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Gamma-ray synthesis of magnetic nanocarrier composed of gold and magnetic iron oxide

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Abstract

Magnetic nanocarrier consisting of iron oxide and gold was synthesized in an aqueous solution by using γ -ray irradiation. UV–vis absorption spectra showed surface plasmon resonance of nano-sized metallic gold. The surface of quasicore–shell structured magnetic iron oxide nanocarriers was almost covered with gold grains after having the gold grains grow over the iron oxides.

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1. Introduction

In recent years, magnetic nanoparticles are studied because of their potential applications as magnetic carriers for various biomedical uses such as cell and DNA separation, drug delivery system (DDS), magnetic resonance contrast enhancement and gene cloning [1–6]. In particular, magnetic beads with a few micrometers in diameter are

already commercialized and used for cell separation, DNA isolation and protein isolation [7]. For these applications, their surfaces are coated with a layer to combine with the functional biomolecule for each purpose and to avoid nonspecific adsorption. However, the commercially available magnetic beads cannot be used as a general purpose carrier. For each biomolecule it is necessary to coat the particles with an appropriate layer, which does not deactivate the biomolecule. On the other hand, gold nanoparticles are also widely studied in the field of biotechnology [6,8–10]. Gold combines firmly with biomolecules possessing mercapto

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groups and exhibits a characteristic reddish color due to surface plasmon resonance. The color changes when gold nanoparticles aggregate with the molecules attached on their surface, for which colorimetric detection of specific biomolecule is possible.

Recently, our group succeeded in synthesizing composite nanoparticles consisting of magnetic iron oxide nanoparticles and gold nanoparticles supported on their surface using γ -ray [11]. The composite nanoparticle takes over both the functions of the gold metal and magnetic maneuverability of the iron oxide. We have proposed that the composite nanoparticle is a very useful magnetic nanocarrier for the applications described above, because gold can serve as a specific tag for the mercapto group included in functional biomolecules. The composite nanoparticles may realize colorimetric detection and magnetic separation of the specific target biomolecules. Another merit of the composite nanoparticles is that they are synthesized in an aqueous solution without harmful surfactants or organic solvents. Carpenter et al. and Kim et al. claimed that iron–gold nanoparticles of a core–shell structure is synthesized by a reversed micelle method in an octane solution using CTAB as a surfactant [12,13]. Their particle must be coated with the surfactant molecules, which are not suitable for the biotechnological applications. We have already confirmed that the gold in our composite nanoparticles combine with molecules possessing mercapto group by using a glutathione as a model compound. However, an adsorption by the magnetic iron oxide surface was still observed. So, it is required to increase the amount of gold nanoparticles covering the iron oxide surface in order to suppress the nonspecific adsorption. The gold layer on the magnetic iron oxide should avoid nonspecific adsorptions.

In this work, we tried to enhance gold deposition on iron oxide by controlling an initial charge of iron-oxide dispersed in the suspension. We aimed at synthesizing core–shell nanoparticles; the surface of iron oxide nanoparticles is almost fully coated with gold layer, by growing the gold grains by a chemical treatment.

2. Experimental procedure

Iron oxide nanoparticles of γ -Fe₂O₃ with average diameter of 26 nm synthesized by physical vapor synthesis which are purchased from Nanophase Tech. Corp. were used as magnetic carriers. It contains γ -Fe₂O₃ particles of several nanometers to a hundred nanometer. Chemicals, such as HAuCl₄, 2-propanol and polyvinyl alcohol (PVA) were purchased from Wako Pure Chemical Industries Ltd. The iron oxide nanoparticles were dispersed in an aqueous solution containing Au(III) ion together with 2-propanol and PVA, then closed up in a glass vial. Concentration of the Au(III) ion, 2-propanol and PVA was fixed at 0.5, 0.125 mmol/l and 10 g/l, respectively. The amount of iron oxide nanoparticles dispersed in the suspension was 1.0 or 0.1 g/l. The suspension was sonicated for 15 min in an ultrasonic bath before γ -ray irradiation to disperse the iron oxide nanoparticles. The suspension was irradiated at room temperature with a ⁶⁰Co γ -rays source at a dose rate of 3 kGy/h for 0–6 h. During the irradiation, suspensions were continuously stirred to maintain the dispersion by rotating the disk on which the vials were mounted [14]. The sample suspension thus obtained was divided into magnetic and nonmagnetic fractions by a permanent magnet. Composite nanoparticles were obtained from the magnetic fraction.

