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Investigation on the adsorption characteristics of anserine on the surface of colloidal silver nanoparticles

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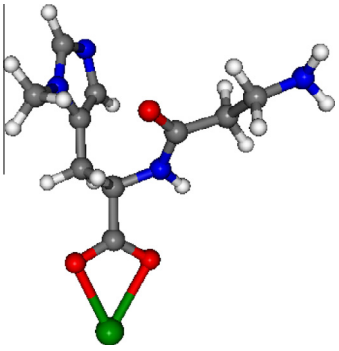
HIGHLIGHTS

- Anserine is a potent anti-oxidant present in animals.
- Optimized structure of silver complex of anserine explains the enhanced Raman modes.
- Concentration dependent SERS studies show changes in the orientation of anserine.

GRAPHICAL ABSTRACT

The surface adsorption characteristics of anserine (an anti-oxidant) with silver nanoparticles were investigated from SERS studies. Optimized structure of the silver complex of anserine explains the enhanced Raman modes in the SERS spectrum.



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ABSTRACT

The surface-enhanced Raman scattering (SERS) studies of anserine (beta-alanyl-N-methylhistidine) was carried out on colloidal silver nanoparticles to understand its adsorption characteristics. The experimentally observed Raman bands were assigned based on the results of DFT calculations. The studies suggest that the interaction of anserine is primarily through the carboxylate group with the imidazole ring in an upright position with respect to the silver surface. Concentration dependent SERS studies suggest a change in orientation at sub-monolayer concentration.

Introduction

Surface-enhanced Raman scattering (SERS) is an effective technique in studying surface-interfacial properties and has been used at molecular level to investigate and characterize the interaction between the substrate and the adsorbate [1–5]. The interaction between bio-molecules and metal surfaces has recently given rise to a large number of investigations due to challenging technological applications in the field of biomaterials, biosensors and biocatalysis. Metal nanoparticles have been exploited for the delivery of drugs [6]. Information such as molecular identity, structure, orientation and nature of bonding of the surface-adsorbed species may provide essential clues on the efficiency of these processes.

The difference in the spectra of the adsorbed molecule on the metal surface in terms of the shifts in vibrational frequencies and

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relative intensities with respect to the molecules in solution provides information on the relative proximity of different parts of the adsorbed molecule to the surface. The "surface selection rules" of Moskovits and Suh [7–11] based on image dipole field theory [12] helps in estimating the orientation of the molecules adsorbed on the metal surface. In the present article, we report the SERS studies of anserine (beta-alanyl-N-methylhistidine), a dipeptide of the amino acid beta-alanine and amino acid derivative methyl histidine. Anserine is present in high concentrations in the muscle and brain of many animals and acts as an anti-oxidant [13]. The imidazole moiety of histidine and its derivatives confers the anti-oxidant activity.

The Raman spectra of solid anserine, aqueous solution of anserine and the SERS spectrum in silver colloid was recorded in order to investigate the nature of binding of the molecule with the silver surface and the probable orientation the molecule assumes on the surface. The experimental Raman data is supported with DFT calculations using B3LYP functional and LANL2DZ basis set. The vibrational frequencies of the molecule and its silver complex were computed at the optimized geometry and compared with the experimental values.

Experimental

Aqueous silver colloid was prepared by the reduction of silver nitrate with sodium borohydride using the method of Creighton et al. [14]. Anserine was obtained from Aldrich and used without further purification. The UV–visible absorption spectra of the silver colloid with and without anserine were recorded using a Jasco V-650 spectrophotometer. Raman spectra of anserine (solid and aqueous solution) and anserine in silver colloid were recorded at room temperature using the 532 nm line from a diode pumped Nd^{3+}: YAG laser (SUWTECH laser, model G-SLM-020 from Shanghai uniwave Technology Co. Ltd.). The laser power used for the Raman measurements was 25 mW. The Raman scattered light was collected at the back-scattered geometry and detected using a CCD based home-built monochromator [15].

