Submicro- and Nanocrystals of Cyano-bridged FeLa Coordination Polymer in Reversed Micelle

Nobuyuki Kondo,[1] Aya Nakajima,[1] Yayoi Sasaki,[1] Masato Kurihara,*[1] Mami Yamada,[2]
Mikio Miyake,[2] Fujio Mizukami,[3] and Masatomi Sakamoto*[1]
[1]*Graduate School of Science and Engineering, Yamagata University,*
1-4-12 Kojirakawa-machi, Yamagata 990-8560
[2]*Advanced Institute of Science and Technology (JAIST),*
1-1 Asahidai, Tatsunokuchi-machi, Nomi, Ishikawa 923-1292
[3]*National Institute of Advanced Industrial Science and Technology, AIST Tohoku,*
4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551

(Received July 4, 2006; CL-060756; E-mail: kurihara@sci.kj.yamagata-u.ac.jp, sakamoto@sci.kj.yamagata-u.ac.jp)

Submicro- and nanocrystals of a d–f heteronuclear coordination polymer, $La[Fe(CN)_6] \cdot nH_2O$, were prepared in the water-in-oil microemulsion using AOT or NP-5 as a surface-protecting agent. When AOT was used, size and shape of the crystals were remarkably influenced by their preparation conditions, whereas little changed when NP-5 was used. These results were explained by the different protecting abilities of anionic AOT and nonionic NP-5.

Prussian blue (PB) and its analogues (PBA) with cyano-bridged polymeric structures have attracted much interest because of their possible use as molecule-based magnets[1] and catalysts.[2] With the development of nanotechnology, tremendous attention has been directed also to nanoparticles/crystals of PB and PBA,[2b,3] and it has become recognized that their size and shape give an effect in tuning properties of their materials.[3j,3l,3m,3o,3t] However, studies are limited to those on the d–d systems comprising only d-transition metal ion(s), as far as nanoparticles/crystals are concerned,[2b,3] and no reports are available on the d–f systems comprising d-transition metal and lanthanide (f-elements) ions. Recently, we reported the fluorescence and morphology of $Eu[Co(CN)_6] \cdot nH_2O$ and $La[Fe(CN)_6] \cdot nH_2O$ prepared in the water/AOT/hexane reversed micelle media (AOT: sodium bis(2-ethylhexyl)sulfosuccinate as a surfactant).[4] Under the respective synthetic conditions, the former coordination polymer was a few nanometer in size[4a] and the latter was observed as a submicro-sized hexagonal disk which was changed into a hexagonal ring.[4b] These results insinuate that particles/crystals with a wide variety of sizes and shapes can be prepared for the d–f systems by controlling the interaction between lanthanide ions located on the crystal surface and surfactants, because lanthanide ions are labile in the ligand substitution and have generally higher coordination numbers compared with d-transition metal ions. Thus, the d–f heterometal systems are the next stimulating targets for studies on the morphology control. From this point of view, in this work, we prepared the $La[Fe(CN)_6] \cdot nH_2O$ crystals employing the reversed micelle technique with AOT or NP-5 (polyethylene glycol mono-4-nonylphenyl ether) as a surface-protecting agent, and the first investigation was undertaken on the effects of preparation conditions on their sizes and shapes.

Typical preparation of $La[Fe(CN)_6] \cdot nH_2O$ crystals was as follows: aqueous $La(NO_3)_3$ and $K_3[Fe(CN)_6]$ solutions (0.25 or 0.5 M) were prepared. Fifty µL of each solution was separately added to 2 mL of a hexane solution (0.2 M) of AOT or a *c*-hexane solution (0.2 M) of NP-5, and the temperature was kept constant at 10, 20, or 30 °C for 1 day. These two clear reversed micelle solutions were mixed to form $La[Fe(CN)_6] \cdot nH_2O$ crystals and the temperature of this mixture was held at the same temperature for 1 to 8 days.

