EXAFS ANALYSIS OF SIZE-CONSTRAINED SEMICONDUCTING MATERIALS

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Abstract   Semiconducting materials such as CdSe, CdS, PbS and GaP are included in crystalline zeolite Y and mordenite and structurally flexible ethylene-methacrylic acid copolymer solid matrices. EXAFS analysis reveals formation of species with dimensions of molecular size up to ca. 13 Å in the crystalline hosts, while the polymer matrices allow agglomeration of larger semiconducting particles. Zeolite anchored structures are distinctively different to small particles with bulk crystal structure as usually found in colloidal systems.

INTRODUCTION

Small semiconducting clusters of nanometer dimensions represent a new class of materials with hybrid electronic and optical properties in comparison to their bulk and molecular counterparts. Widened electronic band gaps and the appearance of discrete absorption peaks in the electronic spectra of small semiconductor clusters have been interpreted as due to quantum size effects and exciton formation[1,2,3]. Structurally defined semiconductors with homogeneous morphology and narrow size distribution are a prerequisite for understanding the physical origin of these effects.

The majority of previous studies have been performed on colloids. For example, small CdS particles of 35 Å diameter could be prepared in aqueous solution by reaction of cadmium salts with H_2S, but the colloids were found to be unstable against aggregation to 125 Å within a day[4]. Some stabilization is obtained by arrested precipitation in non-aqueous solvents at low temperatures or upon addition of complexing agents (e.g., sodium hexametaphosphate) and stabilizers (e.g. colloidal silicon dioxide)[5]. Thus, even smaller CdS particles of 15 to 25 Å diameter could be prepared in acetonitrile, with band gaps between 2.5 and 2.3 eV[6]. Colorless "Q-CdS"

particles (Q = quantum state) made in propanol at -78° C were found to posess almost no semiconductor properties at all[7]. The latter are stable in solution, but very sensitive against light, heat and water. They can be obtained as solid materials only with simultaneous precipitation of cadmium sulfate which is believed to function as a spacer between the extremely small clusters. Larger particles, obtained by warming the alcoholic solution, showed photodissolution within minutes of illumination. The strong tendency to form larger aggregates could not be overcome by arrested precipitation in the case of ZnSe or CdSe[8]. In another approach, surfactants were used as stabilizers in order to aid charge separation in semiconductor colloids for application in photochemical solar energy conversion. Vesicles, or reversed micelles comparted CdS colloids were thus obtained of 550 Å or 100 Å diameter[9].

Different routes have been explored to stabilize small semiconductor particles on supports: Crystalline particles of mainly 800 to 1000 Å diameter have been reported on ultrathin bilayer lipid membranes (45 Å) which were stable for days. They could be removed from solution and arranged as arrays on copper grids[10]. Clays, which consist of stable two-dimensional sheets with ion-exchange capacity, present a potential for the formation of anisotropic semiconductors[11]. However, the flexibility of the interlayer spacing made the loading level of cadmium ions solvent dependent and reversible upon subsequent reaction with Na_2S. When methanol was used as solvent the interlayer space was found to be too small to allow diffusion of S^{2-} anions and bulk CdS was formed on the external surface of the clay. The use of ethylene-methacrylic acid copolymer as matrix for PbS proved to be promising for a systematic control of particle size: films with colors ranging from black to yellow were obtained upon variation of the lead concentration and subsequent reaction with H_2S. Band gaps from 1.0 to 2.2 eV corresponding to particles estimated at 45 to 25 Å were determined[12]. Monodispersed 20 Å CdS particles were produced by an intriguing biosynthetic strategy using yeast bacteria[13].

In order to obtain small semiconductor ensembles of defined size and structure, we have utilized zeolite hosts as stabilizing matrix. Zeolites are crystalline alumino-silicates with known pore sizes, cage structures and cation coordination sites and should therefore provide ideal hosts for this purpose. We have recently demonstrated that extremely small clusters of a variety of semiconductors such as Se, CdS, CdSe, PbS and GaP can be made using this approach[14,15,16,17,18]. The resulting materials, which are stabilized ensembles of only a few atoms, still exhibit exciton peaks in the electronic absorption spectra, characteristic for larger particles of ca. 20-50 Å. In this report we discuss the different structural features of these materials as

determined by EXAFS spectroscopy. Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS) has recently emerged as a technique to analyze systems lacking long range order[19,20]. It provides information about the close environment of the x-ray absorber atom by the following principle: Photoelectrons excited by x-ray absorption are backscattered to the absorber by atoms of the first few neighboring shells. The resulting interference wave pattern carries information about coordination numbers, distances and types of neighbors. A radial distribution function is obtained when EXAFS data are Fourier transformed from momentum space (k, Å^{-1}) to distance space (r, Å). The peaks in those functions are phase shifted by 0.3 to 0.5 Å with respect to their real bond distances. Accurate structural information is extracted by iterative fitting with reference compounds. In the following we will describe the structures of (sub)nanometer particles of CdSe, PbS and GaP clusters obtained by inclusion in zeolite or polymer matrices.

