

Environmental modification of self-assembled plasmonic core-shell cluster (silica-gold nanoparticles) for surface enhanced Raman scattering (SERS)

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Abstract: We fabricated a 3-dimensional core-shell structure of Silica-Gold Nanoparticles and tested it as a substrate for Surface Enhanced Raman scattering (SERS). The environment of the colloidal solution was modified through pH variations to optimize the stability of the solution. Transmission Electron Microscopy (TEM) images show the structure of the cluster and the resonances were investigated through UV-Vis spectroscopy. Zeta Potential value was also measured to further verify the stability. The core-shell structure was used as a substrate and its subsequent Raman spectra were analyzed.

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References and links

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1. Introduction

Complex composites of a core shell system have sparked a lot of interest in recent years within the scientific community. The interest shown towards this complex composite is due to its wide range of applications in various fields such as catalysis, colloidal stability, sensors and nanolasers [1]. Core - shell system takes advantage of the scattering response of a cluster of spherical metallic nanoparticles (NPs) demonstrating a strong magnetic dipole moment. The composite medium that is formed from the excitation of localized surface plasmon (LSP) in metallic NPs exhibits large dispersive effective permittivity. It may have a stronger Mie resonance of a wavelength larger than the LSP resonance. The lowest order of Mie resonance is associated with a magnetic dipole. These randomly arranged spheres can induce a dispersive isotropic effective permeability and is a key feature of the recent interest. There are various ways to fabricate the core-shell system. Generally, this structure is fabricated on plain substrates by a top-down approach using techniques such as focused-ion beam milling or electron-beam lithography. By using these techniques, the fabricated structures are essentially planar (2-D) thin films that are generally unsuitable for complex (3-D) fabrication. These fabricated methods have two peculiarities; periodic arrangement that constitutes a deterministic system and the metal atoms that may be arbitrarily closed spaced leading to a high filling fraction. Alternatively, bottom-up self-assembly technique provides a versatile and low cost route to the construction of complex 3-D materials. The fabricated materials consist of randomly arranged meta atoms thus yielding a smaller filling fraction. In this study, a silica core and the gold shell structure were synthesized using a bottom-up self-assembly technique [2].

Silica nanoparticles are often selected as the core material since they are stable, chemically inert, resistant to coagulation, neutral to redox reaction and transparent in the visible region. Meanwhile, metallic nanoparticles such as the shell structure have a fast nonlinear optical polarizability and a strong optical resonance. This characteristic is associated with Plasmon frequency where for a core shell structure; it can be adjusted over a wide range of spectrum [3]. Even though the Surface Plasmon Resonance (SPR) can be observed in all conducting materials, only gold and silver exhibit its SPR in the visible region [4]. Therefore, due to the tunable Plasmon resonance and chemical inertness, gold is always preferred as shell making material.

However, most applications depend on the plasmonic resonances with an electric dipole character; this does not yield the full potential of the core-shell system. The core-shell spheres when excited produces magnetic dipole in the far field resulting from the oscillating electric dipoles 180° out of phase in both spheres of the system. This magnetic response is the key factor in several applications particularly surfaced enhanced Raman scattering (SERS) that uses complex shaped plasmonic structures [5]. The development of SERS in the 1970's had become a stepping-stone and represented a great advancement in the field of Raman spectroscopy since the fundamental weakness of the Raman signal had been addressed and amplified.

SERS manipulates the localized SPR to give out an amplified electromagnetic field. It can be enhanced through electromagnetic or chemical enhancement routes. In the electromagnetic route, the result is enhanced due to the excitation of surface plasmons by the light source while in the chemical route the charge transfer mechanism is primarily employed. The mechanism involves a resonant of the excitation wavelength with the metal-molecule charge transfer electronic states [6,7]. SERS has vast applications in analytes detection, cancer therapy and spectroelectrochemistry. There are a few factors that can be considered in order to obtain optimum enhanced signal such as enhancing substrate and excitation source. The enhancing substrate is fabricated from plasmonic materials that can have different shapes and sizes with different enhancing factors. In this study, the core shell structure is used as the enhancing substrate. To optimize shelf life and the stability of the core-shell structure, the pH

of the environment is modified with HCl and NaOH and the subsequent Raman signal is investigated.

2. Experimental section

2.1 Core-shell structure assembly

The core - shell structure was assembled using electrostatic forces [5]. Silica sphere was first synthesized using Stöber method with a mean diameter of 333 nm and gold nanoparticles (AuNps) were prepared using Turkevich method with a mean diameter of 20nm. To assemble the core structure, Silica surface was modified using a solution of N-[3-(trimethoxysilyl)propyl]ethylenediamine which would yield a net positive charge while the AuNps exhibits a net negative charge from the citrate capping molecule. Solution of functionalized silica was then added to AuNPs under rigorous stirring and changes from deep red to blue could be observed.

