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A facile synthesis and characterisation of cadmium sulphide nanoparticles (Cds NPs)

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Abstract

Cadmium sulphide nanoparticles (Cds NPs) were successfully synthesized using cadmium acetate and thiourea as the precursor in presence of polyethylene glycol (PEG) at room temperature and maximum of 90°C respectively. The effect of sodium hydroxide was introduced into the CdS NPs preparation. The samples characterized using UV-Vis, FT-IR and SEM studies. The CdS NPs were functionalized using bio molecule of L-Cysteine it gives the reducible size of CdsNPs into self-assembled leaf-like structure.

Keywords: CdS nanoparticles, Cysteine functionalized CdS-NPs, metal sulphides, thiourea functionalized, semiconducting materials.

1 Introduction

In recent years, metallic and metal-oxide nanoparticles are capable of increasing the activities for many chemical reactions due to the high ratio of surface atoms with free valences to the cluster of total atoms. In addition to a high surface area-to-volume ratio for nanoparticle derivatized materials, the size controllability, chemical stability, and surface tenability provide an ideal platform for exploiting such nanostructures in sensing/biosensing and catalytic applications [1]. Inorganic semiconductor nanoparticles such as PbS, ZnS, CdSe and CdS due to their unique electrical, optical and electrochemical properties have been discussed in numerous electrochemical and electrochemiluminescence (ECL) fields [2-5]. CdS semiconductors with a band gap of 2.42 eV indicate superior optical, photophysical and photochemical properties [6]. PANi due to its excellent conductivity, high chemical and electrochemical stability is a good host matrix for the inorganic semiconductors [6]. Composites composed of conducting polymers and inorganic semiconductors indicate the reinforced mechanical, electrical and thermal properties [7] and are valuable for commercial applications like nanoelectronics [8], biosensors [9], photovoltaic and light-emitting diodes [10]. These materials are also predicted as effectual and promising electrode materials in various electrochemical devices [6].

Metal sulphides are of great importance in many scientific and technical fields owing to their outstanding chemical and physical properties. It is well known that the physical and chemical properties of metal sulfides are relative to their phase, morphology, size, crystal defects, surface properties, etc., which, in turn, depend on their preparation methods and preparation conditions. In addition to photo catalysis, cadmium sulfide nanoparticles can be used in various fields of industries such as medicine [11], hydrogen production [12], photovoltaic devices [13], optoelectronics [14], diodes [15], gas sensors [16], etc. For example, in medicine, CdS nanoparticles reveal antibacterial [17], antimicrobial [18], and antifungal [19] activities against micro-organisms. Recently, many methods have been developed to produce CdS nanoparticles such as microwave-assisted co-precipitation [20], the wet chemical method [21], microwave irradiation [22], reverse micellar methods [23], electrochemical deposition [24], solvothermal [25] and hydrothermal [26] processes, green synthesis [27] and biological methods [28]. However, most of the reported low temperature synthesis methods have somewhat difficulties in large-scale production of metal sulfide nanoparticles at low cost [29-33]: either the adopted precursors and equipment were expensive and not easily available; or the synthesis processes were very complex and the reactions were performed in the presence of solvents, in which a great deal of waste water would be produced and the products must be separated from the solvents and dried; or the reaction times were very long, etc.

Cysteine is a nonessential, water-soluble, sulfur-containing amino acid and is usually found in most proteins, although only in small quantities. Cysteine can be used as a strong binding agent through one of its functional groups, the thiol group, and successful examples include the capping agent of Ag^0 [34], Au^0 [35] and Cu^0 [36] and even alloy particles [37]. The sulfur in the SH is divalent and endows cysteine with an additional function, acting as an antioxidant [38]. In addition, the existence of the NH_2 group and COOH in the cysteine molecules will enable the cysteine-capped magnetic particles to have good biocompatibility and good solubility in aqueous solutions.

