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Surface enhanced Raman scattering studies of silver-gold normal and inverted core-shell nanostructures on their efficiency of detecting molecules

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Abstract

The intense significance of biological molecules in our everyday lives has prompted the research into the analysis, identification and quantification of these molecules. Recently, surface-enhanced Raman scattering (SERS) study is identified as one of the effective techniques to detect and quantify such bio-molecules, as these processes are indispensable in order to use them in biological applications. Such detection of molecules by SERS depends predominantly upon SERS active metal substrates such as the typical colloidal silver-gold nanostructures. However, identifying and fabricating suitable metal nanostructures for detecting such biomolecules is an essential need to implement them for practical applications particularly in extensive physiological environments. Herein, we report the synthesis of Ag-Au normal and inverted core-shell nanostructures and investigation of their plasmonic properties to detect drug molecules such as methylene blue and methyl orange using the surface enhanced Raman scattering technique. Our investigation promises for an easy reproduction of biocompatible silver-gold bimetallic core-shell nanostructures that possess excellent chemical stability which can be ideal candidates for a wide range of biomedical applications.

1. Introduction

Surface-enhanced Raman scattering (SERS) has become one of the effective emerging spectroscopic tools to explore different biological entities owing to its excellent sensitivity and molecular detection competences [1]. It is reported that, in SERS, the intensity of the Raman signal that comes from a molecule gets enhanced by many orders of magnitude when the molecules adsorbed to the surface of metallic nanostructures exhibiting atomic scale coarseness [2]. The mechanism of SERS mainly involves the enhancement of electromagnetic field and chemical signals associated with the molecules [3]. Therefore, mostly these molecules are coupled with metallic nanoparticles owing to their excellent surface plasmonic (SP) properties [4]. In the quest of searching such suitable metallic nanostructures for SERS applications, the nanostructures of silver (Ag) and gold (Au) are found to be potential candidates due to their enhanced optical and electronic properties exhibiting distinct localized surface plasmon resonances (LSPR) bands in both UV and visible region of the EM spectrum

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[5]. Consequently, most of the SERS studies have been carried out by using Ag or Au nanostructures [5]. However, though enhanced Raman signals can be obtained from silver nanostructures, they are not desired for the *in vivo* investigations in biological systems. On the other hand, gold nanostructures are widely preferred for the *in vivo* studies, but they show only average SERS effects [3]. Therefore, it would be appropriate to combine silver and gold as a bimetallic system such as alloy or core/shell to make use of their physicochemical properties to probe biomolecules through SERS studies. However, as aforementioned, the silver nanoparticles (Ag NPs) are not preferred as much as gold nanoparticles (Au NPs) are preferred though the plasmonic properties are relatively good in Ag NPs compared to Au NPs. Therefore, choosing a suitable bimetallic system is crucial that depending upon their application for which the system is intended. Studies show that the Ag-Au alloy like structure may cause adverse effects when it establishes interactions with the biological system as Ag exists on the surface of the alloy particles [6, 7]. Whereas, in core/shell like structure, it is possible to determine which metal (either silver or gold) should interact with biological system by making appropriate Ag-Au normal or inverted core/shell structures. It is also possible to widely tune their plasmonic properties by varying the thickness of core or shell layer. The plasmonic response of the system is important as it determines which range of wavelength, either ultra violet (UV) or visible or infra red (IR) should be used as a probing wavelength while studying the biological systems. It is more viable to use visible light for the general biological studies and IR wavelength in the case of studying deeper tissues [8].

Hence, we have synthesized Ag-Au normal and inverted core/shell bimetallic nanostructures and studied their plamonic properties by using UV-visible spectrometer. Also we studied their surface enhanced Raman scattering properties on its efficacy of detecting drug molecules such as methylene blue (MB) and methyl orange (MO) by using Raman spectroscopic technique. The formation of Ag-Au core/shell structure and their SERS mechanism are discussed with suitable schematics in the following sections.

2. Experiment

The typical chemical reduction method was employed for the synthesis of Ag-Au normal and inverted core-shell nanostructures.

