GRAPHICAL ABSTRACT

TITLE

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.

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 $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (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 been used previously 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, $[\text{Zn}(\text{S}_4)_2]^{2-}$ and $[\text{Zn}(\text{S}_6)_2]^{2-}$ 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 to 10 times the sulfur atoms that would remain in the pyrolyzed 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 pre-formed 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 of 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 & METHODS

2.1. Polysulfide preparation

Polysulfide solutions were created by mixing ammonium sulfide (40-48% in H₂O, 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 Polysulfide 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 (NH₄)₂S were injected into each. Polysulfides 1-4 were stable in DMSO and DMF. Polysulfide 4 precipitated sulfur after 24 hours, 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 hours 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 hours, 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 hour. The zinc

solution was added, and the temperature raised to 320°C, at which point the sulfur solution was rapidly injected. After five minutes, 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 minutes at 5000 rpm. The supernatant was discarded, and the white precipitate was rinsed 3x with ethanol, dried in air, and finally taken up in hexanes. This purification cycle was repeated once more before storage (10mg/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 one hour, shaking vigorously every 15 minutes to remove any un-exchanged material from the vial walls. After 1 hour, the solutions were cooled, 2 mL hexanes were injected, and the vials were stirred at room temperature for another 10 minutes to extract the polar phase and excess hydrophobic ligands. The vials were then opened and the contents centrifuged at 4000 rpm for 5 minutes 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 minutes, leaving white precipitates for all the polysulfides, except polysulfide 1, which had a slightly grey 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 cm², sonicated in acetone for 20 minutes, dried under filtered air, and subjected to UV-ozone cleaning for 30 minutes. 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 minutes in a tube furnace under nitrogen gas flow. During the anneal process, the samples were covered with a glass substrate to allow for slower, more controlled ligand volatilization.

2.5. Characterization

UV-Visible spectroscopy (UV-Vis) measurements were performed on a Cary 6000i spectrophotometer. Fourier-transform infrared (FTIR) spectroscopy was conducted on a Thermo Electron Nicolet Nexus 670 spectrometer. FTIR samples were prepared by drop-casting and drying nanocrystals on cleaned Si wafers, or sandwiching liquid samples between two Si wafers.

X-ray photoelectron spectroscopy (XPS) was performed with a PHI VersaProbe Scanning XPS Microprobe instrument with Al (K-alpha) 1486 eV radiation at a power of 51 W and a 0.20 mm spot size. In analyzing the XPS fine scans, each sulfur 2p peak was fit using two Gaussian curves for $j=3/2$ and $1/2$, separated by 1.18 eV. The peaks were fixed to a 2:1 area ratio, and the full-width half-maximums (FWHMs) were kept consistent among all peaks. The polysulfide peak position was found to reside at a binding energy 1.48 eV above the main sulfur peak for all the polysulfide species, and this peak separation was fixed while fitting the peaks for quantification of polysulfide content..[29] X-ray diffraction (XRD) data was collected on an a PANalytical X'Pert PRO x-ray diffraction system using Cu-K α radiation in the Bragg-Brettano geometry using a θ -2 θ scan with programmable divergence slits and a PIXcel detector. In analysis, the signal contribution from Cu K α 2 radiation was stripped algorithmically and the data was baselined before fitting for peaks. Scanning electron microscopy (SEM) was performed using an FEI Magellan 400 XHR Scanning Electron Microscope with a FEG source. Lastly, thermogravimetric analysis was performed using a TA Instrument Q500 thermogravimetric analyzer.

3. RESULTS & DISCUSSION

3.1. Polysulfide ligand characterization

The polysulfide solutions in DMSO solvent were chosen for UV-Vis spectroscopy since polysulfides have been well-documented in this medium.[22,23,30] The spectra, shown in Figure 1, are of samples diluted to the same total sulfur concentration; all are diluted to below 1% concentration of the concentrated stock in order to avoid saturation in the absorbance spectrum.

At such low concentrations, the polysulfide solutions are all blue-green in color, although they range from green to red with increasing sulfide length at full concentration. All of the polysulfide spectra exhibit large absorption peaks at 332 nm and 617 nm, the latter of which caused the blue-green appearance in the diluted samples. The 617 nm transition is insignificant in the full concentration solutions, where the change in color between the polysulfide solutions is determined by the changes in absorption from 429-486 nm. The 617 nm absorption peak is attributed to the S_3^- radical, which in aprotic solvents is formed by the dissociation of S_6^{2-} , explaining the apparent increase in molar absorptivity of this transition at lower concentration.[22] The major changes in absorbance with increasing polysulfide chain length occur at around 370 nm and in the 425-490 nm range.

