Dielectric Dispersion Measurements of CdSe Nanocrystal Colloids: Observation of a Permanent Dipole Moment

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We measure the dielectric dispersion of CdSe nanocrystal colloids and show the existence of large dipole moments of 25 and 47 debye for 34 and 46 Å diameter nanocrystals, respectively. The magnitude is consistent with the expected spontaneous polarization of the bulk wurtzite CdSe lattice and implies a potential drop of ≈0.25 V across the nanocrystal. This effect, which is intrinsic to the wurtzite structure but has been largely overlooked, should be incorporated in the description of the quantum confined electronic states. [S0031-9007(97)03636-3]

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Colloidal CdSe nanocrystal "quantum dots" [1] are well-characterized materials that currently provide one of the best systems for tests of ideas about 3D nanometer scale semiconductors [2]. The size-dependent absorption spectra of the CdSe colloids have several well-defined excitonic features that have been convincingly assigned to states derived from a spherical confinement model using the effective mass approximation and an approximate treatment of the Coulomb interaction [3–5]. Furthermore, the observable fine structure at the band edge has been modeled in great detail using the experimentally measured, slightly prolate shape of the nanocrystal and the exchange interaction [6,7]. While the very slow recombination dynamics and its temperature dependence used to be explained by a phenomenological mechanism based on shallow surface traps [8], at present, however, the fluorescence Stokes shift, the radiative lifetime, and the magnetic field dependence are all explained by the lowest state being a "dark exciton." This complete picture of the nanocrystals electronic structure is nevertheless at odds with several observations. Stark measurements suggested the presence of large changes in the dipole moment upon optical excitation [9]. This is inconsistent with the picture of inversion symmetry but it was later shown that the same Stark measurement could be interpreted by field induced mixing of bright and dark states, and that the inversion symmetry did not have to be lifted [10]. Resonance Raman depolarization [11] and two-photon fluorescence excitation measurements [12,13] showed again that the assumption of near-spherical symmetry is inappropriate. The detailed comparison of the one-photon and two-photon band edge spectra suggested further that the internal ground state polarization of the CdSe wurtzite structure is a natural way of lifting the inversion symmetry with the proper magnitude [13]. Of course, this bulk property does not have to carry over to nanometer particles. We present here the first study of the dielectric dispersion of nanocrystal colloids to directly measure their dipole moment, and we show that the effect of the nanocrystal polarity is large enough to compel giving up the picture of a centrosymmetric confinement potential for the highest hole states.

The CdSe nanocrystals are synthesized, according to Ref. [1], by injection of dimethyl cadmium and trioctylphosphine selenide in a hot bath of trioctylphosphine and trioctylphosphine oxide. Their surfaces are stabilized by trioctylphosphine oxide (TOPO) which leads to strong band-edge luminescence and no deep trap emission [1]. The samples are purified and the size dispersion is further reduced by fractional precipitation [1]. From the absorption spectra of the solutions and by comparisons with data in the literature, size dispersions are between 5% and 10% [1]. For the measurements, the samples are dispersed in alkanes such as hexadecane or 2,2,4,4,6,8,8-heptamethylnonane (HMN) with typically 5 mg/ml of dissolved TOPO to act as a stabilizer. The nanocrystals are highly soluble in these nondipolar hydrophobic solvents. The solvents' viscosities are also such that the nanocrystal rotational relaxation is below our upper frequency measurement limit of a few megahertz.

The mean semiconductor diameters, 34 and 46 Å, are determined from the correspondence [14] between the mean sizes and the first maximum in the optical absorption spectra, 526 and 579 nm, respectively. Measuring the mass of the purified nanocrystal powder, using the calculated mass of a single nanocrystal with its organic capping layer, and measuring the optical density at the first absorption peak, we determine a nominal optical cross section. This is then used to measure concentrations. We obtain cross sections of 5×10^{-16} cm^2 for the 34 Å nanocrystals and 8×10^{-16} cm^2 for the 46 Å nanocrystals. We estimate the error in the cross sections, and thus the volume fractions, to be about 20%. The volume fraction will always refer to the volume fraction of the core semiconductor plus its organic passivating layer.