EXPERIMENTAL

The Cd and Pb samples were prepared via ion-exchange of Cd(II) or Pb(II) cations into zeolites Y, mordenite and/or a polymer matrix of 85% ethylene-15% methacrylic acid copolymer (E-MAA) from aqueous solutions of $Cd(NO_3)_2$ or $Pb(NO_3)_2$ at room temperature. Subsequent dehydration of the zeolites at elevated temperatures and exposure to hydrogen sulfide/selenide at room temperature resulted in orange/yellow samples. Ga was introduced into zeolite Y via gas adsorption of $(Me)_3Ga$, which was then treated with 100 Torr of PH_3 at 570 K. EXAFS data were collected at the National Synchrotron Light Source, Brookhaven National Laboratories, beamline X-11A. The structural analysis was performed using experimentally determined EXAFS data from reference compounds.

CdSe IN ZEOLITE Y[16]

The formation of CdSe within the zeolite matrix was followed by studying both the dehydrated Cd-exchanged precursor sample CdY and the same sample after reaction with H_2Se, CdSeY. Zeolite Y offers two different "reaction vessels" for cation coordination and cluster formation: "supercages" and sodalite cages with 13 and 6 Å diameter, respectively. EXAFS analysis of the precursor sample CdY shows that 70% of all Cd cations are accomodated inside the sodalite cages. The corresponding Fourier transformed EXAFS spectrum is shown in Figure 1.
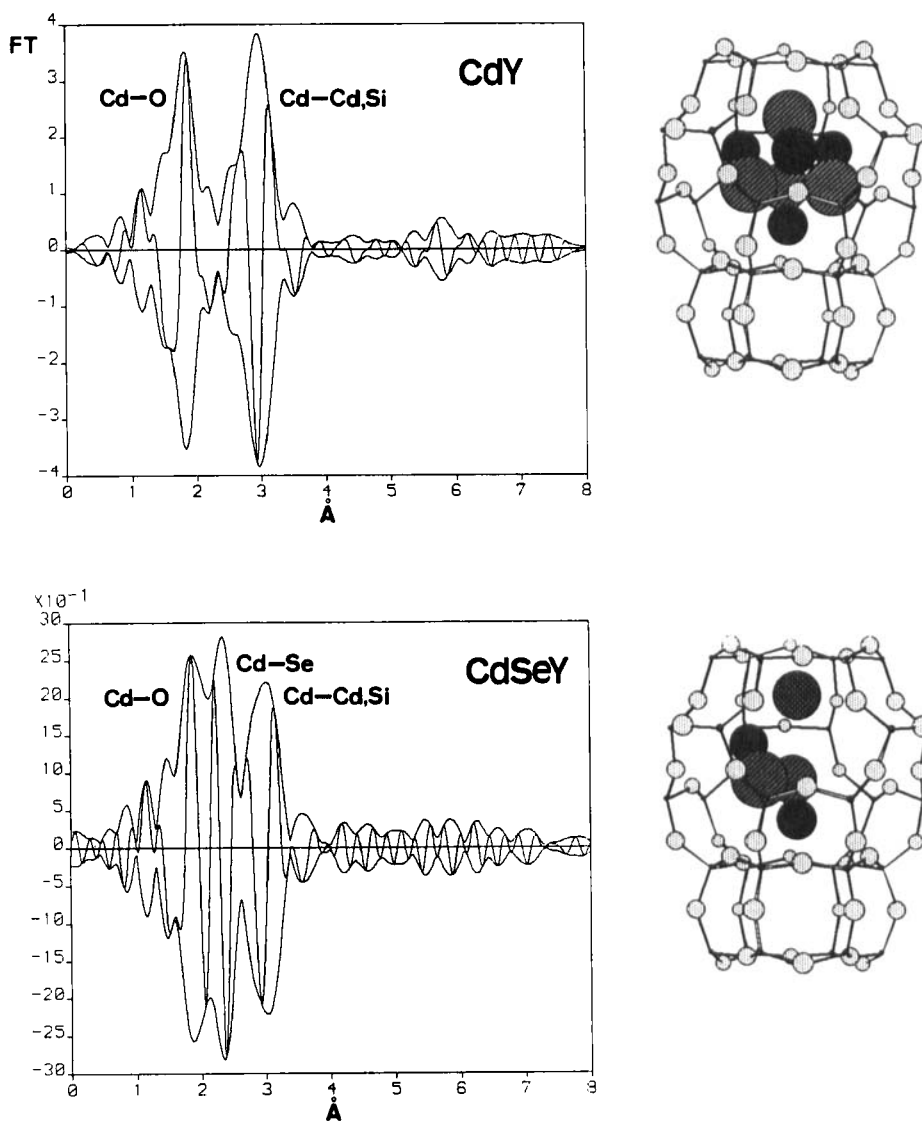
FIGURE 1   Radial distribution functions of cadmium exchanged zeolite Y (CdY) and, after treatment with H₂Se (CdSeY). The corresponding three dimensional representations of cadmium ensembles in the sodalite cage are shown to the right: light dotted - Si framework atoms; large black - Cd ions; large striped - extra-framework oxygen; large dotted - Se ion.

