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Functionalization of Gold Nanorods Toward Their Applications

Koji Mitamura · Toyoko Imae

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Abstract The topics focusing on functionalization of gold nanorods have been reviewed with a view toward their advanced uses. In most cases, as-prepared gold nanorods are hydrophilic and protected by surfactants, since anisotropic growth of gold nanorods by chemical, electrochemical, and photo-induced methods is carried out in aqueous media in the presence of surfactants and additives. Since solvophilicity of gold nanorods predominantly affects on their optical properties, the control of dispersity of gold nanorods in matrices has been performed, without loss of their optical characters, by surface modification and hybridization with small molecules or polymers. As a result of the functionalization procedure, the capability of self-assembly of gold nanorods has been improved. Furthermore, the examples of application using gold nanorods demonstrate that gold nanorod is a promising material.

Keywords Gold nanorod · Functionalization · Synthesis · Dispersion · Surface modification · Hybridization · Self-assembly · Application · Solvophilicity · Hydrophobation · Optical property

Introduction

Uses and demands of metallic nanoparticles are intensively increasing in the industrial and medical fields, due to great variety of their functionalities such as electromagnetic properties, catalytic activity, and so on. Especially, the electromagnetic properties of metallic nanoparticles are valuable in highly sensitive biosensors, nonlinear optical devices, and others [1, 2]. The optical character utilized in the devices is originated from surface plasmon phenomenon, which brings optical absorption and field enhancement of incident light on the metallic nanostructure [3–5].

“Plasmonics” of nanoparticles is an integrated bottom-up technique to fabricate the advanced devices and materials using the surface plasmon resonance (SPR) of nanostructured metals. In this technique, the nanoparticles are mainly used as building blocks. The character and performance of the fabricated devices and materials are largely dependent on composition, dimension (size and shape), and arrangement of the nanoparticles, since the SPR (e.g., wave vector of resonance light) is predominantly changed by these factors of metallic nanoparticles [6, 7]. Therefore, it is vital to fabricate the nanoparticles with controlled dimension and their assemblies in order to construct the advanced materials.

Nanoparticles with specific shapes display more particular and valuable characters in optical properties than spherical ones [8–10]. For instance, while spherical gold particles have only one surface plasmon band at 510–575 nm depending on size and dielectric environment, nanorods provide two intrinsic (transverse and longitudinal) bands and nanoparticles with other shapes reveal two or more shape-depending bands [10]. Among such nonspherical nanoparticles, gold nanorods are more directed to advanced uses such as anticancer agent, near-infrared (IR) filter, and storage media in comparison with other non-

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K. Mitamura
Ecotopia Science Institute, Nagoya University,
Chikusa,
Nagoya 464-8603, Japan

T. Imae (✉)
Graduate School of Science and Technology, Keio University,
Hiyoshi,
Yokohama 223-8522, Japan
e-mail: imae@educ.cc.keio.ac.jp

spheres, since nanorods have a longitudinal plasmon band at near-infrared region, and additionally, the synthesis procedures of gold nanorods with high yield have been developed [11–14].

In this review, we introduce recent topics on synthesis, dispersion, surface modification, and self-assembling of gold nanorods. We provide promising techniques and processes toward further applications using gold nanorods.

Synthesis

There are many conventional methods to synthesize nanoparticles with desired composition and dimension. For example, nanoparticles consisting of noble metals (Au, Ag, Pt, etc.) are synthesized by chemical, electrochemical, sonochemical, and photo-induced methods [15–23]. The nanoparticles with unique and anisotropic shapes are also fabricated under the existence of certain chemicals [11, 24–33]. Indeed, Ag nanoparticles with triangular and hexagonal shapes are prepared by photoreduction in the presence of poly(amido amine) dendrimers [31]. Furthermore, metallic nanocubes, nanowires, and nanostars are also synthesized [25, 26, 30].

