Robust SERS Substrates Generated by Coupling a Bottom-Up Approach and Atomic Layer Deposition

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ABSTRACT This paper reports on the development of a novel thermally stable surface enhanced Raman scattering (SERS) substrate. Specifically, these substrates can withstand high temperatures in air for an extended period of time without the loss of their enhancement capabilities. To accomplish this, we utilized a bottom-up approach, where the polyol reduction process was used to synthesize silver nanowires (NW) that were roughly 90 nm wide to act as the SERS active moiety. Subsequently, the NW were deposited onto a glass substrate and then coated with a thin protective layer of Al_2O_3 via atomic layer deposition (ALD). After heating these SERS substrates at 400°C for 24 h in air, it was found that the coated samples maintained a significant enhancement of the Raman signal, with further heating resulting in effectively no change in the SERS spectrum. The stability imbued by the ALD coating stems from limiting surface oxidation along with impeding aggregation that occurs at the higher temperature, which would otherwise lead to the destruction of the nanomorphology and complete loss of the SERS capabilities. These highly stable SERS substrates highlight the potential application of SERS in investigation of high-temperature chemical reactions and catalytic processes.

KEYWORDS: SERS • ALD • nanowire • robust • bottom-up • silver

INTRODUCTION

Recently, surface enhanced Raman scattering (SERS) has exponentially increased in research interest because of its ability to detect a wide variety of analytes at extremely low concentrations (1, 2). Typically, silver nanostructures are employed as the SERS active species because of their unique plasmonic properties, which lead to a superior enhancement factor of the Raman signal in comparison to other materials (3−5). Further, with the growth in the field of nanomaterials synthesis, many novel silver nanostructures have been developed in order to maximize their SERS capabilities, including spheres, cubes, octahedrons, and wires (6−9). However, there are still a number of limitations associated with current SERS substrates, as silver nanomaterials are prone to rapid surface oxidation when exposed to ambient conditions, which result in the loss of the enhancement capabilites in a short period of time (10). Further, heating the SERS substrate at a high temperature will exacerbate decay of the enhancement of the Raman signal because the elevated temperature will speed surface oxidation and lead to the destruction of the nanostructure through aggregation and oxidation processes.

SERS has been found to be extremely useful in detecting molecules of a biomedical or national security interest (11−14). However, SERS has received only a relatively limited role in the study of catalysis (15−17). This can be primarily attributed to degradation of the enhancement capabilities when the silver substrate is exposed to the harsh conditions such as high temperatures and oxidizing environments that are very common in many catalytic systems (18−20). To extend the use of SERS into the examination of such catalytic systems, there has been great interest in the development of extremely stable SERS substrates (1). As the SERS effect can extend roughly 1−2 nm from the silver surface, one can coat SERS active substrates with an ultrathin layer of a SERS inactive material on the surface to enhance stability (10, 21). Atomic layer deposition (ALD) is an ideal method for the generation of such a coating, because one can easily control the thickness of the layer ranging from a single molecular layer to several hundred angstroms (22). Previous attempts to use this method to generate a protective coating on top of SERS active species have been promising, showing improved stability at room temperature conditions (13). However, attempts at effectively preserving enhancement capabilities in harsh environments have been limited. One attempt has shown only the effects of heating the protected substrates under an inert environment on their localized surface plasmon resonance (LSPR) properties (23). Another example from our group revealed that ALD-coated silver films could retain some enhancement capabilities after heating for a short period of time, roughly 15 min, with further heating eventually leading to the loss of SERS capabilities. However, in this case any specific details concerning the effects of the protective layer on preserving the nanostructure after heating were not discussed (24). Moreover, both of these prior endeavors utilized a top-down approach to generate their SERS active moiety rather than a bottom-up approach. A bottom-up

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approach is more advantageous, as it allows for the utilization of many new silver nanostructure shapes, especially those with sharp features, synthesized via wet chemical processes, which have been shown to have superior enhancement of the Raman signal (25).

