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Spontaneous CdTe → Alloy → CdS Transition of Stabilizer-Depleted CdTe Nanoparticles Induced by EDTA

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Abstract: CdTe nanoparticles stabilized by L-cysteine are chemically transformed into CdS nanoparticles of the same diameter via an intermediate CdTeS alloy without any auxiliary source of sulfur. The reaction is induced by ethylenediaminetetraacetic acid dipotassium salt dehydrate (EDTA), which was demonstrated experimentally to act as a catalyst by partially removing thiol stabilizers from the nanoparticle surface. It is hypothesized that addition of EDTA facilitates Te^{2-} release, and oxidation of Te^{2-} drives the nanoparticle transition process. Unlike many reports on reactions catalyzed by nanocolloids, this is likely to be the first observation of a catalytic reaction in which nanoparticles function as a substrate rather than a catalyst. It opens new pathways for the synthesis of novel nanoscale II−VI and other semiconductors and represents an interesting case of chemical processes in nanocolloids with reactivity increased by depletion of the surface layer of thiol stabilizers. This includes but is not limited to accurate control over the particle composition and crystallization rate. The slow rate of the CdTe → alloy → CdS transition is important for minimizing defects in the crystal lattice and results in a substantial increase of the quantum yield of photoluminescence over the course of the transition.

Introduction

A number of physical and chemical phenomena encompassing optical, electrical, and magnetic properties have been found to be specific to nanoscale objects.[1−7] From a chemical point of view, the metastable nature of nanoparticles (NPs) provides fruitful grounds for the search for new nanoscale structural transformations[8−11] and new morphologies of nanocolloids.[10,12−16] In general, the destabilization process of NPs in solution leads to branched or fractal aggregates without accurate structural control.[17,18] However, by taking advantage of partial destabilization strategy via depleting stabilizers on NP surfaces by simple washing,[8,19,20] CdTe and CdSe NPs were observed to self-reorganize into one-dimensional (1D) nanostructures.[8,19] The partial destabilization method has also been applied to metal, metal oxide, and other NPs, and highly anisotropic Ag and TiO_2 nanostructures have been prepared.[21,22] Very recently, three-dimensional (3D) mesoporous semiconductor chalcogenide aerogel was also prepared by gradual removal of stabilizers from NPs.[23] In this paper, partial destabilization is demonstrated to be an effective synthetic strategy not only to realize shape or geometry transitions, but also to induce in-depth chemical transformation of NPs.

We suggest considering a nanocolloid not as a static object and an end-product, but rather as an intermediate chemical system with a variety of potential routes of structural evolution. Numerous experiments have successfully demonstrated that a simple ion-exchange process can drastically alter the composition of NPs, including the crystal lattice structure, while

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10.1021/ja055366w CCC: $33.50

maintaining the individuality and geometrical attributes of the particles.[9−11,24−33] It should be mentioned that the number of reports on chemical transformation in NPs is still small because of, among other factors, the strong screening effect of stabilizers on the NP surface and the sluggishness of solid-state diffusion.[14,34] Since the partial destabilization strategy should decrease the density of the stabilizer shell and increase the chemical potential of the ions or atoms in the crystal lattice, it must facilitate the chemical transitions between the different particle materials. Using CdTe NPs as an example, we demonstrate the validity of these considerations. ethylenediaminetetraacetic acid dipotassium salt dehydrate (EDTA) was used here to bind to surface Cd sites and, hence, partially removed the thiol shells and reduced the stability of NPs. CdTe NPs transformed into CdS NPs via an intermediate state of CdTeS alloy under ambient conditions. No additional source of sulfur was used except for L-cysteine, which served as the original stabilizer. Looking at the chemical processes in a more general way, EDTA facilitates the chemical transformation while not being a reactant or a product. So, EDTA apparently acts as a catalyst, although the actual stage of the process affected by EDTA requires a separate study. This approach can potentially be applicable to the processes of chemical transformation of NPs to achieve better control over products and to explore the rich chemistry of NPs to generate new NP intermediates along the way to different nanoscale colloids.

Experimental Section

Chemicals. $Cd(ClO_4)_2{\cdot}6H_2O$, L-cysteine, NaOH, H_2SO_4, and EDTA were purchased from Aldrich. Al_2Te_3 powder was purchased from Alfa Aesar. The purity of $Cd(ClO_4)_2{\cdot}6H_2O$, NaOH, H_2SO_4, and EDTA was above 99%, and that of L-cysteine was 97%. All chemicals were used as received. Because Al_2Te_3 is easily oxidized in air, it was kept in a glovebox when not in use.

