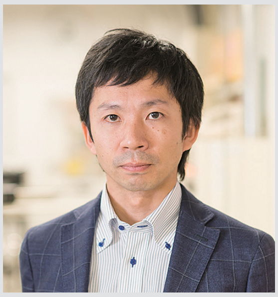
Electronic Property of Functional Organic Materials

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



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Professional Employment

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2009	Visiting Associate Professor, Institute for Molecular Science
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Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However, the mechanisms and the origin of various device characteristics are still under debate. Scientific discussions have been redundant because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is essential to investigate precisely the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the electronic states is very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

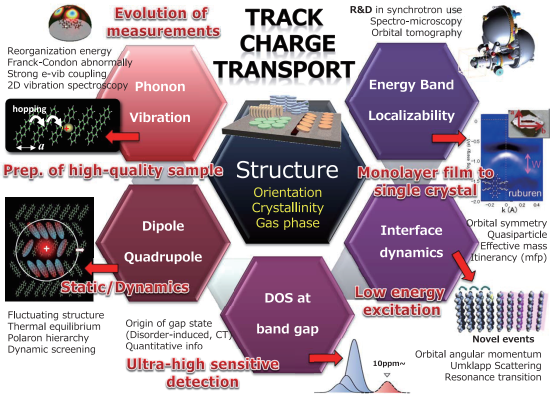

Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- Y. Nakayama, S. Kera and N. Ueno, *J. Mater. Chem. C* **8**, 9090–9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
- S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. Surface Characterization of 2D Covalent Organic Frameworks[1)]

Two-dimensional (2D) covalent organic frameworks (COFs) fabricated through on-surface synthesis were investigated as a honeycomb nanopore template for the growth of 3d-transition-metal nanoclusters (NCs) with a size of 2 nm on a metallic substrate. The evolution of these NCs and their electronic characteristics were studied employing scanning tunneling microscopy/spectroscopy (STM/STS), angle-resolved ultraviolet photoelectron spectroscopy (ARUPS), and X-ray photoelectron spectroscopy (XPS) under an ultrahigh-vacuum (UHV) condition at room temperature. The 2D COFs were synthesized on Cu(111) substrate utilizing 1,3,5-tris(4-bromophenyl) benzene (TBB) precursors, which engendered a honeycomb nanopore array of approximately 2 nm in size. In contrast to the behavior observed in the Co/Cu(111) system producing bilayer-stacking nanoclusters measuring 10–20 nm, STM imaging of Co/COFs/Cu(111) revealed the growth of Co NCs of approximately 1.5 nm within a single COF nanopore. This growth occurred without forming a monolayer film beneath the COFs, providing direct evidence that the 2D COFs on Cu(111) can effectively entrap Co atoms within the nanopore, giving rise to Co NCs (Figure 2). The spectroscopy measurements, STS, ARUPS, and XPS, confirmed the different local densities of states for Co NCs and COFs, corroborating the coexistence of Co NCs and COFs on the surface.

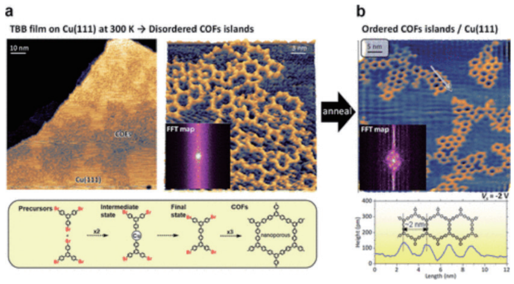

Figure 2. (a) UHV-STM topographic images obtained on the surface of TBB film grown on Cu(111) at 300 K with a schematic model of honeycomb lattice formation *via* the Ullman reaction. (b) STM topographic image of the ordered 2D-COFs islands on Cu(111) after the thermal annealing in UHV. The inset in the bottom panels denotes the FFT map. The figure is after ref 1).

2. Electronic Structure and Many-Body Interactions of Low-Mobility Carriers in Perylene Diimide Derivative[2)]

Despite the rapid progresses in the field of organic semiconductors, aided by the development of high-mobility organic materials, their high carrier mobilities are often unipolar, being sufficiently high only for either electrons or holes. Yet, the basic mechanisms underlying such significant mobility asymmetry largely remains elusive. We perform the ARUPS to reveal the occupied band structures and the many-body interactions for low-mobility hole carriers in a typical n-type semiconductor perylene diimide derivative (PTCDI-C8). The 50-nm thick PTCDI-C8 film consists of many needle-like crystallites, each of which are several hundreds of nanometres along its long axis by AFM, where the long axis of the crystallites was determined to be the crystallographic π-π stacking direction. The band dispersion is observed clearly even for random orientation of the molecular plane by thanks to large anisotropic nature of the BZ structure. The observed HOMO band by ARUPS exhibits strong renormalization to the calculated DFT results based on the single-particle electronic state (Figure 3). The analysis including many-body interactions elucidate that the significant mass enhancement can be understood in terms of strong charge–phonon coupling, leading to an important mechanism of polaron band transport of low intrinsic carrier mobility in organic semiconductor.

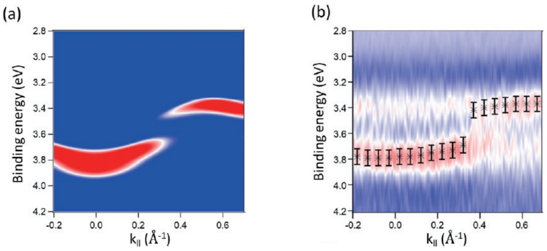

Figure 3. Second derivative plot of a simulated HOMO band dispersion with hole-intramolecular vibration coupling (a) and the observed HOMO by HeII ARUPS (b).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope are developing at BL6U.[3)] The perspectives required for future light-source facility have been discussed with communities.[4)]

References

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