Review Article

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Recent progress and challenges in plasmonic nanomaterials

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Abstract: Owing to their optical, mechanical, and catalytic properties, plasmonic nanomaterials (P-NMs) have been widely used in sensing, disease treatment, as well as energy transfer and conversion applications. Therefore, the synthesis, properties, and applications of P-NMs have garnered significant interest in recent decades. This review surveys the various types of P-NMs, their synthesis methods, their properties, and recent applications. In addition, we summarize the current challenges and future developments in P-NMs. We hope this article will help researchers to gain a deeper understanding of P-NM applications in the field of energy, overcome the current problems associated with P-NMs, and develop novel P-NMs with better characteristics.

Keywords: nanomaterial, noble metal, plasmon, plasmonic nanomaterial

1 Introduction

Recent development in advanced processing and characterization approaches have boosted the research on nanomaterials [1–16]. Nanoscale materials have some advantageous acoustic, optical, electrical, magnetic, and thermal characteristics, which make them potentially applicable in many fields (e.g., energy storage and conversion [17–31] and medical treatment and transportation [32–37]). However, owing to their small size, these materials often exhibit defects and some non-desirable features, such as high surface energy and easy agglomeration, making them non-conducive to long-term storage [38–42]. These drawbacks have significantly hindered the adoption of nanomaterials for practical applications. To alleviate these drawbacks, coping strategies have been sought by many researchers. Feichtenschlager et al. used hydrothermal methods for preparing ZrO2 nanocrystals and modified the surfaces of nanocrystals using coating agents [43]. They found that after such surface modification, the molecular structure of the studied ZrO2 nanocrystals changed significantly. At the same time, the agglomeration behavior of these nanocrystals improved, and the overall performance of the coated materials improved as well. In addition to surface modification strategies, two major strategies have been proposed: (1) innovative synthesis methods and (2) doping based on nanomaterials. Pan and coworkers dispersed nanoparticles (NPs) in a volatile solvent and mixed them with an uncured polymer precursor, obtaining a micro-emulsion [44]. Those NPs were then quickly evaporated to prevent NP agglomeration during the polymer curing stage. This method eliminates the need for NP surface functionalization. It is suitable for preparing nanocomposites (NCs) of various polymers and is promising for novel NCs with novel functions.

To further stimulate the performance of nanomaterials and develop their applications, researchers have proposed a novel family of nanomaterials – plasmonic nanomaterials (P-NMs) [45–56]. Plasmons can be described in the classical picture as an oscillation of electron density with respect to the fixed positive ions in a metal. To visualize a plasma oscillation, imagine a cube of metal placed in an external electric field pointing to the right. Electrons will move to the left side (uncovering positive ions on the right side) until they cancel the field inside the metal. If the electric field is removed, the electrons move to the right, repelled by each other and attracted to the positive ions left bare on the right side. They oscillate back and forth at
the plasma frequency until the energy is lost in some kind of resistance or damping. Plasmons are a quantization of this kind of oscillation. Surface plasmons are those plasmons that are confined to surfaces and that interact strongly with light resulting in a polariton. They occur at the interface of a material exhibiting positive real part of their relative permittivity, that is, dielectric constant (e.g., vacuum, air, glass, and other dielectrics) and a material whose real part of permittivity is negative at the given frequency of light, typically a metal or heavily doped semiconductor. In addition to opposite sign of the real part of the permittivity, the magnitude of the real part of the permittivity in the negative permittivity region should typically be larger than the magnitude of the permittivity in the positive permittivity region, otherwise the light is not bound to the surface. The particular choice of materials can have a drastic effect on the degree of light confinement and propagation distance due to losses. Surface plasmons can also exist on interfaces other than flat surfaces, such as particles, or rectangular strips, v-grooves, cylinders, and other structures. Many structures have been investigated due to the capability of surface plasmons to confine light below the diffraction limit of light.

Compared with the ordinary nanomaterials, P-NMs exhibit a better performance, and their use has led to many novel results in many applications [57–63]. P-NMs consist of cations and free electrons that are present on the surface of the materials. The free electrons collectively oscillate under the action of the photoelectric field. Because of this effect, P-NMs can be activated and yield hot electrons, which makes these materials catalytically active. In addition, the cations and free electrons on the P-NM surfaces can form plasmonic waves, which in turn enhances the light field, resulting in the surface plasmon resonance (SPR) effect, local SPR (LSPR) effect, surface-enhanced Raman scattering (SERS), plasmon resonance energy transfer (PRET), and magneto-optical (MO) effects. These effects further improve the performance of P-NMs; as a result, P-NMs have garnered significant attention.

In the continuing process of exploration and research, researchers have developed many P-NMs with novel and exciting properties. Examples include metal-based P-NMs, carbon-based P-NMs, sulfur-based P-NMs, and plasmonic active-structure nanofilms [64–77]. Among these, metal-based P-NMs and carbon-based P-NMs have attracted the most attention. Metal-based P-NMs exhibit excellent physical and chemical properties. Among the most striking are their plasmon optical properties, which prompted many researchers to study them. Ma et al. used a simple one-pot synthesis method for constructing core–shell (CS) gold nanorod@layered double hydroxide (GNR@LDH) nano-materials (Figure 1a) with good photothermal conversion rates [78]. This excellent performance was attributed to the electron transfer of the upper part of gold (Au) in GNR@LDH, which caused the CS GNR@LDH and layered double hydroxides to have more electron interactions and enhanced the plasmonic absorption effect. The development of this CS GNR@LDH material has established a platform for light-to-heat conversion, antibacterial, tumor therapy, and bioimaging applications. In addition, owing to its good stability and high electrical conductivity, carbon is becoming increasingly valuable for carbon-based P-NMs. Among these, graphite and carbon nanotubes (CNTs) are the two most commonly used carbon-based nanomaterials. Owing to the rich functional groups on the surface of graphene, it has good electrical conductivity, mechanical strength, thermal conductivity, and stability; as a result, it has been widely studied by many researchers. Primo et al. summarized the P-NMs that were prepared by combining biomolecules with different graphite-derived materials [79]. A series of graphene-derived materials, such as graphene oxide (GO), chitosan (CHIT)-modified graphene (GO-CHIT), and chemical reduction GO-CHIT (RGO-CHIT) were reviewed. The covalent immobilization of Au surfaces modified by different graphene-derived materials on solid substrates was discussed. These materials were shown to exhibit excellent SPR effects and are likely to be helpful in the development of biosensors.

At present, the commonly used methods for synthesizing P-NMs include the solvothermal, microwave-assisted synthesis, chemical deposition, self-assembly, and in situ growth methods. Klinghammer et al. used the electrochemical method for depositing Au on the nanopores of an anodized aluminum oxide (AAO) matrix, and then studied their plasmon characteristics [80]. Figure 1b–d show the related tests that were performed for studying these characteristics. Figure 1b shows that this microbiosensor device relies on a large array of Au nanoantennas. The scanning electron microscopy (SEM) image in Figure 1c confirms that vertically aligned nanoantennas are evenly and densely distributed on the substrate. Figure 1d shows the extinction spectra of nanoantennas with different aspect ratios, measured at different positions on the same sample. The synthesis process of this method is simple, easy to implement, flexible, and easy to convert; the disadvantage is that the voltage and current may be unstable, resulting in an uneven preparation of nanomaterials, which affects the performance. Compared with the electrochemical deposition method, the solvothermal method has the advantages of low energy consumption, less agglomeration, and controllable particle shape. Javed et al. successfully synthesized the silver (Ag)/rGO/TiO$_2$ ternary NCs using the solvothermal
method for high-efficiency plasmonic dye-sensitized solar cells (PDSSCs) [81]. However, the disadvantage is that the yield is low, and the uniformity of the size and morphology of the nanomaterials are not satisfactory. In light of this, the in situ growth method has been generating more interest. Owing to its advantages of morphological controllability and stability, the in situ growth method can yield a variety of nanostructures. Therefore, these nanostructures (such as NPs, nanorods [NRs], nanobeams, nanosheets, nanospheres, and shell cores) have also been extensively studied. In addition, researchers have attempted to develop novel methods to further improve the performance of P-NMs. Ji and coworkers used cation exchange-enabled nonepitaxial strategy to obtain Au@Cu$_2$S with controllable CS structure (Figure 2a). Based on experimental and theoretical studies, the aqueous dispersions of as-prepared Au@Cu$_2$S NCs have been confirmed with resonant and off-resonant SPR coupling in both the near infrared (NIR)-I (750–900 nm) and NIR-II region (1,000–1,400 nm). The photothermal conversion efficiency of them can be as high as 43.25% even under 1,064 nm light irradiation. It happens that there is a similar case [36]. Lee et al. developed a novel synthesis method (Figure 2b) using sulfide combined with cation exchange, obtaining a heterostructure with plasmonic metal-semiconductor hybridization: Au nanorod-CdS yolk–shell nanostructures (AuNR-CdS YSNs) [82]. During the experiment, it was found that the key to successful synthesis was the exchange of anions and cations. In addition, Scarabelli et al. developed a method for forming a superlattice of Au NRs aligned from the bottom to the top [83]. Under the illumination by light, the structure exhibited an ultraefficient plasmonic effect. It is worth noting that during this growth process, the agglomeration of colloidal particles was caused by the drying solvent.

