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Optical Activity and Chiral Memory of Thiol-Capped CdTe Nanocrystals

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Semiconductor nanocrystals (NCs) have been receiving much attention as light emitting nanomaterials that have size- and composition-tunable optical properties derived from the quantum confinement effect.[1] Because of their unique properties unlike the bulk, the prospective applications of NCs range from optoelectronics[2−4] to biodetection.[5−7] A couple of recent studies are focusing on CdS NCs capped with a chiral thiol (penicillamine, Pen), motivated by the development of chiral light emitting nanoprobes.[8,9] CdS NCs with D- or L-Pen showed circular dichroism (CD) signals in the range 200 to 390 nm with mirror images identical to one another, which differ from both the free ligand and the Cd−ligand complex.[8] Despite a number of theoretical and experimental studies on the optically active inorganic nanomaterials, the origin of chirality is still under discussion.[8−16] On the basis of density functional calculations, Elliott et al. recently suggested that the chirality of CdS NCs originates from the ligand shell, in which the Pen ligand transmits an enantiomeric structure to the surface layers and associated electronic states.[9] While the model clearly explains the chiral shell and achiral core in CdS NCs, there still seems to be lacking experimental proof for semiconductor NCs.

In this communication, we describe the chiroptical properties of CdTe NCs passivated with chiral thiols. The origin of chirality is discussed by comparing the CD profiles with those of CdS and CdSe NCs capped by the same ligands. The unprecedented chiral memory effect of the CdTe NC surface is also demonstrated by the ligand exchange with an achiral thiol.

CdE (E = chalcogenide; S, Se, and Te) NCs capped with D- and L-cysteinemethylester hydrochloride (MeCys) were prepared by the microwave-assisted heating for CdS[8] and by the aqueous synthetic method for CdSe and CdTe.[17] *R*- and *S*-α-lipoic acids were also used for CdTe NCs as bidentate ligands. The sizes of NCs were found to be 2.5, 2.1, and 2.8 nm for CdS, CdSe and CdTe, respectively, by transmission electron microscopy (TEM). Figure 1 shows the UV−vis absorption and CD spectra of MeCys-capped CdTe NCs together with those of CdS and CdSe NCs. These NCs exhibited absorption peaks at approximately 320 nm for CdS, 470 nm for CdSe, and 540 nm for CdTe NCs, corresponding to the first excitonic transitions that are dependent on the extent of quantum confinement. The order of peak positions shows good agreement with that of the band gap energy of the bulk, since each NC has a sufficiently smaller size than the bulk exciton Bohr radius (a_B = 3.0, 5.6, and 7.5 nm for CdS, CdSe, and CdTe, respectively). The CD profiles of D- and L-MeCys-capped CdTe NCs showed symmetrical mirror images with peaks at approximately 320, 270, 255, 235, and 220 nm, and these were entirely different from those of free D- and L-MeCys.[18] Interestingly, CD profiles for both CdS and CdSe NCs capped with D- or L-MeCys coincided well with those of CdTe NCs, whereas their absorption spectra differed substantially. Meanwhile, neither CdTe nor CdSe NCs showed a CD signal in the range of the first excitonic transition band (above 400 nm). The absence of CD signals in this range indicates that the observed CD signals cannot be attributed to the first excitonic transition in NC cores. While each NC should have a different lattice constant depending on the composition and crystalline form, the outermost Cd atoms of the core are expected to be directly coordinated by ligand-S atoms to form a Cd−S−ligand monolayer for all NCs.[19] Consequently, the CD profile would be attributed to the superposition of the CD signals derived from the direct electronic transition from chiral thiol to the Cd ion and the electronic transitions involving distorted near-surface Cd atoms as described by Elliott et al.[9] The CD profiles depended on the chemical structure of thiols and became dull by increasing the NC size according to the decrease of surface-to-volume ratio.[18] The absence of circularly polarlized photoluminescence of the present CdTe NCs also supports the achiral core model. The experimental data described above strongly indicate that the optical activity of CdTe NCs originates not from the CdTe core but from the surface shell including chiral capping molecules.

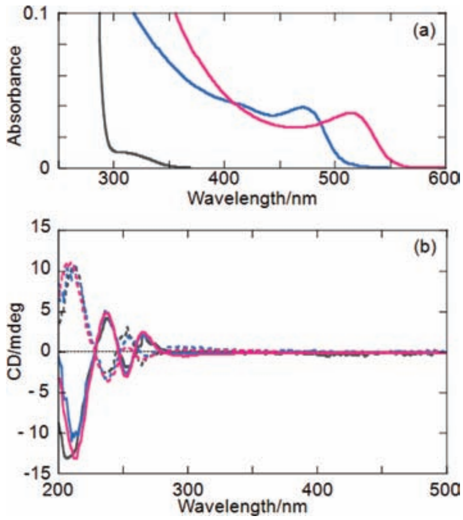

Figure 1. (a) UV−vis absorption spectra of D-MeCys-capped CdS (black), CdSe (blue), and CdTe (red) NCs. (b) CD spectra of D- (solid lines) and L- (dotted lines) MeCys-capped CdS (black), CdSe (blue), and CdTe (red) NCs.