Gold nanorods are synthesized by various methods such as chemical, electrochemical, and photochemical methods in aqueous solutions, where gold nanorods with regulated size (longitudinal, 20–100 nm; transversal, 10–20 nm) are obtained at high yield (>90%) [11–14, 34–36]. The chemical synthesis starts from small gold seeds (2–3 nm) and promotes their anisotropic growth by adding cationic surfactant (hexadecyltrimethylammonium bromide, CTAB), silver ion, and ascorbic acid besides gold ions (Fig. 1A) [11]. CTAB molecules and silver atoms prefer to be adsorbed on (110) facets at the sides of gold nanorods rather than (111) and (001) facets at their edges [37, 38]. Such localized protection by adsorption leads to the deposition of gold atoms only on edges and the production of gold nanorods. Then, CTAB molecules play important roles as a protector and a stabilizer for dispersion in an aqueous phase by forming a bilayer on the gold nanorod. Ascorbic acid is used as a reducing agent and ensures a slow rate of the reduction and growth. The preparation takes, at least, 3 h. This seed-mediated synthesis can produce gold nanorods at high aspect ratio (18±2.5 with short axis 16±3 nm) by repetitive addition of the developing gold nanorods into the growth solutions [39].

In the electrochemical process, acetone and cyclohexane are added besides the CTAB molecules and silver ions [24]. While the latter two chemicals play an important role in gold nanorod growth, the former two chemicals are believed to loosen the micellar framework of CTAB molecules, enhancing the formation of the gold nanorods. In an electrochemical cell, gold ions are supplied from an anode electrode consisting of gold metal and reduced on the cathode (Pt) by applying a current at 5 mA for 20 min (Fig. 1B). The aspect ratios are controllable in this method by varying experimental conditions.

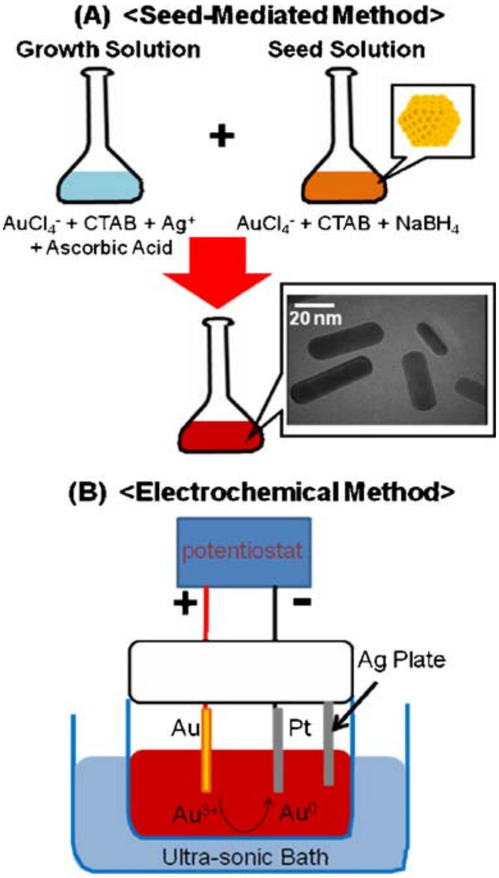

Fig. 1 Schematic illustration of conventional preparation of gold nanorods. **A** Seed-mediated method, **B** electrochemical method

The photochemical synthesis is performed in a solution of CTAB, silver ions, and gold ions [34]. The reduction of gold ions is induced by irradiation of 254 nm ultraviolet light (420 μW/cm^2). In this work, the preparation takes time more than 30 h, but the long irradiation (>40 h) causes degradation and transformation of gold nanorods into spheres. However, the reaction time can be shortened into 30 min at a stronger irradiation (8 mW/cm^2).

