Chapter 1

Introduction
1.1 Introduction to Nanomaterials

The materials having their structured components with one or more dimensions in the nanometer range are designated as nanomaterials. Although, these materials have a long history (Faraday, 1857), but it was only in last few decades (Kroto et al., 1985; Keribeg & Vollmer, 1995; Porel et al., 2007; Abargues et al., 2008; Leong et al., 2008; Meng et al., 2008; Ramesh et al., 2009) that this field has touched new heights. This became possible only due to the invention of revolutionary imaging methods and sophisticated experimental techniques, which made the characterization of these materials easy. Nanomaterials are broadly classified into three categories depending on their one, two and three dimensions, respectively in nanometer range. The materials, such as thin films, surface coatings, etc. where only one of three dimensions is in nanometer range, are categorized as one dimensional nanomaterials. Materials with two of the three dimensions in nanometer scale, like nanowires, nanotubes, etc. and those having all the three dimensions in nanometer range, e.g. quantum dots, fall in the category of two and three dimensional nanomaterials, respectively.

The nanostructured materials have attracted the attention of researchers mainly due to their unique and distinctive properties. Materials, with their constituents having dimensions in micrometer scale, exhibit the properties mostly similar to that of their bulk counterpart. As the dimensions are reduced to nanometer scale, the properties of the materials, like electrical, thermal, optical, mechanical, etc. are changed significantly (Cao, 2004). Such changes in the properties of the material at the nanometer scale are originated mainly due to the following reasons:

(a) Surface to Volume Ratio: The ratio of surface area to volume is actually a measure of the percentage of molecules or atoms that are on the surface of the material as compared to the total number of molecules or atoms in the entire piece of material. As an illustration, figure 1.1 clearly demonstrates how the surface area increases with the reduction in the dimensions of the material. For the single cube of side 1 cm, the volume 1 cm$^3$ comprises the surface area 6 cm$^2$. With the consistent reduction in the dimensions of the cube, a proportional increase in surface area is clearly evident. For the cube of side 0.5 cm, 0.25 cm and 100 nm,
the surface area increases from 12 cm$^2$ to 24 cm$^2$ and finally, to 6,00,000 cm$^2$, respectively for the same volume of 1 cm$^3$. Such an increase in surface area of the material constituents leads to the increased number of atoms on the surface, which are more reactive than those present in its bulk. This is because of the reduced number of nearest neighbours of the surface atoms, presence of unsaturated sites or dangling bonds at the surface etc., which result in their enhanced surface energy. This is responsible for the change in chemical and physical properties of nanoparticles as compared to their bulk counterpart (Nei & Emroy, 1997; Shipway & Willner, 2001; Wang et al., 2004).

**Figure 1.1:** A schematic representation of the increase in surface area of the cube with reducing dimensions for the same volume of 1 cm$^3$.

**(b) Quantum Size Effect:** When the particle size is reduced and attains the limit of the Bohr’s radius, its electronic energy structure changes from continuous energy bands to discrete energy levels (Kubo, 1962; Cotney, 1971; Ventra et al.,
2004), as shown in figure 1.2. Such a transition is termed as the quantum size effect (Daniel & Astruc, 2004). This is the major cause, which is responsible for the modification in the properties of materials at nanometer scale. Also due to this, the continuous optical transitions between the electronic bands become discrete and the properties of the nanomaterials become size-dependent (figure 1.2) (Wang and Herron, 1991; Bharagava et al., 1994; Keribeg and Vollmer, 1995) unlike to that for bulk materials. For example, colloidal solution of gold nanoparticles has a deep red colour, which becomes progressively yellowish with increasing particle size. Such unique properties lead to the wide applications of nano-scale materials into the emerging areas of technological importance (Pillai et al., 2007; Matheu et al., 2008; Atwater and Polman, 2010; Christopher et al. 2012; Liu et al., 2013; Qi et al., 2013).

