

## Two Opposite Effects of Alcohols in the Precipitation of Aqueous Nanocrystals

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In this work, we investigated the alcohols-based purification process of aqueous nanocrystals in simultaneous consideration of the interparticle-distance-dependent total interaction potential and the external structure of nanocrystals. Before nanocrystal precipitation, it is required to overcome an energy barrier, which is basically generated by the interparticle electrostatic repulsion. In the precipitation process of nanocrystals, alcohols possess two opposite effects. On the one hand, the addition of alcohols leads to the decreased relative dielectric constant of the mixture solution and the reduced interparticle electrostatic repulsion, which promotes the precipitation of nanocrystals. On the other hand, the ionic strength in the nanocrystal solution decreases after the introduction of alcohols. This leads to the increased interparticle electrostatic repulsion, which is adverse for the precipitation of nanocrystals. As a result, the precipitation process of aqueous nanocrystals should consider the integrated effects of alcohols. Overall, the current investigation is not only favorable for understanding various unusual experimental observations in the purification process of aqueous nanocrystals but also is a benefit for comprehending nanocrystal behaviors in complex solvent systems, which will greatly help synthetic chemists in establishing protocols for nanocrystal synthesis.

### Introduction

Semiconductor nanocrystals have attracted great fundamental and technical interest in recent years. Compared with organic dyes, semiconductor nanocrystals possess broader emission tunability, superior photostability, longer photoluminescence (PL) lifetime,<sup>1,2</sup> and thus can be extensively exploited as potential candidates for light-emitting diodes, lasers, biomedical tags, and so forth.<sup>3–6</sup> Among various physical and chemical routes of nanocrystal preparation, the colloidal chemistry method is one of the best for synthesizing nanocrystals with high PL quantum yields, narrow size distribution, controllable shapes, and desired surface functionalities.<sup>7–10</sup> The colloidal method usually employs two types of materials: the precursor and the ligand. The former is used to create the cores of nanocrystals, and the latter is used to prevent the aggregation of nanocrystals as well as make nanocrystals dispersible in solvent.<sup>11,12</sup> The colloidal method also makes it possible to synthesize nanocrystals alternatively in aqueous solution and nonaqueous media through the selection of different ligands. Hydrophobic ligands, for instance, trioctylphosphine, oleic acid, and oleic amine, are common ligands for nonaqueous synthesis.<sup>13–17</sup> In comparison, aqueous synthesis usually adopts hydrophilic mercapto-ligands, such as 3-mercaptopropionic acid, thioglycolic acid, 1-thiolglycerol, and so forth.<sup>18–21</sup> Through flexible selection of various precursors and ligands, nanocrystals with different sizes, shapes, composition, and properties can be achieved.<sup>13–17</sup>

No matter which synthesis routes are used, lots of excess ions, ligands, and compounds are introduced into the nanocrystal solution during the preparation process. These excess matters are usually a disadvantage to the subsequent coupling or assembling of nanocrystals with other materials.<sup>22–25</sup> For

instance, in bioimaging applications these excess ions are toxic to the target organism.<sup>26</sup> To remove this excess matter, purification is necessary before the application of nanocrystals. The most common purification method is the addition of nonsolvents into the nanocrystal solution, which can separate nanocrystals from solution by decreasing the solubility of nanocrystals in the mixture solution.<sup>11a,27,28</sup> By controlling the volume fraction of nonsolvents in the mixture solution, a novel technique of size-selective precipitation has also been developed for separating nanocrystals with different sizes.<sup>11a,27,28</sup> Among various nonsolvents exploited for precipitating nanocrystals, alcohols are the typical nonsolvents for both nonaqueous and aqueous nanocrystals.<sup>11a,27,28</sup> For example, methanol or ethanol is used for precipitating hydrophobic CdSe nanocrystals,<sup>11a,27</sup> whereas 2-propanol is exploited for precipitating aqueous CdTe nanocrystals.<sup>28</sup> Although alcohols are always used as nonsolvents, the fundamental mechanism of the alcohols-induced nanocrystal precipitation is usually ignored. On the basis of the precipitation of nonaqueous nanocrystals, alcohols are believed to increase the polarity of the mixture solution, making worse compatibility of hydrophobic nanocrystals in the polar mixture.<sup>11a</sup> However, it is hard to understand that aqueous nanocrystals, which possess good dispersibility in polar solution, can also precipitate by addition of alcohols.<sup>28</sup> Interestingly, some recent works report the dispersibility of aqueous nanocrystals in alcohols or direct synthesis of aqueous nanocrystals in alcohols.<sup>29</sup> These experimental observations indicate the unusual effects of alcohols in the precipitation process of nanocrystals. Anyway, investigating the alcohols-induced nanocrystal precipitation is not only the key for understanding various unusual experimental observations in purification process but also is favorable for comprehending nanocrystal behaviors in complex solvent system, which will greatly help synthetic chemists in establishing protocols for nanocrystal synthesis.

