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Histidine adsorption on nanostructured cerium oxide

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ABSTRACT

Histidine adsorption from neutral aqueous solution on cerium oxide substrates was studied by photoemission with use of synchrotron radiation, soft X-ray absorption spectroscopy and nuclear magnetic resonance. Polycrystalline oxide films and oxide nanoparticles were used as ceria substrates. Independent of the morphology of the support, histidine binds to the oxide through the carboxylic group while the imidazole ring does not participate in the interface formation. Compared to deposition of molecules by evaporation in vacuum, the presence of the solution during adsorption does not alter the histidine bonding to cerium oxide. The present results clearly demonstrate the applicability of the model (*in-situ*) studies of the histidine/CeO_2 interface to the biocompatible techniques of cerium oxide functionalization.

1. Introduction

The interface between biomolecules and inorganic oxide surfaces has attracted considerable attention as a decisive factor in bio-applications of nanostructured oxides [1,2]. Cerium oxide is among prospective materials for bio-electrodes [3–6], drug delivery systems [7–9] and artificial enzymes [4,10–12]. Cerium oxide has unique redox properties. The ability of Ce cations to easily change their oxidation state between 3+ and 4+ in response to electronic interaction or oxygen exchange with their surroundings, together with good biocompatibility, has a strong impact on the development of new systems for bio-applications.

To define the interaction of oxide nanoparticles with a biological medium is an extremely complex task [13]. It is usually solved in an empirical way *via in vitro* and *in vivo* experiments. Another approach is *via* model studies of simplified systems prepared under defined conditions [14–16], in which the bonding of a chosen molecule to the inorganic oxide surface can be well examined. The starting state of the biomolecule can be free in vacuum (deposition by evaporation under ultrahigh vacuum (UHV) conditions) or in solution (deposition from solution). In general the use of any solution introduces an additional level of complexity [17] which is defined by its composition and pH, and as a result may alter the molecular bonding to the oxide. Further complexity comes with variation of the morphology of the oxide substrate.

There are several studies reporting on histidine films on gold (deposition from solution [18] and UHV deposition [19]) and copper (deposition from solution [18]) polycrystalline substrates. The schematic structure of histidine is shown in Fig. 1a. Independent of deposition technique, the film formed on gold consists predominantly of zwitterion histidine molecules, which are weakly bound to the surface through the carboxylate oxygen atoms [18,19]. The bonding mode to copper involves a stronger coordination through the amino nitrogen and carboxylate oxygen atoms. There is no direct evidence for coordination to the gold and copper surfaces through the imidazole (IM) nitrogen atoms [18].

Recently we published a study of histidine adsorption by physical vapor deposition in UHV on well-ordered [14] and polycrystalline cerium oxide [15] films. We found that the polycrystalline structure of the oxide film is an important factor which determines the mechanism of histidine adsorption on the cerium oxide. On the well-ordered single crystalline oxide, histidine bonded *via* the deprotonated carboxylic acid group, the α amino nitrogen and the IM ring, with deprotonation of its amino nitrogen. On the polycrystalline oxide, surface bonding occurred via the carboxylic acid group only, and the IM formed intermolec-

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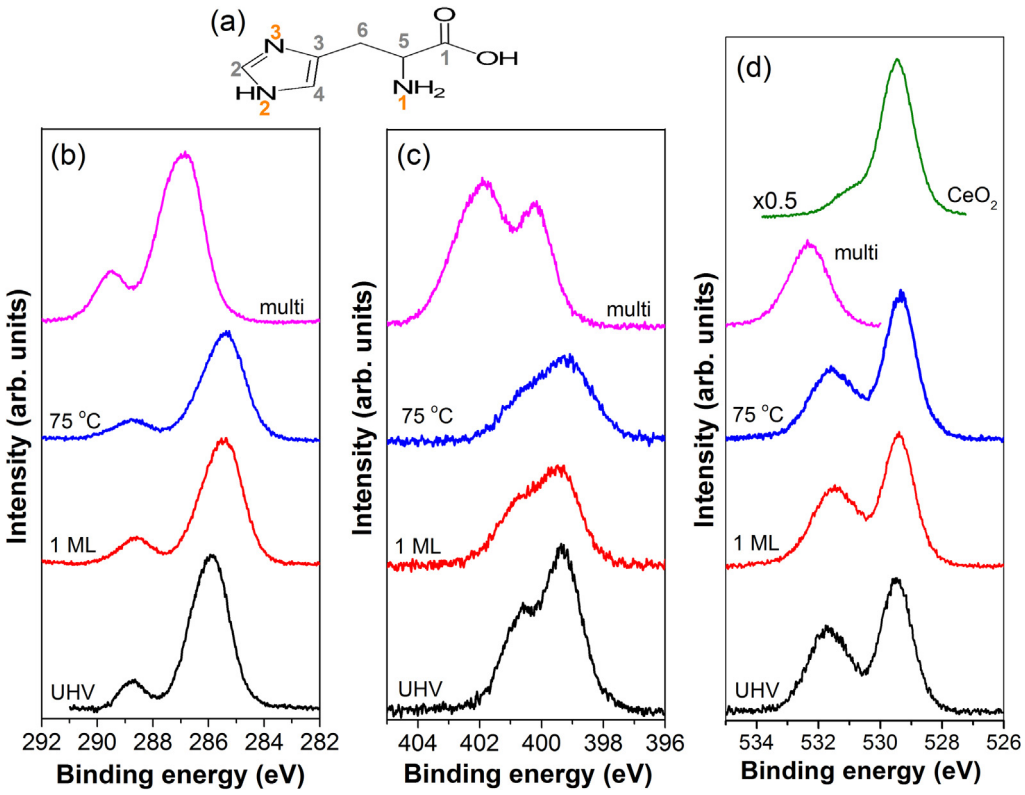

