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SYNTHESIS OF ULTRASMALL $CD_{0.3}ZN_{0.7}$SENANOCRYSTALS VIA MECHANOCHEMICAL ROUTE

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ABSTRACT
Mechanical alloying through severe plastic deformation (SPD) was used to synthesize ultrasmall nanocrystals of ($Cd_{0.3}Zn_{0.7}Se$)with a diameter (d = 1.3 nm) after 20 hours milling time. A high-resolution electron microscope was (HRTEM) used to examine the mechanical deformation on the nanocrystals. The images reveal a bulk-like cluster structure without a distinctive regular shape. The atoms appear to be located entirely at the surface. The energy band-gap of the ultrasmall was determined to be 4.56 eV from UV-Vis absorption spectra.

Keywords: Mechanochemical synthesis; extremely small particles; optical property

INTRODUCTION

Ultrasmall or extremely small nanocrystals are particles with their size ranges from 1-2 nm (Chestnoy, Harris, & Hull, 1986)typically composed of (20 – 100) atoms. They are typically large molecules with exact atomic configurations rather than continuous lattice (Landes, Braun, & El-Sayed, 2001).They are termed "nanoclusters" because of the presence of tens to several thousands of atoms. In this case, it becomes almost impossible to differentiate between the surface and bulk atoms.

Ultrasmall nanocrystals have profound technological applications in micro-fabrication, telecommunication, and information-processing engineering. Their nonlinear optical can be exploited to fabricate optical switches and frequency converters(Remarks, 1991). Their unique broad-emission properties through the entire visible spectrum make them a strong candidate for biological labeling and energy-saving devices. They are used as solid-state lighting sources in the form of white-light-emitting diodes(WLEDs)(Dai, Duty, & Hu, 2010).Their potential applications in photovoltaic industries have been explored by shifting the energy levels to appropriately match the UV-visible spectrum without changing the main size(Teunis, Dolai, & Sardar, 2014).

The synthesis of Ultrasmall nanocrystals via a chemical route method had been reported in binary compounds such as CdSe and CdS (C.Gente,M.Oehring, 1993)(G. Tan, 2003). Chemical route methods involve the use of toxic chemicals that are not environmentally friendly.

In this report, we employ mechanical alloying through severe plastic deformation (SPD) for the synthesis of the ternary compound (CdZnSe). In this method, Intensive deformation under non-isothermal conditions generally occurs in high-energy milling devices(Hellstern, Fecht, Fu, & Johnson, 1989). The synthesis of the ultrasmall binary compound had been reported in CdTe nanocrystals using mechanical alloying. This method is considerably cost-effective devoid of toxic chemical

Experimental Procedure

Elemental Cd, Zn, and Se powders with a purity of 99.9%were purchased from Alta Aesar. The powders were thoroughly mixed with a nominal composition x=0.7 and sealed in an inert atmosphere in a stainless-steel grinding jar with 3 mm diameter steel balls. The ball milling was performed in PM100 (Retsch)with a ball-to-powder ratio of 10:1for up to 20 hours. The sample was milled at 500 revolutions per minute.

The optical spectra were monitored with a UV-Vis absorption spectrophotometer (UV-1650PC SHIMADZU JAPAN). The high-resolution transmission electron microscopy (HRTEM) micrographs were obtained using (Tecnai G F20 Series) at a 200 kV accelerating voltage in dark-field modes

RESULT AND DISCUSSIONS

Optical absorption in milled nanoparticles

The optical absorbance spectra of the nanocrystals were recorded as a function of the wavelength energy in a range of 200-800 nm. We observed the optical properties of mechanically alloyed nanocrystals that exhibit similar large bandgap to nanoclusters prepared via wet chemical methods.

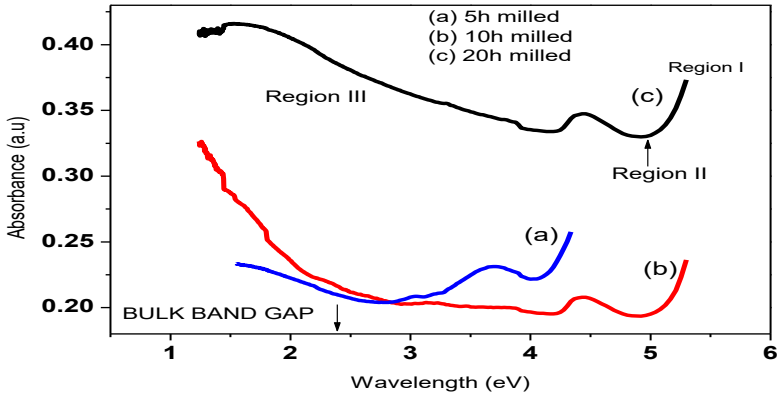

Fig. 1. Absorption spectra for the $Cd_{0.3}Zn_{0.7}$Senanoclusters after 20 hours of milling. The insert shows the absorption features at high photon energy.

