

Surface-enhanced Raman spectroscopy of morphine in silver colloid

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We report the surface-enhanced Raman (SERS) spectra of morphine in silver colloid, and study the silver colloid enhanced effects on the Raman scattering of morphine. The Raman bands of morphine are assigned to certain molecule vibrations. The broad band in the long-wavelength region of the electronic absorption spectra of the sol with added adsorbent at certain concentrations has been explained in terms of the aggregation of the colloidal silver particles. The potential applications of SERS in quantitative measurement of the morphine samples are demonstrated. By using a proper Raman band of morphine, the detection limit of morphine in silver sol is found to be 1.5 ng/ml. The result suggests that it is of great significance to use SERS in illicit drug morphine inspection.

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Surface-enhanced Raman scattering (SERS) is one of the most sensitive techniques for molecular adsorption, single molecule detection, etc., since it is discovered by Fleischmann *et al.*^[1,2]. Many ultra-low concentration analytes including chemical, biological, and medical molecule have been detected through SERS^[3-7]. When the target molecule is attached to silver or gold nanostructure, the nonresonant Raman signal can be enhanced up to 14 orders. Raman spectroscopy and SERS have been widely used in biomedical research^[8-10]. Morphine (C₁₇H₁₉NO₃) is a kind of powerful analgesic drug and attracts more and more scientists. However, there are only few reports on the surface enhance Raman spectroscopy of morphine in silver sol, so a detailed study on the SERS of morphine will be of great interest to scientists in general and clinicians in particular. In this letter, we illustrate the potential applications of SERS in quantitative measurement of morphine that is clinically significant. The SERS spectra of such molecules are found to be very sensitive to the small change of their concentration in silver colloidal solution. The SERS approach may provide a unique and immediate testing method for morphine.

Morphine used in our experiment was supplied by Fuzhou university. The morphine were kept in a refrigerator at about 5 °C, and the excitation power were controlled to be 100 mW. Stable silver sol was prepared according to the process described by Maseil *et al.*^[11]. The silver colloid was aged for two days before being used. And the sol was stored at 5 °C. All required solutions were prepared with distilled and deionized water from a Milli-Q-plus system from the M/S Millipore Corporation (USA). The desired concentration of Morphine in silver sol was attained by mixing a specific volume of

stock solution in ethanol with an appropriate volume of silver hydrosol. Fractional concentrations were obtained by accurate mixing of the sample with a micro syringe and the SERS spectral measurement for a particular concentration was repeated at least three times to ensure reproducibility.

Raman spectra were recorded by a RS2000 Raman spectrometer which was constructed by our group^[12]. The samples were taken in a quartz cell and were excited by 785-nm radiation from a Spectra Physics semiconductor laser. Raman scattering was collected at a right angle to the excitation. The acquisition time was 3 s for every spectrum. The electronic absorption spectra were recorded in a Lambda 950 ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer. All the spectra reported in the figures are original raw data directly transferred from the instrument and processed using the Excel program without signal smoothing.

Figure 1 shows the electronic absorption spectra of Ag sol with and without morphine. The previous research work has shown that the intense band at 425 nm in pure silver colloids (line a in Fig. 1) is a characteristic of the plasma resonance absorption for silver spheres in water^[13]. When a certain amount of the molecules are added, we can see that a new band in longer wavelength region appears (line b in Fig. 1) and the intense band at 425 nm is reduced to some extent. The peak of this stable new band is usually different with the added molecules and their concentration. To the morphine-silver sol system, this peak is at about 990 nm. This behavior is usually believed to be described as the surface plasma resonance of aggregated silver particles.

We recorded the normal Raman spectroscopy and SERS spectra of morphine liquor, and studied the sil-

ver solution enhanced effects on the Raman scattering. Figure 2 shows the near infrared-SERS (NIR-SERS) spectra of morphine in silver sol. A comparison with the NIR-SERS spectra of morphine before adding the silver colloid shows that the intensity of many dominant vibration bands increases greatly which indicates that there is strong interaction between the silver colloids-morphine systems. Just because of the existence of this interaction, morphine molecules can attach on the silver particles surfaces closely, and thus lead to an extra enhancement in the intensity of the Raman vibration mode. No obvious Raman signal could be observed without the addition of silver colloid because the normal Raman signal of morphine liquor is too weak. Table 1 shows the SERS bands of morphine in silver colloid and proposed assignments.

We evaluated the capability for SERS calibration on a Raman instrument for quantification of the compound and chose SERS signal of morphine for the evaluation. Figure 3 exhibits a concentration dependence of the SERS of morphine in silver solution. With the increase of morphine concentration, we can observe that the morphine's SERS signal intensity enhances from the bottom up. These spectral data are good enough for the quantitative measurement of morphine in water. Figure 4 plots the concentration of morphine in silver colloid versus the intensity of the band at 720 cm^{-1} which is the characteristic of morphine. This curve shows that morphine concentration is linearly related to its SERS peak intensity ($R^2 = 0.995$). The detection limit of morphine in silver sol is found to be 1.5 ng/mL . This shows that the SERS approach would provide a unique and fast test method for morphine.