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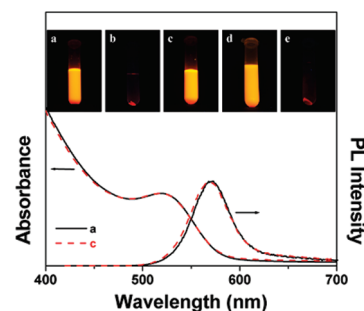
The recent works have reported the external structure of aqueous nanocrystals; namely, aqueous nanocrystals composed of a core, a ligand layer, an adsorbed layer, and a diffuse layer.<sup>30</sup> The main interactions between aqueous CdTe nanocrystals are electrostatic repulsion, van der Waals attraction, and dipolar attraction on the basis of the colloidal Derjaguin–Landau–Verwey–Overbeek (DLVO) model.<sup>30</sup> The electrostatic repulsion mainly originates from the charges of ligands on the nanocrystal surface, and the electrostatic repulsion increases exponentially from the outside of diffuse layer to the ligand layer.<sup>30a,b</sup> What is more, the interparticle interactions have proved to affect the nucleation and growth processes of aqueous nanocrystals.<sup>30a,b</sup> In fact, these works open a door for comprehending various behaviors of aqueous nanocrystals. In this work, we emphasized on investigating the alcohols-based purification process of aqueous nanocrystals in the simultaneous consideration of the interparticle-distance-dependent total interaction potential and the external structure of nanocrystals. Before nanocrystal precipitation, it is required to overcome an energy barrier, which is basically generated by the interparticle electrostatic repulsion. Alcohols have two opposite effects in the purification process. Whether nanocrystals can precipitate from the solution is determined by the integrated effects of alcohols.

## Experimental Section

**Materials.** All materials used in this work were analytical reagents. CdCl<sub>2</sub>, NaBH<sub>4</sub>, NaOH, NaCl, methanol, ethanol, 1-propanol, 2-propanol, acetone, and diethyl ether were commercial available in China. 3-Mercaptopropionic acid and Te powder were purchased from Aldrich. NaHTe solution was prepared by using Te and NaBH<sub>4</sub> according to the reference methods.<sup>31</sup>

**Synthesis of 3-Mercaptopropionic Acid-Capped CdTe Nanocrystals.** CdTe nanocrystals were prepared according to the previous methods.<sup>31</sup> Typically, the mixture of CdCl<sub>2</sub> and 3-mercaptopropionic acid was adjusted to pH 9.1 using 1.0 mol/L NaOH solution and then aerated with N<sub>2</sub> for 30 min. After injection of freshly prepared NaHTe solution into the mixture, CdTe crude solution was obtained. The total concentration of Cd in crude solution is  $5.2 \times 10^{-3}$  mol/L, and the initial molar ratio of CdCl<sub>2</sub>/3-mercaptopropionic acid/NaHTe is 1.0/2.4/0.2. To obtain CdTe nanocrystals with emissions from green to red, the crude solution was refluxed for specific time and then cooled to room temperature in the open air. In this context, if there is no special declaration, CdTe nanocrystals were prepared using the aforementioned method. CdTe nanocrystals with a relatively low concentration were prepared with a similar procedure except the total Cd concentration of  $1.3 \times 10^{-3}$  mol/L. Notably, the as-prepared CdTe nanocrystals were also called the original CdTe nanocrystals to discriminate from the redispersed solution of CdTe precipitates after the purification process.

**Alcohols-Induced Precipitation of Aqueous Nanocrystals.** The typical precipitation process was shown in parts a–c of Figure 1. 2-Propanol (5.5 mL) was dropped into the original CdTe nanocrystal solution (5 mL) until the solution became slightly turbid.<sup>28</sup> The mixture was centrifuged at 4000 r/min for 20 min, and then CdTe precipitates appeared at the bottom of the centrifugal tube. After decantation of the supernatant solution, the precipitates were dispersed into 5 mL water. To discriminate with the original CdTe solution without purification, the dispersed solution of CdTe precipitates was brief as the redispersed CdTe solution in this context.



