CdPd Sulfide Heterostructured Nanoparticles with Metal Sulfide Seed-Dependent Morphologies

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Seed-mediated growth synthesis has provided us with anisotropically phase-segregated CdPd sulfide heterostructured nanoparticles with seed-dependent morphologies and crystal structures.

Recently, anisotropically phase-segregated heterostructured nanoparticles (NPs) have become accessible and received much attention.[1] The close coupling of different components on the nanoscale may significantly improve the application performance, or even create new properties.[2] Especially, a combination of distinct metal chalcogenide NPs would have great potential for various photo-related applications.[3] They may also serve as building blocks for complex nanostructures in nanodevices.[4] Recently, we reported anisotropically two and three phase-segregated metal sulfide NPs consisting of Co_9S_8 and PdS_x (CoPd sulfide NPs).[5, 6] On the basis of our proposed mechanism for the formation of CoPd sulfide NPs in which the crystalline Co_9S_8 phases anisotropically grow on the amorphous PdS_x seed NPs, the PdS_x NPs are the key material for the formation of anisotropically phase-segregated heterostructures.[5, 6] Thus various metal sulfides NPs have potentials as seeds for the designed synthesis of heterostructured metal sulfide NPs with seed-dependent morphologies. Herein, in the light of structural control, we report on the synthesis of unique CdPd sulfide heterostructured NPs by means of the PdS_x and CdS seed-mediated growth methods. Flower-shaped NPs were generated through an interesting crystal structural transformation of amorphous PdS_x seeds into crystalline Pd_xCd_yS induced by cation exchange of Cd^{2+} ions with Pd^{2+} ions. Dumbbell-shaped NPs were formed via linking CdS seeds with small single PdS_x phase, this mechanism being applicable to obtain CdS nanorod chains.

First, the PdS_x seed-mediated growth reaction was carried out to produce PdS_x-CdS heterostructured NPs. Amorphous PdS_x seed NPs of 5.4±0.8 nm in size (Fig. 1a) were synthesized according to our previous work.[6] The PdS_x seeds were reacted with di-*n*-octylether solution containing $Cd(acac)_2{\bullet}xH_2O$ and 1-octadecanethiol ($C_{18}SH$) at 260 °C for 120 min to form the flower-shaped heterostructures (nanoflowers, NFs) as shown in Fig. 1b. It was found from the 2D projection of TEM image that NFs had the faceted dark cores with one to four bright petals of 3 nm (Fig. S1, ESI[†]). Local chemical compositional analysis of a single NF measured by nano-spot energy-dispersive X-ray (EDX) spectroscopy showed that the dark cores had the Pd-rich Pd_xCd_yS phases and the bright petal were composed of CdS (Fig. S2, ESI[†]), suggesting that the Cd^{2+} ions were replaced with Pd^{2+} ions in the PdS_x phases and the nucleation of CdS occurred on the Pd_xCd_yS cores. The size of Pd_xCd_yS cores is similar to that of PdS_x seeds.

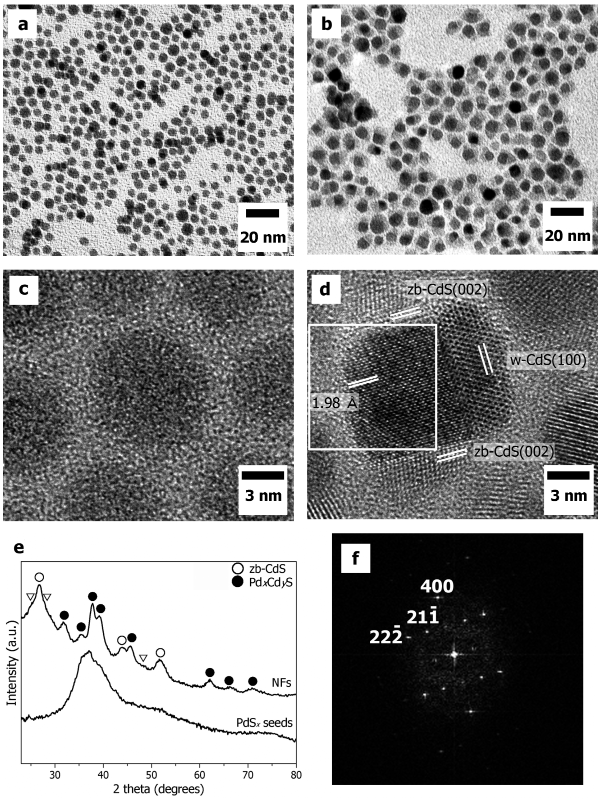

Fig. 1 (a,b) TEM and (c,d) HRTEM images of (a,c) PdS_x seed NPs and (b,d) NFs. (e) XRD patterns of PdS_x seed NPs and NFs. Inverted triangles are assigned to wurtzite-CdS. (f) FFT pattern of rectangular region of (d). Depicted Miller indices of Pd_xCd_yS phase are based on a cubic system.

