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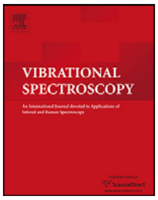

A novel fabrication of Au-coated glass capillaries for chemical analysis by surface-enhanced Raman scattering

Ji Won Lee [a], Kwan Kim [a,*], Kuan Soo Shin [b,**]

[a] *Department of Chemistry, Seoul National University, Seoul 151-742, Republic of Korea*
[b] *Department of Chemistry, Soongsil University, Seoul 156-743, Republic of Korea*

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ABSTRACT

A novel method to deposit a highly surface-enhanced Raman scattering (SERS) active gold film onto the inside surface of a glass capillary is developed. Firstly, Au sol was synthesized by the reaction of $HAuCl_4$ with poly(ethylenimine) (PEI), and then toluene and benzenethiol (BT) were added into the sol. The mixture was flowed through the glass capillary to obtain the SERS active Au film. The SERS activity of the Au-coated glass capillary was dependent on the amount of PEI and BT used. BT could be desorbed from the Au surface by treating with a mild borohydride solution, but maintaining the initial SERS activity. The best SERS enhancement factor at 632.8 nm excitation was on the order of 10^6. The detection limit of adenine is then as low as 1.0×10^{-6} M based on an S/N ratio of 3. All this suggests that the Au-coated capillary is an invaluable device for the microanalysis of effluent chemicals by SERS.

1. Introduction

For several decades, the electroless deposition of metal films has been a continuous research topic in the scientific community because of its immense application prospects [1]. It is especially challenging to coat thin metal films in a controlled way onto the inner surfaces of glass and plastic capillaries and microchannels [2–4]. Gold- and silver-coated capillaries, for instance, can be incorporated into microchip analyzers, running on the basis of surface-enhanced Raman scattering (SERS) spectroscopy [5–8]. On the other hand, the energy losses of hollow-glass waveguides, which are used for the delivery of high-power laser pulses and optical pulse compression, can be reduced significantly by coating the inside surface of the hollow waveguide with a highly reflective metallic layer [9,10].

In principle, the metal film can be deposited inside the capillary, as well as the hollow silica waveguide, by a liquid phase deposition process in which the thickness of the metal film may be controlled by varying the reaction time, the flow rate, the temperature, and the concentration of the reacting solutions [11]. For the case of silver deposition, a photosensitive alkaline silver amine solution is usually mixed with a reducer solution composed of dextrose and a sodium salt of ethylenediaminetetracetic acid, and then the resultant solution is pumped into capillaries. The two primary solutions react to yield a film of metallic silver on the inner surface of the capillary [10]. We have demonstrated recently that silver can also be deposited onto the inside surface of a glass capillary using only an ethanolic solution of $AgNO_3$ and butylamine [12].

There are several ways to form thin films of gold on solid surfaces. These include sol–gel process utilizing organometallic gold precursors with photoirradiation or by irradiating chitosan–$HAuCl_4$ films [13]. Gold films have similarly been obtained by Ar^+ laser-initiated decomposition or UV photolysis of nitro- or methyl-cellulose films containing either $HAuCl_4$ or its ammonium salt [14,15]. Au films can also be formed by attaching gold particles from a colloidal suspension to glass or quartz slides derivatized with 3-mercapto- or 3-amino-propyl trimethoxy silanes. Those nanoparticles can then function as seeds to fabricate conductive Au films [16–20].

We found recently that poly(ethylenimine) (PEI)-capped Au nanoparticles prepared in aqueous phase could be assembled into 2D arrays not only at the aqueous/toluene interface but also at the inner surface of the sampling bottle simply by the addition of benzenethiol (BT) [21]. An Au nanoparticle film could also be formed, through brief contact with the mixture, on the inner walls of capillary tubes. The purpose of this work is to assess the application capability of our Au-coated capillary as a SERS-based chemical analysis system on a microchip. We firstly confirmed that the as-prepared Au-coated capillary is highly SERS active to show intense SERS peaks of BT, and secondly that the BT molecules present initially on Au surfaces can be easily desorbed by borohydride, but maintaining the initial SERS activity. The Au-coated capillary could

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* Corresponding author. Tel.: +82 2 8806651; fax: +82 2 8891568.
** Corresponding author. Tel.: +82 2 8200436; fax: +82 2 8244383.
E-mail addresses: kwankim@snu.ac.kr (K. Kim), kshin@ssu.ac.kr, shin-1979@hanmail.net (K.S. Shin).

