

Synthesis of Guar-Gum-Stabilized Nanosized Silver Clusters with γ Radiation

Jayashree Biswal,¹ S. P. Ramnani,¹ Seema Shirolkar,² S. Sabharwal¹

¹Radiation Technology Development Section, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

²Tata Institute of Fundamental Research, Department of Biological Sciences, TIFR, Mumbai 400005, India

Received 29 December 2006; accepted 27 April 2008

DOI 10.1002/app.30113

Published online 7 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Gamma ray induced synthesis of Ag clusters in the aqueous medium has been carried out using natural polysaccharide guar gum as a stabilizer. The results showed that guar gum is very effective in binding the Ag clusters and restricts their size in the nano region. The surface plasmon resonance band in the wavelength range of 410–425 nm of visible region has confirmed the formation of Ag clusters. The size of the clusters is governed by the concentration of both, i.e. precursor Ag^+ and guar gum. The clusters were characterized by TEM and XRD, which shows that the size of clusters is in the range of 10–30 nm. The results have shown that silver clusters

stabilized by guar gum are stable in acid media and alkaline media is not a desired media for the synthesis. From thermogravimetric analysis it has been demonstrated that incorporation of nano sized Ag clusters within guar gum improves the thermal properties of irradiated guar gum. To the best of our knowledge, the use of guar gum as a stabilizer in the gamma ray induced synthesis of Ag nano clusters is being reported first time in the literature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2348–2355, 2009

Key words: biodegradable; colloids; irradiation; nanocomposites; thermogravimetric analysis (TGA)

INTRODUCTION

The study of metal nanoparticles is of interest in both research and technology, as metal nanoparticles possess specific properties not available in isolated molecules or bulk metals. These characteristics, namely, optical, magnetic, catalytic, and electrochemical properties, are dependant to a great extent on their dimensions, shape, and chemical surroundings and can be advantageously used for the purpose of the development of novel biosensors, chemical sensors, electrooptical devices, material for high-capacity data storage media,^{1–7} and substrates for enhanced Raman spectroscopy.^{8–13} The metal of choice for many of the aforementioned applications, as well as for other applications, is silver because of its facile preparation and the good application properties of the silver colloidal particles.

The synthesis of nanoparticles of metals involves the reduction of metal ion with a suitable reducing agent. The reduction can be achieved chemically,¹⁴ photochemically,¹⁵ by microwave heating,¹⁶ and by high-energy radiation,^{17–19} such as γ and electron beam radiation. Among the various methods mentioned previously, the use of ionizing radiation for the synthesis of metal nanoparticles is promising;

because of the extreme range of reactivity of the species produced by the radiation, it creates redox levels that are hard to achieve by other methods. Furthermore, because of its ability to fine-tune the radiation dose and dose rate, it may offer better control over the size and the size distribution.

It is now well established that polymers are excellent host materials for nanoparticles of metals. When the nanoparticles are embedded or encapsulated in a polymer, the polymer acts as a surface-capping agent. Various synthetic polymers, such poly(vinyl alcohol),^{14,20} poly(vinyl pyrrolidone),²¹ polystyrene,²² and poly(methyl methacrylate),²³ have been used in the synthesis of metal nanoparticles. However, very little work has been carried out in which a natural polysaccharide has been used as a capping agent for the stabilization of metal nanoparticles. Recently, the synthesis of natural-polymer-stabilized selenium nanoparticles by the reduction of selenious acid by ascorbic acid was reported.²⁴ Natural polymers, because of their large abundance, biodegradability, and reactivity (due to the presence reactive functional groups), may show a better ability to stabilize nanoparticles. Guar gum (GG)²⁵ is a naturally occurring edible carbohydrate polymer found in the seeds of *Cyamopsis tetragonolobus*. It is a nonionic, branched-chain polymer, consisting of straight-chain mannose units joined by β -D-(1-4) linkages having α -D-galactopyranose units attached to this linear chain by (1-6) linkages. The structure of GG is shown in Figure 1. The structure of GG is very

Correspondence to: S. P. Ramnani (ramnani@magnum.barc.gov.in).

