



# Silver overlayer-modified surface-enhanced Raman scattering-active gold substrates for potential applications in trace detection of biochemical species



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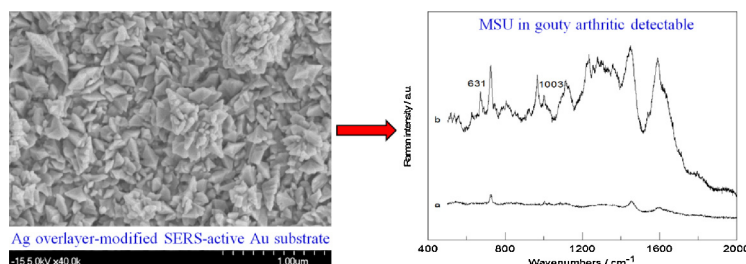
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## HIGHLIGHTS

- Underpotential deposition Ag used for modifying SERS-active rough Au substrate.
- Low limit of detection of  $2 \times 10^{-15}$  M for R6G.
- Trace detection of monosodium urate-containing solution in gouty arthritis.

## GRAPHICAL ABSTRACT

MSU in gouty arthritis is detectable on Ag overlayer-modified SERS-active Au substrate with needle-shape microstructures.



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## ABSTRACT

Because Ag and Au nanoparticles (NPs) possess well-defined localized surface plasmon resonance (LSPR) they are popularly employed in the studies of surface-enhanced Raman scattering (SERS). As shown in the literature and in our previous studies, the advantage of SERS-active Ag NPs is their higher SERS enhancement over Au NPs. On the other hand, the disadvantage of SERS-active Ag NPs compared to Au NPs is their serious decay of SERS enhancement in ambient laboratory air. In this work, we develop a new strategy for preparing highly SERS-active Ag NPs deposited on a roughened Au substrate. This strategy is derived from the modification of electrochemical underpotential deposition (UPD) of metals. The coverage of Ag NPs on the roughened Au substrate can be as high as 0.95. Experimental results indicate that the SERS of Rhodamine 6G (R6G) observed on this developed substrate exhibits a higher intensity by ca. 50-fold of magnitude, as compared with that of R6G observed on the substrate without the deposition of Ag NPs. The limit of detection (LOD) for R6G measured on this substrate is markedly reduced to  $2 \times 10^{-15}$  M. Moreover, aging of SERS effect observed on this developed substrate is significantly depressed, as compared

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with that observed on a generally prepared SERS-active Ag substrate. These aging tests were performed in an atmosphere of 50% relative humidity (RH) and 20% (v/v) O<sub>2</sub> at 30 °C for 60 day. Also, the developed SERS-active substrate enables it practically applicable in the trace detection of monosodium urate (MSU)-containing solution in gouty arthritis without a further purification process.

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## 1. Introduction

Since surface-enhanced Raman scattering (SERS) of pyridine adsorbed on rough Ag electrode was first reported in 1974 [1]. Its widespread applications in detection of chemical species that are present in a system at very low levels have been intensively investigated [2,3]. As shown in the literature [4,5], Raman scattering intensity from molecules close to the surface of certain finely divided metals, especially for nanoparticles (NPs) of Ag, Au and Cu, can be significantly enhanced by a factor of about 10<sup>6</sup>. This SERS effect therefore provides a powerful means of obtaining vibrational information on adsorbate–surface interactions in view of its unique sensitivity and excellent frequency resolution. In SERS studies, noble metals of Au and Ag NPs are most popularly employed because they possess well-defined localized surface plasmon resonance (LSPR) bands in the UV–vis regions. These can promise matching the excitation energies from the laser lights used in measuring SERS spectra [6,7]. As shown in the literature [8] and in our previous studies [9,10], the advantage of SERS-active Ag NPs is their higher SERS enhancement over Au NPs because the molar extinction coefficient of Ag NPs is the highest one among metals [11]. On the other hand, the disadvantage of SERS-active Ag NPs compared to Au NPs is their serious decay of SERS enhancement in ambient laboratory air [12,13], which makes the spectrum reproducibility being poor. Moreover, the corresponding SERS-active moieties on Au are of inherently greater stability than on Ag [14,15].