The first peak in the precursor sample CdY originates mainly from two different oxygen neighbors of the cadmium ions. The second contribution is due to an overlap of a Cd-Cd and Cd-Si interaction, the latter arising from the zeolite framework. A three-dimensional picture of the cation location in the zeolite framework is included in Figure 1. Cadmium ions (black) are coordinated to three oxygens at a distance of 2.44 Å in front of Si-O-Si six-rings (SI' positions) in the sodalite units. The corresponding distance to the Si framework ions was found to be 3.42 Å. Additionally, cadmium is bound to extra-framework oxygen (dark striped; OH or H_2O) at 2.25 Å, thus forming a cube of Cd_4O_4 in the small cage of the zeolite. It seems that the oxygen shell of the sodalite units is well suited for saturation of the coordination sphere of the cadmium ions.

Upon introducing H_2Se, the EXAFS magnitudes corresponding to Cd-O and Cd-Cd interactions are reduced, and a new peak is present from an interaction of cadmium with selenium (Figure 1, CdSeY). Data analysis leads to the following conclusion: extra-framework oxygen is partially replaced by selenium ions, introducing strain to the initial Cd_4O_4 cube. Fragmentation into smaller entities and redistribution of cadmium is the result. Zeolite-anchored ensembles of Cd_2O_2Se in the sodalite cages (see Figure 1) and of CdSe in the supercage are the main products. The Cd-Se bond distance of 2.62 Å is identical to the bulk value of CdSe, but no indication exists for the formation of any bulk material. EXAFS analysis of the Se-edge also reveals the presence of small amounts of selenium helical chains. In contrast, when a similar CdY precursor sample is treated with H_2S, the cube-like structure remains intact, but two oxygens are substituted for sulfur ions which are slightly smaller than selenium[15]. These results are consistent with synchrotron powder X-ray diffraction studies performed on the same samples[16].

PbS IN ZEOLITE Y, MORDENITE, AND METHACRYLIC ACID COPOLYMER[17]

EXAFS data at the Pb absorption edge were taken of the dehydrated lead precursor samples and after treating these samples with H_2S. Data analysis of the precursor PbY shows that lead cations are coordinated to three oxygen atoms of the zeolite Si-O-Si six-rings with a Pb-O bond distance of 2.46 Å, and a Pb-Si distance of 3.42 Å, very similar to the cadmium coordination described above. The coordination sphere is completed by two additional extra-framework oxygens (OH or OH_2). The data suggest interaction with two to three lead ions at a distance of 4.1 and 4.3 Å. This long distance and the size of the cations points to a siting in the large cages which also contain six-ring windows. PbO cubes are thus not likely to exist, in contrast to the cadmium

