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Surface enhanced Raman spectroscopy and quantum chemical studies on glycine single crystal

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ABSTRACT

Adsorption characteristics of glycine (Gly) on silver surface were investigated based on density functional theory calculations and surface enhanced Raman spectroscopy (SERS) technique. The single crystals of Gly were grown by slow evaporation method and characterized by single crystal X-ray diffraction (XRD) technique. Silver nanoparticles (Ag NPs) were prepared by solution combustion method using Gly as fuel. The Ag NPs were characterized by XRD, ultraviolet–visible spectroscopy and high-resolution transmission electron microscopy techniques. The calculated structural parameters of Gly molecule were compared with the experimental observed single crystal XRD data. The structural parameters of Gly after adsorption on silver surface show the slight deviation, which indicates the interaction between the Gly and Ag_3 cluster. Raman and SERS spectra for Gly single crystal were studied experimentally. Raman frequencies were calculated for Gly and Gly adsorbed on a silver surface. Raman and SERS frequencies were assigned on the basis of potential energy distribution calculation and compared with the experimental values. Frontier molecular orbital analysis was carried out for Gly and Gly adsorbed on a silver surface. The band gap value was significantly reduced for Gly after adsorption on the silver surface. The reduction in band gap indicates the delocalization of electrons, which leads to the higher bioactivity of the title molecule. SERS spectral analysis reveals that the Gly adsorbed as a stand-on orientation on the silver surface. Hence, the present investigation has been developed as a model system to understand the interaction of Ag NPs with amino acids.

1. Introduction

Surface enhanced Raman spectroscopy (SERS) is a Raman spectroscopic technique that provides enhanced Raman signal from Raman-active molecules that have been adsorbed onto certain specially prepared metal surfaces. The enhanced Raman signal was observed in the order of 10^4–10^6 and can be as high as 10^8 and 10^{14} for some systems [1,2]. The SERS technique provides the opportunity of using Raman techniques for single molecule detection. The greatly enhanced Raman intensities for molecules after adsorption on certain rouged metal (silver, gold, copper) surface, with the roughness of the nanometer size, has been observed both experimentally as well as theoretically is an interesting phenomenon [3]. SERS technique coupled with the suppression of fluorescence effect, generated considerable interest. SERS is widely used in biomedical applications [4]. It is very important to know the orientation of the adsorbed molecule with respect to the metal surface. Surface selection rules for Raman scattering allow us to obtain such information. According to these rules, the adsorbed molecular vibrations, which have the polarizability tensor component normal to the surface, will be preferentially enhanced [5].

The adsorption of biomolecules on the metal substrates has been widely studied by many researchers due to its potential applications. SERS has become a prominent tool for monitoring the changes in the chemical nature of the molecule adsorbed on silver nanoparticles (Ag NPs). Silver is the most universal substrate due to its broad plasmon resonance in the visible region, high stability and easy preparation [6]. Silver is known to scatter light better than the other noble metal like gold, copper and platinum. Ag NPs have been widely studied due to their useful physical and chemical properties and as the substrates for SERS [7]. Ag NPs, generally associated with their anti-bacterial properties, have also been incessantly gaining momentum recently.

Density functional theory (DFT) is an efficient quantum

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mechanical modeling approach to compute the molecular structures, electrostatic properties and Raman scattering intensities of molecules. The DFT calculations are established to correlate well with the experimental spectroscopic techniques [8]. DFT provides excellent vibrational frequencies of organic compounds, if the computed frequencies are scaled to compensate for the electron correlation, basis set deficiencies and anharmonicity [9]. The influence of molecular structure on the stability and reactivity of the molecules has been drawing attention of many researchers in the recent years [10].

Amino acids are the basic building blocks of proteins. Basically, amino acids are chained together by peptide bonds to form the basic structure of proteins. Glycine (Gly) is an amino acid that often helps trigger the release of oxygen to the energy-requiring cell making process, and it is important in the manufacturing of hormones responsible for a strong immune system [11,12]. Gly is unique among all amino acids with minimal side chain of only one hydrogen atom and it is achiral. It can fit into hydrophilic or hydrophobic environments. Traditionally, Gly has been used for stomach ulcer treatment.

The *ab initio* calculations of the zwitterion form of Gly molecule were reported [13,14]. The SERS investigations of amino acids and their homo peptides adsorbed on colloidal silver was investigated [15]. SERS of amino acids adsorbed on an electrochemically prepared silver surface was studied by Stewart et al. [15]. Raman studies of Gly and its dipeptide in acidic and neutral solutions were carried out [16]. Vijayakumar et al., reported that the non-bonded interactions and its contribution to the NLO activity of glycine sodium nitrate [17]. Padmaja et al., analyzed that the vibrational spectra of L-alanylglycine using density functional theory calculations [18]. SERS study of a tetrapeptide based on histidine and glycine residues, adsorbed on copper/silver colloidal nanoparticles was studied by Cristina Gellini et al. [19]. Rekha et al., reported that the structural and spectroscopic studies of adsorption of naphthalene on Ag NPs [20]. In this present study, the effect of Ag NPs on the enhancement of SERS spectra and the orientation of Gly on the Ag NPs surface was investigated by the experimental and DFT methods.

