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# Plasmonic nanoparticles and their analytical applications: A review

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## ABSTRACT

Plasmonic nanoparticles (NPs) have been reviewed herein for their fascinating optical properties in a wide spectral range and for their various applications. The surface plasmon resonance (SPR) bands of metal NPs can be tuned from visible to near infrared region by varying the shape of the metal NPs. As a result, the tuning of the SPR band over a spectral range is possible by making plasmonic NPs of different shapes. This review emphasizes fundamental studies of plasmonic NPs and nanocomposites with well-defined and controlled shapes that have several analytical applications such as molecular detection and determination in different fields. This review describes how oxidative etching and kinetic control can be utilized to manipulate the shape and optical properties of NPs. This review also describes the specific examples of the sensing applications of the localized surface plasmon resonance studies in which the researchers use both wavelength shift and surface-enhanced Raman scattering sensing to detect the molecules of chemical and biological relevance. The review ends with a perspective of the field, identifying the main challenges to be overcome and suggesting areas where the most promising developments are likely to happen in future.

## KEYWORDS

Nanoparticles; shape-controlled synthesis; localized surface plasmon resonance; surface-enhanced Raman scattering; tip-enhanced Raman scattering

## Abbreviations

|        |                                                               |
|--------|---------------------------------------------------------------|
| AA     | Ascorbic acid                                                 |
| AFM    | Atomic force microscopy                                       |
| APTES  | 3-Aminopropyltriethoxysilane                                  |
| CTAB   | Hexadecyltrimethylammonium bromide                            |
| DDA    | Discrete dipole approximation                                 |
| DNA    | Deoxyribonucleic acid                                         |
| EDX    | Energy dispersive X-ray spectroscopy                          |
| EuTDPa | Tris(dibenzoylmethane) mono (5-amino phenanthroline) europium |

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|                    |                                                                  |
|--------------------|------------------------------------------------------------------|
| HAuCl <sub>4</sub> | Tetrachloroauric acid                                            |
| Irgacure 2959      | 1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methyl-1-propan-1-one |
| LSPR               | Localized surface plasmon resonance                              |
| MWCNTs             | Multi-walled carbon nanotubes                                    |
| NaBH <sub>4</sub>  | Sodium borohydride                                               |
| NaBr               | Sodium bromide                                                   |
| NCs                | Nanocomposites                                                   |
| NPs                | Nanoparticles                                                    |
| NRs                | Nanorods                                                         |
| PTFE               | Polytetrafluoroethylene                                          |
| PVP                | Polyvinylpyrrolidone                                             |
| PVP                | Polyvinylpyrrolidone                                             |
| RNA                | Ribonucleic acid                                                 |
| SDS                | Sodium dodecyl sulfate                                           |
| SERS               | Surface-enhanced Raman scattering                                |
| SPPs               | Surface plasmon polaritons                                       |
| SPR                | Surface plasmon resonance                                        |
| TDAB               | Tetradodecylammoniumbromide                                      |
| TEM                | Transmission electron microscopy                                 |
| TEOS               | Tetraethylorthosilicate                                          |

## Introduction

Nanoparticles (NPs), notable for their small size, high surface area to volume ratios, and strong adsorption capacity, have been the subject of great interest in analytical chemistry (1, 2). Metal NPs-based analytical techniques have become increasingly important in clinical, pharmaceutical, environmental, and food safety fields owing to their high sensitivity, wide linear range, and simple instrumentation, and thus over the past decade, NPs have been widely used for elemental detection and speciation (1, 2). Thus, metal nanostructures have gained considerable attention both fundamentally and technologically because of their many peculiar properties and functionalities compared to their bulk counterparts. One of the most important aspects of NPs is their optical properties. In the nanoscale domain, many metals like silver and gold exhibit strong absorption in the visible region. These optical properties of nanoscale metal particles depend on various parameters such as their dimensions (3), shapes (4), the composition of metal (5), optical properties, and surrounding medium of the particles (5–10). The optical properties of metal nanostructures are magnificent and therefore have enhanced a great deal of excitement in the last few years (1–3, 5–7, 9–11). The variations in color arise from changes in shape, size distribution, surrounding medium and high absorption, which promoted these materials as inorganic chromophores from visible to near infrared region. Owing to this researchers are prompted to find various applications of metal nanostructures as optical sensors and imaging agents (11–14). For example, nowadays nanomaterials are also recognized as excellent candidates to detect biological impurities, such as the presence of *Escherichia coli* in water (15, 16). Through this review, we attempt to show that NPs and core-shell nanocomposites (NCs), i.e., nanomaterials, have well been utilized as new generation water remediation materials (16).

Metal NPs play an important role in many different fields. For example, they can serve as a model system to experimentally probe the effects of quantum confinement on magnetic, electronic, and other relevant properties (17, 18). The metallic NPs have also been used in many areas such as catalysis (19), photography (20), biological labeling (2, 21), photonics (22), optoelectronics (23), information storage (24), and surface-enhanced Raman scattering (SERS) (25, 26).

Metallic NPs can be obtained by various synthetic routes such as electrochemical methods, decomposition of organometallic precursors, and reduction of metal salts in the presence of stabilizers or vapor deposition methods. Sometimes the presence of stabilizer is required to prevent the agglomeration of nanoclusters. In addition, the stabilizers play a crucial role in controlling both the shape and size of NPs (27).

NPs are complicated multi-electron systems where the confinement of electronic motion due to the reduction in size leads to fascinating effects, potentially tunable with particle size and shape. In addition, almost any shape can be produced. These different shaped nanostructures exhibit different absorption spectra or colors. More complex structures such as aggregates, nanocages, and nanoprism usually have more nondegenerate resonances and obtain broad absorption spectrum. It has been shown that due to lower symmetry of structures more nondegenerate modes are obtained (28).

These optical properties exhibited by metal NPs are due to the surface plasmon resonance (SPR), and correspond to the frequency of oscillation at which conduction electrons oscillates in response to the electrical field of the incident electromagnetic radiation. The surface plasmons are essentially electromagnetic waves trapped at the metal/dielectric interface due to the collective oscillations with the free electrons of the metal. This phenomenon was explained by Mie theory and is based on the Maxwell equation on scattering (14). Materials that possess negative real and positive imaginary dielectric constants are capable of supporting the SPR. This resonance is a coherent oscillation of the surface conduction electrons excited by electromagnetic radiation of light. Plasmonics is the study of these particular light interactions that have enabled various applications such as biological and chemical sensing (1, 2, 13, 25, 29–45), lithographic fabrication of the materials (20, 46–48), and surface-enhanced spectroscopies (49–64). However, only gold, silver, and copper NPs exhibit plasmon resonance effects in the visible spectrum, giving rise to intense colored particles. It is due to the fact that resonance frequency of the SPR depends on the shape, size, and surrounding medium of the particles (3, 4, 8, 16, 65). Au and Ag NPs play a significant role in the visible region due to surface plasmon absorption and the surface accessibility for further functionalization (15, 16, 40, 66–68). These NPs are known for their interesting optical properties caused by plasmonic resonance with significant absorption and scattering at 530 nm and 400 nm for gold and silver, respectively. These NPs have been studied for various analytical, environmental, and medical applications such as laser biomedicine, laser-combined imaging, photothermal therapy, cancer research, biosensors, etc. (15, 16, 40, 66–71).

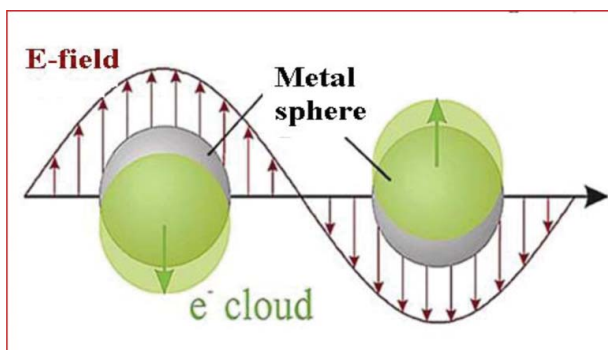
The optical properties of metal NPs have been previously investigated by optical spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM) techniques. Core-shell NPs are very attractive for analytical, biological, biochemical, and biotechnological applications due to their unique properties, especially in tuning of plasmon absorption peak (16, 40, 53, 56, 66, 67). It is also interesting to use core-shell NPs with possible plasmon resonance wavelength in the range of 400–500 nm or in other spectral range. The optical properties of spherical core-shell NPs depend on the values of core and shell radii,

and the optical indexes of refraction and absorption of core and shell metals (16, 53, 56, 66, 67). Extending the Mie theory of radiation, the modeling of optical properties of spherical core-shell particles can be carried out for wavelength in range  $300\text{ nm} \leq \lambda \leq 650\text{ nm}$  (14). In order to obtain high-efficiency factors of absorption, scattering, and extinction of radiation by the core-shell particles, it was observed that the ideal range of shell thickness and core radii should be 0–40 nm and 5–100 nm, respectively. It could be applied for photonic applications in nanotechnology (72). It is possible to control the absorption in the visible range with relatively narrow absorption for each sample by simply controlling two parameters such as shell thickness and core diameter of the particles (53, 56). The controlled and tunable optical properties of metal structures are highly desired for many applications that rely on light absorption of metal such as SERS sensing, imaging therapy, photo catalysis and SPR (16, 40, 53, 56, 66–71, 73). For example, Haes and coworkers explored the long range distance dependence of localized nanosensors using self-assembled monolayer of 11-mercaptopundecanoic acid and  $\text{Cu}^{2+}$  ions adsorbed on arrays of noble metal NPs with various shapes, sizes, and compositions of the materials (74). We have also shown the plasmonic detection of  $\text{Cd}^{2+}$  ions using SERS active core-shell NC (66). In addition, we have also developed highly selective visual monitoring of hazardous fluoride ion in aqueous media using thiobarbituric-capped Au NPs (67) and a new way in nanosensor for sensing  $\text{Fe}^{3+}$  ions in aqueous media (68). Therefore, we have been interested in Au and Ag NPs because they have the strongest plasmonics interaction with light among all metals (15, 16, 40, 53, 56, 66–68). Hence, this review mainly focuses on Au and Ag NPs with different shapes including nanocubes, nanospheres, tetrahedron and octahedron shapes of the particles, etc., where the shape-controlled chemical syntheses of plasmonics metal NPs have also been emphasized. Some unique properties enabled by the shape-controlled synthesis of metal NPs and NCs as well as the advantages of these structures to several analytical applications such as molecular detection and determination in different fields have been highlighted in this review. To summarize our discussion, the specific examples of localized surface plasmon resonance (LSPR) sensing experiments using wavelength shift and SERS have been provided. The review ends with a perspective of the field, identifying the main challenges to be overcome and suggesting areas where the most promising developments are likely to happen in future.

