Article

Revealing the Hemispherical Shielding Effect of SiO$_2$@Ag Composite Nanospheres to Improve the Surface Enhanced Raman Scattering Performance

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1. Introduction

The oxide@metal composite structures were widely investigated in various fields, such as photonic crystals, catalysis and surface enhanced Raman scattering (SERS), etc. [1–4] due to their outstanding physical and chemical properties [5–7]. The composite microspheres of oxide@metal play a significant role in SERS associated with the localized surface plasmon resonance (LSPR) of metal nanoparticles (NPs) [8,9], inducing a charge transfer effect at the oxide@metal interface [10,11]. Thus, many oxide-metal composites have been designed to improve the capabilities of SERS [12–14]. In recent years, SiO$_2$ has attracted increasing interest due to the advantages of easy preparation and modification, high stability and low light loss [15–17]. Meanwhile, Ag is one of the metals with the remarkable properties of SERS because of its strong LSPR and controllable shape to generate lots of hot spots [18–21]. Therefore, in order to achieve better SERS performance, a variety of methods [22–27] were developed to prepare the SiO$_2$@Ag composite nanospheres for surface enhanced Raman scattering effects, and is very consistent with our simulation results.

Keywords: SERS; LSPR; three-dimensional models; upper hemisphere shielding
distributed in all corners of the entire collection of SiO$_2$ nanospheres. However, the structures of simulation are usually two-dimensional and the composite structure uniformly loaded with Ag NPs has significant electromagnetic enhancement everywhere. Therefore, the enhancement factors (EF) obtained by simulating electromagnetic enhancement are usually far from the corresponding experimental EF.

In order to improve the simulation accuracy of electromagnetic enhancement, we used the optical module of Comsol Multiphysics software to construct a three-dimensional structure of the SiO$_2$@Ag composite nanosphere, and simulated the three-dimensional electromagnetic enhancement distribution of SiO$_2$@Ag composite microspheres, finding that light cannot penetrate the upper hemisphere in three-dimensions due to the electrostatic shielding caused by sufficient adjacent Ag NPs, revealing SiO$_2$@Ag hemisphere’s electric field electrostatic shielding effect. At the same time, we designed related experiments to prepare materials similar to the simulated structure, SiO$_2$@Ag composite nanospheres were synthesized, and the effects of different methods for in-situ reduction of silver ammonia ions were characterized and analyzed. We used Rhodamine 6G (R6G) as a probe molecule to study the SERS activity of different concentrations of SiO$_2$@Ag substrate, and tested its EF value to verify the simulation result. In addition, the hydrophobic properties of SiO$_2$@Ag introduced in the fabricated process are studied here, which are often overlooked in SERS.

2. Materials and Methods

2.1. Materials

All chemicals were analytical grade and they were used without further purification. Tetraethyl orthosilicate (TEOS, 99.9%), ammonium hydroxide (NH$_3$·H$_2$O, 25–28%), silver nitrate (AgNO$_3$, 99.5%), glucose (C$_6$H$_{12}$O$_6$, 99.5%), and polyvinylpyrrolidone (PVP, k29–32) were purchased from Aladdin (Shanghai, China). Anhydrous ethanol (EtOH, 99.7%) was supplied from Guangfu Chemical Reagent Factory (Tianjin, China). Deionized water with a resistivity of 18.2 mΩ·cm$^{-1}$ was obtained from a Millipore Simplicity 185 water purification system (Millipore, Co., Ltd., Bedford, MA, USA).

2.2. Modification of SiO$_2$ Nanospheres

The monodisperse colloidal SiO$_2$ nanospheres with 500 nm used in our experiments were prepared by the Stöber method [29,30]. Then, PVP was added to the aqueous solution in which SiO$_2$ nanospheres were dispersed. The solution was stirred at 30 °C for 3 h. Finally, the modified SiO$_2$ nanospheres were obtained through centrifugal washing with ethanol and deionized water, and vacuum drying.

