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Preparation of Au-Ag Alloy Nanoparticles for Surface Enhanced Raman Scattering

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Abstract: Using a laser-based method we study the preparation of Au-Ag alloy nanoparticles for Surface enhanced Raman scattering (SERS). Au and Ag nanoparticles (NPs) were prepared in distilled water by pulse laser ablation using 1064nm wavelength of Nd:YAG laser. Au-Ag alloy NPs were prepared by irradiating the mixture of colloidal Au and Ag NPs with the 532 nm second harmonic wavelength of Nd:YAG laser. The Au NPs, Ag NPs and Au-Ag alloy NPs were characterized by using UV-vis absorption spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction measurements. The Au-Ag alloy NPs were used to fabricate nanostructure substrates for SERS measurement. Raman spectra were measured by a Micro-Raman spectrophotometer (LABRAM HR). Raman scattering enhancement by Plasmon excitation on Au-Ag alloy NPs were investigated.

Keywords: Laser ablation, laser-induced synthesis, Au-Ag alloy nanoparticles, Surface enhanced Raman scattering (SERS).

1. Introduction

In the last ten years, metallic nanoparticles (NPs) have been largely studied because of their light confinement effects at the nanoscale as well as size-and-shape dependent optical properties [1]. Recently, much effort has been devoted to produce bimetallic NPs due to their composition-dependent optical and catalytic properties. Combination of desirable features of mono-metallic NPs and bimetallic NPs is useful to a diverse range of applications related to photonics, catalysis, information storage, chemical/biological sensing, and surface-enhanced Raman scattering (SERS) [2-5]. Au-Ag bimetallic NPs are attractive materials because of their fascinating surface Plasmon resonance absorption (SPR) in the visible spectral region. In Au-Ag bimetallic systems, alloy and core-shell structures often show different optical properties, although the composition of Au and Ag within the nanostructures is the same [6-7]. The SPR absorption peaks, in consequences, the optical properties of core-shell NPs depend not only on the relative composition but also on thickness of the core and

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shell [8-9]. Meanwhile, the SPR absorption peaks of the alloy NPs depend crucially on relative composition of nanoalloys. For example, surface plasmon absorption for Ag-Au alloy NPs can be tuned over a broad range by simply varying the alloy composition. To produce alloy NPs, different physical and chemical methods and combination techniques have been reported to date. For example, Au-Ag alloy nanoparticles were produced by pulsed laser irradiation of bulk alloy metals in water [10], by laser irradiation of mixtures consisting of Au and Ag NPs [11] or by laser irradiation of mixtures of micrometer-sized metal powders NPs[1].

In this work, we report the results on the synthesis of Ag-Au alloy NPs by a two step laser-based method. In the first step, colloidal solutions of Ag and Au NPs were separately produced by pulsed laser ablation (PLA) in distilled water, using the fundamental wavelength (1064 nm) output of a Nd:YAG laser. In the second step, we mixed colloidal Au and Ag NPs at the determined molar ratio and irradiated the colloidal Au-Ag mixture by the second harmonic (532 nm) output of the Nd:YAG to form Au-Ag alloy NPs. By this method one can not need Au-Ag bulk alloys with different compositions that are expensive. Moreover, by the laser based method one can prepare Au-Ag alloy NPs without contamination.

These Au-Ag alloy NPs were used to fabricate nanostructure substrates for SERS measurements. Rohdamine 6G was chosen as a tested analysis to investigate Raman scattering enhancement due to its well defined Raman spectrum. The strong enhancement of the Raman scattering intensity in SERS has been explained by two mechanisms: the electromagnetic and chemical mechanisms [12-14]. According to the electromagnetic mechanism, Raman scattering intensity is enhanced due to the increase of the local electromagnetic field of the adsorbents by the excitation of the surface plasmon resonance. The chemical mechanism is attributed to short distance effects due to the charge transfer between the metal and the adsorbed molecules [12]. The electromagnetic effect is dominant over the chemical effect [15]. The electromagnetic enhancement (EME) depend on the presence of the metal surface's roughness features which is formed in this case by Au-Ag alloy NPs [16].

2.Experimental

Gold and silver NPs were separately prepared by pulse laser ablation of corresponding metal plates (purity of 99.99%), which was placed in the glass vessel filled with 10 mL distilled water. The laser ablation was performed by using the fundamental (1064 nm) of Quanta Ray Pro 230 Nd: YAG pulsed laser (pulse width of 8 ns) operating at 10 Hz. The laser beam was focused by a lens with a focal length of 100 mm.