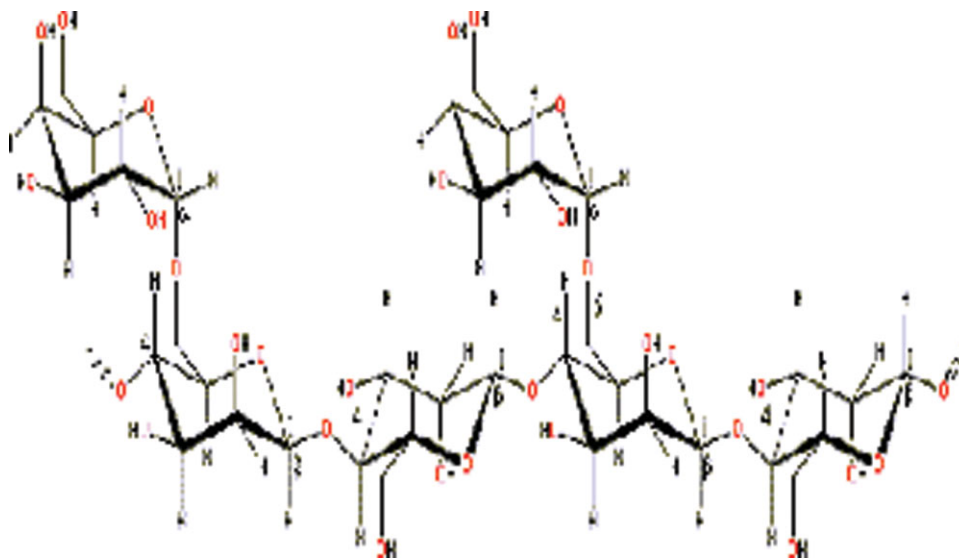


Figure 1 Chemical structure of GG. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

complex, and it has several hydroxyl groups, which can effectively bind metal clusters. To the best of our knowledge, the use of GG in the stabilization of metal nanoclusters prepared by γ irradiation has not reported in the literature. In this article, we report the γ -radiation-induced synthesis of silver nanoclusters in an aqueous medium stabilized by GG.

EXPERIMENTAL

All reagents used were of high purity. AgNO_3 (Sarabhai Chemicals, Vadodara, India) and isopropyl alcohol (M/s S. D. Fine Chemical, Mumbai, India) were used as received. The GG used in this study was from M/s Sigma and was used as received. The molecular weight of GG was determined with the viscosity method with the relation $\eta = kM_v^\alpha$, where η is the intrinsic viscosity, M_v is the viscosity-average molecular weight, and k and α are constants, whose values are 3.8×10^{-4} and 0.732, respectively.²⁶ M_v was found to be 1.9×10^6 . All solutions were prepared in double-distilled water and purged with N_2 gas to eliminate oxygen before irradiation. The concentration of GG used in this study was 0.5% w/v; therefore, the direct purging of N_2 did not pose any problem. Irradiations were carried out in a ^{60}Co γ chamber with a radiation dose rate of 3.5 kGy/h determined with Fricke dosimetry.²⁷ The absorption spectra were recorded on a Shimadzu model 4600 recording spectrophotometer. The X-ray diffraction (XRD) patterns were recorded on a Philips XRD spectrometer (model PW 1729) in the range $2\theta = 10\text{--}70^\circ$. Thermogravimetric experiments were carried out under a N_2 flow with a TGA Mettler 3000 instrument at a heating rate of $10^\circ \text{C}/\text{min}$. The sample for transmission electron microscopy (TEM)

was prepared by the irradiation of the aqueous solution of 0.5% GG containing $1 \times 10^{-3} \text{ mol}/\text{dm}^3 \text{ Ag}^+$ and $0.2 \text{ mol}/\text{dm}^3$ isopropyl alcohol. The radiation dose delivered to the sample was adjusted in such a way so that entire Ag^+ was converted into Ag. A drop of this solution was placed on a carbon-coated copper grid; this was followed by drying. The pictures of the particles were taken by the placement of the grid under TEM (Jeol, model 100 S).

Synthesis of the silver nanoparticles

The silver nanoparticles were prepared by the dissolution of a known weight of AgNO_3 in a 0.5% (w/w) aqueous solution of GG containing $0.2 \text{ mol}/\text{dm}^3$ isopropyl alcohol. The solution was stirred until a viscous homogeneous solution was obtained. It was then purged with N_2 gas to eliminate the dissolved oxygen present in the solution. Because the concentration of GG used was 0.5% (w/w), the direct purging of N_2 gas through the solution did not pose any problem. The resultant solution was irradiated in a ^{60}Co γ chamber to a desired radiation dose. A bright yellow solution, characteristic of silver nanoparticles, was obtained; this was confirmed by ultraviolet-visible (UV-vis) spectrophotometry.

RESULTS AND DISCUSSION

The reduction of silver ions in aqueous solutions in the presence of a polymeric stabilizer generally results in the formation of colloidal silver with a particle diameter of several nanometers. These particles have specific optical properties indicated by the presence of an intense absorption band at 390–450 nm caused by the collective excitation of all the free electrons in the particle.²⁸ To investigate the

