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Synthesis and Applications of Gold Nanoparticles

Juan Li*; Zaizhu Lou*

Institute of Nanophotonics, Jinan University, Guangzhou, 511443, China.

Corresponding Author: Juan Li & Zaizhu Lou

Institute of Nanophotonics, Jinan University, Guangzhou, 511443, China.

Email: lijuan@jnu.edu.cn & zzlou@jnu.edu.cn

Abstract

Gold nanoparticles (AuNPs) have attracted extensive interest for over a century due to their unique plasmonic properties. In this review, we present a short overview of the synthetic methods, variety of shapes and recent applications of AuNPs in optical, catalytic and biomedical areas.

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Introduction

Metallic nanoparticles, especially gold nanoparticles (AuNPs) have attracted tremendous interests due to their intriguing interaction with incident light [1]. Under resonant excitation, the free electrons of AuNPs undergo a collective coherent oscillation, also known as Surface Plasmon Resonance (SPR). The plasmon resonance enables the extremely large electric field enhancements around the AuNPs, giving rise to a variety of light–matter interactions with new mechanisms, such as plasmon-enhanced spectroscopies [2], optical nanoantenna effect [3], photothermal conversion [4], and plasmon-assisted photochemical reactions [5]. Driven by the utilization of these fascinating optical properties, AuNPs have become one of the most remarkable areas of modern nanoscience and nanotechnology.

The SPR properties of AuNPs are known to be tailored by synthetically tuning their sizes and shapes [6]. Various AuNPs with different morphologies have been investigated during the last decade. In particular, the anisotropic AuNPs are more attractive because their optical, electronic, magnetic, and catalytic properties are different from, and most often superior to, those of spherical AuNPs [7]. Besides, the anisotropic AuNPs exhibit intense SPR band in the near-infrared (NIR) region, which makes them suitable for biological diagnostics and photothermal therapy [8-10]. The textured surfaces of anisotropic AuNPs also offer great advantages for Surface Enhanced Raman Scattering (SERS) and catalytic applications [11,12]. In this current review, we present several synthetic method and highlight the applications of various AuNPs in optical, catalytic and biomedical areas.

Synthesis of AuNPs

To date, there are numerous methods for the synthesis of AuNPs, including “top-down” and “bottom-up” approaches (Figure 1) [13]. Considerable efforts have been devoted to the controllable synthesis of AuNPs over their size, shape, solubility, stability, and functionality. Generally, procedures of the AuNPs synthesis basically can be classified into chemical, physical and biological methods.

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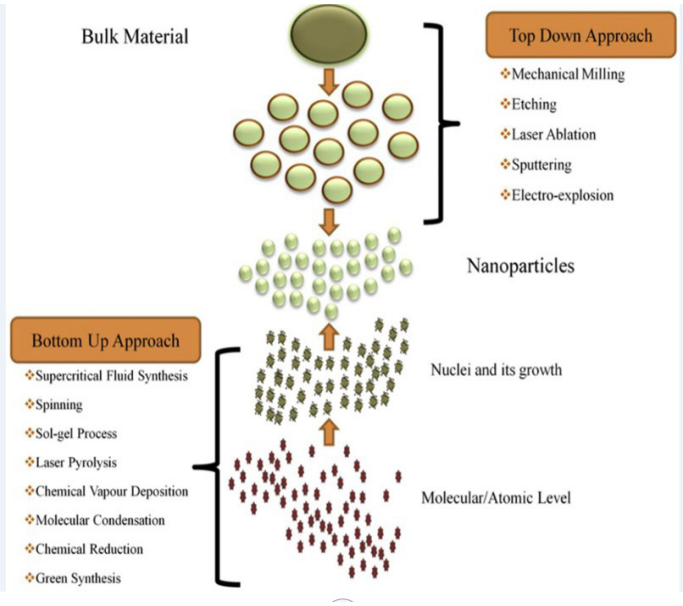

Figure 1: Basic approaches for nanoparticle preparation [13].

