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Laser assisted solid state reaction for the synthesis of ZnS and CdS nanoparticles from metal xanthate

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ABSTRACT

Nanoparticles of CdS and ZnS were produced by a nanosecond laser using zinc (II) and cadmium (II) complexes of ethyl xanthate. Laser pulses with a peak wavelength of 355 nm, pulse repetition rate of 10 Hz, and pulse duration of ~4 ns were used. The sample exposure time were 10 min and 30 min respectively. The obtained nanoparticles were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible spectroscopy (UV–vis) and photoluminescence (PL) spectroscopy. The morphology and optical property of the synthesized nanoparticles were investigated as a function of the time of exposure. Upon extensive irradiation, the crystallinity of the CdS nanoparticles increased while the crystallinity of the ZnS nanoparticles decreased. The average crystallite size of the CdS nanoparticles estimated from the TEM image was 4.8 nm, while the presence of aggregates with no crystalline edges impeded the size determination of the ZnS nanoparticles. The absorption spectra showed that the nanoparticles exhibit quantum confinement.

1. Introduction

Nanocrystalline materials have attracted much attention in recent years due to the change, at nanoscale, which occurs when their crystallite radius becomes comparable to the exciton Bohr radius. Zinc sulfide and cadmium sulfide are among the widely studied II–VI group semiconductors because they show significant quantum confinement effects which influence their electrical and optical properties [1,2]. They have found applications particularly in photovoltaic, photonic, and optoelectronic devices and sensors [3].

The syntheses of the II–VI group of nanoparticles have been achieved using different techniques which include thermolysis of a single-source precursor [4,5], solventothermal [6], sonochemical [7], and colloidal precipitation [8]. However, most of these techniques are complex to perform with limited control over particle size [9].

Recently, interaction of radiation with matter has been reported as an efficient method for the synthesis of nanoparticles. Examples are microwave irradiation [10–13] as well as gamma ray irradiation in oil-in-water systems, the latter which was reported as an efficient method for the synthesis of mesoporous CdS semiconductor nanoparticles [14]. Production of nanoparticles by the use of laser irradiation either in gas or in vacuum has been explored during the last decade [15]. Laser irradiation of bulk molecules and subsequent decomposition into the nanoparticulate forms presents a simple route to the synthesis of nanoparticles. The laser activates the initial decomposition of the precursor and facilitates its conversion to the desired products under mild conditions. The entire procedure takes place in few hundreds of ns interaction time (s), since the nanoparticles are formed from the very first pulses of some nanoseconds (ns) duration [16]. A number of studies have exploited the use laser irradiation of precursor materials for the synthesis of nanoparticles. For instance, syntheses of different noble metal nanoparticles by the ablation of metal surfaces immersed in liquid have been reported [17–20]. The surfactant surrounds each nanoparticle and prevents direct contact of the nanoparticles. The synthesis of II–VI compound semiconductor nanoparticles by the exposure of precursor compounds to laser radiation has been reported. Cadmium sulfide nanowires, and single crystalline three armed (nanotripods) CdS were prepared using a pulsed laser [21,22]. Athanassiou et al. reported the formation of zinc sulfide and cadmium sulfide nanocrystals, by the irradiation of Zn/Cd thiolate precursors with UV laser pulses [23,24]. The starting samples consist of polymers doped with the precursor complex which are decomposed after the absorption of UV light, resulting into the nanoparticles formation.

The precursor compounds used in this present study is the metal xanthate of zinc and cadmium. The decomposition of

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different metal xanthate precursors through thermolysis to produce metal sulfide nanoparticles have been reported [25]. Metal alkyl xanthates were used as the precursors in Lewis base alkylamine solvents. CdS nanoparticles capped with tri-n-octylphosphine oxide (TOPO) have been synthesized by a single-source route using cadmium ethyl xanthate as a precursor [26]. ZnS based thin films have been prepared by the decomposition of Zinc bis(O-ethyl xanthate) [27].However, selection of the solvent and the choice of the temperature for thermal decomposition still require further research [25].

The chemistry of laser synthesis of nanoparticles from a precursor complex is derived from the fact that the absorption of an intensive laser pulse creates transitional or thermo-elastic stresses, which can lead to fragmentation. In particular, the energies of individual chemical bonds in organic molecules are around 400 kJ/mol (e.g C–C, E=347 kJ/mol; H–H, E=437 kJ/mol; N–N, E=388 kJ/mol), which corresponds to the energy of near-ultraviolet (NUV) electromagnetic radiation. An NUV laser pulse with a sufficiently high energy density (i.e., intensity) will cause a large enough perturbation to break these chemical bonds [28,29]. The method has been reported as an effective, flexible and efficient technique for preparing various types of high purity nanoparticles [9].

Here we present our research results on the synthesis of ZnS and CdS nanoparticles by nanosecond laser irradiation of zinc (II) and cadmium (II) ethyl xanthate. The effect of the length of time of the laser irradiation exposure on the sizes and the crystallinity of the prepared nanoparticles were studied. We report the surface morphology of the nanoparticles, the crystalline quality, and the optical properties. To the best of our knowledge, a time dependent study of one-step, non-thermal, solid state reaction syntheses of ZnS and CdS nanoparticles via nanosecond laser irradiation from metal xanthate has not been reported. It is observed that the time of exposure to the laser irradiation has a significant effect on the properties of the nanoparticles synthesized.