In conclusion, we have demonstrated the feasibility

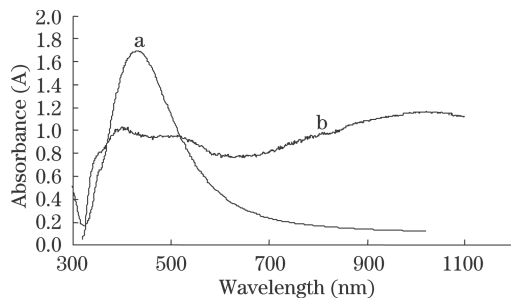


Fig. 1. UV-VIS-NIR absorption spectra of silver sol. (a) Pure sol; (b) with morphine.

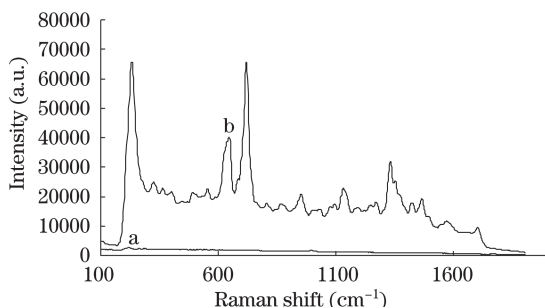


Fig. 2. (a) Normal Raman spectroscopy of morphine liquor without the silver solution; (b) NIR-SERS of the mixture of silver colloids and morphine.

Table 1. SERS Bands of Morphine in Silver Solution and Proposed Assignments^[14-16]

Raman Shift (cm^{-1})	Tentative Vibrational Assignment
401 (w)	Ring
451 (w)	$\gamma(\text{O-H})\text{c}$, $\tau\text{c/p}$
492 (w)	$\gamma(\text{C-C})\text{cp}$
557 (m)	Ring p/c
647 (s)	$\gamma(\text{C-H})\text{c}$
720 (vs)	τa , Ring c, $\gamma(\text{C-H})\text{p}$
807 (w)	$\nu(\text{C-C})\text{c}$, $\gamma(\text{C-H})\text{b/c/p}$
872 (m)	$\nu(\text{C-C})\text{p/c}$, $\nu(\text{C-N})\text{p}$, $\gamma(\text{C-H})$
953 (s)	Ring p, $\gamma(\text{C-H})\text{b/p}$
1032 (w)	Ring p, $\gamma(\text{C-H})\text{m}$, $\nu(\text{C-C})\text{c/f}$
1093 (w)	$\nu(\text{C-O})\text{c}$, $\nu(\text{C-C})\text{c}$, $\nu(\text{C-N})\text{p}$
1129 (s)	$\gamma(\text{C-H})\text{m}$, $\delta(\text{O-H})\text{a}$, Ring a, $\delta(\text{C-H})\text{a/p}$
1190 (w)	$\nu(\text{C-C})\text{f/b}$, $\tau(\text{C-H})\text{b/p}$, Ring a
1248 (w)	$\nu(\text{C-N})\text{m}$, $\tau(\text{C-H})\text{p}$, $\gamma(\text{C-H})\text{c}$
1273 (w)	Ring a, $\delta(\text{O-H})\text{a}$, $\delta(\text{C-H})\text{a}$, $\nu(\text{C-N})\text{p}$
1331 (s)	$\gamma(\text{C-H})\text{b/c}$, Ring a
1424 (m)	$\gamma(\text{C-H})\text{m}$
1467 (m)	$\gamma(\text{C-H})\text{m}$
1572 (m)	$\nu(\text{C-C})\text{a}$, $\nu(\text{C-O})\text{f}$, $\delta(\text{O-H})\text{a}$

vs: very strong; s: strong; m: medium; w: weak; ν : stretch; δ : in-plane bend; γ : out-of-plane bend; τ : torsion; ring: ring breathing; a: ring a; b: ring b; c: ring c; f: ring f; p: pyridine ring; m: N-methyl.

of the SERS technique with Ag colloid for quantitative measurements of the illicit drug morphine samples. We can observe that the silver colloid has very good enhanced

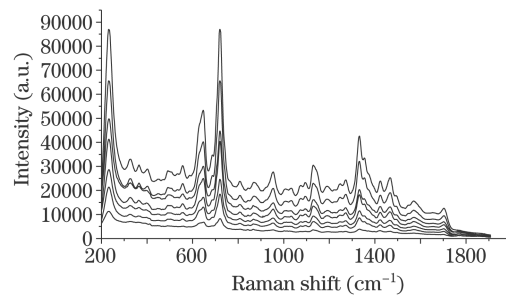


Fig. 3. Concentration dependence of the SERS of morphine in silver colloid.

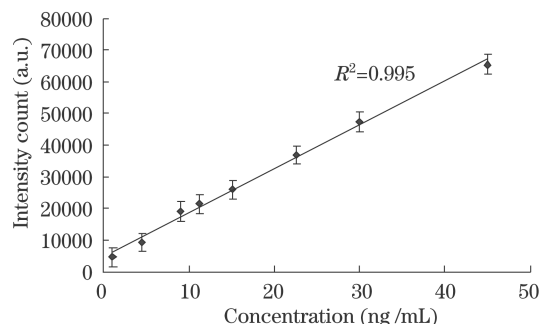


Fig. 4. Concentration dependence of the relative intensity of the 720-cm^{-1} SERS band of morphine.

effects for the morphine. The SERS effect may be due to the surface plasma resonance of aggregated silver particles which can be found in the electronic absorption spectra of the Ag sol with added morphine at certain concentrations. The Raman bands of morphine are assigned to certain molecule vibrations. By using the 720 cm^{-1} Raman band of morphine, it is possible to determine its concentration with a square of the correlation coefficient as 0.995 in the morphine sample.

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