

NON-INNOCENT ROLE OF FLUORINE AS AN ELECTRON DONOR IN OXIDES

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Engineering of reducible oxides is generally focused on the cation sites. As such, anion doping remains an underutilized tool despite its unique potential in altering the defect chemistry and steering redox processes. In this contribution, we explore the possibilities offered by substitution on the anion site on the case of a

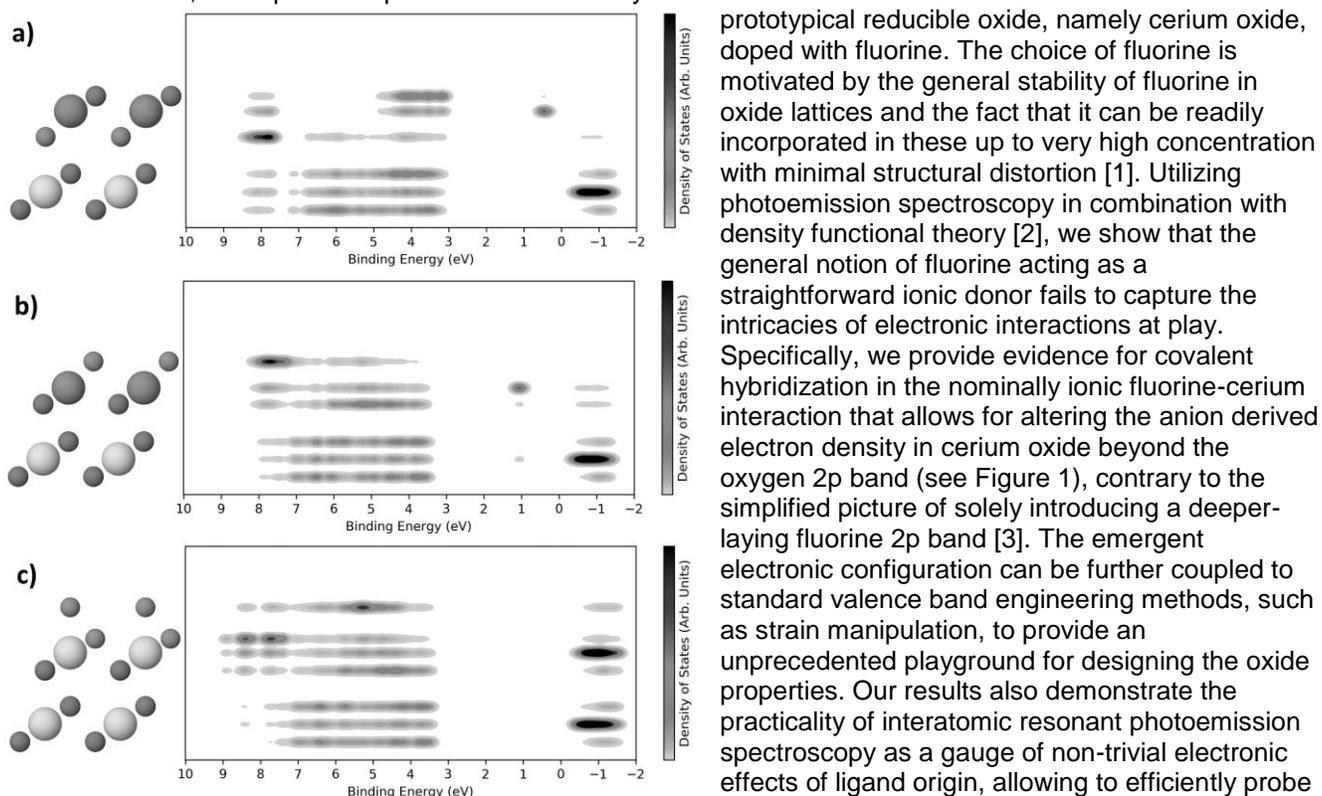


Figure 1 – Calculated projected densities of states of the top two layers of fluorine-doped ceria(111) slabs. Ce^{4+} and Ce^{3+} are represented by large light and dark grey spheres, respectively. The fluorine dopants are distributed as follows: a) in the sub-surface layer, b) in the surface layer, and c) in the surface layer and adsorbed on top. The PDOS are separated vertically. Each line of PDOS is corresponding to the contribution from atoms with which it is aligned in the structural model to the left of each plot. The darker the color, the higher the PDOS.

prototypical reducible oxide, namely cerium oxide, doped with fluorine. The choice of fluorine is motivated by the general stability of fluorine in oxide lattices and the fact that it can be readily incorporated in these up to very high concentration with minimal structural distortion [1]. Utilizing photoemission spectroscopy in combination with density functional theory [2], we show that the general notion of fluorine acting as a straightforward ionic donor fails to capture the intricacies of electronic interactions at play. Specifically, we provide evidence for covalent hybridization in the nominally ionic fluorine-cerium interaction that allows for altering the anion derived electron density in cerium oxide beyond the oxygen 2p band (see Figure 1), contrary to the simplified picture of solely introducing a deeper-laying fluorine 2p band [3]. The emergent electronic configuration can be further coupled to standard valence band engineering methods, such as strain manipulation, to provide an unprecedented playground for designing the oxide properties. Our results also demonstrate the practicality of interatomic resonant photoemission spectroscopy as a gauge of non-trivial electronic effects of ligand origin, allowing to efficiently probe the above-mentioned effects. We note that fluorine doping represents a complement to oxygen vacancy engineering and highlight the fact that, unlike oxygen vacancies, the electronic effects generated by fluorine can persist in an oxidizing environment. The latter represents an important contribution the electronic modification of mixed-anion oxides can provide to a breadth of fields, ranging from superoxide stabilization to resistive switching.

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[2] Duchoň T. et al., Physical Review B 95, 165124 (2017).

[3] Duchoň T. et al., Physical Chemistry Chemical Physics, submitted.