Herein we report on the use of a bottom-up approach that uses Ag nanowires as the SERS active species, which were coated with an ultrathin layer of Al_2O_3 via ALD. It was found that the coated samples continued to exhibit a significant enhancement of the Raman signal even after heating the substrate to 400 °C in air for 24 h. Additional reheating of the substrate for 2 h at 400 °C did not significantly affect the enhancement factor. We have also shown that the ALD layer not only served as a protective layer to impede surface oxidation but also prohibited aggregation that occurs at the higher temperature, thereby preventing the destruction of the morphology.

EXPERIMENTAL SECTION

Ag Nanowire Synthesis. In a typical procedure for Ag nanowires, 5 mL of ethylene glycol (EG, J.T. Baker, lot H24B27) was injected into a vial with a Teflon-coated stir bar and heated in air at 140°C for 1 h. One milliliter of a 4 mM HCl solution in EG was then added to the hot EG. The solution was heated for an additional 10 min. Two solutions of 94 mM $AgNO_3$ in EG and 147 mM PVP ($M_w \approx 5.5 \times 10^4$) were dissolved separately in 3 mL aliquots of EG and were added simultaneously into the vial at a rate of 45 mL/h. The reaction mixture was continuously heated at 140 °C in air for 19 h, after which a grey opaque solution had formed. The solution was then washed with acetone to remove excess organics and centrifuged, yielding a grey precipitate. The nanowires were then stored in ultrapure 18 MΩ deionized water.

Fabrication of the SERS Substrates. Ag nanowires (NW) were deposited onto the glass substrate via drop-casting and allowed to dry in air at ambient conditions. Subsequently, the Ag NW substrate was placed in the center of the ALD reaction chamber, which consisted of a stainless steel flow tube (3.5 cm diameter, 25 cm length) that was heated to 67 °C. The alumina precursor, trimethylaluminum (TMA), and high-purity water were alternately pumped to the reaction chamber using nitrogen as a carrier gas. One complete reaction cycle was 42 s in duration and was composed of the following: (i) TMA reactant exposure time = 1 s; (ii) N_2 gas purging time = 20 s; (iii) water vapor exposure time = 1 s; and (iv) N_2 gas purging time = 20 s. The SERS substrates were placed in the ALD reaction chamber for a total of 4 cycles. The average growth rate per cycle was determined by exposing the Ag nanowire to 40 cycles of the ALD process, which yielded a coating thickness of roughly 12 nm from which we can estimate the average growth rate was ~3 Å/cycle (see the Supporting Information, S1).

Characterization. STEM samples were prepared by drop-casting a dispersion of the nanowires onto carbon-coated copper grids (Formvar/Carbon, 200 mesh, Ted Pella). STEM images were acquired using a Hitachi HD2000 microscope operated at 200 kV. SEM images were taken of as prepared samples for Raman measurements using a field-emission scanning SEM (Hitachi S4700SEM) operated at an accelerating voltage of 5 kV. Raman spectra were recorded with a Renishaw system 1000 Raman spectrometer equipped with an integral microscope (Leica DMLMS/N). The laser line of 632.8 nm from a 25 mW air-cooled He−Ne laser (Renishaw) was used as an excitation source. Raman scattering was collected with a dry objective in 180° configuration. With a holographic grating and a 50 μm slit, a spectral resolution of 1 cm^{-1} was obtained. A
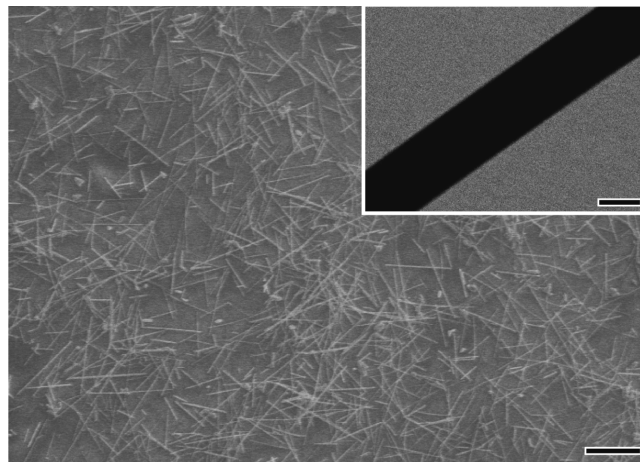

