Capturing Electrons in Motion: Time-Resolved X-ray Photoemission Spectroscopy for Unraveling Charge Transfer Dynamics

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The study of excitations and their dynamics is of great significance in nature and applied technologies. A multitude of fundamental aspects of our world, including chemical processes and transport phenomena, are based on dynamic reaction chains. At the core of numerous emerging concepts concerning the conversion of sunlight into fuel and electricity are interfacial processes that necessitate an optimised, concerted flow of charge and energy at the molecular level. In order to gain a comprehensive understanding of the fundamental dynamics and scaling laws that enable molecular, interfacial, and macroscopic charge and energy transport, it is necessary to connect processes that evolve on spatial and temporal scales spanning orders of magnitude. As interface properties undergo changes during operation, for instance, under the influence of applied electrochemical stimulus or external photoexcitation, and due to the coexistence and competition of multiple bulk and interface processes, detailed in operando characterisation is imperative. Concurrently, interfaces present a challenge in technologies that rely on charge transfer processes. These processes require sophisticated experimental probes to elucidate the underlying physical and chemical mechanisms. In this context, soft X-ray spectroscopy techniques have emerged as a particularly effective means of monitoring the electronic and chemical states of matter, exhibiting the requisite elemental site-specificity and chemical sensitivity to facilitate rigorous testing and enhancement of our fundamental understanding of interfacial chemistry and photophysics in complex systems. Here we present an overview of the diverse experiments conducted in recent years using synchrotron radiation sources and free-electron lasers. The results of these experiments demonstrate that time-resolved XPS provides a unique opportunity to investigate the photo-induced interfacial charge transfer dynamics with exceptional site-specificity and temporal resolution in the picosecond to femtosecond regime across a range of sample systems. Access to the element and chemically specific core-levels provides a unique perspective of the dynamic charge evolution in the direct vicinity of the atom from which the core electron is emitted. This unique capability will enable previously unattainable insights into underlying microscopic mechanisms and thus pave the way for a better understanding of emerging photovoltaic and photocatalytic frameworks.

Keywords: Charge transfer dynamics, Time-resolved XPS, Synchrotron radiation, Free-electron laser (FEL), Energy conversion

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