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Computational Study of the Surface-Enhanced Raman Scattering from Silica-Coated Silver Nanowires†

Brent M. DeVetter¹, Rohit Bhargava^{1,2,3,*}, and Catherine J. Murphy^{3,*}

¹Department of Electrical and Computer Engineering, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL

²Department of Bioengineering, School of Chemical Sciences, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL

³Department of Chemistry, School of Chemical Sciences, Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL

Abstract

Surface-enhanced Raman scattering (SERS) is a popular vibrational spectroscopic technique that can have several applications in chemical and biological sensing. Within the last decade or so, our ability to chemically synthesize nanostructures has improved to the point that the rational design of a variety of SERS substrates is now viable. In this report, we describe a computational study using the finite element method (FEM) to investigate the effects of patchy silica coatings on silver nanowires. We found that varying the degree of silica coating on silver nanowires impacts the enhancement and may be explained through two processes. The first process is a consequence of changes in the dielectric environment surrounding the nanowire due to the silica. As additional layers of silica coat the nanowire, the localized surface plasmon resonance of the nanowire redshifts. The second process is a result of silica distorting the local electric field around the nanowire surface. Anisotropic silica coating can influence anticipated enhancement depending on its spatial localization with respect to excited plasmon modes in the nanowire. We propose that the design of nanostructures with patchy silica coatings can be a viable tool for increasing surface enhancement.

INTRODUCTION

Inelastic light scattering, or Raman scattering, from molecules is an exceedingly rare process with cross sections on the order of 10^{-30} cm² per molecule, roughly 14 orders of magnitude smaller than that of fluorescence (1). Historically, Raman scattering's inherently weak cross sections limited its usage as an analytical technique due to the exceptionally weak signal. A major effort to enhance the signal first presented itself in 1974 when researchers inadvertently discovered a phenomenon now called surface-enhanced Raman scattering (SERS). The researchers discovered that when pyridine molecules were adsorbed to

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*Corresponding authors murphycj@illinois.edu (Catherine J. Murphy) and rxb@illinois.edu (Rohit Bhargava).

roughened silver electrodes its Raman signal mysteriously increased (2). It was later determined that the nanoscale features present on roughened noble metal surfaces support the propagation of surface plasmon polaritons and can subsequently enhance the Raman scattering cross section of nearby molecules (3). In 1997, two reports of single-molecule sensitivities using SERS were published (1, 4). In both cases, molecules were placed in the rough crevices between silver nanoparticles, resulting in extraordinarily high enhancement. The past decade has seen an exponential growth of publications discussing both the fundamental aspects of SERS and numerous, innovative methods for chemical and biological sensing (5).

Surface enhancement occurs when molecules are placed near the surface of plasmonically active nanostructures. Noble metals (typically gold or silver) exhibit a localized surface plasmon resonance (LSPR), in the visible portion of the electromagnetic spectrum, when excited with light. The LSPR is a coherent oscillation of conduction band electrons that generates an evanescent electric field near the nanostructure's surface. Noble metals have optical properties that satisfy the resonance conditions necessary to support an LSPR. Specifically, the resonance conditions require that the complex permittivity ($\epsilon = \epsilon' + i\epsilon''$) of the material have minimal losses ($\epsilon'' \sim 0$) and a negative real component ($\epsilon' \sim 0$) (6). Within the last decade or so, the wet chemical synthesis of plasmonic nanostructures has improved such that the community is now able to reliably and routinely synthesize nanostructures with tunable LSPR maxima such as nanorods (7) and nanowires (8), among others (9).

