Precisely Controllable Synthesized Nanoparticles for Surface Enhanced Raman Spectroscopy

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Abstract

Surface-enhanced Raman scattering (SERS) is a powerful technique for trace molecular detection because of its ultrahigh molecular structure sensitivity and unique fingerprinting spectra. The morphology, size and structure of the plasmonic nanoparticles seriously influence the Raman scattering intensity of sample. In this chapter, we focus on the influence of nanoparticle morphology. By tailoring the plasmonic properties of anisotropic Au, Ag nanoparticles and generating electromagnetic "hot spots" of SERS active substrate, the SERS intensity can be seriously influenced. We also focus on providing a general introduction to understand the main parameters of anisotropic noble metal nanoparticles of SERS performance.

Keywords: surface enhanced Raman spectroscopy (SERS), localized surface plasmon resonances (LSPRs), noble metal nanoparticles, core/shell nanoparticles, controllable synthesis

1. Introduction

The utilization of the enhancement effect of Raman scattering by using the plasmonic effect for nanoparticles (NPs) is mainly determined by the physical and chemical properties of the surface-enhanced Raman spectroscopy (SERS) active substrates. SERS is a powerful technique for ultrasensitive detection through the enhancing of electromagnetic fields (E-field) generated by localized surface plasmon resonance (LSPR) effect [1–4]. It can provide specific fingerprint information about a wide range of target molecules [5]. Noble metal NPs (e.g., Au, Ag, Cu, etc.) display a variety of plasmonic behaviors. The extremely inefficient inelastic light scattering of Raman scattering of the molecules or materials is the most important factor restricting its applications [6]. However, the bottleneck can be overcome when the molecules are adsorbed onto a rough surface of noble metal NPs by enhancing the vibrational excitation of the adsorbed molecules or materials in a process commonly known as SERS. To develop size, shape and chemical composition, controllable anisotropic NPs to generate the “hot spot” can maximize the Raman signal to enhance the molecule detecting capacity. A wide variety of anisotropic noble metal NPs have been developed as a suitable candidate for SERS detecting and sensing. By controlling the size, shape, chemical component and structure of the NPs, the absorption range of noble metal NPs can be tuned form the visible to the near-infrared (NIR) range, and the resonances of noble metal NPs occur in the visible and NIR range of the electromagnetic spectrum [7]. Synthetizing the precisely controllable anisotropic noble metal NPs has proven to be an extremely powerful tool to tune the plasmon resonance for rendering them suitable for ultrasensitive detecting.

By varying the diameters of spherical noble metal NPs, the plasmon resonances of NPs can only be tuned in a relatively narrow wavelength range (always only tens of nanometers). However, the anisotropic shape NPs provide one or several additional degrees of freedom, which allows controlling the plasmon resonance wavelengths, ranging from the visible to the NIR range, by varying the aspect ratio (AR) of the nanorods (NRs) or other topography parameters of NPs.

This chapter focuses on recent researches on the most commonly used anisotropic Ag, Au, and so on noble metal NPs for SERS application. Herein, we focus on the intrinsic shape-dependent SERS property of the precisely controlled anisotropic NPs, synthesized mainly in solution.

2. Nanorods

In the early twenty-first century, the seed-mediated Au and Ag NRs growth method was developed, and this method has become the most popular approach for Au and Ag NRs synthetizing [8]. In general, this method comprises two steps: (1) the synthetizing of the small metal NPs, that is, so-called “seeds” and (2) the overgrowing of the seed to the larger, mature metal NPs. In addition, the shape of the mature metal NPs can be controlled by using the different surfactants, salt precursors and solvents. In this method, the separation of the nucleation and growth of the nanocrystals synthesis process lead to precise control of shape and size and the high uniformity of the metal NRs. In 2001, the precisely size controlled Ag NRs were successfully synthetized by using silver nitrate as the Ag precursor, ascorbic acid (A.A.) as the reductant and cetyltrimethylammonium bromide (CTAB) as the surfactant with the presence of Ag seeds and NaOH [9]. By reducing the amounts of NaOH, the ARs of the Ag NRs increased. As a pioneering Au NRs synthetizing research, the high-crystallinity colloidal Au NRs have been prepared with a high 90% shape yield by

Nikoobakht and El-Sayed [10]. But the Ag ions are always needed in the high shape yield Au NRs synthetic method [11].

The typical UV-vis-NIR spectra of Au and Ag NRs show two obvious plasmon bands, corresponding to the transverse (short wavelength) and longitudinal modes (long wavelength). The transverse mode at ca. 520 nm can be hardly tuned, but the longitudinal mode can be precisely controlled by tuning the AR of noble metal NRs, and the intensity is much stronger than the transverse mode as shown in **Figure 1** [12]. The simulation and experimental studies of the external electromagnetic fields (E-field) distribution indicated that the high localized E-field enhancement at the noble metal NRs tips, so-called hot spots, along the dipolar longitudinal mode [13, 14].

