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Surface enhanced plasmon effects by gold nanospheres and nanorods in Langmuir-Blodgett films

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ABSTRACT

Hydrophobic gold nanospheres and nanorods were synthesized by a reduction method and a seed-mediated growth method, respectively, and by the surface-modification with 1-dodecanethiol. Langmuir-Blodgett (LB) films of gold nanoparticles were prepared at different surface pressures and two-dimensional ordering of nanoparticles was evaluated. A plasmon band of nanospheres slightly red-shifted from 525 nm in water to 543 nm in chloroform but it was 634 nm at LB film. Plasmon bands at 750 and 515 nm of nanorods in water drastically changed to a band at 550 nm in chloroform but it appeared at 621 and 1000 nm. Moreover, Langmuir monolayer of eiocosanoic acid was transferred on LB films of nanospheres on CaF_2 window and transmission surface enhanced infrared absorption spectra (SEIRAS) were measured. A C═O stretching vibration band at 1702 cm^{-1} was strongly enhanced compared to other vibration bands due to the selection rule of SEIRAS. That is, the dipole moment of C═O stretching mode should be on the same direction as the surface enhanced electric field, which is perpendicular to the gold surface. From the comparison of SEIRAS for poly(amido amine) dendrimer on LB films of nanospheres and nanorods, it is apparent that the enhancement effect of nanorod LB film is higher than that of nanosphere LB film, although the surface coverage and the number density of nanorods in LB film are lower than those of nanosphere LB film, suggesting the effect of hot spots.

1. Introduction

Gold nanoparticles have been taken account some applications on industrial and biomedical fields because of their unique physical, chemical, electrical and optical properties. Thus, they have been synthesized through different techniques like laser ablation, vapor deposition electrochemical reaction and chemical reduction methods and produced with varied sizes and shapes [1–10]. At the same time, surface properties of nanoparticles were also emphasized to disperse nanoparticles in medium, and various stabilizers were loaded on the surface of gold nanoparticles. Thiol compounds are one of strongly anchoring reagents on gold surfaces and the selection of thiol compounds changes the surface characters of gold nanoparticles to be hydrophilic or hydrophobic [11–13].

The local plasmon characters of gold nanoparticles are effective for enhancing spectroscopic detection of molecules and can be applied on plasmon devices for sensing and phototherapy. The surface enhanced infrared absorption spectroscopy (SEIRS) [14–16] has been investigated as well as the surface enhanced Raman scattering [17,18] and the surface enhanced plasmon fluorescence [19–21]. On this situation, the enhancement effect depends on the situation of plasmon particles, especially, on the ordering ways of gold nanoparticles, that is, perpendicular, horizontal or random orientations of anisotropic particles [22] in addition to shapes of nanoparticles such as sphere or non-sphere. By the way, well array of gold nanoparticles has been prepared in liquid crystal matrix [23], at air-water interfaces [24], and as Langmuir-Blodgett (LB) monolayers [25–32]. However, such ordered arrays have mainly been prepared from spherical nanoparticles.

We have prepared hydrophobic gold nanorods and their well-ordered array by solvent evaporating [13] or evaporation-induced self-assembling [33]. In the present investigation, we form LB films of hydrophobic gold nanospheres and nanorods and compare their properties as a function of the surface pressure. This particle preparation method provides obvious advantages due to simple process and controllable operation parameters and ordering, and it can be applied to various nanoparticles with any shape and size. After the film preparation, the SEIRAS behaviors on LB films are discussed. Although there are reports of LB Films of gold nanorods, the rods are coated by thick silica shell [34,35]. The gold nanoparticles in the present work are coated by alkanethiol molecules and thus the shell thickness is thin but

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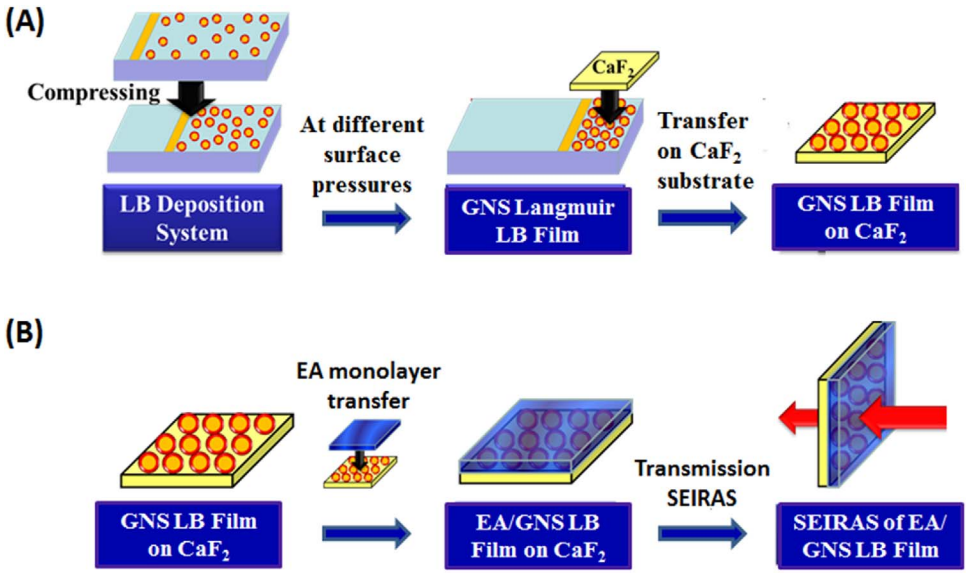
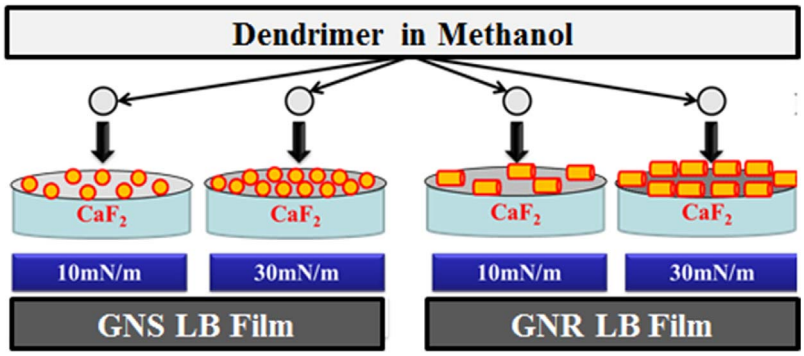


