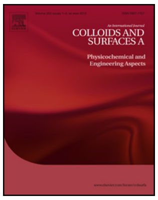
Colloids and Surfaces A: Physicochem. Eng. Aspects 497 (2016) 117–125

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Effects and mechanisms of water matrix on surface-enhanced Raman scattering analysis of arsenite on silver nanofilm

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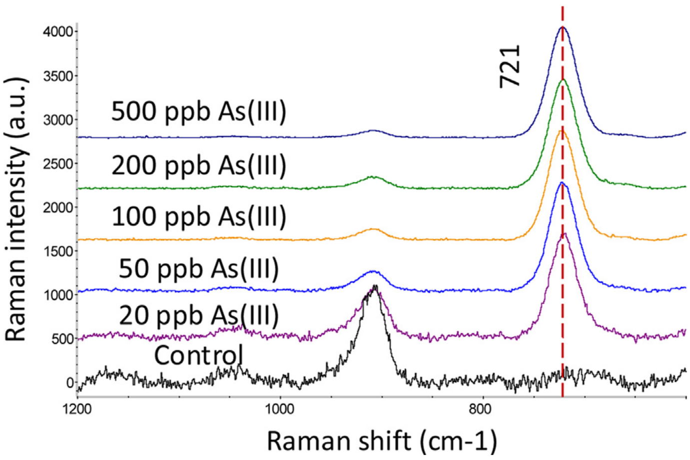
HIGHLIGHTS

- As(III) at low $\mu g\,L^{-1}$ level can be detected by SERS.
- Cl^- can activate the SERS of As(III).
- SERS technology is hopeful to determine inorganic arsenic species in water.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 December 2015
Received in revised form 20 February 2016
Accepted 26 February 2016
Available online 3 March 2016

Keywords:
Surface-enhanced raman scattering
Arsenite
Speciation

ABSTRACT

Ag nanofilm was synthesized using a modified mirror reaction and used as surface-enhanced Raman scattering (SERS) substrate for analysis of arsenite (As(III)). The SERS substrate can detect 20 and 50 $\mu g\,L^{-1}$ As(III) spiked in aged tap water and groundwater respectively. The effect of nine common ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, CO_3^{2-}, HPO_4^{2-}, SO_4^{2-} and Cl^-) in natural water on SERS of 0.5 $mg\,L^{-1}$ As(III) was investigated. Na^+ and K^+ (100 $mg\,L^{-1}$) had no obvious negative effects on the SERS intensity of 0.5 $mg\,L^{-1}$ As(III), but Ca^{2+} and Mg^{2+} significantly decreased that of 0.5 $mg\,L^{-1}$ As(III) as their concentrations increased to 1 and 10 $mg\,L^{-1}$ respectively. NO_3^-, SO_4^{2-} and CO_3^{2-}(HPO_4^{2-}) had negligible, medium and significant inhibition on the SERS of As(III) respectively. The inhibition effect of Ca^{2+} might be through the formation of surface complexes with As(III) on SERS substrate. The inhibition effect of CO_3^{2-}, HPO_4^{2-} and SO_4^{2-} could be explained by the competitive adsorption of anions with As(III) for adsorption sites of Ag nanofilm. It was confirmed that Cl^- can activate the SERS of As(III) alone and in the presence of Ca^{2+}, CO_3^{2-}, HPO_4^{2-} and SO_4^{2-}. The activation effect of Cl^- on SERS of As(III) could be attributed to charge transfer (CE) mechanism.

1. Introduction

Arsenic is one of most toxic inorganic contaminants in natural water. Long term arsenic exposure via drinking water can cause

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http://dx.doi.org/10.1016/j.colsurfa.2016.02.042
0927-7757/

skin, lung, bladder and kidney cancers as well as other health problems. In January 2006, USEPA enforced a new standard for arsenic in drinking water at 10 μg L^{-1} [1]. As well known, arsenite (As(III)) is more toxic than arsenate (As(V)). It is very important to determine the species of arsenic in order to evaluate the toxicity of arsenic in real water. Several analytical methods, such as atomic fluorescence spectroscopy (AFS), graphite furnace atomic absorption spectrometer (GFAAS), and inductively coupled plasma-mass spectrometry (ICP-MS), can accurately measure arsenic in environmental samples to μg L^{-1} concentrations. If combined with HPLC and speciation separation technologies, AFS, ICP-MS and GFAAS can determine the species of arsenic [2,3]. But these experimental instruments are expensive to operate and maintain and always are used off-site.

