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Electrochemical surface-enhanced Raman scattering measurement on ligand capped PbS quantum dots at gap of Au nanodimer

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ABSTRACT

The vibrational characteristics of ligand-capped lead sulfide (PbS) quantum dots (QDs) were clarified via electrochemical surface-enhanced Raman spectroscopy (EC-SERS) using a hybridized system of gold (Au) nanodimers and PbS QDs under electrochemical potential control. Enhanced electromagnetic field caused by the coupling of QDs with plasmonic Au nanodimers allowed the characteristic behavior of the ligand oleic acid (OA) on the PbS QD surface to be detected under electrochemical potential control. Binding modes between the QDs and OA molecules were characterized using synchronous two-dimensional correlation spectra at distinct electrochemical potentials, confirming that the bidentate bridging mode was probably the most stable mode even under relatively negative potential polarization. Changes in binding modes and molecular orientations resulted in fluctuations in EC-SERS spectra. The present observations strongly recommend the validity of the QD–plasmonic nanostructure coupled system for sensitive molecular detection via EC-SERS.

1. Introduction

The discovery of surface-enhanced Raman spectroscopy/scattering (SERS) has opened a new avenue for very sensitive molecular detection because it broke through the sensitivity limitations of Raman spectroscopy. Enhancement of Raman scattering cross section of molecules adsorbed on noble metal nanostructures has been attributed to two major effects induced by the excitation of localized surface plasmon resonance (LSPR): the electromagnetic (EM) enhancement because of the effect of polarization of molecules in highly localized electromagnetic field, and the chemical enhancement achieved through charge transfer interactions of the adsorbed molecules with the metal surface [1–3]. Because of its high sensitivity and fingerprinting capability for chemical structures and enhancement factors of the order of 10^8–10^{12} [4], SERS has been widely used in chemistry [5], biology [6], and medicine [7,8] with various nanoparticle size, shape, and spacing parameters, and massively parallel.

Electrochemical surface-enhanced Raman spectroscopy/scattering (EC-SERS) uses a system consisting of nanostructured electrodes immersed in an electrolyte to obtain vibrational information for molecule characterization and identification. Altering the electrochemical potential of the working electrode, i.e., the Fermi level, modulates the properties of the electrode–electrolyte system including the dielectric constant of the interfacial electrolyte, the coverage and/or adsorption orientation of molecules, and bonding interaction of molecules with the electrode surface. As a result, one can rationally recognize that EC-SERS has an advantage in influencing the physical and/or chemical enhancements of the SERS process, which strongly affects spectroscopic sensitivity [9]. However, thermal fluctuation in solution often produces noise in EC-SERS measurements. Analyses of EC-SERS results using conventional one-dimensional spectra face practical difficulties because of the fluctuation-induced overlap of spectral features. In this sense, two-dimensional correlation spectroscopy (2DCOS), which boasts improved spectral sensitivity over one-dimensional spectra, has attracted extensive interest to clearly visualize dynamic fluctuations in spectra induced by external perturbations [10], especially in SERS and EC-SERS studies [11–17].

Besides noble metals, semiconductor nanostructures can also serve as SERS probes to enhance Raman scattering with an enhancement factor of the order of 10^3–10^6 [18–21]. Synthesized semiconductor nanostructures possess numerous tunable properties, such as band gap energy, geometrical anisotropy, crystallinity, and surface structure. In particular, lead sulfide (PbS) quantum dots (QDs) exhibit strong quantum confinement effect when their size is less than the relatively large Bohr radius of 18 nm [22]. PbS QDs play an important role in SERS characterization by both physical and chemical mechanisms: one aspect is that PbS QDs intensely enhance the EM field generated by LSPR because of their large dielectric constant and semi-metallic properties [23,24]; the other is that the size-induced quantum confinement affects charge transfer resonance between the PbS QDs and capping ligand molecules [25]. Oleic acid (*cis*-9-octadecenoic acid, OA) is a major surfactant used to stabilize not only semiconductor nanostructures but also plasmonic metal nanoparticles by a simple method that involves rapid precursor

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injection [26]. In the case of synthesizing PbS QDs, the formation of strong chemical bonds between the carboxylic acid group of OA and surface Pb atoms (Fig. 1b, top) lowers the surface energy, thus stabilizing the nucleated PbS. OA molecules exhibit highly complex spectral features at room temperature [27], so Raman studies of OA have always deliberately been performed at low temperature [28,29]. This situation means that SERS and EC-SERS studies of OA as a capping ligand are still under active investigation. In this sense, the characteristics of the surface binding structure of OA on PbS QDs should be clarified for further investigation of their contribution toward optoelectronic manipulation.

In this work, we investigate the EC-SERS behavior of the capping ligand of PbS QDs by coupling with gold (Au) triangle nanodimer arrays fabricated via angle-resolved nanosphere lithography (AR-NSL) under near-infrared (NIR) light irradiation. Vibrational spectra of surface OA ligand molecules are clearly observed because of the enhancement induced by the plasmon coupling between Au and the PbS QDs. The effect of electrochemical potential on the SERS characteristics is analyzed by 2D synchronous spectroscopy. The results demonstrate the ability of semiconductor QD–metal nanoparticle coupled systems to facilitate SERS detection of the vibrational properties of molecules in confined spaces.

