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Recent Progress in Applications of Ligand-Stabilized Metal Nanoclusters

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Summary: Due to a nanotechnology boom in science and technology, the metal nanoclusters or nanoparticles stabilized by polymers and organic ligands have achieved much attention recently all over the world. We have studied on the preparation of polymer-stabilized metal nanoclusters by chemical methods, and applied them mainly to catalyses. Here the recent progresses in our group are presented in the structure control of bimetallic and trimetallic nanoclusters and in the applications of metal nanoclusters not only to the catalyses but also to the sensing responsive to pH and molecular recognition, and to the electro-optic properties of liquid-crystalline display rapidly responsive to frequency modulation. Preparation of trimetallic nanoclusters with a triple core/shell structure is especially emphasized to serve as a very active catalyst at a special atomic ratio of three elements.

Keywords: liquid crystal display; metal nanocluster catalyst; self-organization of triple core/shell structure; sensor; trimetallic nanoparticle

Introduction

Due to a nanotechnology boom in science and technology, the metal nanoclusters or nanoparticles stabilized by polymers and organic ligands have achieved much attention recently all over the world. The metal nanoclusters or nanoparticles are considered to serve the development of nanotechnology as one of the most important building blocks to construct nano-organized systems.[1] The colloidal dispersions of metal nanoclusters have long been used as catalysts.[2-6] They are applied to catalysts for hydrogenation, hydrogen generation, hydrosilylation, hydration, oxidation, carbonylation, Heck reaction, Suzuki reaction, and so on. Although sometimes the colloidal dispersions have disadvantage, for example, in separation of the metal from the reaction mixtures on comparison with supported metal catalysts, they have advantages in other cases in

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removal of exhausted reaction heat, exclusion of unexpected effect of supports, and so on, especially in control of the structure of bimetallic nanoclusters. The core/shell structure of bimetallic nanoclusters have been constructed at first by simultaneous reduction of two kinds of precious metal under mild conditions.[4,7,8] Redox potential of two metal ions and coordination ability of protective polymer to metal atoms are the two factors to control the bimetallic core/shell structure.[9] The inverted core/shell structure, in contrast, was constructed by a sacrificial hydrogen method,[10] in which hydride adsorbed on the surface of the core metal serves as a reductant for reduction of precious metal ions to form a shell. This method can be applied to control of the core/shell structure in various pairs of elements.

Metal nanoclusters are applied not only to catalyses but also to sensing, information technology, and so on. Bio-sensing is an interesting field which requires nanotechnology as well. Information technology is another important field, which can develop a new field in science as well. Here the recent progresses in our group will be presented in the structure control of bimetallic nanoclusters and their applications not only to the catalyses but also to the sensing by using plasmon absorption band of Au nanoclusters and the rapid electro-optic response of liquid crystalline display doped with metal nanoclusters.

Self-Organization for Construction of Core/Shell Structure

We have already succeeded in constructing the core/shell structure of bimetallic nanoclusters both by natural properties of metal ions themselves in simultaneous reduction[9] and by sacrificial hydrogen strategy.[10] Recently we have found that the physical mixing of colloidal dispersions of Ag and Rh nanoclusters results in bimetallic nanoclusters with a pseudo-core/shell structure.[11] This is a simple but very strange phenomenon since no change usually occurs by mixing dispersions of two kinds of polymer-protected metal nanoclusters. This self-organization by fusion of two kinds of nanoclusters was at first found in the mixtures of poly(*N*-vinyl-2-pyrrolydone)(PVP)-protected Ag and Rh nanoclusters. The plasmon absorption band of Ag metal nanoclusters disappears in 1 h at room temperature after mixing.[11] One day after mixing, the size of the particles was observed to decrease by measurements with a transmission electron micrography (TEM). The formation of a Rh-core/Ag-shell structure in this fusion is confirmed by distribution analyses of Ag and Rh for each particle with an energy-filtered TEM. Schematic

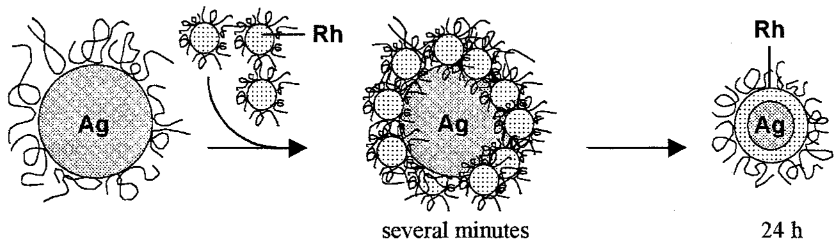

Figure 1. Schematic presentation for self-organizing construction of pseudo-core/shell structure by mixing of Ag and Rh nanoclusters.

