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Research Article

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Effect of Cu doping on the optical property of green synthesised L-cystein-capped CdSe quantum dots

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Abstract: In the present study, the synthesis of water-soluble copper-doped CdSe nanoparticles (NPs) via a low cost, facile, and environmentally benign method is reported. Simple reagents such as selenium powder, cadmium chloride, and copper sulphate were used as selenium, cadmium, and copper precursor, respectively, while L-cysteine was used as a capping ligand without the use of an additional stabiliser. The as-synthesised copper-doped CdSe NPs were characterised using ultraviolet (UV-Vis) absorption and photoluminescence (PL) spectroscopy, Fourier-transform infrared spectroscopy, and transmission electron microscopy. By varying the dopant concentration, the temporal evolution of the optical properties and the shape of the nanocrystals were investigated. The observation and the results showed that the colour of the solution changed rapidly from orange to black, and the PL shifted to a longer wavelength at the high dopant concentration. The micrographic images revealed that the as-synthesised materials are small and could be used for bio labelling.

Keywords: green synthesis, quantum dots, copper, doping, photoluminescence

1 Introduction

In the past two decades, semiconductor nanoparticles (NPs), also known as quantum dots (QDs), have been of considerable interest due to their fundamental as well as their theoretical properties, particularly the quantum confinement effect in which the electrical and optical properties can be changed simply by variation in its particle size [1–3]. The progress made in understanding the properties of semiconductor NPs has stimulated similar efforts in doping semiconductor nanocrystals to control the final properties of these materials [4–6]. Doping, the intentional introduction of impurities, is a common approach for tuning the electronic, optical, mechanical, and magnetic properties of materials. It plays a central role in many areas of modern semiconductor science and technology. This makes them useful for a variety of applications such as bio-theragnostic agent, sensors, photovoltaic cells, solar cells, etc. [7,8]. In previous studies, doped nanocrystals have been synthesised by the aqueous as well as the organometallic methods. Kłopotowski et al. [9] recently reported the synthesis of doped CdSe with Cu through an organometallic method. However, the limitation of this method is the use of expensive and hazardous chemicals. For green synthetic chemistry approach, organic solvents are discouraged, and water is considered as an ideal solvent. Compared with the organometallic route, the cheaper, more straightforward, and less toxic aqueous synthetic approach is an alternative strategy to directly prepare water-soluble nanocrystals, thus making the synthetic approach greener. In this regard, Wageh et al. [10] synthesised Cu-doped CdSe QDs in an aqueous method using water-soluble precursors. However, they have employed 3-mercaptopropionic acid, a highly reactive chemical that can pose potential environmental and biological risks as the capping agent. Therefore, complete synthesis of Cu-doped CdSe QDs in water with mild capping reagents is necessary. In this study,

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we report a facile green synthesis of water-soluble, Cu-doped CdSe NPs using L-cysteine as the capping agent. L-Cysteine is an essential amino acid naturally found in the human body and available in the pharmaceutical market as a dietary supplement. Hence, it is a biocompatible and environmentally suitable material for green synthesis [11,12]. In addition, we have investigated the effect of different copper ion concentrations on the optical and structural properties of the as-synthesised CdSe NPs. The as-synthesised L-cysteine-capped Cu-doped CdSe NPs could be a potential candidate for diverse QD applications.

2 Materials and methods

2.1 Materials

Sodium borohydride ($NaBH_4$), deionised water (HPLC grade), cadmium chloride ($CdCl_2$), selenium powder, copper sulphate ($CuSO_4$), and L-cysteine ester hydrochloride were purchased from Sigma Aldrich, South Africa. All the chemicals were of analytical grade and used as purchased without further purification.

