Understanding X-ray spectroscopy of carbonaceous materials by combining Density Functional Theory with Machine Learning

Anja Aarva,[1,*] Volker L. Deringer,[2,3] Tomi Laurila,[1] and Miguel A. Caro[1,4]
[1]*Department of Electrical Engineering and Automation,*
School of Electrical Engineering, Aalto University, 02150 Espoo, Finland
[2]*Engineering Laboratory, University of Cambridge, Cambridge CB2 1PZ, United Kingdom*
[3]*Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom*
[4]*Department of Applied Physics, Aalto University, 02150 Espoo, Finland*

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Carbonaceous materials are known to have many desirable properties for biological applications. These materials are biocompatible and resistant to bacterial adhesion. Amorphous carbon (a-C), where carbon can be bonded in different ways (sp^1, sp^2 and sp^3 hybridizations) and form various kinds of ring structures [1–3], has been found to be especially interesting.

In practice carbon-based materials always contain elements other than carbon, such as hydrogen and oxygen, which can be present in elementary form or as part of different functional groups on the surface. Their presence can change the electrochemistry, electrical properties, and even mechanical properties of the films considerably [4–8]. Despite the efforts carried out in material characterization [2, 3, 5, 9–11] and studies about electrochemical behavior [4, 5, 9, 11, 12], clear understanding of the relationship between structural characteristics and properties of these materials is still lacking. This is due to highly convoluted data and the resulting difficulties in interpretation of the information obtained.

X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS), can be very powerful tools for analyzing surface characteristics [13–15]. However, interpretation of the experimental data is challenging as discussed above. A literature review about characterization of carbonaceous materials utilizing X-ray spectroscopy [5, 16–25] quickly reveals that the interpretations of the spectra are often controversial. Hence, a simulation tool that can recreate any spectrum from first principles would aid in deconvoluting the spectra remarkably.

In this study, density functional theory-based simulations are employed generate a-C the XAS spectra. We also calculate the Δ-Kohn-Sham (ΔKS) energy shifts which can be used to interpret XPS spectra [26, 27]. We utilize three different a-C models: 1) bulk sample created by geometry optimization [2], 2) surface reconstruction cleaved from the bulk, and 3) a large set of machine learning (ML) based a-C surfaces [28]. Further, graphene and diamond samples are included for reference. The surfaces are functionalized with hydrogen- and oxygen-containing groups: hydrogen (-H), oxygen (-O), hydroxyl (-OH) and carboxylic acid (-COOH). In order to dismantle the complexity of the amorphous samples, the structures are classified by employing ML clustering techniques. The clustering is based on k-medoids [29–31] and the similarity matrix is calculated using the Smooth Overlap of Atomic Positions (SOAP) [32] and ΔKS similarity kernels. We aim to use the calculated spectra in quantitative interpretation of experimental spectroscopy of carbonaceous materials in order to provide atomic-level chemical information about the functional groups present on the surfaces. This information will help us in finding connections between surface chemistry and electrochemical properties, for instance, thus pawing the way towards tailored carbonaceous nanomaterials.

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[*] anja.aarva@aalto.fi

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