

Time effect on the conventional colloidal synthesis of copper selenide nanocrystals

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Abstract. Herein we report on the synthesis of copper selenide nanoparticles using a conventional colloidal method. Furthermore the effect of time on the properties of copper selenide was investigated. The absorption spectra of particles synthesized at varied times were all blue-shifted from the bulk copper selenide, indicative of quantum confinement. The size of the nanoparticles showed a slight increase with increasing synthesis time. The shape of the nanoparticles remained unchanged and was predominated with hexagonal shaped nanoparticles.

1. Introduction

Photovoltaic devices have gained momentum on improving green solar energy consumption. Devices are made based on the optical and electrical properties of chosen materials. Metal chalcogenide semiconductors have been intensively targeted in photovoltaic applications because of their unique properties on the nanoscopic scale [1-3]. Copper selenide nanoparticles have been investigated and proven to exhibit higher properties required for efficient solar cells. Copper selenide can be synthesized in various stoichiometries including CuSe, Cu_{2-x}Se and Cu₃Se₂ [4-8]. Several parameters are controlled to synthesize copper selenide nanoparticles with preferred designed shape and size [9-14]. The investigation of time of synthesis is the main feature for particle growth and size distribution in conventional colloidal method in order to get nanocrystals with desired properties. In this work synthesis time is investigated to prepare copper selenide nanoparticles using the conventional colloidal method and optical and structural properties of the synthesized copper selenide nanoparticles are studied.

2. Experimental

2.1. Chemicals

Copper (I) chloride, selenium, tri-n-octyl phosphine (TOP), hexadecylamine (HDA), triethanol amine (TEA), hexane, methanol, ethanol and acetone were all purchased from Sigma-Aldrich and used as they were obtained.

2.2. Method

Conventional colloidal method (CCM) was used for the synthesis of copper selenide nanoparticles. 6 g of hexyldecylamine (HDA) was heated to 100 °C. Then 1 ml of 1M solution of CuCl in TOP (TOPCuCl) was added to the solution. The resultant solution was then heated to 220 °C where 1ml of 1M solution of Se in TOP (TOPSe) was then added. The content was heated for a further 5, 10, 20, 30, 45 and 60 min. The temperature was then decreased to 60 °C. Methanol was then added to the solution to flocculate the nanoparticles and copper selenide nanoparticles were collected after centrifugation.

2.3. Characterization

The optical measurements of copper selenide nanoparticles were determined using an Analytical Jena Specord 50 UV-Vis Spectrophotometer. The samples were dispersed in toluene and placed in a quartz cuvette. A StellarNet miniature spectrofluorometer, equipped with 395 nm LED as an excitation source was used to analyze the photoluminescence of the nanocrystals after dissolving them in toluene in placing the solution in a quartz cuvette. The X-ray diffraction patterns on crushed samples were conducted using Bruker D2 Phaser X-ray diffractometer. The images of nanoparticles dispersed in toluene were determined by FEI G² Tecnai spirit transmission electron microscope.

3. Results and discussion

3.1. Optical properties of the CCM synthesized copper selenide nanocrystals

The absorption spectra of the as synthesized nanoparticles are shown in Fig.1. The spectra are blue shift in band edges compared to bulk copper selenide which possesses band-edges between 539 nm and 1240 nm depending on their stoichiometries. The spectra revealed that the band edges tend to increase (red shifted) as the time was increased. Typically, particles synthesized for 30 min gave a band edge around 400 nm and they were the most stable nanoparticles and thus most of the characterizations were done on this sample. The increase in the particle sizes with time is attributed to the growth of the nuclei and ultimately to the Ostwald ripening of the nuclei.

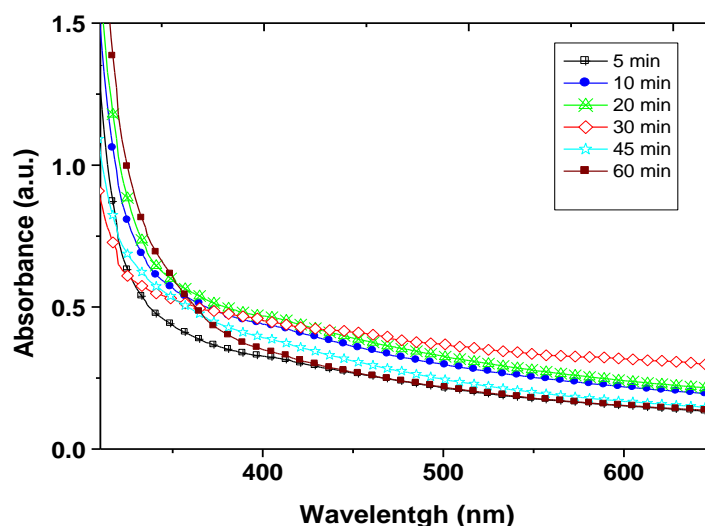


Fig. 1: UV- Vis spectra of copper selenide nanoparticles synthesized at different times.

Shown in Fig. 2 are the photoluminescence (PL) spectra of the as synthesized particles. The sharp peak observed on PL spectrum of particles synthesized for 5 minutes suggests the uniformity of size of particles whilst longer timed synthesis (60 min) yielded a broad range of particles. The emission maxima for all the spectra are located around 450 nm and are red-shifted from the absorption band edges.