Figure 1: (a) Synthesis of GNR@LDH, reproduced with permission [78]. Copyright 2019, American Chemical Society. (b) Representative drawing of the LSPR-based biosensor for real-time detection; (c) SEM images of vertically aligned nanoantennas. (d) extinction spectra of nanoantennas with different aspect ratios measured at different spots on one and the same sample, reproduced with permission [80]. Copyright 2018, American Chemical Society.
Supercrystals near the edge of the dry solvent usually contain more NRs and stacked layers, whereas the supercrystal in the center is composed of upright NRs composed of a single layer, causing unevenness of the substrate. This hinders the rapid transmission of active channels and electrons, causing changes in their characteristic spectra. It was found that agglomeration negatively affects not only nanomaterials, but also P-NMs. To alleviate this effect to the maximal possible extent, researchers have developed several substrate optimization methods to obtain more homogeneous substrates. At present, the main improvement measures amount to using biologically active substrates, electron beam etching technology, the nanosphere template method, and other nontraditional technologies [84]. Jeong et al. adopted the electron beam etching technology, using a simple oxygen plasmon-etching process to sinter porous Au nanoshells for controlling the nanogaps between the particles, and successfully exfoliated the obtained nanomaterials into a single nanotriangular structure, reducing the reunion effect [85]. The apex of the synthesized material had sharp edges, allowing to concentrate the light field in a narrow gap, which made the plasmon between the needle tip and the shell hybrid further increasing the local electric field and enhancing the SERS effect.

It was found that among all of the effects of P-NMs, the enhancement of SERS and LSPR effects can significantly improve the performance of P-NMs. This is because the SERS and LSPR effects strongly depend on the material’s morphology, size, and composition, and even on interparticle gaps. Therefore, the microscopic composition of NPs can be studied by acquiring and analyzing SPR spectra. When a synthesized NC material is excited by a light source, the formed plasmon thermal electrons can be transferred to the NC material. It can increase the number of catalytically active sites, enhance the charge density inside the material, and improve the electron transport speed to improve the photocatalytic performance. Zhang et al. prepared composite nanomaterials with Au NPs supported on porous nitrogen-doped carbon (PNC) [86]. As effective electrocatalysts, these materials exhibited excellent HER performance. Excited by a 532 nm-wavelength light source, Au NPs exhibited LSPR-induced generation of thermal electrons. These electrons were transferred to the PNC’s HER active sites (nitrogen-doped sites), promoting the HER, and the overpotential at a current density of 10 mA/cm² decreased from 196 to 99 mV. The potential mechanism for the high activity of these NCs was attributed to the synergy between the hot electrons exhibiting the LSPR-induced effect of Au NPs and the highly conductive PNC. This increased the thermal electrons’ density of the electrocatalyst and enhanced the rapid transport of electrons. This study demonstrated broad application prospects for both energy conversion and photocatalysis, paving the way for the development of various catalytic reactions. At the same time, the LSPR effect is also extremely sensitive to the surrounding medium, which prompts future research on chemical sensors and biosensors based on optical signals. Regarding the plasmon SERS effect, as early as 1974, Fleischmann first discovered that pyridine on a rough Ag film can yield enhanced Raman spectroscopy. Three years later, the SERS effect was demonstrated, with Figure 2: (a) Synthesis scheme of Au@Cu_{2−x}S CS NCs by cation exchange between Au@CdS nanocubes and Cu⁺ [36], reproduced with permission. Copyright 2020, American Chemical Society. (b) Schematic of the synthesis route of AuNR-Cd S YSNs [82], reproduced with permission. Copyright 2018, Royal Society of Chemistry.
the potential of greatly enhancing the Raman signal of molecules near metal nanostructures. Since then, the SERS effect has garnered significant attention. Mei et al. developed novel three-dimensional Au@Ag NPs [87]. Compared with conventional Au@Ag NPs with smooth Ag shells, these novel NPs were based on Au NPs at the core, and Au NR arrays were grown vertically. The thiol ligand selectively blocked the surface and controlled the anisotropic growth of Ag NPs at the tip of Au NRs, thereby producing high-density homopolymerization (Ag–Ag) and heterogeneous (Au–Ag) hot spots in a single NP. These 3D hotspots increased the SERS effect of 3D Au@Ag NPs 30-fold, compared with the SERS effect of conventional Au@Ag NPs, enabling single-NP-level signal detection. This P-NM exhibits good optical properties and has been successfully applied in the fields of in vivo imaging and quantitative analysis of pollutants. The above examples show that the optical performance and high-efficiency optical and electrocatalytic performance exhibited by P-NMs cannot be ignored. The successful use of these properties and their application to actual needs will bring their advantages to the extreme.

Because P-NMs have excellent optical, magnetic, and mechanical properties [88–104], they have broad application prospects in the fields of energy storage devices, nanosensing technology, and medical treatment [45,105,106]. Although thermochemically induced photochemical synthesis materials have been increasingly reported in recent years, there are still only a few reports on plasmon-enhanced electrochemical catalysis and associated reactions. Moreover, at present, there is still little research on novel P-NM synthesis methods and their energy applications. Bo et al. proposed for the first time a novel solar radiation and postplasmon catalysis (SEPPC) process, in which toluene is effectively oxidized using a highly efficient and stable MnO2/graphene-nanofinshed foam (GFF) catalyst [107]. Using plasmon-enhanced chemical vapor deposition (CVD), GFF was synthesized as both a catalyst carrier and a light absorber. A modified MnO2 nanofin on the GFF was used as a high-performance catalyst, yielding a fin-shaped MnO2/GFF layer. In the SEPPC process, the energy efficiency of the toluene conversion was as high as 12.7 g kW/h, which was ~57% higher than for the postplasmon catalysis (PPC) process (8.1 g kW/h), which does not use solar radiation. In addition, the MnO2/GFF catalyst exhibited an excellent long-term catalytic stability, which was significantly better than that reported in earlier studies. This was mainly owing to the synergistic effect of the thermal effect of the solar hot surface and the MnO2/GFF catalyst, which promoted the decomposition of ozone and enhanced the catalytic oxidation of the catalyst surface. Gelé et al. described the application of plasmon-enhanced nanocatalysis for organic conversion [108].

With regard to the applications of P-NMs, some earlier reviews summarized their applications to biosensing, environmental detection, and energy conversion [55,106,109–114]. Among these, the applications of P-NMs to energy have been very few. Devi and Kavitha summarized the surface metallization characteristics of plasmonic metal-TiO2 composite materials and their performance in energy and environmental applications [115]. Furube and Hashimoto elaborated on the latest advances in plasmonic thermal electron transport and plasmonic molecular drives, in both energy conversion and nanomanufacturing [116]. In addition, Subramanian et al. [117] and Ma et al. [106] reviewed the latest research on the electrocatalysis of plasmon-induced multicomponent nanostructured materials in fuel cell reactions and the nanostructure of plasmonic metal-semiconductor heterostructures. The potential use of materials in photocatalysis applications has been considered.

This review surveys various P-NMs and their synthesis methods that have been introduced recently. The existing applications of P-NMs in the energy field are also reviewed. In addition, the current challenges and future developments of P-NMs are summarized. The authors hope this review of the groundbreaking and extensive body of research will be of importance to researchers and will encourage the development of novel P-NMs, which in turn may help to expand their applicability.

2 Types of P-NMs

Metal-based P-NMs and carbon-based P-NMs are the two most common types of P-NMs. This article focuses on the synthesis methods of these two types of P-NMs. To compare the differences more conveniently, the synthetic method and application of metal-based P-NMs have been summarized in Table 1.