Using an average laser power density of 15.9W/cm^2 we prepared Ag NPs with exposure time of 7 minutes and Au-NPs with exposure time of 15 minutes.

The mixtures of the colloidal Ag and Au NPs were placed into a glass cell and irradiated by nonfocused laser beam with the second harmonic wavelength (532 nm). The absorption spectra of colloidal NPs were recorded by a Shimadzu UV-2450 spectrometer in the 300–800 nm range. The morphology of nanoparticles was studied by transmission electron microscopy (JEM 1010-JEOL). The size of nanoparticles was determined by ImagieJ 1.46r of Wayne Rasband (Nationnal institues of

Heath, USA). The size distribution was obtained by measuring the diameter of more than 500 particles and using Origin 8.5.1 software. The concentration of metal nanoparticles in water was determined by F-AAS technique using a Perkin Elmer AAS-3300 atomic absorption spectroscopy system.

SERS substrate was prepared by dropping metal nanoparticle colloids on a copper wafer. A Rohdamine 6G solution of 10^{-4} M concentration in ethanol was used as a test analyte to study SERS spectrum. Few droplets of the analyte solution were dropped and left to dry on the SERS substrate. R6G molecules will be absorbed onto the metal nanoparticles of the SERS substrate after some minutes. SERS spectra were observed by Micro-Raman spectrophotometer (LabRAM HR).

3. Results and discussion

3.1. Preparation of Ag, Au NPs and Au-Ag alloy NPs

The absorption spectrum of colloidal Ag-NPs is shown in Fig.1.The characteristic SPR absorption peak of Ag-NPs appeared at 395 nm. The XRD patterns of Ag NPs (Fig.2) show 3 peaks at positions $2\theta = 38.1^o$; 44.4^o and 64.4^o corresponding to diffraction from the (111), (200) and (220) planes respectively of a face centered cubic structure of Ag crystal. TEM image and size distribution of Ag-NPs in distilled water are presented in Fig.3. The analysis of size distribution shows that the diameters of Ag-NPs range from 3.7 to 67.6 nm with average diameter of 17.8nm. The concentration of Ag-NPs in water measured by Atomic absorption spectroscopy (AAS) is 32.04 mg/l.

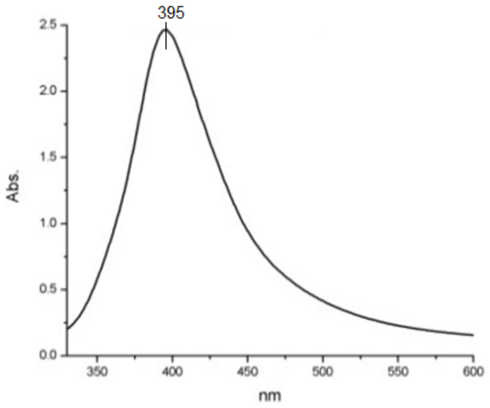

Fig.1. UV-Vis absorption spectrum of colloidal Ag NPs.

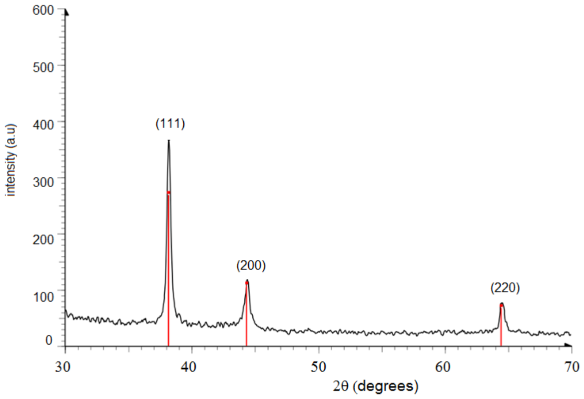

Fig.2. XRD pattern of Ag NPs.

The UV-Vis absorption spectrum of colloidal Au-NPs (Fig.4) exhibits a characteristic peak of Au-NPs at about 521nm. The crystalline structure of Au-NPs was also examined by XRD measurement. The XRD patterns of Au NPs show 3 peaks as Ag-NPs, this is due to close lattice constants of Au and Ag (namely, Au: 4.0786 Å and Ag: 4.0862 Å). The TEM image and size distribution (Fig.5) show Au-NPs are rather spherical in shape with average diameter of 17.1 nm and size ranging from 2.8 to 47.7 nm. The AAS measurement showed the concentration of Au-NPs in water of ca. 97.4 mg/l.

