Communication

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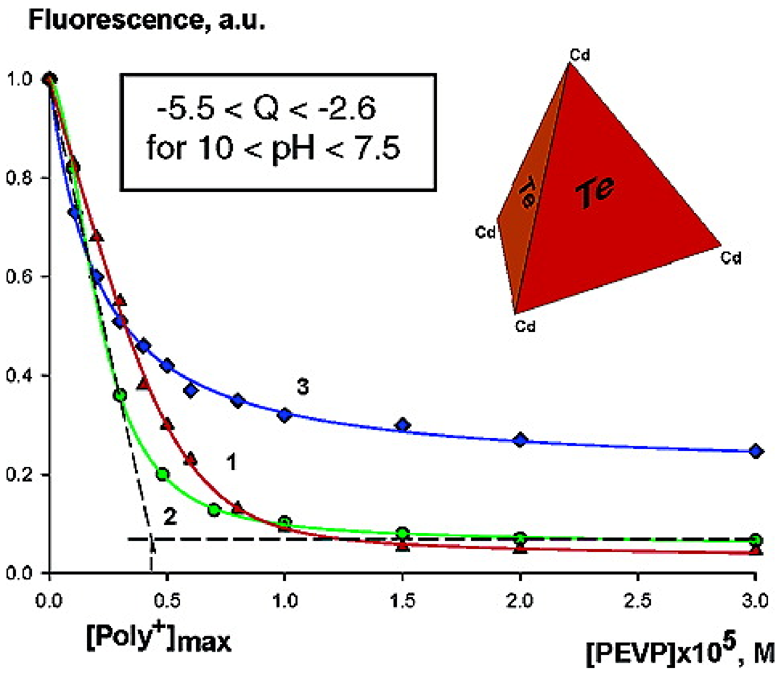

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What Is the Effective Charge of TGA-Stabilized CdTe Nanocolloids?

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The net charge of nanoparticles (Q) is a key parameter which determines their behavior and stability against aggregation in dispersions. Additionally, there are several important reasons related to advanced technologies, based on nanoparticles (NPs), to know Q in liquid media. (1) Stored charge strongly affects optical and electronic properties of NPs[1−3] and, therefore, their applications in photonics, electronics,[4] and analytical chemistry.[5] (2) Q determines different modes of self-organization processes of NPs.[6] (3) It also controls interaction with polymers and, thereby, structure and function of nanocomposites, for instance, those made by layer-by-layer assembly.[7] (4) Last, but not least, Q defines NP interactions with cell membranes, which makes it imperative to know Q for evolving biomedical applications of NPs.[8−11] Despite the obvious importance of Q, very limited information, mostly in the form of indirect data about the net charge of NP colloids, can be found. Scanning probe microscopy can be used to determine the relative and potentially absolute values of Q,[3] but the effect of transferring of NPs from solution to dry surfaces on Q is uncertain. Rockenberger et al.[12] calculated the overall charge for 1.8 nm NPs, $Cd_{54}Te_{32}(SR)_{52}$ (SR is 2-mercaptoethanol residue) tetrahedron, to be $Q = -8$ as the sum of all atomic constituents taking (+2) for Cd, (−2) for Te, and (−1) for the SR residue. Many factors can cause deviations in the value of Q calculated as described above, for instance, adsorption of ions, ionization of acidic stabilizers, replacement of thiols with water, and others. As well, the tetrahedral geometry of $Cd_{54}Te_{32}(SR)_{52}$ may not persist for all the NPs of similar composition, resulting in imperfect geometrical shapes with the defect site. Here, we describe a simple method of quantitative evaluation of Q in aqueous dispersions, which should be applicable to many families of luminescent NPs and does not require the knowledge of exact atomic composition or any assumptions about drying effects.

