

Probing the Electronic Structure of BiVO₄ Coated ZnO Nanodendrite Core-Shell Nanocomposite Using X-ray Spectroscopic and Spatially Resolved Scanning Transmission X-ray Microscopy Studies

Mandar M. Shirolkar¹, Yu-Fu Wang¹, Yu Cheng Shao¹, Kuan-Hung Chen¹, Hsiao-Tsu Wang², Xian-Sheng Qiu¹, Jih-Sheng Yang³, Jih-Jen Wu³, Jau-Wern Chiou⁴, Takuji Ohgashi⁵, Nobuhiro Kosugi⁵ and Way-Faung Pong^{1*}

¹. Department of Physics, Tamkang University, Tamsui 251, Taiwan.

². Department of Physics, National Tsing Hua University, Hsinchu, Taiwan.

³. Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan.

⁴. Department of Applied Physics, National University of Kaohsiung, Kaohsiung 811, Taiwan.

⁵. Institute for Molecular Science, Okazaki 444-8585, Japan.

* Corresponding Author: wfpong@mail.tku.edu.tw

Our mother nature is serving as a persuasive source of innovations for the mankind. The photoelectrochemical (PEC) is one such promising technology route for water splitting for transforming solar energy to chemical energy and mimicking nature's smart technology. Since the discovery of water splitting effect on TiO₂ in the beginning of the 1970s, the worldwide efforts are endeavoring to develop efficient PEC featured semiconducting material/s for solar water splitting, which can unveil the ability to harness visible light, appropriate band alignment with water redox potentials and which are stable in the presence of water. From the point of view of water stability of PEC materials, oxides are generally more stable than sulfides and nitrides or any other compound semiconductors. Nevertheless, in most of the oxide semiconductors, the valence band is formed predominantly by oxygen 2p states that are centered at +2.94 V vs standard hydrogen electrode (SHE), while the O₂/H₂O redox potential is at +1.23 V vs SHE. Thus, the number of suitable oxide semiconductors for PEC operations are limited and careful materials selection scheme is required for efficient PEC properties [1].

In that perspective, recently, it has been reported that ZnO nanodendrites (NDs) coated with BiVO₄ nanolayers core-shell nanocomposite thin film structure forms a multiple-level hierarchical core-shell nanocomposite thin film structure, which is remarkably beneficial for light absorption and charge carrier separation for the competent PEC properties compared to their individual counterparts [2]. As PEC properties are essentially a function of band alignment and atomic – electronic structures, we studied the nanocomposite thin film using various X-ray spectroscopic and microscopy studies. We have probed the origin and nature of localized electron states in core-shell structures using valence band spectroscopy, X-ray absorption spectroscopies and spatially resolved scanning transmission X-ray microscopy (STXM). The valence band studies show band alignment at the core-shell interface, which allows efficient charge transfer between heterostructure. While, X-ray absorption studies essentially show that in core-shell structure tetrahedral environment of V⁵⁺ in BiVO₄ is unusually distorted and the inter-band gap states related to another valence state of Vanadium, namely, V⁴⁺ is present. The presence of multiple valence states of Vanadium gives favorable conditions for small polaron formation in BiVO₄, thereby degrading PEC activities. However, it was observed that V⁴⁺ coordinates with ZnO lattice thereby giving rise to conditions similar to Vanadium doped ZnO. These studies reveal electronic structure over few micrometers length scale within the thin film, which contains hundreds of nanostructures and precise locations of the coordination within individual nanostructure remain unrevealed. Moreover, high-resolution transmission electron microscopy - electron energy loss spectroscopy could not effectively resolve above-mentioned coordination features. On the other hand, STXM is powerful technique and

retains the ability to effectively resolve the observed coordination features efficiently within single or cluster of nanocomposite structure because of its high spatial resolution features. Thus, with STXM measurements, we are able to probe core-shell coordination and the sites in ZnO NDs contributing to V^{4+} doped ZnO within single nanocomposite structure. Figure 1 below depicts STXM results obtained on the core – shell nanostructure.

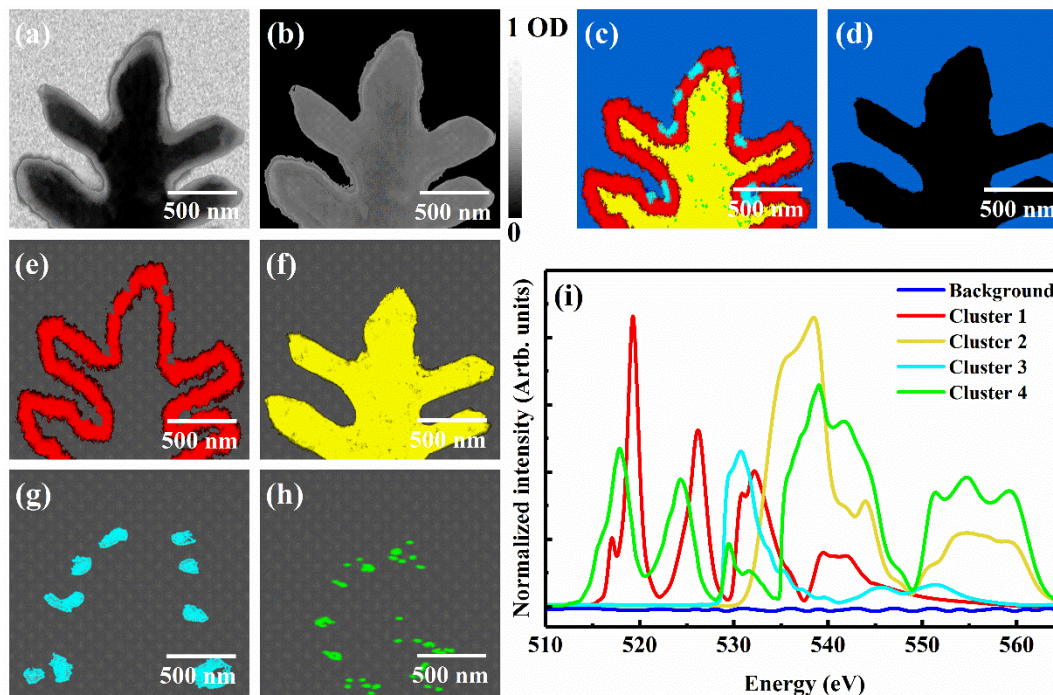


Figure 1. (a) shows transmission electron microscope micrograph of BiVO_4 coated ZnO nanodendrite core-shell nanostructure, (b) shows STXM image of core-shell nanodendrite highlighted in (a), (c) – (h) shows STXM mapping of O – K edge representing various coordination among core and shell structures: Bi – V – O (red), Zn – O (yellow), Bi – O (cyan) and Zn – V – O (green) and (i) represents O – K edge spectra obtained on various clusters.

Thus, our STXM investigations correlate our other synchrotron measurements, thereby we can precisely probe the sites of V^{4+} within core-shell nanostructure, substoichiometric bismuth oxide phase and the possible reason behind the absence of small polaron feature in BiVO_4 nanostructure (observed from valance band spectroscopy) even if multiple valance states of vanadium are present. These insights into the electronic structure of ZnO nanodendrite @ BiVO_4 nanolayers nanocomposite thin film may guide the development and optimization of this material for efficient PEC applications.

References:

- [1] X. Chen, S. Shen, L. Guo and S. S. Mao, *Chem. Rev.* **110** (2010), 6503.
- [2] J. – S. Yang and J. –J. Wu, *Nano Energy* **32** (2017), 232.
- [3] The authors acknowledge funding from Ministry of Science and Technology, Taiwan.