Anisotropically Phase-segregated Co_9S_8/PdS_x Nanoacorns: Stability Improvement and New Heterostructures

Toshiharu Teranishi,*[1] Youhei Inoue,[2] Masaki Saruyama,[1] Masafumi Nakaya,[1] and Masayuki Kanehara[1]
[1]*School of Pure and Applied Chemistry, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8571*
[2]*Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043*

(Received December 22, 2006; CL-061495; E-mail: teranisi@chem.tsukuba.ac.jp)

Stability of anisotropically phase-segregated Co_9S_8/PdS_x nanoacorns, which we recently prepared, was improved by the addition of oleic acid or oleylamine as a stabilizer. Further investigations on the experimental conditions implied the formation of more complex $PdS_x/Co_9S_8/PdS_x$ and $Co_9S_8/PdS_x/Co_9S_8$ heterostructured nanoparticles.

Since the primary structures of inorganic nanoparticles 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.[1–6] Recently, anisotropically phase-segregated nanoparticles, which are different from the conventional alloy and core–shell bimetallic nanoparticles[7,8] in the phase-segregation manner, have been accessible and received much attention because of to both the simultaneous utilization of two different functions and the anisotropic arrangement of distinct functional ligands at the surface of particles.[9–14] 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.[13] Recently, we succeeded in the spontaneous formation of anisotropically phase-segregated Co_9S_8/PdS_x nanoparticles (nanoacorns),[15] whose instability in solution should be improved for further applications. Also, other experimental conditions should be investigated to generalize the processes underlying the heterostructure formation. Here, we report both the improvement of the stability of Co_9S_8/PdS_x nanoacorns and the findings of other new heterostructured nanoparticles.

The Co_9S_8/PdS_x nanoparticles with an acorn shape were prepared as follows. $Co(acac)_2 \cdot 2H_2O$ (0.5 mmol), $Pd(acac)_2$ (0.5 mmol), and 1-octadecanethiol ($C_{18}SH$, 1.0 mmol) were added in di-*n*-octyl ether (13.5 mL). After removing the oxygen under reduced pressure, the solution was heated at 220 °C for 10 min under nitrogen to completely dissolve the precursors and was kept to heat at ca. 240 °C for 30 min to complete the reaction. The black precipitate was obtained by the addition of ethanol (40 mL) to the resulting black solution and the subsequent centrifugation and redispersed in hexane (50 mL). The solution was bubbled by nitrogen and stored in the screw bottle. Compared to the previous preparation procedure,[15] the addition of 1,2-hexadecanediol was omitted, because the $C_{18}SH$ works as a reductant for Co^{II} ions (Figure S1).[16]

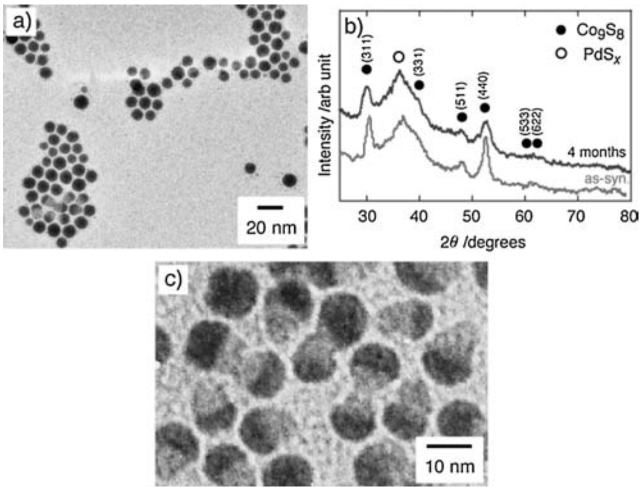

Figure 1. (a) TEM image and (b) XRD pattern of Co_9S_8/PdS_x nanoacorns dispersed in hexane after 4 months. (c) TEM image of $PdS_x/Co_9S_8/PdS_x$ heterostructured nanoparticles that were sometimes observed in the as-prepared sample.

The major drawback of the thiolate-passivated Co_9S_8/PdS_x nanoacorns is their unstability in solution. The chemical stability of nanoacorns was investigated both in solution and in a dry state. The Co_9S_8/PdS_x nanoacorns in hexane were relatively stable in a month, although, after a few weeks, some precipitates started to form both at the bottom and on the surface of the glass bottle. Figure 1a shows a TEM image of nanoparticles still dispersed in hexane after 4 months. We could predominantly observe the dark spherical PdS_x nanoparticles with a minor fragment of nanoacorns. It was found from the energy-dispersive X-ray (EDX) elemental analysis that the nanoparticles in solution were rich in Pd (Co/Pd $\approx$ 30/70) and, in contrast, the precipitates were rich in Co (Co/Pd $\approx$ 50/50–60/40) (Table S1).[16] This result is in good agreement with the TEM observation, giving consideration to the Co/Pd molar ratio of 40/60 for the as-prepared Co_9S_8/PdS_x nanoacorns. In the XRD pattern of the nanoparticles in hexane as shown in Figure 1b, the peaks assigned to the Co_9S_8 phase became small, also indicating the loss of Co_9S_8 phases. Therefore, it was concluded that the Co_9S_8/PdS_x nanoacorns in hexane were relatively unstable, and two phases were gradually separated to survive the PdS_x nanoparticles by the strong passivation of $C_{18}S$ and to precipitate the weakly passivated Co_9S_8 phases. Actually, in some cases, the Co_9S_8 phases coalesce with each other in hexane to form the $PdS_x/Co_9S_8/PdS_x$ heterostructure (Figure 1c), which implies the selective formation of new heterostructured $PdS_x/Co_9S_8/PdS_x$ nanoparticles by modifying experimental conditions.[17] In order to improve the stability of the Co_9S_8/PdS_x nanoacorns, an excess amount of oleic acid, oleylamine, trioctylphosphine, or 1-dodecanethiol was added to the hexane solution of nanoacorns. As shown in Figure 2, the stability of nanoacorns was drastically improved when using oleic acid or oleylamine owing to a strong stabilizing ability to the Co_9S_8 phases (especially to

