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Computational and experimental evaluation of selective substitution of thiolated coumarin derivatives on gold nanoparticles: Surface enhancing Raman scattering and electrochemical studies

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ABSTRACT

Gold nanoparticles (AuNPs) of various sizes were prepared and treated with a mixture of HS-(CH₂)₁₁-NHCO-coumarin (act as Raman reporter) and HS-PEG-(CH₂)₁₁COOH (as co-stabilizer and also to attach biomarkers on activated -COOH) to produce mixed monolayer protected clusters of gold (AuMMPCs). In this paper, we demonstrate the significance of the HS-(CH₂)₁₁-NHCO-coumarin concentration (percentage ratio) on the enhancement factor (EF), and the geometry of the adsorbed ligands on AuNPs of different sizes. The calculated EFs from Raman spectra reveal a significant decrease with an increase in AuNPs sizes. Molecular dynamics calculations were carried out to obtain the adsorption energies for different ratios of HS-PEG-(CH₂)₁₁COOH to HS-(CH₂)₁₁-NHCO-coumarin. It was found that molecules that adsorb strongly on the surface of the metal, underwent changes in their polarizability and consequently enhanced Raman intensities were observed, and this was in agreement with experimental data.

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1. Introduction

The optical properties of nanostructured materials has played a significant role in the development of surface enhanced Raman spectroscopy (SERS). This technique is known to enhance weaker Raman signals by a factor of 10⁴–10⁶ through surface plasmon resonance (SPR) in metal nanostructures [1–3]. Such, enhanced Raman signals for molecules attached to metal nanostructures have been observed with very high sensitivities. Over the past decades, a vast number of studies on SERS have led to great advancement in understanding the underlying mechanisms of this effect. Thus it has been exploited in numerous applications [4] ranging from sensors for chemical species in quantitative approaches [5–7] over optical labels [8,9] to new tools for biophysics [10–12].

Metal nanoparticles (MNPs) exhibit a SPR absorption that is dependent on many factors including the dielectric constants of metals and their surfaces, the inter-particle distances, as well as the size and shape of the NPs [13–17]. The excitation of the SPR absorption results in a strong, local electromagnetic field enhancement in the vicinity of the NPs, as it is responsible for the major enhancement in the Raman spectra of molecules near or attached to the surface of metal NPs [15]. There are four major factors that contribute to the total SERS enhancement effect at varied experimental conditions: (i) electromagnetic enhancement (EM) resulting from excitation of surface electrons of the metallic NP; (ii) charge transfer to and from the metal NP surface, (iii) a resonance mechanism (resonance Raman spectroscopy) where the excitation corresponds to an electronic transition in the molecule, and (iv) an off-resonance enhancement (usually described as excitation to virtual states) due to metal-adsorbate interaction [18–20]. The dependence of the EM contribution to SERS enhancement on NP size has been well investigated in theoretical studies [15,21–24] and experiments on arrays of MNPs of different sizes have also been reported [13,25,26]. Inter-particle coupling plays a significant role in the distribution of the

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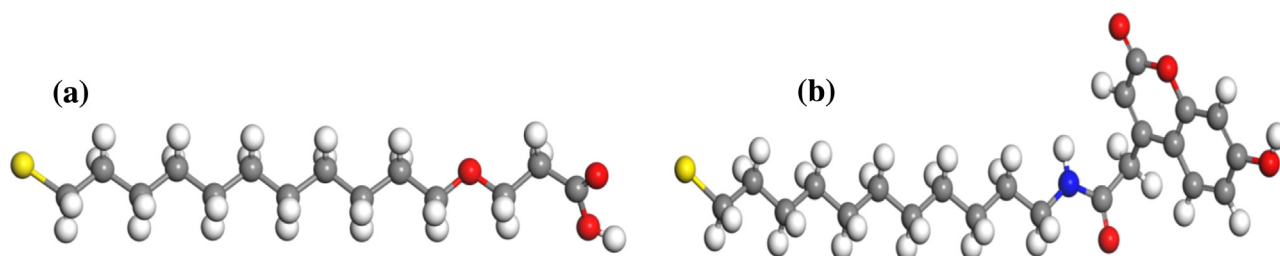


Fig. 1. (a) HS-(CH₂)₁₁-PEG-COOH, (b) HS-(CH₂)₁₁-NHCO-coumarin. Yellow atoms are sulphur, red = oxygen, blue = nitrogen, grey = carbon and white = hydrogen. (Note: for the sake of clarity in the simulated geometries that follows, the H-atom on the S-atom is not shown, although present). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

local field in addition to the different size effects [27–30]. However, Zheng et al. showed that when using NPs in solutions, SERS evaluation can be probed without inter-particle coupling effects [31]. SERS experimental studies carried out using NPs in solution have also revealed that the addition of the analyte can cause some aggregation, which can lead to a huge increase in the SERS enhancement. Also both experimental and theoretical studies have agreed that these aggregated NPs show an extended plasmon band to longer wavelengths that provides optimum enhancement of excitation and scattering fields in the near-infrared region [32–36]. Therefore, to study the effect of the metallic NP size on SERS enhancement, it is important to synthesize a monodispersed NP solution of different sizes with identical dielectric surface properties [37,38].