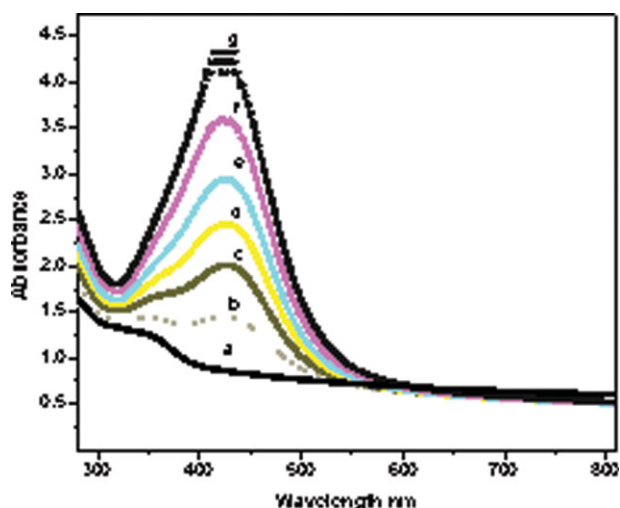
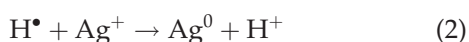
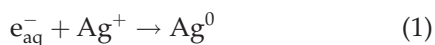


Figure 2 Absorption spectra of GG solutions irradiated at various doses: (a) unirradiated GG and GG irradiated with (b) 0.15, (c) 0.29, (d) 0.46, (e) 0.58, (f) 0.70, and (g) 0.87 kGy in the presence of 1×10^{-3} mol/dm³ Ag⁺ and 0.2 mol/dm³ isopropyl alcohol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

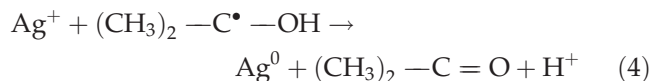
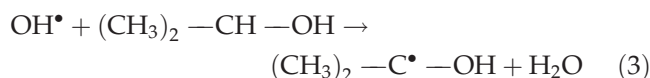
ability of GG to stabilize the Ag clusters, the irradiation of an aqueous solution of GG in the presence of Ag⁺ was carried out. The absorption spectrum of an aqueous solution of 0.5% GG containing 10^{-3} mol/dm³ Ag⁺ and 0.2 mol/dm³ isopropyl alcohol when irradiated with γ radiation with various radiation doses is shown in Figure 2. The unirradiated GG solution showed a shoulder at 350 nm without any peak in the visible region. With increasing radiation dose, the absorption in the region of 300–600 started to develop, with an absorption maxima at 427 nm. Under the same experimental conditions, when irradiation was carried out in the absence of Ag⁺, no absorption band in the region 300–600 nm was observed. Thus, the absorption band observed at 427 nm was attributed to silver clusters stabilized by GG.

When Ag⁺ dissolved in an aqueous solution of GG containing isopropyl alcohol was irradiated with γ radiation, most of the energy was absorbed by water, which resulted in the generation of e_{aq}⁻ (hydrated electron), H[•], and OH[•]. Among these species, e_{aq}⁻ and H[•] were very strong reducing agents: $E^0_{\text{H}_2\text{O}/\text{e}_{\text{aq}}^-} = -2.87\text{V} \times \text{NHE}$, where E^0 is the standard reduction potential, V is the volt, NHE is the normal hydrogen electrode, and $E^0_{\text{H}^+/\text{H}} = -2.3\text{V} \times \text{NHE}$. These species reacted with Ag⁺ and resulted in its reduction to Ag⁰ [eqs. (1) and (2)]:

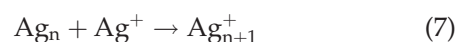
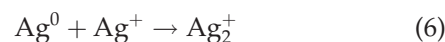
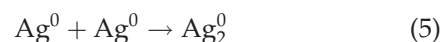


The purpose of the addition of isopropyl alcohol was twofold: (1) it reacted with the OH[•] radical to

form an isopropyl radical, which thus prevented the oxidation of Ag⁰ formed back into Ag⁺ by the OH radical, and (2) the isopropyl radical formed in eq. (3) was highly reducing and reduced Ag⁺ to Ag⁰ [eq. (4)]:



The silver atoms formed in reactions 1, 2, and 4 dimerized when they encountered each other or associated themselves with excess Ag⁺ ions by a cascade of coalescence processes, and these species progressively grew into larger clusters, as shown in the following reactions:



The clusters of silver atoms thus formed were not allowed to grow further because of the presence of GG, which anchored them. The structure of GG is shown in Figure 1. As shown from the structure of GG, there were several OH groups that could bind the growing Ag clusters and also, because of the presence of a long linear chain of mannose units and a side chain of galactose units, the anchored Ag clusters were prevented from growing further by steric hindrance, and thus, they were stabilized. Evidence for the interaction of hydroxyl groups in the stabilization of the silver clusters was obtained from the Fourier transform infrared (FTIR) spectra of the GG-containing Ag clusters. The FTIR spectra of GG and Ag/GG are shown in Figure 3. GG exhibited characteristic bands²⁹ at 3426 and 2926 cm⁻¹ because of the O—H stretching vibrations of the polymer associated with C—H stretching vibrations. Additional characteristic absorption bands of GG appeared at 1418 and 1026 cm⁻¹ because of C—H bending and O—H bending vibrations, respectively. As shown in Figure 3, the band at 3426 cm⁻¹ shifted to 3457 cm⁻¹ in the presence of Ag; also, the band was broader in Ag/GG compared to GG. These observations clearly indicate the interaction of Ag with the —OH group of GG. Similar results were reported earlier in the synthesis of silver nanoparticles stabilized by Konjac Glucomannan, which is structurally similar to GG, by a photochemical reduction method.³⁰

