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# Silver Nanowire Layer-by-Layer Films as Substrates for Surface-Enhanced Raman Scattering

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In this paper, the fabrication of highly stable, surface-enhanced Raman scattering (SERS) active dendrimer/silver nanowire layer-by-layer (LBL) films is reported. Ag nanowires, ~100 nm in diameter, were produced in solution and transferred, using the LBL technique, onto a single fifth-generation DAB-Am dendrimer layer on a glass substrate. The Ag nanowires, and the resulting LBL films were characterized using UV–visible surface plasmon absorbance, while the LBL films were further characterized by atomic force microscopy measurements and surface-enhanced Raman and resonance Raman scattering of several analytes. The dendrimer was found to effectively immobilize the Ag nanowires with increased control over spacing and aggregation of the particles. These films are shown to be excellent substrates for SERS/SERRS measurements, demonstrating significant enhancement, and trace detection capability. Several trial analytes were tested using a variety of excitation energies, and results confirmed effective enhancement of Raman signals throughout the visible range (442–785 nm) with different molecules. Analytes were deposited onto the enhancing Ag nanowire LBL films surface using both casting and Langmuir–Blodgett monolayer transferring techniques.

Surface-enhanced Raman scattering (SERS)<sup>1–3</sup> is an extremely powerful microanalytical technique that is currently receiving a great deal of attention in the literature due to its potential for application toward a wide range of problems. In particular, it is finding extensive use in the fields of biomedicine,<sup>4</sup> thin-film

characterization,<sup>5</sup> and trace analysis.<sup>6,7</sup> Its low-cost, high spatial resolution, ultrasensitivity, and high structural information content make it an especially attractive option, and recent reports of single-molecule sensitivity<sup>8–11</sup> have led to a surge in the number of practitioners. Likewise, we are also currently witnessing a rapid and ongoing expansion of nanoscience, driven by potential applications in fundamental research and nanotechnology.<sup>12–14</sup> There is a clear push to develop novel techniques that allow for control over the size, shape, structure, and morphology of nanostructures produced as well as to uncover the mechanisms responsible for their varied forms.<sup>15,16</sup> Control over these factors, as a start, will mean a more effective and fruitful exploitation of the unique optical and electronic properties of these materials.

In fact, the optical properties that result from surface plasmon resonance in the visible range of the electromagnetic spectrum make metallic nanoparticles particularly attractive for several applications. The enhancements of absorption (visible and IR radiation),<sup>17–19</sup> fluorescence emission,<sup>20–22</sup> and Raman scattering from analytes are widely known<sup>1–3</sup> and represent a distinct

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opportunity to gain information about both enhancing metal nanoparticles and molecular analytes. In particular, SERS, resonance Raman scattering, and surface-enhanced resonance Raman scattering (SERRS) have been identified as optical techniques used with increasing frequency in the characterization of nanomaterials.<sup>23</sup>

Surface-enhancement of Raman signals results when analytes are placed in regions at or near the surface of appropriate noble metallic nanostructures where electromagnetic fields are strengthened dramatically due to dipole particle plasmon resonances (collective oscillations of conduction electrons) of the metal. The contribution of surface roughness to the amplification of optical fields was quickly confirmed after the first reports on SERS,<sup>24,25</sup> and since then, particularly after the first publications on single-molecule spectroscopy using SERS,<sup>26,27</sup> the role of nanostructures in this phenomenon has been fully recognized.<sup>28</sup> Of particular importance for SERS applications is the fabrication of novel silver and gold nanoparticles, producing a variety of shapes including spheres, rods, prisms, and wires.<sup>29</sup> Moreover, the development of a wider variety of improved substrates for enhancement of Raman signals remains one of the most critical challenges facing SERS research today.

The layer-by-layer (LBL) technique, as a method for nanodimension film fabrication, was pioneered by Decher<sup>30</sup> and involves the electrostatic assembly of alternating positively and negatively charged layers. This technique allows for the controlled production of nanoarchitectures and represents a great potential for broadening the possibilities of SERS experiments.<sup>31</sup> In this work, the fabrication of SERS active dendrimer/silver nanowire LBL thin solid films is reported for the first time. Ag nanowires, ~100 nm in diameter, were produced in solution and allowed to self-assemble into a single layer on a single generation 5 (G5) DAB-Am dendrimer layer coating a glass substrate. The Ag nanowires, and the resulting LBL films, were characterized using UV-visible surface plasmon absorbance, while the films were characterized further by atomic force microscopy (AFM) measurements and SERS and SERRS of several analytes. The dendrimer was found to effectively immobilize the Ag nanowires with increased control over spacing and aggregation due to shielding of electrostatic repulsions between the nanoparticles, as was also observed in recent work in our laboratory, where gold nanoparticles were embedded within self-sustained chitosan biopolymer films (submitted paper).

