Chapter 1: Introduction to metal nanoparticles and polymer nanocomposites: principle of radiation induced synthesis

1.1. Introduction

"There's Plenty of Room at the Bottom", the historic remark Richard Feynman made during his lecture delivered on December 29, 1959, is what probably sowed the seeds for the emergence and growth of the concept of nanotechnology. Though not entirely unknown to the ancient and medieval world, the concept of nanotechnology gathered steam primarily during the 1980’s as seminal work and discoveries by researchers from across the globe converged to build up a strong platform on which the future course of this field was to be based. Fundamental works in the field was soon followed by the myriad of applications which further augmented people’s interest in this area and led to growing public awareness. The past decade or so has been witness to massive developments in this field and with every passing year, there has been a phenomenal growth in areas such as basic research, applications in the field of catalysis, sensors, imaging and other applications as well as in disciplines such as quantum dots, polymer nanocomposites, drug delivery systems etc. [1-10]

Nanomaterials are traditionally defined as materials with at least one external dimension in the size range from approximately 1-100 nanometers. These materials owe their uniqueness to their distinct differences from the corresponding bulk materials. The primary characteristics that describe a nanomaterial are i) increased specific surface area, and ii) quantum effects [11,12] These factors can significantly change or enhance properties, such as reactivity, strength, optical and electrical characteristics. As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside. Thus nanomaterials have a much greater surface area per unit mass compared to larger particles
As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles. In tandem with surface-area effects, quantum effects can begin to dominate the properties of matter as size is reduced to the nanoscale [14]. These can affect the optical, electrical and magnetic behaviour of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale. Materials that exploit these effects include quantum dots, and quantum well lasers for optoelectronics.

Another area that has generated tremendous interest over the years is nanocomposite materials, which basically combines the properties of a nanomaterial with those of a suitable matrix in which it is uniformly dispersed. Polymer nanocomposites ie, materials with a polymeric matrix, in particular have emerged as a highly useful class of materials [17,18]. These advanced materials offer enhanced mechanical, thermal, flame retardant, barrier, electrical and chemical properties compared to their constituent elements, which arise due to nanoscale level of mixing between the fillers and the base polymer matrix.

The growth of nanotechnology has simultaneously led to the emergence of a large number of fabrication techniques. One of the important techniques of nanosynthesis involves the use of ionizing radiation sources, such as UV, gamma, electron beam and X-rays. This technique has also shown remarkable growth over the years and has been extensively employed in the current research work.

### 1.2. Nanoparticles

#### 1.2.1. Basic definition and classification

Nanoparticles are defined as nanomaterials which have all three dimensions in the nano regime i.e. within the 1-100nm range. These include colloids and quantum dots (tiny particles of semiconductor materials). Nanoparticles that are naturally occurring (e.g.,
volcanic ash, soot from forest fires) or are the incidental byproducts of combustion processes (e.g., welding, diesel engines) are usually physically and chemically heterogeneous systems and often termed ultrafine particles. Nanoparticles can be classified into five categories:

(i) **Fullerenes and Carbon Nanotubes:** These are crystalline forms of carbon and constitute 28 to more than 100 atoms, forming a hollow sphere. Fullerenes and carbon nanotubes (CNTs) are similar as both can be bonded with organic or inorganic groups to form various products. They find application in Solar and lithium batteries, Electronics, Storage of gases, such as methane and oxygen, Additives to rubber and plastics, treatment of various diseases, including AIDS and cancer, polymer composite, for hydrogen storage and in batteries etc. [19]

(ii) **Metals:** These include noble metal nanoparticles such as those of Gold, Silver and Palladium. These particles have a wide variety of applications and are extensively used in Catalysis, Electronics, Sensing, Photonics, Environmental cleanup, Imaging, Drug delivery etc

(iii) **Ceramics:** Ceramic are objects created from inorganic, non-metallic materials. A wide range of industries use ceramic materials, including Mining, Aerospace, Medicine, Refinery, Food and chemical industries, Packaging science, Electronics, Industrial and transmission electricity, Guided light wave transmission [20-22]

(iv) **Semiconductors (Quantum dots):** Quantum dots are combinations of chemical elements from Groups II and IV or Groups III and V of the periodic table. Sizes range from about 1 to 10 nm in diameter and display unique optical and electronic properties. Quantum dots may be used in semiconductors, insulators, metals, magnetic materials or metal oxides. Medical field uses include imaging, high-speed and high-resolution screening, drug vectors, diagnostic tools, solar batteries etc [23-26]
(v) **Polymeric:** Polymeric nanoparticles include dendrimers and these have potential applications as drug delivery devices, gene therapy and delivery of proteins, peptides and genes through oral route administration, imaging agents, affinity ligands etc [27-28].

