Applied Surface Science 457 (2018) 264–270

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Preparation of phase diagram of gold nanorods in mixture solvent of DMSO and water and its application for efficient surface-modification

Qinghui Shou[a,*], Mitsuhiro Ebara[b], Jiaqi Wang[a], Qinggang Wang[a], Xiangfeng Liang[a], Huizhou Liu[a], Takao Aoyagi[b,c,1,*]

[a] CAS Key Laboratory of Bio-Based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT), Chinese Academy of Sciences(CAS), Qingdao 266101, China
[b] International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 3050044, Japan
[c] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan

ARTICLE INFO

Keywords:
Gold nanorods
CTAB
DMSO
Phase-diagram
Thiols
Ligand-exchange

ABSTRACT

Gold nanorods (AuNRs) have been widely studied in various biological and biomedical fields. The complete removal of a cationic binary surfactant cetyltrimethyl ammonium bromide (CTAB), which is strongly bound to prepared AuNRs, is necessary due to their cytotoxicity as well as further functionalization of the surface. Here, we report an appropriate procedure which can remove CTAB and modify the surface by ω-mercaptocarboxylic acid efficiently. The detachment mechanism of CTAB from AuNR surface varying with the volume ratio of dimethylsulfoxide (DMSO)/water ($V_{\mathrm{DMSO}}:V_{\mathrm{AuNRs}}$) and the concentration of CTAB was also studied. For samples after twice-centrifugation ($C_{\mathrm{CTAB}} = 15\,\mu\mathrm{M}$), CTAB thoroughly detached from AuNRs under the condition of $V_{\mathrm{DMSO}}:V_{\mathrm{AuNRs}} = 0.3\text{–}0.5$, while AuNRs attained colloidal stability at either $V_{\mathrm{DMSO}}:V_{\mathrm{AuNRs}} = 0\text{–}0.2$ or $0.6\text{–}0.9$. Especially, the complete removal of interdigitated CTAB bilayer was confirmed at $V_{\mathrm{DMSO}}:V_{\mathrm{AuNRs}} = 0.5$ by X-ray photoelectron spectroscopy surface composition analysis. Based on the colloidal stability of AuNRs related with the volume ratios of DMSO/water and CTAB concentration, the phase diagram of AuNRs was further drawn. Both the minimal and maximum DMSO-fraction thresholds for efficient removal of CTAB are generally increased with the increase of CTAB concentration. After the removal of CTAB, mercaptohexadecanoic acid (16-MHDA) was utilized for the further modification of AuNRs. In a wide range of CTAB concentration and with high DMSO fraction, there is no aggregation after the modification. This technique may be used to functionalize the surface of AuNRs for use in a diverse range of applications.

1. Introduction

Anisotropic gold nanoparticles such as gold nanorods (AuNRs) have become a new exciting focus as an emerging noble metal nanomaterial with unique properties since the development of the facile seed mediated synthesis method [1–5]. Unlike spherical nanoparticles, the functionalized AuNRs cannot be directly prepared by reduction of gold ions. Therefore, the necessity to use a directing agent appears to ensure one directional growth of the nanostructures into rods. A cationic surfactant, cetyltrimethylammonium bromide (CTAB), is most commonly used shape-directing agent for the high production of AuNRs [1,2]. CTAB is not only the structure directing agent of anisotropic growth, but also the stabilizer that forms bilayers on the surface of AuNRs [6,7]. While AuNRs were found to be less toxic at certain doses, CTAB-capped AuNRs solutions were found to display significant cytotoxicity at a certain concentration. The apparent toxicity of CTAB-capped AuNRs solutions was assigned quantitatively to free CTAB molecules, which originate from inadequate purification and desorption of CTAB from nanorod surfaces [8,9]. These studies indicate that a rigorous purification procedure is required prior to clinical test. To address this issue, a number of studies have been implemented on surface modification of AuNRs; such as layer-by-layer technique [10], surface capping of silicon layers [11], or stealthy PEGylation method [11]. One of the most commonly used strategies is the ligand-exchange of CTAB with hydrophilic ligands with thiols, such as 3-mercaptopropionic acid, 11-mercaptoundecanoic acid, or glutathione [12,13]. Although

---

[*] Corresponding authors at: Smart Biomaterials Group, International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), 1-1Namiki, Tsukuba, Ibaraki 305-0044, Japan (T. Aoyagi).

