Size-Selective Growth and Stabilization of Small CdSe Nanoparticles in Aqueous Solution

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ABSTRACT Using cysteine and its derivatives as capping molecules, we investigated the influence of the physical structure and chemical nature of capping molecules on the selective growth and stabilization of small CdSe nanoparticles (NPs) in aqueous solution at room temperature. Our investigations revealed specific roles for each functional group of cysteine, and we could correlate this structure and nature of the capping molecules with the size, size restriction, size distribution, and stability of the NPs. For selective growth and stabilization of the NPs in aqueous solution, their capping molecules should have at least one functional group with strong nucleophilicity as well as another free, charged functional group. Capping molecules acting as a monodentate ligand were more effective than those acting as a bidentate ligand for restricting the NPs to a smaller size, whereas the former was less effective than the latter for getting a narrower NP size distribution. Capping molecules with relatively bulky spatial geometry near the ligand—NP interface resulted in the formation of NPs with poor short- and long-term stabilities, whereas those having relatively compact spatial geometry near the interface led to NPs with at least moderate short-term stability. We saw that capping molecules having relatively compact outermost spatial geometry led to NPs with excellent long-term stability, whereas those having relatively bulky outermost spatial geometry produced NPs with at most only moderate long-term stability. Our results clearly showed general trends for the possibility of selective growth of stable semiconductor NPs with particular sizes in aqueous solution.

KEYWORDS: aqueous synthesis · semiconductor nanoparticle · selective growth · stability · capping molecule · CdSe · magic cluster

Highly stable colloidal semiconductor nanoparticles (NPs) with precise atomic composition have been of great interest because of their well-defined structures as well as their atomic arrangement-dependent physical, chemical, and optical properties. These kinds of NPs can minimize ambiguities from size dispersion or from poorly defined surfaces and may be very useful as building blocks for functional materials in many scientific and technological fields. Although numerous reports are available about semiconductor NPs with a relatively narrow size distribution,[1−6] those for NPs composed of a specific number of constituent atoms and produced in a macroscopic quantity are scarce.[7,8]

Macroscopic amounts of semiconductor NPs with a narrow size distribution or with a specific number of constituent atoms have been exclusively produced in organic solvents.[1−5,7,8] Murray *et al.*[1] synthesized CdS, CdSe, and CdTe NPs (1.2−11.5 nm in diameter; <5% rms) through pyrolysis of organometallic reagents in a hot coordinating solvent. Herron *et al.*[7] prepared $Cd_{32}S_{14}(SC_6H_5)_{36}$-(*N*,*N*-dimethylformamide)$_4$ clusters (~1.5 nm in diameter) by recrystallization of solid $Cd_{10}S_4(SC_6H_5)_{12}$ in a solution of pyridine and *N*,*N*-dimethylformamide. Recently, Kasuya *et al.*[8] reported semiconductor NPs with precise atomic composition. They fabricated macroscopic quantity of a mixture of stable $(CdSe)_{33}$ and $(CdSe)_{34}$ magic clusters stabilized in toluene. Unfortunately, preparation of the NPs in an organic phase is neither cost-effective nor environment-friendly. Furthermore, it requires that the NPs be stabilized by hydrophobic capping molecules, which are disadvantageous to applications requiring water solubility of the NPs, such as biorelated applications.

Direct fabrication of the NPs in an aqueous phase may be an excellent alternative to an organic phase fabrication. Aqueous phase synthesis can be very simple and is highly reproducible, as well as relatively economical and environment-friendly.[9,10] For this, small organic molecules with both sulfhydryl and carboxyl functional groups (hereafter referred to as "mercapto acids") have been widely adopted as capping molecules.[9−14] The sulfhydryl group can coordinate to the NPs, whereas the carboxyl group can contribute to the electrostatic stabilization of the colloidal NPs as well as to their further surface modification for various applications. Amino acids containing a

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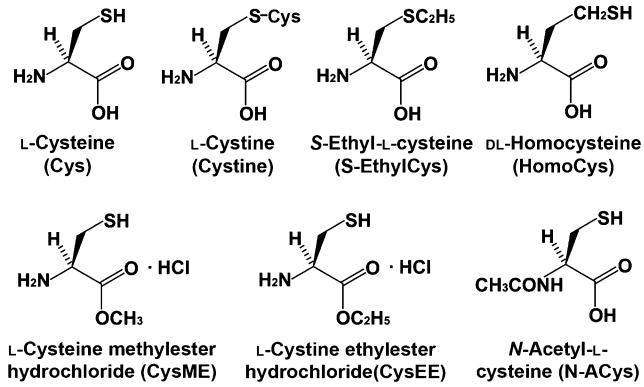

