



Experiment title: Fe magnetic moment switching in catalytic Oxygen Reduction Reaction (ORR) of FePhthalocyanine adsorbed on Ag (110)

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CH-3747

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Report:

Iron Phthalocyanine (FePc) arranged in a $c(10 \times 4)$ superstructure at the Ag(110) surface in the sub-monolayer (ML) coverage range has been recently shown to be catalytically active in the Oxygen Reduction Reaction (ORR) and the structure of the oxygen-coordinating active site has been elucidated at the single molecule level.¹ The present experiment was aimed at studying the evolution of the electronic structure and of the Fe-localized spin and orbital magnetic moment components deriving from the change in Fe coordination upon oxygen dosage by means of X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) measurements at the Fe $L_{2,3}$ edge of FePc. The final goal is showing that the catalytically active interface can be also exploited to control single molecular spins within their specific environment.

An Ag (110) single crystal was used as the substrate. Repeated cycles of 1 keV Ar^+ sputtering and annealing at 820 K were required to prepare a clean and ordered surface. FePc (Alfa Aesar GmbH, 95% purity, mass of a few mg) was dosed in vacuum with a Dr Eberl's NTEZ40 low T evaporator for organics. The Ag substrate was held at RT during FePc deposition and O_2 dosage till saturation. O_2 was dosed in vacuum at a pressure of 10^{-6} mbar through a leak valve. The catalytically active FePc phase corresponds to slightly less than 1 ML of FePc displaying a $c(10 \times 4)$ superstructure (surface density 0.42 nm^{-2}).¹ When a full ML is completed, the system undergoes a sharp phase transition to a denser oblique phase, which is inactive towards ORR. Fine control over the structure of the overlayer is therefore required, which was exerted by means of STM and LEED measurements for each prepared sample. STM also gave a characteristic and direct fingerprint of oxygen binding to FePc in the form

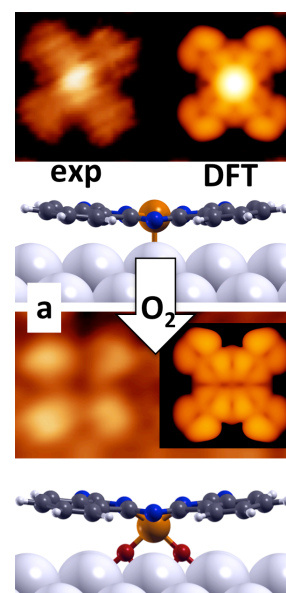


Figure 1

¹ Sedona, F. et al. *Nat. Mater.* 11 (2012) 970-977.

of a bright/dim switch of the Fe-centred density of states (Figure 1). We have insured that the majority of FePcs in the sample were in identical O₂ uptake conditions.

Four types of samples have been measured, namely (1) “clean” (i.e. prior to oxygen dosing) c(10×4)-FePc/Ag(110) obtained in the sub-monolayer (ML) FePc coverage range, which is reactive towards oxygen (Figure 1, top); (2) the oxygen-saturated FePc-(η^2 -O₂)-Ag(110) system resulting from oxygen dosage of the former (Figure 1, bottom); (3) the as-deposited and (4) oxygen-dosed oblique phase.

XAS and XMCD experiments were performed at the Fe L_{2,3} edge, the latter with $\mu_0 H \leq 5$ T applied magnetic field at T=7 K, on both the as-deposited FePc overlayer and on the oxygen-dosed FePc/Ag interface below and above the phase transition. The experiments were performed between grazing and normal incidence at steps of 15 degrees, to fully exploit the data by fitting to angle dependent predictions of the orbital and spin magnetic moment components. The measurements have to be done at T=7 K to stabilize Fe-O bonds, which are labile at RT,¹ and maximize the magnetic signal. A field of H=5 T was sufficient to polarize the magnetic moment to its saturation value.

Both XAS and XMCD results at the Fe L_{2,3} edge for the c(10×4)-FePc/Ag(110) phase show that the Fe-related components of the molecular electronic structure are strongly affected by oxidation (Figure 2), while – most interestingly – the “as-grown” electronic structure is almost fully recovered after annealing, in concomitance with the backward (dim/bright) switch of the Fe-centred density of states in STM images (Figure 1).

