Microwave-assisted polyol method for the preparation of CdSe "nanoballs"

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The microwave-assisted polyol reduction method was applied to the preparation of CdSe "nanoballs". The cubic and hexagonal forms of the CdSe nanoparticles obtained were analyzed by XRD, TEM, HRTEM, UV-VIS, photoluminescence (PL) and photoacoustic spectroscopy. Formation of the hexagonal or cubic form of CdSe depends on the glycol used for reaction. It was found that "nanoballs" are built-up of clusters of CdSe with sizes of a few nanometers. A strong blue shift is observed in the absorption spectrum, as expected for size quantization. A possible reaction mechanism is provided.

Introduction

In recent years there has been considerable interest in semiconductors with nanometer size dimensions due to the quantum size effect exhibited by these nanosized semiconductors.[1–3] Because of the high surface-to-volume ratio of nanoparticles, their surface properties have a significant effect on their structural, catalytic, mechanical, electrical and optical properties. Among the many techniques for their preparation, solution synthetic methods are especially appealing. This is because of their simplicity and low reaction temperatures, compared with the elaborate and expensive CVD and PVD methods. Indeed a variety of solution synthetic methods have been developed for the synthesis of nanosized semiconductors. To name just a few: precipitation in homogeneous solution,[4,5] metathesis reactions,[6] and also synthesis in a confining medium, like zeolites.[7] Among the various semiconductors, the preparation of selenides has attracted special attention. Several methods have been used for their synthesis. Methods such as gas phase reaction between the element (or elements) and gaseous H_2Se, solid state reactions, sonoelectrochemistry, pyrolysis of single source precursors, and pressure reactions.[8–12] In general all these reactions require moderate temperatures (in the case of solid state reactions), and use toxic (H_2Se) or highly sensitive (Na_2Se) precursors or require high-pressure equipment. In the current synthesis the microwave-assisted polyol method is applied to the preparation of nanophased CdSe. The synthesis is conducted without requiring special and/or sensitive reagents or expensive equipment.

Microwave heating (MW) has been known since the early 1940's and has been used successfully in the food industry. The MW method has found a number of applications in chemistry since 1986.[13–16] The number of publications related to the application of microwave irradiation in organic chemistry has shown an exponential growth over recent years. Its extension to inorganic chemistry, on the other hand, has been much slower. The effect of heating is created by the interaction of the permanent dipole moment of the molecule with the high frequency (2.45 GHz) electromagnetic radiation. Polyol solvents like ethylene glycol are very suitable for microwave reactions because of their relatively high dipole moment.[17] Another advantage of using ethylene glycol as a solvent is its reducing power. Previously, a reduction method based on ethylene glycol, and known as the polyol method, was used for the preparation of nanoparticles of pure metals.[18–20] The current synthesis is a continuation of the series of papers devoted to a new method, developed for the preparation of the nanoparticulate chalcogenides using microwave irradiation. We have extended this methodology and successfully applied the polyol method to the synthesis of a variety of chalcogenides.[21–23] In the current report we use the polyol method for the preparation of CdSe nanoparticles.

Experimental

All reagents were of the highest purity. Elemental Se, cadmium acetate (+2), triethylene glycol and ethylene glycol were purchased from Aldrich Co., and used without further purification. All the reactions were conducted in a modified domestic microwave oven (Spectra 900 W) operating in a cycling mode (on: 14 s, off: 6 s) to prevent intense boiling of ethylene glycol. The powder X-ray diffraction patterns of the products were recorded by employing a Bruker AXS D* Advance Powder X-Ray Diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). EDX measurements were conducted using an X-ray microanalyzer (Oxford Scientific) built on a JSM-840 Scanning Electron Microscope (JEOL). The transmission electron micrographs (TEM) were obtained using a JEOL-JEM 100SX microscope, working at a 100 kV accelerating voltage. High resolution TEM (HRTEM) images were obtained by employing a JEOL-3010 instrument with a 300 kV accelerating voltage. A conventional CCD camera, with a resolution of 768×512 pixels, was used to digitize the micrographs. Image processing of these digital images was performed using Digital Micrograph software. HRTEM image calculation, and electron diffraction indexing were performed using an EMS package.[24] Samples for TEM were prepared by placing a drop of the sample suspension on a copper grid (400 mesh, electron microscopy sciences) coated with carbon film and were allowed to dry in air. X-Ray photoelectron spectra (XPS) were recorded using an AXIS, HIS, 165, ULTRA (Kratos Analytical) instrument. Absorption spectroscopy was carried out on a Cary (Varian 1E) spectrophotometer. The photoluminescence (PL) spectra of the as-prepared CdSe were measured using a Perkin-Elmer Luminescence Spectrometer (LS50B). The spectra were recorded at room temperature using 1 cm quartz cuvettes. The samples were prepared by ultrasonically dispersing CdSe nanocrystals