Figure 1. Schematic drawings of cysteine and its derivatives used in this study.

sulfhydryl functional group, such as cysteine (Cys) and homocysteine, have also been used as capping molecules for the NPs.[15−18] However, the structural and optical properties of the resulting NPs were much inferior to those of the NPs fabricated by conventional organic phase synthesis methods.[9−18]

Recently, Park *et al.*[19] reported a simple, convenient method for fabricating highly stable CdSe NPs directly in aqueous solution at room temperature. Use of Cys as a capping molecule enabled fabrication of CdSe NPs with a very sharp, highly stable first absorption peak (1st $peak_{abs}$). The sharpness and position of the peak are very similar to those for the ultrastable $(CdSe)_{33}$ and $(CdSe)_{34}$ magic clusters grown selectively in the organic phase.[8] These findings suggest that the specific physical structure and chemical nature of Cys played critical roles in the selective growth and stabilization of the NPs and hence exerted significant influence on their physical, chemical, electronic, and optical properties. Therefore, a systematic investigation for the influence of various capping molecules, especially those having very closely related physical structures and chemical natures, on the structure and optical properties of the NPs may reveal invaluable information about specific roles for each functional group of the capping molecules, during and after the fabrication of the NPs. The findings might eventually contribute greatly to convenient, cost-effective fabrication in aqueous media of water-soluble, stable semiconductor NPs with an extremely narrow size distribution or with a precise atomic composition.

Herein, we report the influence of the physical structure and chemical nature of the Cys capping molecule on the aqueous phase synthesis of CdSe NPs exhibiting an extremely narrow size distribution and excellent colloidal stability. We synthesized CdSe NPs in aqueous solution containing Cys or one of its derivatives, having very closely related physical structures and chemical natures, and systematically investigated the effects of the capping molecules on the optical (absorption) and physical (size, size restriction, size distribution, and short- and long-term stabilities) properties of the NPs.

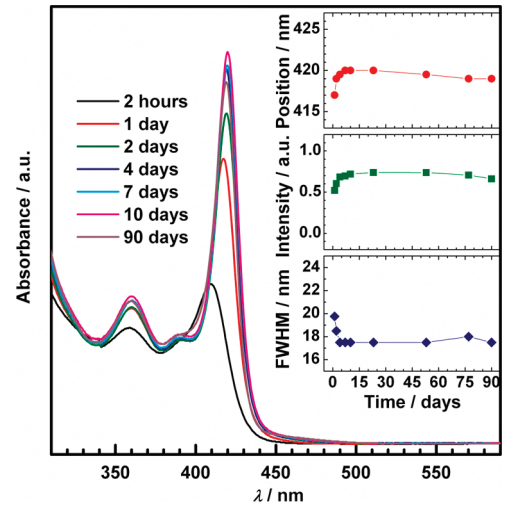

Figure 2. Time-dependent evolution of UV−vis absorption spectra for Cys-capped CdSe NPs. The insets show time-dependent change in the position (top), intensity (middle), and fwhm (bottom) of the first absorption peak.

RESULTS AND DISCUSSION

Cys is an α-amino acid with three functional groups (amine, sulfhydryl, and carboxyl groups). Each of them has lone pair electrons and thus can bear an electric charge, depending on solution pH. This might strongly influence the growth and stabilization of the CdSe NPs and hence affect their physical and optical properties. Each functional group of Cys may have its own roles both during and after the growth of CdSe NPs. To investigate these points, we synthesized a series of CdSe NPs in aqueous solutions containing Cys or one of its derivatives (L-cystine, cystine; *S*-ethyl-L-cysteine, S-EthylCys; L-cysteine methylester hydrochloride, CysME; L-cysteine ethylester hydrochloride, CysEE; *N*-acetyl-L-cysteine, N-ACys; DL-homocysteine, HomoCys). Schematic drawings of the capping molecules used in this study are shown in Figure 1.

Growth and Stabilization of Cys-Capped CdSe NPs. Figure 2 shows time-dependent evolution of absorption features for Cys-capped CdSe NPs. The spectrum obtained at reaction time (t_{rxn}) of 2 h reveals a relatively sharp first $peak_{abs}$ at 410 nm. This peak experiences a gradual red shift and intensity enhancement with t_{rxn} for up to 4 days. After that, absorption features for the NPs experience a minor change with time. The insets of the figure clearly show little change in the position, intensity, and full width at half-maxima (fwhm) for the first $peak_{abs}$ for 3 months (the longest t_{rxn} tested in this study), indicating excellent stability of the CdSe NPs at a particular size. This also indicates that Cys can effectively stabilize and protect the CdSe NPs from further growth, as well as from compositional change, in an oxygen-containing, severe aqueous environment, despite its relatively tiny size.