It is very meaningful to develop a speciation method which can immediately determine the species of inorganic arsenic (As(III) and As(V)) on-site since As(III) is oxidized very fast. Surface-enhanced Raman scattering (SERS) combined with portable Raman spectrometer is a possible method to analyze the species of inorganic arsenic on-site [2,4]. By providing fingerprint of unknown analytes, SERS can identify species of analytes, in addition to its extreme sensitivity down to a single molecule in solution [5,6]. Therefore if a highly sensitive and reproducible SERS substrate of arsenic can be prepared and be used in conjunction with portable Raman spectrometer, it may be possible to develop an economic and rapid method for the monitoring of arsenic in groundwaters, Supefund sites, Resource Conservation and Recovery Act (RCRA) landfills and facilities handling arsenic-containing wastes [2].

The SERS of arsenate at high concentrations using silver sols was reported by Greaves and Griffith [7]. Mulvihill et al. [8] reported the SERS detection of arsenic in groundwater at concentrations lower than 10 μg L^{-1} using standard addition method. However, the effect of co-existing ions in groundwater on SERS analysis of arsenic was not investigated systematically. In previous studies [9], we prepared sensitive and reproducible Ag nanofilm using a modified mirror reaction for SERS analysis of As(V) and As(III). The SERS peak of As(V) and As(III) was at 780 and 721 cm^{-1} respectively. The detection limit of both As(V) and As(III) was 10 μg L^{-1} in DI water. The effects of eight common ions (K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, SO$_4^{2-}$, CO$_3^{2-}$, NO$_3^-$ and Cl$^-$) in natural water on SERS analysis of As(V) were investigated. It was found that Cl$^-$ (50 mg L^{-1}), Mg^{2+} (10 mg L^{-1}) and Ca^{2+} (1 mg L^{-1}) quenched the SERS intensity of 100 μg L^{-1} As(V). Cl$^-$ formed silver chloride with adsorbed Ag$^+$ and decreased the SERS intensity of As(V). The inhibition effect of Ca^{2+} on SERS of As(V) was through its formation of surface complexes with As(V) [9,10]. Also, it was found that the inhibition effect of Ca^{2+} and Mg^{2+} can be reduced dramatically by addition of F$^-$ in As(V) solutions and groundwater samples [10].

In this study, Ag nanofilm was used as SERS substrate for analysis of As(III). The SERS substrate was sensitive to low μg L^{-1} level As(III) spiked in aged tap water and groundwater. In order to understand the effect of water matrix on SERS of As(III), the effects of nine common ions (K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, NO$_3^-$, CO$_3^{2-}$, HPO$_4^{2-}$, SO$_4^{2-}$and Cl$^-$) on SERS analysis of As(III) were investigated and the related mechanisms were discussed.

2. Materials and methods

The procedure about synthesis of Ag nanofilm was reported in the previous study [9]. Briefly, the important modification to reported mirror reaction [11] was the addition of small amount of $Na_5P_3O_{10}$ and Na_2HPO_4 into Tollen's reagent. The additives slowed down mirror reaction and controlled the formation and deposition process of Ag nanoparticles on glass slide. The procedure, called modified mirror reaction, can produce sensitive reproducible Ag nanofilms for the SERS of arsenic. After being synthesized, Ag nanofilm was cleaned by DI water and its surface image was characterized by Zeiss Auriga Small Dual-Beam FIB-SEM.

