

Observation of gold electrode surface response to the adsorption and oxidation of thiocyanate in acidic electrolyte with broadband sum-frequency generation spectroscopy[☆]



Jingjing Wang¹, Mei Xu¹, Zhichao Huangfu, Ying Wang, Yuhan He, Wei Guo, Zhaohui Wang^{*}

State Key Laboratory of Physical Chemistry of Solid Surfaces, The MOE Key Laboratory of Spectrochemical Analysis and Instrumentation, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

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ABSTRACT

The adsorption and oxidation of thiocyanate (SCN^-) on polycrystalline Au electrode surface in acidic electrolyte (10 mM NaSCN/0.1 M HClO_4) have been investigated with broadband sum-frequency generation spectroscopy (BB-SFG). Potential-dependent behaviors of both the surface adsorbed species and the Au nonresonant (NR) electrode surface have been observed through BB-SFG band. A phase change of the S-bounded SCN^- on the Au electrode surface occurs around 0.3 V in both the anodic (increase of surface potential) and cathodic (decrease of surface potential) sweeps. At surface potentials >0.7 V, oxidation and adsorption of the products (AuCN and $\text{Au}(\text{CN})_2^-$) have been observed. Possible oxidation/reduction pathways have been discussed. The Stark slopes of the adsorbed SCN^- SFG bands are significantly different in the anodic scan (before oxidation) from that in the cathodic scan (after the oxidation). The Au surface NR SFG band in the cathodic scan is much stronger than that in the anodic scan at the double layer surface potentials (-0.2 V to 0.5 V). The potential dependent Au surface NR BB-SFG band clearly shows that the adsorption/desorption and oxidation/reduction of surface species will affect the surface electronic structure.

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1. Introduction

Thiocyanate (SCN^-) is a well-studied spectro-electrochemical probe due to its simple structure and strong adsorption on the electrode surfaces [1]. It binds readily to metal ions in three ways: S-bounded, N-bounded and bridged between two metal ions $\text{MSCN-M}'$ or even in three-way-bridging $\text{M}_2\text{SCN-M}'$ [1–4]. SCN^- is a good model system to probe molecule-surface interactions, and understand the primary processes in surface/interface related chemical reactions. For example, Ruthenium Dyes (Ru dyes) show high power conversion efficiency (PCE) due to their broad absorption spectra and long lived excited states. Ru dyes consist of isothiocyanate (NCS) ligands. Both experimental [5] and theoretical [6] studies found that a fraction of Ru dyes can adsorb

on TiO_2 surface through the NCS groups. K.E. Lee et al. observed the blue shift of the N–C stretching, $\nu(\text{NC})$, of N917 Ru dye [7], and C. Pérez León et al. observed similar $\nu(\text{NC})$ blue shift for Ru-bpy dyes [8], they attributed these blue shifts to the participation of the NCS groups in the binding interaction between the dye molecules and the TiO_2 surface. N.W. Duffy et al. found that Ru *bipyridyl dicarboxylic acid photosensitisers* adsorbed on TiO_2 surface through COOH groups [9]. We believe that thoroughly observations of the adsorption and oxidation of SCN^- on metal surfaces may help to better understand how molecules consisting SCN or NCS groups adsorbed on surfaces, and how these groups involved in the surface-related reactions.

Thiocyanate ion adsorbs on the electrode surface via various orientations as well. The C–N stretching mode of SCN^- has a large infrared and Raman cross section, and its frequency is sensitive to electrode potentials (Electrochemical Stark effect) and the orientations of the SCN^- . Generally, the order of the C–N stretching frequency $\omega_{\text{C-N}}$ is bridged, S-bounded, and N-bounded [10]. As potential increases, N-bounded adsorption changes to S-bounded or even bridged [11]. The Stark slopes ($d\omega_{\text{C-N}}/dE$) of

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^{*} Corresponding author.

E-mail addresses: zhwang@xmu.edu.cn, zhwang2009@gmail.com (Z. Wang).