**Figure 1.** Normalized UV and PL ( $\lambda_{\text{ex}} = 400$  nm) spectra of the original CdTe solution (black solid line) and the redispersed CdTe solution (red dash line). The corresponding digital photographs of original CdTe solution and redispersed CdTe solution were shown in pictures (a) and (c) in the insert pictures. Insert pictures: the photographs of nanocrystal solutions under the irradiation of an UV lamp (365 nm); (a) the original CdTe solution, (b) the mixture solution of original CdTe (5 mL) and 2-propanol (5.5 mL) after centrifugation, (c) the redispersed aqueous solution of CdTe precipitates, (d) the mixture solution of redispersed aqueous CdTe solution (5 mL) and 2-propanol (5.5 mL) after centrifugation, (e) the centrifugal solution after addition of NaCl into solution (d).

**TABLE 1: Relative Dielectric Constants of Solvents ( $\epsilon$ ), the Critical Volume Fraction of Alcohols, and the Calculated Critical Relative Dielectric Constant of the Mixture Solution ( $\epsilon_{\text{mix}}$ )**

solvent	$\epsilon$	critical volume fraction	critical $\epsilon_{\text{mix}}$
water	80.1		
ethanol	24.6	0.52	45.7
2-propanol	18.3	0.50	41.9
1-propanol	20.3	0.50	43.6
acetone	20.7	0.54	41.3
diethyl ether	4.3	0.33	49.4 <sup>a</sup>

<sup>a</sup> When diethyl ether was used for precipitating nanocrystals, ethanol must be added simultaneously to improve the compatibility of diethyl ether and nanocrystals. The volume fraction and the calculated  $\epsilon_{\text{mix}}$  had considered the influence of the ethanol.

To measure the minimal volume fraction of alcohols for the complete precipitation of nanocrystals, different volumes of alcohols were dropped into the original CdTe solution under stirring until the supernatant solution exhibited no obvious luminescence after centrifugation. This minimal volume fraction of alcohol was called the critical volume fraction as shown in Table 1. For complete precipitation of 5 mL CdTe nanocrystals, it required at least 5.5 mL ethanol, 5.0 mL 2-propanol, 5.0 mL 1-propanol, 6.0 mL acetone, or 1 mL diethyl ether. Notably, when diethyl ether was used, ethanol (1.5 mL) must be simultaneously added to improve the compatibility of diethyl ether and nanocrystals. The volume fraction of alcohol was calculated by dividing the total volume of alcohol and nanocrystal with the volume of alcohol.

The influence of the centrifugation in Figure 3 was investigated using two shares of CdTe solution. One was the original CdTe solution, and another one was the mixture of original CdTe solution and 2-propanol with equal volume. Both of these shares were centrifuged at 2000 and 10 000 r/min for 20 min before measurements.

For investigating the effect of salts (parts d and e of Figure 1), the mixture of redispersed CdTe solution (5 mL) and 2-propanol (5.5 mL) was divided into two equal portions. NaCl was added into one portion, and another portion adding nothing. Then both of the portions were centrifuged at 4000 r/min for 20 min.

**TABLE 2: Evolution of Zeta Potential ( $\zeta$ ) and Hydrodynamic Diameters ( $d_H$ ) of CdTe Nanocrystals After Addition of 2-propanol<sup>a</sup>**

mixture	$\zeta$ (mV)	$d_H$ (nm)
A	−40.3	4.6
B	−32.7	6.0
C	−24.7	8.7
D	−17.1	10.9
E	−20.1	180.2
F	−11.9	639.1
G	−44.1	6.6

<sup>a</sup> Mixtures A–F were obtained by addition of 0, 0.5, 1.5, 3.0, 5.0, and 10.0 mL 2-propanol into 10 mL original CdTe nanocrystal solution. Mixture G was obtained by addition of 20 mL 2-propanol into 10 mL original CdTe solution, and then the precipitates were redispersed into 10 mL water.

