Capped Bimetallic and Trimetallic Nanoparticles for Catalysis and Information Technology

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Summary: Polymer-capped metal nanoparticles can be recognized as a kind of macromolecule-metal nanoparticle complexes. Here the preparations of the capped bimetallic and trimetallic nanoparticles, in which each particle contains two and three elements of metal, respectively, are presented. They may have a random alloy, a core/shell, or other kinds of structure depending on the preparation method and the combination of elements. The core/shell structure is advantageous to electronically control the activity of metal catalysts. The triple core/shell structured trimetallic nanoparticles were found to have higher catalytic activity than the corresponding monometallic and bimetallic nanoparticles in three cases. Capped metal nanoparticles were also used as a dopant to liquid crystals. Liquid crystal displays, fabricated by metal nanoparticle-doped liquid crystals, showed faster response than those without dopants. Bimetalization could increase the long-term stability in the doped liquid crystal displays. Thus, metal nanoparticles can improve the electronic display system, which occupies an important position in information technology. In addition, $SmCo_5$ nanomagnets were successfully prepared by a chemical method, possibly providing a new building block for information technology. The prepared $SmCo_5$ nanoparticles have a coercivity of 1500 Oe at room temperature. The bimetallic nanoparticles may open a new field in super-high-density magnetic memories.

Keywords: bimetallic catalyst; core/shell structure; information technology; liquid crystal display; macromolecular complex; magnetic memory; metal nanoparticle $SmCo_5$; trimetallic catalyst

Introduction

Macromolecular complexes can be defined as complexes (mainly metal complexes) having organic macromolecule(s) or macromolecular structure(s). Metal nanoparicles capped by macromolecules have been recognized as a kind of macromolecular complexes. For example, more than 10 papers on metal nanoparticles capped by macromolecules were presented as macromolecular metal complex (colloidal) catalysts at the first symposium held in Beijing, China in 1985 in a series of MMC international symposia. In fact, colloidal dispersions of polymer-protected metal nanoparticles have been prepared from the polymer-metal ion complexes via polymer-metal atom complexes, as shown in Figure 1. Thus, polymer-protected metal nanoparticles can be regarded as polymer-metal cluster complexes.[1]

During the production of nanoparticles polymers play an important role to control the size and structure especially in bimetallic systems,[2] and the shape and crystal facet in catalytic ones.[3,4] For example, when the mixtures of two kinds of novel metal ions in solution are subjected to simultaneous reduction under mild reduc-

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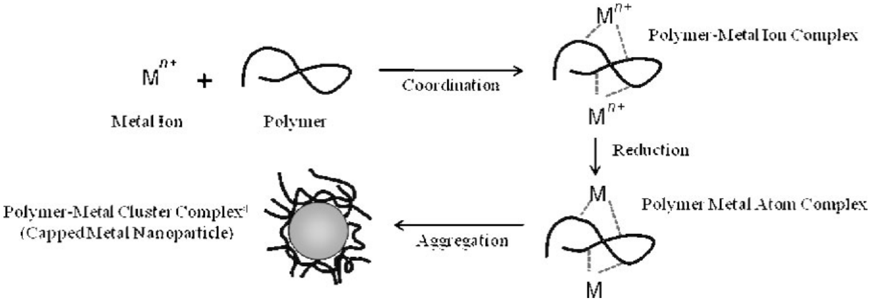


Figure 1.
Schematic presentation of formation of capped metal nanoparticles from polymer-metal ion complexes through polymer-metal atom complexes.

tion condition like alcohol reduction in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP), the bimetallic nanoparticles with a core/shell structure can be produced. During this reaction, PVP can coordinate to metal ions and metal atoms as well as metal clusters. The difference in the coordination ability as well as the redox potential can provide the motive force to control the core/shell structure as shown in Figure 2.[2,5] In addition, we have to emphasize that the polymers added to the solution of metal ions before the formation of metal nanoparticles might coordinate more strongly to

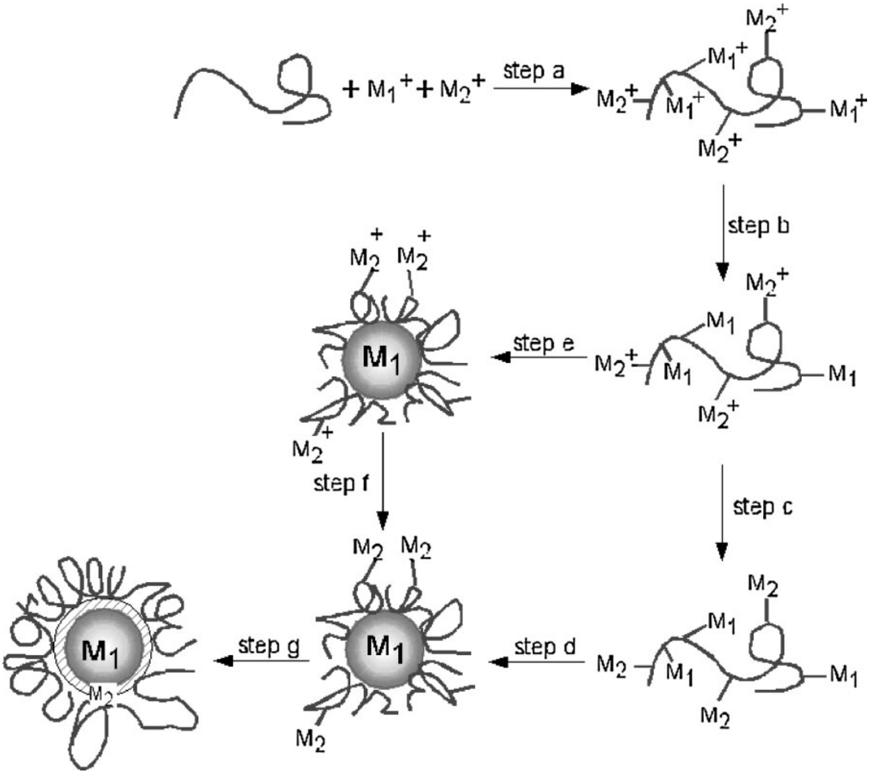


Figure 2.
Schematic presentation of formation of core/shell structured bimetallic nanoparticles by simultaneous reduction of two metal ions.[10]

metal nanoparticles produced than the polymers added after the formation of nanoparticles. Thus, the metal nanoparticles prepared from polymer-metal ion complexes are enough stable to work as an active catalyst for the organic reaction like hydrogenation of olefin in solution.[6]

