STUDIES AND DEVELOPMENT OF RADIATION PROCESSED NANOMATERIALS

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Abstract: Nanotechnology is the emerging technology that deals with processing, manipulating and manufacturing devices and products at the microscopic scale of molecules or atoms with structures smaller than 100 nanometers. Realizing its potential, Government of India spending on R&D in nanotechnology has gone up by an order of magnitude in last 5 years through various national and international programs. High energy gamma radiation and electron beams could be a useful tool to create innovative and newer nano-materials for various applications in medical field for treatment and detection purposes. Considering its certain advantage for producing nano-materials, radiation technology will play a crucial role in development of such materials. Research and development in the area of nano--particles on polymer films, hydrogels, silica particles and their nano-clusters using radiation technology could be a possible route for development of new functional nano-materials.

1. INTRODUCTION

Nanotechnology is one of the fastest growing new areas in science and technology. The preparation and study of metal nanoparticles, nanocomposites, nano-devices etc. are of great interest in both research and engineering. Several methods and techniques have been established for preparation of nanoparticles in large quantities. Methods to achieve desirable shapes and sizes of nanoparticles are available for elements like Silver and Gold. World over, large number of scientists are involved in nanoparticles research and development. Their potential applications in biosensors, drug delivery, nanoelectronics, optical filters, catalysis, home appliances etc. have opened up new issues and challenges. Chemical methods for preparation of nanoparticles are most popular and easy for synthesis by top up approach. Radiation synthesis of nanoparticles have an edge in certain applications because of purity of nanoparticles and possibility of easy template casting.

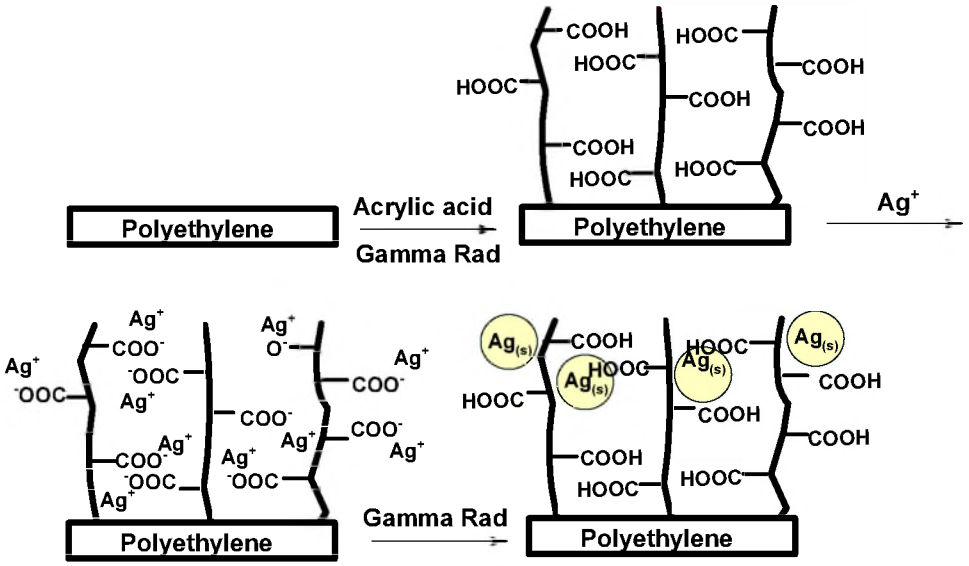
The development of nanoparticle based sensors is an area of great interest. A biological, chemical or biochemical sensor is a device capable of quantitative or qualitative recognition of a target species of interest for example peptides, metabolites, molecules or ions. In the last few years metal nanoparticles have been found to be good candidates for use as sensing indicators. In metal nanoparticles, the surface plasmon mode is restricted due to the small dimensions to which the electrons are confined. Therefore, the resonance frequency of the surface plasmon oscillation of the metal nanoparticle is different from the plasma frequency of the bulk metal. Surface interactions can alter the optical properties and influence the spectral profile of the light scattered by the surface Plasmon resonance of the metal nanoparticles. This feature can be applied as an indicator in sensing interactions. Because of availability of large surface area, nanoparticles/clusters have different surface properties than the bulk material surface. In the proposed study under CRP entitled "Synthesis characterization and applications of radiation processed nano materials for detection of biological important molecules", nanoparticles and ligands attached nanoparticles suitable for detection of specific bio molecules will be investigated. The study will include radiation synthesis and characterization of nano materials including nanoparticles and clusters of silver, gold and copper in different shapes and sizes encapsulated in matrices suitable for detection and estimation of molecules of biological importance. Radiation formation of mixed nano-metal clusters and their suitability for biomolecules detection will also be explored.