1.2.2. Synthesis and stabilization of nanoparticles

The various methods of nanoparticle synthesis are broadly classified under two categories: (a) Top down approach and (b) Bottom up approach. The top down approach involves breaking down of a bulk system into its compositional sub units in the nanoscale regime. Examples of this kind of approach include the various types of lithographic techniques (such as photo-, ion beam-, electron- or X-ray- lithography) cutting, etching and grinding. The bottom up approach, on the other hand, refers to the buildup of a material from the bottom i.e. from smaller units like atoms to bigger units such as nanoclusters. A number of bottom-up approaches have been developed for producing nanoparticles, ranging from condensation of atomic vapours on surfaces to coalescence of atoms in liquids. All types of chemical synthesis, self-assembly and molecular fabrication also fall under the ambit of bottom-up approach [29-31].

Nanoparticles, owing to their extraordinarily large surface areas, are thermodynamically unstable particles and their general tendency is to coalesce and thereby minimize the surface energy to form thermodynamically stable bulk particles. Although any reducing agent, with a suitable redox potential, can ideally reduce a bulk metal to its corresponding nano form, the basic challenge of nanosynthesis lies in the stabilization of the nanoparticles formed so as to retain their unique properties. In the absence of any counteractive repulsive forces, the van der Waals forces between two metal nanoparticles would lead to aggregation. The two most common approaches adopted for nanoparticle stabilization during their fabrication are (i) Steric stabilization and (ii) Electrostatic
stabilization [32,33]. The steric stabilization approach makes use of a capping agent such as a polymer [34,35], surfactant [36], solid support [37] or a ligand [38] having suitable functional groups. These capping agents can get adsorbed onto the colloidal particles and encapsulate them to prevent their agglomeration. This mode of approach is not affected by the salt concentration in the media. These additives cover the system in such a way that long loops and tails extend out into solution. The effectiveness of steric stabilizers can be attributed to the thermodynamic penalty when one tries to confine polymeric chains to smaller volumes. Another explanation is that the hydrophilic nature of the free end of the polymeric chains ensures that they stay associated with water, rather than interact with any other surface and induce coalescence. On the other hand, electrostatic stabilization is a kinetics driven process where the attractive van der Waals forces are counterbalanced by repulsive Coulombic forces acting between the negatively charged colloidal particles. This is realized through the adsorption of negatively charged ions onto the metal nanoparticles surface, which results in the formation of an electrical double layer around the particles [fig. 1.1]. The whole process is explained by the DLVO theory [39]. The theory, in a nutshell, explains the aggregation of aqueous dispersions quantitatively and describes the force between charged surfaces interacting through a liquid medium. It combines the effects of the van der Waals attraction and the electrostatic repulsion due to the double layer of counterions. The theory expresses the overall interaction between two particles or two surfaces in a liquid by the following equation [eqn. 1.1]

\[ W (D) = W (D)_A + W (D)_R \]  

1.1.

Where \( W \) is the net free energy per unit area, \( W(D)_R \) is the repulsive interaction energy due to electric repulsion and \( W(D)_A \) is the attractive interaction energy due to van der Waals interaction. The above relation holds good at smaller separations for smooth
substrates. However, at larger distances the interaction decays more quickly due to retardation effects, while surface roughness may reduce this interaction at smaller distances.

![Schematic representation of nanoparticle stabilization](image)

**Fig. 1.1** Schematic representation of nanoparticle stabilization

### 1.2.3. Optical properties and applications of nanomaterials

The primary importance of nanoparticles lies in their unique optical, chemical, physical and mechanical properties, which can be exploited for a variety of applications. Optical properties, in particular, have been extensively used in the field of optical sensors. Noble metal nanoparticles, such as those of gold and silver, display distinct Localized Surface Plasmon Resonance (LSPR) bands with high extinction coefficients in the visible spectrum.
region. These have therefore been the basis for the development of a large number of nanoparticles based spectrophotometric estimation techniques.

Localized surface plasmon resonance (LSPR) is an optical phenomena generated by light when it interacts with conductive nanoparticles (NPs) that are smaller than the incident wavelength. As in surface plasmon resonance, the electric field of incident light can be deposited to collectively excite electrons of a conduction band, with the result being coherent localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, dielectric environment and separation distance of NPs [40]. The electric field of the incoming light wave induces a polarization of the conduction electrons with respect to the much heavier ionic core of a metal nanoparticle. A net charge difference is felt at the nanoparticle boundaries (surface), which in turn acts as the restoring force that generates periodic dipolar oscillations of the electrons [fig 1.2]. In case of gold and silver nanoparticles, these absorptions can be easily monitored using UV-visible spectroscopy.

