

# Characterization and Surface Charge Measurement of Self-Assembled CdS Nanoparticle Films

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The self-assembly of CdS semiconductor nanocrystals (Q-CdS) as well-defined monolayer and multilayer films on glass, indium tin oxide, and gold surfaces was carried out. These were characterized by ultraviolet–visible spectroscopy, ellipsometry, and scanning tunneling microscopy. The adsorption of the polymeric anion hexametaphosphate (HMP) on the Q-CdS particle surface produced a negative surface charge. The diffuse double-layer interaction forces between a silica probe and the Q-CdS/HMP particle film-covered gold substrate immersed in aqueous solutions were measured using an atomic force microscope. The surface charge and electrostatic potential of Q-CdS particles were obtained by theoretical fits of the force data to solutions of the complete nonlinear Poisson–Boltzmann equation with a knowledge of the silica probe surface potential.

## Introduction

Semiconductor nanoparticles (Q-particles) represent an interesting size regime where a gradual transition from solid-state to molecular properties occurs as the particle size decreases.<sup>1</sup> Characterization and preparation of these nanometer-sized semiconductor particles and their size-dependent physical and chemical properties have been under intensive investigation for the past decade. These research efforts are driven by potential applications in molecular electronics, nonlinear optics, catalysis, and photoelectrochemical cells. One of the recent research directions is to design and assemble both nanometer-scale structures and bulk materials using Q-particles as building blocks.<sup>2,3</sup> A prominent example is the achievement of three-dimensional CdSe quantum dot superlattices reported by Bawendi and co-workers.<sup>4</sup> These novel materials exhibit collective bulk properties which emerge from the ordered array of their constituents.

Self-assembled monolayers (SAMs),<sup>5–7</sup> prepared by spontaneous adsorption of thiolates on gold, provide a convenient and rational approach for controlling the chemical and physical surface properties and the subsequent retention of the surface-active organic molecules on a substrate. Alivisatos and co-workers<sup>8</sup> first demonstrated that a monolayer of dioctyl sulfosuccinate-capped CdS Q-particles could be attached to metal

surfaces using self-assembled difunctional organic monolayer linkers. A multilayer film (up to five layers) of CdSe Q-particles built on an indium tin oxide (ITO) substrate through a bifunctional compound was reported as a component of a light-emitting diode.<sup>9</sup> Recent examples of nanostructured materials also include cross-linked nano-networks of Au particles with controllable electronic properties, both as bulk materials<sup>10</sup> and as thin film multilayer structures.<sup>11</sup> In a previous study,<sup>12</sup> Gordillo and co-workers characterized the multilayer structures of self-assembled Au and CdS nanoparticles by quartz crystal microgravimetry. Here we extend this work and demonstrate that CdS Q-particles can be self-assembled as well-defined monolayer and multilayer films on various substrates. The layer-by-layer film growth process was characterized by ultraviolet–visible (UV–vis) spectroscopy, ellipsometry, and scanning tunneling microscopy (STM).

Q-particle surface charge plays a crucial role in particle stability and is also a very important factor that significantly affects the band positions and the electron-transfer processes across the Q-particle/electrolyte interface. Control and quantitative measurement of Q-particle surface charge and potential are of both practical importance and scientific interest. Unfortunately, due to the limitations of the available techniques, this kind of Q-particle surface charge measurement has not been addressed before. However, recent advances in force measurements associated with the atomic force microscope (AFM) have allowed direct force measurements between a sphere and a flat surface.<sup>13–15</sup>

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These direct measurements of surface forces have significantly advanced our ability to measure surface charge and address interfacial processes.<sup>16</sup> Typically, in an AFM force measurement, the deflection of a microfabricated cantilever is measured as a function of its separation from a surface. In this work, with a well-characterized monolayer of CdS Q-particles on gold as the substrate, the diffuse double-layer interaction forces between a tip modified with a negatively charged silica sphere and the substrate were measured in aqueous solutions with an AFM with and without the adsorbed polymeric anion hexametaphosphate (HMP), a commonly used stabilizer for semiconductor Q-particles synthesized in aqueous solutions. The surface charge and electrostatic potential of CdS Q-particles were calculated from the force data with a knowledge of the silica probe surface potentials. To our knowledge, this is the first quantitative measurement of Q-particle surface charge.