2. Experimental

Materials: All the chemical reagents used for this study were obtained from commercial sources; they are of analytical grade and were used without further purification.

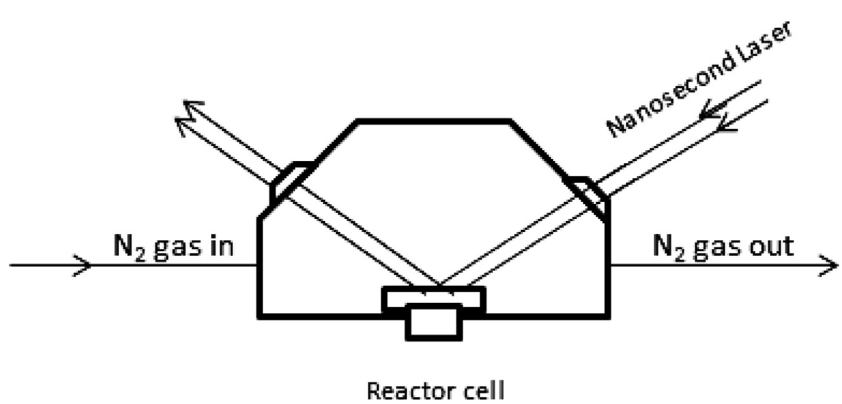
Synthesis of potassium ethyl xanthate: In a typical procedure (Zhang et al.) [30], 0.1 mol KOH powder was added into a beaker containing 0.11 mol absolute ethanol in a thermal bath at 50 °C, followed by intensive agitation. After 45 min, while still stirring, the solution was cooled down to room temperature and 0.10 mol CS_2 was added until a yellowish product precipitated. 100 mL of petroleum ether was added and stirring was continued for another 30 min. The solid precipitate was filtered, rinsed with ethanol and dried at room temperature. Purification of the product was carried out by recrystallization using acetone and petroleum ether. The product was filtered, and dried in vacuum.

Synthesis of cadmium and zinc ethyl xanthate: The precursor complexes cadmium and zinc ethyl xanthate, $[M(C_2H_5OCS_2)_2]$ (M=Cd, Zn), were prepared according to the procedure described as reported [31]. In a typical synthesis, 0.0025 mol of the metal salt (cadmium chloride/zinc chloride) was dissolved in 10 mL distilled water. A solution of potassium ethyl xanthate 0.8 g (0.01 mol) in 10 mL distilled water was added and stirred for 45 min. The white precipitate (pale yellow precipitate for cadmium complex) formed at the end of the reaction was filtered and rinsed several times with a mixture of ethanol-water, and dried under vacuum.

Sample preparation: The microscope glass slides were cleaned by rinsing in diluted HCl, and then sonicated in soap for 10 min, followed by flooding with distilled water. Finally, they were rinsed in acetone and dried in the oven overnight. The samples for laser decomposition were prepared by dissolving 0.5 g of the respective complex in 10 mL chloroform and stirring vigorously to obtain a homogeneous solution. The substrates were casted manually on glass slides to produce thin homogeneous film after evaporation of the solvents. Drying of the samples was carried out in vacuo at room temperature.

Preparation of nanoparticles: The nanocrystals were formed by irradiating the samples with short, high-intensity laser pulses. Third-harmonic pulses at 355 nm from an Nd:YAG Q-switched nanosecond laser (EKSPLA NT342B-SH-10-AW) were used. The pulse repetition rate was 10 Hz, while the pulse length and the pulse duration were <0.13 nm and ~ 4 ns respectively. The energy per pulse emanating from the laser source was determined as 11.00 ± 0.26 mJ and decreased by 15–16% before reaching the sample. Exposure times of 10 min and 30 min were used. The samples were positioned at the center of the reactor cell using microscope glass slides with dimensions 76 mm × 26 mm × 1 mm (LASEC). The laser beam was introduced into the chamber through a quartz window at an angle of $\sim 51^{\circ}$ with respect to the substrate normal to a diameter of ~ 20 mm at the substrate surface.

Sample characterizations: The absorption measurements were carried out using a PerkinElmer Lambda 20 UV–vis spectrophotometer at room temperature. A PerkinElmer LS 55 luminescence spectrometer was used to measure the photoluminescence of the nanoparticles. A Quanta FEG 250 Environmental Scanning electron microscope (ESEM) was used to investigate the surface morphology of the nanoparticles. A thin gold layer was deposited to improve the electrical conductivity for better imaging. A JEOL 2100 TEM, fitted with a LaB_6 electron gun was used for the TEM imaging. Samples were suspended in DMSO, sonicated for 1 min and dispersed on carbon-coated grids. Analysis was done at 200 kV, and images were captured using a Gatan Ultrascan digital



Scheme 1. Schematic diagram of the Laser set-up..