Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Photochemistry and Photobiology A: Chemistry 162 (2004) 625–632
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Photochemical deposition of SERS active silver nanoparticles on silica gel

Subrata Kundu, Madhuri Mandal, Sujit Kumar Ghosh, Tarasankar Pal*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India

Received 27 June 2003; received in revised form 20 September 2003; accepted 1 October 2003

Abstract

Silver nanoparticles with an average size of nearly ∼15 ± 3 nm were deposited onto the commercial silica gel matrix using aqueous solution of silver(I) gelatin complex. Silver(I) gelatin impregnated solid silica gel matrix has been found to produce silver particles with UV-light. The photoproduced silver nanoparticles remained very active for a long time. The surface characterization of the particles with transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDAX) and thermal analysis corroborated the presence of silver nanoparticles on silica surfaces. The resulting silver nanoparticles could easily be leached out from silica gel into an aqueous phase for indirect characterization of the nanoparticles by UV-Vis spectrophotometry. Anchoring of silver nanoparticles on silica gel helped to obtain surface enhanced Raman scattering (SERS) spectra, which was otherwise not possible in solution phase. The solid matrix served as a better catalyst for nitrophenol reduction than the simple silver nanoparticles in aqueous phase.

Keywords: Silica gel; Gelatin; Silver nanoparticle; UV-light; SERS

1. Introduction

Preparation and characterization of metal nanoparticles have been found to be active areas of research because of their potential applications in chemistry, physics, biology, medicine, catalysis and optical devices. These particles having "neglected dimension" bears special properties in many aspects compared to their bulk phase. They find medicinal applications [1], application in catalysis [2] and due to their size and shape dependent optical [3] and electronic properties [4] they are being used in opto-electronic devices [5]. Particularly, semiconductor [6] and noble metal nanoparticles [7,8] have been the areas of research due to their well different physical, chemical and opto-electronic properties. In view of the importance of the surface structure related properties, much effort has been invested in order to create new class of materials through the modification of surface structures.

Metallic nanoparticles, especially silver have attracted maximum attention because they have shown promise in catalysis [2] and surface enhanced Raman scattering (SERS) studies [9]. Incidentally, they have strong optical absorption in visible region. Several workers have demonstrated a large number of routes for the preparation of Ag nanoparticles, for example, wet chemical method [10], photoactivation process [11], γ-radiolysis [12], laser pulse method [13], sonochemical method [14] and so on. It has been a difficult task for always to work with silver nanoparticle in comparison to gold in the nano size regime.

Nowadays, it is a challenge to the scientists to stabilize the metal nanoparticles in solid state/matrix. Different templates, matrixes, LB films, porous aluminates [15], porous carbonate membranes [16], lithographically processed masks [17], micelles [18], different ligands, organic polymers [19] etc. are used to stabilize the metal nanoparticles. In the liquid phase there is a chance of their oxidation, agglomeration and precipitation. So studies have been directed for the improvement of solid matrixes. Recently Cassagneau and Fendler have prepared layer by layer self-assembly of silver nanoparticle capped by graphite oxide nanosheets [20]. Stathatos and Lianos have deposited silver nanoparticle on mesoporous TiO_2 films [21]. Gedanken and co-workers have presented deposition of various nanoparticles such as iron/iron oxide [22], CdS [23], Eu_2O_3 [24] and silver nanoparticle [25] on silica spheres. The silica spheres qualify as hard spherical substrates for the following reasons:

(a) tight size distribution can be achieved over a wider range;

---

* Corresponding author. Tel.: +91-3222-283320;
fax: +91-3222-255303.
E-mail address: tpal@chem.iitkgp.ernet.in (T. Pal).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/S1010-6030(03)00398-8

(b) their surface silanol composition and the extent of hydrogen bonding can be modified by thermal treatment to change their reactivity;
(c) silanol group can form covalent links; and
(d) the isotropic interaction in an aqueous or organic suspension, which helps to form ordered arrays on substrates.

In this report, we have demonstrated the deposition of silver nanoparticles on silica surface via UV-photoactivation technique. Initially, aqueous silver–gelatin complex was impregnated onto silica gel and UV-photoactivation technique was used later on for the generation of the silver nanoparticles on the silica matrix (abbreviated as SNSM). Of all the methods developed for the preparation of metal nanoparticles, the photoactivation technique offers a very simple and reproducible way for the generation of metal particles in the nanometer size regime [11]. The formation of silver nanoparticles were investigated by transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDAX) study, UV-Vis spectroscopy and thermal analysis. The novelty of these particles lies in their SERS activity with small ($\sim 15 \pm 3$ nm) size in the absence of any other added electrolyte [26–29]. So the present work is related with the simple and straight-forward preparation conditions without the use of any harsh reducing agent that might increase the local concentration of the reagent in solution during addition. The procedure required no manipulative skill, hence reproducible [30], unlike the preparation of nanoparticles by the wet chemical method.

