



Synthesis and characterization of mixed monolayer protected gold nanorods and their Raman activities



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ABSTRACT

The cetyltrimethylammonium bromide (CTAB) gold nanorods (AuNRs) were prepared by seed-mediated route followed by the addition of a Raman active compound (HS-(CH₂)₁₁-NHCO-coumarin) on the gold nanorods surfaces. Different stoichiometric mixtures of HS-(CH₂)₁₁-NHCO-coumarin and HS-PEG-(CH₂)₁₁-COOH were evaluated for their Raman activities. The lowest stoichiometric ratio HS-(CH₂)₁₁-NHCO-coumarin adsorbed on gold nanorods surface was detected and enhanced by Raman spectroscopy. The produced mixed monolayer protected gold nanorods were characterized by UV-vis spectrometer for optical properties, transmission electron microscope (TEM) for structural properties (shape and aspect ratio) and their zeta potentials (charges) were obtained from ZetaSizer to determine the stability of the produced mixed monolayer protected gold nanorods. The Raman results showed a surface enhanced Raman scattering (SERS) enhancement at the lowest stoichiometric ratio of 1% HS-(CH₂)₁₁-NHCO-coumarin compared to high ratio of 50% HS-(CH₂)₁₁-NHCO-coumarin on the surface of gold nanorods.

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1. Introduction

Metal nanorods have received widespread interest due to their unique one-dimensional structure; their unusual optical, electric, catalytic properties, their use in chemical sensing, cellular imaging, and therapeutics [1–3]. Specifically, noble metal gold [4–8], silver [9], platinum [10,11], and palladium [12–15] nanorods have garnered great interest, among which gold nanorods have been most extensively studied, due to their plasmonic activity. Most conventional synthetic routes to produce gold nanorods rely on solution-phase reactions such as seed-mediated growth [7,8]. This synthetic route proved to be successful in producing gold nanorods with different aspect ratios thereby rendering them with the desired properties. In this route, gold seeds, size range 3–4 nm, are first synthesized by chemical reduction of gold salt with a strong reducing agent in the presence of a capping agent. These seeds are then added to a solution containing more metal salt, a weak reducing agent, and a surfactant-directing agent. These seeds serve as nucleation sites for the anisotropic growth of gold nanorods. This protocol gives fairly monodispersed and stable gold nanorods [16–18]. The quality of the seed particles can affect the growth mechanism of the nanorod. In general, smaller seeds lead to more

monodispersed nanorods [6,19]. Various capping agents such as cetyltrimethylammonium bromide (CTAB) [18], benzyltrimethylhexadecylammonium chloride [5], tetraoctylphosphineoxide [20,21], and oleic acid [22], have been successfully employed for the creation of rod-shaped particles. However, CTAB has been extensively used. Gold nanorods stabilized with cationic quaternary ammonium surfactants are positively charged, because ammonium surfactants form a bilayer on the surfaces of gold nanorods, with the ammonium head-groups of one monolayer facing the nanorod surfaces [16]. The presence of the surfactant bilayer makes gold nanorods very stable when dispersed in aqueous solutions.

Evidence for rod-shaped particles is usually obtained by transmission electron microscopy, but for gold, the optical spectra of the plasmons are very informative. Nanorods show double plasmon bands, commonly ascribed to light absorption (and scattering) along both the long axis, known as the longitudinal plasmon band, and the short axis known as the transverse plasmon band. Thus, the particle shape dictates on how the wavelengths of light can be absorbed, and elastically scattered. Gold nanorods of an aspect ratio that is between 2 and 5, display plasmon bands with tuneable maxima from ~700 to 900 nm [23,24], while high aspect ratio nanorods exhibit a longitudinal plasmon band past 1200 nm [5,17,25].

A much stronger and more sensitive surface plasmon band for gold nanorods compared to spherical particles [26–29] and the

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ability to form two dimension assemblies [30] make gold nanorods suitable substrates in surface enhanced Raman spectroscopy (SERS) and sensor applications. Therefore, the knowledge on the surface structure of gold nanorods is essential for SERS system development. Gold nanorods have a larger surface area compared to spherical nanoparticles, thus allowing adsorption of a larger number of target molecules on the surface and also a high possibility of yielding more hot spots [31]. These enhanced fields of gold nanorods offer increased sensitivity for chemical sensing modalities such as SERS, in which the Raman intensity from molecules increase enormously, if the molecules are within ~ 10 nm of a metal nanoparticle surface [5,32]. One of the significant advances in the development of SERS is the detection of Raman scattering from a single molecule, as first achieved by two independent groups [33,34]. To date, a SERS enhancement factor of over 10 orders of magnitude may be realized, allowing single-molecule detection even under non-resonant Raman excitation [35,36]. The SERS effect originates primarily from the giant electromagnetic field resonating with the plasmon at the surface of metal nanostructure (silver, gold, etc.) [37,38] as well as from the chemical enhancement owing to the charge transfer resonance between the analyte and the substrate [38]. SERS is of great potential in (bio)-chemical analyses because of its high sensitivity and fluorescence-quenching capability [39]. The presence of CTAB poses a huge threat in utilizing AuNRs for biological applications since CTAB, which is a cationic detergent, shows high cytotoxicity [40–42]. However, Connor et al. reported that the cytotoxicity is not due to the nanorod-bound CTAB layer, but due to the excess CTAB left in the solution, which can be removed by centrifugation [43]. Thus, activation of AuNRs by replacing the CTAB with biocompatible and functionalization-friendly stabilizing agent is essential for the realization of functional nanorod probes that can be used in different application studies.