2.3. Preparation of SiO$_2$@Ag Composite Nanospheres

Firstly, the unmodified SiO$_2$ or pre-modified SiO$_2$ (0.1 g) nanospheres were dispersed in ethanol (13 mL). Secondly, AgNO$_3$ (0.1 g) was dispersed into deionized water (2 mL) and an NH$_3$·H$_2$O (0.6 mL) solution to configure the silver ammonia solution. The freshly prepared silver ammonia solution was slowly added to the mixed solution with continuous stirring, and then the reducing agent was added into the mixed solution. After that, the solution was transferred into a Teflon cauldron and heated at 110 °C for 12 h. Finally, the SiO$_2$@Ag composite nanospheres were obtained through centrifugal washing and vacuum drying.

2.4. SERS Measurement

The SiO$_2$@Ag nanosphere solutions (50 µL) with the concentration of 10 mg/mL were suspended on the silicon wafer. After drying for several minutes, R6G solutions (20 µL) with concentrations ranging from $10^{-10}$ to $10^{-6}$ M were dropped on the SiO$_2$@Ag substrates. The SiO$_2$@Ag substrates were dried to evaporate the aqueous solution. SERS spectra were recorded using a Raman spectrometer system (Xplora plus, HORIBA, Kyoto, Japan) with a 532 nm excitation wavelength.
2.5. 3D Simulated Mode

3D models used for simulation include material types and geometric parameters as shown in Figure 1. Since the nanospheres are hexagonally close packed, the boundary is set to periodic boundary conditions so that the minimum basic unit can accurately replace the overall situation. The minimum basic unit is set to be a core-shell structure, including a dielectric oxide nanosphere of 500 nm as core material and silver nanoparticles on its surface. The diameter of silver nanoparticles is 80 nm in S1 and S2, and it is obvious that the number of silver particles in S3 is far more than that of S1 and S2, so silver particles size is set to 60 nm. In order to simplify the calculation in S3, 1/4, 1/2, and 3/4 height regions of the core are uniformly distributed with silver nanoparticles, and the corresponding silver nanoparticles spacing is about 7.4, 18.5, and 7.4 nm. The wavelength of the incident light is 532 nm, which is consistent with the wavelength of the light source of the experimental equipment, and the generated results are the average value under TE and TM modes.

![Figure 1. Three-dimensional electromagnetic enhancement distribution (stereoscopic view, top view and front view) of SiO$_2$@Ag in S1, S2 and S3.](image)

3. Results and Discussion

Studies have found that the SERS of SiO$_2$@Ag substrate comes from electromagnetic enhancement and chemical enhancement, and the electromagnetic enhancement is absolutely dominant [31–34]. To figure out exactly how the surface electromagnetic enhancement distribution is on the SiO$_2$@Ag composite nanospheres substrates, the three-dimensional SiO$_2$@Ag models are constructed by Comsol Multiphysics (v. 5.3a, COMSOL AB). Ag NPs were distributed on the surfaces of a 500 nm SiO$_2$ core, providing stereoscopic, top, and front views of the electric field distribution shown in Figure 1. To understand simply, S1, S2 and S3 will be respectively used to represent the three samples, where S1 represents sparse but large-sized Ag NPs, S2 is the same as S1 but with some irregular parts, and S3 is dense small-sized Ag NPs. It can be seen from the front view that the high electric field in S1 and S2 are mainly distributed directly under the SiO$_2$@Ag due to the whispering gallery mode of the spherical nanostructure [15,35]. The high electric field in S3 is distributed in the gaps between the Ag NPs in the upper half of the SiO$_2$@Ag mainly...
due to many Ag NPs with close distances confine the incident light contributed to LSPR so 
that most of light cannot reach the lower half of the SiO$_2$@Ag.

