Full Length Article

Electrochemically fabricated gold dendrites with high-index facets for use as surface-enhanced Raman-scattering-active substrates

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ABSTRACT

In this study, cysteine-directed crystalline gold dendrites (Au-Ds) were fabricated on glassy carbon electrodes, which exhibit preferential crystal growth along the ⟨111⟩ direction; Au-Ds exhibited a hierarchical architecture comprising trunks, branches, and nanorod-like leaves in a threefold symmetry, resulting in a high density of sharp tips and edges for hot spots of surface-enhanced Raman scattering (SERS); by this method, analytes present even in a dilute solution were detected. The lowest detection limit for 4-mercaptobenzoic acid (4-MBA) in this study was observed at a concentration of 10 nM, corresponding to a SERS analytic enhancement factor of greater than 8×10^6; this enhancement was determined by monitoring the concentration-dependent SERS spectra of the chemisorbed species as a function of the available crystal surface of Au-Ds. The potential-controlled partial reductive desorption of 4-MBA adsorbed on the Au-Ds surface enabled the selective desorption of some reporter molecules, thereby generating a high exposed crystal surface area of Au-Ds. Notably, the exposed Au(110) and high-index facets of the synthesized Au-Ds in this study have demonstrated potential as excellent SERS substrates as these Au-Ds exhibited strong Raman enhancements over large areas. The major contributors to the observed SERS intensities were found to be 4-MBA adsorbed on the Au(110) and high-index facets of the Au-D/GC substrate (accounting for around 70% of the intensities). The significant decline of SERS intensities of the 4-MBA molecules desorbed from the (110) and high-index facets was attributed to the enhancement of the local electromagnetic field caused by the tips and edges of the Au-D structure.

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1. Introduction

Surface-enhanced Raman scattering (SERS) has widespread application in various fields, such as molecular sensing, catalysis, and advanced materials research [1–5]. Furthermore, one of the most active areas in SERS research involves the development of structured substrates exhibiting high reproducibility and efficient enhancement [5–7]. The surface plasmon resonance (SPR) of SERS-active substrates, attributed to their nanostructures, can efficiently collect and amplify both incident and scattered electric fields near the nanostructure metal surfaces [8–10]. This enhancement of the electric field via SPR is referred to as electromagnetic enhancement, which can extend to greater than several nanometers from the surface of the nanostructured metal. Nevertheless, the scattering of probed molecules under SERS conditions depends on the local enhancement field of hot spots, as well as the binding affinity and positioning of these molecules at a hot spot region [11–13]. For

investigating this spectral enhancement, various nanostructured materials are attracting interest. SERS-active nanostructure materials exhibiting high-index facets have been reported to efficiently increase the density of the hot spots [14]. Hence, it is desirable to create a high density of sharp edges, tips, crevices, interparticle junctions, and other geometries with sharp nanostructures in the detection area for the purpose of obtaining amplified SERS signals of trace chemicals [15].

Nanostructures exhibiting different morphologies demonstrate dramatically different enhancement for SERS. Three-dimensional (3D) nanostructured materials with large surface areas that allow for the formation of hot spots have been reported to be good candidates for increasing SERS sensitivity [16], as high densities of SERS-active sites at the tips, edges, and junction positions of 3D substrates possibly facilitate SERS measurement. In this regard, numerous 3D SERS substrate structures, such as nano-stars [17,18], nano-denrites [8,19,20], nano-flowerers [21], and nano-meatball [22], have been proposed, attributed to their high density of SERS hot spots. Such closely placed nanostructured materials would result in strong local electromagnetic coupling at the branched morphology characterized by sharp edges and nanoscale gaps

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[19,23]. Accordingly, key characteristics of gold dendrites (Au-Ds), such as considerable surface area, chemical stability, wide-range SPR, as well as ease of fabrication and open 3D nanostructure of the material, were identified as beneficial for use as a SERS-active substrate for the detection of trace chemicals.

In this study, a convenient method for the production of a high-density 3D hierarchical architecture comprising sharp tips and high angle edges was described for the purpose of increasing SERS sensitivity was reported. First, reporter molecules (4-MBA) adsorbed on a polycrystalline Au were removed in a stepwise manner from domains exhibiting (111), (100), (110), and high-index facets during a potential-controlled reductive desorption and SERS measurement. To the best of our knowledge, the strategy described herein, which involves the measurement of an active SERS substrate by the selective desorption of probed molecules from Au-Ds for detecting target molecules, has not yet been reported thus far. The use of such Au-Ds with high-index facets for SERS application is promising as they easily exhibit high sensitivity as well as a low detection limit. In addition, by exploiting the ease of electrochemical processing, the Au-D SERS-active substrate can be effectively fabricated in a large area for the design of a device.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate trihydrate ($HAuCl_4 \cdot 3H_2O$, Acros, analytical grade), cysteine, and 4-MBA (Acros, >99%) were used without further purification. For the surface characterization of the electrodeposited Au, glassy carbon plate electrode was used as a substrate for deposition. Before use, the glassy carbon electrode (GCE) surface was polished with alumina slurries (0.3 and 0.05 μm) in sequence by using a nanocloth. The polished GCE was then ultrasonically cleaned in water and ethanol for 15 min, followed by thorough rinsing with DI water.

