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CdS nanoparticles mechanochemically synthesized in a high-energy mill

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This paper describes the structural and surface properties of cadmium sulphide nanoparticles synthesized in a planetary mill. CdS nanoparticles were prepared by the mechanochemical route from cadmium acetate and sodium sulphide precursors. The structure of the as-prepared products was characterized by X-ray powder diffraction which reveals the crystalline nature of CdS nanoparticles. Cubic β-CdS (hawleyite) is the only product of mechanochemical synthesis. SEM, TEM and low temperature nitrogen sorption were used to analyze the particle size and morphology as well as surface composition. The SEM measurements show the aggregates of small nanocrystals in which particle sizes approximately of 2 nm were calculated by application of Williamson-Hall as well as Warren-Averbach method. The TEM confirms the aggregate formation of CdS nanoparticles due to the extremely small particle size and tendency to lower high surface energy. The optical properties of CdS nanoparticles were studied by UV-VIS spectroscopy. UV-VIS spectrum shows an obvious blue shift, which is the result of the quantum size effect. The main advantages of mechanochemical synthesis in the production of CdS nanoparticles is in the formation of uniform crystallites and particles with large surface area in comparison with CdS prepared by chemical route. The cadmium sulphide nanoparticles are obtained in the simple step, making the process attractive for industrial applications.

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1. Introduction

The concept of high - energy ball milling of solids has been applied in the frame of mechanochemistry [1-2], which is now dealing with the new fields of study such as synthesis and characterization of nanocrystalline substances and smart materials for the 21st century.

Mechanochemical synthesis is one possible route which can effectively control and regulate the course of the solid state reactions. The process is characterized by the repeated welding, deformation and fracture of reacting particles during ball-powder collisions, resulting in the formation of nanocomposite mixture of the reactant within each particle. The chemical reaction occurs at the interfaces of the nanometer sized grains that are continually regenerated during milling. As a consequence, reactions, that would normally require high temperatures to occur, due to separation of the reacting phases by the product phases, can occur at low temperature in a ball mill. An important feature of the process is the rapid refinement of the particle microstructure, i. e. grain size or crystallite size, during milling. While powder particle sizes generally decrease only to the micrometer level, a nanometer grain size is developed within each particle. In addition, the high defect densities induced by high-energy milling accelerate the diffusion process [3-9].

The preparation and characterization of various nanocrystalline chalcogenides have attracted considerable attention due to their important nonlinear properties, luminiscent properties and other important physical and chemical properties [10]. The main cause is in their unusual properties based on the high concentration of atoms in interfacial structures and the relatively simple ways of their preparation. Nanoparticles of chalcogenide semiconductors have many potential applications in the area of advanced materials.

Cadmium sulphide is an important semiconductor for a variety of applications including solid-state solar cell windows, laser communications, photoconductors, field effect transistors, sensors, and high-emitting applications. Therefore, much extensive studies on CdS particles and their physicochemical properties has been carried out and many methods have been used for the preparation of this material [11-17]. Some CdS nanoparticles were already synthesized by high-energy milling from chloride precursors [18-20].

The main aim of this work was to prepare CdS nanoparticles by a non-traditional mechanochemical synthesis applying high-energy milling in a laboratory planetary mill and to compare their properties with chemically synthesized CdS particles.

2. Experimental

Mechanochemical synthesis of nanocrystalline CdS was performed in a laboratory planetary mill Pulverisette 6 (Fritsch, Germany). The following milling conditions were used: loading of the mill with 50 balls of 10 mm diameter; weight charge of the total powder mixture in the mill: 10.5

g; ball charge in the mill: 360 g; material of milling chamber and balls: tungsten carbide; rotation speed of the planet carrier: 500 rpm; milling time in an argon atmosphere 5-20 minutes.

CdS nanoparticles were prepared by high-energy milling of cadmium acetate and sodium sulphide precursors according to the reaction

$$(CH_3COO)_2Cd.2H_2O + Na_2S.9H_2O \rightarrow CdS + 2CH_3COONa + 11H_2O \quad (1)$$

The reaction is thermodynamically feasible at ambient temperature, as the enthalpy change is negative. The value ΔH°_{298} =-253 kJmol^{-1} was calculated from thermodynamic data published in [21].