A typical stable absorption spectrum (t_{rxn} = 7 days) exhibits a very sharp first $peak_{abs}$ at 420 nm, together with smaller peaks at 390 and 360 nm. Photolumines-

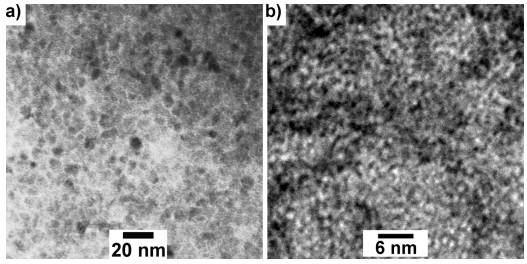

Figure 3. (a) Typical and (b) highly magnified TEM images for Cys-capped CdSe NPs.

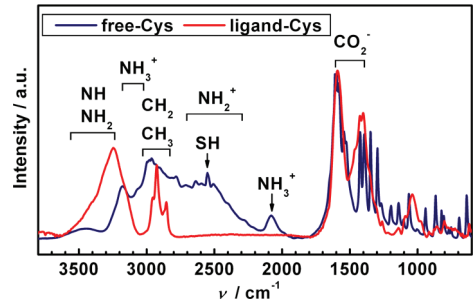

Figure 4. FT-IR spectra for free-Cys and Cys-capped CdSe NPs. Blue solid line for unbound free Cys; red solid line for ligand-Cys coordinated to the CdSe NPs.

cence excitation spectra (unpublished experiments) for Cys-capped CdSe NPs were practically identical to the corresponding absorption spectrum, suggesting that the smaller peaks at 390 and 360 nm could be attributed to the excited states of excitons on the same CdSe NPs. The absorption features for our NPs resemble closely those for CdSe nanoparticles grown selectively in the organic phase.[1,2] They are almost identical to those for the $(CdSe)_{33}$ and $(CdSe)_{34}$ magic clusters stabilized in toluene.[8] The first $peak_{abs}$ position suggests our NPs have an ultrasmall size. TEM images in Figure 3 clearly support this. They show many ultrasmall particles together with bigger agglomerates composed of a few ultrasmall particles, although it is very difficult to determine their definite size from the images due to unclear spot boundaries. From the images, however, it is evident that the size of the NPs is smaller than 2 nm (roughly 1.4−1.8 nm). This observation coincides with previous reports: an ultrasmall size (1.3−1.7 nm) was reported for the organic phase-synthesized, size-selective CdSe NPs showing a sharp first $peak_{abs}$ near 420 nm.[1,2,8] All our attempts to observe lattice fringes for the ultrasmall particles failed. TEM images showing clear lattice fringes for our NPs were only observed when we took high-resolution TEM images at a high beam energy (300 kV), which typically caused melting down of the NPs followed by their growth to larger NPs with crystalline structure (for details, see Supporting Information S1). The extremely small size of our NPs might limit their clear imaging using TEM.[20] Analysis of the XRD spectra (unpublished experiments) for concentrated samples of our NPs revealed an average interparticle distance of 1.73 nm, indicating an ultrasmall size (<1.73 nm) of the NPs. These estimated values accord reasonably well with the size (*ca.* 1.7 nm) calculated using the empirical fitting function[3] based on first $peak_{abs}$ position. Thus, size of the CdSe NPs investigated is reported using the diameter estimated based on their first $peak_{abs}$ position. The sharpness of the first $peak_{abs}$ (fwhm ~ 17.5 nm) for our NPs is much higher than that (fwhm ~26 nm) for the organic phase-synthesized CdSe NPs with the size of *ca.* 1.7 nm and size distribution of ~2.7%.[5] Interestingly, the sharpness is very similar to that (fwhm ~ 18.0 nm) for the $(CdSe)_{33}$ and $(CdSe)_{34}$ magic clusters having slightly different core-cage structures but same physical size.[8] These indicate an extremely narrow size distribution of our NPs.

These observations suggest that our Cys-capped CdSe NPs are selectively grown, ultrasmall NPs having a specific size, extremely narrow size distribution, and excellent stability. They also indicate that Cys is an excellent ligand molecule in aqueous solution for restricting selective growth of CdSe NPs at the size (*ca.* 1.7 nm) exhibiting a first $peak_{abs}$ at 420 nm, as well as for maintaining their extremely narrow size distribution and excellent stability.