Computational details

Geometry optimization was performed for the anserine and its silver complex using the density functional theory (DFT) with B3LYP functional [16] with the LANL2DZ basis set using Gaussian 98 program [17]. The DFT calculations using the LANL2DZ pseudo potentials are an accurate descriptor of the Ag/Au cluster chemistry [18–27]. No symmetry restriction was applied during geometry optimization. The vibrational frequencies for anserine, its anion and its silver complex were computed on the geometry-optimized structures using an analytical Hessian program. The absence of imaginary frequencies confirmed that the ground states of anserine, its anion and its silver complex correspond to a local minimum on the potential energy surface and not to a saddle point. The computed vibrations at the optimized geometry were compared with the experimentally obtained normal Raman and SERS spectra. Fig. 1a and b shows the optimized geometries of anserine and its silver complex. Binding energy of the silver complex of anserine was found to be 154.6 kcal mol^{-1}.

Results and discussion

UV–visible absorption spectrum

The UV–visible absorption spectrum of the silver colloid before and after the addition of different concentrations of anserine (10^{-6}, 10^{-5}, 10^{-4} and 10^{-3} M) is shown in Fig. 2a–e. The absorption

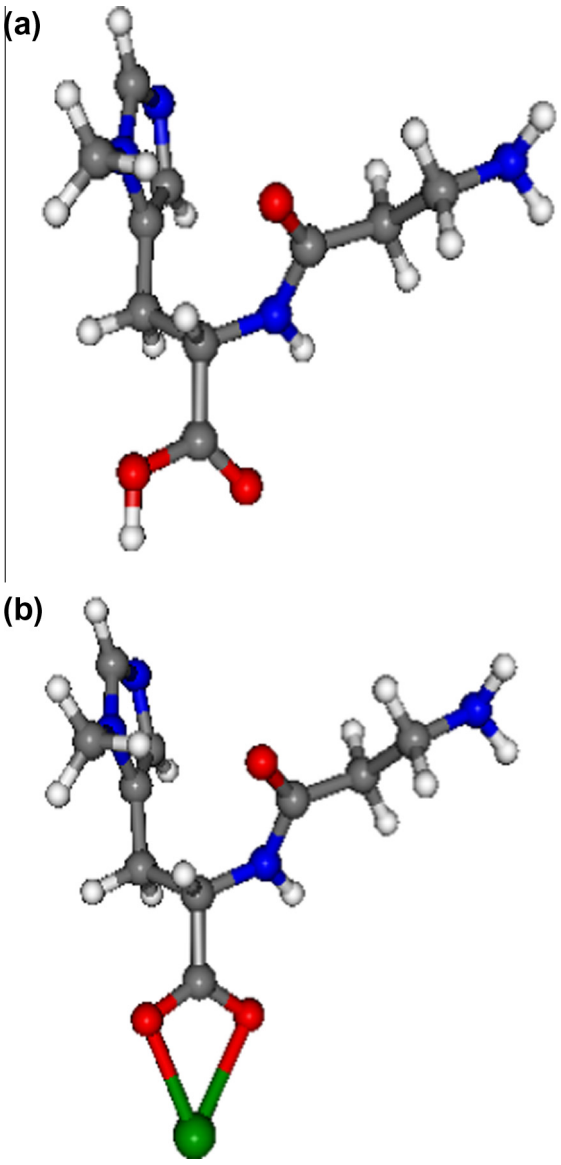

Fig. 1. The optimized structures of (a) anserine and (b) silver complex of anserine.

spectrum of the silver colloid showed a single sharp molar extinction maximum at 380 nm, which is due to the surface plasmon resonant excitation [28]. On addition of anserine to the silver colloid, the absorption spectrum of silver colloid showed an additional band around 530 nm with a decrease in the absorbance of the 380 nm band. The appearance of the red-shifted peak is attributed to a charge transfer/aggregate band [29,30] induced by adsorption of the anserine on the silver surface.

Raman spectra of solid anserine and its solution

The normal Raman spectrum of solid anserine is shown in Fig. 3. The experimental values are compared with the calculated frequencies and the Raman spectrum of solid anserine is tabulated in Table 1.

Anserine is a dipeptide made up of beta-histidine (hist) and L-alanine (ala) and the bands arise from the methylene groups, carboxyl group, amino group, peptide group, imidazole ring (rg) and methyl group. The very intense band in the Raman spectrum is 1042 cm^{-1} attributed to [rg deformation (def), CH_2 (hist) rock, CH (hist)—CH_2 (hist) stretch (str)]. Most of the remaining bands