2. Experimental

2.1. Reagents

All reagents used were of analytical reagent grade without any further purification. Column chromatography silica gel of ~100 mesh size (SRL, India), gelatin powder (Oxo, London), $AgNO_3$ (Merck, India) and 1,2-dimethyl phenyl isonitrile (DMPNC) (Aldrich) were used as received. Double distilled water was used throughout the experiment.

2.2. Instruments

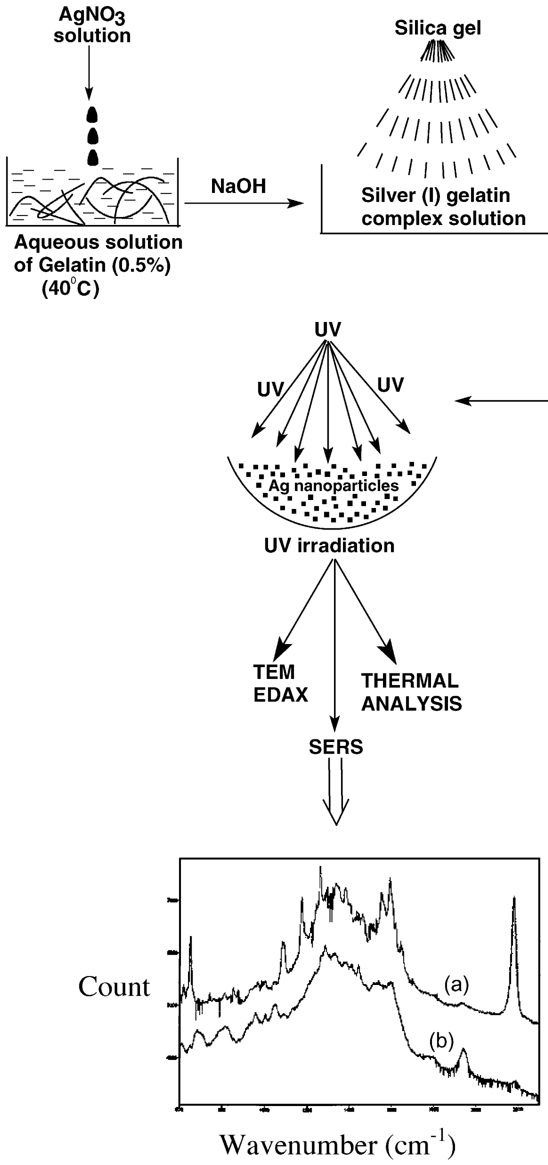
Photoirradiations were carried out with a photo-reactor fitted with ordinary germicidal lamps of wavelength 365 nm (Philips, India). The photo-reactor can produce a flux of 650 lx. The Flux was monitored using a digital Lux meter (Model LX-101), Taiwan. The photo-reactor (intensity of light) was calibrated with an Ophir power meter (NOVA display and 30-A-SH sensor). The number of photons absorbed per unit area of the sample per second from the photo-reactor of 100 lx is 3.03×10^{15}. All UV-Vis absorption spectra were recorded in a Shimadzu (Kyoto, Japan) UV-160 digital spectrophotometer equipped with 1 cm quartz cells. TEM and EDAX analysis were performed with an instrument H-9000 NAR, Hitachi, using accelerating voltage of 300 kV. Very thin epoxy-resin was used to hold the sample powder on 200 mesh copper grid. Thermal analysis was done in Thermal Analyzer, Model DT-40, Shimadzu, Japan. SERS spectra were recorded with a SA Inc. HR-320 spectrograph equipped with Princeton instrument charge coupled device (RE-ICCD) and the measurements were done with Kr laser (200 mW) using 30 nm entrance slit. 1,2-Dimethyl phenyl isonitrile was used as the SERS probe.

2.3. Preparation of silver–gelatin solution and its impregnation in silica gel

The reagent solution was prepared by dissolving 0.5 g gelatin powder (Oxo, London) in 100 ml of warm distilled water (80 °C) with constant stirring which was previously boiled. Then 0.01698 g of solid $AgNO_3$ was added so that the final concentration of $AgNO_3$ in the gelatin solution becomes 10^{-3} mol dm^{-3}. A few drops of 2 mol dm^{-3} sodium hydroxide solution (NaOH) was added to this solution for removing turbidity if appeared in the solution. Then the solution was warmed at 50–60 °C for 5 min and the pH of the solution was adjusted to about 8.0 for all practical purposes [31]. The solution was then cooled to room temperature. Silica gel (used for column chromatography) was added to this solution under stirring condition. Now silver–gelatin complex became homogeneously impregnated over the silica gel surface. The whole mixture appeared like slurry and then turned into a paste. The paste was dried in a vacuum desiccator. The dried mass was all white and remained as such for months together in the dark.

