Abstract

The materials with nanometer grain sizes in one, two or three dimensions have the unique physical, chemical and mechanical properties which neither correspond to bulk material nor to single atom. Because of this fascinating difference, they have been exploited for extensive applications in optics, electronics, magnetics, chemical sensing, biomedicine, micro reactor, etc. Within the past decade, the incorporation of silver nanoparticles into polymer matrix have received more attention as the resultant nanocomposites exhibit better applications in catalysis, drug and wound dressings, optical information storage and surface enhanced Raman scattering, etc., as a result of better processability regarding film formation. The unique and fascinating properties of silver nanoparticles strongly depend upon the size and shape of the particles. Owing to its unique application of nanoscale devices special shaped (cubic, rod shaped, triangular, dendrites etc.) silver nanoparticles are superior to their spherical counterparts. So a growing effort is put into the preparation of special shaped silver nanoparticles including wires, rods, cubes, prisms, discs and dendrites, etc.

Many different approaches are used to prepare special shaped silver/polymer nanocomposites, but controlling simultaneously both size and shape remains an extremely difficult task. Moreover it is difficult to disperse silver nanoparticles homogenously into polymer matrix because of easy agglomeration of nanoparticles. So, convenient and effective ways of preparing silver nanoparticles in polymer materials are in strong demand. The most facile method of preparing silver nano structures is chemical reduction method in the presence of any synthetic high polymer. The polymer

prevents oxidation and coalescence of the particles and provides long time stability. The optical and electrical properties of the nanoperticles can be brought into full play, while the typical advantages of organic polymers (e.g. elasticity, transparency, etc.) are retained in the composite films. Thus, it is worthwhile to prepare different shaped silver nanoparticles and compare their properties in order to achieve any significant inference on shape-property correlation to give better understanding for any possible applications.

In the present thesis we aimed to synthesize special shaped (spherical, cube, dendrite and rod) nanocomposites in polyvinyl alcohol (PVA) matrix and studied their morphological, structural, optical and electrical properties. The thesis is divided into seven chapters. The detail layout of these chapters is shown below.

Chapter-1: Introduction embodies the general introduction which gives the overview of nanoparticles, historical background of noble metal nanoparticles, physical and chemical properties of bulk silver metal and silver nanoparticles. Properties like surface plasmon resonance, band gap, photoluminescence, optical transport properties of silver nanoparticles have been described here. This chapter also includes various available methods of synthesis of silver nanoparticles, advantages of polymer composite nanostructures and application of silver nanocomposites in different fields. The chapter ends with the preview of all the chapters in the present dissertation.

Chapter-2: Experimental deals with the experimaental section where we discuss about the materials and methods of synthesis of various shaped silver/ PVA nanocomposites.

We have obtained spherical shaped silver nanoparticles by adopting chemical reduction method and cubes and dendrites by using photoirradiation method. This chapter gives detail of synthesis procedure adopted with equipments used and also the reaction schematic of nanocomposite formation.

Also this chapter illustrates the different characterizations techniques adopted. UV-Vis spectra for optical absorption study are taken by Cary 300 scan UV-Visible spectrophotometer, Field emission scanning electron microscope (FESEM) and Transmission Electron Microscope images for morphology and particle size determination are taken by FESEM (JSM-6700F, JEOL, Japan) and TEM (JEM-100 CX II) respectively, XRD data for structure study are collected by Scifert XRD 3000 pd diffractometer with Cu-K_{α} (0.15418 nm) radiation, Photoluminescence (PL) are recorded by F-2500FL spectrometer and FTIR images are taken by FTIR (Perkin Elmer Spectrum RXI-FTIR System). Electrical properties viz. I-V Characteristics and Photoconductivity measured by Keithely CV meter (model 595)

