Solvothermal synthesis of luminescent bis-(8 hydroxy quinoline) cadmium complex nanostructures

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Abstract. A facile solution–based route for the synthesis of Bis- (8- hydroxyquinoline) Cadmium (CdQ₂) complex nanorods, nanoflowers (bundles of nanorods) and nanosheets in an oleic acid- sodium oleate- ethanol- H₂O system at 50°C -100°C was reported. Scanning Electron Microscope (SEM) images indicated that longer time and higher temperature would result in nanoflowers, while lower temperature and shorter reaction time would be suitable for the formation of nanorods. However, a novel change in these structures was observed when the concentration of the surfactant (oleic acid) was reduced and we obtained 2-D nanosheets. Fourier- transform infrared (FTIR) spectroscopy was utilized to confirm that the samples were made up of CdQ₂. UV/ VIS spectroscopy was used to determine the different electronic transitions in CdQ₂ molecule. All the samples possessed excellent photoluminescence (PL) properties. Photoluminescence (PL) spectra showed a prominent peak around 500 nm which indicated a strong PL emission in the green region. This methodology could be extended for the controlled, large- scale preparation of other functional complexes, and the obtained nanostructures could be introduced as the basic building blocks for novel optoelectronic devices.

1. Introduction

It is well known that, at the nanoscale, materials exhibit fascinating optical, electronic and magnetic properties that differ drastically from their bulk counterparts [1-6]. Recently, one dimensional (1-D) conducting polymer and small molecule organic semiconductor nanomaterials have attracted much attention because of their unique physical properties and potential applications in fabrication of nano devices. However, the preparation techniques of organic nanomaterials are not diversiform compared with those of inorganic nanomaterials. The novel properties of nanostructured materials enable them to find potential applications in many new and promising fields such as nanofabrication, nanodevices, nanobiology, and nanotechnology [7-12].

Currently, 8- hydroxyquinoline metal chelates are intensively investigated due to their excellent electro- and light- emitting properties, such as field emission, photoluminescence (PL) and electroluminescence (EL) [13-16]. Here, we report the facile solvothermal synthesis of Bis- (8-hydroxyquinoline) Cadmium (CdQ₂) Complex nanorods, nanoflowers and nanosheets in an oleic acid (OA) - Sodium Oleate- ethanol-H₂O system at 50°C-100°C. SEM results show that the reaction time, reaction temperature, and the concentration of the surfactant play a crucial role in the morphology of the samples. Particularly, the reduction in the surfactant concentration results in the formation of (2-D) nanosheets. As far as we know, this significant change in the morphology of CdQ₂ samples has not yet been reported. The photoluminesence (PL) spectra reveal that the samples have excellent...
photoluminescence properties. These findings are very useful to fabricate optoelectronic devices based on CdQ₂ nanostructures [17, 18].

2. Experimental Section

2.1. Materials

All the reagents in this work, including Cadmium chloride(CdCl₂·2½H₂O), 8-hydroxyquinoline (C₉H₇NO), ethanol (C₂H₅OH), Sodium hydroxide (NaOH), and Oleic-acid (CH₃(C₁₁H₂₃COOH), were of A.R grade and used without further purification. De-ionized water was used throughout the process.

2.2. Synthesis of the Samples

In general synthesis, the reaction is mainly on the basis of the precipitation of Cd²⁺ and 8-hydroxyquinoline with a molar ratio 1:2 in a mixed ethanol–water (1:1) solvent at designed temperatures. In detail, NaOH, and oleic acid (OA) were orderly added into the mixed solvent with continuous stirring to produce a homogeneous normal emulsion. Then, the aqueous solution of Cd Cl₂·2½H₂O was poured into the system. Subsequently, the ethanol solution of 8-hydroxyquinoline was rapidly introduced into the solution to start the main reaction and the total volume of the mixture was kept at a certain value 30 mL. After stirring for about 15 min, the mixture was transferred into a 50 mL vessel, which was treated at a designated temperature for appropriate reaction time. Then, the system was cooled at room temperature naturally. The bottom precipitates were thoroughly washed with ethanol twice and then redispersed in ethanol for future use and characterization. The detailed experimental conditions for each sample are listed in table 1 and table 2, respectively.

2.3. Characterization

The sizes and morphologies of the samples were characterized by a Jeol JSM-6510LV Scanning Electron Microscope (SEM). Samples were prepared by placing a drop of a dilute ethanol dispersion of the product on the surface of Aluminium stub. FTIR spectra were conducted with a Perkin Elmer Spectrum 100 series FTIR Spectrometer. UV/ VIS-IR spectra were carried out by using Perkin-Elmer, LAMBDA 950 Spectrometer. PL spectra were taken by using Mini PL/ Raman system, photon system USA with Ne–Cu laser having wavelength of 248 nm.

