

Applications of AuNRs@SiO₂ Matrix Nanocomposites

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Abstract

Gold nanorods (AuNRs/GNR) have unique, controllable and anisotropic local surface plasmon resonance (SPR) properties, which have been widely used in biochemistry, electronics and catalysis. It is of great value and significance to study the synthesis, properties, surface modification and structural regulation of AuNRs. This paper introduces AuNRs and AuNRs@SiO₂. The synthesis of AuNRs@SiO₂ composite nanomaterials with quantum dots, graphene, rare earth materials and magnetic materials is described. The applications of nanocomposites in optics, biomedicine and biosensors are also discussed. The future development of nanocomposites is proposed.

Keywords

AuNRs@SiO₂ Matrix Composite, Application, Review

1. Introduction

This, in recent years, nanotechnology has rapidly developed due to its unique characteristics and range of applications. Nanoparticles (NPs) typically smaller than 100 nanometers in size have been widely used in various products and fields, including environmental, energy, consumer goods, medicine, and life science applications. Gold nanoparticles are stable and have been widely used in biomedical fields for drug delivery [1], biosensors and imaging [2], and cancer diagnosis and treatment [3].

The deposition of silica on inorganic nanoparticles is of significance as SiO₂ and subsequent surface functionalized silane chemistry are now well established and show high biocompatibility. In 1968, the development of the Stöber method inspired 50 years of research on the synthesis, operation, and application of SiO₂ NPs [4]. The addition of cationic surfactants is a common improvement to the

Stöber method to synthesize submicron mesoporous silica of with a variable pore size. The porosity and surface area of these structures enables their use in catalysis, biosensor, physical and chemical research. NPs are now frequently covered with SiO₂, and methods for their covering with noble metals, semiconductors and magnetic NPs have been established [5] [6] [7]. SiO₂ shells can improve the stability of GNRs and impart protection from degradation in harsh thermal and chemical environments, improving the biocompatibility of GNR by providing a barrier between cationic surfactants and the environment [8]. Herein, this paper reviews the progress, properties and applications of AuNRs@SiO₂ nanocomposites.

2. Preparation Method

2.1. Preparation of AuNRs

2.1.1. Template Method

Martin *et al.* [9] [10] [11] first tried to synthesize AuNRs by template method in 1994. This method relies on electrochemical deposition of gold in the pores with nanoporous polycarbonate or alumina membrane as template. Firstly, the template was prepared by electrochemical etching of alumina in acidic solution, and uniform pores with a diameter of 5 - 200 nm were generated on the template. Then, the gold in the pores was electrodeposited at the anode position. Finally, under the protection of the protective agent solution, the template was dissolved and ultrasound was used to release the gold nanorods. The width of AuNRs prepared by this method depends on the diameter of the hole, and the length of the rod depends on the amount of gold deposited in the pores of the template. Due to the uneven deposition of gold, the production of AuNRs will be greatly reduced, and the length of nanorods can not be accurately controlled, so the application of this method is limited. In recent years, with the improvement and innovation of template method, gold nanorods prepared by template method have also been applied in various fields [12] [13] [14].

2.1.2. Electrochemical Route

The earliest electrochemical method to prepare gold nanorods by electrochemical method and photochemical reduction method was proposed by Wang *et al.* At that time, the yield of gold nanorods was high. The growth solution contains two kinds of surfactants: cetyltrimethylammonium bromide and tetraoctyl ammonium bromide. The electrolytic cell containing the growth solution is placed in the ultrasonic cell, and then the gold plate as sacrificial anode and platinum plate as cathode is inserted. Before electrolysis, a proper amount of acetone is added to the cell, and then electrolysis is carried out under constant current [15] [16]. However, electrochemical method has not been well developed in recent years due to the high requirements of equipment. After the seed growth method was used, electrochemical method has been basically eliminated. However, this method has great historical significance for the preparation of gold nanorods.

2.1.3. Synthetic Method

The definition of seed growth method was proposed by Jana *et al.* [17]. Wesner and Wokaum found that when there were small gold nuclei in the solution in 1989, adding hydrogen peroxide and other weak reducing agents into the solution could transform HAuCl_4 into gold, and slowly deposit gold nanorods. The gold nanoparticles can be prepared by changing the size of gold nanoparticles and the ratio of gold ions to gold nanorods. Under the constraint of template, the AuNRs with corresponding aspect ratio are grown directionally [18]. Since then, according to this principle, researchers have done a lot of work to improve and perfect the seed growth method. At present, there are three kinds of seed growth methods: Silver ion-mediated “Seedless” growth method, silver ion-mediated seed growth method, and three-step seed growth method. The seed growth method has low requirements on equipment, mild reaction and can expand production. It is the most successful method for preparing gold nanorods at present. The specific flow chart is shown in **Figure 1** [19], the seed solution was prepared first, and then the aspect ratio of AuNRs was controlled by controlling Ag^+ content. Most preparation methods in research are based on this method [20] [21] [22] [23].

In addition to the above methods for preparing and synthesizing GNRs, there is also electron beam lithography. However, among the many methods to prepare AuNRs, the seed growth method can successfully prepare GNRs with an axial diameter ratio of 1.5 - 20, and obtain polarization peaks of different absorption wavelengths, moreover, the seed method has the advantages of low requirements for reaction conditions and equipment, simple preparation steps, high yield and easy regulation of aspect ratio.

