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A general route to the synthesis of surfactant-free, solvent-dispersible ternary and quaternary chalcogenide nanocrystals†

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A general route to the synthesis of surfactant-free CuInS₂ (CIS), Cu₂CoSnS₄ (CCTS) and Cu₂ZnSnS₄ (CZTS) nanocrystals dispersible in low boiling point solvents is proposed. These nanocrystal inks should be of great interest to the fabrication of thin film absorbers of chalcogenide solar cells.

Advances in high quality semiconducting nanocrystal synthesis^{1,2} and new solution-based processing techniques^{3,4} have opened up new routes to address the challenge of fabricating low cost, high efficiency solar cells. For example, continuous roll to roll processing⁵ has been recently developed for thin film solar cells combining high speed and non-vacuum deposition and involves the use of nanocrystal dispersions. These solar paints can also be printed, sprayed onto large area substrates of thin film solar cells. The most successful synthetic routes developed for producing colloidal semi-conducting nanocrystals involve the use of coordinating solvents⁶ or surface ligands^{7–9} displaying long hydrocarbon chains to inhibit particle growth. Promising material candidates are CuInSe₂ ternary chalcogenides^{10,11} since they possess optimum band gap, high absorption coefficient and radiation stability.¹² More recently, quaternary chalcogenides Cu₂ZnSnS₄ have attracted much interest^{13,14} because Sn and Zn are naturally abundant in the Earth's crust and have relatively low toxicity. Few reports^{15,16} describe the synthesis of the quaternary chalcogenide nanocrystals and to the best of our knowledge, the only works published deal with the arrested precipitation process. Nevertheless, first solar cells fabricated using these building blocks yield low device efficiencies, likely due to the presence of the highly insulating barriers around the nanocrystals. Although much effort have been devoted to remove the growth inhibiting reagents including several ligand exchange stages by mild chemical treatment,¹⁷ complete removal of coordinating solvent or surface ligands has proven to be difficult. A need therefore exists for the fabrication of free-surfactant, ternary or quaternary chalcogenide nanocrystals redispersible in low boiling point solvent required for the subsequent film forming stage. Indeed, the size and surface charge control is extremely difficult as long as conventional reactions^{18–22} are employed such as the reaction between metallic cations (Cu⁺, Sn⁴⁺, Zn²⁺) and various sources of

S^{2–} such as thiourea, thio-acetamide. Here we propose a general route to the fabrication in various solvents of ternary (CuInS₂) and quaternary (Cu₂CoSnS₄, Cu₂ZnSnS₄) chalcogenide dispersed nanoparticles involving the high-temperature polycondensation of tailored oxy-hydroxy-thiourea-Mⁿ⁺ (Mⁿ⁺ = metallic cation) complex precursors. These complex precursors formed in various solvents can be described as ionic, colloidal or slightly aggregated dispersions, depending mainly on the thiourea additions and the OH[–] partial neutralization rate of the metallic cations. Thus, by fine tuning of the precursors composition achieved in a very limited range of OH[–], loosely packed aggregates formed from surface charged ultrafine primary crystallites were produced yielding a family of solvent-dispersible pure chalcogenide nanoparticles.

Formation domains of CuInS₂ (CIS), Cu₂CoSnS₄ (CCTS), Cu₂ZnSnS₄ (CZTS) metal chalcogenides by polycondensation reactions at 200 °C were determined in various solvents such as ethylene glycol, ethanol or isopropanol using CuCl₂·2H₂O, SnCl₄·5H₂O, MCl_x·yH₂O (M = Zn(II), Co(II), In(III)) as metallic salts and respectively thiourea and tetramethylammonium hydroxide