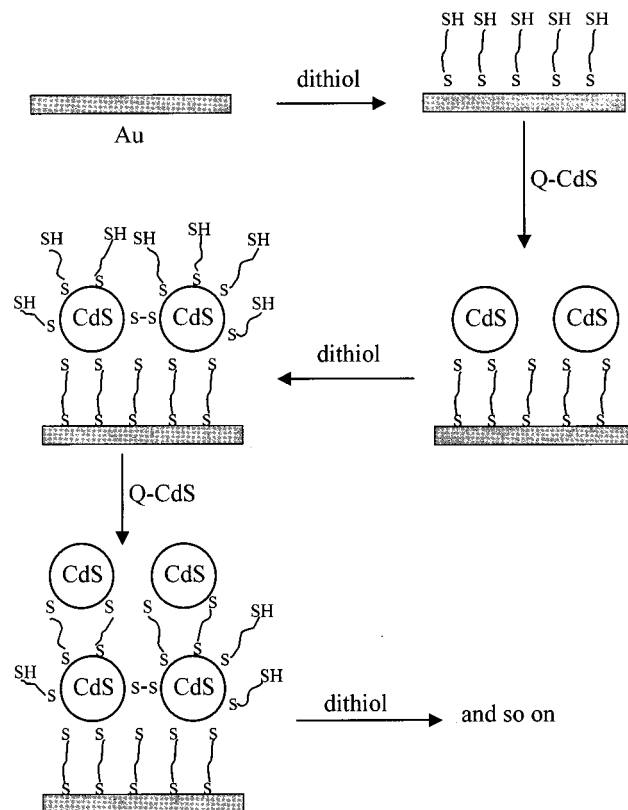
### Experimental Section

**Materials.** 1,6-Hexanedithiol (96%; Aldrich, Milwaukee, WI), 3-(mercaptopropyl)trimethoxysilane (97%; Sigma, St. Louis, MO), and sodium hexametaphosphate (HMP,  $(\text{NaPO}_3)_6$ ; Alfa, Ward Hill, MA) were all used as received. Aqueous solutions were freshly prepared using 18 M $\Omega$  deionized water (Milli-Q Plus, Millipore Corp., Bedford, MA) and deaerated with argon for 20 min immediately before use.

**Preparation of Q-CdS Particles.** Cadmium sulfide particles were prepared in 2-propanol following the method of O'Neil et al.<sup>17</sup> Typically, 0.1 g of  $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was dissolved in 600 mL of 2-propanol, and the solution was degassed with argon for 20 min. After the injection of 5.4 mL of  $\text{H}_2\text{S}$ , the solution was shaken vigorously for 5 min. The resulting clear and yellow-colored solutions were stable for days in the dark at room temperature.

**Preparation of Self-Assembled Monolayers and Multilayers.** Monolayer and multilayer thin films of Q-CdS particles were prepared on thiol-functionalized glass, ITO, and Au substrates. Glass microscope slides (Corning, McGaw Park, IL) were cleaned by immersion in freshly prepared piranha solution (30%  $\text{H}_2\text{O}_2$ :concentrated  $\text{H}_2\text{SO}_4$ , 1:3, caution!) for 20 min at  $\sim 90^\circ\text{C}$ , and ITO-covered glass slides were cleaned by immersion in a boiling 2 M solution of KOH in 2-propanol for 20 min, followed by immersion in boiling 0.1 M  $\text{HNO}_3$  for 5 min to render the surface acidic. Surface silanization with 3-(mercaptopropyl)trimethoxysilane of both ITO and glass substrates was then carried out following the method of Goss et al.<sup>18</sup> Au substrates (for ellipsometry) were prepared by first sputtering a thin layer of Cr ( $\sim 20$  nm) and then 350 nm of Au on clean glass microscope slides. Their quality was confirmed by ellipsometry giving typical values for clean Au ( $\Delta \approx 110$  and  $\Psi \approx 43.5$ ).<sup>19</sup> The freshly sputtered substrates

