

Surface-enhanced Raman spectroscopy of molecules adsorbed on silver nanoparticles dispersed in an agarose gel and their adsorption isotherms[☆]



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ABSTRACT

Surface-enhanced Raman scattering (SERS) was used to obtain adsorption isotherms for two types of SERS-active substrates: silver nanoparticles (AgNPs) dispersed in water (AgNP/sol); and AgNPs dispersed in agarose gel (AgNP/Agar). Rodhamine 6G (R6G) was chosen as the probe molecule to evaluate the two substrates. R6G adsorbs on both substrates following Langmuir isotherms with very similar adsorption constants. The SERS from R6G in AgNP/Agar is ca. 10 times more intense than in AgNP/sol due to the confinement of the R6G molecules within the gel matrix. The AgNP/Agar was further evaluated for the adsorption of methylene blue (MB), crystal violet (CV) and benzotriazole (BTA). The results showed that, for lower surface coverages ($\theta < 0.1$), the observed SERS (or SERRS) spectra corresponded to single molecule events. In this case, each single spectrum presented different relative intensities than from the ensemble averaged spectrum. On the other hand, for higher coverages ($\theta \approx 1$), the relative intensities of a single spectrum were quite similar to those of the ensemble average. Single molecule SERRS events were well identified for MB, because the spectra of the monomer and of the aggregated state differ considerably for this dye. The results also indicate that R6G and CV adsorb on the SERS-active sites forming ion pairs with the adsorbed chloride, while MB and BTA form covalent bonds with Ag atoms on the AgNP surface. In all cases the Gibbs free energy of adsorption were below -30 kJ mol^{-1} , characterizing chemical adsorption.

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1. Introduction

Anomalous intense Raman scattering from pyridine adsorbed on a roughened silver electrode was first observed by Fleischmann et al. [1]. However, the phenomenon was identified as a new effect, called surface-enhanced Raman scattering (SERS), by two independent research groups in 1977 [2,3]. In the 80s, most of the research in the field was dedicated to the understanding of the new surface-Raman phenomenon (see refs. [4–12] for reviews on the subject). Analytical applications of SERS started in the beginning of the 90's and an early review article on this subject was published in 1993 [13]. For recent reviews see Refs. [14–16].

In 1997, two independent research groups, Kneipp et al. [17] and Nie and Emery [18], have shown SERS from adsorbed single molecules (SM). These researchers calculated enhancement factors

as large as 10^{14} . After that, Gresillon et al. [19] observed the excitation of localized surface-plasmon resonances (LSPR) with huge localized electric fields at certain surface sites. Michaels et al. [20] proposed that these surface sites corresponded to the junctions formed by the aggregation of silver nanocrystals and indicated that these “hot spots” were responsible for the observation of SM-SERS. This hypothesis was later confirmed in, at least two key experiments [21,22] and supported by theoretical calculations [23]. Meanwhile, researchers have designed experiments to unambiguously prove the detection of SM by SERS; these included the two-analytes approach [24–26] and tip-enhanced Raman scattering (TERS) techniques [27–29].

Several groups have developed highly efficient SERS substrates [30–32]. Besides having a high density of “hot spots”, efficient SERS substrates should confine the adsorbed molecule to the silver (or gold) nanoparticles (AgNPs) surface. This confinement can be facilitated by a transparent and viscous medium, which avoids or minimizes thermal diffusion of the adsorbed molecules. In this sense, the agarose (Agar) gel appears as an interesting candidate to support a highly enhanced AgNPs gel substrate for SERS [33,34].

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The benefits of Agar as a biodegradable matrix are well-described in the literature [33–38].

In this work, we report on the preparation of SERS-active substrates consisting of a dispersion of AgNPs in agarose gel (AgNP/Agar). In contrast to the processes already described in the literature ([34–38] and references therein), our strategy was to produce activated AgNPs in the agarose gel using an one-step process. In other words, the reduction of Ag^+ was performed within the agarose gel. Our goal was then to obtain adsorption isotherms for molecules on AgNP/Agar by SERS. In this sense, Rhodamine 6G (R6G) was used as a reference SERS probe. A conventional SERS-substrate (AgNPs dispersed in water, AgNP/sol) was used in control experiments. The AgNP/Agar substrate was further used to derive adsorption isotherms for other two dyes, methylene blue (MB) and crystal violet (CV), as well as for benzotriazole (BTA).

2. Experimental

2.1. Chemicals

The chemicals silver nitrate (AgNO_3 – Sigma/Aldrich), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ – Merck), sodium boron hydride (NaBH_4 – Vetec), Rodhamine 6G – R6G ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$ – Sigma/Aldrich), Crystal Violet – CV ($\text{C}_{25}\text{N}_3\text{H}_3\text{OCl}$ – Vetec), Methylene Blue – MB ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$ – Sigma/Aldrich), benzotriazole – BTAH ($\text{C}_6\text{H}_5\text{N}_3$ – Sigma/Aldrich), Sodium Chloride (NaCl – Vetec) and Agar Bacteriological (Acumedia/Neogen) were all of analytical grade. The dyes were recrystallized in water/ethanol solution before use. All glassware was carefully cleaned, first with an alkaline “piranha” solution (70% (v/v) NH_4OH and 30% (v/v) H_2O_2), then with an acidic “piranha” solution (70% (v/v) concentrated H_2SO_4 and 30% (v/v) H_2O_2) and finally rinsed thoroughly with Milli-Q[®] ultrapure water. All water solutions were prepared with Milli-Q[®] ultrapure water.