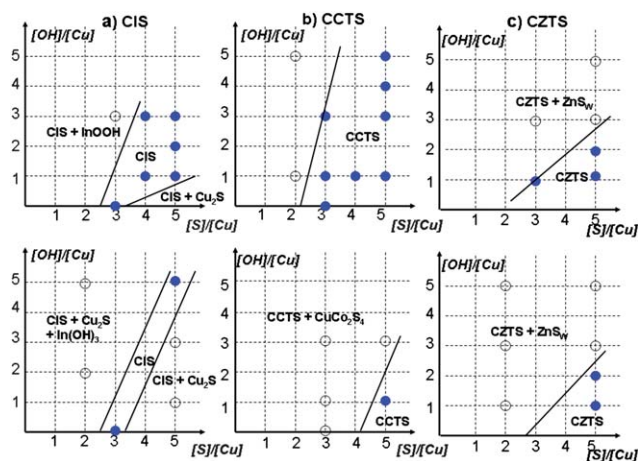


Fig. 1 (a) CIS, (b) CCTS and (c) CZTS formation domains determined in alcohol (top) and in ethylene glycol (bottom) under autogenous pressures at 200 °C—16 h except for CIS in ethanol (150 °C—16 h). Metallic cations were incorporated in stoichiometric ratios in reaction mixtures. Full circles depict ternary or quaternary chalcogenide single phase formation evidenced by X-ray diffraction, Raman spectroscopy and chemical analysis. For syntheses in alcohols, diagrams are given respectively in ethanol for CIS and CCTS, and in isopropanol for CZTS.

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Table 1 Nanocrystals chemical composition determined from chemical elemental analysis (1) or EDS (2) showing nearly stoichiometric composition of CIS and CZTS samples synthesized in ethylene glycol. In contrast, incorporation of Zn is difficult for CZTS syntheses performed in ethanol. The excess of S content is attributed to the presence of thiourea surface species

Compound	Solvent	Reaction mixture composition	Nanocrystal composition
CuInS ₂	Ethylene glycol	(Cu : In) = (1.00 : 1.20)	CuIn _{1.22} S _{2.13} ⁽¹⁾
CuCoSnS ₄	Ethanol	(Cu : Co : Sn) = (2.00 : 1.00 : 100)	Cu _{2.0} Co _{0.77} Sn _{0.96} S _{3.91} ⁽¹⁾
	Ethylene glycol	(Cu : Co : Sn) = (2.00 : 1.00 : 1.00)	Cu _{2.0} Co _{0.85} Sn _{0.96} S _{4.94} ⁽¹⁾
Cu ₂ ZnSnS ₄	Ethanol	(Cu : Zn : Sn) = (2.00 : 1.25 : 1.00)	Cu ₂ Zn _{0.25} Sn _{1.02} S _{3.2} ⁽¹⁾
	Isopropanol	(Cu : Zn : Sn) = (2.00 : 1.00 : 1.00)	Cu _{2.00} Zn _{0.66} Sn _{1.16} S _{4.42} ⁽²⁾
	Isopropanol	(Cu : Zn : Sn) = (2.00 : 1.25 : 1.00)	Cu _{2.00} Zn _{0.75} Sn _{1.19} S _{4.50} ⁽²⁾
	Isopropanol	(Cu : Zn : Sn) = (2.00 : 1.50 : 1.00)	Cu _{2.00} Zn _{0.84} Sn _{1.13} S _{4.52} ⁽²⁾
	Ethylene glycol	(Cu : Zn : Sn) = (2.00 : 1.00 : 1.00)	Cu ₂ Zn _{0.84} Sn _{0.97} S _{4.55} ⁽¹⁾
	Ethylene glycol	(Cu : Zn : Sn) = (2.00 : 1.30 : 1.10)	Cu ₂ Zn _{1.07} Sn _{1.05} S _{4.46} ⁽¹⁾

(TMAOH) as sulfide and OH⁻ sources. Because Cu(II) salt was employed in order to improve the chemical homogeneity of the precursors, production of small crystallite size was promoted by achieving high supersaturation conditions through ascorbic acid addition yielding an increase in [Cu⁺] when employing non-reductive solvents such as ethanol or isopropanol. Crucial parameters describing the complex precursors are sulfide source (S²⁻, HS⁻, thiourea) and OH compositions. Thus, formation diagrams were established with various [OH]/[Cu] and [S]/[Cu] ratios, where [OH] denotes the [OH] concentration, [S] the total sulfur source content, [S] = ([S²⁻] + [HS⁻] + [CS(NH₂)₂]) and [Cu] the total Cu content, [Cu] = ([Cu⁺] + [Cu²⁺]). CIS, CCTS and CZTS single phase formation domains (Fig. 1) in ethylene glycol and alcohols were determined for [S]/[Cu] < 7 and [OH]/[Cu] < 5. X-Ray investigation coupled to Raman spectroscopy indicates larger metallic chalcogenide formation

