Macromolecule-Metal Nanoparticle Complexes for Novel Development of Information Technology and Energy Conversion

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Summary: Macromolecule-metal nanoparticle complexes have achieved a great deal of attention from the researchers since the nanotechnology boom, because nanoparticles can be easily prepared by chemical reactions, often stabilized by complex formation with macromolecules, and can play important roles in the construction of nanostructured materials for novel technologies. Here I would like to introduce three typical examples which are going to be developed in our group and will be potentially applied to novel information and energy-conversion technology, i.e., super-high-density magnetic recording media, fast-responsive liquid-crystal display, and processable thermoelectric materials.

Keywords: Liquid crystal displays; Metal nanoparticles; Nanomagnet; Super-high-density magnetic memory; Thermoelectric materials

Introduction

Material nanoparticles have received much attention recently.[1] However, the metal nanoparticles could not be well dispersed in media without stabilizers. If metal nanoparticles are dispersed in water, poly(*N*-vinyl-2-pyrrolidone)(PVP) is known as one of best stabilizers.[2] In this case, PVP surrounds the nanoparticles and binds to metal nanoparticles at multiple points to form macromolecule-metal nanoparticle complexes.[3] Since many PVP molecules surround a metal nanoparticle to form an organic layer, the surrounding organic layer is called as ‘‘a corona’’ against ‘‘a core’’ which is a metal nanoparticles located at the center, as schematically shown in Figure 1a. If the low molecular weight organic ligands coordinate the metal nanoparticles, assembled or aggregated ligand molecules form the corona as shown in Figure 1b. These coronas can not only stabilize metal nanoparticles by complexation, but also can make the metal nanoparticles well dispersed into a medium and add extra functions to meal nanoparticles.

Meal nanoparticles have been applied to various fields.[1] They are used as catalysts in solution for various organic reactions such as hydrogenation, hydrosilylation, hydrogen generation, hydration, oxidation, C-C bond formation, dehalogenation, and so on.[3] Other applications include hydrogen storage, sensor, optical device, electric circuit, magnet, drug, and so on. From the viewpoint of global problems for human beings, improvement of information technology and energy conversion is very important.

Here I will present a few examples of the application of macromolecule-metal nanoparticle complexes to improve information technology and energy conversion, i.e. nanomagnets for super-high-density magnetic recording media, metal nanoparticle dopants for fast-responsive liquid crystal displays, and semiconducting nanoparticles for potential application to processable thermo-electric materials hybridized with electroconductive polymers.

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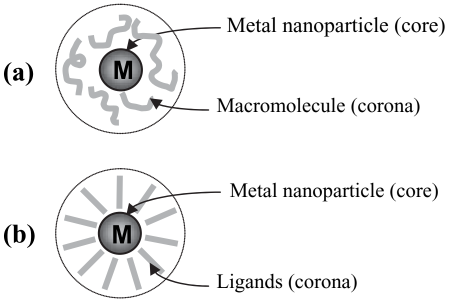

Figure 1.
Schematic model of metal nanoparticles (a core) covered by (a) macromolecules and (b) ligands forming a corona.

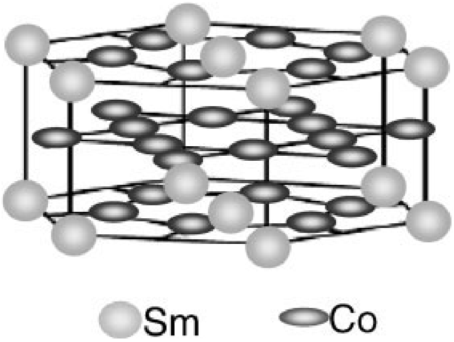

Figure 2.
Crystal structure of bulk alloy of $SmCo_5$ permanent magnet (a $CaCu_5$ type structure).