![Schematic illustration of the collective oscillation of free electrons under the effect of an electromagnetic wave](image)

**Fig. 1.2** Schematic illustration of the collective oscillation of free electrons under the effect of an electromagnetic wave
In case of dilute solutions of spherical metal nanoparticles, the factors governing the resonance conditions can be explained on the basis of the Mie solution to Maxwell’s equations, also termed as the Mie theory [41-43]. The theory, developed by Gustav Mie in 1908, explains electromagnetic scattering by a homogeneous, isotropic sphere. The main assumption of Mie’s theory of the optical absorption by small particles is that the particle and its surrounding medium are each homogeneous and describable by their bulk optical dielectric functions. By solving the Maxwell’s equation for an electromagnetic light wave interacting with small spheres, under appropriate approximations, Mie calculated the scattering and extinction cross sections with multiple oscillations for spherical particles. However, for nanoparticles much smaller than the wavelength of light (2r<λ, or roughly 2r<λ_{max}/10) only the dipole oscillation contributes significantly to the extinction cross-section [44-46]. The Mie theory then reduces to the following relationship (dipole approximation):

\[ \sigma_{\text{ext}}(\omega) = 4\frac{\omega}{c} \frac{V}{\epsilon_m} \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + 2\epsilon_m]^2} \]

Where, where \( \sigma_{\text{ext}} \) is the extinction coefficient, \( V \) is the particle volume, \( \omega \) is the angular frequency of the exciting light, \( c \) is the speed of light, and \( \epsilon_m \) and \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \) are the dielectric functions of the surrounding medium and the material itself respectively. While the first is assumed to be frequency independent, the latter is complex and is a function of energy.

The exploitation of the optical properties of metal nanoparticles, particularly noble metal nanoparticles, is not only confined to their LSPR based applications but also include applications based on other optical properties such as Fluorescence, Light Scattering and Surface Enhanced Raman Spectroscopy (SERS). LSPR properties have been utilized to develop highly sensitive techniques for estimation of trace levels of biologically and environmentally relevant molecules. Several papers have been published which highlight the
application of gold nanoparticles for colorimetric estimation of DNA, proteins, pesticides, metal ions such as Mercury, Lead etc, biologically relevant molecules such as Hydrogen peroxide, dopamine etc [47-51]. Triangular shaped silver nanoparticles have been demonstrated by Haes et al to have high sensitivity towards large proteins and antibodies [52]. LSPR based absorption property has also been used in Plasmonic Photothermal Therapy for selective elimination of cancer cells [53]. Similarly, light scattering properties of gold nanoparticles have been employed by Sokolov et al for cellular imaging of cancer cells [54]. For highly scattering tissues, fluorescence based imaging techniques have been developed which provide greater sensitivity compared to scattering based techniques [55, 56]. Colloidal gold nanoparticles have also been extensively used as SERS substrates to probe components in living cells, especially to study the interaction of various antitumor drugs with their pharmacological targets [57-59].

1.3. Polymer nanocomposites

1.3.1. Basic definitions and classification

Composites, in general, are defined as materials comprising of two or more constituent materials with significantly different physical or chemical properties, which when combined, produce a material with properties different from or superior to those of the individual components. Polymer nanocomposites, in particular, are composite materials in which nanoscopic inorganic particles, with at least one dimension in the nanoscale regime, are dispersed in a polymeric matrix in order to dramatically alter or improve the properties of the polymer. In the last 20 years, there has been a strong emphasis on the development of such polymeric nanocomposites, where at least one of the dimensions of the filler material is of the order of a nanometer. These are high performance materials that exhibit unusual property combinations and unique design possibilities. In general, nanomaterials provide reinforcing
efficiency because of their high aspect ratios [60]. The properties of a nanocomposite largely depend on the size of the filler phases and the degree of mixing between the two phases. The nature of the components used (layered silicate or nanofiber, cation exchange capacity, and polymer matrix) and the method of preparation can be tuned as per requirement to achieve significant differences in composite properties [61]. Similarly, in the case of fibrous or particle-reinforced polymer nanocomposites (PNCs), dispersion of the nanoparticle and adhesion at the particle–matrix interface are the deciding factors in determining the mechanical properties of the nanocomposite. A poor dispersion of the nanofiller can indeed lead to deterioration of the mechanical properties [62]. Additionally, the interfacial bond between the particle and the matrix can be accordingly optimized to tailor the properties of the overall composite. For instance, good adhesion at the interface will improve properties such as interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance [12]. Conventional polymer matrices used include polyurethanes, aliphatic and aromatic urethane acrylates, LDPE, nylon, Poly ethylene terephthalate (PET) etc., whereas the most commonly used fillers, besides metal nanoparticles, are nanoclays (montmorillonites), nanosilica, CNTs, graphene etc.

Based on the type of nanofiller used, polymer nanocomposites can be classified as materials containing nanofillers in the form of:

(i) particles (e.g. minerals, metal nanoparticles)

(ii) sheets (e.g. exfoliated clay stacks)

(iii) fibres (e.g. carbon nanotubes or electrospun fibres) [63-65].

Polymer nanocomposites containing modified organophilic clay (lamellar nanocomposites) can be further sub categorized based on the extent of mixing of clay layers with the polymer chains:
(i) **Phase separated**: These are materials where the nanofillers are not uniformly dispersed throughout the polymer matrix.

(ii) **Intercalated**: In this category, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well defined number of polymer layers in the intralamellar space.

(iii) **Exfoliated**: In exfoliated nanocomposites, the number of polymer chains between the layers is almost continuously variable and the layers stand >100 Å apart.