Noble metal NRs are the most commonly used anisotropic SERS active substrate materials. Tailoring the LSPR relative to the laser excitation wavelength is one of the most significant approaches to obtain a high SERS signals. The search has indicated that the Ag NRs can generate the higher E-field than that of Au NRs under the same wavelength of incident light. In addition, the E-field intensity increases with the increasing of AR for Ag NRs [15]. Han's group developed an efficient platform for investigating the kinetics of catalytic reactions with SERS by using Au@AuPd NRs as the SERS active materials as shown in **Figure 2** [16].

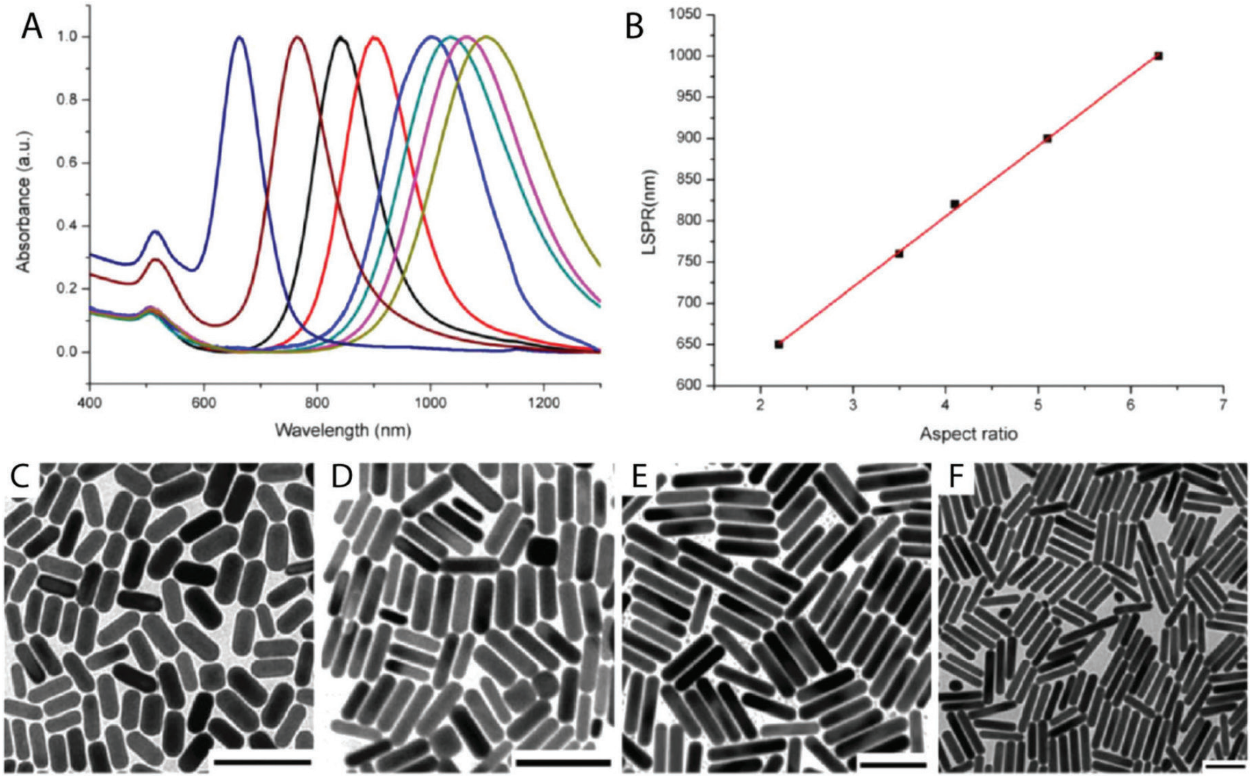

Figure 1. The optical properties and morphology of Au nanorods with different AR. (A) The UV-vis-NIR spectra of Au NRs with different ARs. (B) Relationship between longitudinal LSPR and AR. (C–F) Representative TEM images of Au NRs with different ARs. Scale bars: 100 nm. Adapted from Ref. [12] with permission, Copyright Royal Society of Chemistry.

