



Ag_{core}–Au_{shell} bimetallic nanocomposites: Gold shell thickness dependent study for SERS enhancement



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ABSTRACT

This study reports the synthesized core–shell bimetallic nanocomposites of silver and gold, respectively by varying the thickness of Au shell and studying its role in enhancing the Raman scattering of the molecule. The crystal violet (CV) was chosen as the target analyte molecule and the surface enhanced Raman scattering (SERS) enhancement of this molecule was studied as a function of Au shell thickness. The appropriate thickness of Au nanoshell, deposited on the Ag nanoparticles to obtain the maximum SERS enhancement, was identified and further increase in thickness of Au showed a decrease in intensity of the SERS signals. Among all the fabricated Ag@Au specimens ~30 nm of Ag seed with 8 nm of Au nanoshell showed the maximum enhancement of the SERS signals of CV. The close proximity of discontinuous Au shell acts as SERS hot spots by creating molecular level gap that accommodates the CV molecules responsible for the SERS enhancement up to the order of 10^{13} which is highly reproducible.

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1. Introduction

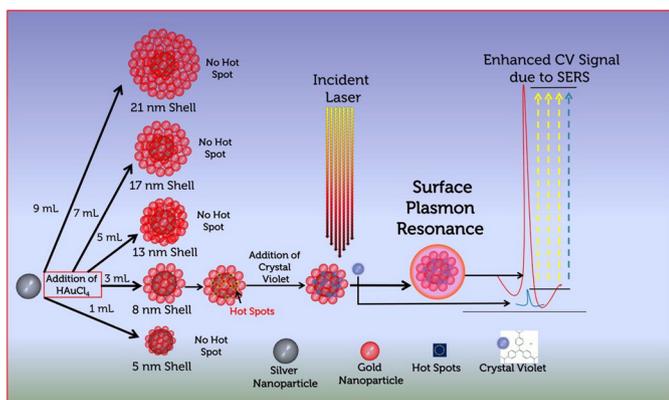
The development of appropriate nanoparticle (NP) and nanocomposite (NC) based substrates as a platform for surface enhanced Raman scattering (SERS) leading to ultrasensitive detection of molecules has been a fascinating area of research [1–5]. It has shown an immense activity with the application and examining variety of strategies with harmonizing performances [1–7]. These efforts include different approaches in the development of new nanomaterials such as top-down methods [8,9] and the self-assembly of NPs in planar platforms [10,11] leading to the development of plasmonic nanosensors [1,7–9, 12–14]. The NPs of different sizes, shapes [7,8], ordered assemblies of metallic structures [11,15,16] and having composition of more than one metal have been explored as SERS substrates [17–20]. The major interest in optimizing the SERS substrates is mainly because of obtaining the spectral information from a single molecule with high specificity and analytical precision [21–23].

Silver and gold NPs are the most frequently used noble metal NPs because they exhibit high SERS effect. When two NPs are adjacent to each other, their interparticle interaction tends to induce plasmon coupling [21], and if any molecule is trapped within this region, shows an extremely high SERS enhancement [22,24]. Therefore, it is necessary to develop a material that combines the SERS enhancement of Ag NPs and the stability of Au NPs and this can be achieved by making bimetallic composite nanostructures which are known to form effective hot spots [25–27].

Few attempts have been made to obtain Ag–Au nanocomposite particles to induce greater SERS enhancement on Au surface of Ag@Au bimetallic NCs. Freeman et al. studied the SERS properties of Ag–clad Au NPs and proposed that deposition of submonolayers of Ag on Au colloid leads to induce aggregation and the SERS enhancement behavior [28]. Rivas et al. have reported the SERS activity of mixed Ag–Au colloids at different excitation wavelengths [29]. It was observed that preparation of Ag@Au mixed colloids allows for the combination of the SERS activities of both metals in a broader interval of the electromagnetic spectrum. Thus, bimetallic NPs are emerging suitable particles for the SERS substrates as compared to their monometallic counterparts. Most recently, we have reported freckled SiO₂@Au NCs as a promising SERS

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Scheme 1. $\text{Ag}_{\text{core}}\text{-Au}_{\text{shell}}$ bimetallic nanoparticles: Gold shell thickness dependent SERS enhancement and role of hot spots in 8 nm shell of gold on silver nanoparticles for excellent Raman signal of crystal violet.

substrate [22]. Thus, in continuation of our interest in synthesis and applications of NPs and NCs [2,3,12–14,22] and the growing endeavors were intended for the synthesis of Ag@Au bimetallic NCs with suitable concentrations of Au in SERS followed by the Au shell thickness dependent study of the SERS enhancement and is reported herein.

