Second harmonic generation from coupled surface plasmon resonances of Au@SiO_2 nanoparticles self-assembled on glass

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Abstract: Self-assembling fabrication of 2-dimensional gold (Au) nanoparticles array on aminopropyltrimethoxysilane–terminated glass substrate with various immersion times into Au sol provided a uniform Au nanoparticles monolayer for the immersion time of 1 hour and it was revealed that excess immersion times gave rise to the formation of colloidal domain structures of Au nanoparticles which, however, induced a second-order nonlinear polarization generating a light in double frequency of Nd:YAG laser.

1. Introduction

Two-dimensional (2D) array of metal nanoparticles on substrate [1] has been of increasing interest to nanoscale-materials scientists and engineers for its practical applications in optical, electrical and biological technologies. Especially an electric functionality of single electron tunneling (SET) [2] with gold (Au) nanoparticles covered with an insulation layer is promising as a nanoscale memory unit working at room temperature, with which a 2D nanoparticles array provides an ultra high density memory disk. In bio-optical science a 2D Au nanoparticles monolayer is purposefully applied to an enzyme-based sensor of glucose [3]. With help of near-field enhancement on nanoscale-roughness of metal surfaces, optical sensors of organic polymers or molecules with high sensitivity are also developed [4]. Several methods for preparing such a 2D array are proposed; Langmuir-Blodgett, sputtering, electrochemical deposition, self assembling, and so on. Our approach is based on a silica-coverage of nanometer-sized Au colloids self-assembly deposited on chemically-modified glass substrate.

The paper discusses second harmonic generation (SHG) from a monolayer of Au nanoparticles fabricated in a variety of immersion times of a chemically-modified glass substrate into Au sol by a self-assembling method. It will be shown that the second harmonic (SH) signals are caused by nonlinear polarizations coming from longitudinal “in-phase” modes of coupled surface plasmons of two or more Au nanoparticles which form aggregation into particles domain on substrate. Recent development of metal particles fabrication using a beam lithography elucidates that two neighboring Au particles of several hundred nm in diameter with surface plasmon resonance (SPR) produce a coupling mode in a lower frequency than a single SPR mode [5]. In the present study smaller particles of 20~30 nm in diameter are adopted for use in order to control single electron transportation and optical nonlinearity. It is important to mention that Au nanoparticles used here for SHG are not in a class of core-shell structured Au nanoparticles with nonlinear optical (NLO) organics in shell [6]. Although such an approach provides an easy way to obtain a strong second-ordered nonlinear polarization thanks to an enhanced near-field, “evanescent field”, around Au nanoparticles, our observation reveals that neighboring Au nanoparticles in plasmon-mode-coupling also give rise to a strong second-ordered nonlinear polarization in spite of the intrinsic structure of cubic symmetry for Au lattice ordering. (Theoretically centro-symmetric structures do not allow second-ordered nonlinearities to be generated.)

2. Experiments

By using $HAuCl_4$, methanol, and sodium(Na)-citrate, Au nanometer-sized particles were synthesized in solution (the length of the major axis was ~35 nm, the length of the minor axis is ~25 nm, aspect ratio = ~ 1.4), which are protected by the surfactants of citrate $(COO^-)_3$ on their surfaces and very stable in a few of months. These particles can chemically be adsorbed on a aminopropyltrimethoxysilane(APTMS)-terminated quartz glass plate with a variety of the immersion times. In order to cover these Au nanoparticles with silica, the nanoparticles monolayer was immersed for 30 min. into a APTMS solution (APTMS:methanol: H_2O(including 0.15N-HCl)= 1:3:3) aged for 2 hours. For several measurements, the films with and without a silica layer were carefully washed with methanol and distilled water, and dried with a cold blower at an ambient atmosphere.

Optical absorption measurements were performed with a UV-Vis spectrophotometer (JASCO, V-570). Atomic Force Microscopy (AFM) images were also collected with SEIKO SPI-4000 in a direct force mode (DFM). SH

signals in Maker-type geometry of transmission were detected using a fundamental light (λ = 1064 nm, pulse width 8~9 ns) of a Q-switched neodium-doped yttrium-aluminum-garnet (Nd:YAG) laser (Spectra Physics Co., GCR-190) at 10 Hz repetition. The incident power of Nd:YAG laser was normally ~ 20 mW in a spot size of 2mmϕ. The usage of filters, R70 in front and HA30 at back of a planer sample, monochromator (Jovin Yvon, HR-320), and boxcar integrator (SRS, model SR250) enabled us more selectively and sensitively to pick up SH signals from the Au nanoparticles 2D monolayer.