Figure 1: UV-Vis spectra of polysulfide dilutions prepared in DMSO showing (a) the spectrum from 300-800 nm (b) the enlarged region from 400-550 nm. The color of each polysulfide trace corresponds approximately to the respective color of concentrated polysulfide solutions in DMSO.

Table 1: Species detected by UV-Vis in each of the five prepared polysulfide mixtures in DMSO and the corresponding wavelength in nanometers. Literature assignments of polysulfide species are in DMSO, unless otherwise indicated. *Indicates tentative assignment.

	Polysulfide Species Detected (nm)					
Experimental	S_2^{2-} *	S_3^{2-} *	S_4^{2-}	S_6^{2-}	S_8^{2-}	$S_3^{\cdot-}$ radical
<i>Monosulfide</i>	-	-	426 (weak)	-	-	617
<i>Polysulfide 1</i>	278	370	429 (weak)	-	-	617
<i>Polysulfide 2</i>	278	372	465 (broad)	-	-	617
<i>Polysulfide 3</i>	278	373	-	483(broad)	483 (broad)	617
<i>Polysulfide 4</i>	278	373	-	486 (broad)	486 (broad)	617
Literature						
<i>Sawyer[22](DMSO)</i>	-	-	420	475	492	618
<i>Badoz[20](DMSO)</i>	-	-	435	-	505	618
<i>Kim[21](DMSO)</i>	-	-	310, 350	340, 450	380, 490	610
<i>Han[23], (DMF)</i>	280	-	420	340, 450	355 (cyclic) 490 (linear)	600

The spectral region of 400-550 nm is expanded for clarity in Figure 1(b), and the region between 260-400 nm is shown in Supporting Information (Figure S1). It is clear that the peak of the absorbance in Figure 1(b) redshifts in going from ammonium monosulfide (at 426 nm) to polysulfide 4 (at 486 nm). This shift is suggestive of a transition in the solution composition to that of longer polysulfides. This conclusion is supported by a more detailed assignment of the different species present in the solutions, as summarized in Table 1 for the transitions near 370 nm and between 400-500 nm for each polysulfide mixture. Each assignment in Table 1 is based on literature, with the exception of the monosulfide, S_2^{2-} , which was not identified in the literature and therefore not assigned in this study.[20–23] The S_2^{2-} assignment of 278 nm should also be considered tentative, as it was not reported in DMSO; however, a value of 280 nm was reported in DMF, close to the assignment used here.[23] It is noted that the wavelengths assigned to S_4^{2-} ,

S_6^{2-} , and S_8^{2-} correspond well to the energies that would be expected for a simple quantum confinement model based on sulfide chain length (L), yielding an $E \propto L^{-2}$ dependence (Figure S2). This model was extended to predict transition wavelengths of 377 nm for S_3^{2-} , 281 nm for S_2^{2-} , and 118 nm S^{2-} . The absorption in the longest polysulfides 2-4 around 373 nm is consistent with the quantum confinement-predicted S_3^{2-} peak at 377 nm. The S_2^{2-} transition of 281 nm is in good agreement with the assignment in DMF, and is consistent with the appearance of a small peak at 278 nm for DMSO polysulfide solutions 1-4 (Figure S1). The 332 nm transition remains unassigned, and although S_3^{2-} is reported at 334 nm in DMF, the trend is inconsistent with expected polysulfide concentrations in this work.[23] The data in Table 1 suggest that each prepared solution contains a mixture of several polysulfides, a result that is consistent with the reported equilibrium between polysulfides of different length.[22] However, the distribution of the polysulfide mixture changes with the sample preparation (going from monosulfide to polysulfide 4, i.e. a higher sulfur:sulfide ratio). Namely, polysulfide solutions prepared with a larger sulfur:sulfide content contain longer polysulfides.

Figure 2: UV-Vis spectra of (a) as-prepared (“Native Ligands”) and polysulfide-exchanged ZnS nanocrystals; and (b) Tauc plot for direct bandgap of ZnS nanocrystals before and after exchange with ammonium sulfide.