precursor samples. Exposure to hydrogen sulfide induces a rearrangement of the intrazeolite lead cations; all outer shell Pb-Pb interactions disappear. The resulting simple radial distribution function with an intense, broad peak is due to a convolution of Pb-O and Pb-S scatterers (see Figure 2, PbSY; S = H_2S, HS$^-$ or S^{2-}).
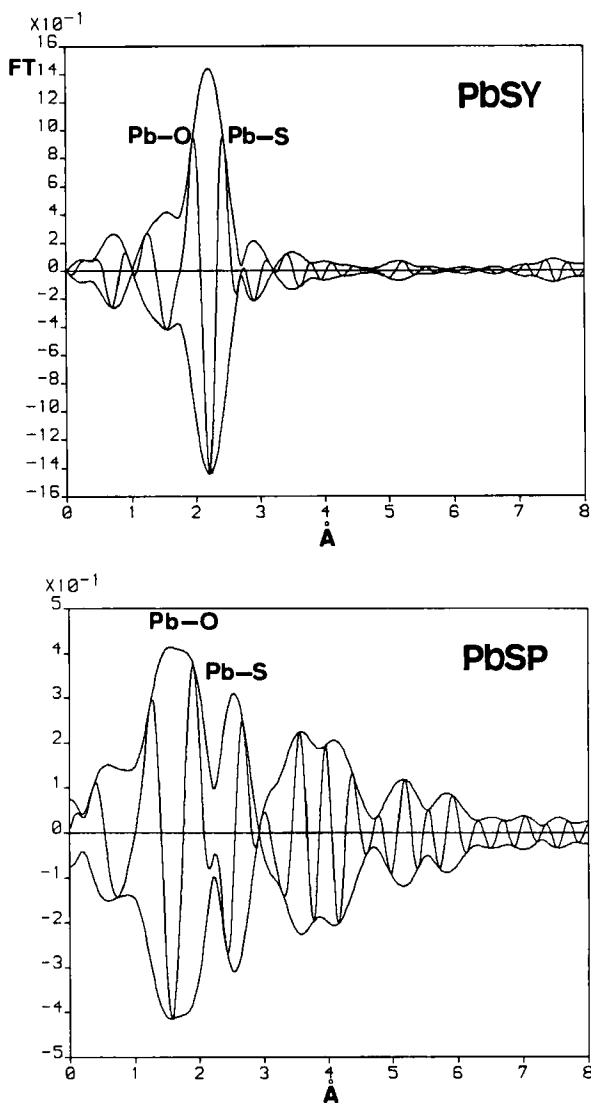

FIGURE 2   Radial distribution functions of lead sulfide in zeolite Y (PbSY) and in ethylene methacrylic acid copolymer (PbSP).

Lead ions are still anchored to the zeolite six-rings (Pb-O = 2.47 Å) but have substituted their two non-framework oxygen ligands for two sulfur neighbors at a distance of 2.77 Å. This value is very short compared to the bulk value for PbS (2.97 Å), but is substantially longer than that for molecular PbS (2.29 Å)[21] and underscores the molecule-like nature of these ensembles. The overall reaction can be formulated as follows:

$$(O_z)_3Pb(OH)_2 + 2 H_2S <\text{-}\text{-}> (O_z)_3Pb(SH)_2 + 2 H_2O$$

(O_z: zeolite oxygen)

As found earlier for selenium loaded zeolites[14], there is no significant influence of the crystal structure of different zeolites on the coordination of the PbS species. Mordenite zeolites with one-dimensional channels would in principle offer the possibility to synthesize semiconducting "wires" in contrast to three-dimensional interconnects as conceivable in zeolite Y. However, the examined mordenite samples contain molecular ensembles almost identical to those found in zeolite Y. It is possible that these ensembles communicate at higher loadings as indicated by optical data[22].

The situation changes remarkably when PbS is formed in polymer films. If the corresponding EXAFS data (Figure 2, PbSP) are compared with those of zeolite-encapsulated lead sulfide, large outer-shell scattering is evident in the polymer samples. The backbone structure of the polymers is more flexible than the rigid inorganic framework of zeolites, and the cluster size of the semiconductor guests now depends strongly upon the metal concentration and heat treatment. It is evident from the radial distribution functions in Figure 2 that the cluster sizes of PbS in the polymer samples are much larger than those of molecular species found in the zeolites. Bond distances of the first Pb-S atom pairs are close to the bulk value of PbS (2.99 Å), and outer peaks up to 6 Å (uncorrected for phase shift) show good agreement with the lead sulfide bulk reference. The conversion to PbS is incomplete as indicated by the remaining Pb-O contribution at a distance of 2.39 Å that is due to polymer carboxylates and/or PbO. Some of the outer shell scattering is unchanged with respect to the precursor sample and is probably due to PbO particles. These results suggest that the limited permeability of the polymer may produce inhomogeneous PbS phases in addition to lead ions and lead oxide. It is interesting to note that the polymer and zeolite samples have very similar optical absorption spectra[12].

