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Microwave Assisted Preparation of CdSe, PbSe, and Cu_{2-x}Se NanoparticlesJunjie Zhu,[†] O. Palchik, Siguang Chen, and A. Gedanken*

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Nanoparticles of various dimensions of II–VI binary chalcogenides CdSe, PbSe, and Cu_{2-x}Se, have been prepared by a very simple fast reaction between acetates or sulfates of Cd, Pb, and Cu and Na₂SeSO₃ in the presence of complexing agents, using microwave irradiation. The nanoparticles were analyzed by X-ray diffraction (XRD), electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Introduction

In recent years there has been considerable interest in semiconductors of nanometer dimensions due to the quantum size effect that they exhibit.^{1–3} Semiconductor selenides have already found applications as sensors, laser materials, optical filters, solar cells, and many other devices.^{4–6} Several methods have been used for the preparation of selenides, such as gas-phase reactions between the element or its compounds and gaseous H₂Se,⁷ solid-state reactions,⁸ chemical bath deposition,⁹ and pyrolysis of single source precursors.^{10,11} Generally all these reactions require high temperatures (~500 °C), and the use of toxic and highly sensitive precursors.

Heating by microwave has been known since the early 1940s and has been used successfully in the food industry. Microwave irradiation as a heating method has found a number of applications in chemistry since 1986, especially in the work of Mingos.¹² Many successful examples of the applications of MW heating in organic chemistry have been reported,¹³ although its expansion to inorganic chemistry has been much slower. The effect of heating is created by the interaction of the dipole moment of the molecules with the high frequency electromagnetic radiation (2.45 GHz). Water has a very high dipole moment which makes it one of the best solvents for microwave assisted reactions. However there are many microwave phenomena which are poorly understood, such as nonthermal effects and the superheating effect.^{12,14}

In this paper, we report a novel method for the preparation of semiconductor selenides. In this method CdSO₄, Pb(Ac)₂, and CuSO₄ react with Na₂SeSO₃ in water in the presence of complexing agents: potassium nitrilotriacetate (N(CH₂-COOK)₃-NTA) for CdSe and PbSe or triethanol amine for Cu_{2-x}Se. All the reactions were conducted in a microwave refluxing system, which was described elsewhere.¹⁵

Experimental Section

Transmission electron microscopy was performed using a JEOL-JEM 100SX Instrument. The powder X-ray diffraction patterns were recorded using a Rigaku 2028 Cu K α X-ray diffractometer ($\lambda = 1.5418$ Å); nickel was used as the filter. X-ray photoelectron spectra (XPS) were recorded using an

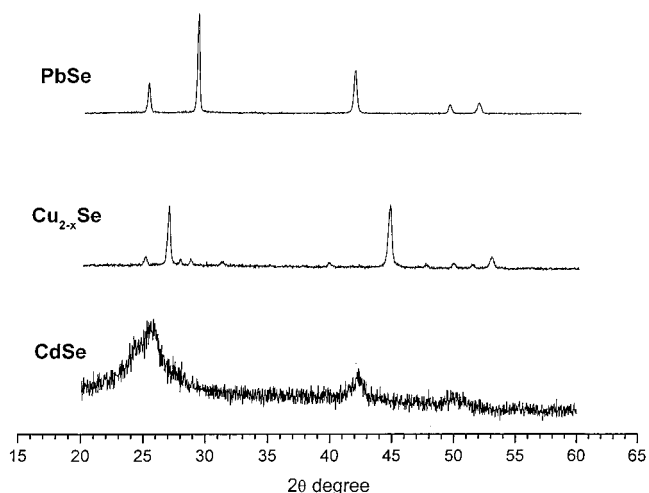


Figure 1. XRD patterns of as prepared selenides: (a) CdSe; (b) Cu_{2-x}Se; (c) PbSe.

AXIS, HIS, 165, ULTRA (KRATOS ANALYTICAL). Reflectance spectrum was carried out on a Cary (varian 1E) spectrophotometer. The PL spectrum was obtained using a Perkin-Elmer Luminescence spectrometer (model LS50B). The excitation wavelength was 650 nm. The electrolyte was based on that by Hodes¹⁶ and Mondal.¹⁷ Selenides were prepared using the following typical procedure. An aqueous solution of CdSO₄, complexed with potassium nitrilotriacetate, was mixed with an aqueous solution of Na₂SeSO₃ to give a final concentration of 80 mM each of CdSO₄ and Na₂SeSO₃ and 160 mM NTA with a pH between 9 and 10 (pH adjustment was made with KOH). Immediately after mixing, the solution was placed in a microwave refluxing system for 10 min at 80% power. (The meaning of 80% power is that the microwave operates in a 20 s cycle: on for 16 s, off for 4 s). The total power is still 900 W. At the end of the reaction the precipitate was centrifuged, washed repeatedly with acetone and dried under vacuum. The compounds obtained were stored under air.

