



Simulation and synthesis of silver dendritic nanostructures for surface-enhanced Raman scattering

Olabode Oladele¹, Chen Chen², Fei Yan², Branislav Vlahovic¹, and Yongan Tang^{1,*}

¹The Department of Mathematics and Physics, North Carolina Central University, Durham, NC 27707

²The Department of Chemistry and Biochemistry, North Carolina Central University, Durham, NC 27707

ABSTRACT

Silver dendritic nanostructures (AgD) is investigated for surface-enhanced Raman scattering (SERS) with simulation and experiments, the simulations showed that there is a significant absorbance over a broad spectrum from the AgD, this indicated that AgD is a good candidate for SERS. The simulations helped to study the parameters of the AgD that affects the SERS and we applied these simulation results for experimental designs, in which our experimental results of synthesis and characterization results of Raman spectrum showed consistence with the simulation results. These simulation results are very helpful in deciding the experimental parameters for efficient and effective synthesizing and reproduction of hierarchical silver dendritic nanostructure. The AgD were produced using displacement redox reaction between AgNO₃ solution and Copper foil. We found that the concentration of AgNO₃ played major role on the rate of reaction, and the rapid growth of the silver nanostructures was observed as the reaction time increases. The structural and morphological evolution of silver dendrites was examined with Scanning Electron Microscope (SEM). The Raman enhancement of AgDs was evaluated using Elman's reagent (DTNB) and Rhodamine 6G (R6G). The silver dendrites have great potential for diverse sensing applications ranging from food safety control, environmental monitoring and assessment, forensic investigation, and to medical diagnosis.

Keywords: Surface Plasmons, Silver Dendrites, Nanostructures, FDTD, SERS.

1. INTRODUCTION

Metal nanostructures (Au, Ag, and Cu) have been purposefully used for different applications such as biological labeling, nanophotonics, nanoelectronics, ultra-sensing, surface-enhanced Raman scattering (SERS) [1]. SERS is one of the most powerful probes for the detection of various analytes/adsorbates molecules down to single-molecule detection limit, in other words enhancement of contaminant that were present in trace [2]. The main enhancement mechanism for high SERS signal is generally agreed to be electromagnetic mechanism (EM), which is

primarily caused by surface plasmon resonance (SPR) [3] from nanostructure (rough metal surfaces). Nanostructures of silver dendrites have received great deal of high considerations because of its hierarchical structure consisting of a main stem and many side branches that possess plenty of active atoms. This special structures lead to their applicability in SERS based sensing [4–7]. The Silver dendrites was considered special because of large presence of hotspots in the ridges, bends and branches of the dendritic nanostructure [8–11]. Another unique property of Silver dendrite is the extra ordinary adsorption property compared to other novel structures and this gave it a better edge to be used as effective SERS substrate [12–15]. We hereby report a straightforward, cost-effective and

* Author to whom correspondence should be addressed.
Email: tangy@ncu.edu

robust method for synthesizing silver dendrites by the galvanic displacement reaction on Copper foil. The process is a simple one, which was carried out at the room temperature and only three materials require for galvanic displacement reaction: copper foil, silver nitrate and water.

2. SIMULATIONS

2.1. Simulation Methods

The finite difference time domain (FDTD) method is a numerical analysis technique used for modeling computational electrodynamics, and it is used to find approximate solutions to the Maxwell's equations over time within some finite computational region, in which space is divided into a discrete grid and the fields are evolved in time using discrete time steps. We utilized MEEP [16], an open-source software with the FDTD method, for simulating the electromagnetic wave propagating in the AgDs. In order to obtain accurate and high efficient simulation results, we set the grid to 10 nm, and applied the parallel computing, which is provided by the Texas Advanced Computer center (TACC) of the Extreme Science and Engineering Discovery Environment (XSEDE) [17]. In the simulations, the Lorentz-Drude model (Eq. (1)) is utilized to describe the dielectric function of the silver

$$\varepsilon = \varepsilon_{\infty} + \sum_{j=0}^k \frac{\sigma_j \omega_j^2}{\omega_j^2 - \omega^2 - i\omega\Gamma_j} \quad (1)$$

Where ε_{∞} is the infinite dielectric constant, ω is the frequency of the incident light, ω_j is the frequency of the critical points, $1/\Gamma_j$ is the constant for lifetime, and σ_j is the strength. These data of the critical points for the dielectric function are from this Ref. [18]; the plot of the dielectric function of silver is shown in Figure 1(a), and these parameters are converted to the MEEP system for simulations shown in Table I below.

