Chapter 7

Overall Summary

Silver nanoparticles have potential application in the field of electrical, electronics, photonics, catalysis, information technology, SERS, biological labelling, optical sensor, etc. The properties are largely governed by the size and shape of the particles. Thus, synthesis of silver nanostructures of different size and shape is of immense interest. In this dissertation, we have reported the synthesis of silver-polyvinyl alcohol (PVA) nanoconposites of various shapes (spherical, cubic, dendrite, rod) and sizes by simple and cheap method. We have also studied their optical and electrical properties and found that these depend upon the shape and size of the nanocomposites. We have used PVA as matrix which simultaneously acts as reducing agent to form silver nanoparticles from its salt and also to stabilize them. PVA has the advantage of being water soluble, transparent and has capability of forming uniform dispersion of nanoparticles.

Spherical shaped silver-PVA nanocomposites are obtained by varying the concentration of silver nitrate ($AgNO_3$) from 1 mM to 5 mM in 3 wt% PVA solution by chemical reduction method. Films cast on different substrates are characterized. Particle size has been found to increase with the increase in concentration. FTIR transmittance shows increase with the increase in concentration and also reveals the cross linking of silver and PVA. I-V curves are linear showing ohmic characterstics upto applied voltage of 0-

20 V. Conductivity increases with the increase in concentration. Out of all these films, particle distribution and size of the particle of 1 mM is the most uniform and in 5 mM, slight change in shape is observed. The PL peak position is observed to have red shift with increase of excitation wavelength from 405 nm to 475 nm due to size selective excitation effect. With the increase in excitation wavelength, the PL peak position increases linearly. PL intensity is maximum for excitation wavelength of 465 nm. However this is little more than the peak position in UV-Vis spectra observed by us which is at 441 nm. This is justified as our surface plasmon resonance peak is much broader. The change in peak position and intensity of PL can be attributed to various particle sizes so that different set of particles of definite size range is active for a particular excitation wavelength.

By irradiating the solution containing spherical shaped nanocomposites with light of wavelength of 475 nm, 510 nm and 650 nm for 23 hrs. we observed predominance of cubic shaped particles in the FESEM picture of the films. FESEM pictures show cubic structures of particle size ranging from 120-150 nm. The UV-Visible absorption spectra shows strong plasmon resonance peak nearly at 435 nm and the peak is broader than that of spherical shape. The XRD pattern shows a strong characteristic peak of silver nano around $2\theta = 38^0$ for (111) crystalline plane and a less intense peak around $2\theta = 44^0$ for (200) crystalline plane. For excitation wavelength of 367 nm, emission band is observed at 418 nm. But for spherical shape, no emission band is observed for the same excitation wavelength. It is worthwhile to note that PL excitation is shifted to lower wavelength (higher energy) as the shape changes from spherical to cubic. I-V curves are linear in the same voltage range i.e. 0-20 V showing ohmic characteristics. We have also observed negative photoconductivity in these films. When the films are irradiated with white light, conductivity decreases and when the light is switched off the current increases to its original value. This property of silver nanoparticles can be used to fabricate optical switch.

By irradiating the solution containing cubic shaped nanocomposites with light of same wavelength of 475 nm, 510 nm and 650 nm for 2 more hrs., we observed formation of nanodendrites through FESEM pictures. These dendrites shows fractal phenomenon. Fractals have good connectivity between different parts and large surface area due to which fractals are excellent catalyst. TEM images show that the length of the branches is 14-15 μm and branches in all direction From the TEM images using box counting method we have calculated fractal dimensions. The fractal dimensions are found to be 1.42, 1.60, 1.71 for 1 mM $AgNO_3$ samples irradiated by these wavelengths 475 nm, 510 nm and 650 nm respectively. We called them as 1B, 1G, 1R. Whereas the fractal dimension for similar 5mM $AgNO_3$ samples (5B, 5G and 5R) are found to be 1.55, 1.57 and 1.62 respectively. We observe increase in fractal dimension with increase in excitation wavelength in both these sets. The increase is more for 1 mM samples though. From the FESEM images the observed thickness of the dendrite is in the range 50-150 nm. It is also observed that with the increase in concentration of $AgNO_3$, the average thickness of the dendrites increases. XRD spectra shows peak at 38.1^0 for (111) plane and the calculated particle size ranges 10-20 nm. UV-Visible spectra show peak at 435-440 nm for 1 mM $AgNO_3$ and at 435 nm for 5 mM $AgNO_3$. Also the peak is broader than that of spherical and cubic shaped nanoparticles. This broad peak in UV-Visible spectra is useful in Surface Enhanced Raman Scattering. PL spectra show emission peak at 660 nm for 1 mM $AgNO_3$ nanodendrites for excitation wavelength of 320 nm, whereas that for 5 mM one is observed at 768 nm for excitation wavelength of 380 nm.

The composite films containing spherical silver nanoparticles are then annealed at five different temperatures (373K, 423K, 473K, 523K and 573 K) in vacuum for 2 hrs. SEM images of the annealed films show that the particle size increase and the shape of the particles become cubic at 523K and nanorods at 573K. XRD spectra shows peak at $2\Theta=38^0$ for (111) plane for all the annealed samples. UV-Visible spectra show a clear blue shift of surface plasmon resonance peak with increase in annealing temperature. This is interesting from application point of view. For 523K sample, the several peaks are observed which may be attributed to multipole resonances, such as quadrupole, octupole, etc. For 573K annealed sample, two peaks are observed which may be attributed to longitudinal and transverse absorptions at 320 nm and 430 nm respectively. PL spectra show peak at 450 nm for excitation wavelength 350 nm with slight red shift with increase of annealing temperature. All these results have been tabulated in table 7.1 for better visualization.

To conclude we may say, we have successfully synthesized silver –PVA nanocomposites of various shapes and sizes. Optical properties viz. UV-Visible spectra and Photoluminescence spectra are seen to depend strongly upon the shape and size of the particles. Using these results we can anticipate fabricating optical device in future. Moreover, we have obtained the phenomenon of negative photoconductivity which might be useful in fabricating optical switch.

Table 7.1 Overall Summary

Studies	Nanosphere	Nanocubes	Nandendrites	Annealed Film
SEM	20- 100 nm	120-150 nm	Thickness 50-150 nm	Size increases from 100 nm to 500 nm with temperature & **nanocubes** and **rods** are formed
TEM			Branch length 14-15μm fractal dimension 1.42 to 1.71	
XRD	38.1^0 for (111) plane	38.1^0 and 44^0 for (111) and (200) plane respectively	38.1^0, 44^0 and 64.6^0 for (111), (200) and (220) plane respectively	38.1^0 for (111) plane
UV-Visible Spectra	423-441 nm	435 nm, broad	435 nm, broader	Blue shift with the increase in annealing temperature
Photoluminescence Spectra	Excitation wavelength-405- 475 nm, Emission wavelength-608 - 720 nm	Excitation wavelength-367 nm, Emission wavelength- 418 nm	Excitation wavelength-380 nm and 320 nm, Emission wavelength- 768 nm and 660 nm	Excitation wavelength-350 nm, Emission wavelength-450 nm, red shift with annealing temperature
Electrical Conductivity (0-20 V)	I-V ohmic	I-V ohmic and negative photoconductivity	I-V ohmic and negative photoconductivity	I-V ohmic