Results and Discussion

XRD Study. The as-prepared chalcogenides were characterized by X-ray powder diffraction, which showed a perfect match with the diffraction pattern published in the literature. The average crystalline size was determined from the Debye–Scherrer equation. The XRD patterns are shown in Figure 1. In

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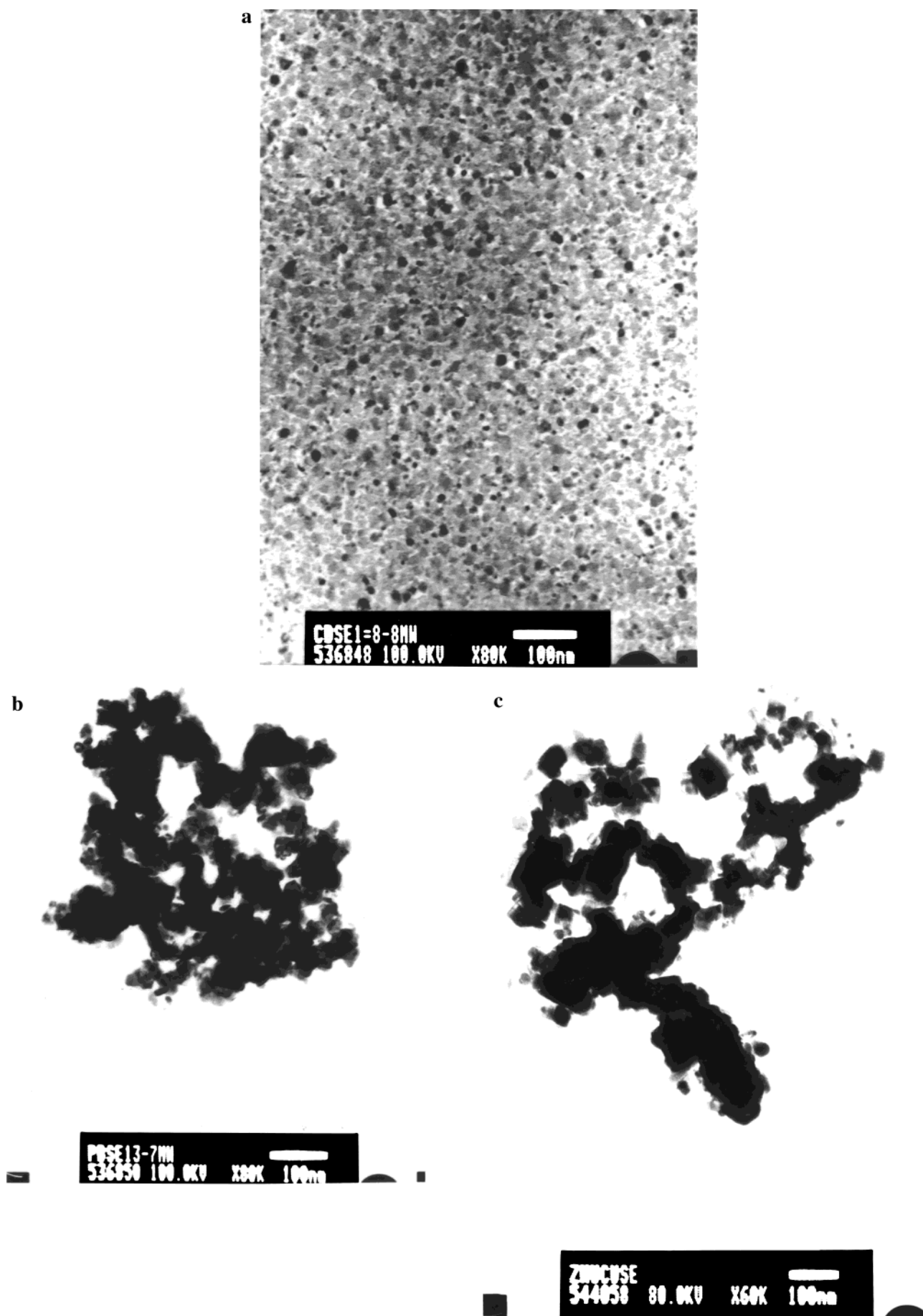


Figure 2. TEM images of as prepared selenides: (a) CdSe; (b) PbSe; (c) Cu_{2-x}Se.