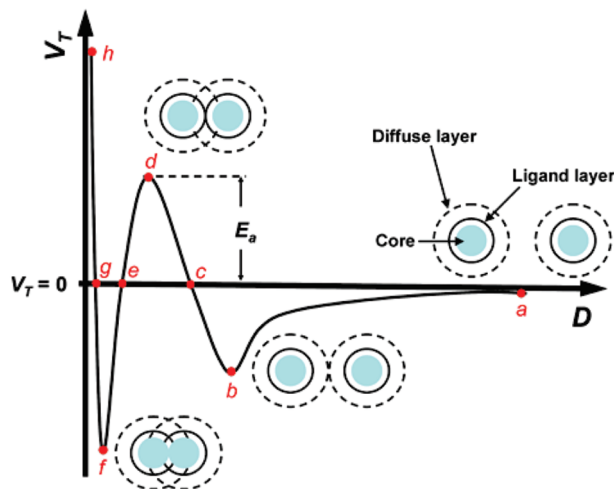
To direct separation of CdTe nanocrystals with a low synthesis concentration (Figure S2 of the Supporting Information), NaCl was added before the addition of 2-propanol, and then the mixture was centrifuged at 4000 r/min for 20 min.

**Characterization.** UV–vis absorption spectra (UV) were recorded with a Shimadzu 3600 UV–vis near-infrared spectrophotometer. Fluorescence experiments were performed with an Edinburg FLS 920 spectrofluorimeter. The excitation wavelength was 400 nm. Dynamic light scattering and zeta potential measurements were performed using a Zetasizer Nano-ZS (Malvern Instrument). The measurements were carried out immediately after the preparation of nanocrystals to avoid the oxidation of nanocrystals. Because of the uncertainties of zeta potential measurements, each sample was measured 10 times, and the average data were listed in Table 2.

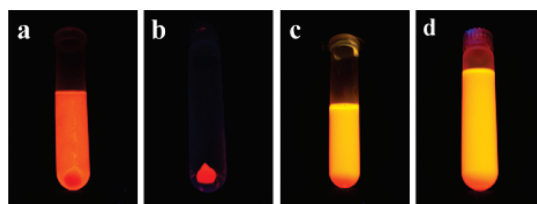
## Results and Discussion

The typical purification process of aqueous CdTe nanocrystals is shown in Figure 1. After addition of a proper amount of 2-propanol, aqueous CdTe nanocrystals can be precipitated, making the supernatant solution colorless (part b of Figure 1). In the same time, the excess ions, ligands, and compounds in nanocrystal solution are dispersible in the supernatant mixture solution in part b of Figure 1. After decantation of the supernatant solution, these excess matters are separated from nanocrystal precipitates, and thus the purification of nanocrystals is realized. These precipitates can redisperse in water. Moreover, the UV and PL spectra of the redispersed nanocrystals are changeless in comparison with that of the original nanocrystals. This suggests the alcohols-based purification process would not seriously affect the optical properties of nanocrystals. Though alcohols are widely used for the purification of aqueous nanocrystals, the fundamental mechanism of alcohols-induced precipitation is still unclear due to lack of a proper theoretical model.

**Theoretical Model for Precipitation.** The recent works about the external structure and interparticle interactions of aqueous nanocrystals have provided us with ideal tools for investigating alcohols-induced nanocrystal precipitation.<sup>30</sup> The expressions of electrostatic repulsion potential ( $V_{\text{elec}}$ ), van der Waals attraction potential ( $V_{\text{vdw}}$ ), and dipolar attraction potential ( $V_{\text{dipole}}$ ) are shown in Note S1 in the Supporting Information. The total interaction potential ( $V_T$ ) is expressed as the sum of various interaction potentials. Because  $V_{\text{elec}}$ ,  $V_{\text{vdw}}$ , and  $V_{\text{dipole}}$  depend on the distance between colloidal particles ( $D$ ),  $V_T$  also relates to  $D$ . On the basis of colloidal chemistry,<sup>32</sup> the schematic illustration of the interparticle-distance-dependent  $V_T$  is shown in Figure



**Figure 2.** Schematic illustration of the interparticle-distance-dependent total interaction potential, and the possible relationship between nanocrystals at states a, b, d, and f.



**Figure 3.** Photographs of centrifuged CdTe solution under the irradiation of a UV lamp (365 nm). Pictures (a) and (b) were the mixture of original CdTe and 2-propanol with equal volume. Pictures (c) and (d) were the original CdTe solution. The centrifugation speeds were 2000 r/min for (a) and (c), and 10 000 r/min for (b) and (d).