Figure 1 shows the UV-visible absorption spectrum of extremely small$Cd_{0.3}Zn_{0.7}$Senanocrystals. In general, the absorption spectrum has three main regions as shown. The first region (I), can be related to optical mobility gap. Region II is associated with weak absorbance due to impurities in the alloyed nanostructure. In region III, the absorption coefficient increases exponentially with photon energy(Kang et al., 2006). This long-wavelength region has been attributed to surface states of the nanocrystals material; representing absorption by trapped carriers (Brus, 1986a). It can be seen that the "tail "of the absorption spectra increases with milling time, which implies smaller nanocrystals are been obtained thus, the surface state increases.

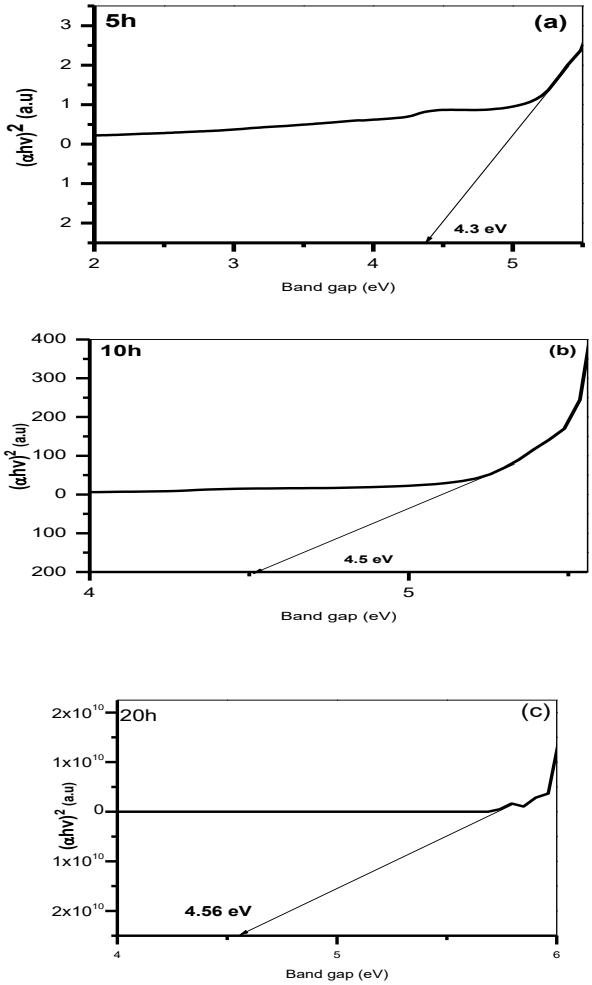

Figure 2 Tauc plots for 5, 10 and 20 h milled samples

The first excited electronic states are partially resolved as shown in Fig. 1(a-c).To obtain an accurate estimate of the energy bandgap, Tauc plots of the milled samples are presented in Fig 2(a-c).It can be seen that the spectra show large blue shifts in the fundamental absorption edge reflecting an increase in the bandgap energy. The band edge blue shift of ~ 2.3eVfrom the bulk (bulk bandgap of $Cd_{0.2}Zn_{0.8}Se$ = 2.42 eV) (Hankare et al., 2006) at the end of 20h of milling is not surprising. Such a large blue shift is commonly observed in mechanically alloyed materials. Tan *el.al* has reported a large blue shift of 3.24 eV and 3.29 eV for CdTe, $Cd_{0.8}Mn_{0.2}Te$ respectively from their respective bulk bandgap energies.(G.-L. Tan, Wang, Wang, Zhang, & Yu, 2011; G. Tan, 2003).It is interesting to compare these large blue shifts with decreasing particle size. It is evident from Table 1 that group II-VI semiconductors exhibit a profound quantum size effect when the particles are further decreased.