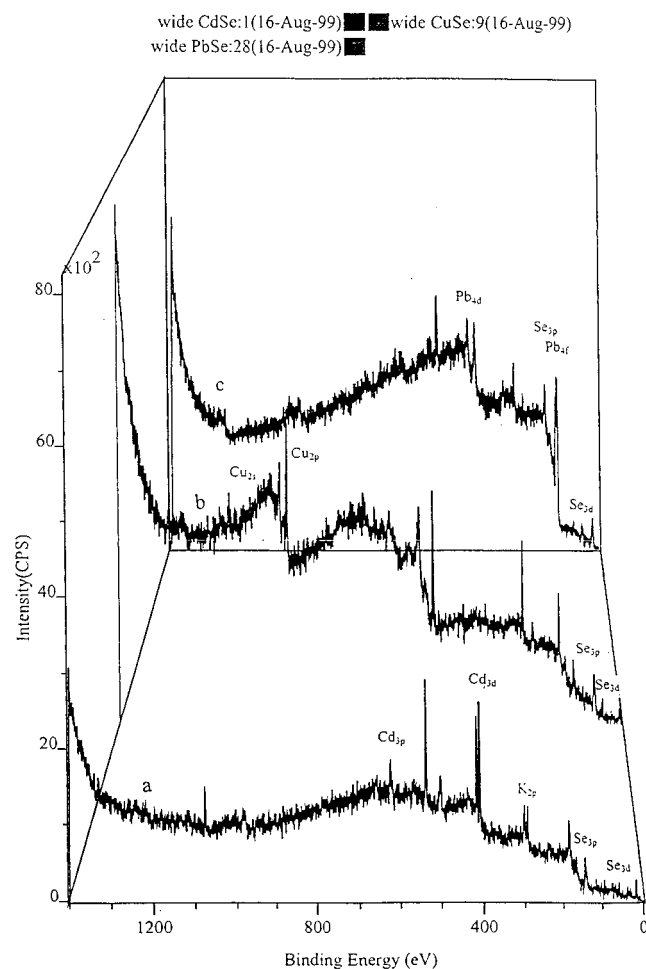


Figure 3. XPS pictures of as prepared selenides: (a) CdSe; (b) Cu_{2-x}Se ; (c) PbSe.

the case of CdSe, the broad XRD peaks indicate a diameter of 4–5 nm. CdSe was obtained in the cubic (sphalerite) phase. Unlike the broad peaks detected for CdSe, the XRD pattern of PbSe presents very sharp and strong peaks, which are indexed as cubic phase PbSe, indicating very good crystallization of the product. No impurity peaks are detected. Crystalline size calculation gives an average diameter of about 40 nm. The strongest peaks detected in XRD pattern of copper selenide are indexed to cubic Cu_{2-x}Se (JCPDS 6-680), but very small peaks that are assigned to Cu_3Se_2 impurity (JCPDS 19-402) are also observed.¹⁸ Grain size is about 50 nm.

TEM Measurements. The morphology of the prepared nanoparticles was studied by Transmission Electron Microscopy (TEM). Figure 2a shows a typical image for CdSe nanoparticles. Their average diameter is 4–5 nm. Figure 2b shows a typical microphotograph of PbSe. The shape of these nanoparticles is irregular, close to spherical, aggregated, with diameters ranging from 30 to 40 nm, which is in agreement with XRD. Figure 2c shows Cu_{2-x}Se nanoparticles. Similar to PbSe, the shape of Cu_{2-x}Se was close to spherical and the average diameter is ~50–80 nm. Aggregation was also observed.

XPS Measurements. The as-prepared nanoparticles were also characterized by X-ray Photoelectron Spectroscopy (XPS) for evaluation of their composition and purity. Wide scan spectra of selenides are shown in Figure 3 a-c. The binding energies obtained from XPS analysis show good agreement with results published by others.^{19–21} In all three cases we observed some impurities of potassium which are present in the complexing agents. The Cd:Se and Pb:Se atomic ratios are 1:1, and in the

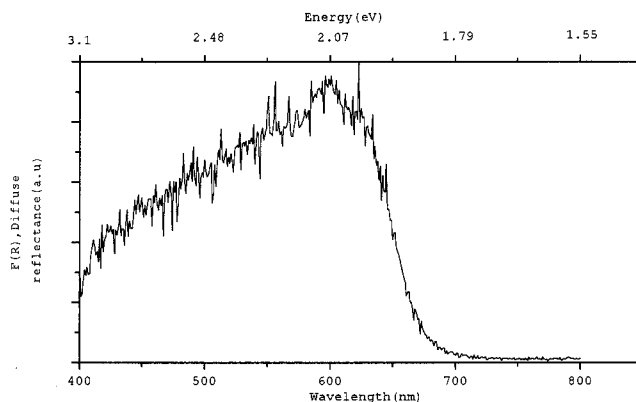


Figure 4. Diffuse reflection spectrum of a glass coated with CdSe nanoparticles.

