Supplementary Material: Synchrotron Radiation Photoemission Spectroscopy of Oxygen Modified $CrCl_3$ Surface

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1. Material preparation:

Starting material details are provided in ref.[1]. Anhydrous chromium(III) chloride (Thermo Scientific) with a purity of 99% was used as a starting material. The powder was stored in an Ar-filled glovebox and XRD characterization is presented in ref.[2]. High-quality single crystals were grown by the self-transport technique, using commercial $CrCl_3$ powder, that was subjected to an oxygen purification process and then enclosed in a 20 cm quartz tube. The tube was placed in a three-zone furnace with a temperature gradient of about 25°C between the hot and cold zones. The hot end of the furnace was heated to 1000°C, held for an hour at a constant temperature, and then gradually cooled to 700°C at a cooling rate of 3°C/hour. Then the quartz tube was kept at 700°C temperature for 7 days. The grown crystals were stored in a glove box filled with argon gas. The samples were eventually cleaved both in vacuum as well as in air for better experimental comparison [3, 4]. Magnetic characterization is provided in ref.[3], Serri et al. demonstrated the larger antiferromagnetic interaction or anisotropy on exfoliated $CrCl_3$ ($\approx$ 10 nm thick) by X-ray magnetic circular dichroism (XMCD) and Magnetic force microscopy (MFM) than in bulk.

2. Cl 2p core level spectra taken at 300°C :

The Cl 2p spectra at 300°C consist of more components than at 150°C. As we mentioned in the main text, such extra components are related to the increasing number of vacancies per unit surface.