Nanomagnets for Super-High-Density Magnetic Recording Media

The density of memory has rapidly increased year by year according to demand of development of information technology. At the present the practical magnetic memory device is prepared by CoCr films compared of submicrometer sized domains prepared by vapor deposition The problems to be solved to make a higher density memories contain thermal fluctuation and noise. These problems can be solved by using monodispersed and smaller domains. S. Sun, et al.[4] proposed the preparation of single-nanometer-sized FePt nanoparticles by a chemical method and their alignement on a substrate. However, they showed superparamagnetism at room temperature. In order to get ferromagnetic nanomagnets, the FePt nanoparticles have to be treated by heat over 500 °C, which is accompanied by sintering to result in larger and nonuniform particles. Thus, the direct synthesis of ferromagnetic nanoparticles with uniform size of single nanometers by a chemical method is strongly desired to construct super-high-density magnetic recording devices.[5–7]

On the other hand some rare-earth alloys are known strong permanent magnet. In $SmCo_5$ bulk alloy having a $CaCu_5$ type structure (cf. Figure 2) is one of such strong permanet magnets practically used all over the world because of strong magnetic anisotropy, high Curie temperature, high coercively, and high saturation magnetization. Few people have already tried to prepare such ferromagnetic nanoalloy. H. Gu, et al.[8] reported the preparation of $SmCo_5$ nanoparticles from samarium(III) acetylacetate ($Sm(acac)_3$) and cobalt(0) octacarbonyl ($Co(CO)_8$), and the heat treatment of the nanoparticles. However, the resulting nanoparticles were unstable under air and did not exhibit any coercively at room temperature. Thus, we have tried to prepare $SmCo_5$ nano-alloy and succeeded to get the nano-alloy exhibiting ferromagnetism at room temperature.[9]

We have prepared PVP-protected $SmCo_5$ nanoparticles by heating the tetraethyleneglycol solution of $SmCl_3$ and $Co(acac)_3$ in the presence of PVP at 300 °C for 3h.The UV-Vis spectral change during the synthesis of $SmCo_5$ nanoparticles is shown in Figure 3, indicating that the band at ca. 250 nm attributed to ionic species disappears in ca. 2 h, i.e., the ionic species change to atomic metals in ca. 2 h heat treatment. The transmission electron microscopic (TEM) photograph and the size distribution histogram of the obtained nanoparticles, shown in Figure 4, exhibit that the average particle size of the $SmCo_5$ nanoparticles is about 33 nm. The composition of obtained nanoparticles was shown to be $SmCo_5$ by inductively coupled plasma (ICP) analysis. The X-ray diffraction pattern of nanoparticles is quite similar to that of bulk $SmCo_5$ materials, indicating a

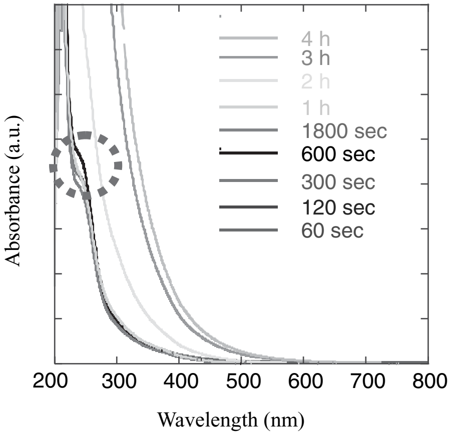

Figure 3.
UV-Vis Spectral Change during the synthesis of $SmCo_5$ nanoparticles starting from $SmCl_3$ and $Co(acac)_3$ in the presence of poly(*N*-vinyl-3-pyrrolidone).

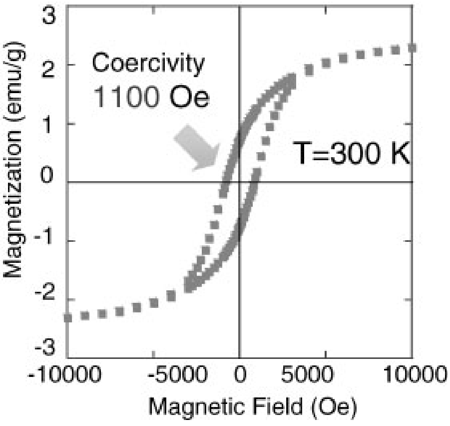

Figure 5.
The Magnetization hysteresis curve at 300 °C of $SmCo_5$ nanoparticles prepared from $SmCl_3$ and $Co(acac)_3$ in the presence of poly(*N*-vinyl-2-pyrrolidone) at 300 °C.