Here, a novel method is presented to prepare core/shell structured bimetallic nanoparticles, which can be applied to prepare trimetallic nanoparticles with a triple core/shell structure as active catalysts. Then, bimetallic nanoparticles developed for information technology, i.e., liquid crystal displays and nanomagnets are introduced. The latter is applicable to super-high-density magnetic memory.

Syntheses of Bimetallic and Trimetallic Nanoparticles with a Core/Shell Structure for Catalyses

Fortunately by accident, we discovered the formation of core/shell-structured Pt/Pd bimetallic nanoparticles by simultaneous alcohol reduction of H_2PtCl_6 and $PdCl_3$ in the presence of PVP.[7] The core/shell-structure of bimetallic nanoparticles was confirmed by extensive studies using an EXAFS technique.[8,9] The formation mechanism, shown in Figure 2,[10] can be applied to the formation of Pt-core/Pd-shell bimetallic nanoparticles, in which M_1 and M_2 are Pt and Pd, respectively.

The core/shell-structured Pt/Pd bimetallic nanoparticles work as an active catalyst for selective partial hydrogenation of dienes.[11] The Pt/Pd (1/4 in atomic ratio) bimetallic nanoparticles with a core/shell structure, in which a nanoparticle with 1.4 nm in diameter consists of a Pt core with 13 Pt atoms and a Pd shell with an atomic layer of Pd, have about three times higher catalytic activity for the partial hydrogenation of 1,3-cyclooctadiene than Pd monometallic nanoparticles with the similar size.[8] This means that the core Pt can provide an electronic effect (a ligand effect) on the surface Pd atoms, active sites of catalysts. Thus, the core/shell structure is very important for catalysis.

We reported the controlled constructions of a core/shell structure by sacrificial hydrogen reduction, where hydrogen adsorbed on the surface of core metal nanoparticles work as reductants of the second metal ions to produce the shell as shown in Figure 3 for the case of a Pd-core/Au-shell structure.[12]

In addition, we found that physical mixture of two kinds of metal nanoparticles in dispersions can spontaneously produce core/shell-structured bimetallic nanoparticles.[13] This reaction was first found from the UV-Vis absorption change observed in the mixture of the dispersion of PVP-protected Ag nanoparticles with that of Rh nanoparticles prepared separately, as shown in Figure 4.[13] The core/shell structure was confirmed by EF-TEM. The reaction mechanism is proposed as shown in Figure 5 based on the EXAFS observation. This is thought to be a self-organized process.

Isothermal titration calorimetry (ITC) studies of the mixing process can clarify the fact that particular combination like Rh and Ag shows a strong exothermic interaction, as shown in Table 1.[14] The core/shell-structured bimetallic nanoparticles thus prepared have found a higher or lower catalytic activity than the corresponding monometallic nanoparticles, depending on the kind of core elements. In the case of the Ag/Rh bimetallic nanoparticles with an Ag core prepared by physical mixing of Ag and Rh nanoparticles, for example, Ag/Rh (1/4) bimetallic nanoparticles have higher catalytic activity than monometallic Rh nanoparticles with the similar size. This is due to an electronic (a ligand) effect of the Ag core on the Rh shell which has active sites for catalysis. Electron deficient property of Rh shell in the bimetallic nanoparticles can enhance the adsorption of olefins on the surface of Rh shell, and enhance the catalytic activity. This is similar to the case of core/shell-structured Pt/Pd bimetallic nanoparticles prepared by the simultaneous reduction.[11] In the case of a Ag core

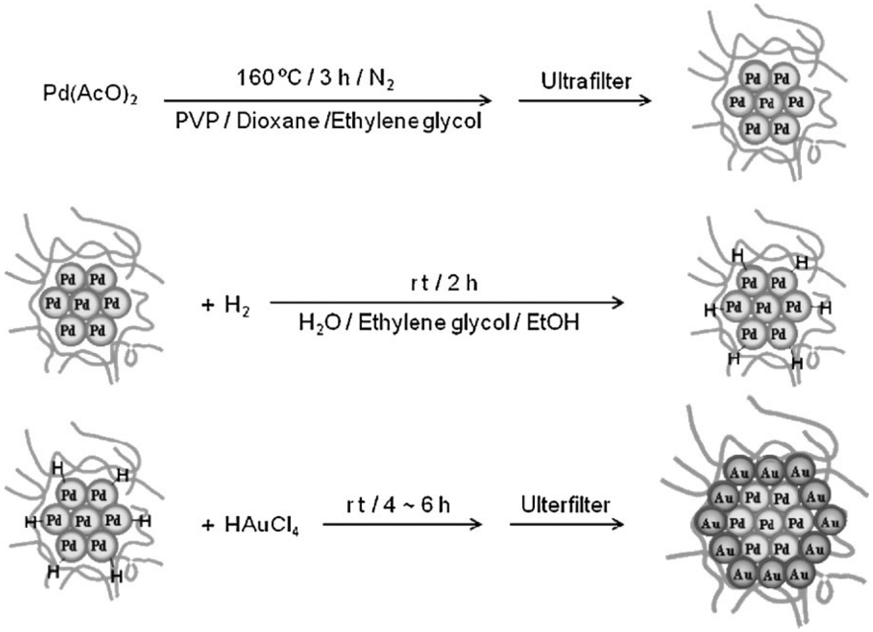


Figure 3.
A sacrificial hydrogen reduction method to produce a core/shell structure.

covered by a Pd shell, in contrast, the catalytic site of Pd shell is electronically enriched by the Ag core. Thus, addition of small amounts of Ag can depress the catalytic activity of Pd. This difference between Rh and Pd can be easily explained by the difference of ionization energy of Rh, Ag, and Pd (Rh<Ag<Pd).