The rational design of SERS nanostructures requires consideration of the mechanisms that lead to surface enhancement of the Raman scattering cross sections of analyte molecules. Researchers have established two primary mechanisms for explaining enhancement in SERS. The first and by far more dominant mechanism is called electromagnetic enhancement (EE). EE originates from the evanescent fields surrounding oscillating or propagating surface plasmons and is tunable by changing parameters such as the composition, geometry or roughness of the nanostructure. The second, and minor, mechanism is called chemical enhancement (CE) and is likely due to a combination of energy transfer and resonance between the plasmonic surface and analyte molecules (10). Due to the dominant magnitude of EE as well as difficulty in understanding and modeling CE, theoretical reports investigating the maximization of enhancement neglect CE and focus on EE. EE may be modeled via electromagnetic simulation tools and can be combined with optimization algorithms to rationally design optimal nanostructures (11). Additional effort is being placed on modeling nanostructures by combining electromagnetic and quantum effects (12). The EE factor, G , is mathematically related to the local electric field: $G = |E_{\text{loc}}(\omega)|^2 |E_{\text{loc}}(\omega + \delta\omega)|^2$, where ω is the excitation frequency and $\delta\omega$ is the Stokes' shifted frequency that is dependent on the vibrational frequencies of the analyte. In general, the Stokes' shift of interest is minimal such that a good approximation can be made to state that SERS is dependent on the fourth power of the local field: $G \approx |E_{\text{loc}}(\omega)|^4$.

Plasmonic nanoparticles are typically treated analytically within the quasi-static approximation. The quasi-static approximation assumes the incident electric field over the entire nanoparticle is constant; this implies that the nanoparticle and surrounding media with electric potential ϕ may be described via Laplace's equation ($\nabla^2 \phi = 0$), making the

mathematics straight-forward and computationally inexpensive. The analytical form of the quasi-static approximation, however, is limited to simple geometries (spheres, ellipsoids). Nanowires cannot be accurately described with the quasi-static approximation because the dimensions of the nanowire are on the same order of magnitude or even larger than the illumination source. Rather than trying to model the field distributions of nanowires analytically, researchers use computational electromagnetic techniques to visualize and understand the fields surrounding them. Techniques such as the finite difference time domain (FDTD) method (13), the finite element method (FEM) (14), T-matrix (15) and the boundary element method (16) have been applied to nanoplasmonic structures. Here, we choose to use a commercial FEM software package, COMSOL Multiphysics, to model the EE and field distribution of silver nanowires. FEM's particular advantage is that it is able to accurately solve for the local electric field near the surface of the metal due to its inherent noncubic mesh grid (14). Furthermore, COMSOL's ability to solve for field distributions in three dimensions allows for us to accurately model anisotropic nanostructures.

Anisotropic nanostructures such as nanorods and nanowires consisting of gold or silver yield higher SERS intensities than equivalent surface area spherical nanoparticles. The usual explanation of this is that areas of increased radii of curvature induce "hot spots" of electric fields at their tips by concentrating the optical fields through what's called the "lightning rod" effect of SERS (17). Molecules placed at areas of concentrated fields will be greatly enhanced through the EE mechanism. Our previous experimental results indicated that colloidal patchy silica silver nanowires yield a higher SERS intensity than fully coated or uncoated silver nanowires (18). Here, we examine this unusual result via electromagnetic modeling to learn if the junction between a metal and a dielectric like silica can provide an unexpected type of SERS hot spot.

RESULTS AND DISCUSSION

All simulations were performed using a commercial FEM software package, COMSOL Multiphysics v4.3a. The three-dimensional scattering domain consisted of a cylindrical scattering boundary condition surrounding the scatterer. Optical constants were obtained from Johnson and Christy (19) and used without any corrective filters. The nanowire is assumed to be cylindrical with hemispherical end caps having a total length ℓ and diameter d . Nanowire dimensions and silica coatings configurations were based on our previous experimental work (18). We assume a nanowire of diameter 30 nm and varying lengths (200, 500 and 1000 nm), following typical parameters from the previous study. The scatterer is assumed to be submerged in pure water ($n = 1.33 + 0i$). Furthermore, the silver nanowire was illuminated with a uniform plane wave (633 nm) and polarized to excite the longitudinal LSPR, unless specified otherwise. Silica beads were created through the geometric intersection of perpendicular silica spheres (of diameter 30 nm) placed 15 nm from the nanowire surface. Furthermore, the silica material was modelled with a relative permittivity of $\epsilon = 4.5 + 0i$. Mesh density was adjusted for each individual scatterer and refined until a convergent solution was obtained.

