

Phase transition of ZnS nanocrystallites induced by surface modification at ambient temperature and pressure confirmed by electron diffraction

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Pentafluorothiophenol, thiophenol, 1-decanethiol, 1-hexanethiol, benzoic acid and cyanoacetic acid, which are confirmed to bind to the surface of ZnS nanocrystallites, induce phase transition of ZnS nanocrystallites from the hexagonal to the cubic phase, with retention of the crystalline size of 3 nm at ambient temperature and pressure.

The crystalline structure of quantum-confined semiconductor nanocrystallites is one of the important factors for determining their photophysical properties.¹ Generally, the difference in the crystalline structure of the solid leads to considerable change in the effective masses of electrons and holes in their electronic bands.² Although it is important to control the crystalline structure of semiconductor nanocrystallites with a definite size, phase transition whilst retaining their size has not been reported at ambient temperature and pressure. There are only a few reports concerning phase transitions at high pressure.³ Generally, the surface of nanocrystallites plays a dominant role in determining the thermodynamics of the system because of their large surface-to-volume ratios. We recently revealed that coordination of solvent molecules, such as *N,N'*-dimethylformamide (DMF), to the surface of CdS⁴ or ZnS⁵ nanocrystallites also plays a crucial role in stabilizing nanocrystallites. In such systems, the crystalline structure as well as size of the CdS⁶ or ZnS⁷ nanocrystallites differs with the choice of solvent used for preparation. Here, we report the first control of the crystalline structure of size-controlled nanocrystallites at ambient temperature and pressure by surface modification.

As reported previously,⁵ transparent colloidal ZnS nanocrystallites (ZnS–DMF) were prepared by introducing H₂S gas to a DMF solution (5 ml) of Zn(MeCO₂)₂·2H₂O (5 mM) with vigorous stirring on an ice bath. After purging ZnS–DMF with N₂ gas for 1.5 h to remove unreacted H₂S, a DMF solution (5 ml) of an organic molecule (2.5 mM), such as thiol, carboxylic acid, or phenol, was added into the 5 ml N₂-purged ZnS–DMF solution ([Zn] = 5 mM) with stirring on an ice bath for 30 min. Normalized absorption spectra of the ZnS–DMF solution after combination with the organic molecules were the same as those before the combination,⁵ indicating that dissolution or growth of the ZnS nanocrystallites in DMF is negligibly small (the change of the size should be within a few Å) under the experimental conditions. The resulting transparent solution was placed on a copper grid covered with amorphous carbon, and dried carefully *in vacuo* at room temp. for transmission electron microscopy (TEM) and electron diffraction measurements (Hitachi H-9000, operating at 300 kV) to determine the size and crystalline structure of the resulting ZnS nanocrystallites, respectively. Their size and crystalline structure did not depend upon the choice of the observed areas, and were not changed by the irradiation by the electron beam in the TEM measurements. FTIR spectra of the ZnS powders dried *in vacuo* were obtained on a Perkin Elmer 2000 FTIR spectrophotometer using the KBr method.

Fig. 1 shows typical TEM images and the size distributions of ZnS–DMF and ZnS–DMF combined with C₆F₅SH. TEM

observation revealed that both ZnS–DMF and ZnS–DMF combined with C₆F₅SH consisted of nanocrystallites with a mean diameter of *ca.* 3 nm. The size distribution and the mean diameter of the ZnS nanocrystallites (2.9 nm before combination) were not significantly changed after combination with the thiol (2.7 nm after combination). However, there lies a crucial difference in the crystalline structure between ZnS–DMF and ZnS–DMF combined with C₆F₅SH. In the electron diffraction pattern of ZnS–DMF [Fig. 2(a)], the apparent diffraction rings assigned to (100), (002), (101), (102), (110) and (103) of the hexagonal ZnS crystallites show that ZnS–DMF has a hexagonal crystalline structure. On the other hand, the diffraction rings assigned to (111), (200), (220) and (311) of cubic ZnS crystallites were observed, while the characteristic ring, (102), which was observed in the hexagonal ZnS crystallites, was not apparent for ZnS–DMF combined with C₆F₅SH [Fig. 2(b)]. The observation of the clear difference in the electron diffraction patterns indicates that the hexagonal structure of ZnS–DMF undergoes a phase transition when combined with C₆F₅SH, giving mainly (> 50%) the cubic phase at ambient temperature and pressure.⁸