At our institute, various groups are working on research, development and applications on nanomaterials, metal nanoparticles, carbon nanotubes, multiwalled carbon nanotubes, etc. for semiconductor, catalysis, polymer composites, antibacterial and biosensor applications. This manuscript describes the recent work being carried out at Radiation Technology Development section.

2. FORMATION OF NANOPARTICLES ON POLYMER SURFACES

Polymers, in general, are relatively cheap and can be easily processed into thin films. One of the methods for incorporating nanoparticle on the surface of polymer films, fibers and other matrices is by producing polymeric brushes on the substrate by either "grafting to" or "grafting from" techniques and then reducing the nanoparticle precursor in these brushes (1,2). The radiation induced synthesis of metallic nanoparticles from metal salt precursor has many advantages compared to conventional chemical and photochemical methods. It is a simple environmental friendly process (additive free) that occurs at room temperatures with the advantage of producing high concentration of metal nanoparticles compared to chemical reduction method. The main advantage of the in-situ method is that all the free silver ions can be washed out thereby preventing undesirable side reactions which results in the agglomeration of the formed nanoparticles. The nanoparticles were produced in two steps. In the first step polyacrylic acid brushes were formed on the surface of PE film by mutual grafting induced by γ-irradiation. In the second step the silver ions were introduced in the brushes and reduced to silver particles by further γ-irradiation. When the transparent films are exposed to radiation, the color of the film changes from rose to purple to dark blue (Fig.1). The radiolytic reduction of silver ions in a solution of sodium polyacrylates has been studied in details by many researchers. They have shown that the color is produced due to the formation of silver-polyacrylate complexes during the early stages of irradiation. The optical transition involved being possibly an acrylate-silver charge transfer. Fig.2 shows the absorption spectra of the films during the early stages of reduction (3). At longer irradiation time (>2h) the transmittance of the films became almost zero and hence the spectra could not be recorded. After 1 h irradiation the film shows a shoulder at 472 nm. After 1.5 h the intensity of the shoulder increases with a slight blue shift and appears at 470 nm. On further irradiation, in 2 h, a strong absorption maximum is seen at 462 nm with a blue shift of 10 nm. All the three films showed an absorption band between 280 nm and 310 nm in addition to the band at about 470 nm. Ershow and Henglein attributed the absorption at the wavelengths, 290 nm and 480 nm to the rose species consisting of about four atoms and an equal number of Ag^+ ions. The blue species (Fig.1) formed at an irradiation time of 8 hours may be attributed to a larger cluster where a linear chain of silver atoms and equal number of silver ions exists along the polacrylate chains with a delocalization of the charge along the chain. In this study the plasmon band could not be observed even after 10h of irradiation, which is more than 40 % of the theoretical value. This suggests that the colored intermediates are more stabilized by the carboxylate groups of the polymeric brushes on the surface of PE films than in corresponding polyacrylate solutions. Another possibility is that the silver ions and the silver clusters are concentrated on a relatively small volume near the surface of the films and only a fraction of the reducing species ($H^{\cdot}$ and e_{aq}^{-}) produced in the bulk media is able to react with intermediate silver clusters or Ag^+.

The species produced during the initial stages (1-2 h) were quite stable in air at room temperature. There was hardly any shift in the wavelength (red shift or blue shift) of the absorption band after aging for one month. However a slight increase in the intensity was observed for all the samples.



Scheme 1. Gamma radiation induced reduction of silver ions in the grafted polyacrylate brushes.

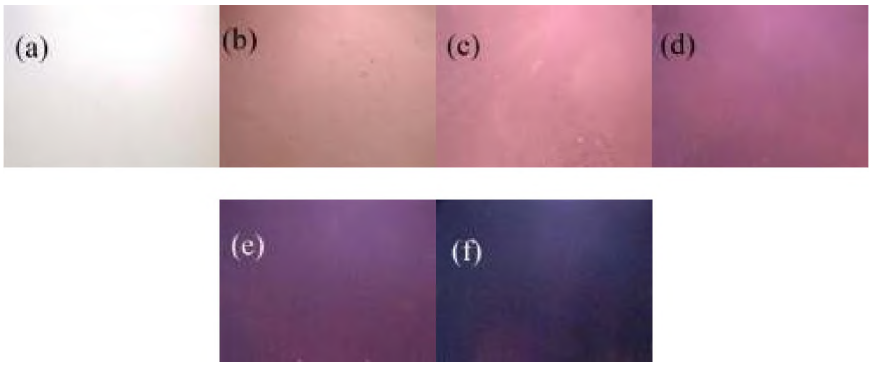


Fig. 1: Silver nanoparticles deposited at PE film exposed to graded doses of gamma radiation.