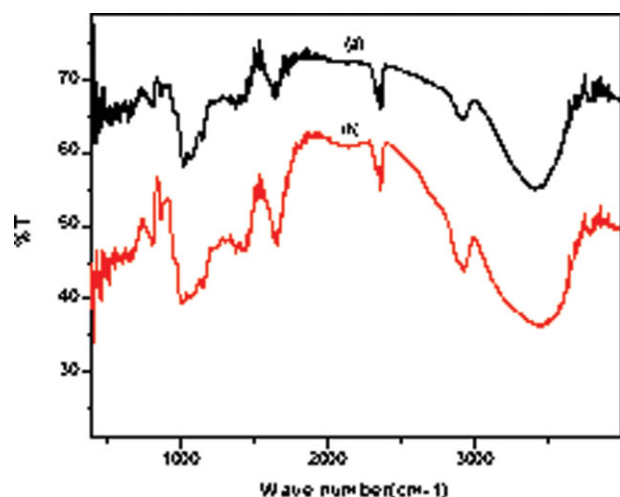


Figure 3 FTIR spectra of (a) GG and (b) Ag/GG. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of the GG and Ag⁺ concentrations

The effect of the GG concentration on the formation of the Ag clusters was studied by the irradiation of a solution containing 1×10^{-3} mol/dm³ Ag⁺ and 0.2 mol/dm³ isopropyl alcohol and various amount of GG. As mentioned earlier, when the aqueous solution is irradiated with γ radiation, most of the energy was absorbed by water, which resulted in the generation of e_{aq}⁻, H[•], and OH[•]. Typically, in the presence of isopropyl alcohol, the yield of reducing species is 6 per 100 eV of absorbed energy.³¹ Thus, a radiation dose of 1 kGy could reduce about 5.7×10^{-4} M of Ag⁺, or in other words, a radiation dose of about 2 kGy in principle is sufficient to bring about the complete reduction of 1×10^{-3} M Ag⁺ to metallic silver. Because GG could also react with the radicals generated from water radiolysis, a higher radiation dose of 3.5 kGy was selected to ensure the complete reduction of Ag⁺. The absorption spectra recorded after irradiation at various concentrations of GG are shown in Figure 4. The spectrum at a low concentration of GG (0.1%) was very broad, with a shoulder at 520 nm and a maximum at 408 nm. However, with increasing concentration of GG, the absorption spectrum became narrower, and the shoulder at 520 nm also disappeared. The narrowing of the absorption spectrum with increasing concentration of GG indicated that the cluster size became more and more uniform. At low concentration, GG was not very effective in stabilizing the Ag clusters, and therefore, there was no control over the cluster size, as evident from the broad absorption spectrum. Similar results have been observed in the synthesis of Ag/chitosan and Au/chitosan by a chemical reduction method with NaBH₄ as a reducing agent.³²

Similarly, we studied the effect of Ag⁺ concentration on the formation of Ag cluster by keeping the concentration of GG fixed (0.5%) and varying the concentration of Ag⁺. The radiation dose delivered to sample was calculated on the basis of the concentration of Ag⁺ (3.5 kGy per 1×10^{-3} mol/dm³). The absorption spectra of the irradiated solutions are shown in Figure 5. As shown in Figure 5, the intensity of the surface plasmon band of the Ag clusters increased with increasing concentration of Ag⁺, and the band was quite symmetrical up to a 2-mol/dm³ Ag⁺ concentration. Further increases in the concentration affected the symmetry of the surface plasmon band, which became quite broad at a Ag⁺ concentration of 3×10^{-3} mol/dm³, and a shoulder at 520 nm also appeared. At high Ag⁺ concentrations, more nuclei were formed and the concentration of GG, which was kept constant at 0.5%, was not sufficient to control the growth and stabilization of the Ag clusters, and hence, the size distribution was not uniform, as evident from the broadness of the surface plasmon band. Thus, it appears that cluster size was governed by both GG concentration and precursor Ag⁺ concentration.