Herein, we report the unassuming synthesis of cadmium sulphide nanoparticles via the liquid–solid reactions of corresponding metal acetates and thiourea in aerobic con-

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ditions were prepared at room temperature and varying the temperature of 60 and 90°C. The prepared CdS NPs were characterization by UV-Vis absorption, FT-IR spectra and scanning electron microscope (SEM). The synthetic CdS NPs prepared from sodium hydroxide method were functionalized with biomolecule of L-cysteine and were studied through UV-vis and FT-IR and their morphology was analyzed by SEM with EDAX.

2. Materials and methods

2.1. Materials

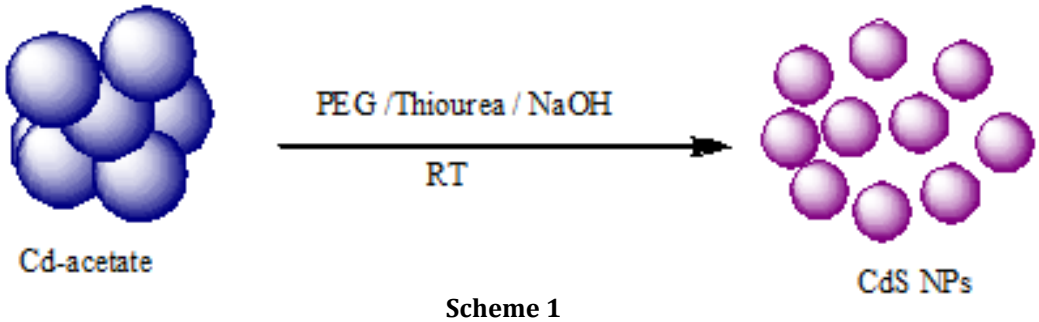
All reagents used were of AR grade. The following chemicals were used at various stages of this synthetic methods of cadmium sulphide (CdS) nanoparticles. Cadmium acetate dehydrate, thiourea, polyethylene glycol (6000), L-cysteine hydrochloride, ethanol, acetone and petroleum ether (MERCK), sodium hydroxide (RANKEM) were used as received. The water used throughout this work was pure, produced by double distillation.

2.2. Characterization

The CdS nanoparticles (CdS NPs) and cysteine modified CdS NPs were characterized by UV-Vis spectroscopy, scanning electron microscopy (SEM), FT-IR spectroscopy. The electronic spectra were recorded on Jasco-550 spectrophotometer in the wavelength range of 190-900 nm. SEM images were captured using a Hitachi S-3400 and JEOL/EO, JSM-6390 scanning electron microscope operated at 20 KV. FT-IR spectra were measured with a SCHIMADZU FT-IR 8400S (4000 – 400 cm^{-1}) spectrophotometer.

2.3.1. Preparation of CdS NPs using PEG and NaOH

The modified procedure [39] described in Scheme 1, was used to synthesize of CdS NPs. Cadmium acetate dihydrate, 0.2655 g (1 mmol) dissolved in 60 ml water and 0.2 g of Polyethylene glycol (PEG) dissolved in 20 ml water were mixed and allowed to constant stirring for 1 h. Afterwards, 0.2284 g (3 mmol) of thiourea which was dissolved in 20 ml water was added dropwise under constant stirring. After 30 minutes, 0.08 g of NaOH (2 mmol) dissolved in 10 ml water was also added to the above mixture drop by drop under constant stirring. The aqueous solution turned into a yellow colloidal solution without any precipitation. Then, this colloidal solution divided into two portions. One portion stirred for 6 h and another portion stirred as well as heated to 80^0 C for 6 h. The resultant solutions were centrifuged at 10,000 rpm for 15 min, and the settled CdS NPs was washed with double distilled water followed by ethanol. After complete washing, the obtained CdS NPs was dried in air



Scheme 1

2.3.2. Preparation of CdS without using PEG

Cadmium acetate dihydrate, 0.2655 g, (1 mmol) dissolved in 60 ml water and 0.2284 g (3 mmol) of thio urea which was dissolved in 20 ml water were mixed and allowed to constant stirring for 1 h. Then, 0.08 g of NaOH (2 mmol) dissolved in 10 ml water was added to the above mixture drop by drop under constant stirring. The aqueous solution turned into a yellow colloidal solution without any precipitation. After the complete addition of NaOH the reaction was allowed to proceed for 6 h. The solution was centrifuged at 10,000 rpm for 15 min, and the settled CdS was washed with double distilled water followed by ethanol. After complete washing, the obtained CdS NPs was dried in air.