Through a series of experiments, these films were shown to be excellent substrates for SERS/SERRS measurements, demonstrating significant enhancement, and trace detection capability. Several trial analytes were tested using a variety of excitation energies, and results confirmed effective enhancement of Raman signals throughout the visible range (442–785 nm) for different molecules, including the observation of both SERS and SERRS. For most measurements, analytes were cast onto the films from aqueous solutions. However, the insolubility of the LBL film substrates was also capitalized upon in this work, through the use of the Langmuir–Blodgett technique<sup>32</sup> to introduce analytes onto the Ag nanowire surface for SERRS experiments. This technique allows for highly controlled deposition of single monomolecular layers onto solid supports and has been employed recently in our group for the detection and spectroscopic study of single molecules using SERRS.<sup>33,34</sup>

## EXPERIMENTAL SECTION

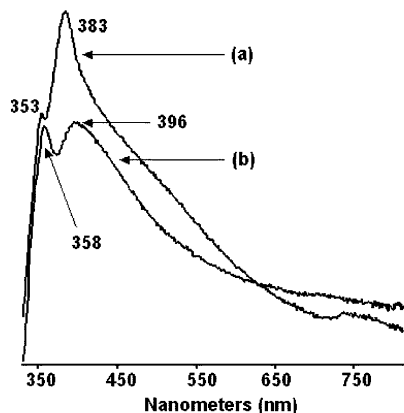
Silver nanowire syntheses were carried out employing the polyol process modified according to Sun<sup>35</sup> and Tao.<sup>36</sup> All glassware was thoroughly cleaned using water, aqua regia, and then deionized water. In a trinecked, round-bottom flask, with magnetic stirring and reflux, a 25-mL 0.36 mol/L solution of poly(vinyl pyrrolidone) (PVP; monomer-based calculation MW = 55 000) was prepared using anhydrous ethylene glycol (Aldrich) as the solvent, and the solution was heated to 160 °C. A 12-mL 0.12 mol/L solution of silver nitrate (Aldrich) in ethylene glycol, at room temperature, was then added dropwise into the hot PVP solution at a rate of 0.625 mL/min. Heating and stirring were kept constant during this step. After the addition of the reactants, the solution was kept stirring for 30 min at the same temperature. The solution was then cooled to room temperature, diluted (1:10) with acetone, and then centrifuged three times at 2 krpm for 20 min. The precipitate was dispersed in ethyl alcohol (a volume equivalent to three times the volume of acetone in the preceding step) and sonicated for 4 min. This dispersion was centrifuged (1.7 krpm, for 20 min) twice. The final precipitate was then suspended in 15 mL of ethyl alcohol and sonicated for 10 min before LBL experiments.

Glass slides were cleaned employing the RCA method<sup>37</sup> before LBL deposition. To prepare the LBL films, substrates were immersed in a 0.1 g/L aqueous solution of DAB-Am 64-polypropylenimine tetrahexacontaamine dendrimer, generation 5 (Aldrich), for 10 min, followed by rinsing with deionized water, drying with nitrogen gas, immersion in a Ag nanowire solution for 3 h, and finally drying with nitrogen gas.

All UV-visible absorption spectra were obtained using a Cary UV-visible spectrometer. AFM was recorded using a Digital Instruments NanoScope IV, operating in noncontact tapping mode with a n<sup>+</sup>-silicon tip. Scan rates of 1 Hz were used with 256 sample

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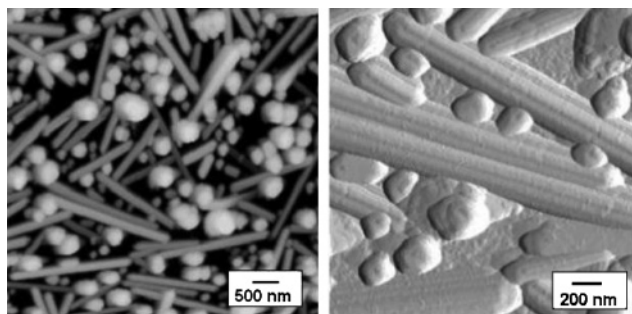
**Figure 1.** Surface plasmon extinction spectra for (a) Ag nanowire solution and (b) Ag nanowire/G5 DAB-Am dendrimer LBL film.

lines and 256 sample points per line. Topographical (height), error (amplitude), and phase images were used for analysis of the surface morphology of the films. The data were collected under ambient conditions, and each scan was duplicated to ensure that any features observed were reproducible.