![Fig. 1.3 Schematic representation of various types of interaction between filler and polymer matrix](image)

**1.3.2. Synthesis protocols**

The three basic methods of polymer nanocomposite fabrication are:

(i) Solution casting (ii) Melt blending and (iii) In-situ polymerization. In solvent casting, the polymer and the nanofiller are dispersed in a suitable common solvent and thoroughly mixed by ultrasonication. The solvent is subsequently allowed to evaporate to leave behind a thin film of the polymer nanocomposite. In the case of melt blending, an extruder or an internal
mixture is used. The polymer and the nanofiller are added in the extruder and subjected to
intensive mixing till a uniform, homogeneous matrix is obtained. The in situ polymerization
method involves mixing of the nanoreinforcement with the monomeric or oligomeric
precursor of the polymer. Once uniform dispersion is achieved, the polymerization is carried
out by using a suitable agent such as a catalyst, a radical initiator or by using high energy
radiation sources such as gamma and Electron beam.

Besides these conventional techniques, some of the other widely used methods for
manufacturing composite parts are wet lay-up, pultrusion, resin transfer molding (RTM),
vacuum assisted resin transfer molding (VARTM), autoclave processing, resin film infusion
(RFI), prepreg method, filament winding, fiber placement technology, etc [66]. However, all
these methods suffer from certain limitations that restrict their utility as commercially viable
techniques for mass production of radiation cured products. Therefore, of late, radiation
curing technique, in particular Electron beam curing, has emerged as the front runner for
large scale production of economical, high quality radiation cured materials.

Radiation curing of a polymeric material involves the use of radiation to generate
radicals, which subsequently result in crosslinking to generate a polymeric matrix of inter
connected polymeric chains. A typical radiation curable formulation comprises of (a) a
multifunctional monomer or oligomer such as urethane acrylates, (b) reactive diluents to
optimize the viscosity and to serve as a crosslinking agent and (c) nanofiller. The components
are chosen as per the desired properties. The thoroughly homogenized reaction mixtures are
exposed to a radiation source till the formulation converts into a non-tacky, uniformly
crosslinked, cured matrix, with the polymer chains held together by the multifunctional
reactive diluent molecules acting as crosslinkers.
1.3.3 Properties and applications

The unique properties of polymer nanocomposites find application in a vast array of fields. Polymer nanocomposite materials possess enhanced thermal, mechanical, optical and electrical properties which are exploited in fields such as:

(i) **Barrier properties and flame retardancy**: Flame retardants are a key component added to potentially flammable materials, including textiles and plastics, to reduce their overall tendency to catch fire. They are widely used in electronics and electrical devices, building and construction materials, furnishings and components of aeroplanes, trains and automobiles. Polymer nanocomposites containing nanoclay as fillers have been found to be
highly efficient flame retardant materials owing to their ability to form protective oxide layers on the material surface [67]. The gas barrier properties of these materials, arising from the dispersion of the clay platelets within the polymer matrix, prevent transport of combustible gases within and out of the system [fig. 1.5]

(ii) **Non linear optical properties**: Optical limiters have received significant attention in the context of the protection of optical components and human eye from laser-induced damages. Polymer nanocomposite films containing metal nanoparticles as fillers have been found to be highly efficient for this application [68] owing to the high polarizability and ultra fast response provided by the metal nanoparticle fillers.

(iii) **Energy storage systems and sensors**: Polymer nanocomposites containing fillers such as carbon nanotubes, graphene etc. possess unique magnetic, thermal, conducting properties which have been exploited for the design of materials such as anodes in lithium-ion-batteries, supercapacitors, organic solar cells and highly sensitive devices for high end sensor applications [69-71].

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**Fig. 1.5** Schematic representation of mechanism of flame retardant property
(iv) **Electronics and automobile sectors:** The addition of conductive nanoparticles to polymers has a strong impact on the resulting composite dielectric properties. With respect to the aspired integration of passive electronic devices, like resistors, capacitors and others, into the printed circuit board (PCB), new composite materials have been developed which provide huge functionality, compatibility to industrial PCB-fabrication, low overall costs, high reliability and extended life cycle. [72-74]. In the automobile sector, enhanced modulus and dimensional stability, improved scratch and mar resistance, superior thermal and processing properties, reduced warpage of components and enhanced impact resistance makes polymer nanocomposites an ideal replacement for traditionally used materials. The key drivers for the use of polymer nanocomposite-enabled parts in the automotive industry are reduction in vehicle's weight, improved engine efficiency (fuel saving), reduction in CO$_2$ emissions and superior performance (greater safety, increased comfort and better driveability) [75].