2.2. Property of AuNRs

Among the numerous nanomaterials, precious metal nanomaterials, as a new type of research field, have been widely concerned by researchers in the past decade. This is due to the special physical and chemical properties of noble metal

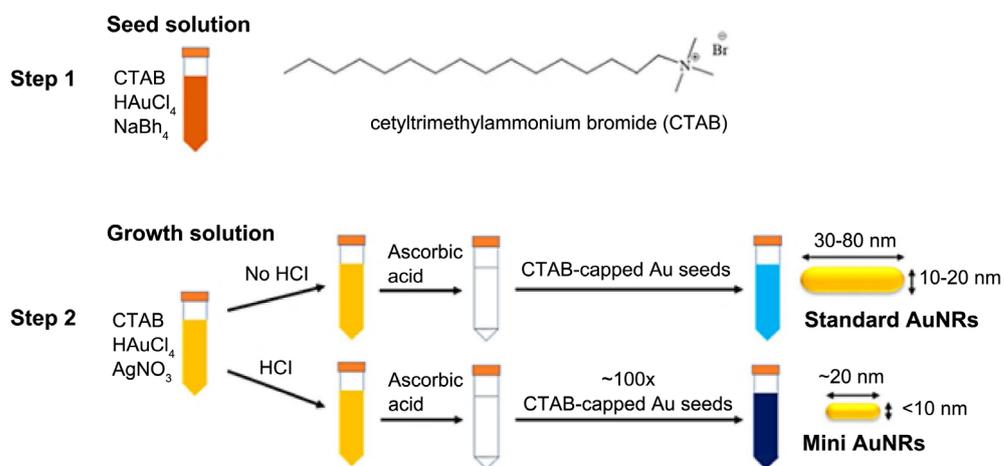


Figure 1. Process diagram of preparing AuNRs by seed growth method [19].

nanoparticles, which have made long-term progress in the fields of information storage, photocatalysis, optoelectronics, biomarkers and surface enhanced Raman scattering [24] [25] [26] [27] [28]. Noble metal nanomaterials have unique local surface plasmon resonance (SPR) peaks and surface enhanced Raman scattering (SERS) as two important properties of gold nanomaterials, these characteristics can be controlled by controlling the size and shape of metal nanostructures [29] [30]. Among different gold nanostructures, gold nanorods are the most widely used, mainly because they have two resonance peaks, LSPR peak and TSPR peak [31] [32], which correspond to the longitudinal and transverse SPR respectively. The position of LSPR is very sensitive to the aspect ratio of gold nanorods. According to the needs, we can change the aspect ratio (AR) of gold nanorods, The SPRL peak is modulated in a large range near the near-infrared region [33], while the position of TSPR is not affected by the aspect ratio of gold nanorods, and is still near the wavelength range of visible light [34]. Moreover, the SERS activity of metal nanoparticles is obviously related to the morphology, size and size of the particles. The larger the size of the nanoparticles, the higher the SERS activity [35]. For gold nanorods, the closer the longitudinal vibration peak is to the laser excitation wavelength, the better the enhancement effect is.

2.3. Preparation of AuNRs@SiO₂

Silicon dioxide as a shell to coat gold nanorods is the mainstream of current application. Because it is the most chemically inert material and is optically transparent, it has the characteristics of adjustable size, easy surface structure modification, mature coating process, etc., and has attracted wide attention in biomedicine, sensing, energy storage and other aspects [36] [37] [38]. The preparation method of silica coated gold nanorods is based on the traditional Stöber method. The structure of Au NRs coated with silica has better controllability and better colloidal stability. Gorelikov *et al.* [39] strongly located CTAB molecules on single nanoparticles were used as templates for the three-dimensional polymerization of tetraethyl orthosilicate (TEOS), the precursor of alkoxy silicon, so as to obtain high yield mesoporous silica coating on nanoparticles, and developed a widely used direct coating method. Chiang *et al.* [40] studied the effects of single factors on the particle size, pore structure and morphology of monodisperse silica nanospheres. Liu *et al.* [41] used the acoustic assisted synthesis method to directly coat PVP activated AuNRs onto silica shell, which was more simple and efficient. Meanwhile, ultrasonic promoted the uniform silicification reaction, which made the silicon shell compact and the coating yield was high. Meng *et al.* [42] prepared gold nanorods by seed growth method, and hydrolyzed tetraethyl orthosilicate in alkaline solution to obtain nano gold structure coated with silica. By coating silicon dioxide on gold nanorods and adjusting the aspect ratio of gold nanorods with different silver ion concentrations in the growth solution, the gold nanoparticles that need to be absorbed in specific UV region can be synthesized. The specific flow chart is shown in **Figure 2**.

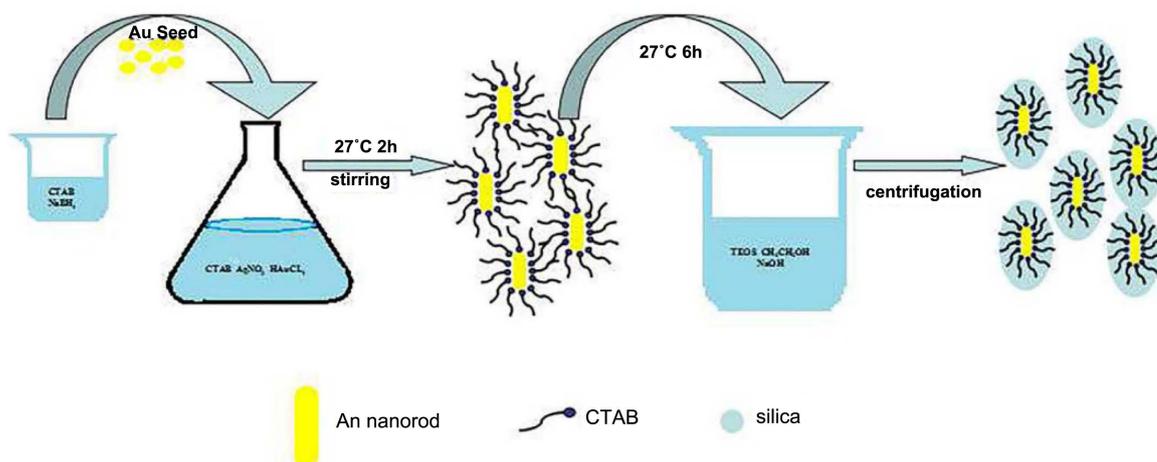


Figure 2. Schematic illustration for the preparation of core-shell Aunanorods@SiO₂ nanostructures [42].