Fig. 1. Schematic structure of histidine (a). C 1s (b), N 1s (c) and O 1s (d) of 1 ML histidine on pollycrystalline ceria deposited from solution and heated to 75 °C compared to histidine deposited by evaporation in UHV [15]. The spectra of multilayer histidine coverage are also shown. The upper curve is multiplied by 0.5 and is the O 1s signal of the clean CeO_2 surface.

ular bonds. We were thus able to determine that histidine-ceria carboxylate bond is independent of the crystalline state, while the IM bond depends on morphology and defect density. The presence of a "free" IM ring provides the possibility for further interaction or linkage with other molecules which may be targets for biosensors [20]. Thus the model experiments on histidine bonding to ceria where two oxide morphologies were considered complement each other and provide comprehensive information on bio-interface formation.

The present article is a continuation of this line of research where the molecules are now introduced from a liquid phase. We show that histidine adsorption from aqueous solution at neutral pH on the polycrystalline CeO_2 film or CeO_2 nanoparticles is the same as for UHV-deposited molecules on polycrystalline oxide films. Synchrotron radiation based techniques (photoelectron spectroscopy (PES), resonant photoelectron spectroscopy (RPES) and near edge X-ray absorption fine structure spectroscopy (NEXAFS)) were used for characterization of the histidine adlayers on the polycrystalline ceria films. Solid-state nuclear magnetic resonance (NMR) spectroscopy was applied to the histidine adsorbed on ceria nanoparticles (NPs).

2. Experimental

The polycrystalline ceria films (20 nm thick) on Si(100) were prepared ex-situ by the nonreactive magnetron sputtering of a CeO_2 target (99.99%, Kurt J. Lesker), see Ref. [15] for details. After insertion in vacuum the CeO_2 films were cleaned by soft Ar^+ ion sputtering (500 V, 10 min) and annealed in O_2 (5×10^{-7} mbar pressure) at 250 °C for 15 min to restore the surface stoichiometry. Such a treatment provides a clean surface with negligible contribution of Ce^{3+} centers. No carbon signal was detected. The surface roughness was about 1.15 nm as determined by Atomic Force Microscopy.

L-Histidine $C_6H_9N_3O_2$ (99.5%) was supplied by Sigma-Aldrich and used without further purification. The saturated water solution was prepared as follows: 0.5 g of histidine powder was added to 10 ml of pure H_2O (18.2 MΩ cm from a MilliQ system) and stirred for 1 h. Molecules were deposited on the CeO_2 samples under a nitrogen atmosphere in a glove bag connected to a fast entry lock of the chamber to avoid exposing the sample to ambient air. Multilayer coverage of histidine was prepared by applying 3 drops of the saturated solution to the ceria surface, leaving for 5 min and drying with a high purity nitrogen jet without any further rinsing. Low coverage, defined as monolayer (ML) coverage, was prepared as follows: 3 drops of saturated solution were placed on the CeO_2 surface, left there for 2 min, dried with nitrogen, followed by rinsing with pure water (2 min) and dried again with nitrogen. Then the sample was inserted in the experimental chamber for measurement.

The experiments were performed at the Materials Science Beamline, Elettra-Sincrotrone Trieste, Italy. A detailed description of the end-station can be found in Ref. [14]. The C 1s, N 1s and O 1s core levels were acquired with photon energies 410, 475 and 630 eV and total resolution of 350, 500 and 700 meV, respectively. The valence band spectra were recorded at 115, 121.4 and 124.8 eV (to monitor Ce 4d–4f resonances in Ce cations), with total resolution of 190 meV. Spectra recorded at 121.4 and 124.8 eV provide the D(Ce^{3+}) resonance enhancements of Ce^{3+} cations (emission from Ce 4f states located at binding energy (BE) of about 1.4 eV) and D(Ce^{4+}) of Ce^{4+} cations (emission from hybridized oxygen cerium states at about 4.0 eV), respectively. The valence band spectrum measured at a photon energy of 115 eV corresponds to off resonance for both Ce^{3+} and Ce^{4+} states and was used as a reference for intensity subtraction between the corresponding features on- and off-resonance. The D(Ce^{3+})/D(Ce^{4+}) resonance enhancement ratio (RER) gives direct information about the oxidation state of surface cerium ions. Al Kα radiation (1486.6 eV) was used to measure the