2.4. Evolution of silver particles on silica gel

It has been reported earlier that silver(I) gelatin solution produced and stabilized silver nanoparticles in aqueous phase [32]. Here is the first report of preparation of silver nanoparticles onto the silica matrix by UV-photoirradiation process. Vacuum dried 0.05 g white (unexposed) silver(I) gelatin impregnated sample were mechanically spread almost as monolayer on a flat glass container and was irradiated in the photo-reactor under UV-light of 650 lx for 20 min. The white solid sample turned brownish black due to the deposition of silver onto the silica surface and was stored in the dark in a vacuum desiccator. Longer exposure time did not cause any deterioration/alteration of the size of the silver nanoparticles and the catalytic property did not alter. The presence of Ag nanoparticles on silica gel were characterized by UV-Vis spectrophotometry after extracting the silver particles into aqueous solution. Routine TEM, EDAX studies, thermal analysis were done for characterization of silver nanoparticles and the whole procedure are shown in Scheme 1. In the present case SNSM sample has been tested successfully as a candidate for SERS studies. While tested silica gel or gelatin or both of them together with silver(I) complex did not show SERS activity. Even the



Scheme 1. Schematic presentation of photo-reduction of silver(I) gelatin complex on silica gel surface to study the evolution of silver nanoparticles on silica matrix for SERS study.

aqueous extract of the silver particles obtained from silica matrix showed no SERS activity.

3. Results and discussion

3.1. Binding of silver with gelatin

Gelatin is widely used in photographic industries [33]. On the other hand, gelatin stabilizes small particles very well and it prevents particle coagulation. Aqueous solution of gelatin formed a colourless, 1:1 weak complex with silver(I) in alkaline medium, which has been found to be very important, inexpensive analytical reagent in recent years [32,34]. The interaction of silver(I) with gelatin was considerably influenced by pH. The binding of silver ions with the $-NH_2$ group of gelatin may be as follows:

$$Ag^{+} + H_2N\cdots COOH + OH^{-} \leftrightarrows H_2N\cdots COOAg + H_2O$$

and

$$H_2N\cdots COOAg + OH^{-} \leftrightarrows AgHN\cdots COO^{-} + H_2O$$

alternatively

$$AgHN\cdots COO^{-} + OH^{-} \leftrightarrows [Ag–N\cdots COO]^{-2} + H_2O$$

and

$$[Ag–N\cdots COO]^{-2} + H_2O \leftrightarrows Ag^{+} + OH^{-} + HN^{-}\cdots COO^{-}$$

where the gelatin skeleton is represented by dotted lines. It is probable that the free silver ions are reduced to silver metal in solid gelatin like the latent image formation in photography. The reduction takes place through a series of steps [35]: the photo generation of electron–hole pairs; the reduction of silver cations to atoms by some fraction of the electrons; the subsequent build up of atoms to evolve clusters. Addition of 1 ml of 0.5% gelatin solution can effectively bind with 453 μg of silver(I) ion at pH ~8 and was verified by the expulsion of free silver by dialysis [36] at 30 °C. Mild reducing agents like ascorbic acid, hydrazine, formaldehyde, carbon monoxide and hydrogen sulfide reduced the complex of gelatin stabilized silver(I) solution with an absorption maxima at 415 nm. This process of generation of silver has given birth to a good number of analytical methods [36–41] to detect different reducing agents while present in water and air samples. It has been shown that at a carefully chosen concentration gelatin moiety becomes a good compromise for binding of silver ion as well as stabilization of silver nanoparticles if produced in solution by wet chemical method [10]. This was due to slow reduction of silver(I) gelatin complex by the reducing agents as mentioned. Again, aqueous solution of silver(I) gelatin complex can be easily impregnated onto silica gel matrix where silver remains as silver ion for months together while kept in the dark. The stability of the silver(I) gelatin complex increased while present in a solid matrix unlike the solution of silver(I) gelatin complex. After impregnation of silver(I) gelatin complex and subsequent drying of the silica gel matrix it has been shown that silver nanoparticles deposit onto the silica matrix upon UV-photoirradiation. From BET analysis the pore specific volume and specific surface area of SNSM were calculated as $0.46086439\,\mathrm{cm^3\,g^{-1}}$ and $321.25177 \times 10^4\,\mathrm{cm^2\,g^{-1}}$, respectively. The reduction is like the 'photographic development' process [33] as described above. Due to the opacity of the silica matrix, UV-light could not pass through the solid material and hence longer irradiation time (20 min) was necessary for quantitative evolution of silver nanoparticles on the silica surfaces. However, higher concentrations of silver nitrate deposited silver nanoparticles on the silica gel matrix under UV-irradiation with lower (<20 min) exposure time. Over exposure did not cause any alteration of the surface structure of the nanoparticle aggregates on the solid matrix unlike the aggregates of silver in solution [42]. Evolution of highly aggregated stable spherical silver nanoparticles (diameter ~25–30 nm) were also observed from UV photoactivation of aqueous solution of silver(I)–gelatin complex. In spite of the stability of these aggregates, they were no way better than the SNSM substrates for SERS and catalysis. So we always used SNSM samples.

3.2. Effect of light

The colour of the silver–gelatin complex after impregnated in silica gel was white. After UV-irradiation, it turned blackish brown. Direct sunlight (visible light) and indoor lighting reduced the complex to some extent if kept for long time (~5 days). This effect was much pronounced when the concentration of $AgNO_3$ was very high ($0.1\,\mathrm{mol\,dm^{-3}}$). Therefore, the white solid complex material was stored in a desiccator with carbon paper covering. Under this condition, the material remained stable for months together.