2.1. Synthesis of Ag_{core}/Au_{shell} nanostructures

In the synthesis process of Ag_{core}/Au_{shell} nanoparticles, 0.5 mM of silver nitrate was taken in 20 mL of 0.1 M cetyltrimethylammonium bromide (CTAB) solution and stirred well for half an hour at room temperature to obtain a homogenous mixture. To this, 20 mL of 0.2 M sodium borohydride (SBH) solution was added drop wise. The color transformation from transparent to yellow indicated the formation silver nanoparticles. Then this silver nanoparticle solution was heated to 90 ºC and 0.3 M of trisodium citrate (TSC) was directly added to the solution and stirred well for 10 minutes. Subsequently, 20 mL of 1 mM gold chloride solution was added drop wise in the above solution. The color transformation from yellow to lilac color indicated the formation of Ag_{core}/Au_{shell} nanoparticles. The process is illustrated in figure 1.
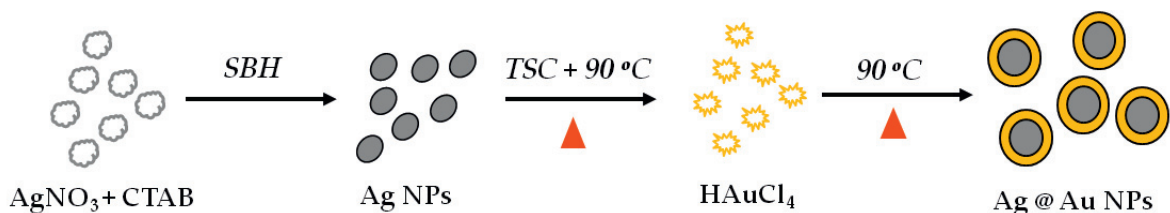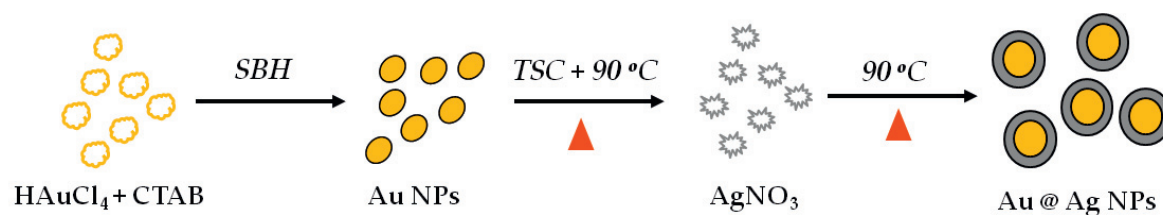

Figure 1. Synthesis process of Ag_{core}/Au_{shell} nanoparticles

2.2. Synthesis of Au_{core}/Ag_{shell} nanostructures

In the synthesis process of Au_{core}/Ag_{shell} nanoparticles, 0.5 mM of gold chloride was taken in 20 mL of 0.1 M CTAB solution and stirred well for half an hour at room temperature to obtain a homogenous mixture. To this, 20 mL of 0.3 M SBH solution was added drop wise. The color transformation from transparent to wine red indicated the formation gold nanoparticles. Then this gold nanoparticle solution was heated to 90 ºC and 0.2 M of TSC was directly added to the solution and stirred well for 10 minutes. Subsequently, 20 mL of 1 mM silver nitrate solution was added drop wise in the above

