



# Density functional theory and surface enhanced Raman spectroscopy studies of tautomeric hypoxanthine and its adsorption behaviors in electrochemical processes



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## ABSTRACT

Hypoxanthine, a purine heterocyclic compound with N and O atoms, has capability to combine metal ions or adsorb on metals. By using density functional theory (DFT) method calculation, the energy, charge distribution, molecular orbital and vibration spectra information of tautomeric hypoxanthine were given. Combined with these DFT results, the influence of pH on the structure of tautomeric hypoxanthine was studied by surface enhanced Raman spectroscopy (SERS). Electrochemical SERS was applied to study the properties of hypoxanthine/gold interface. It is found that the structure of adsorbed hypoxanthine was changed from slightly tilted to upright with negatively moving of potentials.

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## 1. Introduction

Hypoxanthine [1], a family of heterocycles, contains both a pyrimidine ring and an imidazole ring. An outstanding capability of hypoxanthine is that it can possess prototropic [2,3] tautomerism under different environments. The plentiful theoretical calculation has account for its stability [4–6]. It generally isomerizes to be ketonic and enolic forms (Fig. 1). And hypoxanthine is considered to exist two mainly prototropic tautomers, N1H/N9H and N1H/N7H. It is experimentally found that N1H/N9H was more favored than N1H/N7H by miscellaneous technology, such as IR [7], ultraviolet photoelectron spectra [8], NMR [9], etc.

Heterocycles fused heteroatoms can act as an ideal ligand, [10–12] and can be delocalized due to resonance hybridization [13] to interact with metals to transfer charges. In our earlier work, hypoxanthine had been applied in preparing an admirable gold plating bath [14]. The intrinsic adsorption of hypoxanthine would occur in the surface at the growing of gold deposit. For remarkable tautomerism of hypoxanthine, it is meaningful to study its properties for better acquaintance of this molecule.

Surface enhanced Raman spectroscopy (SERS), because of its high sensitivity and resolution, can be applied in studying the adsorption behavior of infinitesimal molecules on the metal surface [15,16]. SERS combined with electrochemistry (EC-SERS) can dynamically track the electrochemical reaction processes [17–19], meanwhile analysis the surface adsorption behaviors of CN<sup>-</sup> [20], SCN<sup>-</sup> [21], 2-hydroxypyridine [22], uracil [23], etc. To better explain the experimentation, density functional theory (DFT) based quantum chemical calculation was used to provide structural and vibrational information of molecules [24,25].

Although many theoretical and experimental researches [4–9,26] had explored tautomeric structure properties of hypoxanthine, there is minority SERS related [27] on the adsorption of tautomeric hypoxanthine. Combined with DFT simulation, tautomeric hypoxanthine was computed to obtain the electron properties and vibrational information. SERS and EC-SERS were applied to investigate the tautomerism and adsorption behaviors of tautomeric hypoxanthine.

## 2. Experimental

### 2.1. Reagent and apparatus

All the chemicals used were analytical grade. H<sub>2</sub>AuCl<sub>4</sub>, HCl (36.0~38.0%), KOH were purchased from Sinopharm Chemical

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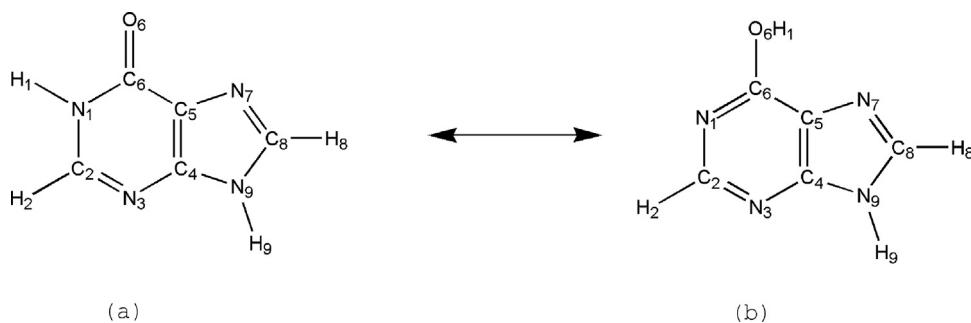


Fig. 1. Structures of tautomeric hypoxanthine: (a) ketonic form; (b) enolic form.

Reagent Co. Ltd. China. Hypoxanthine ( $\geq 99\%$ ) was purchased from Sigma Aldrich. Ultrapure water with resistivity of  $18.25 \text{ M}\Omega \text{ cm}$  for all experiments was purified using Kertone water purification system.

