



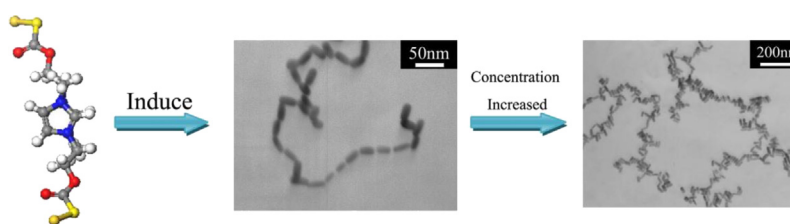
Materials science communication

 π – π stacking interaction induced the assembly of gold nanorodsHongtao Zhou ^{a, b}, Hui Yan ^c, Ailing Zhang ^a, Liqiang Zheng ^{a, **}, Han Jia ^{b, *}^a Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Jinan 250100, China^b College of Petroleum Engineering, China University of Petroleum (Huadong), Qingdao 266580, China^c School of Pharmacy, Liaocheng University, Liaocheng 252000, China

HIGHLIGHTS

- The π – π stacking interactions play important roles in the assembly of gold nanorods.
- The energy calculation demonstrated the stability of face–face stacked orientation.
- The assembly fashion of gold nanorods can be tuned from end-to-end to side-by-side.

GRAPHICAL ABSTRACT



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ABSTRACT

Gold nanorods have been recognized as a good candidate for developing novel nanomaterials due to their exceptional optical properties. However, their assemblies, especially with the assisted ionic liquid, have not been well characterized. In this paper, we report the self-assembly of gold nanorods using thiol-functionalized ionic liquid (1-methyl-3-(2'-mercaptoacetoxyethyl) imidazolium bromide) (TFIL). We found that gold nanorods can self-assemble via two different ways: From end-to-end to side-by-side with the increase of TFIL concentration. The shift of the absorption peak in UV–vis spectrum indicates the change of the assembly fashion. We propose that the π – π stacking interactions between the imidazole rings of TFIL molecules play the most important role in regulating the assembly process. The energy calculation further demonstrated that the face–face stacked orientation was the most stable geometry at high TFIL concentration, which supports the proposed mechanism. These gold nanorod assemblies were shown to yield the large SERS enhancements for Rhodamine 6G.

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1. Introduction

Gold nanorods have received widespread attention between the biosensing and photonics community in recent years. The assemblies of gold nanorods further exhibit unique collective properties that are different from those of both the individual gold nanorods and bulk materials [1]. The assembly of nanorods into 1D arrays has been realized either by employing linear templates or template-free self-assembly method [2–4]. Heung-Shik Park et al. investigated a simple and universal technique for assembling gold

nanorods using self-assembled stacks of lyotropic chromonic materials, without covalent bonding and the linking agent [4]. These self-assembly strategies depend on the presence of many different types of intermolecular interactions. The most common method is to use the thiol-terminated molecules, which can selectively replace the original capping molecule of cetyltrimethylammonium bromide (CTAB), and bind to the gold surfaces at the ends of the rods. If these molecules have an appropriate functional group linked to the thiol group, they can bind to one another, inducing end-to-end assembly of the nanorods [5–7].

As a typical intermolecular interaction among aromatic molecules, the π/π stacking interaction is important in the fields of chemistry and biology. The π/π stacking interaction may control the crystal structure of aromatic molecules, the stability of

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biological systems and their molecular recognition processes [8]. In most reports, the π – π stacking interactions were used to induce aggregation of the organic molecules [9]. Our recent work demonstrated that the π – π stacking interactions can contribute to the ordered arrangement of the capping agents at the surface of gold nanoparticles [10], which led us to further explore the use of π – π stacking interactions in the self-assembly of gold nanorods, which is seldom reported.

In the current study, the thiol-functionalized ionic liquid was used for the self-assembly of gold nanorods. The π – π stacking interactions between the TFIL molecules play important roles in the assembly process. The energy calculation further supports the proposed π – π stacking mechanism.

2. Experimental

Nanorods were made by the well-established seed-mediated method [11]. The gold seed solution was prepared by sodium borohydride reduction of 5 mL HAuCl₄ (0.25 mM) in an aqueous CTAB solution (0.1 M). Seeds were incubated for 3 h, and then a calculated amount of them was added to a previously prepared growth solution (10 mL) containing specific amounts of CTAB (0.1 M), HAuCl₄ (10 mM), ascorbic acid (0.8 mM) and silver nitrate (0.12 mM). This mixture was kept undisturbed for 24 h. Then the gold nanorods were centrifuged after preparation to remove the silver nitrate and excess ascorbic acid.

