Heterostructures Built through Site-Selective Deposition on Anisotropic Plasmonic Metal Nanocrystals and Their Applications

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1. Introduction

Noble metal nanocrystals (NCs) exhibit rich localized surface plasmon resonance (LSPR) properties in response to electromagnetic excitation.[1–3] LSPR arises from collective, coherent oscillations of metal-free conduction band electrons that are confined by the NC surface. Such NCs exhibit strong absorption and scattering, as well as near-field enhancement at LSPR wavelengths. These unique LSPR properties enable plasmonic metal NCs to be promising candidates in enormous applications such as chemical and biological sensing, light-driven catalysis, surface-enhanced spectroscopies, and optical antennas.[4–9] Different plasmonic NCs with distinct properties fit different applications. Fine tailoring of the NC shape, size, structure, composition, and functionalization is hence required. For instance, the longitudinal LSPR wavelength of Au nano-rods (NRs) can be continuously tuned from the visible to infrared region to meet the needs of optical and optoelectronic devices working at various spectral ranges by synthetically changing their length-to-diameter aspect ratio.[3,10] A combination of plasmonic NCs with other functional materials opens up more possibilities. Integrated heterostructures that have been produced include core@shell and yolk@shell nanostructures with plasmonic NCs as the immovable and movable cores, respectively, as well as hybrid nanostructures with the functional material decorated at the specific sites of the plasmonic NC.[11,12] Each component plays a complementary role in producing multifunctionality. For example, bimetallic Au–Pd nanostructures possess simultaneously distinct plasmonic and catalytic activities.[13] Moreover, heterostructures can support strong synergistically enhanced or other new physicochemical properties that are not accessible by the single components alone, such as the tandem effect, enhanced catalytic activity and selectivity, and harvesting of energetic plasmonic hot charge carriers.[11,12,14–16] The relative spatial arrangement of the constituent components can remarkably affect the heterostructure properties, as the plasmonic near field around the metal NC can be very anisotropic and affected by the surrounding medium. In particular, the physical and chemical properties of heterostructures...
constructed from anisotropic plasmonic NCs, such as NRs, nanowires, and branched NCs, are strongly dependent on their morphology.\textsuperscript{(17)} For example, bimetallic heterostructures with Pt nanoparticles grown on the edges of Au triangular nanoprisms exhibit 3–5 times higher catalytic activity than the counterpart heterostructures with Pt nanoparticles grown on the tips and randomly covering the entire surface of the Au nanoprisms.\textsuperscript{(19)} Site-selective deposition of functional materials on plasmonic NCs with precise control of the deposition site is therefore of great significance. In addition, heterostructures with the functional material selectively placed in the different sites of the plasmonic NC are sometimes more advantageous than the corresponding closely packed core@shell nanostructures, because they not only enable strong plasmonic light confinement, but also expose all the components to the surrounding environment.\textsuperscript{(19,20)} For instance, selectively growing CeO\textsubscript{2} at the two ends of Au NRs makes the resultant heterostructures exhibit much higher catalytic activity than Au NRs fully coated with CeO\textsubscript{2}. The higher catalytic activity is believed to result from the enhanced efficiencies of both light harvesting and electron–hole separation.\textsuperscript{(19)} Selective growth of Ag nanoparticles on the branch tips of Au nanostars creates interior plasmonic hotspots where the electromagnetic field is greatly enhanced, allowing the heterostructures to exhibit greatly improved surface-enhanced Raman scattering (SERS) performance.\textsuperscript{(21)} To date, tremendous effort has been made on the fabrication of anisotropic heterostructures composed of plasmonic NCs and other functional components and the study of their enhanced performances in diverse fields, highlighting the importance of selective deposition of a secondary material on the specific sites of plasmonic NCs.\textsuperscript{(12)}

This review is aimed to comprehensively introduce and discuss the recently developed synthetic strategies of heterostructures with the functional material site-selectively deposited on anisotropic plasmonic metal NCs, the unique properties of such heterostructures, and their emerging applications in plasmon-enhanced spectroscopies, catalysis, biomedical technologies, and so on. We will start from the introduction of anisotropic noble metal NCs and their unique plasmonic characteristics. Various types of anisotropic heterostructures composed of different deposition materials will then be discussed. The deposited materials include metals, semiconductors, and dielectric materials like polymers and insulators. The versatile synthetic strategies and the corresponding applications of the site-selectively deposited anisotropic heterostructures will be presented in detail. In the end, we will highlight the pros and cons of these anisotropic heterostructures, as well as point out the perspective and development of this research field. We note that there have been several related review articles, which are devoted to the architectural design of heterogeneous metallic nanostructures, the synthesis and optical properties of hybrid and alloy plasmonic nanoparticles, and the synthetic techniques and corresponding applications of bimetallic nanostructures.\textsuperscript{(22–24)} While these previous articles have mainly focused on heterostructures based on the deposition of metals, we try to expand the related research field. This review article is therefore aimed at the exploration and discussion of heterostructures with site-selectively deposited materials ranging from metals to nonmetallic materials.

2. Anisotropic Plasmonic Metal NCs and Their Heterostructures

Isotropy means uniformity in all directions, while anisotropy refers to a property that exhibits directionally dependent features. Isotropic NCs show identical physical and chemical properties in all directions because of their isotropic geometry and composition. In contrast, anisotropic materials display much richer physical and chemical properties because of their direction-dependent morphology, composition, or material properties. Specifically, engineering the anisotropy of noble metal NCs is a powerful strategy to tailor their plasmonic properties for various applications. The attractive physical and chemical properties of plasmonic metal NCs depend on the type of motion their electrons can execute, which is determined by the degree of the spatial confinement of the electrons.\textsuperscript{(22)} The shape of the anisotropic NCs therefore strongly affects the NC physicochemical properties. For example, plasmonic anisotropic metal NCs exhibit polarization-sensitive optical resonance. In addition, these anisotropic metal NCs can function as seeds in aqueous solutions that direct selective growth of a second material on their specific facets and sites, as different facets and sites are of different surface energies and present varying ligand packing densities that result from the surface curvature.\textsuperscript{(13)}

Due to the aforementioned features, anisotropic plasmonic metal NCs have been widely investigated for biological, catalytic, and spectroscopic applications. These plasmonic NCs include NRs, nanocubes, nanobipyramids, nanostars, nanoparticles, and more irregularly branched structures (Figure 1).\textsuperscript{(3,25–29)} The anisotropic geometry of such NCs provides additional freedoms for the construction of supramolecular assemblies.\textsuperscript{(3,30)} In contrast to their spherical counterparts, anisotropic noble metal NCs usually support rich LSPR features.\textsuperscript{(3,31,32)} For example, elongated, rod-like noble metal NCs such as NRs and nanobipyramids exhibit both longitudinal and transverse LSPRs, which correspond to the electron oscillations along and perpendicular to the length axis of the elongated NCs, respectively, and can be excited by light of different polarizations.\textsuperscript{(3,10)} In addition, the longitudinal LSPR wavelength of rod-like noble metal NCs can be continuously tailored from the visible to near-infrared (NIR) region by synthetically changing the NC length-to-diameter aspect ratio.\textsuperscript{(3,33,34)} Such tunability in LSPR wavelength perfectly meets the needs of biological imaging and therapy applications that require plasmonic responses in the first and second biological transparent windows.\textsuperscript{(35,36)} For instance, the longitudinal LSPR wavelength of Au nanobipyramids can be extended to the second NIR (NIR-II) window (1100–1400 nm) with improved photon penetration in tissues, making Au nanobipyramids promising contrast agents for enhanced optical coherence tomography.\textsuperscript{(17)} In addition, anisotropic NCs with sharp tips, such as nanostars, nanotriangles, or nanobipyramids, exhibit huge near-field enhancement at the tips, enabling the utilization of such NCs for enhanced Raman scattering and study of nonlinear optical properties.\textsuperscript{(38–41)} Moreover, the anisotropic feature affects the catalytic activity of NCs. Plasmonic metal NCs with an anisotropic shape generally offer more active catalytic sites due to the existence of atomic steps, edges, and kinks.\textsuperscript{(42,43)} They also support superior electric field enhancement and optical cross...
sections, leading to increased light absorption and improved generation of hot charge carriers resulting from plasmon decay. As a result, hybrid nanostructures prepared by depositing Pt and Pd on anisotropic plasmonic NCs show enhanced catalytic activity.\[44,45\]

Heterostructures contain two or more components that play complementary and/or synergistic roles in producing multifunctionality. Isotropic plasmonic heterostructures combine isotropic plasmonic NCs with one or more other components that are arranged uniformly, showing identical properties in all directions. Different from them, anisotropic plasmonic heterostructures are composed of plasmonic NCs and other components in a low-symmetry arrangement. In this review, we will mainly discuss on the heterostructures built from plasmonic NCs with anisotropic shapes. Because of the rich properties of their plasmonic component, these anisotropic heterostructures have been widely explored for applications ranging from catalysis and biomedical sensing to medical therapy.\[20\]

3. Different Deposition Materials

Various types of materials, including metals, semiconductors, and dielectric materials like polymers and insulators, have been deposited on anisotropic plasmonic metal NCs. The different deposited materials endow plasmonic NCs with additional physical and chemical properties as well as diverse functionalities, broadening their applications in the fields of self-assembly, biosensing, photocatalysis, nanomanipulation, and so on.

