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Controlling successive ionic layer absorption and reaction cycles to optimize silver nanoparticle-induced localized surface plasmon resonance effects on the paper strip

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ABSTRACT

This study investigates why a silver nanoparticle (SNP)-induced surface-enhanced Raman scattering (SERS) paper chip fabricated at low successive ionic layer absorption and reaction (SILAR) cycles leads to a high SERS enhancement factor (7×10^8) with an inferior nanostructure and without generating a hot spot effect. The multilayered structure of SNPs on cellulose fibers, verified by magnified scanning electron microscopy (SEM) and analyzed by a computational simulation method, was hypothesized as the reason. The pattern of simulated local electric field distribution with respect to the number of SILAR cycles showed good agreement with the experimental Raman intensity, regardless of the wavelength of the excitation laser sources. The simulated enhancement factor at the 785-nm excitation laser source (2.8×10^9) was 2.5 times greater than the experimental enhancement factor (1.1×10^9). A 532-nm excitation laser source exhibited the highest maximum local electric field intensity (1.9×10^{11}), particularly at the interparticle gap called a hot spot. The short wavelength led to a strong electric field intensity caused by strong electromagnetic coupling arising from the SNP-induced local surface plasmon resonance (LSPR) effects through high excitation energy. These findings suggest that our paper-based SILAR-fabricated SNP-induced LSPR model is valid for understanding SNP-induced LSPR effects.

1. Introduction

Raman spectroscopy, discovered by C.V. Raman, is molecular spectroscopy through observation of inelastically scattered light to identify the vibrational states of molecules. Unlike other spectroscopy methods, Raman contains an enormous amount of information regarding the molecular structure itself. Raman has an advantage in that it can be freely selected depending on the purpose of the desired wavelength of the laser chosen to irradiate the molecule [1–3], while it also has disadvantages in the form of low signal sensitivity. This limitation can be overcome through the surface plasmon concentration phenomenon of metallic nanostructures, called surface-enhanced Raman scattering (SERS). When the frequency of an external light and electrons in the nanostructural surface of noble metals is resonated, an electric field is locally concentrated. This phenomenon is referred to as surface plasmon resonance (SPR) and a small area of concentrated electric field is called a hot spot. SERS is another SPR-based spectroscopy in bio-sensing applications [4–16]. The SERS effect shows an enhancement $>10^4$ [17], where a high enhancement factor of $>10^8$ is sufficient for the detection of single molecules [18,19].

Most studies of SERS implementation have focused on the fabrication methods of the SERS substrate using various materials and nanoscale structures. To fabricate the SERS-active regions, time-consuming complex and sophisticated techniques, such as a high temperature process or lithography, have been used [3,20,21]. Alternatively, our research group reported a novel, instrument-free SERS substrate that was fabricated through successive ionic layer absorption and reaction (SILAR) [17]. The silver nanoparticle (SNP)-induced SERS-functionalized paper-based platform achieved high SERS activity (1.1×10^9 enhancement factor, Fig. S1), high reproducibility (4.2% relative standard deviation), and a sensitive limit of detection (1 pM rhodamine B). The platform could enhance the signal with the sensitivity to measure a single molecule. Interestingly, the fundamental material of this substrate is Whatman cellulose chromatography paper (Sigma-Aldrich, St. Louis, MO, USA). Therefore, the fabrication of the SERS substrate is facile, rapid, low-cost, and instrument-free. Additionally, the SILAR technique can control the size and shape of nanoparticles through synthesis conditions of repeated cycles of 20 mM $AgNO_3$ and 20 mM $NaBH_4$. Based on scanning electron microscope (SEM) images from each SILAR cycle, six SILAR cycles with a dense distribution led to superior SERS performance compared to other SILAR cycles with a sparse distribution. In particular,

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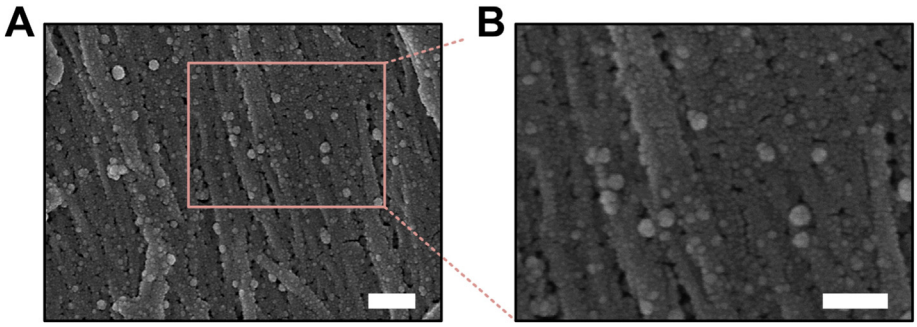