3.3. Stability of SNSM sample

The blackish-brown colour of the complex (after UV-photoirradiation) has been found to remain unchanged for a month together, but its catalytic property decreased a little bit. Therefore, it is better to irradiate the complex once more before it was used as catalyst.

3.4. UV-Vis absorption study

The UV-Vis absorption spectrum (Fig. 1) of the aqueous extract of SNSM sample demonstrates the presence of silver nanoparticles. An amount of 0.05 g of the dry white (unexposed) sample was taken on a flat container and was exposed to UV-light for about 20 min (Scheme 1). Then the exposed silica gel was mixed with 5 ml of water and sonicated for about 15 min. Due to sonication Ag(0) nanoparticles passed into aqueous medium along with gelatin and color of aqueous layer became yellow tinted. UV-Vis absorption spectra of this solution (Fig. 1a) exhibit an intense, broad absorption peak around 435 nm (λ_{max}) due to the surface plasmon excitation of silver nanoparticles and indicates the dispersion of Ag(0) in aqueous gelatin solution. The extracted silver nanoparticles in aqueous medium showed a somewhat broaden band due to aggregation of smaller particles in gelatin moiety. This spectrum was compared with the spectrum of the solution prepared in a similar procedure from the unexposed silica gel impregnated silver(I) gelatin complex (Fig. 1b). The UV-irradiation produced Ag(0) in the solid silica gel matrix. But from the leached out solution obtained from the unexposed silica gel impregnated solid matrix no peak around ~400 nm was observed, hence Ag(0)

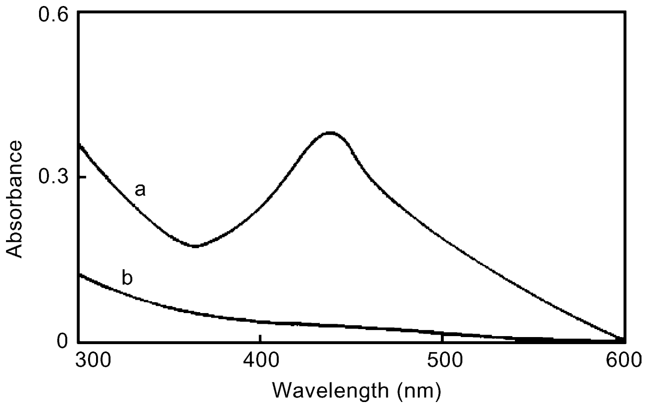


Fig. 1. Absorption spectra of the aqueous solution obtained after sonication of impregnated silica gel (a) after irradiation (plasmon band due to silver nanoparticles at 440 nm) and (b) before irradiation (silver(I) gelatin complex).

was absent. Higher amount of $AgNO_3$ concentration in the silica matrix and subsequent UV-irradiation, of course, darkened the colour of the silica matrix and in that case increased absorbance of the solution owing to the presence of higher amount of silver nanoparticles was noted.

3.5. Energy-dispersive X-ray analysis (EDAX)

The presence of silver, silicon, carbon, sodium and oxygen were examined with EDAX measurement. The EDAX spectrum was also used to obtain a quantitative estimate of the Ag(0) and that authenticated the complete reduction of Ag(I) to Ag(0) upon UV exposure. For the light elements such as oxygen only a rough estimate could be done, because EDAX is a bulk analysis, and oxygen from the silica gel spheres also contributes to the oxygen signal. The silver, silicon and Ag/Si ratio in all samples were identical. The silver content in all samples was about 6.95%. This value is close to the molar ratio of $AgNO_3$/silica gel in the starting solution.

3.6. Electron microscopy studies (TEM)

It has been stated that the colour of Ag–gelatin complex after impregnation in silica gel was white but it turned blackish brown after photoirradiation. The transmission electron micrographs for both the samples (irradiated and unexposed) are shown in Fig. 2a and b, respectively. We observed