Roles of Each Functional Group and Interfacial Structure of Cys. Upon addition of Cd precursor (Cd^{2+} ions), the synthesis solution containing one of the capping molecules without a sulfhydryl group (cystine or S-EthylCys) had white precipitates, whereas a solution containing one of the other capping molecules exhibited neither color change nor precipitates. For our synthesis condition (pH ~12), both the sulfhydryl and carboxyl groups of Cys exist as negatively charged thiolate and carboxylate groups, respectively, whereas the amine group remains uncharged (pK_a = 10.28, 8.18, and 1.96 for $-NH_3^+$, −SH, and $-CO_2H$, respectively).[21] These observations and the pK_a values strongly suggest that the negatively charged thiolate group is mainly responsible for the stabilization of Cd^{2+} ions in the synthesis solution because both cystine and S-EthylCys lack the sulfhydryl group, unlike the others, even though they have uncharged amine and negatively charged carboxylate groups. This can be ascribed to strong nucleophilicity of the thiolate group. Its nucleophilicity is stronger than that of hydroxide ions, and hence, it can easily form stable complexes with Cd^{2+} ions in basic aqueous solution.[22−24] Although both amine and carboxylate groups are capable of forming complexes with Cd^{2+} ions,[10] they are weaker nucleophiles than hydroxide ion. Thus, in the basic aqueous solution containing only cystine or S-EthylCys as a capping molecule, it is reasonable to expect $Cd(OH)_2$ precipitates.

To investigate roles of the other functional groups of Cys further, FT-IR spectra were taken for both free-Cys (free unbound Cys) and ligand-Cys (Cys coordinated to the NPs). The spectrum for ligand-Cys is quite different from that for free-Cys, as shown in Figure 4. The IR

spectrum for free-Cys is very similar to previously reported spectra for free-Cys.[25−27] The spectrum shows typical absorption features corresponding to a zwitterionic form of α-amino acids,[28] along with other features related to the sulfhydryl group: asymmetric (1589 cm^{-1}) and symmetric (1425 cm^{-1}) CO_2^- stretching bands; characteristic combination bands of asymmetric NH_3^+ deformation and hindered NH_3^+ rotation (2150−1900 cm^{-1}); an SH stretching band (2551 cm^{-1}) and nearby complicated bands of the SH involved in hydrogen bond formation; CH_2 and CH stretching bands (3000−2800 cm^{-1}); broad and strong NH_3^+ stretching bands (3176 and 3041 cm^{-1}), characteristic of amine salts. The spectrum for ligand-Cys also shows asymmetric (1591 cm^{-1}) and symmetric (1425 cm^{-1}) CO_2^- stretching bands, indicating the existence of a free carboxylate group. Very distinctive stretching bands at 2926 and 2854 cm^{-1} confirm the presence of hydrocarbons (CH_2 and CH from ligand-Cys). The spectrum, however, shows no combination bands of asymmetric NH_3^+ deformation and hindered NH_3^+ rotation. Furthermore, there is a lack of any combination band at 2700−2300 cm^{-1}, characteristic of secondary NH_2^+.[27] These observations indicate that the amine group of ligand-Cys bears no electric charge at the pH (∼9) of the IR sample solution, where a zwitterionic form of Cys would be expected. A large stretching band at 3246 cm^{-1} and a higher wavenumber shoulder suggest the existence of coordinated NH_2 or NH.[25−28] Absence of any features of an SH stretching mode signifies that S of the ligand-Cys is coordinated to the NPs. All the FT-IR data confirm that both S (sulfhydryl group) and N (amine group) of the ligand-Cys are directly coordinated to the NPs, but its carboxyl group exists as a free carboxylate group.

Primary coordination between the sulfhydryl group of Cys and the surface Cd of the NPs is well expected, considering the strong nucleophilicity of the thiolate group. However, secondary coordination between the amine group and the surface Cd seems to contradict the previous reports about the existence of secondary coordination between the carboxylate group of mercapto acids and Cd^{2+} ions or between the carboxylate group and the surface Cd of Cd-based NPs.[11,13,29,30] This can be explained by considering the reaction solution pH, as well as nucleophilicity of neutral amine and carboxylate groups. The amine group of Cys bears no electric charge in the synthesis solution (pH ∼12), and in general, nucleophilicity of a neutral amine group is slightly stronger than that of a carboxylate group. Thus, the amine group may have priority over the carboxylate group for secondary coordination. The primary and secondary coordination of ligand-Cys may leave the carboxylate group at a spatial position which is unfavorable for coordination to the NPs. Also, it may be possible that the spatial structure of Cys is unfavorable for the secondary coordination of its carboxyl group. This can be partially supported by a previous report about the coordination structure in Cys-capped CdSe/CdS NPs fabricated in aqueous solution at pH 9.2; only primary coordination was observed between the sulfhydryl group of ligand-Cys and the surface Cd.[15] At the pH of 9.2, the amine group should be protonated and thus may not be involved in the coordination, whereas the carboxyl group is expected to exist as a carboxylate form and hence to be involved in the coordination.