2.4. Property of AuNRs@SiO₂

The special surface plasmon resonance (SPR) spectra of gold nanorods make their optical applications more and more extensive. Due to the large surface energy of the metal nanorods, the dispersion system formed is very unstable and easy to aggregate. However, the stability of the nanoparticles is significantly improved after the surface of gold nanorods is wrapped with silicon dioxide, forming a silica shell. Meanwhile, the existence of silica shell does not change the surface plasmon resonance properties of gold nanorods. Therefore, the preparation of core-shell structure of gold nanoparticles and silica, and the study of plasma resonance optical properties related to this core-shell structure, and because of the loading characteristics of this structure, it is not only operable, but also of great significance.

3. AuNRs@SiO₂ Composites and Other Materials

3.1. AuNRs@SiO₂@Quantum Dots

Quantum dots (QDs) are important low dimensional semiconductor materials. The dimensions of QDs in three dimensions are no more than twice the Bohr radius of excitons in the corresponding semiconductor material. QDs are generally spherical or quasi-spherical, with a diameter of 2 - 20 nm with applications in both life sciences [43] and energy storage [44]. Zhou *et al.* [45] synthesized gold nanorods@silica CdTe QD hybrid nanostructures and studied the effect of gold nanorods on the fluorescence of CdTe QDs. The quenching effect was reduced through the coating of silicon dioxide onto the surface of the gold nanorods. Han *et al.* [46] synthesized a novel hierarchical silica coating AuNR@CdSeTe core/shell structures of QDs. Gold nanoparticles were mediated by an initial mesoporous silica layer, covered with a dense silica layer, and then directly assembled into QDs on the surface. Through the plasma resonance effect of Au, the fluorescence of the carbon QDs was enhanced and its material properties realized.

3.2. AuNRs@SiO₂@Graphene

Reduced graphene oxide (rGO) is a derivative of graphene with a 2D carbon honeycomb lattice. As a rising star in material science, rGO has potential applications in energy, catalysis, electronics and molecular sensing. Due to their high biocompatibility, low cytotoxicity and high thermal conductivity, rGO-biomolecular conjugates and rGO-nanoparticle hybrids now offer new directions for electrode materials [47], drug delivery [48] and sensing detection [49]. Zhang *et al.* [50] prepared near-infrared responsive core-shell gold nanorods/mesoporous silica/reduced graphene oxide NPs through electrostatic interactions, which synergistically enhanced both the photo thermal stability and transition effect. These novel near-infrared responsive core-shell hybrid NPs with enhanced photo thermal stability and conversion effects were suitable for photo thermal therapy, bioimaging and drug delivery. Qi *et al.* [51] prepared near-infrared (NIR) responsive core-shell gold nanorods/mesoporous silica NPs through electrostatic and physical absorption, and coated them with PEGylated graphene oxide. Due to the introduction of biocompatible GO-PEG, the hybrid NPs showed unique photo thermal stability under physiological and acidic conditions. The performance of composite graphene AuNRs@SiO₂ has been improved through these methods. The synthetic route is shown in **Figure 3** [51].

3.3. AuNRs@SiO₂@Magnetic Compounds

Chapman *et al.* [52] developed a simple heteropolymerization method to coat magnetite (Fe₃O₄) NPs onto the surface of silica-coated gold nanorods. This method produced Fe₃O₄-SiO₂-AuNRs that maintained the longitudinal surface plasmon resonance of the gold nanorods which were magnetically responsive. Fe₃O₄-SiO₂-AuNRs are of particular interest to biomedical applications as they consist of biocompatible building blocks that are potentially useful for multi-modal imaging or photo thermal therapy with magnetic targeting. Huang *et al.* [53] established a mobile AuNR confined to continuous/permeable IOs nanoshells

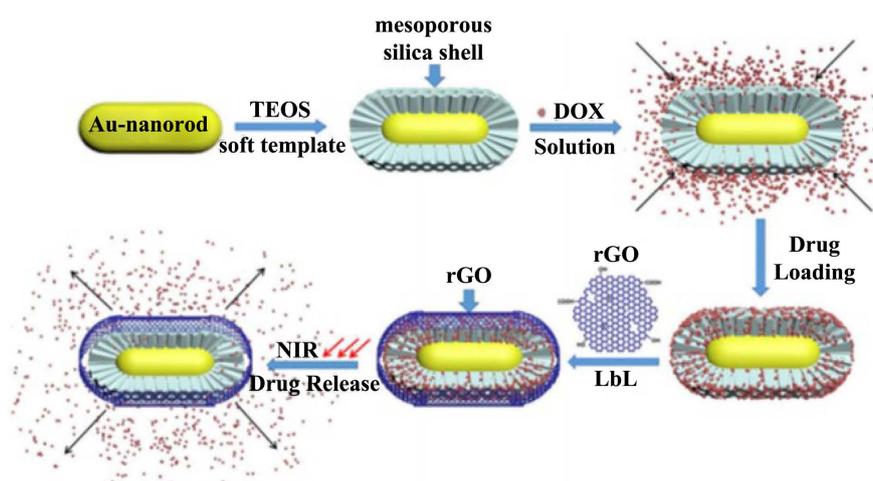


Figure 3. Preparation of Au/SiO₂/rGO nanoparticles [51].

using silica templates, in situ IO deposition and selective template removal, followed by doxorubicin (DOX) loading and dopamine-modified hyaluronic acid (DA-HA) adhesion. Due to the unique coordination between DOX and iron, these multifunctional nanocapsules display unique NIR plasma absorption, excellent magnetic responsiveness and dual-responsive drug release behavior in response to pH/local heating.