Figure 1.2: A schematic representation of electronic energy levels in atoms, molecules, clusters, nanoparticles and bulk.
1.2 Synthesis of Nanomaterials

Nanomaterials can be synthesized either by bottom-up or top-down approach, as discussed below. Under the situation, when both top down and bottom up processes are involved, the technique is referred to as hybrid approach. Figure 1.3 highlights a schematic representation of bottom-up and top-down approach.

a) Bottom-up Approach: According to this approach, constituents of the material are arranged into more complex assemblies atom–by–atom or molecule–by-molecule or cluster-by-cluster (Klabunde, 2001), like that of the growth of a crystal, till the desired dimensions of the material are achieved. Synthesis of nanoparticles by electro-deposition, vapor phase deposition, sol-gel, ion beam epitaxial technique, etc. are some examples of the bottom-up approach (Cao, 2004). This approach generally provides nanostructures with better homogeneity in chemical composition and precise control on their size and shape.

Figure 1.3: A schematic representation of Bottom–up and Top–down approach.
b) **Top–down Approach:** In this approach, the material constituents with larger dimensions are processed to reduce their size until the nanoscale dimensions are achieved. The top-down approach (*Klabunde, 2001; Whitesides & Love, 2001; Schmid, 2004*) often involves the methods, like ball milling, sputtering, etc. However, the limit up to which the size can be reduced depends on the process involved.

### 1.3 Nanocomposites

The direct use of nanoparticles in different applications is limited because of their instability due to their high surface to volume ratio, easily oxidizing nature and contamination to impurities besides the problems associated in their handling due to their small size (*Henglein, 1993*). Such difficulties can be resolved by embedding the nanoparticles into suitable host matrix supplementing the additional benefit of manipulating the shape and organization of nanoparticles (*Biswas et al., 2004; Jiang et al., 2007*). This new class of materials, generally named as nanocomposites, takes the advantage of both the host matrix as well as of the embedded nanoparticles.

Depending upon the nature of the host material and embedded nanoparticles, nanocomposites are generally classified into the three combinations, i.e. Organic-Organic, Organic-Inorganic and Inorganic-Inorganic. In *Organic–Organic combination*, both the host matrix and nano-fillers are of organic nature. Suitable examples are polymers based host matrices dispersed with nanoparticles of biomaterials, conducting polymers, etc. In *Organic–Inorganic combination*, the host matrix and nano-fillers are of organic and inorganic nature, respectively. Nanocomposites of thermoplastic polymers dispersed with carbon nanotubes, metal nanoparticles, etc. fall in this category. *Inorganic–Inorganic combination* contains both host matrix and filler particles of inorganic nature. The relevant examples include ceramic or metal based host matrices with the dispersion of metal nanoparticles, oxide form of nanoparticles, etc.

### 1.4 Polymer–Metal Nanocomposites

Among the nanocomposites, the polymer–metal nanocomposites have gathered a lot of interest because of their potential applications in many diverse fields of science.
and technology (Mayer, 2001; Corbierre et al., 2005; Porel et al., 2005; Sih & Wolf, 2005; Zhu & Zhu, 2006; Porel et al., 2007; Abargues et al., 2008; Leong et al., 2008; Meng et al., 2008; Ramesh et al., 2009; Hariprasad & Radhakrishnan, 2010; Ramesh & Radhakrishnan, 2011; Singh et al., 2012; Sandeep et al., 2013; Qi et al., 2013). This is because of the excellent inherent properties of the polymers (Darraud et al., 1997; Ruck et al., 1997; Hong et al., 2001; Lee et al., 2001; Thompson, 2001; Liu et al., 2002; Singh, 2002; Fink, 2004; Singh et al., 2005; Kondyurin & Bilek, 2008; Hadjichristov et al., 2009) as host matrix coupled with the unique features of metal nanoparticles (Yu et al., 1997; Link & El-Sayed, 1999; Mohamed et al., 2000; Peng et al., 2000; Jin et al., 2001; Hao et al., 2002; Jin et al., 2003).

