Nanoparticle Phase Transfer

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A Temperature-Driven Reversible Phase Transfer of 2-(Diethylamino)ethanethiol-Stabilized CdTe Nanoparticles**

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Nanoparticles (NPs) play an important role in applications such as biological imaging, energy conversion, and environmental remediation due to their unique optical and electrical properties.[1–4] The chemical synthesis of NPs is usually conducted in the presence of either hydrophilic stabilizers in aqueous solution or hydrophobic ligands in an organic solvent. However, the distinct solubility differences of NPs in media with different polarities limit their broader application. For instance, NPs capped with hydrophobic stabilizers can be dispersed and used in organic solvents but not in aqueous solutions, and vice versa.[5,6] Much effort has therefore been devoted to understanding and controlling the phase-transfer behavior of NPs. The successful strategies reported to date can be classified into two types: 1) changing the wettability characteristics of the stabilizers,[7] and 2) changing the composition of the medium.[8] Both these methods involve altering the hydrophobic/hydrophilic properties of NPs by changing the nature of either the stabilizers or the medium to realize repetitive transfers between the immiscible phases. Herein we report a reversible phase transfer of 2-(diethylamino)ethanethiol (DEAET)-stabilized CdTe NPs in water/toluene which is driven solely by temperature. The mechanism of this phase transfer between the two immiscible phases is investigated in detail.

The DEAET-stabilized CdTe NPs were prepared as reported in the literature.[9] DEAET molecules (molecular formula: $(CH_3CH_2)_2NCH_2CH_2SH$) bind to the surface of the NPs through their thiol group, which means that the hydrophilic amino group and two hydrophobic ethyl groups are exposed to the medium. Previous studies have shown that the amphiphilic nature of the ends exposed to the medium endows the NPs with a unique temperature-dependent dispersion behavior in water: they precipitate at 0 °C while they dissolve at higher temperatures (70 °C).[10] These observations prompted us to study the phase-transfer behavior of DEAET-stabilized CdTe NPs in a two-phase system of immiscible liquids.

As shown in Figures 1 A and 1 D, the orange-emitting DEAET-stabilized CdTe NPs are present in the toluene phase at 0 °C. Upon increasing the temperature to 27 °C, however, the NPs partially transfer from the toluene to the aqueous phase (Figures 1 B and 1 E), and at a temperature of 70 °C they are present almost exclusively in the aqueous phase (Figures 1 C and 1 F). The intensity of the corresponding photoluminescence (PL) peaks (Figures 1 D–F) further shows that the partition ratios of DEAET-stabilized CdTe NPs in water/toluene are 1:13 at 0 °C, 3:4 at 27 °C, and 303:1 at 70 °C. From the PL peak positions, the average size of the CdTe NPs is approximately 3.8 nm.[10]

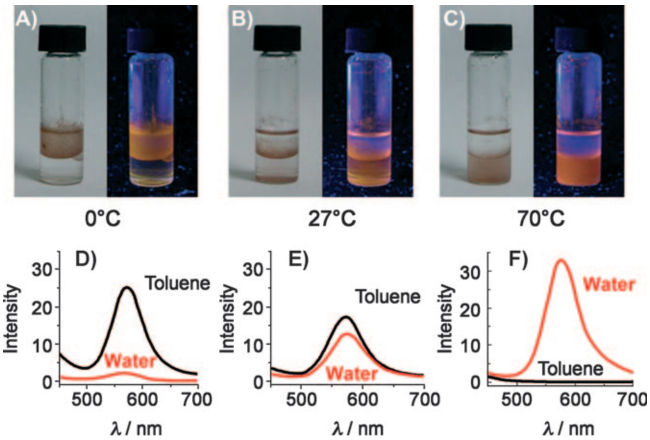

Figure 1. Photographs of orange-emitting DEAET-stabilized CdTe nanoparticles (NPs) in the water/toluene phases taken under daylight (left) and a UV lamp (right) at A) 0 °C, B) 27 °C, and C) 70 °C. The upper layer in the vials is toluene and the lower layer is water. The photoluminescence (PL) spectra of DEAET-stabilized CdTe NPs in the toluene and aqueous phases at D) 0 °C, E) 27 °C, and F) 70 °C. The black line is the PL spectrum of the NPs in the toluene phase and the red line the spectrum in the aqueous phase.

