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Spectroelectrochemical detection of specifically adsorbed cyanurate anions at gold electrodes with (111) orientation in contact with cyanate and cyanuric acid neutral solutions

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ABSTRACT

The adsorption and reactivity of cyanate at Au(111) single crystal and Au(111)-25 nm thin film electrodes is studied spectroelectrochemically in sodium perchlorate solutions and compared to those of cyanuric acid ($C_3N_3O_3H_3$). From the Surface Enhanced Infrared Reflection Absorption spectra obtained under Attenuated Total Reflection conditions (ATR-SEIRAS) it can be concluded that adsorbed cyanate species predominate at the electrode surface for low cyanate concentrations. However, for cyanate concentrations above 1 mM, the similarity of the ATR-SEIRA spectra with those obtained in cyanuric acid containing solutions indicates that some species coming from cyanuric acid is formed and adsorbed at the (111) gold surface sites as the result of an electroless trimerization reaction. Taking into account the results of Density Functional Theory (DFT) calculations, the experimental voltammetric and ATR-SEIRAS results agree with the formation of adlayers of specifically adsorbed triketo-monocyanurate species that adsorb perpendicular to the electrode surface.

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1. Introduction

Cyanate is a simple anion species whose adsorption and oxidation have been studied in the past at various electrode materials [1–11]. Published papers include in situ spectroscopic studies (either infrared [1–11] or Raman [7]) dealing with the identification of the adsorbed species formed from cyanate-containing solutions as well as the corresponding cyanate oxidation products. The adsorption of cyanate was detected as a potential-dependent process as witnessed by the observation of a band around 2220 cm^{-1}, ascribed by most authors to N-bonded cyanate anions [2–6,10]. Besides, Kitamura et al. [3] and Corrigan and Weaver [4] observed both for platinum [3,4] and gold [4] electrodes a band at ca. 2260 cm^{-1} that was attributed to isocyanic acid (HNCO) molecules resulting from the protonation of cyanate anions. This latter process would be induced by the protons released upon the electrochemical oxidation of the electrode surface. Taking into account the calculated optimized adsorbate geometries, adsorption energies and vibrational harmonic frequencies obtained from DFT calculations for cyanate and related species adsorbed at gold [11], we confirmed the assignment of the adsorbate bands between 2100 and 2300 cm^{-1} to the asymmetric OCN stretch of N-bonded, specifically adsorbed isocyanate anions. The observation of absorption bands in a relatively wide spectral region agrees with the coexistence of N-bonded cyanate species with different adsorption sites (mainly top) and tilting angles. In addition, the existence of collective in-phase vibrations at relatively high cyanate coverages also contributes to the widening of the absorption bands. The calculated adsorption energies [11] for cyanic and isocyanic acid indicate that these species adsorb weakly at the studied gold surfaces and, thus, seem not to be at the origin of any of the adsorbate bands.

In the papers commented above, no bands below 1800 cm^{-1} were reported for in situ infrared spectra, which were collected under external reflection conditions [1–11], thus indicating that adsorbed cyanate was the only adsorbate formed from dissolved cyanate anions. However, in a more recent paper, we have reported the first ATR-SEIRAS study of cyanate adsorption at Au(111)-25 nm [12] that changes the picture described above. Both the strong exaltation of the infrared absorption by adsorbates and the removal of interferences due to the bulk solvent characteristic of the ATR-SEIRAS technique [13,14] helped in the observation of new absorption bands in the range between 1800 and 1300 cm^{-1}, not detected previously in the external reflection experiments with gold single crystal electrodes [11]. These bands appear far from the typical wavenumbers for adsorbed cyanate (either adsorbed or in solution), thus suggesting the formation of new adsorbed chemical species. We proposed the formation of species derived from isocyanuric acid ($C_3N_3O_3H_3$) a trimer of isocyanic acid (HNCO) [15]. Cyanuric acid is a highly stable chemical, widely used as a stabilizer for chlorine in the

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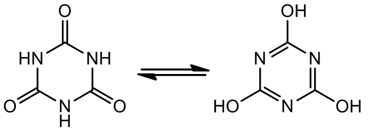
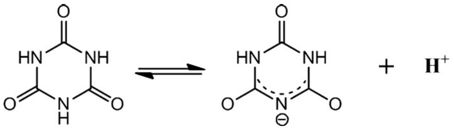
treatment and maintenance of pool water. This high stability is at the origin of the difficulties found for its removal. Some electrochemical treatments (using boron-doped diamond electrodes) have been reported, however, that are successful in achieving the total mineralization of cyanuric acid [16].

The chemical behavior of cyanuric acid and its derivatives has been widely studied, including different synthetic pathways (see the review by Seifer [15] and references therein). There are different tautomeric forms compatible with this molecular species. Some discussion existed in the past regarding the nature of the most stable tautomer (either the triketo (s-triazine-2,4,6-trione) or the trienolic (s-triazine-2,4,6-triol) form, both depicted in reaction (1)).



(1)

This issue is finally settled, after different theoretical and experimental studies that are discussed in detail in the paper by Revan [17]. From these works it is concluded that the triketo form is the most stable tautomer, both in gas-phase [17–20] and in solutions with different solvents [21]. The differences in energy found by Revan [17] (in gas phase) between the triketo form of cyanuric acid and the other tautomers with different degrees of enolization range between 70 and 160 kJ·mol^{-1}. Another relevant property of cyanuric acid is its behavior as a weak acid (with pK_a values 6.88, 11.40 and 13.5 for the successive deprotonations [22]). According to these values, the only species that are expected to exist in significant amounts both in a sodium perchlorate solution and at the electrified interface are the undissociated acid and the monocyanurate anion ($C_3N_3O_3H_2^-$) that results from the first acid dissociation. In this anion the negative charge on the N atom is stabilized by resonance with the two neighbouring carbonyl groups.