in the distilled water. Photoacoustic measurements were conducted employing a homemade instrument which has been described elsewhere.[25]

Procedure for the MW synthesis of CdSe

Cadmium acetate (0.33 g) was dissolved in ethylene glycol (40 ml) by gently heating the solution in the microwave oven for approximately 1 minute. Stoichiometric quantities of Se powder (0.1 g) were then added. The system was purged for several minutes with nitrogen and then the microwave reactor was turned on. The reactions were conducted for 1 hour. In the post reaction treatment the product was centrifuged once with the mother liquid, and a few times with EtOH, at 20 °C, and 8000 rpm. The resulting product was then dried under vacuum overnight.

Results and discussion

In order to study the nature and morphology of the resulting product, techniques such as powder XRD, TEM, HRTEM, SEM, EDX, XPS, UV-VIS, PL and photoacoustic spectroscopy were employed.

PXRD study

The as-prepared CdSe sample was characterized by PXRD, which showed a perfect match with the diffraction pattern available in the PDF-2 database (no. 77-2307). The CdSe sample is obtained in the hexagonal form, with lattice parameters $a = b = 4.32$ and $c = 7.01$ Å. Previously, when CdSe was prepared in our group by other methods[26,27] only the cubic (sphalerite) phase was obtained. In order to calculate the average crystallite size on the basis of the peak broadening, the Debye–Scherrer (DS) equation was employed. The PXRD pattern of the CdSe obtained using the ethylene glycol synthesis is shown in Fig. 1. The calculated average diameter of the nanoparticles is 6.3 nm (the calculation is performed using the peak-fitting program Topas P [Bruker Analytical X-Ray Systems]). No preferred orientation was observed in the growth of CdSe as evidenced from the PXRD data. An impurity in the form of unreacted Se is observed (peak marked by an asterisk in Fig. 1). When the reaction is conducted in triethylene glycol (bp 285 °C) as the solvent and reducing agent, nanocrystals with a perfect CdSe cubic phase (PDF-2 no. 19-0191) are obtained without any impurities. The crystallite size obtained using the DS equation is 8.2 nm. The most intriguing fact is a dependence of the resulting CdSe phase on the nature of the solvent. Two explanations are offered for this observation. The first explanation attributes the observed difference to the boiling points of the two solvents. Triethylene glycol boils at a temperature 87 °C higher than ethylene glycol. However, it is known that the CdSe hexagonal phase is usually obtained at higher temperatures than the cubic phase.[28] Our
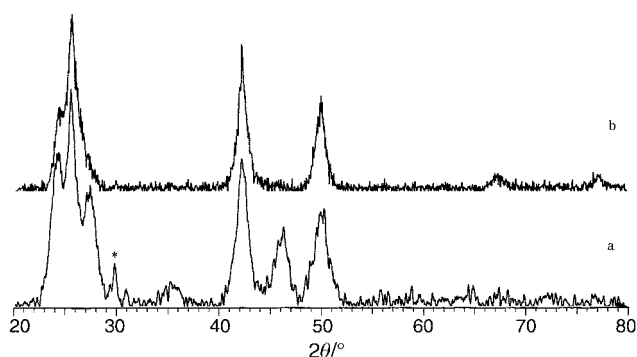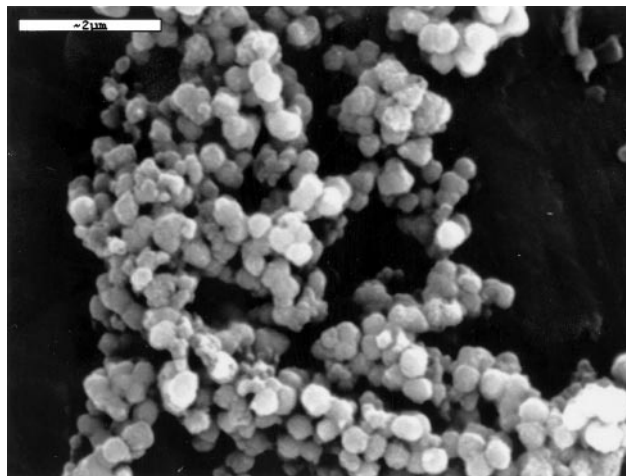