2. Experimental

2.1. Chemicals and materials

Silver nitrate (AgNO_3 , 99.9%), tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%), trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99.9%), methanol (CH_3OH , 99.93%), hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, 99.9%), indium tin oxide (ITO) and crystal violet (CV, Dye content, $\geq 90\%$) were procured from Sigma-Aldrich (U.S.A). They all were of analytical reagent grade and used without further purification. Distilled deionized water (DDW) was used throughout the experiments. All the glassware was cleaned with aqua regia and rinsed with distilled deionized water in all the experiments.

2.2. Synthesis of Ag@Au bimetallic nanocomposites

The bimetallic NCs are interesting class of nanomaterials because the optical property of NPs can be tuned by varying the composition of each metal in the bimetallic NCs. The bimetallic Ag@Au NCs were synthesized by the seed mediated growth approach [30] with minor modifications which resulted in substantial quality improvements of the NCs. For synthesis, 250 mL (5.29×10^{-4} M) aqueous solution of AgNO_3 was boiled to which 5 mL (1%) trisodium citrate was added. The solution mixture

was boiled further for 1 h and cooled to room temperature (25°C) with continuous stirring which led to formation of Ag colloid solution. Then 12.5 mL of Ag colloid solution was diluted with 100 mL of DDW. To this diluted Ag colloid solution, 10 mL $\text{NH}_2\text{OH} \cdot \text{HCl}$ (6.25×10^{-3} M), as a reducing agent, was added in different centrifuge tubes along with 1, 3, 5, 7 and 9 mL of HAuCl_4 (4.65×10^{-4} M) solution so as to obtain five solutions with different thickness of Au nanoshells. All these solutions after mixing were stirred for 40 min and further centrifuged twice with DDW, thrice with methanol and finally the bimetallic NCs thus obtained were redispersed in 10 mL methanol for further investigations.

2.3. Characterization techniques

The optical absorption spectra of the bimetallic Ag@Au NCs were recorded on a 500 UV–VIS–NIR spectrophotometer (Varian, USA). The transmission electron microscopy (TEM) images were recorded using a Philips CM 200 FEG microscope equipped with field emission gun with an accelerating voltage of 200 keV. The samples for TEM were prepared by placing a drop of dilute solution of NCs on carbon coated copper grid and subsequent evaporation of the solvent. Raman spectra were recorded using a Renishaw 2000 Raman spectrophotometer (Renishaw Co., UK) equipped with semiconductor laser having the excitation wavelength 532 nm. The laser power used in all these experiments was maintained at ~ 0.2 mW and the laser beam radii were ~ 1.5 μm .

The SERS spectrum of CV from a solution using bimetallic Ag@Au NCs was not suitable for applications such as sensor in molecular or biomolecular recognition due to the fact that movement of particles in a solution restricts the hot spot formation [31,32]. Thus, the CV samples for the Fourier Transformation Raman spectra were prepared by drop casting 20 μL of 10^{-4} M CV solution (0.4 mg in 10 mL) on ITO. For the SERS sample preparation, 1 mL of 10^{-4} M CV solution was thoroughly mixed with 1 mL of bimetallic Ag@Au NC solution and 20 μL from this mixture was drop casted on ITO followed by drying for ~ 10 h in a vacuum desiccator before any analysis. As the objective was to obtain SERS spectra of CV as well as of CV coated with bimetallic Ag@Au NC samples with varying Au shell thickness so the concentration of CV molecule in every sample was kept constant as 10^{-4} M. Thus, the investigations on bimetallic $\text{Ag}_{\text{core}}\text{-Au}_{\text{shell}}$ NCs as a possible SERS candidate were carried out with varying Au shell thickness.