1.4.1 Polymers as Host Matrices

Polymers, due to their extraordinary properties, such as their easy processability, light weight, flexibility and mouldability, etc. are best suited materials to be utilized as host matrices for the synthesis of nanocomposites. Further, due to high chemical reactivity, the oxidation of nanoparticles occurs readily leading to their agglomeration, which finally results into their larger structures. Therefore, any stabilizing agent is required to enhance their chemical stability retaining their basic properties. A proper choice of the polymer facilitates environmentally safe synthesis without the requirement of any additional stabilizing agent (Nadagouda & Varma, 2007). Also suitable combinations of polymers as host matrices and nanoparticles as fillers lead to the synthesis of nanocomposites possessing novel catalytic, conductive, magnetic or optical properties (Balan & Burget, 2006).

1.4.2 Metal Nanoparticles

Metals exhibit high electrical and thermal conductivity and thus, have tremendous applications in diverse disciplines. The main interest of researchers towards metallic particles lies due to the demonstration of their unique and brilliant colours when their size is reduced to nano-scale. Such a variety of colours is observable due to the interaction of light with metal particles when their size becomes smaller than the wavelength of light (Faraday, 1908). Therefore, metallic nanoparticles act as excellent
chromophores and show plasmonic band in the visible and near infrared region of electromagnetic spectrum (Toshima & Yonezawa, 1998; Huang et al., 2004; Namboothiry et al., 2007; Dahal, 2010). Nanoparticles of noble metals such as gold, silver, platinum and copper have been extensively studied as these particles form stable dispersions and find applications in photography, biological labeling, catalysis, sensors, optoelectronics and photonics (Wohltjen & Snow, 1998; De et al., 2000; Kim et al., 2001; Gudiksen et al., 2002; Krasteva et al., 2002; Obare et al., 2002; Zamborini et al., 2002; Kang et al., 2005; Sonnichsen et al., 2005; Lee & El-Sayed, 2006; Wang & Halas, 2006; Zhang et al., 2006; Sharma et al., 2009). In addition, these nanoparticles show excellent optical properties, which find many scientific applications (Barnes et al., 2003; Naryanan & El-Sayed, 2005; Eustics & El-Sayed, 2006; Homola, 2006; Hu et al., 2006; Ozbay, 2006; Pillai et al., 2007; Awazu et al., 2008; Matheu et al., 2008; Larsson et al., 2009; Atwater & Polman, 2010; Garcia, 2010).

1.5 Surface Plasmon Resonance

Surface Plasmon Resonance (SPR) is defined as the collective oscillation of conduction band electrons at the metal surface when the electromagnetic radiation of wavelength comparable to the size of the particles is incident on the metal surface. Figure 1.4 schematically shows the origin of surface plasmon resonance of a spherical metallic nanoparticle.

In general, when the electromagnetic radiation falls on the metal surface, it displaces the electron cloud of the conduction band from the positive nuclei giving rise to the surface charge distribution, as illustrated in figure 1.4. Due to this surface charge distribution, restoring force due to the Columbian attraction between positive and negative charge center comes into picture, which causes the oscillations of the dipole charges with the periodic phase reversal of the electromagnetic radiation. When the dipole oscillating frequency matches with the frequency of incident electromagnetic radiation, a resonance is occurred and the metal particles on the surface absorb the energy; the phenomenon is known as surface plasmon resonance absorption. The energy corresponding to this absorption band depends on the free electron density, shape & size of the nanoparticle and the dielectric function of the surrounding medium.
In case of noble metal nanoparticles, like Cu, Ag and Au, this SPR absorption band falls in the visible region of the electromagnetic spectrum resulting in their optical response novel for various applications (Atwater & Polman, 2010; Garcia, 2010).

**Figure 1.4:** Schematic of plasmon oscillation for a spherical nanoparticle showing the displacement of the conduction electron charge cloud relative to the nuclei.

### 1.6 Unique Features of Polymer–Metal Nanocomposites

As discussed in the above section, polymer–metal nanocomposites combine the remarkable properties of metal nanoparticles and inherent characteristics of polymer matrix to make them important candidates for various applications, highlighted as under:

- Metal nanoparticles dispersion in the polymer matrix improves the optical, mechanical and thermal properties of polymers, which are very important for
their use in applications, like photonics, sensors, solar cells, optoelectronics, coating, etc. (Tokizaki et al., 1994; Wang et al., 2005; Gradess et al., 2009).