3. Results and Discussions

In the synthesis process, shown in Figure 1, as the consequence of the addition of NaOH, sodium oleate (NaOA) is formed and then coordinate with Cd²⁺ to produce cadmium oleate, which releases Cd²⁺ slowly on the basis of the equilibrium equation to control the nucleation and growth process accurately. The other function of sodium oleate was to produce a buffer media jointly with the superfluous oleic acid which was lucrative for the precipitation between Cd²⁺ and 8-hydroxyquinoline [19]. On the other hand, the interactions such as van der Waals and the hydrophobic force between the alkyl chain and quinoline ring would have made it easier for 8-hydroxyquinoline molecules to collide with Cd²⁺ capped on the surface of sodium oleate to start the main reaction. At last, due to the low solubility of the complex, the final products deposited at the bottom of the container, giving convenience for collection and purification. In order to control the morphology and size of the product and understand the crystal growth behaviours of the purposeful molecule, we investigated the effects of the following factors, reaction time reaction temperatures, reactant concentration, and surfactant concentration. The table 1 and table 2 show the detailed experimental conditions for the synthesis of nanorods, nanoflowers and nanosheets. These morphologies are confirmed by the SEM images, shown in Figure 2 and Figure 3. It can be seen from Figure 2 and table 1 that longer time and higher temperatures (50°C-100°C) would result in the formation of nanoflowers, while lower temperatures (50°C-55°C) would be appropriate for the formation of nanorods.
A novel change in the morphology of the CdQ2 samples has been observed when the concentration of the surfactant (OA) is changed. For instance, when the concentration of the surfactant (OA) was reduced from 3.7 ml to 3.5 ml, the morphology of the samples was remarkably changed from nanorods and nanoflowers to nanosheets. This significant change in the morphology of our samples has been confirmed by the SEM images, shown in Figure 3. Figure 3 and Table 2 indicate that this morphology remains consistent as we increase both the reaction time and temperature (65°C to 85°C). However, at lower temperature and at shorter reaction time (1.0- 2.0 hrs.), the nanosheets appear to be transparent whereas, at high temperatures (75°C to 85°C) and longer time (2.5- 3.0 hrs.), a little thicker nanosheets are obtained, as shown in Figure 3 (d- f).

Table 1. Conditions for different morphologies and sizes of CdQ2 nanorods and nanoflowers

| Samples   | Cd²⁺ (mmol.) | OA (ml.) | NaOH (g) | Temperature T(°C) | Time (hrs) | Morphology              | Length (µm) | Average diameter (nm) |
|-----------|--------------|----------|----------|-------------------|------------|------------------------|-------------|-----------------------|
| Sample-01 | 0.3          | 3.7      | 0.2      | 50                | 2.00       | Nanorods               | 10.92       | 279                   |
| Sample-02 | 0.3          | 3.7      | 0.2      | 55                | 2.5        | Nanorods               | 1.16        | 714                   |
| Sample-03 | 0.3          | 3.7      | 0.2      | 65                | 2.5        | Honeycomb/Nanoflowers  | 50          | 1000                  |
| Sample-04 | 0.3          | 3.7      | 0.2      | 75                | 2.5        | Nanoflowers            | 1.2         | 190                   |
| Sample-05 | 0.3          | 3.7      | 0.2      | 100               | 2.00       | Nanoflowers            | 55          | 882                   |
| Sample-06 | 0.3          | 3.7      | 0.2      | 100               | 2.5        | Nanoflowers            | 3.42        | 560                   |
Figure 2. SEM images of (a) sample 1, (b and c) sample 2, (d) sample 5 and (e) sample 6.