## Surface plasmon resonance

### *Metallic nanostructures*

The physical origin of the strong light absorption by metal NPs is the coherent oscillation of the conduction band electrons induced by interaction with an electromagnetic radiation. This collective oscillation of conduction electrons in metals is known as plasmon. To explain the formation of dipole and origin of plasmon in metals upon interaction with electromagnetic radiations, metals can be considered as plasma of positive ions having equal numbers of conduction electrons. In neutral case, the negatively charged cloud of electron and the positively charged cloud of ions overlap each other. By some external disturbance, such as interaction with electrons or electromagnetic radiations, the charged cloud is disturbed and the electrons moved away from the equilibrium position. If the density of electrons in one region increases, then they repel each other and tend to return to their original position. Due to repulsion, electrons move toward their original equilibrium position with certain kinetic energy. As such,



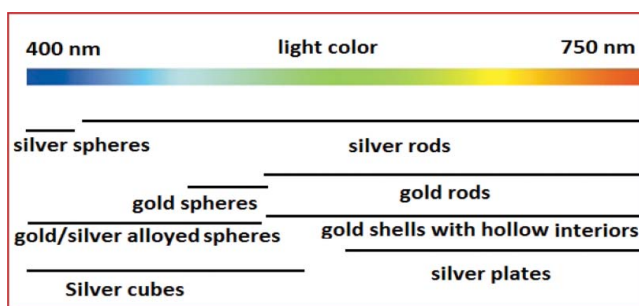
**Figure 1.** Schematic representation of plasmon oscillations from a sphere that shows the displacement of conduction electron charge cloud relative to the nuclei (shown in light green color). Reprinted with permission from Ref. (77).

they oscillate back and forth. As the net charge difference occurs at the NP's boundaries or surfaces, the electrons on the surface are the most significantly involved in oscillations and their collective oscillations are known as surface plasmon. The resonance between these oscillations and incidence light gives rise to an intense peak in the visible range of the electromagnetic region and is known as SPR (75, 76). The scattering of light by small particles is explained involving the Mie theory and is shown in Figure 1, which shows the displacement of the conduction electron charge cloud relative to the nuclei (14, 77).

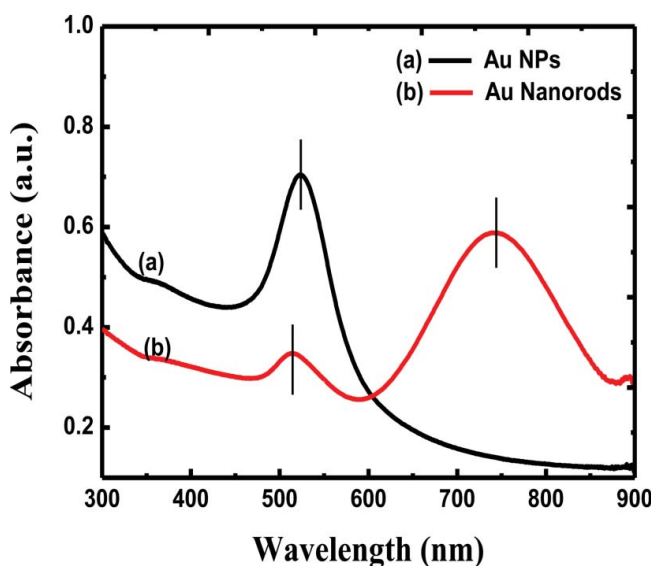
### ***Tuning the surface plasmon resonance band of metallic nanostructures***

Silver and gold NPs have been studied for their unique optical properties in a wide spectral range. These particles show the SPR band in the visible range of the electromagnetic spectrum. The position of the spectrum depends on various factors such as the size, shape, and dielectric constant of the medium in which they are dispersed (3, 4, 8–10, 77). These SPR bands of metal NPs can be varied by changing their sizes in the range of 1–100 nm (15, 16, 53, 56, 66–68). In contrast, surface plasmon band can be tuned in the region from visible to near infrared by varying some of the above mentioned factors (78). In other words, the position of the SPR bands varied in the visible region with various morphologies and structures of gold and silver NPs is shown in Figure 2A (78). When a transition in shape from sphere to rod is made, a single plasmon absorption band shown in Figure 2B(a) splits into two plasmon bands as shown in Figure 2B(b) (68).

At higher wavelengths, a peak is observed due to longitudinal plasmon resonance along longer axis, while at shorter wavelengths, a peak is observed due to transverse plasmon resonance along shorter axis. Nanorods of gold exhibit two SPR peaks as shown in Figure 2B(b) (68), where the transverse mode and the wavelength of longitudinal mode can be tuned in the spectral region from visible to near infrared depending on their aspect ratio (79). Along with the shape and size of the particles, SPR depends on Rayleigh scattering from NPs (80), charge transfer interactions (81), changes in local refractive index (82), aggregation of NPs (83), etc. These kinds of interactions are very useful in the detection of various analytes including biomolecules using metallic nanostructures. Figure 2A clearly shows that tuning of SPR band over a wide spectral range is possible by making nanostructures of different shapes.



(a)



(b)

**Figure 2.** (A) Position of surface plasmon resonance bands tuned using gold and silver nanoparticles of various morphologies and structures. Reprinted with permission from Ref. (78). (B) Surface plasmon resonance spectra of (a) gold nanoparticles and (b) gold nanorods (68).

### Localized surface plasmon resonance (LSPR)

The great interest in plasmonic NPs, especially Au and Ag, is enhanced by their fascinating applications in different fields of analytical chemistry (1–3, 15, 16, 19–26, 33–38, 40, 42–44, 49, 50, 52, 55, 65, 73, 80, 83, 84). Additionally, due to the scattering and absorption of light, plasmonic NPs also enhance the electromagnetic fields. For localized surface plasmon, light interacts with particles much smaller than the incident wavelength. The collective oscillation of free electrons is confined to a finite volume as in the case of metal NPs, the corresponding plasmon is called a LSPR. The LSPR can create intense electric field very close to (within a few nanometers) a particle surface resonance. This near field effect can improve SERS cross sections for the molecules adsorbed onto the surface. Thus, the LSPR depends upon the refractive index of the medium surrounding the metal (Au, Ag, Al, and Cu) NPs, which are examined by the electrodynamics approach. However, the localized studies have been focused on Au and Ag NPs for many years because of their bulk dielectric properties (6, 9). The dependence of

refractive index sensitivity and the figure of merit of plasmonic sensors depending on selected metal NPs with similar geometry show that sensing parameters have shape and width below 20 nm (84). The metals (Au, Cu, and Ag) NPs show much higher refractive index sensitivity, but the figure of merit is higher for Ag compared to other metals (85). The observed sensitivity of nanocubes plasmon is shown to be dependent on various parameters such as surface scattering, dynamic depolarization, radiation damping, and interband transition (86).

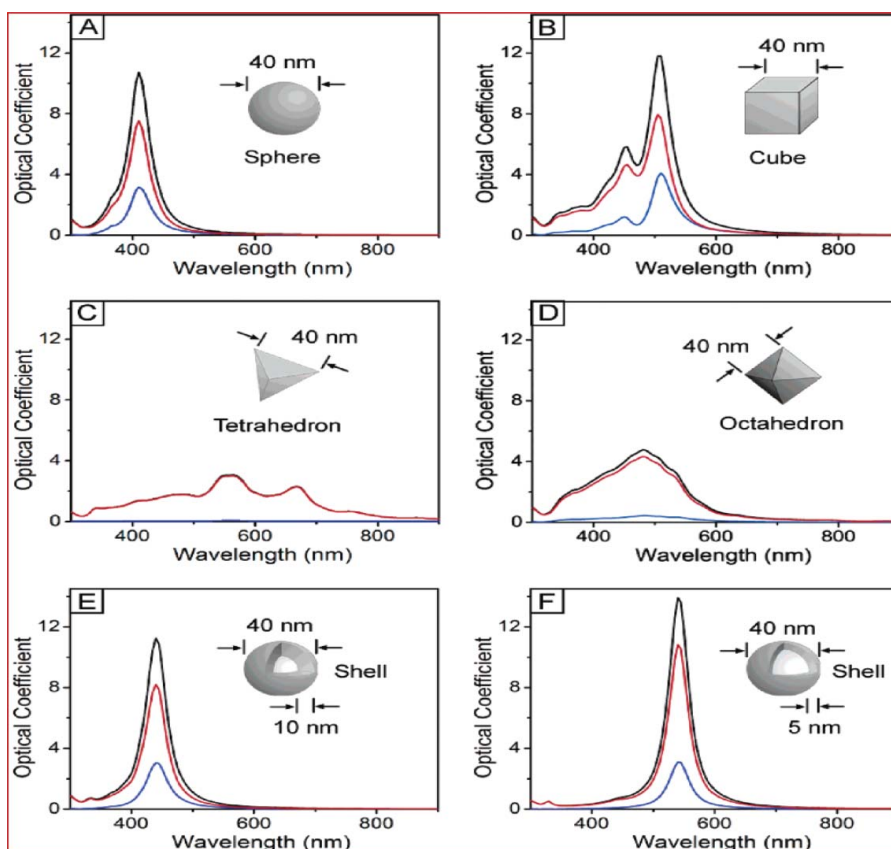
The first synthesis of plasmonic metal NPs was reported more than 150 years ago when Faraday prepared Au colloids by reducing an aqueous solution of Au chloride with phosphorus (87). A variety of chemical methods have been reported during the past few years for preparing high-quality Au and Ag NPs, which have led to systematic studies of LSPR dependencies on the NPs (9, 10, 53, 56, 84–86). This is because the shape of the NPs can significantly affect the interaction of light and thus LSPR (3, 4, 8, 10, 16, 25, 65).

### ***Metal nanoparticle shape and size dependence on LSPR***

The frequency and intensity of plasmon resonance are determined by the intrinsic dielectric properties of the metals, dielectric constant of the medium which it is in contact with and surface polarization. As any variation in shape and size of metallic NPs alters the spectral signature of its plasmon resonance, the ability to change shape and size of the particles and the study of its effect on LSPR are the important and challenging tasks. The interaction of an electromagnetic wave with NPs can be understood by Maxwell's equations (14). Maxwell's equations, based on analytical formulations such as the Mie theory, are desirable for special cases such as solid sphere, concentric spherical shell, infinite cylinder, etc. (14). Numerical calculations with some approximation are required for other particles having arbitrary geometrical shapes. Apart from above-mentioned numerical approaches, the discrete dipole approximation (DDA) has also been used to simulate the interaction of light with metallic NPs having arbitrary shapes (88, 89).

The discrete dipole interaction is used to investigate the effect of shape on LSPR. Dipole approximation calculations are integrated with experimental studies to achieve better understanding of LSPR spectra obtained from NPs' sample (90). These calculations also provide useful guidelines for the design and fabrication of novel plasmonic NPs (90). The LSPR spectra for Ag NPs of various shapes are shown in Figure 3.