Recently we have succeeded in construction of a triple core/shell structure by combination of sacrificial hydrogen reduction or simultaneous alcohol reduction with a physical mixing process (self-organization).[15,16] The Au-core/Pt-shell bimetallic nanoparticles were prepared by simultaneous alcohol reduction in the presence of PVP. The dispersions of Au/Pt (1/4) bimetallic nanoparticles were mixed with the dispersion of 4 times amounts of Rh nanoparticles, prepared separately by alcohol reduction of $RhCl_3$ in the presence of PVP, to produce Au/Pt/Rh (1/4/20) trime-

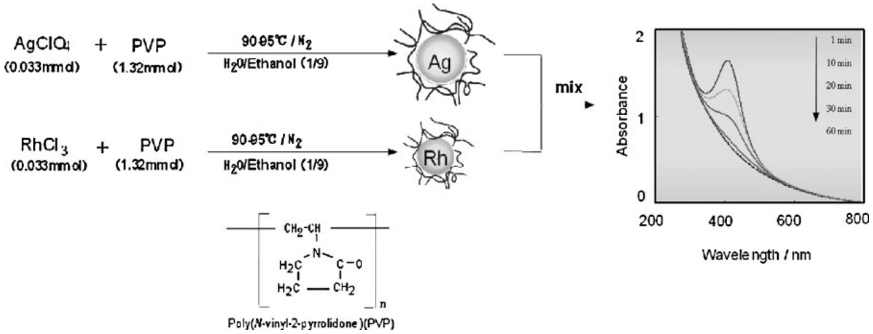


Figure 4.
UV-Vis absorption change in the mixed dispersions of PVP-protected Ag nanoparticles with PVP-protected Rh nanoparticles.[13]

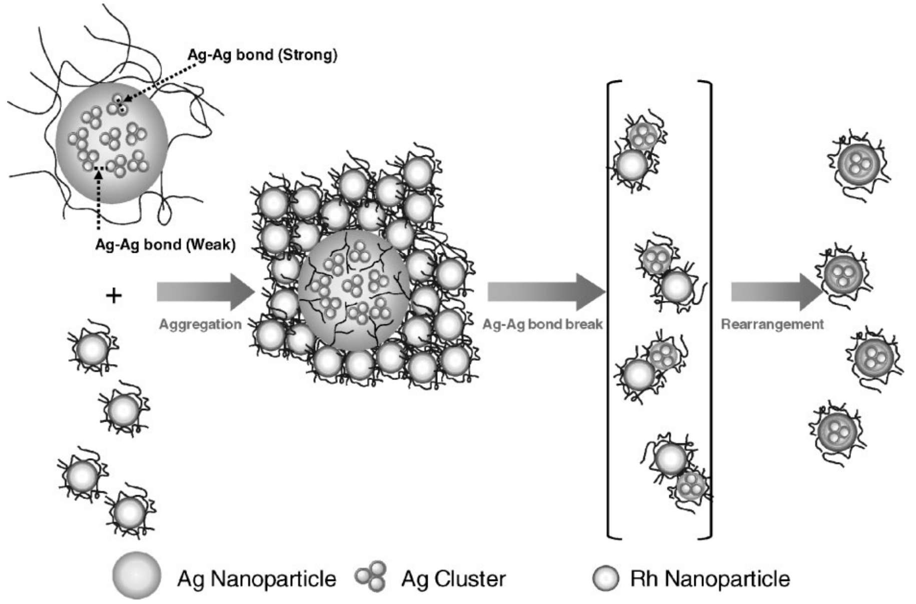


Figure 5.
Schematic presentation for the formation of a Ag-core/Rh-shell structure by physical mixture of PVP-protected Ag-nanoparticles with PVP-protected Rh nanoparticles (Self-Organization).

tallic nanoparticles as shown in Figure 6.[15] TEM photographs of original PVP-protected Au/Pt (1/4) and Rh nanoparticles, as well as Au/Pt/Rh (1/4/20) trimetallic nanoparticle prepared by self-organization, are shown in Figure 7.[15] The trimetallic nanoparticles are enough small in size and have narrow size distribution, suggesting the self-organization process. High resolution TEM and energy-filtered TEM images shown in Figure 8 also support this consideration. We have not the complete evidence for the triple core/shell (Au-core/Pt-interlayer/Rh-shell) structure yet, but the results of the HR-TEM and EF-TEM were not contradictory to the triple core/shell structure. In addition, the trimetallic nanoparticles thus prepared had a higher catalytic activity for hydrogenation of olefin than not only any kinds of monometallic and bimetallic nanoparticles of the corresponding elements but also trimetallic nanoparticles prepared by methods other than the present sophisticated combined method (physical mixing of Rh nanopartilces and Au-core/Pt-shell structured nanoparticles) as shown in Figure 9.[15]

The advantage of the triple core/shell structures had also been confirmed in the case of Pt-core/Pd-interlayers/Rh-shell and Pd-core/Ag-interlayer/Rh-shell trimetallic nanoparticles prepared by self

Table 1.
Isothermal titration calorimetric results by injecting the dispersion of injection particles into the dispersion of particles in a cell.[14]