2.2 Stock solution preparation

Initially, the selenium precursor stock solution was prepared by adding 0.16 mmol of selenium powder to 20 mL of deionised water in a three-necked flask. 0.81 mmol of sodium borohydride was carefully added to this mixture, and the flask was immediately purged with nitrogen gas. The mixture was then stirred for 2 h at room temperature. The entire selenium dissolves in water, giving rise to a colourless selenium solution. On the other hand, the cadmium precursor solution was prepared by adding 0.32 mmol of $CdCl_2$ powder in 20 mL of deionised water. The capping solution was prepared by dissolving 3.2 mmol of L-cysteine ethyl ester hydrochloric acid powder in 20 mL of deionised water.

2.3 Synthesis of CdSe QDs and Cu-doped CdSe QDs

The synthetic approach is straightforward and does not require any special setup. In a typical room temperature reaction, 1.0 mL of cadmium stock solution was added to the ligand solution under constant magnetic stirring. The pH value of the solution was adjusted to the desired pH value by dropwise addition of ammonia solution. This was followed by the slow addition of 1.0 mL of Se stock solution under constant stirring. The reaction was refluxed and allowed to continue for 5 h. The same procedure was repeated for different pH values of 2.45, 4, 7, 9, and 11. For Cu-doped CdSe QDs, a certain amount of copper stock solution was mixed with cadmium solution followed by a similar process for the preparation of CdSe QDs. The as-synthesised QDs were isolated by precipitation with isopropanol followed by centrifugation. The resultant particles were dissolved in water to give a solution of nanocrystallite for further characterisations.

2.4 Characterisation

A Perkin Elmer Lamda UV-vis spectrophotometer was used to carry out absorption spectra in the 200–900 nm wavelength range. Photoluminescence (PL) spectra were recorded on a Perkin Elmer LS 55 luminescence spectrometer. Photoluminescence quantum yield (PLQY) of the samples was calculated using rhodamine 6 G as refernce. A JEOL 2100 TEM operating at 200 kV was used for transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Fourier-transform infrared spectroscopy (FTIR) analysis was performed using Perkin Elmer spectrum Two.

3 Results and discussion

3.1 Effect of pH on the optical properties of CdSe QDs

CdSe QDs were synthesised by simple wet chemical greener method in an aqueous medium using water-soluble precursors at different pH values from acid to alkaline range. Figure 1a and b represents the absorption and PL spectra of CdSe NPs synthesised at different pH values at room temperature after 24 h reaction time. The growth of the particles was observed by the change in the colour of the solution from colourless to slightly yellow. At the pH value between 2.25 and 9, the absorption spectra appear very broad, covering the whole ultraviolet-visible region indicating the particles obtained with low quality. At pH value