The assembly process was initiated by the addition of thiol-functionalized ionic liquid (1-methyl-3-(2'-mercaptoacetoxyethyl)imidazolium bromine; Figure S1) (TFIL) to the purified gold nanorods, and TFIL was synthesized as previously reported [12]. For this,

calculated amounts of TFIL were added to 5 mL of the purified gold nanorod solution. The spectral changes were analyzed by UV–vis spectroscopy (Hitachi U-4100), and the gold nanostructures were characterized by transmission electron microscopy (TEM) (JEM-100CX II (JEOL)).

SERS measurements were carried out on a confocal microprobe Raman spectrometer (Jobin-Yvon HR800). Five milliliters of the obtained aqueous dispersion containing gold nanorod assemblies were first condensed to 50 μ L by centrifugation. The SERS substrate was prepared by dropping the concentrated dispersion onto quartz wafer, which was allowed to dry naturally in air. Then, the quartz wafer covered with the gold nanorod assemblies thin film was immersed into a R6G aqueous solution (10^{-5} M) for 30 min. After drying in the dark at room temperature, it was rinsed with deionized water and absolute ethanol several times to remove the free R6G molecules and dried in air. The SERS measurements were performed with an excitation wavelength of 633 nm and power of 20 mW. Spectra were collected by focusing the laser line onto the sample using a 50 \times objective, providing a spatial resolution of about 1 μ m. The data acquisition time was 10 s for one accumulation. In order to test the reproducibility, measurements at different positions were carried out for each sample.

3. Results and discussion

Gold nanorods are known to show two maxima in the UV–vis spectrum. The first one is due to the plasmon excitation along the long axis, occurring in the NIR region, and is called the longitudinal surface plasmon (LSP) resonance, which will change position according to the aspect ratio of the nanorod. The second is due to an

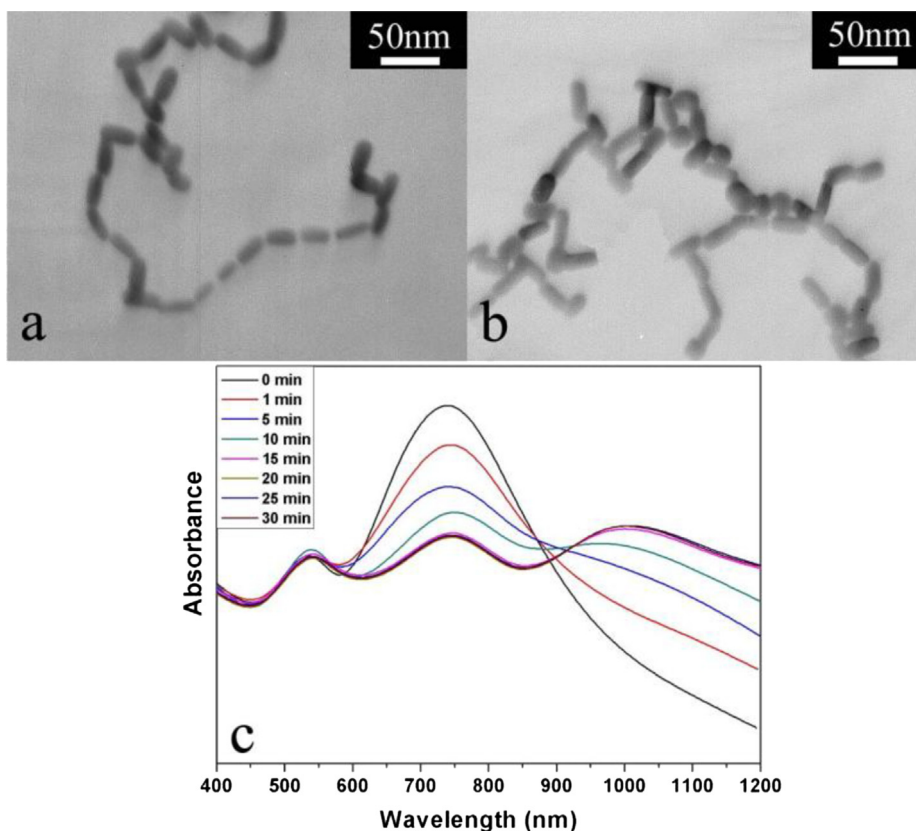


Fig. 1. Representative TEM images (a, b) and the evolution of UV–visible spectra (c) of the gold nanorod assembly in an end-to-end fashion when the concentration of TFIL is 0.2 mM.

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