

Surface enhanced Raman spectroscopy (SERS) and density functional theory (DFT) study for understanding the regioselective adsorption of pyrrolidinone on the surface of silver and gold colloids

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ABSTRACT

The interaction between polyvinyl pyrrolidone (PVP) and the metal atoms on the surface of silver and gold nanoparticles was studied theoretically and experimentally using density function theory (DFT) and surface enhanced Raman spectroscopy (SERS). The attachment of pyrrolidinone and *N*-methyl-2-pyrrolidinone (monomers of PVP) on the surface gold and silver colloids was probed using the SERS and the band assignments correlated through the DFT quantum chemical calculations. Commonly, the adsorption of *N*-methyl-2-pyrrolidinone and pyrrolidinone on the surface of silver and gold colloids occurs through the chemisorption of the nitrogen or carboxylic group of the pyrrolidyl ring, with a possible interaction occurring simultaneously via both the nitrogen and carboxylic groups of the ring. SERS experimental investigations and the subsequent DFT theoretical calculations show that both pyrrolidinone and *N*-methyl-2-pyrrolidinone are selectively adsorbed on silver and gold colloid surfaces preferably via the non-bonding electrons of the carbonyl group.

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1. Introduction

Research into materials at the nanoscale has shown tremendous growth in recent times due to their unique chemical and physical properties [1]. Noble metal nanoparticles are of particular interest to scientists with their applications ranging from microelectronics to biology [2,3]. Numerous methods for the synthesis of nanosized silver and gold have surfaced over the years but only a few have received unprecedented attention. These include the landmark citrate-facilitated reduction of metal chloride salts [4] and the two-phase redox reaction pioneered by Brust et al. [5], with subsequent variations and modifications of these methods reported elsewhere [6,7].

The capping of nanoparticles with polymers such as polyvinyl pyrrolidone (PVP) has been identified as a viable method for producing nanoparticles of tunable morphologies and optical properties [8]. One such method involves the reduction of silver nitrate with dimethyl formamide (DMF) in the presence of polyvinyl pyrrolidone (PVP), a system that has been extensively investigated [9–13]. The selective growth of silver nanoparticles has been

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demonstrated to be closely correlated with the surface interactions with PVP, and a mechanism of this process has been sought [14,15]. Since PVP polymer is a large molecule, a need for a simplified mechanistic investigation is required. Wang et al. [16] has studied the interaction of silver colloids with PVP but further computational studies have never been reported thus far. Herein, we report an investigation into the synthesis and computational study of the interaction of silver and gold nanoparticles with pyrrolidinone and *N*-methyl-2-pyrrolidinone. By observing the interaction of these monomers with silver and gold nanoparticles, we hope to clarify the mechanism for the interaction of these nanoparticles with PVP. In the PVP molecule, the pyrrolidyl group is a suitable molecular system since it has vastly different electrostatic properties. It is believed that during the synthesis of silver and gold nanoparticles in the presence of PVP, the first mechanistic interaction is between the pyrrolidyl group of PVP with silver and gold ions. This is followed by the reduction process and finally the growth of the nanoparticle, which predominantly depends on the ratio of the metal ion-to-PVP in solution. To our knowledge no reports have been made using a combination of experimental results (SERS) and a theoretical method (DFT) to understand the complex formation on the surface of silver and gold by PVP molecules. This was done by looking at the interaction of silver or gold nanoparticles with *N*-methyl-2-pyrrolidinone and pyrrolidinone, respectively.

In order to acquire a better understanding of the interaction between PVP and the metal atoms on the surface of silver and gold nanoparticles, SERS and DFT have been employed to assist in the elucidation of possible mechanisms. SERS is a powerful tool used to characterize the chemical state of bonds formed on metal surfaces and the subsequent molecular conformation on the specific metal surfaces [17,18]. This technique has been successfully applied in many systems designed to understand the adsorption of molecules on the surface of silver and gold colloids [19–23].

2. Experimental

2.1. Chemicals

Silver nitrate, tetrachloroauric acid trihydrate, *N*-methyl-2-pyrrolidinone, anhydrous (99.5%), 2-pyrrolidinone (99%) and trisodium citrate (99%), were purchased from Sigma–Aldrich, and were used without any further purification unless otherwise stated. Double distilled water was used throughout the experiments.

2.2. Synthesis and functionalization of gold and silver colloids

Silver and gold colloids were prepared according to the literature method [24]. Briefly, silver nitrate and gold chloride (90 mg) was each dissolved in 500 mL deionized water and heated to boiling followed by the addition of 10 mL of 1% aqueous trisodium citrate solution. The mixture was allowed to boil for a further 20 min under reflux. Green–grey silver and deep red gold colloidal solutions were obtained for silver and gold nanoparticles respectively. 0.5 mL of aqueous solution of pyrrolidinone (0.01 M) and *N*-methyl-2-pyrrolidinone (0.01 M) was each mixed with 6 mL of the prepared silver and gold colloidal suspensions which were then used for spectroscopic analysis.