Table 2. Conditions for morphology and different sizes of CdQ$_2$ nanosheets

| Samples      | Cd$^{2+}$ (mmol.) | OA (ml.) | NaOH (g) | Temperature (°C) | Time (hrs.) | Morphology | Length (µm) | Average Width (nm) |
|--------------|-------------------|----------|----------|------------------|-------------|------------|-------------|---------------------|
| Sample-07    | 0.3               | 3.5      | 0.2      | 65               | 1.00        | Nanosheets | 926         |                     |
| Sample-08    | 0.3               | 3.5      | 0.2      | 65               | 1.5         | Nanosheets | 7.24        | 788                 |
| Sample-09    | 0.3               | 3.5      | 0.2      | 65               | 2.00        | Nanosheets | 2.08        | 344                 |
| Sample-10    | 0.3               | 3.5      | 0.2      | 65               | 2.5         | Nanosheets | 1.04        | 1000                |
| Sample-11    | 0.3               | 3.5      | 0.2      | 65               | 3.00        | Nanosheets | 4.72        | 313                 |
| Sample-12    | 0.3               | 3.5      | 0.2      | 75               | 2.5         | Nanosheets | 3.2         | 750                 |
| Sample-13    | 0.3               | 3.5      | 0.2      | 85               | 3.00        | Nanosheets | 2.48        | 800                 |
The component of the nanostructures has been identified with FTIR spectra. As indicated in Figure 4 and 5, (similar to congeneric compounds [20, 21]) the peak at 1571 cm$^{-1}$ is an indicative peak of C=C aromatic stretching. Aromatic amine resonance peak of C-N-C at 1280 cm$^{-1}$ and 1387 cm$^{-1}$, C=N stretching at 1425 cm$^{-1}$ and aromatic C-O stretching at 1105 cm$^{-1}$ are observed in the spectrum. The spectra show the characteristics peaks of aromatic ring stretching at 739 cm$^{-1}$, 740 cm$^{-1}$ 793 cm$^{-1}$ and 821 cm$^{-1}$ which can be attributed to the existence of quinoline ring. The cadmium ion is a soft acid which tends to form a stable complex with quinoline by metal nitrogen bond. The Cd-O bond stretching was observed at 505 cm$^{-1}$ while Cd-N bond stretching was observed at 490 cm$^{-1}$. 

Figure 3. SEM images of sample 07, sample 08, sample 09 (a, b, c), respectively, and sample 11, sample 12, sample 13 (d, e, f), respectively.
Figure 4. FTIR Spectra of CdQ$_2$ nanorods (sample 1).

Figure 5. FTIR Spectra of CdQ$_2$ nanosheets (sample 09).

UV/ VIS spectra of our samples are shown in Figure 6. The solvent effect has been observed for the ethanol and water is at 278.43 nm and 262.88 nm, respectively. This is in good agreement with literature value [22]. The aromatic and hetero aromatic (quinoline) shows broad absorption band which consists of multiple peaks in the near UV region between 230-270 nm. E-band is the properties of aromatic structures. The acid produces the positive charge on the nitrogen shifts which shows absorption in the range of 270-290 nm. The nitrogen group is weak absorber in near UV- region (n→π*). Benzene shows a band at 256 nm. The absorption at 279 nm to 356 nm shows the presence of phenyl group in the molecule. The absorption range 226.49 nm 270 nm and 315 nm are observed in quinoline in E$_1$, E$_2$ and B-bands, respectively [19]. Thus we conclude that the broad UV- band is in
the range of 250 nm -450 nm which clearly shows the absorption in the UV- region by CdQ₂. This may be the evidence of the fact that the emission from CdQ₂ may lie in the visible region.

![UV/VIS Spectra of CdQ₂ nanostructures.](image)

**Figure 6.** UV/VIS Spectra of CdQ₂ nanostructures.

![Photoluminescence (PL) spectra of CdQ₂ nanostructures](image)

**Figure 7.** Photoluminescence (PL) spectra of CdQ₂ nanostructures

Photoluminescence (PL) is a very important characteristic for the 8-hydroxyquinoline metal chelates. Figure 7 is the room-temperature PL spectra of CdQ₂ nanostructures (nanosheets) dispersed in ethanol and irradiated by 350 nm of UV light, from which we can see that all the emissions are ranging from 430 to 600 nm and the maximum peak is located around 500 nm. Almost similar spectra are obtained.
for all samples (not shown). The PL spectra reveal that the CdQ₂ samples give a strong emission in the green region with a peak wavelength lies around 500 nm. This property can introduce applications in novel optoelectronic devices, particularly in organic light-emitting diodes.

4. Conclusions
In summary, Bis- (8-hydroxyquinoline) Cadmium (CdQ₂) complex nanostructures have been synthesized via solvothermal chemical route. Reaction time, reaction temperatures, reactant and surfactant concentration are the main influential factors to the size and morphology the final product. Various morphologies such as, nanorods, nanoflowers, and nanosheets have been achieved by changing different parameters. FTIR spectra confirm the formation of CdQ₂ nanomaterial. UV/ VIS spectra indicate a broad absorption band in the range of 250 nm -450 nm. Samples show a strong photoluminescence (PL) in the visible region (430 nm – 600 nm) with a maximum peak located at around 500 nm, indicating a strong green emission.

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5. References
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