2.2. Preparation of Au dendrites and Au nanoparticles

Au-Ds were prepared using a previously reported method with some modifications [8,24]. In brief, the electrodeposition of Au was performed on GCE in an aqueous solution of 1.0 mM $HAuCl_4$ and 0.5 M H_2SO_4 in the presence of 0.1 mM cysteine. A conventional three-electrode system in an electrochemical workstation (CHI 614B) was employed for electrodeposition. A platinum wire and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. Square-wave potential pulses were applied to the GC electrode at a frequency of $5 \, s^{-1}$ for 3000 s. The pulsed potential waveform was utilized for reducing the effect of diffusion limitation on the electrodeposition rate. The lower and higher potentials of the square-wave pulse with respect to the SCE were set at −0.8 and +0.2 V, respectively.

The electrodeposition of Au nanoparticles (Au NPs) was performed by immersing the bare GCE in a solution of 0.1 mM $HAuCl_4$ and 0.5 M H_2SO_4. Square-wave potential pulses were applied to the GCE at a frequency of $5 \, s^{-1}$ for 300 s. A potential step from 0 V to −0.55 V was applied during electrochemical deposition.

2.3. Material characterization

Field emission SEM measurements were made under a JEOL JSM-6700F microscope operated at an acceleration voltage on 3.0 kV. X-ray powder diffraction (XRD) measurements were performed at the BL01C2 XRD end station of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, with an X-ray wavelength λ of 0.775 Å (16 keV). X-ray photoemission spectroscopy (XPS) measurements were conducted at the SPEM end station of

the NSRRC [25]. The photon energy used to obtain Au 4f XPS spectra was 620 eV.

2.4. Surface-enhanced Raman scattering (SERS) measurements

SERS samples were prepared by first submerging the Au-D/GCE and Au-NP/GCE in 1 mL ethanol solutions containing specified concentrations (0.5 mM–10 nM) of 4-MBA for 20 min to achieve chemical adsorption at ambient temperature. Second, the samples were rinsed with ethanol for removing excess 4-MBA, followed by drying under ambient conditions. Raman scattering spectra were obtained by a home-built micro-Raman system [26]. A He–Ne laser system (25 LHR/P 928, CVI Melles Griot) was employed for irradiating samples at 632.8 nm with an output power of 35 mW, which focused on a sample with a diameter of 1 μm using a 40×/0.65 N.A. objective lens (Plan N, Olympus). For each spectrum, the laser exposure time was 10 s. The data collected from six spectra were then averaged for improved statistics.

3. Result and discussions

Fig. 1(a) shows the SEM images of the prepared Au-D/GCE. The SEM images indicated that all of the Au-Ds reach several micrometers in length and exhibit a large rough surface. As shown in the high-magnification SEM image of Au-Ds in Fig. 1(b), several branches radially oriented away from the main stem were observed. Numerous secondary leaves were observed on each branch, resulting in the formation of gold dendrites. Thus, the atoms of rich tip, corner, and edge derived from the Au-D structures were caused by exposure. For further characterizing the composition and structure of Au-Ds, X-ray diffraction (XRD) measurements were conducted. Fig. 1(c) shows the XRD patterns of the hierarchical Au-Ds and Au-NPs obtained on GCE substrates. Diffraction peaks exhibited sharp features, indicative of the formation of highly crystalline Au-Ds. Diffraction peaks corresponding to the (111), (200), (220), (311), and (222) planes of the face-centered cubic (fcc) Au structure were observed, indicating that crystalline Au-D nanostructures are formed. In addition, the intensity ratio of the diffraction peaks was similar to that reported for the diffraction peaks of dendritic crystalline gold [27]. Diffraction peak intensity ratios attributed to the (111) plane relative to those of the (200) and (220) planes were 3.0 and 4.9, respectively, indicating that the presence of cysteine in solution induces the electrodeposition of Au along the (111) direction of the fcc crystalline structure; this observation is attributed to the attachment of cysteine to the Au crystal surfaces, which limits the crystal growth to the ⟨111⟩ direction during electrodeposition, as has been reported previously [20,27]. X-ray photoelectron spectroscopy (XPS) was employed for characterizing the chemical identity of the species on the Au-D surface, and Fig. 1(d) shows the XPS spectrum of Au-Ds. XPS signals of Au-Ds were observed at binding energies of around 285 and 86 eV after the reductive desorption of cysteine, indicative of C 1s and Au 4f electron energy levels, respectively. High-resolution XPS measurement was conducted for examining the electronic states of Au on the GCE. As shown in the inset of Fig. 1(d), the Au 4f spectra were fitted with a pair of doublet peaks at 84.0 and 87.7 eV, corresponding to the $4f_{7/2}$ and $4f_{5/2}$ levels of metallic Au. Hence, the combined results from SEM, XRD, and XPS indicated that numerous crystalline hyperbranched Au-Ds are obtained on the GCE.

The desorption potential of the adsorbed molecules is strongly dependent on the surface of crystalline Au, e.g., Au(100), Au(110), Au(111), and high-index facets. The reductive desorption of thiol molecule occurs on the Au(111) plane at a potential less negative than that occurring on the Au(110) and (100) planes [28,29]. Ohsaka et al. have reported that by the control of the applied poten-