Table I: Energy bandgap in milled crystals and nanoclusters

Material	1st excitonic peak [eV]	Particle size (nm)	Ref.
CdSe	5.77	2-4	(Wu et al., 2007)
	4.2	0.7	(Soloviev & Eichhöfer, 2000)
ZnSe	4.3	2-3	(Chestnoy, Hull, & Brus, 1986),(Brus, 1986b)
CdTe	4.1	1.6	(G. Tan, 2003)
	3.98	5.0	(Patra & Pradhan, 2010)
$Cd_{0.8}Mn_{0.2}Te$	5.06	2.0	(G.-L. Tan et al., 2011)
$Zn_{x-1}Mn_x S$	5.66	< 1.0	(Wu et al., 2008)
$Cd_{0.3}Zn_{0.7}$ Se	4.56	<2.0	This work

The large blue shift with decreasing nanocrystal size as observed from the absorption spectra in fig. reflects the effect of size quantization. Since the electronic wave function experience quantum confinement from extremely smaller CdZnSe particles. The carrier confinement leads to the creation of discrete levels in the conduction and valence bands as the size decreases. With continuous size reduction upon prolonged milling the confinement of charge carriers to the restricted volume of extremely small particles results in a large fraction of the constituent atoms or molecules been at or near the surface. The as-milled nanocrystals are in the strong confinement regime since the Bohr radius of CdZnSe lies somewhere in the neighborhoods of CdSe and ZnSe Bohr radii of (~5.4nm) and (3.65nm) respectively.

We may estimate the size of the corresponding particles by considering the size-dependence shift of the valance band maximum energy in fig.1 (a-c).This shift is attributed to a combination of quantum confinement and loss of dielectric solvation energy in small clusters, which is written as

$$\Delta E = \frac{h^2\pi^2}{2m_h R^2} + \frac{e^2}{2R} . \bar{U}$$

where m_h is the effective mass of the hole, R represents the radius of the clusters while $\bar{U}$ I the average potential over the 1S wave function of the hole crystalline. The expected particle radii are 2.1 and 1.3 nm after 5-20h of milling time respectively. This agrees well with the smallest particles within the wide size distribution as observed by HRTEM.

We now explain the possible origin of these extremely small nanocrystals during severe plastic deformation. It is well-known that with continuous mechanical alloying (MA), micron-sized powder particles became flattened, fractured, and rebounded (Suryanarayana, 2001) with a decrease in the length scale of the microstructure (Pouryazdan et al., 2012). It is important to note that continuous MA by severe plastic deformation is essentially accompanied by an exponential decrease in the particle size of the alloyed components (Delogu & Cocco, 2006b).

$$d = d_f + (d_i - d_f)e^{(-c_1 t)} \quad (1)$$

where d is the particle size, subscripts (i), and (f) represent the initial and final values, respectively, and c_1 is the kinetic constant of the reduction process. The initial and final crystallite size values d_i and d_f, respectively, are the characteristics of each element. Equation (1) describes one possible functional expression for the evolution of particle size with the milling parameters (Delogu & Cocco, 2006a).

Particle size reduction with continuous milling is a common feature of all mechanically alloyed systems. The fundamental factors that determine the minimum particle sizes that are obtained by ball milling are specific energy dose (D_m), which is expressed in J/g and is governed by the angular velocity, ball diameter, and ball-to-power mass ratio in planetary high-energy ball milling (Aleksandar M. Spasic, 2005); alloy composition (Eckert, Holzer, Krill, & Johnson, 1992), (Eckert, Holzer, Krill, & Johnson, 1993); dispersion hardening effect (Koch, 1993).

The energy in planetary mills is 2-3 orders of magnitude higher than that of common mills. The high rate of girding results from the action of centrifugal forces, which arise during the rotation of each grinding jar around its axis ("Apparatus for Mechanochemical Reactions," 2001).

In principle, nanocrystals that are mechanochemically synthesized, store mechanical energy in their topological defects (P.Yu. Butyagin, 1989). These attributes are

characterized by enhanced localized distortions of the crystalline lattice. The degree of mechanical processing during MA determines the extent to which lattice distortions become permanent (Delogu & Cocco, 2005), which translates to the amount of accumulated structural disorder, intimates the mixing of atomic species, plastic deformation, the formation of a stable-phase compound and decrease of crystallite size. Thus, it is important to balance between the formation of a stable phase and the particle-size-dependent optical properties of the new compound during the milling process.

In mechanical treatment, the powder particles continuously experienced the effect of mechanical energy, which is transferred from the milling tools, in the form of high-pressure loads. Besides, the effect of mechanical stress makes the trapped particles slide on one another, which consequently creates shear stress, whose intensity depends on the milling parameters.

