Magnetic Composite Nanoparticle of Au/γ-Fe_2O_3 Synthesized by Gamma-Ray Irradiation

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(Received May 8, 2003; CL-030388)

Magnetic composite nanoparticle of Au/γ-Fe_2O_3 was synthesized in an aqueous phase using gamma-ray. Connection between gold and γ-Fe_2O_3 was confirmed by the magnetic separation technique. TEM observation shows that 5-nm gold particles were dispersed on 20-nm γ-Fe_2O_3 particles. The nanoparticles adsorbed a water-soluble mercaptan, glutathione, and was manipulated by an external magnetic field.

Material scientists have been paying much attention to gold nanoparticles aiming at its application to biotechnology,[1–5] because gold is harmless and firmly combines with compounds possessing biochemical functions such as polypeptides, DNA via mercapto group.[6–8] If the gold nanoparticles are manipulated by the external magnetic field, application range would no doubt spread out, because many other useful techniques, such as magnetic separation, will be easily combined to enhance the functions of the gold nanoparticles. We have successfully synthesized such composite nanoparticles composed of γ-Fe_2O_3 and gold in an aqueous phase using gamma-rays. It has been well known that the radiolysis of aqueous solutions of noble metal ions lead to the formation of nanosized and homodispersed metallic particles.[9,10] We have extended this procedure to composite nanoparticle synthesis. Here we show the synthesis process of our composite nanoparticles and evidences for their affinity with a water-soluble mercaptan.

The present Au/γ-Fe_2O_3 composite nanoparticles were synthesized as follows. A nanoparticle material of γ-Fe_2O_3 obtained by the physical vapor synthesis process with the average diameter of 21 nm was dispersed in an aqueous solution containing $HAuCl_4$, relatively small amounts of polyvinyl alcohol (PVA) and 2-propanol, and then closed up in a glass vial. All the chemicals were supplied from Wako Pure Chemical Industries, Ltd. The amount of gold was 10 wt.% of the γ-Fe_2O_3. The suspension was sonicated for 15 minutes by an ultrasonic bath before γ-ray irradiation. The solution was irradiated at room temperature by a ^{60}Co γ-ray source with a dose rate of 3 kGy/h for 6 hours. During the irradiation, the solution was shaken by rotating the disk on which vials were mounted.[11] The γ-ray irradiation causes radiolysis of water and 2-propanol in the aqueous phase. The processes are expressed as follows:

$$H_2O \rightarrow e^-_{eq}, \quad H^\bullet, \quad OH^\bullet, \quad \text{etc}, \tag{1}$$

$$(CH_3)_2CHOH + OH^\bullet \rightarrow (CH_3)_2^\bullet COH + H_2O, \tag{2}$$

$$(CH_3)_2CHOH + H^\bullet \rightarrow (CH_3)_2^\bullet COH + H_2, \tag{3}$$

where equation (1) represents the radiolysis of water; and equations (2) and (3), the radiolysis of 2-propanol. Gold ions were reduced by H radicals, hydrated electrons and organic radicals generated by the irradiation.

After the irradiation the color of the suspension changed to reddish, reflecting the formation of nanosized gold particles. The particle concentration in the product was about 1.1 g l^{-1}. A considerable fraction of the particles kept suspended in the solution even after a day, though a small fraction settled. The aqueous suspension was made to pass through a magnetic separation column to divide it into magnetic and nonmagnetic components. The absorption spectra of the components were measured with a UV-vis spectrometer, Varian Cary 50. The X-ray diffraction pattern of the nanocomposite powder obtained by drying the magnetic component was measured with a diffractometer, Rigaku RINT2100-Ultima$^+$, by the use of Cu Kα radiation. The size and shape of the composite nanoparticles were investigated by a transmission electron microscope, HITACHI H-8100T.

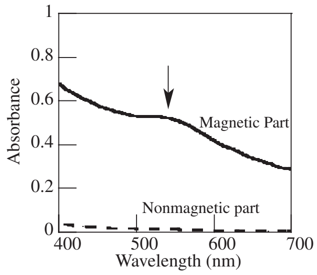

Figure 1. Absorption spectra of the aqueous suspension of the Au/γ-Fe_2O_3 composite nanoparticles. The arrow indicates absorption by the surface plasmon of metallic gold nanoparticles.

Figure 1 shows the typical UV-vis absorption spectra of both the magnetic and the nonmagnetic component of the aqueous suspension of the Au/γ-Fe_2O_3 nanoparticles. Note that a clear absorption band is observed around 540 nm only in the magnetic component, which is ascribed to the surface plasmon of nanosized metallic gold particles formed by the γ-ray irradiation.[10] On the contrary, nonmagnetic component is substantially transparent. Figure 2 shows the XRD pattern of a powder obtained by drying the magnetic part. A broad peak around 38 degrees is due to metallic gold and all the others are ascribed to γ-Fe_2O_3. These results clearly indicate that nanosized metallic gold particles were formed by the γ-ray irradiation and supported on the γ-Fe_2O_3 particles, and monolithic gold nanoparticles were scarcely observed. It should be pointed out that nanosized gold particles exhibiting the plasmon peak are attracted by a magnet. This is quite a novel feature that has not been reported yet.

