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Optical Properties of Amorphous ZnO, CdO, and PbO Nanoclusters in Solution

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We prepared ZnO, CdO, and PbO rock salt-coordinated and ZnO wurtzite-coordinated nanoclusters with a microemulsion method in the AOT reverse micelle. X-ray and electron beam diffraction techniques indicate that all have amorphous structures. The similarity of the UV−visible absorption and photoluminescence spectra at room temperature for ZnO, CdO, and PbO rock salt-coordinated nanoclusters indicates that they are all similar in electronic structure. All prepared nanosystems show strong emission in the visible region, and the emission features depend on the wavelength of the excitation. This phenomenon is considered as a result of localization of the electronic state due to the amorphous structure of nanocluster and surface capping. Time-resolved photoluminescence studies on ZnO, CdO, and PbO nanoclusters were performed. The carrier lifetimes near the band-tail are in the sub- and nanosecond time ranges with different characteristics from that of bulk amorphous semiconductors and nanocrystals. The observed properties can be explained in terms of quantum confinement, structural disorder, and surface polarization.

Introduction

Recent progresses in the preparation and characterization of materials on the nanometer size scale have introduced a new point of view for physics and chemistry in the world of reduced dimensions. By virtue of its size and potential distribution, a quantum dot (QD) structure confines carriers in three dimensions, restricting their degrees of freedom down to zero and creating atomlike levels with discrete density of states.[1−5] The confinement of the electron (hole) wave function can be accomplished for a very small volume of material with a low band gap embedded in material or materials with a large band gap. As the size of QDs decreases, their properties turn into molecular-like ones due to both size and surface effects,[6] and their crystalline and electronic structures change simultaneously. Moreover, the substance with a large band gap as the medium or interface layer could exert strong influence on the electronic states of nanoclusters.

Among other properties, the size-tunable optical properties are probably the most interesting phenomena due to the confinement of the electronic wave function. Quantum-confinement leads to the blueshift of the band edge absorption. This is generally true for II−VI semiconductor nanocrystals. Nevertheless, as we already noticed, surface state or other in-gap states should also play an important role in the determination of the physicochemical properties of the quantum-confined systems. Moreover, their contribution sometimes may become even stronger to compete with the quantum-confinement effect in specific cases.[7] For example, the oxide nanosystems with the prevailing amorphous structure and strong electron−phonon coupling. Hence, it is very important to study very small nanoclusters with narrow size distribution and known surface modification in order to understand their photochemistry and photophysics.

In the past years, a few studies on the quantum-confined effect and surface modifications on the electronic structure of the oxide nanoparticles have been published.[7,8] Reported results indicate that oxide nanoparticles may have different optical properties than the frequently studied II−VI semiconductor nanoparticles. Because of the promising applications in optoelectronics, the investigation of the optical properties of such nanoparticles is of fundamental interest and technological importance.

In this work, small ZnO, CdO, and PbO nanoclusters are prepared with a microemulsion method in AOT reverse micelles in order to see how the surface components and structural disorder influence the absorp-

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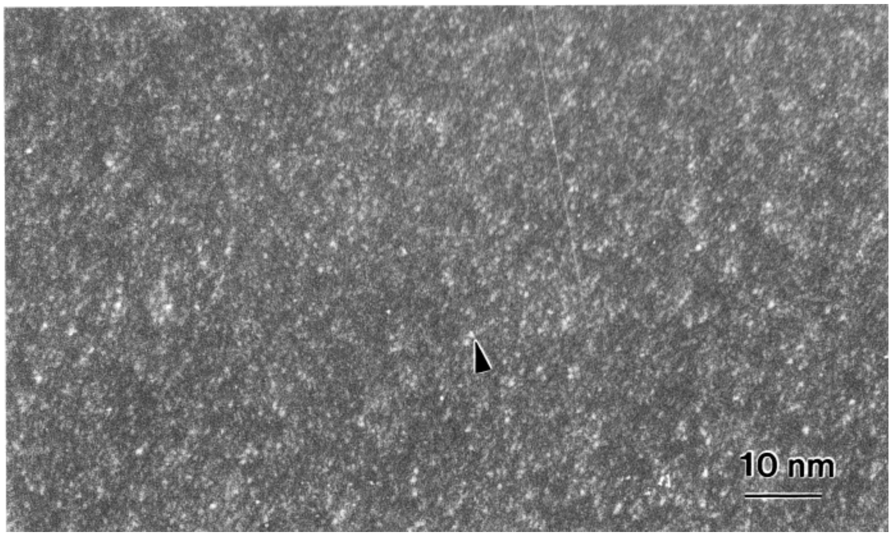