As a model system, we utilize CdTe NPs stabilized by thioglycolic acid (TGA)[13] structurally similar to $Cd_{54}Te_{32}(SR)_{52}$.[8] Their diameter was 1.8−2 nm as determined by TEM and AFM. They displayed strong fluorescence with a maximum $\lambda_{em} = 527$ nm and a quantum yield of 15−25%. A molar concentration of Cd in the prepared suspension was found to be 7.2×10^{-3} M by ICP-AES (IRIS Advantage, Thermo Jarrell Ash). Molar concentration of NP in suspension, [NP], was estimated in two ways. Complete incorporation of Cd into the particles was assumed for both of them. In the first approach, each NP was supposed to carry about 54 Cd atoms,[12] then $[NP] = 1.3 \times 10^{-4}$ M. In the second approach, a density of NP was assumed to be 6.2 g/cm^3, that is, the bulk value of CdTe, which gives $[NP] = 9 \times 10^{-5}$ M. The average between the two above values was taken for the concentration of NPs in the initial suspension: $[NP] = 1.1 \times 10^{-4}$ M. In all experiments here, we used the original dispersion diluted 100 times, that is, with $[NP] = 1.1 \times 10^{-6}$ M.

A cationic polymer, poly(*N*-ethyl-4-vinylpyridinium bromide-*co*-4-vinylpyridine) (94/6) (PEVP), with a degree of polymerization 1100, was prepared by quarternization of poly(4-vinylpyridine) with ethyl bromide as described elsewhere.[14] PEVP is a fluorescence quencher undergoing electron transfer reaction with the excited state of NPs. As expected, addition of PEVP to the NP suspension, $[NP] = 1.1 \times 10^{-6}$ M, was accompanied by a decrease in intensity of the NP fluorescence due to electron transfer quenching. The results obtained at three different pH values of the suspension are represented in Figure 1A. When increasing PEVP concentration, $[Poly^+]$ expressed as moles of positive quarternized units, the fluorescence intensity initially dropped and then stabilized at a certain level, becoming independent of $[Poly^+]$. A linear course of the dependence at low PEVP concentrations for three pH values indicates that nearly all PEVP bind to NPs under these conditions. The maximum concentration at which a complete PEVP binding to the NPs, $[Poly^+]_{max}$, is still observed was estimated as the intersection point of two tangents drawn to both linear sections on the experimental curve (Figure 1A). Thus, obtained $[Poly^+]_{max}$ values were found to be dependent on pH (see Table 1) increasing for high pH. It was also found that binding of PEVP to the NPs was sensitive to the concentration of a salt in the suspension. NaCl concentration suppressed PEVP/NP complex formation (Figure 1B); the binding was completely blocked at $[NaCl] = 0.14$ M. This indicates that PEVP association with CdTe NPs, resulting in the luminescence quenching, is governed predominantly by electrostatic interactions of the positive polycation units with negative NP. This fact may be simple, but not obvious, because one may argue that the structure of PEVP and NP can support van der Waals and hydrophobic interactions between them, as well. The dominant role of electrostatic attraction has special importance here because it allows one to experimentally determine the net charge of the NPs. To confirm this, we measured the surface charge of NPs by its electrophoretic mobility (laser microelectrophoresis; Zetasizer IIc, Malvern Instruments, U.K.) (Figure 2). Importantly, the complete neutralization of the NP surface charge was observed at the PEVP concentration close to $[Poly^+]_{max}$, calculated from the data of Figure 1A. In other words, the above estimated $[Poly^+]_{max}$ is actually equal to the overall concentration of negative charges residing on NPs. Thus, one can calculate the average charge on each NP, Q. This method can also be applied to biomembranes, proteins, and cells

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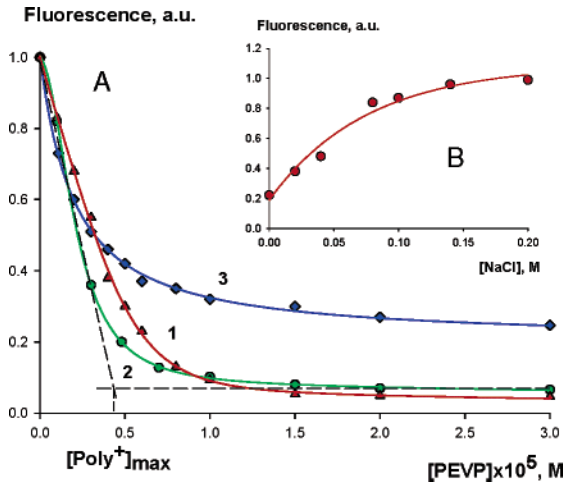