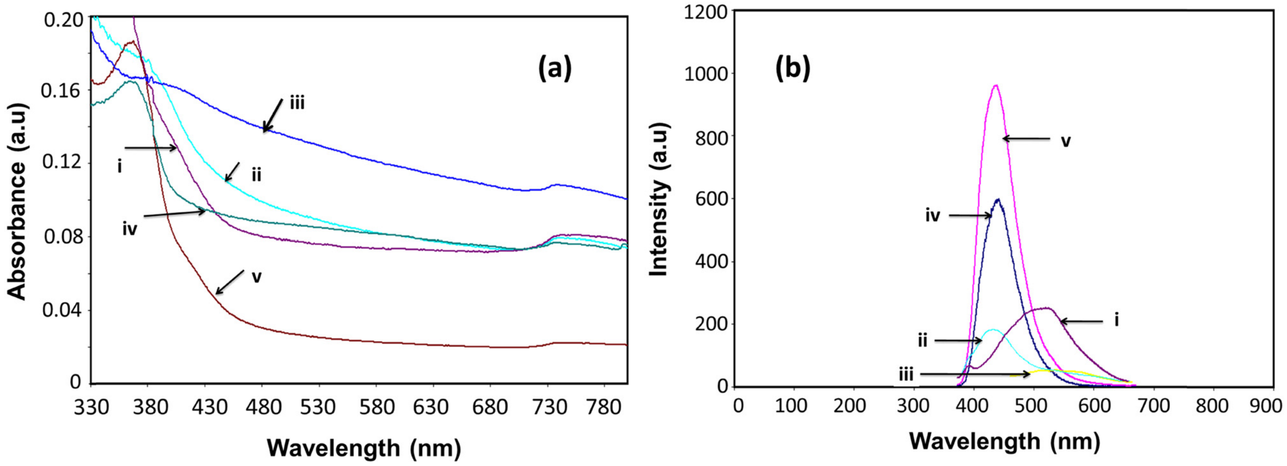

Figure 1: (a) Absorption spectra and (b) PL spectra of CdSe NPs at different pH values (i: pH = 2.25, ii: pH = 4, iii: pH = 7, iv: pH = 9, and v: pH = 11).

of 11, the absorption spectra appeared clearly, showing an excitonic peak at 368 nm. The same trend was also observed in the PL spectra, where the QDs synthesised at pH value of 11 showed the highest intensity and narrow emission, with the peak centred at 435 nm. The syntheses at lower pH value produced broad and/or low-intensity emission peaks. This could be due to the nature of the capping agent L-cysteine at different pH values. At low pH value, the concentration of free thiols in L-cysteine would be inadequate, leading to the improper passivation of the QDs. This could lead to surface defects and aggregation, thus reducing the material quality and PL [13]. However, at high alkaline pH value of 11, the thiol and carboxylic acid group of the L-cysteine ligand are easily deprotonated. This will increase the concentration of the free thiols in the solution as well as the complexation of the surface of the NP by the thiol group. Thus, reducing the surface traps and hence increasing the luminescence intensity. In addition, the repulsion of the negative charge of the carboxylate group on the surface of the NPs by individual NP also prevents particle aggregation and thus, improves the stability of the as-synthesised material [14]. These two factors contribute to the increase in the PL intensity as the pH value increases. Hence, pH value of 11 was chosen for further reaction.

3.2 Optical and structural properties of water-soluble Cu-doped CdSe NPs

Figure 2a and b shows the absorption and emission spectra of 0.5% Cu ions-doped CdSe NPs at different

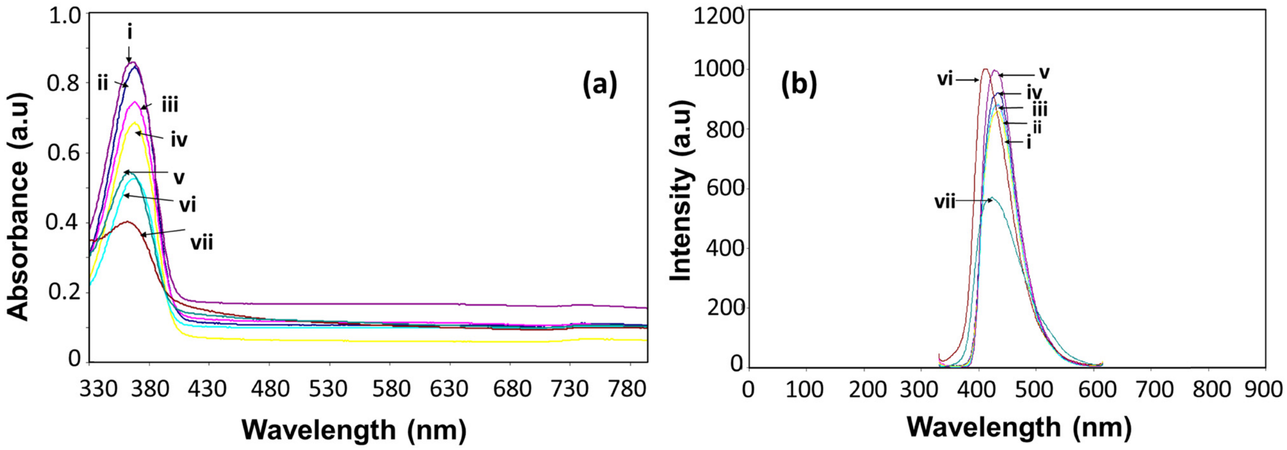

Figure 2: (a) Absorption spectra and (b) PL spectra of 0.5% Cu ions-doped CdSe NPs at different refluxing time (i: 0 min, ii: 2 min, iii: 6 min, iv: 10 min, v: 1 h, vi: 3 h, and vii: 5 h).