Figure 1. Dark-field TEM image of ZnO(R) nanoclusters.

tion, emission, and ultrafast decay of quantum-confined states. This is the first observation of the transient optical behavior of these oxide nanoclusters.

Experimental Section

ZnO, CdO, and PbO nanoclusters were prepared using a microemulsion method described as follows: aqueous solutions of $Zn(NO_3)_2$, $Cd(NO_3)_2$, and $Pb(NO_3)_2$ were added into the AOT toluene/xylene with the ration H_2O/AOT/toluene =1:2:200 to form reverse micelles. These mixtures were stirred and sonicated for more than 1 h. Aqueous solution of NH_3H_2O (1mol/L) was dropped into the above solution to pH = 12 during stirring. White suspended solution was observed. Then, the solution was refluxed for 3−5 h, and it became transparent again. Finally, water was removed by distillation to result in oxide nanocluster organosol. It is interesting that the colorless wurtzite ZnO nanoclusters turned red by heating to 470 K. The CdO and PbO nanoclusters in toluene were light and dark brown, respectively.

The nanoclusters were also studied by transmission electron microscopy (TEM), carried out at 200 kV using a Hitachi HF-2000. A droplet of the solution containing the clusters was dispersed on a ultrathin, holey, amorphous carbon film supported by a cupper grid. The small size and the amorphous structure of the nanoclusters greatly reduced their visibility in conventional bright-field imaging. To image the clusters, we used the mechanism of mass-thickness contrast in TEM, which was performed in dark-field mode by carefully positioning the objective aperture so that the scattering from the nanoclusters was enhanced, whereas that from the substrate was suppressed. Because the scattering power of an atom strongly depends on its atomic number, heavy atoms produces strong higher angle scattering signals.[9] If the objective aperture picks up only a portion of the high-angle scattering signal, the image would show the nanoclusters because of higher atomic number. This is the so-called Z-contrast in TEM measurements.

A Beckman DU-650 spectrophotometer was used to measure absorption spectra. Photoluminescence spectra of ZnO, CdO, and PbO nanoclusters in reverse micelles were obtained using PTI QM-1 and RC-M fluorescence systems.

Temporal emission behavior of these nanoclusters was measured using the time-correlated photon counting technique. The excitation source was 580 nm from a dye laser (Spectra-Physics, model 375B) with a cavity dumper. The dye laser was synchronously pumped by a mode-locked Nd:YAG laser (Spectra-Physics, model 3800). The pulse width was measured using an autocorrelator and was found to be equal to 35 ps. The detection system was a microchannel plate photomultiplier tube (Hamamatsu R1564) coupled with a pulse-to-height converter (ORTEC, model 457), which provided an instrument response function of 40−60 ps (fwhm). The fluorescence decay was collected until there were 4000 counts at the maximum.

Results and Discussion

Our nanoclusters formed in the micropools of water (reverse micelles) in organic solvent. A layer of anionic surfactants capping the surface of nanocluster protects the nanosystem from aggregation and make the particle dissolvable in toluene. So the solvent-nanocluster interaction is negligible. After heating to remove water, the oxides are chemically bound to the surfactant molecules, which can be observed by the FTIR spectra.[10] So, the chemical bonds on the surface exert their force, introducing a larger coulomb potential on the nanoclusters. Under such condition, a modification of the chemical surface may play an important role in alteration of the electronic structure and the optical properties of ZnO, CdO, and PbO nanoclusters.

Figure 1 is an dark-field TEM image of ZnO nanoclusters; the particle size is about 1−2 nm, with a narrow size distribution. Electronic diffraction shows the amorphous structure of the cluster, which is consistent with the results from X-ray diffraction. Other nanoclusters show similar morphologies and structural properties.

