



Photo-responsive spiropyran monolayer protected gold nanorod



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ABSTRACT

The spiropyran monolayer covalently protected gold nanorod (GNR) hybrid was prepared and well characterized for the first time, which was stable, soluble and photo-responsive under certain light irradiation in organic solvent. The photochromism of the densely packed spiropyran monolayer on the surface of GNRS was found having effect on the surface plasmonic resonance (SPR) absorption of gold nanorods, namely inducing the intensity change of the two plasma absorption peaks at 786 and 551 nm of the GNR hybrids. The functionalization of this organic-inorganic GNR hybrid and the photo-tuning of its SPR absorption properties, especially in the not only UV–Vis range but also near-infrared (NIR) spectral area would make important and interesting sense in the area of functional hybrid nanomaterial.

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1. Introduction

Due to the unique and tunable surface plasma resonance (SPR) properties, anisotropic gold nanorods (GNRs) have widely potential and important application in optics, electronics, fabrication of nanocomposites, biomedical, biological detection, cellular imaging and cancer photothermal therapy, etc. [1–10] Great interests of the research in the GNRS field continue to be drawn to focus on the synthesis with controllable size and aspect ratio, the self-assembly and their application in various areas [11–17]. GNRS are mainly prepared in an aqueous solution via a seed-mediated growth method [18–20], in which a surfactant cetyltrimethylammonium bromide (CTAB) is widely employed as a shape-directing surfactant to selectively form a densely packed dynamic layer around the sidewall of a growing GNR with its two ends free from CTAB for an anisotropic growth along the longitudinal axis. The resultant GNRS protected with a CTAB layer on their longitudinal surface are water soluble. However, the dynamic CTAB layer is not stable and it is easy to result in irreversible aggregation of GNRS into gold clusters when either removing excess free CTAB in aqueous solution by centrifugation or solve GNRS in organic solvents thus destroy the CTAB layer. Moreover, the CTAB molecules on GNR surface are toxic to the

biological cells, proteins and tissues, which limit their various functions and potential biologically related applications.

Dispersing the GNRS in organic solvents and functionalizing GNRS with photo-responsive organic molecule via covalent modification to tune their plasmonic properties and expand their various functions are extremely intriguing. So addressing the challenge task to prevent the aggregation propensity of GNRS and make them organic-soluble is necessary, which can be realized by employing the thiol-containing photo-responsive molecule monolayer to modify covalently. A strong covalent S–Au linkage is formed between the thiol molecule and the surface of GNRS, although the thiol molecules are attached onto the two ends primarily [21,22]. Till now only a few organic-soluble GNR hybrids have been reported, examples including polymer adsorption, form a thin organic-silane shell on the CTAB protected GNRS, etc. [23–25] Functionalization of GNRS with thiol monolayer can not only stabilize or solubilize the GNRS in organic solvents, but also tune the properties of GNRS with certain such functional groups contained in thiol surfactants as fluorophore, chiral moieties, electron donors or acceptors and other stimuli-responsive units. In recent years, several organic thiol-monolayer protected GNRS, such as ruthenium (II) trisbipyridine functionalized GNRS [26], organic-soluble photo-responsive azo thiol monolayer protected GNRS [27], chiral thiol-monolayer protected GNRS, porphyrin thiol-monolayer-protected GNRS, hydrophilic thiolated CTAB analogue and cucurbituril pseudorotaxane monolayer covalently protected GNRS [28–30] have been reported.

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Spiropyran, as one of the typical photochromic molecule species, can behave the fact that the $C_{\text{spiro}}-O$ bond undergoes heterolytic cleavage upon UV irradiation resulting in the formation of a zwitterionic conjugated merocyanine (MC) form, and is thermally reversible or by photochemical irradiation with visible light [31–33]. Various functionalities of spiropyran systems, like memories and switches [34–38], dendrimers [39], polymer [40–42] and self-assembled monolayer on nanoparticle surfaces [43–46] etc. have been reported previously. Very recently, spiropyran self-assembled monolayer was employed to modify on polycrystalline gold surfaces and its UV–Vis and NIR light-responsive properties were investigated [47]. Herein, the self-assembled monolayer of a 6-nitrospiropyran modified with a disulfide-terminated aliphatic chain (SPLA) was prepared to protect the entire surface of gold nanorod via strong covalent S–Au bond (Fig. 1) for the first time. Owing to the effective surfactant modification of SPLA monolayer, this GNR hybrid (SGNR) is very stable and soluble in organic solvent without aggregation or decomposition, and also shows obvious photo-responsive properties under UV irradiation of certain wavelength.

2. Experimental

2.1. General information

3,3'-Dimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-indoline]-1'-ethanol (SP), lipoic acid, CTAB and all the solvents were commercial available and used without further purification. UV–Vis–NIR spectra were recorded on a Varian Cary 500 spectrophotometer (1-cm quartz cell used) at 25 °C. ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a tested on an LCT Premier XE mass spectrometer. Elemental analysis was performed

on an elemental Analysensysteme GmbH vario EL III instrument. Transmission electron microscopy (TEM) experiments were done using JEOL JEM-2100 equipment. For the observation, the samples in aqueous solution were dispersed on TEM Cu grids pre-coated with thin carbon film (Cu-400 CN) and then completely dried for analysis.