On applications of SERS technologies in analytical chemistry fields, both SERS enhancement and spectrum reproducibility are important. Therefore, one of the attractive options so far is to synthesize nanocomposites of Au and Ag for obtaining their corresponding advantages in SERS performances of high stability and enhancement, respectively [16,17]. However, new issue should be considered in synthesizing Ag@Au core/shell structures because the Ag core was unavoidably oxidized during the coating process of Au with relatively high reduction potential [18]. On the other hand, core/shell structures of Au@Ag seem to be the promising ones for obtaining the optimal SERS performances in giving consideration to both SERS enhancement and spectrum reproducibility [7,19]. Moreover, in such structure the Ag NPs show improved resistance to oxidation and lower reactivity to Au ions in the galvanic replacement [20]. As reported by Bu et al. [21], Ag core/Au shell NPs were explored as optical sensing agents for the sensitive detection of dopamine (DA) neurotransmitters in SERS measurements. Experimental results indicated that Ag core/Au shell NPs with the lowest surface coverage of Au shell exhibited more sensitive and stronger SERS activity for DA molecules than that of singular Au NPs. As reported by Xia et al. [22], a simple and cost-effective chemical method was introduced to assemble Au NPs on smooth Ag spheres for realizing SERS enhancement by the replacement reaction between chloroauric acid and Ag spheres. They found that the Ag particles decorated with small Au NPs demonstrated the strongest SERS enhancement, while Ag–Au core–shell spheres showed the weakest enhancement. The coverage of Au shell on Ag core cannot be too high for obtaining the optimal total SERS performances. As reported by Pande et al. [23], adsorption of 1,10-phenanthroline (PHEN) on the Au core/Ag shell (Au@Ag) bimetallic nanocolloid surface was investigated. Nanocolloids of different Au core/Ag shell ratio were synthesized keeping the same Au core size. Comparative spectral information revealed the highest SERS effect

from the 1:4 Au core/Ag shell bimetallic nanocolloid of 29 nm size. Cardinal et al. [24] described the modulation of localized surface plasmons in Au nanodumbbells through stepwise Ag coating to form the final core–shell morphology. Optical enhancing properties for SERS were tested with two laser lines, evidencing significantly larger enhancement factors for the bimetallic NPs, as compared to those of Au.

As shown in the literature, the modification of electrochemical underpotential deposition (UPD) [25,26] of metal atoms on metal or metal oxide surfaces is a useful method for functionalizing the surface and tailoring its properties. In addition, the UPD metal has a nobler redox potential than the corresponding bulk metal. It allows an expanded potential window in cyclic voltammetry [27]. Grunder et al. [25] reported probing the halide–metal interaction by monolayer metal deposition at the electrochemical interface. The results indicate that bonding of the halide adlayer is determined by the chemical properties of the first atomic layer of the metal substrate and demonstrates how halide adsorption can stabilize the UPD monolayer. As reported by Mrozek et al. [28], the preparation of Pt-group metal films on roughened Au electrodes by utilizing spontaneous redox replacement of an UPD Cu or Pb monolayer with a Pt-group metal cation solute was described. The SERS signals obtained with the UPD-prepared Pt layers are greater (3–4-fold) than for the directly deposited Pt films. Recently, we have prepared SERS-active Au NPs modified with monolayer of Ag film by using conventional UPD method [29]. The improved SERS effect from the modification of UPD Ag was observed, but was not fully demonstrated due to a lower coverage of UPD Ag on Au NPs. This low effect can be ascribed to the conventional preparation methods were generally used for UPD metals deposited on flat metal substrates [30,31]. However, UPD metals were deposited on a roughened Au substrate in our previous study. In this work, a new strategy for preparing highly SERS-active Ag NPs deposited on roughened Au substrates with high coverage is proposed. The advantages for improving SERS performances on high stability and enhancement are discussed. The potential application in detection of biochemical species by using the prepared SERS-active substrate is also performed.

## 2. Experimental

### 2.1. Chemical reagents

Electrolytes of KCl, H<sub>2</sub>SO<sub>4</sub>, and Ag<sub>2</sub>SO<sub>4</sub>, and reagents of R6G (p.a. grade) were purchased from Acros Organics. Crystals of monosodium urate (MSU, p.a. grade) were purchased from Sigma Organics. All of the chemical reagents were used as received without further purification. The experimental solutions were prepared by using deionized 18.2 MΩ cm water provided from a MilliQ system.

### 2.2. Preparation of SERS-active roughened Au substrates

In electrochemical experiments, a sheet of gold with bare surface area of 4 cm<sup>2</sup>, a 2 × 4 cm<sup>2</sup> platinum sheet, and KCl-saturated silver–silver chloride (Ag/AgCl) were employed as the working, counter and reference electrodes, respectively. All the electrochemical experiments were performed in a three-compartment cell at room temperature (23 °C) and were controlled by a potentiostat

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