FORMATION OF PVA-CAPPED CdSe NANOCRYSTALS UNDER ULTRASONIC WAVES

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Poly vinyl alcohol (PVA)-capped CdSe nanocrystals were prepared using a sonochemistry method. XRD pattern are consistent with that for cubic CdSe. The calculated result from XRD characterization shows that the sizes of particles are less than 10nm. SEM of as-prepared samples shows uniform agglomerated particle distribution. The agglomerates size is found to be less than 300nm based on observed SEM images which aggregated in the form of small nanoparticles. The elemental analysis shows that the prepared samples are exactly stoichiometric.

Introduction

Crystals with dimensions in nanometer range show characteristics that are considerably different from the characteristics of bulk materials. For example, an effective increase in band gap is observed in nanocrystalline CdSe due to quantum confinement effect. Large surface to volume ratio of semiconductor nanoparticles makes them possess characteristics that differ from the bulk semiconductors. Furthermore these characteristics depend principally on their size and shape [1-4]. Considerable interests have been devoted during recent years in CdSe nanocrystal synthesis because of their size quantization effect and wide applications in nanoelectronic devices. However, the suitability of these nanocrystals is limited to their synthetic procedure, size distribution and surface effects. A variety of methods have been described to synthesize CdSe bulk and nanocrystals in thin film form that includes physical vapor deposition, sputtering, spray pyrolysis, electrodeposition, etc.[5,6] In the present work, CdSe nanocrystals were prepared by sonochemistry method.

1. Experimental section

1.1. Materials

Cadmium acetate dihydrate ($C_4H_6CdO_4.2H_2O$, extra pure), sodium sulfite (Na_2SO_3), elemental selenium powder, sodium hydroxide (NaOH, extra pure) and polyvinyl alcohol powder (PVA) were obtained from Merck and employed without future purification. Double distilled water and absolute ethanol were used for washing the particles.

1.2. Instruments

The X-ray powder diffraction (XRD) pattern of product was carried out on Philips X Pert X-ray diffractometer with Cu Kα radiation (λ = 0.154056 nm) at a scanning rate of 0.02 $°s^{-1}$ in the 2θ rang from 20° to 60°. The purity and elemental analysis of the product were obtained by EDAX on LEO 1430 VP instrument. Surface morphology and distribution of particles were performed via LEO 1430 VP scanning electron microscope, using an accelerating voltage of 18 kV. The sample used for SEM observations was prepared by transferring the particles, which at first was dispersed in the ethanol to the SEM stage. After allowing the evaporation of ethanol from the stage, the particles on the stage were coated with a thin layer of gold.

1.3. Preparation of PVA-capped CdSe nanocrystals

PVA and chemically pure reagents were used for the preparation of CdSe nanocrystals. Sodium selenosulfate (Na_2SSeO_3) solutions were prepared via dissolution of 0.2 gr of elemental selenium powder in 50ml of 1.1 aqueous solution of sodium (Na_2SO_3), by magnetically stirring for 2 hour at 80 C applying reflux column system. All the selenium powder was dissolved and the transparent solution was allowed to be cooled to room temperature. The reacting mixtures for the synthesis of CdSe nanocrystals were prepared from 0.2 M cadmium acetate and prepared sodium selenosulfate solutions in 10 mass % PVA solutions in distilled water. The pH of this solution brought to 9 by addition of NaOH. The mixed slowly and the color of mixture gradually changed from milky to orange. This solution was transferred to a 100 ml borosilicate rounded bottom flask and mixed well and irradiated for 1 h at room temperature in open air, using Dr. Heilscher high intensity ultrasound processor UP200H Germany (0.3 cm diameter Ti horn, 200 W/cm^2, 23 kHz). The titanium tip of the horn was immersed directly in the reaction solution. During the sonication of reaction mixture, the temperature increased to about 70°C and remained constant at the end of sonication.

After sonication, the solution was centrifuged (at revolution rate of 4000 rpm) and a plenty of orange precipitates could be observed. The precipitates were washed with double distilled water and absolute ethanol and centrifuged for several times to remove the week bounded species and PVA matrix and finally dissolved in absolute ethanol and then were dispersed on ordinary microscope glass slide and dried at room temperature for one day.