3. Results and discussion

$\text{Ag}_{\text{core}}\text{-Au}_{\text{shell}}$ bimetallic NCs are expected to be SERS-active because both the core and the shell layers are well-known SERS active materials. The bimetallic silver–gold NCs were prepared over Ag seeds by a seed-growth method. Thus, to give an overall illustrative view of the current

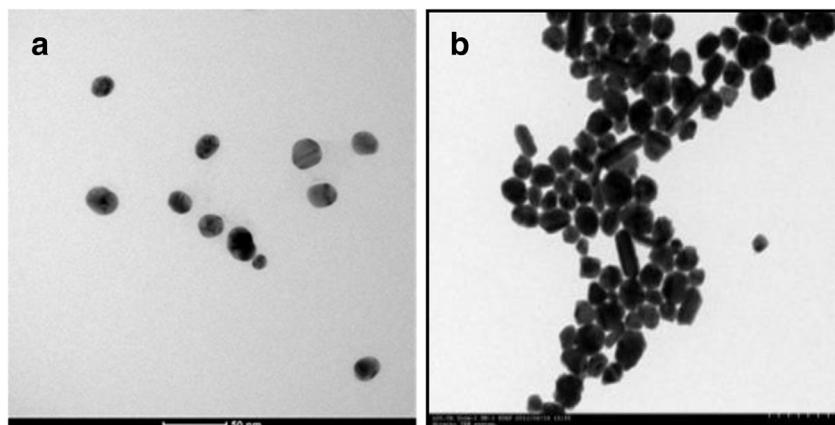


Fig. 1. TEM images of (a) irregular Ag NPs with an average size ~ 30 nm and (b) bimetallic Ag@Au NCs with an average particle size of 38 ± 2 nm.

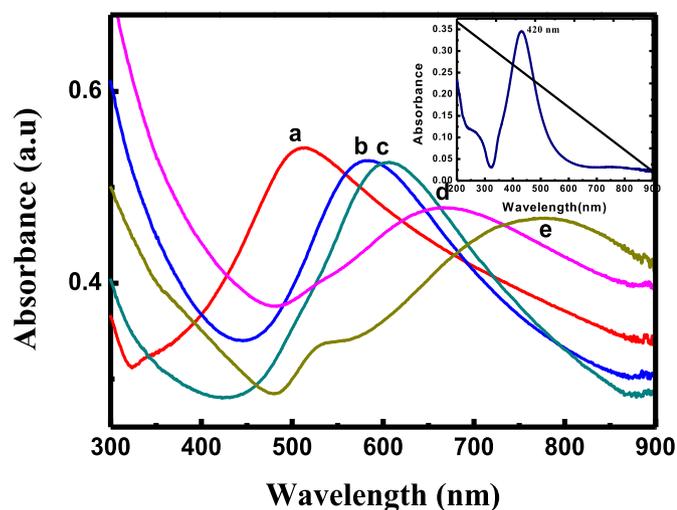


Fig. 2. The surface plasmon resonance of Ag@Au NCs with increasing amounts of 4.65×10^{-4} M Au NPs as: (a) 1 mL (b) 3 mL (c) 5 mL (d) 7 mL and (e) 9 mL. Inset shows the spectrum of Ag NPs.

work, the plausible mechanism and synthesis of Ag@Au NPs of varied Au shell have been presented here as *Scheme 1*. A detailed mechanism in relation to enhancement of SERS signal for the analyte CV has been discussed thoroughly in *Section 3.3*.

3.1. TEM studies of Ag NPs and Ag@Au NCs

Firstly, the size of silver NPs and synthesized bimetallic Ag_{core}-Au_{shell} NCs was studied using transmission electron microscopy. The typical TEM image of Ag NPs as shown in *Fig. 1* (a) which shows that the shapes of Ag NPs were slightly irregular that acts as seeds on which the gold ions reduced to form Au nanoshell and this Ag@Au core shell material acts as a promising SERS substrate. The average size of Ag NPs was calculated to be ~30 nm. *Fig. 1* (b) shows typical TEM images of Ag@Au core-shell NCs where average size of the bimetallic was found to be 38 ± 2 nm. It was confirmed that with the increased Au concentration, the shell thickness also increased.