To grow the gold grains on the γ -Fe₂O₃, we proceeded reduction of Au(III) ions at the surface of composite nanoparticle. The magnetic fraction of the irradiated suspension was mixed with an aqueous solution of HAuCl₄. After stirring 20 min, aqueous solution of NH₃, also purchased from Wako Pure Chemical Industries Ltd., was slowly added to the suspension under vigorous stirring to reduce gold ions. After stirring for 2 h, the aqueous suspension was magnetically separated to magnetic fractions and nonmagnetic fractions. The process was iterated 6 times until the surface of γ -Fe₂O₃ nanoparticles are enough coated with gold nanoparticles.

The UV–vis absorption spectra of the aqueous suspensions were measured by a spectrometer, Varian Cary 50. Au(III) ion concentration, which remains unreduced in the nonmagnetic fraction,

was measured with an improved colorimetric method [15]. The magnetic fraction was dried to obtain the powder, and its X-ray diffraction pattern was examined with a diffractometer, Rigaku RINT2100-Ultima⁺, using Cu-K α radiation. The morphologies of the composite nanoparticles and sizes of noble metal nanoparticles were observed by a transmission electron microscope, HITACHI H-8100 T, operated at 200 kV.

3. Results and discussion

3.1. Characterization of composite nanoparticles synthesized by γ -ray

After the γ -ray irradiation, the suspension became reddish color, which indicates the formation of nano-sized gold particles. After the magnetic separation, the nonmagnetic fraction with 1.0 g/l of γ -Fe $_2$ O $_3$ was transparent, which indicates that there were scarcely monolithic gold particles in the suspension. On the other hand, the nonmagnetic fraction with 0.1 g/l of γ -Fe $_2$ O $_3$ had a reddish color, which indicates the existence of monolithic gold particles. Fig. 1 shows TEM micrographs of the present composite nanoparticles. The magnetic fractions of the particle suspensions were deposited and dried on carbon-coated copper grids. The amount of γ -Fe $_2$ O $_3$ nanoparticles dispersed in the suspension was (a) 1.0 g/l or (b) 0.1 g/l. Small gold grains with average diameters of about 5 nm, which are seen as small and dark grains, are well dispersed on the surface of the γ -Fe $_2$ O $_3$ particles. It should be noticed here that relatively larger gold grains, about 10 nm, were also observed in Fig. 1(b), which will be discussed later. From these micrographs, it was observed that the numbers of gold nanoparticles supported on γ -Fe $_2$ O $_3$ particles are controlled by the initial amount of γ -Fe $_2$ O $_3$ particles charged in the suspension. XRD measurement of the powder obtained from the magnetic fraction showed a peak due to metallic gold. These results are a clear evidence for the formation of composite nanoparticles. In addition, monolithic gold particles were not seen in these micrographs, which indicate that the present magnetic separation is well performed.

