

Chapter 1

Introduction & Literature Review

Chapter 1

This chapter provides a general review of the global field of nanomaterials, particularly plasmonic metal nanoparticles (MNPs), and their properties and applications. In the beginning, a brief introduction of nanotechnology and nanomaterials has been given, which motivates the inherent capacity to impact manufactures now and hereafter with some examples. Notably, plasmonic thin films have garnered significant attention in modern photonics due to their ability to enhance light-matter interactions through localized surface plasmon resonance (LSPR). This enables superior optical, electronic, and sensing properties at the nanoscale. Herein, photoexcitation and relaxation of charge carriers within plasmonic NPs are discussed briefly. This chapter deliberates an overview of the plasmonic MNPs, which has some important photonic applications in the field of solar cells, plasmonic photodetector, transparent conductor, memristor, heat reflector, gas sensor, bio sensor, as well as bio-imaging. These MNPs require a specialized fabrication procedure for their preparation. At the end of this chapter, these materials are discussed in detail with their properties and applications, alongside motivation and the scope of the thesis.

1.1 Nanotechnology

The term “nanotechnology” was first introduced by Prof. Norio Taniguchi of Tokyo Science University Japan in 1974.[1-3] At this scale, unique properties and behaviors emerge, enabling the design and creation of materials, devices, and systems with enhanced functionalities. Nanotechnology encompasses various applications across diverse sectors, including electronics, medicine, energy, and materials science.[4-10] Researchers manipulate and control materials at the nanoscale to exploit novel characteristics, such as increased surface area, improved conductivity, and enhanced reactivity. The potential benefits of nanotechnology include advancements in drug delivery, more efficient energy storage, and the development of smaller and more powerful electronic components.[11-13]

However, ethical and safety considerations accompany the rapid progress in nanotechnology, necessitating careful exploration of its societal implications.

1.2 Nanomaterials

Nanomaterials are the fundamental components of the nanoscience and nanotechnology fields. Research and development processes associated with this are expanding rapidly around the globe. In 1959, physicist and scientist Richard Feynman developed the term "nanomaterial".[\[14, 15\]](#) Nanomaterials have typical particle dimensions between 1 and 100 nm. Furthermore, nanomaterials belong to a class of materials restricted in the bulk materials domain. Nanomaterials exhibit qualities that are completely distinct from their bulk counterparts. The characteristics of these materials are investigated using a precise length scale, which is generally in the nanoscale range. When bulk material is shrunk below the nanometer scale, its physical characteristics alter significantly. The properties of nanomaterials change due to the significant increase in surface-to-volume ratio, leading to high surface tension, which is shown in **Figure 1.1**. This tension causes rapid melting. As particle size reduces, the number of surface atoms increases, impacting free energy and enhancing electronic, optical, mechanical, and thermodynamic properties.[\[16-18\]](#) Surface atoms play a significant role in governing nanoparticle properties. Reducing NP size affects atomic energy levels as the system becomes more constrained, leading to strong variations in optical and electrical properties due to changes in the density of electronic energy levels, known as the quantum size effects.[\[19, 20\]](#) This effect is observed more prominently in metal nanoparticles (MNPs) compared to non-metallic nanoparticles (NMNPs) due to the absence of a band gap and the Fermi level's position in metals.[\[21\]](#) Designing at the nanoscale is crucial for developing new products that replace existing chemicals and materials with enhanced performance and potential cost savings. This also benefits the environment by reducing material usage. Additionally, nanotechnology offers opportunities to organize and improve fabrication processes.

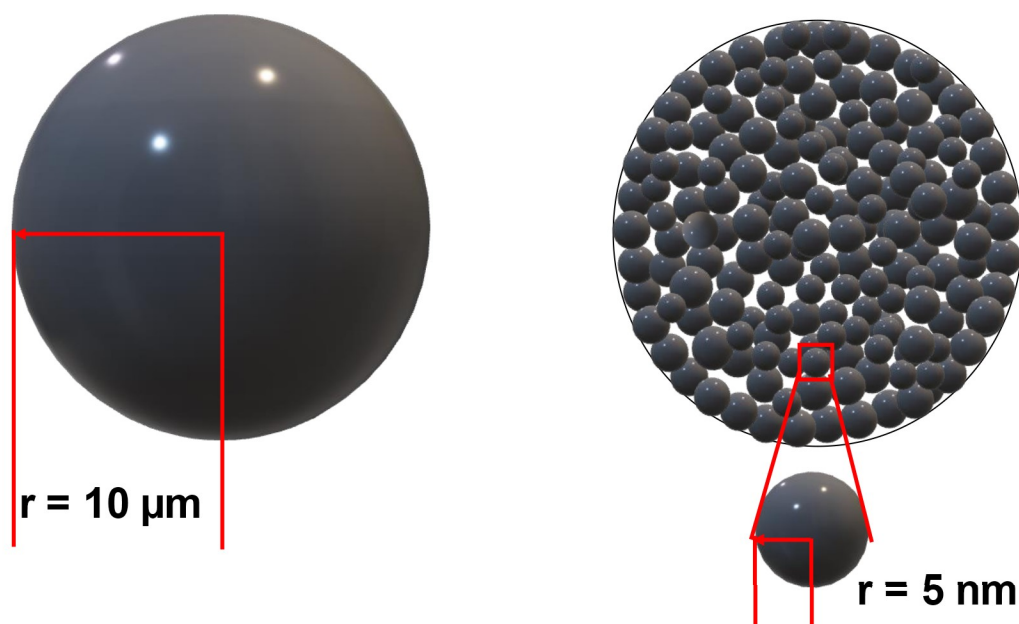


Figure 1.1 Schematic illustration of the difference in surface to volume ratio between a bulk microsphere and microsphere formed by NPs.

1.3 Classification of Nanomaterials

Nanomaterials are generally classified into two major categories: MNPs and NMNPs. The MNPs, such as gold (Au), silver (Ag), copper (Cu), nickel (Ni), platinum (Pt), and palladium (Pd) etc. and their alloys with combination of bi-metal like Ag-Au, Ag-Cu, Cu-Ni and so on are composed of metal components only. Due to their small size and large surface area, these MNPs show unusual electrical, optical, and catalytic properties. On the Other hand, NMNPs, such as tin oxide (SnO_2), titanium dioxide (TiO_2), zinc oxide (ZnO), silver sulfide (Ag_2S), copper sulfide (Cu_2S), tungsten sulfide (WS_2), molybdenum oxide (MoS_2), lead sulfide (PbS), cadmium sulfide (CdS), cadmium selenide (CdSe) and iron oxide (Fe_2O_3), consist of metal atoms bonded to oxygen or Sulphur. These NPs are known for their excellent chemical stability, magnetic properties, and wide range of applications in energy saving smart windows, photodetection, photo-catalysis and biomedical fields.[22-28]

1.3.1 Metal Nanoparticles

A widely recognized definition of a nanomaterial describes it as a material with a structure where at least one of its phases exhibits a nanometre-scale size in at least one dimension. Based on this definition, nano-objects can be categorized into three distinct groups:

- I. 1D nanoscale objects (e.g., thin films)
- II. 2D nanoscale objects (e.g., nanowires, nanorods and nanotubes)
- III. 3D nanoscale objects (e.g., nanoclusters or nanoparticles)

The journey of synthesizing MNPs started in 1856 when Michael Faraday successfully reduced gold chloride with phosphorus, creating gold colloids that exhibited a stable ruby red color. These samples, some of which are still preserved in the Faraday Museum in London.[\[29\]](#) The increasing significance of MNPs in modern science has driven the development of new techniques and enhancements in nanoparticle manufacturing, leading to particles with remarkable properties. One of the most notable properties of MNPs is their optical behavior, which differs greatly from that of single molecules or bulk materials. When reduced to nanoscale, metals like Au and Ag absorb visible light very strongly. These optical characteristics have been known for a long time and were first explained by Mie theory in 1908. This theory, grounded in Maxwell's equations, calculates the particle extinction spectra based on the material's dielectric function and particle size within the visible light wavelength range. Since its introduction, Mie theory has been extensively applied.[\[30, 31\]](#) Typically, standard colloidal results in roughly spherical particles, and a variety of optical methods are used to characterize the spectra of these NPs.