### Scheme 1. Schematic Representation of the Layer Construction of Nanomaterials from Q-CdS Particles and a Dithiol



were thiol-functionalized with 1,6-hexanedithiol by immersion in a 5 mM solution of the dithiol in 2-propanol for at least 1 h followed by thorough rinsing with 2-propanol to remove excess dithiol. The successive formation of Q-CdS monolayers and multilayers was carried out identically for the three different types of thiol-functionalized substrates (Scheme 1). The substrates were alternately immersed in a 2-propanol solution of Q-particles for at least 3 h and in a 5 mM solution of 1,6-hexanedithiol in 2-propanol for at least 1 h. After each dithiol step the substrates were rinsed with copious amounts of 2-propanol to avoid introduction of excess dithiol into the Q-particle solution, which would lead to precipitation of the CdS by covalent cross-linking of the particles.

**UV-Vis Spectroscopy.** A Milton Roy Spectronic 3000 array UV-vis spectrometer was used to monitor multilayer formation on glass substrates and to obtain solution spectra of the particles. The glass samples used were rectangles of  $1 \times 2$  cm<sup>2</sup> made to fit into the sample holder of the spectrometer. Reference spectra were taken with clean uncoated slides prior to recording the spectra of the self-assembled films.

**Ellipsometry.** A Rudolf 2000FT automatic ellipsometer with a He/Ne laser as light source (632.8 nm) was used to monitor multilayer formation on Au substrates. The angle of incidence in all studies was  $70^\circ$ , and commercial software was used to interpret the data. On glass and ITO substrates, ellipsometry could not resolve the thin film formation very accurately, since the refractive indices of these substrates and the Q-particle films are not sufficiently different.

**Scanning Tunneling Microscopy.** Images of Q-CdS multilayer thin films on ITO were obtained with a Nanoscope II STM. The tip was a 0.25 mm Pt/Ir (80/20) wire cut with a hardened steel cutter.

**AFM Force Measurement.** Force measurements were performed with a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) equipped with a piezo scanner having a maximum scan range of  $15 \mu\text{m} \times 15 \mu\text{m} \times 2 \mu\text{m}$ . The AFM force measuring technique is well-documented,<sup>13-15</sup> and the experimental details have been described elsewhere.<sup>20,21</sup> Typi-

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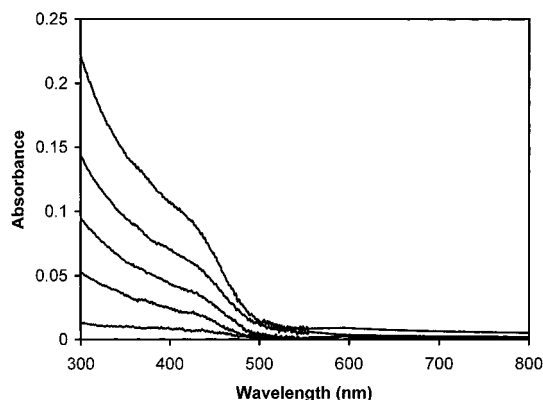
cally, in an AFM force measurement, the deflection of a microfabricated cantilever is measured as a function of its separation from a surface. The spring constant of the silica sphere modified cantilever, determined using the method of Cleveland et al.,<sup>22</sup> was  $0.65 \pm 0.12$  N/m. The very smooth gold surfaces with (111) orientation prepared following the method of Hegner et al.<sup>23</sup> were used as the substrates for the force measurements.

