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Self-Organization of Silver-Core Bimetallic Nanoparticles and Their Application for Catalytic Reaction

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1. Introduction

Metal nanoparticles have received much attentions as a building block of advanced materials for nanoscience and nanotechnology (Bönnemann & Richards, 2001). Their optical, (Fukumi et al., 1994; Lu et al., 1999; Link et al., 1999; Shipway et al., 2000), magnetic (Sun et al., 1999; Teranishi & Miyake, 1999), and catalytic (Kiely et al., 1998; Pileni, 1998; Bradley, 1994; Harriman, 1990; Lee et al., 1995; Toshima et al., 1995; Bonilla et al., 2000; Siepen et al., 2000) properties have been reported with great interests. The character of metal nanoparticle can be altered by the addition of other metals. Bimetallic nanoparticles, composed of two different metallic elements, have been reported to show outstanding characters different from the corresponding monometallic nanoparticles (Harriman, 1990; Yonezawa & Toshima, 1993; Toshima & Hirakawa, 1997, 1999; Toshima & Wang, 1994; Lee et al., 1995). For example, catalytic activities of gold (Au)-core structured bimetallic nanoparticles, gold/platinum (Au/Pt) (Harriman, 1990; Yonezawa & Toshima, 1993; Toshima & Hirakawa, 1999), gold/palladium (Au/Pd) (Toshima & Hirakawa, 1999; Lee et al., 1995), and gold/rhodium (Au/Rh) (Toshima & Hirakawa, 1999), for hydrogenation and/or water reduction are higher than platinum (Pt), palladium (Pd), and rhodium (Rh) monometallic nanoparticles, respectively. Surprisingly, in some cases, a physical mixture of monometallic nanoparticles such as Pt and ruthenium (Ru) nanoparticles in solution shows higher catalytic activity than the corresponding monometallic nanoparticles under a certain condition (Toshima et al., 1995; Toshima & Hirakawa, 1997). This suggests that an interaction between two kinds of monometallic nanoparticles can produce novel nanoparticles. Further, it has been reported that physical mixture of silver (Ag) and other metal nanoparticles, such as Pt, Rh, and Pd, spontaneously forms the bimetallic nanoparticles with Ag-core structure in aqueous solution. This reaction can be used to construct the core-shell structured novel bimetallic nanoparticles. The formed nanoparticles demonstrate superior character for certain catalytic reactions.

In this chapter, the simple method of the preparation of core-shell structured bimetallic nanoparticles by the physical mixing and the application of the formed novel metal nanoparticles for catalytic reaction are described. The topics of the catalytic reaction presented in this chapter are the visible light induced hydrogen generation (Toshima &

Hirakawa, 2003), the removal of reactive oxygen species (Hirakawa & Sano, 2009), and its application to the chemoprevention of ultraviolet induced biomolecules damage (Hirakawa et al., 2008, 2009).

2. Spontaneous formation of silver-core bimetallic nanoparticles

Much attention has been paid to bimetallic nanoparticles, especially those having a core/shell structure (Toshima et al., 2007). From the view point of Au catalysts, bimetallic nanoparticles have received much attention recently. On the other hand, a physical mixture of monometallic nanoparticles such as Pt and Ru nanoparticles in solution shows higher catalytic activity than the corresponding monometallic nanoparticles under a certain condition (Toshima et al., 1995; Toshima & Hirakawa, 1997). Further, it has been reported that physical mixture of Ag and other metal nanoparticles, such as Pt, Rh, and Pd, spontaneously forms the bimetallic nanoparticles with Ag-core structure in aqueous solution (Figure 1). In this section, the spontaneous formation of the Ag-core bimetallic nanoparticles is reviewed.

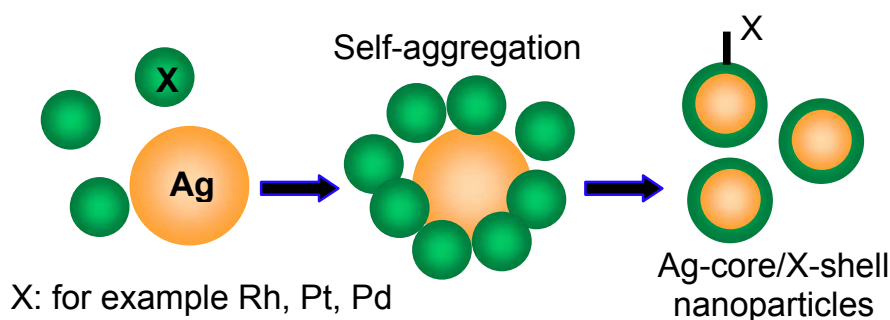


Fig. 1. Schematic diagram of the spontaneous formation of Ag-core bimetallic nanoparticles

2.1 Silver-core/rhodium-shell bimetallic nanoparticles

The interaction between Ag and Rh monometallic nanoparticles in solution by physical mixing was reported. The main reason for using Ag and Rh nanoparticles is the reported prominent characteristics of Rh nanoparticles as a catalyst (Toshima & Hirakawa, 1999), and the expected electronic effect of Ag similar to Au upon enhancement of the catalytic activity of Rh. Furthermore, Ag is inexpensive metal compared with Au. The colloidal dispersions of Ag and Rh monometallic nanoparticles protected by poly(*N*-vinyl-2-pyrrolidone) (PVP), a water soluble polymer, were prepared by an alcohol reduction method (Hirai et al., 1979). Average diameters of Ag and Rh monometallic nanoparticles were 7.5 nm and 2.2 nm, respectively.

2.1.1 Surface plasmon absorption of silver-core bimetallic nanoparticles

Colloidal sol of Ag nanoparticles shows characteristic plasmon absorption around 400 nm (Henglein, 1979). The plasmon absorption band of Ag nanoparticles decreased by addition of Rh nanoparticles and was almost completely extinguished within 30 min after mixing (Figure 2). The parts of plasmon absorption in larger wavelength region were preferentially

extinguished within 10 min, suggesting that influences of Rh nanoparticles on Ag nanoparticles depend on the size of the Ag nanoparticles. When relatively smaller molar quantity of Rh to Ag was added, the plasmon absorption was not completely extinguished. More than 40 atom-mol% of Rh against to Ag was required to extinguish the plasmon absorption band completely.

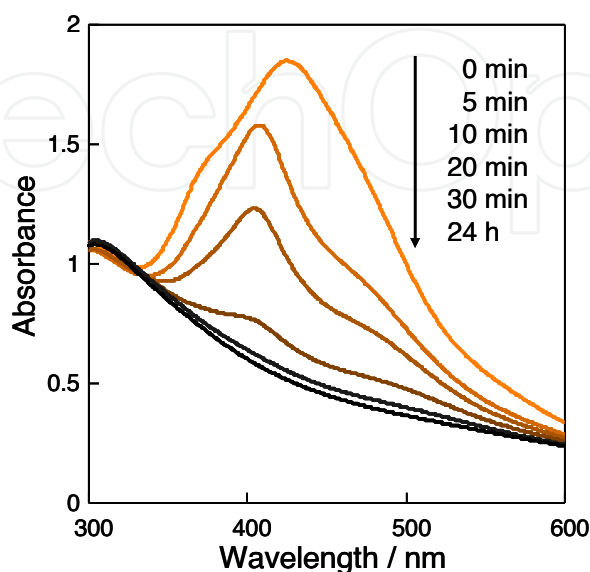


Fig. 2. UV-Vis spectral change of the physical mixtures of dispersions of Ag and Rh nanoparticles. The aqueous solutions of Ag (1 atom-mmol L⁻¹, 50 mL) and Rh (1 atom-mmol L⁻¹, 50 mL) nanoparticles were mixed.