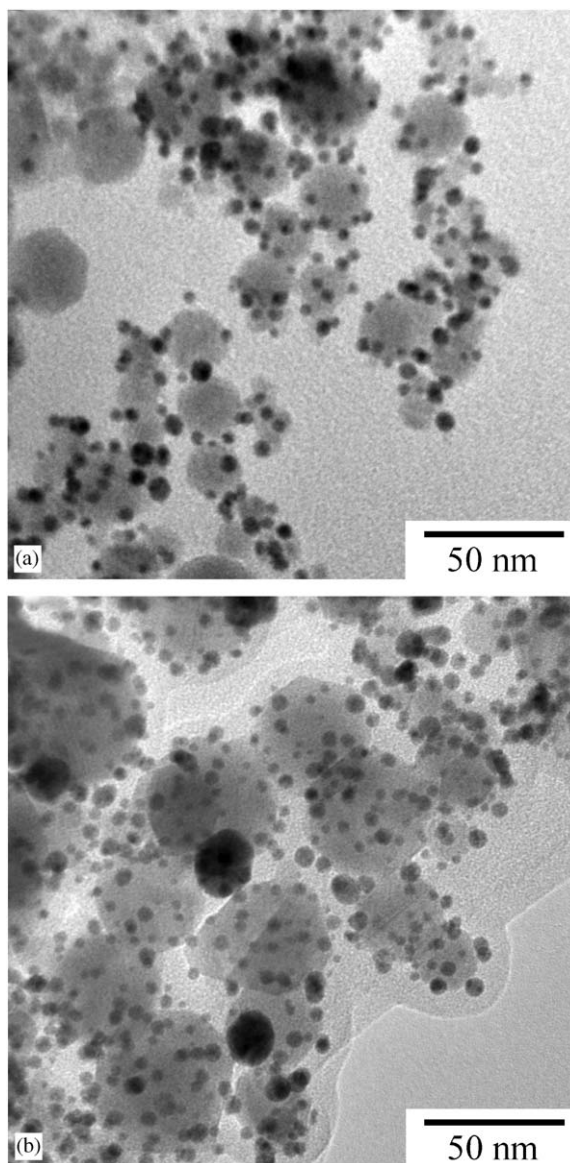


Fig. 1. TEM micrographs of the composite nanoparticles of Au and γ -Fe $_2$ O $_3$ synthesized by γ -ray. The particles were synthesized with 0.5 mmol/l of HAuCl $_4$ and (a) 1 g/l or (b) 0.1 g/l of γ -Fe $_2$ O $_3$ nanoparticles.

Fig. 2 shows the UV–vis absorption spectra of the magnetic fractions of the irradiated aqueous suspensions. Initial concentration of the Au(III) ion was 0.5 mmol/l and the amount of γ -Fe $_2$ O $_3$ was (a) 1.0 g/l or (b) 0.1 g/l. As shown in the figure, each spectrum of the magnetic fraction has a

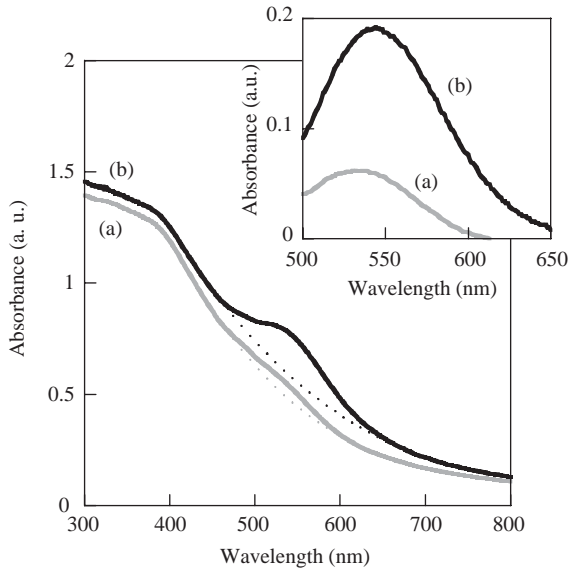


Fig. 2. UV-vis absorption spectra of the magnetic fractions of the γ -ray irradiated suspensions. The suspensions were prepared with 0.5 mmol/l of HAuCl_4 and (a) 1 g/l or (b) 0.1 g/l of γ - Fe_2O_3 nanoparticles. Inset shows background-removed spectra of the magnetic fractions.

shoulder due to the surface plasmon of nano-sized metallic gold. This is also a clear evidence for the formation of the composite nanoparticles. Insets in the figure show background-removed spectra to extract and visually enhance the surface plasmon peak of gold nanoparticles by the procedure as follows. In the region relevant to the plasmon peak, the background spectrum of the γ - Fe_2O_3 nanoparticles are reproduced by a polynomial fitted to the data in the regions at both sides of the peak. We confirmed that the polynomial thus evaluated well described the spectrum of dispersions of the iron oxide nanoparticles only, regardless of their concentrations. The spectrum in the inset was calculated as the difference between the raw spectrum and the background thus evaluated, shown as dotted lines in the figure. Although this procedure is not based on a definite physical theory such as Mie's scattering model [16], the extracted peaks must reasonably reflect the characteristics of gold nanoparticles immobilized on the iron oxide nanoparticles, such as the primary particle size and the agglomeration state. The

plasmon peaks were observed around 535 nm with (a) and 545 nm with (b). This difference in the peak position should be ascribed to the larger gold nanoparticles shown in Fig. 1(b). The difference in the peak intensity should reflect the number of gold nanoparticles supported on the surface of γ - Fe_2O_3 nanoparticles. It should be noticed here that the present composite nanoparticle possesses the optical function of gold nanoparticles. This is one of the promising feature of the present composite nanoparticles for the future applications in colorimetric detection of specific biomolecules.