We noticed that the temperature-driven phase transfer of these NPs was quick and reversible. Thus, the phase transfer was finished within only a few minutes upon raising the

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temperature, and the transfer of NPs between the aqueous and toluene phases could be repeated at least ten times without significantly altering the intensity and position of the PL peaks (Figure S1 in the Supporting Information).

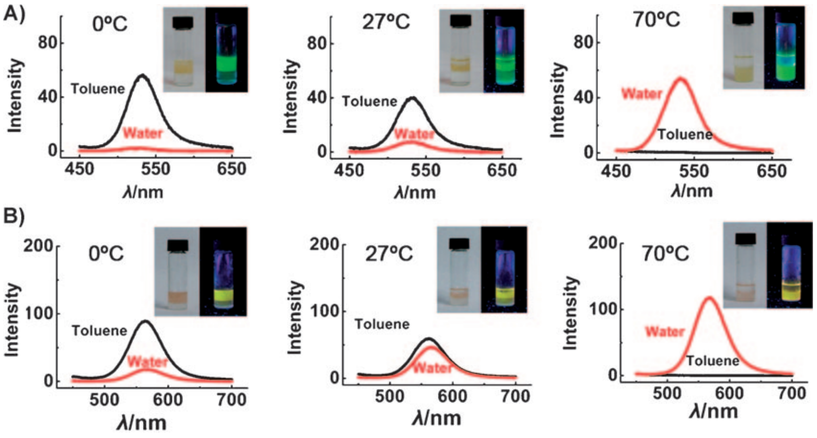

Figure 2. Phase-transfer behaviors of DEAET-stabilized CdTe nanoparticles (NPs) with A) green and B) yellow emission in the water and toluene phases at 0, 27, and 70 °C. The upper layer in the vials is toluene and the lower layer is water. The black line is the PL spectrum of the NPs in the toluene phase and the red line the spectrum in the aqueous phase.

Similar temperature-driven reversible phase-transfer processes have been observed for NPs of varying sizes. Figure 2 shows that green- and yellow-emitting CdTe NPs stabilized with DEAET can also reversibly transfer between aqueous and toluene phases. The partition ratios of green-emitting CdTe NPs in water/toluene (Figure 2 A) are 1:33 at 0 °C, 6:1 at 27 °C, and 41:1 at 70 °C, while for yellow-emitting CdTe NPs (Figure 2 B) the ratios are 1:6 at 0 °C, 1:1 at 27 °C, and 76:1 at 70 °C. From the PL peak positions, the sizes of the green- and yellow-emitting CdTe NPs are estimated to be about 2.5 and 3.0 nm, respectively.[10] The above observation suggests that the phase-transfer behavior is not strongly dependent on NP size.

The hydrophobic ethyl groups of the DEAET stabilizer appear to have an important influence on the phase-transfer behavior of CdTe NPs, as no phase transfer was observed, at any temperature, for CdTe NPs stabilized by 2-aminoethanethiol, which does not contain these two ethyl groups (Figure S2 in the Supporting Information). A couple of questions therefore arise naturally: 1) Why are the DEAET-stabilized CdTe NPs, which should be strongly hydrophobic, able to reversibly transfer between water and toluene phases with changing temperature? 2) Is the temperature-driven phase-transfer behavior the same for DEAET and DEAET-stabilized CdTe NPs?

First of all we resorted to a predictive activity coefficient model (UNIFAC, universal quasi-chemical functional activity coefficient model) to study the partitioning of a trace amount of DEAET between the aqueous (water) and organic (toluene) phases.[11,12] Surprisingly, we found that the relative solubility of DEAET in toluene vs. water increased by a factor of approximately seven as the temperature increased from −20 to 100 °C (Figure S3 in the Supporting Information). We therefore cannot explain the transfer of NPs from the toluene to the aqueous phase at high temperature on the basis of the preference of a single DEAET molecule, as DEAET prefers to be in the organic phase at such temperatures.