It is seen that the crystalline structure of the resulting ZnS nanocrystallites depended on the choice of the added molecules (Table 1). All the thiols, *i.e.* pentafluorothiophenol, thiophenol, 1-decanethiol and 1-hexanethiol, induced the phase transition

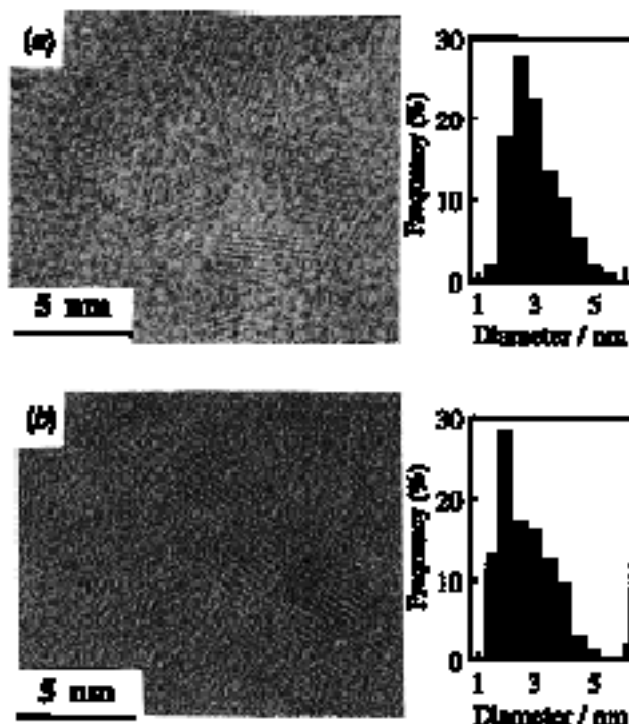


Fig. 1 TEM images and size distributions of (a) ZnS–DMF and (b) ZnS–DMF combined with C₆F₅SH

from the hexagonal to the cubic phase of the ZnS nanocrystallites without changing the crystallite size (3 nm). Additionally, the addition of carboxylic acid, *e.g.* benzoic acid and cyanoacetic acid, could also induce the phase transition. In contrast, combination with phenol, octanoic acid or acetic acid gave the same hexagonal phase as that of 'as-prepared' ZnS–DMF. The behavior of the phase transition depends on the pK_a value of the carboxylic acids and phenol. The carboxylic acids, *e.g.* benzoic acid ($pK_a = 4.19$) and cyanoacetic acid ($pK_a = 2.45$), which have lower pK_a values than acetic acid ($pK_a = 4.76$), were capable of inducing the phase transition, while neither acetic acid, octanoic acid ($pK_a = 4.89$), nor phenol ($pK_a = 9.89$) with higher pK_a values could induce the phase transition.⁹ On the other hand, the phase transition did not depend on the pK_a value of the thiols.¹⁰ These results suggest that the behavior of the phase transition is affected by interactions of the dissociated anions of the respective organic molecules with the surface of ZnS nanocrystallites.

The modified surface of the resulting ZnS nanocrystallites was characterized by FTIR spectroscopy. The surface zinc atoms of ZnS nanocrystallites in DMF are solvated by the oxygen atoms of DMF molecules, and interact with acetate anions derived from the starting zinc acetate;⁵ FTIR analyses of powdered ZnS–DMF combined with carboxylic acid revealed that benzoate and cyanoacetate anions coordinated to the surface of ZnS nanocrystallites *via* the oxygen atoms since the peaks assigned to the C=O stretching vibration of the carboxylate (benzoate, 1536 cm^{-1} ; cyanoacetate, 1623 cm^{-1}) were shifted to lower frequency than those of the free carboxylic acids (benzoic acid, 1688 cm^{-1} ; cyanoacetic acid, 1736 cm^{-1}). In contrast, non-coordination of phenol, octanoic acid and acetic acid molecules was confirmed by FTIR spectra. These observations lead to the conclusion that the phase transition could be induced only when the added molecules react with the surface of ZnS nanocrystallites to form covalent or ionic bonds. For

carboxylic acids with lower pK_a values than that of acetic acid, they must dissociate into the corresponding carboxylate anions in basic DMF to an appreciable extent; the carboxylate anions then coordinate to the ZnS nanocrystallite surface, resulting in the phase transition. On the other hand, since a thiolate anion has high nucleophilicity as a soft base, the thiolate anion readily binds to the surface zinc atom which is a soft acid, even when the concentration of the dissociated thiolate is low.¹¹ As a consequence, the phase transition of ZnS nanocrystallites was independent of the pK_a value of the thiol.