Preparation of L-Cysteine-Stabilized CdTe NPs. The synthesis of L-cysteine-stabilized CdTe NPs followed Rogach and Weller's method.[35,36] In brief, H_2Te gas (generated by the reaction of 0.2 g of Al_2Te_3 lumps with 15 mL of 0.5 M H_2SO_4 under N_2 atmosphere) was passed to nitrogen-saturated $Cd(ClO_4)_2{\cdot}6H_2O$ aqueous solution (0.013 M, 125 mL) at pH 11.5 in the presence of L-cysteine (691 mg) as a stabilizing agent. The reaction mixture was refluxed under N_2 gas for 40 min. ***Caution:*** *Since the intermediate product of H_2Te is highly toxic, a respirator should be worn during the whole synthesis process in order to prevent possible inhalation of toxic gas.*

Chemical Transformation of CdTe NPs. A 10 mL portion of 10 mM EDTA solution was added into 10 mL of L-cysteine-stabilized CdTe NP solution, and the final pH value of the solution was adjusted to 11.5 by adding 2 M NaOH solution. The mixture was heated at 50 °C under air flux for the desired amount of time. The temperature was kept at 50 °C to speed up the reaction, although the same transformation products were also obtained at room temperature. The intermediate products were taken out from the mixture for UV−visible, transmission electron microscopy (TEM), energy dispersion X-ray spectroscopy (EDX), and elemental analysis. To prevent possible influence of free stabilizers and EDTA, NPs samples taken from any stage of the reaction were centrifuged and precipitated by the addition of methanol followed by redissolving into pure water.

Results

Chemical transformation reactions were performed by adding an equal volume of 10 mM EDTA into L-cysteine-stabilized CdTe NP solution (see Experimental Section). The resulting concentrations of Cd, Te, L-cysteine, and EDTA in NP solutions were 9.4, 4.7, 19, and 5.0 mM, respectively. The light-orange NP solution gradually changed to a dark and opaque dispersion in the early stage of the reaction. After 6 h, the solution became clear again, and a bluish-black precipitate appeared on the walls of the glassware. Over the course of the reaction, the hue of the dispersion continuously changed from orange, in the beginning, to yellow, and finally to a white suspension after 48 h. Absorption and luminescence spectroscopy of samples which were taken from the reaction mixture at different intervals of time and diluted with water to provide the optical densities appropriate for UV−visible (around 0.2 at the absorbance peak) and photoluminescence (PL) measurements (about 0.1 at the excitation wavelength) revealed that both the band-edge absorption shoulder and the emission peaks of the NP solution underwent a gradual blue-shift during the first 24 h of the reaction. After 48 h, the absorption spectrum of the NP solution became featureless and showed an increased absorbance in the range of 500−700 nm, while the PL peak shifted back to the red side (Figure 1). The increase of absorbance in the range of 500−700 nm should originate from the scattering of the white suspension in the solution. A similar blue shift of the PL peaks and absorption edge was observed for the oxidation of semiconductor NPs[36,37] or alloying of NPs with another type of semiconductor with higher band-gap.[38,39]

The combination of TEM (Figure 2) and EDX (Figure 3) allows one to understand the stages of CdTe NP transformation started by the addition of EDTA. Statistical analysis of high-resolution TEM (HRTEM) images by carefully discerning the boundaries of NPs reveals that the diameter and size distribution of NPs remain almost unchanged during the whole reaction, i.e., 3.9 ± 0.5 (0 h) vs 3.9 ± 0.5 (12 h) vs 4.0 ± 0.5 nm (48 h) (Table 1). There is no obvious change in the shape of the particles. Previous studies indicated that CdTe NPs with a PL peak at 580 nm had diameters of around 4.0 nm,[8,40] consistent with our TEM observations. Since the diameter remains virtually unchanged during the reaction, the substantial blue shift of PL peaks by as much as 54 nm (217 meV) should be attributed to

