

# Thermal Charging of Colloidal Quantum Dots in Apolar Solvents: A Current Transient Analysis

Marco Cirillo,<sup>†</sup> Filip Strubbe,<sup>‡</sup> Kristiaan Neyts,<sup>\*,\*</sup> and Zeger Hens<sup>†,\*</sup>

<sup>†</sup>Physics and Chemistry of Nanostructures, Ghent University, Krijgslaan 281-S3, B-9000 Gent, Belgium, and <sup>‡</sup>Liquid crystals and photonics, Ghent University, Sint-Pieternieuwstraat 41, B-9000 Gent, Belgium

The synthesis of colloidal nanoparticles (NPs) is an old field of materials chemistry that was redirected in the early 1990s with the publication of a few seminal papers that describe the synthesis of colloidal CdSe and Au NPs stabilized by a molecular monolayer of ligands at the NP surface.<sup>1,2</sup> Typically using ligands with long, apolar alkyl chains, this resulted in NPs that could be dried as a powder and redispersed at will in apolar solvents. Over the last 15 years, this approach has been applied to a large variety of materials, ranging from semiconductors to metal oxides and metals.<sup>3,4</sup> Especially in the case of semiconductor nanoparticles or quantum dots (QDs), this has led to synthesis schemes offering an exceptional control over size, size dispersion, and shape. Due to quantum confinement, these novel nanomaterials have widely tunable electro-optic properties, with possible applications in electro-optic devices,<sup>5–7</sup> biolabeling,<sup>8,9</sup> or sensing.<sup>10–12</sup>

An aspect of these colloidal NP dispersions in apolar solvents that systematically returned in the literature is that of dipoles<sup>13–17</sup> or charges on the NPs.<sup>13,14,18–22</sup> Using an apolar solvent (2,2,4,4,6,6,8-heptamethylnonane) and excess free ligand to stabilize the dispersion, Shim *et al.* showed that dispersions of CdSe QDs in apolar solvents have a nonzero conductivity,<sup>14</sup> a result they related to charges on the QDs. Further confirmation of the fact that QDs can become charged in apolar media came from electrophoretic deposition, which was used to form thin films of CdSe and Fe<sub>2</sub>O<sub>3</sub> QDs.<sup>18,19</sup> Alternatively, the idea that colloidal QDs can become charged upon illumination was demonstrated more directly using electrostatic force microscopy.<sup>20,21</sup> In addition, Shevchenko *et al.* showed that additives like oleic acid and tri-*n*-octylphosphine oxide can change the average charge on colloidal NPs and they proposed a link between charges on colloidal NPs and the

**ABSTRACT** We analyze thermal charging in additive-free colloidal CdSe quantum dot (QD) dispersions by means of the transient electric current resulting from a voltage step applied across the QD dispersion. On the basis of the initial current and the total charge separated, we find that the CdSe dispersion behaves as a 1:1 electrolyte where equal fractions of the QDs carry a single positive or a single negative charge. This conclusion is confirmed by a more detailed fitting of the current transient using the Nernst–Planck–Poisson equations. Using equilibrium thermodynamics, we relate the fraction of charged QDs to the QD charging energy. The magnitude of the charging energy corresponds to values found using known models for the charging energy of either a spherical surface in a dielectric or a charge within a dielectric sphere. However, the experimental dependence of the charging energy on the dielectric constant of the solvent is far less pronounced than predicted by these models. A better correspondence is found based on the charging energy of a spherical surface embedded in a compound medium consisting of the ligand shell and the solvent.

**KEYWORDS:** electrical charges · apolar solvents · charging energy · CdSe · oleic acid · current transient

structure of binary superlattices formed upon self-assembly of dispersed NPs.<sup>22</sup> More recently, the effect of light-induced charging or photoionization of colloidal QDs gained much attention, since the presence of charged QDs complicates the study of carrier multiplication using transient absorption measurements.<sup>23,24</sup>

Leaving aside the special case of photoinduced charging, the present literature leaves a number of questions on charges on colloidal NPs unanswered. Clearly, additives can induce charges on NPs.<sup>22</sup> However, it remains unclear whether additives are required for charging. Shim *et al.* did not use dispersions free of additives<sup>14</sup> and Shevchenko *et al.* find a pronounced imbalance in the charges on PbSe QDs in washed dispersions,<sup>22</sup> suggesting that these solutions do not merely consist of QDs and solvent. In addition, Shim *et al.* suggest that the fraction of charged QDs is related to the QD charging energy,<sup>14</sup> which they interpret as the dielectric confinement energy of a point charge in a dielectric sphere as calculated by Brus.<sup>25</sup> In this way, they predict that

\*Address correspondence to Zeger.Hens@UGent.be.

Received for review November 10, 2010 and accepted January 4, 2011.

Published online January 11, 2011  
10.1021/nn103052r

© 2011 American Chemical Society

the extend of charging should be larger in a solvent with a higher dielectric constant  $\epsilon$ . However, this has not been demonstrated so far, implying that the expression for the charging energy they propose remains to be validated.

In this paper, we address these issues by studying charges on colloidal CdSe QDs, stabilized by oleate ligands in dispersions free of excess ligand,<sup>26</sup> that is, the most simple system possible. For this work, we use a current measurement method that was developed recently for the analysis of charges on inverse micelles in apolar liquids.<sup>27</sup> The method makes use of the current transient following a voltage step applied to a capacitor filled with a CdSe QD dispersion. Using 3.5 nm CdSe QDs dispersed in apolar liquids like dodecane or dioctylether, we find that these dispersions behave as a 1:1 electrolyte, where an equal fraction  $\alpha$  of QDs carries a single positive or a single negative charge. This fraction is considerable, ranging from 0.5% in dodecane to 1.9% in dioctylether. Similar to the work of Shim *et al.*, these values can be rationalized by a thermal charging model where the entropy increase resulting from charging (entropy of mixing) is balanced by the energy it takes to charge a QD (Coulomb energy). The magnitude of the charging energy corresponds to the energy required to charge a spherical shell in a dielectric. However, the dependence on the dielectric constant of the solvent is less pronounced than the  $1/\epsilon$  trend predicted by this simple model. Therefore, we suggest that the ligand shell contributes together with the solvent to the screening of charges on colloidal QDs. In this way, this work introduces a straightforward experimental technique and a conceptual framework to analyze and understand charging of colloidal QDs dispersed in apolar solvents.

