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Gold Nanoparticles Assembled on Sliver Nanoprisms: Its Application to SERS-based DNA Detection in Aqueous Solutions

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1, Introduction

In the past decades, DNA-modified gold nanoparticles have attracted widespread attention due to their novel biochemical properties, such as the excellent biocompatibility, the programmable sequences, and the ability to cooperatively hybridize complementary DNA. Silver triangular nanoparticles (referred to as "nanoprisms" or "NPRs") is a kind of typical anisotropic nanomaterials that can produce massive localized plasmonic field enhancement at their tips, which makes them one of the ideal SERS substrate. Unfortunately, it has previously been demonstrated that the Ag NPRs are extremely sensitive to the changes of ion concentration, and their surfaces, especially the tips, are easily oxidized, which makes it difficult to obtain stable DNA-modified Ag NPRs, hampering its biomedical applications.

Here, using a commercially available alkyl dual-thiol modified DNA, we synthesized stable oligonucleotide-modified Ag NPR conjugates with good reproducibility. After that, DNA-gold nanoparticles were assembled on DNA-Ag NPRs via the selective DNA linkers. Finally, this system was explored as a SERS sensor by marking Raman reporters on gold nanoparticles to detect DNA in aqueous solutions quantitatively, as schematically illustrated in Figure 1.

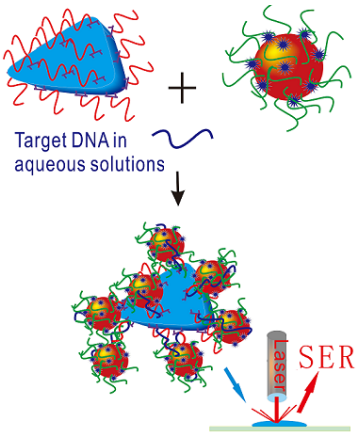

Figure 1. Schematic of gold nanoparticles assembly on Ag NPRs and its application in SERS-based DNA detection in aqueous solutions.

2. Experiments and results

Methods

Gold nanoparticles with an average diameter of 25 ± 5 nm were synthesized by citrate reduction of $HAuCl_4$. Ag nanoprisms were synthesized following a seed-mediated protocol. The prepared Ag nanoprisms with the average edge length of 110 ± 10 nm had an extinction maximum at 755nm. Initially, we labeled DNA-modified gold nanoparticles with Raman molecules (DTNB) for detecting the target DNA. After that, to assemble the DNA-modified gold nanoparticles on DNA-modified Ag NPR, both of nanoparticles were added to PBS buffer, incubated at 70 ℃ for 6 hours in a water bath, and then cooled slowly (1 ℃/min) to room temperature. All aqueous samples were dropped on a glass slide, and their SERS spectra were collected using a confocal microscope.

Results

The gold nanoparticles were successfully assembled on Ag NPRs, which confirmed by the SERS spectra and TEM images. In addition, this system has been used as SERS sensors to detect the target DNA in aqueous solutions. As expect, a good linear response was achieved between SERS signal intensity and the logarithm of target DNA concentration ranging from $10^{-11} \sim 10^{-8}$ M. This result demonstrates that this approach can detect DNA in aqueous solutions directly without "dry" process, and holds a sensitivity that is comparable to or even higher than that of other SERS-based DNA detection methods. Furthermore, duplex target DNA detection was successfully performed by using SERS hybrid probes with two different SERS reporters.

3. Conclusions

We have introduced a SERS-based DNA detection method in aqueous solutions by assembling Au nanoparticles on Ag nanoprisms.

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