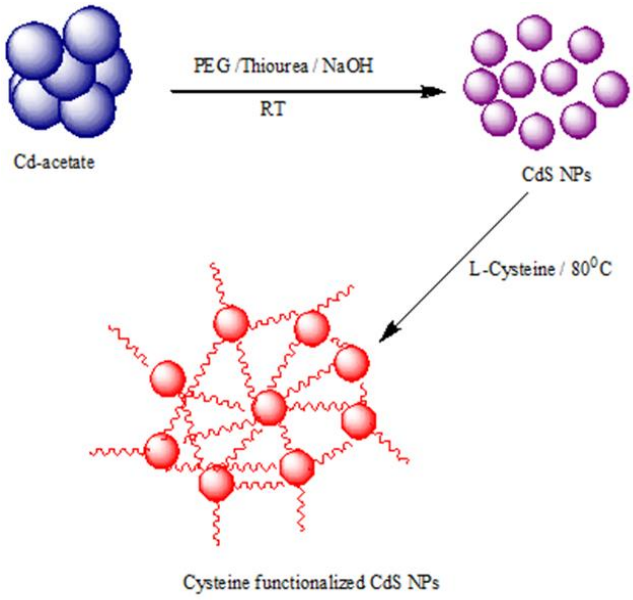
2.3.3. Preparation of CdS NPs using PEG and without NaOH

Cadmium acetate dihydrate, 0.2655 g, (1 mmol) dissolved in 60 ml water and 0.2 g of Polyethylene glycol (PEG) dissolved in 20 ml water were mixed and allowed to constant stirring for 1 h. Subsequently, 0.0761 g (1 mmol) of thio urea which was dissolved in 20 ml water was added drop wise under constant stirring. Then, the above mixture was heated to 60^0 C with constant stirring for 6 h. The aqueous solution was turned into a yellowish orange colloidal solution without any precipitation. The solution was centrifuged at 10,000 rpm for 15 min, and the settled CdS NPs was washed with double distilled water followed by ethanol. After complete washing, the obtained CdS NPs was dried in air. Similarly, only by decreasing mole ratio of Cadmium acetate and thiourea and by increasing temperature to 90^0 C, the CdS NPs were prepared.

2.3.4. L-Cysteine functionalized CdS NPs preparation

0.0109 g of CdS@PEG NPs which was prepared by the procedure described in preparation 1 and 0.1770 g of L-cysteine hydrochloride were dissolved in 30 ml water and the mixture was refluxed at 80^0 C for 6 h. The aqueous so-

lution was turned into a yellowish white solution without any precipitation (**Scheme 2**). The resulting solution was evaporated to dryness on water bath. The resulted functionalized CdS NPs was collected.



Scheme 2

3. Results and Discussion

3.1. UV-vis Spectra

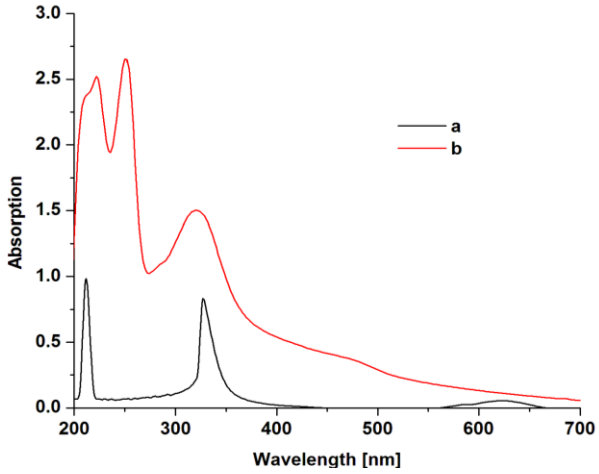


Fig 1. UV-Vis Spectra of the CdS@PEG NPs stirred (a) at room temperature and (b) at 90˚C.

