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Stoichiometric and ultra-stable nanoparticles of II-VI compound semiconductors

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Abstract. Nanoparticles of $(CdSe)_n$ are found extremely stable at $n = 33$ and 34 with structures distinctively different from the bulk fragments. They grow exclusively in large amount with a simple solution method. The diameter is determined as 1.5 nm. Such ultra-stable nanoparticles had been predicted both theoretically and experimentally after the discovery of carbon fullerenes, but not been produced macroscopically in any other element or compound system. First-principles calculations predict that the structures of $(CdSe)_{33}$ and $(CdSe)_{34}$ are puckered $(CdSe)_{28}$-cages accommodating respectively $(CdSe)_5$ an $(CdSe)_6$ inside to form a three-dimensional network of essentially hetero-polar sp^3-bonding.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 78.67.-n Optical properties of nanoscale materials and structures – 78.66.Hf II-VI semiconductors – 36.40.-c Atomic and molecular clusters

1 Introduction

Extensive research has been conducted experimentally and theoretically on nanoparticles of a number of elements and compounds [1–12], especially of groups IV [2–5], III-V [6–8] and II-VI [9–12]. Experimentally, these particles are produced mostly in either gas phase or solution. The former yields very small ones like molecules and the latter large like fragments of essentially the bulk crystals. Very few lie in the intermediate dimension of ~ 1 nm where exotic arrangements of constituent atoms can be realized. In this range, the number of atoms is less than a thousand and hence, measurement on mass number rather than diameter is important in identifying and characterizing them precisely and appropriately. Also important are accurate structural and spectroscopic analyses on mass selected samples of sufficient amount. More of those investigations are needed to reveal fundamental features of the materials phase between molecules and solids. This paper reports the results of our investigation on II-VI compound, particularly on CdSe.

2 Sample preparation

Samples of CdSe nanoparticles have been prepared simply by mixing aqueous solutions of cadmium nitrilotriac-
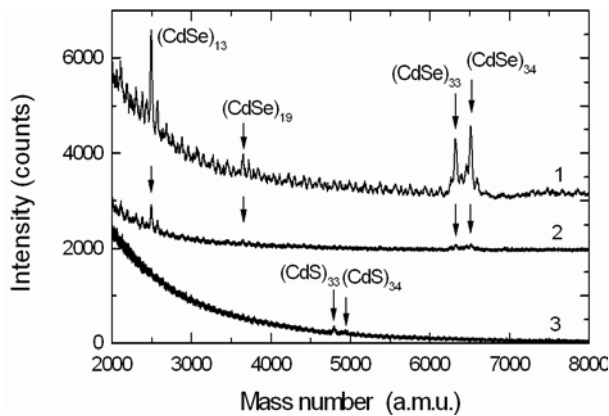
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etate (CdNTA, 1.4 mM, 14 ml) and sodium selenothiosulfate (Na_2SeSO_3, 0.9 mM, 17 ml) together with decylamine ($CH_3(CH_2)_9NH_2$, 4 mM) as a surfactant, followed by adding toluene to the mixed solution at temperature of 45 °C and higher. In alkaline conditions, Na_2SeSO_3 decomposes to yield Se^{2-}. Slow release of Cd^{2+} from CdNTA complex under the presence of surfactants results in only embryonic reaction products at most. By adding toluene onto the solution, the products come together to form nanoparticles in the toluene (upper) side which turns to greenish yellow within 20 minutes, whereas the water (lower) side remains colorless. The total reaction yield is more than 20%.

The sample in toluene was dried on the target plate of a time-of-flight mass spectrometer (Bruker Daltonics, Reflex III) in air. It is introduced in the vacuum measuring chamber and irradiated by the pulsed nitrogen laser for the measurement without injecting cooling gas on vaporized samples.