GaP IN ZEOLITE Y[18]

Intrazeolite GaP was synthezised via vapor-surface reaction in the cavities of zeolite Y. $(CH_3)_3Ga$ was adsorbed in dehydrated NaY at room temperature to give the precursor sample MeGaY (see Figure 3). A single coordination shell is present in the EXAFS, resulting from a Ga-C contribution at 2.04 Å of the adsorbed molecule. Crystallographic data are not available for $(CH_3)_3Ga$, but the obtained distance agrees well with estimated data for interatomic distances. A rather high coordination number of 4.4 may indicate additional interaction with oxygen of the zeolite walls. Si^{29} NMR data suggest a strong interaction with the lattice by deformation of the TOT angle by 0.5°. After treatment with PH_3 at elevated temperatures (470-670 K) a color change from white to yellow-orange was observed. EXAFS data were taken of a sample heated at 570 K. The resulting radial distribution function is shown in Figure 3 (GaPY). The observation of several coordination shells points to clusters larger than single GaP molecules. The position of the first shell (2.04 Å) is unchanged with respect to the precursor sample MeGaY, but is reduced in magnitude. Most likely this indicates the loss of methyl groups and the coordination of unreacted Ga ions to lattice oxygen. For sample GaPY a coordination number of 2.0 was found that correlates with 70% gallium ions sited in six-ring windows. A peak at ca. 2.5 Å (uncorrected for phase shift) is believed to be due to the corresponding Ga-Si interaction. All other peaks in the distribution function can be explained with a GaP phase: Ga-P at 2.37 Å, Ga-Ga at 3.85 Å and a second Ga-P shell at 4.56 Å. These bond distances are very close to bulk GaP values. Based on the fraction that has reacted to GaP (30%), and the coordination numbers for all neighboring shells, the cluster size can be estimated. A 30 atom GaP cluster with zinc blende structure has a diameter of about 11 Å. This estimated size agrees well with all fit results. A cluster this size can easily be accomodated in the large cavity of zeolite Y. We assume that the higher reaction temperatures facilitate the growth to supercage-sized clusters as compared to molecular ensembles formed at room temperature.

In conclusion, we have demonstrated that zeolites can be used as stabilizing matrix for subnanometer clusters ranging from framework-anchored molecular entities (Cd_2O_2Se, PbS_2) to sodalite-encaged $(CdS,O)_4$ cubes of 6 Å size or GaP clusters of 11 Å trapped in the supercages. In comparison, it seems more difficult to control the cluster formation in polymers, which tend to allow agglomeration of the semiconductor clusters.
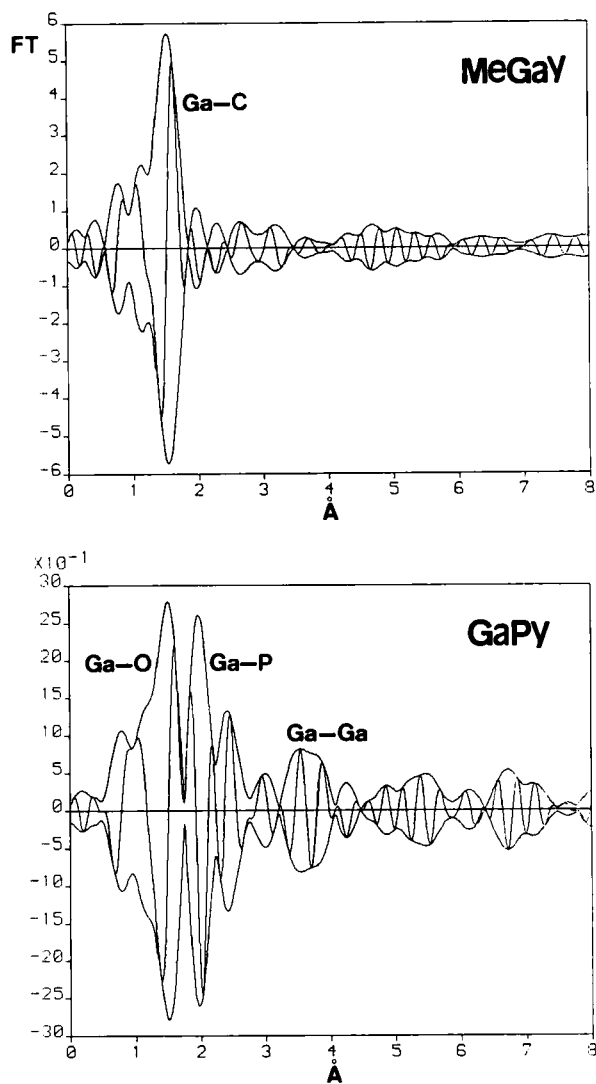
FIGURE 3 Radial distribution functions of $(CH_3)_3Ga$ loaded zeolite Y (MeGaY) and after treatment with PH_3 at 570 K (GaPY).

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