The above observations indicate the following. The sulfhydryl group of Cys stabilizes Cd^{2+} ions in basic aqueous solution. Ligand-Cys acts as a bidentate ligand: the sulfhydryl group is coordinated to the surface Cd, and the amine group is also involved in coordination with the surface Cd. The carboxyl group exists as a negatively charged carboxylate form, and that contributes to the electrostatic stabilization of the colloidal CdSe NPs.

Both the coordination structure and spatial geometry of ligand-Cys might profoundly contribute to its excellent ability as a ligand. The observed absorption and FT-IR spectra for the NPs suggest that the spatial geometry of the bidentate ligand-Cys at its direct interface with the CdSe core surface (hereafter, referred to as "near-interface") is suitable for effectively restricting initial selective growth of the NPs at the size of *ca.* 1.7 nm. Relatively compact near-interface spatial geometry, as well as comparatively strong bidentate coordination, of the ligand-Cys ensures a narrow size distribution of the NPs and prevents them from further change. In addition, the relatively compact spatial geometry of the ligand-Cys at its outermost part (hereafter, referred to as "outermost spatial geometry"), which is the portion directly contacting the molecules of the aqueous synthesis solution, as well as electrostatic stabilization through its negatively charged carboxylate group contributes strongly to the long-term stability of the CdSe NPs.

Effect of Physical Structure and Chemical Nature of Capping Molecules. The absorption spectrum for CysME-capped CdSe NPs (Figure 5a) varies considerably with t_{rxn}. The spectrum at t_{rxn} of 2 h is very similar to the corresponding one for the Cys-capped NPs, except for a slightly broader peak near 420 nm. The peak experiences a rapid intensity drop and broadening as t_{rxn} increases. In t_{rxn} of 3 days, the peak becomes much smaller and broader and a new broad longer-λ tail peak centered at 475 nm appears. Observation of the first $peak_{abs}$ near 475 nm was previously reported for size-selective CdSe NPs stabilized in organic solvents,[1,2,8] indicating that the CysME-capped NPs with the peak at 475 nm may also be the size-selective NPs. After that, the peak near 420 nm becomes gradually smaller, whereas the tail peak shows a slight intensity enhancement without distinguishable extension of its end. All these spectral changes indicate that stable size-selective CysME-capped CdSe NPs are initially grown, and their structure, size, and size distribution are very similar to those

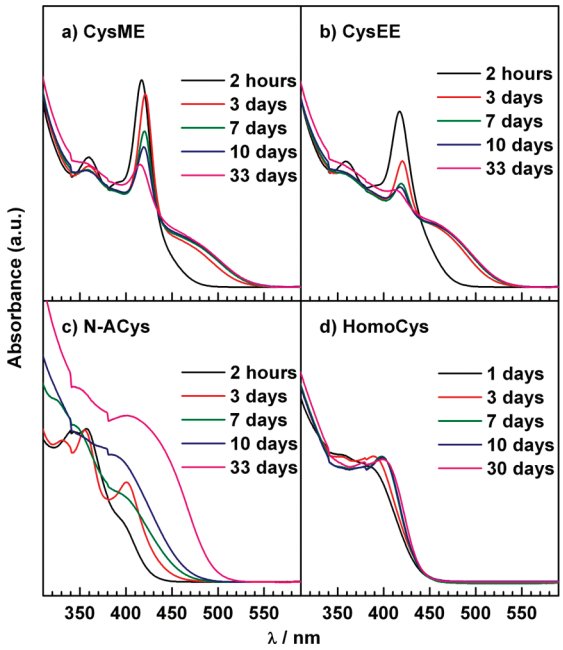

Figure 5. Time-dependent evolution of UV−vis absorption spectra for Cys derivative-capped CdSe NPs. (a) Cysteine methylester (CysME), (b) cysteine ethylester, (CysEE), (c) *N*-acetyl-L-cysteine (N-ACys), and (d) homocysteine (HomoCys).

of the Cys-capped NPs; however, the NPs (*ca.* 1.7 nm) with their first $peak_{abs}$ at 420 nm maintain their stability only for a short time and experience gradual growth to the larger size-selective NPs (*ca.* 2.1 nm) with their first $peak_{abs}$ at 475 nm.[3] In addition, the observations point out that CysME is quite effective both for restricting selective growth of CdSe NPs at the size of *ca.* 1.7 nm and for maintaining their narrow size distribution in the short term, but it is ineffective for maintaining their long-term stability. They also reveal that CysME is quite efficacious for limiting selective growth of CdSe NPs at the slightly larger size of *ca.* 2.1 nm, but it is inefficacious for their narrow size distribution and only moderately effectual for their short- and long-term stabilities.