In the reversed micelle solutions of $K_3[Fe(CN)_6]$ formed by AOT and NP-5, the ν(CN) bands were observed at 2038 and 2040 cm^{-1}, respectively. After mixing $K_3[Fe(CN)_6]$ and $La(NO_3)_3$ in the reversed micelle, these bands were shifted to 2059 cm^{-1}, indicating the coordination of cyano-nitrogens to La(III) to give the three-dimensional network structure consisting of the Fe–CN–La linkages.

Photos (a)–(f) in Figure 1 are the TEM images of samples prepared by mixing 0.25 M aqueous solutions of $K_3[Fe(CN)_6]$

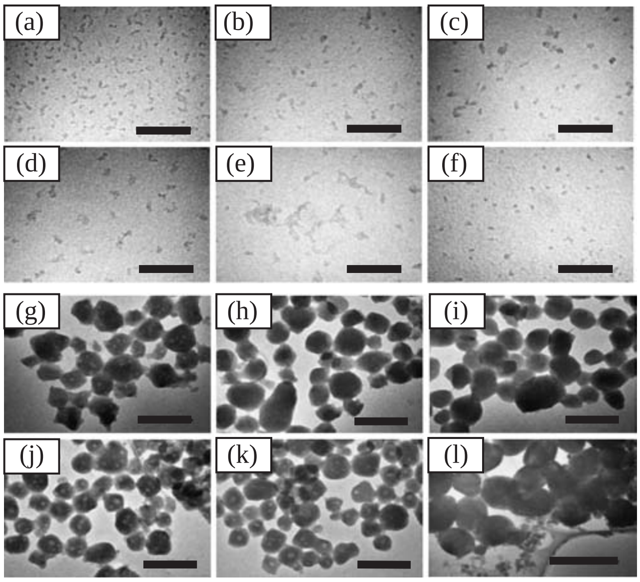

Figure 1. TEM images of $La[Fe(CN)_6] \cdot nH_2O$ prepared in H_2O/AOT/hexane ((a)–(f)) and H_2O/NP-5/*c*-hexane ((g)–(l)), using 0.25 M aqueous $La(NO_3)_3$ and $K_3[Fe(CN)_6]$ solutions. Measurements were performed in 1 day ((a)–(c), (g)–(i)) and in 8 days ((d)–(f), (j)–(l)) after mixing two reversed micelle solutions of $La(NO_3)_3$ and $K_3[Fe(CN)_6]$. Preparation temperatures are 10 °C for (a), (d), (g), and (j), 20 °C for (b), (e), (h), and (k), and 30 °C for (c), (f), (i), and (l). Scale bars are 100 nm for (a)–(f), 200 nm for (g)–(k), 1000 nm for (l).

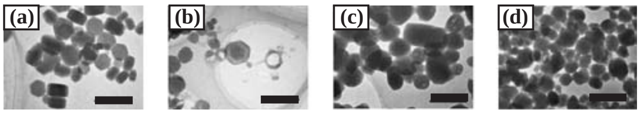

Figure 2. TEM images of $La[Fe(CN)_6]\cdot nH_2O$ prepared at 25 °C in H_2O/AOT/hexane ((a), (b)) and H_2O/NP-5/*c*-hexane ((c), (d)), using 0.5 M aqueous $La(NO_3)_3$ and $K_3[Fe(CN)_6]$ solutions. (a) and (c): taken in 1 day after mixing; (b) and (d): taken in 4 days after mixing. Scale bar is 200 nm.