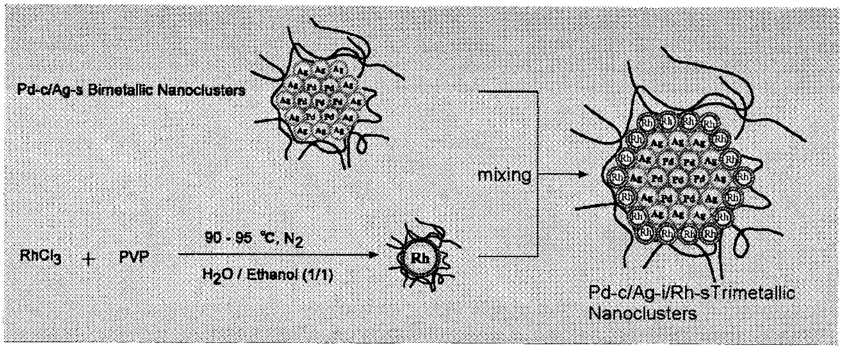

Figure 2. Preparation of triple core/shell-structured Pd/Ag/Rh trimetallic nanoclusters by mixing Pd/Ag bimetallic nanoclusters and Rh nanoclusters.

presentation of this change is shown in Figure 1. When poly(sodium acrylate)(PAA-Na)-protected Ag and Rh nanoclusters are used instead of PVP-protected ones, in contrast, the disappearance of the Ag plasmon absorption band takes a month instead of an hour. This means that the kind of protective polymer is very important to understand this interesting fusion between polymer-protected metal nanoclusters.

This simple procedure for self-organization of a pseudo-core/shell structure is applied to the syntheses of triple core/shell-structured trimetallic nanoclusters. Thus, the PVP-protected bimetallic nanoclusters with a Pd-core/Ag-shell structure, which had been prepared by covering Pd core with Ag shell by the sacrificial hydrogen method, were mixed with PVP-protected Rh nanoclusters in an aqueous solution at room temperature (Figure 2). Thus prepared Pd/Ag/Rh

(1/2/12 mol/mol/mol) trimetallic nanoclusters with a triple core/shell structure have an average diameter of 2.1 nm and their catalytic activity for hydrogenation of methyl acrylate is 19 mol-H_2 mol-M^{-1} s^{-1}, which is more than twice of those of the corresponding monometallic nanoclusters, and is higher than those of the corresponding bimetallic nanoclusters. This high activity of trimetallic nanoclusters can be explained by the sequential electron transfer from the surface element to the inner element by an electromic effect of neighboring elements.

Sensor Responsive to pH and Molecules

The colloidal dispersions of Au nanoclusters have a plasmon absorption band at about 520 nm and have a red color. Addition of inorganic salts like NaCl to this red dispersions makes the color change from red to blue. This is usually an irreversible change. This color change can be applied to highly sensitive detection of target DNA when the Au nanoclusters are modified by the corresponding DNAs.[12-14] In this connection, we have found that the colloidal dispersions of 3-mercaptopropionic acid(MPA)-protected Au nanoclusters show a reversible color change between red and blue depending on pH of the solution.[15] This could be the first report on a reversible color change of Au nanoclusters.

The MPA-stabilized Au nanoclusters were prepared by reduction of $HAuCl_4$ with trisodium citrate in the presence of MPA (Figure 3).[16] The as-prepared dispersion of Au nanoclusters has the plasmon absorption peak at ca. 523 nm and shows a red color. The average diameter of Au nanoclusters was determined to be 2.0 nm (δ = 0.7 nm) by the observation with TEM. The pH of the solution was 5.9. Addition of HClaq to change the pH from 5.9 to 3.8 results in color change from red to purple, having the absorption peak at ca. 532 nm. This large red-shift of the plasmon band is ascribed to a dipole-dipole interaction among the Au nanoclusters forming aggregates. [17] In fact, the TEM photograph of the sample at pH 3.8 shows the large aggregates of Au nanoparticles. Addition of NaOHaq to this purple solution to change the pH from 3.8 to 5.9 results in color change from purple back to red, having the absorption peak at ca. 524 nm. The TEM photograph of the sample shows that the average diameter of Au nanoclusters is 2.1 nm (δ = 0.7 nm), which is quite similar to that of the original. This reversible change of color and TEM photograph of the dispersions of MPA-protected Au nanoclusters can be repeated ten times without any change in color and TEM photograph. This reversible dispersion-aggregation change