Injection particle		Particle in cell	ΔH (kJ/mol)	$\Delta H \times 10^{27}$ (J/particle)
PVP - Rh	→	PVP - Ag	−908	−0.79
PVP - Pd	→	PVP - Ag	−600	−0.43
PVP - Pt	→	PVP - Ag	−414	−0.32
PVP - Ag	→	PVP - Rh	−357	−21.6
PVP - Ag	→	PVP - Pd	−331	−21.2
PVP - Ag	→	PVP - Pt	−189	−11.4

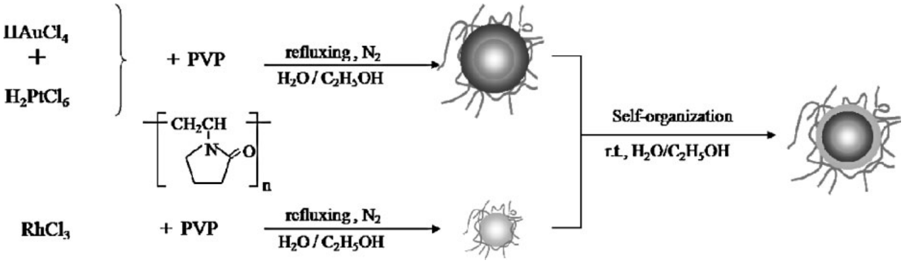


Figure 6.
Synthesis of Au/Pt/Rh trimetallic nanoparticles by combination of simultaneous reduction and self-organization.

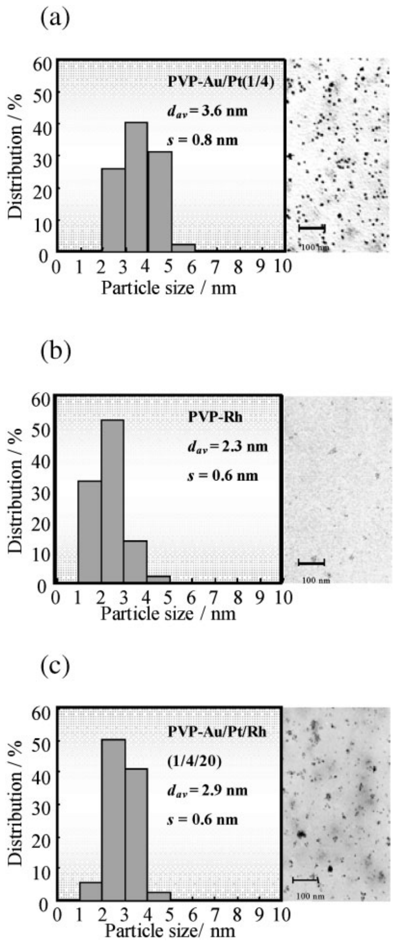


Figure 7.
TEM photographs and size distribution histograms of PVP-protected (a) Au/Pt (1/4) bimetallic, (b) Rh monometallic, and (c) Au/Pt/Rh trimetallic nanoparticles.[15]

organization.[16] The PVP-protected Pd/Ag/Rh (1/2/36) trimetallic nanoparticles have an average diameter of 3.5 nm, while original Pd/Ag (1/2) bimetallic nanoparticles with an inverted core/shell structure and Rh nanoparticles have average diameters of 6.8 nm and 2.5 nm, respectively, as shown in Figure 10.[16] The catalytic activity of the Pd/Ag/Rh trimetallic nanoparticles, prepared by the present sophisticated method using self-organization, is the highest among the corresponding monometallic, bimetallic and trimetallic nanoparticles prepared by other methods. In addition, it is noteworthy that the trimetallic nanoparticles with the smaller size had higher catalytic activity than those with the larger size, among the trimetallic nanoparticles prepared by altering the molar ratio of Pd/Ag to Rh to get the highest activity. Starting from the smallest Pd/Ag (1/2) bimetallic nanoparticles (2.5 nm) with an inverted core/shell structure, the highest catalytic activity was achieved at molar ratio of Pd/Ag/Rh = 1/2/13.5. The catalytic activity is compared with those of other metal nanoparticles in Figure 11.

Capped Bimetallic and Trimetallic Nanoparticles for Information Technology

Information technology is developing so rapidly. Metal nanoparticles should be applied to the development of information technology. Here, two examples were

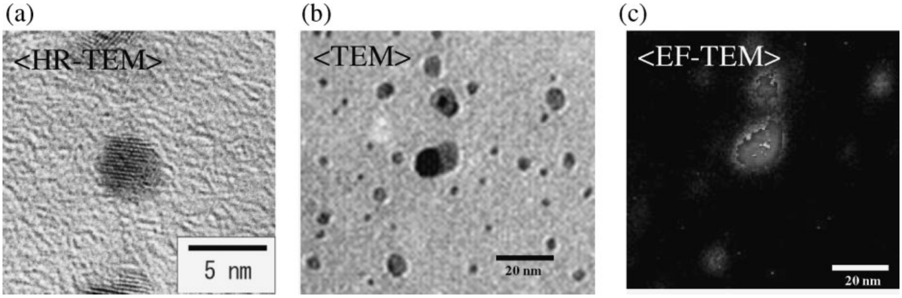


Figure 8.
Images of (a) high resolution TEM, (b) TEM and (c) elemental distribution (Rh, red; Pt, yellow) in energy-filtered TEM of the Au/Pt/Rh (1/4/20) trimetallic nanoparticles.[15]

