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Manipulating semiconductor colloidal stability through doping

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The interface between a doped semiconductor material and electrolyte solution is of considerable fundamental interest, and is relevant to systems of practical importance. Both adjacent domains contain mobile charges, which respond to potential variations. This has been exploited to design sensors, electronic, optoelectronic and other enabling semiconductor colloidal materials. We show that the charge mobility in both phases leads to a new type of interaction between semiconductor colloids suspended in aqueous electrolyte solutions. This interaction is due to the electrostatic response of the semiconductor interior to disturbances in the external field upon the approach of two particles. The electrostatic repulsion between two charged colloids is reduced from the one governed by the charged groups present at the particles surfaces. This type of interaction is unique to semiconductor particles and may have a substantial effect on the suspension dynamics and stability.

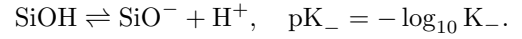
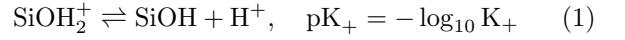
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Semiconductor colloids are of significant fundamental interest and present opportunities for new and exciting applications [1, 2]. A basic property pertinent to any colloidal system is its stability. Semiconductor colloids are no different. Strategies to stabilize such systems employ electrostatic and/or steric [3, 4] repulsion against van der Waals attraction to prevent the particles from coagulation. The balance between electrostatic repulsion and van der Waals attraction is the foundation of the celebrated Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloid stability [5, 6]. We find that the charge density in the doped semiconductor particle interior plays an essential role and can significantly alter the overall interaction. It has been experimentally established that the charge density inside a doped semiconductor in the vicinity of semiconductor-electrolyte interface will shift in response to changes in the electrostatic potential in the electrolyte phase. This effect has been exploited to perform force measurements [7, 8] and is utilized in a significant number of sensing applications that use nanoscale semiconductors [9–13].

We hypothesize that the internal charge redistribution due to external field perturbation should in turn affect the force between two approaching semiconductor colloidal particles. Hence, the DLVO theory has to be revisited when applied to doped semiconductor colloids. In this Letter we provide such a revision based on a general electrostatic analysis. We show that the internal response of the doped semiconductor particles to changes of the potential in the electrolyte may have a dramatic effect on their kinetic stability. In addition, it opens up possibilities to new methods for control and manipulation.

The system under consideration consists of two spherical colloidal particles suspended in electrolyte solution. In order to be specific let the particles have Si cores (other

semiconductors will perform similarly) and the terminal ligands at the surface are $-\text{SiO}^-$ groups [3]. Such oxide layer may naturally form when Si is exposed to air or water that has dissolved oxygen. The $-\text{SiO}^-$ groups are subject to surface charge regulation [14–16] through chemical equilibria with constants K_- and K_+ such that,



We will assume (without loss of generality) that the cores are n-doped. The potential Ψ in the two domains is described by the Poisson equation [17],

$$\nabla^2 \Psi = -\frac{\rho}{\epsilon \epsilon_0} \quad (2)$$

where ρ is the charge density, ϵ and ϵ_0 are the medium dielectric permittivity, and the dielectric constant of vacuum respectively. The charge density in the electrolyte solution is distributed according to Boltzmann's classical statistical mechanics. In contrast, the charge distribution density in the doped semiconductor particle core is subject to quantum exclusion limitations and may have to be described by a temperature dependent Fermi-Dirac distribution [18, 19]. The charge densities are given as,

$$\rho = \begin{cases} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \Psi}{k_B T}\right) & \text{electrolyte} \\ e N_d \left[1 - \chi F_{1/2}\left(\frac{\mu - e \Psi}{k_B T}\right)\right] & \text{semiconductor} \\ 0 & \text{oxide} \end{cases} \quad (3)$$

where e is the fundamental unit of charge, $k_B T$ is the thermal energy, n_i^0 is the bulk number density of species

i , z_i is the charge of ion i , N_d is the number density of donors in the semiconductor, and \hbar is the reduced Planck constant. $F_{1/2}$ is the Fermi integral and is defined as,

$$F_{1/2}(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty dt \frac{t^{1/2}}{1 + \exp(t - x)}, \quad (4)$$

where μ is the Fermi level [19], and the parameter χ is given by,

$$\chi = \frac{1}{4N_d} \left(\frac{2m^*k_B T}{\pi \hbar^2} \right)^{3/2}, \quad (5)$$

where m^* is the effective mass of the electron. The charge density inside the oxide layer is zero.