According to Debye and Onsager [15], the dielectric response due to a dilute concentration n of spherical dipoles is given by

$$\varepsilon' = \varepsilon'_{e,\mathrm{nuc}} + \frac{\varepsilon_d}{1 + (\omega\tau)^2} \qquad (1)$$

and

$$\varepsilon'' = \frac{\varepsilon_d}{1 + (\omega\tau)^2}\,\omega\tau\,, \qquad (2)$$

with the relaxation time $\tau = 4\pi\eta r_H^3/kT$ and the dipole dielectric contribution $\varepsilon_d = 4\pi n\mu^2/3kT$. μ is the screened dipole moment, η is the viscosity of the solvent, and r_H is the hydrodynamic radius, which should be close to the radius of the semiconductor core a, plus its organic capping layer.

In order to get the complex dielectric coefficient $\varepsilon = \varepsilon' + i\varepsilon''$, we measure the complex impedance of a circular, gold-coated parallel plate capacitor with a diameter of about one inch and an annular Teflon spacer 110 or 250 μm thick. A Hewlett Packard 4192A impedance analyzer is used to perform the measurements presented here. These are done with the cell both empty and filled with the nanocrystal colloid and the equivalent circuit is modeled as two capacitors and a resistor all in parallel. When the sample is loaded, the space between the capacitor plates contains a material with real dielectric coefficient ε', and loss factor ε''. Both Teflon and the neat solvents are nearly nondispersive in the frequency range of the measurements with dielectric constants equal to 2.1, and they show negligible or no measurable dissipation. Dissolution of a few percent TOPO did not detectably alter the response of the solvent.

Figure 1 shows the dispersion of the real part of the dielectric coefficient for 34 Å nanocrystals at a volume fraction of 30%. The spectrum contains two features: a Debye relaxation near 3×10^5 Hz, which we associate with the dipolar response of the nanocrystals, and an additional feature dominant below 10^4 Hz. The curve is a least squares fit to the Debye relaxation term (2) plus a constant $\varepsilon'_{e,\mathrm{nuc}}$ and an additional term of the form A/ω^β to fit the rising dispersion at low ω. This low frequency term is due to the macroscopic separation of space charges and represents a breakdown of the assumption of isotropy. It is dependent upon the geometry of the capacitor. A doubling of our spacer thickness resulted in a decrease in A by a factor of 1.8 for a fixed β; however, ε_d changed by less than 1%. ε' has been normalized for slight variations in plate separation, arising from deformation of the Teflon spacer, such that $\varepsilon'_{e,\mathrm{nuc}}$ agrees with a theoretical value taken as the sum of the product of the volume fractions and zero frequency dielectric constants of the solvent, TOPO, and bulk CdSe. Although the static dielectric constant of a nanocrystal may depart from the bulk value [16] and the estimate for $\varepsilon'_{e,\mathrm{nuc}}$ is a crude one, the scatter in our measurements allows these approximations. The normalized value is in most cases less than 10% different from the measured value. We then extract ε_d and τ from the fitting parameters. Curves at different concentrations have similar behavior, showing the Debye relaxation, which is linear in concentration, as well as the large increase in the effective capacitance at low frequency which scales with concentration as a power law with an exponent between 0.5 and 1.5.

Figure 1 shows also the dispersion of ε'' for a volume fraction of nanocrystals of about 7.5%. Again, we must add an additional term to the expected form of the dispersion to account for the conduction of free charges. The line represents a least squares fit to Eq. (2) plus the conductivity term $4\pi\sigma/\omega$ and gives us independent values for ε_d and τ.

Figure 2 shows the average screened dipole moments obtained from the real and imaginary parts through Eq. (1)

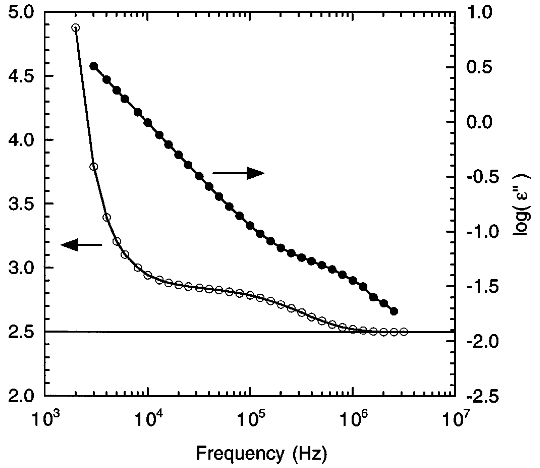

FIG. 1. Dispersion of the real part (open circles) of the dielectric constant for a 30% volume fraction nanocrystal colloid. Dispersion of the dielectric loss (solid circles) for a volume fraction of 7.5%. The nanocrystals have a mean diameter of 34 Å. The lines are least squares fit.