The UV-vis absorption spectra of the colloidal CdS@PEG QDs in water dispersion at different temperature by varying molar ratio of stabilizing as well as reducing agent of thiourea were recorded. When the molar ratio decreases as well as the temperature increases, the absorption red shifts from 230 nm to 238 nm, which suggest that the size of QDs were increase to nanoparticles (NPs) were present due to the rate of agglomeration increases [13, 15, 22]. The results suggest that when the thiourea concentration as well as temperature increases the reaction become faster and the ionic collision were increased and the particles were slowly aggregated to form bigger particles. The results reveal that temperature and reducing as well as capping agent were playing important role in the QDs synthesis.

The chemical reaction process of CdS particles preparation

The CdS particle preparation process can be described as follows. At the beginning, when thiourea was added into the $Cd(CH_3COO)_2$ aqueous solution, the Cd^{2+} was chelated with thiourea to form colorless quadridentate chelate $Cd[SC(NH_2)_2]_4^{2+}$:

$$Cd^{2+} + 4SC(NH_2)_2 \rightleftarrows Cd[SC(NH_2)_2]_4^{2+} \quad \ldots\ldots\ldots \quad (1)$$

Cd^{2+}, $SC(NH_2)_2$ and $Cd[SC(NH_2)_2]_4^{2+}$ all exist in the solution at the same time because reaction (1) is a reversible reaction. Thereafter, during solution stirring and hydrothermal process, a part of thiourea is decomposed to provide S^{2-} to form CdS particles. According to the resonance vibration of thiourea molecule, the reaction process is shown in Fig. 2. Under alkali condition, the decomposition of thiourea will finally produce S^{2-} and NH_3. When OH^- is added, it will promote the thiourea decomposition reaction to the right direction and finally produce S^{2-}, NH_3 and CO_2. At last, the S^{2-} combined with Cd^{2+} to form yellow CdS particles.

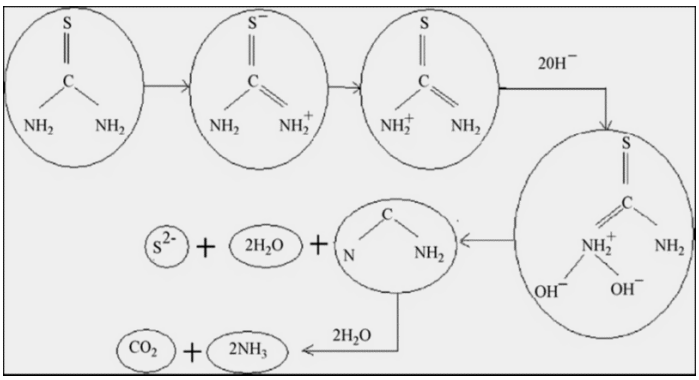


Fig 2. Schematic reaction process of thiourea decomposition

The residue Cd^{2+} might be the reason to induce different chemical phenomenon for different pH modifier. When NaOH is added in the $Cd(CH_3COO)_2$ thiourea solution, at first the Cd^{2+} is combined with OH^- to form $Cd(OH)_2$ white deposition [40].

In the UV-vis spectrum of L-cysteine functionalized CdS NPs (**Fig. 3**), no absorption at 320 nm and new absorption at 276 nm which show the presence of L-cysteine functionalized CdS NPs. It concludes that the L-cysteine act as reducing as well as capping agent, C.A. Mirkin et.al., re-

vealed that the amino acids were self-assembled materials in metal nanoparticles [41]. We expected that the size of the CdS NPs will reduced in the QDs and expect as self-assembled structure of CdS Nps/QDs.