3 Experimental results and discussion

Figure 1 shows spectra of positive ions. The curve 1 is measured without cooling gas on the sample produced at 45 °C. It shows series of 1:1 stoichiometric peaks of $(CdSe)_n$ with dominant ones at $n = 13$, 33 and 34 and

Fig. 1. Time-of-flight mass spectra of positive ions. Curve 1 is for $(CdSe)_n$ prepared in toluene solution, curve 2 powder of $(CdSe)_n$, and curve 3 that of $(CdS)_n$.

Fig. 2. Optical absorption spectra. Curve 1 is as prepared $(CdSe)_n$ and curve 2 the photo-etched $(CdSe)_n$ of bulk fragment.

less dominant one at $n = 19$. It is noted that the intensities of these peaks are so much higher than their off-stoichiometric ones and neighboring. It is also noted that surfactant molecules are not firmly attached to $(CdSe)_n$ and are removed off easily by laser vaporization.

The curves 2 and 3 are similar measurements but on powders of the bulk poly-crystalline CdSe and CdS, respectively, without cooling gas. These curves definitely show peaks at $n = 33$ and 34 of $(CdSe)_n$ and of $(CdS)_n$, although not so dominantly as in the curve 1. This result can be interpreted that these nanoparticles at $n = 33$ and 34 are so stable as to form in the dense vaporization process without cooling gas injection. Similar mass spectra were also obtained from bulk poly-crystalline ZnS, ZnSe and CdTe proving that 33 and 34 are particularly stable molecular numbers not only in CdSe and CdS but also possibly in other group II-VI compounds. Martin et al. [1] find in his measurement on $(ZnS)_n$ enhancement of peaks up to $n = 34$ with helium gas cooling.

Figure 2 displays the result of our optical measurements. The curve 1 is the absorption spectrum of sample prepared at 45 °C. It exhibits very sharp peaks at 415 nm together with 382 nm and 352 nm and no structure above 450 nm where intense absorption of bulk crystalline CdSe would appear. The sharp feature is consistent with the fact that the sample is highly mass-selected at atomic precision found in Figure 1.

This spectral profile is practically identical to those reported by Murray et al. [9] and Ptatschek et al. [10]. Their preparation methods are different from and much more elaborated than ours but result in very similar spectrum. This coincidence is a good indication that $(CdSe)_{33}$ and $(CdSe)_{34}$ are so stable as to form preferably under rather wide varieties of reaction conditions including theirs. Murray et al. [9] estimate the size as 1.2 nm and Ptatschek et al. [10] 1.7 nm under different methods. Ptatschek et al. [10] call this sample a magic cluster as well as three others, each showing a sharp absorption peak at 280, 360 or 540 nm. Similar samples are also produced in our method with additional chemical treatments of solution, and the mass spectra indicate the synthesis
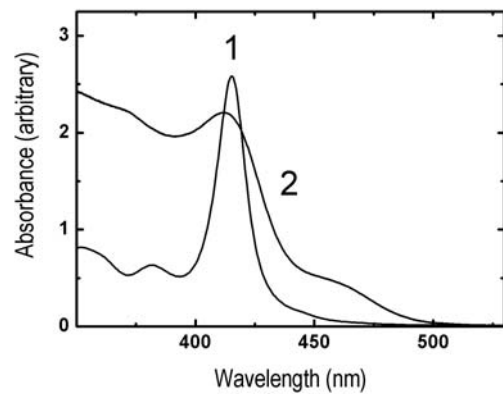
of stable clusters such as $(CdSe)_{13}$. The three peaks observed in the curve 1 in Figure 2, on the other hand, are always found in the same intensity ratio and do not coincide with any of the above three peaks of different sizes. The major component of our sample in toluene, therefore, is identified as only $(CdSe)_{33}$ and $(CdSe)_{34}$.