Figure 2 is the absorption spectra of the ZnO (wurtzite- and rock salt-coordinated), CdO, PbO nanoclusters in organosol. The packing of the CdO and PbO comes from the MO_6 octahedra. The cluster consists of several tens of metal ions.[11] In contrast, ZnO nanocluster obtained after 110 °C thermal treatment have a wurtzite-coordinated structure with a blueshifted absorption. Upon proper 200−250 °C thermal treatment, ZnO nanoclusters coated with ionic surfactant may undergo a transformation into another phase with a rock salt-coordinated nanostructures (a phase exists in bulk

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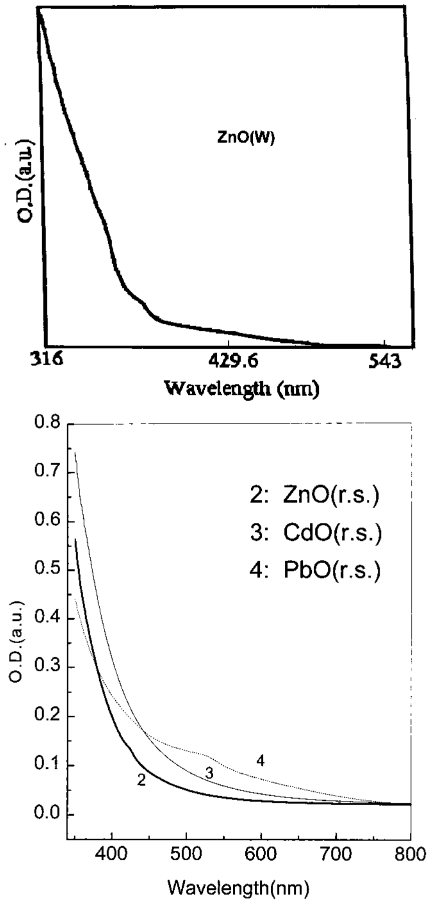

Figure 2. Absorption spectra of ZnO(W) and rock salt-like ZnO, CdO, and PbO nanoclusters.

under high pressure) and indirect band absorption spectra similar to those of CdO and PbO. Thermal treatment leads to formation of this closely packed oxygen structure, which seems to be the result of the surface chemical bonding variation.[7] Such specific character of reorganization may be partially due to structural relaxation caused by the larger Madelung potential introduced by surface modifications. It is reasonable that no long-range order exists in such a small and closely packed structure.

This new phase of ZnO may only appear and exist in specific chemical environments. The surface stretching vibrational frequency of $-SO_3^-$ is between 1600 and 2100 cm^{-1}, which is twice as large as the frequency for the Zn$-$O bond (around 580 cm^{-1}).[12] This acid radical can play the role of donor to impurities around the surface of the nanoclusters and cause the formation of a shallow trap. This environments, together with structural transformation, interplay to induce an electron-multiphonon (LA + LO) enhancement. As a result, multiphonon effects can play a dominant role in structural instability and may cause structural reorganization. This finally leads to the loss of long-range order and to the formation of self-trapped states with a closely packed structure. Figure 3 is an IR transmission spectrum of rock salt-coordinated ZnO nanocluster. In contrast to the wurtzite ZnO, strong absorption below 400 cm^{-1} supports the local rock salt-order structure, because the latter has much more bond contribution from Zn ions, leading to the LO phonon anomaly related to large Zn^{2+} ($<$320 cm^{-1}) displacement.[10] This consideration agrees well with the result of X-ray photoelectron spectroscopy,[13] which demonstrates strong Zn$-$Zn coupling in this surface-capped and rock salt-coordinated ZnO nanocluster. This transformation means smaller particles may lose their long-range order and prefer the local order with octahedral symmetry. So, they will show new electronic structure and optical properties.[10]

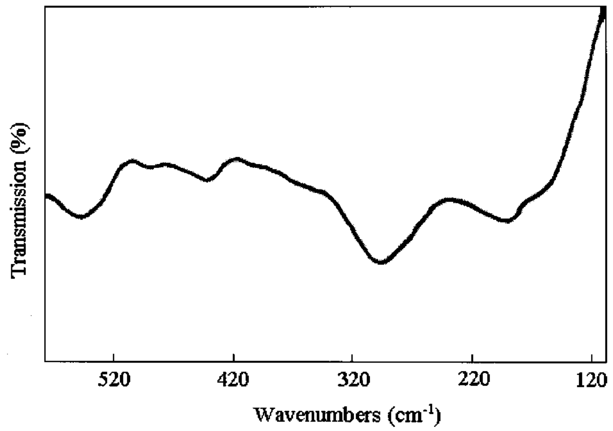

Figure 3. Infrared spectra of ZnO(r) nanocluster.