Fig. 3 shows a time-dependence of the concentration of Au(III) ions in the irradiated suspension. Initial concentration of the Au(III) ion was 0.5 mmol/l and the amount of γ - Fe_2O_3 was constant at 1.0 g/l (see Fig. 1(a) and Fig. 2(a)). Before irradiation, the concentration of Au(III) ion was 0.4 mmol/l, presumably reflecting the adsorption of Au(III) ion onto the surface of γ - Fe_2O_3 nanoparticles. The concentration of the Au(III) ions decreased with irradiation time, and was no longer detected after few hours of

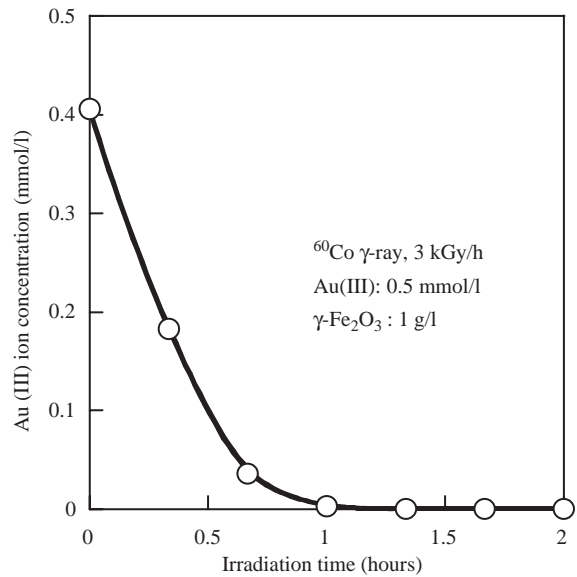


Fig. 3. Time dependence of the concentration of Au(III) ions in the nonmagnetic fraction of the irradiated suspension. The suspension was prepared with 0.5 mmol/l of HAuCl_4 and 1 g/l of γ - Fe_2O_3 nanoparticles.

irradiation. Our group has recently reported the synthesis of similar Au/ γ -Fe₂O₃ composite nanoparticles by sonochemical reduction process [17]. The sonochemical method took only 10 min for the reduction of Au(III) ions, although the volume of the aqueous suspension is restricted by the size of oscillator, about few hundred milliliter per batch. With the present radiochemical process, large reaction vessel, about few liters even with a laboratory scale, is applicable because γ -ray photons easily penetrate the aqueous solution. This would be one of the advantages of this synthesis procedure.

3.2. Synthesis of quasicore–shell nanoparticles

Fig. 4 shows the TEM micrographs of the nanoparticles after the iterative reductions of Au(III) ions at the surface of the composite nanoparticle synthesized by γ -ray. The magnetic fraction used were prepared with 0.5 mmol/l of Au(III) ion and 0.1 g/l of γ -Fe₂O₃ (see Fig. 1(b) and Fig. 2(b)). It clearly shows that the size of gold grains on the γ -Fe₂O₃ increases with reduction steps. After sixth reduction step, gold grains connect with each other and the surface of each γ -Fe₂O₃ particle is almost fully coated with gold grains, in other words, quasicore–shell particles are formed.

Fig. 5 shows the UV–vis absorption spectra of the magnetic fractions before and after the quasicore–shell nanoparticle synthesis. The shoulder due to surface plasmon of gold nanoparticles shows red shift after sixth reduction step. Inset in the figure shows the background-removed spectra to extract and visually enhance the surface plasmon peak of gold nanoparticles. Thus extracted peak also showed a red shift after sixth reduction step, from 545 to 630 nm, which reflects larger and connected gold nanoparticles shown in Fig. 4(b). Fig. 6 shows the extracted peak positions of surface plasmon resonance of each reduction steps. As shown in the figure, the peak position gradually shifted to longer wavelength. These results reflect the formation of large and connected gold grains on the surface of γ -Fe₂O₃ nanoparticles, as shown in Fig. 4(b).