2. The curve upon the abscissa ( $V_T > 0$ ) suggests the case of larger repulsions than attractions, whereas  $V_T < 0$  implies the case of smaller repulsions than attractions. The cross points (points of a, c, e, and g) between the curve and the abscissa indicate the equilibrium states of interparticle interactions ( $V_T = 0$ ). Actually, point a is infinitely closed to the abscissa, which represents the case of infinite far distance between colloidal particles.

In simultaneous consideration of the interparticle-distance-dependent  $V_T$  and the external structure of nanocrystals, it is easy to comprehend the purification process of aqueous nanocrystals. First, when the distance between nanocrystals is far enough, the interactions between nanocrystals are close to 0. This is the case of point a. Second, once the diffuse layers of nanocrystals overlap, the repulsion begin to increase because the electrostatic repulsion increases exponentially from the outside of diffuse layer to the ligand layer aforementioned.<sup>30a,b</sup> As a result, the total interaction potential begins to increase. This should be the case of point b. Third, because the electrostatic repulsion mainly originates from the charges of the ligand layer,<sup>30a,b</sup> the electrostatic repulsion reaches a maximum when the ligand layers of nanocrystals begin to overlap (point d). Fourth, a further decrease of the interparticle distance would lead to the increase of attractions initially (segment d–f), and then the dramatic increase of repulsion (segment f–h). Herein, the repulsion in segment f–h may come from the repulsion of atomic electron atmospheres due to the overlapping of nanocrystal cores. Fifth, points a, c, e, and g ( $V_T = 0$ ) imply the case of equal repulsions and attractions. In other words, they are also the most stable existing states of nanocrystals in solution. Except for these stable states, the other segments on



the curve indicate the instantaneous and unstable existing states due to the much larger repulsions/attractions than attractions/repulsions. The difference between repulsions and attractions would promote nanocrystals to reach the most stable existing states from the unstable states.

Compared with the liquid environment, the core and the ligand layer are the actual solid composition of a nanocrystal,<sup>30</sup> and thus nanocrystals aggregate together once the ligand layers begin to overlap. In other words, point *d* should be a critical state of dispersed nanocrystals and nanocrystal aggregates. Nanocrystals will stably disperse in solution (states *a* and *c*) when the interparticle distance is larger than the distance at point *d*. Similarly, in the case of a smaller interparticle distance than that at point *d*, nanocrystals will aggregate together until they reach the equilibrium states of the aggregates (states *e* and *g*). Obviously, in the precipitation process from dispersed nanocrystals (state *c*) to nanocrystal aggregates (state *e*), it is required to overcome an energy barrier ( $E_a$ ) at state *d*. This energy barrier is mainly determined by the interparticle electrostatic repulsion. Because alcohols promote the aggregation of nanocrystals, they should be able to change the interparticle interactions and the energy barrier. In the following text, we would like to investigate how alcohols affect the interparticle interactions.

**Alcohols-Induced Decrease of the Relative Dielectric Constant of the Mixture Solution.** As shown in Table 1, alcohols possess much smaller relative dielectric constants ( $\epsilon_a$ ) than that of water ( $\epsilon_w$ ).<sup>33a</sup> After addition of alcohols into nanocrystal solution, the relative dielectric constants of the mixture solution ( $\epsilon_{\text{mix}}$ ) is estimated by:<sup>33b</sup>

$$\epsilon_{\text{mix}} = [\phi_w(\epsilon_w)^{1/3} + \phi_a(\epsilon_a)^{1/3}]^3 \quad (1)$$

where  $\phi_w$  and  $\phi_a$  represent the volume fractions of water and alcohols. The relative dielectric constant of original nanocrystal solution is believed to be the same as that of water ( $\epsilon_w$ ). According to eq 1,  $\epsilon_{\text{mix}}$  decreases with the increased addition volume of alcohols. When the volume fraction of alcohols reaches a critical value, nanocrystals would precipitate from the mixture solution. Herein, we would like to define the critical volume fraction as the fraction of alcohols when nanocrystals completely precipitate from the mixture solution. Accordingly, the critical  $\epsilon_{\text{mix}}$  at this fraction is calculated by eq 1. As shown in Table 1, the critical  $\epsilon_{\text{mix}}$  is about 41 in most cases.