solution. The color transformation from wine red to orange indicated the formation of Au_{core}/Ag_{shell} nanoparticles. The process is illustrated in figure 2.
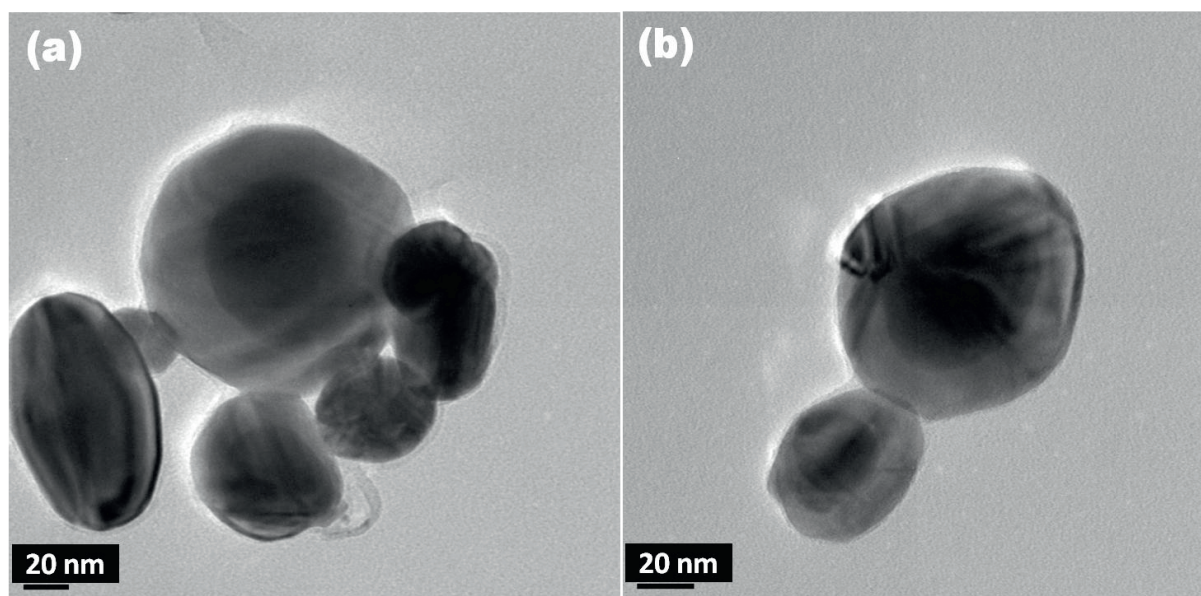

Figure 2. Synthesis process of Au_{core}/Ag_{shell} nanoparticles

2.3. SERS substrate preparations

The substrate which contains the molecules to be studied and the core/shell nanostructures is called as SERS substrate. To prepare the substrate, 5 ml of 1mM methylene blue (MB) and methyl orange (MO) stock solution was prepared and few drops (~2 µL) from this stock solution was added to few micro litres (4 µL) of core/shell nanoparticle solution separately in a glass substrate. Then the Helium-Neon laser (with following parameters: excitation wavelength - 635 nm, spot size - around 600 nm in diameter, laser power - 0.6 mW) was focused on the sample surface and exposed for 30 seconds and eventually the SERS spectra were recorded.

3. Results and discussions

The formed Ag-Au normal and inverted core/shell nanostructures were confirmed by using high resolution transmission electron microscopy technique and the images are shown in Fig. 3 (a) –(b) and Fig. 4 (a) – (b) respectively. The synthesis formulation, as reported in this study, was itself designed in such a way to facilitate the formation of core/shell structuring of Ag-Au.

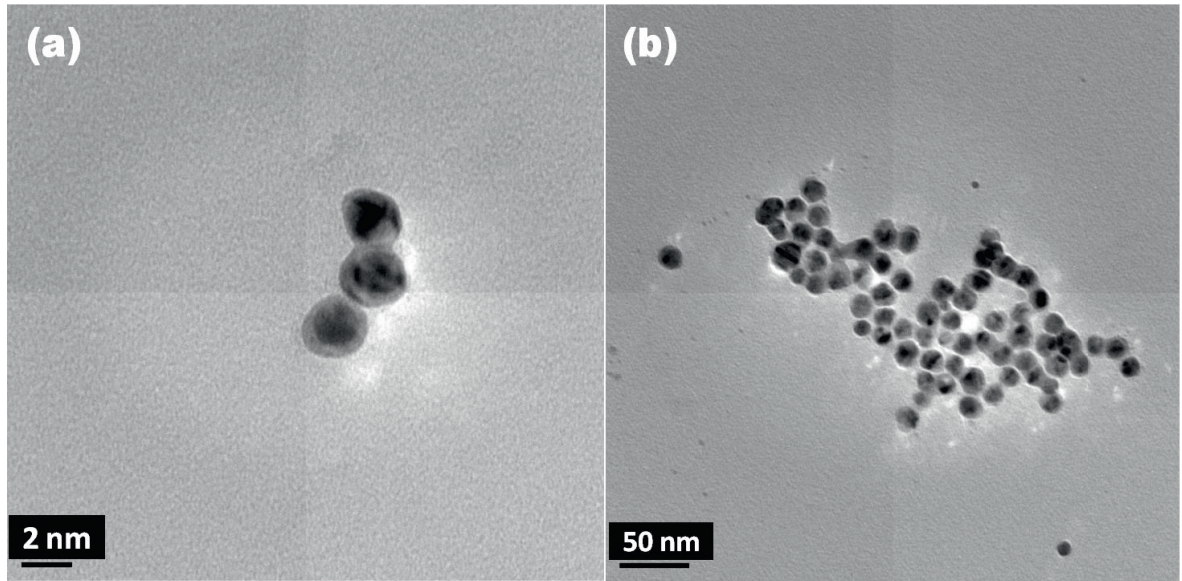*Figure 3(a) – (b). HRTEM images of Ag_{core}/Au_{shell} nanoparticles*