E-mail addresses: shouqh@qibebt.ac.cn (Q. Shou), ebara.mitsuhiro@nims.go.jp (M. Ebara), hhxx1995@qq.com (J. Wang), wangqg@qibebt.ac.cn (Q. Wang), liangxf@qibebt.ac.cn (X. Liang), liuhz@qibebt.ac.cn (H. Liu), aoyagi.takao@nihon-u.ac.jp (T. Aoyagi).

[1] Permanent address: Department of Materials and Applied Chemistry, College of Science and Technology, Nihon University, Chiyoda, Tokyo 1018308, Japan.

https://doi.org/10.1016/j.apsusc.2018.06.261
Received 14 December 2017; Received in revised form 31 May 2018; Accepted 27 June 2018
Available online 28 June 2018
0169-4332/ © 2018 Elsevier B.V. All rights reserved.

alkanethiols are known to form a dense passivation layer on planar gold surfaces, the direct exposure of CTAB-capped AuNRs to alkanethiol agents usually results incomplete removal and uncontrollable aggregation of AuNRs [14].

CTAB forms interdigitated bilayer structure on the surface of AuNRs. The partitioning of CTAB between the gold surface and the solution is pivotal in dynamically controlling the surface ligand-exchange reactions. There have been several reports on this issue by selecting the polarity of organic solvent and mixing ratio with water [15,16]. For example, by mixing AuNRs aqueous solution with dimethyl formamide (DMF) with a certain weight fraction, the efficient removing of CTAB on AuNRs was discovered [15]. This was understood to result from the selective solubility of ammonium group (or alkyl chain) on the surface of AuNRs in high fraction of water (or DMF) [15]. Also, the method to exchange CTAB with PEG-SH was improved remarkably by a so-called two-step method. After modification with PEG-SH, AuNRs were exposed to ethanol and the remaining CTAB was desorbed, and the cytotoxicity to primary human blood monocyte-derived macrophages was further decreased [16]. Therefore, using this concept, the efficient detachment of CTAB from surface has been realized, regardless of the different affinity energy between gold and the CTAB located on AuNRs' shoulder and tail part. However, there are still questions regarding the detachment mechanisms of CTAB from the surface of AuNRs. The concentration of CTAB will directly influence the stability of gold nanorods, which has been investigated by Rostro-Kohanloo et al. [17]. For example, when investigating the partitioning of CTAB between the gold surface and the water-organic solvent mixture solution, the concentration of CTAB is supposed to take a critical role, which has never been explored to the best of our knowledge.

Another practical issue in ligand-exchange reaction is that a majority of hydrophobic thiols are only soluble in water and polar organic solvent mixture with a small portion of water. Up to now, there is still a lack of technique in combining a complete removing of CTAB and a good solubility of thiols in same volume ratio of mixture solvent.

To address this limitation, we proposed a new strategy for the complete removal of CTAB and further modification of the surfaces of AuNRs by careful control of experimental parameters. More specifically, we used a mixture solution of dimethylsulfoxide (DMSO)/water to control the partitioning of CTAB between the gold surface and the solution phase. The rationale behind the selections of DMSO/water ratio and CTAB concentration is discussed in detail regarding the detachment mechanisms of CTAB from the surface of AuNRs. After the removal of CTAB, hydroxyl-terminated alkanethiols were added additionally for the stabilization and further potential functionalization of AuNRs to make them useful for various applications. In this study, we used three steps: (i) removal of free CTAB by centrifugation and adjustment of the concentration CTAB, (ii) ligand-exchange of CTAB capped AuNRs. Mercaptohexadecanoic acid (16-MHDA) was utilized to modify AuNRs. A efficient removal of CTAB should provide chemical functionality for conjugation chemistry, good water solubility, and colloidal stability during modification and purification steps [18].

2. Material and methods

2.1. Reagents and materials

Gold (III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), cetyltrimethyl ammonium bromide (CTAB), sodium borohydride ($NaBH_4$), silver nitrate ($AgNO_3$), L-ascorbic acid, and mercaptohexadecanoic acid (16-MHDA) were purchased from Aldrich. Dimethylsulfoxide (DMSO) and dichloromethane were purchased from Wako Pure Chemical Industries. Milli-Q water was used in the whole experiment. Without specific description, all of the chemicals were used as received.