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then be used for the detection of minute chemical species in flowing phase by SERS. Most importantly, we were able to observe the Raman peaks even when a solution containing weakly chemisorbing species such as nitrophenol, 4-cyanobenzoic acid, and adenine was allowed to flow through the Au-coated glass capillary. We are sure that this work will contribute to the development of SERS-based microchip analyzers since gold deposition is possible not only on glasses but also on plastic microchannels.

2. Experimental

Hydrogen tetrachloroaurate ($HAuCl_4$, 99.99%), branched poly(ethylenimine) (PEI, MW $\sim$25 kDa), benzenethiol (BT, 99+%), 4-nitrobenzenethiol (4-NBT, 80%), rhodamine B isothiocyanate (RhBITC, 97%), 4-cyanobenzoic acid (4-CBA, 98%), 4-nitrophenol (4-NP, 99+%), adenine (99%), and sodium borohydride ($NaBH_4$, 99%) were purchased from Aldrich, and used as received. Other chemicals, unless specified, were reagent-grade. Highly purified water, with a resistivity greater than 18.0 MΩ cm (Millipore Milli-Q System), was used in preparing aqueous solutions.

To prepare PEI-capped Au nanoparticles, 25 mL of 1.4 mM aqueous $HAuCl_4$ solution was mixed with 0.4–1.0 mL of 1% (w/w) PEI, and then stirred vigorously at 80 °C for 2 h. The size of the Au nanoparticles was controlled by the amount of PEI added into the reaction mixture. The reacted mixture was ultracentrifuged and filtered, and then the precipitate was washed with copious amounts of deionized water. The PEI-capped Au nanoparticles thus obtained were re-dispersed in water (5 mL). Toluene (2 mL) was poured over the aqueous Au sol, and then BT (0.6–1.0 mL) was added into the toluene phase. The mixture was subsequently injected using a syringe through the capillary tube: the glass capillary was of dimensions 1.1 mm in inner diameter by 0.2 mm in thickness and 75 mm in length.

The flow of solutions through a capillary tube was controlled using a Sage Instruments Model 341 syringe pump. UV/vis spectra were obtained with a SINCO S-4100 UV/vis absorption spectrometer. Transmission electron microscope (TEM) images were taken on a JEM-200CX transmission electron microscope at 200 kV. Field emission scanning electron microscope (FE-SEM) images and energy-dispersive X-ray (EDX) analysis were taken with a JSM-6700F FE-SEM operated at 5.0 and 15 kV, respectively. X-ray diffraction (XRD) patterns were obtained on a Rigaku Model D/Max-3C powder diffractometer using Cu K_α radiation. Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer. The 632.8 nm line from a 17 mW He/Ne laser (Spectra Physics Model 127) was used as the excitation source. Raman scattering was detected over 180° with a Peltier cooled (-70 °C) charge-coupled device (CCD) camera (400 × 600 pixels). The measured intensity was normalized with respect to that of a silicon wafer at 520 cm^{-1}.

3. Results and discussion

When 25 mL of 1.4 mM aqueous $HAuCl_4$ solution was reacted with 0.4, 0.7, or 1.0 mL of 1% (w/w) PEI, the surface plasmon resonance (SPR) band of Au nanoparticles appeared at 540, 520, and 510 nm, respectively, in the UV/vis spectra (see Fig. 1a). According to the TEM images, the Au particles were mostly spherical, and the average sizes were determined to be 70 ± 19, 27 ± 7, and 10 ± 4 nm corresponding to those SPR peaks, respectively (see Fig. 1b). This illustrates that when the concentration of PEI is low, larger particles are formed [22]. These PEI-capped Au nanoparticles remain stable for at least 2 months without any obvious colloidal aggregation.