The absorption, scattering and extinction spectra for 40 nm silver sphere in water (Figure 3A) and for all the other shapes of the particles were obtained by using the Mie theory (where DDA method was used) (89). The DDA calculated spectra of Ag cube with edge length 40 nm is shown in Figure 3B. In Figure 3B, the absorption spectrum for 40 nm silver spheres shows the presence of two resonance peaks: The main dipole resonance peak is at 410 nm and a smaller quadruple resonance at 370 nm is present as a shoulder peak. The weaker quadruple resonance arising from energy losses make the incident light non-uniform across the sphere and induces a weaker quadruple resonance, characterized by two parallel dipoles of opposite signs (91, 92). Surface polarization is the most important factor in determining the frequency and intensity of plasmon resonance for a given metal NPs because it provides the main restoring force for electron oscillation. Indeed, any variation in particle's shape, size, and the medium will change the surface polarization (93). The nanocubes (Figure 3B) have several distinct symmetries for dipole resonance compared to only one for the sphere (Figure 3A), and hence nanocubes exhibit more peaks than the spheres (94).



**Figure 3.** UV-vis extinction (black), absorption (red), and scattering (blue) spectra calculated for silver nanoparticles of different shapes: (A) anisotropic sphere exhibit spectra with a single dipole resonance peak, (B) a cube, (C) a tetrahedron, (D) an octahedron spectra exhibiting multiple red-shifted resonance peaks, (E) hollow sphere peak exhibiting red-shift and (F) thin-shelled wall peak, exhibiting further red-shift. Reprinted with permission from Ref. (94).

Similar trends are observed for the tetrahedron and octahedron, even though they have reduced scattering cross section because of their different symmetries and smaller structures. The simulated spectra of tetrahedron and octahedron (Figure 3C and D) show red-shifted LSPR peaks because they have even sharper corners than the cubes. The tetrahedron shows the red-shifted resonance of three platonic sides because it has the sharpest corners. The calculated hollow spheres or shells also show the red-shifted resonance peak (Figure 3E and F). This shows that the incident electric field induces surface polarization, i.e., surface charges on both; inside and outside of the shell, i.e., hollow spheres. Hence, the particles must have a dipole moment to compensate the incident field. The charges on the inner surface are of the same sign as those on the outer surface for a given pole. The frequency of oscillation is reduced so as to increase the charge separation. For the thin shells, stronger coupling occurs between inside and outside of the shell leading to an increase in charge separation, and the red-shifted spectra is obtained (Figure 3F). Thus, a metallic nanoshell represents a unique object of radiative and local field properties which can be effectively tuned over a wide range (95).

In summary, the DDA calculations show several pathways in which shapes of metallic nanostructure affect the intensity as well as frequency at which the nanostructure scatters and absorbs the light. First, the resonance frequency value depends on the number of ways a nanostructure can be polarized. Second, for nanostructures, the red-shift in the resonance frequency occurs due to the increase in sharpness at the corners, particle anisotropy, and decrease in the wall thickness (in the case of hollow nanostructures). Third, the resonance peak intensity increases with an increase in the symmetry of effective dipole moment of the NPs.

### ***Advantages and limitations of various nanomaterials***

Large amount of scientific literature is available on the fabrication techniques of nanomaterials in solution which include photochemical (96–101), electrochemical (102–108), chemical reduction (109–112), ultrasound processing (113–115), sonochemical (116), gamma irradiation, ion irradiation (117–125), microwave processing (126–130), etc. In recent years, the synthetic methods of plasmonics NPs involving different routes have become an important area of research, leading to their direct potential analytical applications (29, 96, 102, 104, 107, 115, 117, 119, 125). We have summarized the advantages and limitations of various synthetic methods and the analytical potential of plasmonics nanomaterials in Table 1. Table 1 also describes the advantages and limitations of various methods for different nanomaterials using object reagents and capping agents and reviews various methods used to obtain the desired shape of Au and Ag NMs (131–156).

### ***Shape-controlled synthesis in plasmonics***

In the past two decades, the metallic NPs have evolved for preparing different shapes and sizes of the particles and continuous efforts have been directed toward the shape control synthesis of NPs (3, 4, 8, 75, 77, 86, 94, 106, 116, 124, 128, 130). Wulff's theorem predicts that a single crystal, noble metal NP in an inert gas assumes a truncated octahedron shape at equilibrium (157, 158). In solid-phase synthesis methods, the shapes are different from a Wulff polyhedron due to different anisotropic interactions of different facets with capping agent and solvent. Therefore, the formation of twin structures with energies lower than those of a cuboctahedron occurs. This ascribes that the solution-phase methods of synthesis of plasmonics are more powerful and versatile than vapor-phase methods for the shape-controlled synthesis of noble NPs. Among the various solution-phase methods, polyol reduction is the best established method for generating silver and gold NPs with controlled shape and optical properties (159–164). Herein, we emphasize on the synthesis of metal NPs structures as a model system to fabricate plasmonic NPs with various shapes and LSPR characteristics. Metal NPs can serve as a model system to experimentally probe the effects of quantum confinement on electronics, magnetic, and other related properties.

In the polyol synthesis, the formation of NPs with controlled shapes is facilitated by adding polyvinylpyrrolidone (PVP) as a capping agent. It has been established that the shape taken by PVP in a metallic nanostructure can promote the formation of twin defects included in the initial seed. Different seeds can grow into NPs of different shapes. Figure 4 summarizes all the major shapes that have been observed under different experimental reaction conditions. For example, a single crystal seed can evolve into an octahedron or cuboctahedron or cubes by controlling the relative growth rates along the {100} and {111} directions (164, 165). This type of control is achieved by the introduction of capping agents (166).

Table 1. Different fabrication methods for gold and silver nanomaterials with their advantages and limitations.

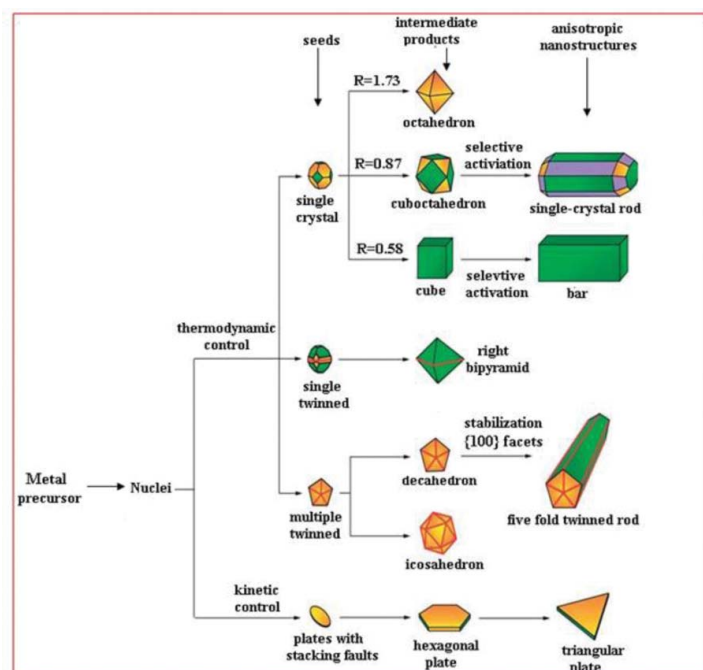
| Plasmonics nanomaterials | Fabrication method      | Capping agent   | Reagents/stabilizer                            | Shapes of particles                                                                               | Advantages                                                                                                                                                                        | Limitations                                                                                                                                               | Ref.  |
|--------------------------|-------------------------|-----------------|------------------------------------------------|---------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| Ag@SiO <sub>2</sub> NCs  | Chemical reduction      | Sodium citrate  | Eu-TDPA                                        | Hollow fluorescent nanobubbles                                                                    | Yield up to 20% enhancement of the fluorescence signal and increase the particle detection sensitivity; used in biological applications such as imaging and sensing               | NCs are not in spherical shape                                                                                                                            | (131) |
| Au@Ag NCs                | Photochemical reduction | Sodium alginate | Sodium alginate and ammonium hydroxide         | Colloids                                                                                          | Exact structures of the NPs are not specified while used photon for reduction                                                                                                     | Low yield of gold and silver NPs                                                                                                                          | (132) |
| Au@Ag NCs                | Radiolysis              | NaCN            | K[Au(CN) <sub>2</sub> ] and NaCN               | Spherical                                                                                         | In the nanosecond, the duration of excitation pulse is much longer than the heat dissipation time whereas in the picosecond, pulses are much shorter than this time scale         | High yield but not uniform; the laser powers are reported to only absorb rather than absolute energies per pulse                                          | (133) |
| Ag@SiO <sub>2</sub> NCs  | Chemical reduction      | APTES           | Sodium silicate and APTES                      | Concentric spherical                                                                              | Core shell NPs with 15 nm gold core and 6 nm silica shell are obtained                                                                                                            | Bulk data are not reliable; need mathematical method taking into account different attenuation through the core and shell; 10% polydispersity also occurs | (134) |
| Au@Pd                    | Sonochemical reduction  | SDS             | SDS, NaBr and palladium black                  | Spherical NPs                                                                                     | Particles are individual monometallic but not bimetallic                                                                                                                          | EDX data showed NPs are individually monometallic and not bimetallic                                                                                      | (135) |
| Ag@Au NCs                | Reduction               | Tyrosine        | Tyrosine, octadecylamine and NaBH <sub>4</sub> | Anisotropic Ag nanostructures originating from spherical Au NPs capped by multilayers of tyrosine | Reduction occurs at high pH (pH 10); particles are stable for a long time                                                                                                         | Particles are not uniform                                                                                                                                 | (136) |
| Ag@SiO <sub>2</sub> NCs  | Sol-gel method          | TEOS            | TEOS and ammonia                               | Spherical NCs and plasmonics waveguide structures                                                 | Uniform shapes, well-controlled dimensions, multiple wave guiding structures with various geometries can be fabricated in a single step by designing templates at low temperature | The reaction required nearly one hour at room temperature for synthesis                                                                                   | (137) |
| Au NRs                   | Seed-mediated growth    | CTAB            | CTAB and AA                                    | Nanorods                                                                                          | 90% yield with minimal purification                                                                                                                                               | Further increase in pH not only leads to a large proportion of rods but high polydispersity occurs                                                        | (138) |

(Continued on next page)

Table 1. (Continued).