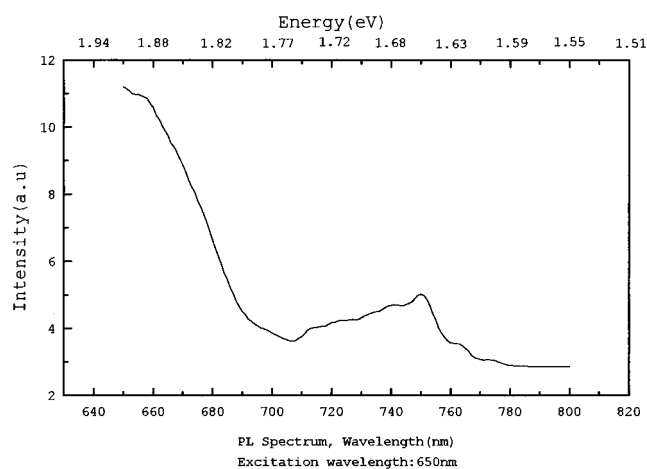


Figure 5. PL spectrum of an ethanol solution containing CdSe nanoparticles. Excitation wavelength: 650 nm.

case of Cu_{2-x}Se the proportions between Cu and Se are 2.2:1. This is because of the presence of a small amount of the impurity of Cu_3Se_2 , which is observed in the XRD analysis.

Optical Properties. We have carried out the optical diffuse reflection spectra measurement of CdSe powder in order to resolve the excitonic or interband (valence-conduction band) transitions of CdSe, which allows us to calculate the quantization energy. Figure 4 depicts the optical diffuse reflection spectrum of the CdSe powder. From the spectrum, we can roughly estimate the band gap of CdSe as ca. 1.90 eV. The value of the band gap energy is larger than that of the reported value for bulk CdSe (ca. 1.70 eV).^{23,24} As expected for quantum-size particles, the position of the first electronic transition was shifted to higher photon energies and became more pronounced with decreasing particle size in accordance with the size quantization effect.^{24–26}

Figure 5 shows the PL spectrum of an ethanol solution containing CdSe nanoparticles. The PL spectrum of the CdSe shows a broad emission band peaked at ca. 750 nm, using a 650 nm excitation wavelength. The band is strongly red shifted in comparison with the absorption edge. This kind of photoluminescence is ascribed to an emission from deep surface traps.²⁴ The broader emission peak at 650 nm may be indicative of size quantization.^{24,27,28}

Effect of Other Factors. In this experiment several other factors were found to affect the quality of the product. The pH of the reactions is one of the most important factors: a pH range of 9–10 is optimal, and no products were obtained at a lower pH. The reason for this dependence is probably due to the

oxidation and reduction potentials of Se and S, which are pH dependent. In addition, if the pH of the solution is lower than 7, free Se is released.

By using different microwave reaction times, different phases of CdSe were obtained. A 10 min irradiation led to the formation of CdSe in the cubic (sphalerite) phase. Longer reaction times caused a phase transition. When the reaction was conducted for 30 min, CdSe was obtained in the cadmoselite phase (PDF2 08-0459). This is a hexagonal phase which differs from the cubic (sphalerite) phase, which is obtained after 10 min. It is worth mentioning that Xie and co-workers²⁹ also obtained the hexagonal cadmoselite phase in a solvothermal reaction carried out at 120° C for 6 h under pressure.

Complexating agents also play an important role: they can slow the reaction rate and cause the particle size to be smaller. Reactions conducted without complexating agents were unsuccessful. In this case immediately after the beginning of the reaction (even before addition of the Na₂SeSO₃) Cd(OH)₂ precipitated.

The small dimensions and high monodispersity of the CdSe and PbSe are intriguing. The small dimensions of CdSe may be related to nucleation and a very slow growth process, which prevents particles from growing during the time scale of the experiment. In the case of PbSe, nucleation and growth are almost simultaneous and fast, yielding lower monodispersity and larger nanoparticles. In sonoelectrochemical experiments, we find similar phenomena, for example, the size of CdSe is smaller than that of PbSe.^{23,30} A comparison reveals that although the size of CdSe is the same as that of the sonoelectrochemical product, the size of PbSe is 3 times larger than that obtained in sonoelectrochemistry. We explain this phenomenon as due to the high rate of the reactions resulting from the microwave irradiation. These findings show that microwave irradiation can influence the selectivity of the nucleation and the growth rates of different compounds.

Summary

CdSe, PbSe, and Cu_{2-x}Se nanoparticles have been prepared by the microwave method. The advantages of this process are that it is a simple and efficient method for producing nanoparticles. We can foresee the upscaling of the process to form large quantities of this kind of nanomaterials.

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