The common concept of quantum confinement with blueshift is true on the following conditions: (1) no structural transition and (2) a particle size generally larger than 2$-$3 nm or by neglecting the surface polarization. The latter was enhanced due to surface polarizable bonding in our samples. There are also examples that other wurtzite or zinc blend semiconductors would prefer a cubic structure, when they are small enough.[14] Therefore, it is not strange that oxide nanoclusters with strong electron$-$phonon coupling also may possess the same structures and similar properties as their sizes get small enough. The carrier dynamics of excited states in such systems may be unique and interesting. In the view of some possible applications, it is important to understand the similarities and differences between the optical properties of such nanosystems.

We consider CdO and PbO structures to be rock salt and rock salt-like, respectively. ZnO nanoclusters have a wurtzite structure originally but acquire a rock salt structure upon thermal treatment. X-ray diffraction and electron beam diffraction techniques have indicated an amorphous character of such small ZnO, CdO, and PbO nanoclusters within reverse micelles.[10,13] It is well-accepted that intrinsic disorder produces a spatial randomness of the atomic potential that gives rise to localized (within a few lattice sites) electronic states. These so-called band-tail states are responsible for the smoothness of the valence and conduction band density of states at their edges. As a result, conduction and valence band edges are not defined in our systems, and their energy gaps are determined by the difference between the conduction- and valence-band mobility

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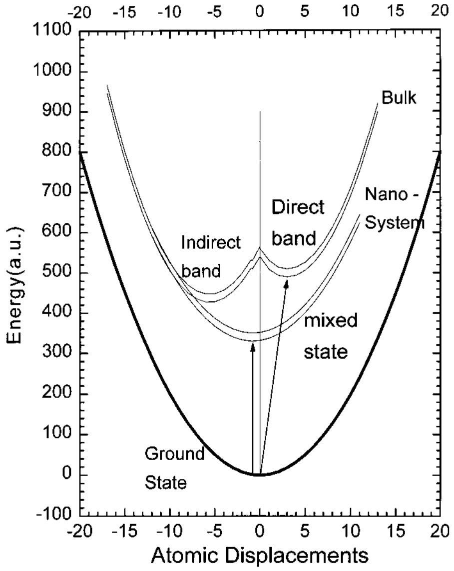

Figure 4. Electronic states diagram of rock salt oxide nanoclusters.

edges. These edges represent the boundary between extended and shallow states. Manifestation of the extended states optical properties in bulk amorphous semiconductors is obvious but not in our nanosystems.

The electronic structure of the studied oxides is similar to that of CdO (rock salt) bulk.[15,16] The direct band gap is 3.0 eV, but the indirect band gap is 2.3 eV. So, the indirect bands dominate their visible absorption and emission. The valence band for CdO is comprised of two O bands with a spin–orbital splitting of about 1000 cm^{-1}.[17] The direct band edge of CdO (rock salt) bulk is around 3.0 eV. The absorption features for CdO, PbO, and ZnO rock salt-like nanocluster are indirect characteristics. Using Tauc's band edge model, we determined the band edges of present samples to be around 580 nm for ZnO rock salt, 600 nm for CdO, 650 nm for PbO. However, the absorption is a direct-band transition for the ZnO(W) (see Figure 2). The weak tail of absorption below the direct band suggests the presence of an in-gap density of states due to structural disorder.

In all, we suggest the following model (see Figure 4) with two main features to understand the observed absorption properties:

(i) Because of strong confinement and structural reorientation, nanomaterial may no longer be described as one with repeated zone structure but the molecular symmetry. Surface bond and disorder modulate the electronic states on an ensemble of harmonic oscillators.