3.1. Metals as Deposition Materials

Metals that have been selectively deposited on the specific sites of anisotropic plasmonic NCs include plasmonic metals (Cu, Ag, Au),\[21,46–49\] catalytic metals (Ru, Pd, Pt),\[18,44,45,50–53\] magnetic metals (Fe, Co, Ni),\[54,55\] and metal alloys such as AgPd, AgPt, and CoFe (Figure 2a–d).\[46,49,55–58\] The deposited metal or alloy improves the plasmonic performance of the anisotropic plasmonic metal NC core or introduces additional functionality like catalytic activity and magnetism.\[59\] The bimetallic or multimetallic nanostructures not only integrate two or more properties within one nanoarchitecture, but they also show novel and enhanced properties resulting from synergistic effects, which are not found in the metal NC core or the deposited material. These unique characteristics have enabled the bimetallic or multimetallic systems to have improved performance in a wide range of applications such as catalysis, sensing, enhanced spectroscopy, bioimaging, and photothermal therapy.\[21,44,59–61\] The physico-chemical properties of the obtained heterostructures are highly dependent on the spatial arrangement and atomic ordering of different metal atoms. For example, Au NRs with Pt nanoparticles selectively deposited at the NR ends show a higher H$_2$ evolution rate than the Au NRs fully covered with Pt.\[45\] The spatial separation of the reduction and oxidation sites leads to efficient charge separation and, as a result, an improved H$_2$ production rate. In a very recent work, AgPt nanoparticles are selectively deposited at the different sites on Au nanocups.\[62\] Au nanocups with AgPt deposited at the opening edge and bottom exhibit the highest photocatalytic activity. In addition, some dimer heterostructures, such as Au–Au, Au–Ag, Au–Cu, and Ag–Cu...

Figure 1. Transmission electron microscopy (TEM) images of anisotropic plasmonic metal NCs with various shapes. a) Au NRs. b) Au nanobipyramids. c) Au hexagonal nanoplates. a–c) Reproduced with permission.\[29\] Copyright 2019, American Chemical Society. d) Au nanostars. Reproduced with permission.\[26\] Copyright 2012, IOP Publishing. e) Ag nanocubes. Reproduced with permission.\[27\] Copyright 2013, American Chemical Society. f) Au nanotriangles. Reproduced with permission.\[24\] Copyright 2014, American Chemical Society.
nanoparticle dimers, have been successfully synthesized.\textsuperscript{[63–67]} These heterostructures exhibit improved properties due to the coupling effects. For instance, Ag–Cu nanodimers exhibit a 3.4 times enhancement in the Faradaic efficiency for $\text{C}_2\text{H}_4$ and a twofold enhancement in the partial current density for the CO$_2$ reduction reaction, compared with the pure Cu nanoparticle counterpart.\textsuperscript{[65]} Moreover, monometallic (Au NR)–(Au nanoparticle) dimers show ideal blackbody absorption at 98–99% in the spectral range from 400 to 1400 nm.\textsuperscript{[68]} These results indicate that accurate control over the deposition site of the metal on anisotropic plasmonic metal NCs is vital to the heterostructure performance. In addition to the deposition site, the number and morphology of the deposited metal will also affect the performance of the heterostructures.

### 3.2. Semiconductors as Deposition Materials

Semiconductors are another type of important materials that are deposited on anisotropic plasmonic metal NCs. Different semiconductors, including metal oxides, sulfides, and selenides, such as TiO$_2$, CeO$_2$, Cu$_2$O, Ag$_2$O, Ag$_2$S, Cu$_7$S$_4$, CdSe, and AgCdSe, have been selectively deposited at the specific sites on Au and Ag NCs (Figure 2e–h).\textsuperscript{[19,69–74]} The LSPR of the plasmonic NC core can greatly enhance the absorption and therefore the photogeneration of electron–hole pairs in the semiconductor component. The metal–semiconductor interface further facilitates the separation of photogenerated charge carriers. As a result, the heterostructures bring an improved harvesting capability of the incident light energy, exhibiting enhanced photothermal conversion and photocatalytic activities.\textsuperscript{[20,72,74]} In addition, the heterostructures can overcome the cytotoxicity and low photothermal stability of the bare colloidal noble metal NCs. For instance, Au NR–Cu$_2$–S heterostructures show an excellent photothermal conversion efficiency, while at the same time exhibit low cytotoxicity and good photothermal stability.\textsuperscript{[74]} In addition, at the metal–semiconductor interface, hot charge carriers induced through the plasmon decay on the plasmonic metal NCs can transfer to the semiconductor conduction or valence...
3.3. Insulating Dielectric Materials and Molecules as Deposition Materials

Apart from metals and semiconductors, insulating dielectric materials and molecules, as well as hybrids of different materials, have also been deposited on anisotropic plasmonic metal NCs through site-selective functionalization. The deposited materials include polymers like polystyrene-poly(acrylic acid), poly(ethylene oxide),\(^{78-81}\) and polyaniline,\(^{82}\) SiO\(_2\),\(^{80,83,84}\) and hybrid materials such as SiO\(_2\)-Pt and TiO\(_2\)-Pt (Figure 2i-1).\(^{52,85}\) Polymers and SiO\(_2\), the deposition sites of which can be controlled by the surfactant capped on the NC core surface or heating, can serve as the templates for the further site-selective deposition of other materials. For example, with the help of a polymer, Ag can be selectively deposited on the exposed surface of Au nanobipyramids and triangular nanoflakes.\(^{79}\) In addition, the deposition of polymers and SiO\(_2\) improves the stability and biological compatibility of colloidal plasmonic metal NCs.\(^{52}\) The deposition of the hybrids of different materials on plasmonic metal NCs to form ternary heterostructures enables synergistic effects that enhance the heterostructure performance. A ternary type of heterostructures has been constructed out of Au NRs, TiO\(_2\), and Pt nanoparticles, where the TiO\(_2\) components are deposited at the NR ends and the Pt nanoparticles are deposited on the side of the NR core.\(^{85}\) The obtained ternary heterostructures exhibit an enhanced photocatalytic activity of H\(_2\) production, with the H\(_2\) evolution rate being 4.3 times than that achieved by Au–TiO\(_2\) dumbbell-like heterostructures without Pt decoration. The enhanced photocatalytic activity is attributed to the efficient migration and injection process of the plasmonic hot electrons generated in the NR core.\(^{85}\) Moreover, site-selective deposition of polymers and biomolecules on anisotropic plasmonic metal NCs is an effective approach for constructing supramolecular plasmonic assemblies.\(^{80,81,86}\)

4. Synthetic Strategies

Seed-mediated growth is a commonly utilized wet chemistry synthesis method that produces a variety of NCs though regulation of the thermodynamic parameters and growth kinetics in liquid media.\(^{11,87}\) This synthetic approach is applicable to the synthesis of single-component NCs and hybrid NCs with lattice-matched components, while it is generally challenging to deposit on the seed a second material whose lattice is largely mismatched with that of the seed. Anisotropic NCs are enclosed by different crystalline facets that have varying surface energies and surface curvature-determined ligand packing densities. A second material is therefore preferentially deposited on facets with high surface energies.\(^{12,20}\) To finely adjust the morphology of the obtained heterostructures, it is essential to control both the shape of the seeds and the reaction kinetics.\(^{12}\) The deposition process can be controlled by varying the synthetic parameters such as the reaction duration, precursor concentration, type, and concentration of the capping agent. Various routes have recently been developed for the preparation of anisotropic heterostructures, including galvanic replacement, capping agent-directed synthesis, surface-protected growth, selective etching, welding-induced synthesis, and so on. These strategies are discussed in this section.

4.1. Galvanic Replacement Reaction

The galvanic replacement reaction is a versatile approach for the synthesis of multimetallic heterostructures for applications ranging from catalysis to biomedical studies.\(^{88}\) The galvanic reaction is an electrochemical process. It involves the oxidation of one metal that serves as a sacrificial template, by the ions of another metal.\(^{89}\) The electrochemical reaction is driven by the difference in the electrical reduction potential between the sacrificial template and the metal ions in the solution. During this process, the oxidation and dissolution of the templating metal are accompanied by the reduction of the ions of the metal to be deposited from the solution. The second metal is therefore deposited at the surface of the templating metal to form multimetallic heterostructures.\(^{90-93}\) The morphology, internal structure, and composition of the resultant heterostructures can be controlled by varying the molar ratio between the reactants, shape of the seed template, and temperature.\(^{88,89,94}\) In general, during the galvanic replacement reaction, the deposition of the second metal tends to occur from the specific sites of the template due to the difference in the chemical reactivity and/or the ligand shielding of the template surface.\(^{91}\) The second metal, therefore, can be deposited at the specific sites of the template through control of the reaction conditions.