2.1.2 Transmission electron microgram of the silver-core bimetallic nanoparticles

Figure 3 shows transmission electron microscopy (TEM) photographs of the physical mixtures of Ag and Rh monometallic nanoparticles. The samples for TEM measurement were prepared by drying the aqueous dispersions of the physical mixtures of Ag and Rh nanoparticles under vacuum in 0, 10, and 30 min, and 24 h, respectively, after mixing. Relatively large particles are attributed to Ag nanoparticles, and rather small ones are Rh nanoparticles. The TEM photographs showed that Rh particles gathered around Ag particle to surround within several minutes, comparable period of the extinction of plasmon absorption. Interestingly, these aggregated particles changed into homogeneous small particles (average diameter = 2.7 nm) after 24 h. Preliminary study has shown that the

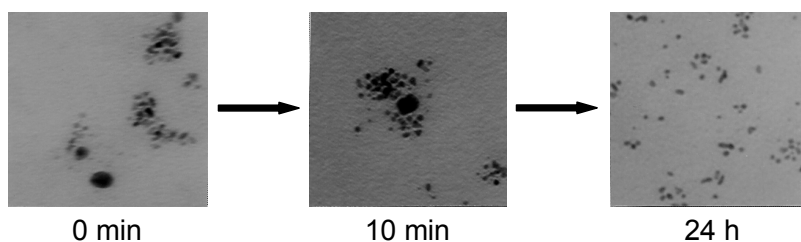


Fig. 3. TEM photographs of the physical mixtures of Ag and Rh nanoparticles. The aqueous solutions of Ag and Rh nanoparticles (1/1, atom-mol/atom-mol) were mixed, and dried after indicated periods.

increase of Rh/Ag molar ratio reduces the average diameter and the size distribution of the nanoparticles. The elemental analysis using characteristic X-ray in high-resolution TEM measurement has shown that the particles produced from their physical mixtures in 24 h are composed of Ag and Rh.

2.1.3 X-ray diffraction of the of silver-core bimetallic nanoparticles

Figure 4 shows X-ray diffraction (XRD) patterns of poly(*N*-vinyl-2-pyrrolidone)-protected Ag and Rh monometallic nanoparticles, and their physical mixture. The sample of the physical mixture of Ag and Rh nanoparticles was prepared by drying the mixtures of their aqueous solutions under vacuum for 24 h after mixing. The XRD pattern of the mixtures of Ag and Rh nanoparticles was similar to that of Rh nanoparticle, suggesting that the surface of the particle produced by mixing Ag and Rh nanoparticles is composed of Rh. Similarly, Au-core/Pt-shell and Au-core/Pd-shell structured nanoparticles have shown the XRD pattern quite similar to that of their surface metals (Yonezawa & Toshima, 1995). These findings suggest that the aggregation of Rh particles around the Ag particle is involved in the extinction of the plasmon absorption.

2.1.4 Mechanism of the formation of the silver-core/rhodium shell bimetallic nanoparticles

Henglein *et al.* reported that lead (Pb) atoms transfer from Pb colloidal particle onto the surface of Ag colloidal particle in physical mixing of Ag and Pb colloidal sols (Henglein *et al.*, 1992). If the extinction of the plasmon absorption is due to coating of the surface of Ag particle by Rh atoms transferred from Rh nanoparticle, at least 28 mol% of Rh to Ag is required assuming that a Ag particle (average diameter = 7.5 nm) is uniformly coated by Rh atoms in a one-atom layer. In the present experiments about 40 atom-mol% of Rh to Ag was

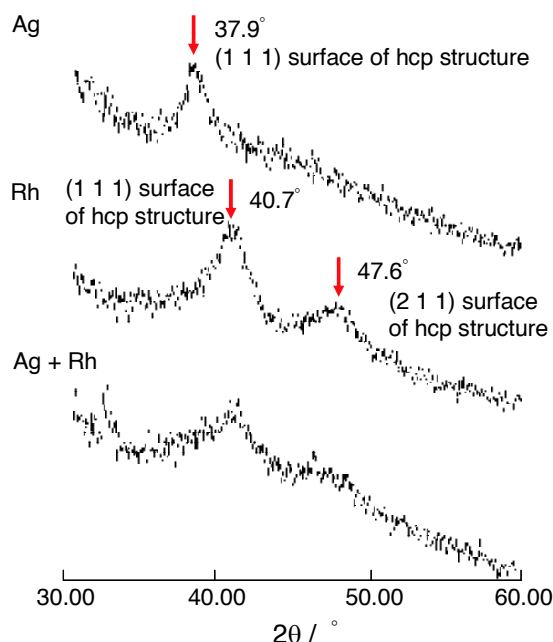


Fig. 4. XRD patterns of Ag and Rh monometallic nanoparticles, and their physical mixture (1/1, atom-mol/atom-mol)

required to completely extinguish the plasmon absorption, which is reasonably supporting the above assumption. These observations suggest that the physical mixture of Ag and Rh nanoparticles spontaneously generates Ag/Rh bimetallic nanoparticles with an Ag-core/Rh-shell structure. The disappearance of the XRD peak of Ag nanoparticles suggests that the core of this bimetallic nanoparticles is not complete Ag, but possibly has a partial Ag/Rh alloy structure. The driving force of the formation of this Ag/Rh bimetallic nanoparticles may be due to the larger binding energy between Ag and Rh atoms than between Rh atoms (Peiner & Kopitzki, 1998). Reduction of diameter of the nanoparticle increases not only its surface energy but also number of the binding sites between Ag and Rh atoms, which stabilizes the total energy. Therefore, the shrinking of Ag/Rh bimetallic nanoparticles might be explained by the balance between the binding energy and the surface energy. The size and the rate of formation of the bimetallic nanoparticles can be controlled by the kind and concentration of protective agents. The self-assembling formation of bimetallic nanoparticle using Ag nanoparticle is applicable to construction of novel nanoparticles.

2.2 Silver-core/noble metal-shell bimetallic nanoparticles

The above mentioned procedure can be used to prepare the Ag-core/noble metal shell nanoparticles, other than Ag-core/Rh-shell nanoparticles. The physical mixing of Ag and other metal nanoparticles, such as Au, Pt, Rh, and Pd particles, produces Ag-core bimetallic particles. The interaction rate between Ag and other metal nanoparticles was determined by the extinction of the surface plasmon absorption of Ag nanoparticle. The initial step of this reaction was investigated by isothermal titration calorimetry (Toshima et al., 2005). This study revealed that the strength of the interaction between Ag and other metals increases in the order of Rh/Ag > Pd/Ag > Pt/Ag.

The formed Ag-core/Pt-shell nanoparticle catalyzed the decomposition of hydrogen peroxide (described later). On the other hand, Au and Au/Ag nanoparticles showed an activity of photocatalytic decomposition of methylene blue (Hirakawa, 2007), although their activities were significantly smaller than that of well-known titanium dioxide photocatalyst (Fujishima et al., 2000, 2008). The physical mixing method is simple and useful to prepare novel bimetallic nanoparticles. These nanoparticles may be used as catalyst and photocatalyst.

2.3 Application to the preparation of trimetallic nanoparticles

This method can be applied to the preparation of trimetallic nanoparticles (Toshima et al., 2007, 2011). It has been reported that the synthesis of trimetallic nanoparticles having a Au-core structure by a combination of the preparation of bimetallic nanoparticles by co-reduction with the formation of core/shell-structured bimetallic nanoparticles by self-organization in physical mixture (Figure 5). The formation of trimetallic nanoparticles has been suggested by UV-Vis spectral change, TEM image change, FT-IR spectra of adsorbed carbon monoxide, XPS spectra and calorimetric studies. The catalytic activity of trimetallic nanoparticles in the molar ratio of Au/Pd/Rh = 1/4/20 was higher than the corresponding monometallic and bimetallic nanoparticles for hydrogenation of methyl acrylate. This high catalytic activity can be understood by sequential electronic charge transfer from surface Rh atoms to interlayered Pt atoms and then to core Au atoms (Toshima et al., 2011).

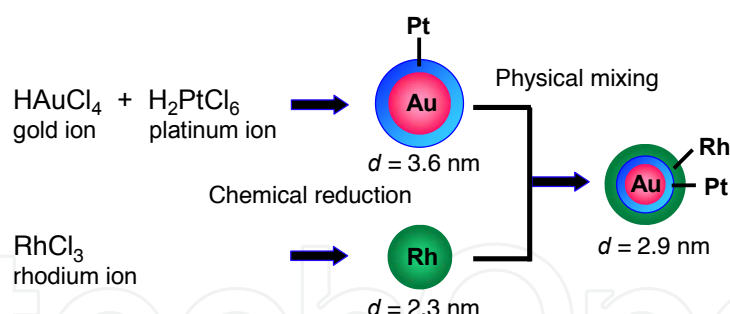


Fig. 5. Schematic diagram of the formation of the trimetallic Au/Pt/Rh nanoparticles

3. Visible-light-induced hydrogen generation by metal nanoparticle catalytic system

Metal nanoparticles are very important materials for nanoscience and nanotechnology (Fukumitsu et al., 1994; Lu et al., 1999; Link et al., 1999; Sun et al., 1999; Teranishi & Miyake, 1999; Akinaga, 2002). A particularly large number of reports have been published on their applications to catalysts (Kiely et al., 1998; Pileni, 1998; Bradley, 1994; Widegren & Finke 2003; Willner et al., 1987; Toshima et al., 1995; Yonezawa & Toshima, 1993). As the catalyst in the homogeneous system, the colloidal dispersions of metal nanoparticles have the advantage that they are soluble or homogeneous in an aqueous solution and transparent to visible light (Kiely et al., 1998; Pileni, 1998; Bradley, 1994; Widegren & Finke 2003; Willner et al., 1987). Thus, colloidal metal nanoparticles are useful for photocatalytic reaction systems. For example, colloidal metal nanoparticles catalyze the water reduction in the visible-light-induced electron transfer system composed of ethylenediaminetetraacetic acid disodium salt (EDTA), tris(bipyridine)ruthenium(II) dichloride ([Ru(bpy)₃]²⁺), and 1,1'-dimethyl-4,4'-bipyridium dichloride (methyl viologen, MV²⁺) (Yonezawa & Toshima, 1993) (Figure 6).