Chemical methods

The scientific chemical synthesis of colloidal gold can be traced back to 1857, Michael Faraday prepared gold hydrosols by reduction of chloroaurate aqueous solution with phosphorus dissolved in carbon disulfide [14]. Later in 1951, Turkevich *et al.* developed a synthetic method for the synthesis of AuNPs by treating Hydrogen tetrachloroaurate ($HAuCl_4$) with citric acid in water [15]. In this method, citric acid acts as both reducing and stabilizing agent and provides spherical AuNPs with a narrow size distribution. In 1994, Brust and Schiffrin achieved a significant breakthrough in the AuNPs synthesis [16]. They reported a two-phase synthetic approach, (the Brust-Schiffrin method), utilizing potent thiol-gold interactions to protect AuNPs with thiol ligands. Here, $AuC1_4^-$ was transferred from aqueous phase to toluene and reduced by Sodium borohydride ($NaBH_4$) in the presence of dodecanethiol. The AuNPs were generated with controlled diameters in the range of 1.5–5 nm. These thiol-protected AuNPs possess superior stability due to the strong thiol-gold interaction and they can be easily handled and further functionalized.

Physical methods

Physical methods enable further manipulation of the AuNPs with tunable features and improve their properties. In 1995, Esumi *et al.* reported a convenient physical method to generate anisotropic AuNPs [17]. In this method, $HAuCl_4$ bound to rodlike cationic micelle surfactants are reduced to Au^0 atoms under the excitation of UV light. The micelle surfactant stabilizes a specific crystal face here, leading to the generation of gold nanorods (AuNRs) by controlled aggregation. Besides, thermolysis [18] and conventional ripening [19] have significantly reduced average particle size and triggered formation of superlattices. The γ-irradiation method provides the AuNPs with controllable size and high purity [20]. The sonochemical method provides an approach for the controllable synthesis of AuNPs within the silica pores and Au/Pd bimetallic particles [21,22].

Biological methods

Biological methods known as green synthesis is another environmental-friendly route to the synthesis of AuNPs. Biosynthesis is important to reduce the harmful chemical and toxic by-products during the conventional synthesis of AuNPs. Green materials such as plants, fungi, algae, enzymes and biopolymers are currently used to synthesize various AuNPs [23-25]. For example, brown seaweed sargassum [26], tannic acid [27] and serum albumin protein [28] have been used to prepare gold nanoplates. Biosynthesis creates highly stable and well characterized AuNPs, which are generally safer for use in biomedical applications since they come from natural materials themselves.

Morphology of AuNPs

Various remarkable AuNPs have been synthesized and can be divided into three parts based on dimensions as discussed in detail below.

One-dimensional AuNPs

AuNRs as a kind of one-dimensional AuNPs have been extensively investigated due to their anisotropic shape, display two separate SPR bands, including transverse (TSPR) and longitudinal plasmon bands (LSPR). AuNRs had been prepared using electrochemical and photochemical reduction methods in aqueous media and nanoporous templates. In 2001, Murphy developed a seed-growth method to generate AuNRs with high yields and good dispersity, which appears as the most favorable one for synthesizing AuNRs [29]. The aspect ratio of AuNRs could also be precisely controlled by varying the amount of seed added to the growth solution (Figure 2a) [30]. Gold nanowires (AuNWs) were synthesized by the tip-selective growth of AuNRs, which have potential applications as nanoscale optical waveguides [31]. AuNWs can also be prepared by UV irradiation, photoreduction, and thermal reduction of $HAuCl_4$ in the bulk phase of the block copolymer (Figure 2b) [32]. Besides, Han and co-workers synthesized Au nanobelts (AuNBs) by ultrasound irradiation of $HAuCl_4$ aqueous solution containing α-D-glucose as a biological directing agent (Figure 2c,d) [33].

