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Research paper

Effect of adsorbate electrophilicity and spiky uneven surfaces on single gold nanourchin-based localized surface plasmon resonance sensors

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ABSTRACT

We present single particle studies on gold nanourchins (AuNUs) for their use as localized surface plasmon resonance (LSPR) biosensors under dark-field (DF) microscopy. First, the LSPR wavelength of single AuNUs was red-shifted as thiol molecules were attached onto the surface. AuNUs with sharp tips showed higher sensitivity for detecting thiol molecules than gold nanospheres (AuNSs) of similar size. Second, the degree of red shift was affected by the electrophilicity of adsorbate molecules on the nanoparticle surface. Last, real-time monitoring of molecular binding events on single AuNUs was achieved with introducing 1 μM of 4-aminothiophenol.

1. Introduction

Plasmonic gold nanoparticles have unique optical properties because of the localized surface plasmon resonance (LSPR) effect [1–3]. The LSPR effect is collective oscillation of conduction electrons at the surface of a nanoparticle stimulated by the electric field of incident light [4,5]. Gold nanoparticles of various shapes, including nanorods [6–11], nanobipyramids [12], nanostars [13–15], nanocubes [16], and nanoshells [17,18], have attracted significant attention due to unique optical properties depending on their three-dimensional (3D) structures. These nanoparticles have been widely used for a variety of applications in biological and chemical sensors [19,20], optical probes [12,21,22], surface enhanced Raman scattering (SERS) substrates [14,23] and photothermal cancer therapy [17,18,24].

Complex gold nanoparticles with spiky uneven surfaces, including nanostars [14,25], nanoflowers [23,26] and nanourchins [27,28], have been extensively employed in SERS studies due to strong electric field enhancement induced by sharp branches on the nanoparticle surface. These complex gold nanoparticles show high sensitivity to target molecules in SERS experiments [29]. The controlled synthesis of gold nanoparticles with sharp tips has been a field of challenging research in the past decade. With the recent advance in the synthetic methods, the reproducible and highly controllable synthesis of monodisperse branched gold nanoparticles has been demonstrated by the zwitterionic surfactant, poly(vinyl pyrrolidone)-sodium dodecyl sulfate aggregations, DNA directed synthetic method, etc. [30–35]. However, our understanding on the optical properties of branched gold nanoparticles is still very limited at the single particle level [36].

Besides SERS-based sensors, LSPR-based biosensors have been widely used to detect target molecules [37–41]. The LSPR sensor is based on the shift of the LSPR peak, which is caused by changes in the medium dielectric constant. The previous studies showed high sensitivity of gold nanoparticles with sharp tips for label-free LSPR biosensing [42,43]. However, branched nanoparticles such as gold nanourchins (AuNUs) and gold bipyramids (AuBPs) have rarely been studied as LSPR-based biosensors compared to gold nanorods (AuNRs). In this regard, it is highly desirable to investigate the capability and performance of single AuNUs as LSPR biosensors. More importantly, our understanding of the effects of electrophilicity of molecules adsorbed onto particle surfaces is still very limited.

In the present study, we investigated the optical properties of AuNUs at the single particle level and tested the capability and performance of single AuNUs as LSPR biosensors compared to Au nanospheres (AuNSs) of similar size. AuNSs were used in this study because they do not have sharp surface branches. We sought to increase understanding of the effect of branches on the optical properties of AuNUs as well as their performance as LSPR sensors. Furthermore, we studied how the electrophilicity of thiolated molecules attached onto nanoparticle surfaces affect the degree of red shift of the LSPR peak. To the best of our knowledge, this is the first study to demonstrate the effect of electrophilicty of adsorbed thiol molecules on LSPR peak shifts in single AuNUs.

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Finally, we tested the potential use of single AuNUs as sensitive LSPR biosensors by monitoring real-time molecular binding events with 4-aminothiophenol.

2. Experimental section

2.1. Sample preparation and characterization

The AuNUs used in this study were purchased from Sigma-Aldrich (St. Louis, MO, USA), while the AuNSs were obtained from Nanopartz (Loveland, CO, USA). The Au nanoparticle solution was first diluted with 18.2-MΩ pure water to a proper concentration. The diluted solution was then sonicated for 15 min at room temperature. Samples were prepared by spin casting the Au nanoparticle solution onto a pre-cleaned glass slide. Then, a 22 mm × 22 mm no. 1.5 coverslip (Corning, NY) was placed on the glass slide. In this study, a silane method with APTES allowed Au nanoparticles to be immobilized on the glass slides. The concentration of Au nanoparticles on the glass surface was controlled to be ~1 μm^{-2} in order to facilitate single-particle characterization and to minimize inter-particle SPR coupling, which can result in a spectral shift. Structural characterization was carried out using a scanning electron microscope (SEM).