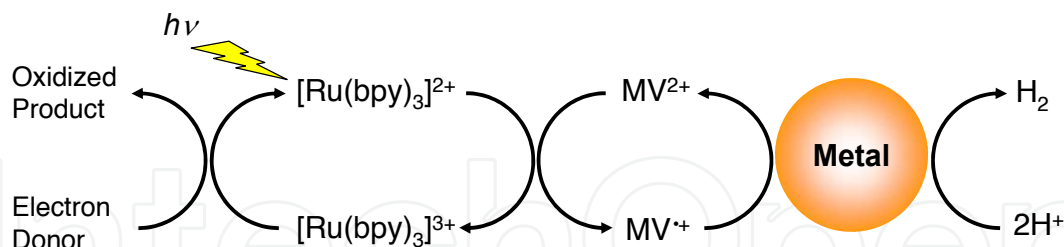


Fig. 6. Schematic diagram of the visible-light induced hydrogen generation using the electron transfer system and metal nanoparticle catalyst

3.1 Catalytic activity of gold-core/platinum-shell bimetallic nanoparticles

The bimetalization of metal nanoparticle can improve the catalytic activity of surface metal. Especially, core-shell structured nanoparticles are important. Several study demonstrated the Au-core/Pt shell metal nanoparticles show higher catalytic activity for the visible-light-induced hydrogen generation than Pt monometallic nanoparticles. The following study is an example of the hydrogen generation using Au/Pt nanoparticle catalyst (Yonezawa & Toshima, 1993). In this study, the Au/Pt bimetallic systems stabilized by polymer and micelle were obtained by alcohol- and photo-reduction of the corresponding metal ions in

the presence of water-soluble polymers and non-ionic surfactant-micelles, respectively. The UV-Vis spectra and the transmission electron micrographs suggest that the polymer-protected Au/Pt bimetallic systems are composed of bimetallic alloy clusters, but the micelle-protected ones are mostly composed of the mixtures of the monometallic Au and Pt particles. The *in-situ* UV-Vis spectra during the reductions can elucidate the formation processes of the bimetallic dispersions which are different from each other depending on the protective reagent. The Au/Pt bimetallic systems can be used as the catalyst for visible light-induced hydrogen generation. The bimetallic system stabilized by the polymer at a molar ratio of Au/Pt = 2/3 is the most active catalyst.

3.2 Application of silver-core/rhodium-shell bimetallic nanoparticles

It has been reported that the catalytic activity of the Ag/Rh bimetallic nanoparticles for visible-light-induced hydrogen generation (Toshima & Hirakawa, 1999) in an aqueous solution composed of ethylenediaminetetraacetic acid, tris(bipyridine)ruthenium(II), methyl viologen, and metal nanoparticle catalyst. The activity is clearly higher than the corresponding monometallic nanoparticles and alloy-structured Ag/Rh nanoparticles, suggesting that the Ag-core shows an electronic effect on the surface Rh as in the case of the Au-core (Yonezawa & Toshima, 1993) and enhances the catalytic activity of the surface Rh. The highest catalytic activity was observed at 1:9 ratio of Ag and Rh atoms (Figure 7). Similar results reported on the other catalytic reactions.

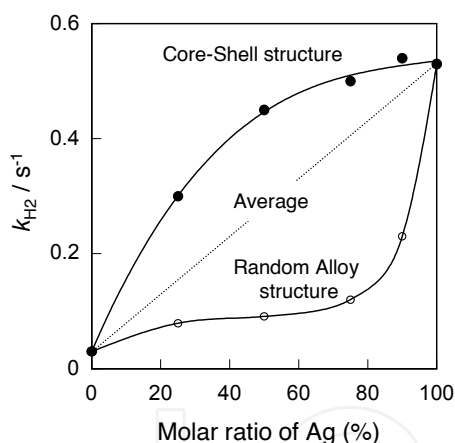


Fig. 7. Hydrogen generation rate coefficient (k_{H_2}) depending on the molar ratio of Ag of Ag/Rh bimetallic nanoparticles. The k_{H_2} indicates the number of generated H_2 molecules on a surface metal atom per one second. The average is the calculated activity of the simple mixture of Ag and Rh monometallic nanoparticles.

3.3 Carbon dioxide reduction by visible-light-induced electron transfer system using metal nanoparticle

A photochemical reduction of CO_2 can be applied to a novel energy storage process for the utilization of solar energy in the future. The above mentioned catalytic system can be applied to CO_2 reduction. The strategy is the catalytic reduction of CO_2 using electrons gathered by an electron transfer system (Willner et al., 1987, Toshima et al., 1995). It has been reported that nanoparticles catalyze the reduction of CO_2 and the generation of methane (Toshima et al., 1995) (Figure 8).

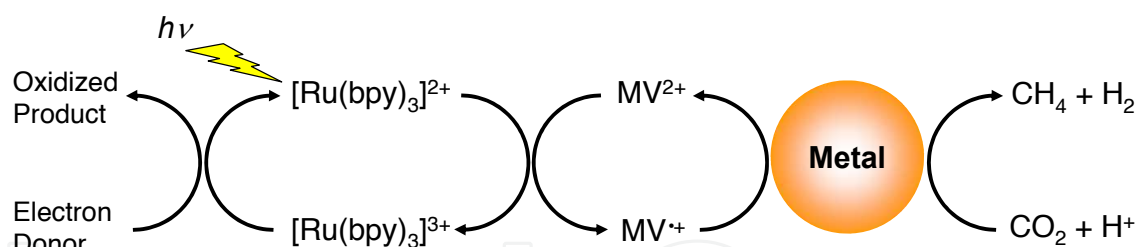


Fig. 8. Schematic diagram of the visible-light induced CO₂ reduction using the electron transfer system and metal nanoparticle catalyst

The possible reaction scheme of the CO₂ reduction is as follows:



This eight-electron reduction of CO₂ is advantageous process compared with other possible CO₂ reduction process from the thermodynamic point of view. Although it is not a study using the silver-core bimetallic nanoparticles, this topic is closely related to the applications of bimetallic nanoparticles to catalytic reaction. Thus, the topic of the CO₂ reduction using metal nanoparticle catalyst is presented here.

Typical reactions were performed by the similar manner to the hydrogen generation. A 20-cm³ Pyrex Schlenk tube was charged with a 10 cm³ aqueous solution, containing EDTA (a sacrificial electron donor), [Ru(bpy)₃]²⁺ (a photosensitizer), MV²⁺ (an electron mediator), NaHCO₃ (a pH adjuster and a CO₂ source), and colloidal dispersion of metal nanoparticles. The mixtures were degassed by freeze-thaw cycles and the tubes were then filled with 1 atm of CO₂. The photo-irradiation was carried out for 3 or 4 h with a 500 W super-high-pressure mercury lamp through a UV cut filter (> 390 nm) in a water bath maintained at 30 °C. About 100 μmol of methane was detected in this system (Toshima et al., 1995). However, it has not been confirmed that methane was actually the reduction product of CO₂.

