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Chemical welding of binary nanoparticles: room temperature sintering of CuSe and In₂S₃ nanoparticles for solution-processed CuInS_xSe_{1-x} solar cells†

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Chemical welding of oppositely charged dissimilar metal chalcogenide nanomaterials is reported to produce a quaternary metal chalcogenide. CuSe and In₂S₃ nanoparticles were synthesized with opposite surface charges by stabilizing with polyacrylic acid and polydiallyldimethylammonium chloride. Upon mixing these nanoparticles at room temperature, the electrostatic attraction induced coalescence of these nanoparticles and led to the formation of CuInS_xSe_{1-x} nanoparticles.

Nano chemical welding is a recently developed technique used to sinter two or more nanoparticles to form a complex structure.^{1,2} In general, sintering or coalescence is a process for eliminating the interparticle pores in a granular material by atomic diffusion³ at relatively high temperatures, $T > T_m/2$, where T_m is the melting temperature, and not under very high pressure, $P < 0.2$ GPa.⁴ Room temperature coalescence or cool welding to join materials without local heating is now used to make complex architecture from nanostructure building blocks.^{1,2,5} Assembly of Au nanoparticles on a liquid interface is a well studied platform for cold welding of Au nanoparticles.² Cold welding of ultrathin gold nanowires was demonstrated by Lu *et al.*⁶ One of the authors have studied in detail the sintering of stabilized silver nanoparticles by using a destabilizing agent.⁵ Even though chemical welding has been demonstrated on metallic nanoparticles, to date, it has not been reported for identical metal compounds or dissimilar metal compounds. Here we observed room temperature chemical welding of CuSe and In₂S₃ nanoparticles to form a new material CuInS_xSe.

I-III-VI₂ semiconductors such as CuInSe₂, CuGaSe₂, CuInS₂, CuInS_xSe_{1-x} and CuIn_{1-x}Ga_xSe₂ (CIGS) are suitable solar absorber materials due to a bandgap of 1–2 eV and a high absorption coefficient of 10^5 cm⁻¹. With these intrinsic properties, CIGS solar cells with a power conversion efficiency of 20% have been demonstrated by vacuum based deposition.⁷ Various groups have recently proposed solution based methods to produce Cu-chalcogenide solar cells with a power conversion efficiency (PCE) between 2 and 15%.^{8–12} This wide distribution of reported PCE is partly due to the difficulty in controlling stoichiometry and grain size. The chemical welding proposed here has great potential to establish an alternative method to grow a big grain from the nanosized particles. In addition, the bottom-up approach for coalescence of CuSe and In₂S₃ to form the CuInS_xSe_{1-x} nanoparticles may offer a better stoichiometry control of the final product.

The coalescence of dissimilar binary metal chalcogenide nanoparticles to form quaternary metal chalcogenides is studied here by stabilizing the binary nanoparticles with oppositely charged polyelectrolytes. The precursor nanoparticles with varying amounts of polymer were used in order to study the importance of morphology and surface charge of precursors during the coalescence and sintering process. In addition, a kinetic study was done to observe the evolution of the process.

PAA (polyacrylic acid, MW 8000) stabilized CuSe nanoparticles were synthesized by reacting CuCl₂ with sodium selenosulphate in the presence of PAA (0.1 vol%) at 90 °C. Similarly PDDA (polydiallyldimethylammoniumchloride MW 100 000–200 000) stabilized In₂S₃ nanoparticles were synthesized by reacting InCl₃ with thioacetamide in the presence of PDDA (0.2 vol%). By room temperature mixing of these poly-cation stabilized CuSe and poly-anion stabilized In₂S₃, destabilization of the nanoparticles happens and they coalesce with each other to form quaternary CuInS_xSe nanoparticles. The experimental steps and the postulated mechanisms are elaborated in Fig. 1. To establish the role of the surface charge on the nanoparticle surfaces during coalescence, we synthesized CuSe and In₂S₃ nanoparticles without any polyelectrolytes under identical conditions and stirred for 24 hours at room temperature (system A). It should be

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Fig. 1 Schematic diagram of electrostatic induced coalescence and sintering.

noted that the polyelectrolyte also has an additional function, as a steric stabilizer. Once the polymer is coated onto the nanoparticles, CuSe nanoparticles acquire a negative surface charge while In_2S_3 nanoparticles acquire a positive surface charge by adsorption of charged polymers, PAA and PDAA, respectively. The ζ -potential of the CuSe nanoparticles solution was -43.0 mV while that of In_2S_3 nanoparticles was $+38$ mV.