3.2. Ligand exchange

The ability to tune the distribution of polysulfide ligands by the solution preparation method is desirable for studying the effect of different polysulfide chain lengths on nanocrystal surfaces. Ligand exchanges were carried out on ZnS nanocrystals using the different polysulfide solutions, and found to be successful in formamide, DMF, and DMSO solutions. Formamide was chosen for subsequent studies as it exhibited the highest exchange efficiency and highest yield upon purification. Figure S3 shows photographs of the polysulfide solutions throughout the exchange process. When the ZnS nanocrystal solution (from the hexane/butanol solvent) is first added to the clear polysulfides, it creates a white opaque nonpolar layer. After the 1 hour exchange process, polysulfide solutions 1-4 largely regain translucency, indicating good dispersion and minimal flocculation of ZnS. The control sample (Figure S3, bottom left), which contained formamide without polysulfide, did not bring nanocrystals into the polar phase, demonstrating the necessity of polysulfide species (this was confirmed with SEM by the absence of nanocrystals in films cast from the control). All polysulfides were stable throughout the 1 hour long, 130°C exchange, as evidenced by the color retention thereafter.

To compare the efficacy of polysulfide ligand exchange, UV-Vis spectroscopy was performed using equivalent concentrations of colloidal nanocrystals before and after exchange (Figure 2). The polysulfide 4 mixture was omitted for the remainder of the study due to its instability, as

sulfur precipitated after a period of 24 hours. Figure 2a shows an absorption onset of about 340 nm for all of the nanocrystal samples, indicating that the ZnS nanocrystals are preserved during the exchange process. The baseline signal in the UV-Vis spectra of the exchanged nanocrystals at shorter wavelengths is indicative of light scattering, suggesting some agglomeration of particles after exchange, whereas the as-synthesized sample is fully colloidally dispersed. Figure 2b shows the fit for direct band gap of the native ZnS and the ammonium sulfide-exchanged ZnS sample. The respective 3.7 and 3.8 eV energies indicated are consistent with the cubic ZnS optical gap of 3.7 eV.[31] As seen in Figure 2a, the absorbance profiles of the other polysulfides were identical to monosulfide, and were omitted for clarity in Figure 2b. The absolute absorbance values at 300 nm were used to estimate the ZnS nanocrystal retention after polysulfide exchange, although scattering may artificially increase these values (Table 2). Excellent retention of over 90% is seen through exchange with the monosulfide and polysulfides 1 and 2, and polysulfide 3 still shows a relatively high yield of 76%.

Table 2: Retention of ZnS nanocrystals upon polysulfide ligand exchange, calculated from UV Vis absorbance at 300 nm, and native ligand remaining, calculated from FTIR absorbance at 2923 cm⁻¹.

Sample	Abs(300 nm)	Exchange Retention (%)	Native Ligands Left (%)
<i>Monosulfide</i>	0.319	92	< 1
<i>Polysulfide 1</i>	0.327	95	< 1
<i>Polysulfide 2</i>	0.337	97	< 0.1
<i>Polysulfide 3</i>	0.263	76	< 0.1
<i>Native Ligands</i>	0.346	100	100

Figure 3: FTIR spectra of (a) neat formamide, (b-e) ZnS nanocrystal films after formamide/polysulfide exchange,, (f) ZnS nanocrystals with native ligands, (g) oleylamine, and (h) oleic acid. The ZnS nanocrystal samples were drop cast onto silicon substrates and dried at 120°C to make solid films.

To determine the species present on the nanocrystal surface, ZnS nanocrystal films on silicon wafers were investigated by FTIR spectroscopy (Figure 3). The ligands on the as-synthesized ZnS nanocrystals include oleylamine, oleic acid, and TOPO. Spectra of neat oleylamine and oleic acid are shown at the bottom of Figure 3. (TOPO showed no additional peaks and was omitted for clarity.) Oleic acid presents C-H stretching modes at 2954, 2923, and 2852 cm^{-1} , a C=O stretch at 1712 cm^{-1} , and a broad O-H stretching signal around 3160 cm^{-1} . Oleylamine yields the same C-H modes as well as a N-H stretch at 3319 cm^{-1} . The native ligands on the as-

prepared ZnS nanocrystals (solid black trace) exhibit a vibrational C-H signature consistent with a mixture of oleic acid, oleylamine, and TOPO, as well as two new bands at 1567 cm^{-1} and $\sim 1455\text{ cm}^{-1}$ appear in the absence of the 1712 cm^{-1} vibration. These new bands express frequencies characteristic of asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetric $\nu_{\text{s}}(\text{COO}^-)$ stretches, indicating O-H dissociation and interaction at the ZnS surface.[32,33] The wavenumber separation $\Delta\nu$ is indicative of the type of interaction between carboxylate and surface metal ion, and can distinguish between monodentate, bridging bidentate, and chelating bidentate.[32–34] The separation observed here of 112 cm^{-1} is most consistent with chelating bidentate, which occurs for the smallest values ($\Delta\nu \leq 110\text{ cm}^{-1}$). Hence, the spectrum of the as-prepared ZnS nanocrystals conforms the presence of oleic acid ligands at its surface, and while oleylamine and TOPO are likely present, they cannot be definitively assigned by IR alone

