

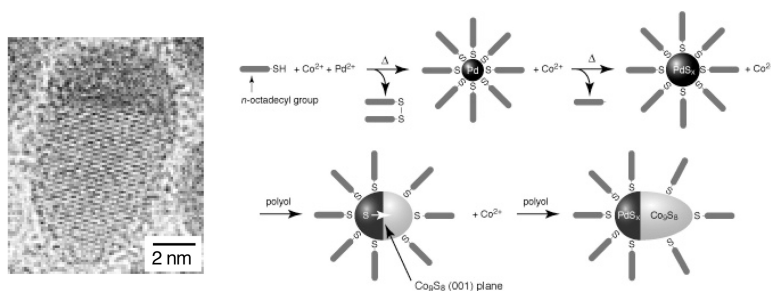
Communication

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Nanoacorns: Anisotropically Phase-Segregated CoPd Sulfide Nanoparticles

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Since the physical and chemical properties of inorganic nanoparticles are determined by their primary structures, such as size, shape, and crystallinity,¹ the control of such structures is quite important for both an elucidation of structure-dependent properties and an application of regularly ordered nanoparticles to nano-devices.² When a nanoparticle consists of two chemical species, the distribution of chemical species inside the particle becomes another determinant for its properties. Such nanoparticles are of standing interest since they can exhibit catalytic,³ electronic,⁴ optical,⁵ and magnetic^{2a,6} properties distinct from those of nanoparticles comprising the corresponding single-chemical species. In general, the nanoparticles with two chemical species obtained by the conventional chemical syntheses have either chemically disordered alloy or core-shell layered structure, both of which are isotropic in the light of phase segregation. If other phase-segregated structures could be spontaneously formed, we would obtain another factor to control the properties of nanoparticles. Through the systematic syntheses of nanoparticles composed of both 3d-transition metal and noble metal for their magnetic studies,⁷ we found that the anisotropically phase-segregated CoPd sulfide nanoparticles were spontaneously formed, in which one phase is made up of cobalt sulfide and another of palladium sulfide. These nanoparticles are named "nanoacorns" from their shape and difference in TEM contrast. Here we report the synthesis, structural analysis, and preliminary formation mechanism of CoPd nanoacorns.

The CoPd nanoacorns were synthesized by the reduction of $\text{Co}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Pd}(\text{acac})_2$ with 1,2-hexadecanediol in di-*n*-octyl ether in the presence of 1-octadecanethiol (C_{18}SH) (see Supporting Information for details). Figure 1a shows a low magnification TEM image of the resulting C_{18}S -protected nanoparticles. The acorn-shaped particles made up of both bright and dark phases having the average size of ~ 14 nm (length) \times 10 nm (width) and the Co/Pd atomic ratio of 40/60 were predominantly observed together with a minor fragment of spherical dark particles. Figure 1b presents nanospot energy-dispersive X-ray (EDX) spectra on the light and dark phases of nanoparticles marked by circles in the enlarged TEM image in Figure 1a. The EDX results of 2.84 keV (Pd L_{α}), 2.99 keV (Pd L_{β}), 6.93 keV (Co K_{α}) and 7.65 keV (Co K_{β}) confirmed that the cobalt and palladium atoms were located at the light and dark phases, respectively. At this stage, we predicted that the CoPd nanoacorns comprised the bright cobalt and dark palladium phases, as shown in Figure 1c.

In the next step, we investigated the crystal structure of CoPd nanoacorns. Figure 2a presents a HRTEM image of CoPd nanoacorns where the Co phases are crystalline, whereas the Pd phases seem to be amorphous. The optical diffractogram (Figure 2b) obtained by the Fourier transform of the crystalline Co phase within the rectangular region in Figure 2a is in good agreement with that

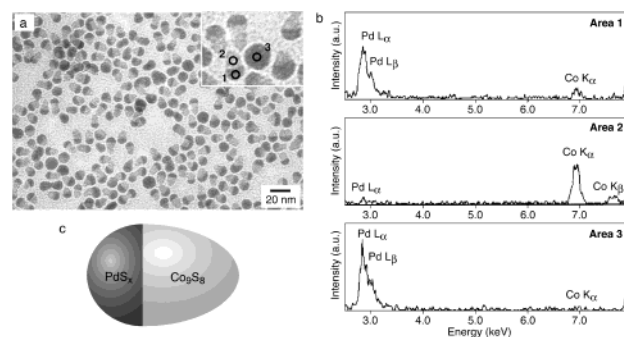


Figure 1. (a) TEM image of CoPd nanoacorns (inset, enlarged TEM image). (b) EDX spectra on bright and dark regions of nanoacorns and dark nanoparticles marked by circles in (a). (c) Schematic illustration of CoPd nanoacorn.