3.4. AuNRs@SiO₂@Rare Earth Materials

Rare earth ions show abundant levels of emission due to their 4f-4f or 5d-4f transitions. The absorption and emission spectra of rare earth ions in both visible and infrared spectral regions correspond to the f-f transition. As 4f electrons are surrounded by 5s and 5p electrons, the position of the emission peak of the spectrum does not change with the external environment. Their unique spectral properties, including narrow emission bands and long luminescence lifetimes, originate from 4f-4f transitions within the ions. Lanthanide-doped organic light-emitting thin films have attracted attention due to their wide applications in solar cells, organic light-emitting diodes, metal ceramics, and optical amplifiers due to their abundant energy levels and wide emission range from ultraviolet to near infrared light [54] [55]. AuNRs@SiO₂@Rare earth composite materials also realize enhanced transition. Wang *et al.* [56] deposited gold@silica hetero-nanorods onto silica through drop casting which were covered with Eu-doped polymer films. Aggregates of the NPs from small to large were regulated by the concentration of the nanorods. Across a wide concentration range, the photoluminescence intensity of Europium (DBM) 3 thin films doped with gold silica nanorods increased ≥ 200 -fold due to the coupling effect of the photons and nanorods. The maximum strength increased by 263-fold. In addition, in the presence of the nanorods, the quantum yield increased from 0.98% to 21.6%, and the lifetime extended from 546.4 to 625.9 s. This enhanced luminescence and extended lifetime were applicable to numerous fields. Lin *et al.* [57], combined Au@SiO₂ nanorods and ligand-free NaYF₄:Tb³⁺ and Yb³⁺@NaYF₄NP to form water-soluble nanocomposites, termed Au@SiO₂/NaYF₄Tb³⁺, Yb³⁺@NaYF₄. Through adjustment of the thickness of the SiO₂ shell and Au@SiO₂ concentration, plasma-enhanced upconversion (UC) and quantum cutting (QC) were obtained and optimized in these nanocomposites. When the thickness of SiO₂ shell was 35 nm, the enhancement factors of UC and QC increased by a maximum of 1.91- and 3.47-fold respectively. These nanocomposites can be applied to biofluorescent labeling, super-resolution imaging and solar cells.

4. Applications

4.1. Optical Field

Gold nanorods have attracted attention due to their unique surface plasmon resonance (SPR) and transverse (SPR-T) and longitudinal (SPR-L) collective oscillations of quasi-free electrons [58]. The GNRs are coupled together due to the

limitations of their electrostatic interactions. SPR coupling can enhance the local electric field in the band gap region. These can be used to enhance optical signals, including Raman signals, fluorescence signals, second harmonic signals and nano-optical tweezers signals [59] [60]. In addition, plasmon coupling between adjacent GNRs leads to large shifts in extinction or scattering spectra, often accompanied by distinct color changes that form the basis for the development of chemical and biological sensors [61] [62] [63]. Lui and colleagues [64] induced the formation of Au with EE and S core-shell structures by depositing SiO₂ onto the prepared GNRs assemblies using dithiol poly(ethylene glycol) (HS-PEG-SH) as the connecting medium. The optical response of the self-assembled AuNRs and their corresponding core-shell nanostructures were simulated through the finite difference time domain (FDTD), showing that the products displayed spectral tunable properties, in addition to thermal stability and biocompatibility.

Lanthanide-doped organic luminescent films display abundant energy levels and can emit from ultraviolet to near-infrared light, with applications in solar cells. Wang *et al.* [56] aggregated these films onto the surface of silicaAu@SiO₂ nanorod thin films with core-shell structures to produce metal-enhanced luminescent substrates. The results showed that through doping Au@SiO₂T, the photoluminescence intensity of Eu(dbm)₃ thin films increased in a concentration dependent manner. Due to the coupling effect between photons and nanorods, the photoluminescence intensity increased by more than 200-fold, with a maximum enhancement of 263-fold, the lifetime of which was 546 s - 625 s, with quantum yield increases from 0.98% to 21.6%. LSPR leads to changes in the density of electron state, altering the radiation attenuation rate and non-radiation attenuation rate by doping Au@SiO₂. This improves the performance of lanthanide luminescent films with broad application prospects in future studies.

Nanogold with surface plasmon resonance properties can absorb visible light bands in the solar spectrum, generate an unbalanced distribution of hot electrons and hot holes in metals, and drive photoelectrocatalytic reactions. Schlathner *et al.* [65] studied the multilayers of open circuit (OC) electrochemical cells through sacrificial photooxidation using citrate ions on AuNM modified electrodes. This increased the optical efficiency of Au@SiO₂@Au photogenerated hot holes in the plasma nanoparticles. Metal NPs have been shown to enhance the electron transfer of surface citrate ions to photoexcited hot holes that occurs simultaneously during hot carrier relaxation. The photocharge rate of AuNMs induced by the photooxidation of ionic hot holes on the surface of citric acid is dependent on the nature of plasmon resonance. The mechanism of photocharging in AuNPs is shown in **Figure 4**.

SPR can improve photocurrents and enhance the photoenergy conversion efficiency of PCE. Che *et al.* [66] used AuNRs@SiO₂ in a photoelectric conversion system and showed that asymmetric gold nanorods not only improve the absorption of light, but couple with N719 dyes to reduce the recombination of photogenerated electrons, prolonging the lifetime of the photoelectrons. Studies

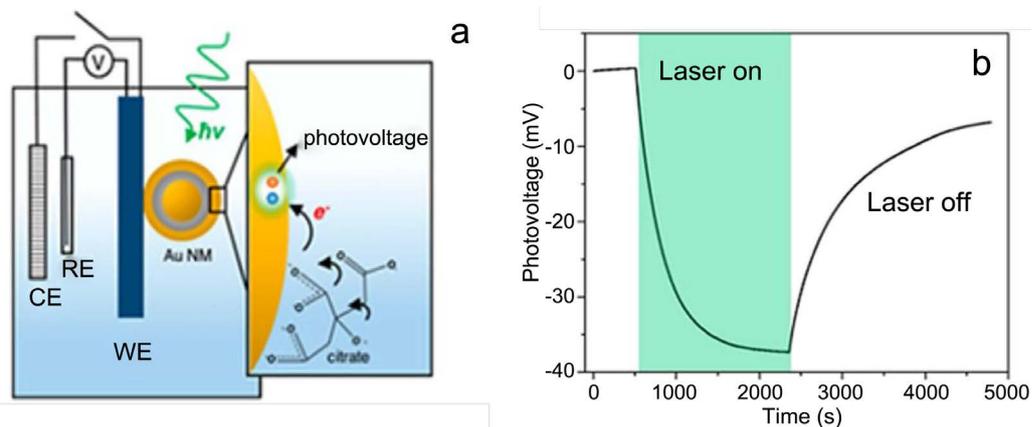


Figure 4. (a) Mechanism of photocharging in AuNPs. (b) OC potential vs time for a AuNM electrode before, during, and after 550 nm laser irradiation [65].