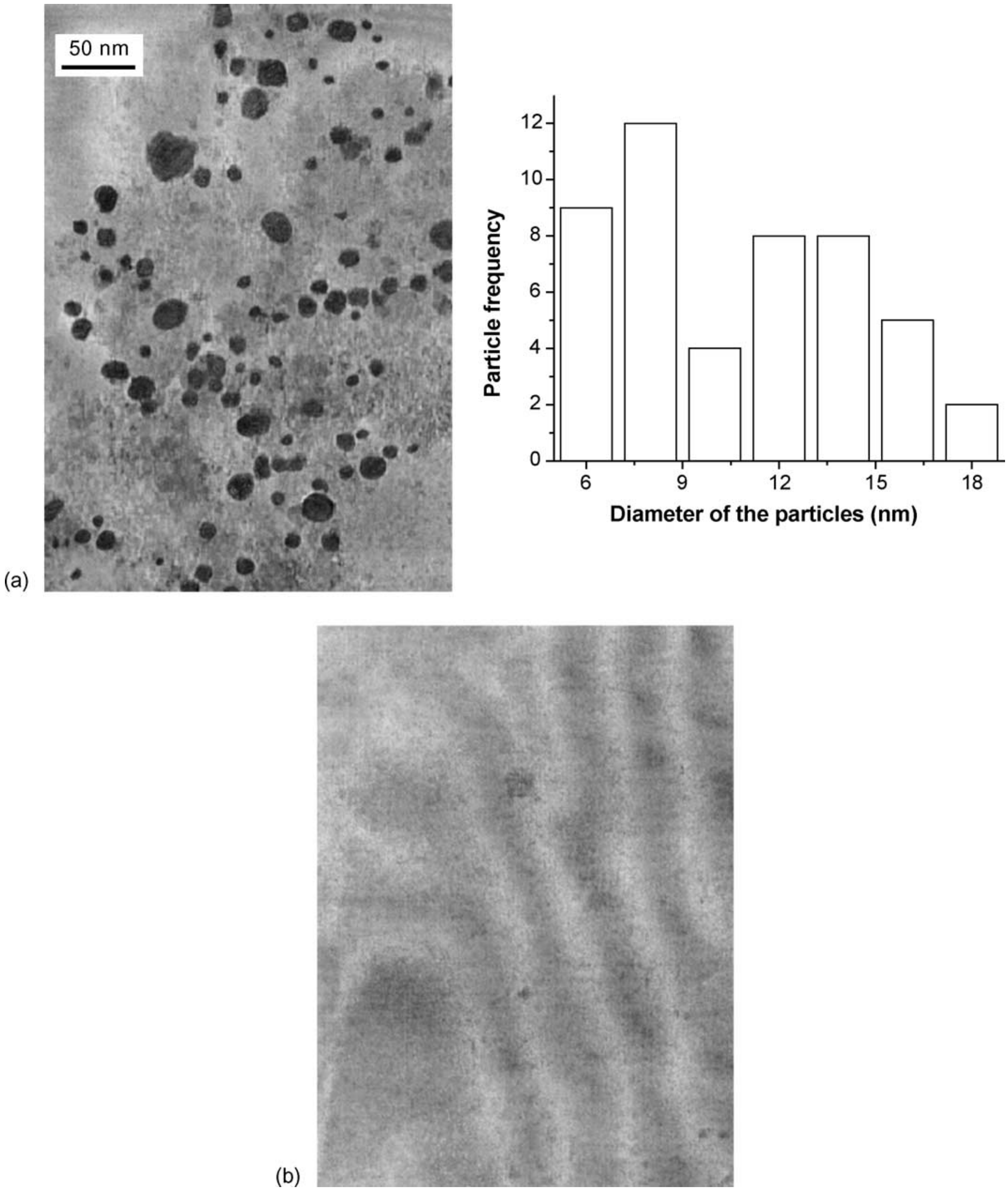


Fig. 2. Transmission electron micrograph (TEM) with histogram of (a) silver nanoparticles after 20 min irradiation and (b) before irradiation (no silver particles is observed).

spherical silver nanoparticles of ∼15 ± 3 nm diameters (Fig. 2a) for SNSM samples. But no trace of silver particles was observed from the TEM micrograph for the unexposed samples (Fig. 2b). The size distributions of the particles are shown in the histogram. In some places the particles were found to remain as aggregates and this was due to presence of gelatin that glue the silica gel matrixes causing aggregation. Higher amount of gelatin (1%) increased such aggregation. This helped us to recognise silver nanoparticles as dispersed material in the gelatin matrix adhering to the silica sphere surfaces.

3.7. Surface enhanced Raman scattering (SERS) study

Since from the discovery of surface enhanced Raman scattering, exhaustive efforts have been devoted in a number of laboratories towards the development of practical substrates to investigate and utilize the SERS effect [43,44]. The cause and the theory of SERS is still a subject of much debate. It is presumed that the oscillating electric field of a light beam induces an oscillating dipole in a colloidal metal particle. This oscillating dipole can be thought of as the free conduction electrons oscillating up and down in phase with the oscillating field. If the natural frequency of oscillation of the conduction electrons (the plasma oscillation frequency) matches the frequency of light, the plasma oscillation is in resonance with light, and the induced dipole becomes practically large. SERS study requires an active substrate for always and the order of enhancement of SERS intensity depends on the microstructure and proximity of the individual particle of the substrate [45,46]. Silver is one of the best materials for making SERS active surfaces since the behavior of its dielectric constant near the Frohlich frequency gives rise to an intense surface plasmon absorption in the visible wave length region.