and $La(NO_3)_3$ which were separately dispersed in 2.0 mL of 0.2 M hexane solution of AOT. The particle sizes are around 10 nm or less in diameter and little affected by both the changes in temperature and the elapse of time. Quite different TEM images were observed for the NP-5/*c*-hexane system ((g)–(l) in Figure 1). In 1 day after mixing, the particle diameters are in the range of 60 to 150 nm, irrespective of the preparation temperature. After 8 days, their shape and size are not apparently changed at 10 and 20 °C, whereas aggregation of the particles considerably proceeds at 30 °C to give much larger particles with the 600–700-nm diameters. Each submicrometer-sized particle is observed as an irregularly aggregated form of nanocrystals and the secondary aggregation of the agglomerates seems to occur depending on the preparation temperature and the reaction time. Further detailed observation of the photos (g)–(l) in Figure 1 reveals that nanoholes appear in the agglomerates, which may be initially formed in the irregular aggregation of nanocrystals, and the hole-size and -number are increased with the elapse of reaction time. These observations suggest that the release of cyano-network components and their recombination still take place after the secondary aggregation. As can be seen in Figure 1l, size distribution of the secondary agglomerates are relatively narrower, suggesting that the particle size may be finally controlled by the balance between the release and recombination rates. Such remarkable difference in the particle sizes between AOT and NP-5 can be explained by the different protecting abilities: compared to the nonionic NP-5, stronger electrostatic interaction of the anionic AOT with La^{III} on the crystal surface is expected to suppress the particle size growth. It has been reported that the more effective electrostatic interaction of cationic polymer PDDA (poly(diallyldimethylammonium chloride)) with the negatively charged PB colloid, compared to nonionic polymer PVP (poly(vinylpyrrolidone)), decreased the particle size.[3o]

Drastic difference in shape was also observed between AOT/hexane and NP-5/*c*-hexane systems, when two aqueous solutions of $La(NO_3)_3$ and $K_3[Fe(CN)]_6$ with higher concentration (0.5 M) instead of 0.25 M were mixed. In the AOT/hexane, hexagonal disks with the dimensions of 50–150 nm in diagonal length and 35–70 nm in thickness were observed in 1 day after mixing (Figure 2a). After 4 days, hexagonal rings appeared with the dimensions being almost the same (Figure 2b). Similar results were recently observed by mixing 0.4 M aqueous solutions of $La(NO_3)_3$ and $K_3[Fe(CN)]_6$, and reasonably explained by the anisotropic interaction of AOT anions with La^{III} ions which are known to be located on the {001} planes and inside the {110} planes from the structural analysis.[4b] In the NP-5/*c*-hexane, spherical particles with the 70–200 nm diameters were formed in 1 day, and their size and shape were little changed even after 4 days (Figures 2c and 2d). In the NP-5 system, the aggregation behavior is not so affected by the preparation conditions.

Results showed that the shape of $La[Fe(CN)_6]\cdot nH_2O$ crystals in the water-in-oil microemulsion can be, to some extent, changed by controlling the surface-protecting ability of surfactant. However, compared with PB and PBA comprising d-transition metal ion(s), the preparation of crystals with narrower size distribution was found to be difficult, probably because of the high lability of lanthanide(III) ions in the ligand substitution sufficient to accelerate the aggregation of particles. In order to overcome this problem, further studies are in progress on the special design of crystal surface.

This work was financially supported by Grant-in-Aid for Scientific Research (Nos. 15750044, 16710069, 17036003, and 17550053) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 For example: a) S. Ferlay, T. Mallah, R. Ouahès, P. Veillet, M. Verdaguer, *Nature* **1995**, *378*, 701. b) O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, *Science* **1996**, *272*, 704. c) O. Sato, S. Hayami, Y. Einaga, Z.-Z. Gu, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 443. d) O. Sato, T. Kawakami, M. Kimura, S. Hishiya, S. Kubo, Y. Einaga, *J. Am. Chem. Soc.* **2004**, *126*, 13176. e) T. Uemura, S. Kitagawa, *Chem. Lett.* **2005**, *34*, 132. f) E. Ruiz, A. Rodríguez-Fortea, S. Alvarez, M. Verdaguer, *Chem.—Eur. J.* **2005**, *11*, 2135. g) T. Nuida, T. Matsuda, H. Tokoro, S. Sakurai, K. Hashimoto, S. Ohkoshi, *J. Am. Chem. Soc.* **2005**, *127*, 11604. h) S. Ohkoshi, T. Matsuda, H. Tokoro, K. Hashimoto, *Chem. Mater.* **2005**, *17*, 81. i) W. Kosaka, T. Ishihara, H. Yashiro, Y. Taniguchi, K. Hashimoto, S. Ohkoshi, *Chem. Lett.* **2005**, *34*, 1278.