3. SILVER NANOPARTICLE HYDROGEL WOUND DRESSING

Uses of hydrogels are known and have several applications in medical field. Drug delivery devices, contact lenses, wound dressing, artificial cartilage's or membranes, vascular prosthesis, gel coated catheters etc., are some of the examples(4). Due to direct relevance to human health, scientists have been continuously exploring these systems. Generally, hydro(water) gels contain 30 -90% of water entrapped in a three dimensional network structure of a hydrophilic polymer. The large water content makes them highly bio-compatible and therefore preferred for use as biomaterials. Some of the hydrophilic polymers used in these applications include poly (vinyl pyrrolidone), poly(ethylene oxide), poly (vinyl alcohol) and poly(acrylic acid). Depending upon the nature of application, the size of these hydrogel can vary from nanometers (nanogels, injectable hydrogels) to centimeters to meters (wound dressing, fire blankets, drug delivery devices and implants). Many times, the wounds are infected. Use of iodine(tincture of iodine) or any water soluble drug makes the dressing

antibacterial gel in which the drug is slowly released to the wound(Fig. 3). In the latest development, silver nano-particles which are known to have bactericidal and healing properties can be incorporated into the dressing making it nano-silver dressing. Silver salts in appropriate concentration and conditions are mixed into the formulation which on irradiation get converted into silver nanoparticles. These nanoparticles diffuse out into the wound on application of the dressing showing bactericidal effects. In normal mixing of Silver ion in polymer and irradiating results in silver nanoparticles formation which get adhered to gel matrix and do not show bactericidal effect. The effectiveness of silver nano-hydrogel to kill bacteria are shown in Fig.ure below The present developed method is not suitable for large scale manufacturing.. Alternative methods are being explored to introduce silver nanoparticles into the PVA gel matrix in different shapes (sheets and cylinder), sizes (50-100 nm) for different therapeutic applications.

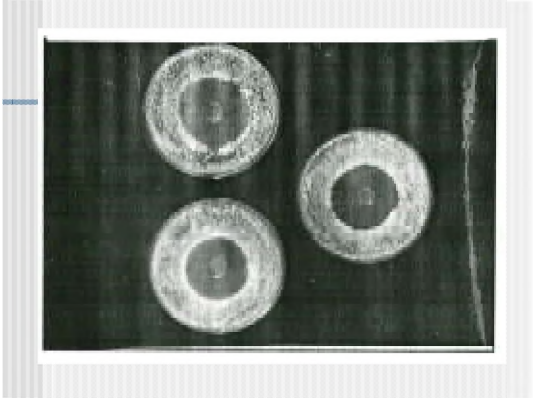


Fig. 2: Bactericidal effect of nano-silver hydrogel (inhibition zones using E.Coli).

4. SILVER NANO CLUSTERS

Small metal clusters are of great interest because oftheir nonlinear optical and special catalytic properties. Radiolytic reduction of aqueous metal ions is a simple,

clean, important and one of the extensively studied techniques, for producing homogeneous colloidal dispersionsof small metal particles Radiolytic reduction of Ag^{+} ions in theaqueous medium is one of the most exhaustively studiedsystems among the different reported metal ions. Various transient intermediates such as Ag^{0}, Ag^{2+},

Ag_3^{2+}, Ag_4^{2+}, etc. have been characterized by the technique of pulse radiolysis, and it finally results in larger Ag clusters with development of Plasmon absorption band at about 380–400nm Similar to the colloidal solutions, the hydrogels containing metal nanoparticles, can also play an important role in catalysis of many important chemical reactions in aqueous medium. But not much work has been reported so far on the radiolytic formation of metal clusters in the hydrogel matrix. The higher stability of a catalyst in gel matrix; uniform distribution without aggregation of small clusters; easy separation of a gel-immobilized catalyst from reaction mixture; accessibility of its large surface area and its repetitive usability, are some of the main advantages offered by such hydrogel systems.In the present work, the radiolytic formation of Ag clusters in aqueous polyvinyl alcohol (PVA) solutionand

PVA hydrogel, have been investigated and the two systems have been compared(5). The effect of Ag^+ ions on the radiation-induced crosslinking of PVA, Figure below, shows the formation Plasmon resonance absorption in gel matrix containing silver ions exposed to graded gamma radiation doses.