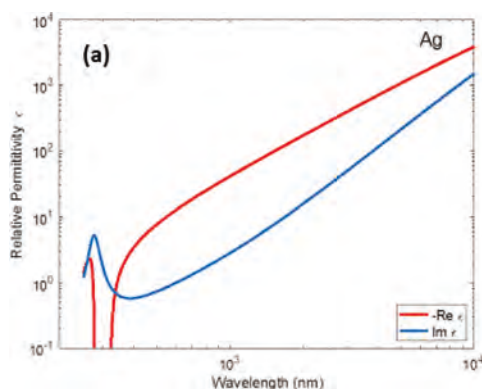


Table I. Parameters of silver dielectric function for simulations.

Parameters for Lorentz-Drude model			Parameters for MEEP simulations		
ω_j (eV)	σ_j	Γ_j (eV)	f (1/ μm)	Γ (1/ μm)	σ
0.00E+00	0.845	0.048	1.00E-20	0.00386	4.44E+39
0.816	0.065	3.886	0.06568	0.31279	7.9247
4.481	0.124	0.452	0.36068	0.03638	0.50133
8.185	0.011	0.065	0.65882	0.00523	0.01333
9.083	0.84	0.916	0.7311	0.07373	0.82655
20.29	5.646	2.419	1.63316	0.19471	1.11334

The cross-section view of yz plane of the unit cell for the simulation is shown in Figure 1(b), the boundaries are set in both x and y directions as Bloch-periodic boundaries, and at both ends of z axis there are a perfect match layer at the outmost to absorb reflections; A plane wave light source is placed next to the PML Layer inside the unit cell on the right end, while the light is traveling in z direction, the AgD is placed in the center of the unit cell, and the transmission spectrum is computed the flux of electromagnetic energy as a function of frequency, it is detected by an optical detector at the left end of the unit cell.

2.2. Simulation Results

We simulated the AgD with variety of lengths and widths, e.g., length of 3 μm and width of 1 μm , while the trunk, branches and sub-branches are cylinders with diameters of 60 nm, 40 nm, and 20 nm, respectively. The simulations show strong localized SPR around the branches and sub-branches of the electric magnetic distribution on the AgD (shown in Fig. 2(a)), the absorbance versus the wavelengths are plotted for two sizes of AgD, 3 μm * 1 μm (Fig. 2(b)) and 4 μm * 2 μm (Fig. 2(c)). Significant absorbance over the broad range of wavelengths from 350 nm to 950 nm are observed, it indicated that AgD is an ideal candidate serving as a substrate for SERS.

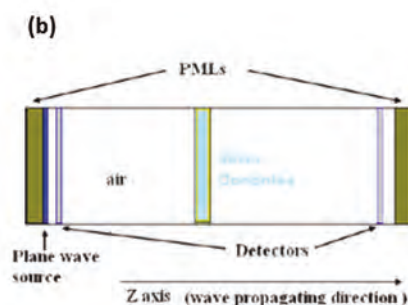


Fig. 1. (a) The plot of the dielectric constant of silver as a function of wavelength, the red line is the negative of the real part of permittivity, and the blue solid line is the imaginary part of permittivity. (b) Schematic of the simulation of silver dendrite unit cell.