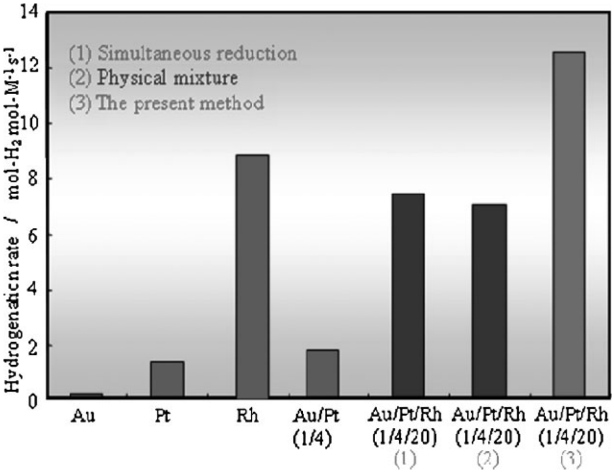


Figure 9.
Comparison of catalytic activities of Au, Pt, Rh, Au/Pt (1/4) and Au/Pt/Rh (1/4/20) nanopartilces prepared by (1) simultaneous reduction, (2) physical mixture of Au, Pt and Rh nanoparticles, and (3) the present self-organization method.[15]

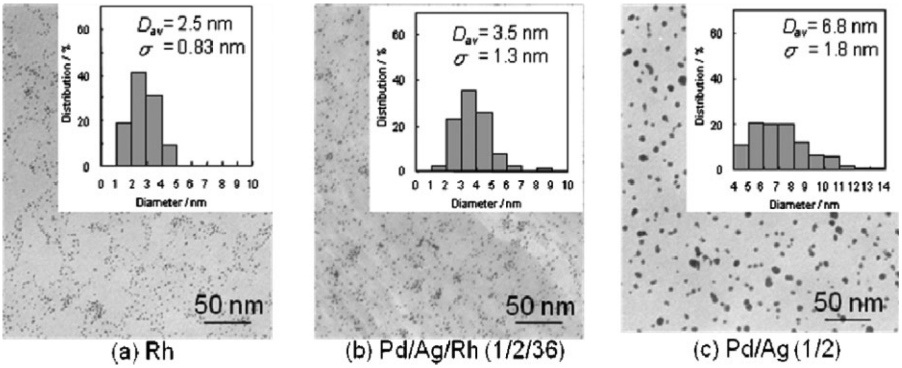


Figure 10.
TEM images and size distribution histograms of (a) original Rh, (b) original Pd/Ag (1/2) bimetallic nanoparticles, and (c) produced Pd/Ag/Rh (1/2/36) trimetallic nanoparticles.[16]

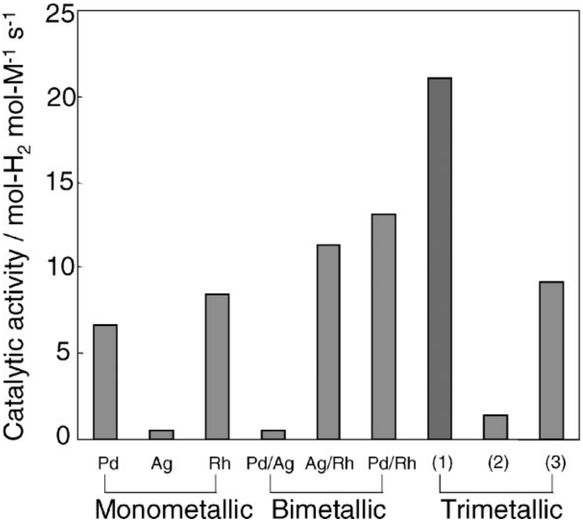


Figure 11.
Comparison of catalytic activities of monometallic, bimetallic and trimetallic nanoparticles for hydrogenation of olefin. Trimetallic nanoparticles (Pd/Ag/Rh = 1/2/13.5) were prepared by (1) the present method, (2) simultaneous reduction and (3) mixture of three monometallic nanoparticles.

presented, which have been investigated in our laboratory.

A liquid crystal display (LCD) is now ubiquitous. It is widely used at any time in any place. From a small-size display in mobile phones to a large-size display in television sets, LCD is the most common electronic display. LCD has already been well-developed. However, it has still some issues. The most important issues will be its response time. Power consumption will be the second. Here we have found that metal nanoparticles may solve these issues. In order to prepare Pd nanoparticles dispersed in liquid crystal media, we used photoreduction of palladium(I) acetate in the presence of 4′-pentyl-4-cyanobiphenyl (5CB) in THF (Figure 12).[17,18] 5CB-capped Pd nanoparticles prepared could be dispersed in 5CB, a typical liquid crystal medium. Dispersions of 5CB-Pd nanoparticles in a 5CB medium can be schematically illustrated in Figure 13. If the mixed solution of palladium(II) acetate and silver perchlorate in THF was used for photoirradiation, dispersions of 5CB-Ag/Pd bimetallic nanoparticles were obtained. TEM images and size distribution histograms at various Ag/Pd ratios as well as HR-TEM images at Ag/Pd = 5/5 of 5CB-Ag/Pd nanoparticles are shown in Figure 14, which also presents elemental analyses of metals by EDS and atomic absorption spectrum. These data indicate the formation of Ag/Pd bimetallic nanoparticles.

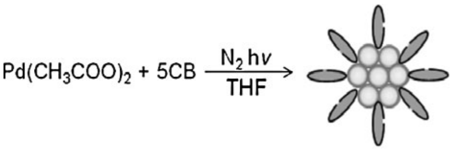


Figure 12.
Synthesis of 5CB-capped Pd nanoparticles by photoirradiation.