Effect of pH on the formation of Ag clusters

In our earlier study on the radiation-induced synthesis of Ag clusters on silica,³³ we observed that the pH of the solution affected the formation of metal clusters. To assess the role of the pH of the solution on the formation of GG-stabilized Ag clusters, solutions of GG (0.5%) containing 1×10^{-3} mol/dm³

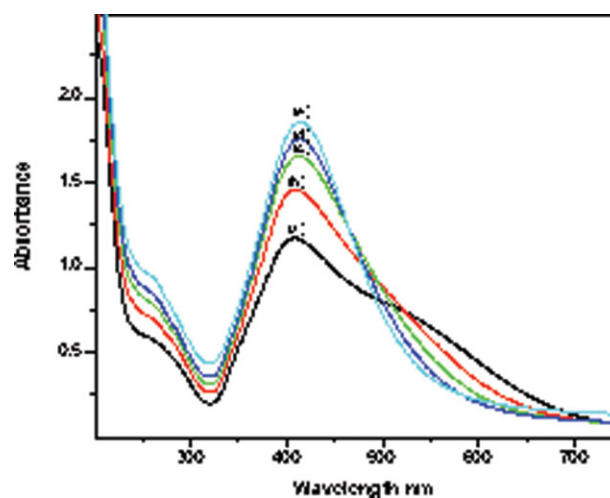


Figure 4 UV-vis spectra of the Ag clusters formed upon irradiation at various GG concentrations: (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, and (e) 0.5% w/v. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

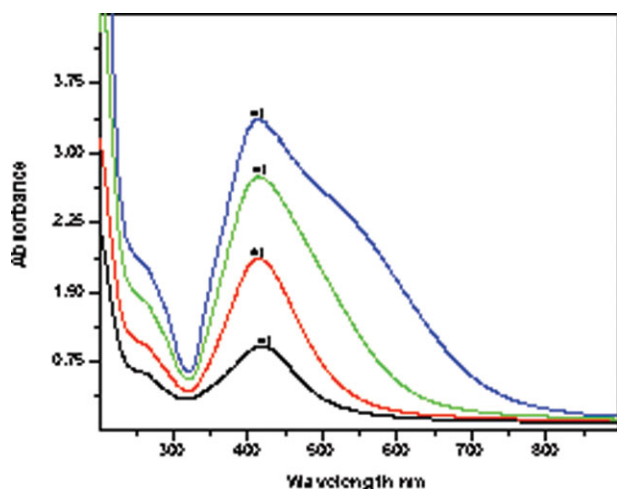


Figure 5 Changes in the surface plasmon resonance band of the Ag clusters upon irradiation at various precursor concentrations: (a) 0.5×10^{-3} , (b) 1.0×10^{-3} , (c) 2.0×10^{-3} , and (d) 3.0×10^{-3} mol/dm³. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

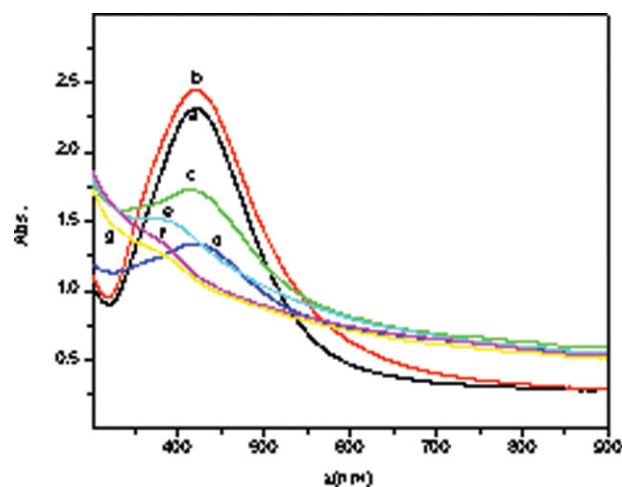


Figure 6 Absorption spectra of the Ag clusters formed upon irradiation at various pH values of the solution: (a) 2.8, (b) 4.8, (c) 5.9, (d) 7.2, (e) 9.1, (f) 10.9, and (g) 11.4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Ag⁺ were irradiated at various pH values, which were varied by the addition of appropriate amounts of KH₂PO₄ or Na₂HPO₄ to the solutions before irradiation. The absorption spectra recorded after the irradiations are shown in Figure 6. The surface plasmon resonance band was symmetrical and had very low absorbance at wavelengths below 600 nm at pH values of 2.8 and 4.75; this indicated narrow size distribution. However, at a pH above 5, the symmetry of band was lost, and it became broad with enhanced absorption at wavelengths above 600 nm. In the alkaline region at pH above 10, no surface plasmon resonance band was observed. In the radiation-induced synthesis of copper nanoparticles,³⁴ in alkaline media, a yellow precipitate of Cu(OH)₂ was obtained. During the chemically induced reduction of silver ions by formaldehyde³⁵ in aqueous media, in alkaline medium, silver nanoparticles were not stable. Similar results were also observed in our earlier study on the radiation-induced synthesis of Ag clusters on silica.³³ Thus, it appears that silver clusters stabilized by GG are stable in acid media and that alkaline media are not desirable for the synthesis.