Whereas the methods mentioned above have to use CTAB molecules at high concentration (>80 mM) in comparison with gold ions (0.1–1.0 mM), the method without CTAB or silver ion has been suggested [40–42]. There, a template such as a porous alumina is employed, and gold ions are electrochemically reduced inside the pores to form gold nanorods. The resultant nanorods are collected by dissolution of the alumina template by acid. This method is convenient to obtain relatively larger gold nanorods (length—several hundred nanometers, width—

several dozen nanometers) than the synthesis methods described above, since there is limitation by template dimension (the pore aspect ratio).

Dispersion in matrices

In order to preserve the optical and chemical characters of gold nanorods, it is crucial that gold nanorods are dispersed in matrices (liquid, solid, and gel phases). There is a report on dispersion of gold nanorods in an alginate gel as a matrix [43]. Alginate is a biocompatible anionic polysaccharide and gelated in the presence of dications such as calcium ions. When calcium ions are added in a mixture of alginate and gold nanorods, the hybrid gel is obtained. Gold nanorods are entrapped and dispersed into alginate hydrogel matrix by electrostatic interaction force, and elemental mapping by energy dispersive X-ray spectroscopy (EDS) shows the existence of gold and calcium alginate gel (Fig. 2A). Even after the hybridization, gold nanorods maintain the optical character. The incorporation into gel has another advantage besides preserving the optical character: It is noticed that the release of gold nanorods is induced by collapse of gel network caused by the monovalent cations (Fig. 2B). The alginate hydrogel (without nanorods) can incorporate drugs instead of gold nanorods in the scope of application to a drug delivery system.

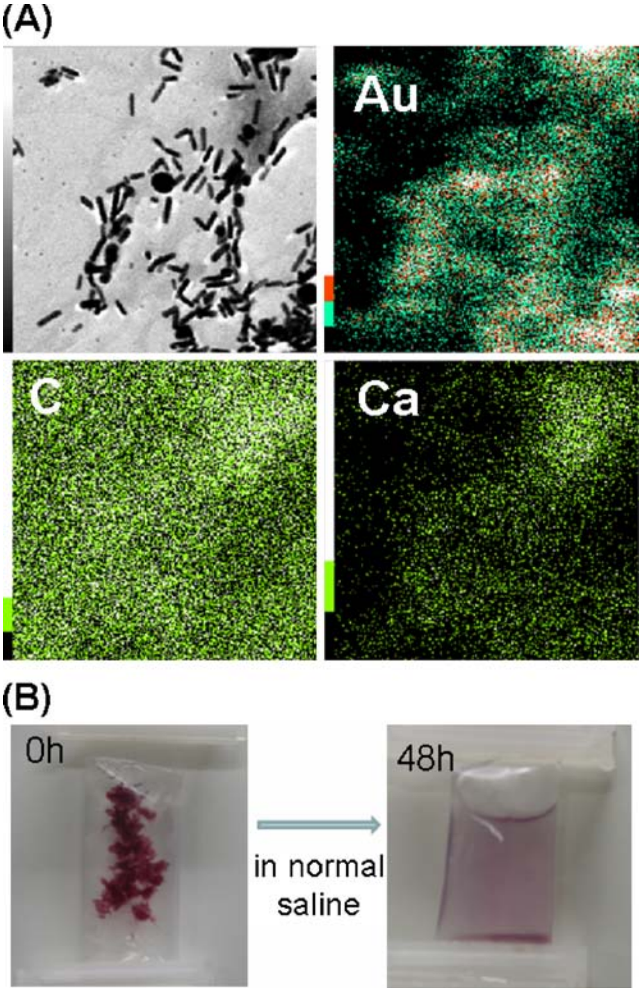

Fig. 2 **A** Scanning transmission electron microscopic image of gold nanorods in gel matrix and EDS elemental mapping for Au, C, and Ca atoms, **B** time development of hybrid gel in a normal saline

In the other example of the dispersion, poly(iso-propylacrylamide) (pNIPAM) gel is a matrix [44, 45]. This gel is thermoresponsible and displays a volume phase transition at 30–40°C by applying thermal stimulus. Gold nanorods are dispersed by hybridizing them with pNIPAM microgel. It has been found that the hybrid gel displays a unique behavior: The gel is reversibly shrunk with/without irradiation of near-IR light. The shrinkage can be caused by the thermal energy that is generated from the gold nanorods excited by absorption of near-IR ray. This phenomenon can be applied to micromechanical system.