In the past decade, the galvanic reaction has been widely used to prepare bimetallic heterostructures based on Au, Pd, and Pt, using Ag as the sacrificial template.\(^{46,56,58}\) A silver shell is found to be crucial for site-selective deposition of a second metal on pregrown plasmonic metal NCs.\(^{56,99,96}\) For instance, the Au–AgPd heterogeneous metal NCs are made by electrochemical or chemical reduction of the Ag layer that is precoated on Au NCs in the presence of a Pd precursor (Figure 3a).\(^{117}\) During the process, the oxidation of the Ag layer leads to the release of electrons,
which are accumulated at the corners or edges of the Au NC due to the high curvature. The Pd precursor is reduced and deposited preferentially at the electron-rich regions. Pd atoms are therefore selectively deposited at the corners or the edges of the Au NC (Figure 3a). Such a strategy is also applicable to Au NCs with various shapes, such as Au NRs and nanobipyramids. Furthermore, the galvanic replacement reaction can be coupled with coreduction, coprecipitation, Ostwald ripening, and Kirkendall processes to generate nanostructures with greatly increased complexity. For instance, different morphologies of (Au NR)–AgPd, including dumbbell-, dandelion-, and lollipop-like structures, have been produced through a galvanic replacement reaction combined with Ostwald ripening (Figure 3b). A dumbbell-like structure is obtained at low AgNO₃ concentrations. As the amount of added Ag⁺ ions is increased, the Ostwald ripening effect during the galvanic replacement reaction combined with the coreduction process drives AgPd from one end to the other, forming a dandelion structure. As the amount of the reductant, ascorbic acid, is increased, the nanodandelion structures are transformed to

Figure 3. Heterostructured metal NC (HMNCs) prepared by galvanic replacement reactions. a) Corner- and edge-selective deposition of AgPd satellite NCs on central Au NCs. Left: Schematic of the growth process. Middle: Scanning electron microscopy (SEM) images. Right: TEM images. Reproduced with permission. Copyright 2013, Springer Nature. b) Dumbbell-, lollipop-, and dandelion-like nanostructures formed by site-selective deposition of AgPd on Au NRs. Top: Schematic of the growth process. Bottom: TEM images. Reproduced with permission. Copyright 2016, Royal Society of Chemistry. c) AgPd-tipped Au nanobipyramids. Top: Schematic of the growth process. Bottom: TEM images. Reproduced with permission. Copyright 2017, American Chemical Society.
lollipop structures. In a similar manner, AgPd- and AgPt-tipped Au nanobipyramids have been produced by first growing a silver layer on Au nanobipyramids and then conducting galvanic replacement reactions (Figure 3c).\cite{46}

The galvanic replacement reaction approach has been widely used for site-selective deposition of a second metal on the surface of pregrown plasmonic metal NCs. Although it is generally challenging to precisely control the deposition site and multiple steps are usually required, this approach allows to produce heterostructures in high yields. In addition, by combining with other processes, this approach can result in heterostructures with sophisticated architectures. Despite the advantages mentioned earlier, we would also note that a sacrificial template material is always needed, which limits the type of heterostructures that can be constructed.

4.2. Capping Agent-Directed Synthesis

Seed-mediated synthesis is the most prevalent methodology for the preparation of NCs with various shapes and compositions. However, in most cases, site-selective deposition does not occur and growth of the second component occurs at all sites on the seed NC. In addition, encapsulation is difficult to be well controlled due to lattice mismatch. It is often challenging to finely control growth at the specific sites of the seed NC. The use of different capping agents on the seed surface is an effective approach for control of the nucleation and growth of a second material in a site-specific manner. The capping agent can selectively bind to the specific facets of anisotropic NC, leading to a remarkable difference in surface energy and improving the interfacial interactions of dissimilar materials.\cite{59,87} Such a difference can allow for the manipulation of the deposition site of a second material on the anisotropic NC seed, as the heterogeneous nucleation of the second material on the plasmonic NC is more favorable than homogeneous nucleation. A very recent study has demonstrated that by appropriate ligands, distinct nucleation energy barriers for secondary nucleation ($E_f$) at the different sites can be introduced on anisotropic NC seeds and the chemical potential of the growth solution can be tailored, leading to site-selective deposition (Figure 4a,b).\cite{48} For example, for a triangular Au nanoprism, the density of the ligand adsorbate varies at different sites with different curvatures. A higher curvature results in a larger average distance ($\delta$) between the ligand molecules. When ligand adsorbates with high binding affinities, such as mPEG6 disulfide, are used, surface sites with higher curvatures and larger $\delta$ values permit easier access to the growth solution for subsequent deposition, leading to lower $E_f$ values at these surface sites. The general trend of the $E_f$ profile for NC growth illustrates the nucleation energy barriers at the corners, edges, and facets, $E_c$, $E_e$, and $E_f$, which follow $E_c < E_e < E_f$. As a result, through the tuning of the supersaturation ($\Delta \mu$) of the growth solution to surmount a certain $E_f$ value by changing the concentration of the reductant ascorbic acid, overgrowth can be well controlled at the corners ($E_c < \Delta \mu < E_e$) and edges ($E_e < \Delta \mu < E_f$) of the triangular prisms, respectively.

The capping agent-directed synthesis approach has been successfully used in site-selective growth of Pt, SiO$_2$, Fe$_3$O$_4$, TiO$_2$, and Cu$_2$O on anisotropic Au NCs.\cite{20,45,52,70,97} The commonly used capping agents include organic ligands (e.g., thiols and amines), surfactants (e.g., cetyltrimethylammonium bromide [CTAB] and sodium dodecyl sulfate [SDS]), polymers (e.g., poly(vinylpyrrolidone) [PVP], poly(acrylic acid) [PAA]), and biomolecules (e.g., peptides).\cite{19,98,99} By this method, Cu$_2$O has been deposited on the different sites of Au hexoctahedral (HOH) NCs (Figure 4c,d).\cite{70} Three types of hetero-NCs (HNCs) are obtained. When PVP is added, Cu$_2$O is deposited on the eight vertexes of the NC that point toward the <111> directions. When a binary mixture of CTAB and SDS is used, the NC surface is covered with Cu$_2$O, except that the eight <111>-oriented vertexes are exposed. When SDS is added, the entire surface of the NCs is covered with Cu$_2$O, that is, (Au core)(Cu$_2$O shell) HNCs are formed. The different architectures are attributed to the difference in the stabilization habit of the surfactants used in the synthesis. In another work, anisotropic overgrowth of TiO$_2$ on the ends of Au NRs using alkyltrimethylammonium bromide (CTAB, n = 12, 14, 16) as the surface-capping agent has been demonstrated.\cite{20} As the surfactant is more densely packed on the side of the Au NR than at the tips, the tips of the Au NR are easier to be accessed by the Ti species, which is obtained by controlling the hydrolysis of TiCl$_4$ through the solution pH or adding NaHCO$_3$ in the reaction solution (Figure 4e,f). The concentration of the surfactant is critical for the formation of the TiO$_2$-tipped Au NRs. For example, when the C$_{16}$TAB concentration is below its first critical micelle concentration (CMC) (0.89 mM), the surfactant bilayer is unstable and easily disrupted, which leads to the coating of TiO$_2$ on the entire Au NR surface. When C$_{16}$TAB concentration is above its second CMC (20 mM), the densely packed surfactant bilayer results in products with only one tip coated or not coated at all. A C$_{16}$TAB concentration in between is therefore appropriate for the preparation of TiO$_2$-tipped Au NRs in high yields. In addition, the shorter hydrocarbon chains of C$_{16}$TAB and C$_{12}$TAB provide weaker hydrophobic interaction among the molecules, which allows for the Ti species to access the catalytic Au surface more easily than C$_{16}$TAB. The yield of the Au NRs that are tip-selectively deposited with TiO$_2$ hence becomes much higher at the optimized surfactant concentration.

Capping agent-directed synthesis is an effective method for site-selective deposition of various materials onto pregrown plasmonic metal NCs. In contrast to the galvanic replacement reaction, this method works for the overgrowth of metals, semiconductors, insulators, and polymers at the specific sites on the core NCs. Nevertheless, it is not an easy task to find an appropriate capping agent, which is the key factor for producing heterostructures with site-selective deposition in high yields by this method.

4.3. Surface-Protected Growth

Surface-protected growth is another versatile approach for selective deposition of a second material on the specific sites of pre-synthesized seed NCs. In this approach, the surface of the seeds is first partially covered with a “protecting agent,” which prevents the access of the growth solution.\cite{112} The commonly used protecting agents include soft agents (e.g., polymers) and hard agents (e.g., silica).\cite{100,101}
4.3. Polymers as Protecting Agents

Polymers have been widely utilized to protect the surface of seed NCs for anisotropic growth of a second material. The most frequently used polymers include thiol-terminated poly(ethylene oxide)-b-polystyrene (PEO-b-PS), polystyrene-b-poly(acrylic acid) (PS-b-PAA), and thiol-terminated polyethylene glycol (HS-PEG).[44,79,83,102] For instance, a polymer shell of PS-b-PAA has been coated on Au NRs. The polymer shell can contract into specific domains through heating in water.[79] The morphology of the (Au NR)-PS-b-PAA heterostructures can be precisely controlled by adjusting the temperature and reaction time. Because of the blockade of PS-b-PAA on the Au NRs, Ag can be selectively deposited on the partially exposed Au NR surface through the reaction between AgNO₃ and the reductant hydroquinone (Figure 4). The location of the deposited Ag is verified by elemental mapping based on energy-dispersive X-ray analysis (Figure 5b). In addition, more complicated nanostructures can be prepared through multistep reactions on the masked Au NRs. For example, a type of structure similar to a bolt with two nuts has been successfully produced by sequentially depositing Pd and Ag on the PS-b-PAA-coated Au NRs (Figure 5c).