2.2 Effect of pH on the stability of core-shell clusters and evaluation of SERS activity

In order to study the pH effect on the stability of the core-shell cluster, the pH of each of the cluster solutions was varied and set to different acidic and basic condition using HCL and NaOH. The pH values of aqueous clusters were set to be 2.12, 2.85, 11.15 and 12.21 with the control sample having a pH of 5.67 (Fig. 1). The pH-modified clusters were then left to age (90 days). The electronic absorption spectra of the clusters were acquired using UV-Vis spectrometer (Cary 50) within the range of 300 to 800 nm for immediate and aged samples. To investigate the SERS activity of the samples, a solution of 1,2-bis(4-pyridyl)ethylene (BPE) was used as a probe analyte. A few drops of solution that contained core-shell clusters were deposited on a substrate and allowed to dry in a desiccator overnight. It was then coated with BPE solution and left to dry again. SERS spectra were obtained at the excitation laser of a 532nm and acquired using Xplora Microraman spectrometer by Horiba Scientific.

3. Results and discussion

Figure 1 shows the TEM images of the as-synthesis SiO₂-Au core shell structure. It consists of dielectric silica spheres with radii of 130 ± 10 nm and decorated by gold nanoparticles with radii of 12.5 ± 10 nm. As can be seen from Fig. 1, self-assembly process allows fabrication of core-shell clusters with sufficient numbers of gold nanoparticles attached to the silica sphere. The structure of the clusters is said to exhibit artificial magnetism based on the model proposed by Simovski for magnetic polarizability. The model states that resonances arising from densely packed metallic NPs exhibit strong Mie-resonances that are directly related to the magnetic dipole moment of the sphere. Therefore, the larger number of metallic nanoparticles per one silica core the stronger its electromagnetic response. In the case of sparsely spaced metallic nanoparticles, local plasmon resonances (LPR) dominates [2, 8].

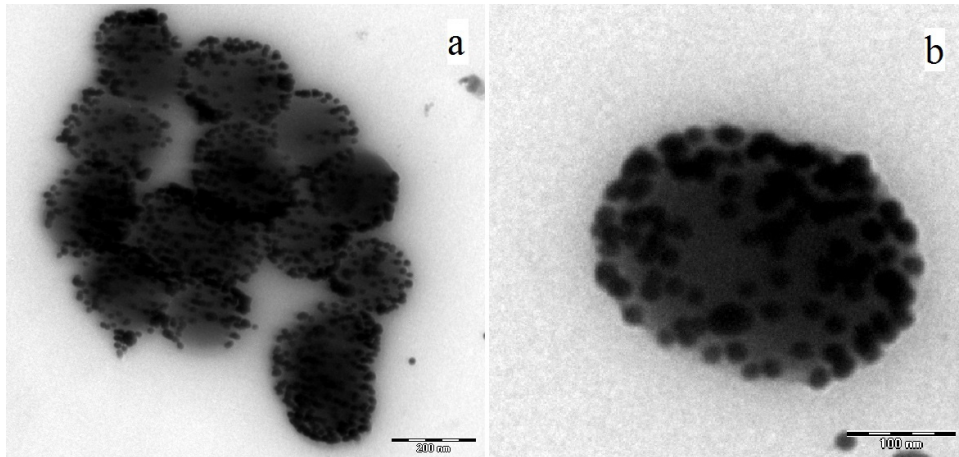


Fig. 1. TEM images of SiO₂-Au core-shell clusters: (a) Random arrangement of core-shell clusters (b) Single core shell structure.

The UV-vis absorption spectra of the core-shell clusters for immediate pH modified samples are displayed in Fig. 2 where the absorption peaks at about 690 nm. These resonances are slightly red-shifted compared to the resonance of the core-shell clusters by Muhlig et. al. [5] is due to the difference in core size [9]. A second peak at the wavelength of SPR of single gold nanoparticles also appeared. This peak is caused by gold nanoparticles that do not cover the dielectric silica due to the excess of gold nanoparticles in the fabrication process and left in solution. The measured resonance, which is strongly red-shifted compared to the isolated gold nanoparticles, can be related to a magnetic dipole moment.