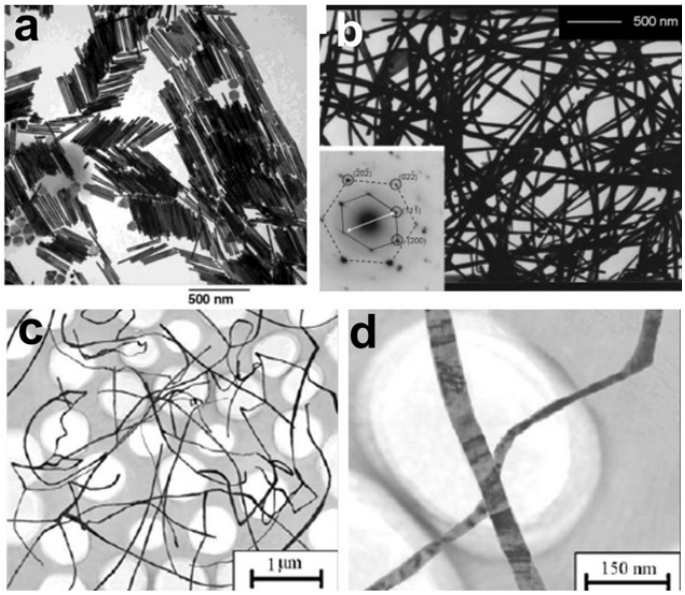

Figure 2: The TEM images of (a) AuNRs [30], (b) AuNWs [32] and (c,d) AuNBs [33].

Two-dimensional AuNPs

The synthesis of 2D Au nanoplates with specific shapes such as triangle, squares/rectangles, pentagons, hexagons and other complex 2D nanoframes have been extensively explored for their specific properties and features. Polymer template method is one of versatile methods to produce gold nanoplates, in which the polymers can act as stabilizers, templates, and reductants. Radhakrishnan prepared polygonal Au nanoplates

in a poly (vinyl alcohol) template through thermal treatment (Figure 3a,b) [34]. In 2004, Wang and co-workers reported a large-scale synthesis of micrometer-scale Au nanoplates by a wet chemical route [35]. In this process, $HAuCl_4$ is reduced by *ortho*-phenylenediamine in aqueous solution to form hexagonal Au nanoplates with preferential growth along the Au (111) plane. Huang and co-workers carried out the synthesis of triangular and hexagonal Au nanoplates by thermal aqueous solution reduction approach (Figure 3c) [36]. Besides, 2D complex nanoframes (rings and triangles with double frames) have been synthesized through selective etching, rim-on deposition and concentric regrowth (Figure 3d) [37].

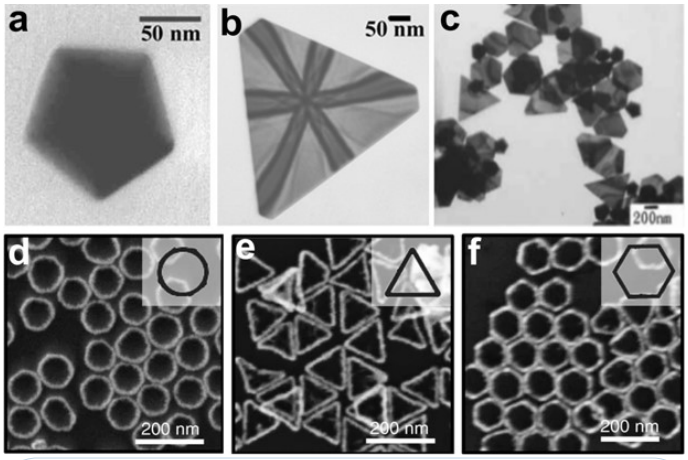

Figure 3: The TEM images of (a,b) polygonal Au nanoplates in PVA films [34] and (c) Au nanoplates with thermal aqueous solution approach [36]. The FE-SEM images of (d-f) 2D complex nanoframes [37].

Three-dimensional AuNPs

Three-dimensional AuNPs with unique spatial-distribution SPR are highly desired due to their great potential for numerous applications. In 2008, Xia research group reported Au nanocages (AuNCs) with hollow interiors and porous walls, which were synthesized by galvanic replacement reaction of silver nanocubes and $HAuCl_4$ (Figure 4) [38]. Gold nanotadpoles as a class of anisotropic 3D nanostructures were synthesized through normal seed-mediated process in the presence of Ag^+ ions and CTAB at room temperature [39]. Gold dendrites with a hierarchical tree-type architecture have attracted much attention due to their fascinating fractal growth phenomena. Hung and co-workers synthesized hyperbranched Au dendrites by electrochemical deposition with a square-wave potential from $HAuCl_4$ solution containing cysteine as the blocking molecule [40]. Besides, 3D AuNPs including monopods, bipods, and multipods [41] such as nanoflowers, nanostars and urchins [42] have also been extensively studied due to their sharp edges and highly localized SPR modes.