2. Results and discussion

The result of the powder XRD pattern of the sample is depicted in Fig. 1. It is compatible with the diffraction pattern of CdSe in cubic structure (JCPDS files No.19-0191). The broadness of peaks indicates the formation of nanosized product. The most common method of determining the particle size is from the width β (FWHM) of the prominent X-ray diffraction (XRD) peaks using Scherrer's formula

$$L = \frac{0.94\lambda}{\beta \cos\theta}$$

Here L is the coherent length, λ is the wavelength of X-ray radiation and θ is the angle of diffraction. In the case of

spherical crystallites, the relation between L and D, the diameter of crystallite, is given by $L = (3/4)\ D$.[7,8].

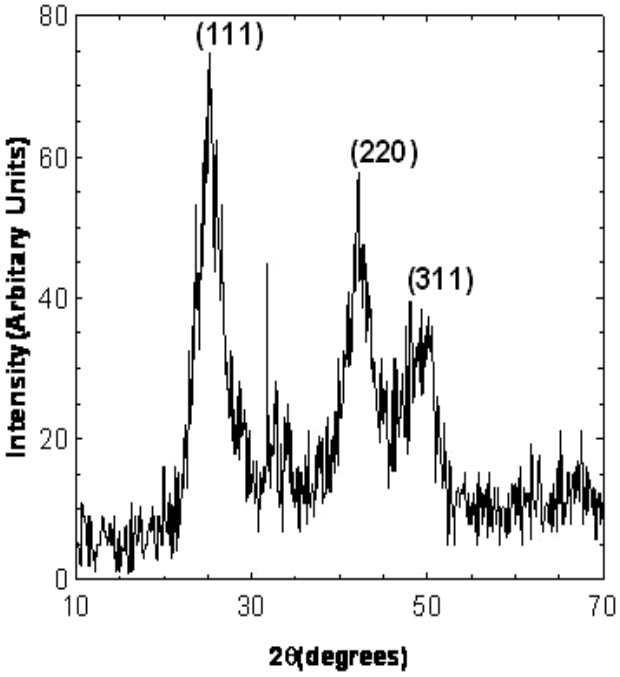

Fig. 1. XRD pattern of as-prepares CdSe nanocrystals by sonochemistry method

Although this technique does not give any proper idea about size distribution, we have estimated the average particle size of the nanocrystallite for as prepared nanoparticles using the above formula, considering three prominent peaks at 25.23°, 42.10° and 50.2°. The average of L obtained from XRD pattern for these picks are less than 20 nm. The surface morphology and the distribution of the product were characterized by Scanning electron microscopy (SEM), which its images are illustrated in Fig. 2a-c at magnifications of 5k, 15k and 30k respectively.

It is obvious from Fig. 3 that produced CdSe consists of spherical nanocrystallites of about 300 nm; aggregated in the form of polydispersive agglomerates with the size in the range of 150-300 nm. Also the particle sizes are calculated by effective mass approximation model [9, 10].

It gives that the size of particle is very small and confirm the obtained results from XRD. The difference between obsereved results from SEM and calculated results from XRD arise from this fact that in fact the particles size is very small (less than 10 nm) and the calculated XRD results are true. The produced nanoparticles were characterized by energy dispersive X-ray analysis (EDAX) for the evaluation of its composition and purity. The EDAX spectrum for the product is shown in Fig. 3. It is evident from the peaks of the figure that the product is completely pure and they correspond to Cd and Se with an average atomic percentage ratio of about 50:50. The elemental analysis confirms the presence of corresponding elements in non-stoichiometric percentage.

The role of sonication and formation of nanoparticles is so important. In this experiment, the presence of PVA is very important in the synthesis of CdSe nanoparticles, since by the help of ultrasonic waves.