Raman scattering experiments were conducted with micro-Raman Renishaw 2000 and Renishaw InVia systems. Several laser excitation energies were employed, including laser lines at 442 (HeCd), 488, and 514.5 nm (argon ion), 633 (HeNe), and 785 nm (diode). All measurements were made in a backscattering geometry using a 50 $\times$  microscope objective with a NA value of 0.75, providing scattering areas of  $\sim 1 \mu\text{m}^2$ . For most SERS/SERRS measurements, 10- $\mu\text{L}$  drops (with 8-mm diameters when dry) of dilute rhodamine 6G (R6G), 2-naphthalenethiol, and sulforhodamine B solutions, of varying concentrations, were cast onto the Ag nanowire/G5 DAB-Am dendrimer LBL substrates. However, to demonstrate further applications for these substrates, 1:10 mixed monolayers of *n*-pentyl-5-salicylimidoperylene (sal PTCD) and arachidic acid (optically noninterfering fatty acid matrix) were transferred to the LBL substrates using the Langmuir–Blodgett technique, for detection of the enhanced Raman signals of the dye.<sup>33</sup>

## RESULTS AND DISCUSSION

Based on the earlier report of Sun et al.,<sup>35</sup> the solution-phase synthesis of uniform nanowires of bicrystalline silver, with diameters of  $\sim 100$  nm and lengths of several micrometers, was successfully completed. The synthesized nanowires were characterized by their surface plasmon absorption in the visible region of the electromagnetic spectrum, and the results are shown in Figure 1. The plasmon absorption of the nanowires in solution is distinctly different from the nanowires in the LBL film with the G5 dendrimer. The spectrum of the LBL film clearly shows two well-resolved maxima at 358 and 396 nm, while a shoulder at 353 nm and a maximum at 383 nm can be seen in the solution phase. A clear red-shifting, broadening absorption is evident for the Ag nanowires in the LBL film, and this can be readily explained by changes in the dielectric function of the medium surrounding the particles,<sup>29</sup> as well as by the apparent aggregation (bundling) of the nanowires. The plasmon absorption of the nanowires (elongated cylinders) is distinctly different from that of a distribution of silver particles in spherical colloidal solutions, or metal island



**Figure 2.** AFM images of Ag nanowire/G5 DAB-Am dendrimer LBL film.

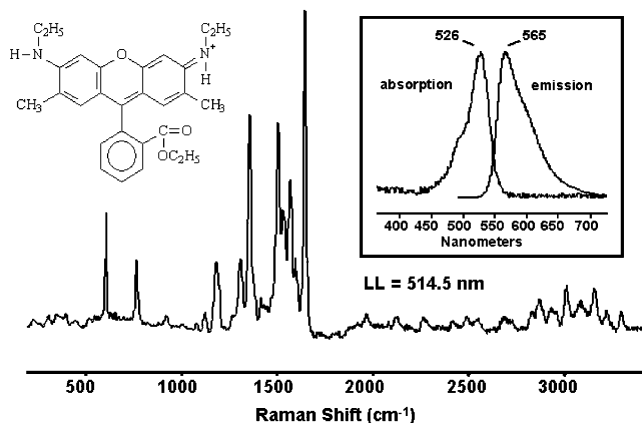
films, showing a characteristic strong blue-shifted maximum below 400 nm, as can be seen in Figure 1. This is in full agreement with the assignment of the transverse plasmon absorption given by Sun et al.<sup>35</sup> For a complete discussion of the surface plasmon absorption of needles and cylinders, the excellent review by Papavassiliou<sup>38</sup> is recommended.

The morphology of Ag nanowires self-assembled on the LBL films is shown in Figure 2. Particles are several micrometers in length, appear bundled together, and have average diameters of  $\sim 100$  nm. Higher magnification images reveal this bundling (lengthwise aggregation) and also show the structures to be many-sided rather than smooth cylinders. This confirms previous results that demonstrated pentagonal cross sections for these wires.<sup>36</sup> Notably, the bundling apparent in these images appears to be directly related to the process of assembling the nanowires onto the dendrimer layer in the LBL film, as it is not observed in images of the wires cast directly onto glass (results not shown). Also in these images, large irregularly shaped particles can be seen interspersed with the nanowires. AFM phase imaging suggests that these particles are Ag, but their contribution to the surface plasmon absorption spectra, or enhancement of the Raman signals, appears to be minimal, as expected from their large size. In fact, the large size of these particles (200–500 nm) largely precludes their effectiveness as enhancing nanostructures for SERS/SERRS experiments, particularly in the visible region of the electromagnetic spectrum. The AFM images of the LBL water-insoluble film show abundant metal nanostructures on the surface of the film, making it an ideal candidate for SERS/SERRS measurements from cast solutions, as well as from single monolayers transferred from the air–water interface to the probing surface using the LB technique. Moreover, the presence of known contributors to high surface enhancement of Raman signals in these films, such as sharp edges and tips, as well as aggregates of particles, is noteworthy.