Optical plasmonic applications

SERS effect

Surface-Enhanced Raman Scattering (SERS) has attracted great attention due to its significant enhancement and excellent selectivity in the detection of various molecules. Electromagnetic (EM) field enhancement resulting from the excitation of surface plasmons on AuNPs surface contributes dominantly to the Raman enhancement. Au nanospheres dimers with a strongly enhanced EM field known as “hot spot” were used as SERS substrate for molecule detection [43]. Besides, AuNPs with sharp protrusions also generate “hot spot”, including nanostars [44], triangles [45], and bipyramids [46]. Wang et al reported different Raman enhancement of Au nanocube dimers in the configuration of corner-to-corner, corner-to-face, and face-to-face [47]. Complex AuNPs aggregates with numerous hot spots were also prepared for SERS measurements. For example, by using nanofabrication techniques or self-assembly methods, ordered AuNPs arrays have been prepared for sensitive analyte detection, as shown in Figure 5 [48]. Song et al prepared Au-areoles array by a selectively electrochemical deposition method to realize efficient detection of femtomol Rhodamine 6G and diverse bioanalytes [49]. In addition, by incorporating AuNPs with other high-performance materials [50,51], the applications of plasmon enhanced Raman spectroscopy can be further improved.

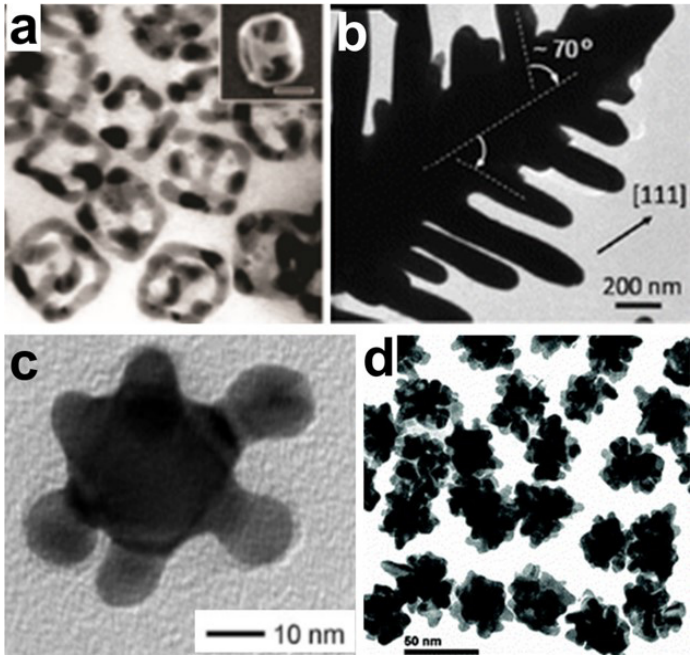

Figure 4: The TEM image of (a) AuNCs [38], (b) Au dendrites [40], (c) Au hexapods [41] and (d) Au urchins [42].