$CaCu_5$ type crystal structure. The magnetization hysteresis in Figure 5 exhibits enough high coercivity (1100 Oe) at room temperature. To our knowledge, this is the first report on rare earth nanomagnet showing ferromagnetism at room temperature. Since the considerably monodispersed $SmCo_5$ nanoparticles were directly prepared by a chemical method without heat treatment, they could be a potential candidate for the fundamental materials to provide super-high-density magnetic recording media.

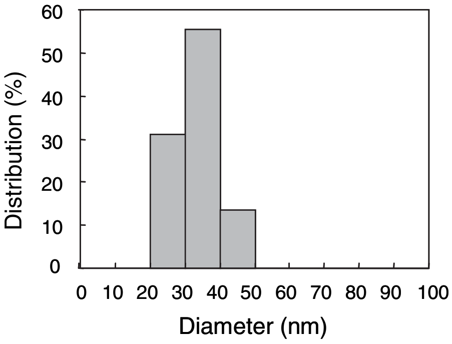

Figure 4.
Size distribution of $SmCo_5$ nanoparticles prepared from $SmCl_3$ and $Co(acac)_3$ in the presence of poly(*N*-vinyl-2-pyrrolidone) at 300 °C.

Nanoparticles for Fast-Responsive Liquid Crystal Displays

A liquid crystal display is a ubiquitous electronic display. It is used in any places at any time. The display is an interface for information between man and machine. A moving picture can transform a lot of information. For this purpose, a liquid crystal display is most useful at the present. In comparison with a plasma display and an electroluminescence display, a liquid crystal display has a disadvantage of slow response.

Recently we have succeeded to combine a nanoparticle technology with a liquid crystal display technology, which have resulted in fast response of a liquid crystal display. Metal nanoparticles protected by liquid crystal molecules were well dispersed in a liquid crystal medium, which is schematically shown in Figure 6. If PVP-protected metal nanoparticles were used as dopants of a liquid crystal medium, the nanoparticles were not dispersed in the medium. Thus, macromolecules or organic ligands, which surround the metal nanoparticles to form a corona, play a very important role to provide a well-dispersed nanoparticles.

Palladium nanoparticles which were protected by a typical liquid crystal molecule, 4-cyano-4′-pentylbiphenyl (5CB) were

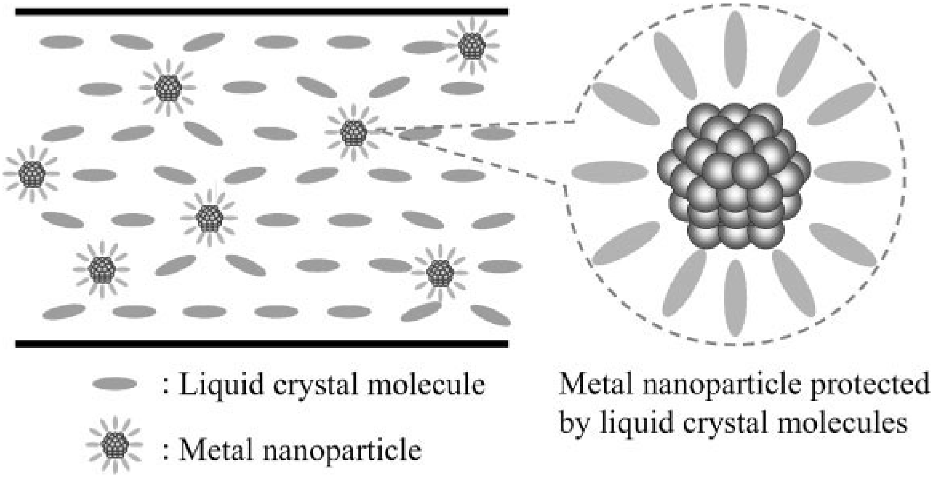

Figure 6.
Schematic model of the structure of metal nanoparticles protected by 4-cycro-4′-pentalbiphenyl (5CB) ligands, and their distribution in 5CB media.

