Polysulfide ligand exchange on zinc sulfide nanocrystal surfaces for improved film formation

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ABSTRACT

The physical and chemical properties of nanocrystals can be modified by changing the ligands attached at their surfaces. A ligand exchange procedure with ammonium polysulfides has been developed to replace the native ligands on cubic zinc sulfide nanocrystals. Several mixtures of polysulfides in formamide and other solvents were prepared with different average chain lengths and used to achieve high yield ligand exchange, as confirmed by UV–vis spectroscopy, infrared spectroscopy and X-ray photoelectron spectroscopy. The results show that polysulfide content can be increased with longer surface ligands and that the exchange process yields compositionally pure surfaces before and after high temperature anneals. X-ray diffraction and scanning electron microscopy show that, when annealed in nitrogen at 525 °C, polysulfide ligands lead to average crystal sizes 2–3 times larger than in the un-exchanged control sample. The ligand exchange procedure itself does not alter nanocrystal size. Nanocrystal inks prepared from the exchanged samples form thin films that exhibit superior grain growth, morphology, mass retention, and composition compared to the un-exchanged material. Overall, polysulfide species are demonstrated as alternative ligands for the surfaces of metal chalcogenide nanocrystals which, when incorporated in an efficient ligand-exchange procedure, can improve the quality of ZnS nanocrystal inks.

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1. Introduction

The deposition of high-quality semiconductor thin films through scalable and affordable methods is of importance in meeting the increasing demand for large area electronics, including photovoltaics, sensors, and displays [1–4]. Many solution-based techniques are attractive as replacements for conventional vacuum-based methods on account of their lower cost, scalability, and potentially higher throughput, although the material quality is generally lower [5–7]. Among the solution methods, two of the most successful strategies have been dimensional reduction (a molecular ink technique) and nanocrystal ink deposition [2,8–10]. Dimensional reduction is a type of ink deposition that relies on dissolving a metal chalcogenide target material through the use of excess, chemically reduced chalcogenide paired with volatile cations to form molecular (or polymeric) precursors that can be heated to form compositionally pure thin films; it has been used in high mobility transistors and the most successful $Cu_2ZnSn(S,Se)_4$ (CZTSS) solar cells, although large scale development may be

hindered by the use of highly toxic hydrazine [11]. Nanocrystal inks, on the other hand, employ inorganic colloidal nanocrystals of the target material and selected solvents to coat thin nanocrystalline films that sinter to form polycrystalline material upon annealing. This strategy enables fast deposition rates, the facile deposition of multi-element systems, and phase and compositional uniformity.

In the present work, we develop an approach aimed at harnessing the benefits of both the dimensional reduction and nanocrystal ink approaches, by incorporating polysulfide ligands at the surface of the nanocrystals. Although polysulfides have not previously been used as surface ligands for nanocrystals, alkylammonium polysulfide species have recently been implicated as the reactive sulfur species in the synthesis of sulfide nanocrystals with oleylamine [12]. Polysulfides have also been shown as effective ligands for inorganic metal complexes, exhibiting chelating binding to metal centers as sulfide chains often four to six sulfurs in length [13]. Specifically, $[Zn(S_4)_2]^{2-}$ and $[Zn(S_6)_2]^{2-}$ complexes containing only sulfur as the ligands have been synthesized [13,14]. Although these complexes are similar to dimensional reduction precursors, consisting of metal ions with excess reduced chalcogen, it is unlikely they could serve alone as molecular inks for quality thin film deposition, as they are generally very bulky, carrying 8–10 times the sulfur atoms that would remain in the pyrolyzed ZnS film. Their large size is exacerbated by the large phase transfer

cations used for their stabilization, such as tetraphenylphosphonium or tetraethylammonium, which are non-volatile and can act as potential sources of film contamination. The pyrolysis of molecular polysulfide and polyselenide metal complexes has previously been used in the preparation of thin films of CuInSe$_2$, and while these approaches were successful in depositing the desired CuInSe$_2$ phase, the resultant films suffered from high porosity and cracking, which was attributed largely to the substantial weight loss of bulky ligands upon pyrolysis [15,16]. Analogous polysulfide metal complexes have shown success as precursors in colloidal nanocrystal synthesis, where bulkiness is less of a problem [17].

In contrast to molecular precursors, our present strategy looks to use polysulfide ligands with a volatile cation (ammonium) on the surface of the nanocrystals, where it will act as a source of excess, contaminant-free, chalcogen during annealing. The aforementioned bulkiness of the polysulfide ligands is expected to be mitigated by formulating an ink using nanocrystals in place of molecular precursors, replacing most of the zinc ions with preformed solid-phase zinc sulfide. Only the ligands on the nanocrystal surface need to pyrolyze in this case, so most of the sulfur, which is in the bulk of the nanocrystal, will be retained in the final film, yielding high mass retention. The use of nanocrystals, along with the substitution of large cations with the smaller, more volatile ammonium, is therefore expected to reduce volume contraction, porosity, and cracking in the final film. Ammonium sulfide and other non-polysulfide, all-inorganic species have already been demonstrated in successful ligand exchanges on the surfaces of several nanocrystals [18,19]. Furthermore, the formation of polysulfides can be accomplished in a facile manner, by dissolving excess sulfur in appropriate solvents containing sulfide salts [20–24].