2.2. Preparation of adsorbates (R6G, MB, CV and BTA) stock solutions

A stock solution (100 mL) of each adsorbate at a concentration of 1.0×10^{-4} M was prepared by dissolving a required mass of the adsorbate in Milli-Q[®] water. Solutions of the adsorbates at

concentrations ranging from 1.0×10^{-5} to 1.0×10^{-8} M were prepared using the corresponding stock solution. Due to the low solubility of BTA in water, a 0.5 M NaOH water solution was used to prepare the BTA stock solution.

2.3. Preparation of the SERS substrates

2.3.1. The AgNP/sol

The colloidal dispersion of silver nanoparticles (AgNP/sol) was prepared as follows [39]: 100 mL of a previously cooled 1.4×10^{-4} M AgNO_3 water solution was added to a 250 mL flask in an ice bath, followed by the addition of 100 mL of an aqueous 1.4×10^{-4} M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ solution. Then, under stirring, 4 mL of an aqueous 2.5×10^{-4} M NaBH_4 solution was carefully added. This mixture was maintained under magnetic stirring for 2 h in the absence of light. The reaction product, a yellowish suspension of silver nanoparticles, was stored in the refrigerator (at 4 °C and under N_2 atmosphere).

2.3.2. The AgNP/Agar films

The silver nanoparticles dispersed in a gel of agarose (AgNP/Agar) were prepared in a one step process, as follows: A 125 mL Erlenmeyer flask containing 10 mL of a 0.01 M aqueous AgNO_3 solution was heated to 85–90 °C for 5 min, followed by the addition of 0.500 g of Agar. The mixture was maintained under stirring and heating for 10 min. Then, 5 mL of an aqueous solution of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (0.047 M) and NaCl (0.01 M) was added dropwise to the mixture that was then stirred and heated (85–90 °C) for 30 min. The resulting gel presented a brown color. The AgNP/Agar films were obtained by spin coating (2000 RPM) of 20 drops of the AgNP/Agar gel on a glass slide during a 15 s spinning time. The AgNP/Agar films were then stored in darkness for further use. The average thickness of the AgNP/Agar films was $98 \pm 5 \mu\text{m}$ (Micrometer gauge: Mitutoyo 293-145).

2.4. Instrumentation and measurements

The SERS measurements were performed on an InVia Raman system from Renishaw (New Mills, UK) equipped with a

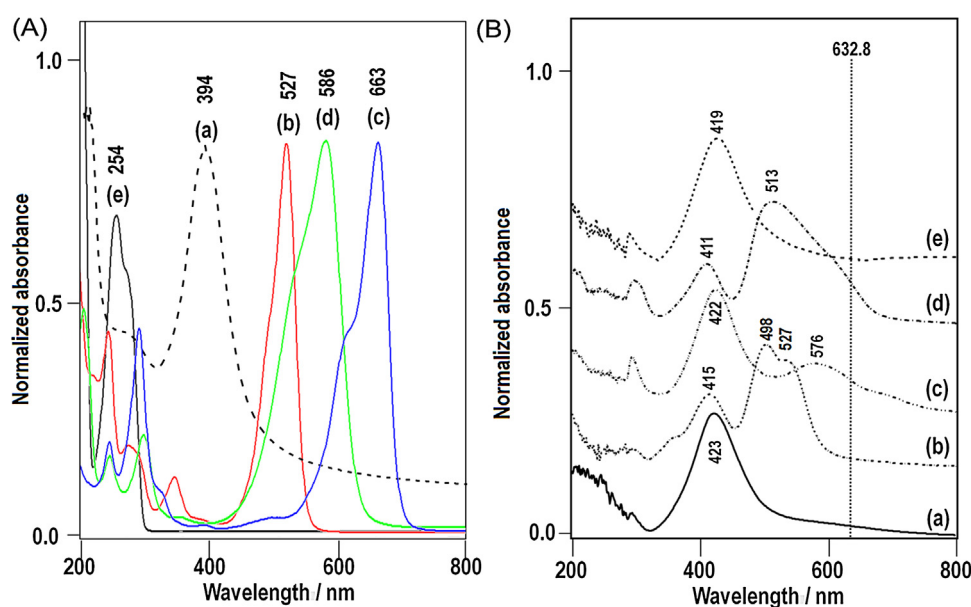


Fig. 1. UV-vis normalized absorption spectra: (A) from the AgNP/sol (a); R6G (b); MB (c); CV (d) and BTA (e), at 2×10^{-6} M. (B) AgNP/Agar films, as prepared (a) and after exposed to 60 μL of a 2×10^{-4} M aqueous solution of the adsorbates R6G (b); MB (c); CV (d) and BTA (e). The vertical dotted line in (B) indicates the laser wavelength used to excite the SERS (SERRS) spectra.

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