This paper reports on the effect of changing HS-(CH₂)₁₁-NHCO-coumarin ratio on the surface of AuNPs. It further demonstrate the adsorption energies in relation to different ratios of HS-PEG-(CH₂)₁₁COOH to HS-(CH₂)₁₁-NHCO-coumarin through molecular mechanics and dynamics calculations. It is expected that those molecules that adsorb strongly on the surface of the metal, will undergo changes in their polarizability and as a consequence changes in the enhanced Raman intensities should be observed. Interestingly, there was correlation observed with either increase or decrease in the binding energies and the Raman signal enhancement due to metal-organic-molecule.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate trihydrate (Sigma-Aldrich, 99.9%), tri-sodium citrate (ACE AR, 99%), HS-PEG-(CH₂)₁₁COOH, HS-PEG-(CH₂)₁₁-OH and HS-(CH₂)₁₁-NHCO-coumarin were obtained from ProChimia Surfaces (Poland). Acetonitrile, H₂SO₄ (98%) and tetrabutylammonium-tetrafluoroborate (TBABF₄) were all purchased from Sigma-Aldrich (South Africa).

2.2. Instrumentation

High purity or ultrapure water with resistivity of 18.1 ΩM was obtained from a Milli-Q Advantage water system purchased from Millipore (USA) and was used in all experiments. Samples were centrifuged in 1.5 mL Eppendorf tubes at 22 °C and 10,000 rpm for 15 min using the Hettich MIKRO 22R cooling centrifuge. Absorption spectra of the solutions were recorded on a Lambda 35 UV–vis spectrometer. Transmission electron microscope (TEM) images were obtained using a JEM-2100F at 200 kV. The TEM grids were prepared by depositing approximately 10 μL of the solution obtained after centrifugation and allowed to dry in room temperature. Raman spectra were acquired using a PerkinElmer Raman Station 400 bench top Raman spectrometer in a range of 100–3200 cm⁻¹. The excitation source was a near-infrared 785 nm laser (100 mW at the sample), with a spot size of 100 μm. The detector was a tempera-

ture controlled Charged Coupled Device (CCD) detector (–50 °C) incorporating a 1024 × 256 pixel sensor. Spectra were acquired using *Spectrum* software and images were acquired using *Spectrum IMAGE* software, both supplied by PerkinElmer (Bucks, UK). All Raman spectra of AuMMPCs samples were acquired by dropping 10 μL of each solution on the gold-coated aluminium substrate and incubated at room temperature (Fig. S1). The electrochemical experiments were carried out using a computer-controlled Autolab Potentiostat/Galvanostat PGSTAT 302N (Eco Chemie, Utrecht, The Netherlands) driven by the General Purpose Electrochemical Systems (GPES). The electrochemical data was collected using glassy carbon electrodes (GCE, r = 1.5 mm) as working electrode, Pt wire as counter electrode and Ag|AgCl as pseudo-reference electrode.

2.3. Synthesis, functionalization and conjugation of AuNPs

2.3.1. Synthesis of citrate AuNPs

In a typical experimental procedure, a solution of aqueous tri-sodium citrate (0.04 M) was added to a boiling aqueous solution of tetrachloroaurate (250 mL, 1.0 mM). The mixture was allowed to boil for 5 min, then removed from heat and stirred for a further 3 h. To obtain different sizes of AuNPs, the volume of the capping agent, aqueous 0.04 M tri-sodium citrate was varied.

2.3.2. Functionalization of AuNPs

The resulting AuNPs were filtered, and then 40 mL aliquots of the 12 nm, 28.5 nm and 40.1 nm AuNPs were treated with 200 μL of HS-(CH₂)₁₁-PEG-COOH (8 mg mL⁻¹). Each 40 mL aliquot of the AuNPs (12 nm, 28.5 nm and 40.1 nm) was coated with HS-(CH₂)₁₁-PEG-COOH and then further divided equally, to be co-stabilized with different percentages of HS-(CH₂)₁₁-NHCO-coumarin (1% and 50%, respectively). For AuNPs stabilization with 1% HS-(CH₂)₁₁-NHCO-coumarin, 0.02 mg of the HS-(CH₂)₁₁-NHCO-coumarin was dissolved in 1 mL of methanol and then thoroughly mixed with HS-(CH₂)₁₁-PEG-COOH (1.98 mg) in 1 mL of methanol. For stabilization with 50% a similar approach was followed using 1 mg instead of 0.02 mg. The mixtures of different percentages (1% and 50% HS-(CH₂)₁₁-NHCO-coumarin) were each added to 20 mL of AuNPs (12 nm, 28.5 nm and 40.1 nm, respectively), and stirred at 800 rpm for 3 h. For the purpose of brevity, from here on HS-(CH₂)₁₁-NHCO-coumarin will only be referred to as “coumarin” and HS-(CH₂)₁₁-PEG-COOH will only be referred to as ‘PEG’.

2.4. Computer simulation

2.4.1. Molecular adsorption

Truncated, octahedral Au nanocrystals of different sizes (diameter = 2.8 nm, 5.2 nm, 7.1 nm and 9.6 nm) were constructed and surfactant adsorption were simulated. A trade-off exists between simulation accuracy and computational time. Since it becomes increasingly more difficult to do accurate molecular mechanics and dynamics calculations on large atomic systems, the aforemen-

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