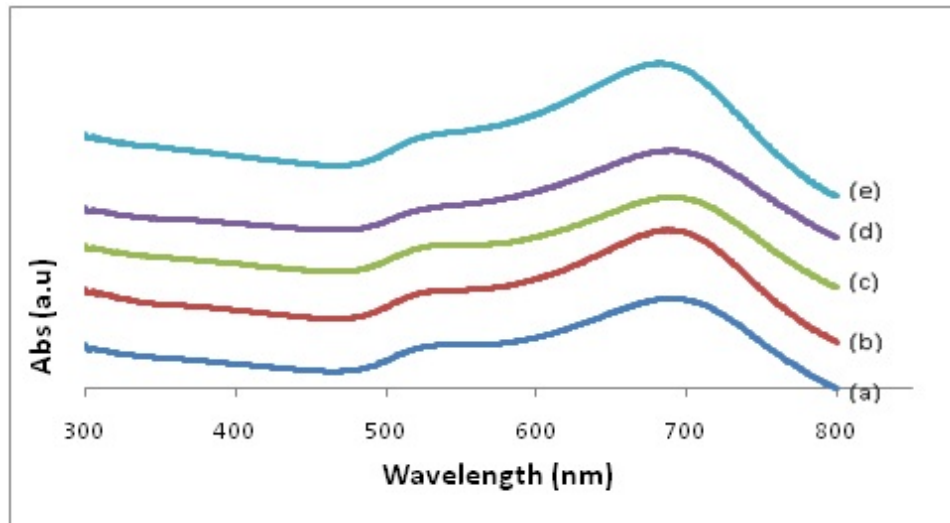


Fig. 2. Absorption spectra of the core-shell clusters for immediate samples at different pH:(a) 2.12 (b) 2.85 (c) 5.67 (d) 11.15 and (e) 12.21.

The absorption profiles for this sample either in base or acidic environment are relatively similar. Changing of pH does not affect its optical properties. Figure 3 shows the absorption spectra of the core-shell clusters for aged samples at different pH. Samples in basic environment show strong absorption spectra while samples in acidic environments show no-absorbance at all. This is due to the high decrease of stability for acidic samples, which makes them become transparent. Meanwhile, the stability of the basic samples remains high and does

not affect their absorption properties. Table 1 shows the zeta potential of the core-shell clusters for aged samples at different pH. Basic samples (pH 11.15 and 12.21) possess the highest zeta potential values (>35), thus confirming the high stability of aged core-shell clusters in basic environments, whilst acid samples possess low zeta potential values and are less stable. These results are in consistent with the UV-Vis results as shown in Fig. 3.

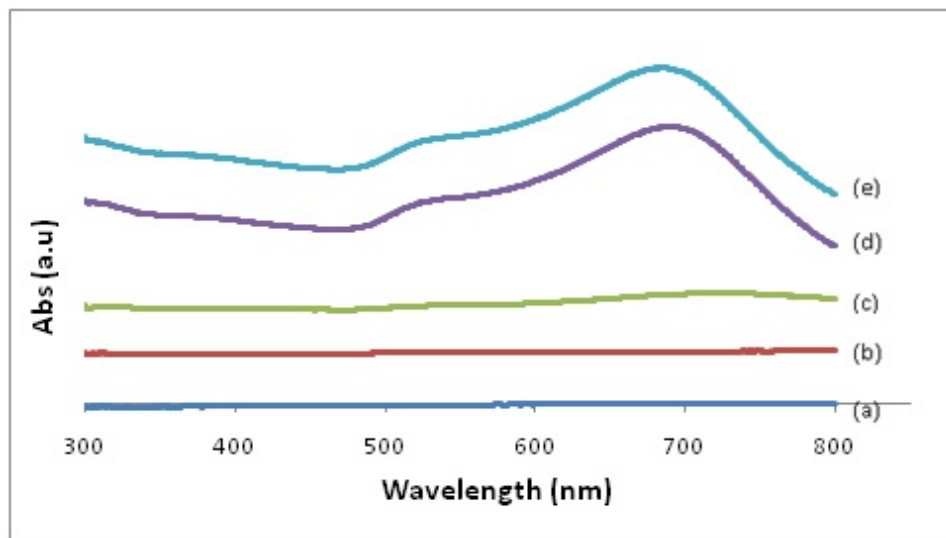


Fig. 3. Absorption spectra of the core-shell clusters for aged samples at different pH: (a) 2.12 (b) 2.85 (c) 5.67 (d) 11.15 and (e) 12.21.

Table 1. Zeta Potential for aged samples of core-shell clusters at different pH values

Sample	pH	Zeta Potential (mV) (Aged)
A	2.12	18.3
B	2.85	17.2
C (control)	5.67	-21.1
D	11.15	-35.4
E	12.21	-45.0

The effect of pH in the SERS experiments using core-shell clusters as the enhancing substrate was evaluated using 1,2-bis (4-pyridyl)ethylene (BPE). Figure 4 displays the spectra of core-shell structure at different pH values. Significant peaks are denoted as modes of (1) to (7). It can be seen that there are variation of intensities for all samples with the lowest one is from acidic samples. Aged acid samples are less stable as compared to basic samples. Its zeta potential values are significantly lower compared to their counterparts. As a result, aged acid samples have barely plasmon resonance (Fig. 3). Thus, the signal on these samples is due to Raman scattering from BPE molecules. At pH 11.15 and 12.21, the intensities are relatively higher than its acidic counterpart. Nevertheless, the highest intensity for BPE is recorded from the control sample that is slightly acidic (pH 5.67). There is also a variation in terms of intensity ratio for modes (1) and (2) in comparison with others works [10, 11]. In this study, the intensity enhancement for mode (1) is higher compared to mode (2) peak ($I_1 > I_2$) which is likely due to the difference in the incubation time since the samples are aged before it was tested [12].