## BACKGROUND

We use the transient current following a voltage step applied over a QD dispersion to detect the presence of charges in QD dispersions and to analyze key properties of these charges, such as their mobility, density, and charge number. If charges are present, an electric field will force them to drift to the oppositely charged electrode resulting in a current  $I$  in the external circuit. In a planar geometry (see Figure 6, Methods section), the current measured in the external circuit can be related to the current density  $J$  in the dispersion as follows<sup>28</sup> ( $S$ , electrode area;  $d$ , distance between the electrodes):

$$I = \frac{S}{d} \int_{-d/2}^{d/2} J(x) dx \quad (1)$$

Under the condition that the QD dispersion contains an initially homogeneous distribution of positively and negatively charged QDs with equal densities ( $n_{\pm}$ ), equal mobilities ( $\mu_{\pm}$ ), and opposite charges ( $Ze$  and  $-Ze$ ), the initial current follows from eq 1 as ( $E$ , electric

field;  $V$ , applied voltage difference):<sup>28</sup>

$$I_0 = 2n_{\pm}\mu_{\pm}ZeES = \frac{2n_{\pm}\mu_{\pm}ZeVS}{d} \quad (2)$$

Here we ignore the capacitive charging upon applying the voltage step. Integrating  $I$  over time yields the total charge  $Q$  transferred between the electrodes through the external circuit. Provided  $V$  is sufficiently high and assuming that charge generation within the dispersion and charge transfer at the electrodes is negligible, the total charge transferred is equal to the total amount of charge initially present in the volume between the electrodes. Hence, we have:<sup>28</sup>

$$Q = \int I dt = n_{\pm}ZeSd \quad (3)$$

This situation of complete separation of charges is uncommon in polar liquids but is described before for charged inverse micelle solutions in apolar liquids.<sup>29</sup>

Equations 2 and 3 show that two relatively simple observables like the initial current  $I_0$  and the total charge  $Q$  enable us to determine the concentration of charges  $Zn_{\pm}$  in a QD dispersion and the mobility  $\mu_{\pm}$  of the charged species. A more elaborate approach consists of fitting the entire transient using the Poisson–Nernst–Planck equations. These describe the concentration of charged particles and the electric field as a function of position and time considering drift and diffusion of charged QDs (Nernst–Planck) and the relation between the electric field and the concentration of charged QDs (Poisson).<sup>28</sup> Under the conditions that screening of the charge on the electrodes by the charged QDs and diffusion can be neglected (this is a valid approximation for sufficiently high applied voltage and sufficiently low concentration of charged species), these equations predict a linear decrease of the current with time:

$$I = I_0 \left( 1 - t \frac{\mu V}{d^2} \right) \quad (4)$$

The value  $d^2/(\mu V)$  is the time it takes for a single charged particle to cross the entire cell denoted as the cell-transit time  $\tau_{tr}$ . For a QD with a hydrodynamic diameter of 7.5 nm, immersed in dodecane, a cell width of 28  $\mu\text{m}$  and a voltage of 5 V,  $\tau_{tr}$  amounts to 92 ms.

## EXPERIMENTAL RESULTS

The typical materials properties of the QDs used in this study have been published.<sup>26</sup> In brief, we use CdSe QDs with an average diameter of 3.5 nm and a size dispersion of 7–8% stabilized by oleate ligands. As shown in the Supporting Information, no free ligands remain in solution with the standard washing procedure, and also dilution down to concentrations of about 1  $\mu\text{M}$  does not release any free ligands.<sup>26</sup>

Figure 1 shows a typical current transient obtained after applying a voltage of 5 V to a 1  $\mu\text{M}$  solution of CdSe QDs in dodecane. We measure an initial current of the order of

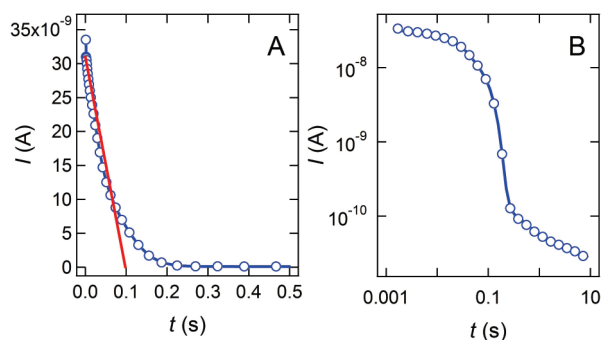


Figure 1. Current transient obtained after applying a voltage step of 5 V to a 1  $\mu\text{M}$  dispersion of 3.5 nm CdSe QDs in dodecane in linear (a) and logarithmic scale (b). The red line in panel a shows the linear decay expected following eq 4 for drift of singly charged QDs in the absence of screening.