Figure 4(a) – (b). HRTEM images of Au$_{core}$/Ag$_{shell}$ nanoparticles

In the synthesis process, the formed core (Ag/Au) nanoparticles acted as host and became kinetically active to reduce the arriving Ag$^+$ or Au^{3+} ions onto the host particles to construct the core-shell structure [9]. The formation of Au$_{core}$/Ag$_{shell}$ is the ideal as the reduction of Ag$^+$/Ag^0 is lower than that of Au^{3+}/Au^0. On the other hand, during the formation of Ag$_{core}$/Au$_{shell}$, the reduction rate of Au^{3+} might be increased than that of the galvanic renormalment rate in the reaction [10]. Mechanistically, the oxidation resistance of the formed Ag core was probably increased and limited the typical oxidation of Ag^0 in the presence of Au^{3+} ions because of its diffusion resistance and charge-transfer may be got increased in the reaction during the formation of Ag$_{core}$/Au$_{shell}$ nanostructures [11]. Furthermore, it was also possible due to the hydrophobic interaction of CTAB with Ag^0 core which inhibited the electron transfer from Ag^0 to Au^{3+} and facilitated the formation of stable Ag$_{core}$/Au$_{shell}$ nanoparticles [12].
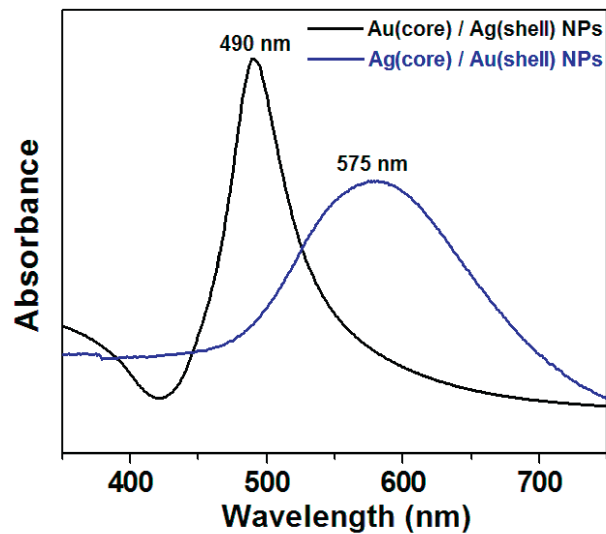