Particle Size and Morphology

Nanocrystalline powders with particle size from bulk to extremely small particles and subsequently approaching atomic or molecular clusters have been synthesized mechanochemically. Intensive (MA) results in extremely small nanocrystals with their surface showing discontinuity with decreasing size. At 5h of milling, no regular surface could be observed for the extremely small particle as indicated by an arrow in Fig.3A (I).With continuous milling i.e. decrease in particle size, an aggregate of

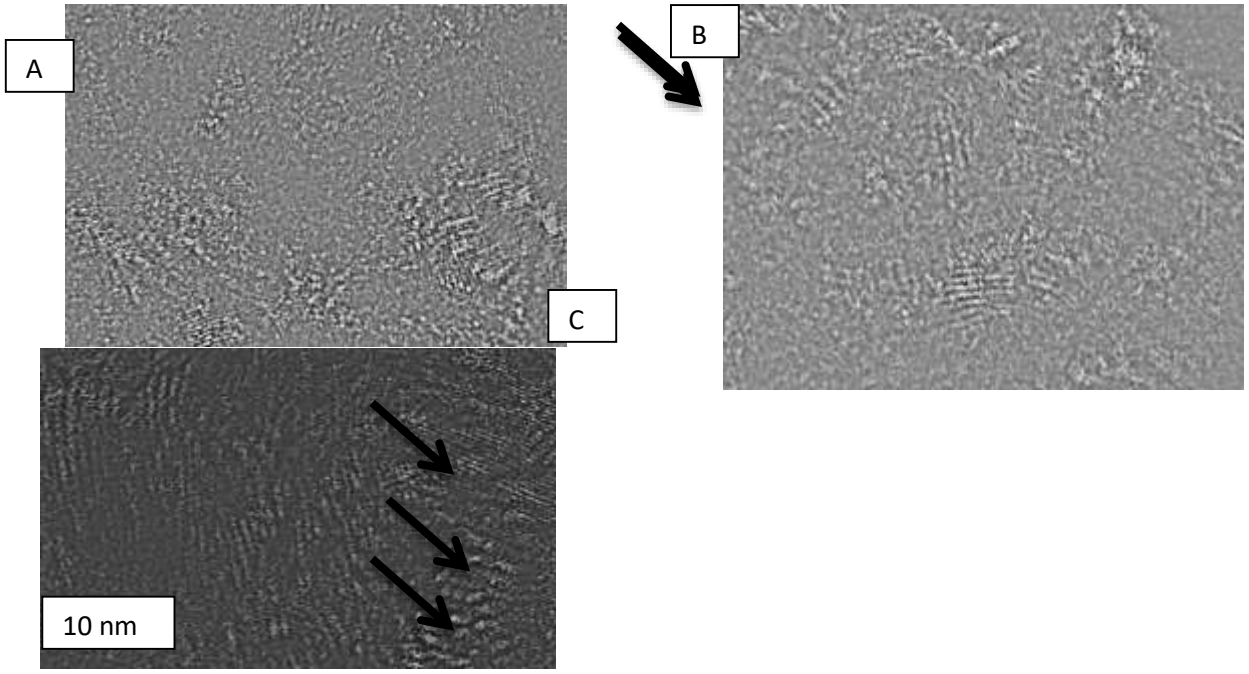

Figure 3: HRTEM images in the dark field mode of a) 5h b) 10 and c) 20h CdZnSe nanocrystals. In the images how no distinctive regular shape with virtually all atoms located at the surface. The arrows are pointing towards cluster like structures

atoms without a continuous lattice structure were observed as shown by an arrow in Fig.1B-C.In contrast to larger nanocrystals within the size distribution, a continuous lattice structure with lattice fringes are well resolved. We think that this cluster-like structure could be the main reason for the large blue shift in the optical spectra of the as-milled samples.

Particle Dispersion in Solvent

The mechanochemically synthesized powder contains wide size distribution ranging from (3 - 1.3) nm. For optical characterization, the powder is dispersed in organic solvents, in which extremely small particles float at the surface while larger particles settled at the bottom of the cuvette. This effect occurs due to a floating force that merely arises from the solvents. In such a case, only the optical properties of extremely small nanoparticles are been determine rather than the entire size distribution. Tan et.al obtained the optical bandgap from the entire size distribution through capping procedure

CONCLUSION

We demonstrated that intensive high energy ball milling results in the synthesis of extremely small nanocrystals. The optical properties of the particles are very similar to that of nanoclusters synthesized via a chemical wet method. Our results elucidate the effect of severe plastic deformation on the shape of the nanocrystal. This study also provides anew synthesis route for ultrasmall nanocrystals with possible applications in solid-state lighting sources (WLED).

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