2. Materials and methods

2.1. Computational details

The molecular structure of Gly was optimized by the DFT/B3LYP method with 6-311G (d,p) basis set using Gaussian 09 program [21]. The structural parameters, Raman vibrational frequencies, the total electron density surface mapped with molecular electrostatic potential and frontier molecular orbital calculations were carried out by the DFT/B3LYP method with 6-311G (d,p) basis set for Gly molecule. The molecular structure of Gly adsorbed on Ag surface was optimized by the density functional theory (DFT) level using PBEPBE functional and LANL2DZ basis set. The LANL2DZ basis set uses an effective core for heavier atoms, which is an established standard choice for the theoretical methods involving transition metals and organometallic complexes. Silver cluster (Ag_3) is identified to be stable and reactive, which has been considered for the theoretical calculations in this study [22]. The structural parameters, theoretical SERS, total electron density surface mapped with molecular electrostatic potential and frontier molecular orbital calculations were carried out by DFT/RPBEPBE method with LANL2DZ basis set for Gly adsorbed on a silver surface. The vibrational modes were assigned with a high degree of accuracy on the basis of potential energy distribution (PED) calculation using the VEDA 4.0 program [23] and also visualized by GaussView 05 program [24].

2.2. Experimental

2.2.1. Materials

Silver nitrate (AgNO) and Gly ($C_2H_5NO_2$) were purchased with 99.5% purity from Sigma Aldrich Chemical Co, St. Louis, Mo, USA. All glasswares were properly washed with distilled water and dried in hot air oven before use.

2.2.2. Synthesis

The Gly single crystal was grown by the method of slow evaporation solution technique. The Gly was dissolved in deionized water and a saturated solution of Gly at 40 °C was prepared. The solution was filtered using Whatman filter paper. The cleared filtrate was left undisturbed for crystallization at room temperature, resulted in the separation of transparent crystals after 3–4 weeks. The crystals were isolated by filtration, washed with little ice-cold water and dried in air. The purity level was increased by successive recrystallization process [25,26]. The prepared samples were transparent and free from any noticeable defects.

Ag NPs were prepared by solution-combustion method using silver nitrate and Gly as an oxidizer and fuel respectively [27]. The silver nitrate and Gly were mixed in the ratio of 2:1 and dissolved in 25 ml of deionized water in a crucible. For the precise and uniform formation of the desired composition of nano scale, this mixture was then stirred on a magnetic stirrer for about 40 min. The uniform aqueous solution was formed and this was subsequently placed on a hot plate at 300 °C. On reaching the point of spontaneous combustion, the solution began to burn, vaporizing the entire solution instantly and the combustion reaction was completed in about 25 min. A loose grayish black colored powder was formed, which was crushed and ground thoroughly to obtain the Ag NPs.

2.2.3. Characterization techniques

The single crystal X-ray diffraction (XRD) analysis of the grown crystal was carried out to identify the cell parameters using Bruker AXS Kappa Apex2 CCD diffractometer. Powder X-ray diffraction (XRD) patterns of Ag NPs were recorded on PANalytical X-ray diffractometer using Cu Ka radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA and the measurements were carried for the diffraction angle range of 2θ = 30–80°. High resolution-transmission electron microscope (HR-TEM) images were recorded using a JEOL 3010, with a lattice resolution of 0.14 nm and a point to point resolution of 0.12 nm, operating at 200 kV. The samples were made by depositing the Ag NPs on a carbon coated Cu grid and the size measurements were performed manually on HR-TEM images. The optical absorption measurements were carried out using Shimadzu UV-3600 UV–Vis–NIR spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD) in the wavelength region 200–500 nm using ethanol as a solvent. The Raman spectrum was recorded by a micro Raman system using a Horiba-Jobin Yvon LABRAM-HR with He-Ne laser and an excitation wavelength of 632 nm. The power of the laser source is 5 mW. The spectral resolution was 1 cm^{-1} and dispersive geometry was employed. SERS spectrum was recorded by mixing solid form of Ag NPs and Gly in the ratio of 1:3. The experimental conditions are same for both normal Raman and SERS measurements.

3. Results and discussion

3.1. XRD analysis

The single crystal-XRD is an analytical technique, which is used to determine the actual arrangement of atoms within a crystalline specimen. It is a non-destructive tool to analyze crystal structure of