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From the development of methods for fitting photoemission spectra to their practical applications: bridging the gap

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We compiled results from the implementation of the practical methods for backgrounds subtraction and the modelling of line-shape in photoemission spectra of catalysis and carbon nanostructures. The methods include the Shirley–Vegh–Salvi–Castle (SVSC) and slope for background subtraction, and the double Lorentzian line-shape for case when asymmetry was found in the spectra. To allow optimization of background and line-shape during the fitting, the *active*-approach was used. The advantages of the use of these practical methods under the *active*-approach were evidenced from the photoemission areas, allowing the assessment of the sulfidation extent $A_{Mo3d\text{-}MoS2}/A_{Mo3d\_Total}$ in the case of catalysis and from the graphitization index A_{sp^3}/A_{sp^2}, for carbon nanostructures.

1. Introduction

Shirley, slope and Tougaard background, Voigt, Doniach Sunjic and Double Lorentzian line-shapes are all well-known fitting tools for those who work in the improvement of methods for the analysis of photoemission spectra for accurate quantitative analysis. However, for the non-surface-analysis community, these methods are not fully understood or even known, and when a photoemission analysis is required, the spectra are left in the qualitative analysis phase or sometimes the spectra are even shown without performing a fitting. In conjunction, the lack of use or misuse of proper fitting tools leads to inadequate evidence of the surface chemistry of materials and their processing.

For this reason, the necessity of increasing the interaction between the surface and non-surface community and providing enough reproducible and comparative information is evident. This work converges with the collaboration of experts from both communities. Particularly in this work, experts in x-ray photoelectron spectroscopy (XPS) and experts in catalysis and carbon nanomaterials.

2. Fitting methods

Working on the side of the surface analysis area, we have published empirical methods for quantitative analysis encompassing the processing of the background and asymmetric line-shape. Both characteristics have been processed under the *active*-approach [1] in which, in contrast with the traditional (*static)* approach, the background is assessed during the optimization of the peak parameters, namely Gaussian, Lorentzian, area, and energy. One of the advantages of this approach is that it allows the incorporation of contributions from various types of backgrounds such as Shirley-Sherwood and slope (numerically equivalent to three-parameter Tougaard background) [2], whose origin is the intrinsic and extrinsic scattering, respectively. Focused on Shirley background, we implemented a variation called Shirley-Vegh-Salvi Castle (SVSC) named after the researchers that spotted that different chemical states produce different background strengths [3].

In the context of line-shape, our contribution has been the Double-Lorentzian line shape, which is useful model the asymmetry. One example of this, are transition metals where the positive core hole interaction with the valence band electrons gives place to a tail in the spectrum at high binding energies. In contrast with Doniach-Sunjic, Double Lorentzian is integrable and thus useful for quantitative analysis.

The backgrounds SVSC, slope, Shirley-Sherwood and the Double Lorentzian line-shape, are processed under the active-approach in the software AAnalyzer®. Different combinations of these tools have been implemented in catalysis and carbon nanostructures applications, employed on a case-by-case basis.

3. Implementation of fitting methods

3.1 Catalysis

In the catalysis area, particularly in sulfide catalysts of Mo promoted by Co or Ni and supported on γ-alumina, it was possible to accurately calculate the sulfidation extent expressed by the XPS area ratio $A_{Mo3d\text{-}MoS2}/A_{Mo3d\_Total}$. We deal with regions in which there are components of different core levels strongly overlapped, namely Mo 3d-S 2s and S 2p–Si 2p, where making a clear distinction between the components related with each core level is crucial. Under these circumstances, the relevance of a method that allows to distinguish between the contributions to the background arising from different components (i.e., chemical states) seems evident. Using SVSC under the *active*-approach, we distinguished between these contributions obtaining the relative percentage (% rel.) of each species present in Mo and S in the catalyst CoMoAl from the resulting spectra fitting. The accuracy of the method was proved through the stoichiometry assessment of the catalyst MoS_2 and the base Al_2O_3, and the results were compared with those obtained using the *static*-approach.

3.2 Carbon nanostructures

Another cutting-edge topic is based on carbon nanostructures -particularly carbon nano-onions (CNOs)- due to their potential use in biomedicine, energy conversion, and environmental applications. Towards their synthesis, a full understanding of the growth mechanism is imperative to control the desirable characteristics on them. In this case, we are exploring the characteristics of the CNOs synthesized through high-temperature nano-diamond annealing. The C 1s spectra was analyzed using the double Lorentzian line-shape to model the asymmetric feature of the sp^2 component, as expected due to the semi-metallic nature of this component. The sp^3 and C-O peaks were fitted with the convolution of Gaussian and Lorentzian (Voigt) distributions. A good indicator of the conversion effectivity from nano-diamonds to carbon nano-onions is the graphitization index, which was calculated from the photoemission peak areas ratio sp^3 to sp^2. For the case of O1s, a component from an indium native oxide from the substrate where the sample was placed, arises. Here, the necessity to discern between the background originated from different chemical species, principally those that do not correspond to the environment of the sample, is evident. This picture is solved using the SVSC background, allowing to obtain accurate relative contributions from the oxygen components related to the sample.

4. Conclusions

The process for quantitative analysis of surfaces through photoemission spectra is not a straightforward task and it requires knowledge of the proper methods for spectra fitting according to the physical and chemical characteristics of spectra and according to the constituent elements as well. We have spotted a wide gap between the surface analysis community and those dedicated to the development of materials and their application. Through this work and the collaborative participation in those areas we expect to shorten that gap through the contribution on the improvement of the analysis, and therefore, towards an improvement on the understanding of the chemistry of materials surfaces and their processing.

5. References

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