During the force measurement, the measured experimental parameters were the cantilever deflection, obtained from the voltage of the sectored photodiode detector, and the substrate displacement, which was given by the piezo scanner voltages. These data were converted to a normalized force (force/radius) vs tip-substrate separation for further analysis. Derjaguin-Landau-Verwey-Overbeek (DLVO) theory<sup>24</sup> was employed to calculate the surface electrostatic potentials between the similarly charged surfaces, i.e., the interaction between two silica surfaces. The electrical double-layer interaction energy between dissimilarly charged surfaces such as the silica-CdS interaction was calculated for the constant-charge limit of the complete nonlinear Poisson-Boltzmann equation using the method of Hillier et al.<sup>20</sup> The Hamaker constants ( $A_H$ ) used for the calculations were  $0.88 \times 10^{-20}$  J<sup>25</sup> and  $1.5 \times 10^{-20}$  J<sup>26</sup> for the silica-silica and silica-CdS interactions, respectively.

## Results and Discussion

### Preparation of Q-CdS Particles and Thin Films.

The UV-vis spectrum of a solution of Q-CdS particles in 2-propanol shows an absorption peak at 370 nm. The significant blue shift of the absorption onset with respect to bulk CdS from  $\sim 520$  nm (bulk CdS) to  $\sim 450$  nm indicates an average particle diameter of  $\sim 3$  nm.<sup>1</sup> This was confirmed by XRD line broadening analysis and TEM studies of identical preparations, which reveal a narrow size distribution between 3 and 3.5 nm.<sup>27</sup> This preparation, introduced first by O'Neil et al.,<sup>17</sup> does not employ a stabilizing agent. This makes the particles particularly useful for covalent attachment to suitably functionalized substrates, since their surface is not blocked by strongly adsorbed ligands, as frequently occurs in nanoparticle preparations. Indeed, in the AFM force measurements described later, we show that HMP-stabilized CdS Q-particles prepared in aqueous solutions cannot be covalently attached to thiol-terminated substrates. Another interesting observation is that the particles precipitate quantitatively upon addition of alkanedithiols without concurrent particle fusion to larger units because the TEM images of such cross-linked particle aggregates show a grain size of the individual particles.<sup>27</sup> The dithiol probably acts as a covalent linking and stabilizing agent as previously observed for cross-linked Au nanoparticles.<sup>10</sup> The resulting powders exhibit a relatively strong, yellow-



**Figure 1.** Absorption spectra of Q-CdS/1,6-hexanedithiol multilayers on glass. The spectra correspond, from bottom to top, to one, two, three, four, and five layers of Q-CdS particles.

orange solid-state photoluminescence typical for Q-CdS particles that is not present in the bulk material.

UV-vis spectra of subsequent layers deposited on glass are shown in Figure 1, indicating regular layer by layer growth. A significant peak broadening is observed, and the absorption onset is red shifted by  $\sim 50$  nm with respect to the particles in solution; this might indicate the emergence of collective electronic properties in this ensemble of coupled particles. A very similar effect has previously been reported by Weller and co-workers who studied spin-coated films of 1-thioglycerol stabilized Q-CdS particles.<sup>28</sup> These films also showed a red shift of the absorbance spectrum which was completely reversible upon dissolution of the films. Whether the red shift observed both in Weller's and in our system is due to collective electronic modes or, as noted in Weller's work, is caused by the change in the dielectric constant of the medium surrounding the particles remains to be elucidated by future studies.

**Ellipsometry.** The formation of monolayer and multilayer thin films of Q-CdS particles on dithiol-functionalized Au substrates was monitored by ellipsometry. In accordance with the UV-vis data obtained from layers grown on mercaptosilanized glass substrates, regular layer-by-layer formation is observed (Figure 2). The average increase of film thickness measured is 2.1 nm per monolayer, i.e., per immersion step in the solution of particles. This is somewhat less than the theoretically expected value of 2.8 nm, assuming a close packing of 3 nm particles. Such a moderate discrepancy is not surprising considering our simplifying assumption that the real part of the complex refractive index of the thin film material is that of bulk CdS ( $n = 2.5$ ).<sup>29</sup> The imaginary part was taken as zero, since the material is transparent for the laser wavelength employed (632.8 nm). The true refractive index of the material is likely to be smaller than 2.5, since the films are composed of CdS particles and aliphatic hydrocarbon chains with a refractive index of  $\sim 1.45$ .<sup>19</sup> Quantum-size effects also influence the optical properties of the individual particles, and collective electronic properties of the particle ensemble might play an important role.

