Journal of Colloid and Interface Science 347 (2010) 90–95

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Surface-enhanced Raman spectroscopy of arsenate and arsenite using Ag nanofilm prepared by modified mirror reaction

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ARTICLE INFO

Article history:
Received 9 February 2010
Accepted 12 March 2010
Available online 16 March 2010

Keywords:
SERS
As(V)
As(III)
Mirror reaction

ABSTRACT

A modified mirror reaction was developed to prepare a sensitive and reproducible Ag nanofilm substrate for the surface-enhanced Raman scattering (SERS) analysis of arsenate (As(V)) and arsenite (As(III)). A good linear relationship between the SERS intensity of As(V) and As(III) and their concentrations in the range from 10 to 500 μg-As/L was achieved using the SERS substrate. As(V) and As(III) appear to be adsorbed on the Ag nanofilm through formation of surface complexes with Ag, based on comparisons of the Raman spectra of the arsenic species in solutions, on the SERS substrate, and in silver arsenate and arsenite solids. As(V) and As(III) species on the SERS substrate and in the solids had the same Raman band positions at 780 and 721 cm^{-1}, respectively. The effect of eight ions in natural waters on the SERS analysis of As(V) was studied. K^+, Na^+, SO_4^{2-}, CO_3^{2-}, and NO_3^- in the range of 0.1–100 mg/L did not interfere with the SERS detection of As(V) for a As(V) concentration greater than 100 μg-As/L. While Cl^- (50 mg/L), Mg^{2+} (10 mg/L), and Ca^{2+} (1 mg/L) were found to quench the SERS intensity of 100 μg/L As(V). Cl^- (at concentrations >10 mg/L) formed silver chloride with the adsorbed Ag^+ and decreased the SERS detection limits for arsenic species. The mechanism of the Ca^{2+} effect on the SERS analysis of As(V) was through the formation of surface complexes with As(V) in competition with Ag. When the Ca^{2+} concentration increased from 0 to 100 mg/L, the amount of As(V) adsorbed in Ag nanoparticles was reduced from 38.9 to 11.0 μg/mg-Ag. When the Ca^{2+} concentration increased to values higher than 1 mg/L in the As(V) solution, the As(V) peak height was decreased in the corresponding SERS spectra and the peak position shifted from 780 to 800 cm^{-1}. The fundamental findings obtained in this research are especially valuable for the development of sensitive and reliable SERS methods for rapid analysis of arsenic in contaminated water.

1. Introduction

SERS, which was discovered three decades ago [1], is a sensitive method for detecting a wide variety of molecules adsorbed on the surface of silver and copper nanoparticles, down to the single molecule range [2,3]. The two well-known mechanisms to account for the origin of SERS are the electromagnetic (EM) and chemical or charge transfer (CT) mechanisms [4,5]. In the EM mechanism, the local electric field increases as a result of coupling between incident light and the electron oscillations at the metallic surface, known as surface plasmons. The CT mechanism is analogous to the resonance Raman process as (1) the metal adatoms and the adsorbed molecule form a CT complex and (2) the energy difference between the Fermi level of the metal and the frontier orbital of the adsorbed species is close in frequency to the incident light. In contrast to the EM mechanism, which is effective in the case of long-range enhancement and is not sensitive to the chemical nature of the molecule and the molecular orientation, direct proximity between the molecules and the surface is required for the CT enhancement.

SERS has been observed with a number of coin metals, mainly copper, silver, and gold. Silver is a very sensitive material for making active SERS substrates. A number of methods, including vacuum evaporation [6], electrochemical oxidation–reduction cycling [7,8], colloidal solution [9], immobilization of Ag nanoparticles [10], and the mirror reaction [11,12], have been explored for preparing silver substrates. Ni and Cotton [11] used conventional Tollen's reagent to form a layer of nano-Ag particles on frosted glass slides, and optimized experimental parameters ($AgNO_3$ concentration, solution temperature, and deposition time) by using 4,4′-bipyridine as the analyte. Saito et al. [12] used an even simpler method to prepare a Ag nanoparticle layer. The two articles noted above showed that the mirror reaction can produce Ag islands of about 40–200 nm both in lateral size and in height.