domains in alcohols compared with ethylene glycol. Interestingly, significant differences were observed between formation conditions of CZTS and CCTS. Whereas CCTS formation was observed both in ethanol and in ethylene glycol, chemical analysis has clearly demonstrated formation of Cu₂SnS₃ rather than the desired CZTS structure in ethanol (Table 1). In contrast, formation of CZTS was successfully achieved in a slightly different alcohol such as isopropanol. This illustrates the crucial effect of the solvent coordination of the Zn²⁺ cation and probably the nature of the zinc-sulfide intermediate clusters on the CZTS structure formation. Moreover, although in some samples the X-ray pattern and the Raman spectrum indicate single-phase formation, non-stoichiometric chemical composition revealed by chemical analysis suggests the presence of some amorphous phase in these samples. Indeed, stoichiometric quaternary chalcogenide compositions such as CZTS were achieved

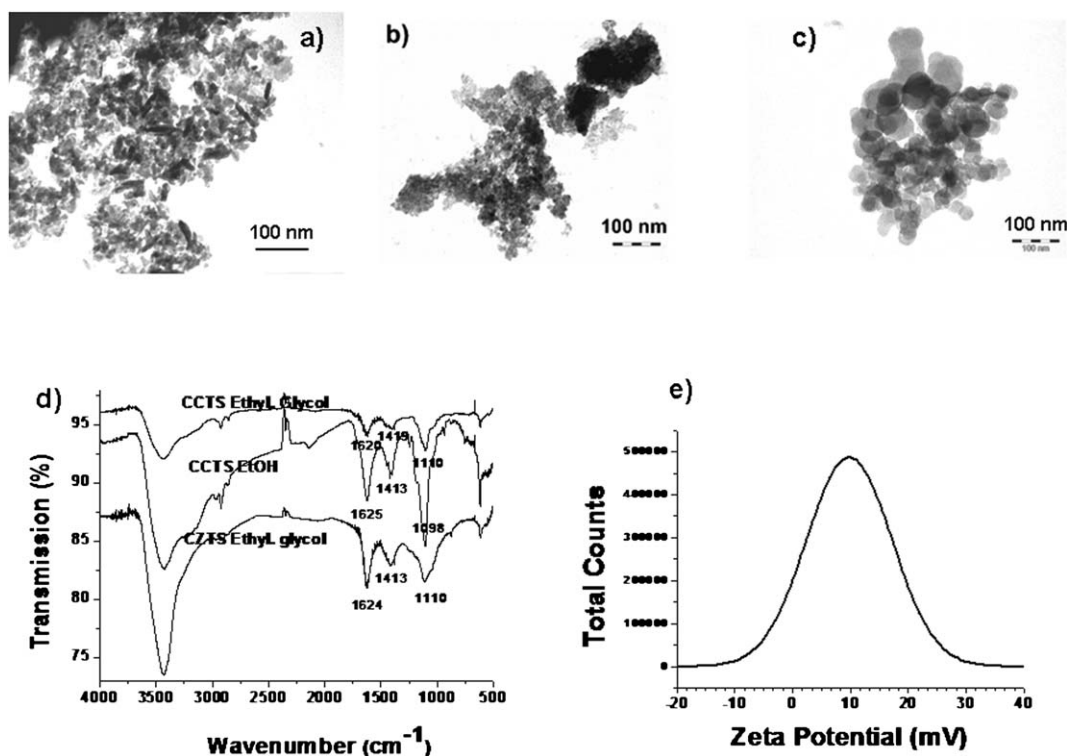


Fig. 2 (a-c) TEM images of CIS, CCTS, and CZTS samples respectively synthesized from precursors prepared with OH⁻ incorporation showing a loose packing of primary crystallites. (d) FTIR spectra recorded on Cu₂CoSnS₄ and Cu₂ZnSnS₄ samples showing peak vibrations attributed to thiourea. (e) ζ Potential of CZTS nanocrystals dispersed in EtOH showing the presence of low surface charge.