During the masked synthesis, the first-step growth of Pd on the exposed NR ends induces further contraction of the polymer, causing a small gap between the Pd- and the PS-b-PAA-coated domains. Ag is therefore selectively deposited in the gap. Moreover, Ag can be selectively deposited on the tips of Au nanobipyramids (Figure 5d,e). By reducing the Ag reduction rate, Au nanobipyramids with one Ag tip can be produced. In addition, site-selectively deposited polymers on anisotropic plasmonic metal NCs can assist in the fabrication of nanoassemblies.[86]

4.3.2. Silica as a Protecting Agent

In addition to polymers, SiO₂ is another versatile protecting agent for selective deposition of a second material on plasmonic metal NCs. The silica block is a rigid, robust protecting layer.[52,101] An approach has been demonstrated for overgrowth of metals (Au, Ag, Pd, Pt) at the specific sites of Au NRs, which are partially blocked by SiO₂ (Figure 5f). At the first step, SiO₂ is selectively deposited at the two ends of the NRs, because the CTAB bilayer is less tightly packed at the NR ends with high curvature. Alternatively, SiO₂ is selectively deposited on the NR side surface when the two ends are blocked by thiol-terminated...
methoxypoly(ethylene glycol). Subsequent metal (M) deposition occurs on the exposed Au surface to give Au/end-SiO\textsubscript{2}/side-M and Au/side-SiO\textsubscript{2}/end-M nanostructures, respectively (Figure 5g–j).

Compared with galvanic replacement reaction and capping agent-directed synthesis, surface-protected growth allows for the control of the deposition site on plasmonic NCs more precisely. In contrast, this approach requires multiple steps and is limited by the selection of appropriate protection agents.

4.4. Other Synthetic Strategies

Apart from the aforementioned approaches, other methodologies have also been developed for the preparation of anisotropic heterostructures. Welding-induced synthesis and selective etching are two of the frequently used approaches. Welding-induced synthesis has been intensively investigated for the preparation of larger nanostructures through welding of small nanoparticles. The welding process is driven by the instability of NCs and the diffusion of metal atoms on the common crystalline facets of neighboring NCs.\cite{103,104} The early welding method based on oriented attachment is, however, largely limited to the same types of nanoparticles due to the requirement of lattice matching.\cite{12,105,106} So far, there have been only a few works on welding of dissimilar nanoparticles through a nonoriented attachment mechanism. For example, multicomponent Au–chalcogenide hybrid nanostructures with specific shapes and morphologies have been formed through welding of dissimilar Au and chalcogenide nanoparticles.\cite{104} After the mixture of citrate/PEG-functionalized Au nanoparticles with Ag\textsubscript{2}S nanoparticles that are modified with bovine serum albumin (BSA), Au–Ag\textsubscript{2}S oligomer-like hybrid nanostructures are formed through weak electrostatic attraction between the dissimilar nanoparticles and repulsion between the same types of nanoparticles (Figure 6a). During the process, atom diffusion between the Au and Ag\textsubscript{2}S domain occurs and the hybrid nanostructures are subsequently welded. The same method has been used to prepare Au–Ag\textsubscript{2}S matchstick-like hybrid nanostructures through welding of Au NRs and spherical Ag\textsubscript{2}S nanoparticles (Figure 6b). The Ag\textsubscript{2}S nanoparticles are selectively attached to the tips of the Au NRs because of the less tightly packed CTAB bilayer at the NR ends. In addition, Au–Ag\textsubscript{2}S tree-burl-like hybrid nanostructures have been obtained through welding of Au nanowires and spherical Ag\textsubscript{2}S nanoparticles (Figure 6c,d).

Selective etching after particle growth is a postsynthetic modification method for tailoring the morphology and aspect ratio of heterostructures. This approach has previously been successfully explored for etching noble metals, where mild oxidation of noble metals is realized by use of cysteamine, Au(III) complex ions, O\textsubscript{2}, and H\textsubscript{2}O\textsubscript{2}.\cite{16,107–109} In general, etching preferentially is initiated from the sharp tips of noble metal NCs.\cite{109} By varying the oxidation condition, the etching site can be well controlled. For example, (Au core)@(Ag shell) nanostructures can be transformed from nanocuboid to rice- and dumbbell-shaped nanoparticles through the surface etching process (Figure 6e–j).\cite{141} The nanocuboids are gradually etched to become the nanorices mainly

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**Figure 5.** Surface-protected growth. a) TEM images of the products obtained by selective deposition of Ag on (Au NR)@PS-b-PAA. Partial coating of the polymer is achieved by heating the core@shell nanostructures in water for 1.5, 2.5, and 4 h at 105 °C, 3 h at 110 °C, and 3 h at 115 °C, respectively (from left to right). b) HAADF–STEM image (left) and elemental mapping images of Au (middle) and Ag (right). Ag is deposited after the bimodal contraction of the core@shell nanostructures at 90 °C for 3 h. c) Nanostructures similar to a bolt with two nuts obtained by sequentially depositing Pd and Ag on the PS-b-PAA-coated Au NRs. Top: HAADF–STEM image (left) and elemental mapping images (right three). Bottom: TEM images and schematic models of two nanostructure samples with Pd segments of different lengths. d) Schematic models and TEM images of Au nanobipyramids with Ag deposited at one tip and two tips, respectively. e) Schematic model and TEM image of Au nanoprisms with Ag deposited at the vertexes. The nanostructures in (a–e) are all produced by polymer-protected growth. a–e Reproduced with permission.\cite{79} Copyright 2018, Springer Nature. f) Schematic showing SiO\textsubscript{2}-protected growth, where the predeposited SiO\textsubscript{2} at the ends and sides directs second growth of a metal on the side and ends, respectively. g–j) TEM images of the Au NR-based Au/end-SiO\textsubscript{2}, Au/end-SiO\textsubscript{2}/side-Pd, Au/side-SiO\textsubscript{2}, and Au/side-SiO\textsubscript{2}/end-Pd nanostructures, respectively. f–j) Reproduced with permission.\cite{142} Copyright 2013, Wiley-VCH.
due to preferential etching of the corners and edges in the presence of Cu\(^{2+}\), ascorbic acid, and cetyltrimethylammonium chloride (CTAC), as the Ag \{100\} facets are selectively stabilized by CTAC (Figure 6f–h). Different facet-selective etching is also observed to lead to the formation of dumbbell-shaped nanostructures, as preferential etching of the Ag \{100\} facets by Fe\(^{3+}\) is dominant in the presence of CTAB (Figure 6i,j).

Both welding-induced synthesis and selective etching work well for the preparation of some specific types of nanostructures while a sophisticated control of the processes remains challenging.

5. Applications

Hybrid nanostructures composed of plasmonic metal NCs and other components such as metals and semiconductors take advantage of LSPR-induced light absorption of plasmonic metal NCs and energy transfer to the adjacent components. Such characteristics can be used for a variety of plasmon-enabled or powered applications, including surface-enhanced Raman spectroscopy, plasmon-enhanced fluorescence, photocatalysis, plasmon-enhanced electrocatalysis, as well as phototherapy. In the following paragraphs, different applications based on anisotropic plasmonic heterostructures are discussed in detail.

5.1. Plasmon-Enhanced Spectroscopies

Compared with their isotropic counterparts, anisotropic plasmonic nanostructures possess better plasmon resonance tunability and larger local electromagnetic field enhancement (hotspots), which contribute to a variety of enhanced spectroscopic applications, such as surface-enhanced fluorescence, Raman scattering, and infrared absorption. Plasmonic NCs can function as optical nanoantennas to strongly transform the far field to the near field, which is beneficial to excitation of adsorbed molecules, as well as interfacial charge transfer between plasmonic NCs and probe molecules. Site-selective deposition of a second material on anisotropic plasmonic NCs provides additional advantages, such as offering larger electromagnetic field enhancement, exposing only electromagnetic hotspots, and preventing fluorescence quenching, which will be described as follows.