have shown that the introduction of GNRs@SiO₂ improves both the light absorption range and intensity of the photoanode. The utilization rate of light can also be enhanced by the complementary induction of plasmon using dye molecules and GNRs, increasing the absorption coefficient within a specific wavelength. The optical coupling of GNRs with TiO₂ was studied using the finite difference time domain method (FDTD). Compared to the anode, the monochromatic photoelectric conversion efficiency (IPCE) of the optimized electrode significantly improved. At 500 - 600 nm and 610 - 710 nm, the overall conversion efficiency improved from 6.4% to 7.5% (Figure 5).

Luna *et al.* [67] discussed the photocatalytic performance of Au-TiO₂/SiO₂ coating on two different building stones. During the experiment, a sol-gel method was used to synthesize Au-TiO₂/SiO₂ photocatalysts for building materials with self-cleaning and decontamination properties. The Au-TiO₂-NPs were integrated into the silica by spraying, so that they were sprayed in the building Material. The sol gelled spontaneously to produce a long-term Au-TiO₂/SiO₂ coating with photocatalytic properties, the integration of TiO₂ in the silica matrix enhances its adhesion to the substrate and subsequent coating durability. AuNPs can effectively improve the photocatalytic activity, self-cleaning and decontamination properties of coated building materials. Bai *et al.* [68] will be doped with SiO₂@TiO₂ double shell (AuNR@SiO₂@TiO₂). A novel composite photoanode was formed by mixing graphene and gold nanorods into dye-sensitized solar cells (DSSCs). The maximum short-circuit current density is 16.26 macm⁻² and the power conversion efficiency is 8.08%, which is 37.7% and 32.9% higher than that of conventional DSSC. These significant improvements in short-circuit current density and power conversion efficiency are attributed to the synergistic effect of LSPR of graphene and AuNRs, as well as the TiO₂ shell of AST, which will also increase the specific surface area and dye adsorption to a certain extent. The paper [69] [70] also carried out the corresponding work, and further explored AuNR@SiO₂. For the application in the field of photosensitive battery, Figure 6 is the schematic diagram of battery structure.

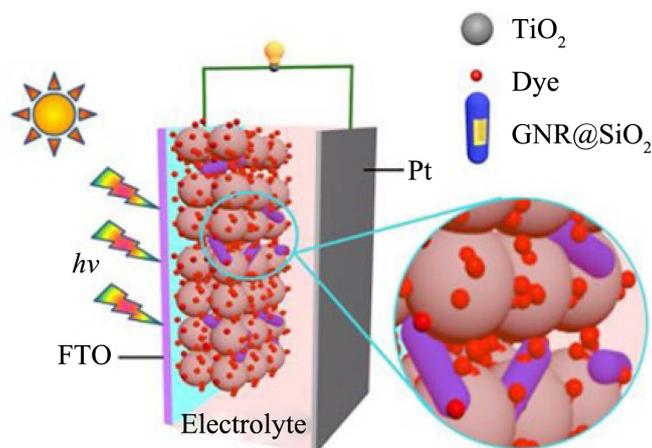


Figure 5. Preparation of Au/SiO₂/rGO nanoparticles [66].

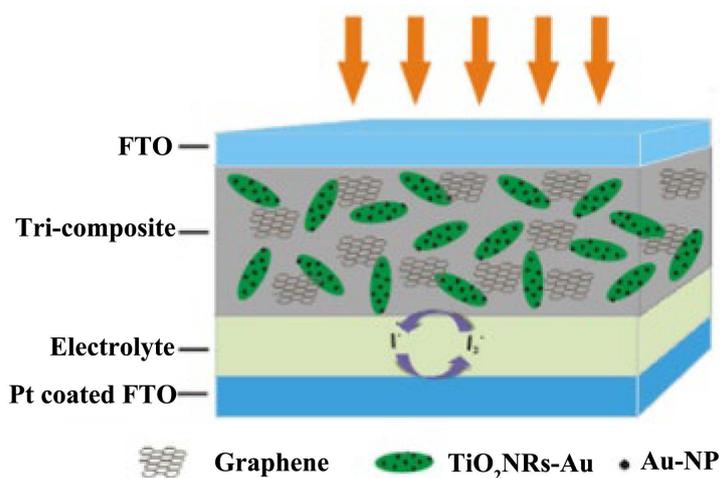


Figure 6. Schematic diagram of the ternary G-TiO₂NRs-Au composite photoanode and the DSSC [70].

4.2. Biomedical Fields

Gold nanorods are useful in a range of biomedical applications, including cell imaging, drug or gene delivery, and cancer therapy, due to their strong and tunable plasmon resonance properties [71] [72] [73] [74]. Photothermal therapy is an emerging anti-tumor therapeutic that involves the artificial injection of photothermal conversion materials into the tumor using targeted recognition technology. Light energy is then converted into heat energy under the irradiation of near-infrared light, generating local high heat in the tumor tissue, leading to cancer cell death. The ability to specifically target tumor cells is critical to the diagnosis and treatment of cancer [75]. Photothermal therapy uses a range of materials with high photothermal conversion efficiency. The photothermal effects of gold nanorods can increase the local temperature to 1000°C in the nanosecond range, highlighting its potential application in tumor radiotherapy [76].

Zhou *et al.* [77] fabricated gold nanorods coated with mesoporous silica by

combining hyaluronic acid (HA) with RGD. AuNRs@mSiO₂-HA-RGD for dual-targeted chemo-photo thermal therapy. The model anticancer drug DOX was loaded onto AuNRs@mSiO₂-HA-RGD mesoporous silica through electrostatic interactions. The resulting product showed a high photo thermal effect with drug loading rates of ~20.16%, and pH- and NIR-triggered drug release characteristics. As a novel dual-target chemotherapy-photo thermal therapy system, DOX-AuNRs@mSiO₂-HA-RGD NIR-induced hyperthermia, drug delivery, and dual receptor-specific targeting, highlighting its potential as an anticancer therapeutic (**Figure 7**).

