Functionalization and Characterization of ssDNA Coated Gold Nanorods

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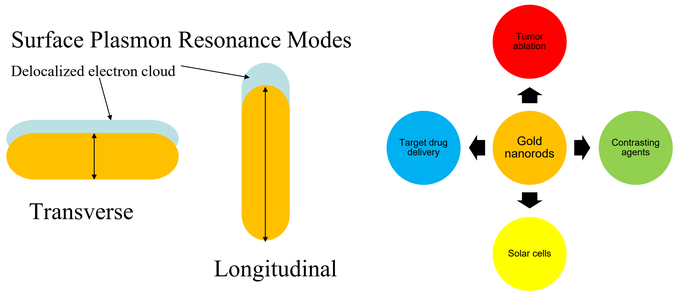
Gold nanorods are versatile nanostructures that find wide application in biotechnology and energy systems. Research has shown that gold nanorods can be functionalized by a variety of ligands. Our research focused on employing a novel procedure for functionalizing gold nanorods with single stranded thiolated DNA. In this work, we followed the established seed mediated, silver assist procedure proposed by Burrows et al for synthesizing highly monodispersed gold nano rods. Once cetyltrimethylammonium bromide (CTAB) coated gold nanorods had successfully been synthesized the nanorods were functionalized using single stranded thiolated DNA. This recoating procedure was conducted in a low pH environment to facilitate a rapid surface modification. The ssDNA coated gold nanorods were then characterized by UV/vis spectroscopy and gel-electrophoresis using SYBRgold intercalating dye. These functionalized gold nanorods can then be further conjugated to larger nanostructures such as DNA origami or DNA functionalized molecules such as silica nanoparticles for future applications.

Introduction

Gold nanorods (GNRs) have found a wide variety of applications in the field of biotechnology and energy cells. These applications can include contrasting agents in photoacoustic imaging, radiative sources in photothermal tumor ablation, delivery mechanisms for chemotherapy drugs and charge carriers in solar cells. The versatility of gold nanorods is due to their tunable optical properties and ability to undergo surface modifications.



The optical properties are defined by the localized surface plasmon resonances, SPR. SPR is the oscillation of conduction band electrons with a frequency matching that of a light source. This coupling allows for light to be absorbed and released as energy. Gold Nanorods show two modes of SPR the transverse and longitudinal modes. Gold nanorods also are capable of undergoing a number of surface chemistry changes. This allows the surface of the GNRs to be functionalized with ligands that stabilize the GNRs in numerous environments.

In this work, we followed the established seed mediated, silver assist procedure proposed by Burrows et al for synthesizing highly monodispersed gold nano rods. Once CTAB coated gold nanorods had successfully been synthesized the nanorods were functionalized using single stranded thiolated DNA. These stable functional GNRs can then be used in future research for conjugation to larger nano systems.

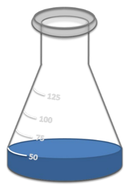
Procedure

Seed Solution Synthesis

- CTAB (micelle structure)
- $NaBH_4$ (strong reducing agent)
- $HAuCl_4$
- Stirred and heated at 28 °C in water bath.

Growth Solution Synthesis

- Dissolved sodium salicylate in CTAB. Stirred and heated at 28 °C in oil bath for 25 minutes.
- Silver nitrate added, precipitate forms.
- Add dilute $HAuCl_4$ plus small quantity of seed solution while being stirred.
- Incubate in hot water bathe at 28 °C for 24 hours.

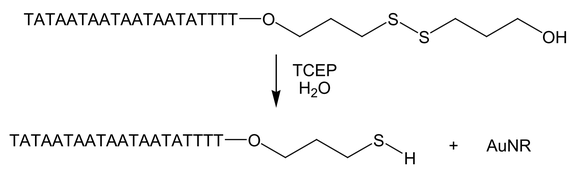


Purification of CTAB gold nanorods

- Centrifugation and washing with DI water.
- UV/vis spectra obtained for purified CTAB coated gold nanorods.

DNA Recoating

- Disulfide bonds cleaved with TCEP (react for 2 hours).



- CTAB-GNRs mixed with SDS and TBE.
- Dilute HCl used to adjust pH to approximately 3.
- Reduced thiolated ssDNA added to low pH GNR solution.
- NaCl Salting agent added. Solution then placed on rocker table for 24 hours.