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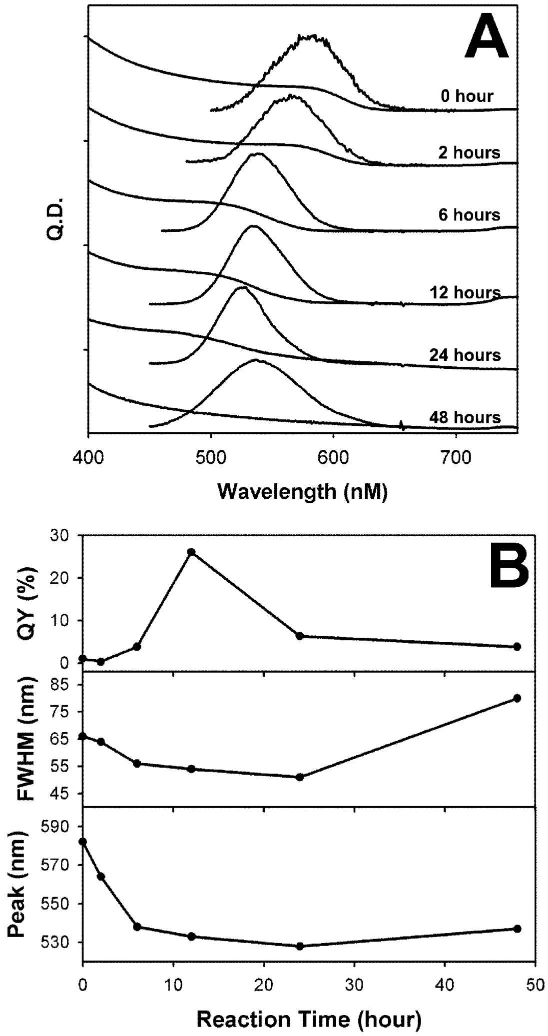

Figure 1. (A) Evolution of UV−visible and PL spectra of CdTe NP solution after addition of EDTA. (B) Time-dependent peak, full-width at half-maximum (fwhm), and quantum yield (QY) curves of PL of NPs.

the formation of a semiconductor alloy. The transition process from CdTe to CdS can also be deduced from imaging single NP by HRTEM, where the distances between adjacent crystallite planes change from 3.8 (0 h) through 3.6 (12 h) to 3.4 Å (48 h) after the addition of EDTA (insets in Figure 2). Again, all NPs here have virtually identical diameters. The distances between the dominant (111) crystal lattices are 3.8 and 3.4 Å for zinc blend-type CdTe and CdS NPs, respectively.[41] HRTEM imaging provides more accurate results than powder X-ray diffractometry because X-ray diffraction peaks displayed intrinsic broadening due to the small diameters of the crystallites.

The transition process of CdTe → alloy → CdS can also be confirmed by elemental analysis from the EDX spectra (Figure 3A−F).[42] Over the course of the replacement reaction, the amount of sulfide inside the NPs gradually increases with a simultaneous decrease in the amount of Te, and, in the end, only CdS is detected after a 48 h reaction period (Table 1). This is further proven by X-ray photoelectron spectroscopy (XPS), clearly indicating the pure product CdS (Figure 3G−I). Note that the sulfur signal detected at the beginning of the