The fraction of the NFs consisting of one, two, three, and four petals were estimated to be 44, 34, 20, and 2%, respectively.

Crystal structure of CdS/Pd_xCd_yS (CdPd sulfide) NFs was investigated by high-resolution TEM (HRTEM) and X-ray diffraction (XRD). The HRTEM observation revealed that the CdS phases possessed both a zincblende structure with stacking faults and a minor fraction of a wurtzite structure (Figs. 1d and S3, ESI[†]). XRD patterns of NFs also demonstrated that the amorphous PdS_x phases completely disappeared and were transformed into crystalline phases and that the CdS phases of NFs were composed of a mixture of zincblende and a small amount of wurtzite (Fig. 1e). The CdS/Pd_xCd_yS interfacial lattice planes of CdS phases correspond to zincblende(*zb*)-CdS (002), (111) and wurtzite(*w*)-CdS (100). Interestingly, the PdS_x seed NPs are amorphous, although Pd_xCd_yS phases have a crystalline nature (Figs. 1c-e). An ionic crystal containing the elements Cd,

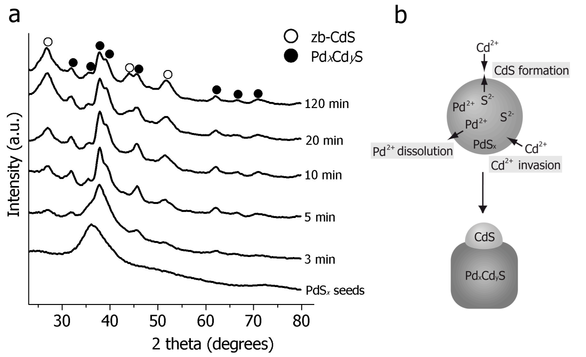

Fig. 2 (a) XRD patterns of CdPd sulfide NFs at various reaction times. (b) Schematic illustration of the formation mechanism of NFs.

Pd and S is not identified in the *Powder Diffraction File* (JCPDS-ICDD). From the detailed HRTEM and fast Fourier transformation (FFT) investigations (Fig. S3, ESI†), we assumed that the Pd_xCd_yS phase belongs to a cubic crystal system with a lattice constant of 7.92 Å. Actually, this assumption of Pd_xCd_yS crystal structure can well explain the diffraction peaks at 2θ = 31.9°, 39.2°, 45.8°, 66.2°, and 71.0° (Fig. 1e and Table S1, ESI†). The detailed crystal structure of the Pd_xCd_yS phase is under investigation using synchrotron-XRD and EXAFS measurements and will be reported in the forthcoming paper.

Next, the formation mechanism of CdPd sulfide NFs was investigated. Although CdS can nucleate independently in the same reaction condition for NF synthesis (Fig. S4, ESI†), the CdS phases preferentially grow on the PdS_x seeds (isolated CdS NPs are rarely observed). This result indicates that the PdS_x seeds behave as the preferential growth substrates for CdS, probably because the CdS phases grow through a sulfur transfer from PdS_x seeds to the Cd precursor, as observed in PdS_x/Co_9S_8 system.[5, 6] Actually, a control experiment of PdS_x seed-mediated growth without an addition of alkanethiol (a sulfur precursor) also demonstrated both the CdS growth on the PdS_x seeds and the formation of Pd_xCd_yS phases (Fig. S5, ESI†), which indicates that the CdS phases nucleate by consuming S^{2-} ions in the PdS_x seeds. It is quite interesting that the crystal structural transformation from amorphous PdS_x to crystalline Pd_xCd_yS phases is induced by the cation exchange of Cd^{2+} ions with Pd^{2+} ions in PdS_x seeds (cf., the cation exchange of smaller Co^{2+} ions does not occur[6]) and that S^{2-} ions subsequently diffuse from the PdS_x seeds to the outside to form the CdS phases. Change in XRD patterns of CdPd sulfide NFs with reaction time demonstrates that the CdS phases grow on the initially-formed Pd_xCd_yS phases (Fig. 2a). X-ray photoelectron spectroscopic analysis revealed that the elements Pd and Cd in Pd_xCd_yS phases were in divalent state (Fig. S6, ESI†), strongly suggesting that the Pd^{2+} ions dissolve into the solution in the course of both the Cd^{2+} invasion and S^{2-} diffusion keep the charge balance of Pd_xCd_yS phases (Fig. 2b).