2.3. Instrumentation

Raman spectra were obtained using a Spex 1877 Triple spectrometer with a CCD detector. The operating wavelength was set at 647.1 nm with a resolution of 2 cm^{-1} using 180° geometry. The output laser power was 150 mW and 200 mW for colloidal solutions, which is known to not induce any changes in the adsorbate–substrate systems.

The optical absorption measurements were done using the Perkin-Elmer Lambda 20 UV–vis spectrophotometer. The samples were measured in a quartz cell of 1 cm path length with water as the reference solvent.

3. DFT calculations and models

All calculations were carried out with Gaussian 03 programs [25] within the density functional theory (DFT) framework. Density functional calculations have been applied in many different studies [19–23], with a reasonable measure of agreement between the theoretical and experimental data. In this study the molecule–metal system structures of silver and gold were optimized using the Becke's three parameter hybrid functional [26] with the Lee et al. [27] (B3LYP) correlation functional employed with the electron core potential basis set LANL2DZ developed by Hay and Wadt [28]. For Ag and Au the LANL2DZ set the electron core potential simulates the 28 and 60 of their total 47 (Ag) and 79 (Au) electrons, respectively. For both heavy elements the remaining 19 electrons are described by all electron basis sets consisting of a (8s6p4d) set of primitive Gaussian type functions contracted to the [3s3p2d]. For C, N and O the LANL2DZ basis consists of a (10s5p) set contracted to the [3s2p] set, while, for H a (4s) set contracted to the [2s] basis set is used. Each sta-

tionary point has been characterized by harmonic frequency calculations at the same level of theory (B3LYP/LANL2DZ) and the Raman active harmonic frequencies have been identified.

4. Results and discussion

4.1. Optical absorption studies

The UV–vis absorption spectra of silver and gold colloids are presented in Figs. 1 and 2. The absorption of the original silver colloids (Fig. 1A) shows a sharp peak located at 411 nm, this is attributed to the surface plasmon resonance (SPR) of silver colloids, which is as a result of the coherent oscillation of the conduction band electrons when interacting with electromagnetic radiation [29,30]. Fig. 1B and C show the spectra after the addition of 2-pyrrolidinone and *N*-methyl-2-pyrrolidinone respectively. The apparent loss of the sharpness and intensity of the spectra showed an onset of aggregation which is most likely due to the multifunctional mode of the ligands adsorbed on the surface of the silver particles. The same phenomenon was observed for the gold colloids (Fig. 2). An absorption maximum at 525 nm was observed, typical for colloidal gold SPR absorption. Fig. 2A and B shows the absorption after the ligands were mixed with the colloids. A secondary peak can also be observed at around 620 nm signifying the aggregation of the gold particles. This observation can be attributed to the time-dependence of the aggregation process for both silver and gold colloids. Longer reaction times are expected to allow for severe aggregation and therefore move the secondary peak to a higher wavelength for the newly formed larger particles, at the same time fading the original SPR intensity of the smaller particles.

4.2. Adsorption of *N*-methyl-2-pyrrolidinone and 2-pyrrolidinone on Ag/Au surfaces

The calculated Raman frequencies were found to be in good agreement with the experimental results as shown in Table 1. Practically, the molecules are adsorbed onto the surface of the silver and gold nanoparticles, and it is possible to calculate the vibration spectra in such a case. A postulate model, M–ON (Fig. 3), that uses both oxygen and nitrogen as “substrates” is not observed [16]. The mass of a silver or gold atom is relatively large making the approximation reasonable, on the other hand in silver, the ligand molecule may not be fixed strongly onto the whole silver particle. Table 1 shows the results of the experimental SERS spectra of 2-pyrrolidinone on silver and gold colloids and the calculated Raman spectra with reference to the model in Figs. 4 and 5. Figs. 4 and 5 show the models for the optimized interaction of silver and gold with 2-pyrrolidinone and *N*-methyl-2-pyrrolidinone respectively.

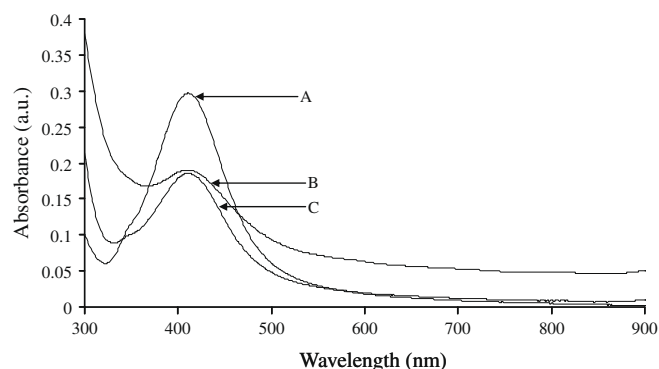


Fig. 1. Optical absorption spectra of (A) original silver colloids, (B) mixed with *N*-methyl-2-pyrrolidinone and (C) 2-pyrrolidinone mixture with the colloids.

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