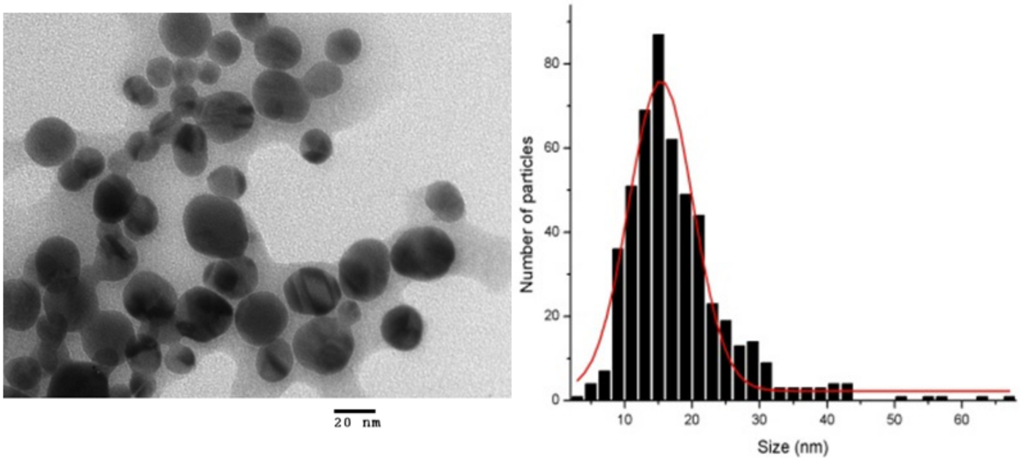

Fig.3. TEM image and size distribution of Ag NPs prepared in distilled water.

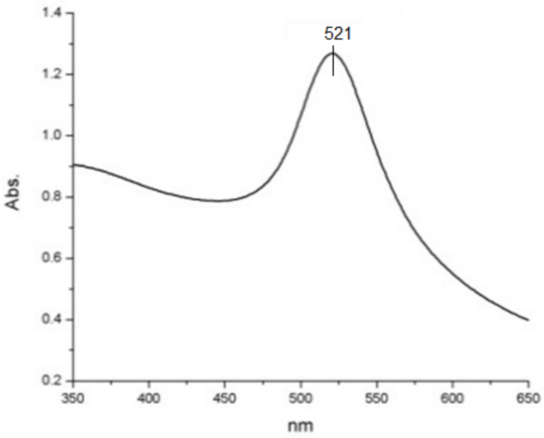

Fig.4. UV-Vis absorption spectrum of colloidal Au NPs.

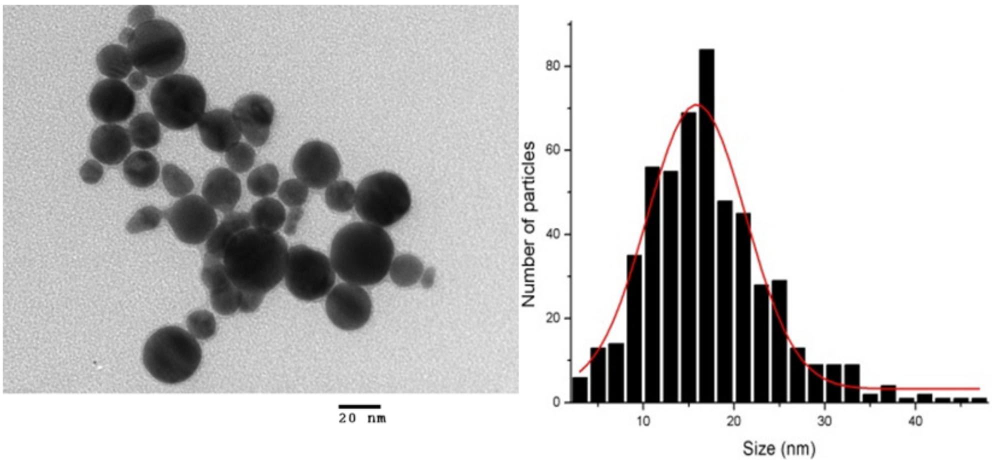

Fig.5. TEM image and size distribution of Au NPs prepared in distilled water.

A mixture of the colloidal Au and Ag-NPs in distilled water was prepared with 1: 1 volume ratio and irradiated by 532 nm wavelength of Nd:YAG laser. The average power density of laser was set at 1.6W/cm^2. Fig. 6 illustrates the absorption spectra of the colloidal Au-Ag mixture in distilled water with different irradiation times.