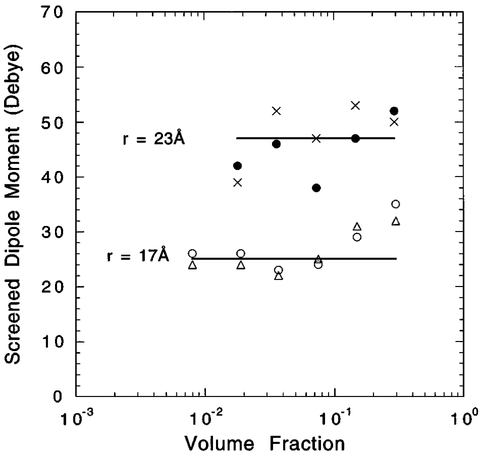

FIG. 2. Measurements of average screened dipole moments. Filled circles and ×'s are from the real and imaginary parts, respectively, of a 46 Å colloid, and open circles and open triangles are from the real and imaginary parts of the dispersion of a 34 Å colloid.

for the two different sizes of nanocrystals plotted against the volume fraction. A summary of the results appears in Table I. The final values of μ and τ reported are averages of the values taken from the real and imaginary parts measured at different concentrations. For a simple theoretical value of the rotational relaxation time we take the hydrodynamic radius to be the sum of the CdSe core radius plus an additional 13 Å for the thickness of the TOPO capping layer in solution calculated from known and estimated bond lengths and angles. This is consistent with close-packed assemblies of similar nanocrystals which are separated by $\approx$20 Å [11,17]. We note that the estimate of τ does not take into account the slightly prolate shape of the nanocrystals [11,17].

The implications of the observed conductivity should be examined. Of particular concern is that a nanocrystal with a point charge located on its surface will appear to have a dipole due to the polarization of the semiconductor lattice. Solving Poisson's equation with appropriate boundary conditions [18] gives a dipole moment of $3ea\varepsilon_1/(2\varepsilon_1 + \varepsilon_2)$, where ε_1 and ε_2 are the static dielectric constants of the surrounding matrix and the nanocrystal, respectively. Using $\varepsilon_1 = 2.1$ [18], $\varepsilon_2 = 10.2$ [19] (bulk CdSe, along the c axis), and $a = 17$ Å, gives a dipole moment of 35 debye for a nanocrystal with one electron on its surface. This immediately raises the possibility that the measured dipole moment is an artifact of dissolution in a solvent with charge impurities. However, an investigation of the conductivity shows that this cannot be the case.

If we assume a "worst-case scenario," that all of the charges participating in the conductivity are charged nanocrystals, we can estimate the number of charged nanocrystals. The conductivity expected from a concentration n of nanocrystals with charge e can be found from the Nernst-Einstein equation for hard spheres with hydrodynamic radius r_H, $\sigma_0 = ne^2/6\pi\eta r_H$. σ_0 represents the conductivity if every nanocrystal carried exactly one charge. For a volume fraction of 2%, we expect σ_0 to be $2.2 \times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for the 34 Å core diameter nanocrystals. Figure 3 shows the ratio of the observed conductivity to σ_0. This ratio is always much less than 1, indicating many more neutral nanocrystals than charged ones. At low volume fraction, the experimental data give a constant $\sigma/\sigma_0 \approx 0.2\%$. Consequently, the expected dipole moment of a charged nanocrystal, 35 debye, cannot account for the observed ε_d by at least a factor of 250. The conductivity measurements therefore support the notion that the measured dipole is an intrinsic property of an uncharged nanocrystal.

TABLE I. Results.