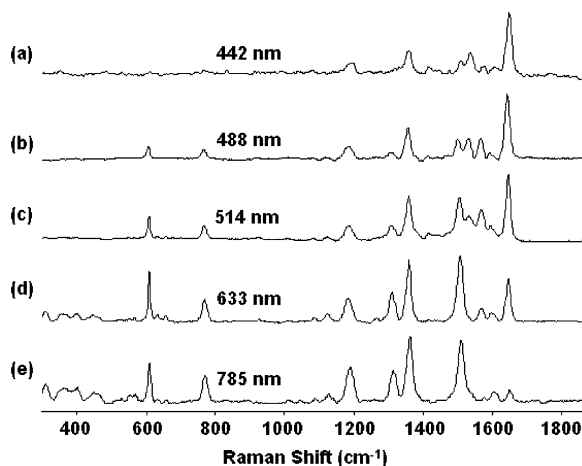
In this work, the ability of new Ag nanowire/G5 DAB-Am dendrimer LBL substrates to produce SERS/SERRS was tested in two ways. First, a known volume (10  $\mu\text{L}$ ) of a solution containing a probe molecule in picomole quantities was cast onto the LBL film, and a section of the surface covered by the solution ( $\sim 1 \mu\text{m}^2$ ) was excited with several laser wavelengths to gather the inelastic scattering in a backscattering collection geometry. R6G and sulforhodamine B, both with absorption profiles in the visible, were selected to investigate the SERRS and SERS enhancement of the substrates, while 2-naphthalenethiol was used as a repre-

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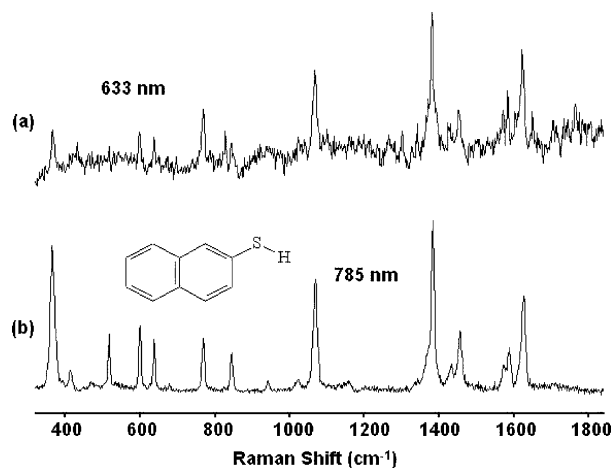
**Figure 3.** Baseline SERS spectrum of R6G on Ag nanowire/G5 DAB-Am dendrimer LBL substrate, recorded using laser excitation at 514 nm, and showing strong overtone and combination bands. Insets show R6G molecular structure and absorption and fluorescence emission of  $10^{-5}$  M R6G solution.



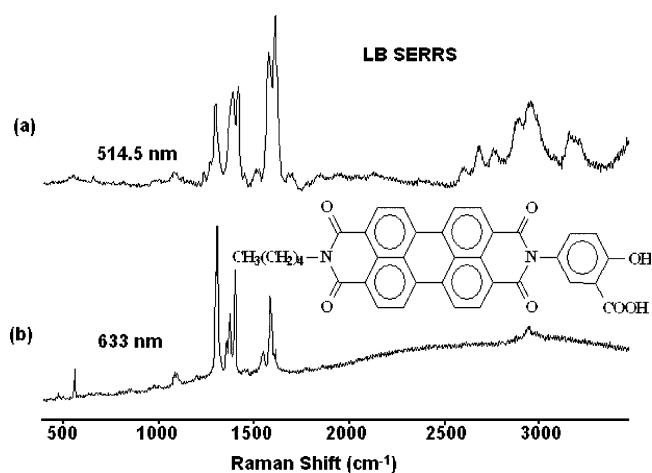
**Figure 4.** SER(R)S of R6G on Ag nanowire/G5 DAB-Am dendrimer LBL substrate recorded using laser excitation at (a) 442, (b) 488, (c) 514, (d) 633, and (e) 785 nm.

sentative nonabsorbing molecule in the visible spectral region. For Langmuir–Blodgett SERS experiments, mixed monolayers of *n*-pentyl-5-salicylimidoperylene were employed. This is a perylene-tetracarboxylic diimide (PTCD) derivative of the series of molecules that we have been testing for single-molecule detection<sup>33</sup> using SERS.