These results are hard to spot in previous studies because the three-dimensional 
models reveal much of the original folded information compared to the two-dimensional 
models, similar to the top view of the three-dimensional models. The EF contributed by 
electromagnetic enhancement [34,36,37] is given by Equation (1):

$$\text{EF} = \frac{I_{\text{SERS}}}{I_{\text{RS}}} \approx \left| \frac{E}{E_0} \right|^4$$

(1)

As shown in three views of Figure 1, the electric field intensity ($E/E_0$) in S1–S3 is 
about 85, 100 between the Ag NPs, and 2–3 times that of their surface, causing the 
SERS to far exceed the surrounding area. According to Equation (1), the corresponding 
electromagnetic enhancements are calculated to be $5.22 \times 10^7$, $3.70 \times 10^7$, and $1 \times 10^8$, 
respectively.

Based on the results of the simulation, we concluded that the probe molecules need to 
be in contact with the bottom of the core material for a structure similar to S1 and S2, while 
the probe molecules need to be distributed between the Ag NPs on the upper surface for a 
structure similar to S3. Therefore, with SiO$_2$ as the representative, we designed relevant 
experiments of S0, S1, S2 and S3 specifically, where S0 represents SiO$_2$ nanospheres.

The colloidal SiO$_2$@Ag composite nanospheres were first characterized by a PHILIPS 
TECNAL-10 transmission electron microscope (TEM), as shown in Figure 2. Figure 2a 
shows the pre-fabricated SiO$_2$ NPs with a diameter of 500 nm used as core material to 
synthesize SiO$_2$@Ag composite microspheres. Ag NPs supported on SiO$_2$ were large and 
sparse, implying that a large amount of [Ag(NH$_3$)$_2$]$^+$ ions were rapidly consumed in the 
solution instead of binding to the surface of SiO$_2$ at 110 $^\circ$C, due to the reducing ability 
of glucose in Figure 2b. S2 (Figure 2c) was prepared under the same conditions as S1, 
but using PVP pre-modifying SiO$_2$ nanospheres. In comparison, S3 represents Ag NPs 
loading in SiO$_2$@Ag obtained using PVP as the reducing agent in Figure 2d. Compared to 
S2, the coverage of Ag nanoparticles coated on the surface of modified SiO$_2$ nanospheres 
dramatically improved.

![Figure 2. TEM images of SiO$_2$ and SiO$_2$@Ag nanospheres substrate with different samples: (a) S0, (b) S1, (c) S2, and (d) S3, scale bar 500 nm.](image-url)

The synthesized SiO$_2$@Ag nanospheres were also characterized by XRD. As exhibited 
in Figure 3a, the XRD patterns of the SiO$_2$@Ag nanospheres displayed diffraction peaks at $2\theta = 38.1^\circ$, 44.3$^\circ$, 64.4$^\circ$, 77.4$^\circ$, 81.5$^\circ$ corresponding to the reflections of (111), (200), (220), (311), (222) crystalline planes of Ag (JCPDS No. 04#0783), indicating that the Ag nanoparticles 
were coated on the surface of the SiO$_2$. Meanwhile, there appeared a broadband 
diffraction angle of 14.78–33.75$^\circ$ corresponding to the characteristic diffraction peaks of 
amorphous SiO$_2$ (JCPDS No. 01-082-1554), and the peak intensity of SiO$_2$ was suppressed 
after the growth of Ag. These results are in very good agreement with Figure 3.
Figure 3. (a) XRD of SiO$_2$ and SiO$_2$@Ag composite nanospheres; (b–e) XPS analysis of SiO$_2$@Ag core-shell NPs ((b) survey spectrum; (c) Ag 3d; (d) Si2p; (e) O 1s spectra); (f) UV-Vis absorption of SiO$_2$(S0) and SiO$_2$@Ag with different samples(S1–S3).