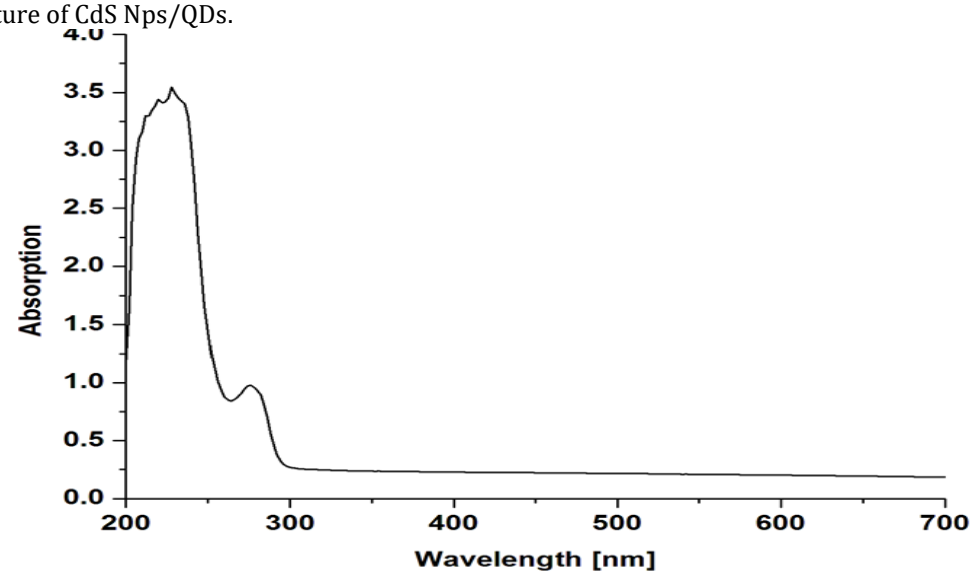


Fig 3. UV-vis spectrum of L-cysteine functionalized CdS NPs

3.2. FT-IR-Spectra

Fig. 4 a shows the FT-IR spectra for the pure CdS NPs prepared by thiourea assisted by hydrothermal method at 60° C and 90° C. When preparation temperature increases, the N-H band at 3406 cm^{-1} is broadening and intensity of the C=S, C-H and N-H were reduced. The stretching frequency of C=S at 1259 cm^{-1} is obtained for CdS NPs synthesized at 60° C. The COO- unsymmetrical stretching at 1390 cm^{-1} is shifted to 1406 cm^{-1}, COO- symmetrical stretching at 1600 cm^{-1} is shifted to 1627 cm^{-1} which indicates that the metal acetate forms to the CdS NPs. In addition, the bands at 472 and 474 cm^{-1} suggest that the Cd^{2+} is formed as CdS NPs capped with thiourea at 60° C and 90° C respectively. The IR spectrum of CdS NPs/QDs prepared in presence of NaOH is given in **Fig 4 b.** and were discussed as follows. The N-H band is broadened and a new band appeared at 2142 cm^{-1}. N-H, C=S stretching were lengthening. The CdS NPs also present as 451 cm^{-1} [42] which is slightly shifted in hydrothermal.