3.2. SPR studies of Ag NPs and Ag@Au NCs

The Ag@Au NCs having 30 nm silver cores with varying gold shell thickness of 5, 8, 13, 17 and 21 nm were synthesized. The size of Ag@

Au NCs increased as the concentration of Au shell increased which was done by adding increasing amount of HAuCl₄ (cf. *Section 2.2*). The optical properties i.e. surface plasmon resonance (SPR) spectra of the synthesized Ag@Au NCs, having Au shell thickness of 5, 8, 13, 17 and 21 nm, were first recorded by UV–VIS spectrophotometer and their respective spectra are shown in *Fig. 2* (a) to (e). The SPR spectra of the Ag@Au NCs exhibit SPR contribution from both; Ag as well as Au plasmon absorptions. *Fig. 2* (a) to (e) clearly shows that the SPR absorption maxima showed red shift as the thickness of the Au shell increased from 5 to 21 nm on the surface of Ag NPs. All the synthesized NCs have shown absorption close to the excitation laser wavelength of 532 nm. *Fig. 2* clearly demonstrates that with adding increasing amounts of 1 to 9 mL of the HAuCl₄ (4.65×10^{-4} M) solution to Ag NPs solution, the red shift was observed in SPR band of Ag@Au NCs from 506 nm (spectrum a) to ~776 nm (spectrum e). This red shift is attributed to an increase in the gold shell thickness in NCs. In other words, the red shift in peak position is due to a decrease in spacing between the neighboring particles on increasing number density of Au NPs on the surface of Ag core.

Along with the red shift in the peak position of Ag@Au NCs, the broadening of the peaks was also observed (*Fig. 2*). The broadening and shift in SPR peaks are mainly due to the reduction in the interparticle distance that enables plasmon coupling between the NPs as well as plasmon coupling within the Ag@Au core-shell NCs. As a result of plasmon coupling, the electron delocalization increases which caused the red shift and the broadening between closely spaced NPs [33]. The significant changes in the relative intensities of some of the SPR peaks were also observed by varying the concentration of Au shell. Thus, the array of properties and application of Ag@Au NCs could be extremely enhanced if the thickness of Au shell is controlled.

The observed red shift in SPR peaks was further supported by the visual change in the color of the Ag@Au NCs as shown in *Fig. 3*. When an increasing amount of Au NPs (4.65×10^{-4} M) solution from 1 to 9 mL was added to the Ag seed solution the color changed from yellow to purple (*Fig. 3*). The change in color from yellow to purple arises because of the increase in the thickness as well as the coverage of the Au shell around Ag NPs.

3.3. Thickness effect of Au nanoshells on SERS activity

To study the gold nanoshell thickness dependent SERS activity herein, the SERS experiments were performed by adsorbing Ag@Au NCs on CV as an analyte molecule. Thus, the SERS spectra of the CV molecule were recorded using bimetallic Ag@Au NCs and compared with the SERS spectrum of pure CV. *Fig. 4* illustrates the SERS spectra of the CV molecule (10^{-4} M) recorded with bimetallic Ag@Au NCs having

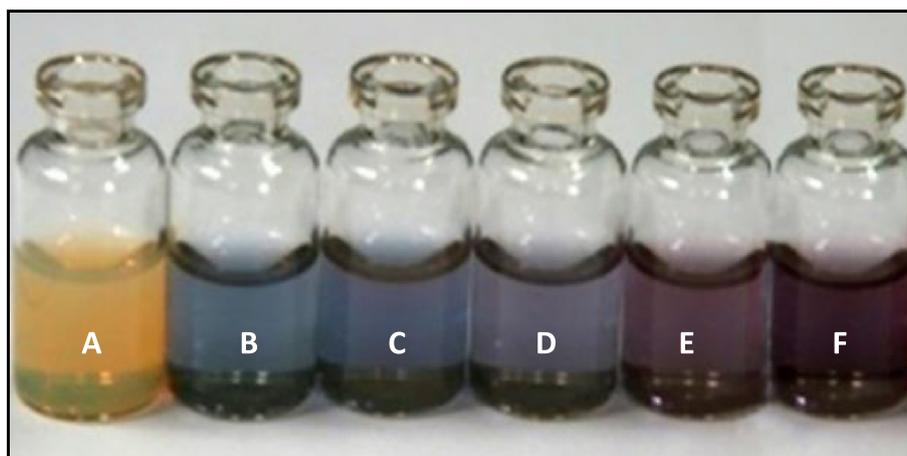


Fig. 3. Visual color change on addition of increasing amount of Au NPs to Ag NPs: (A) only Ag NPs while (B), (C), (D) and (E) are having 1 mL, 3 mL, 5 mL, 7 mL and 9 mL Au NPs respectively in Ag NP seed solution.