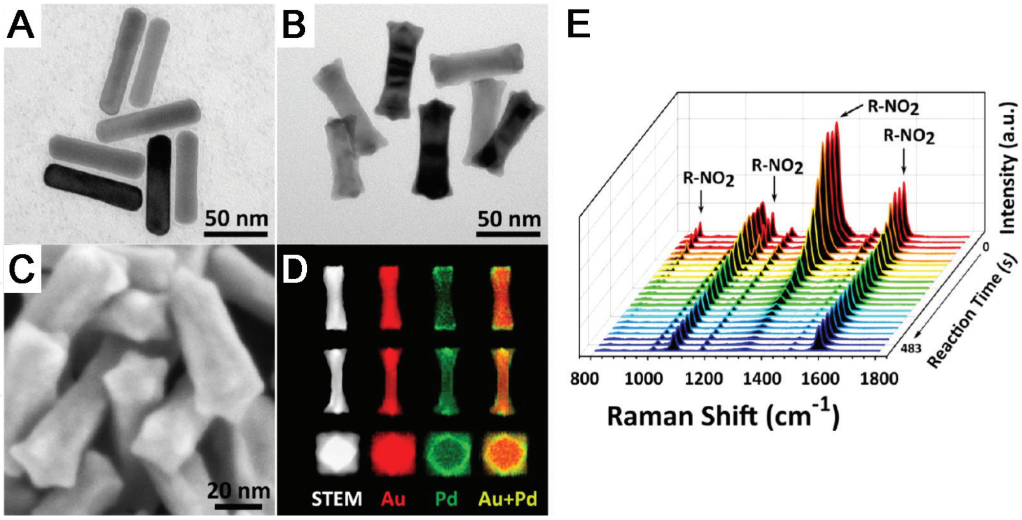

Figure 2. (A) TEM image of the Au NRs seeds. (B) TEM image and (C) SEM image of the Au @AuPd NRs. (D) STEM images of Au@AuPd NRs taken along the [100], [110], and [001] axes (the first column, from the top down), and the corresponding elemental mappings for Au (the second column) and Pd (the third column); the last column shows combined mappings, in which the simultaneous presence of Au and Pd appears yellowish. (E) Successive SERS spectra of the reduction of 4-nitrothiophenol by H_2 collected on a planar platform made of Au@AuPd NRs. Copyright American Chemical Society.

The results indicated that the Ag NRs show the high Raman enhancement than the Au NRs because of the stronger E-field of Ag NRs than that of Au NRs. This phenomenon can be attributed to higher plasmonic intensity at the tips of Ag NRs and higher Rayleigh scattering for Au NRs.

3. Nanoplates

Triangular nanoplates are the circular, triangular or hexagonal nanomaterials in which one of the dimensions is much smaller than the other two. The most commonly used SERS active substrate nanoplates are the Au and Ag nanotriangles and nanohexagons. Because of the sharp corners and edges, the nanotriangles exhibit the strong E-field enhancements. **Figure 3** shows the morphology and optical property of nanotriangles [17].

Au and Ag nanotriangles exhibit the excellent SERS signal because of the high generation of E-field, good assembling behavior and the tunability of the LSPR bands. Although the nanotriangles own the better optical property than that of NRs, the synthetic difficulties of nanotriangles restrict its application as the SERS active substrate materials. Study has shown that the Ag nanotriangles with sharp corners and edges exhibit the larger Raman enhancement than the rounded corner nanotriangles as shown in **Figure 4** [18]. In addition, the zigzag edges of nanotriangles can generate a further enhancement compared