Fig. 2 The SEM images of the hexagonal CdSe "nanoballs" (scale bar equal to 2 μm).

synthesis reveals the opposite behavior. Namely, we obtain the hexagonal phase using the lower boiling point solvent, ethylene glycol. We will therefore relate this result to the kinetically-controlled nature of the MW polyol reaction. The other explanation relates the difference to the complexing power of the glycols. Triethylene glycol is a much stronger complexating agent than ethylene glycol. This is due to the fact that in addition to its two OH groups it is also a diether. This multifunctionality could cause a decrease in the surface energy of some crystallographic planes relative to others, and in this way stabilize the cubic structure relative to the hexagonal structure.

SEM measurements

In order to the study the morphology of hexagonal CdSe we have employed SEM techniques. The SEM micrograph is presented in Fig. 2. It is possible to see spherical (ball-like) particles with very low aggregation. Size measurements conducted on several "nanoballs" yielded an average diameter of 330 nm. It is interesting to note the tremendous difference between the crystallite size obtained from the SEM measurements, and the dimensions calculated from the DS equation.

TEM and HRTEM measurements

The TEM picture of the hexagonal CdSe is shown in Fig. 3a. Similar to the SEM pictures it is possible to see individual low aggregation spheres of CdSe. The interesting fact is the presence of a low density shell around each particle. The mean diameter of the particles including the shell is 350 nm, and the core of the particle is 240 nm. This yields a shell thickness of about 50 nm. In general the sizes obtained by the SEM and TEM (particles including shell) are in good agreement, but they are totally different from the size calculated from the PXRD data. In order to study the structure of this shell we applied HRTEM, which showed (see Fig. 3b) clusters of CdSe with an average diameter ~6–7 nm. An amorphous matrix surrounds the clusters. The density of these clusters increases towards the core. Unfortunately it is impossible to study the core by HRTEM, because it is too thick. TEM micrographs of the CdSe products having a cubic phase structure are shown in Fig. 3c. These nanoparticles have dimensions (diameter) of approximately 6 nm, and are also loosely aggregated.