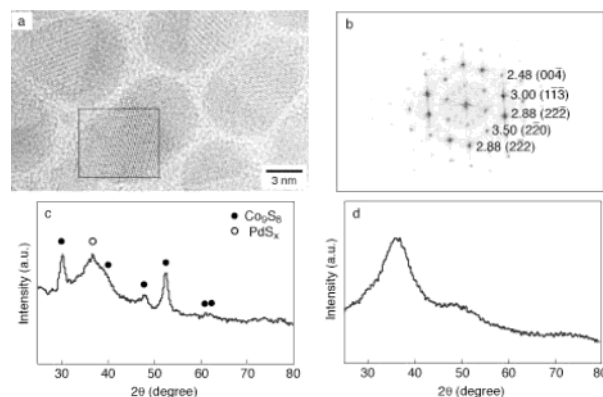


Figure 2. (a) High-resolution TEM image of CoPd nanoacorns. (b) Optical diffractogram obtained by the Fourier transform of the crystalline Co phase within the rectangular region in (a). (c,d) XRD patterns of CoPd nanoacorns and PdS_x nanoparticles.

of the Co_9S_8 (110) plane (see Figure S1). To support this result, we attempted to synthesize the Co_9S_8 nanoparticles in a similar fashion, but in vain, meaning that the Co phase grows in the presence of Pd phase, as described later. Then the powder X-ray diffraction (XRD) measurements were carried out. Figure 2c shows the XRD pattern of CoPd nanoacorns, in which several unidentifiable sharp ($2\theta = 29.9^\circ, 47.5^\circ, 52.2^\circ, 60.9^\circ, 61.7^\circ$), shoulder ($2\theta = 39.4^\circ$), and broad diffraction peaks ($2\theta = 36.4^\circ$) were observed. One shoulder and five sharp peaks are almost precisely attributed to the Co_9S_8 crystalline phase,⁸ which supports the above result. From the detailed HRTEM study (see Figure S2), the interfacial lattice plane of Co_9S_8 phase was concluded to be the (001) plane, the reason remaining to be determined.

Contrary to the cobalt case, the C_{18}S -protected Pd nanoparticles were formed in a polydisperse state (see Figure S3), and their XRD patterns (Figure 2d) also indicate the amorphous phase with the similar broad diffraction peak centered at $2\theta = 36.8^\circ$ similar to that in Figure 2c. Recently, Whitesides and co-workers have

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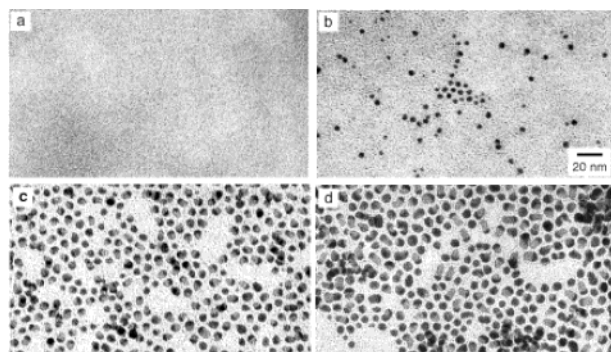


Figure 3. TEM images of CoPd nanoacorns taken for monitoring their growth process: (a) after 15 min heating, (b) after 20 min heating, (c) after 30 min heating, (d) after 40 min heating.