prepared by photoreduction of palladium(III) acetate in tetrahydrofuren (THF) in the presence of 5CB.[10] The 5CB-protected Pd nanoparticles were added to 5CB, a twisted nematic liquid crystal medium. The liquid crystal medium, doped with or without 5CB-protected Pd nanoparticles, was used as a liquid crystal display, the opto-electric properties of which were observed by measuring the transmittance of the display at various applied voltages (V-T curve). The results of V-T curves of the liquid crystal displays at various frequencies are shown in Figure 7. Without Pd dopants, the transmittance of the 5CB liquid crystal display changes from 100% (white) to 0% (black) at the threshold voltage, ca. 1 volt (Figure 7a). This V-T curve does not change when the frequency is altered from 30 to 100 Hz. With Pd dopants, in contrast, the V-T curves change dramatically depending on the frequency. The shift of the threshold voltage depending on the frequency increases with increasing concentration of Pd nanoparticles in 5CB medium (cf. Figures 7b, 7c, and 7d).

This phenomenon is called frequency modulation.[11] We have found that the degree of frequency modulation depends on the kind of metal nanoparticles. Thus, we have prepared 5CB-protected Ag/Pd bimetallic nanoparticles from palladium (III) acetate and silver perchlorate by a photoreduction method in THF in the presence of 5CB.[12]

Figure 8 exhibits a transmission electron microphagh (TEM) and a size distribution histogram of 5CB-protected Ag/Pd (1/1) bimetallic nanoparticles. The average diameter of the bimetallic nanoparticles d_{av} is 2.8 nm and the standard deviation σ is 0.9 nm. The 5CB twisted nematic liquid crystal display doped with 5CB-protected Ag/Pd (atomic ratio = 1/1) nanoparticles exhibits different V-T curves depending on the frequency (Figure 9). The shift of the threshold voltage due to the frequency in liquid crystal display doped with Ag/Pd bimetallic nanoparticles (Figure 9) is larger than that doped with Pd nanoparticles (Figure 7a), which could be attributed to the difference of electroconductivity of the metal nanoparticles dopant.

The liquid crystal display fabricated with 5CB doped with Ag/Pd bimetallic nanoparticles exhibited fast response on comparison with that without dopants. For example, the rising response time t_r and the rising delaying time t_{dr} were 1.9 and 0.9 msec., respectively, when the applied voltage and frequency were changed from 5.1 V and 100 Hz to 17 V (5 cycles) or 5.1 V

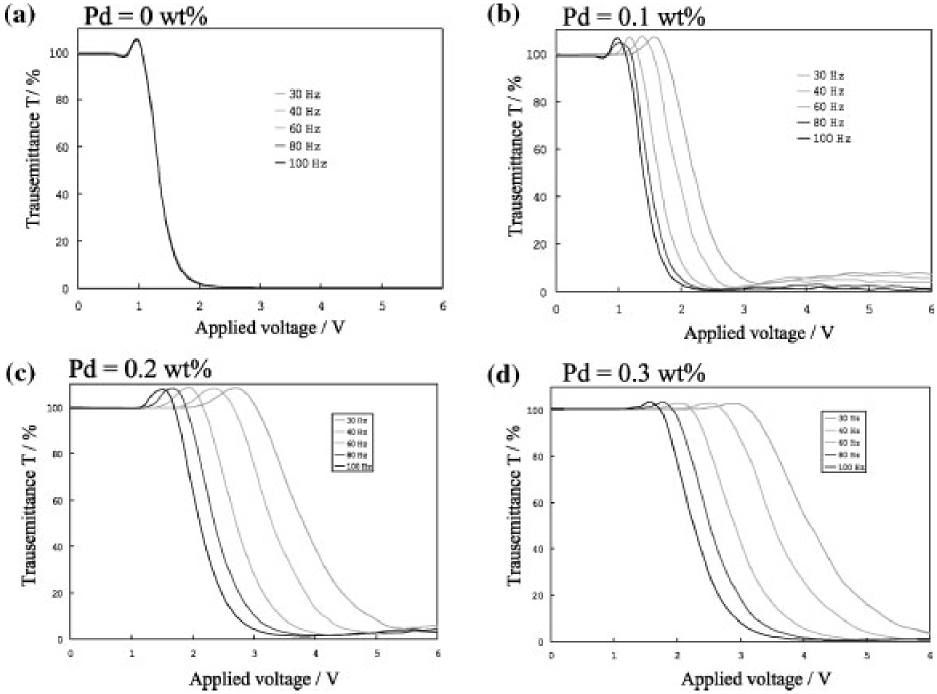

Figure 7.
V-T curves of liquid crystal displays doped with or without 5CB-covered Pd nanoparticles.

and 500 Hz, respectively. These response times were much faster than those of pure 5CB without dopants under the similar conditions (7.8 and 2.1 msec, respectively).