Addition of these metal nanoparticles to liquid crystal media in only 0.1 wt% could improve the response time. Ag nanoparticles had stronger effect than Pd to improve the response time.[18,19] However, Ag nanoparticles were not stable enough to get a long life. So, we used the bimetallic nanoparticles to obtain a stable system. Life time of the metal nanoparticle-doped LCD

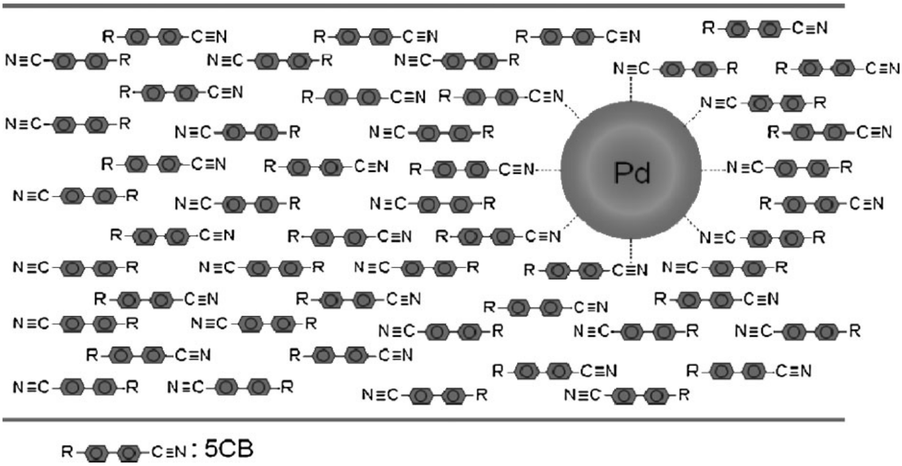
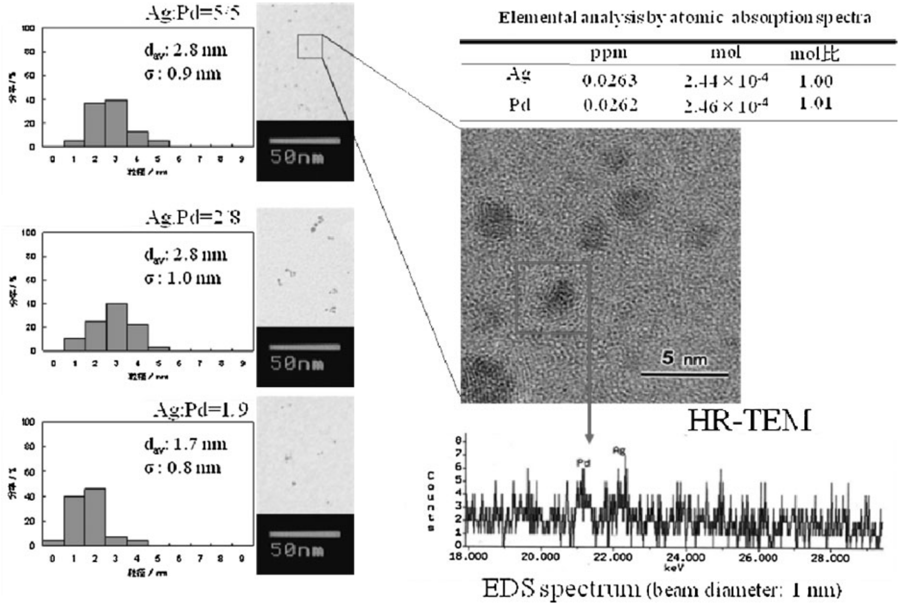


Figure 13.
Schematic presentation of dispersion of 5CB-capped Pd nanoparticles in 5CB medium.

was evaluated at elevated temperature. The results are shown in Figure 15, suggesting that Ag/Pd bimetallic systems are not so bad compared with a stable Pd system.

Now, the result obtained by collaboration with industries is shown.[20] Figure 16 is the practical LCDs. Both pictures were taken at −10 °C when a scene was changed from a numeral list to a picture of a dog. The left-side cell did not contain bimetallic nanoparticles, while right cell did. In a top part of the left picture, there still remain some numbers,


Elemental analysis by atomic absorption spectra

	ppm	mol	mol比
Ag	0.0263	2.44×10^{-4}	1.00
Pd	0.0262	2.46×10^{-4}	1.01

Figure 14.
TEM images and size distribution histograms of 5CB-capped Ag/Pd bimetallic nanoparticles at various Ag/Pd ratios, and HR-TEM image of those at Ag/Pd = 5/5. Elements analyses by EDS and atomic absorption spectra are also shown.

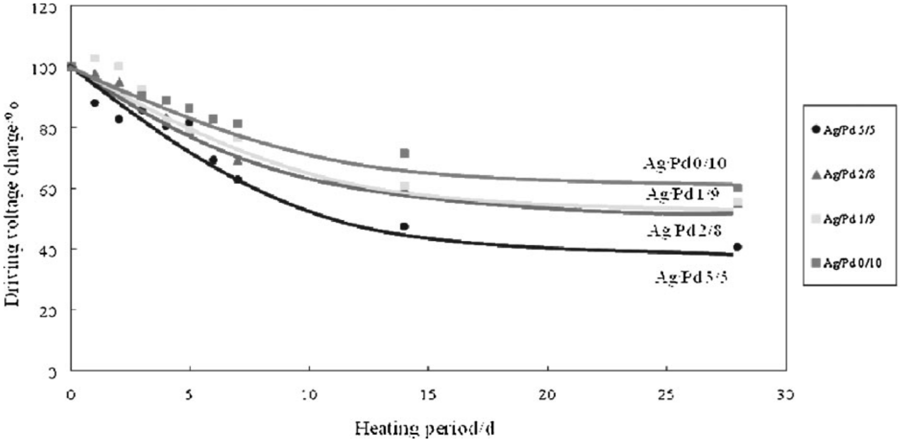


Figure 15.
Comparison of driving voltage change of LCD fabricated by nanoparticle-doped 5CB at 80 °C.

which have been illustrated in the previous scene. On the contrary, a top part of right picture does not contain numbers. This means that the nanoparticle can enhance the response of LCD. This might be because of Maxwell Wagner effect.[20]