(v) **Defence applications:** Polymer nanocomposites have also carved out a niche for themselves in the defence sector. High performance fibres/fabrics have been developed and find wide applications in defence as electrically conductive fabrics, sensors, electromagnetic shielding, microwave absorption, electrical energy storage (capacitors), actuators, and materials for micro UAVs. There are also reports of the promising application of nanocomposites in body armour. [76]

### 1.4. Basic aspects of radiation chemistry

#### 1.4.1. Types and energy of ionizing radiation

Radiation chemistry is a branch of chemistry that studies chemical transformations in materials exposed to high-energy radiations (gamma-rays, X-rays, Electron beams). It uses radiation as the initiator of chemical reactions, as a source of energy that disrupts the sensitive energy balance in stable systems. The energy of ionizing radiation, which also
includes radiation from charged particles (electrons, protons, deuterons, α-particles) or uncharged particle (neutron), lies in the range of \(10^2\) to \(10^7\) eV. Interaction of an atom or a molecule with high energy radiation can result in the formation of a wide range of reactive species such as radicals, cations, anions etc [77-79].

The important advantage of radiation chemistry lies in its ability to be used to produce, and study, almost any reactive atomic species playing a part in chemical reactions, synthesis, industrial processes, or in biological systems. The techniques are applicable to gaseous, liquids, solid, and heterogeneous systems. By combining different techniques of radiation chemistry with analytical chemistry, the reaction mechanism and kinetics of chemical reactions are studied.

### 1.4.2 Interaction of electromagnetic radiation with medium

Electromagnetic radiations such as X-rays (extra nuclear origin) and gamma (γ) rays (originating within the atomic nucleus) belong to the class of ionizing radiations. Gamma rays originating from radioactive isotope sources, such as those derived from \(^{60}\)Co radioisotopes emit radiation of discrete energies (1.332 MeV and 1.173 MeV for \(^{60}\)Co). For a narrow beam, the intensity of gamma radiation transmitted through an absorber is given by the equation:

\[
I = I_0e^{-\mu x}
\]  

(1.3)

Where, \(I_0\) is the incident radiation intensity, \(x\) is the thickness of material through which radiation has traversed and \(\mu\) is the linear attenuation coefficient.

The linear attenuation coefficient is the sum of a number of partial coefficients representing different processes that are initiated within the absorber by the impinging radiation These include (a) photoelectric effect (b) compton scattering (iii) pair production (iv)coherent scattering and (v)photonuclear reactions. The energy of the incoming photon and the atomic number (\(Z\)) of the absorbing material are the two factors that decide the relative
importance of each of these processes. While coherent scattering is predominant for low
energy photons (<0.1 MeV), photonuclear reactions are possible with photons of energies in
the range of 2 to 8 MeV for low Z materials and in the region of 7-20 MeV for high Z
materials.

(i). **Photoelectric effect**: This process is the principal interaction process at low photon
energies (1 keV < \( E_\gamma < 0.5 \) MeV), wherein the photon interacts with a bound electron in an
atom, and ejects it from the atom by transferring its entire energy. The energy of the ejected
electron (\( E_e \)) is given by the difference between the energy of the photon (\( E_\gamma \)) and the binding
energy of the electron (\( E_b \)) (Equation 1.4).

\[
E_e = E_\gamma - E_b \quad \text{(1.4)}
\]

(ii) **Compton scattering**: The Compton scattering process is predominant for photons with
energy typically around 1 MeV. For low Z materials, Compton scattering is the common
phenomenon for photon energies between 30 keV to 20 MeV. In this process a free electron
at rest is struck by a photon that scatters off at some angle to its original path. By the
conservation of momentum and energy, the electron recoils in a specific direction, with a
specific energy. This energy is provided by a reduction in the energy of the incoming photon
(increase in its wavelength). The relation between the various parameters is given by equation
(1.5). The energy of recoil electron is given by the Equation (1.6).

\[
E' = \frac{E_\gamma}{1 + \left(\frac{E_\gamma}{m_e c^2}\right)(1 - \cos \theta)} \quad \text{(1.5)}
\]

\[
E' = E_\gamma - E_e. \quad \text{(1.6)}
\]
iii) **Pair production**: At photon energies above 1.02 MeV another possibility becomes available when matter is struck by the photon: the creation of particle-anti-particle pairs. This process is the reverse of electron-positron annihilation phenomenon and involves the complete absorption of a photon in the vicinity of an atomic nucleus resulting in the formation of an electron and a positron. Since the rest mass of an electron or positron is 0.511 MeV, for pair production to occur, minimum photon energy must be 1.02 MeV (i.e. $2m_e c^2$)

$$E_0 = E_{e^-} + E_{e^+} + 2m_e c^2$$  \hspace{1cm} (1.7)

Therefore, depending on the incident photon energy, the photon gets attenuated and the total linear attenuation coefficient ($\mu$) is given by Equation (1.8).

$$\mu = \tau + \sigma + \kappa$$  \hspace{1cm} (1.8)

where, $\tau$, $\sigma$ and $\kappa$ are the linear attenuation coefficient of photoelectric, compton and pair production process respectively.

**1.4.3. Interaction of electrons with medium**

When an electron hits onto a material, different interactions can occur, which can be broadly categorized as (a) inelastic collision (b) elastic collision (c) emission of
bremsstrahlung radiation and (d) Cerenkov emission. The energy of the electrons as well as the nature of the absorbing material decides the relative importance of these processes.