1.3.2 Non-Metallic Nanoparticles

Non-metals or metal oxides are pivotal in various fields due to their ability to form a wide range of compounds with diverse structural geometries and electronic properties, ranging from metallic to insulating. They are essential in technological applications such as microelectronics, sensors, fuel cells, and catalysts.[\[32-35\]](#) In nanotechnology, NMNPs exhibit unique properties, which are not seen in bulk materials, driven by their small size and high surface area, which introduce significant changes in structural and electronic

characteristics. As the particle size decreases, structural changes occur due to increased surface energy, which can lead to modifications in lattice parameters, thermodynamic stability, and even phase transitions. These changes, along with quantum size effects, alter the electronic properties, including band gaps and conductivity. The surface properties of nanostructured oxides are also profoundly affected, with enhanced chemical reactivity and unique absorption due to the presence of under-coordinated atoms and vacancies, making them highly valuable for catalytic and other chemical processes.

1.4 Various Synthesis Technique of Metallic/Non-Metallic Nanoparticles

The fabrication of MNPs has seen diverse techniques, reflecting the significant role of NP preparation in science and technology. Two primary strategies for developing materials at the nanometer scale are the top-down and bottom-up approaches, which are shown in **Figure 1.2**. The term “nanotechnology” was discovered by Professor Norio Taniguchi of Tokyo University in 1974 to describe highly precise ultrafine dimensions, introducing the top-down approach, which involves physical and chemical methods to obtain atomic-scale materials by removing material from bulk substances. This method, however, is not ideal for producing uniform small particles. About a decade later, K. Eric Drexler introduced the bottom-up approach, which assembles atoms into nanostructures and can yield more uniform particles. The top-down method's drawback is the significant removal of material, while the bottom-up method can suffer from poor monodispersity due to the challenge of maintaining consistent growth rates for all nanoparticles. Various techniques exist to fabricate different types of nanomaterials, such as colloids, clusters, powders, tubes, wires, thin films, and rods, depending on the target material and nanostructure type. NPs can be synthesized by growing, shaping, or self-assembling materials through physical, chemical, biological, or hybrid methods. The top-down approach includes methods like electron beam lithography and photolithography, while the bottom-up approach encompasses physical, chemical, and biological methods, including electrochemical, seeding, and thermal and photochemical reduction methods, with electrochemical and photochemical methods capable of producing uniform nanorods.[[36-39](#)]

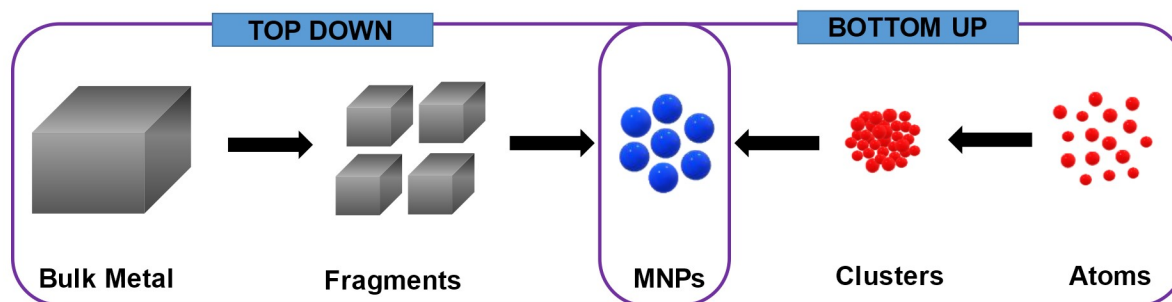


Figure 1.2 Schematic presentation of top-down and bottom-up approach for the synthesis of metal/metal oxide NPs.

Chemical methods have several advantages over physical methods: they are relatively easy and economical, can be conducted at low temperatures, produce large quantities of material, and do not require sophisticated equipment. These methods allow for the preparation of materials in various compositions and are extensively used for synthesizing nanomaterials. In this context, capping materials such as surfactants or polymers are utilized to prevent the aggregation of MNPs in solution. Various shapes, including spheres, cubes, wires, rods, tubes, triangular prisms, tetrahedral NPs, and quantum dots, have been synthesized from metals like Au, Ag, Cu, Pt, etc. and metal oxides like SnO_2 , ZnO, TiO_2 , etc., using different reduction techniques and capping agents. NPs can also be developed using a combination of physical and chemical methods. Therefore, the choice of fabrication procedures depends on the desired physical and chemical properties, such as size, dispersion, mixture homogeneity, and optical properties. Both physical and chemical methods can result in environmental contamination and toxicity. In contrast, biological approaches, specifically green synthesis, are environmentally friendly and less toxic. Still, for the fabrication of opto-electronic devices, physical and chemical methods are superior as they allow making precious NP size, shape and morphology, which is very much crucial for photonic applications.[40-42] The various approaches and methods for NP synthesis are summarized in **Figure 1.3**.

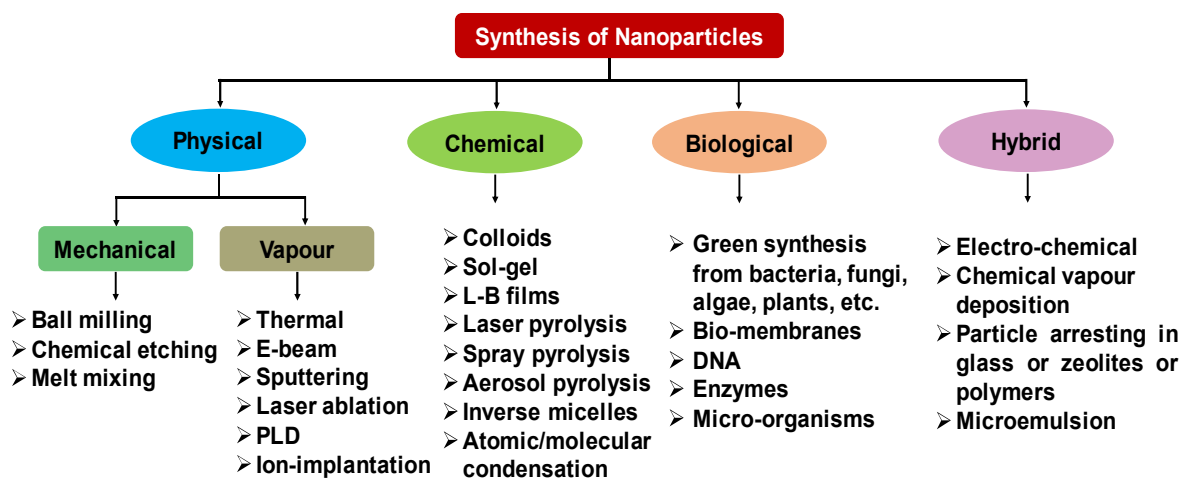


Figure 1.3 Schematic of different synthesis routes for the fabrication of nanomaterials.

In 1951, John Turkevitch reported the synthesis of spherical Au NPs using the citrate reduction method. This technique, which involves reducing Au ions in solution with citrate ions, has become a widely used method for producing Au NPs due to its simplicity and effectiveness. Turkevitch's method remains a fundamental approach in the field of nanotechnology for the preparation of Au NPs.[43, 44] An admired method for creating highly spherical and non-spherical NPs is the seeding system. Typically, spherical NPs are initially developed and then added to a growth solution containing additional metal ions and surfactants to promote anisotropic particle growth. This process often involves seeds fabricated using sodium borohydride, a strong reducing agent. The growth solution employs a weaker reducing agent to partially reduce the metal salt, allowing only the catalyzed reduction on the NP surface. A schematic comparison between in-situ and ex-situ methodologies is shown in **Figure 1.4**.