| Plasmonics nanomaterials | Fabrication method                                     | Capping agent   | Reagents/stabilizer                                | Shapes of particles                              | Advantages                                                                                                                                                                      | Limitations                                                                                                                       | Ref.       |
|--------------------------|--------------------------------------------------------|-----------------|----------------------------------------------------|--------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|------------|
| Au NRs                   | Combination of chemical reduction and photoirradiation | CTAB            | CTAB, AA and TDAB                                  | Nanorods                                         | Using the combination of these two methods, obtained drastic acceleration of the photoreaction and simplification of reaction condition to form the NRs                         | The shape can be varied depending on the irradiation time                                                                         | (139)      |
| Au NPs                   | Photoirradiation                                       | Extracts itself | Mushroom extract                                   | Less spherical Au NPs                            | It is effective for anticancer property and no lethal effect is observed in <i>verocell</i> lines                                                                               | Polydispersity occurs                                                                                                             | (140)      |
| Au NPs                   | Biosynthesis                                           | Extracts itself | <i>Terminalia arjuna</i> extract                   | Spherical Au NPs                                 | No cytotoxic effect of allium cepa root tip cells and gloriosa superb pollen grains                                                                                             | None                                                                                                                              | (141)      |
| Au NPs                   | Biosynthesis                                           | Extracts itself | <i>Abelmoschus esculentus</i> extract              | Spherical NPs with narrow size range of 45–75 nm | Effective antifungal agent; gold NPs are capable of rendering high antifungal efficacy and hence has a great potential in the preparation of drugs used against fungal diseases | None                                                                                                                              | (142)      |
| Au NRs                   | Seed mediated                                          | CTAB            | NaBH <sub>4</sub> , sodium citrate, AA, and CTAB   | Spherical NPs                                    | Particle size can be controlled by varying the seed to metal salt                                                                                                               | Yields are very low; addition of small amount of reducing agent inhibits additional nucleation but promotes nonspherical products | (143, 144) |
| Au NPs                   | Chemical reduction                                     | SDS             | SDS, hydrazine dihydrochloride and AA              | Spherical NPs and NRs                            | Nucleation enhancement 99% as compared to the particle growth                                                                                                                   | Separation of rods and spherical NPs is very difficult                                                                            | (145)      |
| Au-Ag NPs                | Chemical reduction                                     | Oleyamine       | Oleyamine, hexane, toluene and 1,2-dichlorobenzene | Spherical NPs                                    | Nearly monodisperse Au and Ag NPs with adjustable sizes and with exchangeable surfactants                                                                                       | Polydispersity occur                                                                                                              | (146)      |
| Au NRs                   | Seed mediated                                          | CTAB            | CTAB and AA                                        | Rectangle, hexagon, cube, triangle and starlike  | High yield                                                                                                                                                                      | On increasing the concentration of AA, rod length and yield decreases                                                             | (147)      |

|               |                    |                                          |                                                                                                   |                                                           |                                                                                                                                                       |                                                                                                                                                  |       |
|---------------|--------------------|------------------------------------------|---------------------------------------------------------------------------------------------------|-----------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| Ag NPs        | Chemical reduction | CTAB                                     | CTAB and AA                                                                                       | Au hexagonal bipyramids; twinned Ag triangular nanoprisms | High yield and it is more useful than other planar twinned nanoparticles                                                                              | Single-crystalline and twinned product have similar sizes therefore the separation is not possible                                               | (148) |
| Au NPs        | Seed mediated      | CTAB                                     | NaBH <sub>4</sub> , AA and CTAB                                                                   | Seedless nanorods and nanoprisms                          | Seedless approach is used to eliminate chemical reagents; almost identical optical and crystallographic properties up to 90 wt% less reagent material | Seeds exhibit limited active lifetimes after which they may introduce time-dependent heterogeneities in resulting size and shape of nanoparticle | (149) |
| Ag NPs        | Vapor deposition   | PTFE                                     | Ag–Au/polytetrafluoroethylene NCs and hexamethyldisiloxane                                        | Plasma polymerized film                                   | Homogenous NPs                                                                                                                                        | Depend on the coating properties and their water uptake on the oxygen content in the coating films and their thickness                           | (150) |
| Ag NPs        | Electrochemical    | PVP                                      | Two polished Ag plates as the anode and cathode and PVP                                           | Spherical NPs, polyhedron and plate shape                 | Nearly spherical and particles are stable for more than 7 years even under ambient conditions                                                         | Low yield                                                                                                                                        | (151) |
| Ag NPs        | Photochemical      | Cyclohexyl-amine                         | Irgacure 2959, toluene, hexadecylamine, and cyclohexylamine                                       | Polycrystalline                                           | Cluster formation but highly fluorescent Ag NPs are obtained                                                                                          | Majority of polycrystalline nature of particles                                                                                                  | (152) |
| Ag and Au NPs | Photochemical      | Hydroxyl-amine, tetrahydrofuran          | Benzoins as ketyl precursors, benzophenone, hydroxylamine, tetrahydrofuran, and NaBH <sub>4</sub> | Spherical NPs                                             | Unprotected Au NPs are much better catalyst for reduction of HAuCl <sub>4</sub> using hydroxylamine than the surface-protected nanomaterials          | Not stable                                                                                                                                       | (153) |
| Au NPs        | Electrochemical    | Open-end MWCNTs with hydrophilic surface | MWCNT, nitric acid and phosphate buffer                                                           | Thin film of Au NPs on the surface of MWCNTs              | Excellent long-term stability and reproducible uniform modifier films leading to increased reproducible voltametric measurements                      | Polydispersity also occurs                                                                                                                       | (154) |
| Au @Ag NCs    | Biosynthesis       | Neem leaf extract                        | Neem leaf broth ( <i>Azadirachta indica</i> )                                                     | Flat and plate nanoparticles                              | Stable Au and Ag NPs are obtained using neem leaf extract                                                                                             | Flat and plate like morphology with polydispersity occurring                                                                                     | (155) |
| Ag NPs        | Chemical reduction | PVP                                      | PVP, NaOH, and glucose                                                                            | Colloidal nanoparticles                                   | Stable NPs can be obtained by varying the molar ratio of NaOH and silver nitrate                                                                      | At 60 °C, the agglomeration of particles is also influenced by the mixing speed of the reactants, and the speed was slow enough for mixing       | (156) |



**Figure 4.** A schematic illustrating the reaction pathways that lead to metal nanoparticles having different shapes. Green, orange, and purple colors represent the {100}, {111}, and {110} facets, respectively. The parameter  $R$  is defined as the ratio of the growth rates along the {100} and {111} directions, respectively. Reprinted with permission from Ref. (173).

Additionally, the single crystal cuboctahedron and cubic seeds can be subjected to anisotropic growth of 1D nanorods into octagonal cross sections and nanobars with rectangular cross sections (165). A single twinned seed can grow into right bipyramids. When the seeds are multiple twinned, they will evolve into decahedrals, icosahedrons, or five-fold twinned rods. Multiple twinned seeds depend the stability of side {100} surface (166–168). Finally, platelike seed can grow into a hexagonal or triangular plate whose top and bottom faces are {111} facets and side surface is enclosed by mix {100} and {111} facets (Figure 4) (169, 170). Figure 4 clearly shows that first a precursor is reduced to form a nuclei. Once the nuclei have grown past a certain size, they become seeds with a single crystal, single twinned, or multiple twinned structure. If stacking faults are introduced, the seeds will grow into plate-like nanostructures.

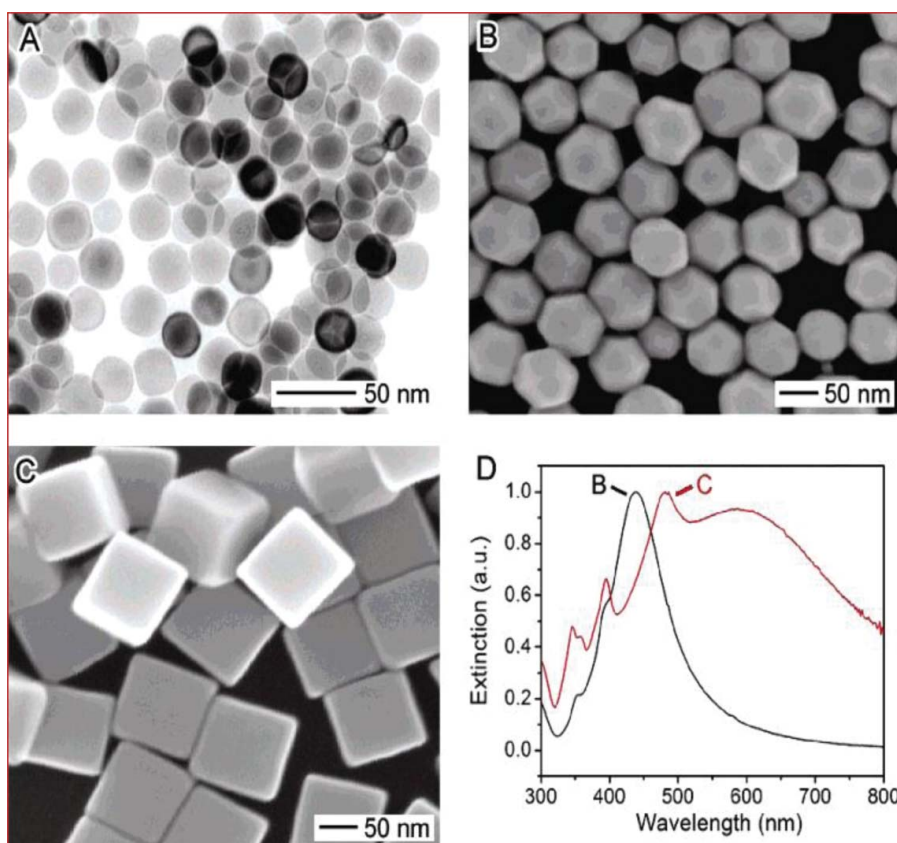
In summary, in order to prepare plasmonic NPs of the desired shape, it is very difficult to control the internal structures of the seeds. In solution-phase synthesis, small clusters of metal atom can be unstable between single crystal and twinned morphologies under an elevated temperature condition (171). Due to this instability, the synthesis usually generates a mixture of single crystal and twinned noble metal nanostructures. Thus, in order to form an entirely single crystal structure, twinned seeds must be removed. Seed structures can be controlled in a number of ways such as oxidative etching and kinetic control (172, 173), and thus the effect of oxidative etching on shape-controlled synthesis is discussed in the next section.

### ***Effect of oxidative etching on shape-controlled synthesis***

Oxidative etching can be utilized to manipulate the shape and optical properties of NPs. At nanoscale levels, metals tend to nucleate and grow into twinned and multiple twinned particles with their surfaces bounded by the lowest energy {111} facets (174). Using oxidative etching technique, multiple twinned seeds can be removed from the solution, promoting the formation of single crystal NPs. In this approach, the selective etching of twin defects is enabled as its defect sites are more reactive than single crystalline regions. This method has been applied for the preparation of silver nanocubes involving the reduction of  $\text{AgNO}_3$  with ethylene glycol in the presence of a capping agent like PVP. Although the shape selectivity mechanism for this process is yet to be fully understood, it is believed that the selective absorption of PVP on various crystallographic planes of silver plays a major role in determining the product morphology. The addition of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{Fe}^{3+}$  to the PVP solution helps toward the generation of nanocubes, bipyramids, and nanowires of silver, respectively. As per a recent study, this oxidative etching mechanism can also be applied to other noble metals like Pt, Pd, Rh, and Ag (164, 175–179).

