



Trace detection and differentiation of uranyl(VI) ion cast films utilizing aligned Ag nanorod SERS substrates

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ARTICLE INFO

Article history:

Received 19 June 2008

Received in revised form 13 October 2008

Accepted 14 October 2008

Available online 1 November 2008

Keywords:

Ag nanorod array

Oblique angle deposition

SERS

Uranyl

Uranyl ion

ABSTRACT

Aligned Ag nanorod arrays prepared by oblique angle vapor deposition (OAD) were utilized to observe the SERS response for cast films of adsorbed uranyl ion complexes. These nanorod arrays consisted of preferentially aligned and tilted cylindrically shaped nanorods (average nanorod length = 858 nm). Routine SERS spectra of cast films of uranyl nitrate resulted in 0.87 pg of material analyzed with a detection limit estimated at 0.87 fg of adsorbed uranyl nitrate. The main spectral feature observed was a strong, broad peak centered at 700 cm⁻¹ assigned to the ν_1 symmetric stretch of the uranyl ion, $\nu_s(\text{UO}_2)$. The complex shape of this band is attributed to multiple uranyl complexes adsorbed onto the Ag surface. Uranyl nitrate cast films formed from ethanol solutions were more uniform and had stronger adsorption to the Ag surface compared to films formed from aqueous solutions. Differentiation of uranyl ion cast films formed from four different uranyl systems (i.e., uranyl nitrate hexahydrate, uranyl acetate dihydrate, uranyl formate monohydrate, and uranyl chloride trihydrate) was accomplished using univariate spectral analysis as well as Partial Least Squares Discriminant Analysis (PLSDA). A simple PLSDA calibration was able to correctly classify 27 SERS spectra of unknown uranyl ion cast films based on the type of anionic ligand present.

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1. Introduction

There is a continuing need to develop methodology that will provide rapid detection, quantification, characterization, and differentiation of uranyl ion complexes. This goal is driven by the need to detect and characterize radionuclides, such as uranium, at nuclear waste repositories as well as the release of these chemicals into the subsurface environment.

In the environment, uranium exists in the form of the uranyl(VI) ion [1]. Most of the work to date in the literature regarding uranyl ion detection and speciation has focused on this ion and its complexes in aqueous solutions. The aqueous solution chemistry of the uranyl ion, also known as the dioxouranium(VI) ion, in acidic [2], neutral [3,4], and basic [5] conditions is fairly well-understood. The uranyl ion complexes that are formed arise from hydrolysis reactions with the dioxouranium(VI) cation [5]. Typical uranyl ion

complexes present in aqueous solutions, which are dependent on pH, include $\text{UO}_2(\text{OH})^+$, $\text{UO}_2(\text{OH})_3^-$, $\text{UO}_2(\text{OH})_5^{3-}$, $(\text{UO}_2)_2(\text{OH})^{3+}$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_3(\text{OH})_7^-$, $(\text{UO}_2)_3(\text{OH})_8^{2-}$, $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$, and $(\text{UO}_2)_4(\text{OH})_7^+$ [5,6]. It is also generally accepted that the uranyl ion in aqueous solution has the ability to complex with a variety of anionic species including nitrate, acetate, carbonate, and bicarbonate [1,5,7–10]. Additionally, there is even a possibility that free water molecules can attach equatorially to the uranyl ion as aquo ligands [11]. Therefore, it is conceivable that many uranyl ion complexes coexist in solution in a complicated equilibrium that makes experimental differentiation of these species quite difficult. It is believed that these complexes and the equilibrium established between them aid in the transport of uranium in the subsurface environment [1].

To date, current techniques capable of both trace analysis and speciation of uranyl ions include electrochemistry [12,13], chromatography [14,15], ICP mass spectrometry [16], as well as numerous spectroscopic methods [17–19]. When comparing these techniques, optically based spectroscopic methods offer specific advantages, such as their noninvasive approach and the ability to

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configure the optical instrumentation for remote and in situ characterization. Of the spectroscopic techniques employed, most of the analysis of the equilibrium chemistry of these complexes in aqueous solutions has been achieved with the use of both infrared and Raman spectroscopy, with the latter being used to a greater extent due to the insensitivity of the technique to water. The uranyl ion vibrations observed by these techniques include the IR active antisymmetric stretch, $\nu_a(\text{UO}_2)$, and the Raman active symmetric stretch, $\nu_s(\text{UO}_2)$ [6,9,20]. It has been documented that both of these vibrations are extremely sensitive to changes in the UO_2^{2+} coordination environment [5,6,8–10]. Because of this, both Raman and infrared spectroscopy have been used to study coordination of organic and inorganic ligands with the uranyl ion.

Although much of the understanding regarding uranyl ion complexation has come from studies of these complexes in aqueous solutions, the interactions of the uranyl ion and its complexes with solid surfaces is vitally important in understanding transport mechanisms in the subsurface environment [10]. To accomplish this task, the vibrational techniques offer the best possibility for sensitive analysis. Raman spectroscopy was used by Maya [21] to study the speciation of hexavalent uranium carbonate complexes on the surfaces of hydrous titania, zirconia, and silica gel. In this study, it was observed that the carbonate ligands were displaced upon adsorption to these surfaces. In a separate study, Raman spectra of uranyl ions adsorbed to montmorillonite were recorded [22]. These authors found that the uranyl ion symmetric stretch was observed to split into two distinct bands, which the authors attributed to two separate species of uranyl adsorbed to the surface. These studies suggest that adsorption of uranyl complexes onto solid surfaces produce species that can be quite different than what is observed in solution.