After the completion of reaction (1) produced CdS nanoparticles have been washed, decantated and dryied according to the flow chart shown in Fig. 1.

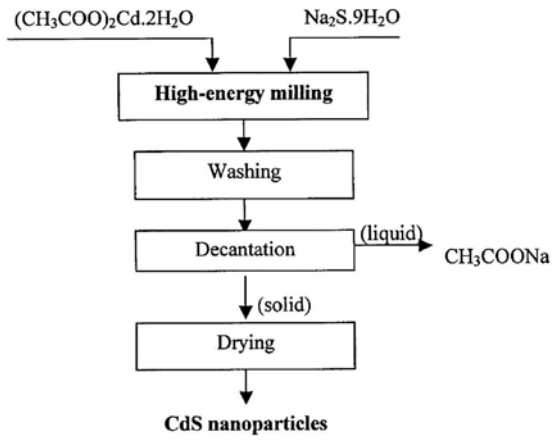

Fig. 1. Flow chart of the CdS nanoparticles preparation.

For comparison the properties of chemically synthesized CdS (Fluka, 98%) have been studied.

The XRD measurements were performed by employing a X-ray diffractometer Siemens D5000 bearing Bragg-Brentano geometrical configuration. The X-ray radiation source was a Cu with $\lambda = 1.5406$ Å. Measurements were made for 2θ values over 20-70° in steps of 0.02° with a count time of 5 s. The Profile software supplied by Bruker/Socabin was used in the pattern decomposition (profile fitting) procedures and in the extraction of the parameters. The profile fitting procedure and principles of the methods were discussed in detail in paper [22].

The specific surface area was determined by nitrogen sorption method at liquid nitrogen temperature using a Gemini 2360 apparatus (Micromeritics, USA).

The synthesized semiconductors were analyzed using FE-SEM LEO 1550 scanning microscope in order to investigate the surface morphology of the nanoparticles. The samples were left uncovered from any conductive material as to keep their original properties.

The transmission electron microscopy was taken on 2000FX TEM microscop (Jeol, Japan).

UV-VIS spectroscopy was performed on spectrophotometer HELIOS GAMMA (Great Britain) in the range 200-800 nm in quartz cell by dispersing of synthesized particles in absolute ethanol by ultrasonic stirring.

3. Results and discussion

The XRD pattern of the chemically synthesized sample (Figure 2) appears to be composed of the hexagonal (α- CdS, greenockite, JCPDS 041-1049) and cubic (β-CdS, hawleyite, JCPDS 010-0454) phases. The peaks at 26.5, 43.7 and 51.9° are associated with both phases. The presence of the small peak at 31.5° also gives evidence for the existence of cubic phases. In addition, the comparison of the relative intensities of the XRD pattern of the sample with JCPDS data files (Table 1) reveals that the peaks associated with both phases of CdS have relatively higher intensity, suggesting once more the presence of both phases in the chemically synthesized sample. However, the hexagonal phase is dominant phase in the sample with regard to low intensity of the 200 reflection and only traces of cubic phase exist in the sample. The small peaks at around 23° are most likely due to the chemical reaction residuals.

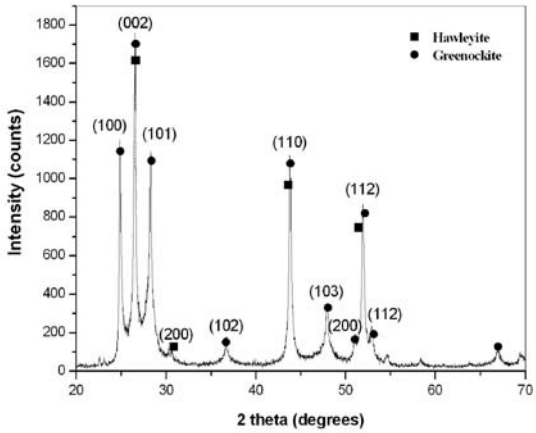

Fig. 2. XRD pattern of the chemically synthesized CdS.