Optical measurements

Results of UV-VIS absorption measurements of solutions of hexagonal and cubic CdSe in water are shown in Figs. 4a and b,
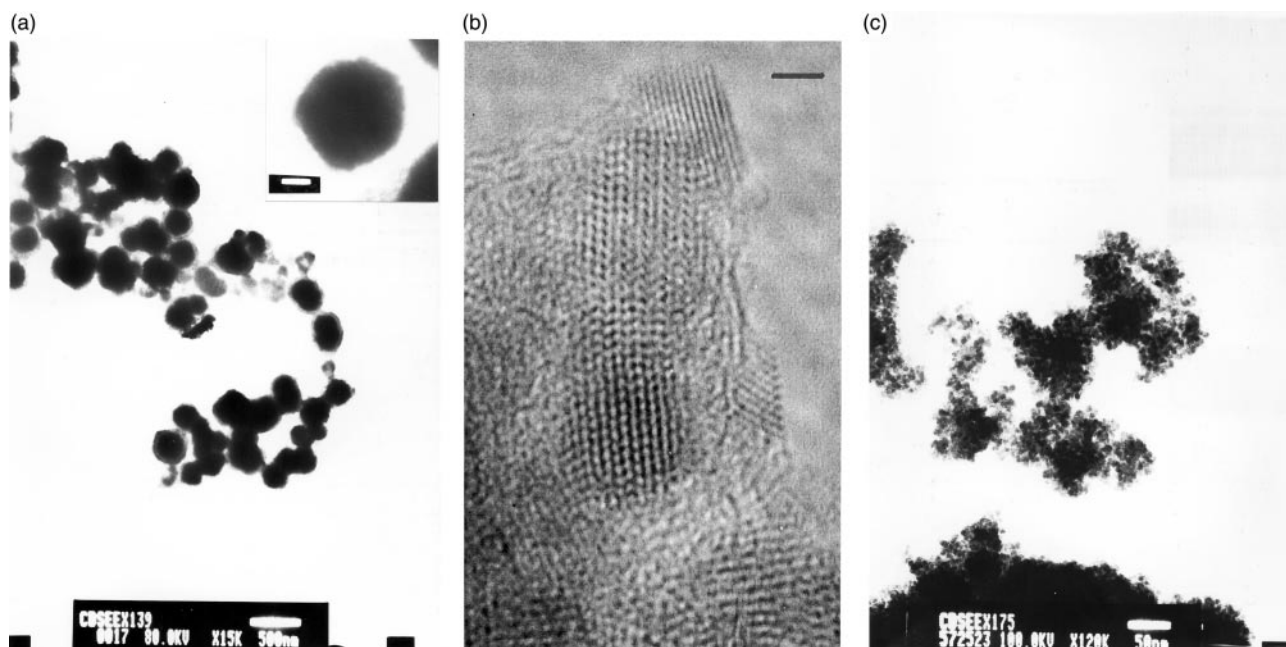

Fig. 1 The PXRD patterns of (a) hexagonal CdSe prepared in ethylene glycol; (b) the cubic form of CdSe prepared in triethylene glycol.

Fig. 3 The TEM pictures of (a) hexagonal CdSe ''nanoballs'' (scale bar equal to 500 nm); insert: higher resolution of the hexagonal CdSe ''nanoballs'' (bar equal to 100 nm); (b) HRTEM image of the shell in hexagonal CdSe (bar equal to 44 Å); (c) cubic CdSe nanoparticles (bar equal to 50 nm).

respectively. The inflection point at 640 nm is taken as a rough estimate for the band gap of hexagonal CdSe, yielding an approximate value of 1.93 eV. Although this can not be considered as a good method for estimating band gaps, it corresponds to the band gaps of particles with a diameter of 8 nm.[29] We present this value only to support the PXRD and HRTEM size measurements. For CdSe particles with a cubic phase structure the corresponding estimated band gap is positioned at 652 nm or 1.90 eV. Both estimated numbers (1.93 and 1.90 eV) are blue shifted relative to the bulk hexagonal (1.73 eV) and bulk cubic CdSe (1.78 eV) phases. The estimation of the band gap (E_g), is based on measuring the wavelength of approximately one-third of the main absorption feature. This approximation is found to be good for quantized semiconductor films as long as their spectral shape behaves like that of a direct bandgap semiconductor.[30]

Photoacoustic measurements

The photoacoustic method, which dates back to the time of Alexander Graham Bell, consists of illuminating the sample with chopped monochromatic light in an airtight cell connected to a microphone. The light is absorbed and converted to heat. The chopped heat then flows to the surface of the sample where it produces an acoustic wave. The wave is detected with a lock-in voltmeter. The signal which is acquired as a function of