Generally, on dispersion of nanoparticles in a liquid matrix, chemicals adsorbed on the nanoparticles dominate the dispersity of nanoparticles, if nanoparticles are modified to increase the solvophilicity. For example, citrate-capped gold nanospheres (terminated with COO^- groups) are dispersed in water, due to the hydrophilicity (mainly electrostatic repulsion) of citrate periphery. On the other hand, nanoparticles covered with nonpolar alkyl chains are usually hydrophobic. The same approach can be approved for gold nanorods, that is, the gold nanorods synthesized by the methods described in previous section can be dispersed in water because of wrapping by bilayers of CTAB molecules. In the meantime, gold nanorods surrounded by hydrophobic shell are dispersed in nonpolar solvent such as chloroform, although there are very few reports on preparation of such hydrophobic gold nanorods. In order to load the desired solvophilicity on gold nanorods, there are two possibilities: (1) development of completely new synthesis process of the required nanorods and/or (2) surface modification of conventionally produced gold nanorods with functional chemicals. The latter one seems easy to achieve versatile functionalization of gold nanorods, because there is possible variation of chemicals for surface modification.

Surface modification

Morphologies of nanoparticles are controllable, to some extent, by modifying the conditions on the conventional synthesis methods. However, in some cases, one needs to attach further "new" functionalities to the as-obtained nanoparticles. Especially, under demand of improvement regarding solvophilicity of nanoparticles, the modification of nanoparticle periphery is performed by using hydrophilic or hydrophobic chemicals. When nanoparticles are prepared in a reverse-micelle system, size of nanoparticles can be well controlled by varying a ratio of [surfactant] to [water], and the obtained nanoparticles usually possess hydrophobic surface with functional alkyl groups [46–49]. However, in general, the additional processes such as surface modification and hybridization with other materials must be adopted, when the specific functionalizations of nanoparticles are required and the nanoparticles are synthesized by procedures at proper conditions befitting chemicals.

In fact, there are some studies about the surface modification and the hybridization of the as-obtained nanoparticles. Metal nanoparticles (Au, Ag) are treated by thiol compounds in order to improve the dispersity in a nonpolar solvent [50–52]. Silver nanoparticles are incorporated in an organic gel [53]. In spite of these efforts, there still remains limitation on the functionalization of gold nanorods. The gold nanorods have difficulty in surface modification due to strong attachment of CTAB on their surface. Moreover, they have cytotoxicity owing to the coexisting CTAB molecules. These problems must be improved for the advanced utilization of gold nanorods.

Since a bilayer of the CTAB molecules are strongly attached on a gold nanorod, surface modification of gold nanorods is a tough work. Wrapping up in an anionic polyelectrolyte, poly(acrylate) (PA), is achieved through the electrostatic interaction with cationic CTAB molecules [54–56]. The research has been extended to layer-by-layer coating on gold nanorods by using PA and polyaniline derivatives. The surface potential (ζ-potential) is reversed at each step of the electrolyte coating. The PA-modified gold nanorods are possible to be immobilized on positively charged solid surface by the electrostatic interaction with carboxyl groups of PAs on gold nanorods.

There are some reports on surface modification by thiol compounds [57, 58]. Hydrophilic thiol compounds such as mercaptopropionic acid (MPA), cysteine (Cys) and thiol-terminated poly(ethylene glycol) (PEG-SH) are mainly used. Small MPA and Cys molecules prefer to be adsorbed on the edge of gold nanorods, leading unique edge–edge aggregation via hydrogen bond between carboxyl groups. Biocompatible gold nanorods can be obtained by PEG-SH modification due to the biocompatibility of PEG, and the PEG-modified gold nanorods are applicable to living cells with the aim of cell staining.