Silver aggregate of an appropriate dimension has been shown to the best-suited metal for SERS studies. Individually silica or gelatin or both of them together were no good for the same study. Even the aqueous extract of the silver particles obtained from silica matrix showed no SERS activity. Therefore, the SERS activity involving SNSM particle was due to the presence of silver in it. It is 'silver' on silica matrix remain active to serve the purpose of a substrate for SERS without the need of any electrolyte for silver

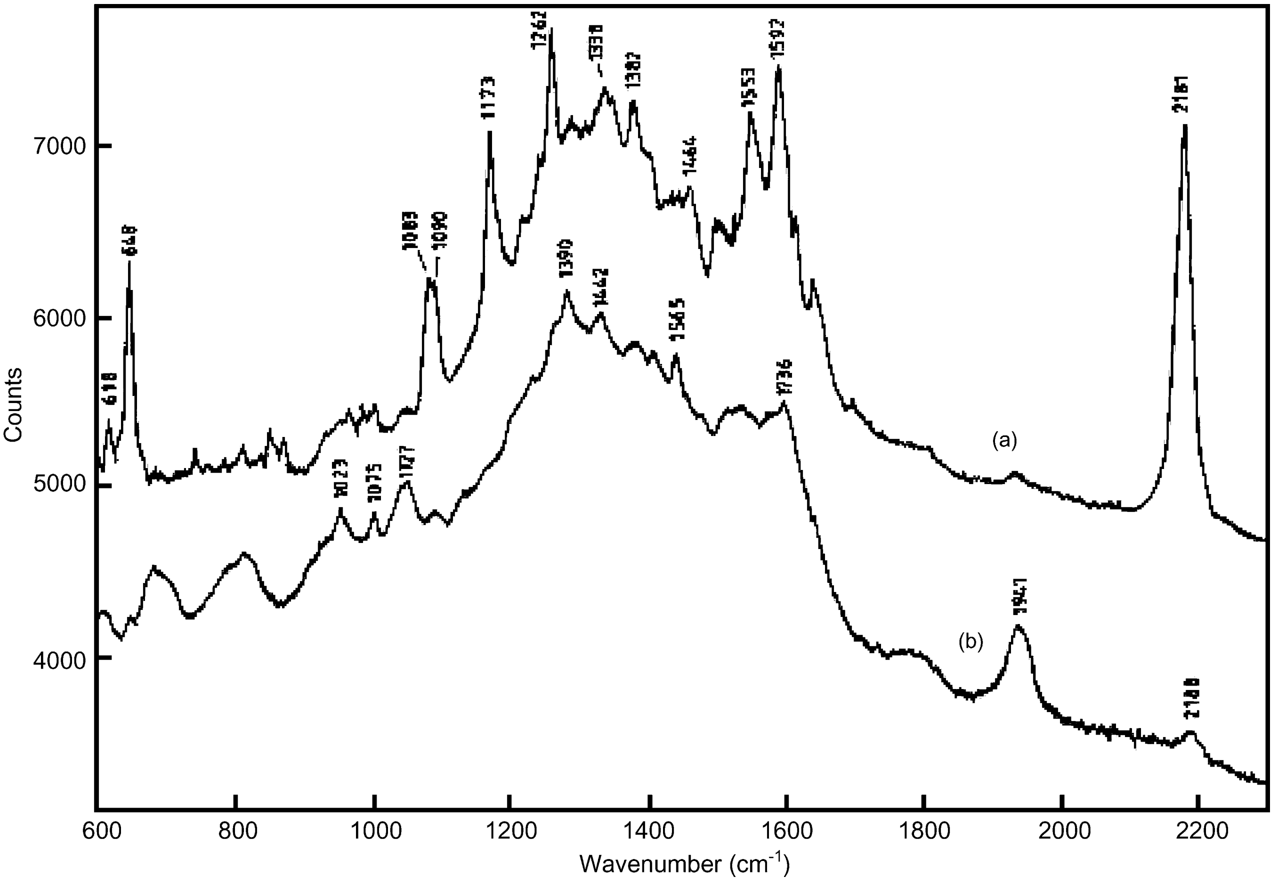


Fig. 3. Surface enhanced Raman scattering (SERS) spectra of 1,2-dimethyl phenyl isonitrile (DMPNC) on the photo produced silver nanoparticles (∼15 ± 3 nm) anchored onto the silica gel surface in the presence of gelatin (a) just after UV-irradiation and (b) after ∼3 months of irradiation. In (a) the NC-stretching band at 2181 cm^{-1} indicates SERS spectra due to adsorption of DMPNC on silver nanoparticle. Other small intense bands below 2181 cm^{-1} due to background of DMPNC. X-axis implies wavenumber (cm^{-1}) and Y-axis implies count.

particle aggregation [26–29]. In turn, it may be said that SERS of DMPNC on SNSM unequivocally speaks the presence of silver in the sample.