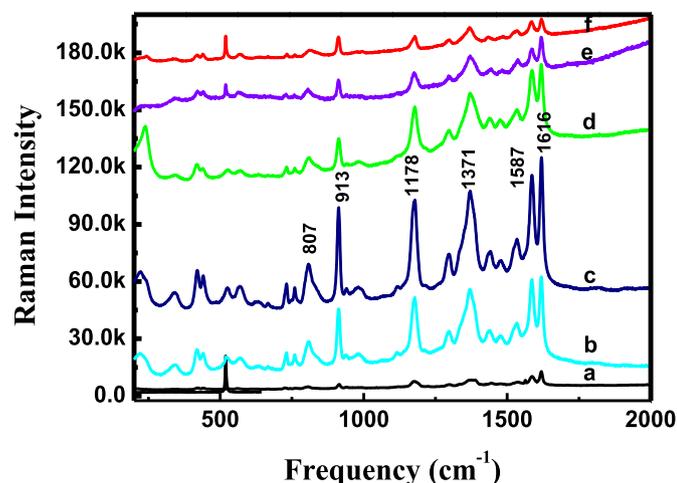


Fig. 4. SERS spectra of (a) CV (10^{-4} M) molecule and CV (10^{-4} M) molecule using Ag@Au NCs with increased Au shell thickness of 5, 8, 13, 17, and 21 nm obtained on addition of the different amounts of HAuCl₄: (b) 1 mL (c) 3 mL (d) 5 mL (e) 7 mL and (f) 9 mL respectively.

different thickness of Au nanoshells as 5, 8, 13, 17 and 21 nm. The different thickness of Au nanoshells on Ag@Au NCs was obtained by adding increasing amounts of 1, 3, 5, 7 and 9 mL of 4.65×10^{-4} M Au NPs. The SERS signal intensity is dependent on the factors like NC surface structure, its coverage with formation of high spatial density of hot spots which led to Raman enhancement i.e. hot spots induced SERS [34,35].

The SERS spectra shown in Fig. 4 clearly show that the SERS intensities increased as the thickness of Au shell was increased up to 8 nm which was obtained by addition of 3 mL (4.65×10^{-4} M) HAuCl₄ solution to Ag seed solution (Fig. 4c). However, in Fig. 4 (d) to (f), there was a decrease in SERS intensities with increased Au shell thickness from 13, 17 to 21 nm that were obtained by addition of 5, 7 to 9 mL of HAuCl₄ solution, respectively. The maximum enhancement of SERS intensity for the CV molecule was observed with Ag@Au NCs having diameter of about 30 nm and 8 nm shell thickness. This enhancement may be due to the incomplete coverage of Ag_{core} by Au shell. As the Au nanoshell grows on the surface of the Ag NPs i.e. Ag_{core}, they generally don't form a continuous shell around the Ag NPs. Rather they form discrete structures with gaps to accommodate a molecule like CV. These molecular level gaps are called as hot spots which lead to very high SERS enhancement.

The SERS signal enhancement may also be due to the fact that the SPR absorption maxima of the bimetallic Ag@Au NCs (572 nm) are close to excitation laser wavelength (532 nm) which gives coupled oscillations responsible for the electromagnetic enhancements. Thus the largest enhancement in the SERS signals of the CV molecule with Ag@Au NCs, having ~30 nm Ag_{core} and 8 nm Au shell was observed (Fig. 4c) and a number of peaks, due to different stretching vibrations in the CV molecule, appeared at 1616 cm^{-1} (vs), 1587 cm^{-1} (vs), 1371 cm^{-1} (s), 1178 cm^{-1} (vs) and 913 cm^{-1} (s) where vs and s

Table 1
Peak position value of the SERS spectra and calculated enhancement factor of CV adsorbed on Ag@Au NCs (when 3 mL of HAuCl₄ solution was added in Ag seed solution).