2.1 Metal-based P-NMs

Metal nanomaterials have important applications in the fields of biomedicine, sensory detection, surface-enhanced active bases, and environmental monitoring, owing to their SPR absorption characteristics. Noble metals themselves have a very high density of free electrons; therefore, plasmonic noble metal nanomaterials have always been of interest to researchers. However, the high cost of precious metals, the loss of light caused by the transition between energy bands and photons, and the shortage of Au and Ag
have caused researchers to devote increasing attention to the research of nonprecious metals. Among these, the key technology for preparing metal nanomaterials is the simultaneous control of the product size and morphology. To date, many methods for preparing metal nanomaterials have been developed; these can be divided into physical and chemical methods. The physical methods involve dispersing a block into small nanosized particles; this is typically achieved using ultrasound, electron sputtering, or gas phase approaches. The chemical methods use a metal compound as raw material, use a chemical reaction for generating NPs, and control the growth of these particles when forming metal NPs, for maintaining them on the nanoscale. As shown in Table 1, metal-based P-NMs prepared using different synthesis methods have different morphologies, properties, and differ in their applicability to a certain extent. In this article, we review metal-based P-NMs obtained using different synthesis methods, mainly the reduction, one-pot, template, and seed-mediated methods.

### 2.1.1 Reduction method

The reduction method is simple, easy to use, and is one of the most commonly used methods for synthesizing NPs. A typical synthesis process involves adding different reducing agents to a solution containing metal ions, and the metal ions are reduced to an aggregate of

| Materials | Method | Application | Ref. |
|-----------|--------|-------------|------|
| Au NRs | Reduction | Cancer cure | [118] |
| HAgNCs | Reduction | Photocatalysis | [119] |
| Co@Pt@Au | Reduction | Biosensing and therapeutics | [120] |
| Ag/ZnO | Reduction | Dye degradation | [121] |
| Au | Reduction | Pressure sensors | [122] |
| Bi-rGO/BiVO₄ | Reduction | Water splitting | [123] |
| MWO | One-pot | Sers substrate | [124] |
| PB-MoO₃₋ₓ | One-pot | Light stability | [125] |
| FeOₓ/TiN | One-pot | Photothermal conversion | [126] |
| CuS-Ptx/SiO₂ | Template | Cancer therapy | [127] |
| Ag/TiO₂ | Template | Sensing | [128] |
| PRX-Ag | Template | Sequencing and detection | [129] |
| Au NPs | Seed-mediated | Data storage and printing | [130] |
| Au NRs | Seed-mediated | Diagnostics | [131] |
| Au NSs | Seed-mediated | Sensing | [132] |
| Au-beads@Ag | Seed-mediated | SERS and biomedical | [133] |
| FeOₓ@PEI-Au@PEI | Seed-mediated | SERS | [134] |
| FeOₓ@Au | Seed-mediated | Attomolar detection | [135] |
| AuNRs/MoS₂ | Seed-mediated | Combination therapy | [136] |
| Au@Pd NRs | Seed-mediated | Photocatalysis | [137] |
| Ag/rGO/TiO₂ | Chemical | PDSSC precipitation | [81] |
| Au | Electrochemical | Plasmonic biosensor | [138] |
| Au/Ag | Self-assembling | Cancer detection | [139] |
| AlNTs-TiO₂ | Colloidal lithography | Ammonia production | [140] |
| MoO₃₋ₓ | Aqueous exfoliation | Energy storage | [141] |
| Noble metal/ZnO | Photothermal | SERS detection | [142] |
| Au | Reactive magnetron | Sensing | [143] |
| J-AgNP | Electrostatic adsorption | Colloidal stabilization | [144] |
| Ag–La/TiO₂ | Ultrasound-assisted wet | Photocatalysis | [145] |
| Au | Seedless and surfactant-free method | Neuroscience | [146] |
| Er³⁺/SiO₂/Au | Seed-mediated | Upconversion emission | [147] |
| Au@Ag NRs | Photothermal nanofurnace | Sers detection | [148] |
| Au-CS UCNPs | Sputtering and thermal annealing | Upconversion emission | [149] |
| Ag–La/TiO₂ NPs | Wet impregnation method | Photocatalysis | [150] |
| Cu–CuO/TNTA | Electrochemical method | Photocatalysis | [151] |

PDSSC: plasmonic dye-sensitized solar cells, TNTA: TiO₂ nanotube array, HAgNCs: hollow Ag nanocubes, and MWO: molybdenum tungsten oxide.
nanometer-sized NPs. The synthesis method of Turkevich is one of the representative synthesis methods for preparing NPs. P-NMs can also be synthesized using the reduction method, and the P-NMs synthesized using this approach exhibit better performance than general nanomaterials. Moreover, the P-NMs synthesized by the reduction method constitute a single precious metal, the P-NM. Huang et al. synthesized plasmonic Au NRs (Figure 3a) using the ascorbic acid (AA) reduction of the Au salt HAuCl₄ solution, using the reduction method [118]. In addition, a microfluidic device embedded with microstructures was designed for aligning with a laser and a dark-field microscope to observe the effects of light and heat on cells in real time. Dadhich et al. synthesized plasmonic hollow Ag nanocubes (HAgNCs; Figure 3b) shows the high-resolution transmission electron microscopy (HRTEM) image with spherical void spaces, using the reduction method [119]. The first step amounted to adding AgNO₃ and folic acid to Milli-Q water. Then, the pH was adjusted with NaOH. Finally, folic acid-capped Ag₂O nanospheres were formed for obtaining HAgNCs during the reduction of hydrazine hydrate (the entire synthesis process is shown in Figure 3c). In the synthesis phase, the folic acid played a unique role as a shape and structure-directing agent. The synthesized HAgNCs were shown to be good catalysts in the dark and sunlight conditions and were shown to degrade a model dye methyl orange. It was found that HAgNC-630 had the best catalytic effect, and the catalytic efficiency in sunlight was 3.3-fold that of solid Ag nanospheres. To improve the performance of single-precious-metal P-NMs, researchers have attempted to dope other single metals based on P-NMs, to form composites with potentially better performance. It was found that most doped substances were metals, metal oxides, and composite films. Katagiri et al. synthesized P-NM Co@Pt@Au NPs, using the reduction method [120]. First, Co–Pt NPs were synthesized by octanol reduction. The resulting NPs were added to HAuCl₄ containing a solution of formaldehyde and 1-octadecene. Then, Au-coated Co–Pt NPs were collected using a magnet, and finally Co@Pt@Au NPs were obtained through ligand exchange synthetic plasmon. In the course of this experiment, the researchers designed and synthesized complex multicomponent NPs through an adjustable reduction reaction. According to the Co/Pt ratio, the distribution of Co and Pt in the NPs was precisely controlled, and a CS structure with Co as the core and Pt as the shell was formed, as shown in Figure 4a–d. The synthesized plasmonic Co@Pt@Au NPs have a great potential for development in transportation and sensing applications. Ziashahabi et al. synthesized a novel cohybrid Ag/ZnO plasmonic nanostructure using the reduction method. The nanostructure was synthesized from ZnO in water using the arc discharge method, and then synthesized by coupling it with Ag using the chemical

Figure 3: (a) Transmission electron microscopy (TEM) images of Au NRs, reproduced with permission [118]. Copyright 2019, Royal Society of Chemistry. (b) HRTEM image of HAgNC-630 and (c) synthesis scheme of HAgNCs, reproduced with permission [119]. Copyright 2018, American Chemical Society.
reduction method [121]. The resulting structure induced the photocatalytic degradation of methylene blue under visible light and darkness conditions. Topcu et al. synthesized a plasmonic Au NP-embedded polyacrylamide (PAAm) composite membrane, using the reduction method [122]. First, HAuCl₄ was reduced with a trisodium citrate solution, for synthesizing Au NPs, after which a poly(vinylpyrrolidone) PVP solution and PAAm were added to the dispersion of Au NPs and left to dry in an oven, finally yielding the PAAm compound membrane. Through related characterization and research, it was found that the synthesized PAAm composite film is a self-supporting flexible polymer film with a strong optical response to mechanical pressure, as shown in Figure 4e. Subramanyam et al. synthesized an rGO/BiVO₄ composite materials (Bi-rGO/BiVO₄) photoanode modified with plasmonic Bi NPs [123]. Bi NPs were synthesized using the chemical reduction method with sodium borohydride as a reducing agent, and the manufacturing of the photoelectrode was completed using the die-casting method. The composite electrode exhibited good light-hydrogen conversion efficiency, considerable incident photon-current efficiency, and low charge transfer resistance, and realized photoelectrochemical (PEC) water splitting. Benefited from the convenient operation, simple equipment, low investment, and good controllability, reduction method is widely used to obtain noble metal P-NMs. However, the biggest

Figure 4: (a–d) TEM images and elemental spectra of Co–Pt NPs prepared with different Co/Pt precursor molar ratios; (a and b) Co:Pt = 60:40 and (c and d) Co:Pt = 70:30. Reproduced with permission [120]. Copyright 2020, American Chemical Society. (e) Appearance of the films used under various pressures. Reproduced with permission [123]. Copyright 2019, Elsevier.
limitation of reduction method is that it can only be used to prepare metals, especially noble metal, rather than metal oxides.

