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Plasmonic response of DNA-assembled gold nanorods: Effect of DNA linker length, temperature and linker/nanoparticles ratio

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ABSTRACT

Optical properties of gold nanorod (AuNR) particles self-assembled with DNA are systematically investigated. The particles assembly is driven by specific base-pair recognition between single strand (ss) DNA linker and DNA anchored to AuNRs, and it results in the distance- and morphology-dependent plasmonic coupling of AuNRs. The longitudinal plasmon band is distinctly affected by tuning the length of DNA linker, the temperature and linker/AuNRs ratio. We observed that the increase of temperature enhances the interparticle interactions and leads to clear distinguishable plasmonic signals between linker lengths up to 100 bases. Both absorbance decrease and shift of the longitudinal plasmon allow for use of AuNR for the DNA sensing applications.

1. Introduction

The assembly of gold nanoparticles (AuNPs) and the control of their hierarchical organization in one, two, and three dimensions are attracting great current interest for applications such as optoelectronic, sensing and drug delivery [1,2]. AuNPs present localized surface plasmon resonance, a collective oscillation of the conduction electron at the metallic surface stimulated by incident light, a property that is greatly affected by the collective interactions of the nanoparticles. For individual gold spheres, typically, the excitation of the plasmon occurs in the visible region and is easily detected with UV–visible spectroscopy or even by eye. A small change in the size, shape, local environment, surface nature, interparticle distance and degree of aggregation of gold nanoparticles leads to a change in their optical properties. The use of gold nanorods (AuNRs) as an alternative to spherical nanoparticles was studied and showed interesting features [3,4]. AuNRs present two surface plasmon resonances (SPRs) – longitudinal and transverse [5]. The longitudinal plasmon band (LPB) maximum is, typically, in the near-infrared region and its position is highly sensitive to the local environment making them more versatile as a platform for biodetection [6]. Also, nanorods, unlike isotropic spheres, can assemble end-to-end or side-by-side providing two distinguishable signals depending on the interaction pathway, potentially leading to a multilevel detection. For end-to-end interactions one expects red shift of LPB while side-by-side assembly affects both plasmon bands and leads to a blue shift in LPB and the red shift of the transverse one, as shown by both discrete dipole simulations [7] and experimental studies [8,9].

Different AuNPs arrangements from multimers [10–13] to 3D well-ordered nanostructures [14,15] were built up thanks to the possibility of using the programmability of DNA base pairing as outstanding strategy for controlled attachment of nanoparticles. In terms of plasmon effect [16], tuning the length and the sequence of DNA and thus the distance between particles and the nanoparticles orientation is attractive in order to modulate the optical properties of nanoparticles-based systems. Therefore, promising nanoparticle-based DNA sensors showing high sensitivity and selectivity were widely developed [17–21].

The use of DNA as a template might provide a variety of rods orientation in the assembled state leading to new and more interesting plasmonic responses. For example, assembly of nanorods in well-defined 2D [22] and 1D [23] architectures has been demonstrated. Moreover, the use of triangular DNA origami structures [24] showed the ability to direct the organization of dimers with control of the distance and angle between rods, which results theoretically and experimentally to diverse plasmonic signatures.

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The length, the flexibility of the DNA linker, the temperature and the ionic strength has shown [13,16,21,25–27] to be very important in defining the performance of spherical nanoparticles-based DNA system as manifested via SPR coupling. However, to date, no specific investigation regarding how these factors may affect the plasmon coupling in AuNR system with DNA mediated interactions has been reported. In order to establish an efficient and reliable method to control the interparticle interactions, the parameters affecting the surface plasmon resonances must be carefully evaluated and characterized.

In the present study, the plasmon coupling arising from the self-assembly of AuNRs driven by hybridization between ss-DNA linker and DNA-functionalized to AuNRs was systematically investigated. DNA linker length, the temperature and DNA linker/AuNRs ratio were studied and discussed in order to determine their effects on the optical properties. Upon adding the linker, a side-by-side AuNRs assembly is immediately induced as noticed by a blue shift of LPB. [23] This trend is observed in our system using flexible DNA linker and elevated temperature of assembly. On the other hand, Parab et al. [28] have reported a red shift of LPB using a more rigid system designed for the detection of 24-mer ss-DNA at room temperature. We also find that temperature significantly affects the interactions between nanorods, which leads to increase in plasmon coupling strength at higher temperatures. The findings might be relevant for a number of biosensing applications, and the results are discussed in the context. We report that whereas, previous studies [28,29] follow the drop of absorbance to detect shorter DNA, LPB blue shift can be used for DNA detection, quantification and length discrimination at least up to 100 bases when the particles get organized in a side-by-side fashion.

2. Materials and methods

2.1. Chemicals and materials

Gold (III) chloride trihydrate ($HAuCl_4{\cdot}3H_2O$), silver nitrate ($AgNO_3$), ascorbic acid 99%, sodium borohydride ($NaBH_4$), cetyltrimethylammonium bromide (CTAB) and phosphate buffer solution 1 M were purchased from Sigma–Aldrich. All the oligonucleotides were purchased from Sigma Life Science. GE Healthcare NAP-5 Columns (Sephadex G-25 DNA grade) were purchased from VWR.

