Materials Chemistry and Physics 160 (2015) 205–211

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Surface-enhanced Raman scattering active gold nanostructure fabricated by photochemical reaction of synchrotron radiation

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HIGHLIGHTS

- Gold nanoparticles were produced by photochemical reaction of synchrotron radiation.
- The gold nanoparticles grew and aggregated into the higher-order nanostructure.
- The behavior is qualitatively explained by analytical estimation.
- The surface-enhanced Raman spectroscopy of 4,4′-bipyridine (4bpy) was demonstrated.
- The substrate fabricated in a suitable condition provides in situ SERS for 1 nM 4bpy.

ARTICLE INFO

Article history:
Received 18 December 2014
Received in revised form
1 April 2015
Accepted 19 April 2015
Available online 23 April 2015

Keywords:
Raman spectroscopy and scattering
Electrochemical techniques
Lithography
Nanostructures
Optical materials

ABSTRACT

The deposition of gold nanoparticles in an electroplating solution containing gold (I) trisodium disulphite under synchrotron X-ray radiation was investigated. The nanoparticles grew and aggregated into clusters with increasing radiation time. This behavior is explained by evaluating the effect of Derjaguin-Landau-Verweyand-Overbeek (DLVO) interactions combining repulsive electrostatic and attractive van der Waals forces on the particle deposition process. The surface-enhanced Raman scattering (SERS) of 4,4′-bipyridine (4bpy) in aqueous solution was measured using gold nanoparticles immobilized on silicon substrates under systematically-varied X-ray exposure. The substrates provided an in situ SERS spectrum for 1 nM 4bpy. This demonstration creates new opportunities for chemical and environmental analyses through simple SERS measurements.

1. Introduction

Discovered over 30 years ago [1–3], surface enhanced Raman scattering (SERS) is a powerful vibrational spectroscopy technique that has attracted a greater interest in the past decade with the development of nanofabrication, such as nanolithography and nano-imprint technologies [1–14]. It enables highly sensitive detection of low concentration analytes by amplifying electromagnetic fields generated by the excitation of localized surface plasmons (LSPs). To this end, gold or silver nanoparticles are typically deposited on nanostructured SERS-active surfaces manufactured by photolithography, nano-imprint lithography [10] or electrochemistry [11]. Alternatively, these substrates exhibit an inherent or reactively synthesized nanostructure [12–14].

Various methods have been developed for preparation of SERS-active nanostructures comprising nanoparticles. Chemical approaches [15–17] are noteworthy because they can be modified by external sources, such as sonochemistry [18–21], ultra-violet (UV) irradiation [22,23], as well as X-ray [24–29] or–γ ray [30] radiation-assisted chemical reduction. Synchrotron radiation has recently utilized to assist the fabrication of nanoparticles, which have not shown SERS-active properties to date. Ma et al. have reported the synchrotron X-ray-enabled synthesis of gold particles on a silicon substrate [24]. Yang et al. [26] and Lee et al. [29] have demonstrated gold and nickel colloidal particles induced by synchrotron X-ray radiation. Gold nanoparticles have also prepared using a laboratory X-ray source [28]. Wang et al. have demonstrated the one-pot synthesis of AuPt alloyed nanoparticles under intense

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http://dx.doi.org/10.1016/j.matchemphys.2015.04.025
0254-0584/

X-ray irradiation [29]. Thus, many studies of synthesis of nanoparticles by X-ray irradiation have been investigated. The galvanic replacement reaction between silver nanowires and an aqueous $HAuCl_4$ solution has been directly observed in real time by transmission X-ray microscopy [31]. These investigations are expected to lead to novel fundamental and engineering applications of nanoparticles. In particular, the easy fabrication of SERS-active substrate has attracted significant attention for chemical analysis and environmental analysis as well as bio-sensing.

In this paper, a synchrotron X-ray-induced nanoparticle preparation method is presented and SERS measurements of 4,4′-bipyridine (4bpy) on the resulting nanoparticles are performed in aqueous solution.

2. Experimental section

Synchrotron radiation induced deposition experiments were performed using beam line BL8S1 at the Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation (Aichi, Japan). A schematic representation of the experimental setup is shown in Fig. 1.