The fast response of doped liquid crystal displays was observed in other systems. Thus, metal nanoparticles are expected to improve the response time of the practical liquid crystal displays.

Nanoparticles for Processable Thermoelectric Materials

From the viewpoints of the increasing consumption of fossil fuel by human being,

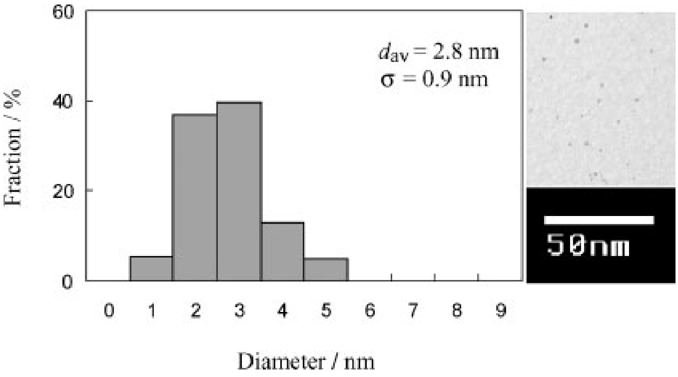

Figure 8.
TEM photograph and size distribution histogram of Ag/Pd bimetallic nanoparticles covered by 5CB ligands.

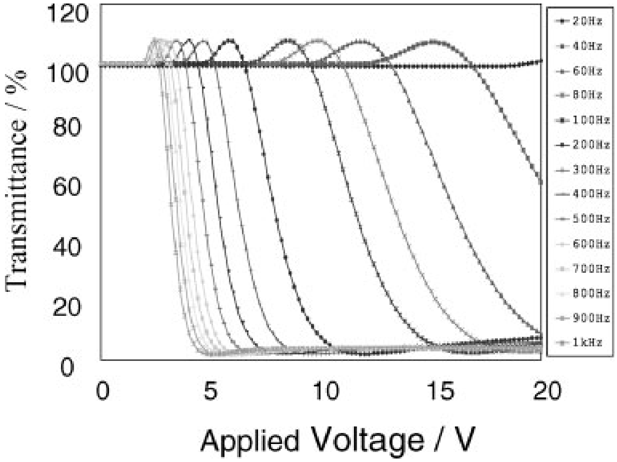

Figure 9.
A V-T curve of 5CB liquid crystal display doped with 5CB-covered Ag/Pd bimetallic nanoparticles at various frequencies.

especially by developing countries and the increasing amount of waste energy due to the low energy conversion, e.g. in automobiles, the thermo-electric materials, which can convert the waste thermal energy to electricity, have received much attention.

As the thermo-electric materials, many kinds of inorganic semiconductors have been proposed. Among them, bismuth telluride Bi_2Te_3 shows an interesting property. However, these inorganic semiconductors are difficult to produce the thermo-electric devices because of hardness. From this point of view, polymer could be an excellent material. In fact, we have reported the thermo-electric property of electroconducting polymers like polyaniline.[13,14] They are processable, but do not have enough efficiency in thermo-electric conversion for practical use.

Here we have successfully prepared Bi_2Te_3 nanoparticles by a chemical method, although we previously reported the Bi_2Te_3 nanoparticles by laser ablation.[15] The prepared Bi_2Te_3 nanoparticles could be combined with polymers to produce processable hybrid thermo-electric materials. The Bi_2Te_3 nanoparticles were at first prepared by reduction of bismuth(III) chloride ($BiCl_3$) and tellirium(IV) ethoxide ($Te(OEt)_4$) in ethanol at 0 °C by $NaBH_4$ in the presence of PVP. Based on the TEM photograph, the prepared nanoparticles had the average diameter of 6.9 nm, which can be increased by refluxing in ethanol resulting in the nanoparticles with a diameter of 18.4 nm.

