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Nanostructures

Anisotropically Phase-Segregated Pd–Co–Pd Sulfide Nanoparticles Formed by Fusing Two Co–Pd Sulfide Nanoparticles**

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As the primary structures of inorganic nanoparticles, such as size and shape, determine their physical and chemical properties, the control of such structures is prerequisite for both the elucidation of structure-dependent properties and the direct assembly of hierarchical structures.[1–8] When a nanoparticle consists of two distinct chemical species, the distribution of chemical species becomes another determinant for its properties and functions.[9–11] In general, this chemical synthesis provides us with chemically disordered alloys or core–shell structures, in which two distinct chemical species isotropically distribute. Recently, anisotropically phase-segregated nanoparticles have become accessible and received much attention as a result of two important features. First, one can simultaneously utilize two different functions such as luminescence and magnetic properties. Second, two distinct functional ligands can be anisotropically arranged at the surface of these particles, thus leading to a directed assembly of micro- and nanostructures. These materials could either be a plasmonic metal and a semiconductor, a plasmonic metal and a magnetic oxide, or other combinations.[12–19] Among them, a combination of distinct metal chalcogenide nanoparticles would have great potential for various applications, including biological labeling, light-emitting diodes, and so on.[18] Recently, we succeeded in the spontaneous formation of anisotropically phase-segregated Co–Pd sulfide acorn-shaped nanoparticles ("nanoacorns").[20] Here we report the synthesis and characterization of a new type of Pd–Co–Pd sulfide heterostructured nanoparticle based on PdS_x seed-mediated growth and demonstrate that this method has a potential to yield various anisotropically phase-segregated heterostructures.

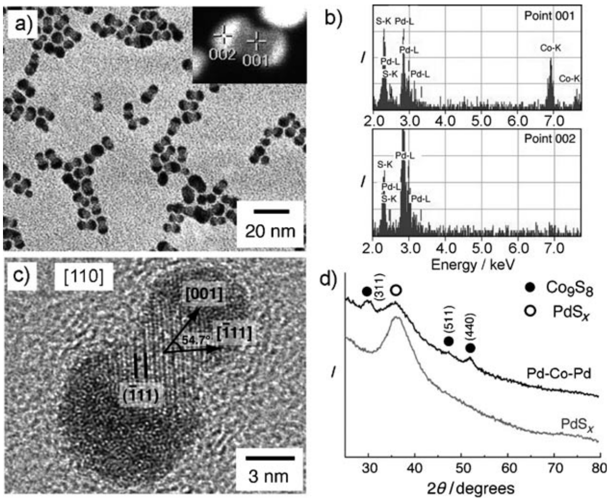

Figure 1. a) TEM image of Pd–Co–Pd sulfide peanut-shaped nanoparticles (inset: STEM-HAADF image). b) EDX spectra of the bright and dark regions of the nanoparticles marked by crosses and labeled as 001 and 002 in the inset to part (a). c) High-resolution (HR)-TEM image of a single peanut-shaped nanoparticle observed in the [110] direction. d) XRD patterns of PdS_x and Pd–Co–Pd sulfide nanoparticles.

On the basis of our proposed mechanism for the formation of Co–Pd sulfide "nanoacorns", in which the Co_9S_8 phases anisotropically grow from preformed PdS_x nanoparticles, the PdS_x nanoparticles are the key material for the formation of heterostructures.[20] Accordingly, the PdS_x seed-mediated synthesis of anisotropically phase-segregated nanoparticles was carried out. The relatively monodisperse PdS_x nanoparticles of (5.6 ± 1.0) nm in size were synthesized as seeds by making use of the spontaneous cleavage of the C–S bonds of 1-octadecanethiol ($C_{18}SH$) on the surfaces of the Pd nanoparticles (see Figure S1 in the Supporting Information).[21,22] The Co_9S_8 phases were anisotropically grown on the surface of the purified PdS_x seeds. Figure 1a shows a low-magnification transmission electron microscopy (TEM) image of the resulting nanoparticles. The peanut-shaped nanoparticles ("nanopeanuts"), made up of bright phases with dark phases at either end and with an average size of approximately 10 nm × 5 nm (length × width), are predominantly observed together with a minor fragment of acorn-shaped nanoparticles, in which the size of the PdS_x nanoparticles is preserved. The compositional variation along the length of the nanopeanuts is apparent in the dark-field scanning transmission electron microscopy (STEM) image taken using a high-angle annular dark field (HAADF) detector (inset in Figure 1a). This Z-contrast image shows the brighter Pd species isolated in the ends and the darker Co species in the core of the peanut-shaped nanoparticles. Figure 1b presents nanospot energy-dispersive X-ray (EDX) spectra of the dark and bright phases of a peanut-shaped Pd–Co–Pd sulfide nanoparticle, as marked by crosses in the STEM-HAADF image. The nanospot EDX results

