Synthesis of Ni$_3$S$_2$/PbS Core-Shell Nanocrystals using Two Precursors

Goh W.L.$^1$ and Chin W.S.$^2$

Department of Chemistry, Faculty of Science, National University of Singapore
3 Science Drive 3, Singapore 11754

ABSTRACT

In this paper, we report our findings in the search for a synthetic route to produce Ni$_3$S$_2$/PbS core-shell nanostructures. We have devised an integrated-step method that uses two single-source precursors, and preliminary findings indicate that this methodology may have potential for Ni$_3$S$_2$/PbS core-shell synthesis. We have found a mild condition that may support layered growth of the PbS shell layer, with some evidence pointing to the formation of a monolayer of PbS shell on the Ni$_3$S$_2$ core.

INTRODUCTION

The synthesis of core-shell nanostructures have proven to be useful in tuning the properties of nanomaterials, achieving results that are beyond the reach of simple size and shape control, such as the enhancement of the photoluminescence quantum yield of a semiconductor nanocrystal core. From reported literature, the general consensus for the requirements of good shell growth is when the lattice parameters of the two components do not differ significantly (Cozzoli et al., 2006). One method of growing core-shell nanocrystals is to achieve selective heterogeneous nucleation of the shell material on the core material while preventing the formation of self-nucleated nanocrystals of the shell material. This is usually done by performing the slow addition of shell molecular precursor to the core at relatively low temperatures, in an effort to promote layered growth of the shell (Cozzoli et al., 2006).

Our investigation in this UROPS project will focus on the synthesis of the Ni$_3$S$_2$/PbS core-shell nanocrystals. The properties of nanosized Ni$_3$S$_2$ are not widely reported and we seek to synthesize Ni$_3$S$_2$/PbS core-shell nanocrystals to determine the properties of Ni$_3$S$_2$ and how they are modified by a semiconductor shell layer.

EXPERIMENTAL SECTION

Nickel (II) thiobenzoate precursor (NiTB), lead (II) thiobenzoate precursor (PbTB) and Ni$_3$S$_2$ nanocrystals were prepared according to methods as reported by Kerk, 2007 and Zhang et al., 2006. Ni$_3$S$_2$/PbS core-shell nanocrystals were prepared by adding oleylamine to a solution of Ni$_3$S$_2$ dissolved in TOP under stirring. A degassed solution of PbTB in TOP was injected into the reaction mixture, and the mixture was aged at 40°C for 20min. For monitoring the progress of shell growth, aliquots were taken from the reaction mixture at regular time intervals. UV-Vis absorption spectra were recorded and TEM slides were prepared. The product was characterized by TEM, XRD and UV-Vis Spectroscopy.

---

1 Student
2 Supervisor, Associate Professor
RESULTS AND DISCUSSION

Synthesis of Ni$_3$S$_2$ Core Nanocrystals

The Ni$_3$S$_2$ core nanocrystals synthesized were observed to be generally spherical with slight faceting (Figure 1a), having a size distribution of 7.06±1.23 nm (Figure 1b). The Ni$_3$S$_2$ core was also characterized by XRD (Figure 1c) and UV-Vis spectroscopy, which records an absorption peak at 460nm that is consistent with the reported findings by Kerk, 2007.

Determining Suitable Conditions for Layered Shell Growth

From reported literature, it is known that PbTB decomposes to form PbS nanocrystals under room temperature conditions in the presence of an amine catalyst (Zhang et al, 2006). To promote layered growth of PbS as a shell layer, we modify the reported procedure by lowering its reactivity. In determining the suitable conditions, we adopted a two-step method which involves synthesizing and drying the Ni$_3$S$_2$ nanocrystals, before redispersing a known mass in the amine solvent, followed by the introduction of PbTB. Reactivity was controlled by using a sterically hindered amine (HDA or oleylamine), by adjusting (lowering) the temperature and adding TOP as a stabilizing agent. The conditions investigated are outlined below:

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Set A</th>
<th>Set B</th>
<th>Set C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$S$_2$ : PbTB</td>
<td>1 : 5</td>
<td>2 : 1</td>
<td>2 : 1</td>
</tr>
<tr>
<td>Amine : TOP</td>
<td>10 : 1</td>
<td>3 : 1</td>
<td>1 : 2</td>
</tr>
<tr>
<td>Amine Type</td>
<td>HDA</td>
<td>Oleylamine</td>
<td>Oleylamine</td>
</tr>
<tr>
<td>Temperature</td>
<td>150°C</td>
<td>80°C</td>
<td>40°C</td>
</tr>
</tbody>
</table>

Our attempts in core-shell synthesis were initially met with difficulties owing to the high reactivity of the system which caused the formation of large cubical (~20nm) PbS nanocrystals. Using Set C conditions, we succeeded in avoiding the overgrowth of such PbS nanocrystals, but it was that observed the dried Ni$_3$S$_2$ powder could not redisperse effectively in amine solvent.