Peak (cm^{-1})	Assignment	EF (at 532 nm)
1616(vs)	C–C stretching vibrations	10^{13}
1587(vs)	C–C stretching vibrations	10^{10}
1371(s)	C–N stretching vibrations	10^7
1178(vs)	C–H bending vibrations	10^8
913(s)	Ring skeleton vibrations	10^6

vs: (very strong); s: (strong).

represent very strong and strong respectively (Table 1). The increase in the SERS peak intensities got suppressed with increased Au nanoshell thickness from 13, 17 to 21 nm i.e. with the increased concentration of HAuCl₄ in the test solution. This decrease in the SERS intensities happened due to the fact that at a higher Au concentration i.e. at larger Au shell the hot spots are no longer available to accommodate the CV molecule i.e. the surface of Ag NPs was completely covered by the Au nanoshells.

In other words, as additional Au was deposited onto Ag network, high intensity pores were no longer accessible which led to the decrease in signals intensities as shown in Fig. 4 (d) to (f). In addition, the coupled vibrations were also no longer available because the SPR absorption maxima shifted to 776 nm (Fig. 2) which resulted in much less electromagnetic enhancement. The maximum experimental enhancement in SERS signals shown in Fig. 4 (c) was confirmed to be in agreement with the theoretically estimated enhancement i.e. enhancement factor (EF) that was calculated with the help of the electromagnetic enhancement theory (EET) using the following formula [22,32] and is shown in Table 1.

$$EF = \frac{I_{\text{SERS}}}{I_{\text{Norm}}} \times \frac{N_{\text{Bulk}}}{N_{\text{Surf}}}$$

The EF for Raman bands observed in the SERS for the CV molecule was calculated by determining the number of analyte i.e. molecules adsorbed in hot spots on the surface of bimetallic NCs. The value of N_{Surf} i.e. the number of CV molecules adsorbed on Ag@Au NCs under the hot spots area was estimated to be 18×10^9 molecules and the value of N_{Bulk} i.e. the bulk sample of CV molecules without Ag@Au NCs was 25×10^{15} . I_{SERS} and I_{Norm} are the intensities of SERS and normal Raman peaks of a particular band, respectively for which EF was to be calculated.

Table 1 clearly shows an excellent enhancement factor i.e. enhancement in the SERS signals of CV on Ag@Au NCs up to the order of 10^{13} . As observed, the most important factor for optimizing the NCs is the different Au nanoshell concentration i.e. thickness of Au nanoshells. By comparing the theoretical and experimental values, it is evident that there exists a maximum enhancement in SERS signals of the CV with a particular shell concentration and SPR absorption maxima. The discrete islands of Au nanoshell on Ag core act as hot spots by creating molecular level gaps wherein CV molecules are trapped and thus show very high SERS signal enhancement. Thus, the study confirmed that the density of the hot spot Ag@Au core-shell bimetallic NCs can be controlled to make them effective SERS substrates.

4. Conclusion

Controllable Au nanoshells of varying thickness were successfully grown on the Ag NP surfaces to introduce hot spots within the shell and thus shifting the core-shell NC SPR absorption close to the laser excitation wavelength. The SERS intensities of the CV molecules on Ag@Au NCs of varying Au thickness were found to be varied with increasing thickness of Au nanoshells. The hot spots were responsible for the enhancement of the SERS signals of analyte CV. The SERS result confirmed that 30 nm size of the bimetallic Ag@Au NCs with 8 nm Au shell thickness is much better Raman signal amplifier to achieve high enhancement of the order of 10^{13} .

