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SERS and electrochemical studies of the gold–electrolyte interface under thiosulfate based leaching conditions

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ABSTRACT

Changes at the gold–solution interface in an alkaline thiosulfate solution under leaching conditions were investigated using surface enhanced Raman spectroscopy (SERS). Oxidation product of thiosulfate, such as tetrathionate, adsorbed thiosulfate and products of thiosulfate decomposition such as adsorbed sulfide or elemental sulfur were identified as the main contributor to the film that forms on the gold surface as a result of direct contact with the thiosulfate solution. The roles of thiourea and ammonia additives on the enhanced leaching kinetics of thiosulfate-based electrolyte solutions were also investigated. The SERS spectra indicate that these two additives form surface complexes with Au(I) and their presence inhibits either the formation or adsorption of the oxygen-containing sulfur species responsible for passivation of the gold surface. Leaching currents were determined from the analysis of current–potential curves and mixed potential theory. The initial leaching rates were higher in the presence of the additives, suggesting that they inhibit the passivating species from interfering with the Au leaching reaction and assist this reaction by forming complexes with the released Au(I) ion.

1. Introduction

Leaching of gold by thiosulfate is the primary non-toxic alternative to the traditional industrial process that involves the use of cyanide as the leaching reagent [1,2]. Initial rates of gold dissolution in the presence of thiosulfate solutions containing copper and ammonia are comparable to leaching rates in cyanide solutions [3]. A difficulty encountered when using thiosulfate as the lixiviant in the gold leaching system, is the decrease in leaching rate after prolonged exposure. This decrease is the result of the formation of a passive layer on the gold surface, which prevents further dissolution of gold. Previous studies have shown that this passive layer on the surface is composed of numerous sulfur species that result from the interaction of gold with thiosulfate. These sulfur species are different from the products formed by electrochemical oxidation of thiosulfate [4,5].

The addition of complexing or organic compounds to the thiosulfate leaching media has been suggested as a means to prevent the passivation of the gold surface and increase the overall leaching current. For example, the addition of ammonia to thiosulfate leaching solution resulted in an increase in the initial gold leaching rate [6,7]. Despite this observation, there are still ambiguities in the literature with regards to the role of ammonia in the leaching of gold. Thiourea is another example of an additive that can increase the rate of gold leaching. Chandra and Jeffrey [8] studied the effect of small additions of thiourea and other organic components to thiosulfate leaching solutions. They found that the addition of thiourea significantly improves the dissolution of gold. Watling [9] studied the effects of adding thiourea to thiosulfate solutions as a function of time using SERS at an applied potential of 0.210 V vs. SHE. The author proposed that thiourea is capable of disrupting networked sulfur—sulfur bonds on the gold surface. To the best of our knowledge, no further studies have been undertaken to investigate the mechanism by which thiourea accelerates gold leaching in thiosulfate electrolytes. The SERS studies in [9] were performed on electrochemically roughened gold substrates, which show a loss in electric field enhancement, and hence Raman intensity, after approximately 15 min due to gold dissolution. In this study, a novel gold nanorod array electrode was developed. It maintained a strong surface enhancement of the Raman signal for an extended period of time. This electrode allowed us to perform long duration studies of the passive layer formed on gold during leaching in thiosulfate solutions. By combining SERS and linear sweep voltammetry, we were able to explain the role of thiourea and ammonia in the enhancement of the gold leaching reaction in thiosulfate solutions. Preliminary results of this work were published in the Proceedings of the 50th Conference of Metallurgist of the CIM, COM 2011 [10].

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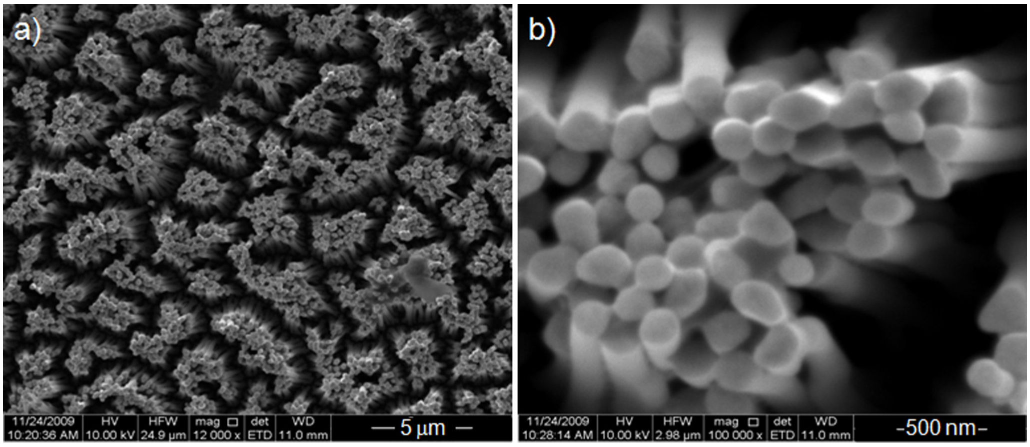

Fig. 1. Scanning electron microscopy images of gold nanorod arrays at a magnification of (a) 12,000× and (b) 100,000×.