2.2. Synthesis of gold nanorods

AuNRs were synthesized using a seed-mediated method [2]. First, Au seeds were prepared as follows: 0.25 mL of an aqueous solution of 0.01 M $HAuCl_4{\cdot}3H_2O$ was added to 7.5 mL of a 0.10 M CTAB solution. After gentle mixing, 0.6 mL of an aqueous ice-cold 0.01 M $NaBH_4$ solution was added all at once, followed by rapid inversion mixing for 2 min. Then the test tube was kept in a water bath maintained at 28 °C for at least 2 h before further use.

To prepare a growth solution, solutions of 0.2 mL of 0.01 M $HAuCl_4{\cdot}3H_2O$ and 4.75 mL of 0.10 M CTAB were mixed to develop a deep yellow color, and then 30 μL of 0.01 M $AgNO_3$ solution was added, followed by gentle mixing by inversion. Then 32 μL of 0.10 M ascorbic acid was added. Finally, 10 μL of seed solution was added, and was gently mixed for 10 s and left undisturbed for at least 3 h. Freshly prepared AuNRs aqueous solutions were centrifuged at 10000 rpm for 15 min. The supernatant was decanted, and centrifuged again after diluting it with Milli-Q water as the same volume of original solution. The centrifugation of AuNR was carried out twice in order to remove the free CTAB as much as possible while keeping AuNRs stable against precipitation. After that, a series solution of CTAB was added to adjust the final concentration of CTAB. Morphologies of the gold nanorods were observed with a transmission electron microscopy (TEM) images were obtained on a JEM-2100F (JEOL, Tokyo, Japan). Number-average diameters were obtained by measuring the diameters of more than 200 particles using SmileView software (JEOL Corp., Japan).

2.3. The stability of AuNRs after mixing with DMSO

The AuNRs were centrifuged twice, in order to reduce the free CTAB and impurities (free gold ions, $AgNO_3$, ascorbic acid, etc.) as much as possible while AuNRs can keep stable against precipitation. A series of CTAB aqueous solutions was then added to make a AuNRs aqueous solution with different concentrations of CTAB. After that, AuNRs in aqueous solution were mixed with DMSO with varied volume ratios from 0.1 to 0.9. The volume ratio was defined to be $V_{\mathrm{DMSO}}:V_{\mathrm{AuNRs}}$. It should be mentioned that subscript of "AuNRs" means AuNRs aqueous solution. The colloidal stability of AuNRs soon after mixing with varying volume of DMSO was investigated by following changes of two characteristic absorptions of AuNRs using UV/Vis/NIR spectrophotometer (V-7200 JascoCorp., Tokyo, Japan). Hydrodynamic diameter was obtained using dynamic light scattering (DLS) (DLS-8000, Otsuka Electronics Co., Osaka, Japan) at 25 °C with a Ne-He laser (λ = 632.8 nm).

The typical procedure to prepare samples to draw phase diagram of AuNRs is as follows: 3 mL of twice-purified AuNRs pellets were diluted with 0.3 mL of CTAB aqueous solution with different concentrations, after which Milli-Q water was added to adjust the total volume of water. The resultant AuNRs aqueous solutions were left undisturbed in a water bath maintained at 28 °C for at least 24 h. Finally, the above samples were mixed with DMSO with varying volume ratios to make an about 3 mL of final mixture solvent solution. The total volume of mixture solvent was calculated using the apparent molar volumes of DMSO/water mixtures at 25 °C [19], which was listed in Table S2. Because of the widely distributed concentration of CTAB from about 1 μM to 10 mM investigated in this work, the total volume of mixture solvent has been regarded as constant. Therefore, through this procedure, the final concentrations of both AuNRs and CTAB after mixing with DMSO with different fractions are constant.

2.4. Ligand-exchange of AuNRs

Mercaptohexadecanoic acid (16-MHDA) was dissolved in mixture solution of DMSO and water, and the freshly prepared solution was added immediately into the AuNRs solution. After mixed by vortex mixer, the solution was stirred for 24 h using magnetic stirrer. The mole

Download English Version:

https://daneshyari.com/en/article/7832946

Download Persian Version:

https://daneshyari.com/article/7832946

Daneshyari.com