(ii) There are indirect transition components as a result of strong surface polarization, like the triplet state absorption in big molecules.

The suggested energy diagram (Figure 4) explains the band edge, redshifted character. We consider the current band edge mobility as an inherited feature of systems with amorphous nanostructures. The following photoluminescence spectra of oxide particles also support our consideration.

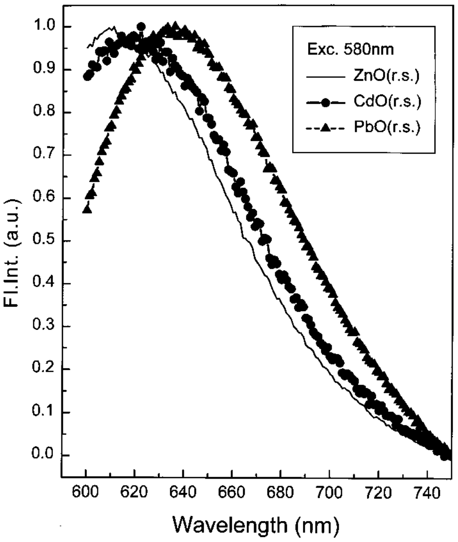

Figure 5. Emission spectra for ZnO (wurtzite), CdO, PbO, and ZnO (rock salt) amorphous nanoclusters for 580 nm excitation.

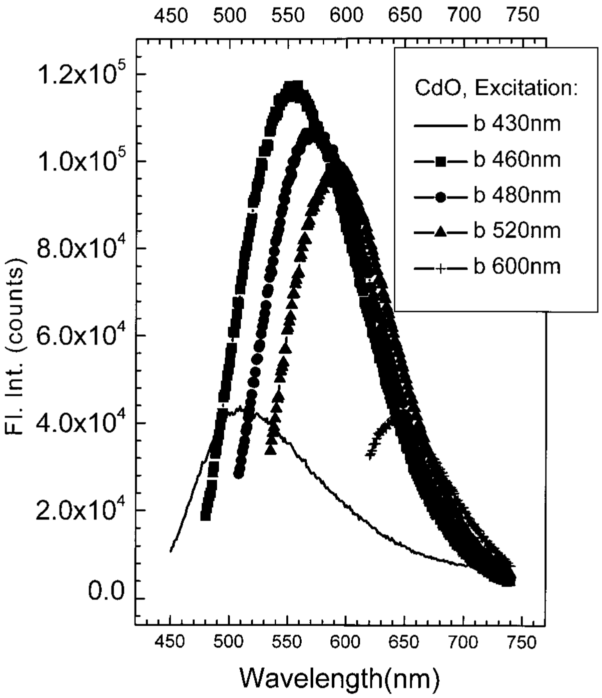

Figure 6. Emission spectra for CdO amorphous nanoclusters for excitations at 430, 460, 480, 520, and 600 nm.

The photoluminescence spectra of ZnO, CdO, and PbO nanoclusters in reverse micelles at room temperature are given in Figure 5. The increase in the Stokes shift for ZnO, CdO, and PbO nanoclusters, in the given order, is clearly seen for excitation at 580 nm. It comes from the difference in their band gaps and the larger polarizability of Pb^{2+} than Cd^{2+} and Zn^{2+} ions.[18] The maximum of the fluorescence band shifts as the excitation wavelength changes (see Figure 6), which is different from that of the crystallite semiconductors.

Photoluminescence from excitation at 580 nm is rather strong despite the fact that the absorption coefficient is low at this wavelength due to the indirect nature. There are several possible explanations: (i)