refluxing times. All the samples show well defined excitonic peak and absorption band edge. The excitonic peak (368 nm) and absorption band edges (400 nm) appear at the same position without any significant shift throughout the reaction time. This signifies that the growth process was not affected by copper doping. The PL emission intensity increased as the reaction time increases and reached its maximum at 3 h, then decays at 5 h. The maximum emission was observed at 436 nm till 3 h, similar to undoped CdSe QDs and slightly blue-shifted at higher reaction times. The PLQY of the CdSe QDs at optimised conditions was calculated to be 20.7%.

3.3 Effect of dopant concentrations

Figure 3a and b shows the absorption and emission spectra of Cu-doped CdSe NPs prepared using different Cu ion concentrations. The different concentrations of the dopant used are shown in Table 1. The colour of the solution changed as the concentration of Cu ion increased from 0.0032% (orange) to 1% (black). The absorption spectra show distinct excitation at 0.0032%, 0.016%, 0.032%, and 0.5% Cu ions dopant level and a broad band-edge at 1%. The absence of excitonic shoulder and the presence of a broad band-edge at 1% Cu ions could be attributed to the defects caused by introducing a large number of Cu ions [15].

The emission spectra show that the PL intensity increases as the concentration of Cu ion increases and reaches a maximum at 0.032% dopant level without any further change at higher concentrations. The PLQY of the QDs at this Cu dopant concentration was calculated to 25.9%. It was noted that the PL peak position remains nearly the same at lower dopant concentrations, while a significant redshift (~52 nm) was observed at higher dopant concentration (1% Cu ions). This increase in the PL intensity as the concentration of the dopant increases can be attributed to the defects caused by high Cu concentration. The Cu level dominates the recombination centre at higher dopant concentration, thus causing a significant redshift in the PL peak position [15].

Table 1: The PL peak and colour of as-synthesised Cu-doped CdSe NPs

% Cu^{2+}	PL peak Cu: CdSe QDs (mm)	Colour of the solution
0.0032	436	Orange
0.016	436	Orange–brown
0.032	436	Brown
0.5	436	Black
1.0	488	Black

3.4 Morphological analysis

The TEM images of the undoped and 0.5% Cu-doped CdSe QDs are shown in Figure 4a and b. In accordance with the optical analysis, the TEM image confirmed the well-dispersed nature of the undoped CdSe QDs produced under refluxing. The particles are in the range from 1.25 to 4.40 nm, with a mean particle diameter of 2.44 nm. On the other hand, the Cu-doped CdSe QDs are in the range from 2.0 to 6.0 nm with a mean particle