3. Results and discussion

From optical absorption spectra of Au nanoparticles assembly on quartz glass, as shown in Fig.1 (a), one can see a growing peak at 520 nm due to the first-ordered ("dipole") SPR of isolated Au nanoparticles with increasing immersion time up to 1 hour, which corresponds to the increasing number of Au nanoparticles on the substrate. Since the chemical moiety of amino ($-NH_2$) group has a stronger affinity to gold metal than the ionic carboxyl (COO^-) group does, the amino-groups in the first layer of the surface of the APTMS-terminated glass substrate allow Au nanoparticles to be attracted on the surface in the sols. Figure 2 (a, b) show AFM images of 2D ordering of Au nanoparticles on the substrate for different immersion times, which consequently clarify that uniform self-assembling 2D array of Au nanoparticles closely-packed can be obtained for the 1 hour immersion. When the immersion time becomes longer than 1 hour, an additional peak around 600~630 nm manifests itself and the SPR peak of isolated Au particles simultaneously decreases, as shown in Fig.1 (b). It is plausible that the long-wavelength peak is interpreted as being a coupled SPRs mode or longitudinal SPR mode [7], which is gradually remarkable with aggregation of two or more Au nanoparticles (see the AFM images in Fig.2).

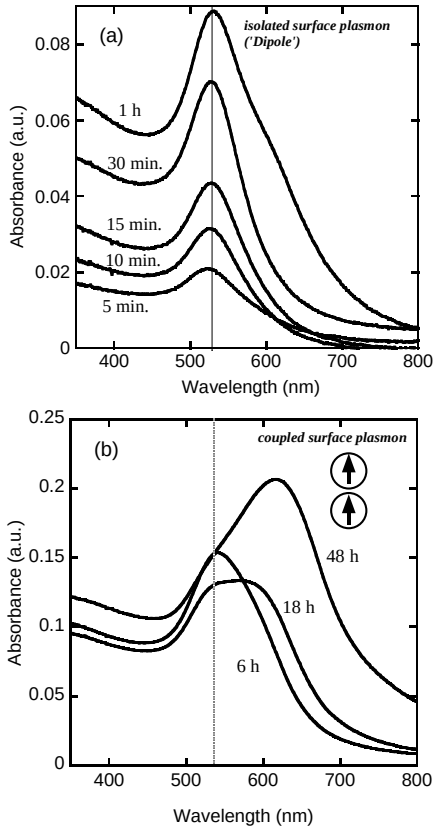

Fig.1 Optical absorption spectra of Au nanoparticles self-assembled on glass with various immersion times.

Clippe et al. [8] first offered a theoretical explanation of coupled resonance modes of two identical clusters, linear chain of particles with larger scale, equilateral triangle, tetrahedron, and fcc cubic-packing clusters, where each particle has a resonance mode. A research group of Creighton and Blatchford [9] experimentally gave clear evidence on the correlation between the long-wavelength resonance mode appearing in visible region and aggregation morphologies of metal nanoparticles. Moreover, they observed that the coupled SPR mode of almost-identical metal nanoparticles induced a large dipole moment resulting in surface enhanced Raman scattering (SERS) of adsorbed organic molecules, pyridine, on metal particles. This finding is substantially important for understanding electromagnetic roles of metal nanoparticles with different aggregation morphologies. In our careful AFM observation for 2D Au nanoparticles monolayers, aggregation of Au nanopartciles can confidently be detected in Fig.2 (b). It is also found that a degree of aggregation is dependent on the immersion time.