Here in our study, 1,2-dimethyl phenyl isonitrile in methanol was used as the SERS probe. It adsorbs well on the surface of silver nanoparticles (methanol evaporates out) and shows good SERS intensity. When it adsorbs NC-stretching vibration near 2125 $\mathrm{cm^{-1}}$ shifts to about 2175 $\mathrm{cm^{-1}}$, so if a band near 2175 $\mathrm{cm^{-1}}$ is appear then it indicates SERS of adsorbed molecule rather than normal Raman of free molecules in solution. The frequency is also dependent on which metal DMPNC is adsorbed. Spectra for the background i.e., solution of DMPNC in methanol showed the NC-stretching band at 2121 $\mathrm{cm^{-1}}$. After its addition onto the silver particle (solid) present in gelatin matrix, the NC-stretching band shifted to 2181 $\mathrm{cm^{-1}}$ (Fig. 3a) and several other bands very close to those for background one. This vast shifts from 2121 to 2181 $\mathrm{cm^{-1}}$ indicates definitely it is SERS spectra, not normal Raman. Single dispersed 15 nm silver particles should have typically low or no SERS enhancement. The observed strong SERS signal most likely arrows from aggregated silver particles that lead to an enhancement [26–29]. In Fig. 3, two spectra are shown, one for freshly prepared silver particles (Fig. 3a) and another for aged (∼3 months' old) silver particles (Fig. 3b). From this spectra it is clear that freshly prepared silver colloid is much more sensitive to SERS, but after a long time, the surface of silver particle presumably get oxidized and SERS activity decreases. It was also observed that the leached out silver particles in aqueous medium showed no promise for SERS studies. It proved that an aggregate of silver particles on solid silica gel was the candidate for SERS.

3.8. Thermal analysis study

Thermal analysis of both the samples (exposed and unexposed) clearly indicate mainly two features: anchoring of silver particles on the silica surfaces and very slow annealing of the small silver particles into larger silver particles (60–80 nm, not shown). The annealing started from 220 °C and ended at ∼500 °C (depicted by an exotherm). The broad exotherm was due to the presence of complex gelatin moiety in the matrix. The presence of gelatin made the anchoring of silver that took place at about 140 °C. Both these phenomena were distinctly observed by the broad exothermic peaks [25], but the temperature was somewhat higher in the presence of gelatin. The water and gelatin loss were observed for both the samples (indicated by the broad endothermic peaks) in the region 80°–125 and 540°–740 °C and a comparison was made with neat gelatin.

3.9. Application as catalyst

It has been already found that silver nanoparticle in solution acts as a very good catalyst for the reduction of different nitro compounds [2a] to the corresponding amino compounds. The particle prepared in this method while incorporated in gelatin matrix has been observed to be a better catalyst than the reported one (in aqueous phase) and the whole experiment of reduction study is under progress.

4. Conclusion

In conclusion, we have presented a new simple method of preparing silver nanoparticle in solid matrix under anaerobic and room temperature condition. The particles were not only found to be stable for a month together but also acted as active SERS substrate and an efficient catalyst. The advantage of this method is that it is very much efficient to produce uniform anchoring of silver nanoparticles on the silica spheres. The method is very much reproducible and particles showed significantly greater surface enhanced Raman scattering signals than the surface made by conventional method. Ongoing research is concerned with the reduction of different nitro phenols using this silver particle as a catalyst made the separation process (after the reaction) simpler.

Acknowledgements

Mr. S. Kundu and Mr. S.K. Ghosh are grateful to the Department of Science and Technology (DST), New Delhi for financial support. Miss M. Mandal thanks Council of Scientific and Industrial Research (CSIR), New Delhi for financial assistance. The authors wish to thank Prof. J.A. Creighton for his help with the SERS studies and for useful suggestions.

References

[1] (a) D. Falkenhagen, Artif. Organs 19 (1995) 792;
(b) L. Polato, L.M. Benedetti, L. Callegaro, J. Drug Targeting 2 (1994) 53.
[2] (a) N. Pradhan, A. Pal, T. Pal, Langmuir 17 (2001) 1800;
(b) N.R. Jana, T. Pal, Langmuir 15 (1999) 3458;
(c) N.R. Jana, T.K. Sau, T. Pal, J. Phys. Chem. B 103 (1999) 115.
[3] (a) H.D. Robert, P.J. Rao, Mater. Res. 11 (1996) 2834;
(b) A. Henglein, Isr. J. Chem. 33 (1993) 77;
(c) N.R. Jana, L. Gearhert, C. Murphy, J. Chem. Soc., Chem. Commun. (2001) 617;
(d) C. Sanchez, G. Soler-Illia, F. Ribot, C.R. Mayer, V. Cabuil, T. Lalot Chem. Mater. 13 (2001) 3061.
[4] S. Link, M.A. El-Sayed, J. Phys. Chem. B 103 (1999) 8410.
[5] N.P. Gaponik, D.V. Talapin, A.L. Rogach, J. Mater. Chem. 10 (2000) 2163.
[6] D. Beydonn, R. Amal, G. Low, S. McEvoy, J. Nanopart. Res. 1 (1999) 439.
[7] A. Takami, H. Kurita, S. Koda, J. Phys. Chem. B 103 (1999) 1226.
[8] U. Kreibig, M. Vollmer, Optical Properties of Metal Clusters, Springer, Berlin, 1995.
[9] T. Pal, N.R. Jana, A. Pal, J.A. Creighton, A.E. Beezer, J. Indian Chem. Soc. 77 (2000) 34.
[10] G. Frens, Nature 20 (1972) 241.
[11] A. Pal, Talanta 46 (1998) 583.