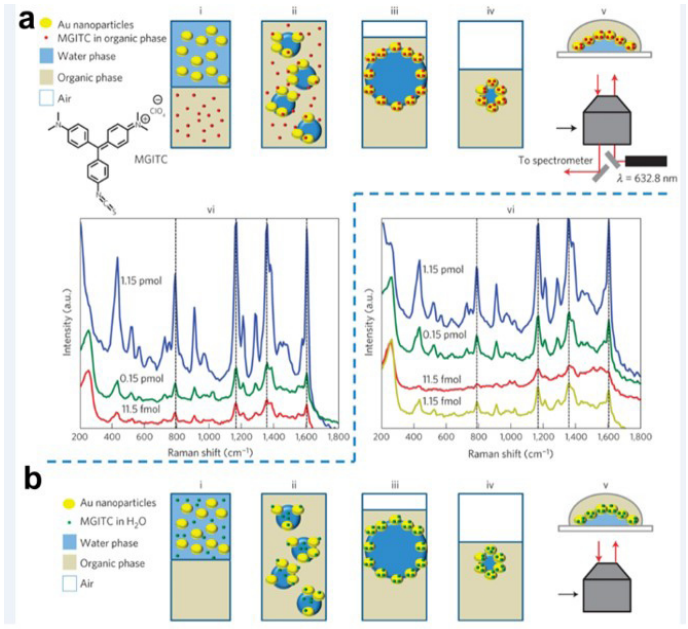

Figure 5: Schematic of nanoparticle assembly at the LLI and MGITC detection [48].

Fluorescence enhancement

Plasmonic AuNPs have been shown to enhance the fluorescence emission and decrease the molecular excited-state lifetimes of adjacent fluorophores. The fluorescence enhancement arises from the combination of enhanced absorption of incident light, modification of the radiative decay rate of the molecule, and enhanced coupling efficiency of the fluorescent emission to the far field [52]. Various AuNPs including nanosphere [53], nanorods [54] as well as nanoporous [55] have been reported to dramatically improve the fluorescence intensity of organic dyes and quantum dots. Specifically, plasmonic AuNPs enhanced upconversion fluorescence have attracted extensive interest because of their potential applications in solar cells, bioimaging and biosensors [56-58]. For example, Pang et al. fabricated a three-dimensional gold nanohole-disc arrays by nanosphere lithography, which could be spectrally coupled to multiple NIR fluorophores for the development of multiplexed biosensors, as shown in Figure 6 [59].

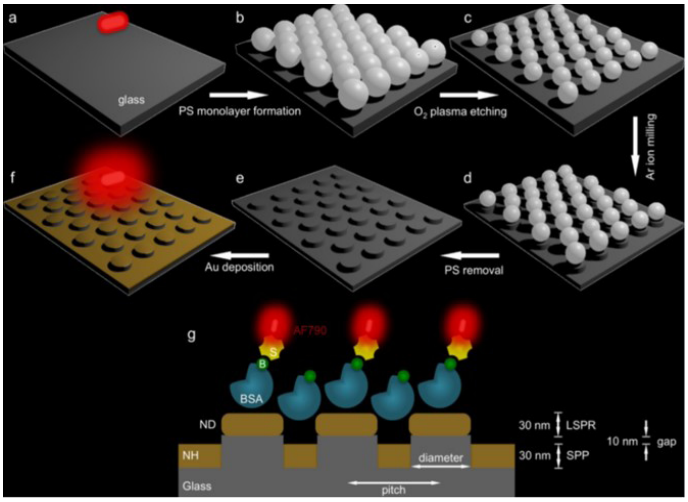

Figure 6: Schematic illustration of three-dimensional Au nanohole-disc arrays for large NIR fluorescence enhancement [59].

Catalytic applications

Catalytic carbon monoxide oxidation with AuNPs on titanium oxide was pioneered by Haruta *et al.* in 1989, which was a breakthrough in catalysis that opened up a wide area of AuNP-catalyzed oxidation reactions [60]. The catalytic activity and selectivity of AuNPs is known to be dependent primarily on the size and shape. Compared to Au nanospheres, anisotropic AuNPs with sharp edges and corners provide more active surface sites for enhanced catalysis. Therefore, catalysis with AuNPs such as gold nanotubes, gold nanodendritic, gold nanopyramids, and gold polygonal have been widely investigated. For example, Huang *et al.* reported the synthesis of dendritic AuNPs with widely exposed active surface to allow the efficient reduction of p-nitroaniline [61]. Branched AuNPs displayed superior catalytic performances for both catalytic reduction of 4-nitrophenol and electrocatalytic oxidation of methanol [62]. Some hybrid bimetallic anisotropic AuNPs also exhibit high activities in various catalytic reactions such as water splitting, contaminants degradation, and photocatalytic organic synthesis [63-65]. For example, Lou *et al.* prepared Pt-edged Au Triangular Nanoprisms (TNPs) as photocatalysts, which provide strong electric field and facilitate the transfer of hot electrons for efficient catalytic hydrogen generation (Figure 7) [63]. Moreover, plasmonic photocatalysts constructed by coupling AuNPs with semiconductors have attracted much attention because of their intense light absorption and efficient charge separation. Shih *et al.* prepared AuNPs modified g-C_3N_4 photocatalyst for significantly enhanced selective catalytic reduction of carbon dioxide to methane [66]. Other semiconductors such as CdS [67], Fe_2O_3 [68], Cu_2O [69], SnO_2 [70] and Bi_2WO_6 [71] have also been used as supports for AuNPs to form plasmonic photocatalysts with LSPR-enhanced catalytic activity.