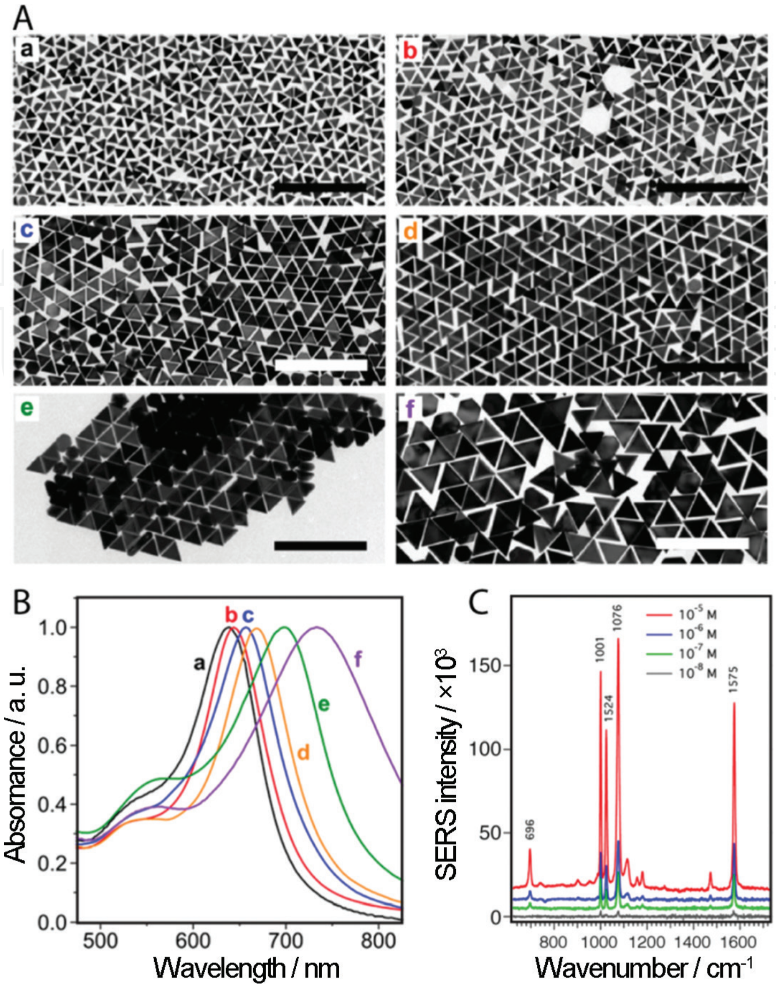

Figure 3. (A) TEM images of Au nanotriangles with different edge lengths (scale bar 500 nm). (B) UV-vis-NIR spectra of the Au nanotriangles depicted in TEM images (a–f). (C) SERS performance of Au NTs in solution for thiophenol (TP) excited at 785 nm and concentrations varying between 10^{-5} and 10^{-8} M. Adapted from Ref. [17] with permission, Copyright American Chemical Society.

to the straight edge nanotriangles. The most widely used Ag nanotriangles synthetizing methods include light-induced synthesis and wet chemistry methods. For the Ag nanotriangles synthetizing methods, polyvinylpyrrolidone (PVP), cetyltrimethylammonium chloride (CTAC) or CTAB acting as the surfactants can induce the Ag growth to the plate-like morphologies with sharp corners and edges [19]. For Au nanotriangles, Scarabelli et al. reported the controllable synthesis of Au nanotriangles with tunable size and high yield (95%) upon simple purification [17]. Tan et al. synthesized Ag nanotriangles with different edge lengths from 30 up to 210 nm with corresponding LSPR band between 485 nm and 1130 nm [20]. Ag nanotriangles SERS substrate was also used for biosensing and measured the E-field of adenosine triphosphate (ATP) with two different incident light wavelengths [20].

