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Synthesis of fullerene $[C_{60}]$ -gold nanoparticles using non-ionic surfactants polysorbate 80 and brij 97

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The synthesis of gold nanoparticles was investigated with non-ionic surfactants such as polysorbate 80, brij 97 and KAuCl₄ in water. The products of gold nanoparticle were well dispersed in water and investigated by UV-vis spectra and TEM. The reaction time for the synthesis of gold nanoparticles was investigated by monitoring the change of color and the change of the peak of the UV-vis spectra in the absence of ultrasonic irradiation and in the presence of ultrasonic irradiation. Gold nanoparticles reacted with 4-aminothiophenol in water and then, diethylether was added, and fullerene[C₆₀] in toluene which was stirred for 24 h. The fullerene[C₆₀]-gold nanoparticles were characterized by UV-vis and MALD-TOF-MS spectra.

Key word: Fullerene[C₆₀], Gold nanoparticle, Non-ionic surfactant, UV-vis spectra, TEM.

Introduction

Metal nanoparticles have exclusively studied, and in 1981, Schimd et al. [1] synthesized the first example of ligand stable gold nanoparticles, Au₅₅(PPh₃)₁₂Cl₆. However, the formation of more stable and isolatable monolayer-protected gold nanoparticles was achieved by nanoparticles; preventing the aggregation of the metal nanoparticles was achieved by Brust et al. [2]. The organic monolayer which binds to the surface of metal particles also stabilizes them from harsh reaction conditions and enhances the solubility in various solvents [3-5]. Other organic compounds with different reactive head groups, such as thiol [6-8], amine [9-11], non-ionic surfactants [34] can protect metal nanoparticles by self-assembly. Among the various metal nanoparticles, gold nanoparticles have drawn remarkable interest in the last few years because of their high stability to oxidation and their optical and well-defined size-related electronic (e.q., quantized charging) properties [12, 13]. The synthesis of monolayer-protected gold nanoparticles [14] is based on the reactive head groups, which provide self-assembly of organic monolayers onto the nanoparticle surface. Gold nanoparticles have been protected with non-ionic surfactants, such as polysorbate 80, brij 97 in an aqueous solution. Non-ionic surfactants such as polysorbate 80, brij 97 alone could be used in the preparation of gold nanoparticles in an aqueous solution at room temperature without any reducing agents. Our investigation has proved that non-ionic surfactants such as polysorbate 80, brij 97 could act not only as a stabilizing agent but also as reducing agents for the synthesis of gold nanoparticles in an aqueous solution at

room temperature. Also, we introduce a somewhat different sonochemical synthetic method. Ultrasonic waves in liquids are known to cause chemical reactions either in homogeneous or in heterogeneous systems [15, 16]. The chemical reactions are promoted by cavitation of liquids caused by ultrasonic waves traveling in the liquid. Cavitation implies the formation of microbubbles in a liquid subjected to sonication, which implode and generate high pressures and temperatures in their surrounding [15, 16]. We have applied an ultrasonic process to the synthesis of gold nanoparticles. Fullerene $[C_{60}]$ -capped nanoparticles have recently begun to attract the interest of nanomaterials researchers [17-24]. Also, we have attempted the synthesis of fullerene $[C_{60}]$ linked gold nanoparticles made with non-ionic surfactants such as polysorbate 80, brij 97 and characterized the products by UV-vis (Ultraviolet-visible) and MALDI-TOF-MS (Matrix-Assisted Laser Desorption Ionization Time of Flight Mass) Spectra.

Experimental

Chemicals

Polysorbate 80 (polyoxyethylene-20-sorbitan monooleate, TWEEN 80), brij 97 (polyoxyethylene-10-oleyl ether, $C_{18}H_{35}O(CH_2CH_2O)_{10}H)$, were purchased from Sigma. Fullerene[C₆₀] was purchased from TCI. Toluene and diethyl ether were purchased from Samchun Chemicals and KAuCl₄ and 4-aminothiophenol were purchased from Aldrich.

