Review Article

Preparation and Progress in Application of Gold Nanorods

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Gold nanorods (Au NRs) have attracted extensive research interest due to their unique optical properties, adjustable aspect ratio, and easy surface modification in the fields of biosensing, bioimaging, and disease diagnosis and detection. In this review, we present a comprehensive review of various methods for preparing gold nanorods including hard template method, electrochemistry method, photochemistry method, seed-mediated growth method, secondary growth method, and amorphous seed method. The unique optical properties of the gold nanorods and its applications in biomedical, detection, catalysis, and information storage will also be discussed in detail.

1. Introduction

Gold nanomaterials, which have attracted the attention of material scientists, biomedical scientists, and physicists, are a kind of metal materials based on gold and having nanostructure. Besides the common properties of nanomaterials such as surface effect, small size effect, macroscopic quantum tunneling effect, and quantum size effect, their unique optical properties relying on morphology have been widely used in biosensor, bioimaging, optical information storage, and catalysis. With the continuous improvement and development of synthesis methods, gold nanomaterials with various morphologies have been synthesized as shown in Figure 1: Au nanospheres [1, 2], Au nanowires [3], Au nanoshells [4], Au nanocubes [5], Au nanoflowers [6], and Au nanotriangles [7].

Gold nanorods, as a kind of capsule-like gold nanoparticles with a scale from a few nanometers to hundreds of nanometers, have more peculiar optical properties than spherical gold nanoparticles due to their localized surface plasmon resonance (LSPR) effect. The anisotropy of the structure leads to different degrees of polarization of electrons in all directions of the gold nanorods, as shown in Figure 2 [8, 9]. Gold nanorods each have independent electron collective vibration in the diameter and long axis directions. Electrons along the short axis of the rod generally resonate with light in the range of 510 nm-530 nm, which is called transverse surface plasmon resonance absorption (TSPR), and the vibration along the long axis is the scattering of the incident light by the rod, which varies widely from the visible region to the near-infrared region, called longitudinal LSPR. Therefore, the longitudinal LSPR peaks of Au nanorods with different aspect ratios by regulating synthesis are shifted from visible light to near-infrared region, and the oscillator strength of the longitudinal LSPR is larger, which makes the longitudinal LSPR play a dominant role in the optical properties of gold nanorods.

Since the gold nanorods have attracted the attention of researchers, synthetic methods and applied research have made great progress. In this review, we will provide a comprehensive overview of the growth preparation and related properties of gold nanorods and their application. At the end of this review, the future development of this ongoing hotspot will be looked ahead. It should be mentioned that there are many excellent reviews summarizing the research work on gold nanorods, but few of them involve the important applications of gold nanorods based on special optical properties in the formation of composite materials after functionalization. Therefore, we will focus on the widely used
preparation methods and the results of gold nanorod applications in recent years. We apologize for not being able to include all of the important works in this field due to the space limitation.

2. Preparation

In order to study the properties of gold nanorods more thoroughly, the researchers have developed many effective methods for preparing gold nanorods with narrower size and shape distribution, higher yield, and lower cost, including hard template method, photochemical method, electrochemical method, seed-mediated growth method, secondary growth method, and amorphous seed method. Among them, the seed-mediated growth method is the most widely used, and it is already the main method of wet chemical synthesis of gold nanorods.

2.1. Hard Template Method. In 1994, gold nanorods were prepared first by the hard template method by Martin [10]. Later, some people used polycarbonate [11], alumina [12], or aluminum film [13, 14] as a template and sprayed a small amount of silver or copper at the bottom of the template as a conductive substrate. The gold ions (III) were reduced in the template channel by electrochemical deposition, and then, they removed the template and the conductive substrate and added a surfactant (polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB), etc.) for protection and dispersion to obtain monodisperse gold nanorods, as shown in Figures 3(a)–3(c). However, this method is limited by the template space to form gold nanorods, which can be extended to the preparation of gold nanotubes and other tubular nanocomposites. Hard template method can effectively control the length-diameter ratio of gold nanorods by controlling the size of template aperture or adjusting electrochemical deposition time, but the operation is very complex and the output is relatively low.