On the basis of the fact that the CdS phases preferentially bind to Pd_xCd_yS phases as discribed above, an effort has been made on a further development of the seed-mediated growth method, in which the CdS NPs were used as seed NPs. In the CdS seed-mediated growth reaction, nearly spherical *w*-CdS seed NPs (10.2±2.5 nm, Fig. 3a) were synthesized according to literature protocols.[7] The reaction of the CdS seeds with $Pd(acac)_2$ and $C_{18}SH$ at 260 °C for 180 min predominantly gave the dumbbell-shaped $CdS/PdS_x/CdS$ NPs (nanodumbbells, NDs), two CdS phases connected by one PdS_x phase, as shown in Fig. 3b. More than 80 % of the NPs had dumbbell-shape (Fig. S7, ESI†), and the average size was 20 nm (length) × 10 nm (width), the size of CdS seeds (10.3±1.9 nm) being almost preserved.

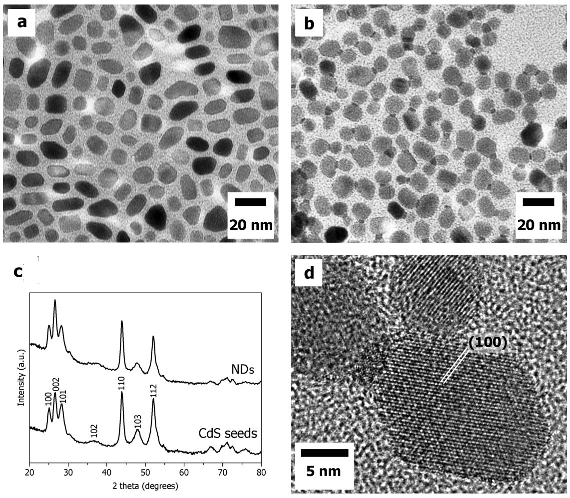

Fig. 3 TEM images of (a) CdS seed NPs and (b) NDs. (c) XRD patterns of CdS seed NPs and NDs. (d) HRTEM image of a single ND.

In the XRD pattern of NDs, the diffraction peaks from *w*-CdS phases were mainly observed even after the PdS_x growth on the CdS seeds (Fig. 3c). The peaks from the PdS_x phases were not detected owing to their smaller volume than *w*-CdS phases (CdS/PdS_x volume ratio is estimated to be ~26.7). According to the HRTEM observation of NDs, an interfacial lattice plane of *w*-CdS phase was (100) planes of *w*-CdS, as observed in NFs (Fig. 3d). Contrary to the NFs, the Pd-rich phases of NDs were *amorphous*-PdS_x, because the Cd^{2+} ions of CdS seeds could not diffuse into newly-grown PdS_x phases. For comparison, we synthesized similar dumbbell-shaped heterostructures by the one-pot synthesis (see experimental details in ESI†), in which the CdS phases were grown on the preformed PdS_x NPs to form dumbbell structures. These dumbbell-shaped NPs have *zb*-CdS/crystalline Pd_xCd_yS/*zb*-CdS structure (Fig. S8, ESI†), which supports our claim that the formation of Pd_xCd_yS phases takes place only when the amorphous PdS_x NPs react with Cd^{2+} ions dissolved in solution.

Next, the formation mechanism of NDs was investigated. On the way to form the NDs, the NP dimers consisting of small PdS_x (1~2 nm) and large CdS phases were obtained when the CdS seed-mediated growth reaction was stopped at 10 min (Fig. 4b). After annealing the purified $CdS\text{-}PdS_x$ dimers with an excess amount of oleic acid and oleylamine at 260 °C for 60 min, almost all the dimers (> 90 %) were converted into dumbbell-shaped NPs as shown in Fig. 4c (an excess amount of surfactants were added for preventing the fusion of CdS phases). Note that further Pd and Cd precursors were not added, meaning that no further crystal growth occurred in this annealing process. This result indicates that the dumbbell-structures are generated by fusing two PdS_x phases of $CdS\text{-}PdS_x$ dimers, as observed in the formation of peanut-shaped $PdS_x/Co_9S_8/PdS_x$ NPs.[6] However, another mechanism including an attachment of PdS_x phases of dimers to