The 995 cm^{-1} band is assigned to the ring-breathing mode of BPE pyridine indicates the vibrational movement of the pyridil nitrogen atom. This band is shifted by 25.3 cm^{-1} and 22.3

cm^{-1} for samples A and B respectively. Meanwhile, the band at 1595cm^{-1} is assigned to the C-N stretching mode of the pyridyl ring. This includes the movement of the pyridyl nitrogen atoms that is blue shifted by 40cm^{-1} . The correlation between these two peaks are directly associated with the vibrational motion of the pyridyl nitrogen. This relationship can be an indication that the pyridyl nitrogen atom is the bridge for the interaction between gold from the core-shell structure surface and BPE molecule [11].

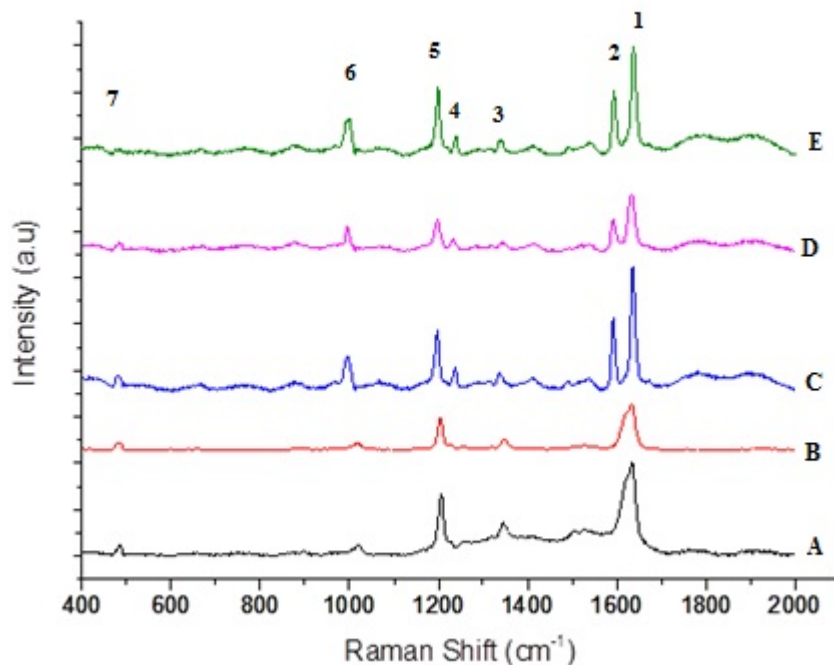


Fig. 4. SERS spectra of BPE on the core-shell substrates at different pH values (a) 2.12; (b) 2.85; (c) 5.67; (d) 11.15; and (e) 12.21.

On the contrary, there are no obvious shifting occurs in other samples with the exception of 1351cm^{-1} band for sample C. This band is assigned to the C-H in-plane bending mode of the pyridyl ring and C-C stretching vibration which red shifted by 13cm^{-1} . Overall, the shift occurred might be due to the geometry of the substrate since the environment's pH will only have an effect on the intensity [13]. Interestingly, acidic samples show significant Raman shift while basic samples shift slightly. In the acidic environment, most of the bands are blue shifted within the range of 26cm^{-1} compared to their counterparts [14]. However, band at 1351cm^{-1} is slightly red shifted while band at 1595cm^{-1} has disappeared for sample A and B. It is most likely that the band has been blue shifted and merged with 1635cm^{-1} band considering that a broad peak is observed within that region. Therefore, this indicates that the surrounding medium plays very important role towards the interaction of electromagnetic radiation with silica-gold nanostructures.

4. Conclusion

Core-shell clusters have been successfully synthesized. UV-Vis spectra show strongly red-shifted resonance due to the magnetic dipole moment. The pH modification on the colloidal solution affects the stability of the samples. Basic samples are highly stable and gave

relatively higher Raman intensities in comparison with acidic samples. However, the maximum Raman signal was recorded from the control sample which has acidic environment (pH5.67) suggests that even though stability can be achieved, which significantly prolongs the storing and shelf life; especially in the sensing application, it has little effect in contributing towards the overall enhancement. Therefore, in order to get optimum stability while having the maximum enhancement, different pH values can be manipulated and the local surface plasmon resonance can be further fine-tuned.

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