Instruments

The UV-vis spectra were recorded on a Varian Cary 500 spectrometer. The synthesized Au(0) nanoparticels were analyzed using a transmission electron microscope (Philips CM10, TEM) at an acceleration voltage of 100 kV. The morphology and crystallite size were studied with a Hitachi H-9000NA transmission electron microscope. TEM

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specimens were prepared by placing a few drops of sample solution on a copper mesh, covered with a carbon film. Ultrasonic irradiation of all samples was conducted in continuous mode with an ultrasonic generator UG1200 (Hanil Ultrasonic Co, Ltd.), set accordingly; frequency 20 kHz, power 750 W, with a horn system configuration, and the horn made of a titanium alloy, Ti-6Al-4V, and a horn tip diameter of 13 mm. The sample was analyzed by MALDI-TOF-MS (Voyager DESTR) with a cyano-4-hydroxy cinnamic acid matrix.

Synthesis

Synthesis of gold nanoparticles by polysorbate 80 and brij 97

In a typical experiment, 0.4 mM of KAuCl₄ was added to each 10 ml of 1 wt.% aqueous solution of polysorbate 80, brij 97 and kept at room temperature. The solution turned yellow to colorless, following a pink color, and then finally to red after 5 h, indicating the formation of gold nanoparticles.

Synthesis of gold nanoparticles by polysorbate 80 and brij 97 under ultrasonic irradiation

In a typical experiment, 0.4 mM of KAuCl₄ was added to each 10 ml of 1 wt.% aqueous solution of polysorbate 80, brij 97 with ultrasonication and kept at 25~43 °C. The solution turned yellow to colorless, following a pink color, and then finally to red after 1 h, indicating the formation of gold nanoparticles.

Synthesis of C_{60} -gold nanoparticles made by polysorbate 80 and brij 97

8.7 mg of 4-aminothiophenol was added to each 100 ml of reduced gold nanoparticles by polysorbate 80, brij 97 in an aqueous solution which appeared a dark red color with stirring for 24 h. 100 ml of diethyl ether and 8 mg of C_{60} dissolved in 100 ml of toluene was added to each above solution in order and then stirred for 24 h. When each solution had separated to two phase, we took the upper solution phase, and dried this in a vacuum oven to obtain products in a solid state.

Results and Discussion

Instead of using reducing agents, we used only non-ionic surfactants such as polysorbate 80, brij 97 and KAuCl₄ to obtain reduced gold nanoparticles Au(0). The synthetic method which made these Au(0) nanoparticles is simple compared to that in previous reports [4, 25-34]. A set of color changes, typical for the preparation of Au(0), was observed during the course of the reaction at room temperature. Initially, the solution turned yellow to colorless, but after 3 h the solution turned pink and then finally red after 5 h. Then the gold surface plasmon band indicative of Au(0) was observed after 5 h at room temperature. A decrease in the intensity of the characteristic surface plasmon band in the UV-vis spectrum for the AuCl₄⁻¹ ion at λ max = 324 nm was observed, featuring a concomitant growth



Fig. 1. UV-visible spectra of gold nanoparticles made using polysorbate 80(a) and brij 97(b) in water.

of new bands in the range of $\lambda \max = 520-540$ nm in Fig. 1(a)($\lambda \max = 527$ nm) and 1(b)($\lambda \max = 522$ nm). These are related to the characteristic surface plasmon band of gold nanoparticles [25], corroborating the formation of Au (0).

The ultrasonic effect on the synthesis of gold nanoparticles by non-ionic surfactants such as polysorbate 80, brij 97 was examined by monitoring the reaction times. When we used ultrasonication to synthesize gold nanoparticle, the color of the solution changed from yellow into red as a final color within 1 h. Even though the color of the solution changed without ultrasonic irradiation, it took a longer reaction time (5 h) than with ultrasonic irradiation to synthesize gold nanoparticles. A decrease in the intensity of the characteristic surface plasmon band in the UV-vis spectrum for the AuCl₄⁻¹ ion at λ max = 324 nm was observed, featuring a concomitant growth of new bands in the range of λ max = 520-560 nm in Fig. 2(a) (λ max = 529 nm) and 2(b) (λ max = 538 nm).



Fig. 2. UV-visible spectra of gold nanoparticles made using polysorbate 80(a) and brij 97(b) in water under ultrasonic irradiation.



Fig. 3. TEM images of gold nanoparticles made using polysorbate 80(a) and brij 97(b) in water.



Fig. 4. TEM images of gold nanoparticles made using polysorbate 80 (a) and brij 97 (b) in water under ultrasonic irradiation.