2.1.2 One-pot method

The one-pot method is simple, convenient, clean, and pollution-free and is one of the most widely considered synthesis methods. Li et al. synthesized surfactant-free plasmonic molybdenum tungsten oxide hybrid nano materials, using the one-pot method \[124\]. Substrates with excellent SERS performance are mainly limited to noble metals (Au and Ag), but it was shown that the synthesized materials could be used as high-performance substrates, with their SERS performance being equivalent to that of noble metals. The study offered novel SERS substrates based on nonnoble metals. Odda et al. also synthesized anoxic molybdenum oxide NP nanoagents (PB–MoO\(_3\)\(_{2−x}\) NCs) functionalized with Prussian blue (PB), using the one-pot synthesis method \[125\]. Thermal nanoagents were shown to be strongly therapeutic with respect to cancer cells, both in vivo and in vitro. Zeng and Xuan synthesized a photonic nanofluid composed of Janus-type magnetic plasmonic Fe\(_3\)O\(_4\)/TiN NPs, using the one-pot synthesis method, the characterization of which is shown in Figure 5a–c \[126\]. The prepared nanofluid exhibited a full spectral absorption of incident sunlight. Those authors described a novel strategy that utilizes full-spectrum solar energy and controls the photothermal properties of nanofluids. One-pot method is one of the most widely considered synthesis methods because it can be used to conveniently and cleanly fabricate most kinds of nanomaterials. However, the conditional control in fabrication is still a major challenge for one-pot method.

2.1.3 Template method

The template method for synthesizing novel nanomaterials has been developed over the past 10 years. In general, we distinguish between the hard and soft template methods, based on their own characteristics and limitations. Soft templates come in many forms and, in general, are easy to construct. Yet, compared with hard templates, the stability of soft templates is poor; thus, the associated template efficiency is typically not sufficiently high. He et al. synthesized plasmonic CuS–PTX/SiO\(_2\) composite nanocapsules using the soft template method of micelles \[127\]. This material exhibited unique colloidal stability, biocompatibility, high light-to-heat conversion efficiency, and NIR laser-stimulated drug release behavior and was judged to be very promising for NIR laser-driven collaborative chemical photothermal cancer treatment applications.

![Figure 5: (a–c): (a) TEM, (b) SEM, and (c) HRTEM images of Fe\(_3\)O\(_4\)/TiN NPs (the dashed circle encircles a nanosphere), reproduced with permission \[126\]. Copyright 2018, Elsevier. (d) Synthesis flowchart of PRX–Ag NRs, reproduced with permission \[129\]. Copyright 2020, Wiley.](image)
Guo et al. reported Ag⁺ ion-doped amorphous TiO₂ hollow spheres produced by etching a silica template and the following exchange of Ag⁺/Na⁺ ions [128]. The resultant material was used for formaldehyde detection. After exposure to increasing concentrations of formaldehyde, plasmonic Ag NPs were generated in situ, and photocurrent amplification was achieved in a proportional manner. This occurred owing to the injection of hot electrons from the plasmonic Ag NPs into the conduction band of amorphous titanium dioxide, which thereby enhanced the photocurrent. Giovannini et al. used peroxiredoxin (PRX) as a template for preparing nanopores, using a simple bioassisted method, and synthesized plasmonic Ag nanomaterials [129]. The spontaneous interaction between precious metals and biological scaffolds allowed to synthesize nanomaterials with unique characteristics that were simple and economical. PRX drove the growth of metallic Ag seeds under wet reduction conditions, and the inner and outer diameters of the generated nanorings were 28 and 3 nm, respectively, as shown in Figure 5d. Template method can more accurately control the size and morphology of nanomaterials than the other methods. However, the main challenges are how to obtain the suitable templates and how to get to remove templates without changing the original structure of nanomaterials.

2.1.4 Seed-mediated method

The particle size uniformity associated with the reduction method is not satisfactory. Compared with the reduction method, the seed-mediated method allows to control the size, shape, composition, and structure of the obtained nanocrystals. Cho et al. synthesized plasmonic chiral Au NPs using a multistep seed-mediated method [130]. The researchers divided the traditional sequence of single-chiral growth steps into two growth stages. First, chiral seed NPs were controllably synthesized from octahedral seed NPs, following which the helicoid was grown uniformly from the synthesized chiral seed NPs. They found that this multichiral evolutionary synthesis method can be applied to the morphology control of water-based nanocrystals, the synthesis of complex nanostructures such as chiral nanomaterials, and the synthesis of plasmonic metamaterials, with high uniformity and repeatability. Similarly, Li et al. used cetyltrimethylammonium bromide (CTAB) as a surfactant and an AA solution as a reducing agent and prepared plasmonic Au NPs using the seed-mediated method [131]. For wavelengths in the 300–700 nm range, by varying the irradiation time, it can be clearly seen from the spectrogram and the TEM image in Figure 6a–c that the obtained Au NRs were gradually oxidized by light into Au particles. The researchers demonstrated the conversion between the photoreduction of Au ions and the photooxidation of Au NRs by varying the wavelength and also demonstrated that the seed-mediated method can not only modulate the color of plasmon resonance in a contactless manner but can also modulate all-optical molding of individual NPs, providing a novel direction for reversibly adjusting the LPR effect. Liu et al. also used the seed-mediated method for synthesizing plasmonic Au nanostars (Au NSs) [132]. First, HAuCl₄ was used as a raw material, and sodium citrate was used as a reducing agent for reducing Au³⁺ into Au seeds; these Au seeds were then added to the PVP and mixed thoroughly to obtain Au NSs. Moreover, in the course of the study, a nanosensor was prepared using a plasmon and the photothermal immunoassay method, in which an enzyme triggered the crystal growth on Au NSs. The sensor detected low levels of alkaline phosphatase and easily read the test by color and temperature. Singh et al. prepared five-twin Au nanobeads by thermally induced seed twin synthesis, followed by the addition of AgNO₃ under magnetic stirring to grow Au-beads@Ag rods, and then converted them into plasmon by current displacement reaction (galvanic replacement reaction) Au nanocapsules [133]. Cetyltrimethylammonium chloride was used as a stabilizer, and an excessive growth of Ag on Au beads produced uniform Au beads@Ag NRs. The volume of AgNO₃ added could be controlled for synthesizing Au-beads@Ag rods of different sizes (Figure 6d and e). In addition, this study also demonstrated that the hollow and porous CS nanostructures inherent in nanocapsules are of great significance in the field of SERS.

In addition to single-metal P-NMs, many researchers have explored single-metal P-NM derivatives, metal oxide P-NMs, and their derivatives. For single-metal P-NM derivatives, the most common derivative is based on single-metal P-NMs doped with metals or metal oxides. Because the performance of a single-metal oxide P-NM is not very good, the research on metal oxide P-NMs basically addresses the composites of metal oxide P-NMs. The composite materials added on the basis of metal oxide P-NMs mainly consist of precious metals and polyelectrolytes. Pinheiro et al. successfully prepared a magnetic plasmonic nanoadsorbent based on Fe₃O₄ and Au, using the seed-mediated method, which was encapsulated in a positively charged polyelectrolyte (polyethyleneimine) (Fe₃O₄@PEI-Au@PEI; Figure 6f and g) [134]. An aqueous solution containing AA and sodium citrate as reducing agents was used for reducing the Au salt to synthesize larger Au NPs (diameter, 70 nm). The final synthesized Fe₃O₄@PEI-Au@PEI was very promising for effective absorption/detection of
tetracycline. Al Mubarak synthesized P-NM Fe₃O₄@Au NPs, using the seed-mediated method [135]. The local Au NPs on the surface were bridged to the Au shell carrying the detection probe of Fe₃O₄@Au core/shell NPs through double hybridization assembly to form an Au substrate, so that the molar detection of microRNA (miRNA)-155 in solution could be performed. The results indicated that plasmonic sensor chip applications for measuring biological binding events are feasible. Runowski et al. synthesized luminescent plasmonic KY₃F₁₀·Yb³⁺·Er³⁺/SiO₂/Au nanomaterials using the seed-mediated method [147]. The surface Au NRs were reshaped into nanospheres at an NIR wavelength of 980 nm, and the color exhibited by the nanomaterials was adjusted by the emission wavelength (yellow to red).