- Non-linear optical properties shown by polymer–metal nanocomposites find applications in non–linear optical devices, electro-optics, etc. (Maier et al., 2003; Lu et al., 2006).

- The surface plasmon behaviour of metal nanoparticles depends on the shape & size of nanoparticles and the surrounding environment of embedded nanoparticles. By changing these parameters, the surface plasmon of metal nanoparticles embedded in polymer matrix can be tuned, which find applications in biological sensors, filters, optical switching devices, etc. (Caseri, 2000; Biswas et al., 2004; Xia & Halas, 2005; Srivastavas et al., 2008).

- When nanoparticles embedded in a dielectric matrix, like polymer, are excited by light, the absorption of light and subsequent surface plasmon oscillations lead to the strongly enhanced electric field (Sarychen and Shalaev, 2000) within the nanoparticles and the interparticle gaps. Such unusual excellent optical features of these nanocomposites find their applications in high efficiency solar cells (Grangvist, 2003), infrared photo detectors, sensors, and solar control glazing windows, etc.

- The superparamagnetism shown by magnetic nanoparticles can be explored by combining magnetic nanoparticles with polymers, which makes them excellent materials for magneto–optical devices, magnetic tapes, magnetic recording, electromagnetic wave absorbers, etc.

- The combination of low refractive index of polymer and high refractive index of metal nanoparticles can be utilized in antireflective coating, high refractive index lenses, optical fibers, waveguides, etc. (Fang et al., 2005; Althues et al., 2007; Li et al., 2010).

- The Surface Enhanced Raman Scattering observed in polymer–metal nanocomposites can be explored in applications, such as active Raman scattering substrates (Erturk et al., 1983; Wang & Li, 1997; Li et al., 2010).
Further, the properties of polymer–metal nanocomposites can be regulated through various treatments like gamma, ultraviolet, X-rays, ion beam irradiation etc. (Gavade et al., 2010; Shah et al., 2010; Gavade et al., 2011; Puiso et al., 2011; Singh et al., 2011). Due to the complexity of the phenomenon involved, it is not possible to probe the overall damage directly; rather one can study individual effects of radiation damage, e.g. chemical changes, structural changes or changes in its mechanical, optical, electrical properties, etc. To understand the basic mechanism responsible for these changes, one must know the interaction process of these radiations with matter as discussed in the next section.

1.7 Interaction of Ionizing Radiations with Matter

The ionizing radiations include all kinds of electromagnetic and corpuscular radiations, e.g. UV–rays, X–rays, gamma rays, ion beam, etc. with energies appreciably greater than the dissociation energy of the bonds present in the material.

1.7.1 Electromagnetic Irradiation

Electromagnetic radiations, while traversing through a material medium, transfer their energy (Evans, 1955; Chapiro, 1962; Leo, 1994) to the medium as a result of photoelectric absorption, Compton scattering and pair production processes. These radiations do not produce ionization directly but lose their energy to the target material by the absorption of photons through any of the processes mentioned above and results into the creation of fast moving electrons. These electrons as a result of their interaction inside the medium produce secondary electrons and so on. Since electromagnetic photons do not lose their energy in a continuous manner and are simply attenuated; therefore, the entire bulk structure of the material gets modified after electromagnetic irradiation. The energy transferred by the electromagnetic rays, especially in polymers, is responsible (Sinha et al., 2001; Saad et al., 2005; Saqan, 2007; Zaki, 2008) for the changes at molecular level, such as chain–scissioning, cross-linking, free radical formation, elimination of volatile species, reordering the chemical bonds, etc. which are finally responsible for the modification in their properties.
1.7.2 Swift Heavy Ions Irradiation