Role of alcohol in the formation of Ag clusters

Although isopropyl alcohol was used as an OH radical scavenger throughout this study, the ability of other alcohols to scavenge the OH radical and the subsequent reactions of alcohol radicals in the reduction of Ag⁺ to metallic silver were also investigated. We studied this by irradiating a 0.5% aqueous solu-

tion of GG containing 1×10^{-3} mol/dm³ Ag⁺ and 0.2 mol/dm³ of various alcohols, including methanol, ethanol, isopropyl alcohol, butanol, and *tert*-butyl alcohol. The solutions were purged with N₂ to eliminate oxygen. The UV-vis spectra of the irradiated samples are shown in Figure 7. As shown in this figure, the intensity of the surface plasmon resonance band in the case of all alcohols except *tert*-butyl alcohol was higher compared to that in the absence of alcohol. This indicates that radicals

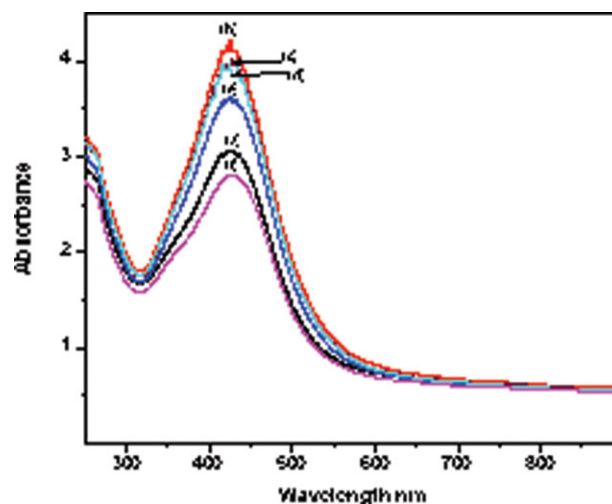


Figure 7 Formation of the Ag clusters in the presence of various alcohols used for scavenging OH radicals: (a) no alcohol, (b) methanol, (c) ethanol, (d) isopropyl alcohol, (e) *n*-butanol, and (f) *tert*-butanol (concentration of alcohol = 0.2 mol/dm³). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

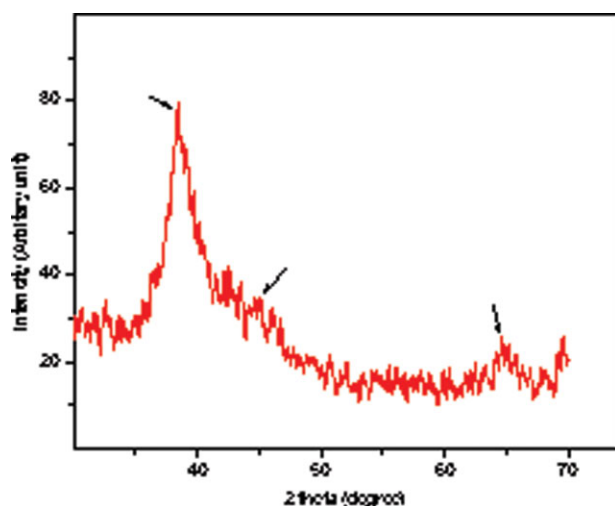


Figure 8 XRD pattern of Ag/GG. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

generated from the reaction of all these alcohols with the OH radical were effective in reducing Ag^+ to metallic silver. Another very important observation that can be made from Figure 7 is that the intensity of the surface plasmon band in the presence of *tert*-butyl alcohol was lower than that in the absence of alcohol. It is known from the literature that the radical produced from the reaction of OH with *tert*-butanol is highly unreactive³⁶ and cannot reduce Ag^+ to Ag, and therefore, in both cases, e_{aq}^- and H bring about the reduction of Ag^+ to Ag. In that case, the intensity of the surface plasmon band should have been same in both the cases. The only difference between these two cases was the fate of the OH radical in the absence of alcohol where it can react with GG. Therefore, it appears that the radical generated from the reaction of OH with GG was able to reduce Ag^+ to Ag and because of this, the intensity of the plasmon band was higher in the absence of alcohol.

Characterization of Ag/GG

The formation of Ag clusters stabilized by GG with γ radiation as a tool for the reduction was successfully demonstrated in the UV-vis spectra, which clearly showed the characteristic surface plasmon band of the Ag cluster in the region 400–450 nm. These clusters were further characterized by several physical techniques, including XRD, TEM, and thermogravimetry. The XRD pattern recorded in the 2θ region of 20–70° is shown in Figure 8. The X-ray diffractogram of metallic silver³⁷ showed prominent peaks at 2θ values of 38.1, 44.25, 64.54, and 77.35 representing the 111, 200, 220, and 311 Brags reflec-

tions. In the XRD pattern, peaks at 2θ values of 38.1, 44.25, and 64.54 were clearly visible, which thus confirmed the formation of metallic silver. The broad bandwidth of the main peak at a 2θ value of 38.1 indicated that the size of clusters was small, which was confirmed from the TEM analysis. The TEM picture of Ag/GG is shown in Figure 9. It showed nearly spherical particles with size distributions in the range 10–30 nm.