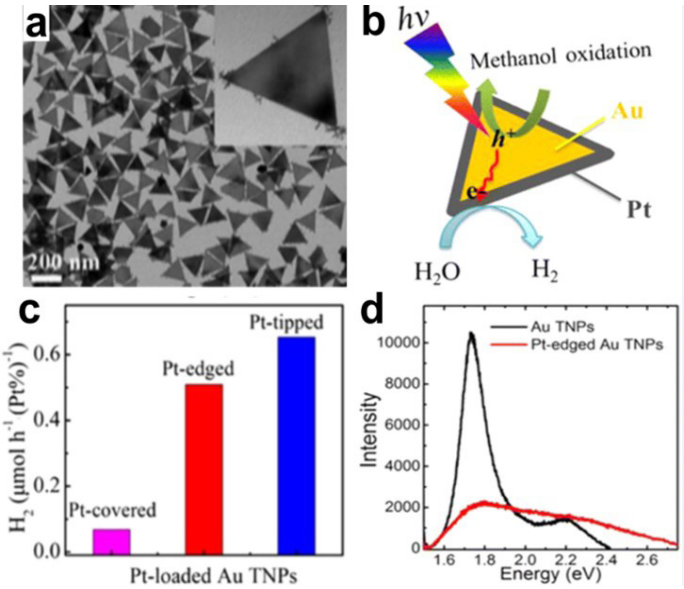

Figure 7: [63] (a) The TEM image of Pt-Au TNPs. (b) Schematic illustration and (c) H2 generation rate over Pt-Au TNPs. (d) Single particle PL spectra of Pt-Au TNPs.

Biomedical applications

Contrast agents in diagnostics

The most important in vivo diagnostics include light scattering imaging, two-photon fluorescence imaging, and photoacoustic imaging [10]. Plasmonic AuNPs such as spherical Au nanoshells, AuNRs, AuNCs, and Au nanostars are efficient contrast agents in biomedical imaging as a result of their unique interaction process with light [72]. For example, the Au nanoshells developed by Halas *et al.* that scatter light in the NIR physiological "water window" have been used as contrast agents for dark-field scattering, photoacoustic imaging and optical coherence tomography [73]. The dark-field imaging based on the light-scattering properties of nonspherical AuNPs (shells, spheres, rods, and cages) have been widely used for cancer imaging through functionalized nanoparticle–receptor binding to cell-surface biomarkers. Nonspherical AuNPs, especially AuNRs, exhibit enhanced two-photon luminescence, making them detectable at single-particle levels under femtosecond NIR laser excitation. He *et al.* reported the detection of circulating tumor cells in vivo by injection of folate-conjugated AuNRs [74]. Photoacoustic imaging are based on the detection of acoustic waves generated by the laser-induced heating of materials. Xia *et al.* used PA to image the cerebral cortex of a rat before and after successive injection of PEGylated AuNCs (Figure 8a) [75]. Gao *et al.* developed a novel photocross-linkable AuNPs for photoacoustic imaging and photothermal therapy of tumors in vivo (Figure 8b) [76].