It is well known, however, that there are important structural differences between the solvation of small and large molecules in an aqueous medium.[13] Contrary to the widely held belief, the hydrophobic effect arises not due to repulsion between aqueous and organic molecules but to a manifestation of the strong attractive forces between water molecules compared to the relatively weak attraction between the organic and water molecule, and between the organic molecules themselves. The network of hydrogen bonds surrounding a small organic molecule such as DEAET in water is not significantly deformed, whereas the solvation of a large hydrophobic species such as a DEAET-stabilized NP disturbs the structure of water to such an extent that it becomes impossible to maintain a hydrogen-bond network adjacent to an extended surface.[13–17] We therefore constructed a minimal theoretical model in order to reconcile the temperature-dependent partitioning of DEAET-stabilized NPs between the toluene and water phases. The goal of this model was to provide a framework to describe the phase-transfer behavior by involving the notion of a "net hydrophobic force". A qualitative explanation of the physicochemical origin of the unique thermosensitivity of DEAET-stabilized NPs is provided in the Supporting Information (Section 2(b)). This unique thermosensitivity was further confirmed by observing the change in contact angle of water on a DEAET-stabilized NP film at different temperatures (Section 3 in the Supporting Information).

Since the phase transfer was observed to be reversible, we also sought to build a thermodynamic model based on the following assumptions: 1) the toluene and water phases have low mutual solubility; 2) the DEAET stabilizer covers the surface of the NPs uniformly, so that it can be visualized as a core/shell assembly; 3) the volume occupied by the NPs is much smaller than the volume occupied by the toluene and water phases. In accordance with the Flory–Huggins lattice theory of polymeric mixtures, the free energy of mixing (the mixing process is shown in Figure S4 in the Supporting Information) can be written as Equation (1),[18] where ϕ_i is the

$$\frac{\Delta G_{\text{mix}}}{NRT} = \phi_{\text{W}} \ln\phi_{\text{W}} + \chi_{\text{W}}\phi_{\text{W}} + \phi_{\text{T}} \ln\phi_{\text{T}} + \chi_{\text{T}}\phi_{\text{T}} \qquad (1)$$

volume fraction of the NP in phase i (T: toluene; W: water) and χ_i is the Flory interaction parameter between an NP and phase i, and N ($= V/\nu_{NP}$) is the ratio of the volumes of the water phase (or toluene, since they are assumed to be equal) and the NPs. The first and third terms on the right-hand side in Equation (1) are entropic in nature, while the second and fourth terms are energetic in origin.

If we assume that the volumes of the water and toluene phases are both equal to V, Equation (2) follows, where n_{NP} is the total number of nanoparticles dispersed between the two phases.

$$n_{NP} = \frac{\phi_W V}{\nu_{NP}} + \frac{\phi_T V}{\nu_{NP}} = (\phi_W + \phi_T) N \qquad (2)$$

To find the equilibrium composition we must determine the minimum of the free energy of mixing. Rearranging Equation (2) gives $\phi_T + \phi_W = n_{NP}/N$, therefore $d\phi_T/d\phi_W = -1$. If we set Equation (3) we obtain, for equilibrium partitioning, Equation (4) where $\chi^* = \chi_W - \chi_T$ approximately represents the strength of the net hydrophobic force.

$$\frac{\partial(\Delta G_{mix}/RT)}{\partial \phi_W} = 0 \qquad (3)$$

$$\frac{\phi_W}{\phi_T} = \exp -\chi^* \qquad (4)$$

Experimentally, the partition ratio for the orange-emitting NPs in water/toluene (ϕ_W/ϕ_T) is 1:13 at 0 °C (Figure 1 D), therefore χ^* is 2.6 (in units of kT), as calculated from Equation (4). Similarly, $\chi^* = -5.7$ at 70 °C, where the value of ϕ_W/ϕ_T is 303:1 (Figure 1 F). The results obtained from the theoretical model are consistent with the experimental results in that the decrease of the net hydrophobic force at high temperature means that the DEAET-stabilized CdTe NPs transfer from toluene into the aqueous phase. Moreover, the fact that hydration of the NP core in aqueous solution at high temperature increases the dipole moment of the NPs, and therefore makes them more hydrophilic, may also contribute to the decrease of the net hydrophobic force.[19]