Since we are considering a system at room temperature, it is appropriate to use the limiting case of the Fermi function where,

$$\chi F_{1/2} \left(\frac{\mu - e\Psi}{k_B T} \right) \rightarrow \exp \left(-\frac{e\Psi}{k_B T} \right). \quad (6)$$

The boundary conditions required to solve Eq. (2), are to match potentials at the interfaces of the semiconductor (subscript “sc”), oxide (subscript “ox”) and electrolyte (subscript “el”) such that the charge regulating boundary condition is enforced at the oxide-electrolyte interface through,

$$\Psi_{ox} = \Psi_{el} = \Psi_s; \sigma_s = \mathbf{n} \cdot [\epsilon_{ox} (\nabla \Psi)_{ox} - \epsilon_{el} (\nabla \Psi)_{el}] \quad (7)$$

while the boundary conditions applied at the semiconductor-oxide interface are,

$$\Psi_{sc} = \Psi_{ox}; 0 = \mathbf{n} \cdot [\epsilon_{sc} (\nabla \Psi)_{sc} - \epsilon_{ox} (\nabla \Psi)_{ox}] \quad (8)$$

where σ_s and Ψ_s are the surface charge and potential governed by the chemical equilibria given in Eq. (1), \mathbf{n} is the vector normal to the surface, and ϵ_{sc} , ϵ_{ox} , ϵ_{el} are the dielectric constants of the semiconductor, oxide and electrolyte respectively.

In this model we use a site dissociation model such that the charge density is given by [14, 20],

$$\sigma_s(\Psi_s) = \frac{e\Gamma\delta \sinh[e(\Psi_N - \Psi_s)/k_B T]}{1 + \delta \cosh[e(\Psi_N - \Psi_s)/k_B T]}. \quad (9)$$

Γ is the number of ionizable groups per unit area at the surface, $\delta = 2\sqrt{K_-/K_+}$, Ψ_s is the potential at the solid-liquid interface (see Eq. (7)), the Nernst potential Ψ_N is given as,

$$\Psi_N = \frac{k_B T}{e} \ln(10)(\text{pI} - \text{pH}) \quad (10)$$

the isoelectric point is given as $\text{pI} = (\text{pK}_+ + \text{pK}_-)/2$, pH denotes the value for the pH far from the interface and pI is the isoelectric point of the solid-liquid interface.

The spatial dependence of the electrostatic potential Ψ and charge density ρ on the distance between two particles with a separation of 10 nm and a particle in isolation is shown in Figure 1. The results presented in the figure were obtained by numerically solving Eqs. (2) and (3). Alternatively the exact analytical solution of Behrens and Borkovec for interacting surfaces with charge regulation [21] can be adapted to obtain the same results. As the distance between the charged particles varies, the potential distribution changes in the electrolyte filled gap between the surfaces as well as in the particle interior. This is due to the fact that the potentials inside and outside of particles are connected through Eqs. (7) and (8). The coupling goes both ways, hence the potential and charge distributions in the electrolyte will be affected by the fact that inner charges respond by internal redistribution to the particle approach.

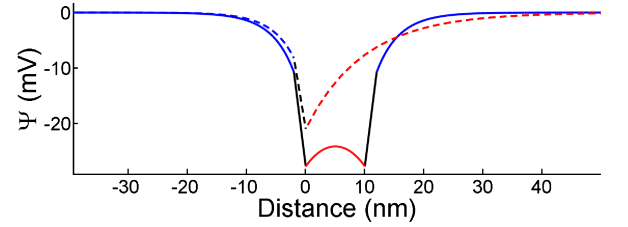


FIG. 1: One dimensional potential distributions in the electrolyte solution (red), oxide layer (black), and the semiconductor (blue) approximated as infinite flat plates. The solid line corresponds to two particles separated by 10 nm, while the dashed line corresponds to the potential distribution of a single particle in isolation. These curves illustrate how the potential distribution inside the semiconductor responds to the presence of an approaching colloid. The particles are covered with $-\text{SiO}^-$ groups with surface density $\Gamma = 8 \times 10^{18} \text{m}^{-2}$. These groups may release or attach a proton according to Eq. (1). The parameters for this calculation are: $\text{pH} = 3.5$, the overall electrolyte concentration is 0.925 mM (adjusted by adding symmetric monovalent electrolyte), $\text{pK}_+ = -2$, $\text{pK}_- = 6$, and the particle doping is 10^{24}m^{-3} . The dielectric permittivities were $\epsilon_{el} = 78.5$ for the electrolyte, $\epsilon_{sc} = 11.7$ for Si, and $\epsilon_{ox} = 3.9$ for the 2 nm thick layer of SiO_2 [22, 23].