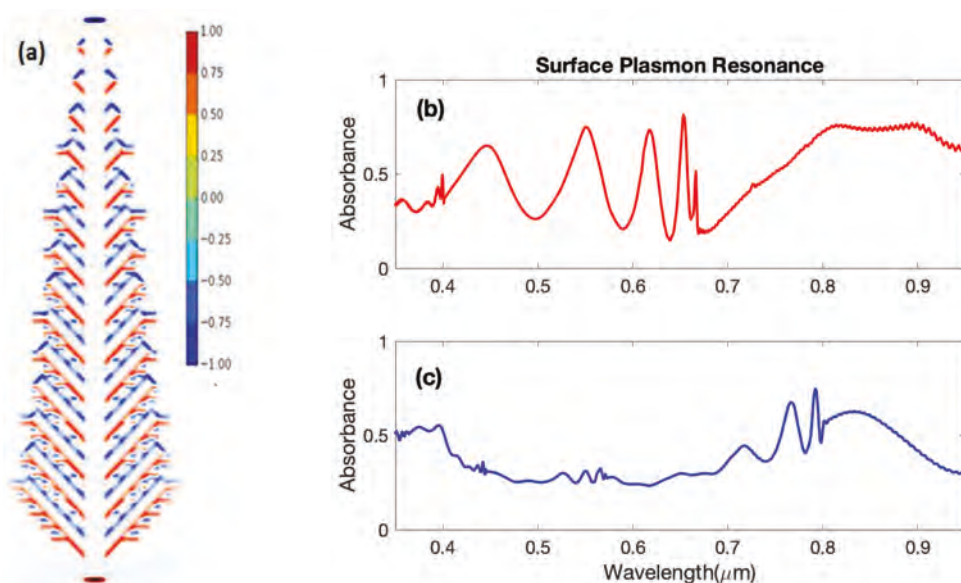


Fig. 2. (a) Localized SPR of silver dendrite with size of 3 μm * 1 μm ; (b) the absorbance versus wavelength of 3 μm * 1 μm silver dendrite, and (c) the absorbance versus wavelength of 4 μm * 2 μm silver dendrite.

3. SYNTHESIZE MATERIALS AND METHODS

3.1. Synthesize Materials

The materials were openly sourced and they are Silver nitrate (AgNO_3), Aluminum foil (with the thickness of 0.3 mm), Graphene oxide, Ethanol, Deionized (DI) water.

3.2. Synthesize Methods

The AgDs were synthesized with galvanic displacement reaction method, whose process is shown in Figure 3. First, size of 4 $\times$ 3 cm^2 copper foil were prepared and grease was removed from the surface by ultrasonic concussion using ethanol and later rinsed with DI water. The Silver nitrate solution of 100 ml, 0.075 M was prepared dissolving 1.275 g into 100 ml of DI water. The clean Cu foil was immersed into the silver nitrate solution for period of 30 seconds at ambient temperature and pressure. The interaction of Cu foil with a solution of silver nitrate is a spontaneous electrochemical process called galvanic displacement. The silver ions in the solution diffuse into the surface of a Cu foil, where it gains electrons from the atoms of copper. This causes the silver ions to lose their charge and become solid silver atoms, this

creates a starting point in which micro and nanoscale crystal structures begin to blossom. The copper, which convert to ions as they lose their electrons to the silver, diffuse outward into the solution [$\text{Cu} + \text{AgNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + \text{Ag}$]. The micro particles were shaking off the Cu surface by ultrasonifying and this was vigorously washed with DI water, and ethanol, respectively in centrifuge machine. This method was repeated for the following concentration of Silver nitrate solution of 100 ml of 0.1 M and 0.05 M respectively.

3.3. Experimental Results

FEI 430 Nano-Scanning Electron Microscope (SEM) was employed to examine the morphology, surface topography and images of the synthesized AgDs (shown in Fig. 4). The sizes and features of the AgDs synthesized is similar to the AgDs in simulations. In order to provide a free and flexible SERS device, we synthesize and deposit AgDs on Graphene Oxide (GO), which was synthesized using Hummer modified method [19]. The AgDs/GO mat allows uniform arrangement of silver dendrite particles in end to end version, in which stronger SERS sensitivity can be

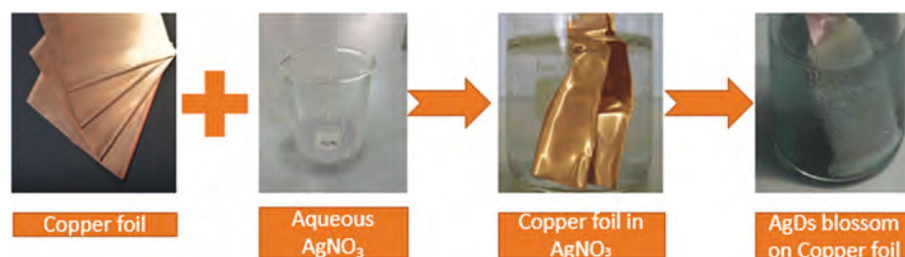


Fig. 3. Galvanic displacement reaction method.