Figure 6: (a) Extinction spectra acquired for increasing irradiation times (0 min for curve 1, 90 min for curve 2, and 180 min for curve 3). (b) TEM images of the Au NRs were taken before oxidation and (c) after 180-min-long oxidation. The scale bars in the insets of (b) and (c) are 10 nm. Reproduced with permission [131]. Copyright 2018, Royal Society of Chemistry. (d and e) TEM image of an Au-bead@Ag NR. (d) Aspect ratio: 2.8 ± 0.2. (e) Aspect ratio: 6.0 ± 0.3. Reproduced with permission [133]. Copyright 2018, American Chemical Society. (f and g) TEM images of Fe₃O₄@PEI-Au@PEI. Reproduced with permission [134]. Copyright 2019, Springer Nature.
To further improve the synthesis methods and improve the performance of synthesized P-NMs, some researchers have proposed combined methods. Younis et al. prepared a dual plasmonic photothermal therapy (PTT) nanoagent Au nanorods/MoS2 (AuNRs/MoS2) by combining the seed-mediated and hydrothermal synthesis methods [136]. First, an Au seed solution was prepared by reducing HAuCl4 with NaBH4, and then PEGylated MoS2 nanosheets were synthesized using the hydrothermal method. Then, the two were ultrasonically mixed to finally prepare Au NR-modified polyethylene glycol-MoS2 nanostructures. Studies have shown that the resultant material could be activated by a single low-power laser, and the proposed simultaneous photodynamic/synergistic PTT effect strategy could effectively reduce the treatment time and achieve a high treatment index. Shahine et al. synthesized a CS bimetallic plasmonic nanostructure (Au@Pd NR) using a combination of the seed-mediated and deposition methods [137]. Au seeds were added to the growth solution consisting of a mixture of CTAB, HAuCl4, and AgNO3 to initiate the growth of Au NRs. Related studies have shown that the plasmon-enhanced nanoenzyme activity of this precious-metal nanostructure can be used for oxidative stress-related therapeutic applications, and the adjustable LSPR in the NIR range has other advantages. Similar to the template method, the seed-mediated method can induce the formation of the P-NMs with particular sizes. However, the source of suitable seeds limits the application of the seed-mediated method.

2.1.5 Other methods

Synthetic methods, such as the solvothermal method, the deposition method, the self-assembly method, photo-lithography technology, and mechanical lift-off methods, have also been considered in recent years. The solvothermal method is simple, inexpensive, green, and environmentally friendly and has always been among the most widely used synthetic methods. However, only a few synthetic approaches have been presented for preparing P-NMs. Javed et al. synthesized an Ag/rGO/TiO2 ternary plasmonic NC using a simple solvothermal method, and the synthesized material was suggested as a photoanode for high-efficiency PDSSCs [81]. The deposition methods for synthesizing P-NMs mainly include the electrochemical and chemical deposition methods. Klinghammer et al. synthesized plasmonic Au nanotubes by electrochemically depositing Au on the nanosized pores of an AAO matrix. On this basis, NaOH was used for etching away the surrounding AAO matrix, leaving only Au nanowires. It was found that a large array (area, ~1 cm²) of Au NRs, arranged vertically and densely packed, can be used for local confinement and amplification of external light signals for reliable biosensing. Shehata et al. synthesized plasmonic Au cerium oxide NPs using chemical precipitation technology; this material can be used as an optical sensing material for lead particles in aqueous media based on fluorescence quenching [138]. Self-assembly is a method to spontaneously polymerize nanostructures using different interactions between specific active groups present in nature. It is a method for preparing novel biologically and chemically developed functional materials. Compared with general synthetic methods, P-NMs synthesized using the self-assembly approach have a more stable structure and exhibit better performance. Li et al. synthesized this plasmon nanostructure by self-assembling Au nanospheres selectively onto hollow Au/Ag alloy nanocubes. They used miRNAs, which are both cancer biomarkers and direct self-assembly triggers, as a target [139]. Through strict nucleic acid hybridization of the miRNA target, Au nanospheres selectively self-assembled to exhibit an ideal interparticle distance (≈2.3 nm). The best SERS signal transmission was achieved for hollow Au/Ag alloy nanocubes. Two synthesis methods, photolithography and mechanical lift-off, were proposed recently. Thangamuthu et al. fabricated large-area plasmonic aluminum nanotriangles (AlNTs) through efficient and scalable colloidal lithography [140]. Etman et al. introduced a simple aqueous exfoliation strategy [141]. This method uses two commercial molybdenum oxide precursors, MoO2 and MoO3, with different weight ratios, to produce a series of plasmonic MoO3-x nanosheets (where x represents oxygen vacancies). It was found that this material can be used as a negative electrode material for lithium-ion batteries. In addition, there are some less common synthesis methods, such as combustion, vacuum evaporation, and thermal dehumidification methods. Although these approaches have not been widely adopted for synthetic P-NMs, each of them has a certain research value. Pathak et al. synthesized noble metal-doped ZnO by combustion and studied the effects of different metals (Ag, Au, and Pd) on the physical properties and on the LSPR performance [142]. The results showed that the combustion technology is a unique method. No further heat treatment was required for synthesizing a nanocrystalline material with a large surface area in a synthetic form. Kong et al. synthesized a plasmonic Au nanoisland (NI) array by vacuum evaporation [152]. A thin film of Au NIs was prepared by evaporating a 5 nm-thick Au layer on a precleaned glass and a silicon substrate in high vacuum, followed by annealing at temperatures in the 200–600°C range, in the presence of argon. Subsequently, Eu3⁺-doped polycrystalline NaYF4 particles were deposited on the Au NI thin
films. Under the plasmon heat and the catalytic effect of Au NIs, polycrystalline NaYF₄ quickly transformed into single-crystal Y₂O₃ (the conversion process is shown in Figure 7a). This novel approach yielded single-crystal transformations at very low temperatures. After laser irradiation, optimized nanocrystals with better crystallinity and stability were produced. Yoshino et al. used thermal dehumidification to condense a coated Au film into nanodots, which is a simple and low-cost method for manufacturing uniform metal nanodots [143]. They successfully manufactured an array of Au nanodots with diameters in the 100–520 nm range, which responded to infrared light and could be used in infrared plasmonic sensors.

To further improve the overall performance of P-NMs, researchers have developed and tested many novel methods. Cao et al. prepared Au@Ag NRs into fully alloyed plasmonic AuAg NRs using a photothermal nanofurnace (TEM images are shown in Figure 7b and c) [148]. It was found that a silica shell can be used as both a thermal insulation layer and a protective layer, thereby promoting the alloying process. In addition, AuAg NRs maintained anisotropic nanostructures well after alloying. Therefore, the prepared AuAg alloy NRs exhibited excellent SPR performance, excellent chemical resistance, and chemical stability, which could be used for SERS detection in practical applications. Guo et al. fabricated Janus plasmonic Ag nanosheets (J-Ag NPs) with two chemically different surfaces, using different electrostatic adsorption methods [144]. This approach avoids corrosive chemicals and high temperatures that can degrade Ag NPs. J-Ag NPs demonstrated a great potential for stabilizing emulsions and forming layered interfacial nanostructures. This novel method can be used for designing P-NMs at liquid–liquid and solid–liquid interfaces for achieving colloidal stability. Joint methods have also been considered. Koneti et al. synthesized plasmonic Au NPs using the reactive magnetron sputtering and deposition methods [145]. First, a thin film composed of Au (Au–TiO₂) dispersed in TiO₂ was obtained by reactive magnetron sputtering. Then, the Au–TiO₂ film was deposited on a substrate using the electrochemical method, following which the sample was subjected to vacuum annealing at different temperatures, at 10⁻³ Pa, to obtain Au NPs formed by the diffusion of Au atoms in the entire matrix. The obtained material featured small-sized Au NPs in the deposited Au–TiO₂ thin film, resulting in a negligible LSPR response. Clarke et al. synthesized Au-CS upconversion NPs (UCNPs) by large-