Knowing the effect of separation on the potential and charge density distributions, in both particle interior and exterior, allows us to derive the pair electrostatic energy of interaction between the two spherical colloidal particles of radius a separated by distance h using the Derjaguin method [5, 6],

$$U_e(h) = \pi a \int_h^\infty dy \int_\infty^y dz \Pi_e(z), \quad (11)$$

where y and z are distance variables. A detailed description of the solution and the assumptions made are given in Supplementary Information, but we should emphasize here that the pressure Π_e depends on the electrostatic

potentials, and hence on the separation distance. The total energy of interaction consists of [5, 6]

$$U(h) = U_e(h) + U_{vdw}(h), \quad (12)$$

with U_{vdw} being the van der Waals attractive energy which for small separations is $U_{vdw}(h) = A_H a / 12h$ where A_H is the Hamaker constant [5, 6, 24].

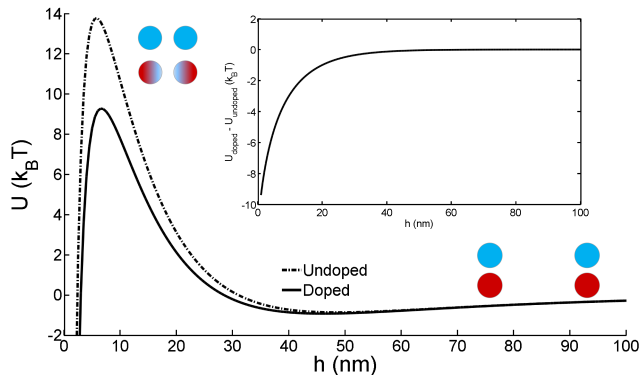


FIG. 2: Interaction between colloids. Interaction energy between undoped (blue particles, full line) and doped (red particles, dashed line) semiconductor colloids. As the particles approach the charge density in the doped particles redistribute which is illustrated by the gradual color change. The Hamaker constant used to generate this plots is $A_H = 5.4 \times 10^{-20}$ J, and the particle radius is $a = 100$ nm. The rest of the parameters are the same as in Figure 1. The inset shows the difference between the two energy curves.

The total interaction energy given by Eq. (12) is shown in Figure 2. The height of the maximum determines the stability against coagulation. Overcoming the barrier brings the two particles into the region of very close separations where the van der Waals attraction completely overpowers the electrostatic repulsion and leads to irreversible coagulation. The difference between the energy maxima for doped and undoped semiconductor colloids, and the parameters listed in Figure 1 and 2 is slightly more than $4 k_B T$. It is due to fact that internal charge density redistribution in the doped semiconductor reduces the potential in the electrolyte gap between the particle surfaces. Hence, the electrostatic repulsion for doped particles is less than that for undoped, which leads to a different energy curve (see Figure 2). The inset shows the energy change that is due to the doping. This is a new type of colloidal interaction that is uniquely characteristic to semiconductor colloids in aqueous suspension and is very significant in both magnitude and range. This effect depends on the doping concentration and decreases as the latter goes down and vice versa.

Suspensions characterized by a combination of van der Waals and electrostatic interactions are thermodynamically unstable and, given enough time, will ultimately coagulate. The energy barrier however provides kinetic

stability that may allow for sufficient time for different applications and processing. The rate equation describing the coagulation of two colloidal particles (formation of doublets) is [25–27],

$$\frac{dn_2}{dt} = k_c n_1^2, \quad (13)$$

where n_2 is the concentration of coagulated pairs (doublets), n_1 is the concentration of single particles, t denotes time, and $k_c = k_0/W$ is the rate constant.

With k_0 we denote the rate constant in absence of any long range interactions and energy barriers (the rate is purely diffusion-limited). The effect of slowing down due to the presence of an energy barrier is taken into account by the stability factor [27–29],

$$W = 4a \int_0^\infty \frac{H(h) \exp[U(h)/k_B T]}{h - 2a} dh, \quad (14)$$

where $H(h) = (4h + a)/4h$ embodies the hydrodynamic effects [30], also see Supplementary Information.