Chapter-3: Spherical Shaped Silver/ PVA nanocomposites describes the synthesis of spherical shaped silver/ PVA nanoparticles by varying the concentration of $AgNO_3$ (1 mM to 5 mM) in PVA and its various characterizations. FESEM images show that the particles are mostly spherical in shape and the particle size increases with the increase in concentration. Out of these, particle distribution and size of the 1mM solution is the best and in 5 mM, slight change in shape is observed. FTIR transmittance is seen to increase with the increase in concentration also indicates the cross linking of silver and PVA. In PL spectra, the peak position is observed to red shift with increase of excitation wavelength from 405 nm to 475 nm due to size selective excitation effect. This indicates definite size range is active for a particular excitation wavelength. With the increase in excitation wavelength, the PL peak position increases linearly. PL intensity is maximum for excitation wavelength of 465 nm. I-V characteristics for all the samples are linear. Electrical conductivity is found to increase with the increase in concentration.

Chapter-4: Cubic Shaped Silver/PVA nanocomposite describes the synthesis of cubic shaped silver/PVA nanocomposite films by photoirradiation method, various characterizations and photoconductivity study. FESEM show cubic structures of particle size ranging from 120-150 nm. UV-Visible absorption spectra show strong plasmon resonance peak at 435 nm. The XRD patterns show a strong characteristic peak of silver nano around $2\theta = 38^0$ for (111) crystalline plane and a less intense peak at around $2\theta = 44^0$ for (200) crystalline plane. PL spectra show band at 418 nm that for excitation wavelength of 367 nm, emission. I-V characteristics are found to linear in the voltage range 0 to 20 Volts. Negative photoconductivity is observed in the kinetics of photocurrent measurement As the light source is switched on, the current decays instantaneously to less than half of its dark value and decrease still further and on switching off the light, it increased instantaneously again to reach the original dark value.

Chapter 5: Silver/ PVA nanodendrites describes the synthesis of silver/ PVA nanodendrites by photoirradiation method and characterization of silver/ PVA nanodendrites. The solution (1mM and 5mM $AgNO_3$) containing nanocubes (as detailed in chapter 4) are irradiated further and by fractional aggregation silver nanodendrites are formed. SEM images show that the thickness of the dendrite is 10-30 nm. TEM images show that the length of the branches is 14-15 μm branching in all directions. XRD spectra show peak at 38.1^0 for (111) plane and the average particle size is 10-20 nm. UV-Visible spectra show peak at 435 nm for 5mM, 435-440 nm for 1 mM and broader.

PL spectra Show for Excitation wavelength of 380 nm, emission band at 768 nm for 1 mM and for Excitation wavelength of 320 nm, emission band at 660 nm for 5 mM nanodendrites.

Chapter-6: Effect of Annealing on Spherical Shaped Silver Nanoparticles describes the effect of annealing on the structural morphology and optical properties of the silver/PVA nanocomposites. The film containing spherical shaped nanoparticles is annealed at different temperatures (373 K, 423 K, 473 K, 523 K and 573 K) in vacuum, and the effects on the surface morphology and the surface plasmon resonance characteristics are investigated. Scanning electron microscopy images show the change in shape and size with the increase in annealing temperature. Silver nanocubes and nanorods are seen to form at annealing temperature of 523 K and 573 K respectively. UV-Visible spectra show a blue shift of surface plasmon resonance peak with the increase in annealing temperature. XRD shows a characteristic peak of silver nano at $2\Theta = 38^0$ for (111) crystalline plane. Photoluminescence spectra show emission peak at 450 nm for excitation wavelength of 350 nm.

Chapter-7: Overall Summary gives the overall summary of the results obtained in different chapters. We have successfully synthesized silver nanoparticle of various sizes and shapes (spherical, cubic, dendrite and rod) by chemical reduction method, photoirradiation method and by annealing. As per our anticipation, we saw definite change in various properties with change in size and shape of the nanoparticles. For better visualization, the results are displayed in tabular form.

Finally in the **Appendix**, the author gives her list of publications in the referred journals and also the conferences/ workshops.