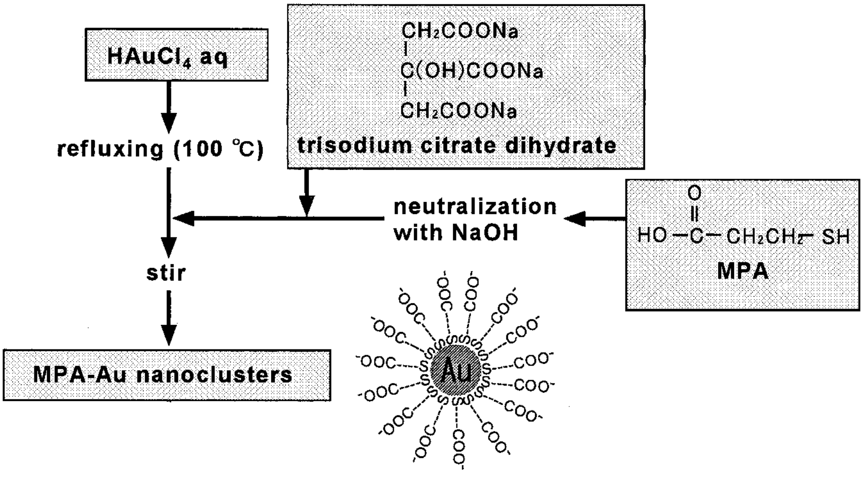

Figure 3. Preparation of MPA(3-mercaptopropionic acid)-protected Au nanoclusters.

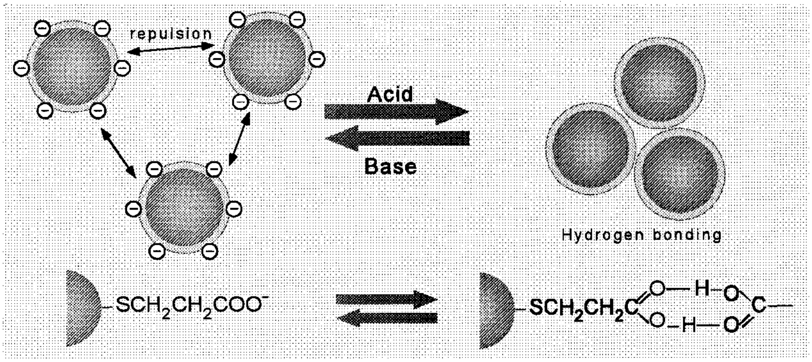

Figure 4. Schematic illustration of reversible color change of MPA-protected Au nanoclusters depending on pH.

could be described to electronic repulsion between carboxylate anions and to hydrogen bonding between carboxylic acids, respectively, which cover the Au nanoclusters as illustrated in Figure 4. When the Au nanoclusters are stabilized by poly(cyclodextrin), the recognition of an organic molecule having a thiol and a hydroxycarbonyl group, like *p*-mercaptobenzoic acid, can be performed by cyclodextrin cavities, resulting in the color change of dispersions of Au nanoclusters.

Frequency-Modulated Liquid Crystalline Display

Application of nanomaterials to information technology is one of the most important research fields of nanotechnology. The merging of nanomaterials and nanotechnology into electro-optic device technology such as liquid-crystalline device may attract the attention of researchers who are interested in inaugurating a new kind of combination of different fields. Here Pd nanoclusters stabilized by liquid-crystalline materials were prepared and applied to electro-optic device, in which a new type of driving system, frequency modulation, is first created for the liquid-crystalline display.[18,19]

Pd nanoclusters protected by 4-cyano-4'-pentylbiphenyl (5CB), a typical liquid-crystalline molecule, were prepared by UV irradiation of the tetrahydrofuran solution of Pd(II) acetate in the presence of 5CB (Figure 5).[20] The 5CB-protected Pd nanoclusters, thus prepared, have an average diameter of 1.9 nm and have high solubility into liquid-crystalline matrices. Addition of 5CB-Pd nanoclusters (1 wt%) into a guest-host type of liquid-crystalline device improves its electro-optic properties, i.e., increases the contrast ratio of the device.