Since the heat treatment of Bi_2Te_3 nanoparticles, prepared by reduction with $NaBH_4$, can make the growth of nanoparticles in size and improve the crystalinity, we have treated the seed nanoparticles by heat in various alcohols at their refluxing temperatures. For example, in ethanol at 80 °C the particle size grew up to 14 nm, and in ethyleneglycol at 198 °C it was 60 nm. The higher the refluxing temperature, the larger the size of nanoparticles. This means that we can control the size of Bi_2Te_3 nanoparticles by controlling the refluxing temperature and refluxing time. X-ray diffraction (XRD) pattern of the nanoparticles prepared by refluxing at high temperature indicated the crystallinity could be also controlled by controlling the refluxing temperature and refluxing time.

These reaction processes can be illustrated as Figure 10. Thus, Bi(II) and Te(III) ions can coordinate to the ligand parts of polymer to form macromolecular complexes. When both ions are reduced by $NaBH_4$ at 0 °C, Bi and Te metal atoms get

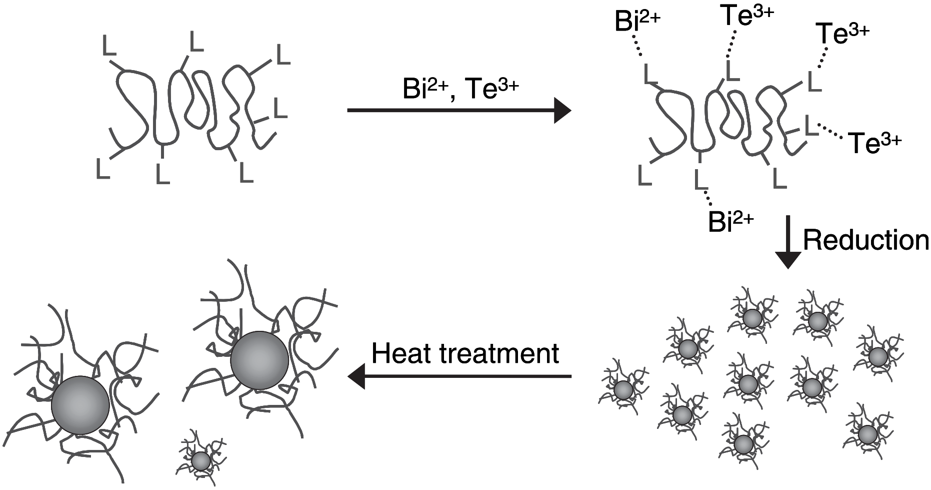

Figure 10.
Proposed formation processes for Bi_2Te_3 nanoparticles by $NaBH_4$ reduction and successive refluxing in solvent.

together to generate Bi_2Te_3 seed nanoparticles, which are unstable under air and have low crystallinity because of weak metallic bond. By heat treatment at the seed nanoparticles by refluxing for a while, aggregation of the seed nanoparticles provide large Bi_2Te_3 nanoparticles, which are rather stable under air and have high crystallinity.

Conclusion

1. Macromolecule-metal nanoparticle complexes were successfully prepared by a chemical method in solution in the presence of polymer(s) (PVP) and/or organic ligand(s), and applied to development of information technology and energy conversions.
2. The capped $SmCo_5$ alloy nanoparticles prepared by a chemical method showed enough high coercivity of 1100 Oe at room temperature without heat treatment, providing a potential application to super-high-density memory storage.
3. Liquid crystal molecule-capped Ag/Pd bimetallic nanoparticles prepared by a chemical method were used as a dopant for twisted nematic liquid crystal display. The doping with the metal nanoparticles can improve the response time of the liquid crystal display, a ubiquitous electronic display.
4. Polyvinylpyrrolidone-capped Bi_2Te_3 nanoparticles prepared by a chemical method had a crystalline structure by successive refluxing, providing a potential application to processable thermoelectric materials.

Acknowledgements: The author expresses his sincere thanks to all the colleagues, especially those who appear in the cited literatures for their intelligent and intensive efforts. This work is supported by Grant-in-Aid for Scientific Research from MEXT, Japan, and Consortium R&D Project for Regional Revitalization from METI, Japan.

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