Semiconductor radius a	17 Å	23 Å
Screened dipole moment μ	25 ± 2 D	47 ± 5 D
Relaxation time τ_{exp}	0.27 ± .03 μs	0.7 ± 0.2 μs
Hydrodynamic radius r_H	29 ± 1 Å	39 ± 3 Å
$\tau_{\mathrm{exp}}/\tau_{\mathrm{theory}}$	0.9 ± 0.1	1.4 ± 0.4

As shown in Fig. 3, there is a dramatic increase in the conductivity per nanocrystal at the higher volume fraction. Using different solvents, different surface modifications, or filtering, we have not yet been successful at significantly controlling this conductivity and, therefore, we do not attempt a quantitative description. Nevertheless, the observed behavior is opposite to that expected for electrolytes [20] where association tends to reduce the molar conductivity at high concentration. It is instead similar to that observed in a variety of conducting colloidal and microemulsion systems [21]; thus this rise of the conductivity is clearly related to the nanocrystals. Qualitatively, this indicates a turn-on of a contact or hopping-related conduction mechanism.

Having firmly established the magnitude of the dipole moment, we can now discuss its origin and impact. First, it is well known that the CdSe nanocrystals have the wurtzite structure, which is polar in the bulk. It is therefore natural to compare the dipole moment to the internal polarization. We can cast μ in the form of an internal polarization P_0, given by [22] $P_0 = \mu(2\varepsilon_1 + \varepsilon_2)/4\pi a^3\varepsilon_1$. This leads to values of 0.9 and 0.7 $\mu\mathrm{C/cm^2}$ for the smaller and larger sized nanocrystals which are comparable to the estimated bulk value [13] 0.6 $\mu\mathrm{C/cm^2}$. This close agreement supports the origin of the moment as being intrinsic to the wurtzite structure. It explains why the dipole moment increases strongly with nanocrystal size and implies that surface polarization or reconstruction does not yet screen out the internal field at these small crystal sizes. The implications are important: Concurrent with the polarization, there is a potential drop along the c axis of the crystal given by [22] $\Delta\Phi = 2\mu/\varepsilon_1 a^2$. For the 34 Å and 46 Å nanocrystals, the potential drop is 0.25 V coincidentally for both—much

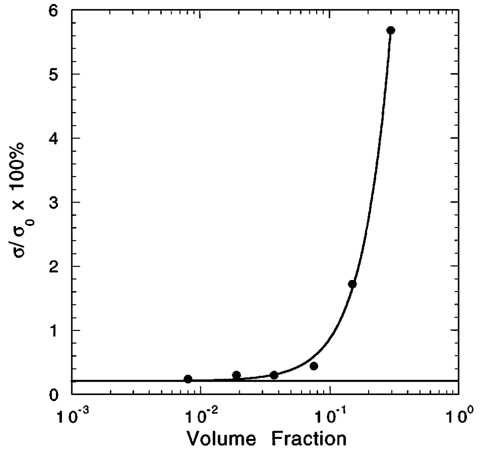

FIG. 3. Conductivity of the 34 Å colloids plotted as a fraction of the conductivity expected for singly charged nanocrystals. At the lower volume fractions, this ratio is about 0.2%. The lines are guides to the eye.

larger than either the exchange or shape effect perturbations. For the 46 Å nanocrystals, calculations based on a centrosymmetric spherical confinement predicted that the shallowest hole state $1S_{3/2}$ is $\approx$100 meV below the top of the valence band [4], while the next state, the $1P_{3/2}$ state, is only $\approx$30 meV farther away. Therefore the potential drop is so large that a complete, nonperturbative reworking of the hole energy levels is required. For the lowest electron states, the confinement and separation energies are of the order of 0.5 eV allowing a better possibility for a perturbative treatment. Qualitatively, the hole should be on one side of the nanocrystal, while the electron remains delocalized to a greater extent. This partial hole localization bears similarity to the trap-state scenario [8] without actually requiring a specific trap state. It reduces the orbital wave function overlap leading to decreased oscillator strengths, increased Frölich coupling to optical phonons, and reduced exchange interaction. Inclusion of this internal polarization should lead to a more consistent description of the nanocrystal optical properties.

In summary, we observe large, permanent, dipole moments for colloidal CdSe nanocrystals. We also measured the rotational relaxation times of the nanocrystals in solution and find that they scale appropriately with nanocrystal sizes including their organic capping layer. Finally, we observed the presence of charges in the solutions and a superlinear increase of the conductivity at high nanocrystal volume fractions. This last point is relevant to optoelectronic measurements of high concentrations or close-packed assemblies of nanocrystals.