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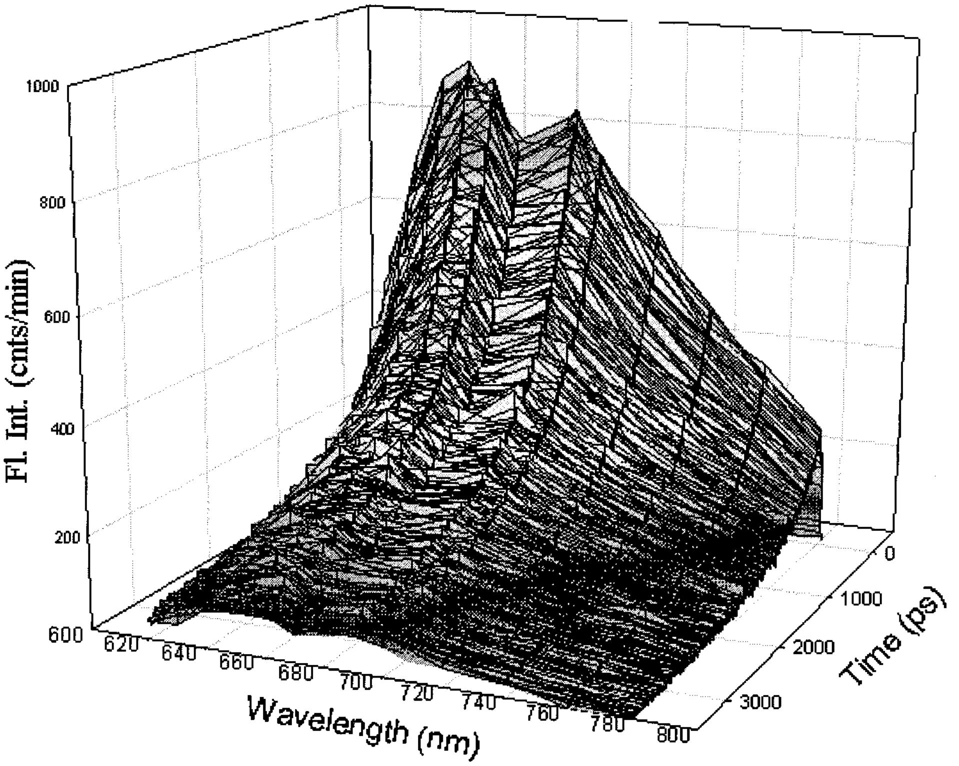

Figure 7. Fluorescence decay spectra for PbO amorphous nanoclusters.

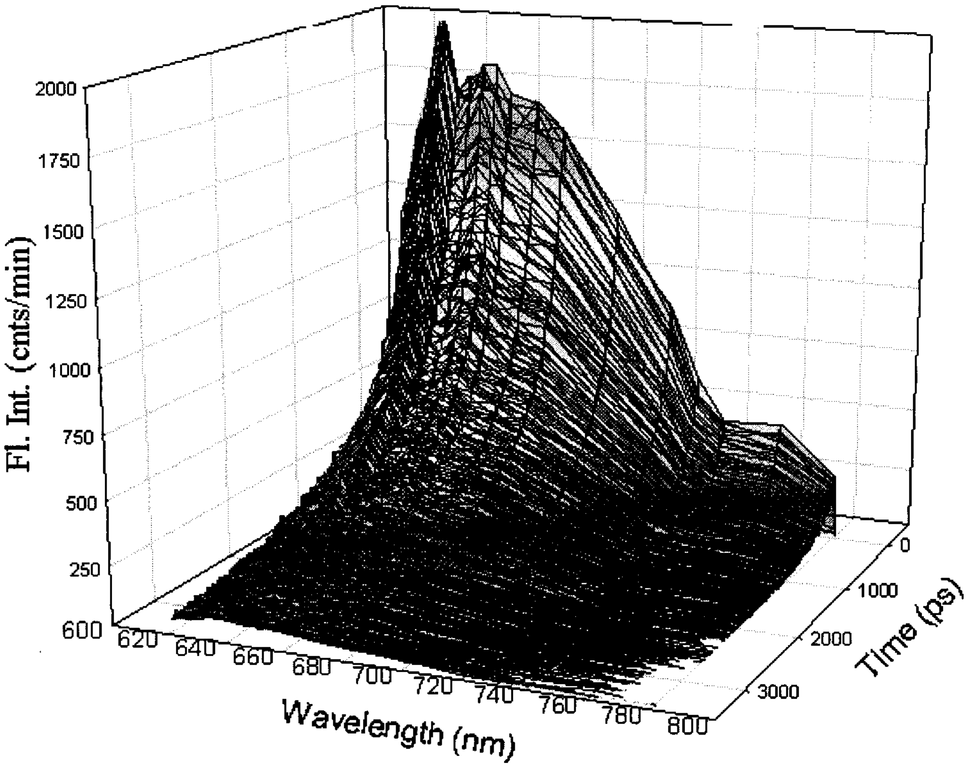

Figure 8. Fluorescence decay spectra for rock salt-like ZnO amorphous nanoclusters.