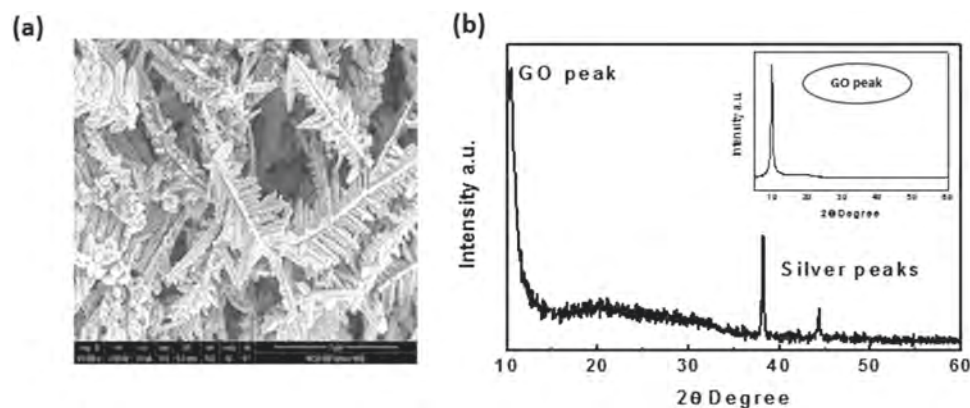


Fig. 4. (a) SEM for Ag nanoparticles of size $3\ \mu\text{m}$, (b) XRD of Ag Dendrites using Graphene as the substrate and the insert is the XRD of the graphene oxide.

easily explored as against single particle aggregates. With the GO substrate analyte easily access the AgDs because of large surface area of the substrate and this give rise to better absorption. We applied X-ray diffraction (XRD) to obtain information on the crystal phases and structure of

AgDs and GO, the plot shows (Fig. 4(b)) various peaks for Graphene and Silver particles is observed that the AgD is completely synthesized and deposited on GO.

Raman Spectrometer (Horiba Scientific Lab RAM HR Evolution) was used to measure the SERS spectra under