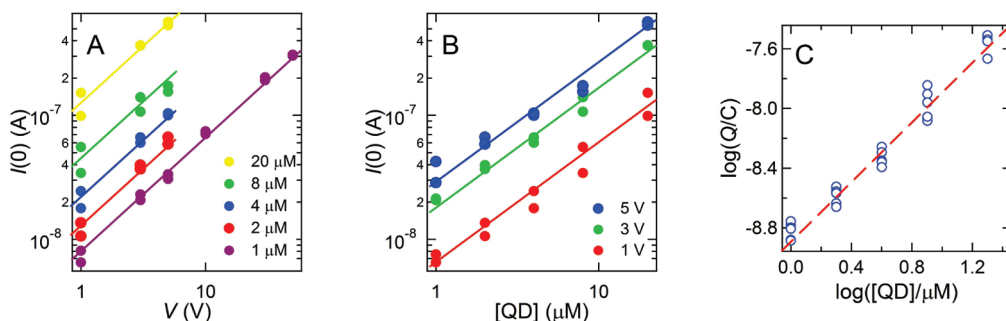


Figure 2. (a) Initial current versus voltage for CdSe QD dispersions in dodecane for different QD concentrations as indicated. (b) Initial current as a function of concentration for the voltages indicated. (c) Total charge versus concentration. At each concentration, measurements at voltages of 1, 3, and 5 V are represented. In all figures, the full lines are guides to the eye with a slope of 1.

10–100 nA, which drops to the 10–100 pA level after about 0.2 s. The red line in Figure 1a indicates the transient expected following eq 4 if the initial current measured were due to drift of singly charged QDs with a hydrodynamic diameter of 7.5 nm. The reasonable correspondence with the measured transient gives a first indication that the current is effectively related to the separation of charged QDs initially present in the dispersion. In that case, the current drop at about 0.2 s corresponds to the time when all charges have been collected at the electrodes, while the small current remaining after 0.2 s is either related to the generation of charged QDs in the dispersion or to charge transfer at the electrodes. Importantly, Figure 1b shows that both the initial current and the total charge can be accurately determined from these current measurements. The steep drop in the current at about 0.2 s provides a clear end point for the integration, making a simple  $I_0$ – $Q$  analysis of the transients based on initial current and total charge feasible.

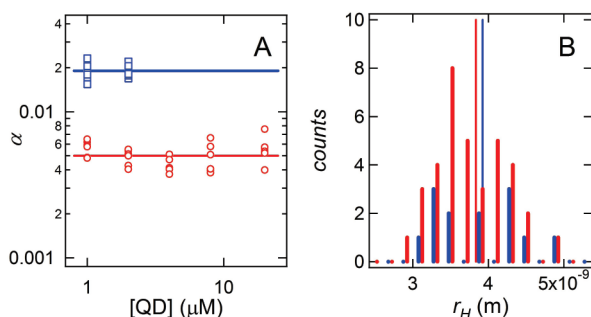
A summary of the  $I_0$ – $Q$  analysis for a series of measurements carried out with CdSe QDs dispersed in dodecane is presented in Figure 2. We find that  $I_0$  increases proportionally with the QD concentration and with the applied voltage (Figure 2a,b). On the basis of eq 2, this means that the concentration of charged species in the QD dispersion is a constant fraction of the QD concentration, and that their electrophoretic mobility is independent of electric field and concentration. The former

conclusion is corroborated by the observation that  $Q$  is directly proportional to the QD concentration as well, yet does not depend on the applied voltage (Figure 4c).

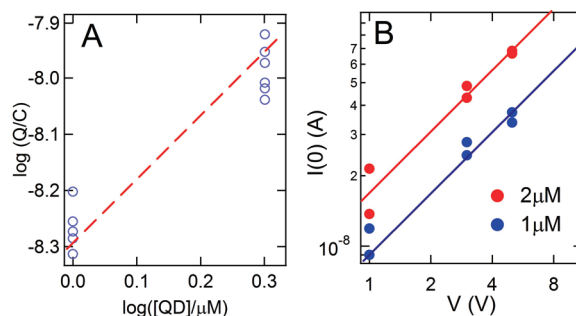
Using eq 3 and assuming that  $Z = 1$ , the concentration of charged particles  $n_{\pm}$  can be calculated. The ratio  $\alpha$  between the concentration of charged QDs  $n_{\pm}$  thus determined and the QD concentration is plotted in Figure 3a. Averaged over all the measurements, we find that  $\alpha$  amounts to 0.5% of the QD concentration. Using this figure, the electrophoretic mobility of the charged particles can be calculated for each data point in Figure 3a by means of eq 2. Figure 3b shows the histogram of the hydrodynamic radii (red bars) calculated from the resulting mobilities according to ( $\eta$ , viscosity of dodecane, 1.34 mPa s<sup>30</sup>):

$$r_H = \frac{Ze}{6\pi\eta\mu} \quad (5)$$

We find that the distribution of the  $r_H$  values thus calculated is centered around an average of 3.85 nm (red line). This corresponds well with the QD radius of 1.75 nm, incremented with a ligand shell thickness of 2.1 nm, a reasonable value for oleate ligands that closely matches the hydrodynamic radius of 3.8 nm found by NMR spectroscopy on similar QDs dispersed in toluene.<sup>26</sup> This correspondence demonstrates that our experimental results are consistent with the assumption made in deriving eqs 2 and 3—in particular that of



**Figure 3.** (a) Ratio  $\alpha$  between the concentration of charged QDs and the total QD concentration for all measurements done in dodecane (red symbols) and dioctylether (blue symbols). (b) Histogram of the hydrodynamic radii calculated for the different measurements in dodecane (red bars) and dioctylether (blue bars). The vertical lines indicate the average hydrodynamic radius found in (red, 3.85 nm) dodecane and (blue, 3.95 nm) dioctylether.



**Figure 4.** (a) Total charge versus concentration for CdSe QD dispersions in dioctylether (b) Initial current as a function of concentration for the concentrations indicated. In both figures, the full lines are guides to the eye with a slope of 1.

an equal concentration of positive and negative charges—and with the hypothesis  $Z = 1$ . This implies that both the fraction of QDs carrying a single positive or a single negative charge is equal to the ratio  $\alpha$  shown in Figure 3a.