XRD pattern of CdS nanoparticles synthesized by high-energy milling in a laboratory mill is displayed in Figure 3. XRD pattern shows mainly the reflections of cubic phase. It is also supported by relative intensity as well. No reflection peaks was found at 2θ = 36.6° and 47.8°, which are present only in the hexagonal form of CdS. The (022) reflection of the cubic phase at about 31° is probably masked due to a large broadening of the (111) reflection. The peaks associated with hexagonal phase

disappear with milling and only the cubic structure is evident in the diffraction pattern of the milled sample. This is in a good agreement with observations of Tsuzuki and McCormick [18] where they mechanochemically synthesized CdS by chloride route. The higher background on the XRD pattern of mechanochemically synthesized CdS implies the formation of some poorhouse material. The amorphization is in fact a highly distorted periodicity of lattice elements, and it is often characterized as a short range order in contrast to the long order of a fully crystalline structure.

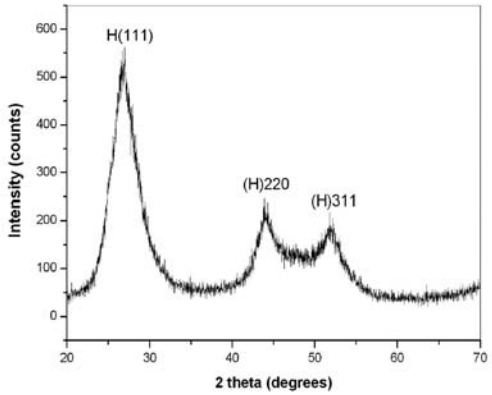

Fig. 3. XRD pattern of mechanochemically synthesized CdS nanoparticles (H-hawleyite).

Table 1. Comparison of the JCPDS diffraction data and experimentally measured data.

Greenockite			Hawleyite		
hkl	*Relative intensity*		*hkl*	*Relative intensity*	
	JCPDS	*measured*		*JCPDS*	*measured*
100	62	70.9	111	100	100
002	91.9	100	200	39.8	--
101	100	66.8	220	80.5	40.4
102	29.2	10.2	311	60.2	34.3
110	48.3	66.2	222	10.2	--
103	50.2	19.2	400	20	--
200	8.1	10.4	311	30	--
112	31	49.0	420	10	--
201	15	12.8	422	30	--

Fig. 4 shows the Williamson-Hall plots for mechanochemically (1) and chemically (2-3) synthesized samples. The scatter of the β_f^{*2} values for the chemically synthesized sample with low correlation coefficient indicates that the crystallite shape differs from a spherical one. In addition, the (10l), $l \geq 1$ reflections show higher deviation than other reflections. The Williamson–Hall plots for the chemically synthesized sample yields very small slopes close to zero which implies the sample is free of strain. Two main crystallite groups are expected in the chemically synthesized sample. For chemically synthesized samples 2 and 3 (10l), $l \geq 1$ the average volume weighted crystallite size are calculated using the intercept of the corresponding lines, being 14.4 nm and 2.6 nm respectively. The crystallite with 14.4 nm is dominant group in the sample. The corresponding plots yield low correlation coefficient (r<0.5).

Regarding the mechanochemically synthesized sample (1), the presence of non zero slope and intercept reveals that both size and strain components exist in the sample. The plot shows high correlation coefficient (r=0.991) and negligible scatter in the β_f^{*2}, suggesting uniform crystallites. The mechanochemically synthesized sample yields larger broadening compared to the chemically synthesised sample. The volume weighted crystallite and maximum lattice strain are calculated 1.92 nm and 3.1×10^{-2} respectively.

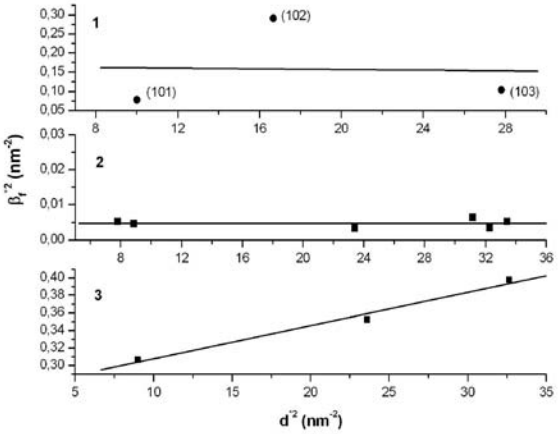

Fig. 4. Williamson-Hall plot of mechanochemically synthesized CdS nanoparticles (1), chemically synthesized CdS (2) and chemically synthesized CdS nanoparticles (10l), $l \geq 1$ *(3).*