The stabilization of MNPs can be achieved through various approaches. In ex-situ fabrication, NPs are dispersed in a solid or liquid medium after their synthesis using different chemical methods. This approach provides stabilization but poses a risk of reaggregation over time. In contrast, in an in-situ fabrication, MNPs are grown directly within the stabilizing medium, which is of great interest due to its technological advantages.[45]

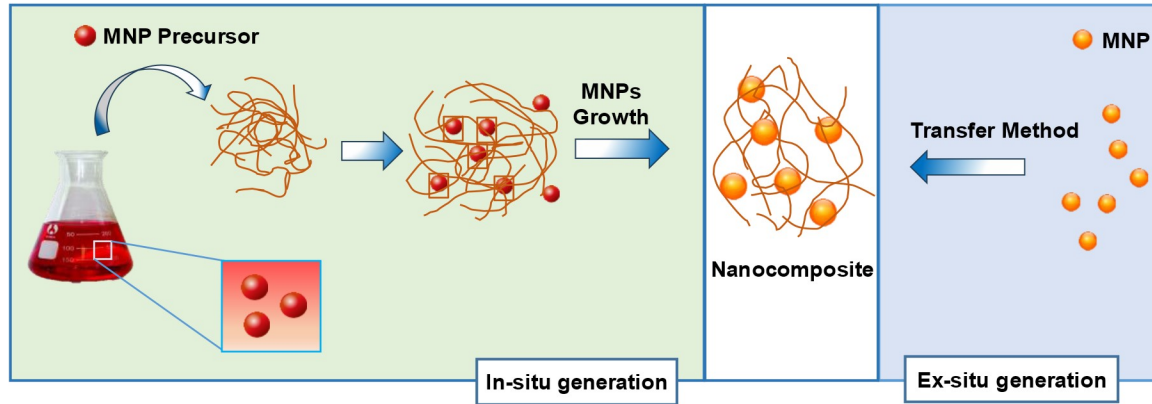


Figure 1.4 Schematic presentation of in-situ and ex-situ methodology for NP synthesis.

1.5 Plasmonic Metal Nanoparticles

The investigation of optical phenomena related to the electromagnetic (EM) behavior of metals has driven the rapid growth of a promising research area known as plasmonics. The intense interaction between EM fields and plasmonic NPs creates new opportunities for technologies that leverage photophysical processes, enhanced by this light-matter interaction. The interaction of these metallic NPs with incoming light causes a collective oscillation of free electrons known as plasmon to become dominant, resulting in the surface plasmon resonance (SPR).[46, 47] Many of these electrons participate in the SPR, resulting in high absorption, scattering, and near-field amplification at the plasmonic NPs natural frequency, which is also known as plasma frequency.[47] Novel metals, including Au, Ag, Cu, Ni, or their bimetallic nano-film, can be employed as free electron systems whose electrical and optical properties are determined only by the conduction electrons. According to the Drude-Lorentz model, metals are considered plasmas because they contain equal numbers of positive ions and conduction electrons.[48] So, in the presence of an incoming plane EM wave, charge displacement occurs within this plasma. Volume or Bulk plasmons are the cases discussed by Pines and Bohm,[49] visualized in **Figure 1.5a**). So, bulk plasmon is the outcome of the generation of forward and backward EM waves (due to charge displacements caused by an incoming plane EM wave), resulting in the formation of an energy gap.[50] The energy of the bulk plasmon[51] is given by **equation 1.1**-

$$E_{\text{bulk}} = \hbar\omega_p \text{ ----- (1.1) where } \omega_p \text{ is the plasma frequency}$$

In the context of metal thin film with finite dimensions and different surrounding dielectric materials, their collective oscillations are known as surface plasmon polaritons (SPPs) or surface plasmons. The resonant interaction of optical waves with free electrons in a metal can generate surface-bound EM modes, often known as surface plasmons, which are typically excited at the interface of a noble metal and a dielectric. These surface plasmons have maximum field intensity at the metal-dielectric interface, with evanescent waves penetrating the surrounding dielectric, making them highly sensitive to refractive index changes near the metal surface, as shown in **Figure 1.5b**). Localized surface plasmons (LSPs) arise when light hits MNPs or metal nanostructures. As the light wavelength is substantially larger than the nanostructure, a plasmon oscillates around it, as shown in **Figure 1.5c**). When light interacts with MNPs or nanostructures, the conduction electrons on their surface oscillate collectively at a particular frequency, known as plasma frequency.[52]

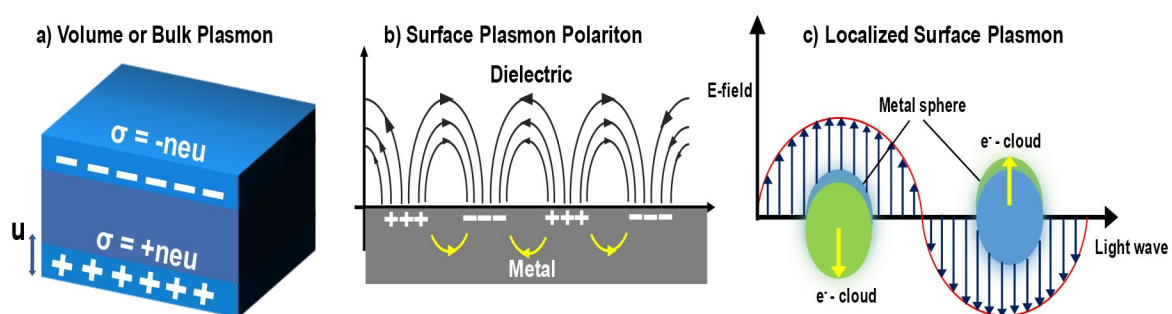


Figure 1.5 Comparative diagrams of **a)** volume or bulk Plasmon, **b)** surface plasmon polariton, and **c)** localized surface plasmon.

LSPR is one primary characteristic of plasmonic MNPs like Ag, Au, Cu, etc. that are widely used in varieties of applications. This effect is typically excited by direct illumination without requiring a specific angle that satisfies the resonance condition, with maximum field intensity at the metal-dielectric interface, decaying exponentially away from it. The light absorption by MNPs originates from the coherent oscillation of conduction band electrons caused by interaction with external EM radiation. In MNPs, a disturbance-like interaction with EM radiation displaces the equilibrium of the negatively charged electron cloud and the positively charged ion cloud, depicted in **Figure 1.6**. This disturbance causes electrons to

oscillate back and forth, creating collective oscillations, which result in strong absorption in the visible to near infrared (NIR) region.[53, 54]

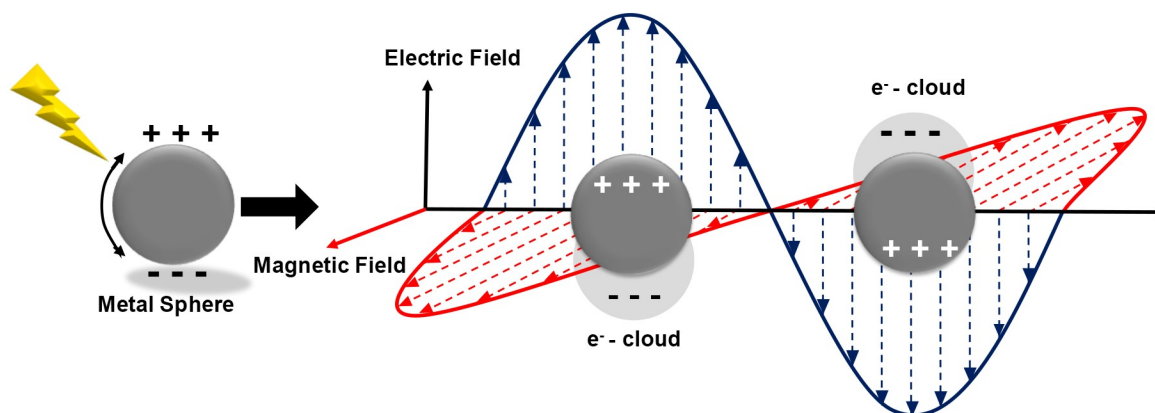


Figure 1.6 Schematic representations of the LSPR effect in plasmonic MNPs.

