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Surface geometry of tryptophan adsorbed on gold colloidal nanoparticles

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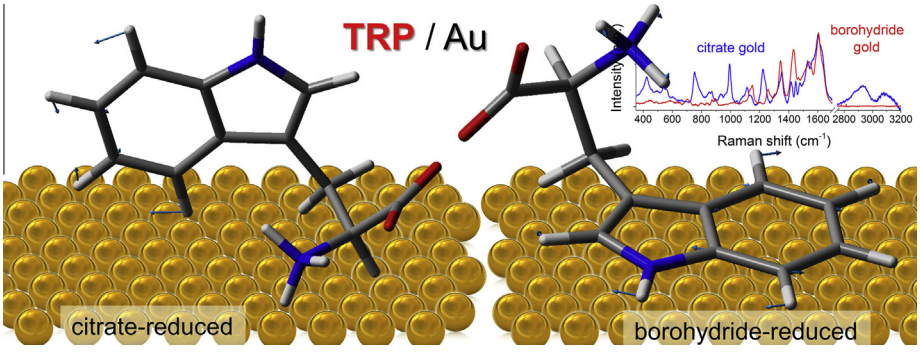
HIGHLIGHTS

- Tryptophan shows two distinct surface-enhanced Raman spectra with gold colloids.
- Indole ring, carboxyl, and protonated amine participate in surface adsorption.
- Perpendicular and flat orientations of indole ring to gold nanosurfaces.
- Several indole ring vibrations are highly sensitive to the surface orientation.

GRAPHICAL ABSTRACT



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ABSTRACT

Two distinct surface-enhanced Raman (SER) spectra of tryptophan depending on the surface adsorption geometry were obtained by using colloidal gold nanoparticles reduced by borohydride and citrate ions. According to the vibrational assignments based on DFT simulations, the SER spectra of tryptamine and 3-indolepropionic acid, and the pH dependence of tryptophan SER spectrum, we found that some indole ring vibrations are very sensitive to the surface adsorption geometry of the molecules. With citrate-reduced gold colloids, tryptophan and related molecules mainly adsorb via the protonated amine group while maintaining a perpendicular geometry of the indole ring to the surface. However, a flat geometry of the indole ring to the surface is preferred on the borohydride-reduced gold colloids where the surface adsorption occurs mainly through the indole ring π electrons. By comparing our results with previous reports on the SER spectra of tryptophan on various silver and gold surfaces, we propose a general adsorption model of tryptophan on metal nanosurfaces.

Introduction

Surface-enhanced Raman scattering (SERS), which was established decades ago, has been successfully applied in many disciplines, including physics, chemistry, life sciences, and engineering [1–5]. The rich information about molecular structures and functions that can be obtained from many types of chemicals and materials makes Raman (vibrational) spectroscopy a general and versatile analytical tool, as long as the infinitesimal Raman cross-sections (on the order of 10^{-30} cm^2 sr^{-1}) are overcome by large signal enhancements originating from metal nanostructures and excitation fields. The Raman intensity of the molecules adsorbed on the nanostructures can be enhanced dramatically either by the increased local electric field near the metal nanostructures (electromagnetic enhancement) or by the increased

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Raman cross-sections in the charge transfer process between the molecules and the metal (chemical enhancement) [3,5].

A wide range of metal nanosurfaces, such as colloidal nanoparticles [6–8], island films [9–11], and roughened electrodes [4,12,13] of silver, gold, and other noble metals, have shown strong enhancements of Raman signals. The extremely large enhancements of surface Raman signals on hot spots often found in the gap regions between metal nanostructures have allowed for surface-enhanced Raman (SER) measurements at the single-molecule level [14,15]. SERS has been applied to study molecular structures and adsorption geometries of all types of molecules, from small molecules (e.g., pyridine and benzene) to macromolecules (e.g., DNA, RNA, and proteins) [5,16,17].

SERS of small amino acids, including glycine and tryptophan (TRP), and short peptides has previously been reported, where carboxyl and amine functional groups of amino acids and peptides are the main surface adsorbing groups [18–32]. However, the findings from previous studies on the spectral features and vibrational assignments in the SERS of small amino acids, such as TRP, are not consistent [20–24,30], which makes it difficult and important to interpret the surface Raman spectrum of TRP and its adsorption geometry in various experimental conditions. It has been generally accepted that TRP adsorbs on Ag surfaces via both carboxylate and amine groups [18,20,25], but the SER spectra of TRP on these Ag surfaces showed clear differences. Recently, Reeves and co-workers reported the detailed adsorption kinetics of small molecules and amino acids on citrate-reduced (CT) gold colloids by steady-state absorption and zeta-potential measurements and concluded that the amino acid might adsorb on CT gold colloidal surfaces via the amine group and the carboxyl group might inhibit the surface adsorption [32].