Due to the first layer effect in the CT mechanism, which provides an additional enhancement of 10^2–10^4 due to electronic interaction between metals and adsorbed species, much work

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doi:10.1016/j.jcis.2010.03.028

has been done to investigate the influence of anions (mainly halides) on the SERS effect [13–16]. In silver sols, the chloride effect includes aggregation of silver nanoparticles, stabilization of sol particles, an increase in the number of active sites, and changes in the adsorption of target molecules. For example, Li et al. [13] observed that a high chloride concentration ($>10^{-3}$ mol/L) can completely quench the SERS intensity of benzoic acid and *p*-aminobenzoic acid using borohydrite-reduced silver sols, arising from changes in the adsorption state of the molecules. Maruyama and Futamata [15] investigated the effect of anions on the SERS of Rhodamine 6G (R6G) using Ag nanoparticles, and found that Cl^- or Br^- ion induced a prominent activation ($>10^2$) attributed to the formation of a Ag–X–R6G complex (X denotes Cl^- or Br^-). In contrast to the many works done concerning the effect of anions on the SERS of analytes, much less information is available about the effects of cations [17,18]. In one study, Niaura and Jakubėnas [18] studied the interaction of adsorbed phosphate anions with alkali metal cations at the Ag/aqueous solution interface by SERS. Formation of ion pairs at the interface was evident from the cation-induced perturbations in the SERS spectra of the anions.

Arsenic is one of the most common contaminants in groundwater worldwide and is a known carcinogen. On 22 January 2001, the EPA adopted a new standard for arsenic in drinking water at 10 μg-As/L which was enforced in January 2006 [19]. Although laboratory instruments, such as atomic fluorescence spectroscopy, graphite furnace atomic absorption spectrometer, and inductively coupled plasma-mass spectrometry, can accurately measure arsenic in an environmental sample to microgram As per liter concentrations, there is still a necessity for development of simple and rapid methods for field assays [20]. A feasible route for arsenic field analysis is to develop a highly active substrate for SERS of arsenic that can be used in conjunction with portable Raman technology [21]. The SERS of arsenate at high concentrations using silver sols was reported by Greaves and Griffith [22]. Recently, Mulvihill et al. [23] reported SERS detection of arsenic in groundwater at concentrations lower than the 10 μg-As/L level using a standard addition method. However, the effect of coexisting ions in groundwater on the SERS analysis was not investigated.

In this paper, we developed a sensitive and reproducible Ag nanofilm using a modified mirror reaction for the SERS analysis of As(V) and As(III). The Raman spectra of different arsenic species and forms were obtained to determine the mechanisms of arsenic interaction with the Ag nanofilm. The effect of eight common ions occurring in natural waters on the SERS of As(V) was investigated, including K^+, Na^+, Ca^{2+}, Mg^2, Cl^-, SO_4^{2-}, CO_3^{2-}, and NO_3^-.

2. Materials and methods

2.1. Materials

$AgNO_3$ (Certified A.C.S.), KOH (Certified A.C.S.), ammonia hydroxide (29.5%), glucose (Certified A.C.S.), methanol (HPLC grade), $Na_3P_5O_{10}$ (purified granular), and Na_2HPO_4 (Certified A.C.S.) were purchased from Fisher Scientific Inc. Other chemicals (NaCl, Na_2SO_4, $NaHCO_3$, KNO_3, Mg $(NO_3)_2$, Ca $(NO_3)_2{\cdot}4H_2O$, H_2O_2 (30%), concentrated H_2SO_4, $Na_2HAsO_4{\cdot}7H_2O$, and $NaAsO_2$) were Certified A.C.S. and purchased from Fisher Scientific Inc. A Coplin staining jar was purchased from Wheaton Science Products. Glass slides were purchased from Fisher Scientific Inc.