For the parameters in Figures 1 and 2, the coagulation rate in an undoped sample will be more than 60 times slower than the doped sample (see Figure 3). This is a significant difference that cannot be ascertained using the conventional DLVO theory. This new effect is entirely due internal mobility and reconfiguration of charges in the doped semiconductor. Figure 3a illustrates how the stability factor W of the colloidal system depends on doping [see Eq. (14)]. The relative coagulation rate is shown in the inset. As the doping level increases, the doped system becomes more unstable and prone to coagulation and precipitation. Figure 3b illustrates how a change in ionic concentration affects the stability of the colloids.

In the limit where the surface potential is small, $|\Psi_s| < 26$ mV we have derived Eq. (15) for the surface potential (see also Supplementary Information). The inverse Debye lengths are given as, $\kappa_{sc} = \sqrt{n_{sc} e^2 / \epsilon_{sc} \epsilon_0 k_B T}$ and $\kappa_{el} = \sqrt{n_{el} e^2 / \epsilon_{el} \epsilon_0 k_B T}$ for the semiconductor and electrolyte phases respectively where n_{sc} and n_{el} are the number densities of ions, also for the semiconductor and electrolyte phases respectively. Eq. (15) allows for the derivation of analytical expressions for the potential distributions in all phases. Further analysis provides insight into the functional form of the surface potential in various limits. In the low doping limit $\kappa_{sc} \rightarrow 0$ we recover the equivalent expression for charge regulation at a dielectric-electrolyte interface. Similarly, when the thickness of the oxide L_{ox} is large such that $L_{ox} \rightarrow \infty$ we again recover the expression for charge regulation at a dielectric-electrolyte interface. In the high doping, or metal-like limit where $\kappa_{sc} \rightarrow \infty$ and $L_{ox} \rightarrow 0$ the effect from the redistribution of charges in the semiconductor region is even stronger, as long as there is an oxide barrier to prevent the release of ions into solution. In the case of a metal-like particle without an oxide, the charge regulation formulas would have to be revisited.

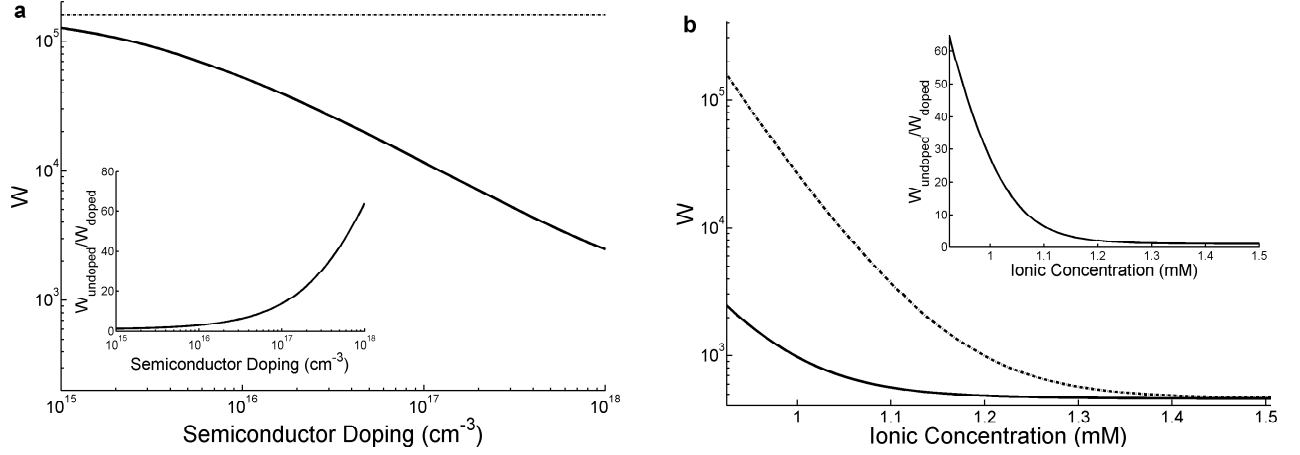


FIG. 3: Differences in stability due to doping. (a) Stability of undoped (dashed) and doped colloids (solid) vs. semiconductor doping concentration. The stabilities are useful for calculating time to coagulation. The inset shows relative stability $W_{\text{undoped}}/W_{\text{doped}}$ vs. doping. The relative stability is useful for calculating relative times to coagulation for undoped vs. doped particles. (b) Stability of undoped (dashed) and doped colloids (solid) vs. ionic concentration of the electrolyte. The relative stability $W_{\text{undoped}}/W_{\text{doped}}$ vs. ionic concentration of the electrolyte is given in the inset. The rest of the parameters are the same as in Figures 1 and 2.