Figure 5. Plasmonic band of Ag-Au normal and inverted core-shell nanoparticles

The plasmonic profile of the synthesized Ag-Au normal and inverted core/shell nanoparticles was studied using UV-visible absorption spectrometer and the results are shown in figure 5. The SPR band of Ag_{core}/Au_{shell} and Au_{core}/Ag_{shell} nanoparticles was observed at 575 nm and 490 nm, respectively. The typical SPR band of gold and silver NPs lies at around 520 and 410 nm, respectively[13]. It is known that the collective oscillation of the surface electrons in the metals is known as surface plasmons (SP) and their disnormalments against the static positive charges causes the polarization in the nanoparticles [14]. Therefore, the absorption and scattering of the incident light by the nanoparticles are depending upon the primary parameters such as size, shape, inhabited dielectric medium and chemical composition [15]. Accordingly, the observed shift in the surface plasmon band was essentially attributing to the contribution of their inter-band transitions to the dielectric functions of the two metals [16]. Therefore the evolution of the plasmonic band Ag-Au normal and inverted core/shell nanoparticles can be estimated from the polarizability of the two metals. The appearance of single plasmonic band in each spectrum (fig. 5) clearly confirmed that the core metal perfectly covered by their respective shell metal without leaving any monometallic elements in the solution. Further, the observed shift in the absorption spectrum of bimetallic Ag-Au core-shell nanoparticles clearly indicated the influence of the metal one over another on their plasmonic properties. The observed plasmonic band showed that the fabricated core-shell systems can be effectively used for SERS applications.
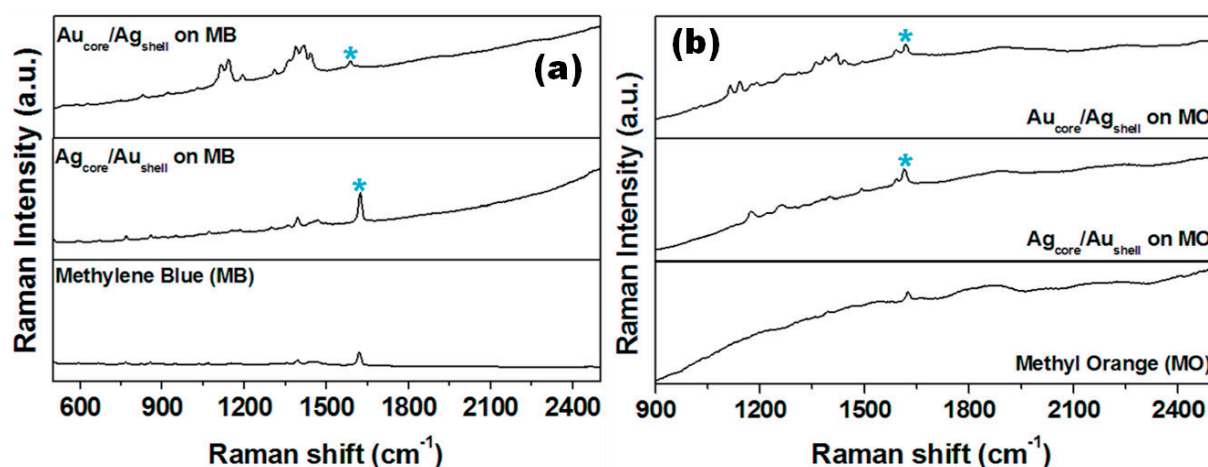

Figure 6(a)-(b). SERS effect of Ag-Au normal and inverted core-shell nanoparticles on MB and MO molecules

SERS studies have been extensively applied for wide range of applications in biological sciences since its discovery in 1974[17]. Especially, the nanoscale noble metals, typically silver and gold are widely used due to their potent interactions with visible light through the resonance with surface plasmons (SP) of the particles [18]. It is known that the SERS is governed by EM field and associated chemical environment of the samples to be studied. The EM mechanism mainly involves the interaction of the electric field produced by the surface plasmons with the charge transition of the molecules adsorbed on the surface of the metal nanoparticles, whereas the chemical mechanism involves the generation of signals by establishing appropriate orbital-level coupling between the molecules and nanoparticles. This coupling essentially transfers the charge that results in a resonant with applied Raman frequency [19] that essentially enhances the scattering effect of probe molecules.

As aforementioned in the 'Experiment' section, the SERS properties of the synthesized Ag-Au normal and inverted core-shell nanoparticles were studied by Raman spectroscopic technique. Both the core/shell structures were studied for their efficacy to detect methylene blue and methyl orange molecules separately and the results are shown in figure 6 (a) - (b). It was observed from the results that the Au_{core}/Ag_{shell} system showed relatively enhanced detection capabilities of MB and MO molecules compared to Ag_{core}/Au_{shell} system through its enhanced (SP) properties. The improved effect of Au_{core}/Ag_{shell} system can be explained as follows. It is known that the gold atoms possess a strong electronic effect on the silver atoms through charge transfer interactions [20, 21]. These interactions in Au_{core}/Ag_{shell} system can be described on account of their electro-negativity values of both metals. It is known that the Au atoms are more electro-negative than the Ag atoms and therefore Au atoms will get electrons from the Ag shell and show pronounced plasmonic properties [22]. Further, the Fermi energy level of Au (about -4.6 eV) is relatively lower than Ag (about -5.0 eV), therefore it is obvious that the charge will be transferred from Ag to Au [10].