Gao *et al.* [78] developed a novel folate-based functionalized AuNRs@SiO₂-FA and studied its cellular uptake in vitro and in vivo. AuNRs@SiO₂-FAIt showed high biocompatibility, cell attachment to folate receptors and ligand receptor-mediated endocytic cell entry into tumor cells (**Figure 8**).

Hou *et al.* [79] developed a simple method to synthesize monodisperse, uniform and well-defined nanostructures of PMGNS NPs of an appropriate size (≤ 100 nm) using the seed growth method. The PMGNS NPs consisted of a superparamagnetic Fe₃O₄ inner core with silica as an intermediate layer coated by gold nanoshells using the seed-mediated growth method. This led to the development of contrast agents for MR and CT imaging, with high photo thermal effects and low cytotoxicity. Further comprehensive evaluation showed that the PMGNS NPs showed high biocompatibility and potential as an MR/CT dual-modality

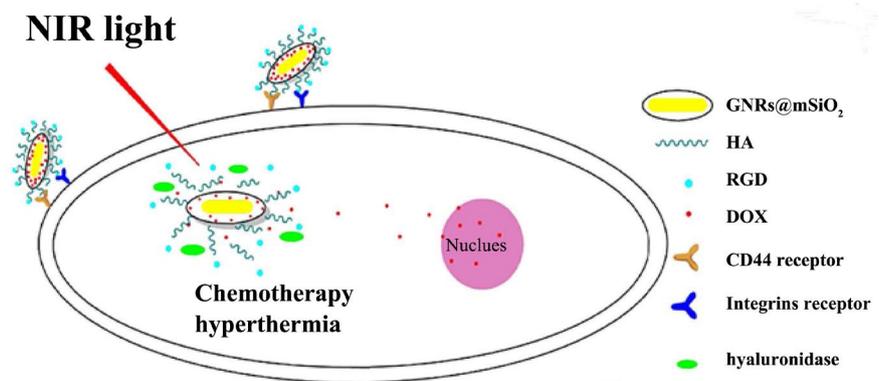


Figure 7. CD44- and integrin-mediated endocytosis of nanoparticles and subsequent chemotherapy and NIR-induced hyperthermia [77].

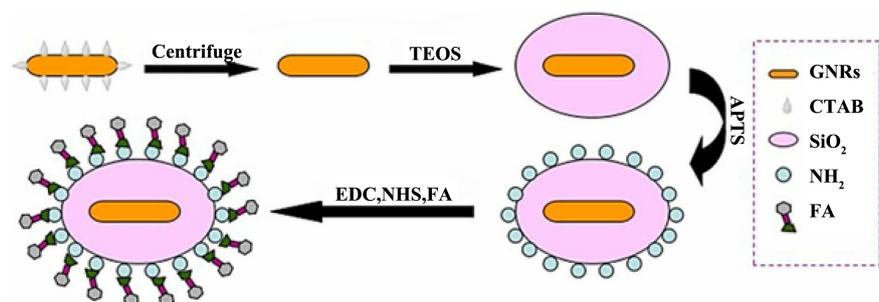


Figure 8. Procedure for the synthesis of GNRs@SiO₂-FA [78].

imaging-guided photo thermal therapeutic for biomedical applications. Xuan *et al.* [80] formed AuNS on the surface of mesoporous silica NPs (MSNs) using the seed-mediated growth method to which the NIR dye cyanine 7 (Cy7) was conjugated. The NPs were then fused to the surface of macrophage membrane (MPCM) vesicles to prepare MPCM-AuNS with utility for *in vivo* imaging in mouse models following intravenous injection. The results showed that MPCM-AuNS guided by the surface proteins on MPCMs, prolonged *in vivo* circulation times and enhanced the accumulation of AuNS in the tumors. When irradiated using near-infrared light, the tumor cells were ablated by the heat energy transformed by the accumulated AuNS. This biomimetic strategy significantly improved the efficacy of AuNS-regulated *in vivo* cancer photo thermal therapy, thereby integrating the advantages of the NIR thermal effects produced by AuNS and the long circulation time and active recognition ability inherited from macrophages.

Zhang *et al.* [81] have grown multifunctional nanocomposites with up to the third generation (G3) grafted polyamide type dendrimers on the surface of gold nanorods coated with mesoporous silica by divergent technology. The AuNRs@SiO₂-G3 nanocomposites have uniform size and excellent stability, which can not only be used as a targeted contrast agent for photothermal cancer treatment, but also be used as a scaffold for the intracellular delivery of anticancer drugs and small interfering RNA (siRNA) to improve the efficiency of cancer treatment, **Figure 9** is the preparation flow chart of the material. Ma *et al.* [82] prepared Au nanorods/mesoporous silica/hydroxyapatite (HAP) nanocarriers with thermal responsive polymer caps for remote drug delivery. *In vitro* drug delivery results showed that the hybrid nanoparticles exhibited excellent drug loading efficiency and unique near-infrared (NIR), heat and pH responsive drug delivery characteristics. The results of cell viability also showed that the P (NIPAM-co-AAC) capped AuNRs/SiO₂/HAP nanoparticles had excellent biocompatibility.