Equation (4) also reveals that the partition ratio of NPs in water/oil phases is strongly dependent on χ^* and that a change of about eight accounts for the dramatic transfer behavior. Furthermore, the partition ratio does not depend directly upon the size of the nanoparticle, although there is an indirect and presumably weak dependence through χ^*. Indeed, the temperature-driven reversible phase transfer of CdTe NPs with varying sizes was observed experimentally (Figures 1, 2 A, and 2 B). The PL data for all these systems can be fitted to the curve $\chi^*(T) = -32.9 + 9829.8/T$, as shown in Figure 3.

The final question concerns how the CdTe NPs reversibly transfer across the water/toluene interface at different temperatures. An intermediate state of the interfacial attachment of CdTe NPs is observed at 27 °C before the NPs fully transfer into either the toluene or water phases (Figures 1 B and 2). The inter-NP forces, which include hydrogen bonding, dipole attraction, electrostatic interaction, and net hydrophobic force, change with temperature, which leads to the interfacial aggregation and subsequent phase transfer of CdTe NPs. A similar transfer process has been discussed previously.[20]

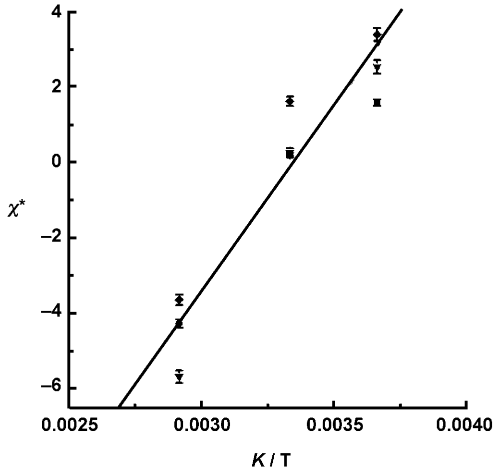

Figure 3. The dependence of the Flory interaction parameter (χ^*) on temperature (K), as inferred from the experimental data using Equation (4). ——: $\chi^* = -32.9 + 9829.8/T$. ◆ green-emitting (2.5 nm), ● yellow-emitting (3.0 nm), and ▼ orange-emitting (3.8 nm) DEAET-stabilized NPs.

In summary, we have shown that DEAET-stabilized CdTe NPs are able to transfer reversibly between aqueous and toluene phases in a process driven solely by temperature. Theoretical studies have revealed that, in contrast to simple DEAET molecules, the net hydrophobic force of DEAET-stabilized CdTe NPs decreases at high temperature, thus favoring the transfer of NPs into the aqueous phase. The different phase-transfer behavior of CdTe NPs with respect to DEAET molecules is ascribed to their size, which is large enough to disturb the hydrogen-bonding network in the water surrounding the NPs and thus increase their solubility in water. These findings could help the further understanding of the unique physiochemical properties of NPs and benefit their future applications in solvents with different polarities.[21]

Experimental Section

Synthesis of DEAET-stabilized CdTe NPs: $Cd(ClO_4)_2 \cdot 6H_2O$ (0.986 g) was dissolved in distilled water (125 mL), then DEAET (0.854 mL) was added and the pH was adjusted to 5.0 with 2 M NaOH. The solution was placed in a three-necked flask and deaerated with N_2 gas for about 30 min. H_2Te gas, generated by mixing Al_2Te_3 (0.2 g) with 0.5 M H_2SO_4 (15 mL) in a separate three-necked flask, was bubbled through this solution. CdTe NPs with varying sizes were synthesized by heating at reflux under nitrogen gas for different times. Thus, green-, yellow-, and orange-emitting NPs were obtained after reaction times of 1, 2, and 10 d, respectively.

Phase transfer of DEAET-stabilized CdTe NPs: An equal volume of toluene was added to the previously prepared CdTe NP solution to study the phase-transfer behavior at different temperatures. The photographs in Figures 1 and 2 were taken with a camera in daylight or under a UV lamp. An LS 55 Luminescence spectrometer (Perkin–Elmer, USA) was used to record the photoluminescence (PL) spectra of NPs in water and toluene.

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