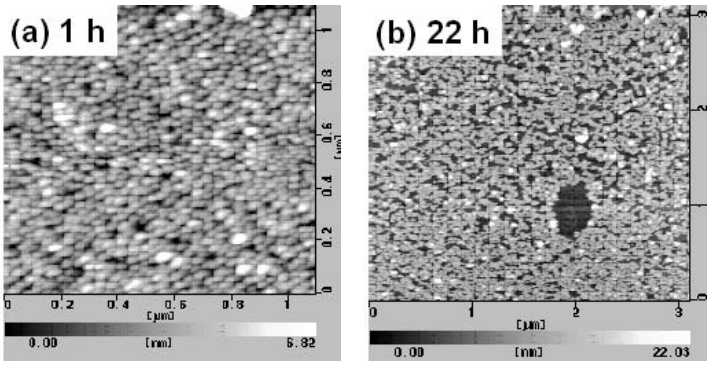

Fig. 2 AFM images of Au nanoparticles self-assembled on glass with a various immersion time.

Figure 3 depicts SH signals as a function of an incident angle against the perpendicular axis of the 2D monolayer with incidence of a Q-switched Nd:YAG laser. In the immersion time of 1 hour there is still no SHG observed, while for quite long immersion times a clear fringe pattern of SH signal can be observed (Fig.3(c,d)). The intensity of SHG appears to be independent of the immersion times if they are much longer than 1 hour. The correspondence with increasing SPR peak around 600~630 nm enables us to infer that nonlinear polarizations resulting in the SH

manifestation are produced by a longitudinal mode of coupled SPRs in aggregation of Au nanoparticles. It is noted that in case (c) and (d) the SH intensities for normal incidence is zero and increases with increasing angle. To generate a substantial SH signal, a given propagation length, so-called “coherent length”, of the incident light inside the media is required. Since the layer thickness is ~ several ten nm, the propagation length at the zero incident angle is not enough to produce SH signals. The result of increasing SH intensity in company with several fringes with increasing angle shows that the incident light experiences the propagation in the film with multi-reflection. The coupled surface plasmon mode is accompanied with a broad bandwidth of ~100nm around at 600 nm, which is very close to the double frequency of Nd:YAG laser (1064nm). Thus, it is believed that the strong intensity of the incident laser produces a second-order nonlinear polarization which is possibly enhanced by the resonance with the coupled surface plasmon mode. For a practical use, the nanoparticles array can be covered by silane-coupling agents. Dipping the array on substrate in the partially polymerized APTMS solution for 30 min. is caused by the silica-coverage of Au nanoparticles with a silica-thickness of ~ 10nm. Even after the silica coverage the SH signal can be maintained. Further experiments of the study have been performed with silica-covered Au nanoparticles.

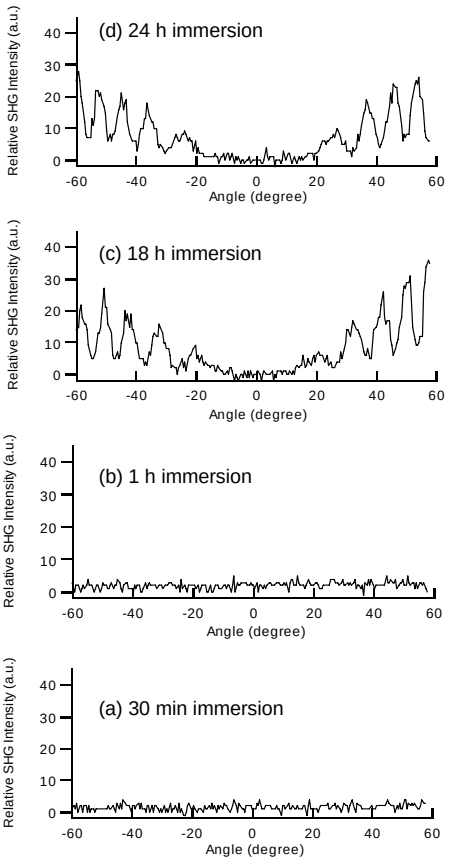

Fig.3 Maker-type fringe patterns for SH signals of self-assembling 2D Au nanoparticles monolayer fabricated for different immersion times.

4. Conclusion

Several examinations with the various immersion times for APTMS-terminated glass into Au sol revealed that the immersion time of 1 hour was enough to obtain a self-assembling Au nanoparticle monolayer in uniform 2D array and that excess immersion times gave rise to the formation of colloidal domain structures due to aggregation of several Au nanoparticles on the substrate, which however induced a second-order nonlinear polarization generating a light in double frequency of Nd:YAG laser (1064 nm).

5.References

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