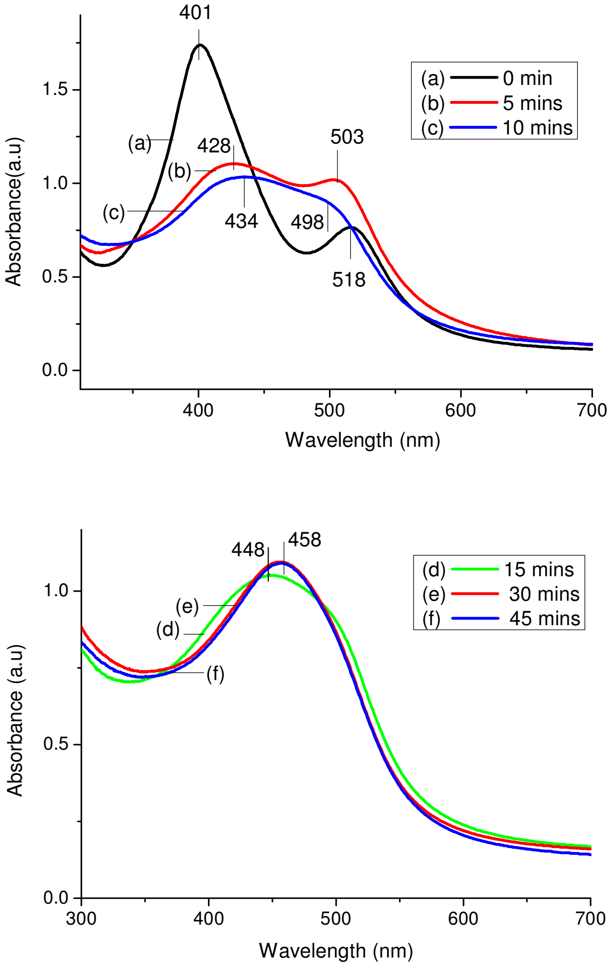

Fig.6. Absorption spectra of a mixture of Au and Ag NPs in distilled water with different irradiation times.

Before exposure to laser light, two distinct absorbance maxima at 401 and 518 nm, (Fig.6.a) corresponding to SPR absorption peaks of Ag and Au NPs respectively, indicate isolated Ag and Au-NPs in the mixture. After the colloidal Au-Ag mixtures were exposed to laser irradiation, the absorption spectra changed. In the first 5 minutes of the exposure, the SPR absorption peak of Ag-NPs tends to shift to longer wavelengths, at 428 nm, whereas one of Au-NPs have trend to move to shorter wavelengths, at 503nm (Fig.6.b). After 10 minutes of irradiation, the SPR absorption peak of Au-NPs disappeared and a weak shoulder was observed at about 498nm, while the SPR absorption peak of Ag-

NPs shifted more to longer wavelengths, at 434 nm (Fig.6.c). With an irradiation time of 15 minutes, only one SPR absorption peak appeared at 448 nm (Fig.6.d). This peak shifted to 458 nm and kept almost unchanged when laser irradiation time increased from 30 minutes to 45 minutes (Fig.6.e and Fig.6.f). This result indicates that the irradiated colloidal solutions contained alloy nanoparticles rather than core–shell nanoparticles, or mixtures of monometallic nanoparticles. It is known that a simple mixture of monometallic Au and Ag nanoparticles has two absorption peaks due to the surface plasmon resonance absorption of Au and Ag-NPs. Core-shell nanoparticles would also exhibit two absorption peaks or only one absorption peak of shell component when the shell becomes thick enough. Under irradiation with an intense pulsed laser at 532 nm which is near SPR absorption peak of Au-NPs, the Au-NPs in the mixed colloidal solution were excited and heated to their boiling point [17]. The absorbances of Au and Ag-NPs at 532 nm are 0.81 and 0.23, respectively. So under laser irradiation at 532 nm, Au-NPs will be more efficiently excited than Ag-NPs of the same size. However, the melting point of Ag is lower than Au (Ag: 961.78^{o}C; Au: 1064.18^{o}C). It is possible that Ag nanoparticles reach the meting point at the same time as Au-NPs at 532nm [18-19]. These heated Au and Ag-NPs may be fragmented into smaller nanoparticles by releasing atoms and clusters. The hot released atoms and clusters have a strong tendency to rapidly recombine into Au-Ag alloy particles on a nanosecond time scale [20]. Also, single atoms or small clusters might diffuse to and aggregate on the surface of preexisting nanoparticles.[21]. Since Au and Ag have almost identical lattice constants, mixing of the two metals is a thermodynamically favorable process. Therefore, alloying process may take place easily to form homogeneous Au-Ag alloy particles. With the increase of irradiation time, sintered structure could be formed.