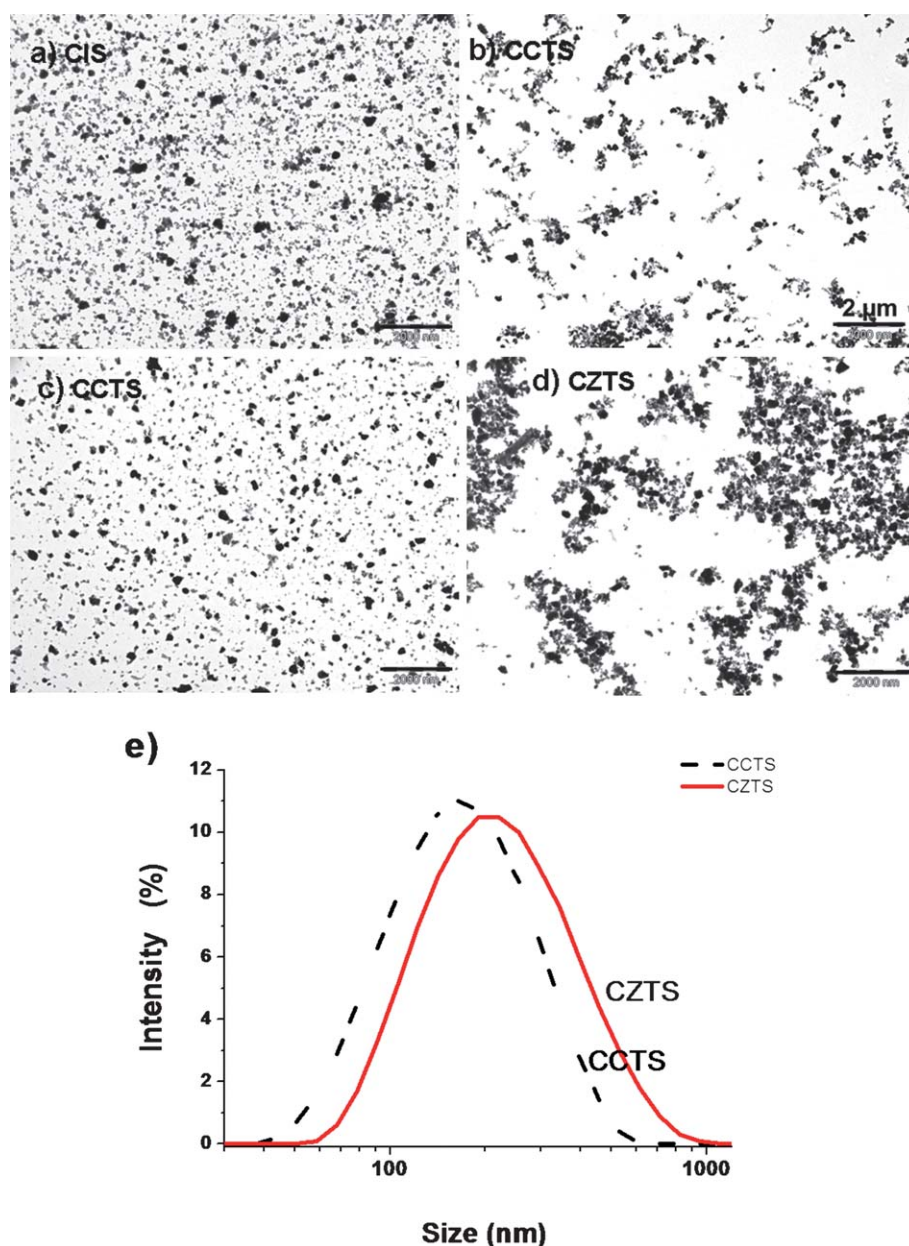


Fig. 3 Low magnification TEM micrographs showing the presence of a large number of nanocrystals dispersed in ethanol. (a) CIS nanocrystals synthesized in ethylene glycol $[\text{OH}]/[\text{Cu}] = 5$, $[\text{S}]/[\text{Cu}] = 5$, (b) CCTS nanocrystals synthesized in ethylene glycol $[\text{OH}]/[\text{Cu}] = 1$, $[\text{S}]/[\text{Cu}] = 5$, (c) CCTS nanocrystals synthesized in ethanol $[\text{OH}]/[\text{Cu}] = 1$, $[\text{S}]/[\text{Cu}] = 5$, (d) CZTS nanocrystals synthesized in ethylene glycol, $[\text{OH}]/[\text{Cu}] = 1$, $[\text{S}]/[\text{Cu}] = 5$. Scale bar: 2 μm . (e) Size distribution of CCTS and CZTS nanocrystals.