(2)

Some precedents exist regarding the study of adlayers of cyanuric acid, either alone or mixed with melamine, as these systems form well-ordered self-assembled monolayers on Au(111) [23–27]. The results of the structural characterization using STM under different conditions indicate that for most of the experimental conditions studied [23, 25–27], in these adlayers the cyanuric acid molecule adsorbs weakly, parallel to the surface, forming hydrogen bonds between neighbouring adsorbates that increase the stability of the adlayer. We are not aware of any published result regarding the adsorption or electrochemical behavior of cyanurate on gold electrode surfaces.

In this work, we extend our preliminary study of the adsorption and reactivity of cyanate at gold electrodes by exploring the behavior in contact with solutions having a wide range of cyanate and cyanuric acid concentration. In order to support the interpretation of the experimental results (in particular, band assignments) we have compared the in-situ ATR-SEIRA spectra recorded in these solutions with the theoretical frequencies obtained by periodic DFT calculations for the most plausible candidate structures to be adsorbed at the electrode surface. Finally, we compare also the voltammetric behavior of cyanuric acid at the (111) preferentially oriented gold thin film electrodes and Au(111) single crystal electrodes, showing the existence of characteristic features of ordered (111) domains.

2. Experimental section

Working solutions were prepared in ultrapure water (18.2 MΩ·cm, Elga-Vivendi) by dissolving either sodium cyanate (96%, Sigma-Aldrich) or cyanuric acid (98%, Sigma-Aldrich) in a 0.08 M solution of sodium perchlorate (99.99%, Sigma-Aldrich). Deuterium oxide (99.9 atom %D, Aldrich) was used as the solvent in some experiments as received. All these solutions were deaerated with Ar (N50, Air Liquide) and maintained under an atmosphere of this gas during the experiments.

The spectroelectrochemical Pyrex glass cells used in this work are equipped with a silicon prismatic window beveled at 60° [28]. A Ag/AgCl/KCl (sat) electrode and a gold wire were used as the reference and the counter electrode, respectively. The working electrode in the ATR-SEIRAS experiments was a 25 nm-thick gold thin film fabricated by thermal evaporation on one of the faces of the silicon prism. Film deposition was carried out in the vacuum chamber of a PVD75 (Kurt J. Lesker Ltd.) coating system at a base pressure around 10^{-6} Torr. A quartz crystal microbalance was used for monitoring the deposition rate (fixed at 0.006 nm s^{-1}), and the thickness of the gold film. The surface quality of these thin films was further improved by electrochemical annealing in the spectroelectrochemical cell filled with a 10 mM $CH_3COONa + 0.1$ M $HClO_4$ solution [29]. Due to its preferential (111) orientation this electrode will be named along the text as Au(111)-25 nm [14]. Some voltammetric experiments were carried out with Au(111) single crystal electrodes (ca. 2 mm diameter), which were prepared from a gold wire (Alpha Aesar 99.999%) following Clavilier's method [30,31]. These electrodes were heated in a gas-oxygen flame before the experiments, cooled in air and protected with a droplet of ultrapure water [31–33].

In situ infrared experiments were carried out using a Nexus 8700 (Thermo Scientific) spectrometer equipped with a Veemax (Pike Tech.) reflectance accessory and a MCT-A detector. All the spectra were collected with a resolution of 8 cm^{-1} and are presented in absorbance units (a.u.) as $-\log(R/R_o)$, where R and R_o represent the single beam sample and reference reflectivity spectra, respectively. Positive-going and negative-going bands correspond, respectively, to gain or loss of species for the sample spectrum with respect to the reference spectrum. Sets of 100 interferograms were collected at different sample potentials and referred to a reference single beam spectrum collected in the working solution either before or after dosing the molecule at the indicated potential.

3. Computational details

Geometry optimization and calculation of harmonic vibrational frequencies for the adsorbates studied (undissociated cyanuric acid and monocyanurate) were carried out using the Projector-Augmented-Wave (PAW) method [34,35] as implemented in the VASP [36–39] code (version 4.6). The density functional chosen was that proposed by Perdew, Burke and Ernzehof [40,41]. The relative energy values reported do not include the correction of zero point vibrational energy. Brillouin zone sampling used the Monkhorst-Pack [42] (3 × 3 × 1) scheme. Smearing was done with the second order method of Methfessel-Paxton [43] (sigma = 0.2 eV). The convergence criteria used were: 10^{-5} eV for electronic convergence, and 0.02 eV/Å for the forces on atoms.

The periodic models of the unreconstructed Au(111) surfaces were slabs of 4 metallic layers, with a (3 × 3) periodicity, separated by more than 12 Angstrom of vacuum. The positions of the gold nuclei (9 per layer, for a total of 36) were kept fixed at their bulk positions, without allowing relaxation. A value of 4.1748 Angstrom was used for the lattice constant, determined from the fitting to a Murnaghan equation of state. This value agrees well with experimental values reported for pure gold crystals (4.065 Angstrom) [44].

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