Unlike nanorods and nanoparticles, nanowires exhibit higher order modes due to their relatively significant dimensions with respect to the illumination wavelength. Figure 1

shows the local field intensity ($|E_{\text{loc}}|^2$) of a silver nanowire ($\ell = 500$ nm, $d = 30$ nm) illuminated with a plane wave. As shown, the longitudinal surface plasmon resonance excites multiple modes along the entire length of the nanowire. As the dimensions of the nanowire increases, higher order modes become more prevalent and the nanowire begins to lose some of its plasmonic activity along the longitudinal axis. The following results assume a longitudinal excitation as a limiting case due to the relative strength of the longitudinal *versus* transverse modes.

To study the effect of patchy silica-coated silver nanowires, we considered four different configurations of silica coatings, as shown in Fig. 2. The investigated dimensions and configurations were based on our previous experimental work (18). Silica coating is typically performed through the addition of a silane such as 3-mercaptopropyltrimethoxysilane (MPTMS) to an aqueous suspension of nanowires. As a result of thiol's strong affinity to metals, silver thiolate bonds will form on the surface of the nanowire. Nanometer-scale thick silica is grown through the addition of sodium silicate. As we have previously discussed (18), thiolated Raman-active molecules compete with MPTMS for the silver surface and can result in patchy silica coatings if low concentrations of sodium silicate are added. Our simulation assumes that the thiolated molecules are immediately adjacent to the metallic surface. In addition, we assume that aggregates and metallic hot spots are negligible or nonexistent. For experimental studies, aggregates in solution can lead unreliable results because the signal intensity is heavily dependent on the positioning of the analyte molecule as well as the distance between metal surfaces. Aggregates concentrate the local electric field by several orders of magnitude, but we currently lack the precision to reliably fabricate subnanometer features in wet chemistry. A framework for understanding signals recorded from suspensions of particles, using an effective medium theory, is then available to extrapolate results from single nanowires to ensemble measurements (20, 21).

To evaluate the differences in EE of the four configurations of silica-coated silver

nanowires, we define a relative enhancement factor: $\xi = \frac{\int \int |E_{\text{loc}}|^4 dS}{\int \int dS}$, where integration is evaluated over the entire silver nanowire surface. Two cases are considered; the first is a silver nanowire of diameter $d = 30$ nm and length $\ell = 200$ nm; and the second is a silver nanowire of diameter $d = 30$ nm and length $\ell = 1000$ nm (Table 1). In both cases, 30 nm diameter silica beads coat the silver nanowire for the sparse and dense configurations (see Fig. 2). The fully coated silver nanowire has a 5 nm thick silica coating completely surrounding it.

The FEM was used to model the extinction of the varying configurations of silica-coated silver nanowires. The absorption and extinction cross sections are expressed as the following (22):

$$C_{\text{abs}} = k \int \int \int \text{Im}\{\tilde{n}\}^2 |\mathbf{E}(\mathbf{r}')|^2 d^3 r' \quad (1)$$

$$C_{\text{ext}} = -k \text{Im} \left\{ \iiint (\tilde{n}^2 - 1) \mathbf{E}(\mathbf{r}') \cdot \mathbf{E}_{\text{inc}}^*(\mathbf{r}') d^3 r' \right\} \quad (2)$$

In this case, k corresponds to the wavevector, $\tilde{n}$ is a ratio between the frequency-dependent index of refraction of silver and the index of refraction of water $\tilde{n} = (n_{\text{Ag}(\omega)})/n_{(\text{H}_2\text{O})}$. The incident electric field $\mathbf{E}_{\text{inc}}$ is assumed to be a time harmonic plane wave. Submicron and nanoscale silver scatterers can exhibit multiple resonances in the ultraviolet–visible spectrum; therefore, we focus on the shift in the LSPR nearest the laser excitation wavelength (633 nm).

In case 1 ($\ell = 200$ nm), we find that complete silica coverage of the nanowire results in the highest predicted enhancement with a nearly $4\times$ higher ξ -factor than an uncoated silver nanowire. In contrast, case 2 ($\ell = 1000$ nm) indicates that a densely coated silica nanowire will yield a higher ξ -factor, but only with an increase of ~ 1.59 compared with uncoated silver nanowires. Case 2 has less dramatic changes in enhancement, possibly because the plasmonic activity for longer nanowires is weaker. Varying degrees of silica will redshift the LSPR because the local dielectric environment around the nanowire changes. In case 2, further, the LSPR is far away enough from the excitation wavelength that small changes in the optical properties of the nanowire do not significantly impact the enhancement.