Scheme 1. Schematic illustration of preparation of (A) gold nanosphere LB films and (B) eicosanoic acid Langmuir monolayer-loaded gold nanosphere LB films.



Scheme 2. Schematic illustration of preparation of PAMAM dendrimer-deposited gold nanoparticle LB films.

enough to protect nanoparticles from the aggregation among them and allows nanoparticles to be dispersed in organic solvents.

2. Experimental section

Citric acid (anhydrous), chloroform (99%), and hexadecyl trimethylammonium bromide (C_{16}TAB, 99%) were purchased from ACROSS Organics. Eicosanoic acid (arachidic acid) and silver nitrate were products from Wako Pure Chemical Industries, Ltd. Carboxylate-terminated generation 4.5 poly(amido amine) (PAMAM) dendrimer (ethylenediamine core, 5 wt% in methanol), sodium borohydride (98%) and sodium tetrachloroaurate(III) dehydrate (99%) were obtained from Aldrich Chemical Co. Inc. Ethyl alcohol, 1-dodecanethiol (*n*-dodecyl mercaptan) and sodium hydroxide pellets were purchased from Shimakyu's Pure Chemicals, TCI, and J. T. Baker, respectively. All chemicals were used without further purification. Ultrapure water ($>$ 18.2 MΩ cm) was used throughout all the experiments.

LB films were prepared on a LB deposition system (Nippon laser & Electronics Lab, LB 140S-MWC). Transmission electron microscopic (TEM) images for specimens on copper grid were taken on a Hitachi H-7000 microscope. Atomic force microscopic (AFM) images were taken on a Digital Instruments NanoScope III, Veeco, for specimens on silicon wafer. Ultraviolet (UV)-visible-near infrared (NIR) absorption spectra for specimens on quartz plate or solutions in quartz cell were recorded on a JASCO V-670 spectrometer, and infrared (IR) absorption spectra for specimens on CaF_2 window were recorded on an FTIR spectrometer (Nicolet, Nexus 6700, Thermo Scientific).

Gold nanospheres were the same one, which was synthesized by the reduction of $NaAuCl_4$ and used before [36,37]: An aqueous solution (1 mM, 50 cm^3) of $NaAuCl_4$ was mixed with an aqueous solution (1 wt %, 5 cm^3) of sodium citrate (prepared from citric acid by the neutralization) and the mixture were heated at 100 °C under stirring. After a wine-red color of gold nanoparticles was ascertained, the solution was cooled down to room temperature. Then the hydrophilic surface of spherical nanoparticles was modified to be hydrophobic [12]: An aqueous solution (10 cm^3) of nanoparticles was shaken with a chloroform solution (2 mM, 10 cm^3) of 1-dodecantiol. After the transfer of the color from an aqueous solution to an organic one was affirmed, the organic phase was separated, the solvent was evaporated and the residue was solved in chloroform. The size of resultant nanospheres determined by TEM was 15 nm in average.

Gold nanorods were same as ones previously synthesized and used [37,38], which were prepared in accordance with a seed-mediated method. The dispersion of produced gold nanorods was dialyzed to remove the excess C_{16}TAB, after the filtration removal of crystallized C_{16}TAB at 4 °C. The surface modification of nanorods by 1-dodecanethiol was carried out at the same procedure as for nanospheres described above. The product was the mixture of rod particles with different aspect ratios of 3.4 (20 nm length, 5.9 nm width) and 1.6 (16 nm length, 10 nm width), which existed with a ratio of 81.8 and 18.2%, respectively [32].

For the preparation of LB films, the suspension of particles in chloroform was spread on water subphase in an LB trough, and chloroform was evaporated. Langmuir monolayer of nanoparticles was compressed up to desired surface pressures at a rate of 10 mm/min and transferred by the horizontal adsorption procedure on distinct