FIGURE 1. Ag nanowires deposited onto the surface of a glass Raman slide where the scale bar is 10 μm; the inset displays a singular nanowire that is 90 nm in diameter (inset 50 nm).
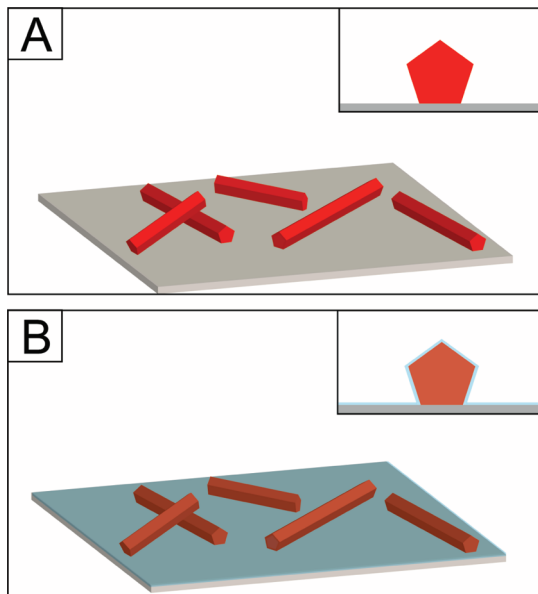
silicon wafer with a Raman band at 520 cm^{-1} was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be better than 1 cm^{-1}. For SERS characterization, an ethanol solution containing a known concentration of 0.1 mM rhodamine 6G chloride (R6G), or alternately 1.0 mM Benzoic acid (BA) in water was applied to the SERS substrate. Raman measurements were performed after evaporation of the ethanol or water. Laser power at the sample was approximately 0.6 mW for R6G and 2.4 mW for the BA measurements. X-ray photoelectron spectroscopy (XPS) was performed by mounting the samples on stainless steel XPS sample carrier and were then placed in a vacuum load lock of the Thermo Fisher Scientific K-Alpha XPS instrument with no other preparation. After suitable evacuation, the samples were transferred into the analysis chamber (base pressure of 6×10^{-10} mbar) and positioned at the focal point of the x-ray gun (monochromatic Al-Kα X-rays), the ion gun (3 kV Ar-ions), and the electron energy analyzer (hemispherical). Surface composition was determined for the as-received samples over the binding energy range from 0 to 1350 eV using a 400 micrometer X-ray spot. High-energy -resolution core level data were also acquired for C 1s, O 1s, Na 1s, Si 2p, Al 2p, and Ag 3d to determine detailed chemistry.

RESULTS AND DISCUSSION

Because a bottom-up approach was selected to make the SERS substrate, the nanowire (NW) morphology of silver was chosen as our SERS active moiety because of its sharp features and high recorded enhancement factor (9). The silver NW were prepared using a protocol previously developed by the Xia group, which involves the incorporation of an oxidative etchant into the polyol reduction process (26). Specifically, HCl was added to a hot ethylene glycol (EG) bath, followed by the simultaneous injection of both silver nitrite and poly(vinyl pyrrolidone) (PVP) dissolved in EG. Figure 1 shows a SEM image of the Ag nanowires produced after 19 h of reaction, after drop-casting on the surface of a glass slide for subsequent SERS studies. As illustrated in the inset of Figure 1, the nanowires produced via this method were approximately 90 nm in diameter, the ideal size domain range for optimum Raman signal enhancement (25).

Displayed in Scheme 1A is a diagram of the glass substrate on which nanowires were deposited via drop-casting