According to Note S1 in the Supporting Information, the relative dielectric constant of nanocrystal solution ( $\epsilon_s$ ) is relevant to the interparticle interactions. After introduction of alcohols into nanocrystal solution,  $\epsilon_s$  decreases from original  $\epsilon_w$  to subsequent  $\epsilon_{\text{mix}}$ . This will lead to the decrease of interparticle electrostatic repulsion and the increase of interparticle dipolar attraction. In Table 2, we also measured the evolution of zeta potential ( $\zeta$ ) and hydrodynamic diameters ( $d_H$ ) after the addition of alcohols into nanocrystal solution. As can be seen,  $\zeta$  decreases with the addition of alcohols, indicating the decreased interparticle electrostatic repulsion. Simultaneously,  $d_H$  increases from 4.6 to 639.1 nm with the addition of 2-propanol from 0 to 10 mL (samples A–F in Table 2). Actually, the size of nanocrystals remains unchanged in the purification process, which is reflected by the unchanging exciton peak position in the UV spectra (Figure 1).<sup>11a</sup> That means  $d_H$  actually represents the hydrodynamic diameters of aggregates in the case of a large addition amount of alcohols, for instance, samples E and F in Table 2. Overall, from the results of Tables 1 and 2, it is easy to deduce that the introduction of alcohols leads to the decreased

$\epsilon_s$  of nanocrystal solution and the decreased electrostatic repulsion. When the electrostatic repulsion decreases to a critical value, the energy barrier  $E_a$  for precipitation can be neglected, and thus nanocrystals precipitate from the solution. In fact, this critical value for precipitation has been implied by Table 1, where nanocrystals completely precipitate from the solution when  $\epsilon_{\text{mix}}$  is close to 41. Note that the addition of alcohols into aqueous nanocrystal solution will simultaneously lead to the decrease of electrostatic repulsion and the increase of dipolar attraction, which all benefit the aggregation of nanocrystals. Because the electrostatic repulsion is easily reflected by zeta potential measurement, we will mainly discuss the electrostatic repulsion on the aggregation process of nanocrystals. A detailed reason is shown in Note S1 in the Supporting Information.

On the basis of the aforementioned discussion, it is easy to comprehend the effect of centrifugation, which is commonly used for the precipitation of nanocrystals. As shown in part a of Figure 3, after the addition of 2-propanol, CdTe nanocrystals cannot completely precipitate from the solution at a low speed of rotation, for instance 2000 r/min. In comparison, almost all nanocrystals precipitate at the rotating speed of 10 000 r/min (part b of Figure 3). In fact, the centrifugal force is an external attraction because it promotes the movement of nanocrystals toward the centrifugal center. The centrifugal force is expressed as:

$$F = mw^2r \quad (2)$$

where  $F$  is the centrifugal force,  $m$  stands for the mass of nanocrystals, and  $w$  is the angular velocity. It is equal to the speed of rotation multiplied by a constant.  $r$  indicates the radius of rotation. According to the eq 2, the larger centrifugal attraction force inflicts upon nanocrystals at the faster speed of rotation. As a result, it promotes nanocrystals to overcome the energy barrier for precipitation. Certainly, if it is insufficient to overcome the barrier after infliction of centrifugal force, nanocrystals will not precipitate. One example is shown in parts c and d of Figure 3. Without the addition of alcohols, nanocrystals cannot precipitate no matter how we adjust the speed of rotation.

**Alcohols-Induced Dilution of Electrolytes in the Mixture Solution.** Though most of the experimental observations are comprehensible according to the aforementioned discussion, there are still some indigestible phenomena. For instance, the recent work has mentioned the direct synthesis of aqueous CdTe nanocrystals in alcohols.<sup>29</sup> Moreover, in this work, we found that the redispersed solution of CdTe precipitates was difficult to precipitate again (parts c and d of Figure 1) even after the addition of the same volume fraction of 2-propanol like the precipitation process of original CdTe solution (parts a and b of Figure 1). Furthermore, CdTe precipitates can partly disperse in methanol solution (part a of Figure S1 of the Supporting Information). Overall, these unusual observations remind us that some other factors in the nanocrystal precipitation process must be ignored.

