Kyushu Synchrotron Light Research Center

（Form: No.5）

Experiment Report for Prefectural Beamline

Proposal no. ： 1711115S
Beamline no.： BL12
Report date ： 03/22/2018

Electronic states of Mg, Sn-doped Ga_2O_3 thin films on ultra-smooth sapphire substrates using a NiO seed layer

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１． Summary（Note: Please include conclusions）

Hybrid materials composed of metal nanoparticles and metal-organic frameworks (MOFs) have attracted attention for various applications because of the synergistic functionality between their constituent materials. However, the charge transfer mechanism is still ambiguous. Here, we studied Pd nanocubes supported by copper(II) 1, 3, 5-benzenetricarboxylate (HKUST-1), denoted Pd@HKUST-1, with the significantly enhanced hydrogen storage capacity. We investigated Cu *L* edge and O *K* edge and the role of oxygen in charge transfer behavior was also confirmed experimentally. This result is beneficial to reveal a charge transfer mechanism from the Pd bands to the Cu-O hybridization bands of HKUST-1 at the Pd/HKUST-1 interface.

２． Purpose of experiment and background

In the previous work, we used hard X-ray photoelectron spectroscopy (HAXPES) at SPring-8 to study the valence band of Pd@HKUST-1 consisting of Pd nanocubes and HKUST-1 MOF compared to Pd nanocubes or

HKUST-1. After HAXPES measurements, Cu in HKUST-1 shows feature of Cu^{2+} ions. While in Pd@HKUST-1, Cu shows features of both Cu^{2+} and Cu^{+} ions in HKUST-1. This may be related to oxygen bands. We also used a density of states (DOS) calculation to predict that oxygen also takes part in the charge transfer behavior. To obtain the clear relation between copper and oxygen, we measured the NEXAFS of the Cu L edge and O K edge. Because Cu is directly binding to O atoms, here we chose CuO and Cu_2O as references.

３．Experimental（Note: Description of sample， method of experiment and analysis, etc.）

The NEXAFS data of Pd@HKUST-1 and HKUST-1 were recorded at BL12, SAGA Light Source. Both a total electron yield and a fluorescence yield were collected. The total electron yield mode can probe the materials with the order of several nanometers beneficial for the study of nanomaterials. While the probing depth for fluorescence measurements of the order of 100 nm for the fluorescence X-rays, used for the bulk references. The overall resolution is about 0.1 eV.

４．Results and Discussions

To reveal the clear relation between copper and oxygen, we measured the NEXAFS of the Cu *L* edge and O *K* edge for Pd@HKUST-1 and HKUST-1. The Cu *L* edge was obtained while Cu 2*p* electrons absorbed the photon energy and then excited into unoccupied 3*d* states. At the O *K* edge, the 1*s* electrons were excited to empty 2*p* states. In Fig. 1(a), the Cu L_3 and L_2 peaks are shifted to the higher energy comparing with HKUST-1, which have the same peak position with CuO (Fig.1 (b)). That is consistent with the previous report of HKUST-1 with bivalent Cu^{2+}.[2] The similarity to CuO with the typical octahedron structure results from the local atomic structure around Cu inside of HKUST-1. The Cu and O atoms construct two connected distorted octahedral. While HKUST-1 is covered to Pd nanocube in the structure, only the interfacial Cu^{2+} reduced to Cu^{+}. There are coexist of Cu^{2+} and Cu^{+} in Pd@HKUST-1, leading to the peak position between the peak of Cu^{2+} and that of Cu^{+}. In Fig. 1 (c), both spectra contains two regions, the sharp π^* region and the broad σ^* region. When we consider the local atomic structure around O, the π^* region originates from electrons excited from O 2*p* hybridized to Cu 3*d* and the σ^* region arises from electrons excited from O 2*p* hybridized to Cu *sp* and also C *sp*. Based on the previous research,[3-6] the peaks were distinguished and marks in gray arrows for the peaks related to C *sp* and in red arrows for those related to Cu 4*sp*. Comparing with the HKUST-1 spectrum, the peak intensity of Pd@HKUST-1 was increased clearly. This suggests that there are more electrons on the oxygen bands. The O K edge of Pd@HKUST-1 was shifted to higher energy side around 532 eV and 545 eV marked in red arrow, which is related to the Cu 3*d* - O 2*p* hybridization and Cu 4*sp* - O 2*p* hybridization, respectively. Comparing with the CuO and Cu_2O references (Fig. 1 (d)), the peak position of HKUST-1 O *K* edge is different from that of CuO because O connects to not only Cu but also C. The energy value of the first peak shifts by 0.4 eV to the higher energy side, much less than the copper oxide bulk. This is because of the amount of the interfacial oxygen binding to Cu. That means, inside of Pd@HKUST-1, interfacial HKUST-1 accepts electrons from Pd 4*d*, and Cu-O hybridization bands are filled. In case of atomic structure of HKUST-1, there are probably two kinds of atomic connection at the interface, Pd-Cu-O and Pd-O-Cu. This means there are Cu-O features and/or Pd-O features may appear in a NEXAFS spectra. Then we also measured the O *K* edge of the standard PdO reference, as the same as the calculated result.[7] The O *K* edge NEXAFS spectra of Pd@HKUST-1 shows only the features of Cu-O, without the features of Pd-O. All the NEXAFS spectra confirmed the involvement of oxygen in the charge transfer behavior, consistent with the calculated results from HAXPES and predicted by the DOS calculation above.

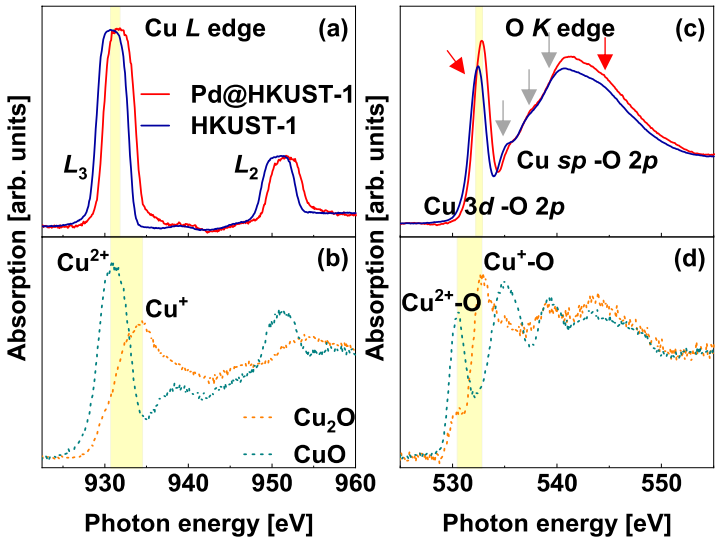

Fig. 1 (a) Cu *L* edge and (c) O *K* edge NEXAFS spectra of HKUST-1 and Pd@HKUST-1.
(b) Cu *L* edge and (d) O *K* edge NEXAFS spectra of CuO and Cu_2O.

５． Future issues

Understanding the link between the charge transfer behavior and chemical or physical properties will allow as to construct new hybrid materials by engineering their electronic structure. This will drive progress in the creation of new functional materials for hydrogen storage, catalysis and other application.

６． References

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７． Publications, patents （Note: Typical deliverables related to this proposal.）

Not yet.

８． Keywords （Note: 2-3 words about samples and experimental methods.）

Metal organic framework, Electronic strucute, Oxygen

９． About the publication of research results

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