3.3.1 Strategy for the demonstration of the methane generation from carbon dioxide

In a heterogeneous system, photoreduction of CO₂ was confirmed by experiments using an isotope (Ishitani et al. 1993). To our knowledge, however, the isotopic method has not been applied to the confirmation of the photoreduction of CO₂ in a homogeneous system using the colloidal dispersion of metal nanoparticles. To confirm the above mentioned methane generation, the following study was carried out. In this study, photoreduction of CO₂ was carried out in a similar system to one reported previously (Toshima et al., 1995), and the generation of methane from CO₂ was confirmed by isotopic experiments. As the catalysts, novel metal nanoparticles, *i.e.*, liposome-protected Pt nanoparticles, were prepared and used in the present system. Colloidal dispersions of Pt and Ru nanoparticles were prepared by photoreduction without using ethanol (Yamaji et al. 1995). Preparation of nanoparticles without ethanol is required, because the coexisting ethanol is decomposed during the photochemical reaction, leading to the formation methane. This methane formation cannot be distinguished from the actual methane generation from CO₂. Protective agents used for the metal nanoparticles were poly(*N*-vinyl-2-pyrrolidone), C₁₂EO, and liposome. The products in the gas phase were analyzed with a gas chromatograph. The characterization of gaseous products was carried out with a gas chromatograph mass-spectrometer.

3.3.2 Methane generation from carbon dioxide reduction

The formation of methane was then clearly detected by gas chromatography (about 19 nmol in the case of the liposome protected Pt nanoparticles system). In order to confirm the methane generation from CO₂, isotope experiments were carried out using NaH¹³CO₃ as a CO₂ source and analyzed by a gas chromatograph mass-spectrometer. Since NaHCO₃ is equilibrated with CO₂ in solution and easily treated, it was a good source of CO₂ in the present experiments. In this experiment, ¹³CH₄ was clearly detected, though the produced methane was not pure ¹³CH₄ and it did contain ¹²CH₄. In the same experiment, the mole ratio of ¹³CO₂ to ¹²CO₂ in the gas phase was about 57:43, which is nearly the same as the isotopic ratio of the generated methane. EDTA works as an electron donor in the system and is known to decompose into CO₂. Therefore, ¹²CH₄ generation possibly occurs through the reduction of ¹²CO₂ generated from EDTA. The effect of EDTA on methane generation was examined in the Pt-liposome system. Methane was detected on visible-light irradiation of the system involving EDTA without CO₂ or NaHCO₃ but could not be detected in the absence of EDTA. These results suggest that the detected ¹²CH₄ is generated by the reduction of ¹²CO₂ originated from EDTA.

3.3.3 Liposome-protected metal nanoparticle catalyst

Liposome was better than other protective-colloid of Pt nanoparticles for methane generation. This is probably explained by assuming that liposome can form a larger and stronger hydrophobic region to concentrate CO₂ around a Pt nanoparticle than C₁₂EO micelle and poly(*N*-vinyl-2-pyrrolidone). In addition, Ru-C₁₂EO showed higher catalytic activity than Pt-C₁₂EO. Thus, Ru-liposome was considered to be an active catalyst for methane generation in the system tested here. The synthesis of Ru-liposome was tried in a way similar to that of Pt-liposome, but the suspension of the Ru-liposome was not active as a catalyst. The resulting Ru-liposome was not as homogeneous, probably because the Ru ion is not miscible with liposome in water.

3.3.4 Summary of the carbon dioxide photo-reduction by metal nanoparticle catalyst

The Pt and Ru nanoparticle catalysts, which were prepared by a photoreduction method of metal salt in water without ethanol, successfully generated methane from CO₂. The methane generation suggests that the eight-electron reduction of CO₂ easily proceeds on metal nanoparticles possibly due to a thermodynamic advantage. This is different from an electrochemical CO₂ reduction using Pt electrodes, on which CO₂ is reduced to CO with adsorbed hydrogen atoms. In the present system using metal nanoparticles, the competition reaction, i.e., the kinetically favorably hydrogen generation, inhibits the methane generation. An increase of CO₂ concentration, the electron supply rate, or both may enhance CO₂ reduction.

4. Catalytic decomposition of hydrogen peroxide by metal nanoparticle

The modification of biomacromolecules upon exposure to reactive oxygen species, including hydrogen peroxide (H₂O₂), dioxide(1-) (superoxide O₂^{•-}), hydroxyl radical (HO[•]), and singlet oxygen (¹O₂), is the likely initial event involved in the induction of the mutagenic and lethal effects of various oxidative stress agents (Kawanishi et al. 2001; Cadet et al., 2003;

Drechsel & Patel, 2008). Therefore, the activity of reactive oxygen species generation by various chemical compounds is closely related to their toxicity, carcinogenicity, or both. For example, hydroquinone, a metabolite of carcinogenic benzene, causes DNA damage via H_2O_2 generation (Hirakawa et al., 2002). Many studies have addressed the role of antioxidants, such as vitamins (Slaga, 1995; Sohmiya et al., 2004) and catechins (Weyant et al., 2001), in protection against cancers and cardiovascular diseases. These antioxidants can scavenge reactive oxygen species and protect against cancer occurrence. On the other hand, every antioxidant is in fact, a redox agent, protecting against reactive oxygen species in some circumstances and promoting free radical or secondary reactive oxygen species generation in others. Indeed, an excess of these antioxidants elevates the incidence of cancer (Nitta et al. 1991; Omenn et al., 1996). Solovieva et al. reported that antioxidants, ascorbic acid (Solovieva et al., 2007) and dithiothreitol (Solovieva et al., 2008), exhibit cytotoxicity via H_2O_2 generation. Relevantly, it has been reported that vitamins A (Murata & Kawanishi, 2000) and E (Yamashita et al., 1998) and catechins (Oikawa et al., 2003) induce DNA oxidation through H_2O_2 generation during their oxidation. H_2O_2 is a long-lived reactive oxygen species which plays an important role in biomacromolecular damage induced by various chemical compounds (Kawanishi et al., 2001; Hirakawa et al., 2002).

4.1 Metal catalyzes decomposition of hydrogen peroxide

Various studies have demonstrated the catalytic decomposition of H_2O_2 by noble metals such as Pt (Keating et al., 1965; McKee, 1969; Bianchi et al., 1962), Pd (Keating et al., 1965; McKee, 1969; Bianchi et al., 1962; Eley & Macmahon, 1972) Ag (Baumgartner et al., 1963; Goszner et al., 1972; Goszner & Bischof, 1974), and Au (Eley & Macmahon, 1972; Goszner & Bischof, 1974). These metals themselves are hardly oxidized by reactive oxygen species, however, it is difficult to use metal powder or foils as anti-oxidative drugs. Recently, Kajita et al. reported that Pt nanoparticles catalyze the decomposition of reactive oxygen species (Kajita et al., 2007). These nanoparticles can be dispersed in water and used as homogenous solutions. Because this removal mechanism is catalytic decomposition, no oxidized product is formed through this reaction. Platinum metal is used as a food additive and is not considered to be a toxic material. This result led us to the idea that inorganic materials, in particular noble metals, rather than organic antioxidants, can be used as novel chemopreventive agents against reactive oxygen species-mediated biomolecules damage. In this section, the examination of the removal of H_2O_2 generated from a chemical compound, hydroquinone, using water-soluble polymer-protected Pt and Ag/Pt nanoparticles are reviewed.

4.2 Catalytic activity of monometallic nanoparticles

4.2.1 Preparation of metal nanoparticles for reactive oxygen scavenger

Colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected Pt, Pd, Rh, and Au nanoparticles were prepared using an alcohol reduction method (Hirai et al., 1979). 50 mL of water/ethanol (1/1, v/v) solution containing 1 mM metal salts and 40 mM poly(*N*-vinyl-2-pyrrolidone) (monomer unit) was refluxed for 2 h, resulting in the formation of typical colored sols of metal nanoparticles. The solvent was removed by vacuum evaporation, and the nanoparticles were dispersed into water to prepare 1 mM/atom (atomic concentration) metal colloidal sols. An aqueous solution of poly(*N*-vinyl-2-pyrrolidone)-protected Ag

nanoparticles (Shiraishi & Toshima, 1999) was prepared from reduction of 1 mM AgNO_3 with NaBH_4 in the presence of 40 mM poly(*N*-vinyl-2-pyrrolidone). The obtained Ag colloidal dispersion was purified with an ultra-filter.

These poly(*N*-vinyl-2-pyrrolidone)-protected metal nanoparticles formed water-soluble sols. The average diameters (d) and standard deviations (σ) of monometallic nanoparticles determined by TEM measurement were as follows: Pt ($d = 2.2$ nm, $\sigma = 1.0$ nm), Pd ($d = 2.0$ nm, $\sigma = 0.9$ nm), Rh ($d = 2.2$ nm, $\sigma = 1.0$ nm), Ag ($d = 10.0$ nm, $\sigma = 1.9$ nm), and Au ($d = 10.2$ nm, $\sigma = 2.0$ nm).