FTIR spectra were collected of the ZnS nanocrystals after polysulfide ligand exchange in formamide solution (Figure 3, color traces) and compared with that of neat formamide. The spectrum of neat formamide (dashed, top) shows N-H stretching modes at 3423 , 3336 , and 3201 cm^{-1} , C-H stretching at 2890 cm^{-1} , a carbonyl C=O stretch at 1686 cm^{-1} , an NH_2 scissor mode at 1608 cm^{-1} , and an in-plane C-H scissor mode at 1390 cm^{-1} , all in good agreement with literature.[35] The exchanged monosulfide and polysulfide ZnS samples exhibit a vibrational signature identical to the neat formamide case, with almost no trace of the native ligands. Since the polysulfides are not IR-active, this data indicates near complete replacement by formamide and polysulfides after exchange (Table 2). **Further identification of polysulfide species may be also achieved through Raman spectroscopy, which was not performed in this study.**[36,37] The C-H stretching region of the spectra is expanded (Figure S4) to better

quantify the extent of native ligand removal. In this region, ZnS nanocrystal samples exchanged with the shorter ligands (monosulfide and polysulfide 1) do retain a weak intensity in the C-H peaks at 2923 and 2852 cm^{-1} , corresponding to the same signals in the native ligand sample. These peaks progressively disappear in samples exchanged with polysulfides 2 and 3, demonstrating an enhanced ability by the longer polysulfides to displace the native ligands. The remaining signal at 2877 cm^{-1} is assigned to a redshifted C-H stretch from formamide.

Figure 4: X-ray photoelectron spectra of dried ZnS nanocrystal films with (a) polysulfide 2 ligands and (b) native ligands.

3.3. XPS analysis

To further examine the nature of the exchanged ZnS surface, XPS was performed on ZnS nanocrystals drop cast then dried on silicon substrates. The full XPS spectra of dried films from ZnS nanocrystals before and after polysulfide ligand exchange are shown in Figure 4. The polysulfide 2 sample (Figure 4a) is chosen because it is representative of all the exchanged

samples. The XPS spectrum with native ligands (Figure 4b) reveals only small Zn signals and is saturated with carbon, oxygen, and silicon signal, owing to the carbonaceous native ligands as well as micro cracking in the film, exposing the SiO₂ native oxide surface of the silicon substrate. The XPS penetration depth is only several nanometers, and the native ligands almost completely obscure the Zn and S from detection, as oleylamine and oleic acid have full chain lengths of 2.0 nm.[38] After the exchange procedure, carbon, oxygen, and silicon are largely absent from the ZnS film surface, and the only major signals are from Zn and S, again demonstrating the efficacy of the ligand exchange. The small remaining carbon and oxygen signals are attributed to adventitious absorption, as the surface of these samples was not sputtered in situ, and some of the polysulfide samples showed no detectable carbon 1s signal at all. The Zn:S atomic ratio was 1.00 in the exchanged polysulfide films, indicating stoichiometric composition.

A comparison of XPS survey scans of both the dried (solvent removed at 120°C) and annealed (525°C in nitrogen) films of the samples from Figure 4 is shown in Figure S6. The ZnS films with native ligands, when annealed at 525°C, do lose most of the carbon signal due to pyrolysis of the long-chain moieties, but both carbon and oxygen linger in the film. The ZnS film that has been exchanged shows very little compositional change between dried and annealed, with the exception of slightly higher oxygen and carbon signals after anneal, albeit significantly less than in the case of the annealed native-ligand film. The surface Zn:S ratios of the annealed films with exchanged and native ligands were 1.09 and 1.00, respectively. Overall, the polysulfide-exchanged ZnS samples show excellent compositional purity both post-exchanged and post-annealed, with lower oxygen and carbon content than the un-exchanged counterparts.