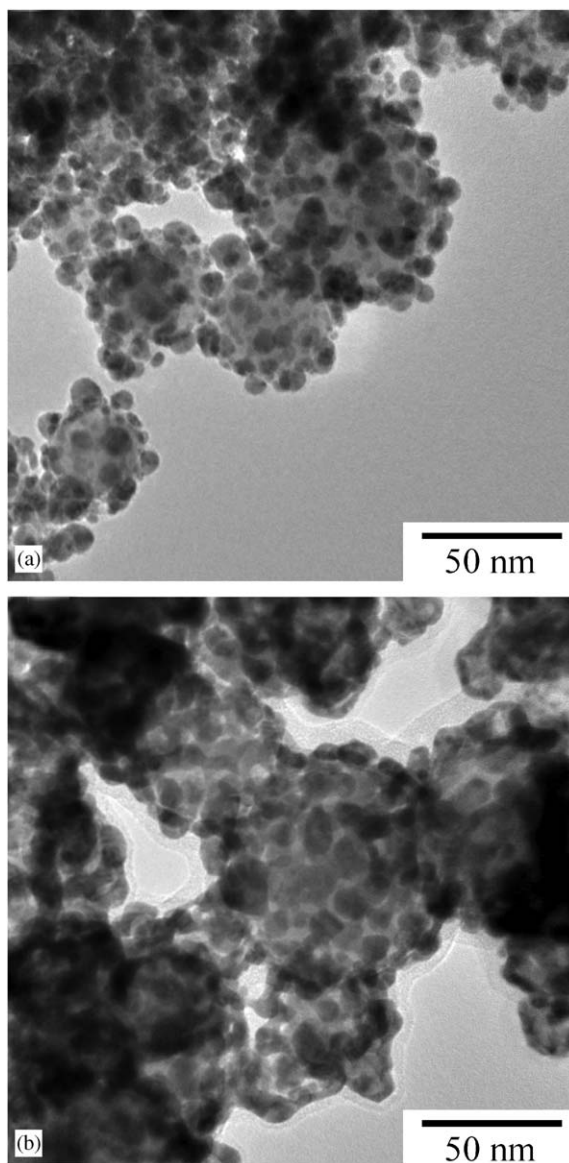


Fig. 4. TEM micrographs of the quasicore–shell nanoparticles of Au and γ -Fe₂O₃ synthesized with iterative reduction of Au(III) ions by (a) 3 times and (b) 6 times.

3.3. Formation process of the composite nanoparticle by γ -ray

Formation process of the composite nanoparticles by γ -ray irradiation is now discussed. As the quantum energy of the ⁶⁰Co γ -ray is 1.25 MeV, it

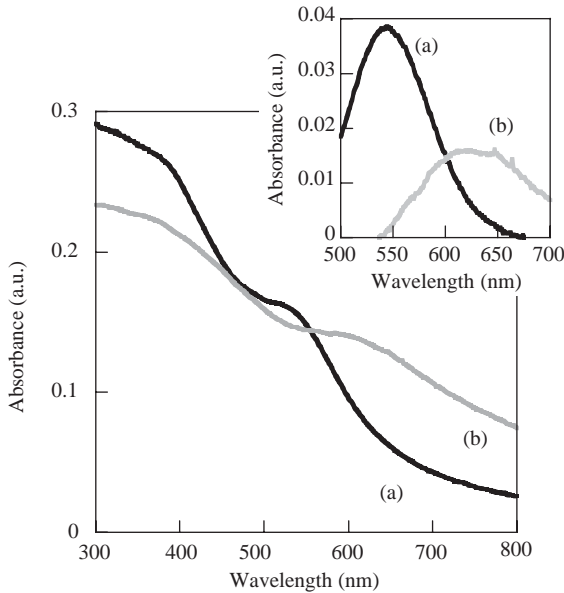


Fig. 5. UV-vis absorption spectra of the magnetic fractions of (a) before and (b) after the iterative reduction of Au(III) ions. The iterative reduction was performed 6 times. Inset shows background-removed spectra of the magnetic fractions.

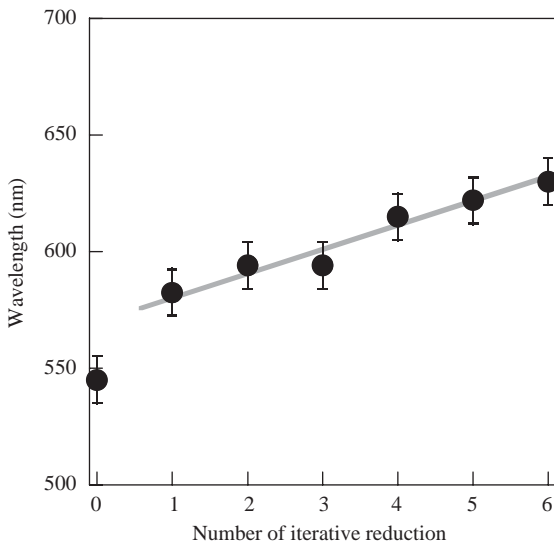
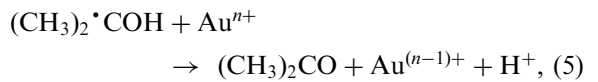
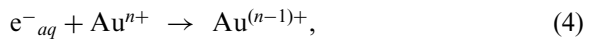
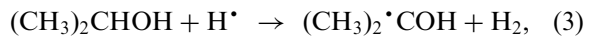
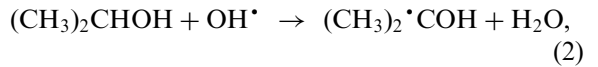
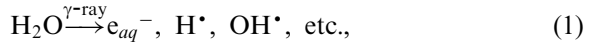