2. Materials and Methods

2.1. Materials

OA and toluene were purchased from Wako. Commercial OA-capped PbS QD (Lot: LNR20HPB; dispersed in toluene; QD concentration: 200 μM; first exciton absorption peak: 753 nm; emission peak: 852 nm) was purchased from Evident Technologies, Inc. Polybead® polystyrene microspheres (PS beads, diameter = 200 nm, Polysciences, Inc.) were diluted in ethanol (Wako). Optically transparent indium tin oxide (ITO)-coated glass (Kuramoto Co., Ltd) was used for the preparation of Au triangle nanodimer arrays. Electrolyte for Raman measurements was prepared with 0.1 M sodium hydroxide (NaOH, 97.0%, Wako).

2.2. Preparation of Triangular Au Nanodimers

The detailed procedure has been reported in our previous publications [30,31]. Briefly, Au nanodimer substrate was fabricated via angle-resolved nanosphere lithography (AR-NSL). Polystyrene microspheres (PS beads) with the average diameter of 200 nm were dispersed on a well washed hydrophilic ITO glass [32]. Triangular Au nanodimer arrays were deposited via electric beam vaporization (quartz crystal monitor CRTM-6000, ULVAC; 3KWE-type electron gun, ANELVA; compound molecular pump TG-800F-B, OSAKA Vacuum Ltd.) between the gaps of the PS beads with well-adjusted repeated condition containing a deposition angle of ±10° and a thickness of 10 nm at a deposition rate of 0.20 nm/s. Then the PS beads were well washed in Milli-Q water via ultrasonication for 1 min. The fabricated Au nanodimers yielding a plasmonic adsorption maximum of 785 nm approximating to the laser wavelength of Raman spectroscopy (Fig. 1a).

2.3. Sensitization of Au Nanodimers With PbS QDs or Oleic Acid

Commercial OA-capped PbS QDs was diluted 100 folds in argon-degased dehydrated toluene. OA molecules were dissolved in methanol with a concentration of 10 mM. The PbS QDs dispersion or the OA solution was respectively drop-casted onto the surface of Au nanodimers, forming a circle of about 2 cm in diameter with a particle density of 1.2 $\times 10^{13}$ cm^{-2} for PbS QDs and a molecular density of 100 nmol/cm^{-2} for OA, respectively. After solvent evaporation, Raman measurements were taken on those samples.

2.4. SERS Measurement

Raman measurements were performed via an inverted Raman spectroscopy of Nanofinder®30 (Tokyo Instruments, SOLAR TII) with a 100× objective lens (Nikon TU Plan ELWD, NA = 0.80, WD = 4.5 mm). NIR laser light of 785 nm (E_{ex} = 1.58 eV) was obtained from a diode laser (Vortex™ 6000 laser controller, Tokyo Instruments). Polarized

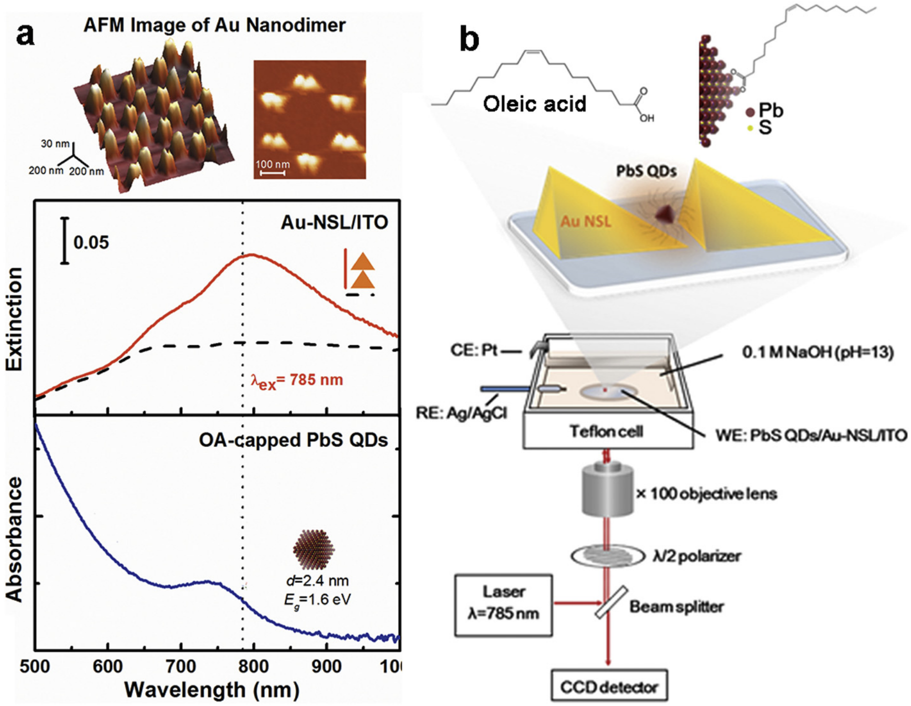

Fig. 1. (a) AFM image (top) and extinction spectrum of triangular Au nanodimers (middle), and absorption spectrum of OA-capped PbS QDs with the 1st exciton peak around 750 nm (bottom). Red (black) line respectively presents the longitudinal (transverse) polarization, the direction that the electronic field of incident light is parallel (vertical) to the long axis direction of the Au nanodimers. Dotted line illustrates the excitation laser light at 785 nm. (b) Schematic of the electrochemical SERS measurement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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