[12] (a) A. Henglein, Ber. Bunsen. Ges. Phys. Chem. 99 (1995) 903;
(b) A. Henglein, Chem. Rev. 89 (1989) 1861;
(c) J. Belloni, Curr. Opin. Colloid Interface Sci. 1 (1996) 184;
(d) A. Henglein, J. Phys. Chem. 97 (1993) 5457.

[13] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. 92 (1988) 531.

[14] Y. Mizukoshi, K. Okitsu, Y. Maeda, T.A. Yamamoto, R. Oshima, Y. Nagata, J. Phys. Chem. B 101 (1997) 7033.

[15] (a) C.A. Foss Jr., G.L. Hornyak, J.A. Stockert, C.R. Martin, J. Phys. Chem. 98 (1994) 2963;
(b) J.C. Hulteen, C.R. Martin, J. Mater. Chem. 7 (1997) 1075.

[16] C. Schonenberger, B.M.I. Van der Zande, L.G.J. Fokkink, M. Henny, C. Schmid, M. Kruger, A. Bachtold, R. Huber, H. Birk, U. Staufer, J. Phys. Chem. B 101 (1997) 5497.

[17] W. Gotschy, A.K. Vonmetz, A. Litner, F.R. Aussenegg, Opt. Lett. 21 (1996) 1099.

[18] H. Bonnemann, R. Binkmann, P. Neileler, Appl. Organomet. Chem. 8 (1994) 361.

[19] K. Esumi, A. Suzuki, N. Aihara, K. Usui, K. Torigoe, Langmuir 14 (1998) 3157.

[20] T. Cassagneau, J.H. Fendler, J. Phys. Chem. B 103 (1999) 1789.

[21] E. Stathatos, P. Lianos, Langmuir 16 (2000) 2398.

[22] S. Ramesh, R. Prozorov, A. Gedanken, Chem. Mater. 9 (1997) 2996.

[23] N.A. Dhas, A. Gedanken, Appl. Phys. Lett. 72 (1998) 2514.

[24] S. Ramesh, H. Minti, R. Reisfeld, A. Gedanken, Opt. Mater. 13 (1999) 67.

[25] V.G. Pol, D.N. Srivastava, O. Palchik, V. Palchik, M.A. Slifkin, A.M. Weiss, A. Gedanken, Langmuir 18 (2002) 3352.

[26] A.M. Michaels, M. Nirmal, L.E. Brus, J. Am. Chem. Soc. 121 (1999) 9932.

[27] P. Hildebrandt, M. Stockburger, J. Phys. Chem. 88 (1984) 5935.

[28] S. Nie, S.R. Emory, Science 275 (1997) 1102.

[29] K. Kneipp, Y. Wang, H. Kneipp, L.T. Perelman, I. Itzkan, R.R. Dasari, M.S. Feld, Phys. Rev. Lett. 78 (1997) 1667.

[30] T.K. Sau, A. Pal, T. Pal, J. Phys. Chem. B 105 (2001) 9266.

[31] T. Pal, D.S. Maity, Analyst 111 (1986) 49.

[32] T. Pal, J. Chem. Edu. 71 (1994) 679.

[33] J. Pouradier, in: T.H. James (Ed.), The Theory of the Photographic Process, fourth ed., Macmillan, New York, 1977, p. 51.

[34] T. Pal, N.R. Jana, P.K. Das, Analyst 116 (1991) 321.

[35] J. Belloni, M. Treguer, H. Remita, R.D. Keyzer, Nature 402 (1999) 865.

[36] T. Pal, A. Ganguly, D.S. Maity, Analyst 111 (1986) 691.

[37] T. Pal, A. Ganguly, D.S. Maity, Anal. Chem. 58 (1986) 1564.

[38] T. Pal, A. Ganguly, D.S. Maity, Bull. Chem. Soc. Jpn. 60 (1987) 3001.

[39] T. Pal, A. Ganguly, D.S. Maity, Talanta 35 (1988) 658.

[40] T. Pal, A. Ganguly, D.S. Maity, Analyst 111 (1986) 1413.

[41] T. Pal, P.K. Das, Anal Lett. 20 (1987) 2011.

[42] P.V. Kamat, M. Flumiani, G.V. Hartland, J. Phys. Chem. B 102 (1998) 3123.

[43] J.A. Creighton, C.G. Blatchford, M.G. Albrecht, J. Chem. Soc., Faraday Trans. 2 (1979) 790.

[44] N.S. Lee, Y.Z. Hsieh, M.D. Morris, L.M. Schopfer, J. Am. Chem. Soc. 109 (1987) 1358.

[45] M.I. Stockman, V.M. Shalaev, M. Moskovits, R. Botet, T.F. Geogr, Phys. Rev. B. 46 (1992) 2821.

[46] J.A. Creighton, D.G. Eadon, J. Chem. Soc., Faraday Trans. 87 (1991) 3881.