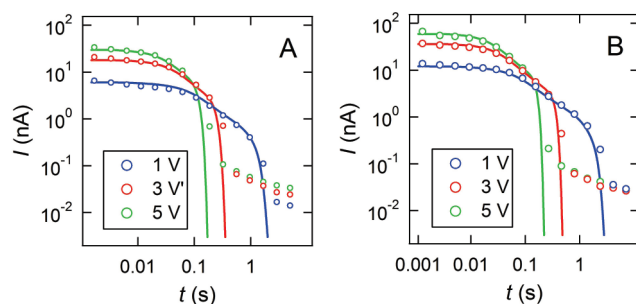
The outcome of the  $i_0$ – $Q$  analysis on a set of current transients recorded on CdSe QDs dispersed in dioctylether is represented in Figure 4. While the data set is less extensive than that obtained with dodecane, they show a very similar result. The initial current is directly proportional to the QD concentration and the applied voltage, while  $Q$  is directly proportional to the concentration and largely independent of the applied voltage. As shown in Figure 3a, we calculate a fraction of charged QDs in dioctylether of 1.9% from the data, a number that is about four times larger than in dodecane. In this case, the histogram of the hydrodynamic radii (calculated using  $\eta_{\text{dio}} = 3.52 \text{ mPa s}$ ) is centered around 3.95 nm (Figure 4b), again confirming the consistency of the analysis.

The relatively simple  $i_0$ – $Q$  analysis of the current transients points toward the conclusion that well purified QD dispersions correspond to a 1:1 electrolyte where a fraction of the QDs carries a single positive charge and an equally large fraction carries a single negative charge. In dodecane and dioctylether, these fractions amount to 0.5% and 1.9%, respectively. To substantiate this result, we expanded the  $i_0$ – $Q$  analysis with simulations of the current transients up to the point where the charges initially present are fully separated. These simulations are based on the combined Poisson–Nernst–Planck

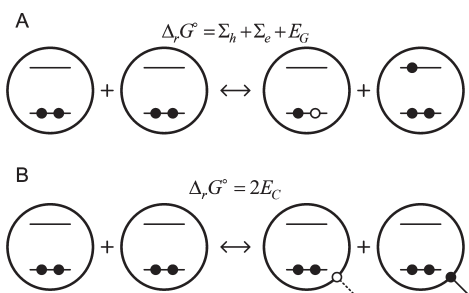
equations, taking a homogeneous distribution of a 1:1 electrolyte of charged QDs as a starting point and neglecting charge generation in the dispersion or charge transfer at the electrodes.<sup>28</sup> As the different parameters entering the simulations are either set by the experimental conditions ( $S$ ,  $d$ , and  $V$ ) or taken from known properties of the QDs and the dispersion ( $\mu$ ,  $\eta$ , QD concentration), the only adjustable parameter in the simulations is the fraction of charged QDs  $\alpha$ . Figure 5 shows a comparison between simulated and measured transients for  $\alpha$  equal to the experimental value of 0.5%. The excellent correspondence for the different concentrations (1 and 2  $\mu M$ ) and voltages (1, 3, and 5 V) clearly confirms the initial assumption that the current transient is due to the separation of oppositely charged QDs with equal concentration and  $Z = 1$ . An aspect worth noting in the transient, especially for the 2  $\mu M$  dispersion, is the  $t^{-3/4}$  dependence of the current on time, prior to the current drop that indicates the end of the charge separation. This behavior is typical for drift of charged particles in the regime where the applied electric field is considerably screened due to the presence of charged QDs at the electrodes.<sup>28</sup>

## DISCUSSION

The analysis of the current transients recorded at CdSe QD dispersions in dodecane and dioctylether clearly shows that these should be considered as a 1:1 electrolyte, containing an equal concentration of QDs with a single positive and a single negative charge.

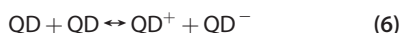


**Figure 5.** Transient currents for (A) 1 and (B) 2  $\mu\text{M}$  solutions of CdSe QDs in dodecane for applied voltages of 1, 3, and 5 V. The dots and lines represent experimental results and simulations, respectively. The simulations are based on the combined Poisson–Nernst–Planck equations assuming a 1:1 electrolyte of charged CdSe QDs, with the fraction of charged QDs as the sole adjustable parameter.



**Figure 6.** Two possible equilibria between uncharged and charged QDs. (A) Charged QDs have either a hole (open circle) in the valence band or an electron (filled circle) in the conduction band. (B) Charged QDs have a positive or a negative surface charge, e.g., resulting from the transfer of a charged ligand (open circle, dashed line = missing ligand; filled circle, full line = additional ligand). The expression of the standard reaction free energy is given for both cases.

This means that we can formally write the equilibrium between charged and uncharged QDs as



Calling  $\alpha$  the fraction of charged QDs with respect to the total number of QDs and  $\Delta_r G^\circ$  the standard free energy change of the charging equilibrium, the chemical equilibrium equation reads:

$$\left(\frac{\alpha}{1-2\alpha}\right)^2 = \exp\left(-\frac{\Delta_r G^\circ}{k_B T}\right) \quad (7)$$

The value  $\Delta_r G^\circ$  takes will depend on the nature of the charge QDs. As shown in Figure 6, if charged QDs have either a hole in the valence band or an electron in the conduction band,  $\Delta_r G^\circ$  amounts to the QD bandgap energy  $E_G$  incremented by the polarization energy of the hole ( $\Sigma_h$ ) and the electron ( $\Sigma_e$ ).<sup>31</sup> In the case of a surface charge resulting, for example, from the transfer of a charged ligand between two QDs,  $\Delta_r G^\circ$  equals twice the energy  $E_C$  needed to bring this charge on a QD. Following eq 7, the experimentally determined fraction of charged QDs is related to  $\Delta_r G^\circ$ . Table 1 shows that the fraction of charged CdSe QDs, which is obtained from the analysis of current transient measurements, leads to an experimental  $\Delta_r G^\circ$  of 270 meV

in dodecane and 200 meV in dioctylether. Typical values of Coulomb charging determined for CdSe using tunneling spectroscopy range from 60 to 140 meV,<sup>31–33</sup> while the sum of the bandgap energy and the electron and hole polarization energy is of the order of 2–3 eV.<sup>31,32</sup> Hence, we conclude that  $\Delta_r G^\circ$  corresponds to twice the QD charging energy  $E_C$  (Figure 6B). The corresponding experimental charging energies  $E_{C,\text{exp}}$  are given in Table 1.