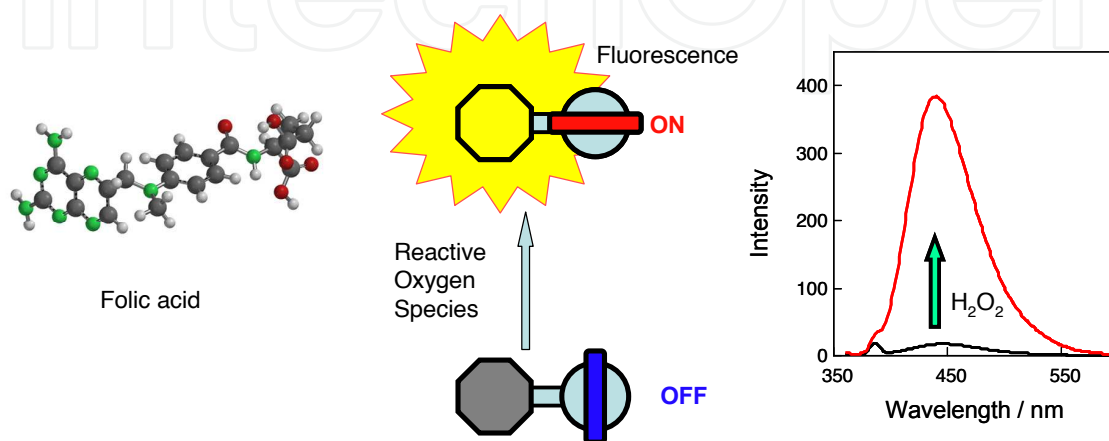


Fig. 9. Fluorimetry of reactive oxygen species (hydrogen peroxide) using folic acid

4.2.2 Method of the detection of hydrogen peroxide

The generated H_2O_2 was measured by a previously reported method using folic acid (Hirakawa, 2006). This assay is based on the fluorescence enhancement of less-fluorescent folic acid via oxidative decomposition by H_2O_2 and copper(II) ion into strong-fluorescent 2-amino-4-oxo-3*H*-pterine-6-carboxylic acid (Figure 9). The concentration of H_2O_2 ($[\text{H}_2\text{O}_2]$) can be determined using a calibration curve. A reaction mixture containing folic acid, copper(II) chloride, and the H_2O_2 sample (or H_2O_2 generator ⁴) with or without the metal nanoparticle in a sodium phosphate buffer (pH 7.6) was incubated in a microtube for 30 min. After incubation at 37 °C, the fluorescence intensity of the reaction mixture at 450 nm was measured using a fluorescence spectrophotometer with 350-nm excitation.

4.2.3 Platinum nanoparticles effectively scavenge hydrogen peroxide

Platinum nanoparticles effectively scavenged H_2O_2 in a dose-dependent manner and showed the highest activity among the metal nanoparticles used in this study (Figure 10). A sample solution of 5 μM /atom Pt nanoparticles, among which 1 μg Pt metal is included, exhibits comparable activity for H_2O_2 decomposition to that of 10 units of catalase. One unit of catalase can remove 1.0 μmol H_2O_2 per min in water (pH 7.0, 25 °C). Poly(*N*-vinyl-2-pyrrolidone) itself did not scavenge H_2O_2 . This experiment confirmed that poly(*N*-vinyl-2-pyrrolidone)-protected Pt nanoparticles can remove H_2O_2 . The mechanism of H_2O_2 removal by Pt nanoparticles can be explained by catalytic decomposition into water and molecular oxygen as follows:



The generation of O_2 gas through the H_2O_2 decomposition was confirmed with a gas-burette as following procedure. The 10 mL of aqueous solution containing 0.1 M H_2O_2 was treated by 10 μg Pt nanoparticles and generated O_2 gas was measured with a gas-burette. The volume of detected gas coincided with that of the theoretically calculated value of O_2 generation from the decomposition of H_2O_2 in the sample solution.

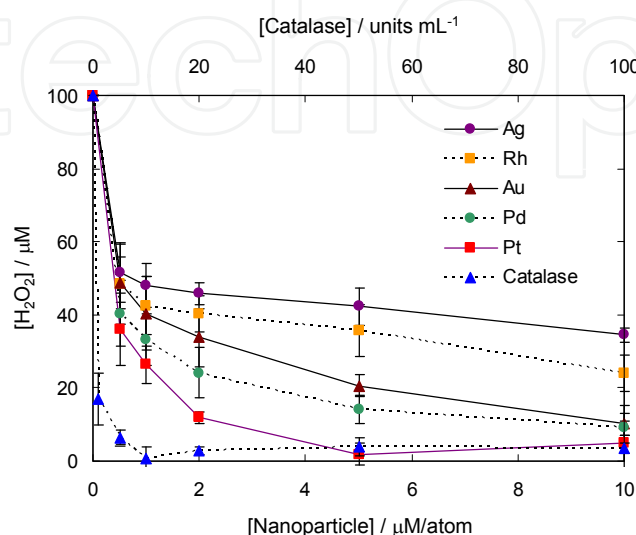


Fig. 10. Removal of H_2O_2 by metal nanoparticles and catalase. The 1 mL of sample solution containing 100 μM H_2O_2 , 10 μM folic acid, 20 μM copper(II) chloride, and indicated concentration of metal nanoparticles or catalase was incubated for 30 min. The concentration of H_2O_2 was estimated from the fluorescence measurement.

4.3 Application of silver-core/platinum-shell bimetallic nanoparticles to catalytic decomposition of hydrogen peroxide generated by chemical compound

4.3.1 Preparation of silver-core bimetallic nanoparticles for hydrogen peroxide scavenger

The catalytic activity of Pt and its modified particles with Ag (Ag/Pt) on the decomposition of H_2O_2 generated from chemical compounds was evaluated, since Pt showed the highest activity. The Ag/Pt nanoparticles were prepared from the following procedure. The absorption spectrum of the sol of Pt nanoparticles is a flat curve (Figure 11), indicating the formation of homogenous particles. Ag nanoparticles exhibited a typical yellow color due to surface plasmon absorption around 400 nm. It has been reported that a physical mixture of Ag and Pt nanoparticles spontaneously forms bimetallic nanoparticles, possibly Ag-core/Pt-shell structured particles (Toshima et al., 2005). The time-course of the absorption spectra of this physical mixture showed the extinction of Ag surface plasmon absorption, and the absorption was completely extinguished within 24 h (Figure 11), suggesting that the surface of the formed bimetallic nanoparticles is composed of Pt atoms. Typical TEM images showed the formation of relatively small particles of Pt and large particles of Ag (Figure 12). TEM photographs showed that the large Ag particles disappeared through interaction with Pt particles, resulting in the formation of bimetallic particles smaller than the parent Ag particles (Figure 12). A similar result has been observed in the case of Ag/Rh bimetallic

nanoparticles (Toshima & Hirakawa, 2003). These findings suggest the formation of self-organized Ag/Pt bimetallic nanoparticles. These metal nanoparticles are stable in water for several months. The Ag/Pt (Ag-atom/Pt-atom, 1/1) bimetallic nanoparticles were prepared using a self-organization method to mix Pt and Ag monometallic nanoparticles according to previous reports (Toshima & Hirakawa, 2003; Toshima et al., 2002, 2005; Matsushita et al., 2007).

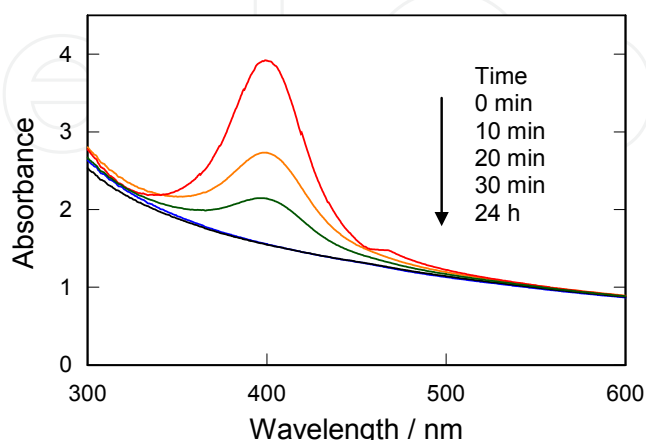


Fig. 11. Absorption spectral change of the physical mixture of dispersions of Ag and Pt nanoparticles. The aqueous solutions of Ag (1 mM/atom, 10 mL) and Pt (1 mM/atom, 10 mL) nanoparticles were mixed and measured at 0, 10, 20, and 30 min, and 24 h after mixing.