quantum confinement (system with quantized levels) and an increase in the carrier lifetime even for the in-gap state; (ii) localization of the carrier due to disorder, surface trapping and a change of the transition rule; and (iii) interfacial Coulombic potential that helps bands to mix and leads to transition rule variance.

In all, the photoinduced carriers can be trapped and hopped in different potential wells within the nanoclusters. A wide-band fluorescence occurs from their excited states such as in an amorphous semiconductor.

The results of time-resolved emission studies on PbO, ZnO (rock salt-like) CdO, and ZnO (wurtzite) nanoclusters are given in Figures 7−9, respectively. Specifically, Figure 7 demonstrates the development of the fluorescence spectral properties in time for PbO nanoclusters. The fluorescence is very broad mainly due to compli-

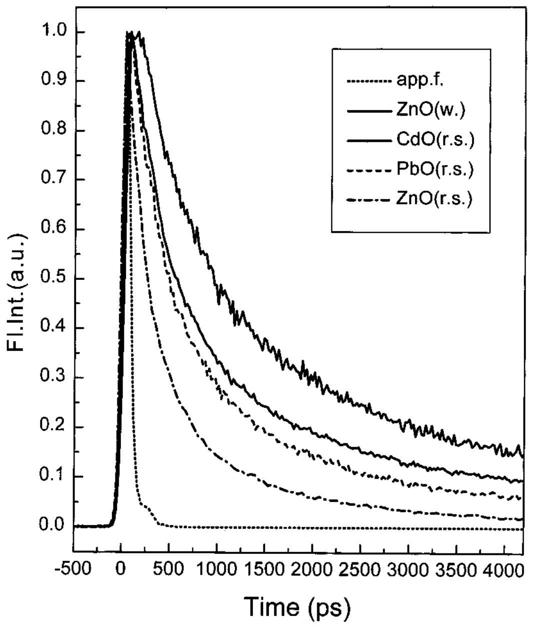

Figure 9. Fluorescence decay for ZnO wurtzite (thick solid line), CdO rock salt (thin solid line), PbO rock salt (dashed line), and ZnO rock salt-like (dashed and dotted line) amorphous nanoclusters at 640 nm.

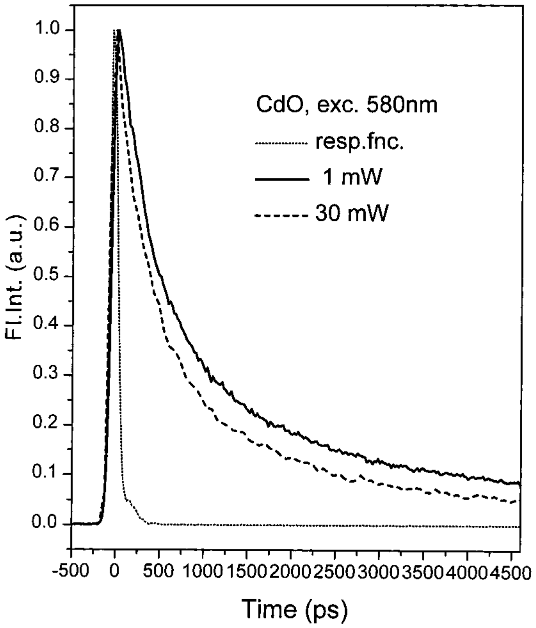

Figure 10. Fluorescence decay at 640 nm for CdO amorphous nanoclusters for different pump intensities: 1 mW (solid line), 30 mW (dashed line), and response function (dotted line).