reported that the unknown palladium sulfide species are generated with the thickness of 1–2 nm at the palladium film surface after the spontaneous cleavage of the C–S bond of self-assembled alkanethiolates.⁹ Tsukuda and co-workers have also demonstrated the formation of the palladium sulfide interlayer at the surface of Pd nanoparticles prepared in the presence of C₁₈SH.¹⁰ Since our reactions have been carried out over 200 °C, it is easily speculated that the C–S bond of C₁₈S is cleaved at the surface of metallic palladium to liberate the sulfur atom, which transforms the Pd nanoparticles to the palladium sulfide ones with an unknown amorphous binary phase (Pd:S = ~2 from EDX quantitative analyses, see Table S1). The S(2p) XPS spectrum of the nanoacorns indicates the presence of sulfurs in both Co₉S₈ and PdS_x phases and those of C₁₈S present at the surface of the nanoacorns, respectively (see Figure S4). These results led us to the conclusion that the CoPd nanoacorns comprise both unknown amorphous PdS_x and crystalline Co₉S₈ phases. In this regard, the thiols are requisite to the formation of nanoacorns. In fact, the sulfur-free protective ligands do not give the nanoacorn formation, but other thiols, such as 1-octanethiol and 1-dodecanethiol, in place of C₁₈SH yield similar nanoacorns as well (see Figure S5).

Our next interest moves to the formation mechanism of the CoPd nanoacorns. First, the decrease in the metal precursors in di-*n*-octyl ether solution was monitored spectroscopically (see Figure S6). After heating the solution for 5 min, the charge-transfer band of Pd(acac)₂ at 328 nm completely disappeared without the significant decrease of Co(acac)₂·2H₂O peak at 272 nm, and the shoulder peak, presumably attributed to the charge-transfer band of palladium sulfide complexes, was observed at ca. 370 nm,¹¹ indicating that the Pd(II) ions were first reduced with C₁₈SH to yield very small Pd_n(SC₁₈)_m clusters.¹² Then the charge-transfer band of Co(acac)₂·2H₂O completely disappeared after 30 min (comparable with 20 min after an addition of 1,2-hexadecanediol). The growth process of nanoacorns has been also monitored by TEM measurement (Figure 3). Although we have confirmed no evidence for the formation of clearly observable nanoparticles within 15 min (Figure 3a), many dark contrast particles have been observed in the next 5 min (Figure 3b). Then the bright contrast Co₉S₈ phases have anisotropically grown from the dark contrast phases to form the nanoacorns after 30 min (Figure 3c). During the subsequent 10 min, the Co₉S₈ phases have grown longer in [001] direction to complete the CoPd nanoacorns formation (Figure 3d). This growth process of nanoacorns is roughly consistent with the UV–vis result. The formation of thermodynamically unfavorable nanoacorns means that the palladium surfaces are always required to produce the free sulfur

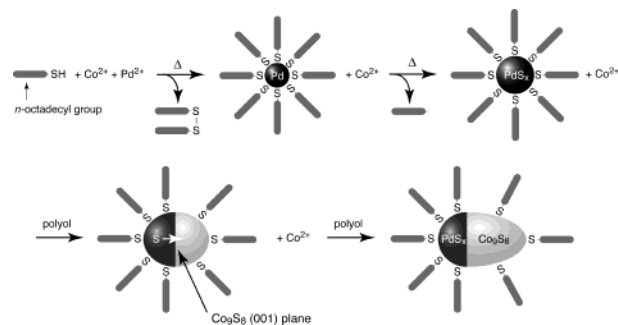


Figure 4. Schematic illustration of the speculated formation mechanism of the CoPd nanoacorns.

atoms and supply them to the cobalt phases. Consequently, we illustrate schematically the formation mechanism of the CoPd nanoacorns in Figure 4.

The results reported here provide the novel potentiality of chemical methods to control the phase-segregation manner of nanoparticles. The syntheses of various nanoacorns are in progress to provide the sort of firm new mechanistic insights into the processes underlying nanostructure formation more generally.

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Supporting Information Available: Synthetic procedure of CoPd nanoacorns, optical diffractogram of Co₉S₈ (110) plane, HRTEM images of nanoacorns, TEM image of PdS_x nanoparticles, EDX and XPS results of nanoacorns, TEM images of C₈S- and C₁₂S-protected nanoacorns, and UV–vis spectral change of nanoacorn solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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