Considering the structures of Cys and CysME, it is reasonable to expect CysME-ligand to act as a bidentate ligand. Thus, ligand-CysME can limit the initial selective growth of the NPs at the size of *ca.* 1.7 nm, like ligand-Cys does. However, its lack of a free, charged functional group which contributes to electrostatic stabilization of the initially grown NPs results in eventual degradation followed by gradual transformation of the NPs to the larger size-selective ones (*ca.* 2.1 nm). Furthermore, the outermost spatial geometry of ligand-CysME is relatively bulky due to its ester group. It seems to be too bulky to maintain the stability of the ultrasmall CdSe NPs with the size of *ca.* 1.7 nm for a long time.

The absorption features for CysEE-capped CdSe NPs (Figure 5b) are very similar to those for the CysME-capped NPs, except for their slightly wider, less intense peak at 420 nm and slightly bigger longer-λ tail peak. These minor differences can be mainly attributed to the structural difference between their ligand molecules. The outermost spatial geometry of ligand-CysEE is slightly bulkier than that of ligand-CysME. Hence, the former is slightly less effective than the latter for stabilizing the ultrasmall NPs with the size of *ca.* 1.7 nm. The effects of CysEE on the selective growth and stabilization of CdSe NPs are very similar to those of CysME.

The absorption features for N-ACys-capped CdSe NPs (Figure 5c) are quite different from those for the Cys-, CysME-, and CysEE-capped CdSe NPs. The spectrum at t_{rxn} of 2 h shows a broad absorption peak near 360 nm as well as a tiny shoulder peak near 400 nm. The 3 day reaction period results in the peak near 360 nm becoming more distinctive, without much change in its absolute intensity, and the shoulder peak becomes much more distinctive and intense, as well. These indicate coexistence of mainly two different sizes of size-selective CdSe NPs exhibiting their respective first $peak_{abs}$ at 360 and 400 nm. Observation of the first $peak_{abs}$ near 360 and 400 nm was also reported previously for the separately synthesized, size-selective CdSe NPs,[2,5,12] suggesting that our N-ACys-capped NPs may also be size-selective NPs of different sizes. The spectrum at t_{rxn} of 7 days shows broadening and a blue shift of the peak near 360 nm, as well as broadening of the peak near 400 nm without much change in its position. These observations imply that N-ACys is unable to maintain stability of the NPs. The peak near 360 nm changes faster than that near 400 nm. The spectra at t_{rxn} of 10 days or longer show a broad peak near 400 nm and a very broad peak near 360 nm. However, both peaks have enhanced absolute intensity, compared with their corresponding peaks at shorter t_{rxn}. These observations suggest continuous formation of the N-ACys-capped NPs with their first $peak_{abs}$ centered near 400 nm as t_{rxn} increases. In addition, the observations indicate that N-ACys is very efficient for restricting selective growth of the ultrasmall CdSe NPs at the sizes (*ca.* 1.2 and 1.5 nm) exhibiting their first $peak_{abs}$ at 360 and 400 nm, respectively.[3] They also indicate that N-ACys is quite effective for initially focusing the narrow size distribution of the NPs, as can be inferred from the sharpness of their first $peak_{abs}$. The fwhm for the two first $peak_{abs}$ ($t_{rxn} = 3$ days) is slightly less than 40 nm. This value is somewhat smaller than fwhm of ~47 nm for the organic phase-fabricated CdSe NPs with a size distribution of ~4.6%.[5] The time-dependent evolution of the absorption spectra signifies that N-ACys is moderately efficient for short-term stability of the NPs with the size of *ca.* 1.2 nm but ineffective for short-term stability of the NPs with the size of *ca.* 1.5 nm. It further indicates that N-ACys is poor at getting long-term stability of the two different sizes of the CdSe NPs.