When CdS nanoparticles were used as a dopant for 5CB, the doped LCD cell can be driven at a lower driving voltage than that without dopant, which could provide a new technique for energy saving.[21]

Another example of application of bimetallic and trimetallic nanoparticles for information technology is the synthesis of novel nanomagnet for super-high-density magnetic memory. At the present the practical magnetic memory devises are constructed by CoCr films, prepared by vapor deposition and composed of domains in submicrometer size. Since each domain keeps one memory, decreases of the domain size can increases the density of memory. S. Sun proposed the

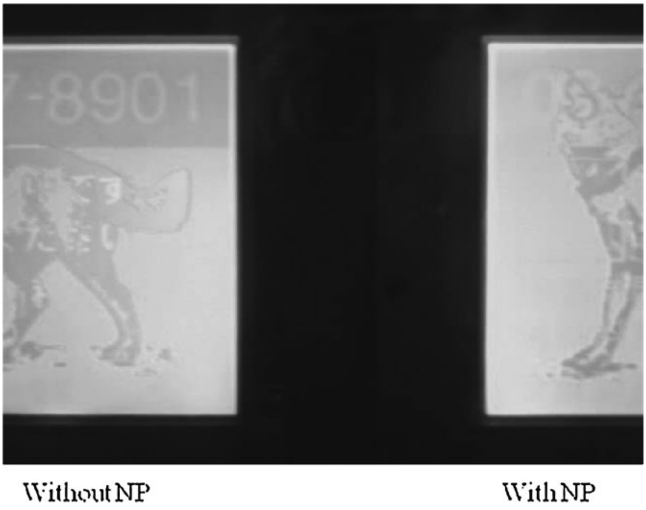


Figure 16.
Pictures of STN-LCDs fabricated with (right) and without (left) Ag/Pd bimetallic nanoparticle dopants at −10 °C.

preparation of single-nanometer-sized FePt nanoparticles by a chemical method and their alignment on a substrate.[22] However, heat treatment over 500 °C is required to transfer the FePt nanoparticles from superparamagnetic to ferromagnetic phase. In addition, the high cost of platinum is another problem for practical use.

$SmCo_5$ bulk alloy having a $CaCu_5$ type crystal structure is known as one of strong permanent magnets composed of rare-earth alloys. Some researchers have tried to prepare $SmCo_5$ nanoparticles having ferromagnetism at room temperature. K. Ono et al.[23] and H. Gu et al.[24] reported the preparation of $SmCo_5$ nanoparticles by a chemical method starting from $Sm(acac)_3$ and $Co_2(CO)_8$. However, their nanoparticles did not have ferromagnetism at room temperature. Quite recently, Tens and Yang reported the preparation of $SmCo_5$ nanoparticles coated by Fe_2O_3 shell, the coercivity of which was shown at 5 K but not at room temperature.[25]

We have synthesized $SmCo_5$ ananoparticles from $Sm(acac)_3$ and $Co(acac)_3$ in the presence of oleic acid and oleylamine in tetraethyleneglycol (TEG) at 280 °C under nitrogen. The products were rich in Co. If small amounts of AuCl were added to reaction mixtures, the products contained three elements at the charged ratio, and the coercivity of 1500 Oe at 300 K.[26] The XRD patterns showed the presence of $SmCo_5$ crystal with a $CaCu_5$ type crystalline structure.[26] HR-TEM photographs, shown in Figure 17, indicate the presence of Au at the central part, which is surrounded by $SmCo_5$ polycrystals and Sm in the outer side. Thus, Au nanoparticles may play a role of a seed for crystal growth of $SmCo_5$ nanoparticles.

Conclusion

Capped metal nanoparticles are recognized as a macromolecule-metal nanoparticle complexe, a kind of macromolecular complex. Here, bimetallic and trimetallic nanoparticles were focused on application to catalysis ad information technology, because both fields are rapidly developing recently.

As for catalysis, recently much attention has been given to the structure design of metal nanopartilces as an active site of the catalyst. Especially, a core/shell structure is interesting from the viewpoint of control of the electronic property of surface metal. Here we propose a novel method, physical mixture of nanoparticles or self-organization. Since the reaction in this method proceeds under mild conditions, it can be applied to construct a triple core/shell structure by surrounding the bimetallic

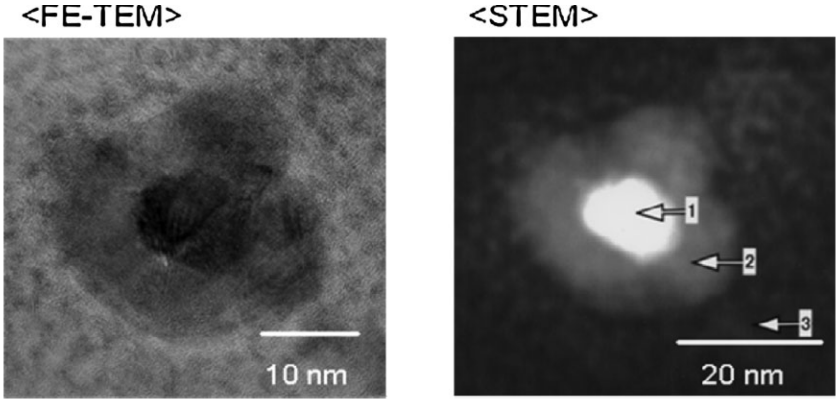


Figure 17.
Structural analysis of $SmCo_5$-Au nanoparticles by FE-TEM and STEM. Spot 1: Au contaminated by Co on the surroundings, Spot 2: Sm-Co alloy, Spot 3: Sm.

nanoparticle having a core/shell structure with the third element without destroying the original bimetallic core/shell structure. Macromolecules play an important role for construction of the core/shell structure. The electron density of the surface element in trimetallic nanopartilces can be affected by the electronic level of elements in inner layers. If the electronic levels or work functions of three elements are aligned so as to enhance an overall electronic charge shift in trimetallic nanoparticles having a triple core/shell structure, then the concept of a sequential potential field[27] can provide the catalyst with the highest activity in the sense of an electronic effect or a ligand effect.