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References

- [1] P. Etchegoin, R.C. Maher, L.F. Cohen, H. Hartigan, R.J.C. Brown, M.J.T. Milton, J.C. Gallop, New limits in ultrasensitive trace detection by surface enhanced Raman scattering (SERS), *Chem. Phys. Lett.* 375 (2003) 84–90.
- [2] P. Khurana, S. Thatai, P. Wang, P. Lihitkar, L. Zhang, Y. Fang, S.K. Kulkarni, Speckled SiO₂@Au core-shell particles as surface enhanced Raman scattering probe, *Plasmonics* 8 (2013) 185–191.
- [3] S. Thatai, P. Khurana, J. Boken, S. Prasad, D. Kumar, Nanoparticles and core-shell nanocomposites: new generation water remediation materials, *Microchem. J.* 116 (2014) 62–76 (and references cited therein).
- [4] M. Fan, G.F.S. Andrade, A.G. Brolo, A review on the fabrication of substrates for surface enhanced Raman spectroscopy and their applications in analytical chemistry, *Anal. Chim. Acta* 693 (2011) 7–25.
- [5] D.-W. Li, W.-L. Zhai, Y.-T. Li, Y.-T. Long, Recent progress in surface enhanced Raman spectroscopy for the detection of environmental pollutants, *Microchim. Acta* 181 (2014) 23–43.
- [6] K.L. Kelly, E. Coronado, L.L. Zhao, G.C. Schatz, The optical properties of metal nanoparticles: the influence of size, shape, and dielectric environment, *J. Phys. Chem. B* 107 (2003) 668–677.
- [7] L.A. Dick, A.D. McFarland, C.L. Haynes, R.P.V. Duyne, Metal film over nanosphere (MFON) electrodes for surface-enhanced Raman spectroscopy (SERS): improvements in surface nanostructure stability and suppression of irreversible loss, *J. Phys. Chem. B* 106 (2002) 853–860.
- [8] J.N. Anker, W.P. Hall, O. Lyandres, N.C. Shah, J. Zhao, R.P. Van Duyne, Biosensing with plasmonic nanosensors, *Nature Mater.* 7 (2008) 442–453.
- [9] M.E. Stewart, C.R. Anderton, L.B. Thompson, J. Maria, S.K. Gray, J.A. Rogers, R.G. Nuzzo, Nanostructured plasmonic sensors, *Chem. Rev.* 108 (2008) 494–521.
- [10] C.J. Addison, A.G. Brolo, Nanoparticle-containing structures as a substrate for surface-enhanced Raman scattering, *Langmuir* 22 (2006) 8696–8702.
- [11] M. Fan, A.G. Brolo, Silver nanoparticles self-assembly as SERS substrates with near single molecule detection limit, *Phys. Chem. Chem. Phys.* 11 (2009) 7381–7389.
- [12] S. Thatai, P. Khurana, S. Prasad, D. Kumar, A new way in nanosensors: gold nanorods for sensing of Fe(III) ions in aqueous media, *Microchim. J.* 113 (2014) 77–82.
- [13] J. Boken, S. Thatai, P. Khurana, S. Prasad, D. Kumar, Highly selective visual monitoring of hazardous fluoride ion in aqueous media using thiobarbituric-capped gold nanoparticles, *Talanta* 132 (2015) 278–284.
- [14] S. Thatai, P. Khurana, S. Prasad, D. Kumar, Plasmonic detection of Cd²⁺ ions using surface-enhanced Raman scattering active core-shell nanocomposite, *Talanta* 134 (2015) 568–575 (and references cited therein).
- [15] J.R. Anema, A.G. Brolo, P. Marthandam, R. Gordon, Enhanced Raman scattering from nanoholes in a copper film, *J. Phys. Chem. C* 112 (2008) 17051–17055.
- [16] Q. Min, M.J.L. Santos, E.M. Girotto, A.G. Brolo, R. Gordon, Localized Raman enhancement from a double-hole nanostructure in a metal film, *J. Phys. Chem. C* 112 (2008) 15098–15101.
- [17] Y. Cui, B. Ren, Jian-L. Yao, Ren-A. Gu, Zhong-Q. Tian, Synthesis of Ag_{core} Au_{shell} bimetallic nanoparticles for immunoassay based on surface-enhanced Raman spectroscopy, *J. Phys. Chem. B* 110 (2006) 4002–4006.