To make clear the encapsulation state of the elements in the SiO$_2$@Ag core-shell NPs, the most widely used XPS analysis was performed to elucidate the chemical composition and the interaction at the interface between Ag and SiO$_2$ [6,38,39]. All binding energies were referenced to the C 1s line at 285.1 eV from carbon, and the spectrum deconvolutions were handled with the XPS Peak Fitting Program. The X-ray photoelectron spectroscopy for SiO$_2$@Ag nanocomposite spheres substrates are displayed in Figure 3b–e. The Ag 3d region in Figure 3c is shown as fitted with two components, by a doublet Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ due to the spin-orbit coupling. The spectrum was well fitted with the typical Ag 3d doublet at the binding energies of 368.1 and 374.1 eV with the spin-orbit splitting of 6 eV. In addition, there is no other minor peak or trace of any other peaks, which reveals that the surface of Ag atoms does not oxidize and these analyses confirm the existence of metallic Ag° particles over the SiO$_2$ NSs surface. We obtained a silicon dioxide signal at the binding energy of Si 2p at 103.2 eV in Figure 3d and this signal was fitted into a Gaussian curve. The fitted peak is assigned to a combination of O–Si+Si–O–Si bonds, which is in good accordance with the O 1s spectrum (Figure 3e). The deconvoluted peaks of the O 1s spectrum show the four Gaussian curves at binding energies of 530.0, 532.4, 533.5 and 534.5 eV; they are attributed to PVP, O–Si, Si–O–Si and O–C bonds, respectively. These results are in very good agreement with the XRD spectrum, with a suppression of peak intensity of amorphous SiO$_2$ NPs in as obtained SiO$_2$@Ag core-shell NPs. Hence, XPS analysis confirms the successful formation of SiO$_2$@Ag core-shell NPs.

To understand these optoelectronic features for SiO$_2$@Ag, the LSPR investigations were handled by UV–visible tests [27,40]. UV–visible absorption spectra of SiO$_2$ and three kinds of SiO$_2$@Ag are demonstrated in Figure 3f. The spectrum measured for bare silica powder was featureless (curve S0). However, upon the deposition of silver, the UV–visible spectrums of S1 to S3 show an adsorption peak at 451, 477 and 432 nm, due to Mie plasmon resonance excitation from the silver nanoparticles. In particular, the two red shifts, one is from 432, 451 to 477 nm; another is from 535 nm to S2’s absorption peak in the near-infrared region, and broadening width of the three main absorption peaks in UV–visible spectra were observed while the dimensions of Ag NPs were grown.

To verify the SERS activity of SiO$_2$@Ag NPs, the SiO$_2$@Ag was spin-coated on the silicon wafer; the associated SEM images are provided in Figure 4. Obviously, Ag nanoparticles in Figure 4a are sparse, while in Figure 4c they are uniformly scattered on the surface
of SiO$_2$ spheres. The difference is that in Figure 4b the Ag nanoparticles are large and sparse and some are even connected into islands. These results are consistent with TEM results, further indicating that the prepared SiO$_2$@Ag nanospheres are in line with the expected simulation design.

**Figure 4.** SEM images of SiO$_2$@Ag nanosphere substrate with 3 different samples: (a) S1, (b) S2, and (c) S3; and the corresponding magnification enlarged by 6 times (d) S1, (e) S2, and (f) S3.

As shown in Figure 5, the water contact angle of S2 is basically 0, indicating that it is hydrophilic, which is the same as S1; while the water contact angle of S3 is about 27 degrees, showing a certain degree of hydrophobicity. These results suggest that R6G in the aqueous solution after evaporating solvent is more distributed on the bottom in S1 and S2, and more on the surface rather than the bottom in S3.

**Figure 5.** Wettability of the SiO$_2$@Ag composite-nanospheres substrates: (a) S2, and (b) S3.

SERS on R6G with the SiO$_2$@Ag composite-nanospheres substrates were carried at 532 nm excitation wavelength. Figure 6a shows the Raman peaks of $10^{-8}$ M R6G spin-coated on the substrate S1, S2, S3, and Figure 6b shows the peak intensity of 0.01M R6G spin-coated on the silicon wafer. Figure 6c shows that the SERS spectra of R6G at different concentrations ranging from $10^{-10}$ to $10^{-6}$ M with the volume of 20 µL, and Raman peaks at 609, 768, 1361, 1510, 1640 cm$^{-1}$ are clearly observed $[23,41]$. The spectra reveal that an R6G concentration as low as $10^{-8}$ M can still exhibit observable signals. The SERS enhancement factors (EF) for R6G on the SiO$_2$@Ag composite-microsphere substrates can be calculated $[23]$ according to Equation (2).