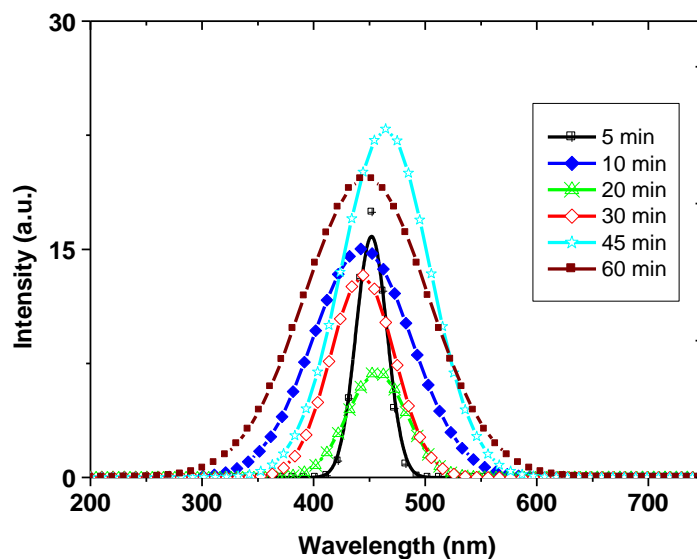


Fig. 2: Photoluminescence spectra of copper selenide synthesized at different times.

3.2. Structural properties of the CCM synthesized copper selenide nanocrystals

Structural properties were investigated for the particles synthesized in 30 minutes as they were the most stable over time. The particles synthesized in shorter synthetic time sintered and gave absorption spectra similar to the 30 minutes spectrum, whilst the particles synthesized at longer times showed a profile similar to a bulk copper selenide. The TEM image of copper selenide nanoparticles synthesized at 30 min (Fig. 3) revealed that the particles are hexagonal in shape, however, the size distribution was not homogeneous and the average particle diameter was about 4.5 nm confirming that the nanocrystals were successfully synthesized. The nanoparticles properties were also confirmed on XRD (Fig. 4) and were mostly found in binary crystalline phase where both hexagonal CuSe (PDF no 000491457) and cubic Cu₂Se (PDF no 010710044) were present.

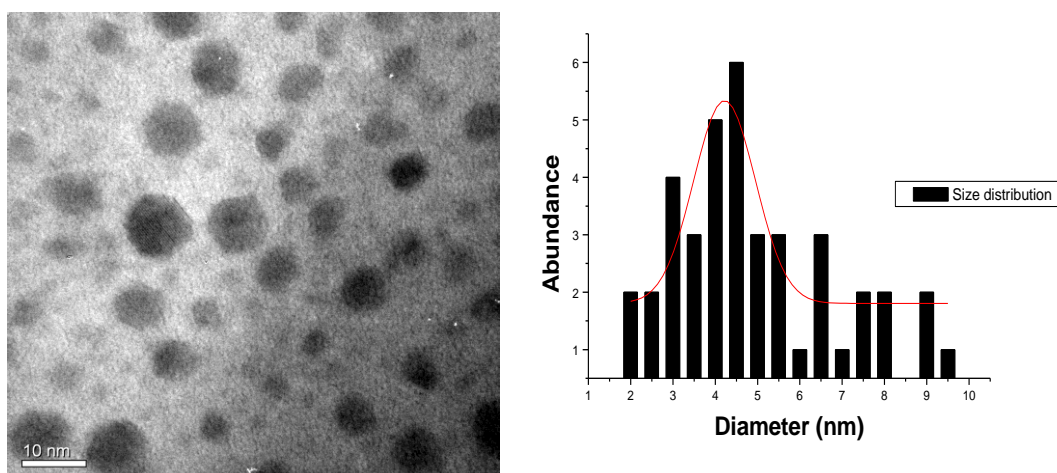


Fig. 3: TEM images of copper selenide synthesized for 30 min and particle size distribution.

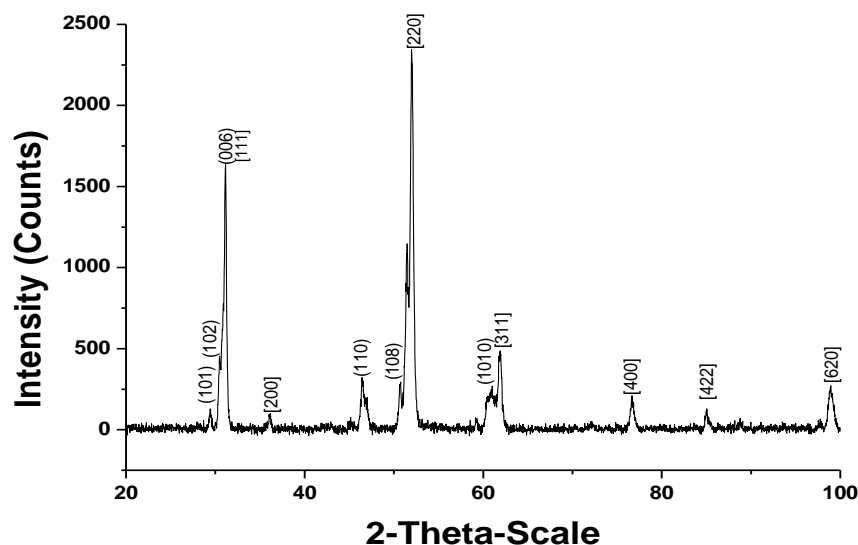


Fig. 4: XRD patterns of [cubic] and (hexagonal) copper selenide nanoparticles synthesized for 30 min.

4. Conclusions

Copper selenide nanoparticles were synthesized at different times with the 30 minutes yielding the most stable particles. The nanoparticles had average diameter of 4.5 nm and were found in a cubic (Cu_{2-x}Se) and hexagonal (CuSe) crystalline phases. The small sizes and crystallinity of the particles make them good candidate as solar material.

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