2.2. Photochemical Method. In 2002, Kim et al. [15] used a cetyltrimethylammonium bromide- (CTAB-) tetradeclayamine (TC12AB) double-surfactant aqueous solution system to reduce chloroauric acid by ultraviolet irradiation at 254 nm for 30 h and changed the content of silver in the system to obtain gold nanorods with different aspect ratios, as shown in Figure 3(f). Niidome et al. [16, 17] prepared gold nanorods by chemically reducing chloroauric acid with ascorbic acid combined with ultraviolet irradiation. The reaction process is that Au (III) was first reduced to Au (I) by ascorbic acid, and then, acetone was added to form carbonyl radicals by photochemistry reaction under ultraviolet irradiation and used as reducing agent to reduce monovalent gold. The gold atoms condense into nucleation, and anisotropic growth forms gold nanorods. It can be seen that the size of the gold nanorods can change as the reaction process changes. In 2009, Placido et al. [18] prepared gold nanorods by photochemistry and discussed the mechanism of silver ions in gold anisotropic growth during the formation of gold nanorods. The method is relatively simple in the process of preparing the gold nanorods, but the precise control of the light intensity and time is difficult, which may cause the quality of the gold nanorods to fluctuate.

2.3. Electrochemical Method. In the electrochemical preparation method, gold plate and platinum plate as anodes and
cathodes, respectively, are embedded in the electrolytic cell solution composed of a mixed surfactant of CTAB and tetra- octylammonium bromide (TCAB). A part of the gold plate loses electrons by ultrasonic temperature-controlled electrolysis to obtain some gold ions, which are moved from the anode to the cathode to be reduced to elemental gold. The other part of the gold plate is reduced and left on the platinum plate interface to encapsulate the gold element reduced at the anode to form gold nanorods. CTAB not only supports the electrolyte but also acts as a rod-shaped micelle template to prevent aggregation of gold nanoparticles. TCAB induces the formation of gold nanorods. Length-to-diameter ratio of gold nanorods was prepared by adjusting the ratio of CTAB to TCAB or by changing the current density. Yu et al. [19, 20] first prepared gold nanorods by this method and later improved the method and realized that the added acetone played a role in loosening micelle structure to prepare longer gold nanorods, as shown in Figures 3(d) and 3(e). The gold nanorod particles prepared by electrochemical method are relatively uniform, but the process is relatively complicated and the whole mechanism of the reaction is not still clear.

2.4. Seed-Mediated Growth Method. The seed-mediated growth method is the most respected method for synthesizing gold nanorods currently. The basic principle is to add a certain amount of gold nanoparticle seeds to the growth solution. And under the action of surfactants, the seed crystals grow into gold nanorods with a certain aspect ratio. The seed-mediated growth method was proposed by Jana et al. [21] in 2001, as shown in Figure 4(a). They added gold seeds protected by sodium citrate into the growth solution in the presence of CTAB and ascorbic acid. Gold nanorods with different aspect ratios can be obtained by changing the amount of gold seeds and chloroauric acid. In the same year, the research group [22] introduced acetone and cyclohexane into the growth solution, which made the micelle skeleton loose, and then enhanced the rod-shaped micelle
structure. By 2004, Sau and Murphy [23] first rapidly reduced \( \text{Au}^{3+} \) to spherical \( \text{Au} \) seed with a diameter of about 5 nm with a strong reducing agent and then prepared a growth solution to make the gold atoms deposit and grow along the one-dimensional direction on the surface of spherical \( \text{Au} \) seeds under the action of the surfactant and eventually grow into a one-dimensional rod-like product, as shown in Figure 4(b).
Recently, Ye et al. [24] reported a new process for the synthesis of gold nanorods by seed-mediated growth method. The basic operation is to use aromatic salicylates as an additive to promote the interaction of CTAB micelle template to form a more stable template structure, while maintaining a low concentration of CTAB. Thereby, the high yield and good uniformity of gold nanorods were achieved, and at the same time, the amount of CTAB was reduced. Furthermore, by adjusting the amount of seed crystals in the growth solution, the concentration of the reducing agent, and the amount of the surfactant and some parameters, the effective control of the morphology of the formed product is achieved.