The interesting ability of ligand-N-ACys can be ascribed to its *N*-acetyl group. Weak nucleophilicity of the *N*-acetyl nitrogen prevents it from coordinating to the surface Cd. Thus, N-ACys can coordinate to the NP

TABLE 1. Effects of Capping Molecules on the Selective Growth and Stabilization of CdSe NPs[a]

capping molecule	peak position[b] (nm)	nanoparticle size[c] (nm)	size restriction	size distribution focusing	stability	
					short-term	long-term
Cys	420	1.7	0	0	0	0
CysME	420	1.7	0	0	0	X
	475	2.1	0	X	Δ	Δ
CysEE	420	1.7	0	0	Δ	X
	475	2.1	0	X	Δ	Δ
N-ACys	420	1.7	X	X	X	X
	400	1.5	0	0	X	X
	360	1.2	0	0	Δ	X
HomoCys	420	1.7	X	X	X	X
	400	1.5	0	Δ	0	0

[a] 0 = Excellent; Δ = moderate; X = poor. [b] First absorption peak. [c] Estimated diameter based on a calculation using an empirical fitting function[3] for CdSe NPs.

only through its S, so it acts as a monodentate ligand. This claim can be supported by the difference in the first $peak_{abs}$ positions for the N-ACys- and Cys-capped CdSe NPs. The former shows the peak at shorter λ than the latter. This is unlikely if N-ACys acts as a bidentate ligand because it is bulkier than Cys and hence less effective for stabilizing smaller NPs. Monodentate ligand-N-ACys may take a less bulky near-interface spatial geometry than bidentate ligand-Cys. Thus, ligand-N-ACys can limit the initial selective growth of the NPs at the sizes (*ca.* 1.2 and 1.5 nm) smaller than that (*ca.* 1.7 nm) of Cys-capped CdSe NPs. However, its outermost spatial geometry seems to be too bulky, due to the *N*-acetyl and carboxylate groups, to maintain stability of the ultrasmall NPs, resulting in eventual destabilization and overall poor stability of the NPs.

HomoCys-capped CdSe NPs experience a gradual red shift of their first $peak_{abs}$ with increasing t_{rxn} up to 7 days, and then they maintain the peak at 400 nm (Figure 5d). The CdSe NPs are very stable, as indicated by the small peak feature change and absence of any longer-λ tail formation even at t_{rxn} of 1 month. These observations signify that HomoCys is highly effective for restricting selective growth of CdSe NPs at the size (*ca.* 1.5 nm) exhibiting a first $peak_{abs}$ at 400 nm as well as for maintaining their short- and long-term stabilities. In addition, HomoCys is moderately effectual for their narrow size distribution, as can be inferred from the moderately sharp first $peak_{abs}$. Its fwhm (t_{rxn} = 7−30 days) is ~44 nm, which is slightly smaller than the fwhm of ~47 nm for the organic phase-synthesized CdSe NPs with a size distribution of ~4.6%.[5]

The specific ability of ligand-HomoCys can be attributed to the CH_2 between the SH and $CH_2CH(NH_2)CO_2H$ moieties. It is natural to expect coordination between S of HomoCys and the surface Cd because of the strong nucleophilicity of the thiolate ion. Due to the CH_2, the amine group may be located too far from the NP surface to be involved in coordination. Therefore, HomoCys coordinates to the NP only through its S, acting as a monodentate ligand. The similarity in the first $peak_{abs}$ position (400 nm) for the N-ACys- and HomoCys-capped CdSe NPs strongly supports our claim that both N-ACys and HomoCys act as a monodentate ligand because they lack an amine nitrogen strong enough or close enough to coordinate to the NP. Therefore, ligand-HomoCys can effectively restrict selective growth of the NPs at the size (*ca.* 1.5 nm) smaller than that (*ca.* 1.7 nm) of Cys-capped CdSe NPs. Due to the relatively simple and compact structure, ligand-HomoCys can take relatively compact near-interface and outermost spatial geometries. In addition, it has a free, negatively charged carboxylate group contributing to electrostatic stabilization of the NPs. Therefore, it is very effective for maintaining short- and long-term stabilities of the CdSe NPs with the size of *ca.* 1.5 nm.