One variation of Raman spectroscopy, surface-enhanced Raman spectroscopy (SERS) is an excellent approach for the study of uranyl ion complexation and adsorption to surfaces. SERS has emerged as a remarkably sensitive spectroscopic technique capable of single molecule detection. SERS involves an enhancement in the intensity of spectral bands for analytes that are either physically in contact with or in close proximity to ideally structured metallic surfaces. Although SERS has been a widely utilized optical technique for trace analysis of environmental pollutants, its use for uranium detection and quantification has been minimal [23]. Clavijo et al. [24] first reported SERS spectra for uranyl superphthalocyanine (UO_2SPc) on silver with an overall SERS enhancement of 10^2 . Dai et al. [25] were the first to report SERS detection of uranyl nitrate adsorbed onto the surface of a silver-doped sol–gel film with an overall SERS enhancement of 10^5 . Utilizing modified silver colloids, Teiten and Burneau reported detection limits as low as 5×10^{-9} M for adsorbed uranyl ions [8,26]. Tsushima et al. [10] investigated the adsorption of uranyl ions onto Ag and Au colloidal particles and reported that the significant spectral shift to lower wavenumber for the symmetric stretch of the UO_2^{2+} ion was indicative of strong adsorption of the uranyl species to the Ag or Au particles. These authors also observed displacement of ligands from the uranyl complexes upon adsorption to gold, but minimal displacement upon adsorption to silver. More recently, Bao et al. [23] reported a detection limit of 8.5×10^{-8} M for dry cast films of adsorbed uranyl ions using silver sol–gel substrates similar to that used by Dai et al. [25] These authors note that they were able to detect a uranium content of 0.2 ng using this method [23].

Recently, aligned Ag nanorod arrays produced by oblique angle vapor deposition (OAD) have been shown to be a very sensitive SERS substrate (i.e., SERS enhancements $>10^8$) [27,28]. These arrays are uniform and have extremely large electromagnetic field

enhancements when utilized as SERS substrates. OAD is a nanofabrication method and is a type of physical vapor deposition that involves tilting the substrate away from the direction of the vapor source in such a way that the vapor impinges upon the substrate at incidence angles greater than 75° . This approach produces nanorod arrays that grow preferentially towards the direction of deposition. OAD represents a flexible nanofabrication technique in which one can easily tune the size, shape, density, composition, and arrangement of the nanorod arrays, thus producing highly sensitive, reproducible, and stable SERS substrates.

In this study, aligned Ag nanorod substrates prepared by OAD were utilized to observe the SERS response for adsorbed uranyl ion complexes. Furthermore, the SERS data was analyzed in a multivariate fashion using Partial Least Squares Discriminant Analysis (PLSDA) in an attempt to differentiate adsorbed uranyl ion complexes formed from four different uranyl systems. The overall goal of this approach was to further develop methodology that will allow for rapid, ultrasensitive detection of various uranyl systems while also developing a unique multivariate approach to aid in the differentiation of the numerous uranyl complexes that occur upon adsorption to solid surfaces. The initial approach towards investigating the differentiation capabilities of this method explored uranyl complexes formed from solutions of four different uranyl compounds (i.e., uranyl nitrate hexahydrate, uranyl acetate dihydrate, uranyl formate monohydrate, and uranyl chloride trihydrate).

2. Experimental

The Ag nanorod substrates used in this study were fabricated using OAD on a custom-designed electron-beam evaporation system that has been described elsewhere [27,28]. Glass slides were used as the supporting substrate for the deposition of the nanorod arrays. The glass substrates (Fisher Scientific) were typically 0.5 in. \times 0.5 in, cleaned with piranha solution, rinsed with deionized water, and dried under a stream of nitrogen prior to use.

Prior to deposition, the base pressure in the OAD system was $<10^{-7}$ torr. The source material for evaporation was Ag pellets (99.999%, Kurt J. Lesker Company, Clairton, PA). For the fabrication of the SERS substrates, a 20 nm adhesion layer of Ti (99.999%, Kurt J. Lesker Company, Clairton, PA) was deposited along the surface normal of the glass substrates at a rate of 0.2 nm/s followed by the deposition of a 500 nm Ag layer (rate = 0.3 nm/s). Next, the substrates were tilted to an angle of 86° relative to the vapor source and the substrate surface normal followed by the oblique deposition of 2000 nm of Ag (rate 0.3 nm/s). This overall thickness corresponds to nanorod lengths around 860 nm as monitored by a scanning electron microscope (SEM). To test the SERS enhancement of the fabricated substrates, cast films of trans-1,2-bis(4-pyridyl)ethene (BPE) (Sigma–Aldrich, St. Louis, MO) were analyzed. BPE is a common reporter molecule used to test the sensitivity of SERS substrates.

Uranyl nitrate hexahydrate, uranyl acetate dihydrate, uranyl formate monohydrate, and uranyl chloride trihydrate (International Bioanalytical Laboratories, Bradenton, FL) were purchased and used as received. 8.5 mM solutions of these compounds were prepared by dissolving the uranyl compound in either 18 M Ω deionized water or absolute ethanol (200 proof, 99.5%, Sigma–Aldrich, St. Louis, MO) and used immediately. Dilutions of these stock solutions provided the low concentration solutions used for the SERS analysis. For the SERS analysis, a 1 μL aliquot of a given uranyl ion solution was placed onto a Ag nanorod substrate. The solution was allowed to dry prior to analysis. Sample spot sizes were typically ~ 1.2 mm when using water as the solvent and ~ 4 mm when using ethanol as the solvent.

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