(a) **Inelastic Interactions**: If energy is transferred from the incident electrons to the sample, then the energy of the electron after interaction ($E_{el}$) with the sample is consequently reduced compared to its initial energy $E_0$:

$$E_{el} < E_0$$

The energy transferred to the specimen can yield different signals such as X-rays, Auger or secondary electrons, plasmons, phonons, UV quanta or cathodoluminescence. Inelastic scattering is the only process that generates excited or ionized species in the absorber material and results in significant chemical or biological change. Secondary and tertiary electrons are generated as the incident primary electrons are slowed down. The average amount of kinetic energy lost per unit length by electron through coulomb interaction with atomic electrons in a medium is defined as the specific energy loss or stopping power ($S$) of the medium and is defined by the Bethe’s Equation (1.9).

$$S = -\frac{\text{d}E}{\text{d}x} = \frac{2\pi e^4 N_0 Z}{m_0 v^2} \left[ \ln \frac{m_0 v^2 E}{2l^2 (1-\beta^2)} - \left( 2\sqrt{1-\beta^2} - 1 + \beta^2 \right) \ln 2 + 1 - \frac{1}{2} \left( 1 - \sqrt{1 - \beta^2} \right)^2 \right] \quad (1.9)$$

Where, $e$ and $m_0$ represents the charge rest mass of electron, $v$ is the velocity of electron, $N_0$ is the number of atoms cm$^{-3}$ in the medium, $Z$ is the atomic number and $l$ is the mean excitation potential of the electrons in the stopping material, $\beta$ is the ratio of $v$ to the speed of light $c$.

(b) **Elastic scattering**: In this case, no energy is transferred from the electron to the sample and essentially leads only to a change in the direction of motion of electrons. As a result, the electron leaving the sample still has its original energy $E_0$:

$$E_{el} = E_0$$
This phenomenon is more common for electrons with low energy and target with high atomic number.

(c) **Emission of bremsstrahlung radiation**: Bremsstrahlung, or ‘braking radiation’, is emitted by high energy electrons moving in the electric field of a nucleus of an atom. The electron gets decelerated and emits energy in the form of electromagnetic radiation, at the expense of its kinetic energy. Bremsstrahlung emission is negligible below 100 KeV but increases rapidly with increasing energy, and is the dominant process at electron energy between 10 - 100 MeV.

(d) **Cerenkov emission**: Cerenkov radiation takes place when charged particles such as electrons move through a dielectric (i.e., electrically polarizable) medium at a phase velocity greater than the speed of light in that medium. Emission of this radiation (see Figure 1) occurs as the charged particles lose energy inelastically via electric field interactions with the transiently polarized medium. This radiative emission is the predominant process at high electron energies and for high Z materials.

### 1.4.4. Interactions of charged particles

When a charged particle enters into a medium, it interacts with electrons and nuclei in the medium. These interactions are called "collisions" between charged particles and the atomic electrons and nuclei and can lead to either ionization or excitation within the medium. The four primary types of interaction of charged particles with matter are:

(a) **Inelastic or soft collisions**: In this type, the Coulomb force due to moving particle affects the atom as a whole, leading to excitation of the atomic electrons or ionization of the atom. This is the main process of energy transfer for charged particle interaction with matter.

(b) **Hard collisions**: In this type of interaction, the charged particle exerts enough impulse to eject an electron from the atom.

(c) **Inelastic collisions with a nucleus**: The Coulomb force interaction here is mainly with
the nucleus and if the charged particle has enough energy, it can leave the nucleus in an excited state. The nucleus subsequently decays with the emission of nucleons or gamma rays.

(d). Elastic collisions with a nucleus: These types of interactions are known as Rutherford scattering. There is no excitation or emission of radiation in this case and the particle loses energy through recoil of the nucleus.

Fig. 1.7 Schematic representation of interaction of electrons with medium
1.4.5 Distribution of active species in the system – track structure

The energy lost when a high energy charged particle is slowed in a medium gives rise to a trail of ionized and excited species along the path of the particle. This trail is commonly referred to as a track [fig 1.8]. A photon imparts a large fraction of its energy to a single electron which subsequently excites and ionizes a large number of molecules along its track. The population of reactive species generated within the track depends on the energy of the impinging radiation.

The electrons liberated in the ionization process can possess a wide range of energies. If the energy of these secondary electrons is less than 100 eV, their range in solids and liquids is short and the ionizations and excitations caused by these electrons also remain restricted to a small range, leading to the formation of small spurs containing reactive species. In water, the isolated spurs contain on an average six active species for every 100eV of energy absorbed. Secondary electrons with high kinetic energy (between 100 and 500eV) deposit their energy to form dense regions of ionization, which look like large spurs. These elongated spurs are called blobs. For electrons of still higher energy (500 to 5000eV) the spurs overlap to form short tracks which are more or less cylindrical in view. In this case, the events are so close to each other that they cannot be considered as isolated. [79]. The typical energy distribution for a 440 keV Compton electron in water is spurs (64%), short tracks (25%) and blobs (11%).
1.5. Radiation dosimetry: Radiation-chemical yield and Fricke Dosimeter