The assembly of nanoparticles into homogeneous 2-dimensional (2D) arrays is usually difficult to achieve due to their uncontrolled coagulation [23,24]. We discovered recently that a fairly homogeneous Au film can be fabricated on a bottle wall by adding consecutively toluene and BT into the PEI-capped Au solution [21]. A 2D Au film is also formed at the toluene–water interface, and the film can be transferred onto a separate glass substrate immersed in the mixture. The Au film formed on a mica substrate by adding BT showed an UV/vis absorption band at $\sim$700 nm (see Fig. 1c). The Au film thickness is subtly dependent upon the amount of BT added into the toluene phase. Its absorbance increased upon increasing the amount of BT up to 1.0 mL. The red shift of the SPR band as much as $\sim$200 nm from that in aqueous solution and the increase in its absorbance are indicative of the close-packing of Au nanoparticles in the film state [25]. Much the same Au film could be fabricated immediately onto the inside surface of a glass capillary by injecting a mixture comprised of BT, toluene, and PEI-stabilized Au colloid through the capillary tube.

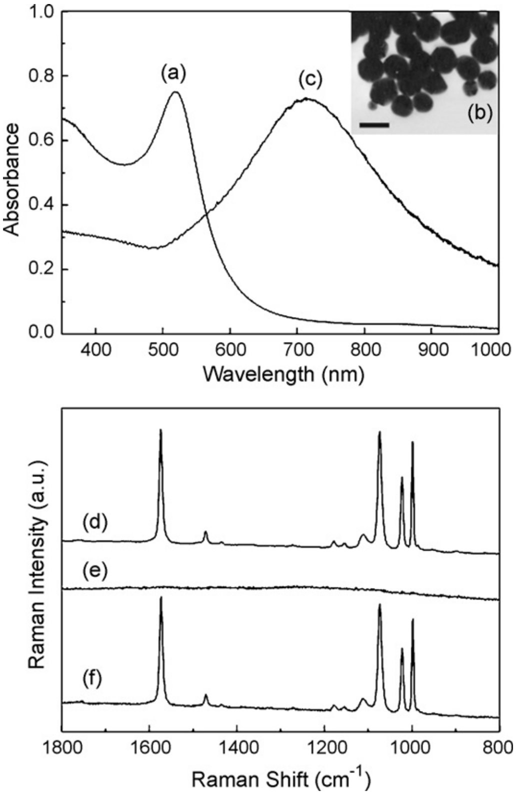

Fig. 1. (a) UV/vis spectrum and (b) TEM image (scale bar = 50 nm) of PEI-capped Au sol obtained by heating an aqueous mixture of 25 mL of 1.4 mM $HAuCl_4$ and 0.7 mL of 1% (w/w) PEI at 80 °C for 2 h. (c) UV/vis spectrum of Au film formed at the toluene–water interface by adding consecutively toluene and 1.0 mL of BT into above PEI-capped Au sol. SERS spectra of BT on Au measured (d) as prepared in (c) and (e) after treating with 0.1 M borohydride for 30 min, and then (f) after readsorption of BT.

As one would expect from the intense SPR band at $\sim$700 nm in the UV/vis spectra, strong Raman peaks of BT were observed from the Au film assembled on glasses. It must be a SERS spectrum of BT. A fairly intense BT SERS spectrum was also measured at 632.8 nm excitation by focusing the laser light axially through the capillary wall, as shown in Fig. 1d. The most intense SERS peaks of BT were observed from an Au-coated capillary fabricated using a mixture of 1.0 mL of BT, 2 mL of toluene, and 5 mL of Au sol comprised of 27 nm sized Au nanoparticles. Subsequent experiments were thus conducted using those capillaries. In order to use those capillaries in probing the adsorption characteristics of other adsorbates, BT should not interfere with these molecules.