Figure 5: XPS spectra of (a) the sulfur 2p peak in ZnS nanocrystal film after polysulfide 2 exchange and 525°C nitrogen anneal; and (b-e) un-annealed polysulfide-exchanged ZnS nanocrystal films. The percentage indicates the contribution of the polysulfide component to the total sulfur peak.

Furthermore, the sulfur 2p peak was used to identify polysulfide species on the ZnS surface.

Figure 5a shows the sulfur 2p peak of a typical polysulfide-exchanged ZnS film after a 525°C

anneal under nitrogen, which is found to be well fit by two spin-orbit split peaks, with binding energy of 161 eV for the $2p_{3/2}$ level and 162.2 eV for the $2p_{1/2}$ level (blue curves). This signal originates solely from sulfur in the ZnS lattice, as all polysulfides were removed through the 525°C annealing process. In Figure 5b-e, the best fit included a second sulfur peak 1.5 eV higher in binding energy, at 162.5 and 163.7 eV for the respective 2p spin-orbit splitting values. This binding energy is consistent with the polysulfide state of sulfur.[29,39] The same peak positions, peak widths, and relative intensities in a 2:1 ratio are used for each of the spectra, providing a good quality of fit in each case. Notably, the polysulfide content increases with chain length, as is expected for the presence of longer polysulfides on the surface, and it tapers off at 22% for polysulfide 2 and 3, as calculated from the 2p peak fitting. No difference in binding energy was detected between the polysulfides of different chain length, indicating a similar chemical environment among the S-S bonded species. The trend of increasing polysulfide content with longer chain length was also examined using the sulfur 2s peak, which, while less sensitive, nonetheless corroborated the same trend (Figure S5). Higher oxidation states of sulfur would be expected to appear in the 164-170 eV range, but no other sulfur XPS peaks were observed, indicating that this procedure, in which samples were largely maintained in inert atmospheres, is resistant to oxidation and contamination.

Figure 6: X-ray diffraction plots of ZnS thin films on glass annealed at 525°C cast from (a) un-exchanged and (b-e) mono- and polysulfide-exchanged ZnS nanocrystals. The vertical lines correspond to the XRD peaks in the and cubic ZnS reference (PDF #01-071-3733).[40]

3.4. Structural and morphological properties

The structural properties of the annealed films were examined with XRD (Figure 6). Equivalent volumes of both as-synthesized and polysulfide-exchanged ZnS nanocrystal inks were cast on glass substrates and annealed under nitrogen at 525°C. All films showed peaks consistent with the cubic zinc sulfide structure, registering the (111), (220), and (311) reflections and no aberrant signals. The films annealed with native ligands showed very low crystallinity (black curve). Crystallization increased markedly after all polysulfide exchanges, exhibiting much higher integrated XRD intensity, and demonstrating success of the ligand exchange in promoting crystallinity. In addition to increased intensity, the average grain size increased as well, as

calculated by the Scherrer formula (Figure S7, circles). The average particle size increased from 4.2 nm in the native ligand film to up to 8.9 nm in the polysulfide 2 mixture. This is a small but significant increase. Moreover, larger increases are expected for materials systems with a lower barrier to recrystallization, such as those with lower melting points and higher vapor pressure, as bulk ZnS melts at 1718°C.[41]

Figure 7: Scanning electron micrographs of ZnS films on silicon annealed at 525°C under nitrogen, cast from (a) native ZnS nanocrystals, and (b-e) ZnS nanocrystals exchanged with monosulfide and polysulfides 1-3, respectively. (100 nm scale bar for all images)

To further assess the film quality, the film morphology of annealed films was studied with SEM (Figure 7). Films prepared from ZnS nanocrystals with native ligands clearly generate the smallest particles (Figure 7a), and all films made from polysulfide-exchanged ZnS nanocrystals have significantly larger average features (Figure 7b-7e). Particles within the exchanged films retain isotropic dimensions, as is consistent with coalescence of smaller spherical grains. The average feature size in the films from Figure 7 was measured with particle sizing software. The results (Figure S7, squares) show a dependence on the ligand. The native ligand films give an average particle size of 4.0 nm, while the average particle size of all of the polysulfide films is greater than 9 nm. The polysulfide 1 mixture gives the largest average feature at 16 nm, and the