The illumination of a metallic nanostructure triggers a series of complicated processes in different time scales, leading to various possible outcomes.[55] These include the rapid internal relaxation or ejection of hot carriers, the generation of strong optical near-fields, and the re-emission of photons. The initial stage in hot carrier excitation begins with photon absorption (**Figure 1.7a**), where the probability of absorption is related to the square of the local electric field inside the metal. In metallic nanostructures, light absorption is further amplified by the LSPR effect.[56, 57] This enhancement results in an antenna-like effect, allowing the structure to collect light from an area larger than its actual size.[58, 59] Consequently, these MNPs or nanostructures act as an EM hotspot. The concentrated light field generated by this effect has been extensively studied and applied in surface-enhanced processes such as surface-enhanced Raman spectroscopy (SERS), surface photochemistry, and the photoexcitation of nearby quantum emitters.[60, 61] In nanostructures, plasmon resonances can be damped non-radiatively by generating hot electron-hole pairs through Landau damping or radiatively by photon re-emission (**Figure 1.7b**). Landau damping is a purely quantum mechanical phenomena that transfers a plasmon quantum into a single electron-hole pair excitation within a timescale (τ) ranging from 1 to 100 femtoseconds (fs).[62] The plasmon-induced electric field, acting as a time-dependent perturbation on the metal's conduction electrons, facilitates transitions from occupied to unoccupied electronic states. However, because the transition matrix elements for electron-hole pair formation are

relatively small, the most likely direct outcome of plasmon decay is the creation of a single electron–hole pair, with a possible carrier distribution illustrated in **Figure 1.7b**). The distribution of charge carriers depends on multiple factors, including plasmon energy, particle size, plasmon mode symmetry, and the material’s electronic structure and density of states.^[63] Landau damping contributes to the imaginary part of a metal’s dielectric permittivity in the visible spectrum. Understanding this imaginary component is crucial for optimizing hot carrier generation. For example, adjusting a subradiant plasmon mode to energy levels where the imaginary component of the permittivity is high allows for the optimization of hot carrier production. This tuning can be achieved by leveraging the geometric tunability of LSPRs in MNPs or by designing composite structures composed of noble metals combined with metals exhibiting strong intraband transitions. Following plasmon decay, the hot electrons rapidly redistribute their energy among lower-energy electrons through electron–electron scattering mechanisms, such as Auger transitions.^[64] While hot carrier relaxation dynamics have been well studied for extended surfaces, little is known about these processes at the nanoscale. For extended MNP surfaces, time-resolved studies^[65] suggest that relaxation times range between 100 fs and 1 picosecond (ps), leading to the formation of a high-temperature Fermi–Dirac-like distribution with an elevated effective electron temperature (**Figure 1.7c**). Hot electrons are those electrons that are not in thermal equilibrium with the atomic lattice of the substance. These hot electrons follow a Fermi distribution but exhibit an increased effective temperature. In the final stage, heat is transferred from the metallic nanostructure to its surroundings, a process that occurs over a timescale ranging from 100 ps to 10 nanoseconds (ns), depending on factors such as material composition, particle size, and the thermal conductivity of the ambient atmosphere (**Figure 1.7d**).

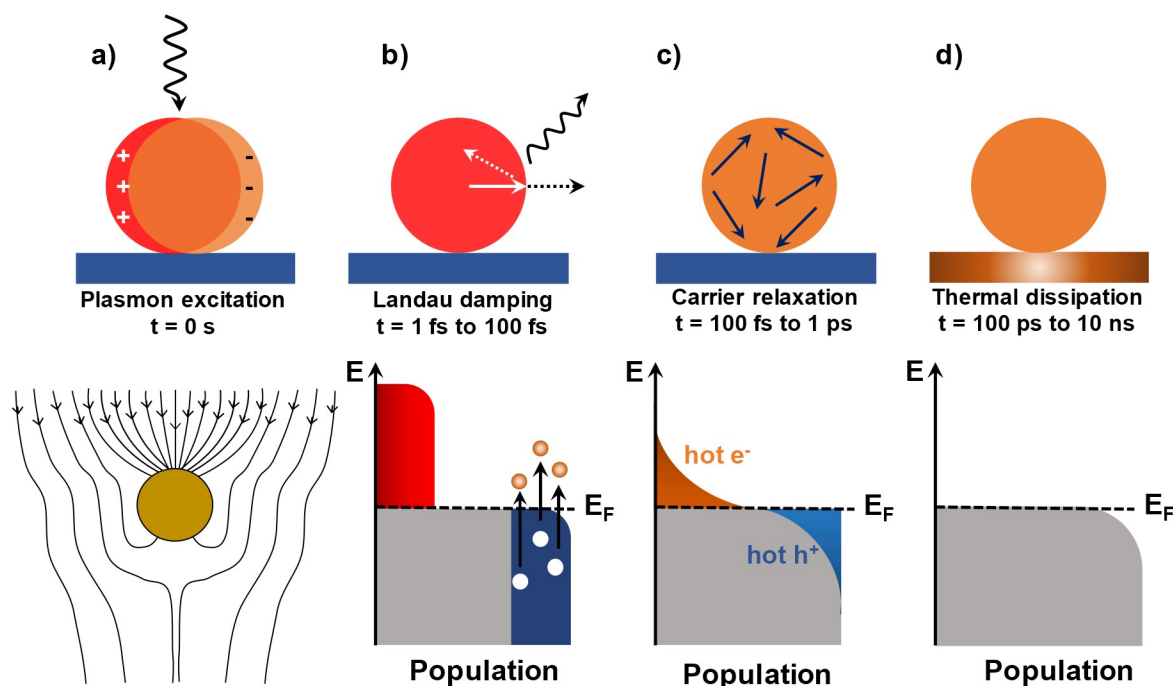


Figure 1.7 **a)** Excitation of a LSPs redirects the Poynting vector, channeling the flow of light toward and into the NP. Following plasmon excitation, the distribution of electronic states changes, with hot electrons appearing in the orange regions above the Fermi energy (E_F) and hot holes occupying the blue regions below E_F . **b)** Within the first 1–100 fs after Landau damping, electron–hole pairs form a thermal distribution that undergoes decay either by photon re-emission or through carrier multiplication driven by electron–electron interactions. During this brief period, the hot carrier distribution remains highly non-thermal. **c)** hot carriers undergo energy redistribution through electron–electron scattering processes, occurring within a timescale of 100 fs to 1 ps. **d)** Thermal conduction facilitates the transfer of heat from the metallic structure to its surroundings over a longer timescale, ranging from 100 ps to 10 ns.

Following light absorption and LSPR excitation in these nanostructures, EM decay occurs on a fs timescale. This decay can occur either radiatively, by emitting photons, or non-radiatively, by transferring energy to hot electrons, as illustrated in **Figure 1.8a**). In the non-radiative pathway, surface plasmons initially decay into single-electron excited states, which may subsequently lead to photoemission if the electron's energy surpasses the work function of the material.^[66-69] Non-radiative decay in noble-metal nanostructures can occur via

intraband excitations within the conduction band or interband excitations involving transitions between other electronic bands (such as d bands) and the conduction band. In Ag, the d band energy levels are positioned 4 eV below the Fermi energy level, allowing only intraband excitations. Conversely, Au exhibits significant interband excitations under light exposure due to the shorter energy gap of 2.4 eV between its d-states and the Fermi level.[70, 71] Since Ag only undergoes intraband transitions, hot electrons can be efficiently excited above the Fermi energy within the same band, making it more favourable for hot electron collection to the conduction band of metal-oxide at the metal–semiconductor interface compared to Au. However, Au remains the most stable plasmonic nanoparticle among noble metals. When a bi-metallic Ag–Au nanostructure is illuminated, it experiences fewer interband excitations than Au alone, as its d-states are shifted further from the Fermi level. This provides enhanced stability along with improved charge carrier collection. Once photo excited, electrons dissipate energy through electron–electron and electron–phonon interactions, ultimately converting into heat. An electron-donor solution or a hole-transporting layer (HTL) is required to promote hole transfer to the counter electrode in order to maintain charge balance and electrical current. **Figure 1.8b)** illustrates the parabolic density of states (DOS) in the conduction band of a plasmonic nanostructure where the Fermi energy is used as a function of energy.[72-74] A highly effective method for capturing these hot electrons is the formation of a Schottky barrier with a suitable semiconductor. **Figure 1.8c)** presents a Schottky barrier between a plasmonic nanostructure and an n-type semiconductor, such as titanium dioxide (TiO_2). Due to its high DOS in the conduction band, TiO_2 serves as an excellent electron-accepting metal oxide, enabling rapid electron injection. Hot electrons with energies exceeding the Schottky barrier energy (Φ_{SB}) can be transferred into the semiconductor, with emission efficiency depending on their energy.[75] Following electron injection into the adjacent semiconductor, the plasmonic nanostructure becomes positively charged due to electron depletion. An electron-donor solution or a hole-transporting layer (HTL) is required to promote hole transfer to the counter electrode in order to maintain charge balance and electrical current.