However, despite the Au_{core}/Ag_{shell} system showed all the characteristic peaks of the probed molecules, the major characteristic peak of both MB and MO molecule (marked with asterisk symbol) was well pronounced in the SERS spectrum when the Au_{core}/Ag_{shell} system was used to probe the molecules. Therefore it may be presumed that, as in the case of using or detecting MO and MB, the Au_{core}/Ag_{shell} can be used merely to detect the presence of probe molecules, whereas Ag_{core}/Au_{shell} can be used for detailed study of the probe molecules such as whether the molecule is chemically bound with the biological system which can be studied through observing any Raman shift in the corresponding peak of the chemical bonding. Figure 7 schematically illustrates the SERS results of both Ag-Au normal and inverted core-shell nanoparticles as observed in this study. However, in general, the mechanism of SERS effect still remains a subject of debate [23, 24].
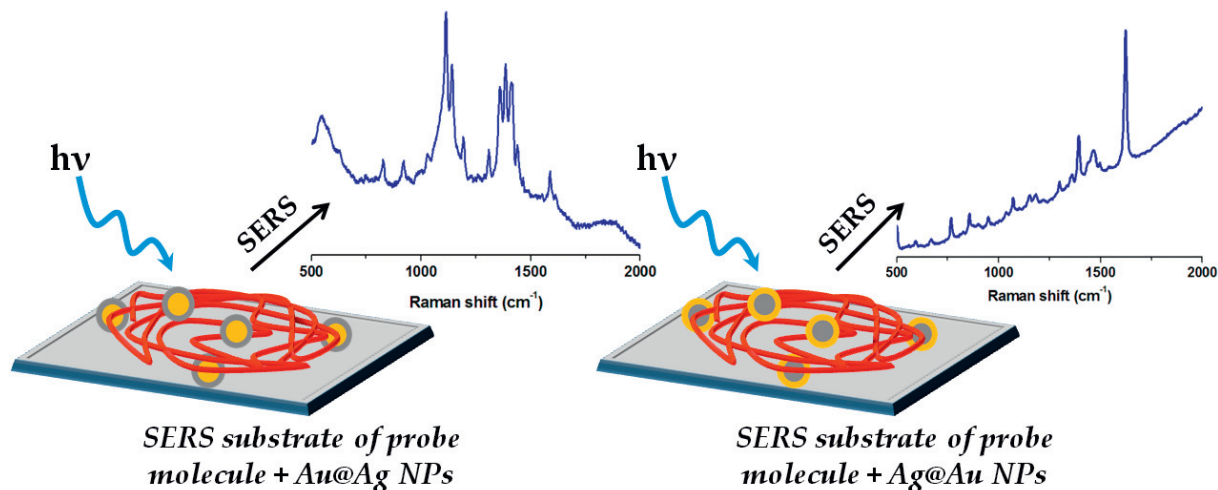

Figure 7. Schematic illustration of SERS effects of Ag-Au normal and inverted core-shell nanoparticles on MB and MO molecules

4. Conclusions

Ag-Au normal and inverted core-shell nanoparticles were synthesized by chemical reduction method. The synthesized nanoparticles were examined for their core-shell structure by high resolution transmission electron microscopy technique. Their plasmonic absorption band was observed by UV-visible spectrometer and it was appeared at 490 and 575 nm for Au_{core}/Ag_{shell} and Ag_{core}/Au_{shell} system respectively. The surface enhanced Raman scattering property of both systems was studied on methylene blue (MB) and methyl orange (MO) by confocal Raman spectroscopy. Among the two systems, the Au_{core}/Ag_{shell} nanoparticles showed an enhanced capability of detecting the probe molecules by displaying all their characteristic molecular signature peaks. However, the Ag_{core}/Au_{shell} nanoparticles clearly displayed the major peaks of the probe molecule with significant intensity. These observations were essentially revealed that former can be used for the detailed study of the probe molecules and the latter can be used to check the presence of probe molecule as in case of MO and MB.