Raman spectra were recorded on a Renishaw inVia Raman Microscopy with a Leica DM2500M microscope at a  $632.8 \text{ nm}$  He–Ne laser source. The laser power was ca.  $0.7 \text{ mW}$ . The long focus distance microscopy objective with  $50\times$  magnifications was used for laser illumination and signal collection.

Electrochemical and electrochemical-SERS measurements were obtained by a CHI 810B electrochemical workstation (Shanghai, China) with three-electrode system. EC-SERS tests were carried out in a specially designed cell (Fig. 2) which described in previous report [17,28] and improved to accommodate for our study. As shown in Fig. 2, it contains a dismantlable working electrode at the bottom of electrolytic cell. Gold electrode was acted as the working electrode. A Pt wire ring in the interior of cell to form a closed circuit and acted as the auxiliary electrode. The Ag/AgCl ( $3 \text{ mol/L KCl}$ ) electrode inserted in the side is the reference one. The solution can inject into the cell through the hose from the side.

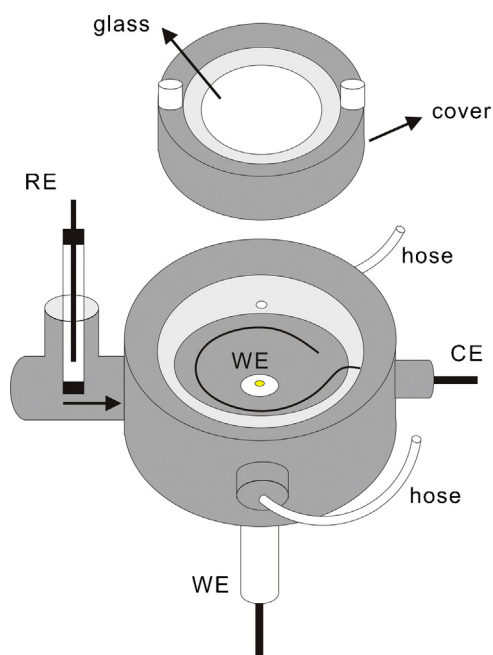


Fig. 2. Schematic diagrams of Raman electrolytic cell.

## 2.2. Preparation of Gold nanoparticles.

Gold nanoparticles (Au NPs) were prepared by the standard sodium citrate reduction method [29].  $200 \text{ mL}$  of chloroauric acid ( $0.01 \text{ weight}\%$ ) were brought to a boil. Then  $2.0 \text{ mL}$  of sodium citrate ( $1 \text{ weight}\%$ ) was added to the boiling and stirring solution quickly. The mixture was refluxed and stirred for  $30 \text{ min}$  and then cooled to room temperature. Finally, gold nanoparticles with about  $50 \text{ nm}$  nanometer were obtained.

## 2.3. Pretreatment of gold electrode.

The gold electrode with diameter of  $3 \text{ mm}$  was polished by alumina grit with the size of  $0.05 \mu\text{m}$ . The polished electrode was immersed in  $0.5 \text{ mol/L H}_2\text{SO}_4$  solution for electrochemical clean. The potential was circularly swept from  $-0.3 \text{ V}$  to  $1.5 \text{ V}$  at  $100 \text{ mV/s}$  scanning rate until the curves were overlapped. Then washed the electrode with ultrapure water, and finally dried the electrode before use.

## 2.4. Preparation of SERS substrate.

Firstly,  $1.0 \text{ mL}$  gold colloid was centrifuged at  $6000 \text{ rpm}$  for  $5 \text{ min}$  and removed the supernatant. Next, the prepared gold electrode was spread by  $2.0 \mu\text{L}$  concentrated gold nanoparticles and then dried at room temperature. Then the electrode was immersed in  $0.1 \text{ mol/L KCl}$  solution in the three-electrode system, the potential was applied constantly at  $-1.0 \text{ V}$  (vs. Ag/AgCl) for  $10 \text{ min}$  to remove the citrate. Finally washed the electrode for many times and immersed in the examined solution after stability for SERS measurement.

## 2.5. Calculation methods

DFT calculation was performed by Gaussian 03 software. All simulations were using B3LYP functional method in the polarizable continuum model (PCM) with water as solvent. Meanwhile basis set of  $6-311++G^{**}$  was used for C, H, O, N, whereas LANL2DZ basis set for gold.

## 3. Results and discussion

### 3.1. Quantization property of tautomeric hypoxanthine

Hypoxanthine is a heterocyclic compound, in which the isomerization would happen for amide group under different environments. In consequence, there exist two forms hypoxanthine, ketonic form and enolic form.  $\text{N1H/N9H}$  hypoxanthine is more frequent existence in solution than  $\text{N1H/N7H}$  hypoxanthine [5] and it is selected to DFT calculation. In our calculations, the total

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