Fig.7 shows a TEM image and the size distribution of Au-Ag alloy NPs in the mixed colloidal solution after an exposure time of 45 minutes. As seen in the image, there are two types of morphology corresponding to formation of nanoparticles that are isolated spherical particles and sintered structure. The spherical NPs have a size ranging from 8.4 to 75.3 nm, their average diameter is of 29.4 nm.

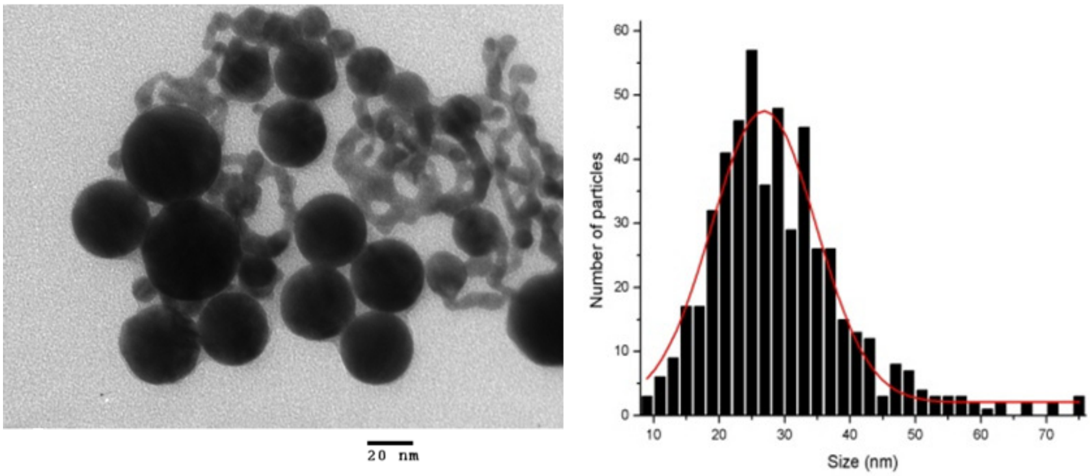

Fig.7. TEM image and size distribution of Au-Ag alloy NPs in distilled water.

3.2. SERS measurement from Au-Ag alloy nanostructure

A layer of Au-Ag alloy NPs was prepared on a copper plate to produce a SERS substrate. In order to examine the Raman enhance effect of the SERS substrates, three types of different samples were prepared: R6G on Cu substrate without Au-Ag alloy NPs (R6G/Cu sample); R6G on Cu substrate with mixture of Au and Ag NPs (R6G/Au/Ag/Cu sample) and R6G on Cu substrate with Au-Ag alloy NPs (R6G/Au-Ag alloy NPs/Cu sample). The spectra measured by Micro-Raman spectrophotometer of these samples are shown in Fig.8. Obtained results show that Raman signal was enhanced strongly by using the SERS substrate. The SERS spectra of R6G are in good agreement with the published results of R6G Raman spectrum. Strong peaks at 1358 cm^{-1}; 1510 cm^{-1} and 1645cm^{-1} are assigned to the C-C stretch. The 613 cm^{-1} peak which is assigned to the C-C-C deformation in-plane vibration was experimentally observed at 612 cm^{-1}. It is explained by the plasmon-generated electric field [22, 23, 24]. The 775 cm^{-1} peak is assigned to the C-H deformation band out-of-plane vibrations. The 1185 cm^{-1} peak belongs to the C-H deformation in-plane vibration. These wave numbers are slightly different from those in the normal Raman spectrum of R6G. It indicates that there is a slight change in the secondary structure of R6G because of the interactions between R6G molecules and Au-Ag alloy NPs [22].