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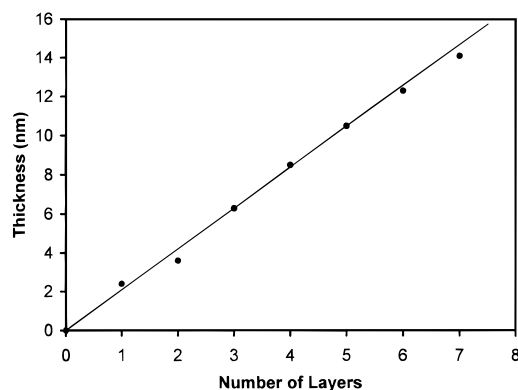
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**Figure 2.** Film thickness (solid circles) of the self-assembled Q-CdS particles as determined by ellipsometry as a function of the number of layers. The refractive index of the thin film was assumed to be 2.5, the same as that of bulk CdS. The average increase of film thickness is 2.1 nm per monolayer.

Indeed, with a smaller refractive index, larger values of film thickness are calculated, but based on our still limited knowledge of this composite material, it is difficult to estimate its true refractive index. The best reasonable assumption we can make at present is that it can be approximated by using the index of bulk CdS.

**Scanning Tunneling Microscopy.** Aggregating colloids generally fuse together and form larger units with bulk properties. Systems in which closely connected nanoparticles maintain their original size and individuality are relatively rare and of great current interest for the design of novel nanostructured materials with potential applications in nonlinear optics, sensor science, catalysis, and microelectronics. Indications that our thin films represent such a material are their photoluminescence, the UV-vis spectrum that shows the presence of Q-particles, and the TEM observation of cross-linked nanostructures precipitated from solution. The surface of Q-CdS films deposited on ITO-coated glass slides was inspected by STM to corroborate the proposed film structure of individual particles covalently linked by dithiol spacer molecules. The STM image shown in Figure 3, despite the roughness of the underlying ITO substrate, shows clearly a disordered assembly of relatively uniform particles in the expected size range of 2.0–4.5 nm. In contrast to a previous report on STM images of films of ligand-stabilized CdS particles,<sup>30</sup> these films are very stable and no particle removal was observed upon repeated scanning. This suggests that the particles are indeed covalently linked to the substrate and to each other to form a stable, nanostructured thin film material.

**AFM Force Measurement.** The Q-particle surface charge plays a crucial role in particle stability and is also an important factor in electron-transfer processes across the Q-particle/electrolyte interface. Although direct measurement of Q-particle surface charge in solution is difficult and has not been reported, one can measure the surface charge of the Q-particles through force measurements when they are anchored on a smooth surface. Typically, to measure quantitatively the surface charge of a substrate, the surface electrostatic potential of the probe must be known in an AFM