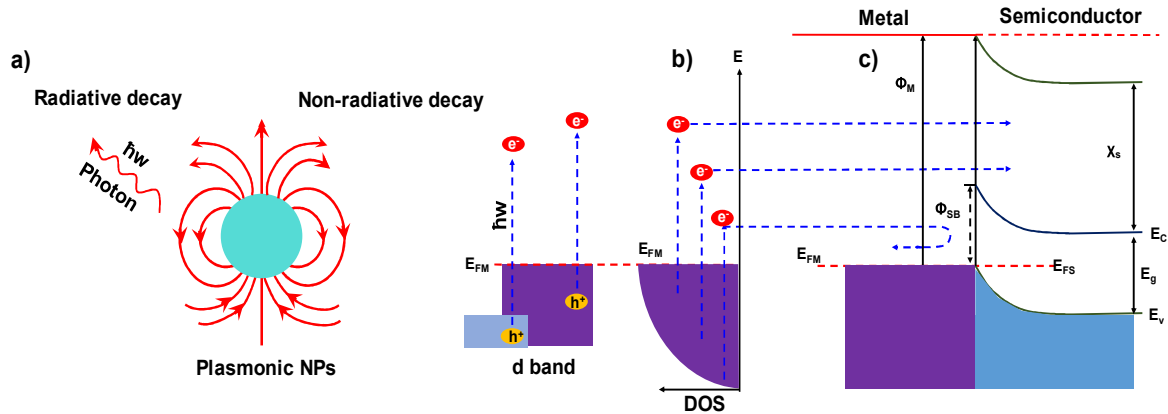


Figure 1.8a) LSPs decay either radiatively, by emitting photons, or non-radiatively, by exciting hot electrons **b)** plasmonic energy conversion excites electrons from occupied energy levels above the Fermi energy **c)** hot electrons with sufficient energy overcome the Schottky barrier $\Phi_{SB} = \Phi_M - \chi_S$ and are injected into the conduction band E_C of a neighboring semiconductor. where Φ_M represents the metal's work function and χ_S denotes the semiconductor's electron affinity.

These novel MNPs can be easily combined with other materials (e.g., zinc, titanium, tin, silicon, carbon, and various polymers) for photonic applications.[76, 77] Their synthesis is generally environmentally friendly compared to other nanomaterials. The plasmonic properties of noble MNPs, especially their large scattering and absorption cross-sections, strong field enhancement, and the ability to form various reproducible morphologies, make them superior to many other nanomaterials. These optical properties enable a wide range of applications in imaging and sensing, associated with enhanced chemical signals, which is schematically shown in **Figure 1.9**. The reproducibility of their fabrication protocols and tunable optical properties makes metallic plasmonic NPs dominant in both theoretical study and practical applications within the field of plasmonics.[78-84]

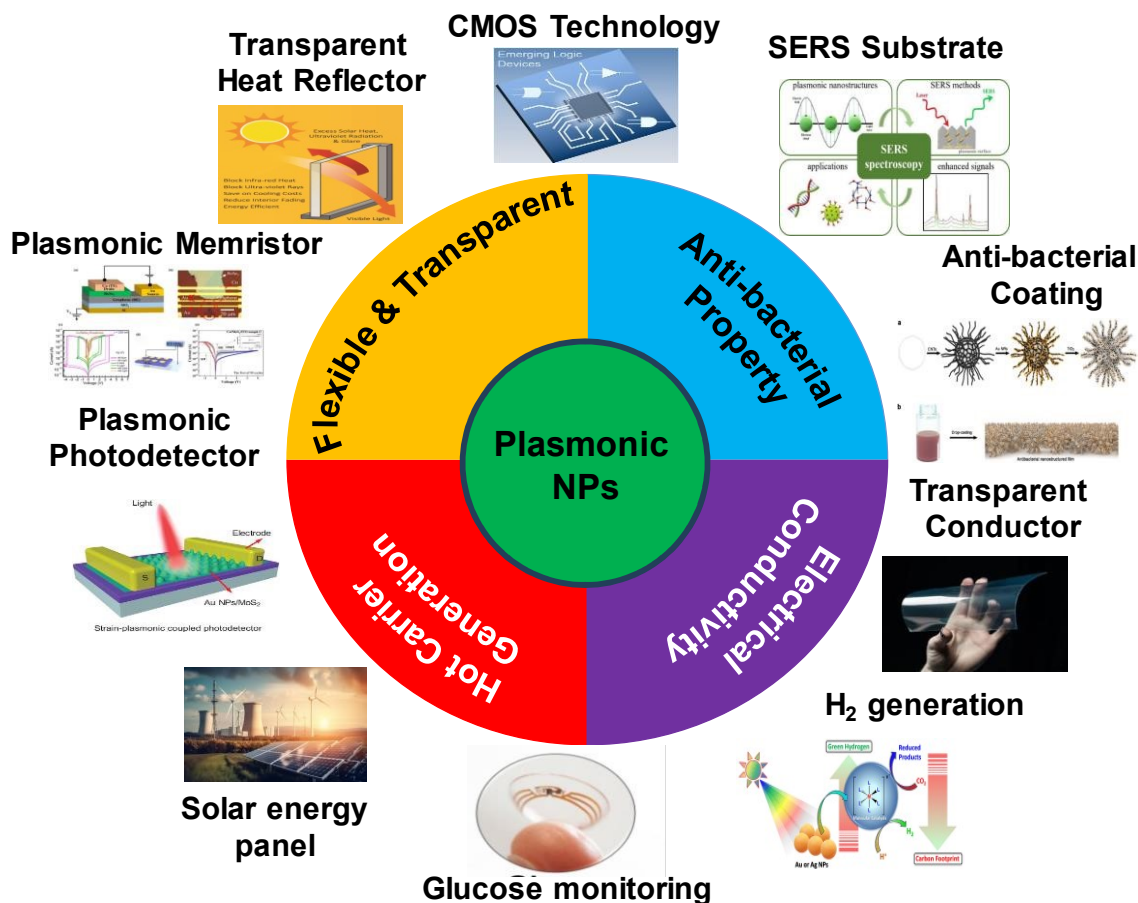


Figure 1.9 Schematic presentation of wide-range photonic applications of plasmonic NPs.

1.5.1 SPR Band Position of Plasmonic MNPs

Both Au and Ag NPs have plasmonic resonance in the visible range with strong absorption at wavelengths of $\sim 520\text{-}550\text{ nm}$ and $\sim 420\text{-}480\text{ nm}$, respectively.[85] The spectrum position depends on diverse factors like size, shape and surrounding dielectric medium. These SPR bands of MNPs can be tuned by varying their size range of $1 - 100\text{ nm}$. In **Figure 1.10**, we can observe that a single broad plasmon absorption band breaks into two plasmon bands as the shape changes from a sphere to a rod. The peak is caused by transverse plasmon resonance along the shorter axis at a shorter wavelength and longitudinal plasmon resonance along the longer axis at a higher wavelength. It is observed that nanorods of Au exhibit two SPR peaks, one for the transverse mode and another for longitudinal mode, which can be tuned in the spectral region depending on their aspect ratio.[86] Along with the different

shapes and sizes of the particles, surface plasmon resonance depends on Rayleigh scattering, charge transfer interactions, changes in the local refractive index and agglomeration of metal NPs. Due to their broad applications of plasmonic NPs with different shapes, they have been synthesized by various routes such as sphere, cubes, rods, bimetallic core-shell, and so on.[85, 87-89]

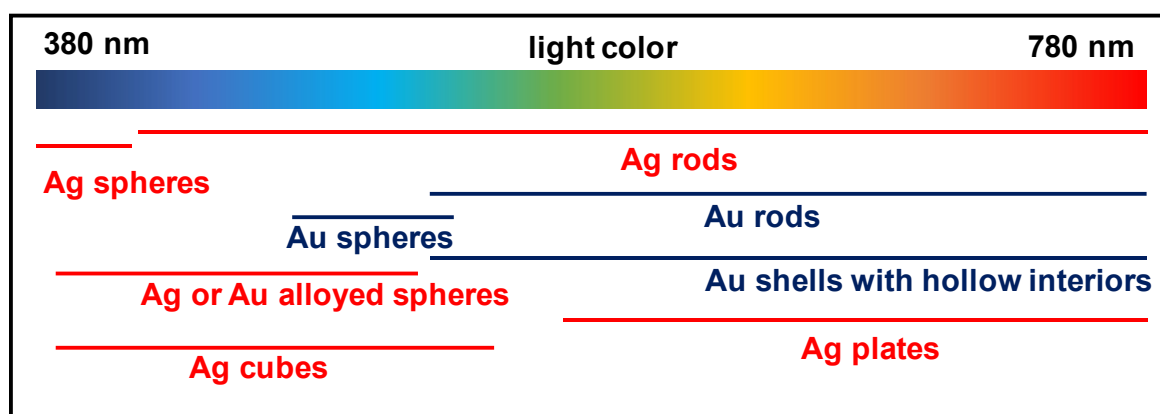


Figure 1.10 Schematic of SPR band position of plasmonic (Ag or Au) MNPs.

