In-situ Electronic Structure Study Capability with Photon-in/Photon-out Soft-X-Ray Spectroscopy

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We have built the chemical cells for *in-situ* photon-in/photon-out soft-x-ray spectroscopy studies of various systems on beamline 7.0 at ALS to demonstrate a unique way to handle the real systems (gas and liquid phases in ambient pressure and temperature) under UHV experimental chamber for electronic structure studies.

Soft-x-rays are ideal for studying electron transitions between a localized core state and a valence/conduction state; thus soft-x-ray spectroscopy has unique features that make it a powerful tool to extract information about electronic properties. In general, soft-x-ray absorption spectroscopy (XAS) probes the local ***unoccupied*** electronic structure; soft-x-ray emission spectroscopy (XES) probes the local ***occupied*** electronic structure; and resonant inelastic soft-x-ray scattering (RIXS) probes the low-energy excitations, such as charge transfer, proton energy transfer etc.

Hydrogen storage is the most challenging task for the hydrogen economy. Solid-state hydrogen storage by chemisorption and/or physisorption is attractive from a technology point of view, but it has encountered tremendous challenges in terms of storage capacity and kinetics. We have studied the electronic properties of hydrogen storage materials to gain insight into chemisorption and physisorption mechanism for hydrogen storage, e.g. carbon nanostructures and metal organic framework.

We have used also photon-in/photon-out soft-x-ray spectroscopy to study the electronic states of liquid water mixed with the simplest type of alcohol, methanol. The ability to determine the mixing properties of different liquids is of great importance: many vital chemical and biological processes take place in aqueous solutions. The emission spectra obtained in this study reveal that the water and alcohol molecules in solution form complex hydrogen-bonded networks. The results illustrate the technique's potential to provide new information about the microscopic origins of the properties of liquids and solutions.

The growth of cobalt nanocrystals suspended in liquid with diameters of nanometers has also been investigated using in-situ x-ray spectroscopy. A sharp absorption peak associated with the ligand molecules is found to increase in intensity upon reducing the nanocrystal size. X-ray Raman features due to d-d and charge-transfer electronic excitations of ligand molecules attached to nanocrystals surface are identified. The study reveals the defined local symmetry for the surface of ε-Co phase nanocrystals, which is originated from a dynamic interaction between Co nanocrystals and surfactant + solvent molecules.