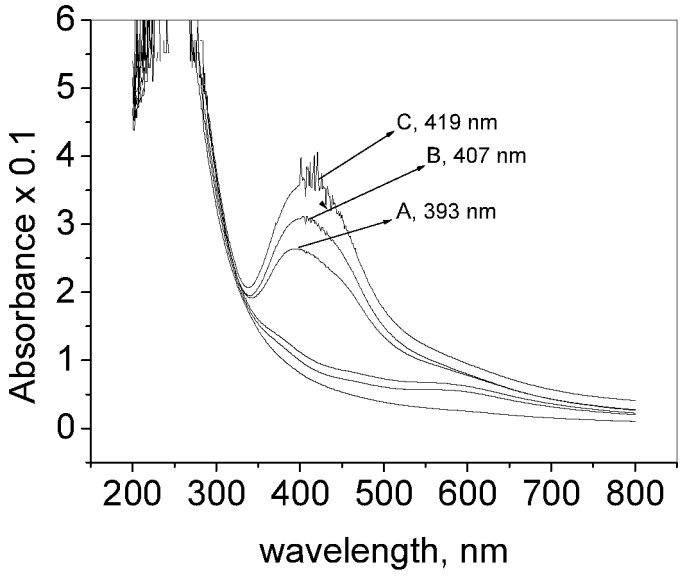


Fig. 3: UV-Visible spectrum of 8% PVA aqueous solution containing silver ions and exposed to graded gamma radiation showing formation of clusters(Doses C>B>A).

5. SYNTHESIS AND CHARACTERIZATION OF AG@SiO_2 USING GAMMA RADIATION AND ITS EXPLORATION FOR CATALYTIC DECOMPOSITION OF N_2O

Silver clusters on SiO_2 support have been synthesized using ^{60}Co gamma radiation. The irradiation of Ag^+ in aqueous suspension of SiO_2 in the presence of 0.2 mol dm^{-3} isopropanol resulted in the formation of yellow suspension. The absorption spectrum showed a band at 408 nm corresponding to typical characteristic surface plasmon resonance of Ag nanoparticles. The effect of Ag^+ concentration on the formation of Ag cluster indicated that size of Ag clusters does not vary with the Ag^+ concentration, which was varied from $4x10^{-4}$ to $5x10^{-3}$ mol dm-^{3}. Presence of oxygen during irradiation hampers the formation of Ag clusters. The results showed Ag clusters are stable in the pH range of 2 to 9 and start agglomerating in the alkaline region at pH above 9. The effect of radiation dose rate and ratio of Ag^+/SiO_2 on the formation of Ag clusters have also been investigated. The prepared clusters have been characterized by X-Ray diffraction (XRD) and Transmission Electron Microscopy (TEM), which showed the particle size of Ag clusters to be in the range of 10-20 nm(6).. A sample containing 5% loading of Ag on SiO_2 has been prepared by irradiating aqueous suspension of 5% SiO_2 containing 5 mol dm^{-3} isopropanol and 23 mmol dm^{-3} of Ag^+ to a radiation dose of 60 kGy. This sample has been explored for its catalytic activity in decomposition of N_2O to N_2 and the results showed that ~ 80% conversion can be achieved at 600^0 C.

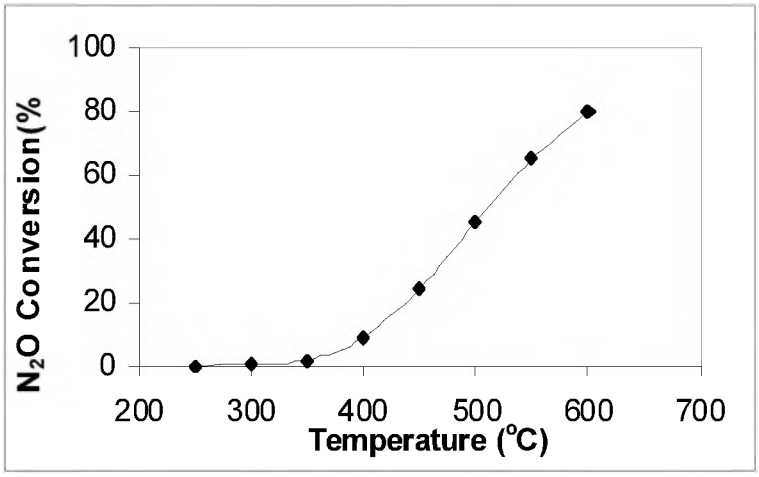


Fig. 4: TEM of Ag on mesoporous silica.

