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Adsorption behavior of terephthalic acid on Au(1 0 0), Au(1 1 1) and Au(1 1 0) electrodes in neutral solution

Yasunari Ikezawa*,[1], Ryoko Masuda

Development of Chemistry, Faculty of Science, Rikkyo University, Nishi-Ikebukuro, Toshima-ku, Tokyo 171, Japan

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ABSTRACT

Adsorption of terephthalic acid on Au(1 0 0), Au(1 1 1) and Au(1 1 0) electrodes in neutral solution has been investigated using in situ Fourier transform infrared (FT-IR) spectroscopy, differential capacity measurements and scanning tunneling microscopy (STM). At negative potentials, the terephthalate anions in solution adsorb in a flat orientation onto the electrode via the π electrons of the aromatic ring. At positive potentials, the terephthalate anions adsorb in a vertical orientation via the oxygen atoms of one of the carboxyl groups as a form of dianion. At more positive potentials, the anions adsorb in a vertical orientation as a form of hydrogen terephthalate. For the three electrodes examined, the overtone and/or combination bands, due to vertically oriented hydrogen terephthalate, were observed at 2642 and 2517 cm^{-1}, respectively. For the Au(1 1 1) electrode, STM observations indicated a flat orientation in the form of terephthalic acid.

1. Introduction

The adsorption of anions at electrode/solution interface is one of the main topics in surface electrochemistry. The adsorption of aromatic carboxylic acids and their derivatives has been investigated using infrared reflection absorption spectroscopy (IRAS) and surface-enhanced IRAS [1–7]. These spectroscopic techniques have already been used to study the adsorption and phase formation of simple carboxylic acids, such as benzoic acid (BA) [1–3], *p*-nitrobenzoic acid [4,5], fluorobenzoic acid [6] and terephthalic acid [7] on various single crystal gold electrodes. Previous studies of benzoic acid suggest that the flat-lying orientation of benzoic acid dominates at less positive potentials, while vertical orientation of the benzoate ion, where both oxygen atoms are directed towards the metal surface, dominates at more positive potentials.

In contrast, carboxylic acids can provide hydrogen bonds with selectivity and directionality that determine the size and shape of the surface nanostructures. For example, terephthalic acid [8], isophthalic acid [9] and a wide variety of their derivatives [10] are known to form one-dimensional tapes and ribbons.

There are three chemical states of terephthalic acid in aqueous solution: terephthalic acid (TPA), hydrogen terephthalate (HTP$^-$) and terephthalate (TP^{2-}). TPA is a planar molecule, which can have two adsorption configurations: via two oxygen atoms of the COO$^-$ group (vertically adsorbed type) and via the π electrons of the benzene ring (flat-lying type). Therefore, many adsorption states are possible when a combination of the adsorption configuration and the number of donated protons is considered. The investigation of a diversity of such adsorption is effective for the interpretation of the adsorption configuration.

In this report, we present in situ Fourier transform infrared (FT-IR) spectra of TPA at Au(1 1 1), Au(1 0 0) and Au(1 1 0) electrode/solution interfaces. The behavior of the adsorbed species is qualitatively investigated for each single crystal electrode and in particular, the number of donated protons and adsorption configuration of the adsorbed species are discussed. Scanning tunneling microscopy (STM) measurements were carried out for the Au(1 1 1) electrode.

2. Experimental

The working electrodes used were Au(1 1 1), Au(1 0 0) and Au(1 1 0) electrodes (MaTeck, 8-mm diameter and 4-mm thick). The working electrodes were annealed in a hydrogen flame and quenched with ultra pure water before each experiment. A gold wire was used as the counter electrode. A α/β mixed-phase Pd/H electrode was used as the reference electrode. However, potentials are reported with respect to a Ag/AgCl electrode in saturated KCl solution for 0.1 M NaF, and with respect to RHE for 0.1 M $HClO_4$.

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* Corresponding author.
E-mail address: ikezawa@rikkyo.ac.jp (Y. Ikezawa).

[1] ISE member.

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NaF and $HClO_4$ (Merck suprapure) were used as the supporting electrolyte. TPA (99.0%, Kanto Chemical) was used without further purification. All solutions were prepared with a Milli-Q water. All solutions were sufficiently de-aerated with nitrogen gas before and during the experiments.

Potential control and current measurements were accomplished using a potentiostat (H-501, Hokuto Denko) connected to a personal computer. The spectro-electrochemical cell used was the same as that described previously [11]. Cyclic voltammograms were recorded at 50 mV/s. For the differential capacity measurements, a small (3.5 mV/rms, 30 Hz) sinusoidal perturbation was superimposed onto the voltage ramps (2 mV/s), and the real and imaginary components of the impedance were measured with a lock-in analyzer (LI-5640, NF Corp.). The measurements were performed between −0.8 and 0.6 V (vs. Ag/AgCl).

