SUMMARY OF Ph.D. DISSERTATION

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Title

Investigation of the Electronic States of Organic Semiconductor Molecules, Semiconductor Surfaces and Decorated Nanostructured Surfaces by Photoemission Spectroscopy

Abstract

Organic semiconductors with π-conjugated molecular system play key roles as functional nanomaterials for photonic and electronic devices. Nanostructures designed finely by the molecular clusters and nanoparticles are also nanometer-scaled functional units attracting a lot of attention as advanced nanomaterials in the next generation because they exhibit novel optical, catalytic, and magnetic properties. The functionality in these nanostructured materials depends strongly on the behavior of electrons. The investigation on the electronic states of organic semiconductors and nanostructured materials enables us to understand the intrinsic mechanism of their advanced functionality. For the fundamental understanding of the electronic properties of the nanostructured materials, however, it is indispensable to develop a new methodology for measuring the electronic states with a high sensitivity as well as that for producing well designed nanostructures. In this thesis, the investigation on the static and dynamic electronic states are described in two viewpoints of (1) organic semiconductor molecules by anion photoelectron spectroscopy, and of (2) semiconductor surfaces and decorated nanostructured surfaces by two-photon photoemission (2PPE) spectroscopy. In particular, the latter reveals both occupied and unoccupied states of the nanostructured surfaces simultaneously because its photoemission process goes through unoccupied excited states.

In Chapter 1, the research background and the content of each chapter in this thesis are described, and in the following Chapter 2, the experimental methods of ultraviolet photoemission spectroscopy (UPS) and 2PPE measurements, and the fabrication of nanoparticles are described.

In Chapter 3, the features of anion photoelectron spectra for various oligophenyls and their adiabatic electron affinities are described.

In Chapter 4, 2PPE spectra were measured for a hydrogen-terminated Si(111) surface [H-Si(111)], where dangling bonds are terminated by hydrogen atoms and the H-Si(111) surface provides an ideal supporting substrate for nanometer-scaled functional units. In addition to the electronic states investigated previously by UPS and inverse photoemission spectroscopy (IPES), the surface resonance and the image-potential state on H-Si(111) were revealed for the first time.

In Chapter 5, 2PPE spectra were measured for Ag nanoparticles (NPs) on H-Si(111), in which Ag NPs were monodispersed on a substrate surface. For the deposition of Ag NPs, a new deposition method was established for size-selected ligand-free metal NPs. For 2PPE measurements, the influence of the local surface plasmon resonance (LSPR) on the photoemission process was measured by using laser excitation tuned to LSPR of Ag NPs. By changing the coverage of Ag NPs on H-Si(111), the enhanced photoemission from H-Si(111) substrate surface was observed at low coverage of 0.05 MLE, while photoemission from Ag NPs was enhanced at higher coverage. Combined with the polarization dependence, it was experimentally demonstrated that the near-field light emitted from Ag NPs via LSPR is significantly concerned in the enhanced photoemission process.

In Chapter 6, the results in this thesis are summarized.