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confirms that the cobalt and palladium atoms are mainly located in the dark and bright phases in the STEM-HAADF image, respectively (see Table S1 in the Supporting Information). The Co/Pd molar ratio is estimated to be 43/57 from X-ray fluorescence analysis and is consistent with that of Co–Pd sulfide nanoparticles. The crystal structure investigation of these peanut-shaped nanoparticles, including HRTEM (Figure 1 c) and X-ray diffraction (XRD) measurements (Figure 1 d), reveals that the peanut-shaped nanoparticles have an amorphous PdS_x/crystalline Co_9S_8/amorphous PdS_x heterostructure, as is observed for Co–Pd sulfide acorn-shaped nanoparticles. From the detailed HRTEM study, two interfacial lattice planes of Co_9S_8 phases are concluded to be the (001) plane, in similar fashion to Co–Pd sulfide acorn-shaped nanoparticles, which strongly suggests that the Pd–Co–Pd sulfide peanut-shaped nanoparticles are formed from two Co–Pd sulfide nanoparticles by fusing the Co_9S_8 phases facing each other. In addition, when an equimolar ratio of $C_{18}SH$ and $[Co(acac)_2]$ was employed (acac = acetylacetonate), Pd–Co–Pd sulfide peanut-shaped nanoparticles formed predominantly when the $[Co(acac)_2]/[Pd(acac)_2]$ molar ratio was less than or equal to one, while only the aggregate of Co–Pd sulfide acorn-shaped nanoparticles was obtained with $[Co(acac)_2]/[Pd(acac)_2]$ molar ratios of two (see Figure S2 in the Supporting Information).

The growth process of the Pd–Co–Pd sulfide peanut-shaped nanoparticles was monitored by TEM measurements. After 10 min (Figure 2 a), the bright-contrast Co_9S_8 phases start to anisotropically grow from the dark-contrast PdS_x nanoparticle seeds, resulting in the formation of spherical Co–Pd sulfide acorn-shaped nanoparticles, with minor fragments of PdS_x nanoparticles and Pd–Co–Pd sulfide peanut-shaped nanoparticles (Table 1). As reported previously,[20] as Co_9S_8 nanoparticles are not formed in the absence of PdS_x phases and the C–S bonds of thiols are not cleaved at the surfaces of the Co_9S_8 phases, the free sulfur atoms are therefore supplied from the PdS_x phases and transferred to the Co phases to form the Co–Pd sulfide acorn-shaped nanoparticles. During the subsequent 20 min (Figure 2 b, c), the percentage of peanut-shaped nanoparticles increases with reaction time without significant growth of the bright-contrast Co_9S_8 phases of the Co–Pd sulfide acorn-shaped nanoparticles. After 40 min (Figure 2 d), almost all the particles are converted into Pd–Co–Pd sulfide peanut-shaped nanoparticles. This result implies that once the spherical Co–Pd sulfide “nanoacorns” are formed, the less-passivated Co_9S_8 phases of the “nanoacorns” are easily fused at their further growth stage in the $[00\bar{1}]$ direction to yield Pd–Co–Pd sulfide peanut-shaped nanoparticles. In the fusion process, two Co–Pd sulfide nanoparticles appear to fuse by facing each other with their Co_9S_8 phases aligned in the same crystallographic orientation (Figure 2 e and Figure S3 in the Supporting Information).