2.2. Single particle scattering microscopy and spectroscopy

DF microscopy imaging was performed under a Nikon inverted microscope (ECLIPSE Ti-U) in this study. In DF mode, the microscope utilized a Nikon Plan Fluor 100× 0.5–1.3 oil iris objective and a Nikon DF condenser. An Andor iXon^{EM}+ CCD camera (iXon Ultra 897) was employed to record DF images of Pt-AuNRs. The collected images were analyzed with Image J. Furthermore, DF scattering spectra were acquired with an Andor spectrometer (SHAMROCK 303i, SR-303I-A) and an Andor CCD camera (Newton DU920P-OE). When taking a spectrum, the scanning stage moved the sample to the desired location so that only the scattered light from the selected location was collected by the objective. The scattered light was directed to the entrance of the spectrometer, dispersed by a grating (300 l/mm, center wavelength, 700 nm), and detected by the Newton CCD camera. The background was measured at a region without any particles. Data analysis was performed with specially designed Matlab programs.

3. Results and discussion

AuNUs with an average diameter of 100 nm were purchased from Sigma-Aldrich (St. Louis, MO, USA), while AuNSs with an average diameter of 100 nm were obtained from Nanopartz (CO,

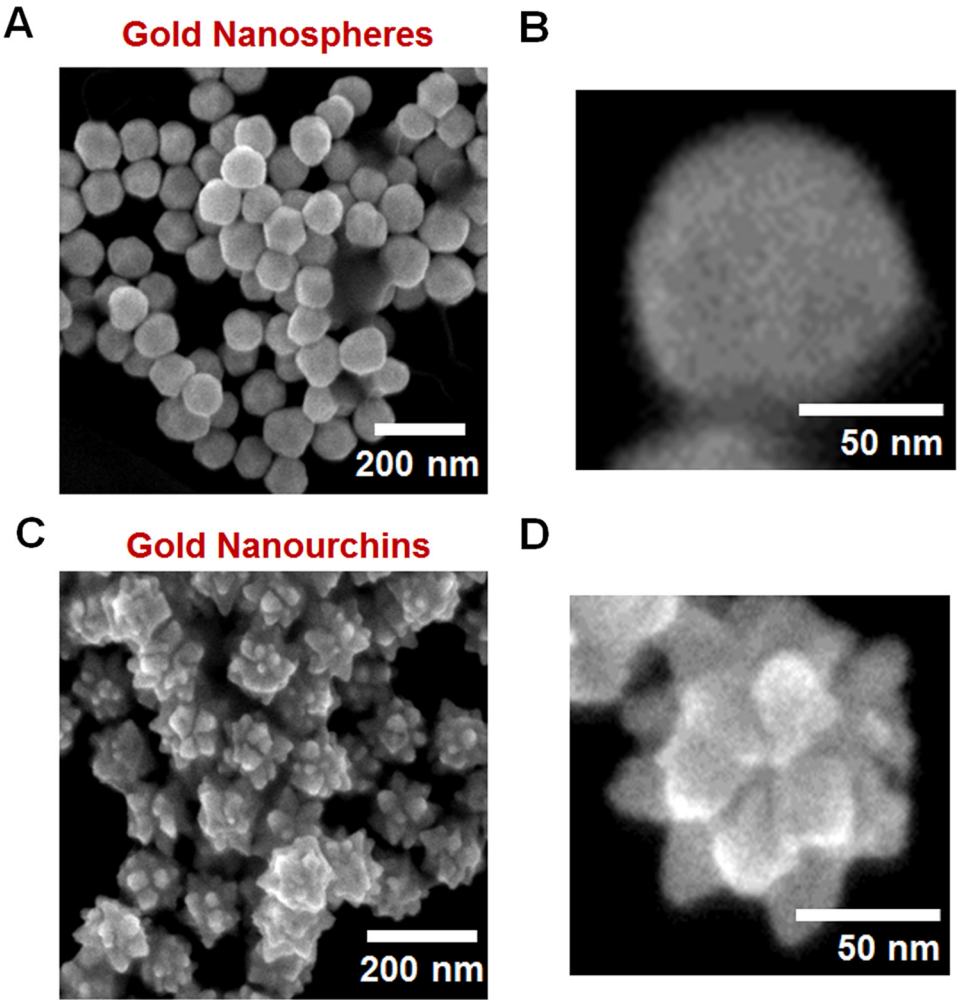

Fig. 1. (A) SEM image of gold nanospheres with diameter of 100 nm. (B) Enlarged SEM image of single gold nanophere. (C) SEM image of gold nanourchins with sharp tips. (D) Enlarged SEM image of single gold nanourchin with diameter of 100 nm.