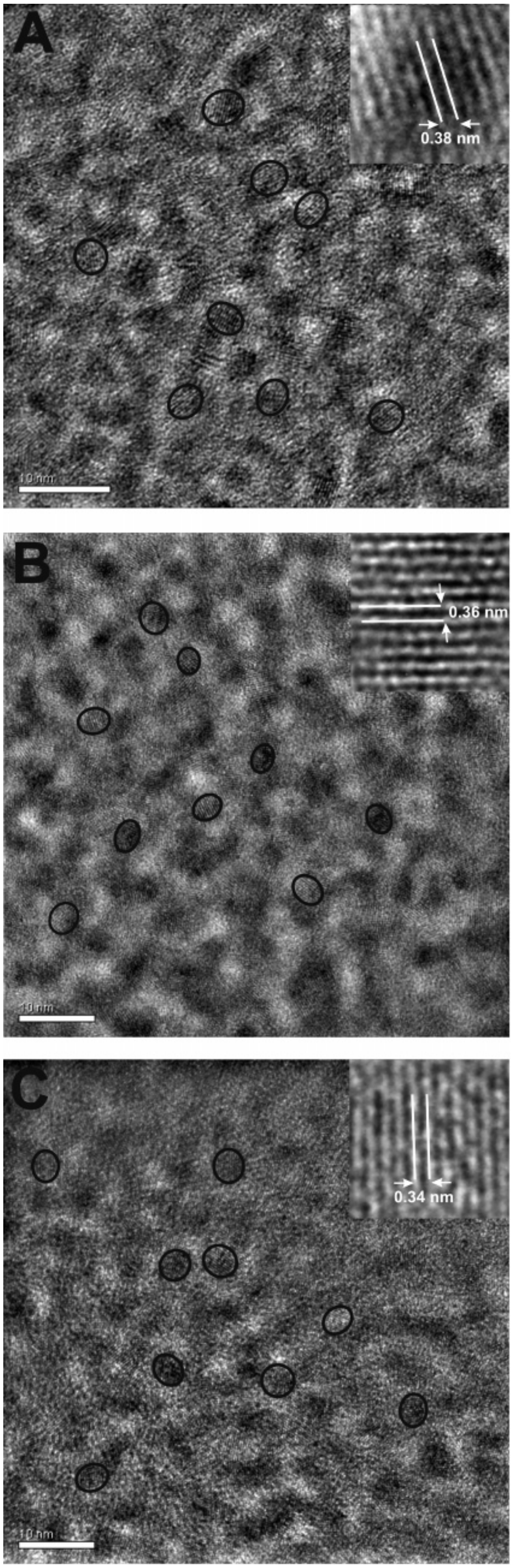

Figure 2. TEM of NP samples taken from reaction solution at 0 (A), 12 (B), and 48 h (C) after addition of EDTA. Black circles mark single NPs.

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(41) *Handbook of chemistry and physics*; CRC Press: Boca Raton, FL, 2003.

(42) To prevent a possible effect of the free stabilizers, NP samples taken from any stage of the reaction were centrifuged, precipitated by addition of methanol, and redissolved into pure water. The NP samples with removal of free stabilizers were then dropped onto the girds for TEM imaging and EDX analysis.