The QD charging energy is essentially an electrostatic quantity. Shim and co-workers proposed that it corresponds to the expression derived by Brus for the work needed to create a charge in a dielectric sphere with dielectric constant  $\epsilon_c$  at a distance  $r$  of the center of the sphere:<sup>25</sup>

$$E_{C,\text{th1}} = \frac{e^2}{8\pi\epsilon_0 r_c} \sum_{l=0}^{\infty} \left[ \frac{(\epsilon_c/\epsilon_{\text{sol}} - 1)(l+1)}{\epsilon_c(\epsilon_c/\epsilon_{\text{sol}} l + l + 1)} \left(\frac{r}{r_c}\right)^{2l} \right] \quad (8)$$

A complication with this expression is the interpretation of the radii  $r$  and  $r_c$ . Table 1 shows which value  $E_{C,\text{th1}}$  takes for the CdSe QDs used here if we set, following Shim *et al.*,<sup>14</sup>  $r$  and  $r_c$  equal to 1.6 and 1.95 nm, respectively, together with dielectric constants of 2 (dodecane), 5.5 (dioctylether), and 10.4 (CdSe). One readily sees that eq 8 yields the correct order of magnitude for the charging energy, confirming the relation between the presence of charged QDs and the QD charging energy. This demonstrates that the charging of QDs in apolar solvents can indeed be described as thermal charging, driven by the balance between the entropy increase resulting from charging (entropy of mixing) and its energy cost (charging energy).<sup>14</sup> Hence, the larger the value of  $E_C$  is, the more difficult it will be for the QDs to get charged, while a reduction of the charging energy will promote the presence of charge on the QDs. In addition, the link between the experimentally obtained values  $E_{C,\text{exp}}$  for QD charging and  $E_{C,\text{th1}}$  accounts for the absence of QDs carrying two or more elementary charges. Doubling the charge leads to a 4-fold increase of the charging energy, which results in a negligible fraction of doubly charged species, in accordance with the observations.



**TABLE 1. Standard Free Energy Change of the Charging Reaction, Experimental Charging Energy, and Various Theoretical Charging Energies As Determined from the Fraction of Charged CdSe QDs for the Solvents Indicated**

solvent	$\alpha$	$\Delta_r G^\circ$ (meV)	$E_{C,exp}$ (meV)	$E_{C,th1}$ (meV)	$E_{C,th2}$ (meV)	$E_{C,th3}$ (meV)
dodecane	$0.005 \pm 0.001$	$270 \pm 10$	$135 \pm 5$	219	206	166
diethylene	$0.019 \pm 0.003$	$200 \pm 6$	$100 \pm 3$	43	75	107

A closer inspection of the  $E_{C,th1}$  values shows that, while yielding the right order of magnitude, it strongly overestimates the influence of the dielectric constant of the solvent on the fraction of charged QDs. Because of the factor  $\epsilon_c/\epsilon_{sol} - 1$  in the numerator of eq 8,  $E_{C,th1}$  strongly drops with increasing  $\epsilon_{sol}$  to become zero when the dielectric constants of the solvent and the QDs match. As this strong dependence of the charging energy on  $\epsilon_{sol}$  is not observed, the use of eq 8 to model the QD charging energy is questionable.

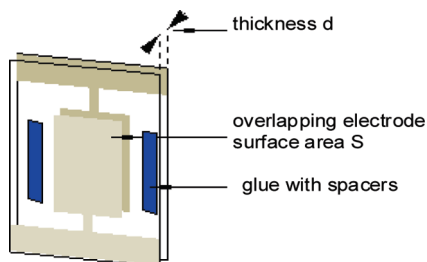
An alternative approach to estimate the charging energy is the energy, indicated as  $E_{C,th2}$ , needed to homogeneously charge a spherical surface with a radius corresponding to that of the inorganic core of the QD, in a solvent with a dielectric constant  $\epsilon_{sol}$ :

$$E_{C,th2} = \frac{e^2}{8\pi\epsilon_0\epsilon_{sol}r_c} \quad (9)$$

Looking at Table 1, we find a better correspondence with the experimental charging energies, but  $E_{C,th2}$  still overestimates  $E_{C,exp}$  in dodecane (206 vs 135 meV), while it underestimates it in diethylene (74 vs 100 meV). This suggests that in reality, a charge on the QDs is better screened than predicted by eq 9 in dodecane, yet screening is less effective in diethylene. A way to solve this paradox is to look at a QD as a dot/ligand core/shell system, immersed in a solvent with a given dielectric constant. A similar model, albeit for an electrolyte solution, has been introduced before to describe the capacitance of monolayer protected gold clusters.<sup>34</sup> Again considering the particle charge as a homogeneously distributed surface charge, we can estimate  $E_C$  in that case as (see Supporting Information,  $\epsilon = \epsilon_{lig}/\epsilon_{sol}$ ):

$$E_{C,th3} = \frac{e^2}{8\pi\epsilon_0} \left( \frac{1}{\epsilon_{lig}r_c} + \frac{1}{\epsilon_{sol}(r_c + r_{lig})} - \frac{1}{\epsilon_{lig}(r_c + r_{lig})} \right) \\ = \frac{e^2}{8\pi\epsilon_0\epsilon_{sol}r_c} \left( \frac{\epsilon r_c + r_{lig}}{\epsilon r_c + \epsilon r_{lig}} \right) \quad (9)$$