4.3. Detection

Glycoproteins regulate cell growth, proliferation and signaling. Accordingly, the aberrant expression of glycoproteins leads to disease occurrence, with many

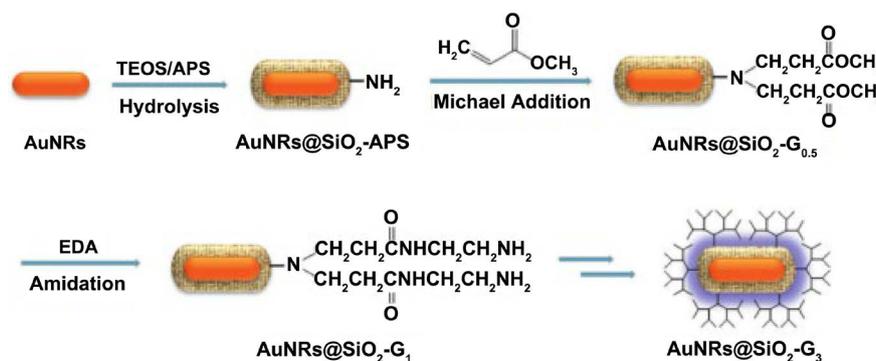


Figure 9. Preparation of multifunctional AuNR@SiO₂-G3 nanocomposites [81].

employed as disease biomarkers for clinical diagnosis. Due to the low detection efficiency of glycoproteins in biological samples, improving the selectivity and sensitivity of glycoprotein detection is an important requirement for clinical diagnosis and treatment. Molecular imprinting is an effective technique to simulate the molecular recognition of natural receptors. Molecularly imprinted polymers (MIPs) show high recognition ability and chemical stability, are easy to synthesize, and have been used for chromatographic separation, sensors, drug delivery and other fields. MIP based on the affinity of borate shows high specificity, affinity and anti-interference, and can be used as an alternative to natural antibodies for the detection of target substances in complex samples.

Sun [83] used in situ growth methods and immobilized AuNR layers on the surface of PAD, and introduced MPBA to the electrode surface through Au-S bonds to capture target glycoproteins and prepared borate affinity-based MIP and $\text{SiO}_2@Au/\text{dsDNA}/\text{CeO}_2$ composites. The formation of hybrid chains and the large surface area of $\text{SiO}_2@Au$ enhanced the sensitivity of the platform permitting rapid and accurate glycoprotein detection. The schematic diagram of the detection method is shown in **Figure 10**.

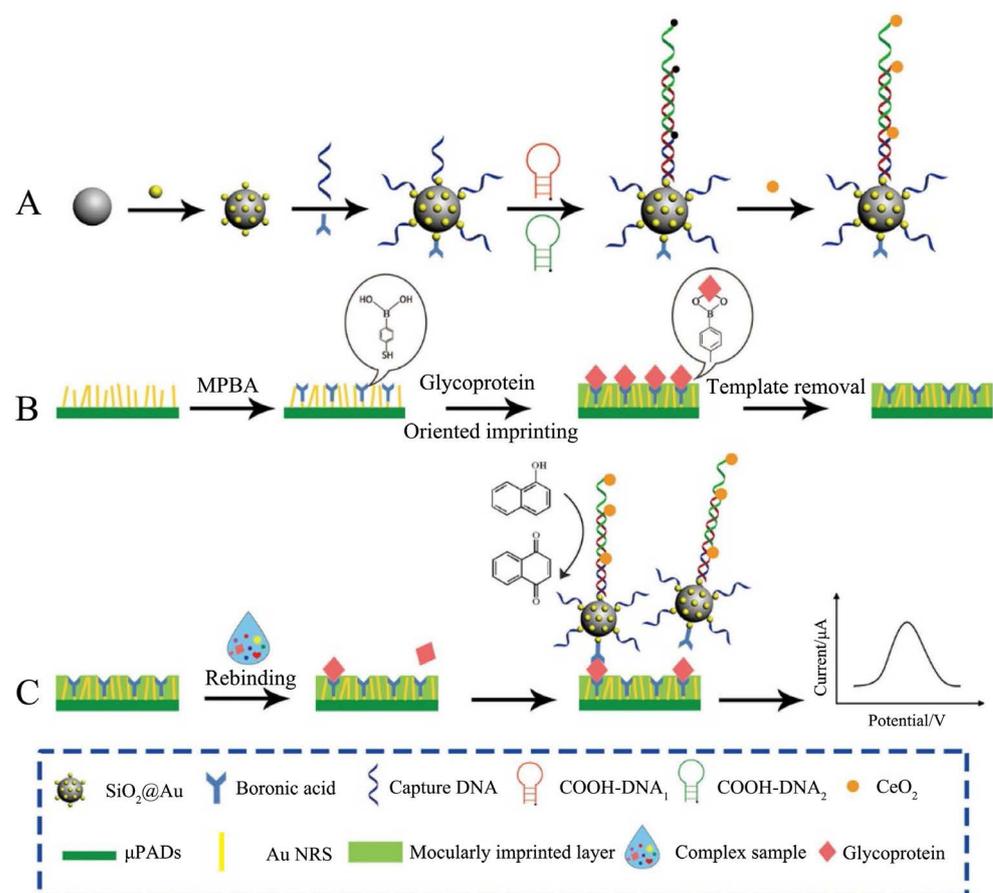


Figure 10. Schematic illustration of the proposed approach for the detection of glycoprotein: (A) preparation of the $\text{SiO}_2@Au/\text{dsDNA}/\text{CeO}_2$ signal tag; (B) synthesis of the Boronate affinity-based glycoprotein imprinted film; and (C) fabrication procedure of the sensing Platform and the Electrochemical detection of OVA [83].

Gan [84] *et al.* showed that multilayered AuNR@Ag@SiO₂ doped into the MIP matrix of molecularly imprinted polymers can significantly accelerate electron transfer and enhance the electrochemical signals. AuNR@Ag@SiO₂@MIP/GCEAs were prepared as a novel electrochemical sensing platform and theobromine THb was quantified with a detection limit of 8.0 nM at a range of 10 - 100 nM, The flowchart is shown in **Figure 11**. Tribrominated biphenyls in food and environmental samples were extracted and determined. The recovery rates ranged from 92.20% to 107.1%, with a relative standard deviation of <4%. This sensor provides a reliable means for the detection of alkaloids in complex environments and lays the foundation for the development of reusable, sensitive and selective electrode materials.

Chen *et al.* [85] used AuNR@SiO₂ to detect temperature jumps through the photoexcitation of gold nanorods coated with SiO₂ using a confocal fluorescence thermometer and 1064 nm pulsed laser to accurately monitor calorific energy. A spatially and temporally resolved method was established to perform these experiments, permitting the study of protein dynamics as a whole without segmenting the target protein (**Figure 12**).