The oxygen-saturated sample shows a XMCD signal twice as large as in the as-deposited c(4×4) phase, which indicates a larger magnetic moment in the oxidized sample with respect to the molecule adsorbed on clean silver, in accordance with preliminary DFT calculations showing that the spin density on the Fe atom within the FePc macrocycle increases by a factor of two as a consequence of oxygen coordination (Figure 2). As far the the shape of the XMCD is concerned, the Fe L_{2,3} edge for the c(10×4)-FePc/Ag(110) phase has a distinctly metallic character, while the oxygen-saturated sample displays a pronounced molecular character. As expected, no significant changes have been observed in XAS and XMCD on dosing oxygen on the higher density oblique phase.¹

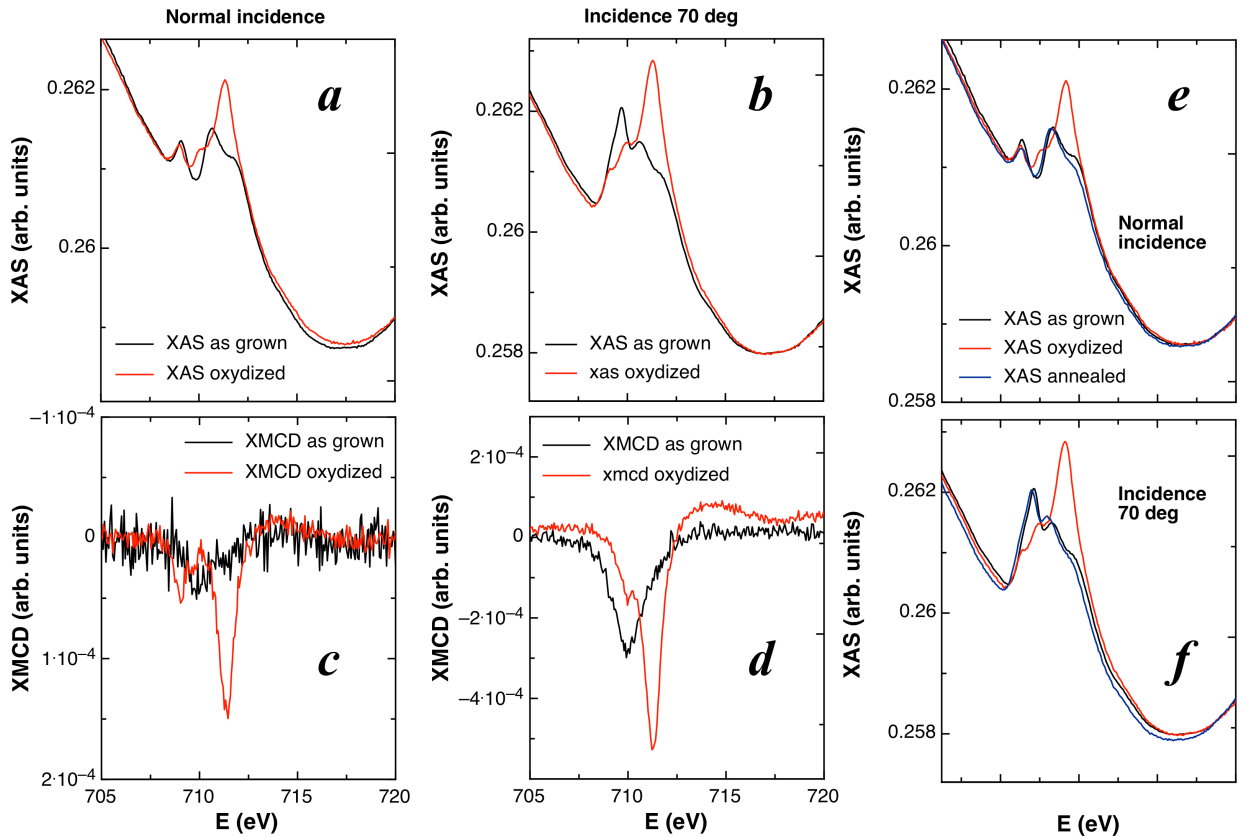


Figure. 2 XAS (panels a and b) and XMCD (panels c and d) spectra obtained on as-grown and oxidized c(10×4)-FePc/Ag(110) phase for normal (a and c) and 70° off-normal incidence (b and d). Panels e and f show the recovery of the electronic structure upon annealing.