When an energetic ion penetrates through the material, it loses energy mainly by two nearly independent processes: (i) elastic collisions of the incident ion with the nuclei of the target atoms, usually referred to as nuclear energy loss \((dE/dx)_n\) (ii) inelastic collisions of the incident ion with the atomic electrons of the target atoms, generally expressed as electronic energy loss \((dE/dx)_e\) (Ritchie & Claussen, 1982; Fink & Chadderton, 2005). The relative contribution of the energy loss through these two processes depends upon the nature of the incident ion and the target material parameters. For MeV heavy ions, usually the electronic energy loss dominates while the nuclear energy loss remains almost negligible. However, when the ion velocity reduces to the extent that the ion behaves almost as a neutral atom, the ion-matter interaction occurs via hard sphere scattering and under this situation the nuclear energy loss starts dominating over electronic energy loss. Thus, for swift heavy ions, where the ion velocity remains considerably higher than that for its orbital electrons, the electronic energy loss remains into picture with nuclear energy loss to be almost negligible.

Finally, the energy deposited by the swift heavy ions during their passage, particularly in polymers, leads to the processes of macromolecular destruction, chain–scissioning, cross–linking, free radicals formation, carbonization, oxidation, etc. These processes are responsible for the modification in the optical, electrical, thermal, mechanical and chemical properties of the polymeric material.

1.8 Motivation

Due to the unique features of polymer-metal nanocomposites and the feasibility to tune their structural, electrical, optical, mechanical, thermal and other properties as a result of electromagnetic and ion beam irradiation, these nanocomposites are promising futuristic materials in device applications at a larger scale (Mayer, 2001; Corbierre et al., 2005; Sih & Wolf, 2005; Zhu & Zhu, 2006; Avasthi et al., 2007; Puiso et al., 2011; Sharma et al., 2011). The characteristic features of polymer-metal nanocomposites not only depend on the concentration and dispersion of the embedded metal nanoparticles but also on their size, shape and orientation within the polymer matrix. These
parameters of embedded nanoparticles, which are responsible for the change in the properties of polymer-metal nanocomposites, can be regulated through irradiation (Abyanesh et al., 2007; Bernard et al., 2011; Puiso et al., 2011; Sharma et al., 2011) besides their synthesis mechanism. Although, sufficient literature is available related to the synthesis and characterization of polymer-metal nanocomposites (Khanna et al., 2005; Gautam & Ram, 2009; 2010) but the studies related to irradiation induced effects on their optical, electrical, thermal and structural behaviour are scarce.

Motivated with the feasibility of tuning the properties of polymer-metal nanocomposites as a result of irradiation, in the present work, we have concentrated on a comprehensive study related to the effect of gamma, ultraviolet and swift heavy ion irradiation on the optical, electrical and structural behaviour of PVA-Ag nanocomposites. The observed changes in the optical and electrical properties have been tried to be correlated with the induced structural changes, revealed through X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and Raman Spectroscopy. The selection of PVA in PVA-Ag nanocomposites is due to its high dielectric strength, good charge storage capacity, dopant-dependent electrical and optical properties and capability to act as good stabilizing and capping agent for embedded metal nanoparticles (Khanna et al., 2005; Bhajanti et al., 2007; Mahendia et al., 2010; Voue et al., 2011) while silver nanoparticles provide interesting optical and electrical properties.

1.9 Objectives of the Present Study

The following were the specific objectives of the present study:

1. To synthesize PVA–Ag nanocomposites by in-situ chemical reduction method and preparation of their films by solution casting method.
2. To reveal the size distribution and dispersion of embedded nanoparticles through Transmission Electron Microscopy.
3. To study the optical, electrical and structural behaviour of prepared PVA–Ag nanocomposite films using UV–Visible spectroscopy, I-V measurements, FTIR and Raman Spectroscopic techniques and XRD analysis.
4. To analyze the variation in optical, electrical and structural properties of prepared PVA–Ag nanocomposite films as a result of gamma, UV and swift heavy ion irradiation at different doses.

5. To understand the irradiation induced changes in optical and electrical behaviour of PVA–Ag nanocomposite films in terms of induced structural changes.

In order to meet the objectives as stated above, the procedure followed for experimental measurements, obtained results and their interpretation are presented in the subsequent chapters.
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