$$\Psi_s = \frac{\Gamma \delta e \sinh(e\Psi_N/k_B T)}{[\delta \cosh(e\Psi_N/k_B T) + 1] \left[\epsilon_0 \epsilon_{el} \kappa_{el} \tanh\left(\frac{\kappa_{el} h}{2}\right) + \frac{\epsilon_0 \epsilon_{ox} \epsilon_{sc} \kappa_{sc}}{\epsilon_0 + L_{ox} \epsilon_{sc} \kappa_{sc}} + \frac{\Gamma \delta e^2 (\cosh(e\Psi_N/k_B T) + \delta)}{k_B T (\delta \cosh(e\Psi_N/k_B T) + 1)^2} \right]} \quad (15)$$

The internal mobility of charges (electrons and/or holes) in semiconductor materials has been experimentally demonstrated and utilized in different sensing applications [1, 2, 7–12, 31–33]. In this Letter, we used first principle continuum electrostatics [17] to develop a simple model that allows one to find the effect of the internal charge mobility on the external potential distribution and hence, on the electrostatic interaction between two approaching colloidal spheres. The internal charge redistribution manifests itself as a reduction of the electrostatic repulsion (or alternatively can be defined as an apparent additional attractive contribution to the energy see the inset in Figure 2). While one may think that this interaction is similar to the van der Waals attraction, the truth is that it has a very different functional dependence on separation. Instead of following a power law it decays almost exponentially, which is due to its electrostatic origin. It is very interesting that the effect of reduction in electrostatic repulsion is primarily dependent on the doping level and much less on whether the semiconductor particles are n-doped, p-doped or mixed. In addition to the n-doped particle interaction (the dashed line in Figure 2) we have computed the interaction potentials between p-doped particles as well as that between an n-doped and a p-doped particle. All these curves practically collapse onto a single one, which is almost indistinguishable from the dashed curve in Figure 2. This means

that the main reason for the observed effect is that there is a dynamically responsive charged fluid in the particle interior that responds to potential perturbations. The polarity of the inner charges is practically unimportant.

The surface chemistry plays a key role in determining the strength of the interaction between semiconductor dopants and the electric double layer. The difference between the chemical equilibria constants $\Delta pK = pK_- - pK_+$ determines the strength of the charge regulation at the interface [34]. Large ΔpK allow for larger changes in the surface potential as the distance h is varied. Particle surfaces with low ΔpK would show little change in stability with doping, while surfaces with large ΔpK (i.e. silica, $\Delta pK = 8$) allow for relatively large changes in surface potential and hence exhibit large changes in stability due to doping.

The new type of interaction, we have identified, has significant implications on the processing and handling of semiconductor colloids. First obvious conclusion is that doped colloids will be less stable and much more prone to coagulation than their undoped counterparts. Figure 3 gives an idea about the relative time windows for kinetic stability. As mentioned above, the average lifetime for a suspension of silicon colloid with $10^{18}/\text{cm}^3$ doping level will be more than 60 times shorter than that for an undoped sample with the same surface chemistry. This effect can be exploited to separate doped from un-

doped particles in aqueous suspensions, or even sort the particles based on their doping. Heavily doped particles will precipitate faster and can be separated from the rest by simple filtration or centrifugation. They then can be redispersed using sonication. The procedure can be repeated multiple times to obtain particles with narrow distribution of the doping levels.

Increasing the pH beyond the isoelectric point leads to an increase in the value of the surface potential and hence, increase the repulsion and stability of the suspension. Similar will be the effect of reducing the background electrolyte concentration, which will extend the range of the overall electrostatic repulsion. Colloidal suspensions can be used to fabricate ordered crystal-like structures that have excellent properties for photonics applications [35]. Figure 2 implies that among other things the particle doping may have an effect on the spacing and ordering in crystals composed of semiconductor colloidal particles. Doped particles will be spaced on the average closer than undoped particles. For example a close inspection of the energy curves in Figure 2 show that the average doped particles spacing will be about 2 nm smaller than that for the undoped. We are convinced that better understanding of the interface between semiconductor materials and electrolyte solutions will be instrumental in the effort to design novel “smart” materials at the micro and nanoscale.

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