2.2. Synthesis and preparation

2.2.1. Synthesis of SPLA

The surfactant SPLA was synthesized via an esterification reaction between commercial 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran and lipoic acid in the presence of N,N' -dicyclohexylcarbodiimide (DCC) and N,N -dimethylpyridin-4-amine (DMAP). The reaction detail is described as following: a solution of 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran SP (1.41 g, 4 mmol) and lipoic acid (0.91 g, 4.4 mmol) in 40 mL CH_2Cl_2 was cooled to 0 °C. DCC (1.24 g, 6 mmol) and a small amount of DMAP (95 mg, 0.78 mmol) were added to the solution. Then the solution was allowed to stir at room temperature for 12 h. The reaction was then quenched by addition of water. The CH_2Cl_2 solution was filtrated and then washed by dilute sodium carbonate solution and water. Then the lower CH_2Cl_2 layer was collected and dried over anhydrous MgSO_4 . After evaporating most of the CH_2Cl_2 , the crude product was purified via column to afford SPLA as a brown solid (1.82 g, 84.0%). ^1H NMR (CDCl_3), δ ppm = 8.04 (d, 1H), 8.02 (s, 1H), 7.22 (t, 1H), 7.11 (d, 1H), 6.94 (d, 1H), 6.92 (t, 1H), 6.77 (d, 1H), 6.70 (d, 1H), 5.90 (d, 1H), 4.29 (m, 1H), 4.19 (m, 1H), 3.52 (m, 2H), 3.44 (m, 1H), 3.22–3.11 (m, 2H), 2.48 (m, 1H), 2.35–2.26 (m, 2H), 1.90 (m, 1H), 1.43 (m, 2H), 1.30 (s, 3H), 1.18 (t, 3H). ^{13}C NMR (CDCl_3), δ ppm = 173.180, 159.348, 146.631, 141.032, 135.607, 128.269, 127.776, 125.902, 121.767, 119.862, 118.375, 115.492, 106.675, 62.356, 56.225, 52.780, 42.332, 40.155, 38.425, 34.487, 34.054, 33.857, 28.690, 28.637,

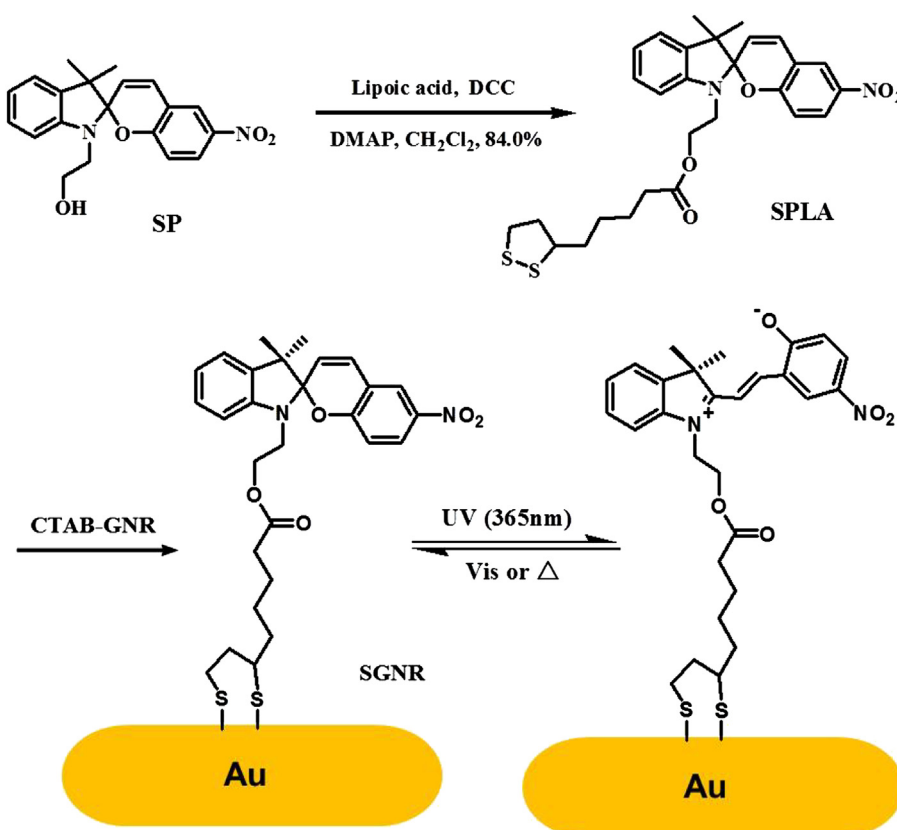


Fig. 1. Synthesis of SPLA and schematic preparation of SPLA monolayer protected gold nanorods (SGNR).

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