Actually, in the purification process, the excess electrolytes and polyelectrolytes, including various ions, ligand, and Cd-ligand compound in original nanocrystal solution are separated. Because of the separation of these excess electrolytes, the ionic strength in the redispersed nanocrystal solution will be far less than that in the original nanocrystal solution. Consequently, the decreased ionic strength will lead to the increased electrostatic repulsion in the redispersed nanocrystal solution according to the relationship between ionic strength and the electrostatic

repulsion as shown in Notes S1 and S2 in the Supporting Information. In our experiment, the  $\zeta$  potential measurement in Table 2 also confirms the increased electrostatic repulsion of the redispersed nanocrystal solution (sample G) than that of the original nanocrystal solution (sample A) after purification process. As a result, it requires more alcohols to lower down the electrostatic repulsion of the redispersed nanocrystal solution to the critical value for precipitation. This is the reason why the redispersed CdTe nanocrystals are more difficult to precipitate than original CdTe nanocrystals after the addition of 2-propanol (parts a–d of Figure 1). In the proving trial, after the addition of NaCl into redispersed solution, nanocrystals can easily precipitate (part e of Figure 1). This implies that the ionic strength in nanocrystal solution significantly affects the interparticle electrostatic repulsion and the precipitation process of aqueous nanocrystals.

Because the excess matters in original CdTe solution are dispersible in alcohols, the ionic strength in the alcohol–nanocrystal mixture solution is lower than that of the original nanocrystal solution due to the increased volume of the mixture after the introduction of alcohols. Consequently, the electrostatic repulsion increases because of the diluted ionic strength after the addition of alcohols. Notably, this dilution effect of alcohols is opposite to the aforementioned one that decreases the electrostatic repulsion by lowering  $\epsilon_{\text{mix}}$ . Experimentally, the dilution effect of alcohols is reflected by the following observations.

First, the precipitation of CdTe nanocrystals relates to their preparation concentration. When nanocrystals are prepared at a relative high concentration, for instance  $5.2 \times 10^{-3}$  mol/L in Figure 1, they can directly precipitate from the solution after the addition of the proper amount of alcohols. In comparison, it is very difficult to precipitate nanocrystals from the solution just by the addition of alcohols when nanocrystals are prepared at a relatively low concentration, for instance  $1.3 \times 10^{-3}$  mol/L in Figure S2 in the Supporting Information. Actually, nanocrystals with a high preparation concentration possess much higher ionic strength in solution, and therefore the interparticle electrostatic repulsion is much lower. This has been proven by the previous work.<sup>30a</sup> As a result, it requires only a small amount of 2-propanol to reduce the electrostatic repulsion to the critical value for precipitation. In contrast, it needs a large amount of 2-propanol to precipitate nanocrystals with a low preparation concentration due to the low ionic strength in solution. Simultaneously, the dilution effect of alcohols becomes prominent because of the large addition amount of alcohols. Consequently, the dilution effect partly offsets alcohols-induced decrease of electrostatic repulsion through lowering  $\epsilon_{\text{mix}}$ . The integration of these two effects makes nanocrystals with a low concentration difficult to precipitate from the solution just by the addition of alcohols (part a of Figure S2 in the Supporting Information). In previous reports about the precipitation of nanocrystals with a low preparation concentration, the condensation manipulation is usually adopted before the introduction of alcohols.<sup>28c</sup> In fact, this condensation actually increases the ionic strength in solution, which can weaken the influence of the dilution effect, and thus nanocrystals can precipitate with a small addition amount of alcohols. In the proving trail (part b of Figure S2 in the Supporting Information), without the need of condensation, CdTe nanocrystals with a low concentration can directly precipitate from the solution simply by complementing NaCl into the alcohol–nanocrystal mixture solution. This also indicates that the dilution effect of alcohols is greatly weakened in the case of high ionic strength.

Second, Table 1 also implies the dilution effect of alcohols. As can be seen, the critical volume fraction of alcohols relates to their  $\epsilon_a$ , for instance, the fraction is respectively 0.5 for 2-propanol ( $\epsilon_a$  is 18.3) and 0.33 for diethyl ether ( $\epsilon_a$  is 4.3). Because of the smaller  $\epsilon_a$  of diethyl ether, it only requires a very small amount of diethyl ether to reduce the electrostatic repulsion to the critical value. The smaller addition amount of diethyl ether also leads to a less prominent dilution effect than that of other alcohols. As a result, the critical  $\epsilon_{\text{mix}}$  of diethyl ether (49.4) is much higher than that of other alcohols (about 41) due to the smaller offset of the dilution effect to the electrostatic repulsion. From another viewpoint, these results also indicate the critical  $\epsilon_{\text{mix}}$  relates to the ionic strength in solution because the small volume fraction of diethyl ether will lead to the high ionic strength in the mixture solution. As shown in part b of Figure 1, CdTe precipitates cannot disperse in the supernatant solution ( $\epsilon_{\text{mix}}$  is 41.9) but they can partly disperse in methanol ( $\epsilon_a$  is 32.7) after removal of excess matters in the supernatant solution (part a of Figure S1 in the Supporting Information). Note that the precipitates cannot disperse in diethyl ether ( $\epsilon_a$  is 4.3) as shown in part b of Figure S1 in the Supporting Information. Obviously, the critical  $\epsilon_a$  is intermediate 32.7 and 4.3 after removal of the excess matters in solution, which is much smaller than the critical  $\epsilon_{\text{mix}}$  (41.9) before the separation of excess matters.