First, gold nanoparticles were prepared by X-ray irradiation of electroplating solutions and their surface properties and elementary analysis were determined by scanning electron microscopy (SEM). The electroplating solution consisted of a gold (I) trisodium disulphite solution at pH 8.0 produced by Electroplating Engineers of Japan Ltd. and distributed by Tanaka Holdings Co. Ltd. By X-ray irradiation, gold nanoparticles were synthesized from a 18 μL solution containing 2–3% $Na_3Au(SO_3)_2$ and 1.4–1.9% $NH_2CH_2CH_2NH_2$ etc., according to a published procedure [32]. As a result, the Au content of the solution was adjusted to 1.3%. The solution was deposited on a 10 mm^2 silicon substrate sealed by a SiN membrane-protected silicon and polytetrafluoroethylene (PTFE) plates (Fig. 1a). This assembly was covered by SUS frame holder (Fig. 1b). The PTFE plate between SiN membrane and Si substrate protects the solution seeping from the SUS frame holder as show in Fig. 1. This frame holder structure enables us to sustain the solution without leakage under the atmospheric pressure at ambient temperature. The specimen was placed on the stage and bombarded with an unmonochromatized X-ray beam ranging from 8 to 12 keV through a Pt mirror and beryllium and polyimide windows. The beam was attenuated using 500 μm-thick aluminum plate, before passing through SUS mask (Fig. 1a). The inset of Fig. 1a shows the X-ray photon intensity on the solution with or without the SUS frame. Low energy X-rays were cut down and intensities were significantly attenuated in the presence of the SUS mask [33]. All experiments were performed at room temperature and under the atmospheric pressure. After synchrotron X-ray exposure, the specimen was washed using deionization water to remove residual dross from its surface.

3. Results and discussion

3.1. Surface characterization and elemental analysis

Fig. 2 shows SEM images of an Au pattern deposited in 5 min by X-ray irradiation. As shown in Fig. 2a, it can be seen that a slit pattern is well defined. (not shown here, several slit patterns were well appeared.) When magnified, the slit patterns was found to contain nanoparticles (Fig. 2b). Quasi-spherical grains exhibiting almost uniform nanometric sizes were created in the irradiated area (Figs. 2b–d). Figs. 2c and d show energy dispersive x-ray spectroscopy (EDX) elemental maps of Si*Kα* and Au*Mα*, respectively. These EDX maps indicated that the nanoparticles mostly consisted of Au with a small amount of C. At this stage, we could not reveal where carbon atoms were in nanoparticles. These results are in good agreement with the previous experiments [24–30].

Synchrotron X-ray radiation has been reported to split water into proton and hydroxyl radicals as [34–36].

$$H_2O + x - ray \rightarrow OH + H \quad (1)$$

In the electroplating solution, the regeneration of H_2O by the coupling of the proton and hydroxyl radicals is expected to give an electron. Therefore,

$$Au(SO_3)_2^{2-} + e \Leftrightarrow Au + 2SO_3^{2-}. \quad (2)$$

Next, high-resolution SEM observations were performed at different X-ray irradiation times to investigate the grain growth and surface morphology. Fig. 3 shows the resulting SEM snapshots. The grains become denser and their interconnections remained random with increasing irradiation time (Figs. 3a–e). Elementary nanoparticles ranging from a few to several tens of nanometers gradually aggregated into nanoparticles. Figs. 3(a–ii) and (d–ii) clearly show that the nanoclusters consist of elementary nanoparticles, consistent with the formation of higher-order nanostructures. As a

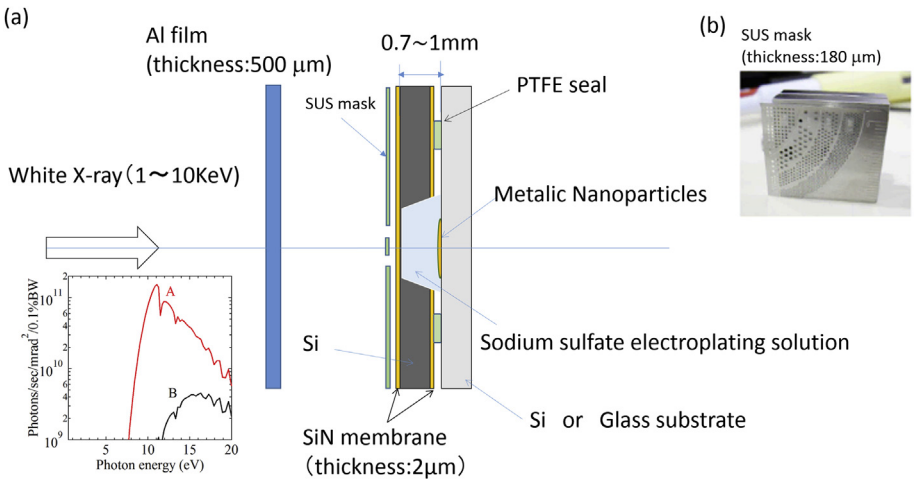

Fig. 1. (a) Experimental setup for the X-ray irradiation of the $Na_3Au(SO_3)_2$ electroplating solution. The inset shows photon intensity distribution as a function of photon energy across the electroplating solution (A) without and (B) with the SUS mask. (b) Photograph of a 180 μm-thick SUS mask.