Table 1: Distribution of nanostructured materials with reaction time (see also Figure 2).

Reaction time [min]	Distribution [%][a] PdS_x	Co–Pd	Pd–Co–Pd	others
10	52	21	27	trace
20	22	36	41	1
30	13	44	42	1
40	2	14	77	7

[a] Estimated by counting approximately 1000 particles.

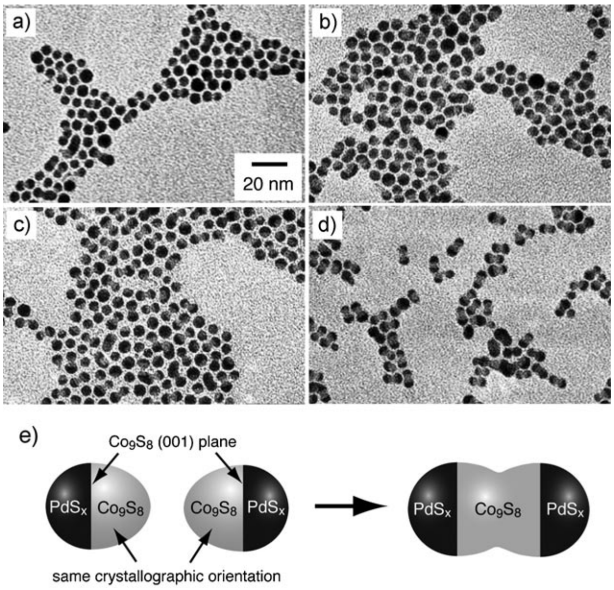

Figure 2. TEM images of Pd–Co–Pd sulfide nanoparticles, monitoring their growth process with time after heating: a) 10 min, b) 20 min, c) 30 min, and d) 40 min. e) Schematic illustration of the speculated formation mechanism of Pd–Co–Pd sulfide peanut-shaped nanoparticles.

The question now arises as to what condition promotes the fusion of the Co–Pd sulfide “nanoacorns” to form Pd–Co–Pd sulfide “nanopeanuts”. It was found that the Co_9S_8 phases of the Co–Pd sulfide nanoparticles were unstable in solution as a result of the comparatively lower passivation by thiols, leading to the precipitation of the Co_9S_8 phases and/or the partial coalescence of two Co_9S_8 phases.[23] We consider that the key factor that determines whether the fusion of two Co_9S_8 phases proceeds or not is the amount of the passivating agent, $C_{18}SH$, present when growing the Co_9S_8 phases. Figure 3 shows the TEM images of the resulting nanostructured materials obtained at $C_{18}SH/[Co(acac)_2]$ molar ratios of 2, 3, 5, and 10 (the amount of $[Co(acac)_2]$ was fixed at 0.25 mmol). Note that a near-equimolar amount of $C_{18}SH$ with respect to $[Co(acac)_2]$ is consumed as a sulfur source for the formation of the Co_9S_8 phases. When a molar ratio of two was employed, the peanut-shaped nanoparticles still formed as a main product (Table 2). As the molar ratio was raised to three, the acorn-shaped Co–Pd sulfide nanoparticles were predominantly generated with a minor proportion of the peanut-shaped Pd–Co–Pd sulfide nanoparticles. A further increase in the molar ratios led to the formation of the acorn-shaped Co–Pd sulfide nanoparticles only, with similar sizes to those obtained at $C_{18}SH/[Co(acac)_2] = 3$ (Figure 3 c, d). This tendency is true of 1-dodecanethiol when used as a protective agent in place of $C_{18}SH$ (see Figure S4 in the Supporting Information). It seems reasonable to conclude that the less-passivated Co–Pd sulfide acorn-shaped nanoparticles ($C_{18}SH/[Co(acac)_2] = 2$) easily form peanut-shaped Pd–Co–Pd sulfide nanoparticles through the fusion of two Co_9S_8 phases, whereas