Fig. 3(a) shows a TEM micrograph of Au (0) nanoparticles synthesized in a 1 wt.% polysorbate 80 aqueous solution. Also, Fig. 3(b) shows a TEM micrograph of Au(0) nanoparticles synthesized in a 1 wt.% of brij 97 aqueous solution. Fig. 4(a) and 4(b) show transmission electron microscopy (TEM) images of Au(0) nanoparticles synthesized in the different non-ionic surfactant solution which Fig. 4(a) is 1 wt.% polysorbate 80 aqueous solution under ultrasonic irradiation and Fig. 4(b) is 1 wt.% brij 97 aqueous solution under ultrasonic irradiation. All bearing gold nanoparticles bore both guasi-spherical shapes. 4-aminothiophenoxide gold nanoparticles were synthesized as reduced gold nanoparticles, Au(0) reacted with 4aminothiophenol using a modified Brust reaction. Here, we suggest a non-ionic surfactant-induced reduction mechanism of a gold salt that could involve the repeat unit (-CH₂- CH₂-O-) (Fig. 5, scheme1) a, b of polysorbate 80, and brij 97 in the reaction with gold nanoparticles, polysorbate 80, and brij 97 have oxyethylene groups(-CH₂-CH₂-O-) and have proved to be efficient reducing agents as non-ionic surfactants. Also, C_{60} and 4-aminothiophenoxide gold nanoparticles made a product in which C_{60} is linked with 4-aminothiophenoxide gold nanoparticles by amination.

The peak of C_{60} linked 4-aminothiophenoxide gold nanoparticles made using polysorbate 80 was shifted to 328 nm in a toluene solvent as compared to C_{60} (336 nm in toluene) from the UV-vis spectra in Fig. 6(a). Also, we prepared aminothiophenoxide gold nanoparticles by the reaction of Au(0) and 4-aminothiophenol. Then, we synthesized fullerene[C_{60}]-4-aminothiophenoxide gold nanoparticles by amination. The reaction mechanism in the formation of fullerene[C_{60}]-4-aminothiophenoxide gold



Fig. 5. (Scheme 1) Chemical structure polysorbate 80 and brij 97.



Fig. 5. (Scheme 2) Synthesis of fullerene $[C_{60}]$ linked 4-aminothiophenoxide gold nanoparticles made using non-ionic surfactants; polysorbate 80 and brij 97.



Fig. 6. UV-visible spectra of C₆₀ linked 4-aminothiophenoxide gold nanoparticles made using polysorbate 80 (a) and brij 97 (b) in toluene.

nanoparticles is shown in Fig. 5, scheme 2. The peak of C₆₀ linked 4-aminothiophenoxide gold nanoparticles made using with brij 97 was shifted to 328 nm (as a shoulder) in the toluene solvent as compared to C_{60} (336 nm in toluene) by the UV-vis spectra in Fig. 6(b). The MALDI-TOF-MS analyses reported in Fig. 7(a) and 7(b) show the formation of HC₆₀(HNC₆H₄)SAu because the MALDI-TOF-MS spectrum shows a peak from HC₆₀(HNC₆H₄)SAu, at m/z = 1042 in the toluene solvent. The reaction mechanism for the formation of fullerene $[C_{60}]$ -4-aminothiophenoxide gold nanoparticles is shown in the scheme 2 of Fig. 5. Finally, fullerene[C₆₀]-gold nanoparticles are interesting materials for the formation of hybrid nanomaterials. It is suggested that fullerene[C₆₀]-gold nanoparticle structures may be promising candidates for novel sensor materials, catalysts, and for the bottom-up fabrication of single-electron transistors [18].

Conclusions

We knew that polysorbate 80, brij 97 could act both as reducing agents and stabilizing agents to make gold nanoparticle in an aqueous solution at room temperature.

We found that the time of synthesis of gold nanoparticles with polysorbate 80, brij 97 under ultrasonic irradiation was shorter than in the absence of ultrasonic irradiation.

Gold nanoparticles reacted with 4-aminothiophenol in water to synthesize 4-aminothiophenoxids gold nanoparticles and then, with diethylether and fullerene[C_{60}] in toluene added and stirred for 24 h it was possible to synthesize fullerene[C_{60}]-4-aminothiophenoxide gold nanoparticles by amination. UV-vis, TEM, MALDI-TOF-MS spectra were used to confirm the products of reduced gold nanoparticles, and fullerene[C_{60}]-4-aminothiophenoxide gold nanoparticles, and fullerene[C_{60}]-4-aminothiophenoxide gold nanoparticles.

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