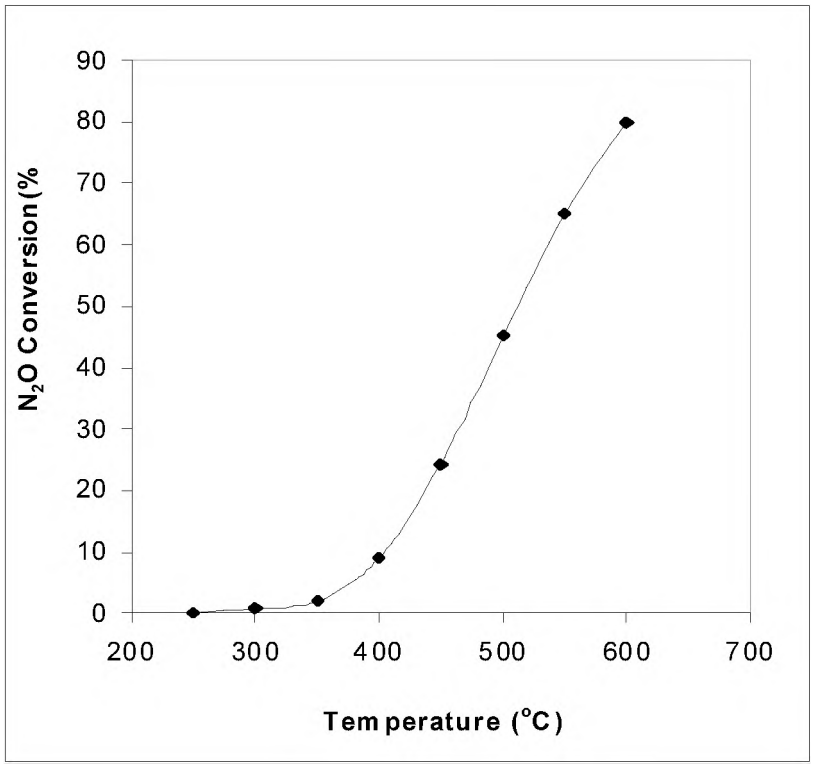


Fig. 5: Activity profile of Ag/SiO2 catalyst in N2O decomposition.

6. NANO-COMPOSITES

Different compositions of ethylene vinyl acetate (EVA)/multiple walled carbon nanotube (MWNT) nano-composites were prepared by melt mixing and subjected to different doses of gamma radiation. The efficiency of radiation vulcanization was analyzed by sol-gel analysis, Charlesby-Pinner parameter estimation and crosslinking density measurements.

Gamma radiation induced crosslinking was found to increase with MWNT fraction in EVA-MWNT nano-composites (po/qo in the range: 1.15-0.98). These results ruled out the possibility of a significant neutralization of single ionization spurs by MWNT addition. The incorporation of MWNT also resulted in increased hardness and higher density of the nano-composite matrix. The efficiency of multifunctional acrylates as crosslinking aid in the radiation-induced vulcanization of EVA-MWNT nano-composites was also investigated. The results established lower efficiency of methacrylates than of acrylates in the radiation vulcanization process.

REFERENCES

[1] BOYES, S., G., AKGUM, B., BRITTAIN, W., J., FOSTER, M.D., "Synthesis, characterization and properties of polyelectrolyte block copolymer brushes prepared by atom transfer radical polymerization and their use in the synthesis of metal nanoparticles", Macromolecules **36** (2003) 9539-9548.

[2] TSENG , C., WANG, C., Chen, C., "Polypropylene fibers modified by plasma treatment for preparation of Ag nanoparticles", J. Phys. Chem. B **110** (2006) 4020-4029.

[3] SANJU, F., LALIT, V., SUNIL, S., "Gamma radiation induced in situ generation of silver nanoclusters on the surface of PE films", Radiat. Phys. Chem. (2009).

[4] Lalit, V., "Role of natural polysaccharides in radiation formation of PVA–hydrogel wound dressing", Nucl. Instrum. Meth. Phys. Res. B **255** (2007) 343–349.

[5] MANMOHAN, K., LALIT, V., SANJU, F., "Radiolytic formation of Ag clusters in aqueous polyvinyl alcohol solution and hydrogel matrix", Rad. Phys. Chem. **73** (2005) 21–27.

[6] RAMNANI, S.P., SABHARWAL, S., VINOD KUMAR, J., HARIPRASAD REDDY, K., RAMA RAO, K.S., SAI PRASAD, P.S., "Advantage of radiolysis over impregnation method for synthesis of SiO_2 supported nano-Ag catalyst for direct decomposition of N_2O", Catal. Comm. **9** (2008) 756-761.

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