Figure 3 shows the typical TEM micrograph of the Au/γ-Fe_2O_3 composite nanoparticles. It clearly shows that individual nanosized gold particles, which are seen as smaller and darker grains, are well dispersed on the surface of the γ-Fe_2O_3 particles. The average size of the gold grains determined from the micrographs was about 5 nm.

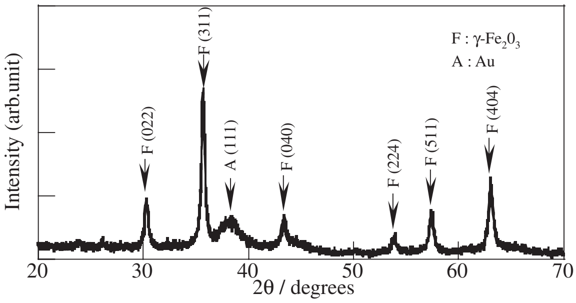

Figure 2. X-ray diffraction pattern of the Au/γ-Fe_2O_3 composite nanoparticles obtained by drying magnetic component.

Adsorption of biochemical compounds onto our composite nanoparticles was tested by using glutathione (GSH, supplied from Wako) as a model compound. GSH was added to the suspensions of the present Au/γ-Fe_2O_3 composite nanoparticles, so that the concentration of GSH was 100 ppm. After stirring for two hours, the nanoparticles were removed by the magnetic separation technique. Concentration of GSH remaining in the nonmagnetic solution was measured by the enzymatic recycling technique.[12,13]

The amount of adsorbed GSH onto the nanoparticles was calculated from the decrement in GSH concentration, which is tabulated in Table 1. For comparison, we also measured amounts of GSH adsorbed onto (1) monolithic gold nanoparticles, (2) monolithic γ-Fe_2O_3 nanoparticles with PVA and (3) monolithic γ-Fe_2O_3 nanoparticles without PVA. The monolithic gold nanoparticles were synthesized by using gamma-rays as well with PVA.[9,10] The data for (2) and (3) were obtained by just mixing γ-Fe_2O_3 and GSH, so that they were free of γ-ray irradiation. In Table 1 these data are also given and compared.

From Table 1 we can see that the present composite nanoparticles best adsorbed GSH, more than the sum of adsorption by gold and γ-Fe_2O_3 with PVA. This indicates that the affinity between gold and GSH is not spoiled at all even when the gold grains are supported on the γ-Fe_2O_3 nanoparticles. This is a very promising feature from the viewpoint of application, though further investigation is required. The monolithic γ-Fe_2O_3 nanoparticles also adsorbed GSH, but coexsisting PVA seemed to prevent the adsorption, possibly because molecules of PVA could compete with GSH. The monolithic gold nanoparticles, of course, adsorbed GSH, and its amount was much more than γ-Fe_2O_3 in spite of the smaller weight of gold (see the second column of Table 1). These data reflect the stronger bond between GSH and gold than that between PVA and gold, and this is considered partially due to the higher specific surface area of the gold nanoparticles. The adsorption of GSH by the present composite nanoparticles is not equal to the sum adsorption by gold and γ-Fe_2O_3 with PVA. It might be partially ascribed to the difference in effective surface area between the monolithic gold and composite gold.

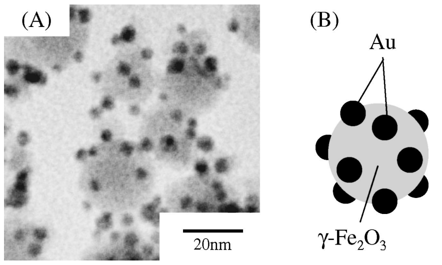

Figure 3. Typical TEM micrograph (A) and a schematic structure (B) of the Au/γ-Fe_2O_3 composite nanoparticles.

Table 1. Adsorption of GSH onto the surface of the nanoparticles

Nanoarticles	Amount ($g\,l^{-1}$)	PVA ($10\,g\,l^{-1}$)	Adsorbed GSH ($\mu mol\,l^{-1}$)
*Au/γ-Fe_2O_3	1.1	Contained	72
*Au	0.1	Contained	40
γ-Fe_2O_3	1.0	Contained	23
γ-Fe_2O_3	1.0	None	42

Initial concentration of the GSH; 100 $\mu mol\,l^{-1}$,
*; Gamma-ray irradiated suspension)

To summarize, we have successfully synthesized magnetic composite nanoparticles composed of individual nanosized gold particles supported on γ-Fe_2O_3 in an aqueous solution using γ-rays. We have confirmed that these particles exhibit the absorption band due to the plasmon of nanosized gold particles, and adsorb glutathion. We have also observed that the plasmon and glutathion involved with the composite nanoparticles are attracted by a magnet. This material would combine with biochemical compounds and be manipulated by the external magnetic field. Therefore, a wide range of its application is expected.

The authors thank Prof. K. Niihara and Dr. T. Nakayama for their help in TEM observation.

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Published on the web (Advance View) July 7, 2003; DOI 10.1246/cl.2003.690