Determining Suitable Conditions for Ni$_3$S$_2$/PbS Core-Shell Synthesis

The two-step method used earlier was eventually redesigned into an integrated-step method to bypass the difficulties associated with redispersion of Ni$_3$S$_2$. This involves excluding the drying step and performing the core and shell synthesis sequentially in a single experiment. Set C conditions were retained and the effects of varying the amine concentration were investigated:
In summary, approximately spherical nanocrystals were observed for all sets, and formation of large PbS nanocrystals was not observed (Figure 2a). HR-TEM images were obtained to determine the lattice spacing and identify the nanocrystals, in which the majority of the nanocrystals were identified as Ni$_3$S$_2$ (Figure 2b, 2c). For Sets 1 and 2, besides the typical Ni$_3$S$_2$ nanocrystals observed, patches of “grainy” area containing what appears to be extremely small nanocrystals were observed (Figure 2a, denoted by red circle). Based on our HR-TEM observations, the few PbS nanocrystals that we found were all identified in this “grainy” area, which leads us to suggest that the “grainy” area contains primarily self-nucleated PbS nanocrystals. This is supported by EDX data (Figure 2d) that detects Pb composition to be 4 times higher in the “grainy” area than normal. It should also be noted that this “grainy” area was not observed in Set 3, but nevertheless the presence of Pb was recorded by EDX, which may suggest the formation of a PbS shell layer.

Figure 2: (a) TEM images (b), (c) HR-TEM images and (d) EDX of Ni$_3$S$_2$/PbS nanocrystals. Time evolution for the UV-Vis absorption spectra of Ni$_3$S$_2$ nanocrystals for (e) Set 1, (f) Set 3.

The UV-Vis spectra for all sets were recorded (Figure 2e, 2f) from 300nm to 1600nm. However, the expected PbS absorption peaks (at ~1000nm) arising from the presence self-nucleated PbS nanocrystals was not observed. Thus, we postulate that there are 3 possibilities to explain the observations. The first possibility is that the PbS nanocrystals formed were of insufficient concentration to register a clear absorption peak. A second possibility is that most of the PbS nanocrystals were removed unintentionally during the work-up. The third possibility is that a thin monolayer of PbS shell had formed around the Ni$_3$S$_2$ core, which may not register an absorption peak nor will its lattice be observable under HR-TEM.

For Sets 1 and 3, a blue shift from the original Ni$_3$S$_2$ absorption peak was observed, and available data seems to indicate that the blue shift increases with reaction time. We suggest that
the observed blue shift in the UV-Vis spectra is attributed to the growth of a PbS shell over the Ni$_3$S$_2$ core. However, we also acknowledge that another equally reasonable explanation is that the blue shift may be due to the overlapping spectrum of discrete Ni$_3$S$_2$ and PbS nanocrystals. Nevertheless, for the case of discrete nanocrystals, one would expect the magnitude of blue shift to be greater in Set 1 than in Set 3. This is because the former has a higher amine concentration, which would lead to the formation of more PbS nanocrystals. However, the UV-Vis data does not support this prediction; at 20 min reaction time for Sets 1 and 3, the blue shift remains virtually identical at 19 nm and 20 nm respectively.

To further analyze the feasibility of shell formation in the experiment, the thickness of the PbS shell layer was calculated by using data obtained from the EDX elemental composition. Our model assumes that the Ni$_3$S$_2$ core nanocrystals are spherical with a diameter of 7 nm. The molar ratio of both reagents was equated to determine the expected volume of the PbS layer, using the derived equation:

\[
\text{Volume}(\text{PbS}) = \left(\frac{3\beta}{100}\right)\frac{\rho(\text{Ni}_3\text{S}_2)M(\text{PbS})}{\rho(\text{PbS})M(\text{Ni}_3\text{S}_2)}\text{Volume}(\text{Ni}_3\text{S}_2)
\]

In our calculations, the density of bulk Ni$_3$S$_2$ (5.82 g/cm$^3$) and PbS (7.40 g/cm$^3$) were used. Our model assumes that the packing of the Ni$_3$S$_2$ and PbS nanocrystals are similar as that of the bulk material. From the volume of the PbS shell, the shell thickness can be then determined.

Based on this simplified model, we calculated that the maximum shell thickness for Set 1 and 3 is 0.9 Å and 0.4 Å respectively. While these values are smaller than the dimensions of PbS lattice parameter (a = 5.9 Å), it should be noted that the model assumes a uniform shell growth on all Ni$_3$S$_2$ present. A possible scenario is that only a fraction of the Ni$_3$S$_2$ core present had undergone proper shell growth, which would decrease the average shell thickness value. Given that such a shell layer would be very thin, it would probably not be observable under HR-TEM. Admittedly this model is a simplification, as it does not accounts for the effects of surface restructuring which will alter the packing structure of the core surface and shell layer, but nevertheless it serves as a good approximation to determine the approximate shell thickness.

**CONCLUSION**

In conclusion, we have determined the condition at which excessive self-nucleation of PbS nanostructures may be avoided. The two precursor integrated-step method for core-shell nanocrystal synthesis was investigated, but evidence of shell growth has thus far been inconclusive. A possible explanation for the lack of shell growth confirmation is that a monolayer of PbS shell material was formed, which would not be observable under HR-TEM but may be responsible for the observed blue shift in the UV-Vis spectra.

**REFERENCES**

