Environmentally Benign Synthesis of Starch Capped CdSe Nanoparticles at Room Temperature

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***Abstract*—Starch capped CdSe nanoparticles have been successfully synthesized at room temperature by a simple, environmentally benign solution growth technique. The powder product was well characterized by powder X- ray diffraction (XRD), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). It is investigated that as synthesized powder has a zinc-blend (cubic) structure of CdSe with diameters of the particles are in the range of 25-30 nm. The transmission electron microscopy (TEM) image showed that the particles are small and are notspherical in shape. The UV–vis absorption and photoluminescence spectroscopy (PL) showed that the particles exhibited quantum confinement in their optical spectra with emission in the red region. The Fourier transform infra-red (FTIR) analysis confirmed the capping of the nanoparticles by the starch**.

Keywords:* *CdSe Nanoparticles; Photoluminescence; X-ray diffraction; Starch capped; optical properties.

I. INTRODUCTION

Nanostructured materials have unique characteristics that cannot be obtained from conventional macroscopic materials. Hence they have attracted a great transaction of attention in the last few years. Novel optical, electronic, magnetic, chemical and structural properties are displayed by nanomaterials, owing to the quantum size effects and surface effects, and might find many important technological applications. An extremely active and prolific field in nanomaterials is finding ways to control size and morphology of the nanoparticles since the properties and applications of the nanoparticles are largely dependent on their size and morphology. Such properties construct semiconducting nanostructures suitable for several kinds of applications, from anti reflecting coatings [1] to biomolecular detection [2] and light emitting devices [3]. Among the family of II–VI semiconductors CdSe [4], is the foremost candidates since of their favorable electronic and optical properties for optoelectronic applications. In particular CdSe quantum dot (QD) is an important II–VI semiconductor having a wide optical band gap, making it a very attractive material for optical applications, especially in nanocrystalline form. CdSe can have two different crystal structures cubic zinc blende and hexagonal wurtzite and a direct band structure. CdSe quantum dots of appropriate size can have an absorption edge and emission peak anywhere in the visible spectrum. This led to CdSe nanoparticles to be used for opto-electronic devices, laser diodes, nanosensing and biomedical imaging [5].

Many synthetic methods have been developed for the preparation of monodispersed nanoparticles of various semiconductor materials, ranging from aqueous precipitation route to high temperature hot injection method. Most of these methods usually involve the use of sophisticated equipments, complex or toxic reagents which are not environmentally benign, and use many variables for the synthesis of CdSe nanoparticles. There are reports on room temperature synthesis of CdSe nanoparticles involving costly and hazardous techniques with or without surfactant/stabilizing reagents [6-8]. As a result of these toxicity concerns, the search for QDs with high photostability and biocompatibility, prepared via a greener, sustainable and environmentally benign method, is still an area of immense interest.The toxicity of the ingredients has posed a major concern regarding the use of nanoparticless in biological application. Some researchers have reported the synthesis of CdSe nanoparticles via a simple environmentally benign method using cysteine and starch as passivating agent [9,10].

In this work we have adapted a simple method to synthesize starch capped CdSe nanoparticles. The as-prepared CdSe nanoparticles were characterized by XRD, SEM and TEM for crystal structure and particle size. The optical characterization by UV–vis absorption spectra and FTIR spectroscopy was made. The photoluminescence (PL) spectrum of the prepared sample was also recorded. The results indicated stable and well dispersed CdSe nanoparticles with fairly narrow size distributions.

II. EXPERIMENTAL

Commercially available cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), selenium metal powder (Se) and sodium sulfite crystal ($Na_2SO_3{\cdot}7H_2O$) and precursor, water soluble starch $[(C_6H_{10}O_5)x$ was purchased and were used to synthesize the

CdSe nanoparticles. All the reagents were of analytical grade and used as received. Double distilled water was used in all the experiments

A stock solution of 0.5 mol l^{-1} sodium selenosulfate (Na_2SeSO_3) was prepared by refluxing the aqueous solution containing 1.0 mol l^{-1} NaS_2O_3 and 0.5 mol l^{-1} elemental Se under stirring for 3 h. In a typical procedure, the aqueous solution of cadmium chloride (1.0 ml, 0.1 mol l^{-1}) was added to the aqueous solution of soluble starch (100 ml, 0.05 wt%) in a glass beaker with constant stirring and 1.0 ml as-prepared 0.5 mol l^{-1} Na_2SeSO_3 aqueous solution was introduced, then ammonia solution was added to adjust the pH value to 10 – 11. The mixture was stirred for 2 h to obtain a red transparent solution and aged for 12 h. The red transparent solution was then extracted with acetone to obtain red precipitate. The precipitate was washed several times with acetone and dried at room temperature for 3 h [11].

