the capping ligands are expected to be HS^- rather than S^{2-} . Indeed, the infrared spectra, between $800\text{--}1700 \text{ cm}^{-1}$, of the nanocrystals drop cast and dried on ATR crystals from water and formamide is consistent with this picture and exhibit infrared absorptions that can be assigned to vibrations of SO_4 in K_2SO_4 and in KHSO_4 ,¹⁸ which are expected to form when K_2S and KHS oxidizes in air in presence of moisture (see ESI†).

Extraction into an intermediate phase such as formamide and washing the excess K_2S is necessary for successfully preparing aqueous dispersions of CZTS nanocrystals. We observed significant changes in the CZTS nanocrystals when high concentrations of K_2S was present in aqueous dispersions. Specifically, combination of

CZTS nanocrystals, excess K_2S and water leads to the formation of zinc hydroxystannate (ZnSn(OH)_6). The aqueous solution becomes basic upon hydrolysis of K_2S in water *via* $\text{K}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{KOH} + \text{KSH}$ and ZnSn(OH)_6 forms, likely through the reactions of OH^- ions with CZTS. For example, Fig. 6 shows the XRD from a CZTS nanocrystal film cast from an aqueous dispersion with excess K_2S . Specifically, the CZTS nanocrystals were cleaned only once after extraction before dispersing them in DI water. Sharp (200) and (220) diffractions from ZnSn(OH)_6 clearly indicate the presence of this reaction product.

In summary, we report a method for dispersing CZTS nanocrystals in polar solvents. These dispersions are achieved by extracting oleic acid capped CZTS nanocrystals dispersed in toluene into a K_2S solution in formamide. The nanocrystals are electrostatically stabilized with inorganic S^{2-} in formamide and HS^- in water. Examination of the nanocrystals by optical absorption, TEM, XRD and Raman spectroscopy show that the extraction process does not change the nanoparticle size and the structure, provided that care is taken not to expose the crystal to high concentrations of K_2S in water.

This work was supported primarily by the MRSEC Program of the NSF (NSF DMR-0819885). Partial support from Institute for Renewable Energy and the Environment (IREE grant RL-0004-11) is also acknowledged. Part of this work was done in the UMN Characterization Facility, which receives partial support from the NSF-MRSEC program.

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