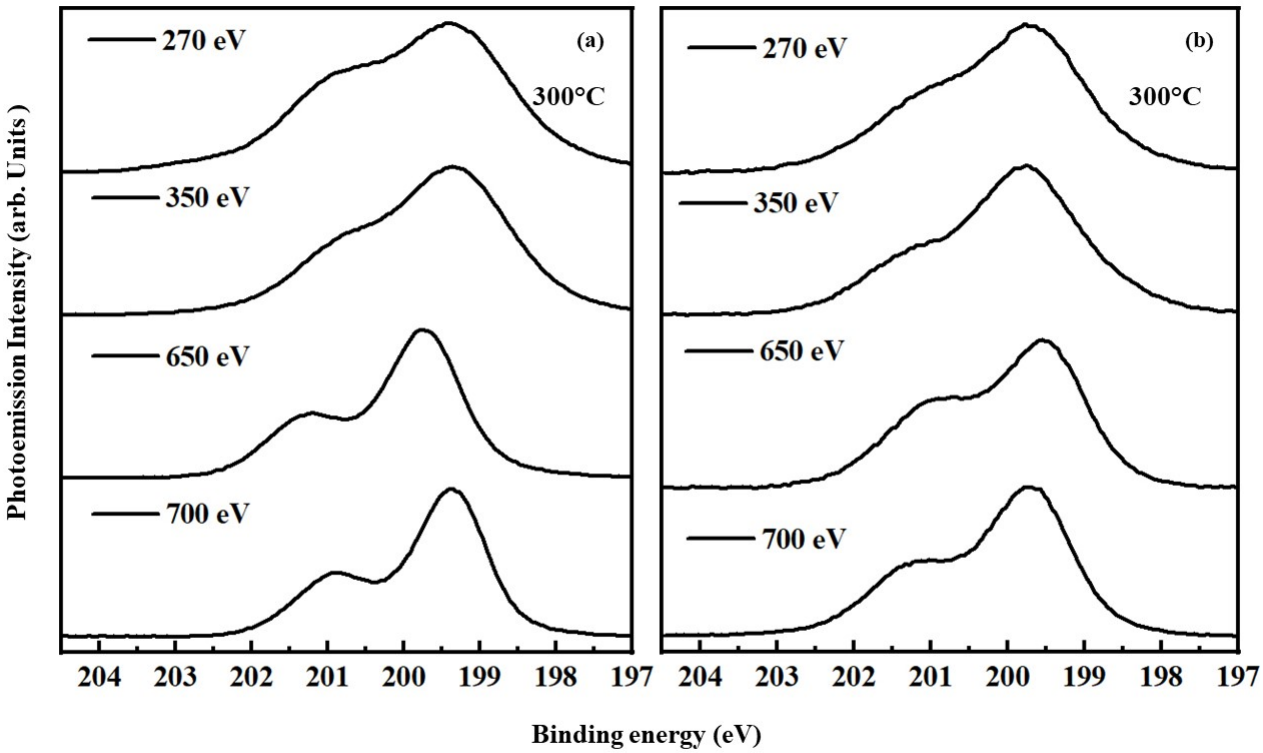

Figure SM1: Cl 2p core level spectra including data at 300 °C with different incident photon energies:(a) UHV cleaved spectra. (b) Air cleaved spectra.

3. Cr3p Spectra

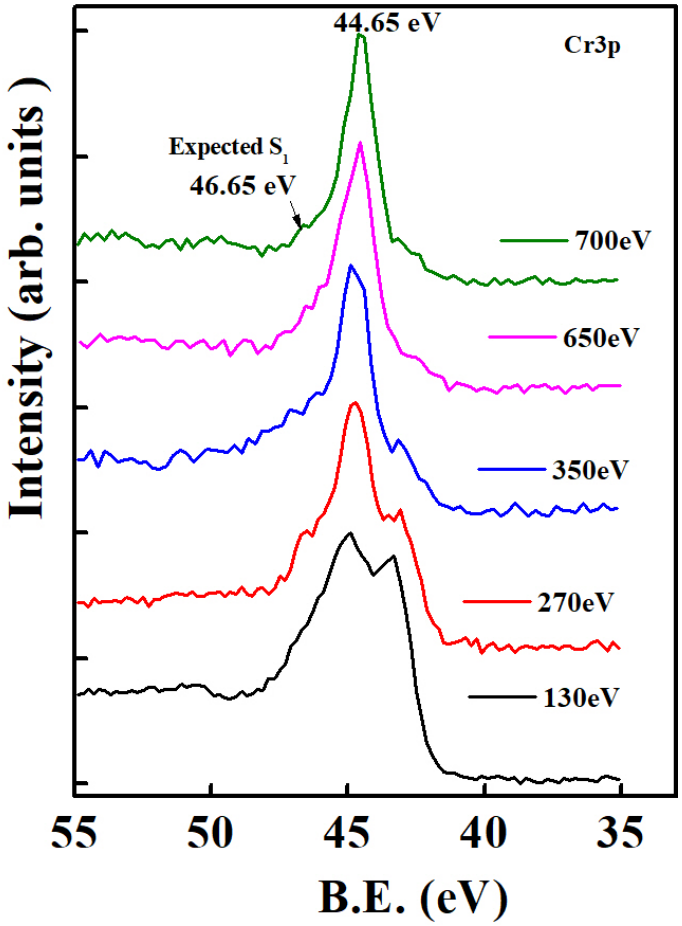

Figure SM2: Cr 3p core level spectra including satellite features at 150 °C with different incident photon energies.