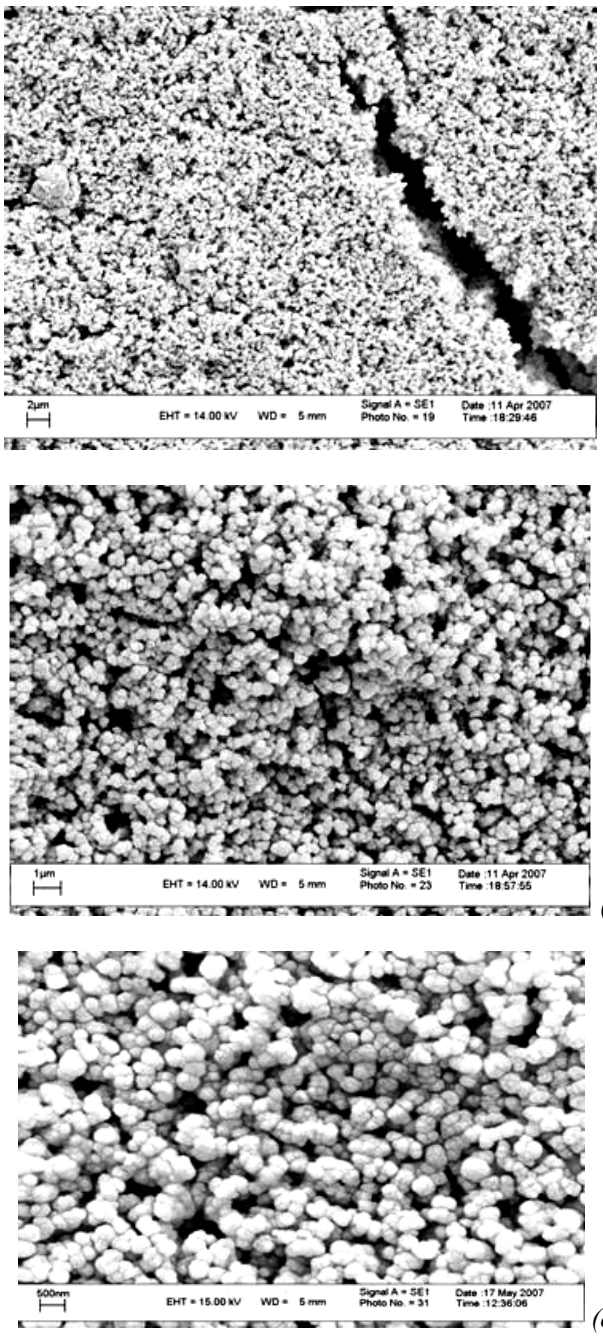

Fig. 2. SEM image of CdSe nanocrystals, magnification *(a)* - 5k; *(b)* – 15k; *(c)* – 30k.

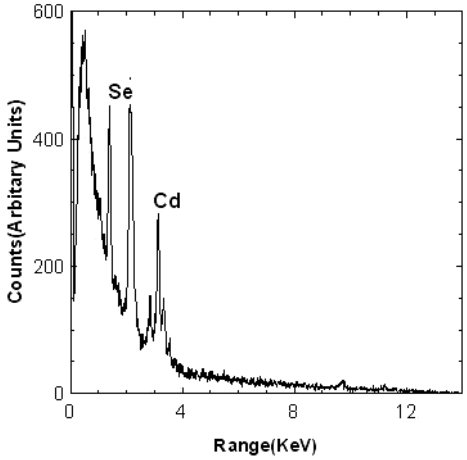

Fig. 3. EDAX spectrum of as-prepared CdSe nanocrystals by sonochemistry method

Conclusion

A novel and simple method for preparation of CdSe nanoparticles using ultrasonic waves has been described. The product are nanocrystallites, in cubic structure, with an average diameter of less than 10 nm, highly pure and having higher band gap of about 4.7 eV compared to its bulk value, demonstrating a big blue shift due to CdSe nanostructure nature.

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PVS ÖRTÜKLÜ CdSe NANOZƏRRƏCİKLƏRİNİN ULTRASƏS DALĞALARININ KÖMƏYİ İLƏ ALINMASI

Ultrasəs dalğalarının köməyi ilə polivinil spirtli (PVS) örtüklü CdSe nanozərrəcikləri alınmışdır. Struktur tədqiqatlarına əsasən, alınmış CdSe nanozərrəcikləri kubik guruluşa malikdir. Rentgen tədqiqatlarından nanokristalların ölçüləri təyin edilmişdir (10 nm-dən kiçik). Elektron mikroskopik tədgigatlarının nəticələri göstərdi ki, bu zərrəciklər orta ölçüsü 300nm olan bircins aqlomerat əmələ gətirir. Element analizinin nəticələrinə əsasən alınmış nanokristallar stexiometrik tərkibə malikdirlər.

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ФОРМИРОВАНИЕ НАНОКРИСТАЛЛОВ CdSe В ПВС ОБОЛОЧКЕ С ПОМОЩЬЮ УЛЬТРАЗВУКОВОЙ ВОЛНЫ

Методом ультразвука были получены наночастицы CdSe в оболочке поливинилового спирта (ПВС). По результатам структурных исследований установлено, что наночастицы CdSe имеют кубическую структуру. По данным рентгенографических исследований были рассчитаны размеры нанокристаллов, которые были меньше 10 нм. Результаты исследования СЭМ показали, что полученные частицы образуют однородные агломераты со средним размером 300 нм. Элементарный анализ показал, что полученные образцы имели стехиометрический состав.

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