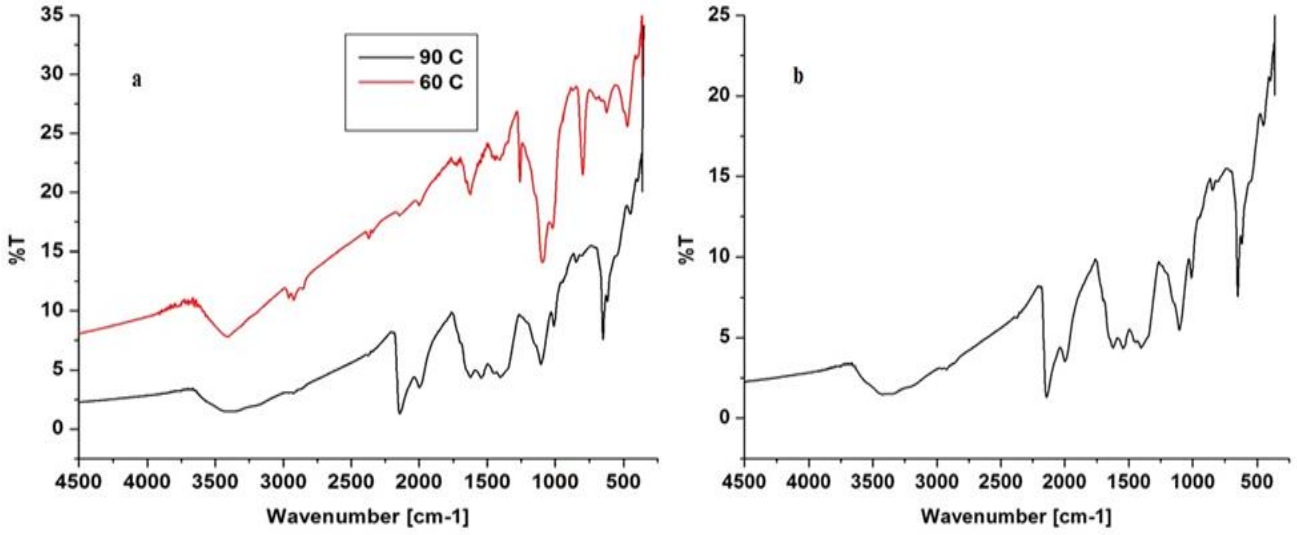


Fig 4. IR spectra of (a) CdS@PEG NPs prepared without using NaOH and (b) CdS@PEG NPS prepared using with NaOH

3.2. FT-IR-Spectra

The FTIR spectrum of L-Cysteine functionalized CdS NPs is given in **Fig 5.** In IR spectrum L-cysteine show the functional groups like S-H, N-H, and COO^- at 2561, 3377 and 1623 cm^{-1} respectively. In our CdS NPs functionalized with L-cysteine, these functional group frequencies were shifted to 2557, 3442, 1579 and 1689 cm^{-1} respectively (**Fig 5**.). The bands appeared at 457, 487 and 648 cm^{-1} also suggested the formation of cysteine as functionalized with CdS.

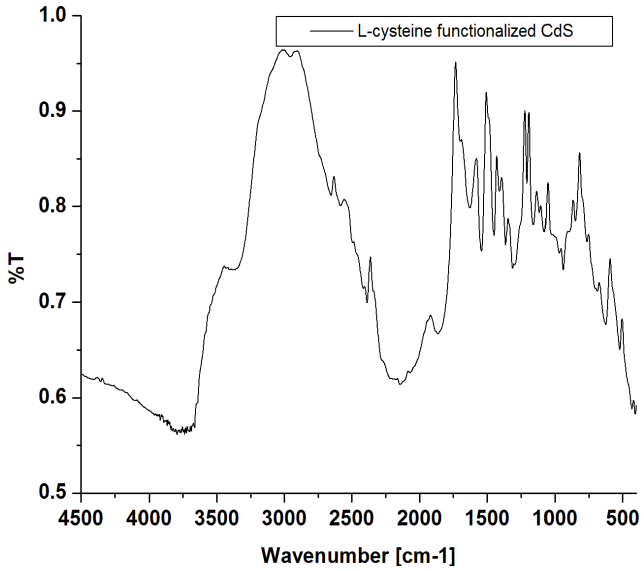
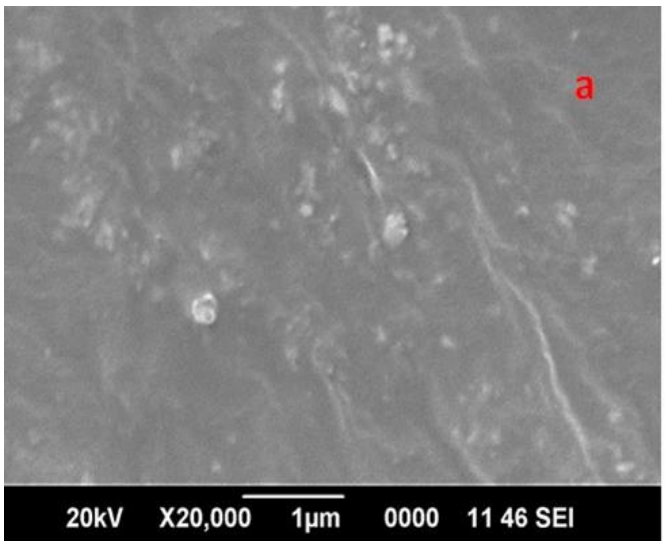