The main conclusion of this Letter is that the measured dipole moments are consistent with the expected bulk internal polarization for CdSe indicating little surface screening and that the relatively large corresponding potential drop across the nanocrystal implies that the electronic calculations based on spherical or weakly prolate nanocrystals must be thoroughly revised, in particular at the band edge. Since the effect is thought to arise from the wurtzite CdSe lattice, an important experimental test will be to perform similar studies of well-defined nanocrystals with cubic or zinc blende lattices. In addition, the larger delocalization and wave function overlap expected for these other materials should be beneficial to optical applications.

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[1] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).

[2] For reviews, see M. L. Steigerwald and L. E. Brus, Annu. Rev. Mater. Sci. **19**, 471 (1989); A. P. Alivisatos, J. Phys. Chem. **100**, 13 226 (1996); A. Henglein, Chem. Rev. **89**, 1861 (1989).

[3] J. B. Xia, Phys. Rev. B **40**, 8500 (1989); P. C. Sercel and K. J. Vahala, Phys. Rev. B **42**, 3690 (1990).

[4] A. I. Ekimov *et al.*, J. Opt. Soc. Am. B **10**, 100 (1993).

[5] D. J. Norris, A. Sacra, C. B. Murray, and M. G. Bawendi, Phys. Rev. Lett. **72**, 2612 (1994); D. J. Norris and M. Bawendi, Phys. Rev. B **53**, 16 338 (1996).

[6] M. Nirmal *et al.*, Phys. Rev. Lett. **75**, 3728 (1995); M. Chamarro *et al.*, Phys. Rev. B **53**, 1336 (1996); Al. L. Efros *et al.*, Phys. Rev. B **54**, 4843 (1996); U. Woggon, F. Gindele, O. Wind, and C. Klingshirn, Phys. Rev. B **54**, 1506 (1996).

[7] D. J. Norris, Al. L. Efros, M. Rosen, and M. G. Bawendi, Phys. Rev. B **53**, 16 347 (1996).

[8] M. G. Bawendi, P. J. Carroll, W. L. Wilson, and L. E. Brus, J. Chem. Phys. **96**, 946 (1992); M. Nirmal, C. B. Murray, and M. G. Bawendi, Phys. Rev. B **50**, 2293 (1994).

[9] V. L. Colvin and A. P. Alivisatos, J. Chem. Phys. **97**, 730 (1992); V. L. Colvin, K. L. Cunningham, and A. P. Alivisatos, J. Chem. Phys. **101**, 7122 (1994).

[10] A. Sacra, D. J. Norris, C. B. Murray, and M. G. Bawendi, J. Chem. Phys. **103**, 5236 (1995).

[11] J. J. Shiang, A. V. Kadavanich, R. K. Grubbs, and A. P. Alivisatos, J. Phys. Chem. **99**, 17 417 (1995).

[12] M. E. Schmidt *et al.*, Phys. Rev. B **53**, 12 629 (1996).

[13] M. E. Schmidt *et al.*, J. Chem. Phys. **106**, 5254 (1997).

[14] M. G. Bawendi (private communication).

[15] N. E. Hill, W. E. Vaughn, A. H. Price, and M. Davies, *Dielectric Properties and Molecular Behavior* (Van Nostrand Reinhold, London, 1969).

[16] L. W. Wang and A. Zunger, Phys. Rev. B **53**, 9582 (1996).

[17] C. B. Murray, C. R. Kagan, and M. G. Bawendi, Science **270**, 1335 (1995).

[18] This is an approximation $\varepsilon_t = n_D^2$, where $n_D = 1.4390$; the index of refraction at the sodium *D* line comes from the manufacturer, Aldrich Chemical Corp., Milwaukee, WI.

[19] *Semiconductors: Other Than Group IV Elements and III-V Compounds,* edited by O. Madelung (Springer-Verlag, Berlin, 1992), p. 29.

[20] P. H. Rieger, *Electrochemistry* (Chapman & Hall, New York, 1994), p. 115.

[21] A. M. Cazabat, D. Chatenay, P. Guering, and W. Urbach, in *Physics of Complex and Supermolecular Fluids,* edited by S. A. Safran and N. A. Clark (John Wiley and Sons, New York, 1987), p. 585, and references therein.

[22] C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973), Vol. 1, p. 134.