Detecting Organic Molecules Using Au Nanoparticle Dimers with Supramolecular Interactions

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ABSTRACT

In this work, we have developed a controlled method of functionalization of colloidal nanoparticles in solution based in using rigid molecules as linkers (Cucurbituril molecules) which allow us to obtain reproducible hot spots in gold nanoparticle dimers, due to the control of the gap size between the plasmonic structures with subnanometer precision, and at the same time enables placing analyte molecules precisely within these junctions of ultrahigh field enhancement. This novel protocol allows to obtain dimers of Au NPs using cucurbit[6]uril as linker in a reproducible manner that are stable over several days. The sensing performance of these dimeric structures, is by far superior to previous work using supramolecular interactions, as demonstrated by measuring the SERS response of this system using cucurbituril linker as the host and methyl viologen as the guest molecule.

Keywords: plasmonic nanoparticles dimers, self-assembled nanoparticles, quantitative SERS, cucurbit[6]uril, host-guest, sensing.

1. INTRODUCTION

Noble metal nanoparticle (NP) aggregates have long been recognized for their unique plasmonic properties, particularly their capability to couple to each other through near- and far-field interactions, giving rise to a variety of interesting optical phenomena, such as strongly confined and enhanced electromagnetic fields generated between the NPs, and to tune the plasmon resonance frequencies just by changing geometrical parameters, such as nanoparticle size,[1] shape, [1],[2] crystal face,[3] surface roughness,[4] and particle-particle spacing [5]-[10].

The synthesis and fabrication of surface enhanced Raman spectroscopy (SERS) substrates have evolved from electrochemically roughened metal surfaces to random nanoparticle aggregates and finally to rationally designed nanostructures. Nowadays, our current ability to control the interparticle spacing (and therefore to control the magnitude of the enhanced field in the gap – "hot spot") as a function of the nanoparticle specific functionalization is the subject of great interest. The generation of controlled nanostructures (NEs) with specific geometrical position of the NPs in the final architecture of the NE and with a precise interparticle distance between the NPs is a very interesting and challenging research topic. For this purpose, the selection of a particular NP linker is crucial. There are a lot of previous work in which the properties of Cucurbituril (CB) molecules has been pointed out, as this barrel-shaped molecule not only generates subnanometer gaps, but also allow to localize an analyte molecule precisely in the gap of the NPs [11]. Nevertheless, in general, the agglomeration of NPs occurs through the carbonyl groups of the portals of the CB molecule, and those interactions leads to a random NE [11]-[13].

In the present work we have developed a method of functionalization of colloidal nanoparticles in solution based in using rigid molecules as linkers (cucurbit[6]uril CB[6] molecules) which allow obtaining reproducible hot spots due to the control of the gap size between plasmonic structures with subnanometer precision, and allowing placing analyte molecules precisely within these junctions of ultrahigh field enhancement. This novel protocol allows to obtain dimers of Au NPs using cucurbituril as linker in a reproducible manner that are stable over several days. The SERS performance of these plasmonic structures is found to be several fold greater than those reported previously using similar host-guest interactions.

2. RESULTS

The dimer formation is based in the surface modification of the metal NP with cysteamine (Cys) previous incubation with cucurbituril molecules. The pH of the solution was controlled in such a way as to ensure that the amine group of the cysteamine is protonated. This positive charged amine group interacts through H-bonds with the carbonyl groups of the portal of the cucurbituril molecule. The dimer generation is based in a stoichiometric control between the cysteamine functionalized NPs (Cys-NP) and the CB[6] molecule (Cys-NPs / CB[6] ratio 2:1).

The gap of the junction Cys-CB[6]-Cys is around 1.8 nm (see Figure 1–A), giving rise to a significant SERS enhancement, (around 10^8) making it possible to detect picomolar concentrations very easily. In that sense, the host-guest properties of the CB[6] molecule were used to detect the average SERS enhancement produced by adding Methyl Viologen (MV) as plasmonic probe (see Figure 1–B). The values of the average analytic

enhancement factors (AEF), reveal that the AEF is as good as that obtained for the cucurbituril itself, being around 10^8.

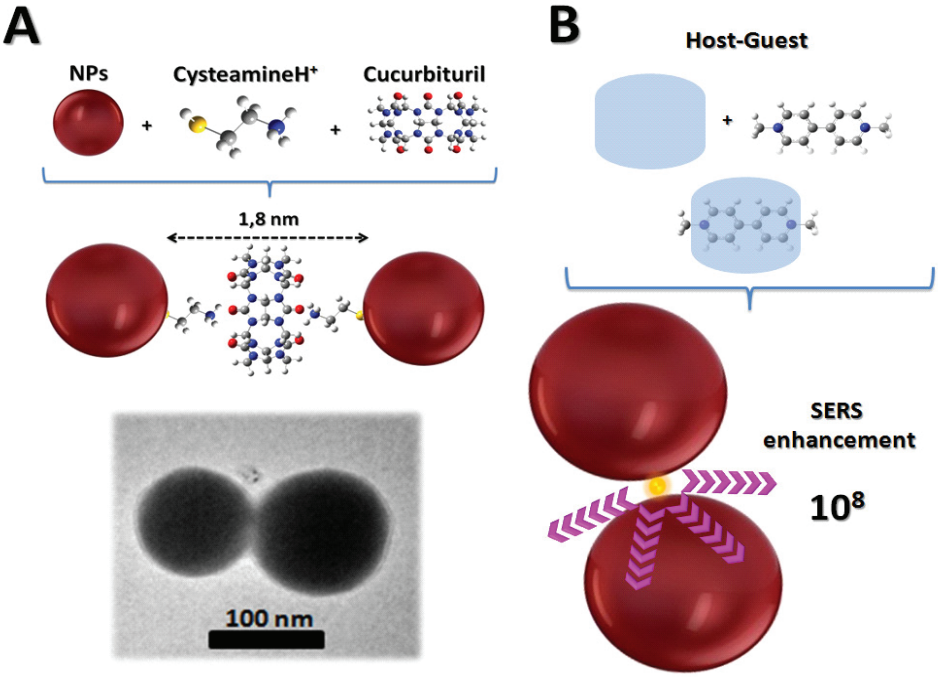

Figure 1. Schematic representation of Cucurbituril-linked Au nanoparticle Dimer and the application to the detection of methyl viologen.

The optical behavior of the dimers is in good agreement with electrodynamics calculations of the near and far field properties simulated using the Generalized Multiparticle Mie Theory (GMM).

3. CONCLUSIONS

We present in this work a novel strategy to induce NPs agglomeration in a controlled way (dimer formation) that generates NEs with improved optical properties (near field enhancements of 10^8) preserving the detection properties due to the supramolecular host-guest chemistry of the cucurbituril linker.

These dimeric structures can be obtained in a reproducible manner and are stable over several days. This supramolecular SERS which is an improvement with respect of the cucurbituril-linked NEs described in literature.

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