with Zn excess ($\text{Cu} : \text{Zn} : \text{Sn} : \text{S}$) = (2.0 : 1.3 : 1.1 : 10) mole in the reaction mixture. In comparison with the conventional approach involving reactions between metallic cations and a sulfide source, fine inspection of formation diagrams indicates a significant extension of metal chalcogenide formation domains achieved with OH^- addition. Corresponding XRD patterns and Raman spectra confirmed that these samples could be fully identified as single phase ternary or quaternary chalcogenides. As expected, small primary crystallite sizes were determined of around 4–8 nm, as calculated from the Scherrer equation using the full-width at the half-maximum of the chalcopyrite (112) peak. For CIS or CCTS samples, these primary crystallites correspond to crystallites observed by HRTEM. Interestingly, TEM observations reveal a loose aggregation of the ternary and quaternary

chalcopyrite primary crystallites when samples are synthesized from precursors with OH^- addition regardless of the solvent used. The TEM observations are consistent with the N_2 absorption–desorption BET curves showing the presence of pores of larger size (40 nm) and larger volume ($73 \text{ cm}^3 \text{ g}^{-1}$) for these samples prepared with OH^- addition. We take advantage of this loose aggregation to produce by ball-milling discrete ternary and quaternary chalcogenide nanocrystals in the size range 150–250 nm. Redispersion of these ball-milled nanocrystals was achieved in polar solvents arising probably from the presence of surface species such as thiourea and evidenced both from S and C chemical analysis and FTIR spectra recorded on these samples. Peaks were observed at 1626 cm^{-1} , 1410 cm^{-1} and at 1110 cm^{-1} and attributed respectively to NH_2 bending deformation,

C=S stretching vibration and NH₂ rocking vibration²³ (Fig. 2d). Indeed, the presence of thiourea surface species probably causes the positive surface charge²⁴ as determined from the ζ potential curves (Fig. 2e) indicating slightly positive CIS, CCTS, and CZTS nanocrystal charged surfaces in polar solvents such as ethanol or acetonitrile. Because the nanocrystals surface charge was relatively low, solvent-redispersibility of the ternary and quaternary chalcogenide nanocrystals was only achieved in dispersions displaying low ionic strength. Typical conditions of preparation of pure ternary and quaternary chalcogenide solvent-redispersible nanocrystals *via* the polycondensation of tailored oxy-hydroxy-thiourea-Mⁿ⁺ complex precursors were thus determined from a rationale study performed in various solvents. In a typical experiment, Cu₂ZnSnS₄ nanocrystals in ethylene glycol were synthesized using the following molar ratios: 2.0CuCl₂·2H₂O : 1.3ZnCl₂·6H₂O : 1.1SnCl₄·5H₂O : 10CS(NH₂)₂ : 2.0 TMAOH. The resulting mixture was transferred into a Teflon-lined stainless steel autoclave for 16 h at 200 °C. After washing, the precipitated solid was ball-milled in EtOH using 0.3 mm ZrO₂-Y₂O₃ balls. Decrease in ionic strength of the suspensions was achieved through EtOH washing and CZTS nanocrystals dispersion was collected after size selection performed by centrifugation at 3000 rpm. Fig. 3 shows TEM images of discrete CIS, CCTS and CZTS nanocrystals of mean size ranging from 150 nm (CCTS) to 250 nm (CZTS) and dispersed in ethanol (Fig. 3e). These nanocrystals which consist of aggregates formed from 5–8 nm primary crystallites display substantial stability up to 5 days, allowing formation of ternary and quaternary chalcogenides thin films of solar cells.

In conclusion, a novel approach for the synthesis of surfactant-free solvent-redispersible metallic chalcogenide nanocrystals is proposed. Ternary and quaternary chalcogenide nanocrystals displaying surface charge were obtained by high-temperature polycondensation of complex precursors designed in a narrow range of OH⁻ addition corresponding to the partial neutralization of the cations. The ability of generating surfactant-free solvent-redispersible nanocrystals renders this approach appealing, particularly for the ink-based fabrication of CZTS solar cells.

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