Apart from organic modification, inorganic coatings based on silica (SiO_2) have been reported [59, 60]. As the precursor of silica shell, sodium silicate or tetraethoxysilane (TEOS) has been employed. In a case of the former one, the silica shell of 7–10 nm thickness surrounds gold nanorods. Although the silica shell in this case does not seem to be uniform on the nanorods, it is reported in the latter investigation that the thicknesses (10–50 nm) of silica shells are controllable by amount of TEOS. The hydrophobation of gold nanorods is accomplished through deposition of organosilane (octadecyltrimethoxylsilane, ODS) on silica shell. However, in this process, there is triple repetition of polyelectrolyte coating before the formation of silica shell.

In a different strategy, the hydrophobation of gold nanorods is successfully obtained using same organosilane as a coating agent without any silica shell [61]. After polymerization (formation of Si–O–Si bond) between organosilane molecules, gold nanorods have been wrapped with the organisilanes and converted to hydrophobic ones, as shown in Fig. 3. This hydrophobation can be done at three steps, i.e., (1) anchoring of mercaptopropylsilane (MPS) on gold nanorods, (2) hydrolysis of MPS and ODS, and (3) dehydration condensation (polymerization) among organosilanes. The fewer steps of processes are advantageous in the modification.

The surface modification of gold nanorods varies their dispersity in matrices and the affinity between gold nanorods. For instance, the interaction between CTAB-capped gold nanorods is repulsive due to their positive surface

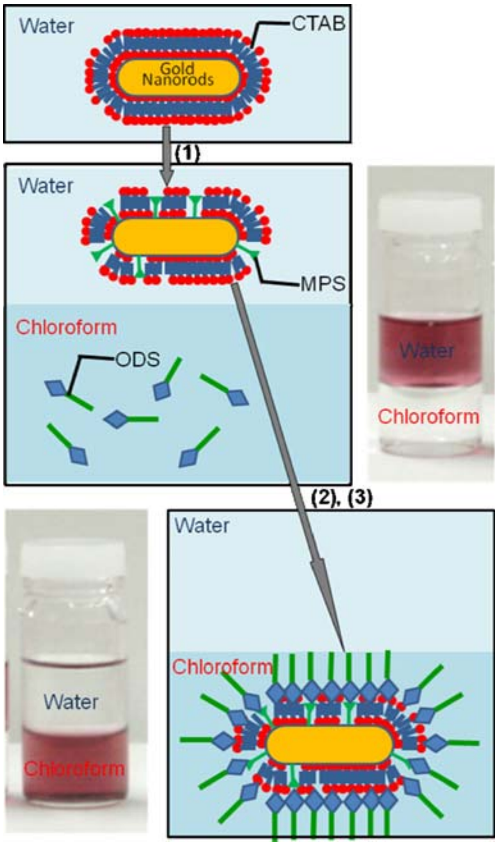

Fig. 3 Schematic illustration of hydrophobation of gold nanorods. *1* Anchoring of MPS on gold nanorods, *2* hydrolysis of organosilanes, and *3* dehydration condensation among organosilanes

charges, and it leads gold nanorods well dispersed in water. On the other hand, for hydrophobic gold nanorods, strong repulsive force like electrostatic one does not act between each other, except structural (steric) hindrance. Thus, arrays of gold nanorods in self-assembly vary, depending on their surfaces modified by different chemical species.