When any material is exposed to ionizing radiation, the amount of energy deposited in unit mass of the material is termed as the absorbed dose. It expressed in terms of joules per kilogram (SI units) and its special name is gray (Gy). Another important parameter associated with the absorption of radiation dose by a material is the radiation chemical yield. Radiation chemical yield of any material is the number of molecules transformed per 100eV of energy absorbed. It is defined in terms of its G value. In the SI system, the unit of G is expressed as mol/Joule. G values reported in terms of number of species formed per 100 eV can be converted to SI units using the following relationship (1.10).

\[ G \text{ (mol} \, J^{-1}) = G \text{ (number per 100ev)} \times 1.036 \times 10^{-7} \]

Dosimetry refers to the process of determining the amount of dose delivered by any radiation source to a particular system. The Fricke dosimetry system provides a reliable means for measurement of absorbed dose to water, based on a process of oxidation of ferrous ions to ferric ions in acidic aqueous solution by ionizing radiation. In situations not requiring

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Fig. 1.8 Schematic representation of distribution of active species in medium
traceability to national standards, this system can be used for absolute determination of absorbed dose without calibration, as the radiation chemical yield of ferric ions is well characterized. The dosimeter is an air-saturated solution of ferrous sulfate or ferrous ammonium sulfate that indicates absorbed dose by an increase in optical absorbance at a specified wavelength. A temperature-controlled calibrated spectrophotometer is used to measure the absorbance.

1.6. Radiation chemistry of water

1.6.1 Primary yields

The radiation chemistry of water is of significance since water is the basic component in most biological and chemical systems. [80]. Ionizing radiation produces abundant secondary electrons that rapidly slow down (thermalize) to energies below 7.4 eV, the threshold to produce electronic transitions in liquid water. For both the primary charged particle and the secondary electrons, this slowing down process is accomplished by transfer of energy to the medium in a sequence of discrete events. Depending on the amount of energy transferred to the electron, the molecule can undergo (a) Ionization (b) excitation or (c) thermal transfer. The initial event is the transfer of energy sufficient to cause (multiple) ionizations or excitations in water molecules, resulting in the formation of spurs [79]. Direct ionization of water produces a radical ion and a free subexcitation electron (E < 7.4 eV).

\[
\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e^- \quad (1.10)
\]

Energy transfer can produce a water molecule in an excited state.

\[
\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^* \quad (1.11)
\]

The time scale for the creation of these species is on the order of 10^{-16} seconds. In the next step, the three initial species begin to diffuse and react with each other or other molecules in the medium. Energetically unstable positively charged ions (H_2O^+) undergo ion
molecule reaction in $10^{-14}$ seconds producing \`OH radicals [81]. The radical ion of water can
dissociate to produce a hydroxyl radical and a hydrogen ion.

$$\text{H}_2\text{O}^+ \rightarrow \text{H}^+ + \text{HO}^-$$  \hspace{1cm} (1.12)

The excited water molecule can dissipate excess energy by bond breakage to produce
hydroxyl and hydrogen radicals.

$$\text{H}_2\text{O}^* \rightarrow \text{HO}^- + \text{H}$$  \hspace{1cm} (1.13)

Subsequently, the electron released during ionization gradually loses its energy to fall
below the ionization threshold of water and finally gets localized in a potential energy well
long enough to get captured by water through dipolar interactions to generate a solvated
electron: [82]. The entire process is completed in about $10^{-12}$ seconds.

$$\text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}_{aq}^- \text{surrounded by a “cage” of water}$$  \hspace{1cm} (1.14)

After $\sim 10^{-12}$ sec, the chemically reactive species viz. HO-, H-, $\text{e}_{aq}^-$ are still located in
the vicinity of the original $\text{H}_2\text{O}^*$, $\text{H}_2\text{O}^+$ and $\text{e}_{aq}^-$ species that caused their creation. These
species now begin to migrate randomly about their initial positions. As this diffusion
proceeds, individual pairs may come close enough together to react with each other.
A variety of reactions are possible in the track of the charged particle.

$$\text{HO}^- + \text{HO}^- \rightarrow \text{H}_2\text{O}_2$$  \hspace{1cm} (1.15)

$$\text{HO}^- + \text{e}_{aq}^- \rightarrow \text{OH}^-$$  \hspace{1cm} (1.16)

$$\text{HO}^- + \text{H}^- \rightarrow \text{H}_2\text{O}$$  \hspace{1cm} (1.17)

$$\text{H}^+ \text{e}_{aq}^- \rightarrow \text{H}^-\text{n}$$  \hspace{1cm} (1.18)

$$\text{e}_{aq}^- + \text{e}_{aq}^- + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-$$  \hspace{1cm} (1.19)

$$\text{e}_{aq}^- \text{e} + \text{H}^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{OH}^-$$  \hspace{1cm} (1.20)

$$\text{H}^- + \text{H}^- \rightarrow \text{H}_2$$  \hspace{1cm} (1.21)
Most of these reactions remove chemically reactive species from the system. With time (~$10^{-6}$ sec) all of the reactive species diffuse sufficiently far so that further reactions become unlikely.