Figure 5A provides an illustrative summary of single crystal seeds and nanocubes. In the polyol synthesis, after a certain reaction time,  $\sim 20$  nm spherical single crystal seeds were produced as shown in Figure 5A. Figure 5B and C shows single crystal seeds that were grown into truncated or sharp cubes depending on the kinetics of the reaction. The truncated cubes take more time for surface reconstruction to reduce the surface area and increase the surface of the lowest energy {111} facets at the corners. The normalized extinction spectra of truncated and sharp nanocubes suspended in water are shown in Figure 5D. The main resonance dipole peak for the truncated cubes is located at 440 nm, which is similar to that of a sphere of similar size. The dipole resonance is more pronounced for 90 nm cubes with sharp corners and most intense peaks are red-shifted to 600 nm. This confirms the general trend predicted by DDA calculations that nanostructures with sharp corners display red-shifted extinction peaks and that the number of peaks exhibited by a nanostructures increases with the number of ways in which the electron density can be polarized (179). High yields of the single twinned seeds necessary for the growth of right bipyramids have only been produced in the presence of  $\text{Br}^-$ , which may be due to the fact that  $\text{Br}^-$  is less corrosive than  $\text{Cl}^-$ . If NaBr is added to the reaction mixture in place of NaCl, then it leads to high yields of single crystal seed. Without the addition of  $\text{Br}^-$  or  $\text{Cl}^-$ , Ag precursor is reduced quickly to form multiple twinned particles. Thus,  $\text{Br}^-$  enables sufficient etching to eliminate the seeds with multiple twin defects but not so much as to eliminate those seeds with only single twin defect (180). Thus, the concentrations of corrosive anions also play a critical role in controlling the shape of silver NPs during the polyol process (172).

A high-resolution transmission micrograph of single twinned seed in which the {111} facets are obtained from a 15 h reaction sample is shown in Figure 6A. These single twinned seeds grow to form right bipyramids as shown in Figure 6B (75 nm) and in C (150 nm) with their edge lengths increasing with the reaction time. Figure 6D shows normalized extinction spectra for right bipyramids size with edge lengths of 75 nm and 150 nm. The most intense peak shifted from 530 nm to 742 nm with an increase in edge length because of increased charge separation and energy loss related to the large particle. Additionally, bipyramids are significantly sharp where the two halves of the bipyramids meet, leading to a red-shift of the main resonance peak. Such sharp corners improve localized field enhancement for Raman scattering.

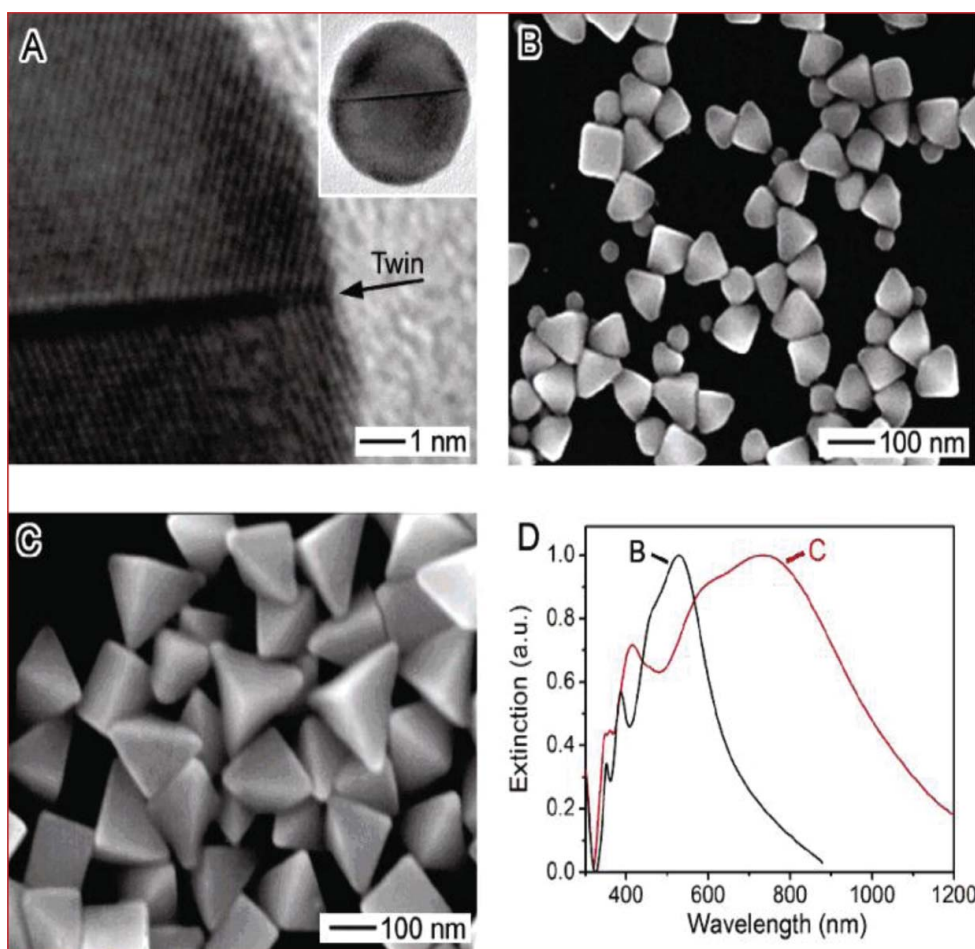


**Figure 5.** (A) Transmission electron micrograph of single crystal seeds. (B) Scanning electron micrograph of truncated nanocubes. (C) Sharp nanocubes. (D) Localized surface plasmon resonance spectra of aqueous suspensions of silver nanocubes (C) (red-shifted) showing several peaks compared to the spectrum of the truncated cubes (B) resembling more to the LSPR spectrum of nanospheres. Reprinted with permission from Ref. (94).

Triangular plates are also an important class of silver NPs. The sharp corners and edges of triangular plates generate a large electromagnetic field that makes these NPs an interesting candidate for various spectroscopic techniques (181, 182). The growth of triangular plates with controllable sizes and high yields remains a challenge in the synthesis of NPs different shapes and sizes (183–192). This is because the formation of plate-shaped seeds in the solution is not thermodynamically favored. For plate-shaped seeds or other nanostructures, one must achieve kinetic control to slow the reduction in the synthesis of metals or clusters (169, 177, 193, 194). In the case of Au and Ag, it has been suggested that the desired shape can be achieved during the growth of NPs. As crystal growth proceeds, initially these nanoplates achieve a circular cross section, which then evolves into hexagonal and then triangular shapes with an increase in their lateral dimensions (194–197).

### Localized surface plasmon resonance (LSPR) sensing

The previous section described the shape-controlled synthesis of metal NPs having different shapes and their impact on LSPR. The development of plasmonic NPs possessing distinct



**Figure 6.** (A) High-resolution transmission micrograph of single twinned seed, which grows to form right bipyramids (B) at 75 nm (C) at 150 nm (D). The localized surface plasmon resonance spectra taken of aqueous suspension of (B) silver nanocubes and (C) silver bipyramids. Reprinted with permission from Ref. (94).

shapes (and hence distinct LSPR spectra) have wide applications such as biological labeling and biomedical applications (198, 199), photothermal therapy (200), LSPR and SERS sensing (201, 202). This section focuses on two different sensing modes like SERS and wavelength shift involving LSPR and their applications to several systems involving the sensing of molecules of biological and chemical interest.

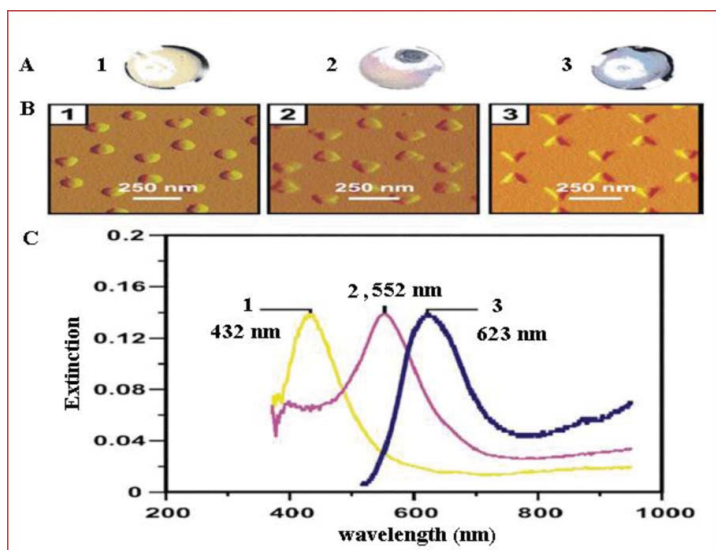
### Wavelength shift

The most common method of the LSPR sensing is the wavelength shift measurement wherein the change in the maximum or minimum of the LSPR extinction curve is a function of change in the local dielectric environment caused by the analyte absorption. The sensitivity of the local dielectric environment is correlated to the sensing of biological molecules like proteins and antibodies. Research has been performed for a number of systems in which either the bulk solvent refractive index or the wavelength of a molecular adsorbate is changed, leading to

the detection of biological toxins (203, 204). This principle of local environment has been used to measure the shift in wavelength maxima on binding of either streptavidin or antibiotin to biotin functionalized NPs arrays, i.e., for multiplexed biosensing (205, 206).

In order to systematically study the LSPR response of noble metal NPs to changes in their dielectric environment, a technique is required to produce NPs with desired shape, size, and monodispersity. The chemical synthesis method has been used for this purpose for noble metal nanostructures. These approaches are utilized to fabricate high concentrations of a wide variety of NPs with varying monodispersity and tunable optical properties. The LSPR nanosensors have been useful in detecting metals, biological molecules (9, 36, 43, 74) as well as antigen–antibody reaction (43, 82, 200–202, 204–206). At the nanoscale, the LSPR nanosensor is a refractive index based sensing device that shows the extraordinary optical properties of noble metallic NPs such as Au, Ag, and Cu (36, 74, 82, 205, 207). The LSPR refers to the ability of the conduction electrons in the NPs to oscillate collectively, inducing the electromagnetic field surrounding the NPs, which then determine the sensing volume in which the refractive-based sensing can occur (74, 208). Since the conduction electrons oscillate collectively to only a certain specific wavelength of light, NPs show selective photon absorption, which is easily monitored using ultraviolet–visible spectroscopy (3, 209). Presently, the limit of detection for the LSPR nanosensors has been found to be in the low-picomolar to high-femtomolar region (205).