The SERS and SERS spectra of R6G obtained from Ag nanowire–dendrimer LBL substrates are illustrated in Figures 3 and 4. The insets of Figure 3 show the molecular structure of R6G, as well as the absorption and emission spectra of the stock solution of the dye used in the SERS experiments. It can be seen that the 633- and 785-nm laser excitation lines are not in resonance with the observed electronic transitions of the molecule, and therefore, we can refer to these enhanced spectra as SERS. When laser excitation is in electronic resonance with the molecular system, however, we can refer to the observed enhanced spectra as SERS. This is the case for this molecular system at 442-, 488-, and 514-nm laser excitation. Figure 3 shows the SERS spectrum observed for R6G employing 514.5-nm excitation, on Ag nanowire LBL films. Shown are the fundamentals, in the spectral region up to 1700  $\text{cm}^{-1}$ , and also the combinations and overtones (excited-state phenomenon), clearly seen in the 1900–3500- $\text{cm}^{-1}$  region. Accounting



**Figure 5.** SERS of 2-naphthalenethiol on Ag nanowire/G5 DAB-Am dendrimer LBL substrate recorded using laser excitation at (a) 633 and (b) 785 nm. Also shown is the molecular structure of 2-naphthalenethiol.



**Figure 6.** SER(R)S of 1:10 mixed *n*-pentyl-5-salicylimidoperylene/arachidic acid Langmuir–Blodgett monolayer on Ag nanowire/G5 DAB-Am dendrimer LBL substrate recorded using laser excitation at (a) 514 and (b) 633 nm. Also shown is the molecular structure of *n*-pentyl-5-salicylimidoperylene.

for the total amount of molecules used, and the area probed by the Raman microscope, detection levels below attomole quantities have been achieved using low laser energy densities at the sample.

Notably, all laser excitation lines from the visible, starting at 442 nm, to the near-infrared, at 785 nm, provide strong SERS or SERS with these substrates, as shown in Figure 4 for the R6G molecule. The relative intensities in the SERS/SERS spectra vary as laser excitation is brought in and out of resonance with the molecular electronic transition, revealing differences in the excited and ground states of the molecule. Similar SERS/SERS results (not shown) were obtained for sulforhodamine B on Ag nanowire/G5 PAMAM dendrimer LBL substrates as well.

The SERS spectra of 2-naphthalenethiol, recorded with two laser excitation wavelengths, 633 and 785 nm, are shown in Figure 5. Under identical experimental conditions (laser power, grating, accumulation time, and acquisition optics), the 785-nm excitation is more efficient for SERS. This is clearly a peculiarity of SERS, since the fourth power dependence of the scattering intensity would render the opposite result for normal Raman, and the surface plasmon absorption maxima of the films are clearly to the

blue of 785 nm. This result can be explained, however, on the basis of so-called "hidden resonances",<sup>39</sup> where small percentages of the particle population (hot spots) provide the largest enhancement contributions.

Finally, these LBL films are water insoluble and therefore offer the possibility for use as substrates for LB SERS/SERRS.<sup>40,41</sup> Here a single mixed LB monolayer was transferred by z-deposition to the Ag nanowire/G5 DAB-Am dendrimer LBL substrate. Mixed LB monolayers were prepared by spreading a mixed solution containing arachidic acid and *n*-pentyl-5-salicylimidoperylene in a 10:1 ratio at the air–water interface of a Langmuir trough. Again probing an area of  $\sim 1 \mu\text{m}^2$ , the SERRS spectra presented in Figure 6 are the result of detecting less than 1 amol of *n*-pentyl-5-salicylimidoperylene molecules. A change in the relative intensities of the vibrational bands with different excitation energies is once more the result of molecular resonance with the dye molecules at 514.5 nm and not at 633 nm.

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## CONCLUSIONS

A versatile new substrate for enhanced optical applications has been developed and characterized by UV–visible surface plasmon absorption, AFM, and SERS measurements. The presented Ag nanowire/G5 DAB-Am dendrimer LBL substrates are water insoluble and can be used for solution casting, and Langmuir–Blodgett applications, allowing the transfer of monolayers at the air–water interface. The application of these substrates to ultra-sensitive analysis is illustrated with small molecules and dyes, examining both resonant (SERRS) and nonresonant (SERS) surface-enhanced Raman scattering with several laser lines.

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