Scheme 1. Schematic Diagram Illustrating the ALD Coating of Ag Nanowire Substrate: (A) Nanowires (red) That Had Been Deposited onto the Glass Substrate (grey), with the Inset Displaying a Cross-Sectional View of a Singular Nanowire; (B) NW-Covered Slide Was Then Coated with a Protective Al_2O_3 Layer (blue) on the Surface via ALD; Cross-Sectional Diagram in the Inset Shows the Thin Layer of ~1.20 nm Al_2O_3 That Encapsulates the NW
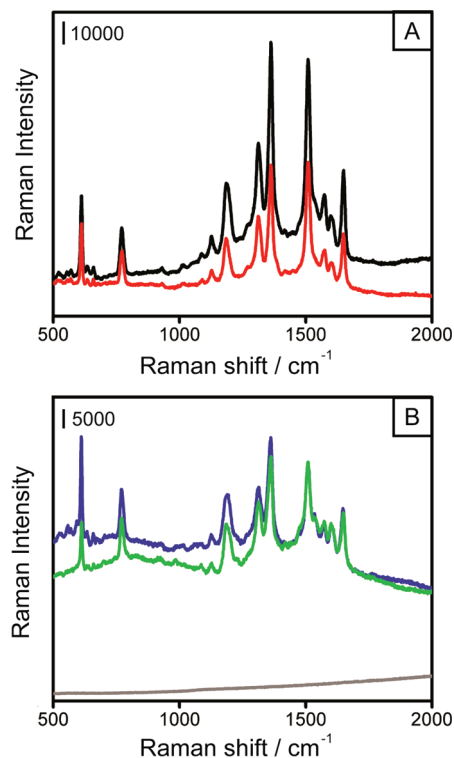

FIGURE 2. SERS spectra of Rhodamine 6G adsorbed onto coated and uncoated Ag NW substrates: (A) bare Ag nanowires (black) and coated (red); (B) effects of heating the substrate at 400 °C in air for 24 h for both the coated (blue) and uncoated (grey), and upon reheating of the coated sample for an additional 2 h (green). The concentration of R6G is 0.1 mM.

Table 1. EFs for the SERS Substrates for Uncoated, Coated, Heated, and Reheated for R6G; For R6G, we investigated the vibrational mode at 1512 cm^{-1}

coating thickness (nm)	EF		
	R6G	heat	reheat
0	4.4×10^4	6.4	N/A
~1.2	3.0×10^4	1.08×10^4	1.07×10^4

and allowed to dry in air prior to being placed inside an ALD reaction chamber. Alumina was chosen as the coating layer for the Ag NW SERS substrates primarily for two reasons: (1) the precursor is highly reactive and binds to the silver surface without pretreatment, and (2) the Al_2O_3 layer will not undergo a phase transition until 800°C, leading to high stability of the protective layer. To prepare the Al_2O_3 layer, we utilized trimethylaluminum (TMA), which was chemisorbed onto the exposed surfaces of the silver NW and bare regions of the substrate. This was directly followed by a hydrolysis step, which reactivated the surface for the next adsorption cycle. The ALD process was then allowed to proceed for a total of four cycles, to insure that there would be a minimization of any pinhole defects and allow for an even coating of the substrate (Scheme 1B). After removing the slides from the ALD reaction tube, we then used STEM to characterize a single coated NW and estimated the thickness of the Al_2O_3 over-coating layer to be ~1.20 nm.

To test the SERS abilites of the silver nanowire substrates coated with Al_2O_3, we first examined the enhancement of Rhodamine 6G (R6G), specifically the region around a wavelength at 1512 cm^{-1}. For our purposes, we calculated the enhancement factor (EF) for all spectra using the equation below