Silver NPs fabricated from nanosphere lithography technique (NSL), produced consistent red-shift with increase in density and thickness of adsorbate layers (82, 203). NSL is a powerful fabrication technique used to produce arrays of NPs having controlled shape, size, and inter-particle spacing (203, 210). By using NSL, researchers have demonstrated that nano-scale chemosensing and biosensing can be realized through shifts in the LSPR extinction maximum of the tunable silver NPs as shown in Figure 7. This is due to the electromagnetic coupling between NPs. The wavelength shifts are caused by adsorbate induced local



**Figure 7.** Ag nanoparticle substrate fabricated by NSL. Top row: photographs of nanoparticle substrate. Middle row: AFM images of Ag nanoparticle substrate. Bottom row: normalized UV–vis spectra of nanoparticle substrate. Reprinted with permission from Ref. (212).

refractive index changes in comparison with charge transfer interactions at the surfaces of NPs (211, 212).

Biological sensing has been demonstrated for large proteins and antibodies (43, 213). LSPR has been widely used to monitor a broad range of analyte surface binding interactions including adsorption of small molecules (9, 35, 36, 43, 74, 200–202, 204, 205, 209, 214–216), protein adsorption on self-assembled monolayer (217–219), ligand receptor binding (220–223), antibody–antigen binding (43, 224), protein–DNA interaction (225), and DNA and RNA hybridization (226–229). LSPR sensing has also been demonstrated for sensing of biomarker for Alzheimer's disease in clinical sensing (213, 230) and amyloid-beta derived diffusible ligand (29, 231–233).

Moreover, the LSPR sensing approach can be broadly generalized to allow the diagnosis of any disease with an associated biomarker and antibody pair such as ovarian cancer (234). An alternative approach of LSPR sensing is by attaching chemically synthesized NPs to a substrate using a solid-phase technique. Using this method, chemically synthesized gold and silver NPs are covalently or electrochemically attached randomly to a transparent substrate and could be used for the detection of proteins (234). In this approach, signal transduction depends on changes in the NPs' dielectric environment induced by the solvent or target molecules and not by NPs coupling. Another approach is chip based, and using this method a solvent refractive index sensitivity of  $76.4 \text{ nm RIU}^{-1}$  has been found and a detection of 16-nM streptavidin has been achieved (235, 236). This chip-based approach has several merits, including a simple fabrication technique that can be demonstrated in most laboratories as real-time bio-molecules detection using UV–vis spectroscopy and a chip-based design allowing multiplexed analysis. However, the sensitivity of the sensor has been very limited by NPs coupling (235, 236).

Haynes and Van Duyne have investigated the effect of dielectric substrates on the LSPR extinction of metallic arrays (237), while Pinchuk et al. have compared the effects of dielectric, semiconductor, and metallic substrates on NPs (238). It can be concluded from both these investigations that plasmon resonances are red-shifted, which is related to the particles in a vacuum because of interactions as determined by the dielectric constant of the substrate and the distance between the particle and substrate (237, 238). If the particles are in contact with the substrate, then the size of red-shift depends on the particle that is in contact with the substrate (238). Thus, it is important that the enhancement of the substrate's LSPR be properly matched with Raman scattering and excitation wavelength (237–239).

### ***Surface-enhanced Raman scattering (SERS)***

Another application for LSPR sensing in which it plays an important role is SERS sensing. Here, we describe the various examples in which SERS is used for applied biological sensing experiments. Raman scattering is a fingerprinting technique for the chemical identification of molecules. Hence, it is used for molecular detection in various fields such as molecular electronics, plasmonic photothermal therapy, single molecule detection, pollutant identification, food minerals, molecular imaging, biomolecules, biowarfare agents, and explosives (16, 25, 26, 35, 40, 50–52, 54, 55, 59, 61, 62, 66–69, 178). As SERS is inherently a weak scattering process, it is necessary to deliberately enhance the scattering signal. To enhance the Raman signal, various improvement methods have been used (15, 16, 40, 53, 56, 66–68). These also include the introduction of intense lasers as photon sources to increase the number of photons for interaction with matter, enhancement of the electric field, and the substrate

modification for the reaction to take place. One of the most important applications of nanostructures is SERS. It is based on the enhancement of Raman scattering of an analyte molecule on a roughened metal substrate surface (53, 56, 240–244). However, due to the dependence of the SERS activity on the parameters of the metal substrate structure such as distance from the substrate, orientation, conformation of the molecules, strength of interaction between the molecule and substrate, SERS spectrum differs substantially from normal Raman spectrum for the same molecule in terms of peak intensity distribution and vibrational modes detection (245, 246).

Over the past 15 years, SERS has emerged as a very powerful technique for the detection of ultra-low concentrations of various analytes and single-molecule detection (16, 25, 26, 35, 40, 50–52, 54, 55, 59, 61, 62, 66–69, 178, 247–250). Using SERS technique, one can amplify Raman signals by several orders of magnitude (53, 56). The amplification of signals in SERS is due to the interaction of photons with metals producing large amplifications of the laser field through excitations generally known as plasmon resonance (251). SERS mainly takes place due to chemical and electromagnetic interactions with the analyte molecule/metal surface (252–255). Hence, it is an extremely useful analytical tool for chemical, biochemical, and biomedical sensing. Signal enhancement due to chemical component is because of the interaction between electronic states of molecules and those of the metallic substrate through charge transfer, leading to surface plasmon resonance enhancement with Raman excitation lasers (256). On the other hand, electromagnetic enhancement is a result of the increase in the electric field at sharp points on rough surfaces or regions in the small gaps between NPs or nanostructures (53, 56). SPR of metallic substrates also helps in the process of signal enhancement. The enhancement of signals depends on selective vibrations as well as overall proximity of the laser excitation wavelength to the SPR wavelength of the substrate. Ag and Au NPs, due to their strong LSPR in the visible range, are good candidates for SERS (15, 16, 40, 53, 56, 66–68). For a given NP, the tunability of SPR to match with the selected laser wavelength leads to the increase in Raman signal.

Raman signal enhancement is also related to other surface enhancement phenomenon such as SPR and surface-enhanced fluorescence (257–266). SERS and surface-enhanced fluorescence have regularly been used for quantitative analysis, detection of various analytes and label-free protein detection. Therefore, several research groups have published a lot of progress in this area (16, 25, 26, 35, 50–52, 54, 55, 59, 61, 62, 66–69, 178, 217, 247–250, 261, 264, 265). Further research has to be performed to improve the efficiency of the Raman signal using a variety of new substrates (15, 16, 53, 56) or techniques such as tip enhanced Raman spectroscopy (TERS) (267, 268). However, TERS instrumentation is relatively expensive. This technique is also used for protein detection and structure study (269). The advantage of TERS application is the sensitivity enhancement of U-shape probe (270). A fiber optics U-shape probe-based biosensor of different bending radii has been fabricated by Satija et al., and it was reported that the probe with bending radius around 0.982 mm possesses the maximum sensitivity and used as a point sensor (270). This type of sensors has been used for the detection of glucose in blood and other samples (271, 272). As a point sensor, they require a very less amount of blood sample ( $\sim 150 \mu\text{L}$ ) for sensing, which makes them more suitable for commercialization and better than commercial sensors that generally require about 1.5 mL of blood for the detection of glucose. For the measurement of analyte, only the tip of U-shape probe has to be in contact with the sample (271, 272). The response time of proposed sensors is very low and response curves were obtained immediately after immersing the sensing probe in the glucose sample (271–273). These kinds of sensor developments are

still in progress and the device can be commercialized, after optimization of various associated parameters with it for the detection of glucose (271–274).

The assembly of the SERS substrate, which provides enhanced electromagnetic fields, is a must for the glucose monitor, whereby glucose has to approach the metal surface. To develop a glucose sensor for sensing application, researchers have prepared a mixed self-assembled monolayer that has both hydrophilic and hydrophobic components and assembles alumina-modified silver film over nanosphere (FON) substrate. With this functionalized SERS substrate, detection of glucose concentration has been demonstrated using SERS both *in vitro* and *in vivo* (275, 276). The sensor developed by Lyandres et al. provides real-time information on potentially harmful fluctuations in glucose levels (276). SERS also has great potential in high-throughput protein detection (277–289). Several studies have been carried out in recent past to establish SERS active probes applications (277–288). Raman dyes labeled Au NPs have been used to detect proteins and antibodies for immunoassay (277–280). Some SERS probe studies have used fluorescein-labeled antibodies to recognize antigens on metal substrates (290) and also for label-free protein detection (277, 281, 288).

Recently, metal colloids such as Au and Ag NPs and metal NCs have commonly been used as SERS active substrates for biomolecules detection as well as immunoassay (291, 292). A comparative study of SERS emanating from silver–gold core–shell bimetallic NPs and Ag as well as Au NPs for immunoassay concluded that Ag NPs can produce a large SERS effect than Au NPs (293). Other studies have shown that the SERS spectra of proteins on silver films are difficult to reproduce because of protein multi-absorption and aggregation of Ag NPs (294, 295).

Based on strong SERS signal/activity it was concluded that the silica–silver core–shell (SSCS) substrates have a great potential for the investigation of protein–protein, DNA–protein, and DNA–RNA interactions (224–229, 277, 282). The SERS has also been applied in the field of cellular sensing and analysis (296). Generally, NPs are small enough to fit into cells without hindering their normal function. However, there is size limit beyond which they will not be stable inside the cell. If NPs' size is below 20 nm, then the particles might escape out of the cell. If NPs are greater than 80 nm, then they can damage or impede the function of the cell (296). Hence, size factor of the NPs plays a critical role in the SERS study of living cells. The studies by Chithrani and Chan on intercellular SERS research involved imaging at various positions within the cell with resolution greater than 1- $\mu$ m (297) where different types of Raman signals were observed, indicating a very complex chemical environment within the cell. It has also been observed by Kneipp et al. that Au NPs tend to aggregate within the cell and become immobile (298). Their study concluded that strong signals from SERS activity were obtained only when cell functioned normally (298).

Recently, in order to improve intercellular sensing and to minimize negative interaction, a small SERS probe using silica-encapsulated hollow Au NPs for immunoassay has been developed by Ko et al. and is proved to perform better than the Au NPs probe (299). The unique structural and optical properties of hollow Au nanospheres provide various benefits like small size, spherical shape, and tunable and smaller absorption from visible to near IR region (291–301). When the size of a material is reduced to the nanoscale, at or below the characteristic length scale that determines their properties, the material acquires completely new properties (302). Recently, Mahmoud et al. have reported the application of hollow and solid metallic NPs in sensing as well as in nanocatalysis and presented a summary of the difference between the solid and hollow NPs in nanocatalysis (302). These authors have also

shown that the observed superior catalytic properties of hollow NPs are due to the catalysis occurring within the cavity of the hollow NPs. The SERS also meets the requirements for a rapid, sensitive, and specific detection technique in the area of food safety (303). The SERS-based approach has been reported for the detection of water-insoluble molecules by applying a hydrophobic surface modification onto the surface of enzymatically generated Ag NPs. Most recently, Jahn et al. have presented a novel SERS-based approach for the detection of illegal water-insoluble molecules, i.e., food dyes, such as Sudan III in presence of riboflavin, as a water-soluble competitor. They have also demonstrated its applicability for the determination of Sudan III in spiked paprika extracts (303).