Postsynthetic ligand-exchange experiments often provide helpful insights for the origin of optical activity for nanoparticles.[13,15,16] Since thiol-capped water-soluble CdTe NCs are metastable due to the relatively weak coordination of Cd-thiol[20] and the electrostatic repulsion between ligands on the NC surface,[21] the MeCys was easily exchanged with 1-dodecanethiol (DT) by a simultaneous phase transfer method.[18,22] Elemental analyses suggested that more than 92% of D-MeCys molecules were exchanged with DT[18] and DT-coated CdTe NCs were stably dispersed in chloroform. As shown in Figure 2b, no significant change was observed in absorption spectra after the ligand exchange. Furthermore, TEM

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measurements did not give any change of mean diameter for NCs. Surprisingly, both DT-capped CdTe NCs gave symmetrical mirror CD profiles which were almost identical to those of the original enantiomeric MeCys-capped CdTe NCs above 260 nm, even though they were capped predominantly with an achiral thiol. The chiral structure of CdTe NCs should be stored on the surface of NCs.

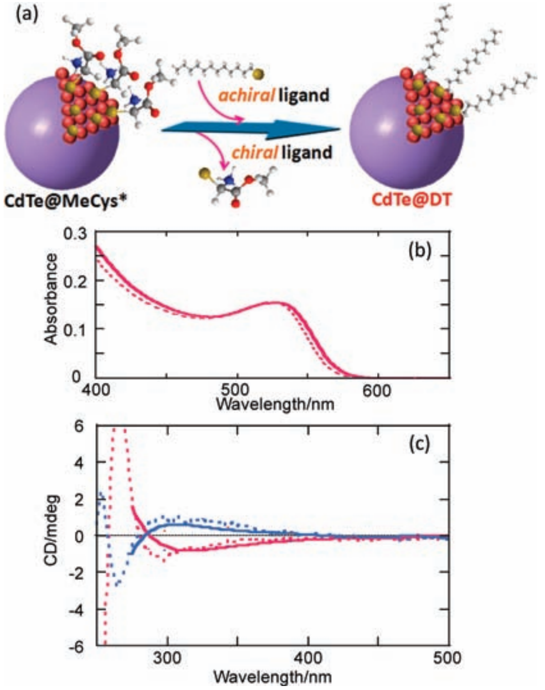

Figure 2. (a) Schematic illustration of ligand-exchange reaction. (b) UV−vis absorption spectra of D-MeCys-capped CdTe NCs (dotted line) and DT-capped CdTe NCs (solid line) after ligand-exchanged from D-MeCys. (c) CD spectra of D-MeCys (red) and L-MeCys (blue)-capped CdTe NCs (dotted lines) in water and DT-capped CdTe NCs (solid lines) in chloroform ligand-exchanged from D-MeCys (red) and L-MeCys (blue) -capped CdTe NCs. The spectra for DT-capped CdTe NCs were available only above 260 nm due to the limit of solvent transparency.

In principle, the crystalline order in a nanocrystalline sample decreases with respect to the bulk due to surface induced stress and strain. Temperature dependent extended X-ray absorption fine structure (EXAFS) measurements for thiol-capped CdS[23] and CdTe[24] NCs gave the enhanced static disorder parameters, which were dependent on the size, or the surface-to-volume ratio of NCs. In both the core and surface, the lattice distortions were observed for thiol-capped CdTe NCs, and the degree of distortion was more significant for the Cd−S shell than for the cubic CdTe core.[24] The surface of thiol-capped CdTe NCs is therefore inherently distorted and the presence of a chiral ligand appears to direct such distortions into enantiomeric compositions. Two plausible mechanisms could be suggested for the introduction of chiral structures. First, the chiral ligand preferentially adsorbs on the chiral surfaces as observed for some high Miller index surfaces of transition metals.[25] The stronger interaction of chiral lignds with such intrinsically chiral surfaces may maintain and selectively grow the chiral surface. Second, even for the achiral surface, the asymmetric adsorption of chiral molecules induces the chiral facet as reported by Zhao.[26] Both the two mechanisms eventually contribute to the formation of the chirally distorted kink structures on the surface of NCs by the interaction of MeCys ligand molecules with the surface of NCs. Because the ligand-exchange reaction would occur in an immediate and concerted manner by the large excess DT molecules, the chiral kink structures are stored during the ligand-exchange process, providing an unprecedented chiral memory effect of CdTe NCs. It should be noted that the response of optical activity of gold nanoparticles to ligand exchanges showed a clear contrast to the present system.[16] The difference should be attributed to the relatively high mobility of gold atoms on the surface of nanoparticles.[27,28] The chiral memory was robust enough to be preserved for at least 1 year under ambient conditions, whereas it disappeared by heating above 190 °C[18] which is substantially higher than the Debye temperature of the CdS shell of thiol-capped CdTe NCs.[24]

In summary, we have experimentally proposed that the optical activity of chiral thiol-capped CdE NCs originates from distorted Cd−S−ligand surfaces. The robust chiral memory on the surface promises to give us a new platform for chiral transcription, resolution, and amplification based on inorganic nanoparticles.

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Supporting Information Available: Detailed synthetic and experimental procedures and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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