The curve 2 in Figure 2 is the absorption spectrum of sample synthesized at a higher temperature and then irradiated with an intense 442 nm light beam. Before irradiation, this spectrum had a peak at 460 nm. Electron diffraction measurements indicate that the average diameter of particles was less than 2 nm and the structure is bulk crystalline-like. Upon 442 nm light irradiation, particles in the sample reduced their sizes by photo-etching processes in the toluene solution to yield a new peak appearing and shifting in time to a shorter wavelength from the original 460 nm peak that is gradually diminishing. The new peak in the curve 2 is at 412 nm and close to 415 nm of the curve 1, indicating that the particle diameter is reduced to about 1.5 nm. The peak shifts much more by shorter wavelength irradiations. The peak width stays nearly constant and is much broader than in curve 1. These results show that bulk crystalline-like particles of CdSe are produced in any diameter with rather wide distribution without particular size being more favorable or stable. This behavior is expected in an etching process of bulk crystalline particles, where diameters can be reduced nearly continuously by removing atoms little by little from their surfaces. The sharp peak at 415 nm in curve 1 in contrast to curve 2 provides a strong evidence that $(CdSe)_{33}$ and $(CdSe)_{34}$ are preferentially synthesized in solution over other $(CdSe)_n$ and have structures distinctively different from the bulk fragment to provide a strong selective stability at $n = 33$ and 34.

First-principles calculations [3,12] predict that the structures of $(CdSe)_{33}$ and $(CdSe)_{34}$ are puckered $(CdSe)_{28}$-cages consisting of alternately connected Cd and Se ions forming 4- and 6-membered rings, and accommodating respectively $(CdSe)_5$ and $(CdSe)_6$ inside to form a three-dimensional network of essentially hetero-polar sp^3-bonding. The empty $(CdSe)_{28}$-cage is basically that
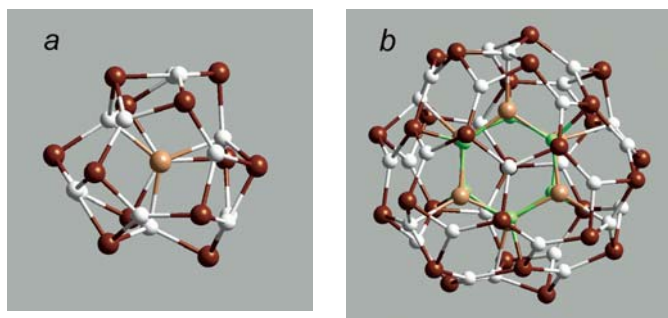
Fig. 3. Calculated structures of (a) $(CdSe)_{13}$ and (b) $(CdSe)_{34}$.

given by Seifert et al. [8] for $(BN)_{28}$. He proposed polyhedron $(BN)_n$ including isomers made up of 6 squares and $x-4$ hexagons with $x = 4$ or $x > 5$. Because of more polar nature of CdSe compared with BN, our $(CdSe)_n$-cages are favorably more puckered than $(BN)_n$ with Se-ions being outside and Cd-ions slightly inside. Further stabilization takes place by filling the center with more ions than empty. In a $(CdSe)_{28}$-cage, there is just a right space for $(CdSe)_5$ and $(CdSe)_6$ at the center. This core-cage structure explains the extreme stability of $(CdSe)_{33}$ and $(CdSe)_{34}$. The other strong peaks at $(CdSe)_{13}$ and $(CdSe)_{19}$ are interpreted as, respectively, $(CdSe)_{12}$-cage and $(CdSe)_{18}$-cage with $(CdSe)_1$ at the both centers. The calculated results of $(CdSe)_{13}$ and $(CdSe)_{34}$ are shown in Figures 3a and 3b. The geometry of $(CdSe)_{19}$ is found less symmetric than $(CdSe)_{13}$ and $(CdSe)_{34}$ and is hence less stable. The series of stable species at $n = 13, 19, 33$, and 34 are thus explained systematically. The magic numbers usually show

no consecutive number of stable species because stable ones tend to lie between unstable ones. The core-cage structure can give reasonable answer to our observation of stable 33 and 34.

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