Limitations in Determining Oxidation States in Condensed Matter at the Sub-Nanometric Scale

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Oxidation state is a fundamental concept used to predict the behavior of compounds in chemical reactions[1,2]. Determining the oxidation state becomes even more important but complex when dealing with nanoclusters, where the properties of solid matter strongly depends on the number of atoms[3]. In the present work, we highlight the challenges in determining the oxidation state of size-selected clusters using synchrotron-based High-Resolution X-ray Photoelectron Spectroscopy, a technique commonly recognized for providing unambiguous fingerprints of the different oxidation state[4]. We investigated the oxidation of W_n (n=13, 25) nanoclusters deposited on epitaxial graphene at 40 K monitoring in-situ the evolution of W 4f spectral components growing at higher binding energies (BEs) compared to metallic W, attributed to the formation of tungsten oxide species. To shed light on the formation of these new components, we performed density functional theory simulations including calculations of core-electron BEs in the final-state approximation. The lack of crystalline order leads to a broad distribution of core levels that can be grouped in six different families, defined by the number of O atoms bonded to a specific W atom in the clusters. We found a strong linear relationship between valence, computed using Pauling's formula[5], and the calculated W $4f_{7/2}$ core levels. However, when the number of oxygen atoms bonded becomes large (n>3), the large variability of W-O interatomic distances causes the core levels of different families to overlap, making difficult to precisely assess W oxidation state, whose assignment should be reviewed in the case of nanostructures.

[1] Resta, R. *Charge state in transitions*, Nature 453, 735 (2008)
[2] Jablonka, K. M. et al., *Using collective knowledge to assign oxidation states of metal cations in metal–organic frameworks*, Nat. Chem. 13, 771–777 (2021)
[3] Tyo, E. et al., *Catalysis by clusters with precise numbers of atoms*, Nature Nanotech. 10, 577–588 (2015)
[4] Morn, R. et al. *The oxidation of Platinum under wet conditions observed by electrochemical X-ray Photoelectron Spectroscopy*, J. Am. Chem. Soc. 141, 6537-6544 (2019).
[5] Pauling, L. *Atomic radii and interatomic distances in metals*, J. Am. Chem. Soc. 69, 542-553 (1947).