A New Evidence of the Thermodynamically Stable Nanophase: CdS in 4M KOH-tert-butanol solution

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Supplementary Information

Nanoparticle Synthesis and Transformation. 3 nm CdS nanoparticles were synthesized in water by the dropwise addition of 0.1 M Na2S to 0.1 M CdCl2 at room temperature. 9 nm CdS was purchased from Aldrich. Bulk CdS was obtained by treating 3 nm nanocrystalline CdS in vacuum for 3 day at 850 °C. CdS nano-sheets were obtained by treating 3 nm, 9nm, and bulk CdS in 4M KOH-tert-butanol solutions (2.24g KOH and 10ml tert-butanol) at 180°C and in hydrothermal autoclaves. The times for sample treatment are prolonged to ensure the attained products present the characteristic nanostructures. After hydrothermal treatment, samples were quenched to room temperature. The solid material was separated by centrifuging and quickly washed with excess water and ethanol to remove the basic solution, without altering the nanosheets. CdS is poorly soluble in KOH-tert-butanol solutions, and we ensured that CdS was present in excess in each experiment.

X-ray Diffraction. A PANalytical X’Pert PRO diffractometer with Cu KR radiation (45 kV, 40 mA) was used to identify the crystal structures of initial and treated samples. If the full width at half-maximum (fwhm) intensity of each peak equal to the machine resolution, the sample can be regarded as bulk material.

Scanning Electron Microscopy. SEM analyses were performed using LEO-1530 scanning electron microscopy (SEM) equipped with an Oxford-INCA energy dispersive X-ray (EDX) spectroscopy. Samples were prepared for SEM study by dispersing CdS powders onto a silicon die support.

High-Resolution Transmission Electron Microscopy. HRTEM analyses were performed using a JEOL JEM2010 HRTEM. Samples were prepared for HRTEM study by dispersing CdS powders onto a holey carbon support.

To check the solubility of CdS in different concentration under prolonged coarsening times, the autoclave containers were taken out and quenched to room
temperature; the clear supernatants was quickly extracted and further centrifuged once. This whole process was done within 4-5 min. After that, the content of cadmium in the whole sample was detected by inductively coupled plasma (ICP) (Ultima2).

**Supplementary Figure S1.** Electron Microscopy images for Initial sample of CdS. 

a) TEM image of 3nm CdS ; b) TEM image of 9nm CdS ; c) SEM image of bulk CdS.

**Supplementary Figure S2.** Electron Microscopy images of 3nm CdS coarsening in 2M KOH-tert-butanol solution at 180 °C for 25 days . a) ,b) TEM image of the sample ; c) SEM image of the sample. The TEM and SEM images show out 3nm CdS grew into bulk material after coarsening.
**Supplementary Figure S3.** a) Typical AFM images of nanosheets from 3nm CdS coarsening in 4M KOH-tert-butanol solution at 180 °C for 7 days. b) Size distribution of thickness of the monolayer nanosheets from AFM measurements. The fragments of monolayer nanosheets were obtained by a powerful ultrasonic treatment. AFM measurements indicate the average thickness of a single nanosheet is about 8.5 nm.( thickness based on the statistics of 30 fragments )

**Supplementary Figure S4.** Illustration of a possible mechanism of the formation of nano-sheet stackings (including SEM measurements). SEM of the nano-sheet stackings from damaged side face.

As shown in Figure S4, the formation of nano-sheet stackings may be described by a model in which (001) faces of CdS nano-sheets provide nucleation sites for the coalescence of other nano-sheets. Figure 1d show that the concentration of Cd$^{2+}$ increase with the KOH concentration, the (001) faces of CdS may adsorb more KOH, that means the concentration of Cd$^{2+}$ would be much higher on the (001) faces of CdS. Usually, the growth of nanomaterials is spontaneous in the solution, with the thermal perturbation, crystal nucleation would be favored to occur in the area with high concentration. Thus in the systems, the probability of crystal nucleation on the (001) faces would be much higher and the nano-sheets would be favor to coalesce. As
shown schematically above, these simple assumptions appear reasonable for a good qualitative description for the observed nano-sheet stackings.

Supplementary Figure S5. XRD data of the 20nm ZnS and bulk ZnS treating in 4M KOH-tert-butanol solution at 180 °C for 14 days. The resulting sample was separated by centrifuging and quickly washed with excess water and ethanol to remove the basic solution, the XRD data show that the nanophase materials obtained by the hydrothermal treatment of ZnS in 4M KOH-tert-butanol solution at 180 °C are equivalent whether 20 nm ZnS nanoparticles or bulk ZnS are chosen as the starting material.

Supplementary Figure S6. XRD data of the 3nm CdSe and bulk CdSe treating in 4M KOH-tert-butanol solution at 180 °C for 60h. The resulting sample was separated by centrifuging and quickly washed with excess water and ethanol to remove the basic solution, the XRD data show that the nanophase materials obtained by the hydrothermal treatment of CdSe in 4M KOH-tert-butanol solution at 180 °C are equivalent whether 3 nm CdSe nanoparticles or bulk CdSe are chosen as the starting material.