Fig. 2a and b show the XRD patterns of the as-synthesized In_2S_3 and CuSe nanoparticles without any polymer, which matched with the standard patterns of CuSe (ICSD 76960) and In_2S_3 (ICSD 202353) respectively. The XRD pattern of the final product of system A, obtained *via* room temperature mixing of nanoparticles without any polyelectrolyte, is shown in Fig. 2c. The pattern clearly shows that the final product is a mixture of precursor nanoparticles, confirming that coalescence of the CuSe and In_2S_3 nanoparticles did not occur without the charges on the surfaces. As for the charged nanoparticles synthesized using polyelectrolytes (system B), the XRD is shown in Fig. 2d. We observed that all the reflections in the XRD pattern resemble the standard $\text{CuInS}_x\text{Se}_{1-x}$.¹³

To confirm the formation of CuInSSe and the absence of binary nanoparticles, Raman analysis was performed. Fig. 3a and b show the Raman spectra of CuSe and In_2S_3 nanoparticles without any polyelectrolytes. Fig. 3c shows the Raman spectrum for system A, with peaks corresponding to the active modes of

Fig. 2 XRD patterns of (a) In_2S_3 without polymer, (b) CuSe without polymer, (c) system A: CuSe and In_2S_3 without polymer after 24 hours and (d) system B: 0.1 vol% PAA-CuSe and 0.2 vol% In_2S_3 after 24 hours stirring. Vertical lines on the x-axis represent the standard data of CuInSSe (ICSD 656272).

Fig. 3 Raman spectra of (a) In_2S_3 without polymer, (b) CuSe without polymer, (c) system A: mixture of CuSe without polymer and In_2S_3 without polymer after 24 hours and (d) system B: mixture of 0.1 vol% PAA-CuSe and 0.2 vol% In_2S_3 after 24 hours stirring.

CuSe at 260 cm^{-1} as well as In_2S_3 at 300 cm^{-1} and 365 cm^{-1} .^{14,15} The Raman spectrum for the final product of system B in Fig. 3d shows 2 peaks: one at 178 cm^{-1} which is the $A_1[\text{Se-Se}]$ mode from CuInSe_2 and the other at 288 cm^{-1} which is the $A_1[\text{S-S}]$ mode from CuInS_2 . This indicates the existence of a quaternary CISSe phase in this region. This observation of A_1 bimodal behavior of the $\text{CuInS}_x\text{Se}_{1-x}$ quaternary phase was in agreement with the observation of Bacewicz *et al.*, who reported Raman spectra of $\text{CuInS}_x\text{Se}_{1-x}$ for different “ x ” values.¹⁶

To understand the formation mechanism of $\text{CuInS}_x\text{Se}_{1-x}$ nanoparticles, the reaction dynamics were investigated. The samples were extracted from the coalescence reaction mixture of system A at different times and characterized. XRD patterns of the final product for different samples at the start of the coalescence reaction, at 10 hours and at 24 hours are shown in ESI† (Fig. S1). In general, when the reaction time is shorter than 24 hours, the diffraction peaks of the XRD patterns can be attributed to a mixture of CuInSSe (ICSD 656272) and CuSe (ICSD 76960), as the peak intensity for the synthesized In_2S_3 in the presence of PDAA is quite low because of its small particle size (see Fig. S2, ESI†).

The quantitative phase analyses of the products obtained by Rietveld refinement are 17 wt% CuInSSe and 83 wt% CuSe at 5 hours, 43 wt% CuInSSe and 57 wt% CuSe at 7.5 hours, 63 wt% CuInSSe and 37 wt% CuSe at 10 hours and 78 wt% CuInSSe and 22 wt% CuSe at 15 hours, as illustrated in ESI† (Fig. S1). After 24 hours we found that the final product is pure $\text{CuInS}_x\text{Se}_{1-x}$ without any CuSe phase, as supported by XRD and confirmed by Raman analysis as shown in Fig. 3d.