In this paper, we have shown two distinct surface Raman spectra of TRP adsorbed on gold colloidal nanoparticles reduced by two different reducing agents and compared these results with those reported in previous studies that used various silver and gold nanosurfaces. More relevant vibrational assignments in the Raman spectra of TRP and related molecules, i.e., tryptamine (TMN, which lacks a carboxyl group) and 3-indolepropionic acid (IPA, which lacks an amine group), as well as surface adsorption geometries are sought.

Experimental

Chemicals and synthesis of gold colloidal nanoparticles

All of the chemicals, including TRP, TMN, and IPA, were purchased from Sigma Aldrich and used without further purification. The molecular structures of TRP and the related molecules are shown in Fig. 1.

Colloidal gold solutions were synthesized using two reducing agents. The CT gold colloid was obtained by reducing a boiling aqueous $HAuCl_4$ solution with sodium citrate under vigorous stirring [33,34]. The borohydride-reduced (BH) gold colloid was synthesized by adding sodium borohydride to $HAuCl_4$ solutions at ice temperature [8,29,35]. The SERS samples were prepared by adding 20 μL of a concentrated analyte solution to 1 mL of the gold colloidal solution to have a final concentration of 5×10^{-6}–1×10^{-3} M. SER enhancements of 10^3–10^4 were estimated for SERS with the CT colloid and higher enhancements of 10^4–10^5 were found with the BH colloid. Drops of 0.1 M NaOH or 0.1 M HCl solutions were added to adjust the solution pH when needed. A drop of the colloid solution evaporated on a copper grid was used for the TEM analysis on a Tecnai G^2 F30 (300 kV).

Raman measurements

A custom Raman microscope setup with a 20× objective lens was used to measure the Raman scattering. A HeNe laser (5 mW at 632.8 nm, linearly polarized; 05-LHP-141, Melles Griot) was used to excite the sample and a holographic notch filter was used to suppress the Rayleigh scattering. An imaging spectrograph (SP300i, Princeton Instruments) with a 1200 gr/mm grating was used to disperse Raman signals and a back-illuminated CCD array (DU401A-BR-DD, Andor Technology) was used to measure Raman intensities. The Raman signal from a small amount of sample dropped on a glass slide was accumulated for 60 s in general.

DFT simulation

The ground-state vibrational spectrum of TRP was simulated using the density functional theory (DFT) method available in the Gaussian 09 software package [36]. We adopted the optimized geometry of the zwitterionic form of TRP by Chuang and Chen [20] and used the BL3YP/6-311G basis set in the vibrational spectrum simulation. A molecular graphics package, Molekel, was used to visualize the vibrational normal modes [37].

Results and discussion

Absorption spectra and TEM images of gold colloids

The absorption spectra of both gold colloidal solutions are shown in Fig. 2. The absorption band of the CT colloid, centered at 540 nm, was much broader (~110 nm) than that of the BH colloid (~70 nm), centered at 535 nm, which indicates a wider distribution in the sizes and shapes of the nanoparticles with the CT colloid. TEM images of both colloidal nanoparticles shown in Fig. 3a and b are consistent with the absorption spectra, where the CT colloid appeared more inhomogeneous (40–50 nm diameter on average but mixed with much larger nanostructures) than the BH colloid (30–40 nm diameter in average) [33]. When small amounts of analytes are added, the plasmon resonance band of the BH gold colloid appeared at ~785 nm with TRP (5×10^{-5} M or higher), while that of the CT gold colloid appeared at ~870 nm

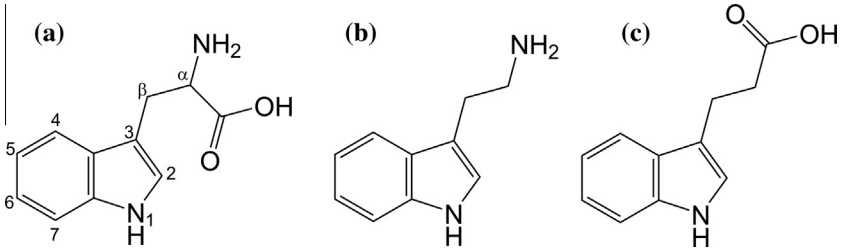

Fig. 1. Chemical structures of (a) tryptophan (TRP), (b) tryptamine (TMN), and (c) 3-indolepropionic acid (IPA).