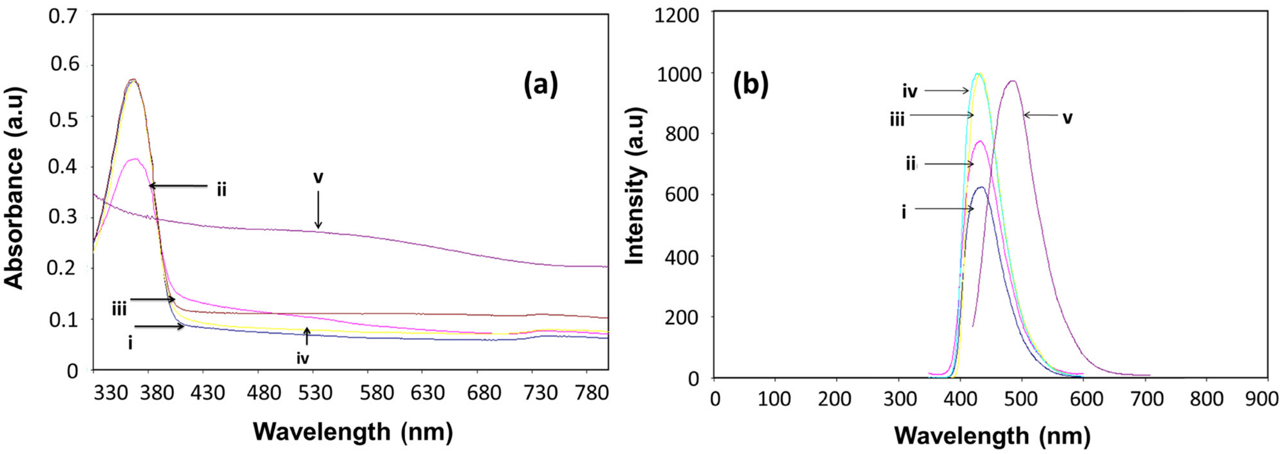

Figure 3: (a) Absorption spectra and (b) PL spectra of Cu-doped CdSe NPs at different % of Cu ions (i: 0.0032%, ii: 0.016%, iii: 0.032%, iv: 0.5%, and v: 1%).

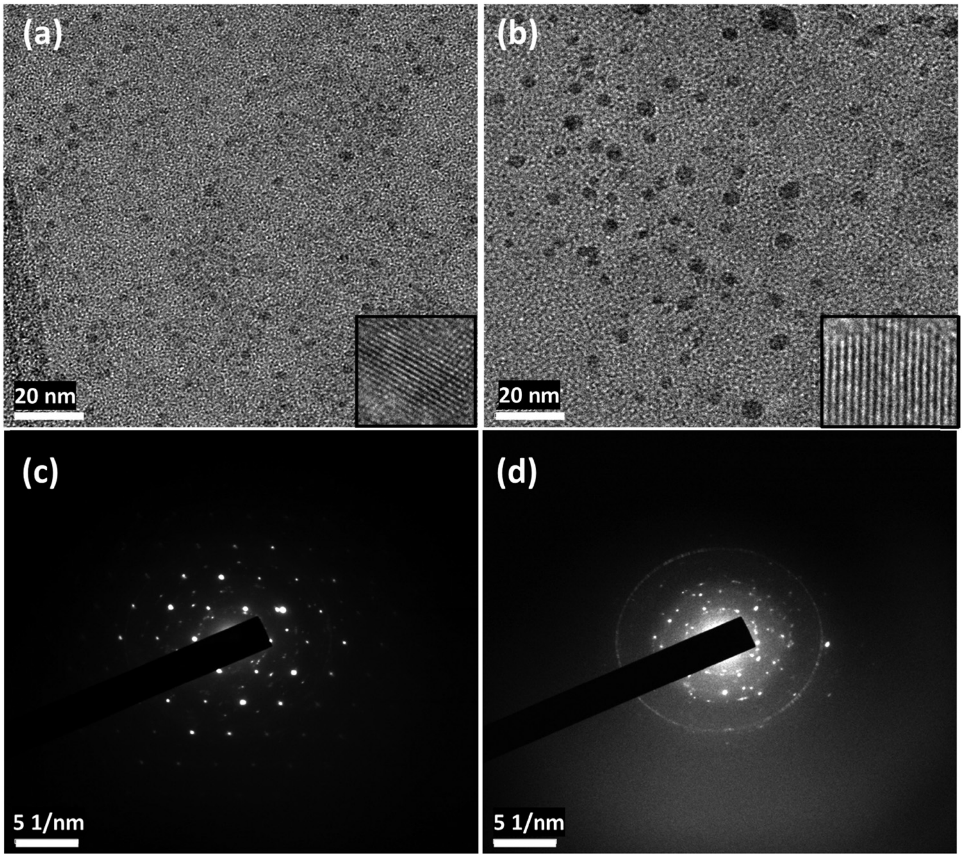

Figure 4: TEM images of (a) CdSe QDs and (b) 0.5% Cu-doped CdSe QDs. SAED patterns of (c) CdSe QDs and (d) 0.5% Cu-doped CdSe QDs.

diameter of 3.57 nm. The increase in size could be attributed to Cu doping. The HRTEM images (insets of Figure 4a and b) showed that nearly spherical particles with the clear lattice fringes indicate the crystallinity of QDs. The SAED pattern (Figure 4c and d) of both undoped and Cu-doped CdSe QDs shows sharp and clear singular reciprocal points indicating that the obtained NPs are highly crystalline.