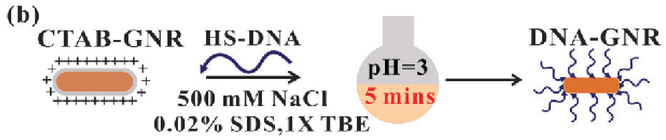
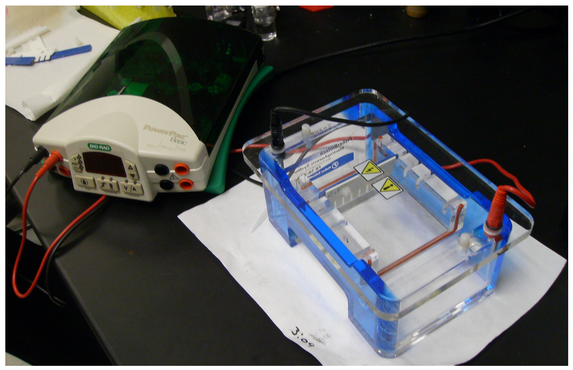


Image credited to: Dangwei Shi; Chen Song; Qiao Jiang; Zhen-Gang Wang; Baoquan Ding; Chemical Communications, 2013, 49, 2533-2535.

Gel electrophoresis

- 1% agarose prepared in a 1 X TBE buffer.
- Dilute SYBRgold dye added to gel.
- Gel molded
- Lanes loaded.
- 100V applied.
- Gel imaged under UV illumination using SYBR photographic filter.

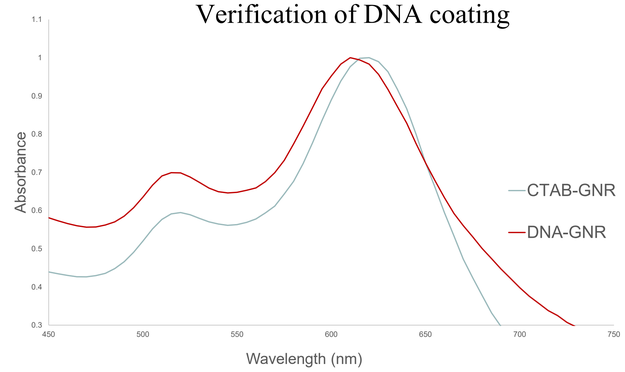


Results

DNA Recoating Procedure

The synthesis of gold nanorods as described above produced CTAB coated GNRs with a λmax of 620nm corresponding to the longitudinal SPR mode giving a blue coloration. These CTAB-GNRs were then coated with ssDNA and the efficacy of the procedure described above was assessed by UV/vis spectroscopy at the a λmax of 620nm.

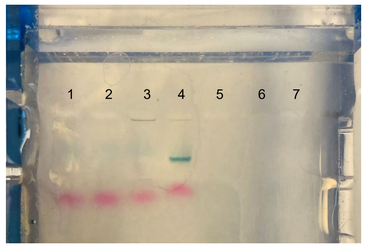
Verification of DNA coating



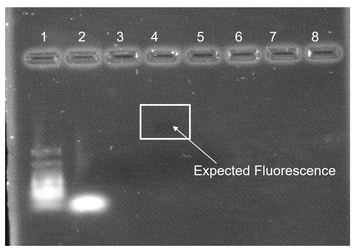
The shift in the λ_{max} of the ssDNA conjugated gold nanorods compared to the CTAB-GNR complex is indicative of a surface chemistry change. Here the weakly absorbed CTAB is being replaced by covalently bonded thiolated ssDNA. This change in the dielectric environment changes the wavelength of the longitudinal SPR.

Gel electrophoresis

The result from the UV spectrum is not sufficient to support that the GNRs were successfully coated with ssDNA. Gel-electrophoresis allows us to visualize the effectiveness of the recoating procedure by observing if the negatively charged –ssDNA-GNR complex pulls through the gel.



Lane 1: DNA ladder
Lane 2: ssDNA + loading dye + 1 X TBE
Lane 3: CTAB-GNR + loading dye
Lane 4: ssDNA-GNR + loading dye



Lane 1: DNA ladder
Lane 2: ssDNA + loading dye + 1 X TBE
Lane 3: CTAB-GNR + loading dye
Lane 4: ssDNA-GNR + loading dye

As expected, the CTAB coated GNRs in lane 3 showed no migration through the gel. It is evident however, that the ssDNA coated gold nanorods in lane 4 are migrating towards the positive electrode suggesting a successful recoating procedure. However, the result of the SYBRgold dye on the ssDNA-GNR complex in lane 4 is negative. It can be seen that SYBRgold does intercalate and fluoresce single stranded DNA as evidenced by the band in lane two.

Future Research

Ongoing efforts are being directed towards getting the ssDNA-GNR complex to fluoresce under UV illumination using SYBRgold. These functionalized GNRs can then be conjugated to DNA origami structures as well as ssDNA functionalized silica nanoparticles currently being developed by fellow lab partners. The potential applications of these nanostructures can then be explored.

Acknowledgements

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