1.6 Properties of Plasmonic MNPs

Plasmonic MNPs are renowned for their unique optical properties, primarily due to the LSPR effect, where conduction electrons oscillate in resonance with incident light. This leads to strong light absorption, scattering, and enhanced EM fields.[76, 90] Beyond optical properties, these materials also exhibit significant catalytic activity due to their high surface area and active sites, which are enhanced by the LSPR effect, enabling efficient energy transfer and boosting reaction rates. These NPs have various forms, such as mono-metallic, bi-metallic nanocomposite, metal/semiconductors nanocomposite, etc. The physical and chemical properties of these nanostructured materials are closely related to their shape, size and chemical composition.[91-96] By changing their size, it is possible to tune their different physical properties, including optical, mechanical, electronic, magnetic, photo-catalytic, etc., which are listed in **Figure 1.11**.

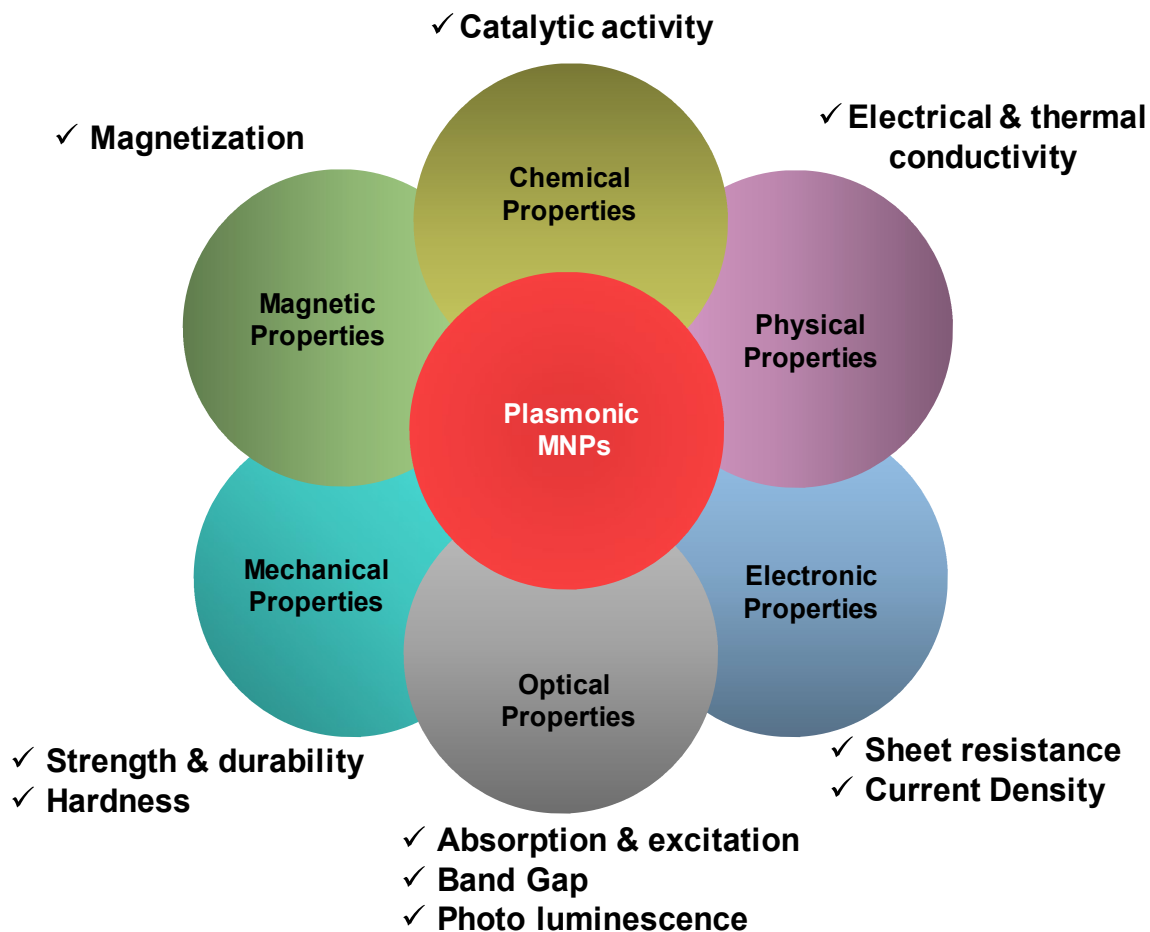


Figure 1.11 Schematic illustrations of different size dependent physical properties of plasmonic MNPs.

1.7 Different Applications of Plasmonic Thin Films

Plasmonic thin films of metal, metal-oxide semiconductor or their nanocomposite have drawn significant attention due to their strong potential applications. These materials have been fabricated for numerous applications like plasmonic photodetector, solar cell, transparent conductor, transparent heat reflector, memristor, SERS, photocatalysis, gas sensor, biosensors, energy storage device, therapeutic and drug delivery, anti-bacterial coating, etc.[97-105] A few applications are explored below in detail.

1.7.1 Plasmonic Photodetector

A photodetector is an electronic device that converts a light (photons) signal into an electrical signal and works by absorbing photons, which generate charge carriers (electrons and holes) within the material, leading to a measurable current or voltage. A plasmonic photodetector leverages the interaction between light and free electrons in metal nanostructures, known as plasmonics, to enhance its performance. By concentrating light into very small volumes and increasing the local EM field, these photodetectors achieve higher light absorption, leading to a stronger photocurrent and improved photo-detectivity. These devices can be designed in three different geometries, such as photoconductors, photodiodes, and phototransistors, as illustrated in **Figure 1.12**. The performance of a plasmonic photodetector is typically evaluated using key parameters, including external quantum efficiency, responsivity, detectivity and transient time response curve. A high-performance plasmonic photodetector should have high detectivity and responsivity with fast response. Whereas external quantum efficiency tells the spectra sensitivity of the device at a particular wavelength range. The key device parameters are discussed in the following section.

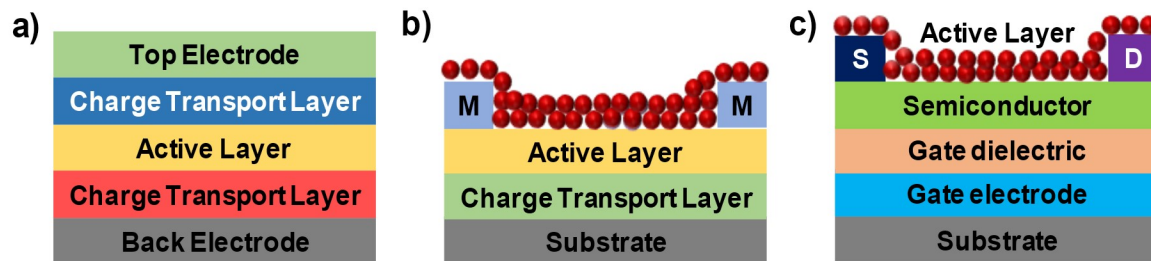


Figure 1.12 Schematic representation of different photodetector geometry a) photodiode b) photoconductor c) phototransistor.