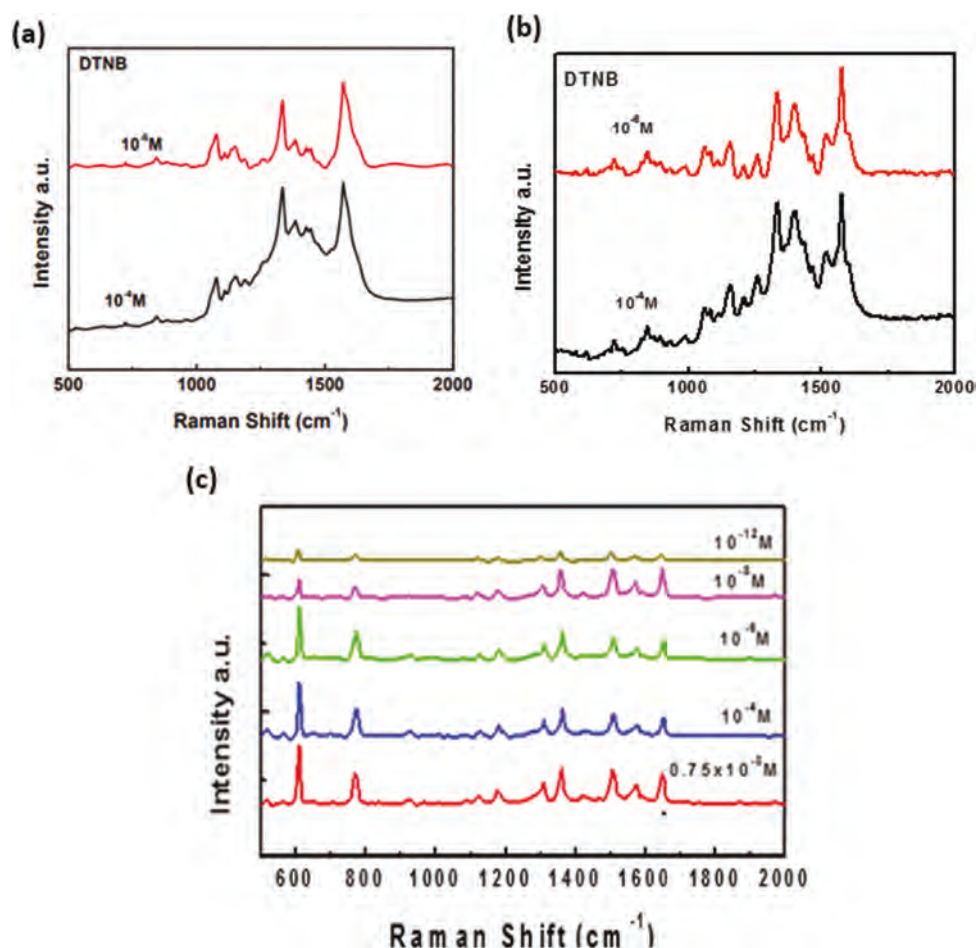


Fig. 5. (a) Silver dendrites SERS performance using DTNB with concentration of 10^{-6} to 10^{-8} M, (b) AgDs and graphene oxide using DTNB with concentration of 10^{-6} to 10^{-8} M. (c) SERS spectra of AgDs/graphene oxide using R6G with concentration of 10^{-3} to 10^{-12} M.

the following conditions: laser wavelength of 785 nm with power of 5 mW, and integration time of 20 s. The substrate was prepared for the SERS by putting a small sample of silver dendrites on a slide and allowed a little drop of DTNB and R6G solutions (shown in Fig. 5). The sample is left to dry in air before the measurements in Raman spectrometer. The SERS performance using DTNB (Figs. 5(a and b)) and R6G (Fig. 5(c)) were employed as probe to characterize SERS spectra intensities from AgDs. The experiments showed that AgDs and/or AgDs with GO have great SERS using DTNB with concentration of 10^{-8} M, and the AgDs with GO have significant SERS using R6G with concentration of 10^{-8} M.

4. DISCUSSIONS AND CONCLUSIONS

Our Simulations show that good absorbance from silver dendrites with sizes of $3\ \mu\text{m} \times 1\ \mu\text{m}$ to $4\ \mu\text{m} \times 2\ \mu\text{m}$ in the broad wavelength range from 350 nm to 950 nm, these results helped us to design the synthesis parameters for similar features of silver dendrites. We successfully grew $3\ \mu\text{m}$ AgDs on Cu foil with 0.05 M and 0.075 M of concentration silver nitrite for 30s. Our experimental results showed significant SERS with DTNB and R6G, this matched our simulation results well. However, it is important to report that for Cu foil reaction with 0.05 M silver nitrate the micro particles growth was slow and the silver particles take 180s to fully blossom, and for 0.1 M the particles grows too quickly in 20 s but they are large which made them unsuitable for SERS application. Moreover, Cu foil reaction with 0.075 M produced micro particles of controlled size, and moderate growth.

There is possibility of synthesizing controllable, hierarchical Silver nanostructure via galvanic displacement reaction on Copper foil with Silver nitrate in large quantities within a very short time. In achieving this effort, it is discovered that silver nitrate concentration and reaction time are very crucial. The Raman scattering was successfully detected using DTNB and R6G because of its abundant hotspots site, which were shown in simulation results of Figure 2(a), and tremendous adsorption capacity. Moreover, the Silver nanostructure made on copper-foil will provide new opportunities, simple approach to develop remote and portable SERS-based sensors that could be used to detect contaminants.

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