- [18] N.R. Jana, Silver coated gold nanoparticles as new surface enhanced Raman substrate at low analyte concentration, *Analyst* 128 (2003) 954–956.
- [19] G.V.P. Kumar, S. Sruthi, B. Vibha, B.A.A. Reddy, T.K. Kundu, C. Narayana, Potent for surface-enhanced Raman scattering studies of biomolecules, *J. Phys. Chem. C* 111 (2007) 4388–4392.
- [20] A. Shen, L. Chen, W. Xie, J. Hu, A. Zeng, R. Richards, J. Hu, Triplex Au–Ag–C core-shell nanoparticles as a novel Raman label, *Adv. Funct. Mater.* 20 (2010) 969–975.
- [21] E.C.L. Ru, M. Meyer, P.G. Etchegoin, Proof of single-molecule sensitivity in surface enhanced Raman scattering (SERS) by means of a two-analyte technique, *J. Phys. Chem. B* 110 (2006) 1944–1948.
- [22] P. Khurana, S. Thatai, J. Boken, S. Prasad, D. Kumar, Development of promising surface enhanced Raman scattering substrate: freckled SiO₂@Au nanocomposites, *Microchem. J.* 122 (2015) 45–49.
- [23] U.S. Dinish, F.C. Yaw, A. Agarwal, M. Olivo, Development of highly reproducible nanogap SERS substrates: comparative performance analysis and its application for glucose sensing, *Biosens. Bioelectron.* 26 (2011) 1987–1992.
- [24] D.P. Fromm, A. Sundaramurthy, A. Kinkhabwala, P.J. Schuck, G.S. Kino, W.E. Moerner, Exploring the chemical enhancement for surface-enhanced Raman scattering with Au bowtie nanoantennas, *J. Chem. Phys.* 124 (2006) 061101.
- [25] C. Wang, J. Fang, Y. Jin, M. Cheng, Fabrication and surface-enhanced Raman scattering (SERS) of Ag/Au bimetallic films on Si substrates, *Appl. Surf. Sci.* 258 (2011) 1144–1148.
- [26] R.A. Alvarez-Puebla, J.P. Bravo-Vasquez, P. Cheben, D.-X. Xu, P. Waldron, H. Fenniri, SERS-active Ag/Au bimetallic nanoalloys on Si/SiO₂, *J. Colloid Interface Sci.* 333 (2009) 237–241.
- [27] Y. Yang, J. Shi, G. Kawamura, M. Nogami, Preparation of Au–Ag, Ag–Au core-shell bimetallic nanoparticles for surface-enhanced Raman scattering, *Scripta Mater.* 58 (2008) 862–865.
- [28] R.G. Freeman, M.B. Hommer, K.C. Grabar, M.A. Jackson, M.J. Natan, Ag-clad Au nanoparticles: novel aggregation, optical, and surface-enhanced Raman scattering properties, *J. Phys. Chem.* 100 (1996) 718–724.
- [29] L. Rivas, S. Sanchez-Cortes, J.V. Garcia-Ramos, G. Morcillo, Mixed silver/gold colloids: a study of their formation, morphology, and surface-enhanced Raman activity, *Langmuir* 16 (2000) 9722–9728.
- [30] M.S. Shore, J. Wang, A.C. Johnston-Peck, A.L. Oldenburg, J.B. Tracy, Synthesis of Au (core)/Ag(shell) nanoparticles and their conversion to Au/Ag alloy nanoparticles, *Small* 10 (2010) 1–5.
- [31] S.A. Kalele, N.R. Tiwari, S.W. Gosavi, S.K. Kulkarni, Plasmon-assisted photonics at nanoscale, *J. Nanophoton.* 1 (2007) 12507–12526.
- [32] N. Tiwari, M.Y. Liu, S. Kulkarni, Y. Fang, Study of adsorption behavior of aminothiophenols on gold nanorods using surface-enhanced Raman spectroscopy, *J. Nanophoton.* 5 (2011) 053513–053527.
- [33] J. Nam, Y.S. Ha, S. Hwang, W. Lee, J. Song, J. Yoo, S. Kim, pH-responsive gold nanoparticles-in-liposome hybrid nanostructures for enhanced systemic tumor delivery, *Nanoscale* 5 (2013) 10175–10178.
- [34] K.A. Willets, S.M. Stranahan, M.L. Weber, Shedding light on surface-enhanced Raman scattering hot spots through single molecule super-resolution imaging, *J. Phys. Chem. Lett.* 3 (2012) 1286–1294.
- [35] T. Chen, H. Wang, G. Chen, Y. Wang, Y. Feng, W.S. Teo, T. Wu, H. Chen, Hotspot-induced transformation of surface-enhanced Raman scattering fingerprints, *ACS Nano* 4 (2010) 3087–3094.