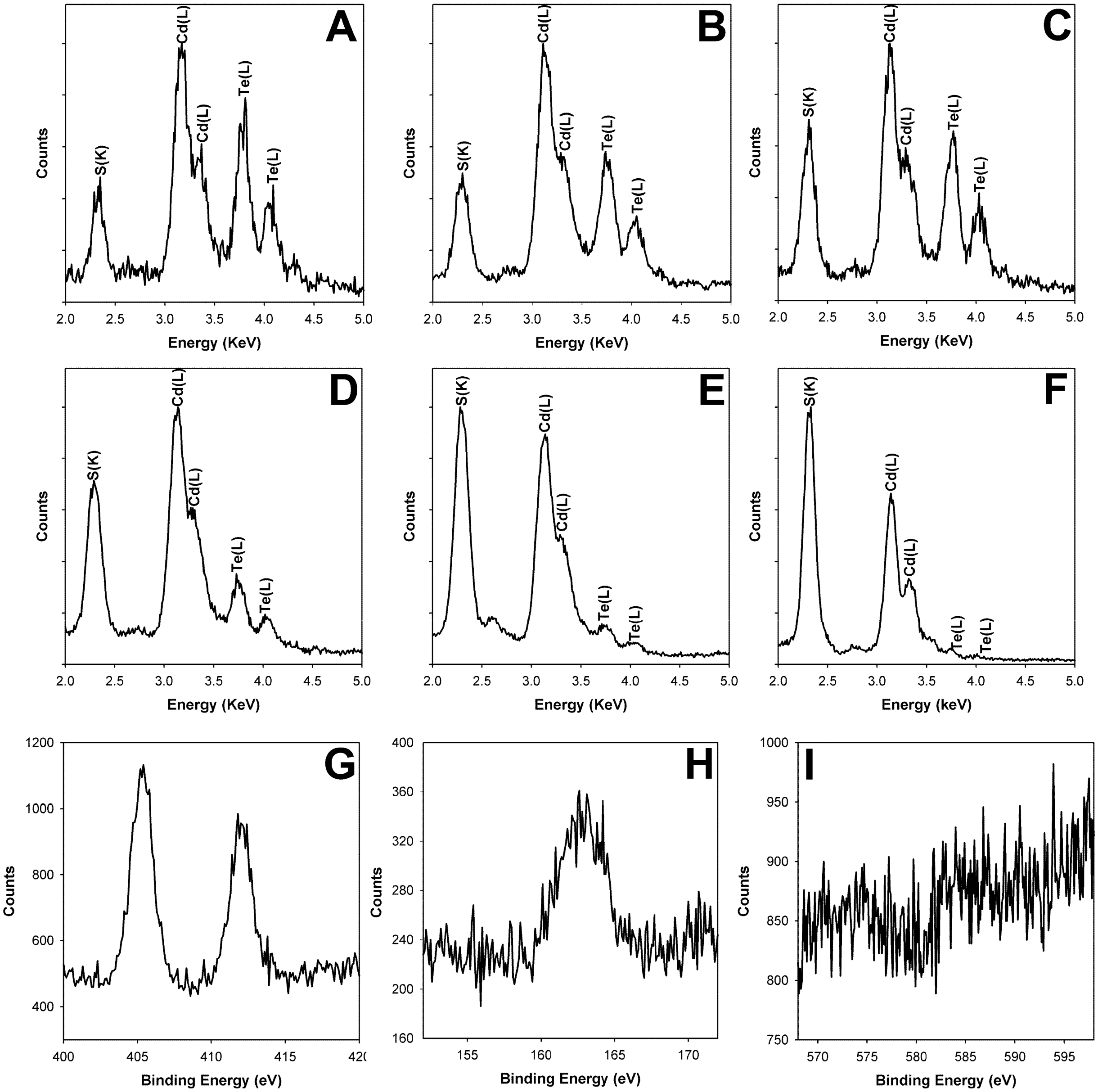

Figure 3. Typical EDX spectra of CdTe NPs undergoing chemical transformation, taken from reaction solution 0 (A), 2 (B), 6 (C), 12 (D), 24 (E), and 48 h (F) after addition of EDTA. XPS spectra of NPs undergoing chemical transformation for Cd 3d5 (G), S 2p3 (H), Te 3d5 (I) binding energy regions after 48 h of reaction.

Table 1. Time-Dependent Elemental Composition, Diameters, and Crystal Lattices of NPs during Transformation Reaction

reaction time (h)	elemental composition (%)[a]			diameter (nm)[b]	crystal lattice (Å)[b]
	Cd	Te	S		
0	48.0 ± 2.9	36.7 ± 2.9	15.2 ± 1.8	3.9 ± 0.5	3.8
2	50.8 ± 0.5	29.6 ± 0.8	19.6 ± 0.8		
6	48.6 ± 0.9	27.3 ± 2.0	24.0 ± 2.0		
12	53.5 ± 1.0	15.0 ± 0.7	31.5 ± 1.0	3.9 ± 0.5	3.6
24	49.6 ± 2.5	4.4 ± 1.1	46.0 ± 2.1		
48	40.7 ± 1.2	0	59.3 ± 1.2	4.0 ± 0.5	3.4

[a] Average values for at least 20 measurements from EDX spectra at different positions of samples. [b] Average values for at least 200 measurements from different NPs in TEM images.

reaction (0 min in Table 1) is attributed to the L-cysteine stabilizers.

EDX data can also give important information about the degree of stabilization of NPs. Based on the average size of 3.9 nm and the ratio between Cd and S being 3.16 (48.0/15.2), CdTe NPs immediately after the addition of EDTA are estimated to contain ~483 atoms of Cd and ~153 molecules of thiol stabilizers. This gives a surface density of thiol stabilizers on the NP surface of about 3.2/nm^2, which is noticeably lower than the previously reported density of 5−10/nm^2.[43] In addition, a closely packed monolayer of L-cysteine stabilizers on a CdTe surface is calculated to have a density of 6.4/nm^2. The decrease in the surface density of thiols clearly shows that immediate addition of EDTA partially removes the stabilizers from NP surfaces.

Discussion

Looking over the existing data about CdTe NPs from our group and others, one can see that these NPs show considerable chemical stability, even under fairly harsh conditions.[36] Without EDTA, CdTe NPs can remain absolutely unaltered for at least

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[43] Zhang, H.; Zhou, Z.; Yang, B.; Gao, M. *J. Phys. Chem. B* **2003**, *107*, 8−13.

three months under similar ambient conditions. Addition of EDTA destabilizes CdTe and triggers the transition to CdS. Previously, the stabilizer-depleted CdTe NP solution obtained after the methanol rinsing step has been demonstrated to decompose and then form Te nanorods after interacting with EDTA (eqs 1 and 2).[20,44] We can use the information about this reaction to understand the mechanism of the CdTe → alloy → CdS process. Knowing that EDTA induces the oxidation of CdTe to Te,[45] we hypothesize that the reactions here can be described by the following set of chemical equations:

$$\mathrm{CdTe_{(NP)} + EDTA^{4-} \rightleftharpoons CdTe_{(NP)}Cd(EDTA)^{2-} + Te^{2-}} \quad (1)$$