Surface plasmons exhibit an electromagnetic field that is strongly confined within a metallic interface, which is extremely sensitive to smaller changes in the refractive index associated with the binding of target biomolecules to ligands tethered at the sensor surface (304). Biosensor research has been devoted to various signal transduction methods including optical (304–307), radioactive (308), electrochemical (309–311), bimetallic Au–Ag nanoplate array as a highly active SERS substrate (312), piezoelectric (313, 314), magnetic (315), and mass spectroscopy (316, 317). Signal transduction depends on changes in the NPs' dielectric environment induced by solvent or target molecules. In case of LSPR based sensing, signal transduction also depends on the sensitivity of surface plasmon to inter-particle coupling where the presence of multiple particles in a solution supports localized surface plasmons that are able to interact electrochemically through a dipole coupling mechanism. The broadening and red-shifts of the particles in LSPR can be easily monitored by using UV–vis spectroscopy. Heas and Van Duyne have developed noble metal NPs based LSPR sensors that retain the optical properties of SPR sensors (205).

### ***Tip-enhanced Raman scattering***

The TERS is an emerging branch of SERS in which a sharp metallic tip is used (318) where the probe of a scanning tunneling microscope or atomic force microscope is brought in proximity of the analyte to increase their TERS, i.e., Raman signals (318–321). In this technique, the shape of laser-irradiated metallic tip confines optical energy well below the conventional diffraction limit. All nanoscale metallic tips exhibit local field enhancements because of an electrostatic optical lighting rod effect. TERS is useful because of the fact that the detection techniques using far field spectroscopy tool with the sub-wavelength imaging resolution are enabled by plasmonics. Therefore, the combination of Raman chemical fingerprinting and near-field optical imaging has numerous applications in physics, chemistry, biology, and medical sciences (318–327). In addition to its nanoscale resolution, it can extend the capability of SERS in many fields as microdevices in medicine (319). SERS substrate is prepared on to the probe of a scanning probe microscope. The TERS signals can be achieved for analytes that cannot be brought into contact with a metallic substrate. In the TERS, both the sharpness of the tip and smoothness of the surrounding surface are important, leading to a precise control over the intensity and location of the hot spot. However, reproducible and reliable synthesis methods remain a very challenging task. The Raman signal can be monitored as a function of tip-sample distance, which can provide valuable information on the near-field response of the tip (327). Single molecule sensitivity has been developed for TERS (328–333). Using this technique, Zhang et al. have demonstrated improved anthrax biomarker detection (332, 334). The Raman signals of molecules directly below the tip are dramatically enhanced in this technique.

Since the tip radius is only a few tens of nanometers, the lateral resolution reported for TERS is approximately 10–50 nm (318, 319).

## Miscellaneous applications of plasmonics

### *Application of plasmonics in biological field*

The SPR has widely been used to measure binding interactions between biomolecules (197, 198, 204–207, 211, 212, 219, 223, 225, 228, 229, 243, 246, 264, 271, 332, 334–336). The SPR absorption is not due to chromophores but due to resonant electron oscillations induced absorption at the metal sample interface when an in-plane wave vector of the incident light matches the wave vector of the surface plasmon. Therefore, the surface plasmon wave vector is observed by the incident free space wave vector and dielectric constant of the metal film (337–340).

It is interesting to note that the SPR angle is very sensitive to the dielectric constant of the metal because the resonance occurs on the metal interface. Therefore, the sensitivity of SPR to biomolecules binding at the surface is due to interactions of evanescent field with the sample (336). Another application of plasmonics in biology is the use of metallic colloids as probes (336). The suspension of metallic colloids shows brilliant colors due to absorption and scattering of light. While the color of particles and surface plasmon absorption band somewhat depend on the size of spherical NPs, they strongly depend on the shape of the NPs (341). For metals such as silver and gold, almost any color or absorption in any part of UV–vis spectrum can be produced by controlling the structures or shape of the NPs. Therefore, various examples on the synthesis of non-spherical nanostructure have been reported in the literature including aggregates, nanorods, nanocages, nanowires, nanospheres, nanoprisms, and nanoplates, and their different plasmon sensing behaviors have been well demonstrated (342–351).

### *Application of plasmonics in photothermal imaging and therapy*

Plasmonic NPs play an important role in various biomedical applications such as imaging and therapy. This technique depends on processes such as antibody–antigen interaction, while the metal nanostructures serve as the light absorber and thermal energy converter. The conjugation of NPs with antibodies complements the properties of the NPs with the selective and specific recognition capability of the antibodies to antigens (352–355). Herein, a few examples of the application of plasmonics in photothermal imaging and therapy are described (352–358) where nanostructures have been conjugated to biological targets such as tissues or cancer cells (355). The metal nanostructures absorb light and convert it into thermal energy and have been used for imaging *in vitro* and *in vivo* sample target or for therapeutic treatment like cancer cell destruction or ablation of the sample (357). Jain et al. have reviewed some interesting SPR-enhanced properties of noble metal NPs and their applications to biosystems (353), while Huang et al. have presented a review with special focus on the involvement of NPs for cancer diagnosis and therapeutics (354).

For the photothermal imaging and therapeutic application, it is desired to match the absorption of the nanostructures with the wavelength of the laser applied. However, as NPs shapes are complex and its size is large for biomedical applications, smaller shape and sized NPs are desired for effective delivery to the locations of interest for the purpose of detection, imaging, etc. In addition, the NPs also can be tuned in the desired manner for photonics-based imaging and therapy of cancer using SPR (358).

### ***Application of plasmonics in solar cells***

Photovoltaics are considered to have the potential to contribute immensely in solving the problem of climate change. In the last few decades, several research groups have studied the application of plasmonics nanostructures towards the reduction of conventional material usage and improvement of the efficiency of photovoltaics (359, 360). The plasmonics devices have been utilized to enhance the performance of solar cells through the enhancements of electric field in the absorber and by enhancing the path length of light through the absorber. There has been a great deal of research on thin-film solar cells over the past decades (360, 361). To date, various options of photovoltaics have been reported where surface plasmon polaritons (SPPs) are propagation excitations that arise from the coupling of the light with collective oscillations of the conduction band electrons propagating at the metal–dielectric interface (362, 263). Stuart and Hall pioneered the scattering from NPs, leading to enhanced absorption (364). Several research groups have reported the enhancement of absorption and photocurrent in a variety of solar cell designs involving metal NPs (365–371). The metal NPs act as dipoles and have the advantage that the light striking the metal NPs is scattered into the material with higher permittivity (372, 373). The scattering allows the NPs to act as an anti-reflective coating (374). In an study, Spinelli et al. have confirmed that the NPs arrays of silver placed on top of high refractive index substrates exhibited high transmittance than standard reflection coatings (375). Back et al. and other researchers have confirmed that localized surface plasmons due to metal NPs has been successful in tunable light for solar cells due to which reflection is enhanced (376–378). However, another route to enhance the absorption path length is to couple incident photons to SPPs by nanostructuring the back contact, i.e., reflectors of thin-film solar cells (379–382). Therefore, the localized surface plasmon interaction by imbedded Ag NPs provided substantial and efficient enhancement in solar cells and have been true in the case of other reports (379–382).

### ***Applications of plasmonics in the field of biosensors***

Development of sensors is critical to the detection and analysis of various chemicals, toxicants, and biologically important compounds in the areas of clinical, environmental monitoring, security and food safety, etc. Lately, SPR has been applied to the development of biosensors (383–387). The SPR biosensors can detect the interaction of biomolecules without labeling, i.e., they can be used for label-free biomolecules detection. Therefore, SPR biosensors have been used in interaction studies and screening of varieties of moieties like carbohydrates, receptors, proteins, cells, different types of bacteria, clinical diagnostics, military defense, etc. (306, 307, 310, 311, 313, 314, 380–382). Due to their salient features like good detection sensitivity, label-free and real-time detection capabilities, SPR-based biosensors have been used in many applications such as detection of bacteria, allergens, pesticides, viruses, etc. For SPR-based biosensors, depending on the size of the target sample, four different types of assay formats such as direct assay, competitive assay, sandwich assay, and inhibition assay have been developed (383).

In the direct assay format, the recognition molecules are immobilized on the surface of the SPR chip. The sample then binds to immobilized recognition element. The direct assay is used for medium and large molecular weight analytes (384). In the competitive assay format, two samples are used: one is free and other is conjugated to larger protein such as

bovine serum albumin competing for the same recognition molecules immobilized on the surface of the SPR sensor. The signal is proportional to the amount of the target sample (385). In the sandwich assay, secondary recognition molecule is captured by an immobilized recognition element by using secondary recognition species to improve the detection range (386). In the inhibition assay format, a conjugate sample is immobilized on a fixed concentration of an antibody and is passed over the SPR surface immobilized sample derivative (387). In the last decade of research, the SPR biosensor technique has received great interest (383–387). Some applications of the SPR biosensors like pesticides, allergens, bacteria, virus, etc. are presented in the following sections.

### Plasmonic detection of pesticides

The pesticides analysis is extremely important due to their adverse effect on human health and also due to the fact that large amounts of pesticides are commonly used. The United States Environmental Protection Agency (USEPA) has recommended the maximum allowable concentrations for most common pesticides like Atrazine and Simazine as  $3 \text{ ng mL}^{-1}$  and  $4 \text{ ng mL}^{-1}$ , respectively. Therefore, various efforts have been directed to develop sensors for the detection of pesticides at extremely low levels (388–401). A list of pesticides detected using SPR biosensors, showing the sensing materials and techniques used, and the detection limit/range are presented in Table 2.