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Figure 7: (a) Schematic of the fast transformation of RE³⁺-doped luminescent crystals with plasmonic Au NIs. Reproduced with permission [152]. Copyright 2020, Royal Society of Chemistry. (b and c) TEM images of original Au@Ag NRs-2.5 and fully alloyed AuAg NRs-2.5. Reproduced with permission [148]. Copyright 2018, American Chemical Society.
scale dewetting of plasmonic Au NPs onto CS UCNPs by sputtering and thermal annealing dehumidification [149]. The dehumidification method allows precise control of the shape and size of Au NPs over a wide range; thus, by adjusting their plasmon resonance to match the emission wavelength of the Er³⁺ emitter in NaYF₄ UCNP17, the film thickness, annealing temperature, and annealing time can be simply changed. The design and integrated manufacturing methods of Au-CS-UCNPs provide a novel direction for exploring plasmon-enhanced upconversion emission. Dal’Toé et al. prepared lanthanum-doped titanium dioxide decorated with Ag plasmon NPs, using a simple green ultrasound-assisted wet impregnation method combined with photodeposition [150]. In addition, Sang et al. used TNTA photoanodes for synthesizing plasmonic Cu–CuO/TNTA in a two-step electrochemical method using environmentally friendly copper-based nanomaterials, followed by the sensitized synthesis with Eosin Y dye Eosin Y/Cu–CuO/TNTA [151]. This material enhances the transfer of interfacial charge and further increases the photocurrent density. In addition, the synthesis of most NIR-sensitive particles uses the seed-mediated synthesis method, but the surfactants used in the process (such as CTAB) are cytotoxic, and the process is complex. To resolve this problem, Lee et al. attempted to synthesize biocompatible plasmonic Au NSs using seedless and surfactant-free methods [146]. This method requires only biocompatible chemicals, 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid buffer and Au ions (HAuCl₄). The results demonstrated that the synthesized Au NSs can regulate nerves in response to the NIR irradiation.

### 2.2 Carbon-based P-NMs

When carbon-based nanomaterials are used as plasmonic materials, graphite and CNTs are the two most commonly used carbon-based nanomaterials. Table 2 summarizes the carbon-based P-NMs on their synthetic method and application.

As early as 1958, researchers discovered that graphene has a layered structure (with a single-layer structure and a multilayer structure) and also learned that its layered structure originates from sp² bonded carbon atoms. In 2004, Novoselov et al. reported single-layer graphene prepared by mechanical peeling [153] and also demonstrated that graphene has good electrical conductivity, mechanical strength, thermal conductivity, and stability. As a result, graphene has garnered significant attention. Owing to the unique properties of graphene, an increasing number of studies have been conducted in recent years, considering it as a plasmonic material. Qiu et al. [160] adopted the idea of Chuntonov and Haran [161–163] and proposed a plasmonic trimer composed of graphene nanodisks. It was found that graphene nanostructures are more compact than general graphene structures and may have better applications in the optical field. Kanidi et al. [154] combined graphene and silicon to form a P-NM, which fully demonstrated the mechanical properties of graphene and the scalability of silicon. P-NMs were predicted to have good application prospects in disease diagnosis, sensing, and optics. Wang et al. synthesized GN@(γ-FeOₓ@AuNP)@[C₆₀(>DPAF-C₉)]ₙ P-NMs using the deposition method [155]. In addition, photo-induced changes in the relative dielectric properties of these materials were studied.

Owing to the controllability of the content and type of surface free radicals, GO and reduced graphene oxide (rGO) have been of increasing interest to researchers. Primo et al. synthesized GO-CHIT materials using a combination of an ultrasonic treatment and an amidation reaction [79]. Then, the obtained GO-CHIT was reduced with excess NaBH₄ to obtain the RGO-CHIT material. Then, GO, GO-CHIT and RGO-CHIT were characterized. Finally, the influence of the nature and number of graphene nanomaterials and the amount of immobilized

| Materials            | Method              | Application              | Ref. |
|----------------------|---------------------|--------------------------|------|
| Graphene             | Mechanical peeling  | Optical field            | [153]|
| Graphene@silicon     | Mechanical peeling  | Disease diagnosis        | [154]|
| GN@[C₆₀(>DPAF-C₉)]ₙ | Deposition          | Biosensing               | [155]|
| GO-CHIT              | Ultrasonic treatment| Photocatalysis           | [79] |
| AuAg@Au/RGO-C₃N₄    | Deposition          | Disease treatment        | [156]|
| AuPLGA               | Hummers             | CO₂ detection            | [32] |
| CNTs                 | CVD                 | Methylen blue detection  | [158]|
| eW-Au@CQDs           | Chemical reduction  | LSPR-based gas sensor    | [159]|
| CNTs                 | CVD                 |                          |      |
protein on the electrochemical and plasmonic properties of the relevant platform were clearly defined. Relatively speaking, GO has been the most studied graphene derivative as a P-NM. Wang et al. used the method of preparing Au@Ag (the synthesis process is shown in Figure 8a) [164]. Hou et al. synthesized Ag seeds, AuAg@Au, and RGO-C₃N₆ precursors [156]. On this basis, 10 µL RGO-C₃N₆ and 10 µL AuAg@Au were added dropwise to the electrode surface, and finally, the electrode modified with the AuAg@Au/RGO-C₃N₆ material was prepared. This study demonstrated that the AuAg@Au/RGO-C₃N₆ plasmonic material exhibits outstanding photoelectric properties. Chauhan et al. adopted the modified Hummers method for preparing hybrid plasmonic carbon nanomaterials, which are Au polyactic-co-glycolic acid (AuPLGA) NS-decorated graphene oxide nanosheets and IR780 loaded GO nanosheets [157]. Research has shown that they are very promising for disease treatment.

Laser ablation, arc discharge, and CVD are the main methods used for preparing CNTs [32]. When CNTs are used as P-NMs, they are mostly used in the field of sensing. Allsop et al. used the changes in the optical properties of CNTs to prepare an LSPR-based gas sensor for detecting gaseous CO₂ [159]. Cheung et al. found that the strong π-plasmon absorption of single-walled nanotubes (SWNTs) in the ultraviolet region is more sensitive to ion binding than absorption in the visible and NIR regions [165]. On this basis, they designed a special SWNT, which is an SWNT modified with carboxyl-terminated phospholipid-polyethylene glycol (PL–PEG–COOH; SWNT/PL–PEG–COOH).

Through scanning transmission electron microscopy (STEM), SEM, and AFM characterization (Figure 8b–d), a small bundle of SWNTs was demonstrated in the sample SWNT/PL–PEG–COOH. In sensing applications, it was found that the sample can be used for detecting Fe³⁺ metal ions. Therefore, researchers have proposed that when a specific binding chelating agent is attached to the surface of CNTs, it can be used for detecting specific metal ions. In addition, to improve the environment and to reduce the waste, Devi et al. attempted to extract useful substances from electronic waste products to produce carbon quantum dots (CQDs) [158]. The study found that e-waste-derived CQDs (eW-CQDs) have good optical properties. In addition, the researchers also made eW-CQDs into plasmon nanostructures (eW-Au@CQDs) using a one-step chemical reduction strategy, in which eW-CQDs acted as reducing agents. At room temperature, a solution of 1 mM HAuCl₄ and 0.3 M eW-CQD was continuously stirred at a ratio of 1:9 to prepare eW-Au@CQDs. After the reaction was completed, the solution was filtered through a syringe filter. Finally, the samples were stored at 4°C until further use.

2.3 Other materials

In addition to metal-based P-NMs and carbon-based P-NMs, there are other types of P-NMs, such as sulfur-based P-NMs and plasmon-active nanostructured films. Owing to the

![Figure 8: (a) Schematic of the preparation method. (b–d) STEM, SEM, and atomic force microscopy (AFM) images of SWNT/PL–PEG–COOHs, respectively. Reproduced with permission [164]. Copyright 2016, Springer Nature. (b–d) STEM, SEM, and AFM images of SWNT/PL–PEG–COOHs, respectively. Reproduced with permission [165]. Copyright 2016, Royal Society of Chemistry.](image-url)
uniqueness of sulfur in nature, structure, and function, sulfur-based P-NMs have very good application prospects in mesoscopic physics and in the manufacturing of nanoscale devices. However, poor conductivity is a major problem with sulfur-based materials. At present, the best way to overcome this problem is to dope on this basis with good-conductivity materials, such as carbon, metals, and conductive polymers. In this regard, Teng et al. summarized and discussed the current research and challenges of sulfur-based materials and their plasmonic applications. Compared with general P-NMs, the preparation of plasmonics-active nanostructured thin films (PANTFs) on solid substrates has better physical stability. Among them, the SiO$_2$ substrate is the most widely used substrate for preparing PANTFs, owing to its advantages of low cost and easy preparation. In addition, excellent flexibility makes polymethyl methacrylate, polyethylene terephthalate, and polycarbonate polymers the most commonly used polymer substrates for creating PANTFs. To this end, Bhattarai et al. summarized the synthesis of PANTFs and outlined their sensitivity to biosensing [64].

