

CHEMICAL



Here, outstanding chemical research is introduced as major achievements at SPring-8. The research areas include programmed arraying of metal complexes in supramolecular systems, Compton scattering of electrons in nanoconfined water, one-dimensional crystals inside carbon nanotubes, a new class of aluminum-based interstitial hydrides as a hydrogen storage material for fuel cell vehicles, and synchrotron infrared spectroscopy of water. Further remarkable research results achieved by applying SACLA (XFEL) to subjects concerning sequential multiphoton multiple ionization of atoms and attosecond X-ray interaction with core-hole atoms are also introduced.

Supramolecular systems, such as macrocyclic, tetrapyrroles have been studied with the aim of developing functionalized molecular assemblies due to high expectations from their photophysical, electrochemical, magnetic, and catalytic properties. X-ray crystal structure analyses of a facially stacked ionic complex between cyclic tetrapyrroles, and a fourfold rotaxane were performed at the single crystal structure analysis beamline BL02B1. Emergent functions related to nanomagnetism, conductivity, or catalysis via intermolecular electronic communications among the stacked metal complexes should be developed.

Water molecules form a tetrahedral network in ice, and a distorted, slowly changing tetrahedral network in bulk water. The proton in a water molecule exists within a covalent bond in a nearly harmonic well. Since the potential well is due to the distribution of electrons, the valence electrons in nanoconfined water should be distributed very differently from the case of an individual molecule. This conjecture was tested using X-ray Compton scattering. Measurements of the momentum distribution of electrons at the high energy inelastic scattering beamline BL08W indicate that the ground states of electrons and protons in nanoconfined water qualitatively differ from the typical weakly interacting molecules.

SCIENCE

A physical problem found in free-standing 1D crystals is the metal-insulator transition, which is referred to as the Peierls transition. Suppression of the Peierls transition was tested by encapsulation of 1D crystals inside the cylindrical nanocavity of carbon nanotubes (CNTs), with the aim of preserving an enclosed 1D crystal as a 1D quantum conductor. The formation of unprecedented 1D crystals of elemental sulfur inside single-walled CNTs and double-walled CNTs was demonstrated at the powder diffraction beamline BL02B2. The most striking achievement in this study is that the 1D sulfur crystals exhibit a metallic character under ambient pressure, whereas bulk sulfur requires ultra-high pressures to become metallic.

To realize a hydrogen-based economy, safe and efficient hydrogen storage is a key technological challenge. For fuel cell vehicle applications, hydrogen storage materials should be mainly composed of light elements ($Z \leq 20$) to achieve a high gravimetric hydrogen capacity. Interstitial hydrides are favorable as hydrogen storage materials because the hydrogenation and dehydrogenation reactions should proceed simply, and their thermodynamic properties are tunable by the addition of other elements into the alloy. The synthesis of a new aluminum-based interstitial hydride, Al_2CuH_x , was achieved at the JAEA materials science beamline BL14B1. This finding may help to expand the diversity of aluminum-based hydrides and accelerate the development of practical hydrogen-storage materials.

Polymers chemically grafted to the surface of substrates, which are known as polymer brushes, are often used to modify surface properties such as hydrophilicity or hydrophobicity, friction, and adhesiveness. Superhydrophilic surfaces are particularly attractive due to their potential applications for self-cleaning, antifogging, antifouling, and water lubrication systems. The wettability of water on cationic poly(2-(methacryloyloxy) ethyl trimethylammonium chloride) (PMTAC) brush prepared on a silicon wafer was examined by synchrotron infrared (IR) spectroscopy at the infrared materials science beamline BL43IR. The structure of water existing under and even outside the droplet prevents the complete wetting of the highly hydrophilic polyelectrolyte brushes.

Since the detection of anomalous signals from naturally occurring sulfur atoms in a protein at an XFEL photon energy of 7.3 keV, which is far from the sulfur *K*-edge (~ 2.5 keV), the multiphoton ionization of the deep inner-shells and cascade decays has been investigated to reveal the pathways of multiphoton multiple ionization due to the newly developed XFEL at SACLA. Ionization of a heavy atom, Xe, progresses rapidly by repetition of the inner-shell photoionization and subsequent Auger/Koster-Kronig decay within the XFEL's short pulse duration. Understanding the ionization dynamics by high-intensity hard-X-ray beams may provide useful input for future molecular imaging experiments.

A similar phenomenon was observed in the photoabsorption processes of Kr gas. In addition to being of basic interest in the field of X-ray nonlinear optics, the X-ray interaction with core-hole atoms is very important for analysis of XFEL experiments. To investigate the X-ray interaction with the core-hole states, X-ray fluorescence from Kr atoms illuminated by the focused XFEL beam of SACLA was measured. A double core hole (DCH) is created, and the usefulness of DCH has been discussed to determine the pulse duration in the sub-10-femtosecond range.

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