Third, the dilution effect of alcohols is also reflected by changes of  $d_H$  in Table 2. Aforementioned,  $d_H$  mainly reflects the hydrodynamic diameters of CdTe aggregates in the case of a large addition amount of alcohols (samples E and F in Table 2). However, in the case of a small addition amount of alcohols, CdTe nanocrystals will not aggregate. As a result,  $d_H$  still reflects the hydrodynamic diameters CdTe nanocrystals. In fact, according to the values of  $d_H$ , it is very easy to estimate whether  $d_H$  represents the hydrodynamic diameters of aggregates or nanocrystals because the sizes of the aggregates are much larger than that of nanocrystals. In Figure S3 in the Supporting Information, we also plotted the evolution of  $d_H$  at different volume fractions of 2-propanol according to the results of Table 2. As can be seen, the dramatically increased  $d_H$  for samples E and F should represent the hydrodynamic diameters of aggregates. As for samples B–D, the  $d_H$  increases a little in comparison with that of original CdTe nanocrystals (sample A). That means  $d_H$  of samples B–D should represent the hydrodynamic diameters of nanocrystals. What is more, before the appearance of aggregates, the hydrodynamic diameters of nanocrystals increase slightly along with the increased volume fractions of alcohols from sample A to sample D. This is mainly caused by the dilation of diffuse layer due to the alcohols-induced decrease of ionic strength in solution.<sup>30a,32,34</sup> Though the dilation of diffuse layer would lead to the increase of electrostatic repulsion, the measured  $\zeta$  potential actually decreases after addition of 2-propanol (Table 2, and Figure S3 in the Supporting Information). This attributes to alcohols-induced decrease of the electrostatic repulsion by lowering  $\epsilon_{\text{mix}}$ .

## Conclusions

We investigated the alcohols-induced precipitation of aqueous nanocrystals on the basis of the colloidal DLVO model and the external structure of nanocrystals. Before precipitation, nanocrystals need to overcome an energy barrier, which is basically generated by the interparticle electrostatic repulsion. In the precipitation process of nanocrystals, alcohols have two opposite effects. First, it promotes nanocrystals to overcome the energy barrier for precipitation by decreasing  $\epsilon_{\text{mix}}$  of the mixture

solution and the interparticle electrostatic repulsion. Second, the introduction of alcohols also leads to the decreased ionic strength in mixture solution, which makes the interparticle electrostatic repulsion increased. In simultaneous consideration of the multiple effects of alcohols, nanocrystals with a high synthesis concentration can directly precipitate from the solution after addition of alcohols. In comparison, assisted manipulations, for instance condensation or addition of salts, are necessary before the precipitation of nanocrystals with a low concentration. According to this study, the different precipitation behaviors of nanocrystals in the purification processes of aqueous nanocrystal are easily comprehensible. Moreover, the current work also benefits for comprehending nanocrystal behaviors in a complex solvent system, which will greatly help synthetic chemists in establishing protocols for nanocrystal synthesis. We expect that the current work aids deep insight into nanocrystal behaviors at various chemical, physical, or biological environments in practical applications from academic to technical interests.

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**Supporting Information Available:** Expression of electrostatic repulsion, van der Waals attraction, and dipolar attraction, expression of Debye length, photographs of the redispersed solution of CdTe precipitates in methanol solution and diethyl ether solution, photographs of the mixture of CdTe nanocrystal solution and 2-propanol before and after addition of NaCl, and evolution of  $\zeta$  and  $d_H$  of CdTe nanocrystals versus the volume fractions of 2-propanol in the mixture. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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