Generally, ZnS crystallizes to form the cubic structure at room temp. because the internal energy of the cubic phase is slightly lower than that of the hexagonal phase.¹² Thus, the hexagonal structure of ZnS–DMF must be formed due to the metastability caused by the effective coordination of DMF molecules to the ZnS nanocrystallite surface,⁵ which should stabilize the phase during growth. The formation of nanocrystallites with metastable crystalline structure is often observed.¹³ The formation of chemical bonds between the surface zinc atom of ZnS nanocrystallites and the added thiolate or carboxylate anion should lead to a change of the surface energy of ZnS nanocrystallites. This change of the surface energy could induce the phase transition from the metastable phase (hexagonal) to the stable phase (cubic) at ambient temperature and pressure, because the difference in the internal energy of ZnS between the hexagonal and the cubic phase is quite small (13.4 kJ mol^{-1}).¹² Further study is required for quantitative description of the surface energy to induce the phase transition.

In conclusion, control of crystalline structures of quantum-confined semiconductor nanocrystallites was achieved at ambient temperature and pressure through the phase transition from the hexagonal to the cubic structure by the chemical modification of the ZnS nanocrystalline surface with organic molecules for the first time.

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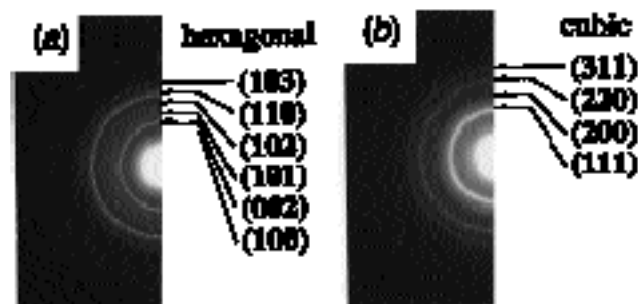


Fig. 2 Electron diffraction patterns of (a) ZnS–DMF and (b) ZnS–DMF combined with $\text{C}_6\text{F}_5\text{SH}$

Table 1 Dependence of crystalline structure of ZnS nanocrystallites on adding reagents

Added reagent	pK_a in water ^a	pK_a in DMF ^b	Crystalline structure
None			Hexagonal
$\text{C}_6\text{F}_5\text{SH}$	< 6.615 ^c		Cubic
$\text{C}_6\text{F}_5\text{SH}$	6.615 ^d		Cubic
$\text{C}_{10}\text{H}_{21}\text{SH}$	<i>ca.</i> 10 ^e		Cubic
$\text{C}_6\text{H}_{13}\text{SH}$	10.3 ^d		Cubic
$\text{CH}_2(\text{CN})\text{CO}_2\text{H}$	2.45 ^f		Cubic
$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	4.19 ^f	12.3	Cubic
$\text{CH}_3\text{CO}_2\text{H}$	4.76 ^f	13.5	Hexagonal
$\text{C}_7\text{H}_{15}\text{CO}_2\text{H}$	4.89 ^f		Hexagonal
$\text{C}_6\text{H}_5\text{OH}$	9.89 ^f	> 16	Hexagonal

^a Acidic dissociation constants in water at 25 °C. ^b Acidic dissociation constants in DMF at 25 °C. See ref. 14. ^c The value of pK_a of $\text{C}_6\text{F}_5\text{SH}$ must be lower than that of $\text{C}_6\text{H}_5\text{SH}$ because of the higher electronegativity of $\text{C}_6\text{F}_5\text{S}^-$. See ref. 15. ^d See ref. 10. ^e The value of pK_a of $\text{C}_{10}\text{H}_{21}\text{SH}$ must be the nearly same as that of $\text{C}_6\text{H}_{13}\text{SH}$. ^f See ref. 9.

Notes and References

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