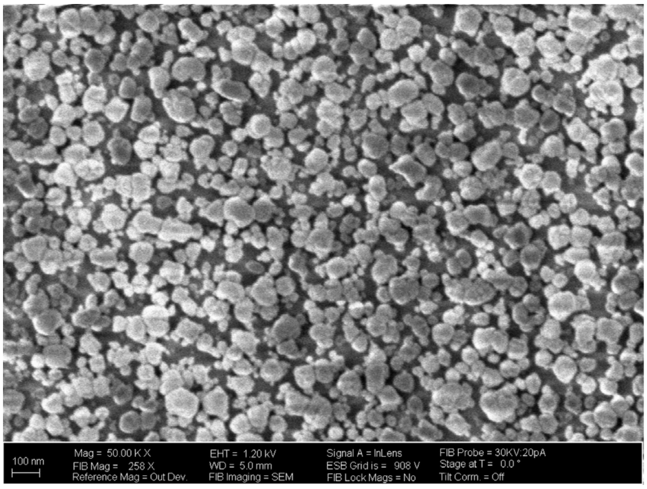

Fig. 1. SEM image of Ag nanofilm.

SERS analysis was performed by transferring 10 μL solution samples onto the SERS substrate. SERS spectra of As(III) were scanned using a Nicolet Almega XR dispersive Raman spectrometer with a laser source at 780 nm and the power of 35 mW. Each analysis was performed with 10 exposures, 3 s each exposure, and 10% of the laser power. The diameter of laser spot size was 3.1 μm.

To evaluate the effect of natural water matrix on SERS analysis of As(III), As(III) was spiked in aged tap water and groundwater sample collected in northern New Jersey, USA. The characteristics of the aged tap water were as follows: pH = 7.4, K = 1.0, Na = 36.2, Ca = 26.2, Mg = 11.9, Fe = 0.05, Si = 3.6, Cl$^-$ = 58.5, and SO$_4^{2-}$ = 14.6 mg L^{-1}. The characteristics of the groundwater were: pH = 7.3, Na = 41, Ca = 36, Mg = 16, Fe = 1.5, Si = 33, S = 16, P < 0.02, Cl = 4.5, TOC = 1.3 mg L^{-1}; total As = 73.2, As(III) = 4.6 μg L^{-1}. After samples were spiked and mixed well, 10 μL solution of each sample was transferred onto the surface of Ag nanofilm and then single SERS spectrum of each sample was collected. The experiment conditions were carefully controlled in order to get the SERS intensity of As(III) against its concentration in real water samples.

To understand the effects of common ions on SERS analysis of As(III), the SERS spectra of 0.5 mg L^{-1} As(III) in solutions containing ions (1–100 mg L^{-1} of Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, CO$_3^{2-}$, NO$_3^-$, Cl$^-$, HPO$_4^{2-}$and SO$_4^{2-}$respectively) or binary ions (20 mg L^{-1} Ca^{2+} combined with 30–90 mg L^{-1} CO$_3^{2-}$, 18–53 mg L^{-1} Cl$^-$, 48–144 mg L^{-1} HPO$_4^{2-}$, and 48–144 mg L^{-1} SO$_4^{2-}$respectively; 30 mg L^{-1} CO$_3^{2-}$(48 mg L^{-1} HPO$_4^{2-}$and 48 mg L^{-1} SO$_4^{2}$–) combined with 18–53 mg L^{-1} Cl$^-$; 0.5 mg L^{-1} As(V) and 0–100 mg L^{-1} Cl$^-$) were scanned using mapping mode (9 points, step size: X = Y = 100 μm). The stock solutions of anions and cations were prepared by their sodium and nitrate salts respectively. To study the effect of Cl$^-$ on the surface morphology of Ag nanofilm, 10 μL solution of 1, 10, 50 and 100 mg L^{-1} Cl$^-$ was dropped on Ag nanofilm respectively. After solutions dried, the SEM images of Ag nanofilms were recorded by Zeiss Auriga Small Dual-Beam FIB-SEM.

3. Resluts and discussion

3.1. SERS substrate

The SEM image (Fig. 1) shows that Ag nanofilm was consisted of Ag nanoparticles (or nano islands). The characteristics of the SERS substrate were published in our previous papers [9,10]. Briefly, Ag