size trend is identical to that from XRD. The absolute size estimates from SEM are larger than those from XRD for the ligand-exchanged nanocrystals, which is accounted for by the different measurement techniques. A given particle sized by SEM can be comprised of multiple smaller grains that have sintered together without becoming a single crystal. In this case, SEM detects the aggregate size, while XRD measures the smaller grains. In the ligand exchanged samples, those smaller grains were still significantly larger than the un-exchanged samples (8.9 vs. 4.2 nm for polysulfide 2), demonstrating that crystal growth is occurring. The sizes of un-exchanged samples as measured by both SEM and XRD converge on 4 nm, indicating that neither sintering nor crystal growth occur without the polysulfide exchange. Porosity is a concern in these films, as significant voids are evident across all films, with the pores larger in the ligand-exchanged films than in the film from native ligands. These pores are presumed to originate from volume contraction upon annealing through volatilization of ligands as well as from empty space between deposited nanocrystals. Future strategies for decreasing porosity include employing larger nanocrystals and a broader size distribution of nanocrystals, using more concentrated inks, and allowing for longer, slower drying times.

This study allows us to isolate the impact of surface ligands on recrystallization during annealing. As evidenced, polysulfide ligands facilitate the formation of larger grains upon annealing of the ZnS films compared to the native ligands. However, the effect is a function of ligand exchange temperature. The 130°C temperature of the polysulfide ligand exchange used in the experiments described above was found to be high enough to drive complete transfer of ZnS nanocrystals into the polar phase, but low enough to prevent any ripening process before the high-temperature anneal. On the other hand, ligand exchange performed at higher temperatures

(200°C) did not provide as clear a benefit because ripening occurred even during the exchange and drying process. Scanning electron micrographs of ZnS nanocrystals exchanged in polysulfide 1 at 200°C for various durations are shown in Figure S8, comparing before and after high temperature anneal. The dried samples show a steady increase in diameter with prolonged 200°C liquid-phase exchange, reaching diameters as large as 30 nm after 20 minutes. Subsequent high-temperature annealing gave only minor increases in particle size for these samples. While these higher temperatures produced even larger crystals than the 130°C exchange, this increase came before annealing. The 200°C process is therefore not expected to provide any more benefit to film formation than if larger nanocrystals had been used as starting material, which would likely introduce more porosity into the films. Overall, the 130°C process was found to give superior conditions for film deposition by increasing film crystallinity only upon annealing.

3.5. Thermogravimetric analysis

Lastly, the mass loading of the polysulfide inks was investigated with thermogravimetric analysis. Mass percentage as a function of temperature is plotted from 150°C to 600°C in Figure 8. Below 150°C, the ethanol and hexane solvents evaporate, and above that temperature, the remaining mass loss is attributed only to surface ligands. The ZnS nanocrystals with native ligands show steady mass loss from about 175°C to 500°C and an overall mass loss of 38% (retention of 62%). All of the polysulfides show much lower mass losses, with values of 11-13%. The final mass percentages are very similar across all of the sulfide ligands, though minor differences are observed in the mass-temperature profiles (enlarged, Figure S9). Overall, all of the polysulfides show marked improvement over native ligands in minimizing mass loss during annealing. The elevated ink loadings of 87-89% demonstrated by the polysulfides is desirable in

mitigating volume contraction during annealing in order to minimize cracking and increasing film density.

Figure 8: Thermogravimetric analysis of ZnS nanocrystal solutions with native, monosulfide, and polysulfide 1-3 ligands.

4. CONCLUSIONS

Various ammonium polysulfide solutions were prepared in aprotic solvents, and were shown to contain a distribution of sulfide chain lengths, centered around the desired length. Cubic ZnS nanocrystals 4.0 nm in diameter were synthesized with long-chain hydrophobic ligands and successfully exchanged into polar solvent upon the addition of polysulfides in a high-yield process. FTIR spectroscopy and XPS demonstrated the near-complete removal of nonpolar ligands from the nanocrystal surface and the presence of polysulfides in their place. The surface polysulfide content increased as expected with longer sulfide chains. XRD and SEM demonstrated that the 130°C ligand exchange procedure used did not ripen nanocrystals after an hour of exchange, and moreover the polysulfide exchange enabled increases in grain size of 2-3 times over the un-exchanged control after 525°C annealing in inert environment. The

exchanged-nanocrystal films exhibited much improved mass retention on annealing compared to native-ligand nanocrystals as demonstrated by TGA. Overall, we introduce the polysulfide species as an alternative ligand for metal chalcogenide nanocrystal surfaces, demonstrate a facile and efficient ligand-exchange procedure, and show that these ligands can improve the crystallinity of ZnS nanocrystal inks.

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