It is well known that GG, like other naturally occurring polymers, undergoes chain scission when exposed to ionizing radiation; this results in a decrease in the molecular weight.³⁸ The changes occurring in thermal properties of GG upon irradiation and after the formation of a composite with Ag were studied with thermogravimetric analysis. For this, a sample containing a 5% loading of Ag nanoparticles in the GG was prepared by the irradiation of 50 mL of a 5% aqueous solution of GG containing 220 mg of AgNO_3 with a radiation dose of 56 kGy. The 5% loading of Ag was chosen so as to obtain noticeable changes in the thermogram. The radiation dose was selected to achieve the complete conversion of Ag^+ to metallic silver. We precipitated the irradiated solution by adding it to acetone followed by washing with acetone to eliminate radiolytic products. Finally, it was dried at 50°C *in vacuo*. Similarly, a 5% solution of GG was also irradiated in the absence of Ag^+ . The thermograms of unirradiated GG, irradiated GG, and GG irradiated in the presence of Ag^+ are shown in Figure 10. The decomposition of unirradiated GG started at 278°C, whereas GG irradiated in the absence of Ag^+ started decomposing at much a lower temperature ($\sim 237^\circ\text{C}$). The observed decrease in the decomposition temperature



Figure 9 TEM images of the Ag clusters formed upon irradiation in aqueous GG solution (bar length = 100 nm).

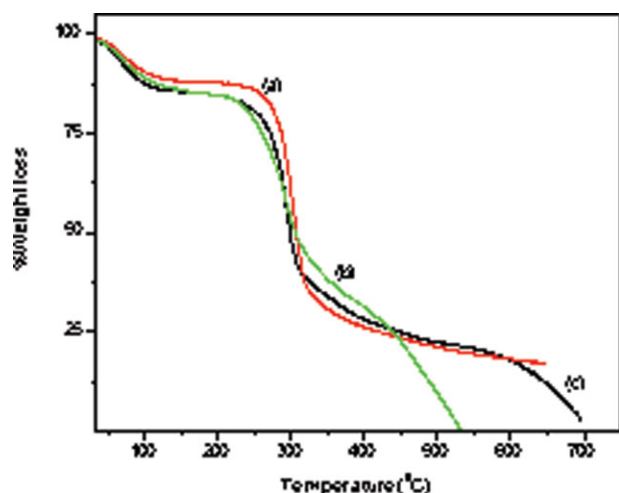


Figure 10 Thermograms of (a) GG, (b) irradiated GG, and (c) GG irradiated in the presence of Ag^+ . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

was due to the degradation of GG upon irradiation. As mentioned earlier, GG belongs to the class of natural polymers that undergo depolymerization when exposed to ionizing radiation such as γ rays. The reduction in the molecular weight was responsible for the decrease in the observed decomposition temperature. Alternatively, when GG was irradiated in the presence of Ag^+ , this resulted in the formation of Ag; the decomposition of the resultant Ag/GG composite started at 258°C , which was higher than the one observed for the GG irradiated in the absence of Ag^+ . In both the cases, that is, in the absence and the presence of Ag^+ , the radiation dose delivered to the GG solution was the same. Thus, it appears that presence of nanosize silver, which acted as a filler, in the irradiated GG was responsible for the improvement in its thermal properties. The analysis of the latter part of thermogram also indicated that the thermal properties of irradiated guar were improved upon the incorporation of Ag. As shown in Figure 10, the complete decomposition of irradiated GG in the absence of Ag^+ was over at a much lower temperature (530°C), unlike the one irradiated in the presence of Ag^+ , where complete decomposition was not even over at 700°C . Similar results were also reported for the Ag/PVA nanocomposites synthesized with the chemical reduction method.¹⁴

CONCLUSIONS

GG was a very effective stabilizer for Ag clusters generated by γ radiation. The size of the clusters was in the nanodomain. An acid medium was best for the generation of Ag clusters in the presence of

GG. The incorporation of Ag clusters in the GG improved the thermal stability of the irradiated GG.

The authors thank A. K. Tyagi, Chemistry Division, Bhabha Atomic Research Centre, for his help with the XRD of the Ag/GG and Hari Kumar, Food Technology Division, Bhabha Atomic Research Centre, for providing the spectrophotometer to record the UV-vis spectra.