5.1.1. Surface-Enhanced Raman Scattering

A great variety of anisotropic plasmonic heterostructures have been developed for use in the enhancement of Raman scattering, which originates from strong mutual excitation-induced dipole in the molecule and that in the plasmonic NC. This phenomenon is well known as SERS. The SERS effect is dominantly ascribed to local enhancement of electromagnetic fields near the surface of plasmonic metal NCs, which can be scattered by probe molecules. The SERS enhancement factor is approximately proportional to the fourth power of the local field enhancement. Therefore, local field enhancement that is strongly affected by the morphology of anisotropic plasmonic heterostructures can bring huge impact on the SERS enhancement factor. In addition, charge transfer resonance can also arise from the electronic interaction between the molecular orbital and the metal conduction band and couple to the vibrational states of adsorbed...
molecules. This chemical mechanism gives rise to an additional SERS enhancement factor of $10^2$–$10^3$.[126] Anisotropic plasmonic metal NCs possessing sharp tips and corners can highly concentrate light into local electric fields. Electromagnetic hotspots, where the Raman signals of molecules can be greatly enhanced, are located typically at the sharp tips, corners, and interparticle gaps.[126,127] Anisotropic plasmonic heterostructures that are synthesized through selective overgrowth of a second component on anisotropic plasmonic metal NCs can have well-adjusted plasmon resonance wavelengths that match the excitation laser wavelength and/or the vibrational peak wavelengths of the probe molecule, providing dramatic enhancement in SERS activity.[115,128,129] For example, coating Ag on the surface of Au NRs continuously shifts the longitudinal dipole plasmon resonance of the NR. In addition, compared with the core@shell nanostructures, heterostructured anisotropic plasmonic metal NCs can produce richer plasmon modes and concentrate more light to their nanoscale edges, tips, and crevices for enhancement of the SERS signal.[21,56] If probe molecules are encapsulated within selectively deposited components, the molecules can approach closer to the tips and corners of anisotropic plasmonic metal NCs where the electromagnetic field is maximized.[126] For example, Au NRs with SiO$_2$ selectively deposited on the rod ends, which is realized through control of the molar ratio of CTAB to the precursor tetraethyl orthosilicate (TEOS) during the deposition process,[130] exhibit greater SERS enhancement factors for crystal violet than both of the bare, CTAB-capped Au NRs and the (Au core)/(SiO$_2$ shell) nanostructures (Figure 7a).

Furthermore, the nanogaps between the distinctive components of heterostructures can cause plasmon coupling and serve as electromagnetic hotspots for the great enhancement of the SERS activity.[131] In most plasmonic substrates for SERS, hotspots are generally generated through nanoparticle aggregation and self-assembly. These hotspots are called exterior nanogaps.[132,133] However, the generation of interior nanogaps within individual nanostructures provides more reproducible and reliable SERS signals. Anisotropic Au–Ag bimetallic nanostructures

![Image](https://example.com/image.png)

**Figure 7.** Plasmon-enhanced spectroscopies. a) Raman spectrum of crystal violet on dumbbell-like (Au NR)–SiO$_2$ heterostructures. The bands at 912, 1173, and 1379 cm$^{-1}$ arise from the ring skeletal vibrations, C–H in-plane bending vibrations, and N-phenyl stretching, respectively. The bands at 1535 and 1620 cm$^{-1}$ correspond to the ring C–C stretching vibrations. The inset shows the schematic model of the heterostructure. Reproduced with permission.[130] Copyright 2019, American Chemical Society. b) SERS enhancement provided by the interior hotspots generated by the gaps formed between Ag nanoparticles grown on the tips of Au nanostars. The samples 1–3 are the heterostructures obtained by adding AgNO$_3$ in different amounts during overgrowth. Sample 4 is the mixture of the Au nanostars and Ag nanoparticles. The molecule 2,5-bis[(1-(ethyl 5-(1,2-dithiolan-3-yl)pentanoate)-3,3-dimethyl-2,3-dihydroindole-2-yldiene)methyl]-cyclobutendiylium-1,3-diolate (named as M1) serves as both the selective capping agent and a SERS reporter. Reproduced with permission.[21] Copyright 2018, American Chemical Society. c) NIR fluorescence emission spectra of free NIR fluorophore CF790 and CF790 attached to Pt-end-deposited Au NRs (CF-PEA NRs). The fluorophore CF790 is attached to the Au NRs through PEG linkers. By varying the linker molecular weight from 1, 3.4, 5, to 10 k, the distance between the fluorophore and the Au NR can be varied. The strongest fluorescence signal is obtained in the CF$_{3k}$-PEA NRs with the PEG molecular weight of 5 k. d) NIR fluorescence images of MCF-7 cancer cells treated with free CF790 and the CF$_{3k}$-bPEA NRs for 6 h, respectively. CF$_{3k}$-bPEA means that the biocompatibility of the CF$_{3k}$-PEA NRs is improved through further biofunctionalization. c,d) Reproduced under the terms of the Creative Commons CC-BY license.[53] Copyright 2019, The Authors. Published by Wiley-VCH.
with interior hotspots have been synthesized through selective overgrowth of Ag nanoparticles on the tips of Au nanostars. The interior nanogaps in the obtained anisotropic Au–Ag bimetallic nanostructures can be well tailored through the change of the amount of the silver precursor AgNO₃. The SERS enhancement factor increases dramatically with the decrease in the nanogap size. Under 785 nm light excitation, the Au–Ag nanostructures display a maximal enhancement factor of 43 for the SERS signal, as well as better Raman signal reproducibility, compared with the bare Au nanostars (Figure 7b). In comparison with the result from the control experiment, the Au–Ag nanostructures with Ag deposited on the tips of the Au nanostars exhibit much larger SERS enhancement than a mixture of the Au nanostars and similarly sized Ag nanoparticles. This result indicates clearly that the Raman enhancement is originated from the ultrasmall nanogaps among the branches of each Au nanostar. Such nanogaps serve as the intensive hotspots for SERS.

5.1.2. Surface-Enhanced Fluorescence

In addition to Raman scattering, fluorescence can also be enhanced by anisotropic plasmonic heterostructures. The enhanced electromagnetic field induced by LSPR can promote energy transfer to adjacent fluorophores, leading to magnified fluorescence signals when the LSPR band of plasmonic nanostructures overlaps with the absorption and/or emission band of the fluorophore. In addition to energy matching between LSPR and fluorescence excitation/emission, the distance between plasmonic nanostructures and fluorophores also plays an important role in plasmon-enhanced fluorescence. The Förster radius, which is defined as the distance between a molecular donor and acceptor for 50% energy transfer efficiency, is in the range of 4–9 nm for typical organic fluorophores as donors and acceptors, whereas the spacing for fluorescence quenching when a fluorophore is placed close to a plasmonic nanostructure has been found to be roughly less than 5 nm. Capping plasmonic nanostructures with spacer materials is an effective approach for control of the distance between the plasmonic nanostructure and the fluorophore so as to achieve fluorescence enhancement. For instance, SiO₂ shells can generally serve as spacer layers to modulate fluorescence enhancement. Optimal fluorescence enhancement can often be obtained at the most appropriate shell thickness.

Polymers are also commonly used to control the distance between fluorophores and plasmonic nanostructures. For example, Au NRs with Pt deposited at the ends support large electromagnetic field enhancement at NIR wavelengths. A NIR fluorophore CF790 is attached to the Pt-end-deposited Au (PEA) NRs through PEG linkers for the enhancement of fluorescence intensity. PEG linkers with different molecular weights are used to control the distance between CF790 and the plasmonic nanostructure. The LSPR wavelength, 808 nm, of the plasmonic heterostructures matches the fluorescence emission band of CF790 at 806 nm. The confined electromagnetic field can promote energy transfer to the neighboring PEG-linked CF790 molecules, leading to NIR fluorescence amplification. When PEG linkers of different molecular weights are used, the hybrid nanostructures exhibit reduced or amplified fluorescence signals (Figure 7c). At the molecular weight of 1 k for the PEG linker, the nanostructures denoted as the CF₁k-PEA NRs show a reduced fluorescence intensity than the free CF790, whereas the other samples all give amplified fluorescence signals. The strongest fluorescence signal is obtained for the CF₅k-PEA NRs with the molecular weight of the PEG linker being 5 k. In vivo experiments also reveal that MCF-7 breast cancer cells treated with CF₅k-PEA NRs show the most remarkable fluorescence enhancement under NIR fluorescence microscopy (Figure 7d).

5.2. Catalysis

Site-selective deposition of nanomaterials with catalytic activities onto anisotropic plasmonic NCs can result in largely improved catalytic performance. The enhanced performance is mainly attributed to the combination of the advantages of plasmonic light harvesting, the catalytic properties of the deposited components, more active sites, and enhanced charge separation at the interface of the different materials. The applications of anisotropic heterostructures in photocatalysis, electrocatalysis, and plasmon-enhanced electrocatalysis are discussed in detail below.