External Quantum Efficiency (EQE)

EQE is the ratio of the number of charge carriers generated and collected by a photodetector to the number of incident photons on the device and measures the effectiveness of converting incoming photons into an electrical signal[106] and is given by the **equation 1.2-**

$$\text{EQE} = \frac{J_{\text{ph}}}{e\phi} = \frac{J_{\text{ph}} \times h\nu}{eP_0} \text{----- (1.2)}$$

where h , ν , c , P_o , e , Φ , J_{ph} and λ is plank constant, frequency, speed of light, output power, electronic charge, the flux of incident photon, photocurrent density and wavelength of the incident light respectively.

Responsivity (R_λ)

Responsivity is a measure of a photodetector's ability to convert incident light into an electrical signal, expressed as the output current or voltage per unit of incident light power.[106] It can be derived from EQE and is given by using **equation 1.3-**

$$R_\lambda = \frac{hc \times EQE}{e\lambda} \text{----- (1.3)}$$

Detectivity (D^*)

The detectivity of a photodetector quantifies its signal-to-noise ratio within a 1 Hz bandwidth, normalized to the detector's area. This critical parameter determines the sensitivity of the device. Taking into account that the primary source of noise originates from the device's dark current, the detectivity[107] can be expressed mathematically as shown in **Equation 1.4-**

$$D^* = R_\lambda / (2eJ_d)^{1/2} \text{----- (1.4)}$$

where J_d denote the dark current density

1.7.2 Plasmonic Solar Cells

Photovoltaics have strong potential to play a crucial role in addressing environmental issues by providing sustainable energy solutions. In recent years, research has focused on.[108-110] For optimal light absorption, photovoltaic layers need to be sufficiently thick. However, indirect band gap materials like crystalline silicon require high-quality production to ensure effective carrier diffusion through thick layers. Currently, around 60-70% of solar cells use crystalline silicon wafers, which are typically 200-300 μm thick, and these wafers account for about 40% of the total cost of the solar cell.[111] In recent years, organic & perovskite

photovoltaics have developed in different research groups throughout the world. Still, power conversion efficiency needs to improve for that photovoltaics. Plasmonic NPs based photovoltaics has driven significant research into thin-film solar cells, in which film thickness is usually 1-2 μm and can be deposited on low-cost substrates such as glass or plastic. However, the major challenge with thin-film solar cells is their inefficient absorption of near band gap light.[112] The progress of solar cells are categorized in four different generations by the development of different materials, which is schematically presented in **Figure 1.13**.

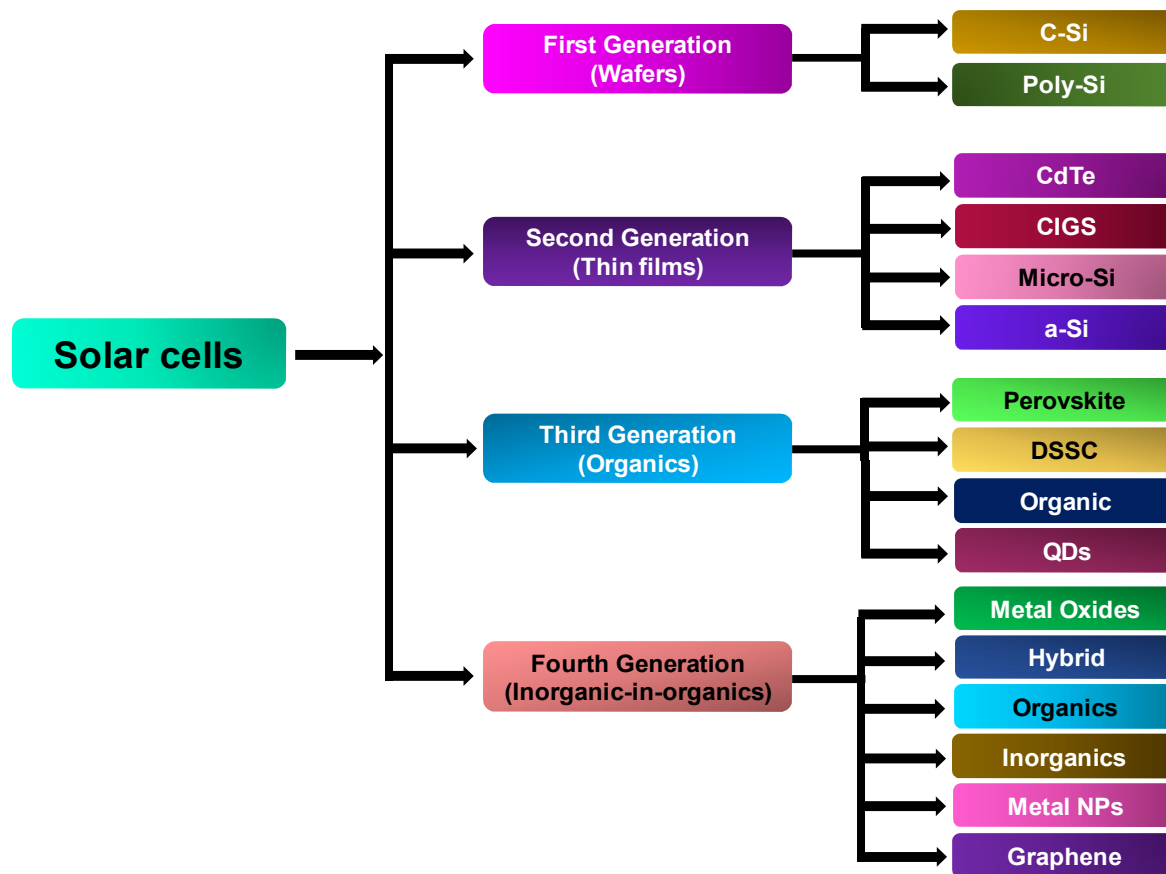


Figure 1.13 Schematic of four different generation solar cells with different materials.

Plasmonic NPs can significantly enhance the efficiency of solar cells by increasing the absorption of light in the active material.[113] These NPs exhibit LSPR, where the conduction electrons resonate with incident light and enhance strong EM fields around the NPs. This resonance enhances the local light intensity, broadening the absorption spectrum

and enabling the solar cell to capture more sunlight across various wavelengths. Additionally, plasmonic NPs scatter light, increasing the optical path length within the active layer, which is particularly beneficial in thin-film solar cells. This scattering effect enhances the probability of photon absorption, leading to greater exciton (electron-hole pair) generation. Besides, plasmonic NPs also produce "hot electrons" that are injected into the conduction band of the active material and contribute to additional photocurrent generation. The size, shape, and distribution of the NPs are essential to optimizing these effects without introducing recombination sites that could negate the benefits. Overall, plasmonic NPs play a key role in improving light absorption, enhancing charge carrier generation, and increasing the power conversion efficiency (PCE) of solar cells, especially in organic and perovskite thin-film photovoltaic devices.

1.7.3 Transparent Conductor & Heat Reflector

Transparent and flexible conductors play a vital role in the advancement of efficient, stretchable, and wearable optoelectronic devices.[\[114, 115\]](#) At the core of these systems lies transparent conductive film (TCF), which must maintain both high optical transparency in the visible spectrum and excellent electrical conductivity, even under significant strain deformation. A key challenge in developing flexible and stretchable electronics is the creation of cost-effective TCFs. Till now, indium tin oxide (ITO) has been the most widely used transparent conductor, offering high transmittance (>90%) and low sheet resistance (10–25 Ω /sq).[\[116, 117\]](#) However, ITO is inherently brittle and susceptible to cracking.[\[118\]](#) Additionally, the limited availability of indium, along with the high-cost sputtering techniques used in ITO film fabrication, makes it less suitable for low-cost and large-area applications.[\[119\]](#) For instance, in photovoltaics, the use of ITO in TCFs accounts for more than 50% of the total material and processing expenses. To address these limitations, alternative TCF materials and cost-efficient solution-phase coating processes are urgently required to enable the production of affordable, flexible electronics. Several emerging materials, including conductive polymers, metal grids, carbon nanotubes (CNTs), graphene, metal/metal-oxide interfaces, and random networks of metal nanowires (such as silver and copper nanowires), are being explored as potential next-generation replacements for ITO.[\[120-122\]](#) Solution processed plasmonic material shows emerging merits because of

their low cost, ease of scalable fabrication, and flexible/stretchable/wearable features to fabricate transparent conductors and heat reflectors.[123, 124] Transparent heat reflectors mainly reflect light in NIR/IR region and allow visible light to pass through the film, which is strongly applicable for the development of energy efficient smart windows.[125, 126] Fabrication of these novel TCF materials is possible via low-cost physical methods, including spin-coating, drop-casting, spraying, dip-coating techniques alongside with thermal or sputtering deposition techniques. However, these solution-processed techniques are difficult to scale up and are frequently employed for laboratory demonstrations. There is a pressing demand for a large-scale, large-area fabrication technique with industrialized potential.