2. Experimental

2.1. Reagents

All solutions were prepared with Milli-Q water (18.2 MΩ cm) and adjusted to a pH of 10 using NaOH (Sigma–Aldrich, 99.99%) to prevent thiosulfate decomposition. Thiosulfate solutions were prepared from sodium thiosulfate pentahydrate (Acros, >99%). Thiourea (Sigma–Aldrich, 99%) and ammonium thiosulfate (Alfa Aesar, 99%), were used as additives to the thiosulfate leaching solution.

2.2. Surface enhanced Raman spectroscopy experiments

A Raman imaging microscope (Renishaw Model 2000) was used for all Raman experiments. A near IR (NIR) diode laser with a wavelength of 785 nm and an output power of 300 mW was used as the excitation source. The Raman instrument was equipped with a CCD array detector. The spectrometer was calibrated using the Raman active vibration of silicon at 520 $\mathrm{cm^{-1}}$prior to each experiment. SERS spectra were accumulated using 1–25% of the laser power to avoid laser-induced decomposition of species on the gold surface. A holographic grating (1200 grooves $\mathrm{mm^{-1}}$) and a slit width of 50 μm allowed for a spectral resolution of ~1 $\mathrm{cm^{-1}}$. The exposure time was 5 s with 10 accumulations. The spectra were collected in static mode to minimize amount of time required for data acquisition. In order to cover the entire spectral range of interest, two individual spectra, centered at 400 $\mathrm{cm^{-1}}$ and 900 $\mathrm{cm^{-1}}$, were recorded for each immersion experiment and then combined into a single spectrum. Gold nanorod array electrodes were used as the substrates to provide adequate Raman enhancement. Anodized aluminum oxide filters (Whatman Anodisc 13) with a 0.1 μm pore size, 13 mm diameter and a thickness of 60 μm, were used as templates for electrodeposition of gold. A thin film of gold of approximately 70 nm was vapor deposited on the backside of each filter to ensure good electrical contact with a gold slide connected to a potentiostat/galvanostat (HEKA PG 590). The gold coated filter was mechanically attached to the gold slide using a homemade Kel-F® holder with the uncoated side facing the open part of the holder. The holder assembly was connected to a potentiostat by a gold wire and placed in a typical three-electrode glass cell using a gold foil as the counter electrode and a saturated calomel electrode (SCE) as the reference. Gold plating solution (Metalor ECF 60, 10 g/L Au with E3 brightener in a 200:1, v/v ratio) was de-aerated with argon for 30 min and used for electrodeposition of the gold nanorods through the pores of the gold coated filter by applying a constant potential of −0.65 V vs. SCE for a period of 6 h. The anodized aluminum oxide template was then dissolved in a 1 M NaOH solution at room temperature. Fig. 1 shows SEM images of these electrodes after filter removal. It should be noted that the use of gold nanorod electrodes allows for time-dependent studies in solutions where the rate of gold leaching is high. This is a crucial advantage with respect to electrochemically roughened electrodes where the enhancement is lost after short period of leaching [5,9].

2.3. Linear sweep voltammetry experiments

A typical three-electrode glass cell was used for the electrochemistry experiments. The reference electrode was a saturated calomel electrode (SCE) and placed in a separate compartment to avoid cross contamination between the investigated solution and reference electrode. The two cells were connected via a salt bridge. A gold coil was used as the counter electrode and placed in a separate compartment in contact with the solution through a glass frit. A solid polycrystalline gold electrode, made in – house from a gold wire (Alfa Aesar, 99.95%) was used as the working electrode in a hanging meniscus configuration with an exposed area of 0.22 ± 0.01 $\mathrm{cm^2}$. A potentiostat/galvanostat (HEKA PG 590) connected to an acquisition board (National Instruments PCI 6052E) was used for electrochemical experiments involving sweep voltammetry measurements. Custom written software provided by Professor Dan Bizzotto (University of British Columbia) and Professor Ian Burgess (University of Saskatchewan) was used for data acquisition.

3. Results and discussion

3.1. Identification of species present in the passive layer

The composition of the passive layer formed on the gold surface at the open circuit potential (*ocp*) in a 0.1 M sodium thiosulfate solution was characterized using SERS. The time-dependent changes of the gold–thiosulfate interface were studied using nanorod electrodes. The spectra acquired in this experiment are shown in Fig. 2 (the spectral region from 700 to 600 $\mathrm{cm^{-1}}$ was omitted since no Raman peaks were observed). The peaks observed in the 900 $\mathrm{cm^{-1}}$ region, have lower intensity than those observed in the 400 $\mathrm{cm^{-1}}$ region. The intensity of all recorded spectra centered at 900 $\mathrm{cm^{-1}}$ were multiplied by a factor of ten to provide sufficient intensity to present all spectral peaks on a single graph. The most prominent features of the spectrum recorded 5 min after placing the electrode in the thiosulfate solution included a band at around 1025 $\mathrm{cm^{-1}}$ and three peaks centered at 438, 383 and 300 $\mathrm{cm^{-1}}$. As time progressed, a broader band at around 260 $\mathrm{cm^{-1}}$ developed and there was a