5.2.1. Photocatalysis

Photocatalysis based on anisotropic plasmonic heterostructures has received significant attention due to the attractive integration of plasmonic metal NCs with semiconductors or other types of catalytic components. In such heterostructures, the plasmonic NC usually acts as a source to provide charge carriers, and the semiconductor or other material usually provides active sites for adsorbing and activating reactant molecules. The combination of plasmonic metal NCs and catalytic components significantly improves light absorption and therefore the photocatalytic activity of the latter, because the LSPR of the metal NC can concentrate light energy and the enhanced local electromagnetic field can boost electron–hole pair generation in the catalytic component. The heterostructures can also efficiently extend the photocatalytic activity of catalytic metals or semiconductors to the visible and even NIR region through the plasmonic hot carrier injection mechanism. Plasmonic hot charge carriers can overcome the Schottky junction barrier formed between plasmonic metals and semiconductors and are injected into the semiconductor even when the photon energy is smaller than the bandgap of the semiconductor. Conventional core–shell nanostructures bury the plasmonic metal NC core completely inside the shell, which prevents hot charge carriers that remain in the metal core from being accessible by reactant molecules when the other type of hot charge carriers are injected into the shell material and hence lower the photocatalytic activity. In comparison, anisotropic plasmonic heterostructures with both the plasmonic and catalytic components exposed are highly desirable. They allow both hot electrons and hot holes to be readily accessible by reactant molecules and participate in reactions simultaneously. Plasmonic metal NCs can function as plasmonic nanoantennas for efficient light harvesting, whereas site-selectively deposited catalytic components provide active sites for reactions. In addition, the
intimate interfacial contact between plasmonic metal NCs and site-selectively deposited components promotes effective electron transfer between the two components within a hybrid nanostructure.\textsuperscript{20,44}

Anisotropic plasmonic heterostructures exhibit great potential in a large variety of industry- and environment-based reactions, including H\textsubscript{2} generation,\textsuperscript{18,20,45,70,72,86,146} N\textsubscript{2} photofixation,\textsuperscript{19} reduction of 4-nitrophenol,\textsuperscript{57,147,148} dye photodegradation,\textsuperscript{69} Suzuki coupling,\textsuperscript{13,44} resazurin reduction,\textsuperscript{50} etc.

Hydrogen generation is one of the most frequently studied photocatalytic applications of anisotropic plasmonic heterostructures. Site-selective overgrowth of a second component, such as semiconductors and metals, enriches the plasmonic properties of metal NCs and broadens their applications in highly efficient H\textsubscript{2} generation.\textsuperscript{20} Cuprous oxide, a p-type semiconductor with a bandgap of \(\approx 2\) eV, was overgrown on the specific sites of HOH Au NCs that are enclosed with 48 triangular high-index \{321\} facets and offer a large number of vertexes (Figure 4c,d).\textsuperscript{70} Selective overgrowth of Cu\textsubscript{2}O on the HOH Au NCs is controlled through the judicious selection of surfactants. Among all the synthesized anisotropic HNCs, Au\textsubscript{core}–Cu\textsubscript{2}O, with Cu\textsubscript{2}O deposited at the vertexes of the HOH Au NCs, exhibits the highest visible light photocatalytic H\textsubscript{2} production efficiency because of the existence of electromagnetic hotspots at the vertexes (Figure 8a,b). The enhanced photocatalytic H\textsubscript{2} generation performance is attributed to the LSPR-induced hot hole transfer mechanism, where the hot holes generated by the plasmonic HOH Au NCs are injected into the valence band of Cu\textsubscript{2}O because Cu\textsubscript{2}O is a p-type semiconductor, as well as the plasmon-induced resonance energy transfer process. In addition to semiconductors, metals can also be grown on plasmonic metal NCs to achieve better photocatalytic H\textsubscript{2} generation performance. Site-specific overgrowth of Pt on Au NRs is achieved with the assistance of a binary surfactant of CTAB and 5-bromosalicylic acid.\textsuperscript{45} At an appropriate surfactant concentration, the close packing of the surfactant molecules at the rod side surface gives rise to Pt-tipped Au NRs (Figure 8c), where the Pt nanoparticles are selectively deposited on both ends of the Au NRs. The Pt-modified Au NRs are used as photocatalysts for H\textsubscript{2} production under visible and NIR illumination. The H\textsubscript{2} production increases linearly with the light illumination time for the Pt-modified Au NRs (Figure 8d). Compared with the Pt-covered Au NRs and Au nanospheres, the Pt-tipped Au NRs give the highest H\textsubscript{2} production rate. Moreover, the high catalytic activity of the Pt-tipped Au NRs can be further proved by their higher internal quantum efficiencies, which is believed to result from the fact that site-selective deposition of Pt facilitates charge separation (Figure 8c).

In addition to photocatalytic H\textsubscript{2} generation, anisotropic plasmonic heterostructures have also been demonstrated for plasmon-enhanced N\textsubscript{2} photofixation.\textsuperscript{19} Crystalline CeO\textsubscript{2} has been deposited at the two ends of Au NRs through site-selective overgrowth. The presence of oxygen vacancies on the surface of CeO\textsubscript{2} can facilitate the adsorption and activation of N\textsubscript{2} molecules. Given the as-obtained heterostructures enable efficient generation of plasmonic hot charge carriers, and improved charge separation ability because of the spatial separation of the reduction and oxidation sites, they give rise to remarkably enhanced N\textsubscript{2} photofixation performance in the NIR region (808 nm) compared with the counterpart core@shell nanostructures (Figure 8e,f).

Reduction of 4-nitrophenol is another type of photocatalytic reaction that can be enhanced by plasmonic heterostructures. (Au NR–CeO\textsubscript{2} heterostructures have been used for this reaction. Half-encapsulated (Au NR)@CeO\textsubscript{2} structures are synthesized using the soft template CTAB and through control of the hydrolysis of cerium acetate. CeO\textsubscript{2} is controlled to be preferentially deposited at one end of the Au NR.\textsuperscript{148} The as-synthesized anisotropic Au–CeO\textsubscript{2} heterostructures exhibit excellent photocatalytic 4-nitrophenol reduction performance under NIR laser illumination because they can substantially promote hot electron generation and transfer, as well as electron–hole separation (Figure 8g). The introduction of CeO\textsubscript{2} enhances the stability of the colloidal Au NRs and maximizes the synergistic effect for the improvement of the photocatalytic activity. The control experiments clearly indicate that the end-CeO\textsubscript{2}-deposited Au NRs give the shortest reaction time and possess the highest photocatalytic activity, compared with the bare Au NRs, mixture of the bare Au NRs and CeO\textsubscript{2} nanoparticles, and the (Au NR core)@(CeO\textsubscript{2} shell) nanostructures.

In addition, the decomposition rate of methylene blue is improved when Au–TiO\textsubscript{2} dumbbell-like nanostructures assembled on Au films are used as the photocatalyst (Figure 8h).\textsuperscript{69} The dumbbell-like nanostructures are prepared by selectively growing TiO\textsubscript{2} at the two ends of the Au NRs through control of the concentration of the dodecyltrimethylammonium bromide surfactant. A portion of the hot electrons generated from the plasmon decay in the Au NRs can overcome the Schottky barrier at the metal–semiconductor interface and be injected into the conduction band of TiO\textsubscript{2} to cause the decomposition of methylene blue. The particle-on-film nanocavities display an enhanced photocurrent and reaction rate, which can be ascribed to the increase in light absorption due to the extremely strong electromagnetic hotspot created in the nanocavity. The enhanced local field facilitates electron–hole separation and at the same time promotes direct optical excitation of the \(d\)-band transitions in the Au film to generate extra hot electrons. In the long-wavelength region, the decomposition of methylene blue is driven by the hot electrons generated through the excitation of the longitudinal dipole plasmon resonance of the Au–TiO\textsubscript{2} heterostructures. In contrast, in the short-wavelength region, the decomposition of methylene blue is attributed to the excitation of the \(d\)-band electrons of the Au film. Such dual-channel generation of hot charge carriers accelerates greatly the decomposition of methylene blue.

In addition to the reactions mentioned earlier, resazurin reduction and Suzuki coupling reactions have also been shown to be improved by photocatalysts based on anisotropic plasmonic heterostructures.\textsuperscript{13,44,50} Site-specific overgrowth of Pd on both ends of Au NRs has been realized in the presence of CTAB at low concentrations. The obtained bimetallic heterostructures can be used as strong light absorbers in the NIR range and efficient photocatalyst in the resazurin reduction reaction (Figure 8i).\textsuperscript{150} The reduction of resazurin to resorufin can proceed with the assistance of hydrazine as the reducing agent. However, the reduction rate is extremely slow without a photocatalyst. The bimetallic heterostructures can photocatalyze the reaction at a greatly improved rate. The Suzuki coupling reaction
has also been photocatalyzed by anisotropic heterostructures made of Au nanobipyramids end deposited with Pd.\[44\] The Pd-tipped Au nanobipyramids can plasmonically drive the Suzuki coupling reaction between bromobenzene and m-tolylboronic acid (Figure 8j). The Au nanobipyramid serves as a plasmonic nanoantenna to absorb light efficiently, whereas the deposited Pd nanoparticles function as the active sites for the target Suzuki coupling reaction. Breaking of the C─Br bond in bromobenzene is the rate-determining step for the reaction. Bromobenzene molecules are first adsorbed on the Pd nanoparticles. The energy transfer from the Au nanobipyramid to the Pd nanoparticles is efficient due to the bonded contact between the two components. The hot electrons generated in the heterostructures can be injected from the Pd nanoparticles to the unoccupied molecular orbitals of the adsorbed bromobenzene molecules and therefore weaken the C─Br bond (Figure 8j).\[44\] The deposition of Pd nanoparticles at the sharp ends of the Au nanobipyramids is found to give the highest photocatalytic activity, which is ascribed to the fact that more hot electrons are generated at electromagnetic hotspots.\[13,44\]
5.2.2. Electro catalysis and Plasmon-Enhanced Electro catalysis