The Raman analysis of the final product for different reaction times also supports the observation of XRD (Fig. S3, ESI†). At 0 hour, peaks corresponding to the precursor nanoparticles are detected and the final product shows the peaks of $\text{CuInS}_x\text{Se}_{1-x}$.¹² The intermediate spectra show a combination of individual nanoparticle spectra, indicating the presence of CuSe and In_2S_3 together with the final product $\text{CuInS}_x\text{Se}_{1-x}$.

To further investigate the morphology and crystal structure of the precursors and the final product, TEM was carried out. Fig. 4a shows the TEM image of CuSe nanoparticles with an average size of around 20 nm. These nanoparticles are

Fig. 4 TEM images of (a) CuSe, (b) In_2S_3 and (c) $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$. Insets are the SAED of the respective samples. (d) The STEM-EDX of $\text{CuIn}(\text{S}_x\text{Se}_{1-x})_2$.

polydispersed and high resolution TEM shows nanorods with lengths up to 60 nm (S4a, ESI[†]). The size of In_2S_3 nanoparticles was very small, as shown in Fig. 4b, and this could be a result of the high molecular weight polymer used as compared to the polymer used for CuSe. Fig. 4c shows the TEM image of the final product of system B. Nanoparticles with different shapes and sizes were observed. The selected-area electron diffraction patterns (SAED) of CuSe, In_2S_3 and $\text{CuInS}_x\text{Se}_{1-x}$ nanoparticles are shown in the insets of Fig. 4a–c, respectively. For CuSe nanoparticles, the diffraction rings observed were in agreement with the (102), (110) and (108) of CuSe (ICSD 76960). The diffraction rings of the In_2S_3 nanoparticles exhibit a continuous ring pattern, an indication of smaller grain size,¹⁷ in agreement with the (113) and (440) of In_2S_3 (ICSD 202353). SAED of $\text{CuInS}_x\text{Se}_{1-x}$ nanoparticles shows 3 diffraction rings made up of discrete spots which match with the (116), (312), (204), (220) and (112) of the chalcopyrite CuInSSe (ICSD 656272).

Careful analysis of SAED patterns confirmed that the final product is not a mixture of CuSe and In_2S_3 , also there is no identical ring pattern to support the presence of CuInS_2 or CuInSe_2 . Scanning transmission electron microscope (STEM)-energy-dispersive X-ray (EDX) of the final product shows a uniform distribution of elements for particles of different sizes (Fig. 4d), which infers that the final product is not a mixture of CuSe and In_2S_3 . High Resolution TEM (HRTEM) analysis also supports the formation of $\text{CuInS}_x\text{Se}_{1-x}$ after coalescence (S4, ESI[†]). $\text{CuInS}_x\text{Se}_{1-x}$ nanoparticles show an ordered crystalline structure, with an inter-planar d -spacing of 3.14 Å, 3.26 Å and 5.04 Å corresponding to the (103), (112) and (010) planes of chalcopyrite CuInSSe (ICSD 656272). The FFTs also match with that of standard data of $\text{CuInS}_x\text{Se}_{1-x}$. Whereas the HRTEM analysis of individual nanoparticles exhibits clear lattice spacing with identical values of standard CuSe and In_2S_3 data.

To demonstrate the potential of these coalesced particles for solar energy harvesting, we fabricated the photovoltaic device by spray depositing the coalesced particle on Mo-coated soda lime glass.¹⁸ The final device with 0.105 cm² effective area resulted in power conversion efficiency of 1.04% under one-sun, air mass 1.5 global illuminations. Details of the device parameter and the current-voltage characteristic are given in the ESI[†] (S5).

The stabilization and destabilization of the nanoparticles helps to promote coalescence of binary nanoparticles to form quaternary chalcogenide nanoparticles. We observed the formation of $\text{CuInS}_x\text{Se}_{1-x}$ nanoparticles after 24 hours of stirring of the mixture of PAA capped CuSe and PDDA capped In_2S_3 at room temperature. The precursor nanoparticles with varying amounts of polymer were used in order to study the importance of morphology and surface charge of precursors in the coalescence and sintering process. In addition, a time study was done to observe the evolution of the process.

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