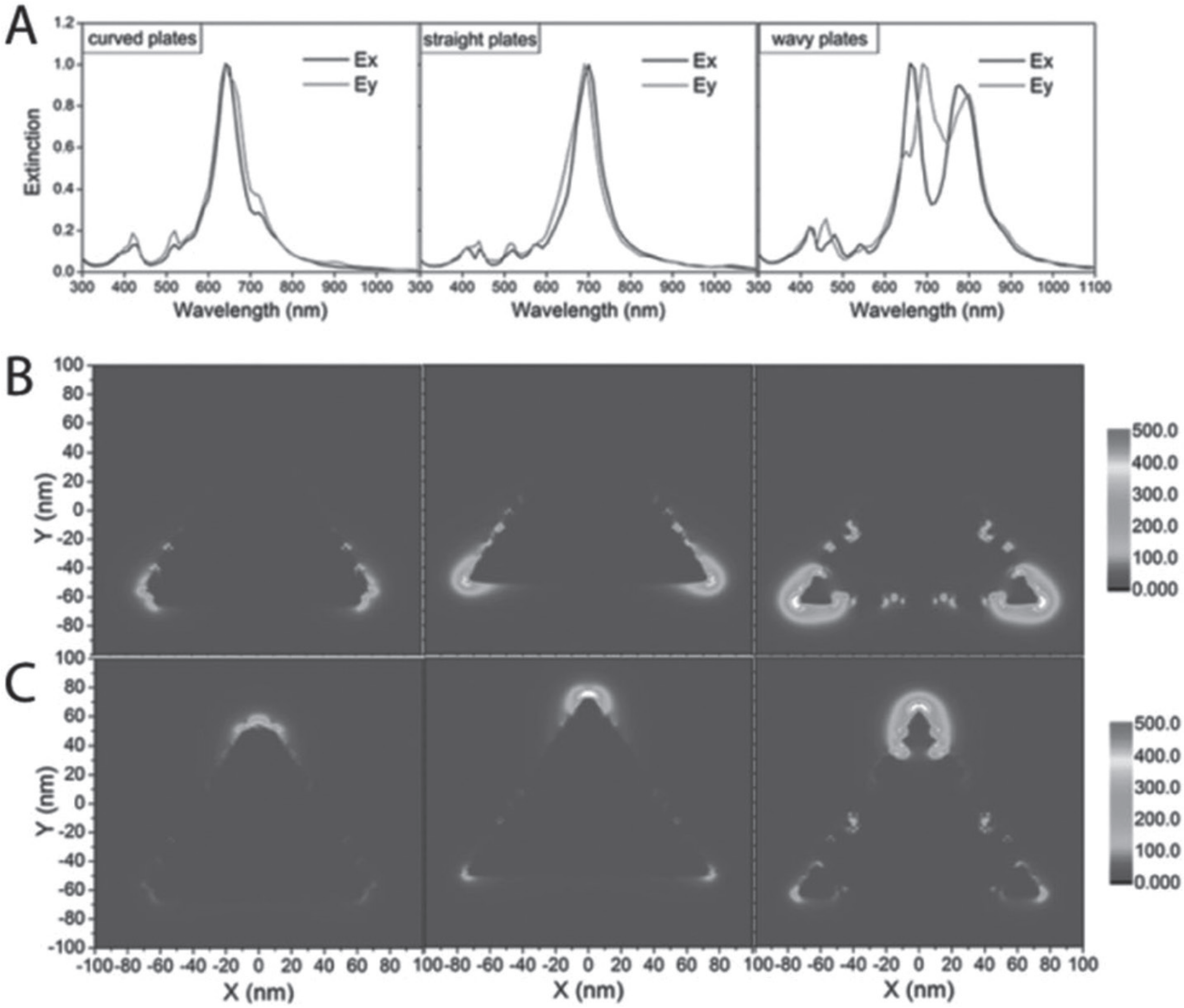

Figure 4. (A) The simulation results of Ag nanotriangles with curved, straight and zigzag edges, using finite-difference time-domain (FDTD) calculations. (B and C) E-field amplitude patterns of nanotriangles with E-field along the x-axis (Ex) and y-axis (Ey), for B and C, respectively. Adapted from Ref. [18] with permission, Copyright Wiley-VCH.

4. Nanocubes

From the synthetic angle, Ag nanocubes (NCs) can be easily obtained with high crystallinity, monodispersion and uniformity than that of Au NCs. In the most commonly used Ag NCs synthetizing method, the Ag ions of the $AgNO_3$ are reduced by ethylene glycol in the presence of HCl and PVP [21, 22]. These Ag NCs were single crystals and were characterized by a slightly truncated shape bounded by {100}, {110} and {111} facets (**Figures 5** and **6**).

The synthesis of monodisperse Au NCs is still a huge challenge. The key parameters such as reproducibility and fine size control still require further optimization. The most commonly used synthetizing method is also based on seed-mediated growth, in combination with CTAC, CTAB or CPC (cetylpyridinium chloride) acting as the surfactants. By precisely controlling the