Table 1 shows the resulting values obtained by taking a ligand shell thickness  $r_{lig}$  of 2.1 nm and setting  $\epsilon_{lig}$  equal to the dielectric constant of oleic acid (3.1). In this case, screening by the solvent is partially replaced by screening by the ligand shell, which reduces the effect of  $\epsilon_{sol}$  on  $\epsilon_C$  in a way that is in line with the experimental data (more screening for dodecane, less for diethylene). Although the correspondence is not perfect yet, this model describes quite well the limited solvent dependence of the charging energy.



**Figure 7. Scheme of the measurement cell showing the overlapping electrodes with surface  $S$  the glue with spacers and the thickness  $d$ .**

While this work introduces a clear view on thermal charging in colloidal QD dispersions in combination with a straightforward experimental approach to determine the fraction of charged QDs and the charging energy, it also shows a number of directions for future research. The first concerns the nature of the charge QDs. The magnitude of  $\Delta_r G^\circ$  excludes an interpretation of the charge as a delocalized electron or hole in the QD conduction or valence band and therefore points toward charges localized on the QD surface. On the other hand, the experimental charging energy is more in line with theoretical expressions based on a distributed charge ( $E_{C,th2}$  and  $E_{C,th3}$ ) than a localized charge ( $E_{C,th1}$ ). This raises the question of how we should understand this surface charge. A second concerns the role of additives. Probably, the adsorption of an additive that can bind as an ion to the QD surface or that can release ionic ligands may shift the distribution of charged QDs in the direction of more positively or more negatively charged QDs.<sup>22</sup> However, the present work shows that in the absence of additives, the charging of QDs can be understood from a thermodynamic equilibrium with a  $\Delta_r G^\circ$  that amounts to twice the QD charging energy and charge balance at the level of the QDs (*i.e.*, an equal number of positively and negatively charged QDs). In the presence of additives, positively and negatively charged QDs will still be in thermodynamic equilibrium. This means that preferential positive or negative charging of QDs requires that additives affect the charge balance. Hence, a proper, thermodynamic understanding of this preferential charging requires a view on the countercharge. Third, this work shows that charges are present in QD dispersions in apolar solvents, yet it does not address possible mechanisms of charge generation, which is clearly of importance for applications where rapid charging or discharging is important, such as

electrophoretic deposition<sup>18,19</sup> or (avoiding of) photoionization.

## CONCLUSION

We have analyzed thermal charging in additive-free colloidal CdSe QD dispersions. To do this, we have used a recently developed approach based on the transient electric current resulting from a voltage step applied across a QD dispersion. On the basis of the initial current and the total charge separated, we find that the CdSe dispersion behaves as a 1:1 electrolyte where equal fractions of the QDs carry a single positive or a single negative charge. This conclusion is confirmed by a more detailed fitting of the current transient using the Nernst–Planck–Poisson equations. Using equilibrium thermodynamics, we relate the fraction of charged QDs to the QD charging energy. The magni-

tude of the charging energy corresponds to values found using the charging energy of either a spherical surface in a dielectric or a charge within a dielectric sphere. However, the experimental dependence of the charging energy on the dielectric constant of the solvent is far less pronounced than predicted by these models. A better correspondence is found based on the charging energy of a spherical surface embedded in a compound medium consisting of the ligand shell and the solvent. By combining a novel experimental technique with a conceptual framework for analyzing thermal charging in QD dispersions in apolar media, this work provides a starting point to further investigate various aspects of thermal charging of QDs, such as the nature of the charge, the role of additives, the understanding of the charging energy and the analysis of charging mechanisms.

## METHODS

**Quantum Dot Synthesis.** CdSe nanocrystals were synthesized according to the procedure of Jasieniak *et al.*<sup>35</sup> A selenium stock solution was made by heating a mixture of Se powder (0.2727 g, 99.999%, Alfa Aesar) in *n*-octadecene (ODE, 25 mL, 90% Alfa Aesar) under nitrogen atmosphere at 195 °C for 145 min. Then the mixture was cooled to room temperature, resulting in a stable yellow transparent solution. For the nanocrystal synthesis, cadmium oxide (CdO, 0.4275 g, 99.999%, Strem) and oleic acid (OA, 10 g, 90%, Sigma-Aldrich) were mixed and heated to 250 °C until all CdO was dissolved. Next, 2.5 mL of Cd-oleate was added to 26.4 mL of ODE and stirred vigorously for 1 h at 100 °C under nitrogen flow. The temperature was then raised to 160 °C, and 7.2 mL of ODE-Se was injected to start the reaction. The temperature of the mixture dropped after injection, and the reaction continued at 235 °C for 12 min. After reaction, equal volumes of toluene and isopropyl alcohol were added, and the particles were precipitated by adding methanol. Afterward, the particles were further purified twice by resuspension in toluene and precipitation with methanol. Concentrations were determined according to recently published UV/vis extinction coefficients.<sup>36</sup>

**Current Transient Measurements.** Electric current transient measurements have been performed on CdSe QD dispersions inserted between two planar electrodes, made by two 2.5 × 2.5 cm<sup>2</sup> glass plates (Delta technologies) on which electrodes of indium tin oxide (ITO) with a surface area *S* of 1 cm<sup>2</sup> where defined using photolithography (see Figure 1). The two glass plates are glued together with UV curing glue (Norland Optics) mixed with spacer beads (Figure 7).