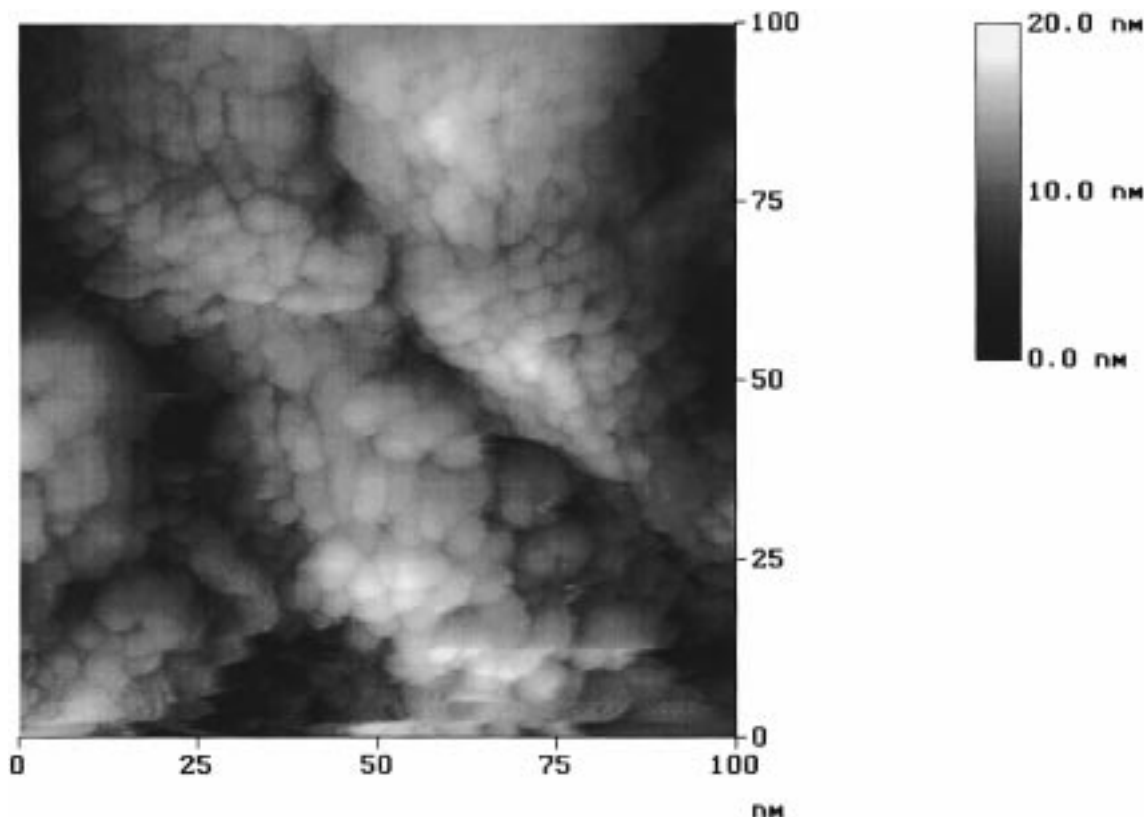
force measurement. Force measurements between a silica sphere and a silica substrate were conducted to determine the silica surface potential ( $\psi_p$ ) under conditions similar to those used while probing the double layers at the gold substrates covered with monolayers of Q-CdS particles, as described previously.<sup>13,20,21</sup> Solutions of 0.1, 1.0, and 10.0 mM NaCl at pH 5.5 were examined. The silica surfaces are negatively charged in a solution at pH 5.5 and diffuse double layers form at the interfaces. AFM force measurements can probe the double-layer structure and thickness as the tip penetrates the double layer. Generally, these force-distance curves exhibit an exponential dependence with distance that agrees with standard DLVO theory.<sup>24</sup> The measured silica surface potentials were  $-19$ ,  $-37$ , and  $-65$  mV for 10.0, 1.0, and 0.1 mM NaCl solutions, respectively. The corresponding Debye lengths,  $\kappa^{-1}$ , of the diffuse double layers were 3.2, 10.8, and 24.1 nm, in good agreement with those calculated from the free ion concentration of the solutions.<sup>31</sup>