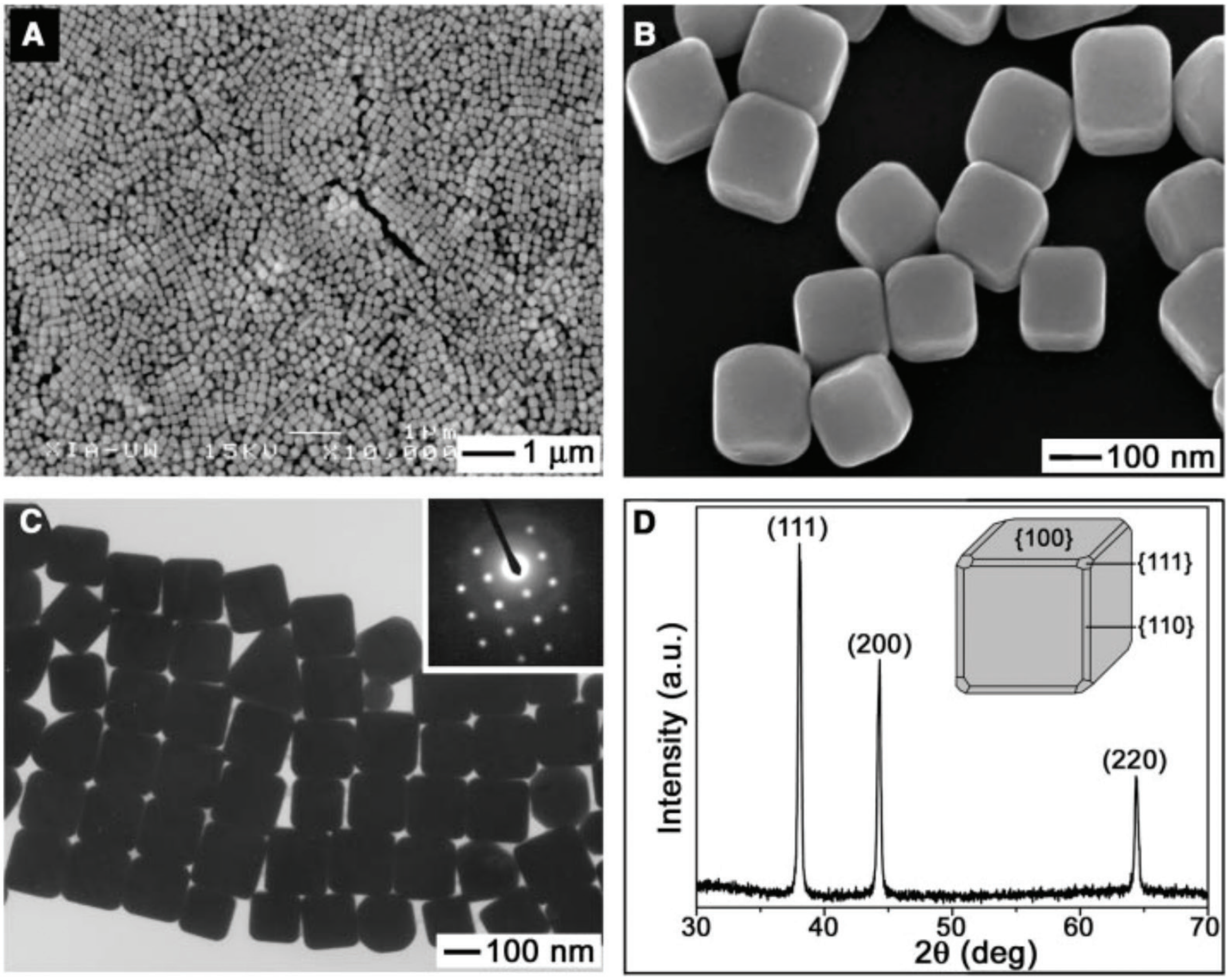

Figure 5. (A) Low- and (B) high-magnification SEM images of Ag NCs. (C) The TEM image of the same batch of Ag NCs. Inset: Diffraction pattern of an individual cube. (D) The XRD pattern of the Ag NCs. Adapted from Ref. [22] with permission, copyright science.

dynamic process, reductant concentration and the selective absorption facet of surfactants, the Au NCs can be obtained with requested shape and single crystal structure [23]. The simulation results indicated that the dipolar LSPR charges of Ag and Au NCs tend to accumulate at corner sites [24, 25]. Due to the strong LSPR and hot spots highly localized at corners, NCs are excellent candidates as SERS substrates. When the other symmetric Au NPs such as rhombic dodecahedra and octahedra were used as the SERS active substrate materials, the SERS signal of these Au NPs was still observed [26].

Because certain facets show higher chemical activities, concave NCs can also be prepared via modifications of the seed-mediated growth method, where CTAC provides control over the concave morphology of the final product. Thereby, the concave NCs can effectively enhance the performance as the SERS active substrates. The LSPR band of concave NCs red-shift obviously compared to the NCs with flat faces. Because of the sharp corner of concave NCs, the higher E-field enhancements can be expected [27].