A nonuniform silica coating distorts the electric field around the nanowire surface and modifies the relative enhancement. As shown in Fig. 3, several configurations of silica coatings were investigated for a 500 nm long silver nanowire. An uncoated silver nanowire is depicted in Fig. 3a with an enhancement $\xi = 21.8$. In Fig. 3b, four silica beads (diameter 30 nm) were placed at electric field minima and have a negligible effect on enhancement. Conversely, in Fig. 3c the silica beads were placed at electric field maxima and heavily distort the electric field at the surface, reducing the enhancement to $\xi = 0.55$, nearly $40\times$ less than that of uncoated silver. The shift in LSPR as a function of the location of silica beads in Figs. 3b,c was calculated to be ~ 10 nm. In Fig. 3d complete surface coverage of 5 nm thick silica is shown to partially distort the surface field. These results are in agreement with the work of Mahmoud *et al.* (23) who found that silver nanocubes are sensitive to anisotropic changes in the surrounding dielectric medium. In this respect, patchy silica-coated silver nanowires are predicted to have differences in enhancement as compared with uncoated or fully coated nanostructures. The positions of the silica patches are shown to be crucial for changes in enhancement and understanding these is essential to understanding whether patchy silica coatings can enhance or reduce the capability of coated nanowire sensors. The results also provide impetus for new synthesis schemes to obtain designed composites at the nanoscale.

CONCLUSION

In this study we investigated the EE of silica-coated silver nanowires using the FEM. Computational techniques elucidate the properties of plasmonic nanostructures without the need for developing complex analytic solutions that are limited to specific geometries or materials properties and dimensions. Our results indicate shorter aspect ratio silver nanowires are more likely to be affected by differences in silica coating. We attribute this

observation to the relative position of the longitudinal LSPR with respect to the laser excitation wavelength as well as the increased plasmonic activity of shorter aspect ratio nanowires. In addition, silica on the surface of the nanowire can distort the local electric field, which is strongly dependent on the position of the silica coating. In this sense, silica coating has some limited ability enhance sensing by modifying electric fields, but will require the development of precise and controlled synthesis schemes to realize the advantages of patchy nanowires. With the appropriate consideration of the LSPR and silica configuration, it may be possible to engineer nanowires with higher enhancements for SERS applications.

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Figure 1. Finite element method (FEM) simulation of incident light ($\lambda = 633$ nm) on a silver nanowire ($\ell = 500$ nm, $d = 30$ nm) suspended in water ($n = 1.33$). (a) Plane wave light polarized such that the longitudinal mode is excited and (b) transverse mode excited.

Figure 2.

Schematic representation of the investigated silver nanowire configurations. (a) uncoated silver (b) completely formation of silica coating a silver nanowire (c) sparsely coated silver nanowire (d) densely coated silver nanowire. All silica spheres were modeled with a radius of 15 nm and (e) absorption cross section C_{abs} of each configuration ($\ell = 200$ nm, $d = 30$ nm) under longitudinally polarized light near the excitation wavelength; solid line—uncoated silver; dash-dotted line—sparsely coated silver; dotted line—densely coated silver; dashed line—completely coated silver.

Figure 3.

Local electric field intensities of silver nanowires ($\ell = 500$ nm, $d = 30$ nm) demonstrating the distortion of the electric field. (a) Uncoated $\xi = 21.8$ (b) four silica beads placed at the electric field minima $\xi = 21.7$ (c) four silica beads placed at center maxima $\xi = 0.55$ (d) 5 nm thick silica surrounding the entire nanowire = 6.93 and (e) absorption cross section C_{abs} of configuration (b)—solid line and (c)—dotted line.

Table 1

Simulation results of two different aspect ratios of patchy silica silver nanowires. A factor ξ characterizes the predicted relative enhancement.

Length (l) (nm)	Diameter (d) (nm)	Configuration	ξ
200	30	Uncoated	7.54
		Complete	29.2
		Sparse	9.65
		Dense	15.8
1000	30	Uncoated	5.98
		Complete	6.09
		Sparse	4.61
		Dense	9.23