With the monolayers of CdS Q-particles covalently bound to the gold substrate, the forces between a silica probe and the substrate were measured in 0.1, 1.0, and 10.0 mM NaCl aqueous solutions at pH 5.5. There were no measurable long-range electrostatic interactions between the silica probe and a gold substrate covered with a monolayer of Q-CdS particles, indicating that the Q-CdS particle surface was uncharged. In other words, there was no specific adsorption of  $\text{Cl}^-$  on the particle surface. Sodium hexametaphosphate (HMP), a polymeric anion when dissolved in water, is a commonly used stabilizer for semiconductor Q-particles synthesized in aqueous solutions. The gold substrate with a monolayer of Q-CdS particles was immersed in an aqueous 5 mM HMP solution for 30 min and then rinsed thoroughly with deionized water. With the adsorption of HMP on the particle surface, electrostatic repulsive forces were observed between a silica probe and the Q-CdS/HMP film-covered gold substrate in aqueous solutions (pH 5.5) at different NaCl concentrations (Figure 4, solid lines). Force measurements conducted in a 0.9 mM NaCl and 0.1 mM HMP aqueous solution at pH 5.5 also confirmed the adsorption of HMP onto the particle surface, and the force measurement results were identical to the experimental results with the HMP-treated substrate in NaCl solutions not containing HMP. In the control experiments, neither the bare gold surface nor the 1,6-hexanedithiol-covered gold surface showed any appreciable repulsive forces in 0.9 mM NaCl and 0.1 mM HMP aqueous solutions at pH 5.5. In a separate experiment, the 1,6-hexanedithiol-covered Q-CdS particle surface was immersed in an aqueous solution containing HMP. The AFM force measurement results showed that the surface remained uncharged, indicating that HMP does not adsorb on the thiol-covered particle surface. These results indicated that HMP was indeed adsorbed on the surface of Q-CdS particles and not on the surfaces of bare gold or SAM.

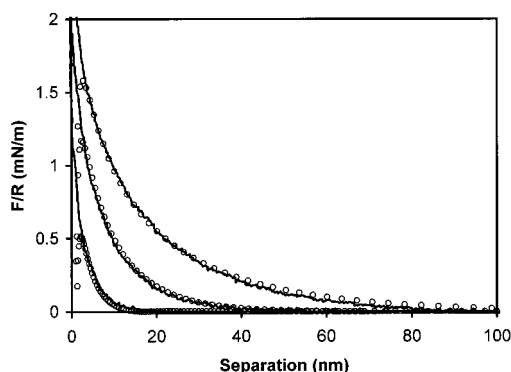
The diffuse double layer reflects the magnitude of surface charge of a substrate immersed in an aqueous solution. In this work, a silica probe interrogates the

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**Figure 3.** Typical STM image of Q-CdS particle layer covalently linked to ITO substrate. The bias voltage was 700 mV (substrate positive) with a set point current of 1.5 nA.



**Figure 4.** Measured (solid lines) and theoretical (circles) force between a silica probe and the Q-CdS/HMP-covered gold substrate in aqueous solutions at pH 5.5. The force curves correspond to, from bottom to top, 10.0, 1.0, and 0.1 mM NaCl solutions. All calculations include both electrostatic and van der Waals interactions, with  $A_H = 1.5 \times 10^{-20}$  J for the  $\text{SiO}_2$ -CdS interaction. The best fit parameters for all force curves are given in Table 1.

surface of the Q-particles covalently bound to the gold substrate. In Figure 4, the repulsive forces between the negatively charged silica tip and the Q-CdS/HMP-covered gold substrate can be explained in terms of the nature of the diffuse double layer. In the force measurement, the silica spherical tip probes the diffuse double layer near the gold substrate as it moves through the double layer, which consists of counterions that compensate the charge residing at the interface. For example, in a 1.0 mM NaCl aqueous solution at pH 5.5 and with the adsorption of HMP on the particle surface, the net surface charge of the gold substrate becomes negative and a diffuse double layer with a net positive charge (a higher local concentration of  $\text{Na}^+$  and  $\text{H}^+$  and

lower local concentration of  $\text{Cl}^-$  and  $\text{OH}^-$ ) forms near the gold substrate. As the negatively charged silica probe (with its own positively charged diffuse double layer) penetrates the double layer near the gold substrate, the overlap and interaction of the two positively charged double layers results in an electrostatic repulsive force.

