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A SERS characterization of the stability of polythionates at the gold–electrolyte interface

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ABSTRACT

A gold nanorod (AuNR) array electrode was employed to record SERS spectra as a function of immersion time in electrolyte solutions of tetrathionate, trithionate, the $[Au(S_2O_3)_2]^{3-}$ complex, sulfide and thiosulfate. The generalized two-dimensional correlation spectroscopy was employed to deconvolute broad bands in the SERS spectra. The results show that the polythionates, tetrathionate and trithionate, and the $[Au(S_2O_3)_2]^{3-}$ complex decompose to form cyclo-S_8, polymeric and monoatomic sulfur at the gold surface. The relative amount of these different forms of sulfur in the film formed at the surface depends on the nature of the electrolyte species. The decomposition of tetrathionate leads predominantly to the formation of cyclo-S_8. Comparable amounts of all three forms of sulfur are formed in the solution of the $[Au(S_2O_3)_2]^{3-}$ complex. Monoatomic sulfur is formed predominantly at the gold surface in solutions of trithionate and thiosulfate. In contrast to the previous suggestions, the results of this study demonstrate that polythionates are not present in the passive layer during gold leaching from thiosulfate solutions at a prolonged leaching times.

1. Introduction

Recent studies of the Au leaching process have employed thiosulfate as the alternative complexing ligand to cyanide for gold extraction from ores containing carbonaceous components which preferentially absorbs gold and gold–cyanide complexes [1–5]. Thiosulfate assists gold dissolution in the presence of an appropriate oxidant such as dissolved oxygen by forming a soluble $[Au(S_2O_3)_2]^{3-}$ complex as shown in Eq. (1) [6,7].

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \leftrightarrow 4[Au(S_2O_3)_2]^{3-} + 4OH^- \quad (1)$$

However, the kinetics of this process are inhibited by the formation of a passive layer on the Au surface that impede the lixiviant reagents from reaching the underlying Au atoms, thereby preventing full recovery of Au from the ore [5].

Previous characterizations of thiosulfate in Au leaching conditions have used techniques such as Raman spectroscopy [8–10], atomic absorption spectroscopy [2,11], chromatography [12], electrochemistry [13–15], and others [16,17]. Several of these investigations have suggested that the oxidative decomposition of thiosulfate into several different species under typical Au leaching conditions is the predominant problem with the Au leaching process. For example, thiosulfate has been proposed to be oxidized into tetrathionate as shown in Eq. (2) [7]. Additionally, the decomposition of tetrathionate into trithionate and thiosulfate, Eq. (3), as well as trithionate decomposition into thiosulfate and sulfite, Eq. (4) [12,16,18], have also been observed.

$$2S_2O_3^{2-} + \frac{1}{2}O_2 + H_2O \rightarrow S_4O_6^{2-} + 4OH^- \quad (2)$$

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \quad (3)$$

$$2S_3O_6^{2-} + 6OH^- \rightarrow S_2O_3^{2-} + 4SO_3^{2-} + 3H_2O \quad (4)$$

Several reports have shown suppressed leaching kinetics in the presence of these polythionates supporting the hypothesis that tetrathionate and trithionate may play a significant interfacial role in inhibiting the Au leaching process [9,19–21]. Eqs. (3) and (4) were developed based on studies of tetrathionate and trithionate electrolyte solutions. However, these electrolytes may decompose at the Au surface and the composition of the interface and the bulk of the solution may be significantly different. Several groups have identified elemental sulfur as a stable decomposition product of thiosulfate adsorbed at the

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Au surface [8,15,17,22–24]. It has been suggested, but not confirmed, that elemental sulfur and sulfides could possibly be formed through Eq. (5) [25] or through decomposition of tetrathionate, Eq. (6) [26].

$$S_2O_3^{2-} + H_2O \rightarrow S^0 + SO_4^{2-} + 2H^+ + 2e^- \quad (5)$$

$$10S_4O_6^{2-} + 34OH^- \rightarrow 13S_2O_3^{2-} + \frac{38}{3}SO_3^{2-} + \frac{4}{3}S^{2-} + 3H_2O \quad (6)$$

Surface enhanced Raman spectroscopy (SERS) is a technique that uses a SERS active substrate to provide unique information concerning the composition of the passive layer formed at a Au surface during the Au leaching process. Watling et al. [8] employed SERS on an electrochemically roughened Au electrode surface to investigate the composition of the passive layer during Au leaching in a thiosulfate solution. However, due to the high Au leaching rate, the SERS active centers were quickly dissolved and the enhancement of the Raman signal was lost after about ~15 min of the leaching experiment. To overcome this problem Baron et al. [9] developed a Au nanorod (AuNR) array electrode and were able to record Raman spectra during gold leaching experiments that lasted several hours. The SERS spectra of the passive layer recorded after much longer leaching time were observed to be quite complex and consisted of many overlapping bands, causing the band assignment to be a difficult task. Species such as tetrathionate, trithionate and thiosulfate gold complex were believed to be the constituents of the passive layer. However the SERS spectra of these species adsorbed at the gold electrode were not available and hence Raman spectra of these compounds in solutions were used as a reference for band assignment in SERS spectra of the passive layer. Fig. 1 shows Raman spectra for aqueous solutions of sodium salts of thiosulfate, trithionate, tetrathionate and the $[Au(S_2O_3)_2]^{3-}$ complex. These spectra illustrate that in a solution the bands belonging to different species are sufficiently well separated to allow identification of individual components in their mixture. However, for species adsorbed at the electrode surface these bands may become broader and the presence of additional species may further convolute assignment of species at the gold surface. Therefore, the objective of this study is to record SERS spectra of tetrathionate, trithionate and the $[Au(S_2O_3)_2]^{3-}$ complex at the AuNR electrode and to investigate the interfacial stability of these compounds during prolong exposure of the AuNR to their solutions. The results of this study will complement the work of Baron et al. [9] and Nicol et al. [27] and will allow for more precise assignment of bands in SERS spectra of a passive layer formed during gold leaching in a thiosulfate electrolyte.