$$EF = (I_{SERS}/I_{Bulk})(N_{Bulk}/N_{ads})$$

where N_{bulk} is the number of analyte molecules in the focal volume and I_{bulk} is the intensity of the Raman signal as calculated from the peak area of the 1512 cm^{-1} band for spectra taken of the analyte on a bare glass slide, whereas N_{ads} and I_{sers} are the same parameters when the SERS substrate is utilized. First, the uncoated nanowire sample was tested, which yielded a large EF of the dye molecule of 4.4×10^4 (Figure 2A; Table 1). Subsequently, the Al_2O_3 coated sample was analyzed and we could see a reduction in the EF to 3.0×10^4 (Figure 2A; Table 1). The reduction in intensity was caused by the increased separation between the SERS active NW and the analyte; however, the thickness of the Al_2O_3 was thin enough for the analyte to be absorbed within the electromagnetic field of the silver NW. The coated and uncoated samples were then placed into a furnace and heated to 400°C in air for 24h. These samples were removed from heating and the effects of the oxidizing environment were analyzed by reapplying R6G (Figure 2B). We found that the uncoated sample had almost completely lost any enhancement capabilities, most likely due to a combination of the oxidation and aggregation of the nanomaterials (Figure 2B). In contrast, the coated sample continued to exhibit substantial enhancement of the Raman signal with the EF
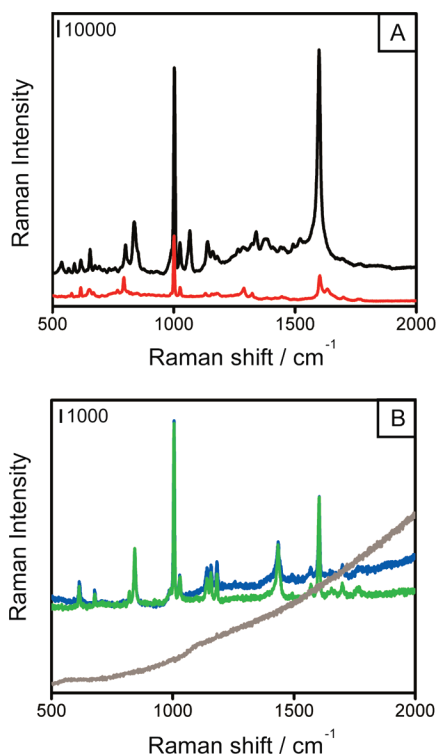
FIGURE 3. SERS spectra of benzoic acid (BA) adsorbed onto coated and uncoated Ag NW substrates: (A) bare Ag nanowires (black), and coated (red); (B) effects of heating the substrate at 400 °C in air for 24 h for both the coated (blue) and uncoated (grey), and upon reheating of the coated sample for an additional 2 h (green). The concentration of BA is 1.0 mM.

only being reduced to 1.08×10^4 (Figure 2B, Table 1). The primary reason for the stability was that the Al_2O_3 layer slowed the diffusion of the oxygen to the surface of the nanowires thereby limiting any surface oxidation that would lead to the destruction of the enhancement capabilities. The low level of surface oxidation was confirmed via high-resolution X-ray photoelectron spectroscopy which could only detect a small Ag−O shoulder in the spectra of the heated SERS substrate (see the Supporting Information, S2). To determine if the reduction in the SERS signal would continue with additional heating, we returned the sample to the furnace to heat for an additional 2 h. After removal, the measured R6G spectrum was nearly identical to the spectrum after the initial 24 h heating, with nominally the same EF (Figure 2B, Table 1). The stabilization of the SERS signal indicates that the oxidizing environment has limited effect on the plasmonic properties and enhancing capabilities of the protected NW.

To more completely understand the enhancement capabilities of the overcoated NWs, we replaced the R6G analyte with benzoic acid (BA) in order to remove any enhancement caused by the resonance of the dye. Figure 3A shows the spectrum of the BA after drop casting onto the surface of the bare nanowires, with strong bands at 1002 and 1599 cm^{-1} characteristic of the ring breathing mode and carbon−carbon stretch, respectively. The band at 1002 cm^{-1} was used to calculate an EF of 2.48×10^3 (Table 2). When the coated substrate was analyzed, a reduction in the intensity of the spectrum was observed with an EF of 6.76×10^2, which is

Table 2. EFs for the SERS Substrates for Uncoated, Coated, Heated and Reheated for BA; for BA, We Investigated the Vibrational Mode at 1002 cm^{-1}

coating thickness (nm)	EF		
	benzonic acid	heat	reheat
0	2.48×10^2	0	N/A
~1.2	6.76×10^2	2.81×10^2	2.79×10^2