In the present work, zinc sulfide nanocrystals are chosen as a simple test system for these ligands. The crystal structure and surfaces are similar to those of chalcopyrite and kesterite materials, and by choosing a simple binary element system, we can reduce the confounding effects of multiple phases on the crystallinity. Moreover, zinc sulfide nanocrystals are of interest in a number of applications, including electroluminescent materials, LEDs, and photovoltaic buffer layers [25–27]. We demonstrate that polysulfide ligands easily replace the native hydrophobic ligands of zinc sulfide nanocrystals, significantly enhance the composition and mass retention of nanocrystal inks, and increase the crystallinity of annealed ZnS films.

2. Materials and methods

2.1. Polysulfide preparation

Polysulfide solutions were created by mixing ammonium sulfide (40–48% in H$_2$O, Sigma–Aldrich) and elemental sulfur (Sigma–Aldrich, 99.99%) in solvents including dimethylsulfoxide (DMSO), dimethylformamide (DMF), formamide (FA), and butanol. Five mixtures of polysulfides were prepared at molar [sulfur:sulfide] ratios of 0, 1, 3, 5, and 7, which will be referred to as Monosulfide and Polysulfides 1–4. For each solution, septa vials were charged with 0.0, 1.0, 3.0, 5.0, and 7.0 mmol sulfur, evacuated and purged with nitrogen 3 times, and 5 mL of the desired solvent and 1.0 mmol (NH$_4$)$_2$S were injected into each. Polysulfides 1–4 were stable in DMSO and DMF. Polysulfide 4 precipitated sulfur after 24 h, and Polysulfides 3 and 4 were unstable in butanol. Polysulfides in DMSO were used for spectroscopic characterization, and polysulfides in formamide were most successful in ligand exchange.

2.2. Nanocrystal synthesis

Zinc sulfide nanocrystals were synthesized by hot injection, from a modified synthesis by Riha et al. [28]. Zinc acetate dihydrate (3.0 mmol, 0.6585 g, Sigma, 99.999%) was dissolved in 3 mL oleic acid (Alfa Aesar, tech) and 3 mL oleylamine (Aldrich, 98%) in a septa-cap vial and degassed for 2 h at 150 °C to make a clear solution. In a separate vial, elemental sulfur (1.5 mmol, 0.0481 g) was dissolved in 3 mL oleylamine and sonicated at room temperature for 2 h, forming a clear red solution. A 3-neck roundbottom flask was charged with trioctylphosphine oxide (TOPO) (Aldrich, 99%, 4 g) and degassed at 140 °C for 1 h. The zinc solution was added, and the temperature raised to 320 °C, at which point the sulfur solution was rapidly injected. After 5 min, the reaction was cooled to room temperature. ZnS nanocrystals were isolated from the clear orange product by precipitation with a mixture of 3 mL butanol, 6 mL ethanol, and 1 mL methanol, and centrifugation for 10 min at 5000 rpm. The supernatant was discarded, and the white precipitate was rinsed 3× with ethanol, dried in air, and finally taken up in hexanes. This purification cycle was repeated once more before storage (10 mg/mL stock in hexanes), and again directly preceding ligand exchange.

2.3. Ligand exchange

For each ligand exchange procedure, 0.5 mL of stock solution of ZnS nanocrystals (terminated with oleic acid, oleylamine, and TOPO), was precipitated, dried, and taken up in 0.25 mL hexanes and 0.25 mL butanol. This solution was injected into a nitrogen-purged septa-cap vial with stirbar along with 1.5 mL formamide (degassed), and 0.5 mL of the desired polysulfide mixture in formamide. In this process, very thin 21 gauge needles were used with oblique angles of entry to the septum to avoid creating pathways for heated gas to leave during the exchange process. These vials were then stirred on a hotplate, raising the vial temperature to 130 °C, for 1 h, shaking vigorously every 15 min to remove any un-exchanged material from the vial walls. After 1 h, the solutions were cooled, 2 mL hexanes were injected, and the vials were stirred at room temperature for another 10 min to extract the polar phase and excess hydrophobic ligands. The vials were then opened and the contents centrifuged at 4000 rpm for 5 min to clearly separate the nonpolar and polar layers. A very small amount of white precipitate was seen in polysulfides 1 and 2, indicating that some of the ZnS may have been only partially exchanged, while polysulfides 3–5 showed only a well-defined interface between transparent layers. The polar layer for each polysulfide was extracted into a fresh centrifuge vial. To precipitate the exchanged nanocrystals, a mixture of 3 mL isopropanol, 1 mL butanol, and 2 mL hexanes was added. The solution was stirred and then centrifuged again at 4000 rpm for 5 min, leaving white precipitates for all the polysulfides, except polysulfide 1, which had a slightly gray color. The supernatant was discarded, and the precipitate was taken up in 1 mL of ethanol to form a final ink solution. Ethanol was chosen for volatility and ease of casting films, though many polar solvents can be introduced at this phase.

2.4. Film formation

Silicon wafers and soda lime glass substrates were cut to 1 cm^2, sonicated in acetone for 20 min, dried under filtered air, and subjected to UV-ozone cleaning for 30 min. To prepare dry films for analysis, films were drop-cast onto silicon and glass substrates in nitrogen-evacuated vials, and allowed to dry slowly at 120 °C to allow full evaporation of ethanol in the case of polysulfide-exchanged samples, or hexane for native ligand samples. A subset of the dried films was also annealed at 525 °C for 75 min in a tube furnace under nitrogen gas flow. During the anneal process, the