Synthesis and Surface Characterization by Raman Spectroscopy of Water-Dispersible ZnS:Mn Nanocrystals Capped with Mercaptoacetic Acid

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Semiconductor nanocrystals have been extensively studied due to their size-dependent optical properties and wide applications.[1,2] Many efforts have been made to develop nanoparticles with superior optical characteristics, *e.g.*, higher quantum yields, more accessible absorption wavelengths, and wider absorption and narrower emission bands. The incorporation of transition metal ions into semiconductor nanocrystals induces radiative recombination of excited electron-hole pair at doping ion sites rather than at surfaces, which shifts photoluminescence wavelength and increases quantum efficiency.[3-9] Therefore, transition metal-doped semiconductor nanocrystals have great potential applications as a novel material for display and light-emitting devices.

The functionalization of surfaces is another important aspect of nanoparticle fabrication.[10] In particular, it is important to make nanoparticles water-dispersible for many biological applications. Surfactants play important roles in the control of dispersed particle sizes, optical properties, and solubility by passivating nanocrystal surfaces.[11] Here, we report on the synthesis and properties of water-dispersible Mn^{2+}-doped ZnS nanoparticles stabilized by mercaptoacetic acid (ZnS:Mn-MAA). MAA is widely used as a capping agent in the synthesis of nanoparticles.[12] MAA is also the simplest molecule that has two terminal functional groups, a thiol and a carboxylic acid, which can be deprotonated, allowing it to bind to the surfaces of nanoparticles. In this respect, it would be interesting to determine the nature of surface-bound MAA and, in particular, to determine which functional group is involved in this binding. Here, we present the Raman spectra of MAA adsorbed on the surfaces of ZnS:Mn nanocrystals and propose a structure for surface-bound MAA based on spectral analyses and density functional theory (DFT) calculations.

Experimental Section

To synthesize ZnS:Mn-MAA nanoparticles, we employed a modified co-precipitation method used to produce mercaptopropionate (MPA)-capped Mn-doped ZnS nanocrystals.[13] Briefly, solutions of 1 M $ZnSO_4$ (5 mL), 0.1 M $MnSO_4$ (1.5 mL), and 1 M MAA (20 mL) were mixed, and titrated to pH 10.3 with 2 M NaOH. After bubbling the solution with N_2 for 30 minutes to purge air. Na_2S aqueous solution (1 M, 4.5 mL) was injected quickly and refluxed for

20 hours. The solution color became yellow as the reaction progressed. ZnS:Mn nanocrystals were precipitated by adding ethanol to the mixture and recovered as a white powder by centrifuging. They were subsequently washed and dried in an oven. These crystals were then subjected to X-ray diffraction (XRD, Bruker D5005), high-resolution transmission electron microscopy (HR-TEM, JEOL JEM3010). and Fourier-transform Raman spectroscopy (Bruker. FRA106/S, resolution: 1 cm^{-1}) for characterization. The ZnS:Mn-MAA powder was highly soluble in water and was subjected to UV/vis (Perkin-Elmer) and fluorescence (Shimadzu) spectroscopy in aqueous solution.

Results and Discussion

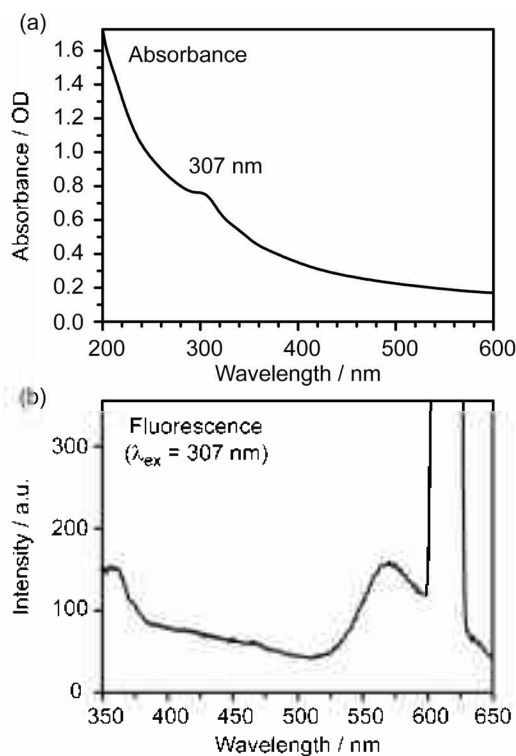The optical properties and morphology of the nanocrystals

