

X-ray surface scattering study of Pt (111) / CO /acidic solution interface.

Yuriy V. Tolmachev¹, Andreas Menzel¹, Andrei Tkachuk², Yong S. Chu² and Hoydoo You¹

¹Materials Science and ²Experimental Facilities Divisions, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439 USA.

We studied ordered structures formed on Pt (111) surface in 50 mM H₂SO₄ and 0.1 M HClO₄ + 10 mM NaBr in the presence of solution phase CO. Both (2×2)-3CO and ($\sqrt{19}\times\sqrt{19}$)R23.4°-13CO commensurate super-lattices found previously in STM studies [1] were confirmed by x-ray surface scattering measurements. The (2×2) reflections are observed at negative electrode potentials [2] and they are replaced by the ($\sqrt{19}\times\sqrt{19}$)R23.4° reflections positive to the CO oxidation pre-wave (see Fig. 1). Two rotational domains were found for the latter structure. Resonant x-ray surface scattering spectra measured at the superlattice reflections through Pt L_{III}-edge (data not shown) showed considerable Pt contribution to superlattice scattering factor at grazing incidence ($L < 0.35$) but not at larger angles suggesting that there is a possibility of buckling - type adsorbate induced reconstruction.

We also studied polarization dependence of the resonant surface scattering spectra. We found that p-polarized spectra in the presence of adsorbed CO for all scattering directions show a bipolar shape with a dip corresponding to Pt Fermi level energy followed by a peak at 6 eV higher than the Fermi level. The peak in the bipolar-shape spectra is present neither in s-polarized spectra nor in the absence of adsorbed CO (see Fig. 2). We attribute the presence of the peak to the surface resonance x-ray scattering [3] of Pt 2p_{3/2} electrons to the 2π* empty of electronic states of adsorbed CO as previously suggested in a XANES study of Pt nanoparticle with and without adsorbed CO [4].

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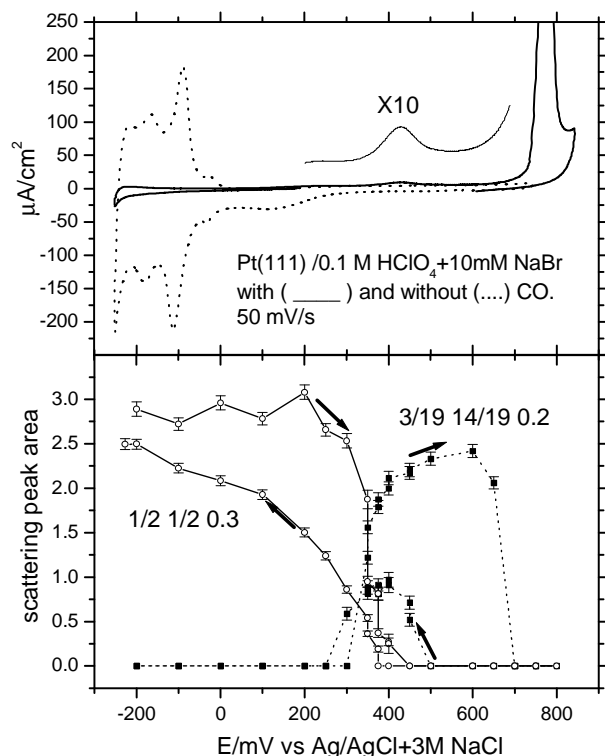


Fig.1. Cyclic voltammogram (upper panel) and x-ray cyclic voltammograms (XCV) for (2×2) and ($\sqrt{19}\times\sqrt{19}$)R23.4° superlattice peaks (lower panel) of Pt (111) facet. Neighboring data points in XCV were acquired with 3 min delay period. A Kapton film was placed over the electrode forming a thin layer cell for X-ray measurements.

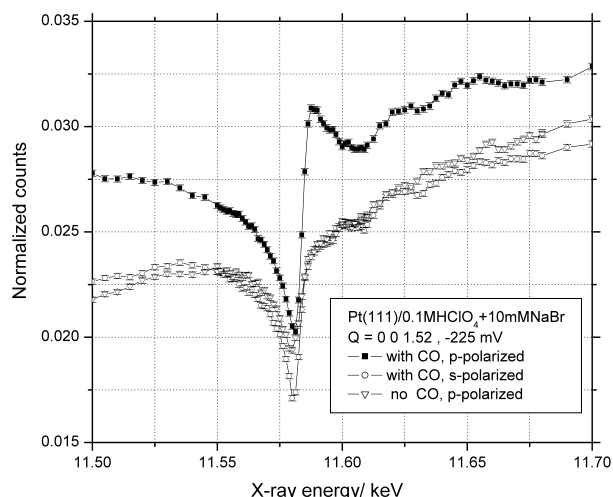


Fig.2. s- and p- polarized Pt L_{III}-edge surface resonant x-ray scattering spectra at the first specular anti-Bragg peak with and without adsorbed CO.