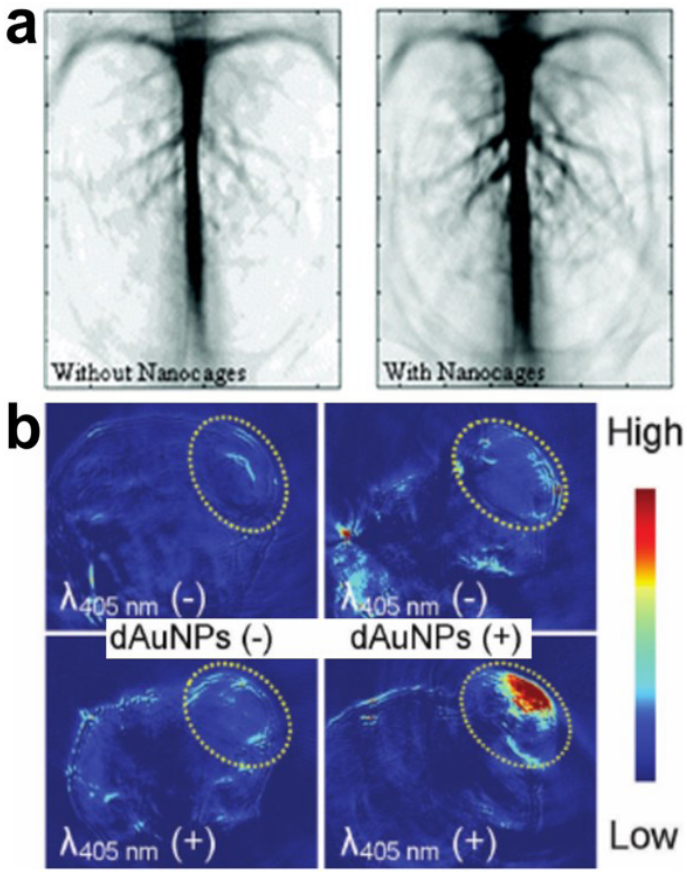

Figure 8: **(a)** Photoacoustic tomography of a rat's cerebral cortex with and without AuNCs [75]. **(b)** Photoacoustic images and quantified signal of the tumorous sites of mice receiving treatments with intravenous delivery of AuNPs [76].

Photothermal cancer therapy

Photothermal Therapy (PTT) known as thermal ablation or optical hyperthermia has been widely explored as a minimally invasive approach to cancer therapy [77]. It is a process based on localized heating due to intense light absorption for selective destruction of tumor cells. In general, NIR (700-1100 nm) light is preferred for such an application, as it can penetrate biological tissues deeply due to low absorption/scattering by hemoglobin and water in this so-called transparent window. Various AuNPs including nanoshells, NRs [78], NCs [79] and nanostars [80] that absorb and convert NIR light into heat, have been shown to be effective in photothermal therapy. Halas reported silica@Au nanoshells functionalized with antibodies for photothermal therapy in mice with subcutaneous tumors of 1 cm size [81]. El-Sayed and co-workers pioneered the application of AuNRs conjugated with anti-EGFR antibodies for selective photothermal therapy to human oral cancer cells [78]. Xia and co-workers demonstrated the photothermal destruction of breast cancer cells in vitro through the use of immuno-AuNCs [82]. In addition, to further enhance photothermal response, hybrid nanostructures composed of AuNPs and other materials including carbon nanotubes [83], graphene oxide [84], and black phosphorus [85] have also been explored. For example, Kim prepared hybrid AuNP/GO sheets by tightly packing α-synuclein-coated AuNPs on GO flakes, which stably adhere to the tumor cell surface and exhibit a remarkable photothermal effect.