Figure 1. (a) UV-visible absorption spectrum and (b) fluorescence spectrum of MAA-capped ZnS:Mn nanocrystals. The fluorescence spectrum was obtained by excitation at 307 nm.
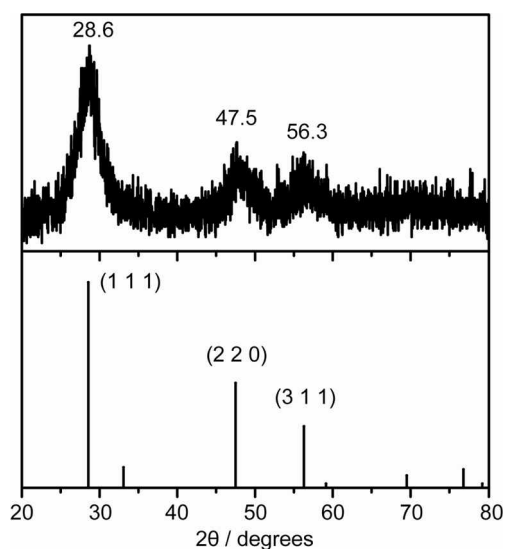
Figure 2. XRD spectrum of ZnS:Mn-MAA nanocrystals. The lower panel shows the XRD spectrum of bulk ZnS in a zinc blende form.

Figure 4. FT-Raman spectra of (a) ZnS:Mn-MAA nanocrystals, (b) sodium mercaptoacetate, and (c) neat MAA solution. All spectra are offset for clarity and the spectrum of sodium mercaptoacetate in (b) is inverted to better allow comparison with (a).

produced were determined. Figure 1 presents the UV/vis and fluorescence spectra of ZnS:Mn-MAA nanocrystals in water. The absorption spectrum shows a steep increase toward shorter wavelengths with a shoulder at 307 nm. Previously, small absorption bands have been reported at 287 and 290 nm for other types of Mn-doped ZnS nanocrystals of size 3 nm and 3.2 nm, respectively.[13,14] In the present study, a slight red-shift in the absorption band to 307 nm suggests a particle size larger than ~3 nm. Figure 1(b) shows the fluorescence spectrum obtained by exciting at 307 nm. The second-order diffraction of the excitation wavelength appears at 614 nm. Despite the interference of light used for excitation, a fluorescence band is clearly visible with a peak at ~570 nm. The large Stokes shift is attributed to the $^4T_1 \rightarrow {}^6A_1$ transition of the Mn^{2+} doping agent.[8,9]

The structural properties of ZnS:Mn nanocrystals were investigated by XRD and HR-TEM. Figure 2 shows the
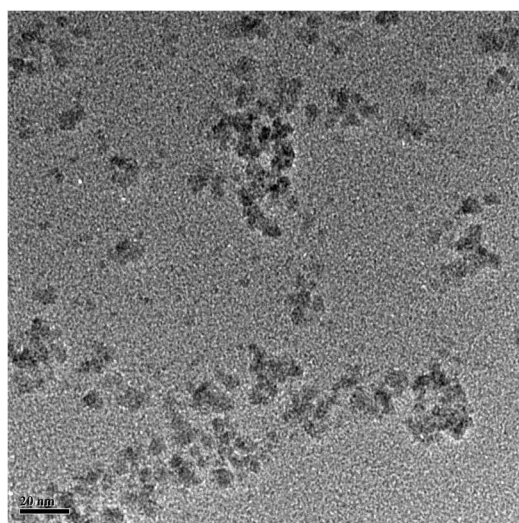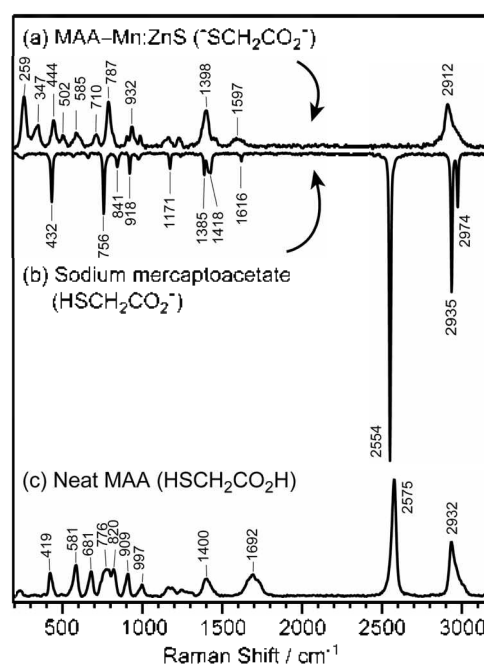

Figure 3. HR-TEM image of ZnS:Mn-MAA. The scale bar indicates 20 nm.

measured XRD pattern of ZnS:Mn-MAA along with that of bulk ZnS. The observed lines at 28.6°, 47.5°, and 56.3° correspond to the (111), (220), and (311) planes of the zinc-blende form of ZnS. The transmission electron micrograph in Figure 3 shows that the average particle size is 3.8 ± 0.5 nm.