The seed-mediated growth method involves many factors, such as environmental conditions, process parameters, growth promoters, dispersants, active agents, and pH, which bring many uncertainties to the quality of gold nanorods. Wu and others [25] found that adding nitric acid to the growth solution can obtain large-aspect ratio gold nanorods with better dispersibility and higher yield. Smith and Korgel [26] reported the effect of different batches of CTAB on the quality of gold nanorods, as shown in Figure 4(c). Ye et al. [27] found that the length-diameter ratio of gold nanorods could be adjusted by mixing sodium oleate and CTAB. Xu et al. [28] synthesized gold nanorods with different aspect ratios under alkaline conditions by changing the reducing agent to hydrogen peroxide (H₂O₂), as shown in Figure 4(d). It can be seen that the preparation of gold nanorods by seed-mediated growth method has extremely low requirements on equipment, simple operation, uniformity, good dispersibility, low cost, and relatively high yield and is the most widely used method for synthesizing gold nanorods.

2.5. Secondary Growth Method. The secondary growth of gold nanorods was reported by Kozek et al. [29] in 2013. Gold nanorods with high aspect ratios were prepared by adding hexadecyl dimethyl benzyl ammonium chloride (BDAC) into the growth solution of existing gold nanorods. The mechanism is that phenyl substitutes methyl to weaken the bonding force of BDAC at the end, which leads to the rapid growth of the end, so that gold nanorods with larger aspect ratios can be obtained. This is a new method for synthesizing gold nanorods with larger aspect ratios, as shown in Figure 4(e). This method of secondary growth uses gold nanorod initial solutions with different aspect ratios for secondary growth. It can also be used for the preparation of different topography or other types of metal nanoparticle.

2.6. Amorphous Seed Method. The amorphous seed method is nucleation and growth in the same solution, which can produce smaller-size gold nanorods. Moustafa et al. [30] reported that silver nitrate solution, chloroauric acid solution, and ascorbic acid solution were sequentially added to an aqueous solution of CTAB. After mixing uniformly, the fresh sodium borohydride solution was ingested. The gold nanorods could be prepared by stirring on a desktop whirlpool agitator, as shown in Figure 4(f). In this method, strong and weak reductants are added into the growth solution at the same time. Strong reductants first promote the growth of gold nuclei, while weak reductants promote the growth of rods. Compared with the seed-mediated growth method, this method has fewer reagents and lower cost. Triangular gold nanoparticles can be prepared by changing the concentration of ascorbic acid or replacing silver nitrate with sodium iodide [31].

3. Application of Gold Nanorods

The results show that the gold nanorods have two absorption bands: longitudinal LSPR band and TSPR band. The TSPR band has less dependence on the length-diameter ratio of the rods, and the TSPR band is fixed and the array strength is weak. However, the longitudinal LSPR band is very sensitive to the refractive index of the surrounding medium which is dependent on the length-diameter ratio of the nanorod. Meanwhile, with the increase of the length-diameter ratio of the prepared gold nanorod, the longitudinal LSPR has a significant red shift and is very sensitive to any change of the refractive index of the surrounding medium. Therefore, the enhancement of longitudinal LSPR brings about the optimization of the optical, thermal, and acoustic properties of gold nanorods, which leads to more extensive applications in sensing, biomedicine, and detection. Longitudinal LSPR has great dependence on the size, morphology, and surrounding medium environment of gold nanorods, so it can be used in different sensing applications by changing the aspect ratio of gold nanorods prepared. Longitudinal LSPR enhances the probability of interband radiant transitions, making it possible to achieve two-photon luminescence (TPL) [32, 33] and multiphoton luminescence (MPL) [34, 35] which are difficult to achieve. This property has been proved to be useful for biological effectiveness in the past few years [36]. After the longitudinal LSPR is enhanced, the absorption energy can release a large amount of energy to the gold nanorods and can be released to a rapid nonradiative form of the surrounding environment to generate high heat so that the gold nanorods can be used as heat for treating major diseases such as cancer reagent [37, 38]. Longitudinal LSPR provides a strong surface electric field enhancement effect on gold nanorods. According to the principle that electromagnetic enhancement enhances Raman scattering, gold nanorods can be used as Raman enhancers to enhance the molecular Raman scattering near the surface, which is called Surface-Enhanced Raman Scattering (SERS). It can be seen that gold nanorods can be used as SERS substrate materials for biomedical imaging or detection [39].

