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Surface enhanced Raman scattering from layered assemblies of close-packed gold nanoparticles

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ARTICLE INFO

Article history:

Received 27 July 2007

Received in revised form

30 August 2007

Accepted 8 September 2007

Published on line 19 September 2007

Keywords:

Surface enhanced Raman scattering

Enhancement factor

Gold

Au

Nanoparticle

Surface plasmon

Benzenethiol

Thiophenol

Electromagnetic effect

Chemical effect

ABSTRACT

A synthetic method of ordering hydrophilic gold nanoparticles into a close-packed two-dimensional array at a hexane–water interface and subsequent transferring of such structure onto a solid substrate is described. By repeating the transfer process, multilayered gold nanoparticle films are formed without need of linker molecules. Their surface enhanced Raman scattering (SERS) efficiencies are compared as a function of the number of layers. It is shown that both the number of layers and the particle size contribute to SERS phenomenon. Judging from the noticeable dependence of SERS efficiency on the nanometer scale architecture, the close-packed nanoparticle formation at an immiscible interface presents a facile route to the preparation of highly active and relatively clean SERS substrates by controlling both the particle size and the film thickness. Among the investigated samples, the gold nanoparticle film assembled with quintuple layers of 30 nm diameter particles showed the maximum SERS efficiency.

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1. Introduction

The elucidation of the microscopic processes, such as molecular adsorption, catalysis, and corrosion, is of fundamental interest for solving challenging problems in surface chemistry. One of the primary objectives in the study of surface science is the understanding of adsorbate–surface interactions at the molecular level. In order to investigate surface adsorption and its dynamics, a myriad of surface-characterization techniques

have been utilized. In particular, surface enhanced Raman scattering (SERS) has been extensively utilized as a major tool for unveiling the vibrational characteristics of adsorbates on noble metal surfaces owing to its enormous signal enhancement effect. It is a general understanding that the SERS from noble metal nanostructures has two major contributions: one is a local field enhancement induced by localized surface plasmon resonance, and the other is a charge-transfer resonance between an analyte and a metal surface [1]. The

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doi:10.1016/j.aca.2007.09.026

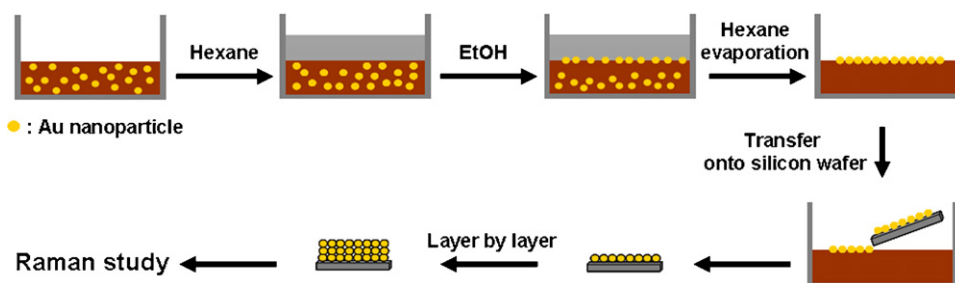


Fig. 1 – A schematic representation of AuNP film formation at a water–hexane interface and subsequent transfer onto a 3-mercaptopropyltrimethoxysilane modified substrate.

local field enhancement is very sensitive to the size and structure of the noble metal. Especially, sharp edges of the nanometer-sized metals or their gaps may create extraordinarily high local field and serve as “hot spots” in the SERS [2–11].

While investigating the nature of the hot spot and its role in SERS is currently a subject of intensive attention, constructing an effective SERS substrate which takes the best advantage of the nature of the local field enhancement and other SERS effects is a primary interest for practical applications. For the diagnostic purposes, the SERS substrate should be easily prepared and stable in air as well as produces a large enhancement for adsorbate vibrational modes. For this purpose, some of recent developments are worth mentioning; silver nanoparticles tethered to a deposited silver film [12], reduction of Ag^+ on Cu foil [13], deposition of Ag onto soft-lithographically patterned nanowells [14], silver nanoparticles sitting on porous alumina membrane [15], photochemical modification of gold film [16], and gold-coated photonic crystals [17]. In all the mentioned contributions, a common effort has been exerted on developing stable nanostructures with high signal enhancement.

For synthesizing reproducible SERS substrates, there are two general requirements. One is the tunability of roughness within tenths of nanometer scale, which leads to the generation of the hot spots in a given substrates. Although a particular shape of a single nanoparticle may behave as a hot spot, collective interaction of electromagnetic field within a nanoarchitecture can lead to the generation of hot spots [3–12]. In this respect, assembling nanoparticles into three-dimensional multilayer is worth a special attention since it can create maximum density of hot spots due to the close proximity of nanoparticles of one another. However, construction of the three-dimensional multilayer has commonly required linker or capping molecules to overcome electrostatic repulsion between nanoparticles [18,19]. The presence of the linker or capping materials often prevents the utilization of the structure as SERS substrates for other adsorbates, which significantly limits a scope of material analysis using the SERS technique.

In this paper, we report that it is possible to construct three-dimensional multilayered film with close-packed gold nanoparticles (AuNPs) by using a Langmuir–Blodgett (LB) method. The constructed film is relatively free of linker

molecules, and therefore would be more suitable for the SERS substrate. The method is based on entrapping the particles at an interface of water and nonpolar liquid with a tunable contact angle [20–22]. To be more specific, to an aqueous solution of AuNPs is added hexane to form the water–hexane interface. The surface nature of the AuNPs is hydrophilic and prefers the water environment. However, as a small amount of ethanol is added, the dielectric constant of the water layer decreases and the AuNPs become destabilized. As the contact angle of the AuNP at the water–hexane interface approaches 90° , the majority of the destabilized AuNPs are collected at the interface. While hexane is removed spontaneously by evaporation, the AuNPs are floated sparsely on the surface of water. As the solution is compressed along the interface, the AuNPs on the water surface are packed into one large film of a monolayer or a close-packed layer. The resulting AuNP film is transferred to a flat substrate for SERS investigation. This series of transformation is summarized in Fig. 1.

The nanoparticle entrapment at the water/oil interface was recently theoretically studied by Reincke et al. [22]. They considered this process in terms of a thermodynamic evaluation of the self-assembly of charged nanoparticles at the water/oil interface. The chemical potentials of the nanoparticles in the bulk phase and at the water/oil interface were considered by taking into account the interfacial energies, the van der Waals interactions, and the electrostatic interactions. They derived an equation by setting the chemical potential for charged nanoparticles at the interface to be equal to the one in the bulk phase, which showed an isotherm of the interfacial particle coverage as a function of the surface charge density of nanoparticles. The equilibrium interfacial coverage increases with decreasing the surface charge density (σ). When ethanol was added, the σ value decreased, which led to an increase in the interfacial coverage, as represented by the adsorption of nanoparticles to the interface. When the ethanol concentration in the aqueous phase was increased, the interface became completely filled with nanoparticles. However, there is a lower limiting point for the σ value that can be achieved by adding ethanol. Ethanol decreases the dielectric constant of water by forming a mixed phase. The dielectric constants for water and ethanol are 80 and 25 at 293 K, respectively. Therefore, an entrapped nanoparticle must retain a certain electrostatic repulsive force because the com-

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