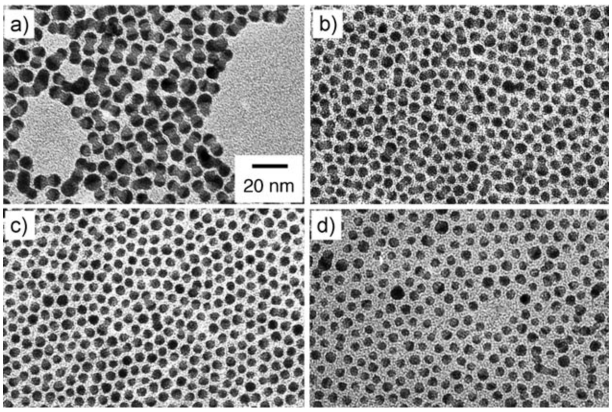

Figure 3. TEM images of Pd–Co–Pd sulfide peanut-shaped nanoparticles and Co–Pd sulfide acorn-shaped nanoparticles obtained at $C_{18}SH/[Co(acac)_2]$ molar ratios of a) 2, b) 3, c) 5, and d) 10.

Table 2: Distribution of nanostructured materials at different $C_{18}SH/[Co(acac)_2]$ ratios (see also Figure 3).

$C_{18}SH/[Co(acac)_2]$	Distribution [%][a]			
	PdS_x	Pd–Co	Pd–Co–Pd	others
2	2	33	47	18
3	3	63	29	5
5	4	77	17	2
10	4	82	11	3

[a] Estimated by counting approximately 1000 particles.

the fusion is suppressed for the "nanoacorns" synthesized at $C_{18}SH/[Co(acac)_2] = 3$ as a result of the sufficient passivation of Co_9S_8 surfaces by thiols (see Figure 4).

In conclusion, we have reported the synthesis and characterization of new heterostructured PdCoPd sulfide peanut-shaped nanoparticles based on the PdS_x seed-mediated growth method. Metal sulfide seed-mediated engineering is expected to result in many kinds of phase-segregated heterostructures and provide firm new mechanistic insights into the processes underlying nanostructure formation. Furthermore, the study on the structure-specific functions, such as a directed assembly of heterostructured nanoparticles, is currently in progress.

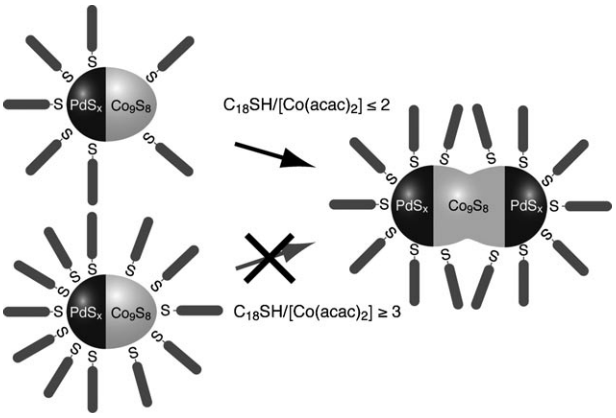

Figure 4. Schematic illustration of the synthesis of Pd–Co–Pd sulfide peanut-shaped nanoparticles and Co–Pd sulfide acorn-shaped nanoparticles using the PdS_x seed-mediated growth method.

Experimental Section

The Pd–Co–Pd sulfide peanut-shaped nanoparticles were synthesized by a seed-mediated growth method. The PdS_x seeds were first synthesized by heating a solution of $[Pd(acac)_2]$ (0.25 mmol), octadecanethiol ($C_{18}SH$, 0.25 mmol), and oleylamine (2.5 mmol) in di-*n*-octyl ether (5.0 mL) at 250°C for 30 min under nitrogen. After purification with mixed solvent (ethanol/hexane), the PdS_x seeds, $[Co(acac)_2]$ (0.25 mmol), and $C_{18}SH$ (0.25 mmol) were taken in di-*n*-octyl ether (10 mL). This mixture was heated at 230°C for 40 min under nitrogen and purified with mixed solvent (ethanol/hexane).

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