With continuous economic developments, a large number of new organic substances continue to be artificially synthesized, including drugs, personal care products, and flame retardants. As traditional wastewater treatment and drinking water treatment processes are generally unable to effectively remove such pollutants, these types of organic matter usually exist in both natural and tap water at trace concentrations, collectively termed organic micro pollutants.

Wei *et al.* [86] designed double-sided gold nanorod/silica composite structure (AuJNRs) in which the presence of silica guaranteed the colloidal stability of the gold nanorods. The uncovered side of the gold nanorods provided an active site



Figure 11. Schematic illustration of the preparation procedure of AuNR@Ag@SiO₂@MIP [84].

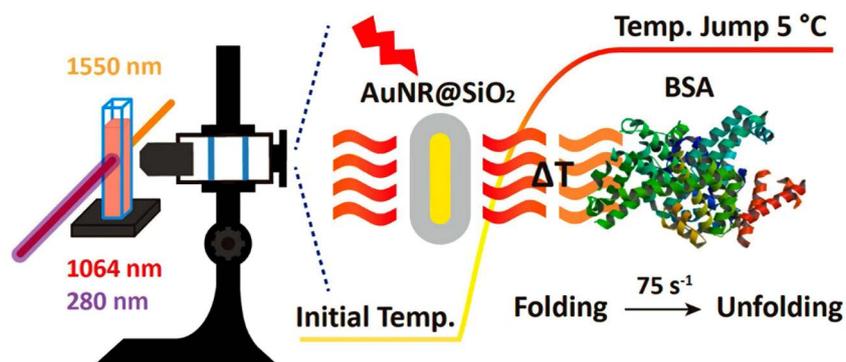


Figure 12. Schematic illustration of the AuNR@SiO₂ as Temperature Jump Photo thermal Convertors Coupled with a Confocal Fluorescent Thermometer to Study Protein Unfolding Kinetics [85].

for the catalysis of the advanced oxidation reaction of persulfate. The experimental results showed that using local surface plasmon resonance for energy conversion, photons in the visible and near infrared bands of sunlight were converted into heat and hot electrons, driving the degradation of organic micro pollutants through the advanced oxidation of persulfate. This not only provides an ideal platform for studying plasmon-based photochemistry in aqueous phases, but also creates new opportunities for the development of solar-based water treatment technologies. Zhang *et al.* [87] combined auro and Rhodamine B (RB) as the core and silica as the shell to construct a novel core-shell hybrid nanostructure, Poly(sodium 4-phenylenesulfonate) (PSS) uses a negatively charged polyelectrolyte to change the surface charge of AuNRs and acts as a linker to capture RB on AuNRs in an electrostatic manner. Due to the overlapping of the maximum fluorescence emission peak of Rb at 580 nm and the fluorescence spectra of AuNRs at 560 nm, the strong green fluorescence of compound nanostructures excited at 488 nm was observed. Therefore, the red fluorescence and enhanced green fluorescence of hybrid nanostructures were obviously observed, so as to explore the potential application of hybrid nanostructures to replace traditional fluorescent dyes in cell two-color fluorescence labeling.

Cao *et al.* [88] proposed a new platform based on go Cys AuNRs hybrid nanostructure system to absorb R6G dye molecules for SERS detection. Go Cys AuNRs composites can be easily prepared by combining go sheet with AuNRs by using Cys molecules as functional bonds. Raman measurement shows that the signal intensity of R6G molecule is very high and the detection limit is as low as 5×10^{-6} M. Luo *et al.* [89] proposed an plasmon near-infrared photodetector for detecting 980 nm illumination by coating plasma on SLG/InP Schottky junction diode AuNR@SiO₂. The specific flow chart is shown in Figure 13. In use AuNR@SiO₂. After surface modification, some key indicators including responsivity, detection rate and response time were significantly improved. In addition, the linear dynamic range and noise equivalent power are much better than other devices with similar geometry.

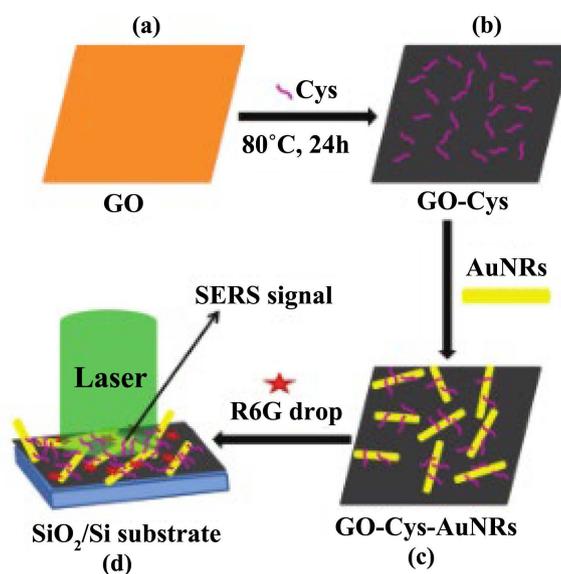


Figure 13. Schematic illustrations of the fabrication process of the GO-Cys-AuNRs composite substrate and its application in SERS for Rhodamine 6G dye molecules [89].

5. Conclusion

This article reviews the related development history, preparation methods and properties of AuNRs and AuNRs@SiO₂, and elaborates on the preparation processes of AuNRs@SiO₂ and the composite forms of other materials, discussing their application in the fields of optics, medicine and detection. The interest in Au nanocomposites continues to rise as does their application in biomedical fields. However, many challenges remain, including the control of the content of the reagent added during large-scale synthesis which dictates the morphology and properties of the final product. Safety remains the top priority in biomedical applications with further studies on the toxicity of AuNRs@SiO₂ now required. We also need to further try in the AuNRs@SiO₂. The substrate is modified by doping other materials such as nanotubes to broaden the field of vision, so as to explore more applications.

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Conflicts of Interest

The authors declare no conflict of interest.

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