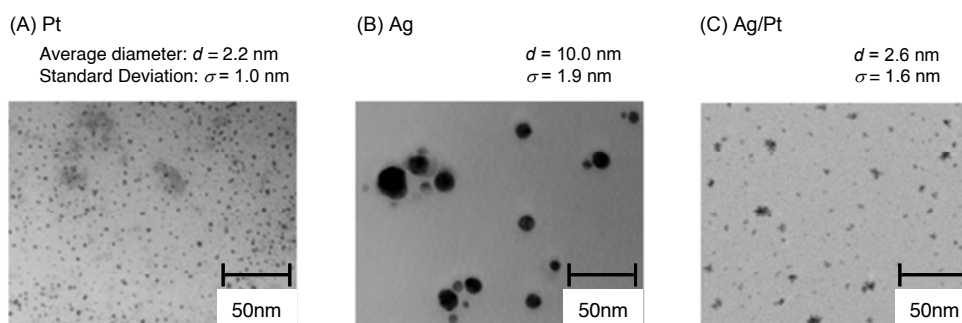


Fig. 12. TEM photographs of metal nanoparticles. The sample of Ag/Pt nanoparticles was prepared by drying the mixtures of the aqueous solutions of Pt and Ag monometallic nanoparticles 24 hour after mixing.

4.3.2 Hydrogen peroxide formation from hydroquinone and its removal by metal nanoparticles

Hydroquinone, which is a metabolite of carcinogenic benzene, was used as H_2O_2 source. This compound can generate H_2O_2 through autooxidation (Figure 13) (Hirakwa et al., 2002). Under these experimental conditions, hydroquinone generated H_2O_2 in a dose-dependent manner (Figure 14). Twenty units/mL catalase effectively removed H_2O_2 generated from this system, and 10 μM /atom (2 μg /mL) Pt nanoparticles exhibited a comparable activity to that of this catalase. Silver nanoparticles showed apparently weaker activity for H_2O_2 removal than Pt nanoparticles. The bimetalization of Pt with Ag apparently suppressed the catalytic activity per unit atom.

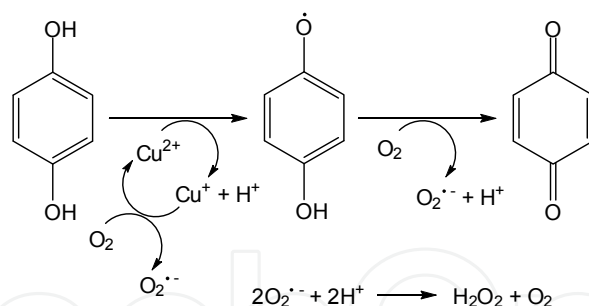


Fig. 13. Schematic diagram of hydrogen peroxide formation by the autooxidation of hydroquinone

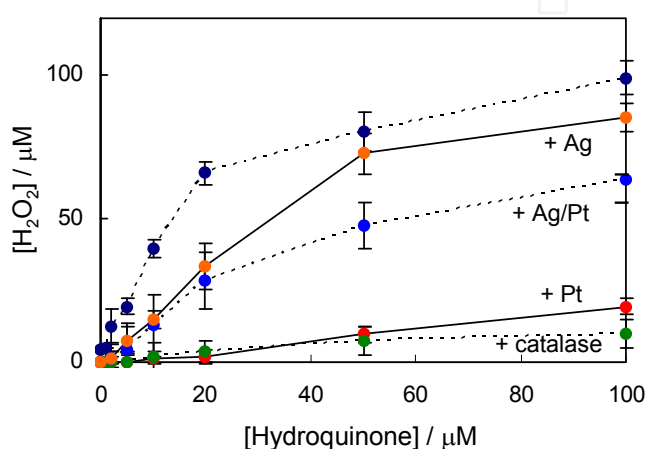


Fig. 14. H_2O_2 generation through autooxidation of hydroquinone in the absence or presence of metal nanoparticles and catalase. The 1 mL of sample solution containing 10 μM folic acid, 20 μM copper(II) chloride, and indicated concentration of hydroquinone with or without 10 μM /atom metal nanoparticles or 20 units/mL catalase was incubated for 30 min. The concentration of generated H_2O_2 was estimated from the fluorescence measurement.

4.3.3 Activity of silver-core/platinum-shell nanoparticles on hydrogen peroxide decomposition

Figure 15 shows the removal activity of H_2O_2 generated from a high concentration of hydroquinone (50 μM) by metal nanoparticles. These metal nanoparticles and catalase scavenged H_2O_2 in a dose-dependent manner. The activity of the 10 μM /atom (2 $\mu\text{g}/\text{mL}$) Pt nanoparticles was comparable to that of 20 units/mL catalase, and Pt completely scavenged H_2O_2 over 20 μM /atom (4 $\mu\text{g}/\text{mL}$). The activity per atom of the Ag/Pt bimetallic nanoparticles was almost the same as that of the Ag monometallic nanoparticles.

To investigate the effect of Pt nanoparticles on H_2O_2 generation through the autooxidation of hydroquinone, NADH consumption during this autooxidation was measured. The consumption of NADH during the autooxidation of hydroquinone was measured by a previously reported method (Oikawa et al., 2003). A sample solution containing 100 μM NADH, 50 μM hydroquinone, and 20 μM copper(II) chloride was incubated at 37 $^\circ\text{C}$ in the absence or presence of 20 μM /atom Pt nanoparticles. The concentration of NADH was determined by the measurement of absorbance of NADH at 340 nm using a microplate

absorbance reader. The oxidized form of hydroquinone can be reduced into the parent hydroquinone by NADH (Hirakwa et al., 2002). The concentration of NADH was gradually decreased through the redox of hydroquinone and Pt nanoparticles hardly inhibited NADH consumption (data not shown). This result indicated that Pt nanoparticles do not inhibit the H_2O_2 generation itself, because H_2O_2 is produced through the autooxidation of hydroquinone.

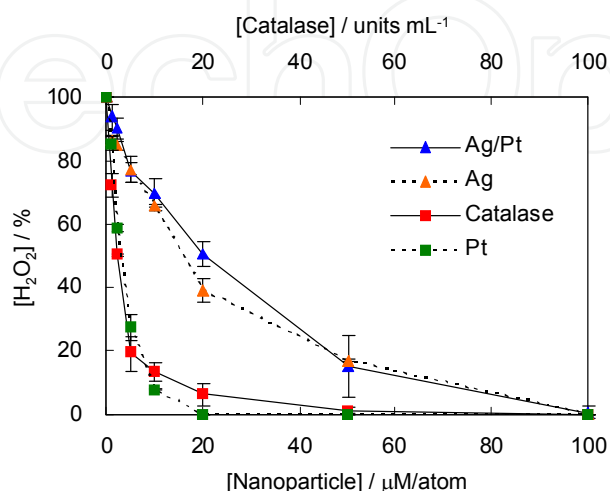


Fig. 15. Removal of H_2O_2 generated through the autooxidation of hydroquinone by metal nanoparticles and catalase. The 1 mL of sample solution containing 10 μM folic acid, 20 μM copper(II) chloride, 50 μM hydroquinone, and indicated concentration of metal nanoparticles or catalase was incubated for 30 min. The concentration of H_2O_2 was estimated from the fluorescence measurement.

4.4 Summary and possible mechanism of hydrogen peroxide decomposition by metal nanoparticles

Poly(*N*-vinyl-2-pyrrolidone)-protected metal nanoparticles, in particular Pt nanoparticles, exhibited a removal effect on H_2O_2 generated through autooxidation of hydroquinone (Figure 16). The removal of H_2O_2 by these metal nanoparticles can be explained by a catalytic reaction similar to that by catalase, which decomposes H_2O_2 into H_2O and O_2 . The formation of H_2O_2 during autooxidation of hydroquinone is through $\text{O}_2^{\bullet-}$, which is generated from a reduction of O_2 by hydroquinone (Hirakawa et al., 2002). Because the lifetime of $\text{O}_2^{\bullet-}$, which dismutates into H_2O_2 through reaction with H^+ , is short (~ 0.1 ms), the scavenging of $\text{O}_2^{\bullet-}$ by a metal nanoparticle can be negligible. The H_2O_2 removal activity per metal atom of these metal nanoparticles occurred in the following order: $\text{Pt} > \text{Ag} \approx \text{Ag/Pt}$. The activities of H_2O_2 decomposition per metal atom consisting of these metal nanoparticles ($\mu\text{M-H}_2\text{O}_2/\mu\text{M-nanometal}$) have been estimated, and the resulting values are 4.2, 12.2, and 3.8 for Ag, Pt, and Ag/Pt, respectively. Further, the activity on the surface area of the Ag/Pt nanoparticles (17 $\mu\text{M-H}_2\text{O}_2/\text{cm}^2\text{-nanometal}$) was also smaller than that of Pt (49 $\mu\text{M-H}_2\text{O}_2/\text{cm}^2\text{-nanometal}$). These findings showed that the Pt nanoparticles have the highest catalytic activity for H_2O_2 decomposition in the metal nanoparticles used in this experiment and the activity of Pt nanoparticles is suppressed by modification with Ag.