As for information technology, two examples, a liquid crystal display and a super-high-density magnetic memory, are presented. Addition of capped metal nanoparticles to liquid crystal media as a dopant can improve the response time of the liquid crystal display. The capped metal nanoparticles may work as a disturbant to the ordered liquid crystal media, resulting in easy movement of liquid crystal molecules. Another example is novel syntheses of $SmCo_5$ nanomagnet. Usually magnetic properties require an enough large domain size. Thus, metal particles in a single nanometer size are difficult to be ferromagnetic at room temperature. We have succeeded in syntheses of $SmCo_5$ nanomagnets in a single nanometer size with assistance of Au metal. Au nanoparticles may work as a seed to construct magnetic $SmCo_5$ nanoparticle crystals with a $CaCu_5$ type structure.

Metal nanoparticles will be applied to a variety of fields in the near future. Bimetallization or trimetallization can improve the properties of metal nanoparticles. In addition, organic ligands, especially macromolecules may play an important role to construct and stabilize the nanoparticles, and disperse the nanoparticles into the proper media for application.

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[1] H. Hirai, N. Toshima, in: "*Tailored Metal Catalysts*", Y. Iwasawa, Ed., D. Reidel Pub. Co., Dordrecht **1985**, pp. 87–140.

[2] T. Yonezawa, N. Toshima, *J. Chem. Soc., Faraday Trans. 91*, **1995**, 4111.

[3] M. A. El-Sayed, *Acc. Chem. Res. 34*, **2001**, 257.

[4] Y. Ziang, Z. Wu, D. Lin, Z. Jinag, W. Chu, Z. Li, Y. Ma, W. Zhon, S. Zio, *Nano Lett. 6*, **2006**, 2290.

[5] N. Toshima, In: "*Macromolecular Nanostructured Materials*", N. Ueyama, Ed., A. Harada, Kodansha/Springer, Tokyo/Berlin **2004**, Chapter 3.3, pp. 182–186.

[6] H. Hirai, Y. Nakao, N. Toshima, K. Adachi, *Chem. Lett.* **1976**, 905.

[7] N. Toshima, K. Kushihashi, T. Yonezawa, H. Hirai, *Chem. Lett.* **1989**, 1769.

[8] N. Toshima, M. Harada, T. Yonezawa, K. Kushihashi, K. Asakura, *J. Phys. Chem. 95*, **1991**, 7448.

[9] M. Harada, K. Asakura, Y. Ueki, N. Toshima, *J. Phys. Chem. 96*, **1992**, 4927.

[10] N. Toshima, H. Yan, Y. shiraishi, in: "*Metal Nanoclucters in Catalysis and Materials Science. The Issue of Size Control*", B., Corain, G., Schmid, N. Toshima, Eds., Elsevier, Amsterdam **2008**, Chapter 3, pp. 49–75.

[11] N. Toshima, T. Yonezawa, K. Kushihashi, *J. Chem. Soc., Faraday Trans. 89*, **1993**, 2537.

[12] Y. Wang, N. Toshima, *J. Phys. Chem. 13*(101), **1997**, 5301.

[13] K. Hirakawa, N. Toshima, *Chem.. Lett. 32*, **2003**, 78.

[14] N. Toshima, M. Kanemaru, Y. Shiraishi, Y. Koga, *J. Phys. Chem. B 109*, **2005**, 16326.

[15] N. Toshima, R. Ito, T. Matsushita, Y. Shiraishi, *Catalysts Today 122*, **2007**, 239.

[16] T. Matsushita, Y. Shiraishi, S. Horiuchi, N. Toshima, *Bull. Chem. Soc. Jpn 80*, **2007**, 1217.

[17] Y. Shiraishi, N. Toshima, K. Maeda, H. Yoshikawa, J. Zu, S. Kobayashi, *Appl. Phys. Lett. 81*, **2002**, 2845.

[18] H. Shiraki, S. Kundu, Y. Sakai, T. Masui, Y. Shiraishi, N. Toshima, S. Kobayashi, *Jpn. J. Appl. Phys. 43*, **2004**, 5425.

[19] J. Thisayukta, H. Shiraki, Y. Sakai, T. Masumi, S. Kundu, Y. Shiraishi, N. Toshima, S. Kobayashi, *Jpn. J. Appl. Phys. 43*, **2004**, 5430.

[20] S. Kobayashi, N. Toshima, *Information Display 23*, **No.** *9*, **2007**, 25.

[21] Y. Du, N. Toshima, *Bull. Chem. Soc. Jpn. 80*, **2007**, 2446.

[22] S. Sun, C. B. Murray, D. Wellen, L. Folks, A. Moser, *Science 287*, **2000**, 1989.

[23] K. Ono, Y. Kakefuda, R. Okuda, Y. Ishii, S. Kamimura, A. Kitamura, M. Oshima, *J. Appl. Phys. 81*, **2002**, 8480.

[24] H. Gu, B. Xu, J. Rao, K. Zheng, X. X. Zhang, K. K. Fung, C. Y. C. Wong, *J. Appl. Phys. 93*, **2003**, 7589.

[25] X. Teng, H. Yang, *J. Nanosci. Nanotechnol. 7*, **2007**, 356.

[26] T. Matsushita, J. Masuda, T. Iwamoto, N. Toshima, *Chem. Lett. 36*, **2007**, 1264.

[27] N. Toshima, in: "*Macromolecular Complexes: Dynamic Interaction and Electronic Processes*", E. Tsuchida, Ed., VCH Pub., New York **1991**, pp. 331–352.