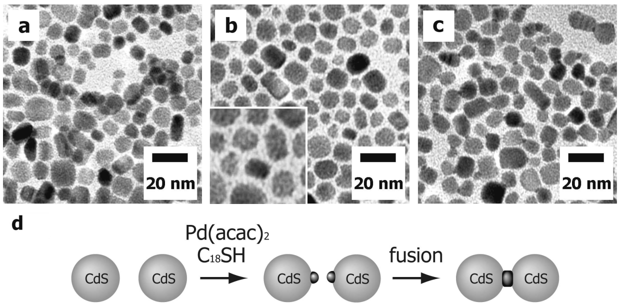

Fig. 4 TEM images of (a) CdS seed NPs, (b) CdS-PdS$_x$ dimers, and (c) CdPd sulfide NDs obtained by annealing CdS-PdS$_x$ dimers. (d) Schematic illustration for the formation mechanism of NDs.

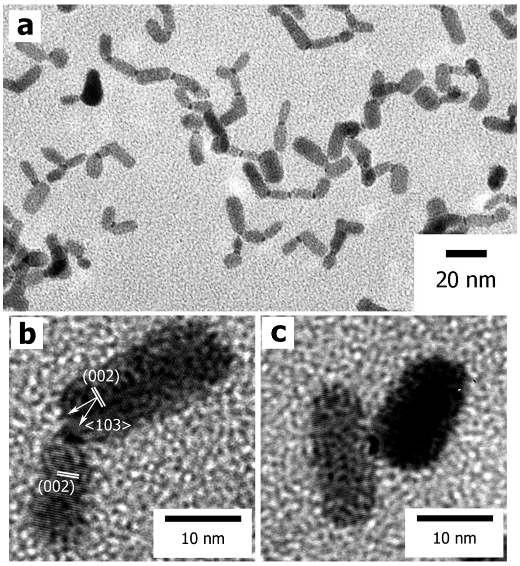

Fig. 5 (a) TEM image of CdPd sulfide nanochains. (b) HRTEM image of CdPd sulfide nanochain focused on the interface of CdS/PdS$_x$ phases. (c) HRTEM image of T-shaped CdPd sulfide heterostructures.

the surface of isolated CdS NPs also should be considered. In order to confirm this possibility, the mixture of the same amount of CdS-PdS$_x$ dimers and CdS NPs were heated at the same annealing condition (Fig. S9, ESI†). As a result, a large amount of free-standing CdS NPs was observed, which indicates that the fusion of PdS$_x$ phases is responsible for the formation of NDs (Fig. 4d).

By utilizing this formation mechanism, the self-assembly of CdS nanorods (NRs) was carried out via a linkage of CdS NRs with PdS$_x$ phases. CdS NRs (6 × 16 nm, Fig. S10, ESI†) were synthesized using the reported procedure.[7] The CdS NR seed-mediated growth reaction was carried out in the same condition of spherical CdS seed-mediated growth reaction. As shown in Fig. 5a, PdS$_x$ phases grew preferentially at either end of CdS NRs and fused to link NRs, resulting in the formation of one-dimensional chains. The longest CdPd sulfide nanochains have the length longer than 50 nm aligning more than four CdS NRs. In this case, interfacial planes of CdS seeds were *w*-CdS (103) or (002) planes, which was different from the case of NDs (*w*-CdS (100)), probably due to a nonepitaxial growth of PdS$_x$ on the CdS seeds. Because the side walls of NRs may be strongly protected by H$^+$, the reactivity of side walls is lower than that of both ends,[7, 8] leading to the selective growth of the PdS$_x$ phases on either end of NRs. A minor fragment of T-shaped heterostructures were also observed, which resulted from the PdS$_x$ growth on the highly reactive defect site on the side wall of CdS NRs (Fig. 5c).

In conclusion, we have demonstrated that the CdPd sulfide heterostructured NPs with metal sulfide seed-dependent morphologies can be selectively synthesized from the various seed-mediated growth methods. These results exhibit that various metal sulfide can be candidates as building blocks for creating the desired functional heterostructured NPs. We are currently studying the structure-specific functions of these new NPs such as a directed self-assembly.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, charaterization techniques, TEM and STEM-HAADF images, HRTEM images, corresponding FFT patterns, and nano-spot EDX results of NFs, TEM image of CdS NPs in the absence of PdS$_x$ seed-NPs, TEM and XRD of CdPd sulfide NPs without an addition of alkanethiol, XPS spectra of Pd$_x$Cd$_y$S phases, and TEM images of NDs and CdS nanorods. See DOI: 10.1039/b000000x/

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