X-ray diffraction patterns have been obtained using a Rigaku Rotating Anode (H-3R) diffractometer. XRD patterns were studied by using Cu Kα radiation (wavelength 1.54 A°) XRD data were collected over the range 20°– 70° at room temperature. The particle size was calculated by using the Debye–Scherrer formula. A JSM – 5600 LV SEM instrument was used for SEM photograph. Tecnai 20 G2 (FEI make) Transmission Electron Microscope was used to take the TEM photograph. Absorption spectra of the samples prepared were recorded with the help of UV-visible spectrometer (SHIMADZU). The FTIR spectra were recorded by the help of FTIR spectrometer (SHIMADZU) in the range of 500cm^{-1} to 4,000cm^{-1}. Photoluminescence of the sample was recorded using a Perkin Elmer Luminescence Spectrometer LS 45.

III. RESULT AND DISCUSSIONS

The X-ray diffraction of CdSe powder sample is shown in Fig. 1. The broaden diffraction peaks indicated the nanocrystalline nature of the sample. There existed three diffraction peaks at 2θ = 24.9°, 43.2° and 49.9°, which corresponded to the (1 1 1), (2 2 0), and (3 1 1) planes of cubic CdSe and were consistent to the reported results in the literature [11]. Moreover, the intensities and positions of the diffraction peaks of CdSe showed are approximately same as of the literature values. The average crystalline sizes of the CdSe nanocrystals and has been determined using Scherrer's formula from the width of first peak.

$$D = \frac{K\lambda}{\beta\cos\theta}$$

The scale factor (k) in the formula accounts for the shape of the particle and is generally taken to have the value 0.9. According to the XRD spectra, the crystallite size of CdSe was calculated to be about 28 nm.

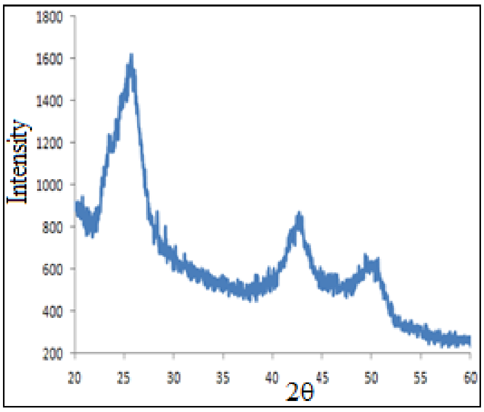

Fig. 1XRD patterns of CdSe nanoparticle

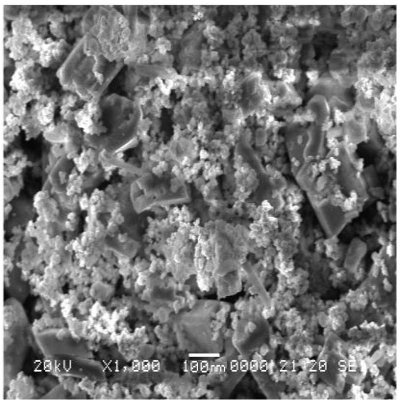

Fig. 2 SEM photograph of CdSe nanoparticle

A typical SEM image of CdSe nanocrystals is shown in Fig.2. It can be seen that some of the particles were highly agglomerated. As observed in the experiments, nanoparticles were made within the first few minutes, but after a few minutes, those particles were agglomerated and their size becomes larger. The average particle size was supposed to be in the range 30-40 nm. It is very clear that particles are not spherical.

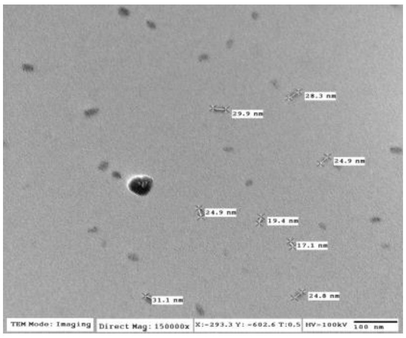

Fig. 3 TEM photograph of CdSe sample

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of highly-focused, mono-energetic beam of electrons is bombarded in vacuum on a very thin solid specimen and interacting with the sample as it passes through. A typical TEM image of CdSe nanoparticles are shown in Fig.3. The particle size was calculated with the help of the scale shown on the lower right corner of the HRTEM figure, which is 100nm. The average particle size of the prepared samples was in the range 25nm – 30nm. These results are similar to the results obtained from XRD pattern.