¹ These authors contribute to this work equally.

different SCN^- orientation are significantly different. Therefore, the adsorption orientation of SCN^- can be approximately estimated according to the frequency of the C–N stretch and its Stark slope ($d\omega_{\text{C-N}}/dE$).

Thiocyanate on the electrode surfaces has been studied extensively by *in situ* vibrational spectroscopies, such as, potential-difference infrared spectroscopy (PDIR) [12], attenuated total internal reflection infrared spectroscopy (ATR) [13], surface-enhanced Raman spectroscopy (SERS, SHINERS) [14–16] and sum frequency generation spectroscopy (SFG) [3,17,18]. Due to the relatively low sensitivity of Raman scattering, rough coinage metal surfaces usually were utilized to produce surface enhancement in Raman spectroscopy. However, different electrode roughness treatments make various surface structures which could introduce extra complexity of surface processes. As the electrolytic solution is strong IR absorbers, many electrochemistry interfaces are not accessible with IR.

Sum Frequency Generation spectroscopy (SFG) is a second-order nonlinear spectroscopic technique that occurs only at interfaces where the inversion symmetry is broken. With the surface/interface selectivity and high sensitivity, SFG spectroscopy has been used to investigate many electrochemical interfaces [19–25]. The stretching vibration of adsorbed species (CN^- , CH_3S , CO , COO^-) on electrodes was observed with a significant potential dependence. In addition, the electrode surface itself (e.g. Au, Ag and Cu electrode) can also give a SFG signal. Thus, not only the species adsorbed on the electrode surface can be investigated by SFG spectroscopy, but also the electrode itself. Rambaud et al. [18] investigated the shape of the SCN^- SFG bands under the influence of the nonresonant (NR) contribution from the polycrystalline Au electrode surface and electrodeposited metallic thin films (Ni, Co). The NR contribution from gold is much larger than that from other metal electrodes (Ag, Co, Ni, Pt) due to the interband transition of Au lies in the visible range. Tadjeddine et al. systematically modelled the metal surface contribution [26] (and references therein), and showed the difference between the phases of the NR contributions of SFG and DFG (difference frequency generation) spectroscopy of electrochemistry interfaces [26–28]. The electrode NR contribution is potential dependent and drastically depending on the nature of the electrode material. Although the metal NR contribution makes the SFG spectrum more complicated, by monitoring the contributions of the metal surface can bring insight on the surface electronic properties of the electrode.

In broadband SFG (BB-SFG), the NR contribution from the metal surface appears as a broadband peak which represents the spectral profile of the input IR pulse [29–31]. Thus, it is more intuitive to observe the metal NR contribution at different surface potentials and adsorption/desorption of surface species. In this paper, we use BB-SFG to study the adsorption and oxidation of thiocyanate ion on polycrystalline gold electrode surface in acidic electrolyte.

2. Experimental method

SFG is a second order nonlinear optical process [32–34]. Since the second order susceptibility $\chi^{(2)}$ vanishes in centrosymmetric or isotropic media, only surface species contribute to the SFG signal due to the breaking of the symmetry at the interface. In BB-SFG, a picosecond visible light ω_{VIS} and a femtosecond IR ω_{IR} are used to generate the SFG signal at $\omega_{\text{SFG}} = \omega_{\text{VIS}} + \omega_{\text{IR}}$. For SFG spectroscopy of electrochemistry systems, the SFG intensity can be written as,

$$I_{\text{SFG}} \propto |\vec{P}_{\text{SFG}}|^2 = |\chi^{(2)}(\omega_{\text{IR}}, \omega_{\text{VIS}}) \vec{E}_{\text{IR}} \vec{E}_{\text{VIS}}|^2$$

$$\chi^{(2)}(\omega_{\text{IR}}) = \chi_{\text{ads}}^{(2)} + \chi_{\text{met}}^{(2)} = \frac{A_{\text{ads}}}{\omega_{\text{IR}} - \omega_{\text{ads}} + i\Gamma_{\text{ads}}} + \frac{A_{\text{met}}}{\omega_{\text{IR}} - \omega_{\text{met}} + i\Gamma_{\text{met}}}$$