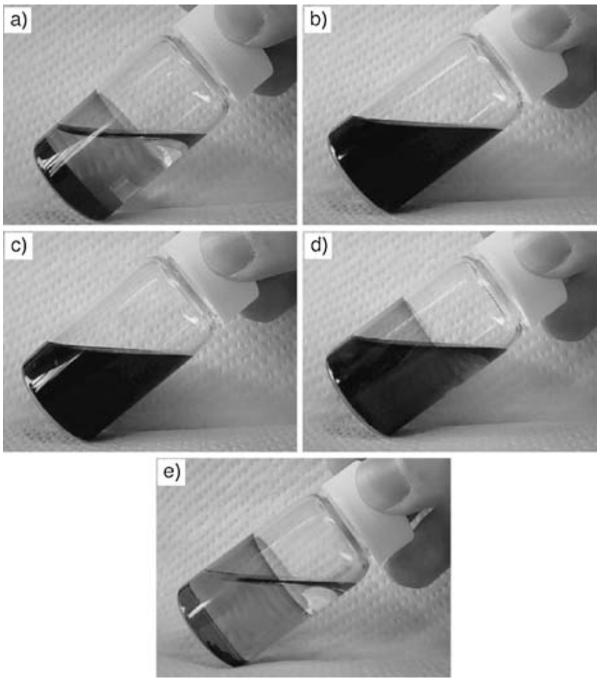

Figure 2. Photos of the Co_9S_8/PdS_x nanoacorns after 40 days. (a) as-prepared, (b)–(e) post-treated with an excess amount of (b) oleic acid, (c) oleylamine, (d) trioctylphosphine, (e) 1-dodecanethiol.

the surface cobalt ions).[18] On a contrary, the thiolate-passivated Co_9S_8/PdS_x nanoacorns immobilized on a TEM grid remain unchanged, indicating that the Co_9S_8/PdS_x nanoacorns are quite stable in a dry state.

It was found from the previous studies that the size of the Co_9S_8/PdS_x nanoacorns could be controlled from ≈7.5 nm (length) × 6.5 nm (width) to ≈14 nm (length) × 10 nm (width) by changing the kind of alkanethiols.[15] Then, we examined to change the volume ratio of Co/Pd phases within the Co_9S_8/PdS_x nanoacorns by altering the mole ratio of metal precursors. Figure 3a shows a TEM image of Co_9S_8/PdS_x nanoacorns prepared at the molar ratio of $Co(acac)_2{\cdot}2H_2O/Pd(acac)_2 = 1/2$ (total amount: 1.0 mmol). The polydisperse Co_9S_8/PdS_x nanoacorns with 7.5 nm (length) × 7.5 nm (width)–15 nm (length) × 12.5 nm (width) were observed. These nanoacorns have an acorn shape, and the volume ratio of Co/Pd phases was smaller than that for nanoacorns prepared at the Co/Pd precursor ratio = 1/1, as expected. On the other hand, in the case of the Co/Pd precursor ratio = 2/1, the obtained nanoparticles did not have an acorn but an irregular shape (Figure 3b). The careful observation reveals that almost all particles consist of small PdS_x and large Co_9S_8 phases, among which a new type of $Co_9S_8/PdS_x/Co_9S_8$ heterostructured nanoparticles (indicated by white circles in Figure 3b) were found to be formed as a minor fragment owing to the large Co/Pd precursor ratio. A HRTEM image (inset in Figure 3b) also demonstrates that these heterostructured nanoparticles are composed of amorphous PdS_x phases with crystalline Co_9S_8 phases at either end. Selective preparation of such heterostructured nanoparticles by modifying the experimental conditions is now in progress.

In conclusions, we have reported the improvement of the stability of the Co_9S_8/PdS_x nanoacorns and the findings of new heterostructured nanoparticles. The selective synthesis of $PdS_x/Co_9S_8/PdS_x$ nanoparticles (nanopeanuts) has been already achieved.[17] The selective preparation of $Co_9S_8/PdS_x/Co_9S_8$ heterostructured nanoparticles will be reported in the forthcoming papers to provide the sort of firm new mechanistic insights into the processes underlying nanostructure formation more generally. Furthermore, the study on the structure-specific functions such as a directed assembly of heterostructured nanoparticles is under way.

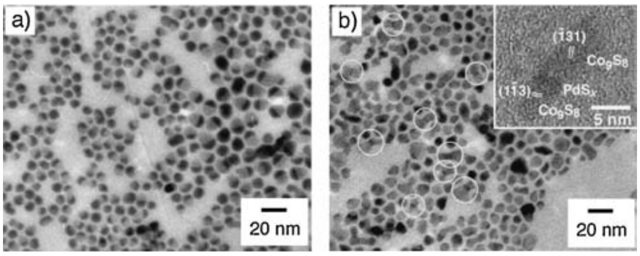

Figure 3. TEM images of heterostructured nanoparticles prepared at the molar ratios of $Co(acac)_2{\cdot}2H_2O/Pd(acac)_2 =$ (a) 1/2 and (b) 2/1 (total amount: 1.0 mmol). The white circles in (b) indicate the novel $Co_9S_8/PdS_x/Co_9S_8$ heterostructured nanoparticles (inset, HRTEM image).

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