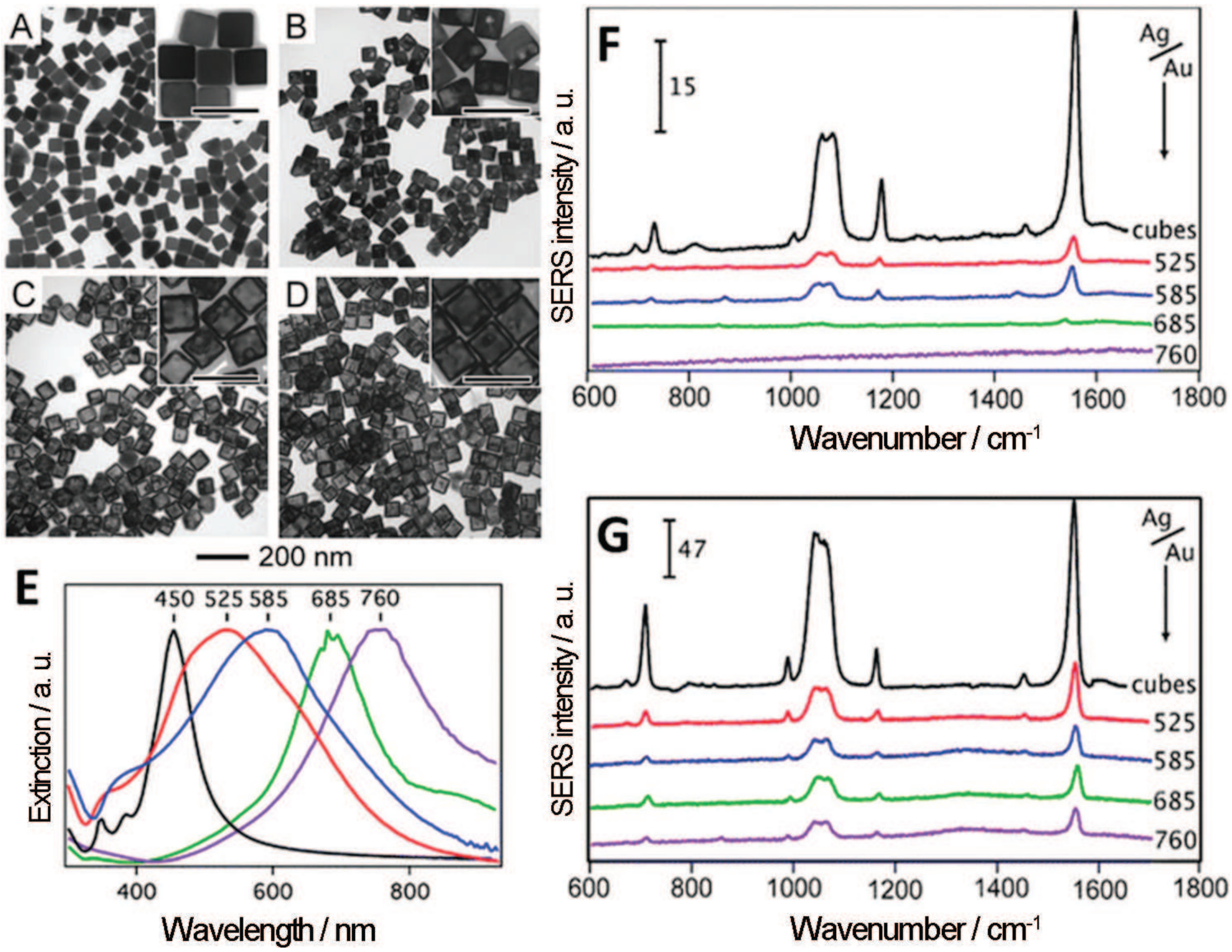

Figure 6. (A–D) TEM images of nanocages at degrees of galvanic replacement. (E) UV-vis-NIR spectra of nanocages with varying Au amounts. (F and G) SERS spectra of 1,4-BDT with nanocages used as the SERS substrate. Adapted from Ref. [28] with permission, copyright Royal Society of Chemistry.

When the inner atoms are etched, the nanocubes can be transformed to nanocages. Galvanic replacement is the most common method for synthetizing hollow nanocages. Au nanocages can be created by galvanic replacement by using Ag NCs as the templates with chloroauric acid in water phase [21]. A valuable property of Au nanocages is the red-shifting of LSPR bands into the NIR range, which is particularly useful for biological sensing and detecting applications. In addition, the galvanic replacement can also produce the bimetallic Au-Ag alloy nanocages, in which the SERS intensity shows a strong relationship between excitation wavelength and Au [28].

5. Nanostars

Nanostars and nanoflowers, so-called branched NPs, are formed by a central body and several arms or tips. These nanoarms and tips can effectively enhance the Raman scattering signal. A lot of synthetic methods based on wet chemistry, for example, the seed-mediated growth and other methods, have been reported for the preparation of nanostars for Au, Ag and other noble metals. For the seed-mediated growth method, in the presence of Ag ions, Au ion can be reduced by ascorbic acid and CTAB or CTAC acting as the surfactants or using N,N-dimethyl-formamide (DMF) as solvent and reductant in the presence of PVP as surfactant. For template-based methods, using mesoporous silica as the template, Au nanotips can be grown on the surface of mesoporous silica. The seed-mediated growth method can also be used to synthetize Ag nanostars. In the presence of the sodium polyacrylate as the seeds, Ag ion can be reduced to Ag nanostars by ascorbic acid as the reductant.

The UV-vis-NIR spectra of Au nanostars indicate that it shows a plasmon band in the range from 600 nm to 1200 nm, corresponding to tailor the sharpness and/or AR of the tips as shown in **Figure 7** [29, 30]. EELS mapping showed an extremely high E-field intensity at the tips of the nanostars, which can enhance the Raman signal efficiently [31].

Nanostars show a higher E-field at the resonance wavelength than that of NRs or nanospheres with the similar dimers. The SERS detection limit can achieve to enhance the Raman signal via the plasmon coupling between the adjacent Au tips or between the Au tips and Au core. Au nanostars acting as the SERS active substrate material can achieve an ultra-sensitive 4-mercaptobenzoic acid (4-MBA) detection, with the detection limits as low as 10 fM [32]. Based on the SIE-MoM, by increasing the surface coverage, the relatively constant enhancement can be observed [33].