3.1. Application in Biomedicine. In the near-infrared region, the background of scattering of light by organisms is weak, while gold nanorods have strong scattering. And due to Rayleigh scattering by surface plasmon resonance enhanced, gold nanorods with larger aspect ratios are particularly suitable for imaging reagents. According to this characteristic, (1) Huang et al. [40] have successfully applied gold nanorods to cells to achieve surface plasmon resonance imaging, thus leading to great practice of using their photothermal effect to kill tumor cells. (2) Malignant tumor cell surface epidermal growth factor receptor (EGFR) [41] is
Figure 5: (a) Light-scattering images of anti-EGFR/Au nanospheres after incubation with cells for 30 min at room temperature. (b) Light-scattering images of anti-EGFR/Au nanorods after incubation for 30 min at room temperature [40].

Figure 6: (a) Schematic diagram of amalgam reaction of Hg and gold nanorods. (b) Hg and gold nanorod head reaction to make nanorods long/decrease in diameter ratio [47].
overexpressed relative to benign tumor cells. Gold nanoparticles modified with anti-EGFR can be used as contrast agents to realize the labeling imaging of tumor cells, as shown in Figure 5. (3) Ding et al. [42, 43] used gold nanorods modified with polyelectrolyte to scatter imaging of tumor cells by electrostatically labeling specific antibodies. (4) The Ben-Yakar group at the University of Texas [44] used the two-photon luminescence (TPL) feature of gold nanorods for three-dimensional fluorescence imaging of biological samples and realized the imaging of skin cancer cell A431 with high resolution.
expression of EGFR. Gold nanorods are controllable in size and morphology, large in surface area, and easy for surface modification; have high stability and low toxicity; and can also be used for drug carriers or photothermotherapy. Among them, Cole et al. [45] found that gold nanorods have high photothermal conversion efficiency, which provides a theoretical basis for photothermal therapy. Wijaya et al. [46] found that the DNA strands can be selectively released by laser irradiation of DNA-loaded gold nanorods, which provides a new direction for medical drug delivery. From this point of view, the application prospect of gold nanorods in biomedicine is very broad.

3.2. Application in Detection. Exposed or surface-modified gold nanorods can be assembled in an orderly manner under the action of certain molecules or ions or agglomerate in an unordered manner to cause changes in their characteristic spectra. Based on this principle, the presence of these specific molecules or ions in solution can be detected and determined by amalgam reaction. Rex et al. [47] used an amalgam reaction limited to the ends of gold nanorods to complete accurate and reliable analysis of fg/L mercury ions by the extinction spectral changes caused by the reduction of the aspect ratio of nanorods, as shown in Figure 6. Zhu et al. [48] prepared a thiolated DNA probe adsorbed on gold nanorods and formed a gold nanorod SS assembly with PCD signal by T-Hg2+-T interaction by selective complexation of thymine on mercury ions, which can be used to detect mercury ions. Wang et al. [49, 50] used the reaction between antibody antigens to demonstrate the color detection based on silica-coated gold nanorod membranes. They used ascorbic acid to reduce mercury ions, which also caused significant color by amalgam reaction.
with gold and achieved the detection of mercury ions. The introduction of mesoporous silica can further improve the biosafety of the material, and the silicon layer can also protect gold nanorods as nuclei.

