Synthesis of high quality monodisperse Nickel Oxide Nanocrystals

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Abstract. Monodisperse nickel oxide (NiO) nanocrystals with a particle size of 2.7±0.7nm have been synthesised using low temperature reflux of hydrated nickel acetate and methanol. It has also been possible to create NiO nanocrystals without refluxing. The fabrication of NiO nanorods with size varying from 2 – 10 µm in length and about 0.25µm in width and crystalline pellets with approximate dimensions of 150nm by 300nm was also achieved.

1. Introduction

The unique quantum properties displayed by nanomaterials make them very attractive to use for a wide range of applications. There has been extensive research in the synthesis and potential applications of these materials and structures which include nanocrystals, nanorods, nanowires, nanofilms and core shell structures to name but a few. Nickel oxide has attracted particular interest due to a wide range of beneficial properties such as catalytic behaviour, anomalous electronic and magnetic properties. These properties open up numerous potential applications such as catalysis, electrochromic windows, sensors, magnetic resonance imaging, targeted drug delivery, solid oxide fuel cells as well as functional layers, dye-sensitized photocathodes and electrodes in solar cells [1-6].

Here we report the successful synthesis of Nickel oxide nanocrystals with optical and electrical properties tailored for applications in solar cells. NiO is an inherently p-type semiconductor with numerous potential applications in solar cells mentioned above. The band gap of nickel oxide is 3.55 eV which is considered to be a wide band gap and therefore it would not be possible to use it as an efficient single junction solar cell device. Nickel oxide nanocrystals with an average size of 2.7±0.7nm have already successfully been synthesised and now attempts are being made to add a Zinc oxide shell to form a p-n junction. It is hoped that successful synthesis of these Nickel oxide nanocrystals will allow them to be used as a functional layer in a tandem solar cell exploiting the higher energy end of the solar spectrum.

Nickel oxide nanocrystals are synthesized by reflux of alcohol solutions of hydrated metal acetate under ambient conditions, following a method similar to that used by Wu et al. for ZnO [7,8]. Chemical and physical properties, including the configuration of deposited nanocrystals, are measured using transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDX), selected area electron diffraction (SAED) and high angle annular dark field HAADF imaging. Optical
properties are measured using spectrofluorometry, photoluminescence, and a novel ‘nanocrystal test bed’ semiconductor device which is being developed at Leeds by Malvi et al.

TEM images, EDX spectra and SAED confirm the successful synthesis of high quality NiO nanocrystals. The highly crystalline NiO nanocrystals produced are spherical with excellent dispersivity and an average size of 2.7±0.7nm. This tight size distribution is very important for practical applications as the properties of the nanocrystals vary with size particularly the optical and electrical properties which are both of paramount importance when it comes to solar cell applications. Numerous samples have been produced and variations to the synthesis have been successfully attempted to control the size of the particles. Particles have even been produced without the application of heat which is unique in terms of producing nanocrystals of this quality. NiO nanorods have also been produced which is an exciting prospect as these structures are also showing great promise in photovoltaic applications.

2. Methodology

The synthesis of NiO nanocrystals via simple reflux methods similar to Wu et al. [7,8]. Hydrated metal acetate was added to methanol in the ratio of 0.03:4.00 and refluxed for 6 hours under ambient conditions, at a temperature of 67°C (the boiling point of the solution) and vigorous stirring. The above ratio was the starting point from which the concentration of the metal ions was varied by adding more metal acetate at various times during the reflux. In addition to this the reflux times were also varied. Cooling to room temperature (23°C) the organic capping agent 3-aminopropyl trimethoxysilane (AM), which has the chemical formula H$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$ is added to different samples at different times. A similar reflux hydrolysis method has been reported to produce CuO nanocrystals [9].

3. Results

TEM, EDX and SAED analysis confirm the synthesis of NiO nanocrystals. It can be seen from figure 1 that the NiO nanocrystals produced have a tight size distribution with an average particle diameter of 2.5±0.5nm. Figure 2 is the SAED pattern taken from the same area as the TEM image in figure 1 and confirms that the lattice spacings are consistent with that found in NiO. The NiO nanocrystals produced here were done so after a 6 hour reflux with the above mentioned Ni : methanol ratio.

Figure 1. TEM image of NiO nanocrystals capped with AM. The nanocrystals can clearly be seen and their crystalline structure is also evident.

Figure 2. SAED pattern of the NiO nanocrystals produced. The atomic spacing from the electron diffraction confirms that the structure is NiO.
NiO nanocrystals produced here were done so after a 6 hour reflux with the above mentioned Ni : methanol ratio. In figure 3 the nanocrystals produced are also from a 6 hour reflux but are uncapped. They are the same size as the capped sample and the electron diffraction pattern clearly shows that they are crystalline.

Figure 3. TEM image of NiO nanocrystals produced after a 6 hour reflux. This sample is uncapped

Figure 4. SAED pattern of the NiO nanocrystals produced. The atomic spacing from the electron diffraction confirms that the structure is NiO.

Figure 5 shows a TEM image of an eight hour reflux. The NiO particles produced here are significantly larger and elongated rod like particles. There are not any small circular nanocrystals present in this sample.

Figure 6 shows nanocrystals produced from just mixing hydrated nickel acetate with methanol and ultrasonicing the solution. This is a remarkable result as in all methods seen in the literature for producing NiO nanocrystals require significantly large temperatures. Note the nanocrystals produced are the same size as those produced in the 6 hour reflux with the same concentration. The same results are achieved for 2 hour and 4 hour reflexes respectively.
In figure 7 the nanocrystals produced are from a 6 hour reflux which had the same initial concentration as mentioned above and in the previous refluxes. However after two and four hours the same mass of nickel acetate was added. Therefore the final concentration of nickel ions in the methanol was tripled. As can be seen the nanocrystals produced are the same size as the previous refluxes.

However as seen in figure 8 there are some larger particles produced which are micron sized. These micron sized particles show signs of agglomeration. It was possible to separate these large particles from the small nanocrystals via sedimentation as the micron sized particles tend to sink to the bottom of the container. When the sample was sonicated before being deposited on the TEM grid the nanocrystals could be seen around close to the larger particles but not dispersed all along the grid like when these larger particles were not present.

4. Summary

It can be seen from the above images that the NiO particles produced have a consistent size of 2.7±0.7nm and that some of the conventional approaches to increasing the size have little effect. However it is also possible to produce very large particles with increased reflux time and concentration which can easily be separated from the smaller particles via filtration and sedimentation. Remarkably it is possible to produce nanocrystals without heating which seems to be unprecedented when producing nanocrystals.

References

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