**Table 2.** Some examples of pesticides detection using SPR biosensors along with materials and techniques used and the detection limit/range.

| Pesticide detected                                    | Sensing materials                                                                    | Detection limit/range                                                     | Instrument/ sensor type              | Ref.  |
|-------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------|--------------------------------------|-------|
| Fenamithion and acetamiprid in water                  | Cd–Te quantum dots with <i>p</i> -sulfonatocalix[4]arene                             | 0.12 nM and 0.34 nM                                                       | Luminescence                         | (388) |
| Parathion                                             | Gold electrode                                                                       | 291.26 Da                                                                 | Quartz crystal microbalance          | (389) |
| Aldrin, dieldrin, chlorpyrifos                        | Tissue fats and rendering oils                                                       | $0.005\text{--}0.1 \mu\text{g g}^{-1}$                                    | Laser induced breakdown spectroscopy | (390) |
| Organophosphorous                                     | O-ethyl O-4-nitrophenyl phenylphosphonothioate                                       | $0.01 \mu\text{g mL}^{-1}$                                                | Immuno-chromatographic based sensor  | (391) |
| Carbaryl                                              | Inhibition immunoassay using BSA-CNH conjugate                                       | $1.3 \mu\text{g mL}^{-1}$                                                 | $\beta$ -SPR                         | (392) |
| Atrazine                                              | Competition immunoassay using atrazine-HRP-conjugate                                 | $5 \text{ ng mL}^{-1}$                                                    | Biacore-2000                         | (393) |
| 2,4,5-Trichlorophenoxy acetic acid                    | Poly-o-toluidine Zr(IV) phosphate nanocomposite                                      | $1 \mu\text{M}$                                                           | Electrochemical                      | (394) |
| Melamine                                              | 18-Crown-6 ether functionalized Au NPs                                               | 6 ppb                                                                     | Optical                              | (395) |
| Pirimicarb                                            | Molecular imprinted nano-polymers (methacrylic acid with carboxyl functional groups) | $8 \times 10^{-6} \text{ M}$                                              | Piezoelectric                        | (396) |
| Methyl parathion                                      | Nano-ZrO <sub>2</sub> /graphite/paraffin                                             | $2 \text{ ng mL}^{-1}$                                                    | Electrochemical                      | (397) |
| Methyl parathion                                      | Fe <sub>3</sub> O <sub>4</sub> @Au nanocomposite                                     | $0.1 \text{ ng mL}^{-1}$                                                  | Inhibition-based enzyme biosensors   | (398) |
| Chlorphrifos and fenthion                             | Tangerine juices                                                                     | $0.20 \pm 0.04 \mu\text{g L}^{-1}$ and $0.50 \pm 0.06 \mu\text{g L}^{-1}$ | Immunoassays-based biosensors        | (399) |
| 16 pesticides from different chemical groups in water | Polydimethylsiloxane and polyacrylate                                                | $0.015\text{--}0.13 \mu\text{g L}^{-1}$                                   | Gas chromatography based sensor      | (400) |
| Paraxon                                               | Indirect immunoassay                                                                 | 1–100 ppb                                                                 | LSPR                                 | (401) |

**Table 3.** Some examples of bacteria detection using SPR biosensors.

| Analyte                                  | Assay format                              | Detection limit/range                                                  | Instrument/ sensor type               | Ref.  |
|------------------------------------------|-------------------------------------------|------------------------------------------------------------------------|---------------------------------------|-------|
| <i>Listeria monocytogenes</i>            | Subtractive inhibition immunoassay        | $10^5$ cfu mL <sup>-1</sup>                                            | Biacore-3000                          | (402) |
| <i>E.coli</i> O157:H7                    | Sandwich assay                            | $10^3$ – $10^7$ cfu mL <sup>-1</sup>                                   | Optical fiber probes                  | (403) |
| <i>E.coli</i> O157:H7                    | Sandwich assay                            | $2$ cfu mL <sup>-1</sup> / $30$ – $3 \times 10^4$ cfu mL <sup>-1</sup> | SPR biosensor                         | (404) |
| <i>E.coli</i> O157:H7                    | Sandwich assay                            | $10^3$ cfu mL <sup>-1</sup>                                            | SPR biosensor                         | (405) |
| <i>E.coli</i> O157:H7                    | Direct immunoassay                        | $10^7$ cfu mL <sup>-1</sup> / $8.7 \times 10^6$ cfu mL <sup>-1</sup>   | Commercially available Spreeta sensor | (406) |
| <i>Yersinia enterocolitica</i>           | Direct immunoassay                        | $10^2$ – $10^7$ cfu mL <sup>-1</sup>                                   | Wavelength division multiplexing      | (407) |
| <i>Legionella pneumophila</i>            | ELISA immunosorbent assay                 | $10^8$ cfu mL <sup>-1</sup>                                            | SPR biosensor                         | (408) |
| <i>Staphylococcus aureus</i>             | Direct immunoassay                        | $10$ cfu mL <sup>-1</sup>                                              | SPR biosensor                         | (409) |
| <i>Campylobacter jejuni</i>              | Indirect immunoassay                      | $10^3$ cfu mL <sup>-1</sup>                                            | SPR biosensor                         | (410) |
| <i>Listeria monocytogenes</i>            | Direct immunoassay                        | $10^7$ cfu mL <sup>-1</sup>                                            | Biacore-3000                          | (411) |
| <i>Vibrio cholerae</i> O1                | Direct immunoassay                        | $3.7 \times 10^5$ cfu mL <sup>-1</sup>                                 | SPR biosensor                         | (412) |
| <i>Acidovorax avenae</i> subsp. citrulli | Direct, subtractive, sandwich immunoassay | $1.6 \times 10^{-6}$ cfu mL <sup>-1</sup>                              | SPR biosensor                         | (413) |

**Plasmonic detection of bacteria**

Generally, the detection of bacteria using SPR biosensors is not an easy task for several reasons. Still, rapid methods for the detection of bacteria are essential, and thus great efforts have been directed to develop methods for their detection in food, industrial, and environmental monitoring, clinical diagnostics and biodefense, food poisoning, water contamination, etc. (402–413). Miyajima et al. have devised a fiber-optic fluoroimmunoassay system with a flow-through cell for rapid on-site determination of *E. coli* O157:H7 by monitoring fluorescence dynamics (403), while highly sensitive detection of pathogen *E. coli* O157:H7 by electrochemical impedance spectroscopy was reported by Santos et al. (404). SPR has not only been used for the development of simple biosensors but researchers from the Laboratory for the Analysis of Surfaces of Materials, École Polytechnique de Montreal, Canada have developed a method for the differential detection of methicillin-resistant, methicillin-susceptible, and borderline oxacillin-resistant *Staphylococcus aureus* by SPR (409). Plasmonic detection has widely been used in environmental pollution remedial management for their unique physicochemical properties, and thus Charlermroj et al. have developed strategies to improve the SPR-based immunodetection of bacterial cells (413). Table 3 provides some examples of bacteria that have been previously detected using SPR biosensors (402–413).

**Table 4.** Some examples of allergens detection using SPR biosensors alongwith assay format and detection limits.

| Analyte detected                                 | Assay format                       | Detection limit                 | Sensor type/instrument | Ref.  |
|--------------------------------------------------|------------------------------------|---------------------------------|------------------------|-------|
| Shrimp allergen Pen a 1 (tropomyosin)            | L-cysteine modified gold electrode | $0.15 \mu\text{g mL}^{-1}$      | Electrochemical        | (414) |
| Cytokine allergen                                | Label-free immunoassay             | $19 \text{ ng mL}^{-1}$         | Label-free biosensor   | (415) |
| $\beta$ -Casein                                  | Sandwich assay                     | $85 \text{ ng mL}^{-1}$         | Biacore-3000           | (416) |
| Peanut protein                                   | Direct immunoassay                 | $0.7 \text{ ng mL}^{-1}$        | SPR biosensor          | (417) |
| Soluble extracts of <i>Lolium perenne</i> pollen | Direct immunoassay                 | $0.1$ – $1 \mu\text{g mL}^{-1}$ | Biacore                | (418) |
| Histamine                                        | Indirect competitive immunoassay   | 3 ppb                           | SPR biosensor          | (419) |

**Table 5.** Some examples of virus detection using SPR biosensors along with assay format, i.e., sensing materials used and detection limits.

| Types of viruses            | Assay format/sensing material                     | Detecting limit/range                    | Sensor type/instrument                        | Ref.  |
|-----------------------------|---------------------------------------------------|------------------------------------------|-----------------------------------------------|-------|
| Epstein-Barr                | Direct immunoassay                                | 0.2 ng mL <sup>-1</sup>                  | Wavelength division multiplexing based sensor | (420) |
| Maize chlorotic mottle      | Enzyme-based immunosorbent assay                  | 1–1000 ppb                               | SPR biosensor                                 | (421) |
| Avian leukosis              | Fe <sub>3</sub> O <sub>4</sub> @gold quantum dots | 115 TCl D <sub>50</sub> mL <sup>-1</sup> | Immuno-based sensor                           | (422) |
| Hepatitis B virus DNA       | Au NPs and fluorescein                            | 15 pmol L <sup>-1</sup>                  | Fluorescence spectrometer                     | (423) |
| Hepatitis B virus DNA       | Sandwich immunoassay                              | 50 aM                                    | SERS-based sensor                             | (424) |
| Herpes simplex virus type 1 | Direct immunosensa                                | 10 <sup>-4</sup> fringes                 | Young interferometer sensor                   | (425) |

### Plasmonic detection of allergens

In the last few years, awareness of allergens has led to a growing demand for rapid, reliable, and sensitive devices for identifying and quantifying allergens. Table 4 provides several types of examples of allergens that have been easily detected using SPR biosensors (414–419). The quantification of the major shrimp allergen Pen a 1 (tropomyosin) has successfully been attempted by Jiang et al. using a mast cell-based electrochemical biosensor (414). Muller-Renaud et al. have been successful in quantification of  $\beta$ -casein in milk and cheese using an optical immunosensor (416), while Kobayashi et al. have developed an SPR immunosensor for the detection of histamine based on an indirect competitive immunoreaction (419).

### Plasmonic detection of viruses

Viruses rapidly spread in the environment and may cause devastating effects on human health and their social as well as economic development. Therefore, several harmful viruses like Hepatitis B, Avian Leukosis, etc. have been detected in recent years using SPR tools. Table 5 provides some examples of viruses that have been previously detected using SPR biosensors (420–425).

### Concluding remarks and future perspectives

Plasmonic NPs play an important role because of their fascinating properties including photothermal imaging, optical, photonics and SERS properties. Both theoretical and experimental calculations have indicated that the plasmonics absorption strongly depends on the structure of the NPs. Any morphological change in plasmonic NPs causes a spectral shift because of the charge separation. The oxidative etching and kinetic control has been utilized to manipulate the shape and optical properties of NPs in the polyol synthesis process that effectively generates NPs of different shapes such as cubes, bars, rods, bipyramids, and triangular and hexagonal plates. In this review, we have emphasized on the shape-controlled synthesis of various NPs and also studied different capping agents and their fascinating analytical applications in different fields.

Finally, the use of LSPR spectroscopy for the biological and chemical synthesis sensing has been discussed using recent reports from the literature. LSPR spectroscopy provides a new direction in analyzing and for further sensing experiments owing to enhanced LSPR shifts. The applications of both wavelength shift and SERS sensing have shown that a variety

of chemically and biologically relevant molecules, like biomarkers of Alzheimer's disease, glucose detection, protein detection, etc., can be easily detected. The plasmonic NPs research continue to grow fast and these LSPR-based sensing experiments will improve as well as lead to high sensitivity, faster and reversible responses, and an ever broadening scope of applicability in different areas of research, especially in analytical and bioanalytical chemistry.

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