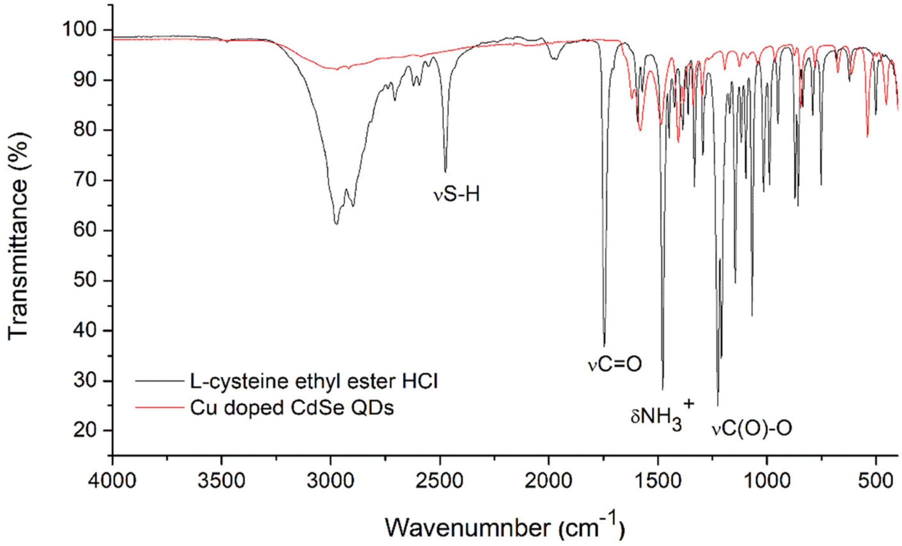

Figure 5: FTIR spectra of L-cysteine ethyl ester and L-cysteine-capped QDs.

3.5 FTIR analysis

The capping nature of QDs by L-cysteine was investigated using FTIR spectra. Figure 5 shows the FTIR spectra of L-cysteine ethyl ester hydrochloride which was used in the synthesis and L-cysteine-capped Cu-doped CdSe QDs. L-Cysteine ester reveals the characteristic FTIR peaks such as υS–H at 2,474 cm^{-1}, υC=O at 1,745 cm^{-1}, δNH_3^+ at 1,478 cm^{-1}, and υC(O)O at 1,225 cm^{-1}. The FTIR spectrum of QDs shows significant differences in comparison with L-cysteine ester spectrum. The ester group peaks (υC=O and υC(O)O) disappeared indicating that the ester group was hydrolysed to the parent L-cysteine at the reaction conditions. In addition, importantly υS–H peak of L-cysteine ester also disappeared indicating that thiol was deprotonated, and the cysteine capped to QD surface via its sulphur as it has strong affinity towards metals like Cd. The FTIR results confirmed the capping of L-cysteine on the QDs.

4 Conclusion

We have reported the synthesis of Cu-doped NPs via a facile, "green", and environmentally benign method using L-cysteine as a capping agent. By varying the pH and dopant concentration, the temporal evolution of the optical properties of the undoped and Cu-doped CdSe QDs were investigated. In comparison with other pH ranges, the CdSe QDs synthesised at pH value of 11 show the highest PL intensity. The PL emission intensity of Cu-doped CdSe NPs increased as the Cu doping increased and reached their maximum at 0.5%, and the emission peak position become redshifted with further high Cu doping. The TEM images confirmed that the as-synthesised materials are small and retain their shape even after doping. The resultant NPs are non-air sensitive, highly water-soluble, and of good quality, which would be of immense utility for potential biological application.

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Conflict of interest: Authors state no conflict of interest.

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