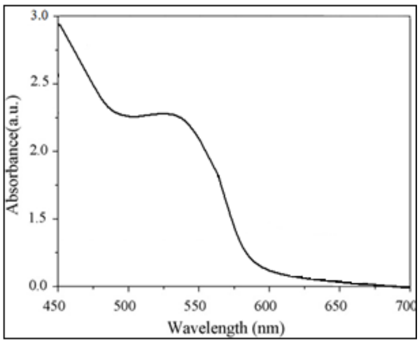

Fig. 4 Absorption spectra of nano CdSe sample

Fig. 4 shows the optical absorption spectra of the CdSe nanoparticle. The starch capped sample exhibited an absorption edge at 585 nm blue-shifting as compared with bulk CdSe. The observed blue shift in the absorption edge is the reflection of increase in the band gap owing to quantum confinement effect. Band gap of standard material of CdSe (bulk) is 1.74 eV, and the band gap of synthesized CdSe in lab was 2.11 eV on the basis of absorption spectra. In addition, the starch capped sample exhibited higher optical sensitivity than the bulk.

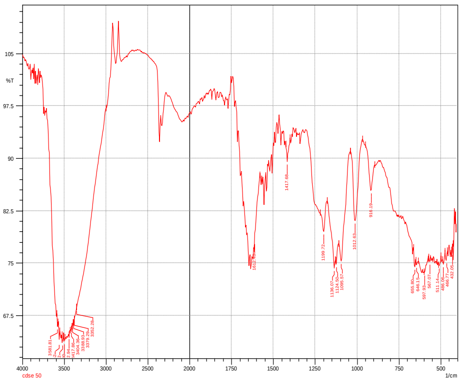

Fig. 5 FT-IR spectra of nano CdSe sample

Fig. 5 shows the FT-IR spectrum of as-prepared CdSe nanoparticle. The IR absorption of the CdSe powder was determined with KBr. Before taking the IR of the sample the sample was dried at room temperature. The most pronounced IR absorption bands occurred at 3508 cm^{-1} (OH), 2930–2918 cm^{-1} (CH_2), 1643 cm^{-1} (C C), 1402 cm^{-1} (CH_2), 1083 cm^{-1} (C-O). The broad peak at 3508 cm^{-1} is assigned to –OH stretching intra molecular hydrogen bonds due to the small quantity of H_2O on the sample. The peak observed at 1643 cm^{-1} is assigned to OH of water absorbed from the molecular precursors. O-H stretching vibration peak is observed at 2342 cm^{-1} due to the presence of starch in our sample. The spectrum peaks observed in fig.5 at wave numbers of 2030, 1600 and 1465 cm−1, respectively, are related to C H vibrations in the alkyl chain of the surface modifiers.

Fig. 6 shows the photoluminescence spectrum of CdSe nanoparticle. PL spectrum shows a strong single emission peak is observed at 673nm, in comparison with that of bulk CdSe at 730 nm. The excitation wavelength was 450 nm. There is a large blue shift in the PL spectrum of as-prepared CdSe nanoparticles as compared to bulk. This effect may be related to the quantum confinement effects.

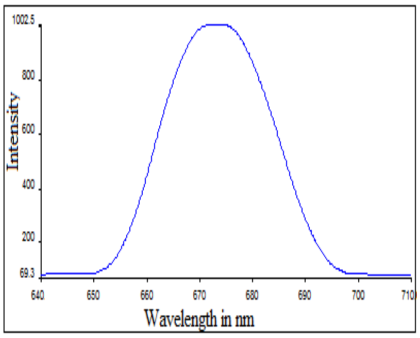

Fig.6 Photoluminescence spectra of nano CdSe

IV. CONCLUSIONS

The well dispersed CdSe nanoparticles were synthesized by using soluble starch as capping agent. This method is a simple, cheap and efficient “green” route for producing nanoparticles. The synthesis of the nanoparticle was made at room temperature and normal pressure. The size of the synthesized CdSe nanoparticle was found to be 28 nm using XRD and TEM. The SEM photograph showed agglomeration. The optical absorption spectra showed blue shift for the nano CdSe nanopaticles. The FT-IR spectra show the presence of starch in the sample. The PL spectrum showed a strong quantum effect and a remarkable increase in the intensity as compared to bulk. This property can be used in future devices. Starch is environmentally benign and renewable, the starch capped CdSe nanoparticles can be widely used as catalysers, luminescent probes and biomedical labeling and so on. This method may be used for the preparation of other semiconductors nanoparticles.

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