The distance *d* between the electrodes (28 μm) was determined by interferometry (Perkin Elmer Lambda 950). The measurements are performed using a custom-built setup consisting of a Keithley 428 current amplifier and a National Instruments USB-6212 data acquisition module for the synchronized generation of voltages and the sampling of the electric current with a time and current resolution of 100 μs and 0.1 pA, respectively. The cell is placed inside a close metallic box to screen it from light and external electric fields. Prior to the measurements, the electrodes are short-circuited for 1000 s. Then, a positive voltage ranging from 1 to 5 V is applied during 20 s and the current transient is measured. Afterward, a negative amplitude pulse with the same voltage is applied for half of the time. As verified by consecutive experiments, this ensures that the QD dispersion is at equilibrium prior to each measurement and avoids that particles remain adsorbed at the electrodes. For the *I<sub>0</sub>*–*Q* analysis of the transients, we neglect

the contribution of the dodecane (see the Supporting Information).

**Current Transient Modeling.** Simulations of transient currents are based on solving the Nernst–Planck–Poisson (PNP) equations assuming a 1:1 electrolyte of charged CdSe QDs. These equations essentially describe drift and diffusion of charged nanoparticles in the QD dispersion upon application of a voltage step. As an initial condition homogeneous and equal concentrations of positively and negatively charged particles are taken. The small distance between the electrodes compared to the electrode area justifies the use of a one-dimensional approximation. The concentrations of positively and negatively charged particles are calculated as a function of time and position between the electrodes using a forward Euler approach. The electric current in the external circuit is then calculated using Ramo's theory in order to compare the simulations to the experimentally available data. The concentration of charged particles is taken as a fixed fraction of the total particle concentration and the mobility is taken from the average mobility extracted from the measurements using the theory in the Background section, which is in good agreement with the expected mobility using Stokes law and the hydrodynamic radius of the particles.

**Acknowledgment.** The authors acknowledge BelSPo (IAP 6.10, photonics@be), the FWO–Vlaanderen (Grant No. G.0.144.08) and Ghent University (NB-Photonics) for research grants. Z.H. acknowledges the IWT (IWT-SBO Metacel) for a research grant.

**Supporting Information Available:** Current transient simulations in diethylene and the derivation of equation 10. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115*, 8706–8715.
- Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. Synthesis of Thiol-Derivatized Gold Nanoparticles in a 2-Phase Liquid–Liquid System. *J. Chem. Soc., Chem. Commun.* **1994**, 801–802.
- Murray, C. B.; Kagan, C. R.; Bawendi, M. G. Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies. *Annu. Rev. Mater. Sci.* **2000**, 545–610.

- Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of Monodisperse Spherical Nanocrystals. *Angew. Chem., Int. Ed.* **2007**, *46*, 4630–4660.
- Rauch, T.; Boberl, M.; Tedde, S. F.; Furst, J.; Kovalenko, M. V.; Hesser, G. N.; Lemmer, U.; Heiss, W.; Hayden, O. Near-Infrared Imaging with Quantum-Dot-Sensitized Organic Photodiodes. *Nat. Photonics* **2009**, *3*, 332–336.
- Luther, J. M.; Law, M.; Beard, M. C.; Song, Q.; Reese, M. O.; Ellingson, R. J.; Nozik, A. J. Schottky Solar Cells Based on Colloidal Nanocrystal Films. *Nano Lett.* **2008**, *8*, 3488–3492.
- Caruge, J. M.; Halpert, J. E.; Wood, V.; Bulovic, V.; Bawendi, M. G. Colloidal Quantum-Dot Light-Emitting Diodes with Metal–Oxide Charge Transport Layers. *Nat. Photonics* **2008**, *2*, 247–250.
- Medintz, I. L.; Uyeda, H. T.; Goldman, E. R.; Mattoussi, H. Quantum Dot Bioconjugates for Imaging, Labelling and Sensing. *Nat. Mater.* **2005**, *4*, 435–446.
- Parak, W. J.; Pellegrino, T.; Plank, C. Labelling of Cells with Quantum Dots. *Nanotechnology* **2005**, *16*, R9–R25.
- Snee, P. T.; Somers, R. C.; Nair, G.; Zimmer, J. P.; Bawendi, M. G.; Nocera, D. G. A Ratiometric CdSe/ZnS Nanocrystal pH Sensor. *J. Am. Chem. Soc.* **2006**, *128*, 13320–13321.
- Gill, R.; Bahshi, L.; Freeman, R.; Willner, I. Optical Detection of Glucose and Acetylcholine Esterase Inhibitors by H<sub>2</sub>O<sub>2</sub>-Sensitive CdSe/ZnS Quantum Dots. *Angew. Chem., Int. Ed.* **2008**, *47*, 1676–1679.
- Chen, Y. F.; Rosenzweig, Z. Luminescent CdS Quantum Dots as Selective Ion Probes. *Anal. Chem.* **2002**, *74*, 5132–5138.
- Blanton, S. A.; Leheny, R. L.; Hines, M. A.; Guyot-Sionnest, P. Dielectric Dispersion Measurements of CdSe Nanocrystal Colloids: Observation of a Permanent Dipole Moment. *Phys. Rev. Lett.* **1997**, *79*, 865–868.
- Shim, M.; Guyot-Sionnest, P. Permanent Dipole Moment and Charges in Colloidal Semiconductor Quantum Dots. *J. Chem. Phys.* **1999**, *111*, 6955–6964.
- Klokkenburg, M.; Houtepen, A. J.; Koole, R.; deFolter, J. W. J.; Erne, B. H.; van Faassen, E.; Vanmaekelbergh, D. Dipolar Structures in Colloidal Dispersions of PbSe and CdSe Quantum Dots. *Nano Lett.* **2007**, *7*, 2931–2936.
- Shanbhag, S.; Kotov, N. A. On the Origin of a Permanent Dipole Moment in Nanocrystals with a Cubic Crystal Lattice: Effects of Truncation, Stabilizers, and Medium for CdS Tetrahedral Homologues. *J. Phys. Chem. B* **2006**, *110*, 12211–12217.
- Nann, T.; Schneider, J. Origin of Permanent Electric Dipole Moments in Wurtzite Nanocrystals. *Chem. Phys. Lett.* **2004**, *384*, 150–152.
- Islam, M. A.; Herman, I. P. Electrodeposition of Patterned CdSe Nanocrystal Films Using Thermally Charged Nanocrystals. *Appl. Phys. Lett.* **2002**, *80*, 3823–3825.
- Islam, M. A.; Xia, S. G. Electrostatic Properties of Maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) Nanocrystalline Quantum Dots Determined by Electrophoretic Deposition. *J. Phys. Condens. Mater.* **2009**, *21*, 285301.
- Krauss, T. D.; O'Brien, S.; Brus, L. E. Charge and Photoionization Properties of Single Semiconductor Nanocrystals. *J. Phys. Chem. B* **2001**, *105*, 1725–1733.
- Krauss, T. D.; Brus, L. E. Charge, Polarizability, and Photoionization of Single Semiconductor Nanocrystals. *Phys. Rev. Lett.* **1999**, *83*, 4840–4843.
- Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. Structural Diversity in Binary Nanoparticle Superlattices. *Nature* **2006**, *439*, 55–59.
- McGuire, J. A.; Sykora, M.; Joo, J.; Pietryga, J. M.; Klimov, V. I. Apparent versus True Carrier Multiplication Yields in Semiconductor Nanocrystals. *Nano Lett.* **2010**, *10*, 2049–2057.
- McGuire, J. A.; Sykora, M.; Robel, I. n.; Padilha, L. A.; Joo, J.; Pietryga, J. M.; Klimov, V. I. Spectroscopic Signatures of Photocharging Due to Hot-Carrier Transfer in Solutions of Semiconductor Nanocrystals under Low-Intensity Ultraviolet Excitation. *ACS Nano* **2010**, *4*, 6087–6097.
- Brus, L. E. A Simple-Model for the Ionization-Potential, Electron-Affinity, and Aqueous Redox Potentials of Small Semiconductor Crystallites. *J. Chem. Phys.* **1983**, *79*, 5566–5571.
- Fritzing, B.; Capek, R. K.; Lambert, K.; Martins, J. C.; Hens, Z. Utilizing Self-Exchange To Address the Binding of Carboxylic Acid Ligands to CdSe Quantum Dots. *J. Am. Chem. Soc.* **2010**, *132*, 10195–10201.
- Strubbe, F.; Beunis, F.; Neyts, K. Determination of the Effective Charge of Individual Colloidal Particles. *J. Colloid Interface Sci.* **2006**, *301*, 302–309.
- Beunis, F.; Strubbe, F.; Marescaux, M.; Beeckman, J.; Neyts, K.; Verschuere, A. R. M. Dynamics of Charge Transport in Planar Devices. *Phys. Rev. E* **2008**, *78*, 011502.
- Verschuere, A. R. M.; Notten, P. H. L.; Schlangen, L. J. M.; Strubbe, F.; Beunis, F.; Neyts, K. Screening and Separation of Charges in Microscale Devices: Complete Planar Solution of the Poisson–Boltzmann Equation. *J. Phys. Chem. B* **2008**, *112*, 13038–13050.
- Caudwell, D. R.; Trusler, J. P. M.; Vesovic, V.; Wakeham, W. A. The Viscosity and Density of *n*-Dodecane and *n*-Octadecane at Pressures up to 200 MPa and Temperatures up to 473 K. *Int. J. Thermophys.* **2004**, *25*, 1339–1352.
- Bakkers, E.; Hens, Z.; Zunger, A.; Franceschetti, A.; Kouwenhoven, L. P.; Gurevich, L.; Vanmaekelbergh, D. Shell-Tunneling Spectroscopy of the Single-Particle Energy Levels of Insulating Quantum Dots. *Nano Lett.* **2001**, *1*, 551–556.
- Jdara, L.; Liljeroth, P.; Stoffels, E.; Vanmaekelbergh, D.; Speller, S. Size-Dependent Single-Particle Energy Levels and Interparticle Coulomb Interactions in CdSe Quantum Dots Measured by Scanning Tunneling Spectroscopy. *Phys. Rev. B* **2006**, *73*, 115305.
- Klein, D. L.; McEuen, P. L.; Katari, J. E. B.; Roth, R.; Alivisatos, A. P. An Approach to Electrical Studies of Single Nanocrystals. *Appl. Phys. Lett.* **1996**, *68*, 2574–2576.
- Hicks, J. F.; Templeton, A. C.; Chen, S. W.; Sheran, K. M.; Jasti, R.; Murray, R. W.; Debord, J.; Schaaf, T. G.; Whetten, R. L. The Monolayer Thickness Dependence of Quantized Double-Layer Capacitances of Monolayer-Protected Gold Clusters. *Anal. Chem.* **1999**, *71*, 3703–3711.
- Jasieniak, J.; Bullen, C.; van Embden, J.; Mulvaney, P. Phosphine-free Synthesis of CdSe Nanocrystals. *J. Phys. Chem. B* **2005**, *109*, 20665–20668.
- Capek, R. K.; Moreels, I.; Lambert, K.; De Muynck, D.; Zhao, Q.; Van Tomme, A.; Vanhaecke, F.; Hens, Z. Optical Properties of Zincblende Cadmium Selenide Quantum Dots. *J. Phys. Chem. C* **2010**, *114*, 6371–6376.