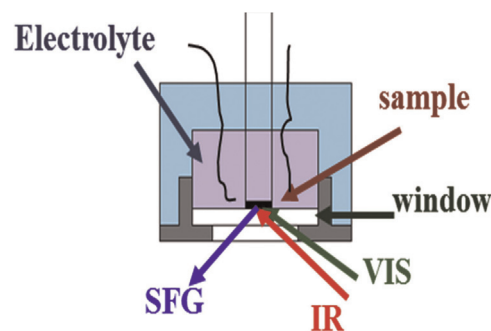


Fig. 1. Schematic of the spectro-electrochemical cell.

where $\chi^{(2)}$ is the second-order surface susceptibility. It comprises two contributions: $\chi_{\text{ads}}^{(2)}$ is the resonant part arising from the adsorbates, and $\chi_{\text{met}}^{(2)}$ is the part due to the metallic substrate. A_{ads} is the oscillation strength, and Γ is the half width of the vibrations.

Our BB-SFG setup is based on a fs Ti:sapphire laser system [29,30,35]. A portion of the output of a fs laser system (Legend Elite Duo) pumps an optical parametric amplifier (OPA) followed by different frequency generation (DFG) to produce the broadband IR (150 fs, 160 cm^{-1} FWHM). Another portion of the output is frequency-doubled by a second harmonic bandwidth compressor, and then pumps an OPA to generate the narrowband visible (VIS, 2.5 ps, $\sim 7 \text{ cm}^{-1}$ FWHM). The IR and VIS focused onto the sample by a parabolic mirror. The incident angle of IR ($6 \mu\text{J}$, centered at 4700 nm) and VIS ($3 \mu\text{J}$, 760 nm) are 60° . The generated sum frequency beam was collected by a spectrograph (Andor technology, SR-303i-B) with a CCD camera (Andor technology, DU920P-BR-DD). All spectra were taken with p-polarized SFG, p-polarized VIS and p-polarized IR with 80 s acquisition time.

A spectro-electrochemical cell (as shown in Fig. 1) with an IR and visible transparent 1 mm CaF_2 window has been used to perform BB-SFG on polycrystalline gold electrode. A polished polycrystalline gold disc with a diameter of 5 mm was used as working electrode. The reference electrode was 99.99% platinum wire (the potential is calibrated by a saturated calomel electrode). A large Pt ring (99.99%) served as the counter electrode. The above-mentioned electrodes are connected to a CHI604D electrochemical work station. During the SFG experiment, the poly Au electrode was pushed against the CaF_2 window in order to form a thin-layer configuration similar method as Bron et al. used in Ref. [4]. (Experimental details can be found in Supporting material S-1.)

The cyclic voltammogram (CV) measurements are performed in the potential range of -0.2 V to 0.9 V with the sweep rate of 100 mV/s . In both the CVs and the BB-SFG spectra measurements, the electrode surface potential scanned from the negative extremity to higher potentials in the anodic scan (increasing), followed by the cathodic scan in opposite way of varying the surface potential (decreasing).

The electrolyte solutions were prepared using triply distilled water ($\geq 18.2 \text{ M}\Omega \times \text{cm}$, total oxidizable carbon $\leq 4 \text{ ppb}$) made by Millipore-Q ultra-pure water system. NaSCN ($\geq 98.0\%$) was from Sigma-Aldrich. H_2SO_4 (98%), HClO_4 (71–72%), NaClO_4 (AR), NaOH (AR), H_2O_2 (30%) were from Sinopharm Chemical Reagent Co., Ltd. N_2 (99.99%) was from Linde group.

3. Results and discussion

3.1. Cyclic voltammogram of the electrode in 10 mM NaSCN/0.1 M HClO_4

Fig. 2 displays the CV of the polycrystalline Au electrode in 0.1 M HClO_4 electrolyte in the range of -0.2 V \sim 0.9 V with the sweep rate

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