Theories describing the forces between interacting double layers in electrolyte solutions are well-developed. Generally, for similarly charged surfaces at low surface potentials, the linearized form of the Poisson-Boltzmann equation yields the same results as the DLVO theory. For dissimilarly charged surfaces, the complete nonlinear Poisson-Boltzmann equation must be solved because of the presence of an additional Maxwellian stress term that represents an induced image charge. In this work, the method of Hillier et al.<sup>20</sup> was used to calculate the electrical double-layer interaction between the silica and Q-CdS surfaces. This model of the interaction force between two dissimilarly charged surfaces has been successful in matching experimental observations for a variety of systems for separations ranging up to the last 3–5 nm.<sup>20,21,32,33</sup> At these closer separations, nontrivial surface roughness introduces uncertainties in the location of the plane of surface charge and introduces a nonideality in the model of spherical surface geometry. The solvent force also begins to dominate the behavior under these conditions.

The surface electrostatic potentials ( $\psi_s$ ) of the Q-CdS/HMP-covered gold substrate can be calculated from the

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**Table 1. Force Data Analysis Results of the Q-CdS/HMP-Covered Gold Substrate as a Function of NaCl Concentration<sup>a</sup>**

NaCl concentration (mM)	surface potential, $\psi_s$ (mV)	Debye length, $\kappa^{-1}$ (nm)	surface charge, $\sigma$ ( $\mu\text{C}/\text{cm}^2$ )
0.1	-73	24.1	-0.289
1.0	-45	10.2	-0.347
10.0	-22	3.4	-0.464

<sup>a</sup> Force data obtained between a silica sphere and the Q-CdS/HMP-covered gold substrate in aqueous solutions at 25 °C and pH 5.5. The silica probe surface potential,  $\psi_p$ , was -65, -37, and -19 mV for 0.1, 1.0, and 10.0 mM NaCl solutions, respectively. The corresponding Debye lengths,  $\kappa^{-1}$ , of the silica probe's diffuse double layers were 24.1, 10.8, and 3.2 nm.

force data. With a knowledge of silica probe surface potentials, the surface electrostatic potentials of the Q-CdS/HMP-covered gold substrates were obtained by theoretical fits of the force data to solutions of the complete nonlinear Poisson-Boltzmann equation with a boundary condition that assumed a constant surface charge. Generally, this constant surface charge boundary condition provided a better fit than if a constant surface potential was assumed, as in previous work with a variety of systems. Figure 4 shows the fit of theoretical curves (open circles) to experimental force data at several different NaCl concentrations. As shown, the theoretical curves fit the experimental force data very well at all distances except for separations of less than 5 nm. All calculations include both electrostatic and van der Waals interactions, with  $A_H = 1.5 \times 10^{-20}$  J for the  $\text{SiO}_2$ -CdS interaction. Given the particle size of 3 nm, the location of the plane of surface charge was moved 3 nm positive of the contact position in all these calculations. The best fit parameters for all force data are given in Table 1. The particle surface charges ( $\sigma$ ) in Table 1 were calculated from the corresponding surface potentials and the measured Debye lengths of the dif-

fuse double layers using the relationship  $\sigma = \epsilon_0 \epsilon_s \kappa (2kT/e) \sinh(e\psi/2kT)$ , where  $\kappa$  is the reciprocal Debye length of the electrolyte solution with a dielectric constant,  $\epsilon_s$ , which is taken to be 78.49 and is assumed to be independent of surface charge change, and  $\epsilon_0$  is the permittivity of free space.<sup>34</sup>

## Conclusion

The layer-by-layer growth of Q-CdS particle films on glass, ITO, and gold surfaces was described. The well-defined monolayers and multilayers of self-assembled Q-CdS particles were characterized by UV-vis spectroscopy, ellipsometry, and scanning tunneling microscopy. The diffuse double-layer interaction forces between a silica probe and the Q-CdS/HMP-covered gold substrate were measured using an AFM in aqueous solutions. The Q-CdS particle surface charge and electrostatic potential, calculated from the force data by solving the complete nonlinear Poisson-Boltzmann equation with the knowledge of the silica probe surface potential, yielded the surface charge on the particles.

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