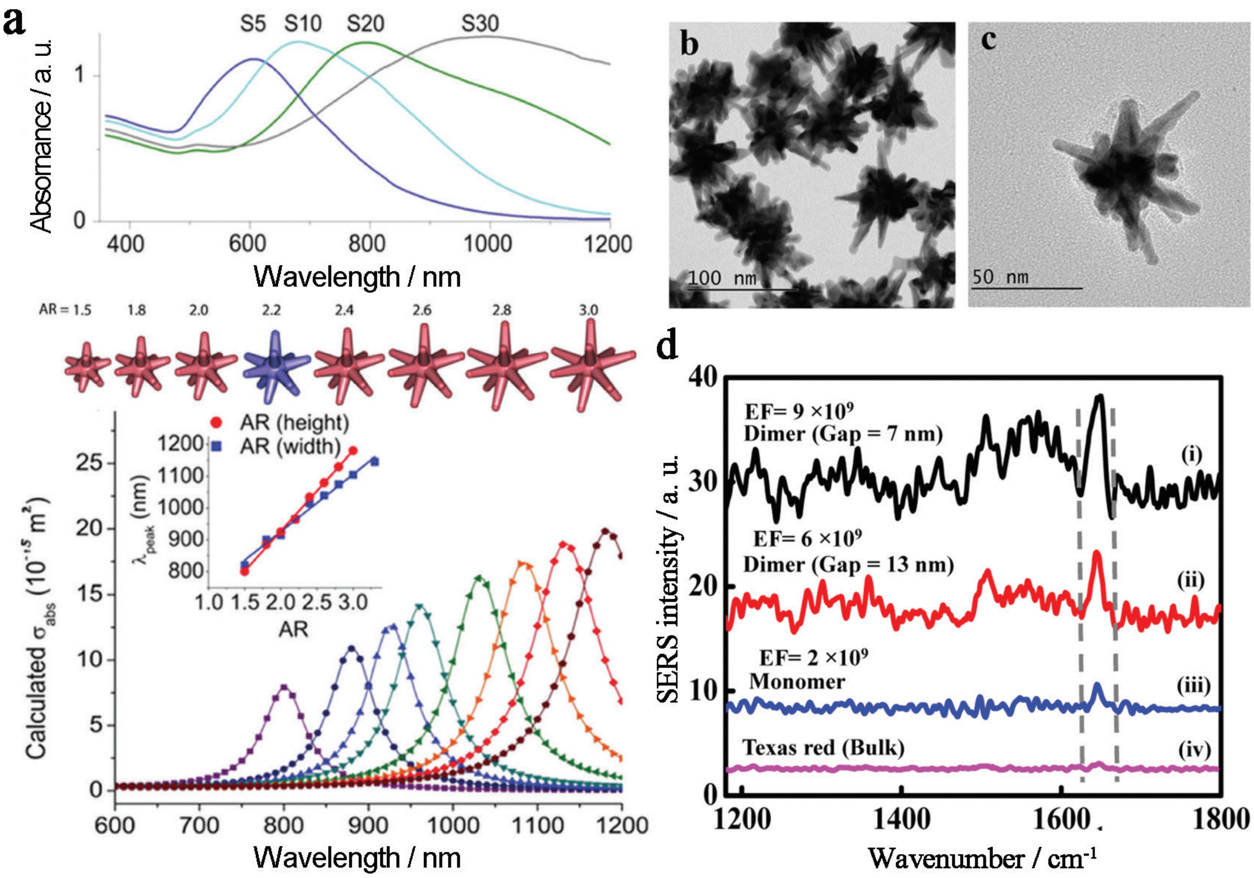

Figure 7. (a) Optical properties of Au nanostars with different branching degrees. An increase in the branching produces a red-shift in the corresponding spectra. Adapted from Ref. [30] with permission, Copyright IOP Publishing. (b and c) TEM images of Au nanostars. (d) SERS spectra of Texas red (TR) dye bound to Au nanostar dimers with average gaps of 7 nm (curve (i)) and 13 nm (curve (ii)), and TR dye bound to Au nanostar monomer on DNA origami (curve (iii)) and bulk TR dye (curve (iv)) recorded using 532 nm laser. Adapted from Ref. [34] with permission, Copyright American Chemical Society.

6. Conclusions and outlook

In summary, the synthesis of precisely controllable anisotropic NPs, with high uniformity and yield, plays the significant role in the SERS detection and imaging. This chapter has demonstrated that the recent research efforts to synthesize the anisotropic noble metal NPs with different morphologies, the E-field distribution, the key morphological parameters to achieve the strong E-field and ultra-sensitive SERS detection. The biggest influence of SERS performance is the effective near-field Raman scattering enhancement, which can be achieved by tuning the LSPR wavelength of the anisotropic noble metal NPs matching with the excitation light wavelength to induce the strong plasmon oscillation. In addition, the anisotropic NPs with high curvature give rise to the highest polarizability at the corners and edges. Many other factors can also powerfully impact the SERS signal output, for example, the binding affinities of analytes to the SERS active materials, the stability of the analyte-NPs system and so on. The interplay of these factors offers a huge potential for the NPs used as SERS active material, and the multifunctional design of the anisotropic noble metal NPs can be applied for the specific application and creates the next generation SERS substrate.

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