Fig. 1. SEM images of the paper-based SERS platform fabricated from two SILAR cycles. Each SEM image was acquired using an S-4700 field emission scanning electron microscope (FE-SEM; Hitachi, Tokyo, Japan) at an accelerating voltage of 5 kV. (A) Scale bar = 150 nm. (B) Scale bar = 100 nm.
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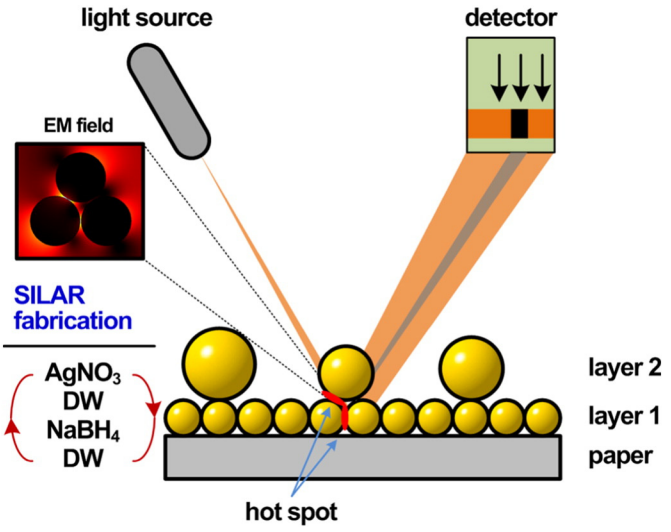
although the structure of SNPs fabricated at two SILAR cycles might not generate the hot spot effect (Fig. 1A), the actual SERS activity at two SILAR cycles (SERS enhancement factor = 7×10^8) was approximately 63% of that at six SILAR cycles. Therefore, the objective of this paper is to clarify the reason for high SERS performance despite SILAR-synthesized SNPs being an inferior nanostructure for SERS enhancement. An evidenced-based, multi-layer concept was introduced to explain this phenomenon.

2. Methods

2.1. Experimental Design

High-precision topographical investigation techniques, such as a self-made focused ion beam (FIB) machine [22] and a NANOS N8 NEOS atomic force microscope (AFM) machine (Bruker, Herzogenrath, Germany), [13] were used to confirm the elaborate nanostructure of the SILAR-fabricated SNP paper strip. However, FIB processing was not performed due to ion charging of the dielectric paper substrate. Additionally, the fiber structure of the paper could not be stably fixed as well as there was no tip to measure the tiny SNPs. SEM images of the paper-based SILAR-fabricated SNP platform illustrate dense attachment of tiny SNPs to the cellulose fibers and sparse attachment of relatively large SNPs to the cellulose fibers (Fig. 1). Therefore, we hypothesized that the multi-layered structure of SNPs on the paper substrate leads to the generation of high SERS activity in spite of the inferior structure of SILAR-synthesized SNPs, as in the case of two SILAR cycles (Scheme 1). The presence of a high SERS effect after two SILAR cycles might be caused by oscillation of electrons charged in a few nanometers between the SNP–SNP interfaces in the two layers, related to the formation of new SNPs synthesized at the initial SILAR processing stage (Layer 1) and growth of preexisting SNPs through the aggregation and transformation of nanoparticles (Layer 2). Based on this hypothesis, the maximum local electric field intensity on the paper-based SILAR-fabricated SNP-induced LSPR model was used as a representative value for each SILAR cycle. The SPR simulation in the frequency domain was used to solve the electromagnetic (EM) field problems in the differential form of Maxwell's equation [23–26].



Scheme 1. Conceptual diagram of multi-layer metallic SNP-induced SPR generation on the SILAR-fabricated paper strip. Hot spots (red colors) occurred at SNP–SNP interfaces in Layer 1 and SNP–SNP interfaces in Layers 1 and 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

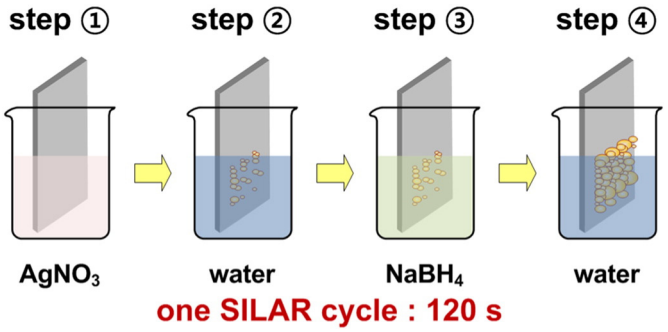
2.2. SILAR Fabrication

SNPs were directly synthesized on the paper using the SILAR approach, in which $AgNO_3$ and $NaBH_4$ aqueous solutions reacted (Eq. (1)). The SILAR fabrication consisted of four steps (Scheme 2); the cellulose paper was immersed in a 20 mM $AgNO_3$ solution of silver ions and rinsed with deionized water. Then, it was treated in a 20 mM $NaBH_4$ reductant and rinsed to remove non-reacted residues. Each step was sufficiently treated within 30 s and one SILAR cycle was performed for 2 min [17].

$$2AgNO_3 + 2NaBH_4 \rightarrow 2Ag + 2NaNO_3 + H_2 + B_2H_6 \quad (1)$$

2.3. Numerical Theory

Surface plasmon is an EM wave that propagates along noble metal surfaces. This light wave interacts with the free electrons of the



Scheme 2. Conceptual diagram of SILAR process used to synthesize SNPs on the cellulose strip. One SILAR cycle consists of four successive steps such as ① treatment in silver-containing solution for the absorption and partial reduction of silver with $AgNO_3$, ② washing with H_2O for elimination of excess reagents, ③ treatment in reductant solution for full reduction of silver with $NaBH_4$, and ④ rewashing with H_2O for elimination of nonreacted reagents and nonattached particles [17,27].