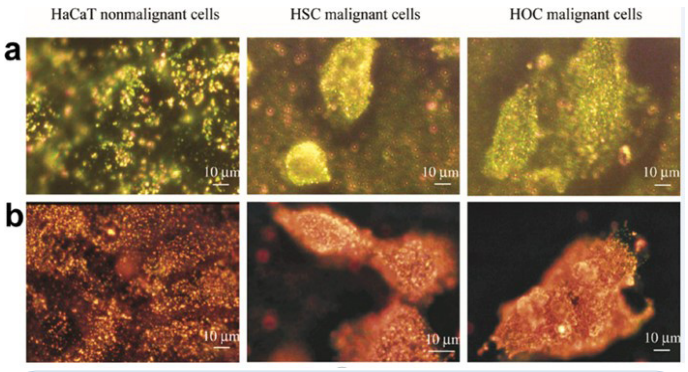

Figure 9: [78] Light scattering images of (a) anti-EGFR/Au nanospheres and (b) anti-EGFR/Au nanorods after incubation with cells for 30 min at room temperature.

Drug delivery

The biocompatibility, stability and nontoxicity of AuNPs make them an efficient nanocarrier in drug delivery systems without significant side effects. Various drugs such as peptides [86], proteins [87] and anticancer agents [88] can be immobilized on the surface of AuNPs, mostly by direct binding through -S or -N, bonding with ligands, simple physical adsorption and hydrogen bonding. For example, Wang *et al.* developed a drug delivery system that tethers doxorubicin onto the surface of AuNPs via an acid-labile linkage, inducing elevated apoptosis of MCF-7/ADR cancer cells [89]. The Au nanostars coated with SiO_2 shells has been designed as nanocarriers to load and release doxorubicin, causing high lethality of HeLa cancerous cells under the NIR radiation (Figure 10) [90]. AuNCs with hollow structures can also serve as "pockets" for drug release. Xia *et al.* filled the hollow interiors of AuNCs with a phase-change material, which acted as a "gatekeeper" to control the release of hydrophobic or hydrophilic drugs in response to temperature increase [91]. Besides, the positively charged AuNRs can adsorb cargos such as DNA oligonucleotides, RNA oligonucleotides, and siRNA [92].

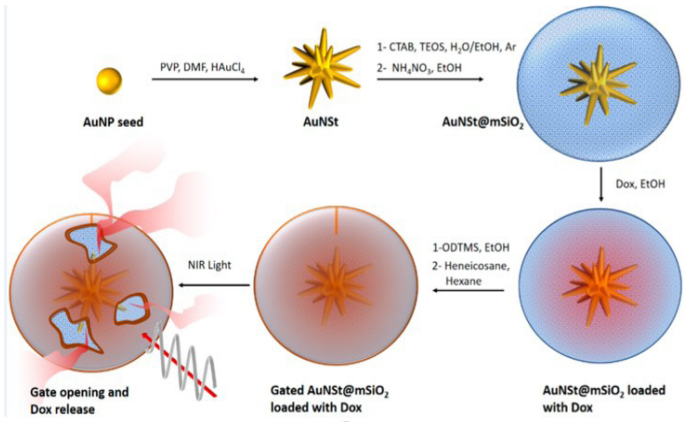

Figure 10: Representation of the drug photorelease system AuNSt@$mSiO_2$@Dox@paraffin based on AuNSts coated with a mesoporous silica shell and paraffin as a thermosensitive molecular gate. The delivery of the entrapped cargo (Dox) is triggered by NIR laser irradiation [90].

Conclusion

In recent years, AuNPs have attracted particular attention as a result of their unique features. Obviously, there has been a great promotion in the synthesis and functionalization of AuNPs, which make them a versatile platform for a wide range of applications. However, despite of much effort done towards the controlling synthesis, an integrative approach is still lacking

covering all length scales for on-demand synthesis of AuNPs. Besides, the reproducibility and toxicity of AuNPs also need to be significantly improved for further practical applications in biomedicine. To date, various AuNPs have been developed for cancer theranostics with high success rates in cell culture and animal models, but still unable to be translated into commercial clinical use. One large barrier is that the AuNPs synthesis is known to be irreproducible, and no two AuNPs batches are the exact same. Variation in AuNPs structure/composition may affect cancer targeting ability and penetration along with photothermal heating efficiency. In addition, the long-term toxic effects of AuNPs is not well-understood and could also vary with structure/composition. In these regards, there is considerable room for further basic science advancing the understanding of biological interactions with AuNPs. Work is still underway to expand the applications of AuNPs.

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