$$\mathrm{2Te^{2-} + O_2 + 2H_2O \rightarrow 2Te + 4OH^-} \quad (2)$$

$$\mathrm{4HSR + O_2 \xrightarrow{OH^-} 2RSSR + 2H_2O} \quad (3)$$

$$\mathrm{Te^{2-} + 2HSR + 2OH^- \rightarrow Te + 2R + 2S^{2-} + 2H_2O} \quad (4)$$

$$\mathrm{CdTe_{(NP)}Cd(EDTA)^{2-} + S^{2-} \rightleftharpoons CdTeS_{(NP)} + EDTA^{4-}} \quad (5)$$

where HSR represents l-cysteine. Cd(EDTA) (eq 1) initially forms on the surface of CdTe NPs ($\mathrm{CdTe_{(NP)}Cd(EDTA)^{2-}}$). Note that the stoichiometry and structure of the surface complexes should allow for a limited degree of variability, depending on the local environment of Cd atoms. Also, some freely dissolved low-molecular-weight metastable species similar to CdTe-(EDTA) may be produced as well;[20] however, they will follow a similar set of redox reactions and give the same product. Regardless of the potentially fascinating details, the fact that $\mathrm{Te^{2-}}$ forms and reaction 1 takes place is quite certain based on previous studies on stabilizer depletion.[20] Without the methanol rinsing step as for the preparation of Te nanowires,[20] large amounts of the stabilizers are allowed to remain in the reaction system. This makes chemical reactions here more complex than for Te nanowire production, since the thiol stabilizers can also be involved in reactions via either the oxidation by air (eq 3) or the reduction by $\mathrm{Te^{2-}}$ (eq 4).[46−48] Importantly, the equilibria is driven from left to right by production of Te in eq 2. Excess of L-cysteine also shifts the equilibrium in the same direction in eq 4, which results in the production of $\mathrm{S^{2-}}$. The latter reacts with Te-deficient $\mathrm{CdTe_{(NP)}Cd(EDTA)^{2-}}$, replaces former Te atoms, and releases EDTA at the same time.

Pieces of evidence supporting the proposed mechanism include the following facts: (1) Blank experiments showed that neither a mixture of $\mathrm{Cd^{2+}}$ and L-cysteine (pH 11) nor EDTA-free CdTe NP solution is transformed to CdS under identical reaction conditions. (2) As expected from eqs 2 and 4, Te nanorods were formed from oxidation of $\mathrm{Te^{2-}}$. They were identified by SEM images of bluish-black precipitates on the walls of the reaction vessel (Supporting Information). (3) The EDTA-induced replacement reaction of NPs was also observed to happen even in darkness, which demonstrates that photocorrosion does not contribute to the formation of Te nanorods and CdTeS NPs. (4) The pH value of the reaction media was observed to decrease from 11.5 to 9.4, as expected from eq 4. The oxidation of thiols in eq 3 does not change the pH of the solution. Equation 2 might increase the pH, but evidently, reduction of thiols by $\mathrm{Te^{2-}}$ is the dominant route, leading to a decrease in the pH value of the solution, as well production of $\mathrm{S^{2-}}$. For a complete picture of proton release, it is useful to remember that EDTA can also participate in the proton equlibria. The ionization constant, pK_a, between $\mathrm{EDTA^{4-}}$ and $\mathrm{HEDTA^{3-}}$ is 10.24,[41] so in the later stages of the CdTe → alloy → CdS transformation the complexing agent may actually take part as $\mathrm{HEDTA^{3-}}$. (5) Compared to $\mathrm{Te^{2-}}$ anions (redox potential is −1.14 V for $\mathrm{Te^{2-}/Te}$), $\mathrm{S^{2-}}$ anions (redox potential is −0.48 V for $\mathrm{S^{2-}/S}$) are more stable in solution under ambient conditions.[41] This difference in chemical properties is the actual driving force for the whole process. (6) Elemental analysis of the ultimate products centrifugally segregated from the reaction media, measured by using a Perkin-Elmer 2400 Series II analyzer, gave an atomic ratio of C, H, and N (present only in the organic shell) of 2.8:6.7:1. This atomic ratio correlates very well with that in L-cysteine, $\mathrm{C_3H_7NO_2S}$, i.e., 3:7:1. This analysis indicates that EDTA, with formula $\mathrm{C_{10}H_{16}N_2O_8}$ and atomic ratio 5:8:1, has little effect on the composition of the stabilizer shell in the product and is, therefore, mostly released from the products according to eq 5. (7) Infrared spectral measurements confirmed that the structures of EDTA remained unaltered after the sequence of reactions (Supporting Information). (8) The net result of the entire process is the gradual replacement of CdTe with CdS, which corresponds very well with the blue shift of the PL peak (Figure 1).