2.2. Nanorods synthesis

The gold nanorods were synthesized by the seed-mediated method. [30] First, a gold seed solution was prepared by the borohydride reduction of 0.25 mM $HAuCl_4$ in an aqueous 0.1 M cetyltrimethylammonium bromide (CTAB) solution. Subsequently, the seed solution was added to a 10 ml growth solution containing 0.1 M CTAB, 0.5 mM $HAuCl_4$, 0.7 mM ascorbic acid and 0.06 mM silver nitrate. The solution was aged for 24 h to ensure the complete formation of AuNRs. This protocol gives CTAB-stabilized gold nanorods, 40 nm ± 3 nm long, with an average diameter around 12 nm ± 1.7 nm (Fig. S1a and b). The concentration of gold nanorods was determined at the LPB peak maximum using molar extinction coefficient $\varepsilon = 4 \times 10^9\ M^{-1}\ cm^{-1}$ [31].

2.3. Nanoparticle modification with DNA

Single-stranded thiolated-DNAs were immobilized on the surface of the nanorods through S–Au bonds following the procedure that we have developed previously. [23] First, DNA for particle functionalization was reduced by adding dithiothreitol (DTT) solution and purified with a sephadex column (NAP-5, GE Healthcare) by elution with 10 mM phosphate buffer (pH = 7.4). From the gold nanorods stock solution, two different batches of particles were, separately, functionalized with Sequence-A DNA and sequence-B DNA (see Table S1 for DNA sequences). Before DNA functionalization, the gold nanorods were centrifuged twice and supernatant was exchanged with purified water in order to remove the excess of CTAB. Typically, an excess of 3000 purified DNA per nanorods was added to 1 ml of a purified solution of AuNRs (~2 nM), and the mixture incubated for at least 12 h at room temperature. The salt aging process was carried out in the presence of 1% w/v sodium dodecylsulfate. The mixture was brought to 10 mM concentration of phosphate buffer (pH = 7.4), and left for 1 h. Afterwards, the salt concentration was increased stepwise in order to reach a final concentration of 0.5 M of NaCl, and the samples incubated overnight. The solution was freed of excess DNA by three consecutive centrifugations and supernatant exchange of phosphate buffer 10 mM, pH 7.4 and 0.5 M of NaCl. The average number of thiolated DNA strands attached to AuNRs, about 500–600 DNA per AuNRs, was determined from changes in the DNA concentration before and after rods functionalization, as measured by UV–visible spectroscopy [32].

The DNA–AuNRs were stable for at least 2 weeks at this salt concentration. The final concentration of AuNRs was adjusted to 0.35 nM.

2.4. DNA–AuNRs assembly at 25 °C

Particle assembly was carried out at 25 °C by combining equimolar amounts ([AuNRs] = ~0.35 nM) of sequence-A and sequence-B DNA-capped gold particles with the corresponding DNA linkers (see Table S1 for DNA linker sequences) in 100 μl solution of 10 mM phosphate buffer, 0.5 M NaCl, pH = 7.4. The UV–visible spectra of the assembled AuNRs were monitored from 1000 to 450 nm using a Shimadzu UV-2550 spectrometer (wavelength accuracy is ±0.3 nm and the photometric accuracy is ±0.004 absorbance) with temperature controlled cell holder.

For ease of data comparison, we have normalized the absorption of all spectra by the maximum of the longitudinal resonance of the AuNRs sample before linker addition. The shift of the LPB ($\Delta\lambda$) and the absorbance drop at the maximum position of the DNA-capped AuNRs located at 770 nm versus time of incubation were plotted in order to follow in detail the LPB responses arising from AuNRs self-assembly.

2.5. Thermal profile procedure

For temperature dependent studies we have used the following procedures. Heating process: The corresponding linker at linker to AuNRs ratio 100 was incubated in an equimolar mixture of sequence-A and sequence-B DNA-capped gold AuNRs at 25 °C for 30 min to initiate gold nanorods assembly. Then, the different samples were heated to a corresponding temperature and UV–visible spectra were taken after 5 min incubation at the required temperature.

Annealing process: After 15 min at 70 °C, each sample was cooled down to 60 °C. UV–visible measurement was performed after 10 min incubation time. All absorption spectra were normalized at the longitudinal plasmon band maximum.

2.6. DNA–AuNRs assembly at 60 °C

Particle assembly was carried out at 60 °C by combining equimolar amounts ([AuNRs] = ~0.35 nM) of sequence-A and sequence-B DNA-capped gold particles with the corresponding DNA linkers in 100 μl solution of 10 mM phosphate buffer, 0.5 M NaCl, pH = 7.4. For the Linker/AuNRs (R) ratio studies, the same