Electrocatalysis based on anisotropic plasmonic heterostructures plays a vital role in sustainable energy applications. Upon light illumination, the electrocatalytic performance can be improved through the mechanisms of hot electron injection and plasmonic sensitization. Plasmon-enhanced electrocatalysis has recently triggered many interests in carbon-free production of useful fuels and conversion of greenhouse gases.[149,150] The plasmon-enhanced electrocatalytic efficiency can be ascribed to the synergetic benefit of the photoelectric, photothermal, and structural effects. First, hot charge carriers generated from the plasmon decay in the metal NC, leading to increase in the charge carrier density of the adjacent selectively deposited component and facilitating electrocatalytic reduction and oxidation reactions.[151,152] Second, anisotropic plasmonic heterostructures can serve as light absorbers and efficiently convert light energy into heat, building a localized heating system to drive catalytic chemical reactions.[153] Third, site-selective overgrowth of a second component on an anisotropic plasmonic metal NC can be leveraged to provide more accessible active sites, larger surface areas, as well as higher electrical conductivity, which all contribute to higher electrocatalytic activities.[58,149] Desired defects such as oxygen vacancies can also be introduced into the catalytic reaction system through the selectively deposited component to provide more active sites and therefore manipulate the reaction kinetics. Aside from increase in the catalytic reaction rate, heterostructures made of noble metal NCs and semiconductors generally also have long-term chemical and thermal stability.[154]

Photoelectrochemical H2 generation has been demonstrated on Au–CdSe dumbbell-like heterostructures, which are synthesized through the selenization reaction with an appropriate selenium precursor.[149] The as-synthesized dumbbell-like heterostructures make use of the plasmon enhancement of the Au NRs as well as efficient electron–hole pair generation and separation (Figure 9a). The H2 generation efficiency of the heterostructure photoanode is enhanced by nearly four times compared with that of the core@shell nanostructures under light illumination over 700 nm (Figure 9b). The Faradic efficiency (FE), which is defined as the percentage of the electrons participating in a given electrochemical transformation, reaches 96%, indicating that nearly all electrons contribute to the H2 production on the counter electrode. Incident photon-to-current conversion efficiency (IPCE) measurements at different monochromatic light wavelengths confirm that the longitudinal dipole LSPR of the Au NRs contributes to the enhanced photoelectrochemical performance. The measured IPCE action spectrum matches the absorption spectrum of the Au–CdSe dumbbell-like heterostructures. The photon energy absorbed by the Au NRs can be transferred to the CdSe components at the rod ends through plasmon–exciton interaction. A portion of the hot electrons generated from plasmon excitation can surmount the Schottky barrier (≈0.7 eV) and be injected into the conduction band of CdSe. This direct hot electron migration from the Au NR to CdSe reduces electron–hole recombination. The generated hot holes can be consumed by the hole scavenger on the side of the Au NR, leading to remarkable photocurrent for H2 evolution on the Pt counter electrode.

Pd-tipped Au NRs have also been used as the catalyst for photoelectrochemical H2 evolution (Figure 9c).[51] The Au NRs convert light into heat, causing the local surface temperature to elevate rapidly. Their LSPR promotes electron–hole generation. The Pd components serve as the electron acceptors and provide electrocatalytic active sites. In comparison with the core@shell nanostructures, the Pd-tipped Au NRs provide a larger active surface area, more active sites, a higher H2 evolution rate, lower onset overpotential, and a higher exchange current density. The Tafel slopes measured under different illumination conditions (Figure 9d) suggest that the heterostructures follow the Heyrovsky–Volmer reaction mechanism for the H2 evolution reaction, indicating the dissociative adsorption of H2 molecules as the rate-determining step. The decreased Tafel slopes reveal the accelerated kinetic process and enhanced electrocatalytic performance under visible–NIR illumination. In another example, AgPt-tipped Au nanostars are used for photoelectrochemical catalysis (Figure 9e). They exhibit a remarkable H2 evolution and methanol oxidation performance under visible–NIR illumination.[58] The photoelectric effect, photothermal effect, and modified electronic state all contribute to enhanced activity, stability, and tolerance to CO poisoning. The oxidation peaks at ≈0.8 V in the methanol oxidation curves reveal preliminary methanol oxidation in the forward scan (Figure 9f). On the contrary, the peaks represent the further oxidation of methanol and carbonaceous intermediates in the backward scan run. The AgPt-tipped Au nanostars offer a higher mass activity for the methanol oxidation reaction (MOR).

Electrocatalysis without light illumination has also been widely investigated for anisotropic plasmonic heterostructures. Compared with photoelectrochemical catalysis, the activation of reactants in electrocatalysis is achieved by electric energy only. Anisotropic plasmonic heterostructures, such as Pd–Au heteropentamers,[155] AgPd nanodendrite-tipped Au nanoparticles,[149] as well as Au–Cu Janus heterostructures,[156] have recently been synthesized for electrocatalytic applications. The electrocatalytic performances of anisotropic plasmonic heterostructures are superior to those of the corresponding core@shell nanostructures due to the following reasons. First, anisotropic plasmonic heterostructures provide more active sites, especially at the corners and edges, compared with the core@shell nanostructure counterparts. The simultaneous exposure of the different components of the heterostructures brings the synergetic effects. The heterostructures also possess high thermal and chemical stability that ensure their repetitive uses without considerable degradation. During the reaction process, anisotropic heterostructures can enhance the reversibility of the electrocatalytic process and promote electron transfer. For example, Pd–Au heteropentamers that are synthesized through site-selective overgrowth of Au on Pd tetrahedral nanoparticles exhibit improved electrocatalytic efficiencies (Figure 9g,h).[155] The electrocatalytic activity of the Pd–Au heteropentamers has been investigated using the quasireversible redox reaction of catechol molecules. The screen-printed carbon electrodes (SPCEs) are modified with the Pd–Au heteropentamers. The electrodes modified with the Pd nanotetrahedra and that without modification are also prepared for comparison. The measurements of the peak-to-peak potential separation (∆E) between the anodic and cathodic voltammetric peaks reveal that ∆E is the lowest for
Figure 9. Electrocatalysis and plasmon-enhanced electrocatalysis. a) Schematic showing plasmon-enhanced photoelectrochemical H₂ production. b) Photoelectrochemical H₂ production rates using different photoanodes under light illumination at wavelength $\lambda > 700$ nm and an external bias of 0.4 V against the reversible hydrogen electrode (RHE). The photoanodes are made of Au–CdSe dumbbell-like nanostructures, Au@CdSe nanostructures, respectively. a,b) Reproduced with permission.[149] Copyright 2019, Wiley-VCH. c) Schematic of the reaction mechanism for electrocatalytic H₂ production with Pd-tipped Au NRs as the catalyst under light illumination. d) Tafel plots of Pd-tipped Au NRs under various illumination conditions. The plots are derived from the H₂ evolution reaction polarization curves. c,d) Reproduced with permission.[51] Copyright 2018, Wiley-VCH. e) Schematic showing the electrocatalytic H₂ evolution (HER) and MOR mechanisms using the AgPt-tipped Au nanostars as the catalyst under light illumination. f) Mass-normalized cyclic voltammogram (CV) curves of AgPt-covered, -edged, and -tipped Au nanostars in the dark and under visible–NIR light illumination. e,f) Reproduced with permission.[149] Copyright 2019, Elsevier. g) Schematic showing the oxidation reaction of catechol to o-benzoquinone and Pd–Au heteropentamers prepared by site-selective overgrowth of Au on Pd tetrahedral nanoparticles. h) CVs (first scan) of catechol with H₂SO₄ as the electrolyte when the SPCEs modified with Pd–Au heteropentamers of the Au domain sizes at 5 and 7 nm were used, respectively. g,h) Reproduced with permission.[149] Copyright 2020, American Chemical Society. i,j) FE and partial current densities, respectively, of the C₂ products when the Au nanobipyramids, Cu nanospheres, (Au nanobipyramid core)@Cu shell) nanostructures, mixture of the Au nanobipyramids and the Cu nanospheres, Au nanosphere-based Au–Cu Janus nanostructures, and Au nanobipyramid-based Au–Cu Janus nanostructures are used as the catalysts. k) Schematic of the proposed reaction mechanism of the electrochemical CO₂ reduction catalyzed by the Au nanobipyramid-based Au–Cu Janus nanostructures. i–k) Reproduced with permission.[156] Copyright 2021, Wiley-VCH.
the electrode with the Pd–Au heteropentamers (Figure 9h). Moreover, the increased currents show the improved electrocatalytic efficiency. These results clearly reveal that the Pd–Au heteropentamers can accelerate electron transfer and enhance the reversibility of the electrocatalytic process.