3 Properties of P-NMs

In the continuing exploration and research of P-NMs, researchers have found that the P-NMs themselves have many excellent properties, including optical, magnetic, and other properties. Among these, the optical properties of P-NMs are the most prominent. Owing to these excellent properties, P-NMs can be widely used in various fields. In what follows, we review the main features of P-NMs.

3.1 Optical properties

Among all of the properties of P-NMs, optical properties are the most important for many applications; therefore, there is a need to optimize these properties for widening the usage scope of P-NMs. In contrast, improving the optical properties of these materials may help to further expand their application market; however, P-NMs can also be added to other materials, to improve the optical properties of resultant materials. Shahine [166], Yang et al. [167], Clarke et al. [149], and others have studied methods for enhancing the optical properties of P-NMs. They coupled metal NPs to semiconductor nanostructures, and excitons and plasmons interacted to form a hybrid system. Owing to the plasmon-mediated emission interaction on the metal surface, it can be used to adjust the characteristics of photoluminescent agents, such as enhancing or quenching light. The integration of NPs affects the absorption and photoluminescence properties of other nanomaterials, thereby adjusting the photocatalytic activity of the entire chemical system (the enhancement effect is shown in Figure 9a–d). Prusty et al. studied the unique structural characteristics of tunable NIR LSPR spectroscopy and high free-electron-density 2D nano-materials, which provide attractive alternative energy conversion products for plasmon-based precious-metal-based nanostructures [168]. In the study of PPC by Odda et al., a simple size/morphology control method was adopted. The prepared PB-MoO$_{3-x}$ NC featured uniform-size particles (size, ~90 nm), had high water dispersibility, and strong light absorption in the first biological window [125]. This intense light absorption was caused by the plasmon resonance in the oxygen-deficient MoO$_{3-x}$ semiconductor. In addition to luminescent agents, P-NMs can also act as photocatalysts. Cho et al. used the photocatalytic properties of P-NMs to dominate the photocatalytic disinfection process of Escherichia coli and enhance the chirality of chiral reactions [123,130]. When P-NMs are used as photocatalysts, they can also be applied to the energy field, in addition to the medical field. In terms of the solar energy utilization, the PEC effect of P-NMs can improve the absorption of radiation, enhance the quantum confinement effect and photosensitivity effect, and increase the conversion efficiency of the solar energy to hydrogen, or for preparing materials for the solar energy conversion. Metal-based P-NMs are the most commonly used P-NM photocatalyst materials. The SPR effect of metal-based P-NMs (such as Au, Ag, and Al) can improve the light absorption characteristics of organic photovoltaic cells (OPVs) and has been widely used. By introducing different metal nanostructures between adjacent layers of the active layer, buffer layer, electrode, or OPVs, multiple plasmon mechanisms have been demonstrated [144]. In a study by Thangamuthu et al., plasmonic AlNTs were used for studying the effect of plasmon on the production of photocatalytic ammonia [140]. Through electrochemical photocurrent measurements, the problem of plasmonic near-field coupling to semiconductors and AlNT generating hot electrons was studied in detail. The results confirmed the successful production of ammonia by decomposing nitrogen at room temperature and atmospheric pressure. From the results obtained, it is clear that the use of a plasmonic aluminum structure can significantly increase the rate of ammonia production. In addition, when P-NMs are used as photocatalysts, they can decompose pesticides to alleviate environmental pollution. Studies have shown that P-NMs decomposed a typical organic pesticide, Pb–TiO$_2$.
when used as photocatalysts, and exhibited high photo-degradation performance with respect to pesticides under 60 min of irradiation by sunlight [169]. In addition, P-NMs can also be used as key intermediates for constructing optical switches and tunable dielectric graphene nanomaterials and can be used for enhancing oxidase activity and cellular effects [170]. The above-mentioned extensive research shows that the optical properties of P-NMs have been widely used.

### 3.2 Magnetic properties

In addition to their optical properties, P-NMs also exhibit good magnetic properties. The magnetic properties of P-NMs can not only be used for synthesizing advanced nanomaterials but also for detection, diagnosis, and treatment of diseases in the medical field. Katagiri et al. designed CS NPs with excellent magnetic properties and...
plasmon resonance: Co@Pt@AuNPs. First, Co@Pt NPs were synthesized using the ethanol reduction approach [120]. Then, Au was successfully coated on the Co@Pt NPs by uneven nucleation to form Co@Pt@Au NPs. Because Co@Pt NPs have excellent magnetic properties and a small lattice mismatch, the addition of Au coating increased the plasmon resonance effect, so Co@Pt@Au NPs exhibited excellent magnetic properties and plasmonic body response. These high-loudness hybrid nanosilicon graphene materials will greatly benefit from optoelectronic devices. Laser-structured plasmonic silicon is easy to manufacture, and its scalability, excellent electromagnetic (EM) enhancement performance, and successful integration with graphene provide convenience for sensing, photonics, optoelectronics, and medical diagnosis applications.

### 3.3 Other properties

The properties of P-NMs include but are not limited to optical properties and magnetic properties. Other properties are likely to affect the application range of these materials as well. Here, we mainly discuss the mechanical properties and chemical stability of P-NMs, which is relevant for sensing applications.

Kanidi et al. transferred graphene to uncoated nanostructured silicon and nanostructured silicon with Au NPs, using a graphene transfer process, and integrated silicon nanoarrays with graphene using laser processing [154]. Compared with traditional deposition and lithography methods, this manufacturing approach relied on a one-step method, which is cost-effective, allows to quickly process silicon in water using lasers, and is suitable for large-scale manufacturing. Excellent mechanical properties of graphene, combined with a scalable three-dimensional (3D) plasmonic nanostructured silicon substrate, enhanced the EM radiation characteristics of the P-NM and the substances with which it interacted. In addition to its good mechanical properties, the obtained P-NM also exhibited very good chemical stability. Cao et al. synthesized fully alloyed AuAg NRs in a photothermal furnace [148]; these AuAg NRs could convert absorbed light into heat energy. The silica shell in the synthesized material served as both a thermal insulation layer and a protective layer, for promoting the alloying process. The synthesized AuAg NRs exhibited improved plasmonic properties derived from Ag and were chemically stable in a corrosive environment derived from Au. The experiment explored the chemical stability of the Au–Ag CS NRs and fully alloyed AuAg NRs. The UV-vis spectra showed that, after the fully alloyed NRs were kept in a mixed solution for 48 h, they still maintained their good plasmonic performance, whereas the band intensity exhibited only a small drop (~6%; Figure 9e). The plasmon energy band of these Au@Ag NRs exhibited a rapid red shift, indicating that the Ag shell was etched (Figure 9f). Guo et al. fabricated J-Ag NPs with two chemically different surfaces, using different electrostatic adsorption methods [164]. J-Ag NPs showed great potential for stabilizing emulsions and forming layered nanostructures at the interface potential. This novel method can be used for designing P-NMs at liquid–liquid and solid–liquid interfaces, for achieving colloidal stability. Topcu et al. [122] studied pressure sensors containing P-NMs. Nanostructures based on Au NPs are promising, owing to their plasmonic properties. In this study, based on polyacrylamide (PAAm) and Au NPs, a self-supporting flexible polymer film with a strong optical response after mechanical stress was prepared. This proposed a simple red–green–blue space-based algorithm that can be used for smartphone-assisted detection of applied pressure.

### 4 Energy applications of P-NMs

With increasing environmental pollution, reduction in the availability of fossil fuels, and increasing demands for clean energy, attention has turned to using wind, tidal, solar, and electrical energy sources that can alleviate the above-mentioned issues. Moreover, electrocatalysts and photocatalysts have been playing key roles in energy applications. Appropriate photocatalysts and electrocatalysts contribute to the sustainable use of water and air, increase the utilization of visible light, and stimulate the potential of energy storage devices, such as batteries and superchargers.

When the size of metal particle is considerably smaller than the wavelength of incident light, confinement of surface plasmons in the metal particle occurs as localized SPs, which present resonance effect as LSPR if the oscillation frequency coincides with the frequency of incident photons. The intensity and frequency of LSPR highly depend on the morphology, size, dispersion, composition, and the surrounding dielectric environment of the metal nanostructures. Benefited from EM fields near the surface of plasmonic metal nanostructures are greatly enhanced under LSPR excitation, light absorption could be distinctly boosted near the resonant frequency, which could competently meet the demands of solar-driven reactions. Besides, the intrinsic catalytic activity of metal nanostructures will also...
contribute to the photocatalysis process. Through creation of energetic charge carriers and broadening of the absorption spectrum, these plasmonic metal nanostructures could effectively promote photocatalytic performance in H₂ production, CO₂ reduction, and other photoredox reactions.