a greater percentage reduction in comparison to the R6G studies (Figure 3A, Table 2). Further, there is also a difference in the relative intensities when comparing the ring breathing 1002 cm^{-1} and the C−C stretching 1599 cm^{-1} modes in the spectrum (27). In the case of the bare sample, the dominant peak is that of the C−C stretching mode; however, after coating, the ring breathing mode has the largest intensity. These two effects are most likely caused by the dielectric layer, ending any chemical enhancement that may take place between the silver surface and the absorbed BA, leaving only electromagnetic enhancement of the analyte. After heating under the same conditions as before, a reduction in the intensity of the spectrum occurred although the coated sample maintained a relatively high EF 2.81×10^2 (Figure 3B, Table 2). In this case, SERS spectrum of the uncoated sample showed merely background fluorescence (Figure 3B). Finally, after reheating, the EF remained largely unchanged at 2.79×10^2, once again demonstrating the stability provided by the overcoating layer (Figure 3B, Table 2). Moreover, for the heated and reheated samples we can also see the appearance of the COO− stretching peak at
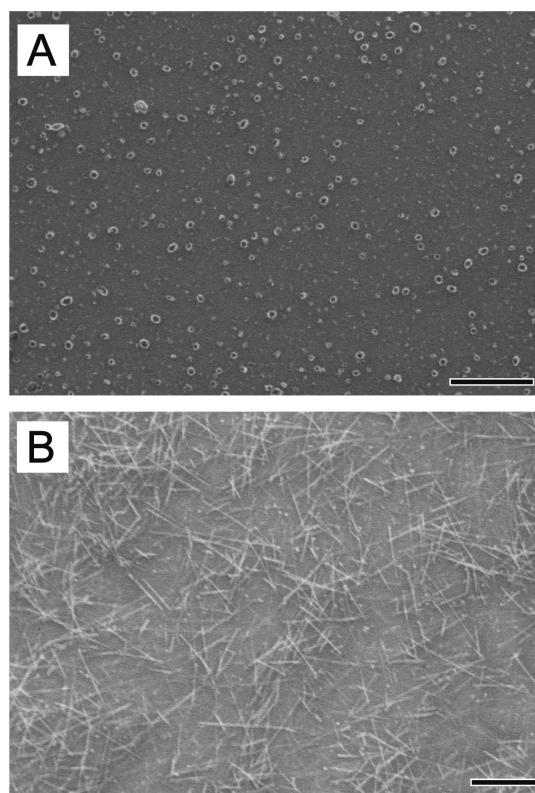

FIGURE 4. SEM images of the (A) uncoated Ag NW substrates and (B) coated after heating at 400 °C in air for 24 h; scale bar is 10 μm.

1440 cm^{-1}, which may be due to the heated substrates having −OH groups exposed on the surface that leads to the BA binding vertically to the surface of the alumina, in place of a mix between both vertical and horizontal binding that occurs on bare silver (28).

Because of the utilization of the well-defined shape of the NW as our SERS active moiety rather than the random form of the silver island films used previously by our group, we can easily detect the stabilizing effect of the Al_2O_3 layer on the morphology of the Ag nanostructures. When the un-coated SERS substrate was heated to 400 °C for 24 h, a drastic change in the morphology was noted (Figure 4A). Specifically, the nanowires that had previously been ap-proximately 90 nm in diameter were transformed into particles that ranged from 1 to 10 μm in size; most likely the result of an aggregation process induced by the elevated temperature. The loss in SERS capabilities for the uncoated substrates can be primarily attributed to the growth of the silver NW into these micrometer sized particles. Figure 4B illustrates the stability of the nanostructure imbued by the Al_2O_3 overcoating layer. In this case, the size and morphol-ogy of the nanowires remained essentially unchanged, as the Al_2O_3 layer bound directly onto the silver surface im-peded the migration of silver ions upon heating, leading to no significant changes to the nanostructure. Moreover, the coating limited atmospheric oxygen from diffusion to the surface of the NW via a similar process.

CONCLUSIONS

In summary, we utilized a bottom-up approach by syn-thesizing silver nanowires as a SERS active species and afterward coating them with an ultrathin layer of Al_2O_3 via ALD. We found that the ∼1.20 nm thick overcoating layer led to a truly temperature- and time -stable SERS substrate that can feasibly extend the use of SERS into the field of high-temperature catalysis. Specifically, we found that the coated NW substrates were effective SERS substrates with the enhancement factor of the silver nanowires being slightly reduced after coating of the dielectric layer. Subsequently, when these varying SERS substrates were heated in air for 24 h at 400 °C, the coating acted as a protective layer enabling the nanowires underneath to maintain their en-hancement capabilities along with preserving their nano-morphology in comparison to the bare sample, which was rendered useless.

Supporting Information Available: STEM image of a Ag NW that been placed in the ALD reaction chamber for a total of 40 cycles of the ALD process; high-resolution XPS data for an Al_2O_3-coated SERS substrate after the sample had been heated at 400 °C in air for 24 h (PDF). This material is available free of charge via the Internet at http://pubs. acs.org.

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