3.3. Application in Optical Information Storage and Catalysis. It is found that the large-capacity information storage device can be prepared by using the wavelength tunability and polarization dependence of gold nanorods because the nanorods excite and accumulate photon energy to absorb deformation after absorbing radiation. Based on the sensitivity of the length–diameter ratio of gold nanorods to their longitudinal LSPR wavelengths, gold nanorods with different aspect ratios can record their deformation with lasers of different wavelengths, thereby increasing storage density. Chon et al. [51] used laser irradiation to gold nanorods and then used longitudinal LSPR for spectral encoding of high-density optical storage after deformation of gold nanorods. Pérez-Juste et al. [52, 53] prepared a PVA-Au nanorod composite film and found that when the film was irradiated with a laser, by changing the polarization angle of the incident light, the irradiated and nonirradiated areas were significantly different due to the size of the gold nanorods, so this phenomenon can be used for optical printing. Qu et al. [54] attached silver nanoparticles to the surface of the gold nanorods and cross-linked the composite to the Pt/n-Si/Ag photon-electrode pipeline. It was found that the introduction of the gold nanorods significantly enhanced the photocatalytic activity, and the spectral dependence indicated the catalytic enhancement derived from the longitudinal LSPR, as shown in Figure 7. Small-sized Pt nanoparticles have good catalytic performance, but in order to maintain the dispersibility of Pt nanoparticles, gold nanorods can be used as a substrate to immobilize Pt nanoparticles. Wang et al. [55] deposited a submonolayer of Pt on gold nanorods to improve the catalytic performance of formic acid oxidation. He et al. [56] deposited AgPt alloy on gold nanorods to significantly inhibit CO poisoning.

4. Concluding Remarks and Prospects

Since the development of gold nanorods as a research hotspot, research on its synthesis methods and applications has continued to develop and mature. Several preparation methods and plasmon resonance effects of gold nanorods and their applications in many aspects are reviewed. In simple terms, the seed-mediated growth method is a widely used method for preparing gold nanorods by wet chemical methods. According to the requirements of practical applications, ideal quality of gold nanorods can be obtained by adjusting the seed content, silver ion content, solution pH, reaction time, and temperature of the growth system. The good solvent dispersibility and biocompatibility of gold nanorods have made it a great concern in biomedical and biochemical testing and have achieved good results. And the optical properties induced by the enhancement of surface plasmon resonance dependent on its aspect ratio make the research on optoelectronic devices, sensors, and so on have continuous progress. With the continuous updating of the characterization method of nanomaterials, researchers have locked their attention on functionalized gold nanorods in recent years. For example, Nguyen et al. [57] used a binary mixture of CTAB and potassium oleate (KOL) as surfactant to prepare gold nanorods with high uniformity and low cost efficiency, and a highly ordered vertical array is formed on the glass dish substrate by self-assembly technology. The surface-enhanced Raman spectrum enhancement factor of the gold nanorods of this structure can reach 10⁷, which can lead to completely low-cost requirements for trace detection of organics, as shown in Figure 8. Wang et al. [58] prepared a novel nanomaterial GNRs/PPy/m-SiO₂ core-shell hybrid consisting of gold nanorods, polypyrrole (PPy), and mesoporous silica. After loading the anticancer drug doxorubicin (DOX), the photothermal properties of GNRs/PPy@m-SiO₂-DOX resulting from the longitudinal LSPR of gold nanorods and the additional electronic oscillation caused by the conductivity of PPy were studied. They found that NIR-induced photothermal effects were beneficial to drug release, as shown in Figure 9. Researchers prepare new composite materials by means of self-assembly, hybridization, alloying, and doping or based on the unique optical properties of gold nanorods, which can be used to broaden and deepen the applications in biomedicine [59, 60], sensing [61], and catalysis [62]. We also believe that in the near future, the application of composite materials based on special optical properties of gold nanorods will continue to progress and deepen. It will also be a new research hotspot for the biological safety of materials themselves and material removal when they are used for human beings.

Conflicts of Interest

The authors declare no competing financial interest.

Acknowledgments

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