$$EF = \frac{I_{SERS}/C_{SERS}}{I_{RS}/C_{RS}}$$  (2)
Correspondingly, EF was calculated within the same area of the laser spot. Meanwhile, the corresponding EF values are calculated to be about $0.81 \times 10^7$, $1.43 \times 10^7$, $2.41 \times 10^7$ for the vibrational peak at $1361 \text{ cm}^{-1}$. These results indicated that the synthesized SiO$_2$@Ag composite nanospheres were effective and ultrasensitive when used as a SERS substrate for detection. Furthermore, the experimental results are in good agreement with the simulation results considering that the actual number and spacing of Ag NPs prepared are weaker than the ideal state in the simulation. It should be noted that there are some irregular Ag NPs of experimentally prepared S2, hot spots between such Ag NPs causing electromagnetic enhancement, but these structures are simplified into a smooth block without these hot spots in the simulation model. Therefore, it causes a slight mismatch between the experimental and simulated values.

The good conformity and reproducibility of the SERS signal are also essential for as-prepared SiO$_2$@Ag SERS substrates. In this work, the SERS enhancement distributed on the surface was measured by randomly collecting the SERS signal intensity from 10 different batches of SiO$_2$@Ag nanocomposite spheres substrates. Figure 6d shows the intensity distribution of the peaks at $611 \text{ cm}^{-1}$ of the R6G with a concentration of $10^{-6} \text{ M}$ collected on 10 different batches of SiO$_2$@Ag substrates; the blue line shows the average intensities. The relative standard deviation (RSD) value of the peaks at $611 \text{ cm}^{-1}$ is 0.03, indicating that intensities of the SERS spectra with little fluctuations around the average intensity are almost similar. The deviation required by actual SERS measurement was less than 0.2 [42], and the SiO$_2$@Ag base prepared in this paper could meet the needs of practical applications. Therefore, the SiO$_2$@Ag SERS substrates with ultrahigh activity and reproducibility have potential ability in practical applications.

By comparing and analyzing the calculated results with the experimental results, it is found that due to the shielding effect of the upper hemisphere, the reagents in the lower hemisphere were ineffective. Therefore, if the hydrophobic surface could be designed
during the experiment, not only could the amounts of reagents be saved, but the SERS performance could also be improved.

4. Conclusions

In summary, this work simulated the three-dimensional electromagnetic enhancement distribution of SiO$_2$@Ag composite microspheres, revealing SiO$_2$@Ag hemisphere’s electric field electrostatic shielding effect. The simulation results illustrated that the surface electromagnetic enhancement distribution of SiO$_2$@Ag nanocomposite spheres could be tuned by altering the number of Ag NPs coated on the surface of the dielectric Oxide nanospheres. Additionally, the upper hemispherical shielding effect is caused by the LSPR of a large number of Ag NPs, which does not depend on the core materials. In order to verify the calculation results, SiO$_2$@Ag composite nanospheres were synthesized and the SERS performance of SiO$_2$@Ag composite nanospheres substrate was studied. The experimental results are in good agreement with the simulated ones, although there is a slight mismatch between the experimental and simulated values in S2; this is because there are some irregular Ag NPs in the experiment, and the hot spots between these Ag NPs lead to electromagnetic enhancement, but in the simulation model these structures are simplified to a light slider, without these hot spots. When the Ag NPs distribution state is S3, the SiO$_2$@Ag nanocomposite-spheres substrate has the best SERS performance, with an EF value of $2.41 \times 10^7$. By comparing and analyzing the calculated results with the experimental results, it is found that the obtained SiO$_2$@Ag nanocomposite spheres substrates have high sensitivity, uniformity, reproducibility and therefore they have huge potentials for qualitative and quantitative analytical detection. However, due to the hemispherical shielding effect, the probe molecules falling below the SiO$_2$@Ag lose their effect and cause weak Raman signals. In order to further improve SERS performance and save reagent consumption, the SERS base can be designed as a hydrophobic surface, and this model can be extended to other Oxide@Ag nanocomposite spheres substrates.

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