2.2. Methods

A mirror reaction has been used for preparation of the silver substrates for SERS [11,12]. However, it is very difficult to use the reported methods to prepare a reproducible and reliable SERS substrate. An easier and more reproducible process was developed by modification of the reported procedures in this study. In the modified mirror reaction, 20 μL of 3.2 wt.% KOH solution was added to 18 mL of a 2 wt.% $AgNO_3$ solution. The solution was mixed with a magnetic mixer to form a fine brown precipitate of Ag_2O. Then ammonium hydroxide (29.5%) was added to the mixture drop by drop until all the precipitates were dissolved. After sufficient 6 wt.% $AgNO_3$ solution was added to turn the solution yellow, a drop of 6 wt.% ammonium hydroxide solution was added and the solution became colorless. The solution was mixed with 3 mL methanol, 10 μL 10 wt.% $Na_3P_5O_{10}$, and 40 μL 5 wt.% Na_2HPO_4 consecutively to form a yellow colloid. Finally, 6 mL 35 wt.% glucose was added and mixed. The glass slides, which had been cleaned in a mixture of three parts of concentrated H_2SO_4 and one part of H_2O_2 (29.5%), were immersed in the colloidal suspension for an hour at 20 °C to form a Ag nanofilm on them. Then, the substrates were taken out and rinsed with DI water (18.2 MΩ cm).

The surface image of the resulting Ag nanofilm was characterized by atomic force microscopy (AFM, Digital Instrument Nanoscope). The tapping mode was performed using Olympus OTESP tips, at a 2.543 Hz scan rate. In order to study the surface ζ potential of the Ag nanofilm, Ag nanoparticles were prepared by the modified mirror reaction. The modified mirror reactions were carried out in a 50-mL centrifuge tube following the same procedures as discussed above, except that no glide slides were immersed in the solution. After 1 h, the nanoparticles were centrifuged at 10,000 rpm and were washed twice using DI water. The Ag nanoparticles were dispersed again using ultrasonic waves. The Ag nanoparticle concentration was 55 mg/L, and the background electrolyte was 0.01 mol/L KNO_3. The pH of the suspension was adjusted using NaOH and HCOOH for measurement of the ζ potential using a Zetasizer Nano-ZS (Malvern Instruments Ltd.).

Raman spectra were obtained using a Nicolet Almega XR dispersive Raman spectrometer with a laser source at 780 nm and 35 mW. SERS analysis was performed by transferring 10-μL solution samples onto the SERS substrate. To obtain a calibration curve for As(V) and As(III), the sample exposure was 3 times with exposure time 3 s each. For other solution samples, the exposure was 16 times with exposure time 10 s each. The laser power used for As(V) was 17.5 mW. To avoid As(III) oxidation, the laser power for As(III) was 0.35 mW.

As(V) adsorption experiments were conducted with a suspension containing 47 mg/L of Ag nanoparticles and 0.01 mol/L of KNO_3 as background electrolyte. The initial As(V) concentration was 50 μg-As/L and the initial Ca^{2+} concentration varied from 0 to 100 mg/L in the suspension. The suspensions were mixed for 18 h at an equilibrium pH of 7.0.

3. Results and discussion

3.1. Characteristics of SERS substrates

The main modification to the reported mirror reaction was the addition of $Na_5P_3O_{10}$ and Na_2HPO_4 to Tollen's reagent. When HPO_4^- was added to the $Ag(NH_3)_2^+$ solution, a yellow Ag_3PO_4 colloid with a K_{sp} of 8.89×10^{-17} was formed [24]. The additives slowed down the mirror reaction and controlled the deposition process of Ag nanoparticles on glass slides, thus generating a reproducible and sensitive Ag nanofilm. The morphology of the prepared Ag nanofilm is shown in Fig. 1A, and the roughness is highlighted in the cross-section in Fig. 1B. The metal islands were about 40–75 nm in height and were about 50–150 nm in lateral size. The ζ potential of Ag nanoparticles versus pH is shown in Fig. 1C. The pH_{pzc} was about 4.1.

3.2. SERS of As(V) and As(III)

The SERS spectra of As(V) in the range of 10–500 μg-As/L are shown in Fig. 2A. The signal to noise ratio for a 10 μg/L As(V) solu-