Coordination-resolved electron spectrometrics

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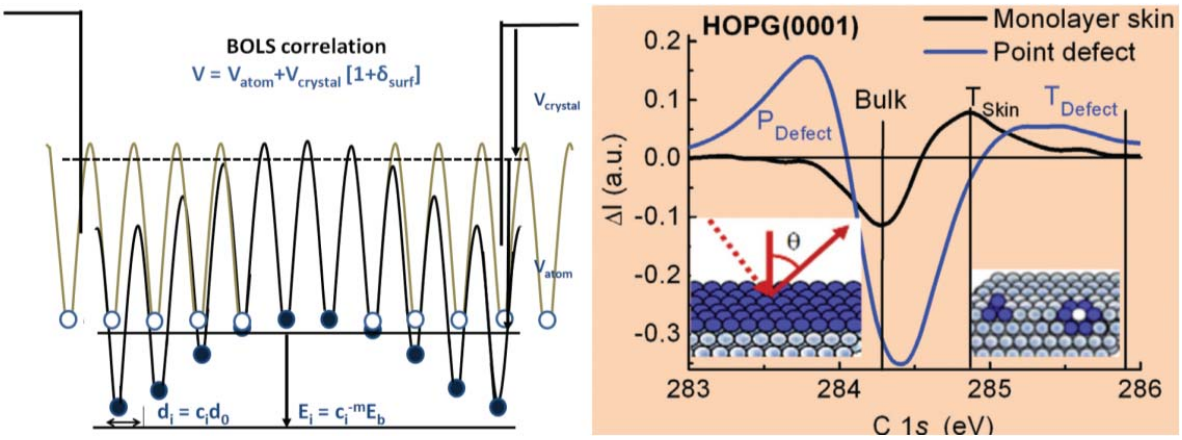
(42,200 Words, 434 Refs, 30 Eqs, 22 Tables; 60 Figures in separate files to be linked)

Electron Spectrometrics resolves atomistic, dynamic, local, and quantitative information of bond length, bond energy, charge quantum entrapment and polarization, energy density and atomic cohesive energy pertaining to adatoms, point defects, monolayer skins, terrace edges, impurities, interfaces, atomic clusters, nanograins, and the joint effect of under- and hetero-coordination. This strategy may lead to a subject area of coordination-resolved bond-electron-phonon-photon Spectrometrics



Keywords: adatom, point defect, kink edge, atomic chain, nanoribbon, solid skin, impurity, interface, alloy, nanostructure, entrapment, polarization, localization, work function, electroaffinity, Hamiltonian, crystal potential, potential screening, band gap, size emergence, photocatalysis, toxity, dilute magnetism, Dirac-Fermi polaron, hydrophobicity, plasmonics, STSM/S, UPS, XPS, AES, APECS, ZPS.

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Abstract

Formation of bond between hetero-coordinated atoms and relaxation of bond between undercoordinated atoms and the associated electron entrapment and polarization mediate the performance of a substance at these irregularly-(or ill- for short) coordinated atomic sites. However, resolving such atomistic, dynamic, local, and quantitative information is beyond the scope of available methods. We report herewith the recent progress in coping with this challenge in terms of “atomistic electron spectrometrics”. Strategies include the bond order-length-strength correlation, nonbonding electron polarization, and local bond average (BOLS-NEP-LBA) notation and the theory-enabled zone-resolved photoelectron spectroscopy (ZPS). Strategies have enabled verification of theoretical predictions regarding the undercoordination effect on the electron energetics of adatoms, atomic clusters, kink edges, point defects, monolayer skins, nanocrystals, the hetero-coordination effect on interfaces and chemisorbed skins, and the coupling effect of ill-coordination on properties of defected TiO_2 and ZnO nanocrystals. Practice has resulted in clarification, correlation, formulation of electron binding energy with quantification of the local bond length, bond energy, energy density, atomic cohesive energy, and the energy levels of an isolated atom and their coordination–resolved shifts for these ill-coordinated systems. Perturbation to the Hamiltonian by bond contraction, bond nature alteration, and electron polarization dictates intrinsically the energy shift, of which the extent is proportional to the local bond energy at equilibrium. Polarization of the nonbonding states by the densely locally entrapped bonding electrons or by nonbonding lone pair screens-and-splits the crystal potential, which in turn offsets the entrapped states negatively. Most strikingly, entrapment dominance entitles Pt adatom and CuPd alloy acceptor-type catalysts while polarization dominance makes Rh adatom and AgPd alloy donor-type catalysts. Isolation and polarization of the dangling σ bond electrons by the entrapped bonding electrons create Dirac-Fermi polarons surrounding graphite atomic vacancies and graphene zigzag edges. Extension of the electron spectrometrics to the coordination-resolved phonon and photon relaxation dynamics of a substance under multifield would be even more appealing, fascinating, promising, and rewarding.