Self-assembly

It is known that size-defined nanoparticles form ordered assembly. Actually, gold nanoparticles with very narrow size distribution are two dimensionally packed in hexagonal array. The assemblies of nanospheres are realized, since the closed packing is structurally preferable and thermodynamically stable [20]. Similarly, size-regulated nanorods are also expected to form ordered array but will be assembled in a different manner from that of nanospheres according to their structural anisotropy. It has been reported that CTAB-capped gold nanorods are two dimensionally arranged [62–64]. The assembly is formed by evaporation of a solvent. In other report, two-dimensional self-assembly of CTAB-capped gold nanorods at water/oil interface has been demonstrated by using a flocculating agent such as dodecanethiol [65, 66]. The partial replacement of CTAB molecules by thiols lowers solubility of gold nanorods in water and leads to the flocculation at the interface. Furthermore, using electrostatic interaction between CTAB and adipic acid, the formation of self-assembly can be controlled by pH. At low pH (2.0), the gold nanorods are individually dispersed but at high pH (>10), gold nanorods form assembly [67]. This assembly formation relies on pKa (4.4–5.4) of adipic acid. As a peculiar case, there is a report of one-dimensional arrangement of gold nanorods induced by MPA [57, 58]. The arrangement is realized by specific adsorption of MPA molecules on the edge and formation of hydrogen bond between carboxylic groups. The one-dimensional array displays a longitudinal plasmon band at a longer wavelength than the individual gold nanorods due to the plasmon coupling between constitutive gold nanorods.

As described above, there are several reports on one and two dimensionally ordered assemblies. However, there are also few reports on more highly ordered structure such as three-dimensional assembly. The CTAB molecules on gold nanorods usually form bilayer in aqueous dispersion, but the structure can partially vary to monolayer with assembly formation [64]. Because of such variation of layer structure and due to resultant nonuniformity of CTAB layers, it can make difficult for hydrophilic gold nanorods to form more uniform and ordered structure.

Meanwhile, hydrophobic gold nanorods adequately treated are expected to form the more ordered structure,