Fig 5. FT-IR spectrum of CdS@PEG QDs functionalized with L-cysteine

3.3. SEM-Morphology study



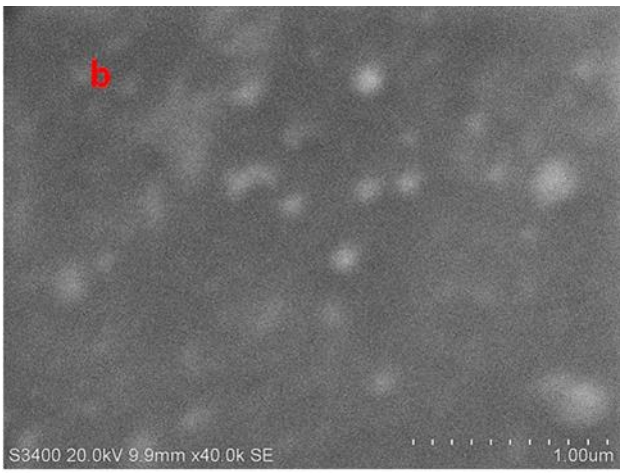


Fig. 6 SEM image of (a) CdS@PEG without NaOH and (b) CdS NPs with NaOH

Fig 6 shows the structure and size of CdS NPs/QDs were using SEM. Fig. 6 a and b reveal that the CdS NPs were spherical in nature and the size of the particle is 70 nm. In the absence of NaOH the PEG form the 2D structure with spherical CdS NPs. SEM images of the L-cysteine functionalized CdS NPs synthesized using NaOH and thiourea as reducing agent in the presence of PEG are given in Fig 7. The morphology of the CdS NPs is spherical and they were uniformly assembled in leaf like structure. The average size of the CdS particles is 50 nm. We are unable to achieve the QDs. The Energy dispersive spectrum (EDS) results revealed the presence of Cd, S and some of Oxygen.

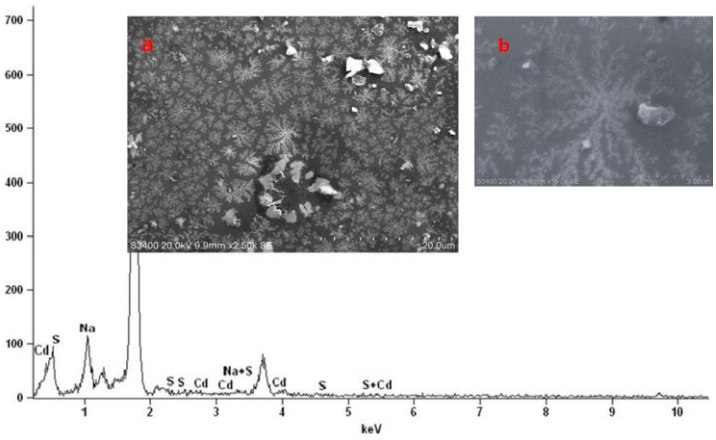


Fig 7. EDAX-SEM image of L-cysteine functionalized CdS NPs low magnification (a); high magnification (b).

4. Conclusion

We were attempted to prepare the CdS QDs but we get only the CdS NPs at low temperature (90° C) and room temperature reaction between metal acetate and thiourea in air. The proposed method is simple, mild and cheap which makes it very suitable to be scaled up for industrial production of semiconducting nanomaterials but not in

QDs. From this scale up method introduce the inert atmosphere and increasing concentration of thiourea is achievable to the QDs in low temperature. A common and cheap sulfur source in synthesizing metal sulfide is thiourea which has melting point of 185.2℃ and a decomposition point of around 198℃. Thus, when thiourea is used as a reactant, it will take on a liquid state and behave just as a liquid reactant at temperatures between around 185.2 and 198℃, which can enormously increase the interfaces and contact surface areas with the other solid reactants and accelerate the reaction rate, leading to the lowered reaction temperature and even the improved properties of the resultant product. However, to our knowledge, the large-scale production of metal sulfide nanoparticles through the direct liquid–solid reactions of corresponding metal acetates and thiourea in air at low temperatures (e.g., 185–198℃) has not been investigated yet. We conclude that low temperature method can be achievable, in future CdS QDs can be achievable it changes into the increasing concentration of thiourea and temperature.

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Conflict of Interest:

The author declares the no conflict of interest.

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