2. Materials and methods

Tetrathionate ($Na_2S_4O_6 \cdot 2H_2O$, Sigma Aldrich, >98%), trithionate ($Na_2S_3O_6 \cdot xH_2O$ prepared following the procedure outlined by Kelly and Wood [28]), thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$, Acros, >99%), and $[Au(S_2O_3)_2]^{3-}$ complex ($Na_3Au(S_2O_3)_2 \cdot xH_2O$, Alfa Aesar, 99.9%) electrolyte solutions were prepared to a concentration of 0.1 M using MilliQ water (18.2 MΩ cm) and pH adjusted (pH = 10) with NaOH (Sigma Aldrich, 99.99%). Electrolyte solutions of sulfide (Na_2S, Sigma Aldrich) were prepared to a 0.1 M concentration and pH adjusted to a value of 10 using dilute HF.

Gold nanorod substrates [9] were fabricated by bonding an alumina template (Whatman 0.2 μm Anodisc 13) to gold coated silicon wafers with low density polyethylene. Gold was electrodeposited into the alumina pores with a 0.1 M $KAu(CN)_2$ (Sigma Aldrich, 98% purity) and 0.1 M KCN (Sigma Aldrich, 99% purity) electrolyte solution (pH = 10). An acid washed three electrode glass cell was used with the wafer-template assembly acting as the working electrode, a gold foil as the counter electrode, and a Ag/AgCl as the reference electrode. Each Au deposition procedure began with purging the electrolyte solution with argon for 30 min and a HEKA PG590 potentiostat was employed for Au deposition by applying a potential of −0.95 V vs. Ag/AgCl for 6 h. Once Au deposition was deemed complete, the samples were rinsed with water and placed in 1 M NaOH (Sigma Aldrich, 99.99%) for one hour to remove the alumina template. Adsorbed cyanide was removed by electropolishing in 3 M HNO_3 with an applied potential of +1.3 V vs. Ag/AgCl for 60 s, followed by +1.1 V vs. Ag/AgCl for 60 s, and finally by rinsing with water for 60 s. Three cycles of this procedure usually resulted in clean SERS active substrates absent of any Raman bands characteristic of contamination. An example of the SERS spectrum recorded in water at the AuNR electrode is shown as the bottom curve in Fig. 2.

A Renishaw model 2000 imaging microscope equipped with a near IR laser (785 nm wavelength and 300 mW power output) and a CCD array detector was employed for collection of all spectra. A spectral resolution of 1 cm^{-1} was achieved using a holographic grating, 1200 grooves mm^{-1}, and a slit width of 50 μm. Each investigation began with calibration of the spectrometer to the vibrational Raman band of silicon ca. 520 cm^{-1}. Raman solution spectra of the thiosulfate, tetrathionate, and trithionate electrolytes were collected with 10%

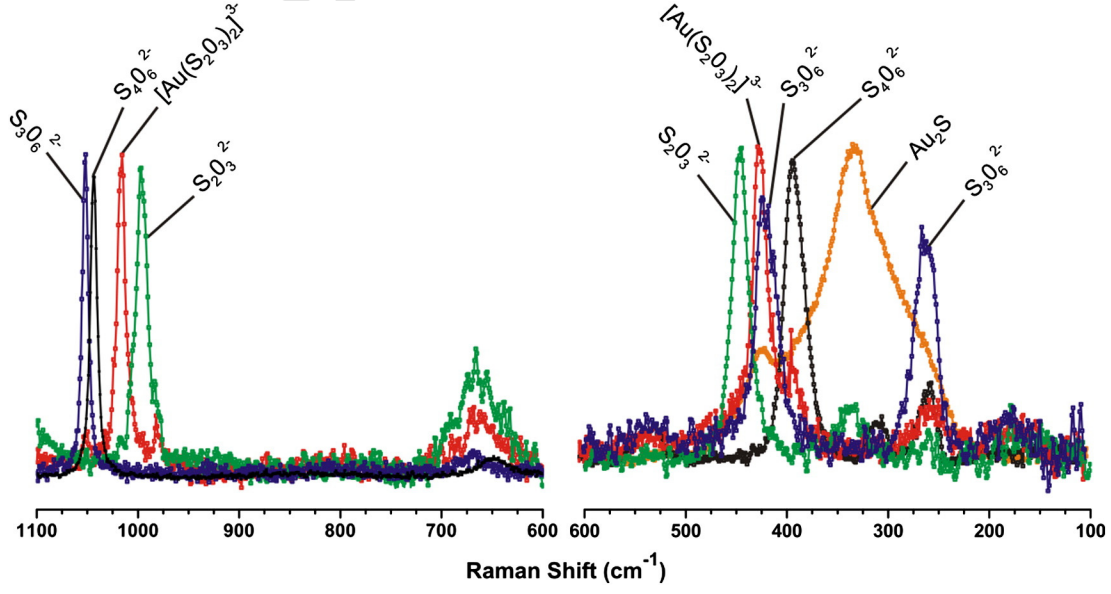

Fig. 1. Solution Raman spectra of 0.1 M electrolyte solutions of $Na_2S_4O_6$, $Na_2S_3O_6$, $Na_3[Au(S_2O_3)_2]$, $Na_2S_2O_3$, and solid Raman spectra of Au_2S.

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