Table 2. Concentration Dependence of EDTA on the Transition Reaction of CdTe NPs[a]

concentration	0.2 mM	0.6 mM	1 mM	5 mM	25 mM
time	32 days	14 days	5 days	2 days	0.8 days

[a] The time refers to the periods when PL peaks of NPs shift from 580 to 524 nm. The variation of time for three time measurements is less than 20%.

According to the series of chemical equations above and the fact that it remains unaltered during the process, EDTA functions as a catalyst in the CdTe → alloy → CdS process. To confirm this presumption, we tested the effect of the concentration of EDTA on the transition speed of CdTe → CdS (Table 2). The higher the starting concentration of EDTA, the shorter the time needed to complete the process. This is in full agreement with the classical description of catalytic reactions.

Thus, the catalytic function of EDTA has strong experimental support and may be considered to be established. However, the question remains, at which stage of the transition is the activation energy the most affected? We ran a variety of quantum mechanical calculations on model clusters of CdTe and CdS with and without EDTA, similar to those described previously using the PM3 algorithm.[49−51] We attempted to establish a

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(44) To some extent, washing of CdTe with methanol, as was done in this case, may also be considered a catalytic trigger, therefore making assignments of chemical functions more obscure in this case.

(45) $\mathrm{Te^{2-}}$ anions have a strong tendency to donate electrons, because $\mathrm{Te^{2-}/Te}$ pairs have a negative redox potential of −1.143 V. The final product of $\mathrm{Te^{2-}}$ anions is elemental Te, which has been shown in the past to produce rods and wires.

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difference between the total energies of the potential intermediate structures, but unfortunately the results were inconclusive because the actual energy differences are quite small compared to the overall energy of the clusters. To some degree this failure may be related to the limitations of the PM3 algorithm; however, it may also indicate that the effect of EDTA as a catalyst here may not necessarily be on the activation energy of a particular fairly defined intermediate structure but rather for an intertwined dynamic process such as ion/molecular diffusion through the stabilizer shell, for instance the release of Te^{2-} (eq 1). Without EDTA, the release of Te^{2-} is frustrated by the dense L-cystein shell and strong binding to Cd^{2+}. So, EDTA is likely to create defects in the stabilizing shell, which decreases the energy barrier of the process of Te^{2-} release.

In this respect, a point that needs to be made is that the replacement of L-cysteine by EDTA is not extensive, as can be seen from the dissociation constant, K_{diss}, for the $Cd(EDTA)^{2-}$ complex, which is $10^{-16.4}$.[41] This is 10−20 orders of magnitude larger than the solubility product: K_{sp} values for CdTe and CdS are 10^{-33} and 10^{-26}, respectively.[20,52] Therefore, the equilibrium between the complex and NP is shifted toward nanocolloids. It should be mentioned, though, that the approximate comparison of these numbers can be somewhat misleading, because EDTA complexation of Cd^{2+} on the surface can take place without complete detachment of Cd^{2+} from the lattice of CdTe of the NPs, which is sufficient for triggering Te^{2-} release and the sequence of chemical reactions shown above. Surface complexation to form $CdTe_{(NP)}Cd(EDTA)^{2-}$ is thermodynamically more favorable than detachment of the complete ion, $Cd(EDTA)^{2-}$, due to the high bonding energy between Cd and Te. This consideration will change the thermodynamic balance between the constants above to give a more prominent presence of EDTA on the CdTe core. While thermodynamic estimates of the extent of surface complexation and stabilizer replacement are difficult, EDX data presented above (Table 1) give an experimental evaluation of stabilizer replacement which indicates a relatively low degree of destabilization as well.

Consequences of the Catalytic Nature of the Process on the NP Properties. The optical properties of nanoparticles determine their importance to fundamental science and potential applications. So, it would be instructive to see how the nature of the transformation process can affect the emission/absorption characteristics of NPs. Slow release of Te^{2-} and the reduction rate of L-cysteine following EDTA binding (eq 4) guarantee a low level of supersaturation with respect to CdS monomers.[53] This is important for the control of optical and other properties of the resulting alloy and CdS nanocolloids. First, it is necessary to avoid nucleation of individual CdS NPs. The reaction conditions here are far from the concentration of intermediates when this might happen. During 2 days of reaction, the concentration of reactants, such as L-cysteine, is 19 mM, which is substantially lower than the concentration of sulfur sources in other studies (for instance, as high as 200 mM), indicating CdS nucleation only on existing NPs.[37,39] PL spectra (Figure 1), EDX, and XPS results (Figure 3) indicate the formation of alloy particles rather than independent populations of NPs from different semiconductors.