1.7.4 Plasmonic Memristor

Plasmonic memristors, which combine the unique properties of plasmonic nanostructures and memristive behavior, hold significant promise for advanced applications in neuromorphic computing, high-density data storage, and optical signal processing.[127, 128] The integration of plasmonic nanostructures, such as metal NPs or nanowires, into memristive devices enhances their functionality by enabling strong light-matter interactions at the nanoscale. This results in the possibility of light-assisted switching, where optical signals can modulate the resistance states of the memristor, thereby enabling faster and more energy-efficient data processing. In neuromorphic computing, plasmonic memristors can mimic synaptic behavior with high precision, offering potential for artificial neural networks that process information similarly to the human brain but with much greater speed and efficiency. Additionally, the plasmonic enhancement can lead to more pronounced and stable resistive switching, improving the performance and reliability of the memristor. In optical signal processing, the ability to control memristive states with light opens avenues for integrated photonic circuits, where data can be processed and stored optically, significantly reducing the energy consumption and enhancing the speed of optical communications.

1.7.5 Surface Enhanced Raman Spectroscopy (SERS) Substrate

SERS is a highly sensitive and selective vibrational spectroscopy technique that leverages the inelastic scattering of photons by molecular species. Its advantages, including ultra-sensitivity, non-destructiveness, speed, and fingerprinting capabilities, make it ideal for analytical and sensing applications.[129, 130] Despite its potential, the high cost and low reproducibility of SERS signals limit its broader application. Developing versatile, stable, flexible and reusable nano-engineered SERS substrates offers a promising solution to these challenges. In recent time, plasmonic SERS-active nano-substrates with varied morphologies have gained significant attention due to their ability to create dense hot spots, enhanced stability, tunable morphology, and surface functionalization.

1.7.6 Chemical and Bio-Sensors

Chemical and biosensors are devices designed to detect and quantify specific chemical substances or biological entities, often at extremely low concentrations. These sensors are essential for a number of applications, such as industrial process control, food safety, healthcare diagnostics, and environmental monitoring.[131-133] Chemical sensors typically detect analytes like gases, pH, ions, or organic compounds, while biosensors are tailored for biological molecules such as glucose, proteins, DNA, or pathogens. The performance of these sensors hinges on their sensitivity, selectivity, and ability to produce rapid and reliable results, often necessitating the detection of trace amounts of analytes in complex matrices. Plasmonic materials have emerged as a transformative technology in the development of advanced chemical and biosensors. These materials exhibit LSPR and collective oscillations of surface electrons that occur when illuminated by light at specific wavelengths. This resonance amplifies the local EM fields near the material's surface, significantly enhancing the detection capabilities of sensors. When incorporated into chemical or biosensors, plasmonic materials enable ultra-sensitive detection by boosting signal intensities and allowing for the real-time monitoring of molecular interactions at the sensor surface. This sensitivity, combined with the ability to functionalize plasmonic surfaces for specific target recognition, makes plasmonic materials ideal for creating highly responsive and selective

sensors, pushing the boundaries of detection limits and enabling new applications in diagnostics and environmental monitoring.

1.7.7 Anti-bacterial Coating

Plasmonic MNPs like Ag, Au, and Cu are known for their unique antibacterial properties, largely driven by their ability to harness LSPR effect. Upon exposure to light, especially in the UV-Visible range, the excitation of plasmons leads to the formation of reactive oxygen species (ROS) such as hydroxyl radicals, superoxide anions, and singlet oxygen. These ROS can disrupt bacterial cell membranes, damage intracellular components like DNA and proteins, and ultimately lead to bacterial cell death. Furthermore, the small size and high surface area of plasmonic NPs enable them to penetrate bacterial cells more efficiently, enhancing their antimicrobial effects. In addition to oxidative stress, Ag^+/Au^+ released from Ag/Au based plasmonic NPs, interact with bacterial enzymes and disrupt essential biological processes. These properties make plasmonic NPs highly suitable for applications in antibacterial coatings for medical devices, wound dressings, water filtration systems, food packaging, and even air filtration systems, providing a non-toxic, efficient, and long-lasting antibacterial strategy that is increasingly important in the fight against antibiotic-resistant bacteria.[\[134-137\]](#)

1.8 Motivation and Scope of the Thesis

Nanotechnology is the emergent technology of different areas of electronics and optoelectronics including display, sensor, photovoltaics and many other photonic applications. These materials have been developed for various purposes, including improve chemical and colloidal stability, fabrication of photovoltaic devices, prevention of bacterial infection, enhancement of photoluminescence, etc. which enables advanced photonic technologies. Particularly, plasmonic thin films have garnered significant attention in modern optoelectronics due to their ability to enhance light-matter interactions through LSPR. This enables superior optical, electronic, and sensing properties at the nanoscale. These thin films, typically made from metal NPs like Ag, Au, and Cu are used to improve device efficiency in applications such as transparent conductors, solar cells, transparent heat reflectors,

photodetectors, biosensors, and anti-bacterial coating. Their sensitivity to environmental changes makes them ideal for chemical and biological sensing, while their light-trapping capabilities enhance energy harvesting and photonic applications. As electronics continue to miniaturize and demand higher performance, plasmonic thin films offer a scalable, cost-effective solution with promising integration into next-generation technologies like quantum computing, wearable devices, and flexible electronics. With advancements in solution-based fabrication techniques, their future in energy-efficient systems, healthcare diagnostics, and photonics is particularly bright.

Researchers are increasingly interested in plasmonic thin film devices fabricated via solution-processed techniques because they offer a groundbreaking combination of cost-effectiveness, scalability, and versatility, particularly for large-area and flexible applications. Solution processes such as spin-coating, dip-coating, and inkjet printing allow for the mass production of high-performance plasmonic devices without the need for expensive equipment or controlled environments, unlike sputtering or lithography techniques. Solution processing also allows seamless integration of plasmonic nanoparticles with other materials, enhancing their optical and electrical properties, thus paving the way for high-performance, low-cost devices in industries ranging from renewable energy to healthcare. As research continues, the ability to fabricate these devices with precision and scalability is positioning solution-processed plasmonic thin films as a transformative technology in modern electronics.

To address the higher cost of these photonic technologies, We have introduced a novel cost-efficient technique where an ion-conducting metal oxide (ICMO) ceramic is used as initial material. This ceramic contains some light ions like Li^+ , Na^+ , K^+ , etc. and these mobile ions can move through the crystal channel easily. By taking advantage of these mobile ions, We have chemically implanted conducting ions like Ag or Cu inside the dielectric matrix. This innovation helps to fabricate plasmonic thin film with much more stability, making it feasible for multi-functional photonic applications. To utilize this phenomena, We have successfully fabricated an ion conducting dielectric $\text{Li}_4\text{Ti}_5\text{O}_{12}$ initially and then by doing surface chemistry, we have developed an Ag- TiO_2 plasmonic thin film. Using Ag- TiO_2 thin film, We have successfully fabricated a narrowband plasmonic hot electron-based photodetector

in photoconductor geometry. The device shows a very good detectivity with conclusive evidence of hot electron generation from the plasmonic part. This approach shows a record detectivity of a plasmonic photodetector with a photoconductor geometry.

Furthermore, by employing surface engineering with an ultra-thin plasmonic layer and Ag-TiO₂ thin film, I have successfully developed flexible transparent conductors, transparent heat reflectors, plasmonic solar cells, photodetectors, and active SERS substrates using a low temperature solution process and physical vapor deposition technique.

From the next chapter onward, the thesis carries forward detailed studies encompassing material characterization and device engineering, systematically addressing the experimental investigations and their outcomes in a structured manner.