wavelength is normalized against the absorption of carbon black powder, a 100% absorber. The instrument operates over the wavelength region 300 to 1600 nm. The spectrum is independent of the nature of the sample unlike reflectance spectroscopy, where the nature of the surface can have a marked effect on the spectrum. It is particularly useful for particulate matter, which causes turbidity and scattering so that conventional absorption spectroscopy is not very helpful. The method is completely non-destructive. The photoacoustic spectra show features that are much better resolved than in the absorption spectra. The PAS of both cubic and hexagonal forms of CdSe are shown in Figs. 5a and 5b. One can see very clear differences between the band edges. Note that below 620 nm the spectra of the two forms are very similar as they are above 780 nm. The band gap for the hexagonal form (see Fig. 5a) lies at 635 nm (1.95 eV) and for the cubic form (see Fig. 5b) at *ca.* 682 nm (1.82 eV). In this case as in the case of UV-VIS absorption measurements we observe a blue shift due to the size quantization. The quality of results obtained from photoacoustic measurements are much better than in the case of UV-VIS measurements because, as mentioned previously, the PAS method is independent of scattering and other factors.
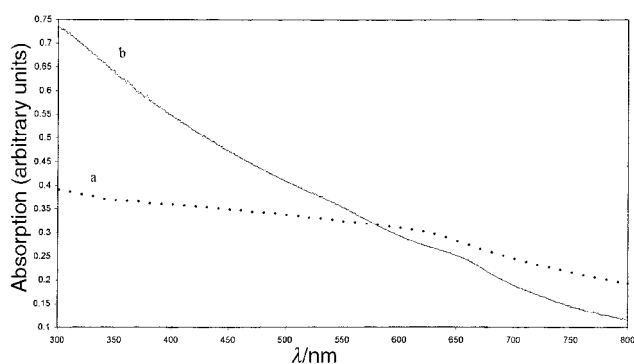

Fig. 4 The UV-VIS absorption spectrum of the (a) hexagonal CdSe ($E_g = 1.93$ eV); (b) cubic form of CdSe ($E_g = 1.90$ eV).
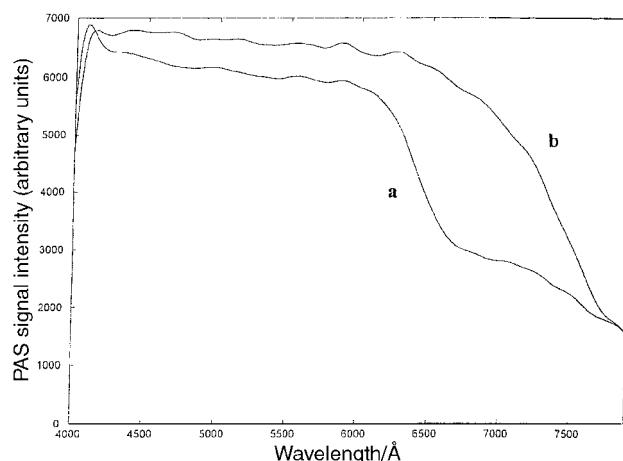

Fig. 5 The photoacoustic measurements of (a) hexagonal CdSe ($E_g = 1.95$ eV); (b) cubic CdSe ($E_g = 1.82$ eV).
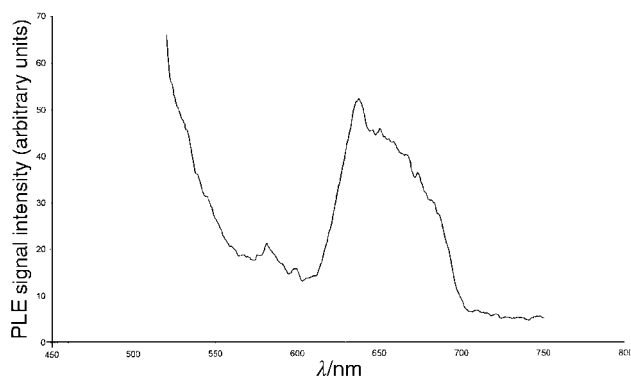
Fig. 6 The photoluminescence spectrum of hexagonal CdSe. The excitation wavelength is 480 nm. Emission peak at 640 nm (1.93 eV).

Photoluminescence studies

Fig. 6 shows the room temperature photoluminescence spectrum of the hexagonal CdSe obtained in ethylene glycol. The excitation wavelength was 480 nm. The PL spectra consist of a sharp emission peak at 640 nm (1.93 eV), and a shoulder at approximately 660 nm. The PL emission at 660 nm is assigned to the surface states and defects, which can only be fully resolved at low temperature. The sharp emission band is blue shifted by 80 nm relative to the PL peak of bulk CdSe (720 nm), indicating the existence of a quantum size effect. On the basis of the previously measured dependence of the position of the PL peak *vs.* crystallite size, the average diameter of 5.3 nm is obtained.[31] This value is smaller than the size measured by the other techniques, but within the error limits of those techniques.