The chemical development of the track is over by $10^{-6}$ sec. The species formed can subsequently react with solutes present in the system. In water, $10^{-7}$ seconds is the lifetime of the radicals reacting at a diffusion-controlled rate with a solute whose concentration is $10^{-3}$ mol dm$^{-3}$ [79,80,82].

1.6.2 Important reducing radicals in aqueous solutions

The primary radicals viz. hydrated electron ($e_{aq}^-$) and the hydrogen atom (H·) are reducing in nature. The high redox-potential of $e_{aq}^-$ ($E^\circ = -2.9$ V vs NHE) makes it a powerful reducing agent capable of reducing a range of metal ions to their zero valent states (Table 1.2). Its reactions with solutes are best understood in terms of availability of a suitable vacant orbital in the solute molecule for the electron to get localized [65,72].

1.6.3 Important oxidizing radicals in aqueous solutions

The primary oxidizing radical generated during water radiolysis is Hydroxyl radical (·OH) ($E0 = 2.8$ V vs NHE). In strongly basic solution (pH > 11.9), it is deprotonated to give $O^-$. 

1.7 Synthesis of metal nanoparticles and nanocomposites by high energy radiation: advantages of radiolytic method

As previously discussed, numerous techniques have been developed and demonstrated over the years for fabrication of metal nanoparticles and polymer nanocomposite coatings. However, with growing environmental concern and greater emphasis being laid on green chemistry, most of these techniques, which involve harsh reaction conditions or use of harmful chemical reagents have been found to be inadequate to meet the stringent regulatory
requirements. Therefore, of late, the focus has shifted to the application of radiation technology for fabrication of materials in large scale. The numerous benefits of using radiation technology can be summarized as follows:

(a) Unlike chemical methods, the radiolytic route of synthesis does not require the use of harmful chemical reducing agents or initiators to carry out the reactions. Radicals generated in situ during radiolysis are sufficient to carry out the reactions. Thus materials prepared via radiolytic route are cleaner since they are devoid of chemical impurities.

(b) Compared to conventional methods, radiolytic reduction/ curing techniques ensure more uniform and complete reaction to produce materials with superior properties.

(c) Radiation sources can initiate reactions at room temperature and therefore do not require the use of high temperature.

(d) Radiation sources such as Electron beam provide high throughput and fast processing and are therefore commercially viable options to achieve bulk production of processed materials.

1.8. Scope of the thesis

Noble metal nanoparticles and polymer nanocomposite materials are being explored for their applications in diverse fields ranging from sensing to materials with superior mechanical and thermal properties. Radiation technology presents itself as an attractive tool for fabrication of these materials owing to the multitude of advantages it offers vis a vis conventional methods of synthesis. Radiation induced synthesis of metal nanoparticles as well as radiation induced curing of polymer nanocomposite films are environment benign techniques with minimal carbon footprint, and can rightly be highlighted as the technology of the future. Moreover, the technique provides materials with superior properties and offers better control over reaction parameters. In this work, radiation sources such as \( ^{60} \text{Co} \) gamma, Electron beam and Synchrotron radiation source have been exploited to engineer nanomaterials for sensing
applications and polymer nanocomposite films for various optical, tribological and thermal applications. The materials designed have been studied and thoroughly characterized using numerous techniques such as UV-visible spectroscopy, TEM, SEM, AFM, Thermal analysis etc. Brief descriptions of the chapters in this thesis are presented below.

Chapter 2 describes the materials, instrumentation and methods employed during the course of the doctoral work.

Chapter 3 highlights the gamma radiation synthesis and characterization of uniformly dispersed Gold nanoparticles stabilized by a biocompatible polymer Poly(N-vinyl-2-pyrrolidone) (PVP). The sensing property of the PVP stabilized Au nanoparticles was also investigated for estimation of trace levels of hydrogen peroxide and mercury ions in aqueous solutions.

Chapter 4 presents a comparative study of the synthesis and structural characterization of PVP stabilized Silver nps fabricated using $^{60}$Co gamma, Electron beam and Synchrotron radiation techniques. Silver nanoparticles synthesized via gamma radiolytic route were also demonstrated to have good sensing property by highlighting their application as a LSPR based optical sensor for estimation of trace levels of uric acid in human and bovine serum samples.

Chapter 5 describes the application of gamma and electron beam irradiation techniques for synthesis of polymer nanocomposite films for various targeted applications. Aliphatic urethane acrylate based films containing in situ metal nanoparticles and other nanofillers were designed using Electron beam irradiation technique. Non tacky, homogeneous, thin films obtained by this technique were characterized by techniques such UV-visible spectroscopy, TEM and FE-SEM analysis, and subsequently studied for their optical limiting applications. Similar films containing organophillic modified montmorilonite clay as nanofillers were also fabricated via gamma radiation curing technique and their mechanical
and thermal properties thoroughly studied. The films were also demonstrated to have flame retardant properties, thus making them potential candidates for flame retardant materials.