Second, the newly formed CdS monomers are likely to prefer depositing on the surface defects with high energy when they are formed slowly. This typically eliminates the states associated with such defects, which act as recombination sites for excitons. The improvement in the optical properties of NPs following the transformation reaction can indeed be seen in the fact that the quantum yield (QY) of NP luminescence dramatically increases with a simultaneous decrease of the full-width at half-maximum (fwhm) of the peaks (Figure 1B). Formation of core−shell-like structures is possible here.[37] However, considering the continuity of the replacement of CdTe with CdS and easy interdiffusion along contact interfaces between CdS and CdTe,[54] the formation of NPs with a sharp border between the CdS shell and CdTe core is unlikely. Gradient structures are more plausible than core−shells for this reaction system for NPs composed of alloys. Ultimately, atomic diffusion in nanoscale semiconductors should result in compositionally uniform NPs, which also correspond to a local thermodynamic minimum.

The QY of alloyed CdTeS NPs in our case reaches 27%, which can be further increased by careful adjustment of the reaction conditions. As a comparison, reported upper limits of QY for negatively charged CdS NPs are 10−15%,[36,55] with commonly known dominance of trap emission.[56] Interestingly, only ∼5% of Te in the CdTeS alloy NPs is sufficient to keep band-edge emission strong (Figure 1 and Table 1); for instance, in the particles obtained after 24 h, this is potentially due to elevation of the absolute energy of the valence band above the threshold of thiol oxidation.[57,58]

It is also necessary to address why, in the final stages of the transformation reaction, bathochromic shift, QY decrease, and fwhm broadening of PL peaks are observed (Figure 1B). This tendency should be ascribed to the complete transformation of CdTe to CdS and related to the onset of well-known nonradiative relaxation processes in CdS, such as hole transfer to thiols and subsequent surface erosion.[56] The optical characteristics of the transformed CdS NPs can further be discerned by photoluminescence excitation spectra, showing a distinct peak around 380 nm with virtually no features around 500−550 nm, where the adsorption of CdTe might have been observed (Supporting Information).

The catalytic nature of the process offers a new and convenient method for product control. Once we know the time course of the reaction, these processes can be easily controlled by removal of EDTA and addition of suitable stabilizers to obtain colloids with desired properties. For instance, this was done for partially transformed alloy NPs, with 36% S vs 12% Te (Table 1) obtained after 12 h reaction time. The catalytic reaction was interrupted by adding methanol, and the partially replaced NPs were centrifuged, precipitated, and then redissolved into pH 11.5 solution in the presence of 9 mM $Cd(ClO_4)_2$ and 19 mM L-cysteine, which was similar to the composition of the original CdTe NPs. The QY of thusly made NPs was 32.9%. This demonstrates the accurate tuning of the properties

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of the resulting nanoparticles taking advantage of the catalytic nature of the product. The same approach can be easily extended to other NP systems that can be partially destabilized by adding a complexing agent.

Conclusions

Partial destabilization can be considered as a convenient and multifaceted tool in the chemistry of NPs which enables profound transformations of CdTe nanocolloids. In the case presented here, it induces a complete chemical makeover from CdTe to CdS via an intermediate alloy state. Oxidation of Te drives the reaction, although this process does not occur before addition of EDTA. Similar to catalysis in molecular reaction, EDTA accelerates the transition while remaining unaltered in the process, as demonstrated by a variety of means. The specific process most affected by addition of EDTA is hypothesized to be Te^{2-} release.

The CdTe → alloy → CdS process is relatively slow; hence, the structure of products can be easily controlled by addition or removal of EDTA by centrifugation or precipitation. These findings should be considered as a starting point for the utilization of this approach in nanoscale synthesis with the potential to control both geometrical parameters of NPs and their atomic composition.

Acknowledgment. This work was supported by NSF-CAREER, NSF-Biophotonics, NIH-NASA, AFOSR, and OCAST. The authors thank Dr. Zhenli Zhang for helping with the molecular modeling of CdTe NPs and CdTe−EDTA complexes, and Mr. Hsien-Yeh Chen for IR measurements.

Supporting Information Available: SEM and EDX data on Te nanorods formed during the reaction; infrared spectra of EDTA before and after the replacement reaction; PLE spectrum of NPs after 24 h of reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

JA055366W