Table 1. Excited States Lifetimes of ZnO, CdO, and PbO Nanoclusters

compounds	τ_1 (ns)	τ_2 (ns)	E_g (eV)
PbO rock salt-like	0.26−0.29	2.04−2.13	1.91
CdO rock salt	0.35−0.4	2.47−3.2	2.066
ZnO wurtzite	0.55−0.79	3.21−4	2.14

cated band tail states and state hopping involvement. There is no energy relaxation to the red in time. That is essentially a relaxation process different from what is occurring in the amorphous bulk matter, in which there is very long state due to relaxation. Another interesting feature is that their lifetimes are about the same for the different emission states. We consider these properties to be a result of quantum confinement and carrier localization. A similar profile is seen in Figure 8 for ZnO (rock salt-like) nanoclusters. The general similarity of the physical nature of these compounds is obvious from our data.

A comparative representation of fluorescence decays at 640 nm for all prepared systems is given in Figure 9. The corresponding lifetimes values are given in Table 1. There are two lifetime components: a fast one is found in the range of 100−500 ps, and a slow one varies from 1 to 4 ns, depending on the sample. The slow component reflects relaxation processes from band-tail states, whereas the fast one may be related to high-lying extended states. It is clear from the Table 1 that an excitation decays quicker in systems with a smaller band gap. This general trend is reasonable because a smaller band gap should lead to better overlap of ground and excited-state wave functions and hence to faster relaxation. On the other hand, the nearer the excitation wavelength to band gap, the longer the lifetime, which should be due to more relaxation channels. Furthermore, the electron−phonon interaction may be larger for heavier atoms, and the surfactant takes part in the relaxation process due to bonding with clusters. Finally, a smaller effective electron mass factor should correlate with the shorter lifetimes of excited state in PbO clusters.

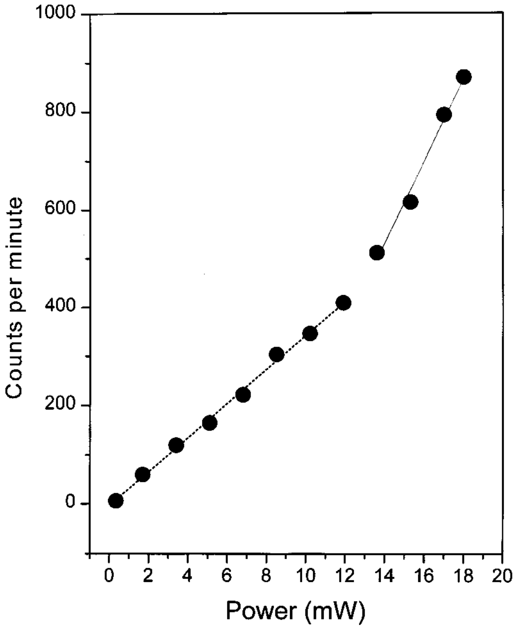

Figure 11. Dependence of CdO amorphous nanocluster fluorescence intensity on the power of laser radiation.

After performing time-resolved fluorescence measurements for CdO particles with different intensities of laser pulse, we find the reduction in the lifetime when the pump intensity is increased (Figure 10). This indicates the presence of a direct transition around the band edge and means that in this system we may form a state with some resonance or mixing between the core and the surface. The interaction of the second exciton with the first may lead to cooperative radiation and lifetime reduction. Finally, we find that the CdO fluorescence intensity depends nonlinearly on power of the laser pulse (see Figure 11). This supports the possibility of cooperative radiate decay in CdO amorphous nanoclusters.

Conclusion

ZnO, CdO, and PbO rock salt-coordinated nanoclusters of the size of 1−2 nm (with similar electronic spectra) have been prepared. These rock salt-coordinated ZnO nanoclusters form from wurtzite coordinated by the thermal treatment. This occurs due to the size and surface effects. X-ray diffraction and electron diffraction techniques indicate their amorphous structures. They all have clear emission in the visible region. The excitation-wavelength dependence of the fluorescence indicates a localization of the electronic state due to amorphous structure and surface capping. ZnO, CdO, and PbO all have the similar UV−visible absorption and photoluminescence spectra at room temperature and hence possible similar structure. Time-resolved photoluminescence just near their band-tail demonstrates sub- and nanosecond time components, which facilitate the understanding of excited states in disordered nanosystems. This is very different from that in the bulk amorphous semiconductor and semiconductor nanocrystals.

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