As early as 1972, TiO₂ semiconductors were developed, realizing the photolysis of water. To determine suitable photocatalysts, extensive research has been conducted, and many semiconductor Au photocatalysts, such as ZnO, SnO₂, ZrO₂, and CdS, have been put forward. However, many problems remain associated with the use of these semiconductor materials as photocatalysts. The main problems are the low quantum rate, low solar energy utilization rate, and unclear mechanism of heterogeneous photocatalytic reactions of these materials. Much effort has been made to overcome these problems. Attempted improvement methods fall into two categories: (1) increasing the absorption wavelength by doping and (2) adding electron capture agents for effectively separating generated electrons and holes. Novel photocatalysts, P-NMs, have been proposed. Among them, composites of precious metals and semiconductor metals are the most commonly considered P-NM photocatalysts. LSPR is a characteristic of P-NMs, which can extend the absorption range of light into the visible range. Moreover, the plasmonic effect of P-NMs can enhance the collection of visible light, extend the lifetime of charge carriers, improve the connection between electron and hole pairs, and stimulate the potential of redox reactions.

Plasmonic Au/TiO₂ NPs synthesized by Yuan et al. were demonstrated to have perfect heterogeneous interfaces [171]. Related characterizations have also been carried out, including using HRTEM, X-ray photoelectron spectroscopy, Fourier-transform infrared, and PEC tests. A linear scanning voltammetry test (scanning rate, 20 mV/s; light intensity, 110 mW/cm²; xenon lamp power, 150 W) was performed for comparing the photocatalytic activities of TiO₂ NPs and plasmonic Au/TiO₂ in response to the UV-vis light irradiation. Figure 10a and b clearly shows that plasmonic Au/TiO₂ NPs exhibit better photocatalytic activity and corrosion resistance than TiO₂ NPs. In addition, the photocatalytic activity of this P-NM was shown to depend on the distance between Au and TiO₂. In addition to noble metal and semiconductor metal composite materials, nonnoble metal, semiconductor metal composite materials, and single-metal materials also have potential as P-NM photocatalysts. Sang et al. synthesized TiO₂ nanotube arrays decorated with plasmon Cu, using the electrodeposition approach [151]. Cu plasmons enhanced the collection of visible light and increased the photocurrent density. Dadhich et al. made a simple modification based on a previously proposed synthesis method for plasmon photocatalyst HAgNC. The catalytic efficiency of the finally synthesized HAgNC-630 in sunlight was 3.3-fold higher than that of solid Ag nanospheres [119].

The above review suggests that based on the photoelectric catalytic performance of P-NMs, they can be suitably used in energy applications. In fact, P-NMs not only serves as good photoelectric catalysts but can also be used as energy-storing materials. The plasmonic effect of precious-metal-based nanomaterials can be utilized in energy storage devices, such as solar cells and supercapacitors, for improving their performance. Yang et al. [167] doped plasmonic Au NPs based on CsPbBr₃ perovskite nanotubes and found that the LSPR effect of the plasmonic Au NPs significantly improved the optical performance of the CsPbBr₃ perovskite nanocubes. Therefore, hybridization of perovskite halides with P-NMs is promising for improving the performance of photovoltaic devices (such as solar cells and supercapacitors). Deng et al. successfully embedded synthesized Au@Ag@SiO₂ NCs into a perovskite film of a perovskite solar cell (Figure 10c–f) [108]. Clearly, as Figure 10 shows, the original perovskite surface was not dense and was very rough. Following the embedding of Au@Ag@SiO₂ NCs, the roughness and density of the perovskite surface significantly improved. Interestingly, with increasing the amount of Au@Ag@SiO₂ NCs, the improvement of the perovskite surface became more obvious. These results clearly show that embedding of plasmonic metal NPs strongly enhances the absorption of induced light and carrier separation ability, thereby increasing the photocurrent density and improving the performance of perovskite solar cells. Javed et al. synthesized Ag/rGO/TiO₂ anode materials using solvothermal methods. Owing to the LSPR effect of these materials, the performance of plasmon dye-sensitized solar cells improved [81]. In addition to precious-metal-based P-NMs, nonprecious-metal-based P-NMs were also considered for energy applications. Smith et al. synthesized plasmonic aluminum NPs using the solution method and studied the plasmonic energy transfer kinetics [172]. It was found that the transient optical response of plasmonic aluminum NPs is mainly determined by the evolution of the scattering cross-section, compared with plasmonic precious-metal-based NPs. Interestingly, a dual interface model suggested that the natural oxide layer of these plasmonic aluminum NPs caused rapid heat transfer. Subramanyam et al. synthesized Bi-rGO/ BiVO₄ supported by plasmonic Bi NPs, and adapted them for anode applications and PEC water splitting [123]. Owing to the surface plasmon behavior of Bi NPs, the resultant composite electrodes exhibited excellent energy conversion.
efficiency, high current density, and low charge transfer resistance.

5 Conclusions and outlook

Compared with ordinary nanomaterials, P-NMs exhibit better performance and are very promising. Thus, in this article, we provided a brief overview of P-NMs. We summarized the relevant recent literature on metal-based P-NMs and carbon-based P-NMs. We showed that metal-based P-NMs exhibit excellent physical and chemical properties. In particular, their plasmon optical properties have garnered significant attention. Metal-based nanomaterials have important applications in the fields of biomedicine, sensory detection, surface-enhanced active bases, and environmental monitoring due to their SPR absorption characteristics. The first materials considered for metal-based P-NMs were the two precious metals, Au
and Ag. Noble metal-based materials have high density of free electrons; thus, plasmonic noble metal-based nanomaterials have been a research focus. However, precious metals also have disadvantages, such as low supply, high cost, and optical loss due to transitions between bands. Moreover, in subsequent research, it was found that non-precious metal-based materials also have very good properties. Therefore, attention has been slowly switching to nonnoble-metal-based P-NMs. In addition, due to its good stability, electrical conductivity, mechanical strength, and thermal conductivity, carbon is becoming increasingly valuable for carbon-based P-NMs. The main types of considered carbon materials are graphene and CNTs.

For next-generation P-NMs, reduced production cost and increased scalability are equally crucial to ensure excellent energy storage and conversion performance. The construction of functional P-NMs can be controlled by simple methods. The main synthesis methods of P-NMs are the reduction, one-pot, template, seed-mediated, deposition, solvothermal, and self-assembly methods. We mainly reviewed the synthesis methods of metal-based P-NMs. These methods are heavily biased toward the reduction, one-pot, template, and seed-mediated methods. Both the reduction and one-pot methods have the advantages of simple synthesis and easy realization, but they also suffer from poor uniformity of the synthesized particles’ sizes. The template method is a recently developed synthesis method and has the characteristics of diversity and easy construction. However, its template efficiency is not sufficiently high due to its poor stability; the seed-mediated method is relatively better. Seed-mediated method can provide amazing control over the size, shape, composition, and structure of nanocrystals.

Many effects have been discovered for P-NMs, such as the SPR effect, the LSPR effect, the SERS effect, the PRET effect, and the MO effect. Among these, the enhancement of the SERS and LSPR effects can significantly improve the performance of P-NMs. As a result, P-NMs exhibit excellent optical, magnetic, chemical, and mechanical properties. The present review focused on the optical and magnetic properties of P-NMs, and we discussed the utility of the optical properties for energy applications. When a synthesized NC material is excited by a light source, the formed plasmon thermal electrons can be transferred to the NC material, thereby increasing the number of catalytic active sites, potentially enhancing the charge density inside the material, and improving the electron transport speed, thus improving the material’s photoelectric catalytic performance. Although the number of proposed thermochemically induced photochemical synthesis materials is constantly increasing, there are still only a few reports on plasmon-enhanced electrochemical catalysis and its reactions. Moreover, at present, there is still little research on the novel methods of synthesizing P-NMs and their energy applications. However, when P-NMs act as photoelectrocatalysts, the advantages of multiple catalytic active sites and faster electron transmission speed still have good market prospects in the energy field.

In summary, this review provides an introduction to the types and synthesis methods of P-NMs, the characteristics of P-NMs, and the energy applications of P-NMs. Although the materials have exhibited good performance, there is still a long way to achieve industrialization and commercialization of these materials. Cost is the fundamental problem to hinder industrialization and commercialization of these materials that complex synthesis is an important reason. We hope this review can provide an insight to identify new technique to determine the potential of P-NMs with different compositions and help researchers find easier approach to obtain these nanomaterials.

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