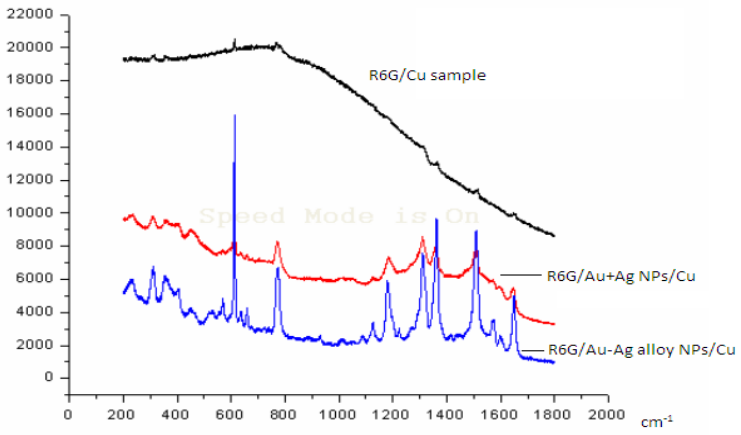

Fig.8. Raman spectra of R6G on SERS substrates.

4. Conclusion

Au and Ag-NPs were prepared in distilled water by pulse laser ablation using 1064nm wavelength. Au-Ag alloy NPs were produced by 532nm wavelength in laser irradiation of a mixture of Au and Ag-NPs in distilled water. SERS substrates were successfully prepared by using Au-Ag alloy NPs and a strong enhancement in Raman scattering spectra was obtained when used the SERS substrates. The obtained results showed that by using laser pulse -based method Au-Ag alloy NPs with different Au/Ag molar ratios as well as alloy NPs of different metals in clean liquids can be produced for SERS applications.

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References

[1] Jin Zhang et al J. Phys. Chem. B 107 (2003) 6920-692

[2] R.Jha, A.K. Sharma, J. Opt. A-Pure Appl. Opt. 11(2009) 045502

[3] A.K.Sharma, B.D.Gupta, Nanotechnology 17 (2006) 124

[4] R.A. Alvarez-Puebla, J.P. Bravo-Vasquez, J. Colloid Interface Sci. 333 (2009) 237 .

[5] E. Hao, S.Y. Li, R.C. Bailey, S.L. Zou, G.C. Schatz, J.T. Hupp, J. Phys. Chem. B 108 (2004) 1224

[6] J.Hodak, A. Henglein, M. Giersig,G. Hartland. J. Phys. Chem. B , 104 (2000) 11708.

[7] J.Abid,;H.Girault, P. Brevet. Chem. Commun. (2001) 829.

[8] A.N.Shipway, E. Katz, I.Willner. ChemPhysChem 1(2000)18.

[9] L.Rivas, S. Sanchez-Cortes, J.V. Garcia-Ramos, G. Morcillo. Langmuir 16(2000) 9722.

[10] Lee.I, Han.S.W, Kim.K. Chem. Commun 1(2001) 782 -1783.

[11] Peng.Z, Spliethoff.B, Walther.T and Kleinermanns.K, J. Phys. Chem. B 110 (2006) 2549- 2554

[12] Alan Campion and Patanjali KambhampatiChem. Soc. Rev. 27 (1998) 241

[13] K.Kneipp, M. Moskovits and H.Kneipp Topics Appl. Phys. 103 (2006) 1-18

[14] A.M.Michaels, M.Nirmal and L.E.Brus J.Phys.Chem B 104 (2000) 11965

[15] N. Félidj, J. Aubard, G. Lévi, J. R. Krenn, M. Salerno, G. Schider, B. Lamprecht, A. Leitner, and F. R. Aussenegg Phys. Rev. B 65(2002) 7

[16] J.I.Gersten J.Chem.Phys.72 (1980) 5779

[17] S. H. Sun, C. B. Murray, D. Weller, L. Folks and A.Moser, Science (1989)287.

[18] D.D.Evanoff, G. Chumanov. J. Phys. Chem. B 108(2004) 3957.

[19] D.D.Evanoff, G. Chumanov. Chem Phys Chem 6 (2005)122.

[20] A.Dawson, P.V Kamat. J. Phys. Chem. B 105 (2001) 960.

[21] F.Mafune, J.Kohno, Y. Takeda, T.Kondow. J. Phys. Chem. B 106 (2002) 8555.

[22] A. Sabur, M. Havel and Y. Gogotsi J. Raman Spectrosc 39 (2008) 61.

[23] T.R.Jensen, M.D.Malinsky, C.L.Haynes, and R.P.Van Duyne J. Phys. Chem. B 104**,** 45(2000) 10549

[24] N.M. B. Perney, F. J. G. de Abajo, J. J. Baumberg, A. Tang, M. C. Netti, M. D. B. Ch lton, and M. E. Zoorob .Phys.Rev.B 76 (2007) 035426