References

- Riboh, J. C.; Haes, A. J.; McFarland, A. D.; Yonzon, C. R.; Van Duyne, R. P. *J Phys Chem B* 2003, 107, 1772.
- Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J Am Chem Soc* 2001, 123, 1471.
- Zynio, S. A.; Samoylov, A. V.; Surovtseva, E. R.; Mirsky, V. M.; Shirshov, Y. M. *J Sensors* 2002, 2, 62.
- Hulteen, J. C.; Treichel, D. A.; Smith, M. T.; Duval, M. L.; Jensen, T. R.; Van Duyne, R. P. *J Phys Chem B* 1999, 103, 9846.
- Henry, A. C.; McCarley, R. L. *J Phys Chem B* 2001, 105, 8755.
- Fuller, S. B.; Wilhelm, E. J.; Jacobson, J. M. *J Microelectromech Syst* 2002, 11, 54.
- Yin, Y.; Lu, Y.; Sun, Y.; Xia, Y. *Nano Lett* 2002, 2, 427.
- Creighton, J. A.; Blatchford, C. G.; Albrecht, M. G. *J Chem Soc Faraday Trans 2* 1979, 75, 790.
- Laserna, J. J.; Cabalin, L. M.; Montes, R. *Anal Chem* 1992, 64, 2006.
- Vlckova, B.; Solecka-Cermakova, K.; Matejka, P.; Baumurk, V. *J Mol Struct* 1997, 408/409, 149.
- Felidj, N.; Aubard, J.; Levi, G. *Phys Status Solidi* 1999, 175, 367.
- Feng, Z. C.; Liang, C. H.; Li, M. J.; Chen, J.; Li, C. J. *Raman Spectrosc* 2001, 32, 1004.
- Etchegoin, P.; Liem, H.; Mahar, R. C.; Cohen, L. F.; Brown, R. J. C.; Milton, M. J. T.; Galop, J. C. *Chem Phys Lett* 2003, 367, 223.
- Khanna, P. K.; Singh, N.; Charan, S.; Subbarao, V. V. S.; Gokhale, R.; Mulik, U. P. *Mater Chem Phys* 2005, 93, 117.
- Sato, T.; Onaka, H.; Yonezawa, Y. *J Photochem Photobiol A* 1999, 127, 83.
- Patel, K.; Kapoor, S.; Dave, D. P.; Mukherjee, T. *J Chem Sci* 2005, 117, 53.
- Gutierrez, M.; Henglein, A. *J Phys Chem* 1993, 97, 11368.
- Belloni, J.; Mostafavi, M. In *Radiation Chemistry: Present Status and Future Trends*; Jonah, C.; Rao, M., Eds.; Elsevier: Amsterdam, 2001; p 411.
- Mieisl, D. *IAEA Techdoc* 2004, 1438, 125.
- Chou, K. S.; Ren, C. Y. *Mater Chem Phys* 2000, 64, 241.
- Khanna, P. K.; Gokhale, R.; Subbarao, V. V. S. *J Mater Sci* 2004, 39, 3773.
- Wu, D.; Ge, X.; Huang, Y.; Zhang, Z.; Ye, Q. *Mater Lett* 2003, 57, 3549.
- Monti, O. L. A.; Fourkas, J. T.; Nesbitt, D. J. *J Phys Chem B* 2004, 108, 1604.
- Zhang, H. Y.; Zhang, J.; Wang, H. Y.; Chen, H. Y. *Mater Lett* 2004, 58, 2590.
- Whistler, R. L. *The Encyclopedia of Polymer Science and Technology*; Wiley: New York, 1969; Vol. 11.
- Reddy, T. T.; Tammishetti, S. *Polym Degrad Stab* 2004, 86, 455.
- McLaughlin, W. L.; Boyd, A. W.; Chadwick, K. N.; McDonald, J. C.; Miller, A. *Dosimetry for Radiation Processing*; Taylor & Francis: London, 1980.
- Creighton, J. A.; Eadon, D. G. *J Chem Soc Faraday Trans* 1991, 87, 3881.

29. Mundargi, R. C.; Agnihotri, S. A.; Patil, S. A.; Aminabhavi, T. M. *J Appl Polym Sci* 2006, 101, 618.
30. Tian, D.; Hu, W.; Zheng, Z.; Liu, H.; Xie, H. Q. *J Appl Polym Sci* 2006, 100, 1323.
31. Hund, J. F.; Bertini, M. F.; Zhand, G.; Levantis, C. S.; Levantis, N.; Tokuhira, A. T.; Farmer, J. *J Phys Chem B* 2003, 107, 465.
32. Huang, H.; Yuan, Q.; Yang, X. *Colloids Surf B* 2004, 39, 31.
33. Ramnani, S. P.; Biswal, J.; Sabharwal, S. *Radiat Phys Chem* 2007, 76, 1290.
34. Joshi, S. S.; Patil, S. F.; Iyer, V.; Mahumuni, S. *Nanostruct Mater* 1998, 10, 1135.
35. Chou, K. S.; Ren, C. Y. *Mater Chem Phys* 2000, 64, 241.
36. Ramnani, S. P.; Bhattacharyya, P. K.; Dhanya, S. *Radiat Phys Chem* 1992, 40, 519.
37. MacDiarmid, A. G.; Chiang, J. C.; Helper, M.; Huang, W. S.; Mu, S. L.; Somasiri, N. L. D. *Mol Cryst Liq Cryst* 1985, 121, 173.
38. Jumel, K.; Harding, S. E.; Mitchell, J. R. *Carbohydr Res* 1996, 282, 223.