References

[1] (a) Streltsov, S., Oleinikov, V., Ermishov, M., Mochalov, K., Sukhanova, A., Nechipurenko, Y., Grokhovsky, S., Zhuze, A., Pluot, M., Nabiev, I. 2003. Biopolymers *72*, p. 442 (b) Podstawka, E., Ozaki, Y., Proniewicz, L. M. 220. Appl. Spectrosc. 58, p. 570.
[2] Moskovits, M. 1985. ReV. Mod. Phys. 57, p. 783.
[3] Pavan Kumar, G. V., Shruthi, S., Vibha, B., Ashok Reddy, B. A., Tapas K. Kundu, and Chandrabhas Narayana, 2007. J. Phys. Chem. C 111*,* p. 4388.
[4] Henglein, A., Brancewicz, C. 1997. Chem. Mater. 9, p. 2164,
[5] (a) Wilcoxon, J. P., Martin, J. E., Provencio, P. 2001. J. Chem. Phys. 115, p. 998, (b) Liz-Marzan, L. M. 2006. Langmuir 22, p.32.
[6] Cui, Y., Ren, B., Yao, J. L., Gu, R. A., Tian, Z. Q. 2006. J. Phys. Chem. B 110, p. 4002.

[7] Ferrando, R., Jellinek, J., Johnston, R. L., 2007. Chem. Rev. 108, p. 845.

[8] Prodan, E.; Nordlander, P. 2003. Nano Lett. 3, p. 543.

[9] Ghosh, S. K.; Kundu, S.; Mandal, M.; Nath, S.; Pal, T. 2003. J. Nano part Res. 5, p. 577.

[10] Surojit Pande, Sujit Kumar Ghosh, Snigdhamayee Praharaj, Sudipa Panigrahi, Soumen Basu, Subhra Jana, Anjali Pal, Tatsuya Tsukuda, and Tarasankar Pal, 2007. J. Phys. Chem. C 111, p. 10806.

[11] Li, Z. Y., Chen, Y. Y., Palmer, R. E., Wilcoxon, J. P. 2005. Appl. Phys. Lett. 87, p. 243103.

[12] de Cointet, C.; Khatouri, J.; Mostafavi, M.; Belloni, J. 1997. J. Phys. Chem. B 101, p. 3517.

[13] Santanu Pyne, Priyanka Sarkar, Samita Basu, Gobinda Prasad Sahoo, Dipak Kumar Bhui, Harekrishna Bar, Ajay Misra, 2011. J. Nanopart. Res. 13, p. 1759.

[14] Moskovits, M., Sloufova, I. S., Vlckova, B. 2002. J. Chem. Phys.116, p.10435.

[15] Yang, W.-H., Schatz, G. C., and Van Duyne, R. P. 1995. J. Chem. Phys. 103, p. 869

[16] Lazarides, A. A., L. K. K., Jensen, T. R., Schatz, G. C. 2000. J. Mol. Struct.: THEOCHEM 529, p. 59.

[17] Fleischmannn, M., Hendra, P. J., MacQuillan, A. 1974. J. Chem. Phys. Lett. 26, p. 163.

[18] Link, S., Wang, Z. L., El-Sayed, M. A. 1999. J. Phys. Chem. B 103, p. 3529.

[19] Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. 1979. J. Chem. Soc.,Faraday Trans. 75, p. 790,

[20] Jeanmaire, D. L.; Van Duyne, R. P. 1977. J. Electroanal. Chem. 84, p. 1.

[21] Henglein, A. 1993. J. Phys. Chem. B 97, p. 5457.

[22] Pal, T., Sau, T. K., Jana, N. R. 1997. Langmuir 13, p. 1481.

[23] Kneipp, K., Wang, Y., Kneipp, H., Perelman, L. T., Itzkan, I, Dasari, R., Feld, M. S. 1997. Phys. ReV. Lett. 19, p. 1667.

[24] Xu, H. X.; Kall, M. 2002. Phys. ReV. Lett. 89, p. 246802.