In addition, Au nanobipyramid-based Au–Cu Janus nanostructures have been synthesized for the electrochemical CO2 reduction reaction.156 The as-obtained Au–Cu nanostructures enable the generation of H2, CO, CH4, C2H6, and C2H4 and possess higher C2 product (C2H4 and C2H2) selectivity than the related Au nanobipyramids, Cu nanospheres, (Au nanobipyramid core)@Cu shell) nanostructures, and mixture of the Au nanobipyramids with the Cu nanospheres. The Janus nanostructures exhibit the highest C2 FE of 46.4% (Figure 9i). The Janus nanostructures also display a maximal partial current density for C2 production at −1.118 V, which is 6.4 times higher than that of the Cu nanospheres at −1.06 V (Figure 9j). The improvement of C2 selectivity of the Janus nanostructures, with the enhanced C2 FE and partial C2 current density, can be ascribed to the synergistic effect of the Au and Cu components. The possible electrocatalytic mechanism is shown in Figure 9k. The spatially separated Au and Cu components, with an intimate contacted interface, enable a tandem catalytic process that results in higher C2 production. In the first step, the Au nanobipyramid contributes to CO2 adsorption and activation, where the active sites can stabilize the COOH* intermediate, facilitating the conversion of CO2 to CO. In addition, the high-index facets of the Au nanobipyramid induce the adsorption and hydrogenation of CO2 for the generation of the COOH* intermediate. The atomic steps on the Au nanobipyramid also maximize the contact interface with the Cu component, optimize the binding of the intermediates in the C2 production process, and accelerate the generation of the C2 products.

5.3. Photothermal Conversion and Therapy

Photothermal conversion and therapy under NIR laser illumination is an emerging field due to the deep penetration of NIR light in blood and tissues. Photothermal therapy enables the destruction of cancer tissues by local heating.157,158 Although small-sized Au nanospheres have been shown to possess excellent photothermal conversion efficiencies, the poor plasmon wavelength tunability hinders their potential applications within the NIR biological transparency windows. The small-sized 28 × 8 nm Au NRs have been proved to be the most effective in plasmonic photothermal heat generation for the optimization of photothermal therapy treatment.159 Various anisotropic plasmonic Au NCs, including NRs, nanobipyramids, and nanostars, have been widely investigated for highly efficient photothermal therapy.160–162 Anisotropic plasmonic heterostructures are also emerging as potent theragnostic platforms for both photothermal conversion and photogeneration of reactive oxygen species (ROSs), resulting in cell apoptosis. Anisotropic plasmonic heterostructures can promote charge carrier separation due to the Fermi-level alignment between disparate metals and therefore can result in much higher ROS production efficiencies.13,3,162

One of the most representative heterostructured phototherapy agents is AgPd-tipped Au nanobipyramids, whose LSPR wavelength can be extended to the NIR region.146 Dense SiO2 is coated on the AuPd-tipped Au nanobipyramids to render them highly biocompatible (Figure 10a). The obtained heterostructures possess excellent photothermal therapy efficacy toward U-87 MG cancer cells in the second biological transparency window. Under laser illumination at 1064 nm that matches the plasmon wavelength of the heterostructures, the cell viability values are found to be (91 ± 3)%,(58 ± 15)%,(19 ± 2)% at power densities of 1.18, 1.96, and 2.74 W cm−2, respectively (Figure 10b). The photothermal therapy efficacy is verified by the nearly undetectable green fluorescence of the U-87 MG cells (Figure 10c).

The Pt-end-deposited Au NRs shown in Figure 7c,d also exhibit excellent photothermal conversion properties (Figure 10d,e).53 Under laser illumination, a large amount of ROSs is also generated on the Pt part of the heterostructure because of plasmonic hot electron generation and efficient electron–hole separation. The photothermal therapy efficacy of CF3-b-PDEA@siRNA NRs is evaluated through thermal infrared imaging. After laser illumination at 808 nm, the temperature of the tumor region of mice, which are intravenously administered with CF3-b-PDEA@siRNA NRs, rapidly increases from 30 to 45 °C within 10 min and the tumor cells are damaged as a result (Figure 10f). Under laser illumination, the CF3-b-PDEA@siRNA NRs also efficiently generate hot electrons, leading to the generation of ROSs, including singlet oxygen, superoxide radicals, and hydroxyl radicals through chemical transformations. The generation of ROSs results in the enhanced photodynamic therapy performance for the tumor cells. Both the photothermal conversion and the ROS generation mechanisms contribute to the overall phototherapy efficacy.

6. Summary and Outlook

We have introduced the recent works on the heterostructures of anisotropic plasmonic NCs with site-selectively deposited components. We have highlighted the preparation strategies of such heterostructures and their applications. The heterostructures with various shapes and compositions are generally prepared by galvanic replacement reactions, capping agent-directed synthesis, surface-protected growth, and some other methods such as welding-induced synthesis and selective etching. The prepared anisotropic heterostructures show great potential in applications ranging from plasmon-enhanced spectroscopy, catalysis, to photothermal conversion, and phototherapy. Although great efforts have been made to investigate the anisotropic heterostructures, there still remain many unanswered questions. The diversities of the heterostructures in material and structure are still limited. The technologies in controlling the heterostructure compositions and morphologies are far from mature. The detailed mechanisms in the heterostructure growth and their performance/property enhancement are unclear. New applications of such heterostructures require further exploration. In our opinion, future research should focus on the following aspects.

First, new approaches in preparing the heterostructures to enrich their libraries are in demand. We have shown that a large number of previous studies in this field have been devoted to the preparation of hybrid heterostructures based on site-selectively depositing other components onto plasmonic metal NCs.
However, due to the distinct differences in the bonding nature and crystalline structure among materials, most of the demonstrated methods are delicate, material specific, and require multiple steps in synthesis. New, simple, and versatile synthetic approaches for the fabrication of the anisotropic heterostructures are therefore highly desired. In addition, the hybrid heterostructures are achieved by introducing a second material onto well-controlled deposition sites of plasmonic metal NCs. Currently, the introduced deposition materials include metals, semiconductors, polymers, and insulated dielectrics like SiO₂. Few studies have been devoted to selective deposition of new functional nanomaterials, such as mesoporous nanostructures, metal–organic frameworks (MOFs), quantum dots, etc. Site-selective deposition of such new nanomaterials on plasmonic metal NCs is beneficial for enhancing the optical sensing performance of plasmonic nanostructures, including sensing selectivity and response speed. For instance, Raman signals can be enhanced if MOFs are site-selectively deposited on the hotspots of anisotropic plasmonic NCs due to the concentration of target analyte molecules through the ordered porous structure of MOFs. Furthermore, the integration of multiple functional materials at different sites on plasmonic NCs can open more possibilities. For example, depositing two types of catalytic materials that catalyze oxidation and reduction reactions separately at different hotspots on plasmonic NCs can significantly improve the catalytic performance and offer opportunities for exploring new catalytic reactions. It is therefore highly desired to develop synthetic methods to prepare such heterostructures.

Second, the detailed mechanisms of the site-selective deposition approaches, which are crucial for the fine composition and morphology control of the heterostructures, still require thorough and deep understanding. Further understanding of the mechanisms favors the design and preparation of anisotropic heterostructures. It is also important to re-examine all the parameters during deposition, including the precursor concentration, temperature, reaction time, template, surfactant, and solvent. For instance, the alkyltrimethylammonium bromide surfactant with a longer hydrophobic chain (C₁₆TAB) leads to a lower yield in the synthesis of TiO₂-tipped Au NRs than those of C₁₄TAB or C₁₂TAB. Based on the understanding and accumulation of experiment results, simple models and pictures have to be built to support the understanding of the synthetic mechanism. Such
models can facilitate the fabrication of anisotropic heterostructures with specific architectures. They can also offer guidelines in the design of the anisotropic heterostructures for specific applications.

Apart from the above perspectives in the synthesis and mechanisms of the anisotropic plasmonic heterostructures, there is one more significant aspect, that is, applications, which lack comprehensive understanding and require further investigation. The anisotropic plasmonic heterostructures have been shown to exhibit enhancement activities for spectroscopies, catalytic reactions, photothermal conversion, and phototherapy. Enhancement in these applications is far from being optimized. Effort made on the understanding of the detailed enhancement mechanisms will promote the improvement of the heterostructure performance in various applications. More studies relying on advanced techniques, including ultrafast spectroscopies and in situ measurements of individual nanostructures, are needed. In addition, studies on the involved charge/energy transfer processes at the interface have remained limited because the processes are complicated and the interface is difficult to be probed. Ultrafast spectroscopies are highly desired for the understanding of the involved carrier transfer processes. The improved understanding of the charge/energy transfer processes is expected to dramatically improve the application performances. Great effort also needs to be made on the exploration of the scope of catalytic reactions based on the anisotropic plasmonic heterostructures. Given their great potential, the anisotropic plasmonic heterostructures are expected to be used in a broader range of applications beyond the currently investigated areas. For example, new plasmonic materials, such as Mg and Al, can enrich the applications of plasmonic heterostructures in many biotechnological applications.

In a word, there still exist many opportunities in the development of various heterostructures with site-selective nanomaterial deposition on plasmonic NCs and the exploration of their applications. The improved preparation techniques and the deepened understanding of the mechanisms in the growth and performance/property enhancement of such heterostructures will greatly extend their applications in sensing, biomedicine, solar energy harvesting, and plasmonic photocatalysis.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anisotropic heterostructures, photocatalysis, plasmon-enhanced fluorescence, plasmon resonances, surface-enhanced Raman scattering

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