To further widen the applications of gold nanorods in SERS technique, it is crucial to fabricate SERS-active metallic nanostructures with both high enhancement performance, good reproducibility and lesser cytotoxicity. In this paper, we report on the synthesis of Raman active gold nanorods achieved by replacing CTAB molecules on the surface of a nanorods by mixture of HS-(CH₂)₁₁-NHCO-coumarin as a Raman reporter and HS-PEG-(CH₂)₁₁-COOH through ligand exchange. These SERS active gold nanorods can potentially be used to develop a highly sensitive SERS diagnostic probe due to gold nanorods Raman enhancement, and the terminal -COOH in HS-PEG-(CH₂)₁₁-COOH can be used to attach biomolecules for various applications.

2. Experimental

2.1. Chemicals

Hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O, >99.9%), cetyltrimethylammonium bromide (CTAB, 99%), L-ascorbic acid (AA, >99%) and sodium borohydride (NaBH₄, 99%) were all used as purchased (Aldrich). Silver nitrate (AgNO₃, A.R.) was from Fluka and methanol (Merck). Ultra-pure (18 M Ω) water was used for all experimental solutions. HS-PEG-(CH₂)₁₁-COOH and HS-(CH₂)₁₁-NHCO-coumarin were obtained from ProChimia Surfaces (Poland).

2.2. Preparation of Au seeds

In a typical procedure, 250 μ l of an aqueous 0.01 M solution of HAuCl₄·3H₂O was added to 9.75 ml of 0.1 M CTAB solution in glass beaker. The solutions were gently mixed by swelling the beaker. The solution appeared bright brown-yellow in colour. Then, 600 μ l

of an aqueous 0.01 M ice-cold NaBH₄ solution was added all at once, followed by rapid stirring for 2 min. The solution developed a pale-brown-yellow colour. The solution was then transferred into a centrifuge tube and kept at room temperature for 2 h.

2.3. Preparation of Au nanorods

In a typical experiment, 9.5 ml of 0.1 M CTAB was added to 75 μ l of 0.01 M AgNO₃, followed by the addition of 500 μ l of 0.01 M HAuCl₄·3H₂O and then gently mixed by swelling. The solution appeared bright brown-yellow in colour. Then 110 μ l of 0.1 M AA was added to it. The solution became colourless upon addition and mixing of AA. Finally, 70 μ l of seed solution was added, and the reaction was left undisturbed in an oven at 40 °C.

2.4. Functionalization of gold nanorods

In a typical experiment, 2 ml of each centrifuged gold nanorods were transferred to two 10 ml test tubes. Different stoichiometric ratios of HS-(CH₂)₁₁-NHCO-coumarin and HS-PEG-(CH₂)₁₁-COOH (1% and 50%) were used too co-stabilize nanoparticles with CTAB. For 1% a mixture of HS-(CH₂)₁₁-NHCO-coumarin (0.02 mg) and (2 mg) of HS-PEG-(CH₂)₁₁-COOH in methanol, was added to 2 ml centrifuged CTAB gold nanorods and swirled for 24 h. The same procedure was used for 50% mixture of HS-(CH₂)₁₁-NHCO-coumarin (1 mg) and (1 mg) HS-PEG-(CH₂)₁₁-COOH in methanol.

2.5. Instrumentation

High purity or ultrapure water with resistivity of 18.1 Ω M was obtained from a Milli-Q Advantage water system purchased from Millipore (USA) and was used in all the experiments. Samples were centrifuged using the Hettich MIKRO 22R cooling centrifuge. The samples were centrifuged in 1.5 mL Eppendorf tubes at 22 °C and 10,000 rpm for 15 min. Absorption spectra of the solutions were recorded on a Lambda 35 UV-vis spectrometer. Transmission electron microscope (TEM) images were obtained using a JEM-2100F at 200 kV. The TEM grids were prepared by depositing approximately 10 μ l of the solution obtained after centrifugation and allowed to dry in air. Raman spectra were acquired using a PerkinElmer Raman Station 400 benchtop Raman spectrometer. The excitation source was a near-infrared 785 nm laser (100 mW at the sample), with a spot size of 100 μ m. A spectral range of 200–3200 cm⁻¹ was employed. The detector was a temperature controlled Charged Coupled Device (CCD) detector (-50 °C) incorporating a 1024 \times 256 pixel sensor. The spectra were acquired using Spectrum software and images were acquired using SpectrumIMAGE software, both supplied by PerkinElmer (Bucks, UK). The zeta potential measurements were performed using a Malvern ZetaSizer.

3. Results and discussion

The seed-mediated method for gold nanorods synthesis was adopted from an earlier publication [7]. Two steps were followed to fabricate monodispersed and stable nanorods as shown in Fig. 1. In the first step, sodium borohydride, which is a strong reducing and nucleating agent was employed to reduce gold ions to form monodispersed spherical nanoparticles acting as seeds for nanorods. In the second step these nuclei were then added in the solution containing CTAB surfactant stabilized gold complex in the presence of ascorbic acid and silver nitrate for efficient growth of one-dimensional gold nanorods. The last step represents the functionalization of CTAB-capped gold nanorods with a Raman active alkanethiol. The results below are based on 1% and 50% mixture, which clearly show that our prepared gold nanorods yield

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