The Warren-Averbach analysis based on Fourier analysis provides detail information regarding to crystallite size, lattice strain and their distributions. For the mechanochemically synthesized CdS (cubic phase), the Warren–Averbach method was applied to calculate both strain and crystallite size components. The three intensive reflections were used for calculation. The analysis once more revealed a narrow fraction of crystallites in the sample. The average surface weighted crystallite size was obtained 1.55 nm and the root mean square strain (RMSS) at L=1 nm, $< \varepsilon_{L=1nm}^2 >^{1/2}$, accounted for 1.7×10^{-2}. As discussed in work [22], the results of the Williamson–Hall plots and Warren-Averbach methods with regard to their relationships are in a good agreement.

The results of the chemically synthesized sample using the Warren-Averbach and Scherrer approach for

different reflections and direction [10l] $l \geq 1$ are given in Table. 2. Since the chemically synthesized sample is free of strain, the Scherrer equation can be applied successfully for calculation of the weighted crystallite size. From the Warren-Averbach method, the average surface weighted crystallite size for (10l), $l \geq 1$ and other reflections are calculated about 2.4 and 6.2 nm, respectively, corresponding to the volume weighted crystallite size of 2.5 and 12.4 nm obtained using Scherrer equation. The results of the Scherrer equation show directly good agreement with the results of the Williamson- Hall plots because both the methods measure the volume weighted crystallite size. The obtained results from the Warren-Averbach method and Williamson hall plots are comparable.

Table 2. The obtained crystallite sizes for chemically synthesized CdS using Warren-Averbach and Scherrer methods.

Reflection	Warren-Averbach	Scherrer
(100)	6.8	12.7
(111)	7.1	13.5
(110)	6.4	14.3
(200)	4.9	10.0
(112)	7.3	13.3
(201)	4.5	10.8
Average	**6.2**	**12.4**
(101)	2.9	3.4
(102)	2.4	1.7
(103)	1.8	2.6
Average for (10l)	**2.4**	**2.5**

Surface morphology of the synthesized CdS nanoparticles with estimated size from 20-30 nm is depicted in Figure 5. Individual nanoparticles have tendency to form nanoparticle agglomerates during milling process and both entities can be clearly seen.

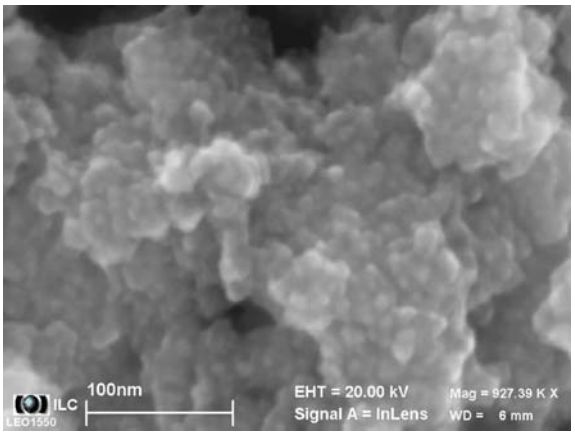

Fig. 5. SEM of mechanochemically synthesized CdS nanoparticles.

The particle morphology of CdS nanoparticles was also observed using TEM. Image of the mechanochemically synthesized CdS is presented in Figure 6A. Because of the extremely small dimensions and high surface energy of the as-prepared CdS nanoparticles, it is easy for them to aggregate. So, it was difficult to determine precisely the size of CdS nanoparticles by simple viewing the TEM image.

We suppose that each particle is composed of fine nanocrystallites, whose sizes were determined by XRD technique. Thus, each particle observed in the TEM micrographs was of polycrystalline nature. Selected area electron diffraction (SAED) pattern corresponding to random orientation of CdS particles is shown in Figure 6B. The presence of (111), (220) and (311) planes clearly suggests presence of hawleyite phase.