4. Valence Band

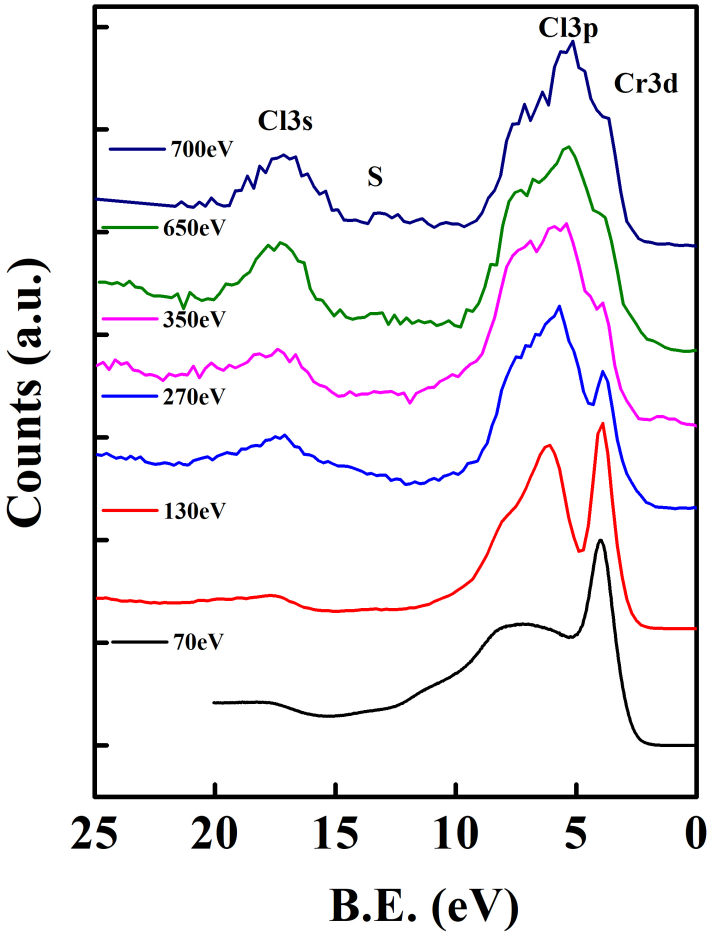

Figure SM3: VB spectra including satellite features at 150 °C.

Additional information on the correlation of the electronic structure can be obtained from the satellites energy as shown in Fig SM 2 and Fig SM3 respectively. The satellite features are mainly related to the metal-ligand hybridization and electron-electron interactions confirming the nature of $CrCl_3$ MH compound, while a trend towards charge transfer is observed on the surface sensitive spectra when the satellite is missing.

5. CTM4XAS (charge transfer multiplets for XAS/XPS) :

The CTM4XAS program is used to analyze the charge transfer effect for 2p and 3p core level spectra of transition metals recorded by X-ray absorption (XAS), X-ray photoemission (XPS), or electron energy loss spectroscopy (EELS). More details on the software can be found in ref [5]. We applied the theoretical model on Cr 2p and Cr 3p in the most probable valence state i.e. (Cr^{+3}). This calculation consists of set of appropriate parameters for charge

transfer, such as the crystal field (10Dq), the charge transfer energy (Δ), the average Coulomb interaction (U^{dd} - U^{pd}), and the energy splitting (e^g and T^{2g}). For Cr 2p,the Slater integral and spin- orbit coupling (SO) reduction were used as default (i.e., 100%), but for the Cr 3p core-level spectra, the value of the SO coupling reduction was kept at zero. Our spectra here consist of two principal components, one related to the multiplet effect (majority) and the other to charge transfer (minority). Consequently, two calculations were performed and compared to the experimental spectra. The linear combination of the two contributions as a whole is then shift rigidly to fit the experimental energy.

6. Corrected XPS atomic sensitivity for photon energy:

To determine the surface composition of the exfoliated $CrCl_3$ flakes, the atomic sensitivity factor correction was calculated using the following formula, taking into account the variable kinetic energy of the photoemitted electrons:

$$\frac{S_{Cr}}{S_{Cl}} = \left(\frac{\sigma_{Cr}}{\sigma_{Cl}}\right) * \left(\frac{K.E._{Cr}}{K.E._{Cl}}\right)^{0.66} [6] \tag{SM1}$$

For better understanding, we have presented a numerical example of the sensitivity correction at 700 eV photon energy:

$$\left(\frac{K.E._{Cr}}{K.E._{Cl}}\right)^{0.66} = \left(\frac{130}{500}\right)^{0.66} = 0.44 \tag{SM2}$$

So, the corrected sensitivity ratio is :

$$\frac{S_{Cr}}{S_{Cl}} = 0.44 * 3.1 = 1.38 \approx 1.4 \tag{SM3}$$

All atomic sensitivity ratios have been calculated in a similar way for other elements.

References

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