Figure 1. (A) Addition of PEVP to the CdTe NPs. Measurements were done 3 min after mixing of the nanocolloids and the polyelectrolyte solution. [NP] $=1.1 \times 10^{-6}$ M; phosphate buffer $= 10^{-2}$ M; pH 10 (**1**), 8.5 (**2**), and 7.5 (**3**); $\lambda_{ex} = 360$ nm. (B, insert) Effect of NaCl concentration on the fluorescence intensity of CdTe NPs complexed with PEVP. Measurements were done 3 min after addition of NaCl to CdTe/PEVP complexes. [NP] $= 1.1 \times 10^{-6}$ M; [PEVP] $= 5 \times 10^{-6}$ M; phosphate buffer $= 10^{-2}$ M; pH 8.5; $\lambda_{ex} = 360$ nm.

Table 1. Effect of pH on the Average Charge on CdTe Nanocolloids

pH	$[\text{Poly}^+]_{max}$ ($\times 10^5$ M)[a]	Q[b]
10	0.61	-5.5 ± 1.1
8.5	0.46	-4.2 ± 0.8
7.5	0.29	-2.6 ± 0.5

[a] $[\text{Poly}^+]_{max}$ is determined as shown in Figure 1. [b] Ratio of $[\text{Poly}^+]_{max}/[\text{NP}]$.

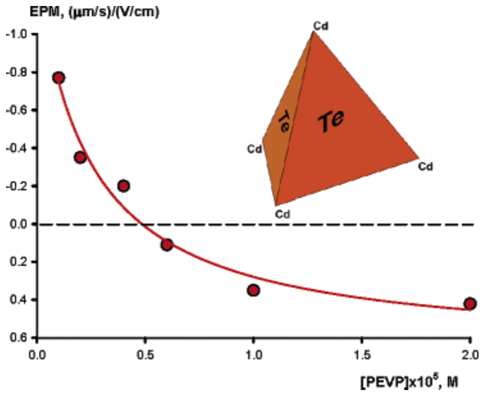

Figure 2. Effect of PEVP on electrophoretic mobility (EPM) of CdTe NP colloids. Measurements were done 3 min after constituents mixing. [NP] $= 1.1 \times 10^{-6}$ M; phosphate buffer $= 10^{-2}$M; pH 8.5.

for which dissociation of fluorescent dye was previously used.[15] The data represented in Table 1 show a decrease of Q from -5.5 to -2.6 when changing pH from 10 to 7.5. Experimental Q was less negative than the net charge calculated for a very similar tetrahedral NP[12] ($Cd_{54}Te_{32}(SR)_{52}$).[8] Physical and chemical adsorption of Cd(2+) ions on (a) Te-rich side planes of the tetrahedrons (see insert in Figure 2), and (b) terminal $-$COOH groups of TGA is the likely reason for this deviation. In fact, it takes only three Cd(2+) to change Q from -8 to -2, especially when bonding with Te atoms exposed on the side planes is taking place. On the other hand, the acidic ionization of terminal $-$COOH groups of TGA should also contribute to the net charge. The evidence of their contribution can be seen in the pH dependence and a clear trend of concomitant increase in $-Q$ and pH. How many of the carboxyl groups are actually ionized, whether in the form of free $-COO^-$ or ion-pairs with Cd(2+), remains an open question. Note that some part of the TGA stabilizers can completely detach from the surface of CdTe.[6] Overall, the manifold of exchange reactions creates a complex chemical system determining the particle charge and NP interactions. Thus, the first experimental measurements of net charge of water-soluble NPs in their native environment are described. The proposed technique offers an experimental method for further research on ionizable NPs, which are important for fundamental studies on optical/electron properties, self-organization of NPs, and practical applications in the biomedical field and analytical chemistry.

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