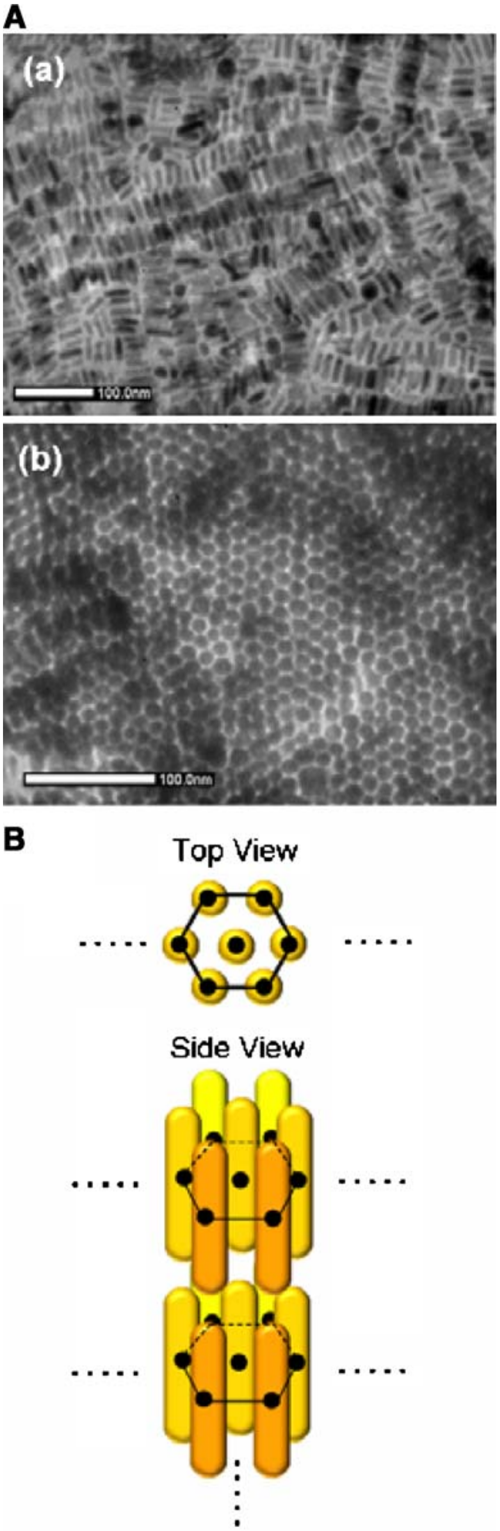

Fig. 4 **A** TEM images of two-dimensional self-assemblies of gold nanorods. (*a*) Parallel arrangement, (*b*) vertical arrangement. **B** Illustration of three-dimensional self-assemblies of gold nanorods

since such gold nanorods take less fluctuation of CTAB layer structure. Actually, two-dimensional self-assemblies of hydrophobic gold nanorods are successfully fabricated on a solid substrate [61]. In Fig. 4A, transmission electron microscopic (TEM) images of the typical self-assemblies are shown. Gold nanorods are arranged in order just similarly to smectic phase in liquid crystal or perpendicularly oriented with hexagonal packing.

These cases provide the possibility to extend the nanorod assembly to three-dimensional ones. The formation of such assembly has been succeeded by condensation and solidification of the gold nanorods [61]. It is confirmed by small angle X-ray diffraction investigation. The gold nanorods are packed in hexagonal array and the two-dimensional hexagonal sheets are three dimensionally accumulated (Fig. 4B). As described above, the hydrophobation can improve the assembling ability and form more highly ordered self-assemblies in comparison with the conventional gold nanorods.

Application

Many advanced uses of gold nanorods are proceeding in industrial and medical fields by using their unique optical characters originating from SPR. There are several reports on phototherapy using gold nanorods. Capability of gold nanorods as anticancer agents has been demonstrated [68, 69]. There, the surface of gold nanorods is modified with folate derivative. After the folate compounds are bound on a folate receptor on a cell membrane, the gold nanorods are activated by irradiation of near-IR ray and provide serious damage to cells. In this technique, there is a major merit that the activity of gold nanorods to the cells is controllable by irradiation of the near-IR ray, which can reduce the damage to normal cells.

Gold nanorods are also focused as a nonlinear optical material. There is a report on two-photon luminescence (TPL) from gold nanorods [70–72]. It is concluded that the efficient TPL are observed, when gold nanorods are under SPR condition along longitudinal direction. The TPL character can be utilized in photo-switching device, photosensor, and so on. Furthermore, gold nanorods are directed toward photo-induced memory. It has been reported that gold nanorods reshape into nanospheres and the reshaped nanorods do not display any more the absorption band at near-IR region [73]. If the condition of the reshaping corresponds to “0” and untouched gold nanorod means “1” in digital expression, the memory using the reshaping of gold nanorods can be developed.

Surely, application of gold nanorods is intensively spread in the medical and industrial fields. It is due to the unique and useful properties of gold nanorods. Further advanced studies and application are carried out all over the world for creating attractive materials using gold nanorods.

Conclusion

Gold nanorods are expected as novel materials due to their valuable characters. Meanwhile, nanorods conventionally prepared have some problems such as surface reactivity and biotoxicity to be solved before application, especially in the medical field. In this review, a possible proposition for the solution of such problems is described. The various synthesis methods have been introduced. CTAB is used in most of cases of synthesis, and this chemical tightly covers onto gold nanorods and importantly biotoxic. The procedures for lightening these demerits are first the hybridization and second the surface reformulation by biononotoxic materials. As a result, such procedures have provided new materials which can control the release of gold nanorods. Moreover, different types of solvophilic gold nanorods have been developed. Especially, hydrophobic gold nanorods show high ability of self-assembling, where the gold nanorods form two- and three-dimensional assemblies. It can be concluded that the recent findings concerning to gold nanorods promise key techniques and methodologies in nanotechnology using gold nanorods.

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