Fig. 6. Dependence of the iterative reduction on the surface plasmon peak position. The peak positions were obtained from background-removed spectra of the magnetic fractions.

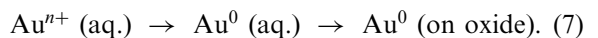
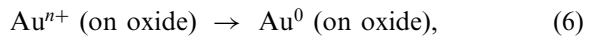
deposits its energy to iron oxide and water almost equivalently for each mass [18,19]. The mass of iron oxide is merely about 0.1 or 0.01% of the

aqueous phase, so that almost all the γ -ray energy is first deposited to water in order to emit electrons. The secondary electrons bring about subsequent radiochemical reactions to reduce Au(III) ions. Elemental processes for the reduction of gold ions by the γ -rays were proposed for the formation of monolithic noble metal nanoparticles as follows [20,21]:



where Eq. (1) represents water radiolysis and Eqs. (2) and (3) represent radiolysis of 2-propanol. Generated hydrogen atoms H^\bullet and hydrated electrons e_{aq}^- are strong reductants capable of reducing gold ions Au^{n+} to lower valences and finally to metallic state. The secondarily generated radical of $(\text{CH}_3)_2^\bullet\text{COH}$ also efficiently reduces the gold ions. These in situ generated reductants transform the gold ions Au^{n+} to $\text{Au}^{(n-1)+}$ according to Eqs. (4) and (5), leading to the formation of gold nanoparticles. These reactions occur very homogeneously from the macroscopic viewpoint of material but very sparsely from the atomic scale viewpoint.

In the presence of iron oxide nanoparticles in the irradiated suspension, the following two processes should be taken into account on the formation of composite nanoparticles:



Eq. (6) means formation of gold metal on iron oxide, while (7) means that gold metal formed in the aqueous phase are immobilized on iron oxide. Occurrence of Eq. (6) was reported for the Ag/SiO₂ system investigated by the pulse radiolysis technique [22,23]. It should be recalled here that in

our experimental condition most of the Au(III) ion remain in the aqueous phase, as shown in Fig. 3. These aqueous gold ions should contribute to forming gold nanoparticles free from iron oxide particles. So it is reasonable to assume that the Eq. (7) occurs in the present synthesis. Of course, occurrence of reaction (6) is not excluded by the present experiments and still expected. It should be recalled that when the amount of γ -Fe₂O₃ nanoparticles was 0.1 g/l, some monolithic gold particles were formed and that some larger gold particles were observed in Fig. 1(b), while not in Fig. 1(a). Fewer amounts of γ -Fe₂O₃ nanoparticles probably lead to the long migration distance of gold nanoparticles initially formed in an aqueous phase, which results in a formation of monolithic gold nanoparticles and larger gold grains on γ -Fe₂O₃ nanoparticles.

4. Conclusion

Magnetic composite nanoparticles consisting of magnetic iron oxide and gold were synthesized in an aqueous solution using γ -ray. Number of gold grains supported on the iron oxide was controlled by initial amount of iron oxide particles. The quasicore-shell nanoparticles were successfully synthesized by an iterative reduction of Au(III) ions at the surface of composite nanoparticles synthesized by γ -ray. UV-vis absorption spectra of the composite nanoparticles showed surface plasmon resonance of nano-sized gold, which were significantly affected by the number and size of gold grains on iron-oxide surface. Radiochemical reduction of Au(III) ions lead to the formation of gold nanoparticles in an aqueous phase, which are immobilized on the surface of magnetic nanoparticles. Thus a synthesized composite nanoparticle carries functions of gold and magnetic iron oxides, so that it would be a magnetic nanocarrier suitable for biomedical applications.

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