The form of the MAA adsorbed on the ZnS:Mn nanoparticles is inferred from Raman spectra. FT-Raman spectra of ZnS:Mn-MAA nanocrystals were obtained and compared with those of neat MAA solution and sodium mercapto-acetate.[15,16] The overall spectrum of the ZnS:Mn-MAA nanoparticles was found to closely resemble that of sodium mercaptoacetate except for 2554 cm^{-1} and low frequency regions, as shown in Figure 4(a) and (b). The absence of S-H stretch at 2554 cm^{-1} in Figure 4(a) suggests that MAA exists as a thiolate on the nanocrystal surface. In addition, due to deprotonation of carboxylic acid group, the C=O stretching band of neat MAA at 1692 cm^{-1} [Fig. 4(c)] switched to an antisymmetric OCO stretch at ~1600 cm^{-1} and a symmetric OCO stretch at ~1400 cm^{-1} [Fig. 4(b)]. Since the OCO stretch of MAA adsorbed on ZnS:Mn closely matches that of sodium mercaptoacetate, we consider that MAA is adsorbed in a dianionic form and carboxylate is left free as in sodium mercaptoacetate.

Spectral analysis of the low frequency region is rather challenging. MAA/nanoparticle binding restricts low frequency bending, twisting, and torsional motion and shifts these bands considerably compared with those of free MAA. New peaks appear at 259 and 347 cm^{-1}, and these are possibly assigned to transverse and longitudinal optical phonon, respectively.[17,18] Alternatively, DFT calculations [B3LYP/6-

Table 1. The measured Raman frequencies of MAA adsorbed on ZnS:Mn nanoparticles and of sodium mercaptoacetate along with the DFT-calculated harmonic frequencies using B3LPY/6-31G(d). The vibrational assignment is based on the DFT calculations. In the DFT calculations, geometry optimization was performed for a Zn-$^-$SCH$_2$CO$_2^-$ complex at the same level of theory and the same size of basis set. A scale factor, 0.9613, was used for vibrational frequencies

ZnS:Mn-MAA	Mercaptoacetate	DFT	Assignment
259 s		256	TO (ZnS) or ν(Zn–S)
347 m			LO (ZnS)
444 m	432 m	388	δ(CCO)/ρ(OCO)
502 w			
585 m	563 vw	532	γ(CCO)/ω(OCO)
710 w	660 vw	652	δ(OCO)
787 s	756 m	784	ν(CS)
	841 w	844	ν(CC)
932 m	918/972 m	863	ρ(CH$_2$)
1170 w	1171 w	1183	ω(CH$_2$)
1398 s	1385 m	1305	ν_s(OCO)
	1418 m	1419	δ(CH$_2$)
1597 w	1616 vw	1658	ν_{as}(OCO)
	2554 vs		ν(SH)
2912 s	2935 s	2904	ν_s(CH$_2$)
2951 shoulder	2974 m	2955	ν_{as}(CH$_2$)

Abbreviations: ν, stretch; δ, in-plane bend; γ, out-of-plane bend; ρ, rock; ω, wag; TO, transverse optical phonon; LO, longitudinal optical phonon; vs, very strong; s, strong; m, medium; w, weak; vw, very weak

31G(d)][19] using a primitive Zn-$^-$SCH$_2$CO$_2^-$ complex yield a Zn-S stretching vibration of 256 cm^{-1}. It is unlikely that the thiolate coordinates to Mn instead of Zn because very small amounts of Mn (only 3% of Zn) were used. Raman spectral assignments based on the DFT calculations are listed in Table 1. Further calculations using a better model such as $^-$SCH$_2$CO$_2^-$ on a two-dimensional ZnS surface are required to definitively assign the low frequency Raman region and to determine the structure of the adsorbate.

In conclusion, we have synthesized water-dispersible ZnS:Mn nanocrystals by using MAA as a capping agent. Optical characterization shows that the prepared ZnS:Mn-MAA nanoparticles absorb at 307 nm and fluoresce at 570 nm. XRD and HR-TEM measurements reveal that the nano-

crystals have a zinc-blende structure with a mean particle diameter of 3.8 nm. Raman spectral analysis and DFT calculations suggest that MAA is deprotonated at both its thiol and carboxylic acid groups and that the thiolate group is bound to nanoparticle surfaces.

Supporting Information. Detailed DFT calculation results are available *via* the internet at *http://www.kcsnet.or.kr/bkcs*.

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