2 a) I. Kim, J.-T. Ahn, C. S. Ha, C. S. Yang, I. Park, *Polymer* **2003**, *44*, 3417. b) M. J. Yi, S.-H. Byun, C.-S. Ha, D.-W. Park, I. Kim, *Solid State Ionics* **2004**, *172*, 139.

3 a) S. P. Moulik, G. C. De, A. K. Panda, B. B. Bhowmik, A. R. Das, *Langmuir* **1999**, *15*, 8361. b) P. Y. Chow, J. Ding, X. Z. Wang, C. H. Chew, L. M. Gan, *Phys. Status Solidi A* **2000**, *180*, 547. c) S. Vaucher, M. Li, S. Mann, *Angew. Chem., Int. Ed.* **2000**, *39*, 1793. d) C. W. Ng, J. Ding, P. Y. Chow, L. M. Gan, C. H. Quek, *J. Appl. Phys.* **2000**, *87*, 6049. e) S. Vaucher, J. Fielden, M. Li, E. Dujardin, S. Mann, *Nano Lett.* **2002**, *2*, 225. f) P. Zhou, D. Xue, H. Luo, X. Chen, *Nano Lett.* **2002**, *2*, 845. g) L. Catala, T. Gacoin, J.-P. Boilot, É. Riviére, C. Paulsen, E. Lhotel, T. Mallah, *Adv. Mater.* **2003**, *15*, 826. h) J. G. Moore, E. J. Lochner, C. Ramsey, N. S. Dalal, A. E. Stiegman, *Angew. Chem., Int. Ed.* **2003**, *42*, 2741. i) J. M. Domínguez-Vera, E. Colacio, *Inorg. Chem.* **2003**, *42*, 6983. j) T. Uemura, S. Kitagawa, *J. Am. Chem. Soc.* **2003**, *125*, 7814. k) Z. Li, J. Zhang, T. Mu, J. Du, Z. Liu, B. Han, J. Chen, *Colloids Surf., A* **2004**, *243*, 63. l) P. H. Zhou, D. S. Xue, *J. Appl. Phys.* **2004**, *96*, 610. m) E. Dujardin, S. Mann, *Adv. Mater.* **2004**, *16*, 1125. n) N. Bagkar, R. Ganguly, S. Choudhury, P. A. Hassan, S. Sawant, J. V. Yakhmi, *J. Mater. Chem.* **2004**, *14*, 1430. o) T. Uemura, M. Ohba, S. Kitagawa, *Inorg. Chem.* **2004**, *43*, 7339. p) M. Yamada, M. Arai, M. Kurihara, M. Sakamoto, M. Miyake, *J. Am. Chem. Soc.* **2004**, *126*, 9482. q) T. Uemura, S. Kitagawa, *Chem. Lett.* **2005**, *34*, 132. r) Q. Kong, X. Chen, J. Yao, D. Xue, *Nanotechnology* **2005**, *16*, 164. s) L. Catala, C. Mathonière, A. Gloter, O. Stephan, T. Gacoin, J.-P. Boilot, T. Mallah, *Chem. Commun.* **2005**, 746. t) M. Cao, X. Wu, X. He, C. Hu, *Chem. Commun.* **2005**, 2241.

4 a) N. Kondo, A. Yokoyama, M. Kurihara, M. Sakamoto, M. Yamada, M. Miyake, T. Ohsuna, H. Aono, Y. Sadaoka, *Chem. Lett.* **2004**, *33*, 1182. b) N. Kondo, M. Kurihara, M. Yamada, M. Miyake, M. Nishijima, T. Ohsuna, F. Mizukami, M. Sakamoto, *Chem. Lett.* **2005**, *34*, 590.