XPS studies

XPS was used in order to derive compositional information about the as-prepared compounds. In Figs. 7a and 7b we represent the high-resolution XPS spectra. For both crystallographic forms of CdSe, peaks of $Cd3d_{5/2}$ and $Cd3d_{3/2}$ were detected at approximately 404.5 and 411.3 eV (see Fig. 7a). The peaks of the unresolved doublet of Se ($3d_{5/2,\ 3/2}$) are measured at 53.4 eV (see Fig. 7b). The energies for Cd and Se are in good agreement with the literature values for the binding energies of Cd and Se.[32–34] For both the hexagonal and cubic CdSe no peaks apart from Cd, Se, C and O are detected. There is no evidence for the appearance of shake-up peaks. The areas under the bands of Cd and Se are measured in order to the calculate the Cd : Se ratio. A non-linear least-square curve-

fitting program was employed to evaluate the areas, with an estimated error of ∼10%. This is due to the uncertainty in the precise shape of the background.[33] In the case of hexagonal CdSe the ratio Cd : Se is approximately 2 : 1, but in the case of the cubic form it is 1 : 1. It should be noted that XPS monitors only the surface of the particles. We explain this difference in stoichiometry and the Cd_2Se ratio as being due to the presence of the low density shell around the "nanoball" existing only for hexagonal CdSe (see Fig. 3a and the insert). Additional information about the structure of this shell is obtained from the analysis of the carbon peaks observed in the XPS spectrum. XPS, being a surface analysis method, always detects the contamination peaks of carbon and oxygen absorbed from the atmosphere and/or solvent. For hexagonal CdSe the percentage carbon content is always higher than for cubic CdSe. The Cd_2Se is related to the shell observed for the hexagonal phase and is depicted in Fig. 3a–b. It does not show any crystallinity and is accordingly assigned to an amorphous phase. We associate the formation of the amorphous phase with the presence of a relatively high percentage of carbons (up to 8%). Any attempt to account for the Cd : Se 2 : 1 ratio would be speculative at this stage.

Conclusions

To summarize, CdSe nanoparticles are prepared in two different solvents, ethylene and triethylene glycol, using the microwave-assisted polyol reduction method. When ethylene glycol is used "nanoballs" having a 346 nm diameter are detected by TEM and SEM. They are composed of much smaller, 6–7 nm diameter, hexagonal CdSe phase particles. When triethylene glycol is used as the solvent, particles and not nanoballs are obtained. We have also demonstrated that they are agglomerated 6 nm diameter CdSe particles having a cubic phase structure. The main advantages of the current process are its simplicity, efficiency, and the relatively low temperatures required.
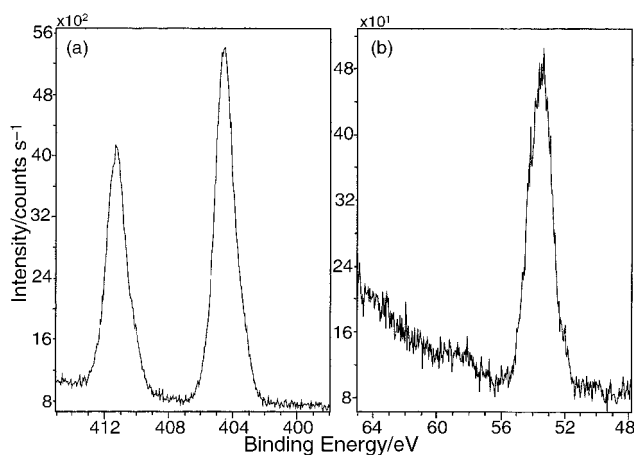
Fig. 7 The HR-XPS pictures of hexagonal CdSe: (a) doublet $Cd3d_{5/2}$ and $Cd3d_{3/2}$ were observed at approximately 404.5 and 411.3 eV and (b) the peak of the unresolved doublet of Se ($3d_{5/2,\ 3/2}$) was observed at 53.4 eV.

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