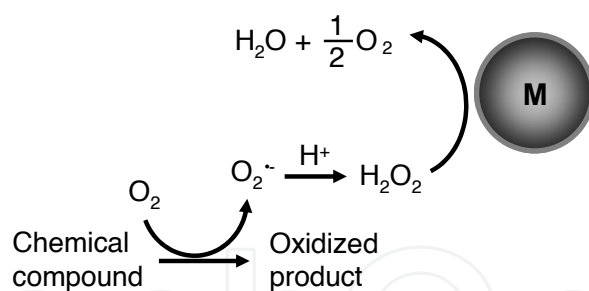


Fig. 16. Hydrogen peroxide generation from an autooxidation of chemical compound and its catalytic decomposition by metal nanoparticle

H_2O_2 is a long-lived reactive oxygen species and plays an important role in DNA damage (Kawanishi et al., 2001, Hirakawa et al., 2002). Indeed, various chemical compounds, including carcinogens, generate H_2O_2 during redox reaction (Kawanishi et al., 2001, Hirakawa et al., 2002). Molecular oxygen is easily reduced by various compounds, leading to the formation of $\text{O}_2^{\cdot-}$. Formed $\text{O}_2^{\cdot-}$ is rapidly dismutated into H_2O_2 . Although H_2O_2 itself is not a strong reactive species, it can generate highly reactive $\text{HO}^{\cdot}$ through a Fenton reaction or a Haber-Weiss reaction. Furthermore, H_2O_2 can penetrate a cytoplasm membrane and be incorporated into the cell nucleus. Therefore, H_2O_2 is considered to be one of the most important reactive species or a precursor participating in carcinogenesis. The removal of H_2O_2 is an effective method for cancer chemoprevention. Furthermore, protective agents against H_2O_2 are important to treat *acatalasemia*, a genetic deficiency of erythrocyte catalase inherited as an autosomal recessive trait. Antioxidants, such as vitamins A and E, are effective protective agents. However, the oxidized products of antioxidants or these molecules themselves promote the formation of secondary H_2O_2 (Yamashita et al., 1998; Murata & Kawanishi, 2000). Indeed, an excess of these antioxidants elevates the incidence of cancer (Nitta et al., 1991; Omenn et al., 1996). A catalyst consisting of an inorganic stable material is not oxidized and does not generate secondary reactive oxygen species. Water-soluble nanoparticles of noble metal may become novel protective agents against reactive oxygen species.

In summary, Pt, Ag, and Ag/Pt nanoparticles effectively scavenge H_2O_2 generated from autooxidation of a highly concentrated hydroquinone. Platinum nanoparticles exhibited the highest catalytic activity among these nanoparticles. Pt is a very stable metal against various chemical compounds and permitted as a food additives. The noble metal nanoparticles may be used as novel chemopreventive agents for cancer or other non-malignant conditions induced by chemical compounds through H_2O_2 generation.

5. Application of metal nanoparticles to prevention of ultraviolet radiation induced biomolecules damage

Exposure to solar ultraviolet radiation is undoubtedly linked to skin carcinogenesis and phototoxic effect. Photosensitized reaction by ultraviolet radiation, especially ultraviolet-A (UVA) radiation (320~400 nm), is considered to cause toxic effect through oxidative biomolecules damage including DNA damage (Hiraku et al., 2007). Photosensitized formation of reactive oxygen species, such as hydrogen peroxide, superoxide, hydroxyl radicals, and singlet oxygen, is involved in UVA-induced biomolecules damage. As

mentioned above, the application of metal nanoparticles to scavenge reactive oxygen species through catalytic decomposition.

5.1 Traditional methods of chemoprevention to biomolecules damage by ultraviolet radiation and its problem

Many studies have addressed the role of antioxidants, such as vitamins and catechins, in protection against cancers and cardiovascular diseases. These antioxidants can scavenge reactive oxygen species and protect against cancer occurrence. On the other hand, every antioxidant is, in fact, a redox agent, protecting against reactive oxygen species in some circumstances and promoting free radical or secondary reactive oxygen species generation in others. Indeed, an excess of these antioxidants elevates the incidence of cancer. It has been reported that antioxidants, ascorbic acid and dithiothreitol, exhibit cytotoxicity via H_2O_2 generation, and their toxic effects are significantly enhanced by vitamin B_{12} . H_2O_2 is a long-lived reactive oxygen species which plays an important role in biomacromolecules damage induced by various chemical compounds.

5.2 Preventive action of metal nanoparticles on ultraviolet-sensitized oxidation of molecules

As mentioned above, metal nanoparticles catalyze the decomposition of reactive oxygen species. Because this removal mechanism is catalytic decomposition, no oxidized product is formed through this reaction. Platinum metal is used as a food additive and is not considered to be a toxic material. This result led us to the idea that inorganic materials, in particular noble metals, rather than organic antioxidants, can be used as novel chemopreventive agents against UVA-induced biomolecules damage.

Recently, it has been reported that the removal of reactive oxygen species generated from a photocatalytic reaction of titanium dioxide (TiO_2) particles using water-soluble polymer-protected Pt, Rh, and Pt/Ag bimetallic nanoparticles. Silver, a relatively inexpensive noble metal, is also used as a food additive, and bimetalization with Ag may improve the catalytic activity of other metal nanoparticles.

5.2.1 Preparation of metal nanoparticles for ultraviolet protection

The colloidal dispersions of poly(*N*-vinyl-2-pyrrolidone)-protected Pt and Rh nanoparticles were prepared from an alcohol reduction. The size (particle diameter) of these nanoparticles is about 2 nm. The aqueous solution of poly(*N*-vinyl-2-pyrrolidone)-protected Ag nanoparticle was prepared from a reduction of silver nitrate by sodium borohydride in the presence of poly(*N*-vinyl-2-pyrrolidone). The Ag-core/Pt-shell (Ag-atom/Pt-atom, 1/1) bimetallic nanoparticle was prepared using a physical method to mix Pt and Ag monometallic nanoparticles according to the previous reports (Toshima et al., 2005).

5.2.2 Evaluation model for the biomolecules damage by ultraviolet radiation

TiO_2 (anatase) and methylene blue were used as a model of the UVA-induced reaction. The sample solution containing methylene blue and TiO_2 dispersion in sodium phosphate buffer (pH 7.6) with or without metal nanoparticle was irradiated with a UVA lamp (365 nm, 1

mW cm⁻²). The decomposition of methylene blue was evaluated by absorption measurement at 659 nm. TiO₂ is a well-known photocatalyst (Fujishima et al., 2000, 2008). When exposing to UVA light, the reduction-oxidation activity of TiO₂ has a significant biological impact, as is exemplified by its bactericidal activity. Photo-irradiated TiO₂ effectively decomposed methylene blue (Figure 17). Various reactive oxygen species contribute to the photocatalytic reaction of TiO₂. Especially, hydrogen peroxide is long-lived reactive oxygen species and plays an important role in oxidative biomolecules damage. Molecular oxygen is reduced by photoexcited materials, leading to the formation of superoxide. Formed superoxide is rapidly dismutated into hydrogen peroxide. Although hydrogen peroxide itself is not a strong reactive species, it can generate highly reactive hydroxyl radicals through a Fenton reaction or a Haber-Weiss reaction. Furthermore, hydrogen peroxide can penetrate a cytoplasm membrane and be incorporated into the cell nucleus. Therefore, hydrogen peroxide is considered to be one of the most important reactive oxygen species participating in UVA carcinogenesis and phototoxicity. Since other reactive oxygen species, such as directly produced hydroxyl radicals (Hirakawa et al., 2004) and singlet oxygen (Hirakawa & Hirano, 2006), rapidly quenched in aqueous solution, hydrogen peroxide should be key reactive species in this experiment. The TiO₂ and methylene blue could be used as a simple model of UVA-induced oxidation.