Table 1 summarizes effects of the capping molecules on the selective growth of CdSe NPs and their stabilization. Cys permits attainment of the size-selective, ultrasmall CdSe NPs exhibiting excellent short- and long-term stabilities. Cys acts as a bidentate ligand and crucially contributes to the selective growth of the NPs at the specific size (*ca.* 1.7 nm) as well as to their narrow size distribution. Its carboxyl group contributes to the long-term stability of the NPs through electrostatic stabilization. The relatively compact structure of Cys allows it to take relatively compact near-interface and outermost spatial geometries. These can help the ultrasmall NPs to maintain their excellent short- and long-term stabilities. Both CysME and CysEE can act as bidentate ligands and restrict the selective growth of the CdSe NPs at the specific size (*ca.* 1.7 nm). However, due to the relatively bulky outermost spatial geometry and the absence of a free, charged carboxyl group, CysME and CysME are less effective than Cys for stabilizing the ultrasmall CdSe NPs for a long time, resulting in their gradual transformation to larger ones (*ca.* 2.1 nm). N-ACys enables the selective growth of the ultrasmall CdSe NPs of different sizes (*ca.* 1.2 and 1.5 nm). It can act as a monodentate ligand and hence take a more compact near-interface spatial geometry than those acting as bidentate ligands (Cys, CysME, and CysEE), even though the former is bulkier than the latter. In this regard, N-ACys can effectively restrict the selec-

tive growth of the NPs at the sizes smaller than that of Cys-capped CdSe NPs. However, its outermost spatial geometry is too bulky to maintain the stability of those ultrasmall NPs, resulting in their destabilization and poor stability. HomoCys can provide an excellent route to the selective growth of ultrasmall CdSe NPs (*ca.* 1.5 nm) showing excellent short- and long-term stabilities. HomoCys can act as a monodentate ligand and hence take a more compact near-interface spatial geometry than those acting as bidentate ligands. In this regard, it can effectively restrict the selective growth of the NPs at the size (*ca.* 1.5 nm) smaller than that of Cys-capped CdSe NPs. In addition, its outermost spatial geometry is relatively compact, helping the ultrasmall NPs to maintain their short- and long-term stabilities without further growth.

CONCLUSIONS

We investigated the influence of the physical structure and chemical nature of capping molecules on the selective growth and stabilization of small CdSe NPs in aqueous solution at room temperature under ambient atmosphere, using Cys and its derivatives as model capping molecules. A series of investigations, using these capping molecules with very closely related physical structures and chemical natures, revealed specific roles for each functional group of Cys as well as influence of the physical structure and chemical nature of capping molecules on the size, size restriction, size distribution, and short- and long-term stabilities of the CdSe NPs.

The sulfhydryl group of Cys stabilized Cd^{2+} ions in basic aqueous solution. The sulfhydryl group of ligand-Cys was coordinated to the surface Cd; its amine group was also involved in coordination with the surface Cd; however, its carboxyl group existed as a negatively charged carboxylate form, and it contributed to electrostatic stabilization of the colloidal CdSe NPs.

Our investigations indicated the following tendencies. For the selective growth and stabilization of the semiconductor NPs in aqueous solution, their capping molecules should have at least one functional group with strong nucleophilicity as well as another free, charged functional group. Monodentate ligands were more effective than bidentate ligands for restricting size of the NPs smaller, whereas the former was less effective than the latter for getting a narrow size distribution of the NPs. The capping molecules with a relatively bulky near-interface spatial geometry resulted in NPs with poor short- and long-term stabilities, whereas those having a relatively compact near-interface spatial geometry led to NPs with at least moderate short-term stability. The capping molecules having a relatively compact outermost spatial geometry led to NPs with excellent long-term stability, whereas those having a relatively bulky outermost spatial geometry produced NPs with at most moderate long-term stability. Our results clearly showed general trends for the possibility of the selective growth of stable CdSe NPs with particular sizes in aqueous solution through selecting and designing appropriate capping molecules.

EXPERIMENTAL METHODS

CdSe NPs were synthesized by sequential addition of the desired amounts of 1 M NaOH, Cys or one of its derivatives, 0.15 M $CdSO_4 \cdot 8/3H_2O$, and 0.05 M Na_2SeSO_3 into deionized H_2O at room temperature with mild magnetic stirring and under ambient atmosphere.[19] Typical concentrations of chemicals in the initial synthesis solution were $[Cd^{2+}] = 1.5$, $[Se^{2-}] = 0.375$, [Cys or its derivatives] = 13.2, [NaOH] = 37.5 mM. Resulting colloidal solutions were kept at room temperature in the dark with continuous magnetic stirring. UV−visible absorption spectra were recorded with a U-2000 (Hitachi) spectrophotometer. FT-IR spectra were recorded with an IFS 66 V (Bruker) FT-IR spectrophotometer. FT-IR samples were prepared by pressing Cys with KBr into pellets or by applying MR-3 ion-exchange resin-cleaned Cys-capped CdSe NPs (pH ~9) on a Si substrate followed by drying in vacuum. TEM images were obtained with a JEM-2000 (JEOL) microscope operated at 200 kV. Supporting Information is available for the experimental details (S2).

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Supporting Information Available: HRTEM image and related data and their interpretation (S1). Experimental details (S2). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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