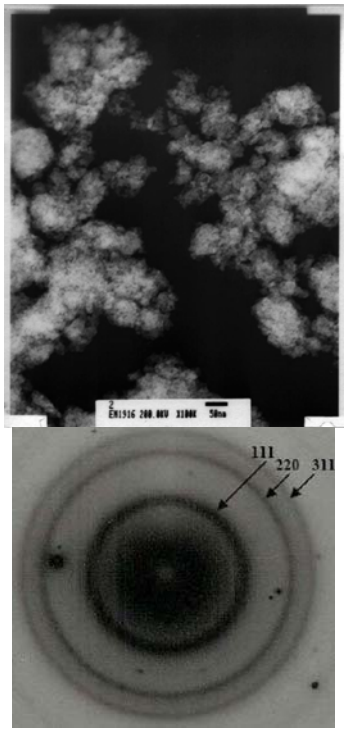

Fig. 6. Transmission electron micrographs (A) and SAED (B) of mechanochemically synthesized CdS nanoparticles.

The optical properties of CdS nanoparticles can be elucidated from the UV-VIS spectrum of the as-synthesized product. UV-VIS optical absorption spectrum of the mechanochemically (1) and chemically (2) synthesized CdS particles are shown in Figure 7. The spectrum of mechanochemically synthesized nanoparticles (1) showed that the onset of the optical absorption 464 nm was blue-shifted compared with that for bulk CdS which is 512 nm. This blue shift was caused by strong quantum confinement effect, due to the decrease in particle size [23]. The band gap of CdS nanoparticles was calculated to be about 2.67 eV, greater than that of 2.42 eV estimated

for the bulk CdS [24]. The relation between this shift and the crystallite size is defined by Brus equation [23]. According to this equation we calculated for mechanochemically synthesized CdS the crystallite size 2.1 nm which is in a good agreement with XRD analysis. The typical UV-VIS spectrum of the chemically synthesized CdS particles is shown in the same Figure, where the curve (2) has an onset at 500 nm with calculated band gap (2.48 eV) and calculated crystallite size 3.5 nm.

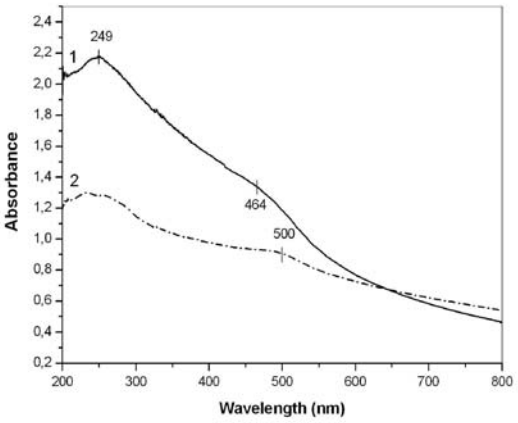

Fig. 7. UV-VIS spectra of mechanochemically synthesized CdS nanoparticles (1) and chemically synthesized CdS nanoparticles (2).

The specific surface area of chemically synthesized CdS particles (13 m^2g^{-1}) is 5-times lower in comparison with mechanochemically synthesized CdS particles. The specific surface area of mechanochemically synthesized CdS nanoparticles (54-60 m^2g^{-1}) increased with the increasing milling time. It is further advantage of mechanochemical synthesis of CdS nanoparticles.

4. Conclusions

The presented paper describes structural and surface properties of the cadmium sulphide nanoparticles synthesized in the planetary mill. The cubic structure of which the peaks associated to (111), (220) and (311) planes were clearly identified. Cadmium sulphide nanocrystallites with particle size 2 nm synthesized in the planetary laboratory mill show quantum-size effect. The mechanochemically synthesized CdS nanoparticles in comparison with chemically synthesized CdS are distinguished by their physicochemical properties. The advantage of mechanochemical synthesis in the production of CdS nanoparticles is in the production of particles with large surface area as well as the uniform crystallites compared with CdS synthesized by chemical route. High-energy milling has considerable possibility for easily scaling up the production of nanocrystalline materials under ambient conditions in reasonable time without the invention of any solvent.

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