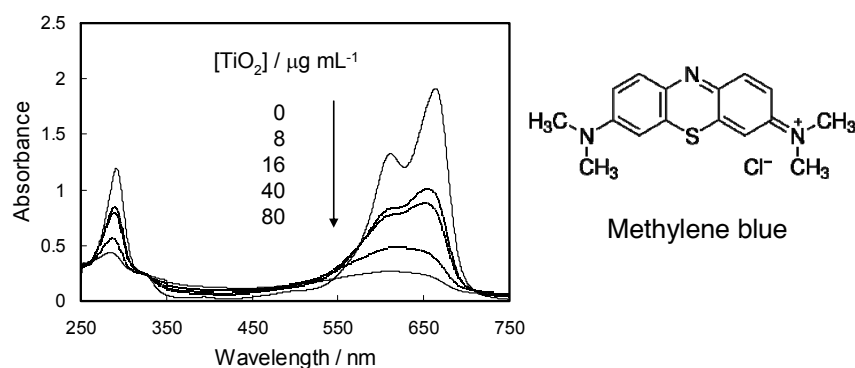


Fig. 17. UV-Vis absorption spectra of methylene blue photocatalyzed by TiO₂. The sample solution containing 10 µM methylene blue and indicated concentration of TiO₂ in 10 mM sodium phosphate buffer (pH 7.6) was irradiated (Ex = 365 nm, 1 mW cm⁻²) for 30 min.

5.2.3 Preventive action of metal nanoparticles on ultraviolet radiation induced biomolecules damage

Poly(*N*-vinyl-2-pyrrolidone)-protected metal nanoparticles, in particular, the Pt nanoparticle, inhibited the methylene blue decomposition photocatalyzed by TiO₂ (Figure 18). Poly(*N*-vinyl-2-pyrrolidone) itself did not inhibit the methylene blue decomposition. This inhibitory effect can be explained by the catalytic decomposition of H₂O₂ generated through TiO₂ photocatalysis. These nanoparticles decomposed H₂O₂ into H₂O and O₂ similar to catalase. In the case of H₂O₂ decomposition, the Pt nanoparticle showed the highest catalytic activity per unit atom. The activity of a 1 µg Pt nanoparticle was comparable to that of 5 units of catalase. One unit of catalase can remove 1.0 µmol H₂O₂ per 1 min in water (pH 7.0, 25°C). Unexpectedly, the bimetalization with Ag did not show improvement effect and rather decreased the inhibitory effect of Pt nanoparticle on the decomposition of methylene blue.

The UV-Vis absorption spectra of these metal nanoparticles were hardly changed by the photocatalytic reaction, suggesting that the noble metal nanoparticles are stable for reactive oxygen species and UVA irradiation. Organic antioxidant undergoes oxidation in the removal process of reactive oxygen species, leading to the formation of various oxidized products and may produce secondary reactive oxygen species. In the case of noble metal catalyst, these effects can be negligible.

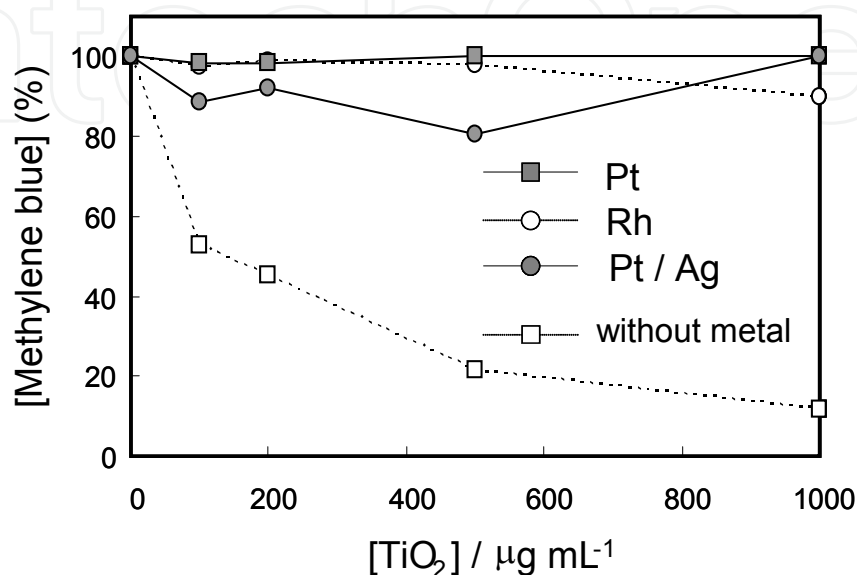


Fig. 18. Inhibitory effect of metal nanoparticles on methylene blue decomposition photocatalyzed by TiO₂. The sample solution containing 20 μg mL⁻¹ metal nanoparticle, TiO₂, and 10 μM methylene blue in 10 mM sodium phosphate buffer (pH 7.6) was irradiated (Ex = 365 nm, 1 mW cm⁻²) for 30 min.

5.3 Summary of the ultraviolet protection by metal nanoparticles

Pt, Rh, and Pt/Ag nanoparticles effectively inhibited the methylene blue decomposition photocatalyzed by TiO₂. TiO₂ photocatalytic system was used as a UVA-induced reactive oxygen species generation. The most important reactive oxygen species in this photocatalytic reaction is H₂O₂, because of its long lifetime in aqueous solution. This inhibitory effect of metal nanoparticle can be explained by the removal of H₂O₂. Unexpectedly, the activity of Pt nanoparticle was not improved by the bimetalization with Ag. Platinum is a very stable metal against various chemical compounds and is used as food additive. A poly(*N*-vinyl-2-pyrrolidone)-protected Pt nanoparticle may be used as a novel preventive agent for UVA-induced biomolecules damage through reactive oxygen species generation.

6. Conclusion

Physical mixture of Ag and other metal nanoparticles, such as Pt, Rh, and Pd, spontaneously forms the bimetallic nanoparticles with Ag-core structure in aqueous solution. These monometallic nanoparticles can be easily prepared from an alcohol reduction of the corresponding metal ions in the presence of water-soluble polymer such

as poly(*N*-vinyl-2-pyrrolidone), a protective colloid. Aqueous sol of Ag nanoparticles exhibits the surface plasmon absorption around 400 nm. The surface plasmon absorption was diminished through interaction with other metal nanoparticle in the physical mixture of these nanoparticles. This phenomenon was explained by that the Ag nanoparticle was coated by other metal. The transmission electron micrograph and X-ray diffraction measurement confirmed the formation of the Ag-core bimetallic nanoparticles. This reaction can be used to construct the core-shell structured novel bimetallic nanoparticles. The formed nanoparticles act superior character for certain catalytic reactions. The catalytic activity of the silver/rhodium bimetallic nanoparticles for visible-light-induced hydrogen generation in an aqueous solution was examined. This system composed of an electron source, a photosensitizer, an electron relay, and metal nanoparticle catalyst. The activity is clearly higher than the corresponding monometallic nanoparticles, suggesting that the silver-core enhances the catalytic activity of the surface rhodium. On the other hand, the catalytic activity of the decomposition of hydrogen peroxide was decreased by this bimetalization. Platinum nanoparticle effectively catalyzes hydrogen peroxide decomposition. The Ag-core/platinum shell bimetallic nanoparticle, which was prepared by the physical mixing of Ag and Pt nanoparticles, demonstrated lower activity of the decomposition of hydrogen peroxide than the monometallic Pt nanoparticle. Metal nanoparticles can be applied to various catalytic reactions. The bimetallic and trimetallic nanoparticles demonstrate superior activity in the certain reaction. The self-assembly formation of Ag-cored nanoparticle may be convenient method to prepare novel metal nanoparticle catalyst.

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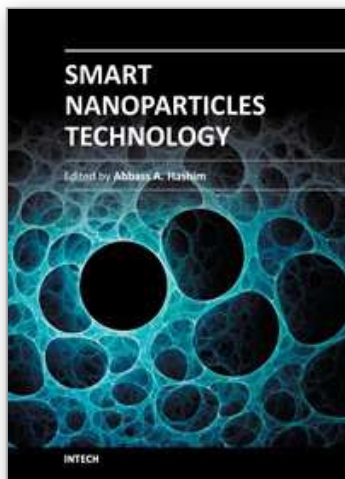
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