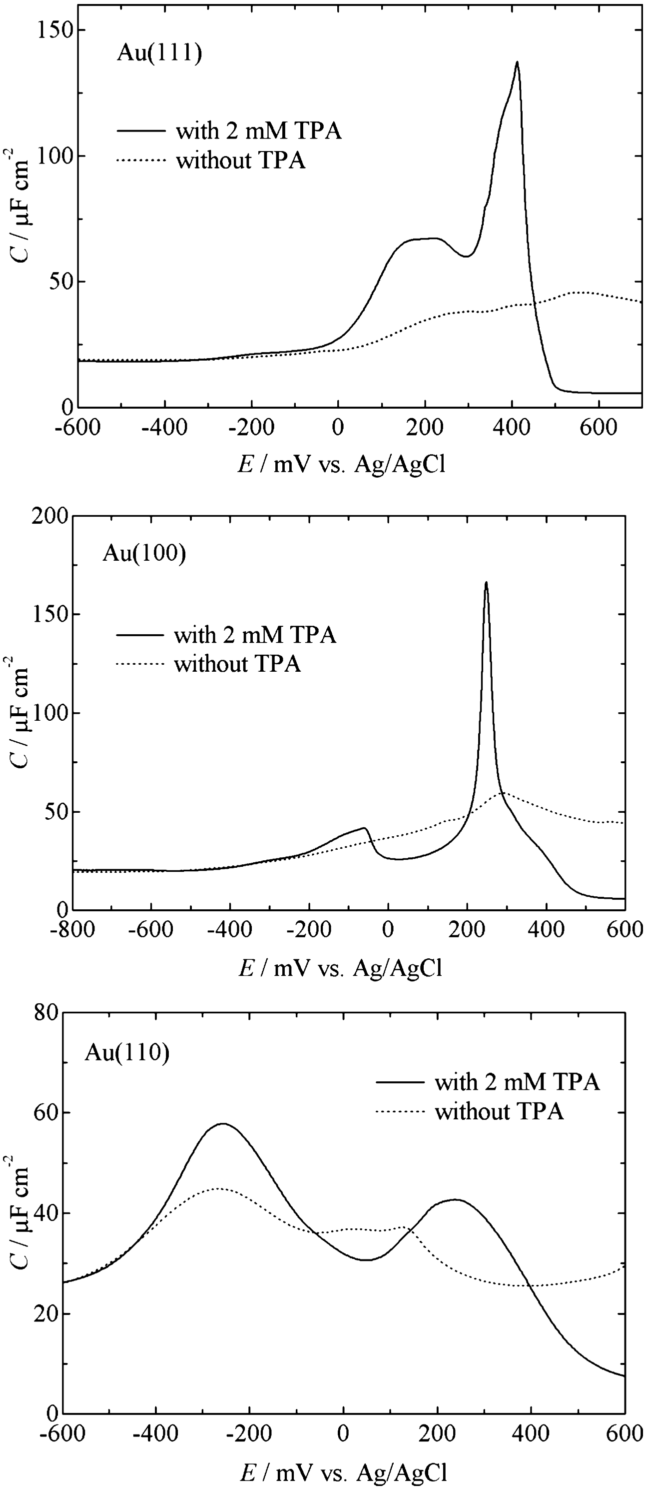

Fig. 1. Differential capacity curves for Au(1 1 1), Au(1 0 0) and Au(1 1 0) electrodes in 0.1 M NaF solution, with (solid line) and without (dashed line) 2 mM terephthalic acid.

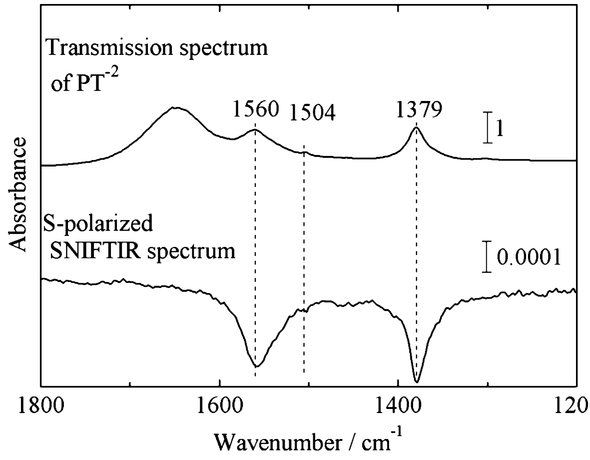

Fig. 2. Transmission spectrum of 0.1 M terephthalic acid in 0.5 M NaOH and the s-polarized spectrum for the Au(1 1 1) electrode at 200 mV in 0.1 M NaF solution containing 2 mM terephthalic acid.

In situ FT-IR measurements were performed using subtractively normalized interfacial Fourier transform infrared reflection spectroscopy (SNIFT-IRS) [12,13]. The IR window was made of CaF_2 beveled at 65°. The SNIFT-IRS measurements were carried out on a spectrometer (JEOL, JIR-5500) equipped with a HgCdTe (MCT) detector (Judson Technologies, LLC) cooled by liquid nitrogen. An attenuated total reflectance (ATR) attachment modified to a single reflection type and a polarizer was also used [14]. 500 scans were collected and averaged for each spectrum. All experiments were carried out at 25 ± 1 °C.

The in situ STM experiments were carried out with a Nanoscope E (Digital Instruments). The (1 1 1) facet on the Au single-crystal bead was prepared by melting an Au wire (0.5 mm in diameter), which was used as the electrode. The single-crystal surface was cleaned by flame annealing and then cooled in nitrogen-saturated Milli-Q water before use. The STM tips were tungsten wires (0.25 mm in diameter) electrochemically etched in 0.1 M $NaNO_2$ and insulated with clear nail polish to minimize the faradic current occurring at the chip. A α/β mixed-phase Pd/H electrode

Table 1
Frequency (cm^{-1}) and assignment of observed band for terephthalate (TP^{2-}) and hydrogen terephthalate (HTP^{-}) in 0.1 M NaF

Solution	Adsorbed	Calculated	Mode
TP^{2-}			
1308		1288	ν (ring) as
1365	1366	1311	ν (OCO) sy
1502		1459	ν (ring) sy
1560		1646	ν (OCO) as
HTP^{-}			
	1282	1168	ν (C–COOH)
	1321	1328	ν (C–OH)
	1390	1296	ν (OCO) sy
	1421	1385	ν (ring) as
	1506	1459	ν (ring) sy
	1581	1583	ν (ring) sy
		1681	ν (OCO) as
	1720	1724	ν (C═O)