5CB-protected Pd nanoclusters can also be used as a dopant to fabricate a twisted nematic liquid-crystalline device, where the sign of dielectric anisotropy ($\Delta\varepsilon$) of the twisted nematic liquid-crystalline molecule of medium is opposite to that of the liquid-crystalline molecule used for a dopant. The electro-optic properties were measured for the devices with and without 5CB-Pd nanoclusters. The relationship between the transmittance of the device vs. the applied voltage in the device doped with 5CB-Pd nanoclusters is much different from that without 5CB-Pd nanoclusters. That is, the relation curves without Pd nanoclusters are not responsive to the frequency, while those with Pd nanoclusters are responsive to the frequency, as shown in Figure 6. This means that, without Pd nanoclusters, the white-and-black response depends only on the applied voltage, while, with Pd nanoclusters, the response depends not only on the applied voltage but also on the frequency.[18] In other words, frequency-modulation in a twisted nematic liquid-crystalline device is successfully developed by using Pd nanoclusters. One of the most important advantages of this frequency-modulation system is a quick response as a display. Although a conventional liquid-crystalline display has the response time of about 30 ms, the present

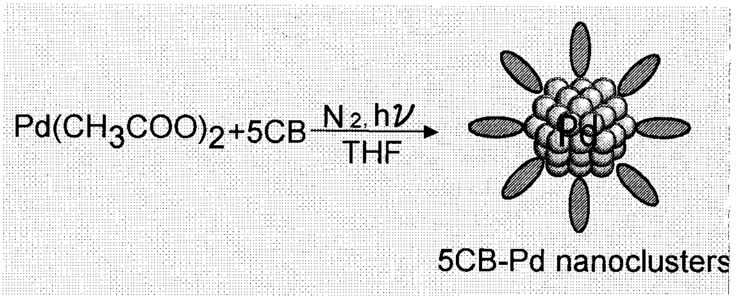

Figure 5. Preparation of 5CB-Pd nanoclusters

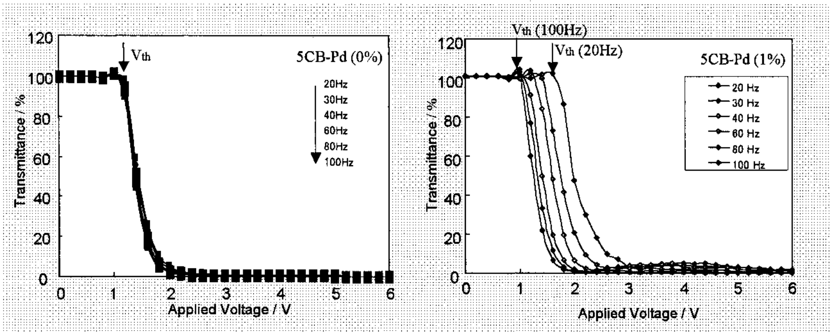

Figure 6. Relations of transmittance vs. applied voltage in the twisted nematic liquid-crystalline device doped with 5CB-protected Pd nanoclusters.

frequency-modulated display has the response time of 3.4 ms, which is about one tenth of that of the conventional one.

Conclusion

Various kinds of metal nanoclusters, stabilized by coordination of organic molecules with high or low molecular weight, have been developed to apply not only to catalyses but also to optical and electro-optical properties. The core/shell structure of bimetallic nanocluster can be constructed by 1) simultaneous reduction, 2) sacrificial hydrogen strategy, and 3) self-organization in mixing. Triple core/shell-structured trimetallic nanoclusters can be constructed by combination of the first simultaneous reduction method or the second sacrificial hydrogen method and the last self-organizing physical mixing method. The trimetallic nanoclusters with triple core/shell structures work as much more active catalysts for hydrogenation of olefin than the corresponding bimetallic or monometallic nanoclusters.

Ligand-stabilized metal nanoclusters can also be applied to sensors responsive to reversible pH change by using their optical property, and to liquid-crystalline devices responsive to frequency-modulation by using their doping effect on electro-optical properties.

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