

## Supporting Information

### Plasmonic Ag@Ag<sub>3</sub>(PO<sub>4</sub>)<sub>1-x</sub> Nanoparticle Photosensitized ZnO Nanorod-Array Photoanodes for Water Oxidation\*\*

Yan-Gu Lin<sup>ad</sup>, Yu-Kuei Hsu<sup>b</sup>, Ying-Chu Chen<sup>c</sup>, Sheng-Bo Wang<sup>c</sup>, Jeffrey T. Miller<sup>d</sup>,  
Li-Chyong Chen<sup>\*c</sup>, and Kuei-Hsien Chen<sup>\*ac</sup>

[\*] <sup>a</sup> *Dr. Yan-Gu Lin and Dr. Kuei-Hsien Chen*

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan.

<sup>b</sup> *Prof. Yu-Kuei Hsu*

Department of Opto-Electronic Engineering, National Dong Hwa University, Hualien, 97401, Taiwan.

<sup>c</sup> *Ying-Chu Chen, Sheng-Bo Wang, Dr. Li-Chyong Chen, and Dr. Kuei-Hsien Chen*

Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan.

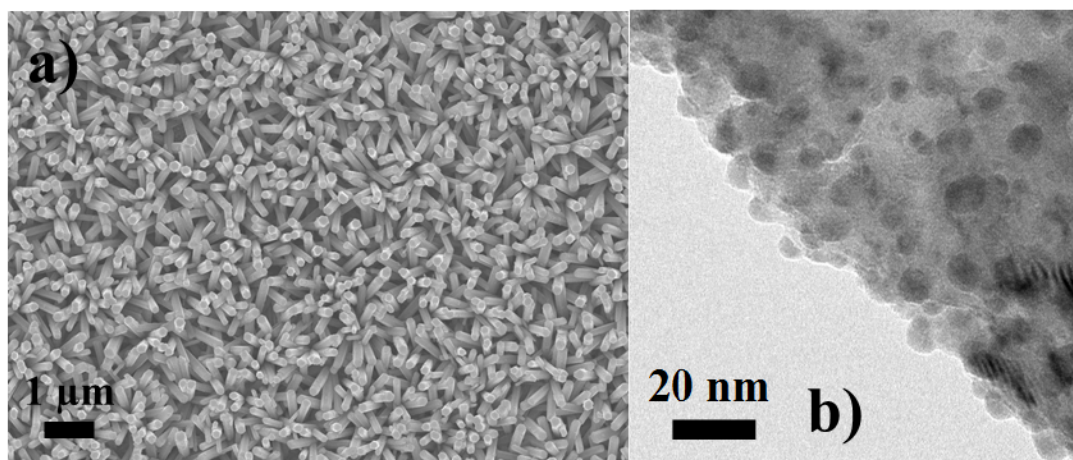
<sup>d</sup> *Dr. Yan-Gu Lin and Dr. Jeffrey T. Miller*

Chemical Sciences and Engineering Division, Argonne National Laboratory, IL 60439, USA

E-mail: yglin@anl.gov

[\*\*] **Acknowledgements**

This work was supported by the National Natural Science Council, Ministry of Education, Taiwan, and AOARD under AFSOR, US. We gratefully thank NSC, IAMS, NTU and Argonne National Laboratory for financial support for this project.



**Fig. SI 1** (a) SEM image of pristine ZnO NRs on ITO substrate. (b) Typical TEM image of the ZnO NRs loaded with Ag@Ag<sub>3</sub>(PO<sub>4</sub>)<sub>1-x</sub> NPs at Ag deposition time of 3 min.

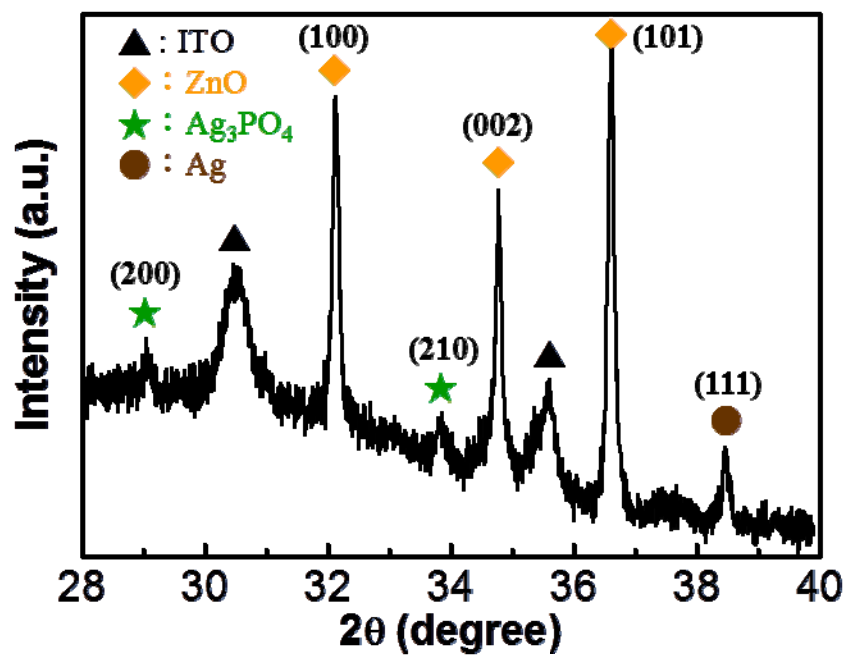
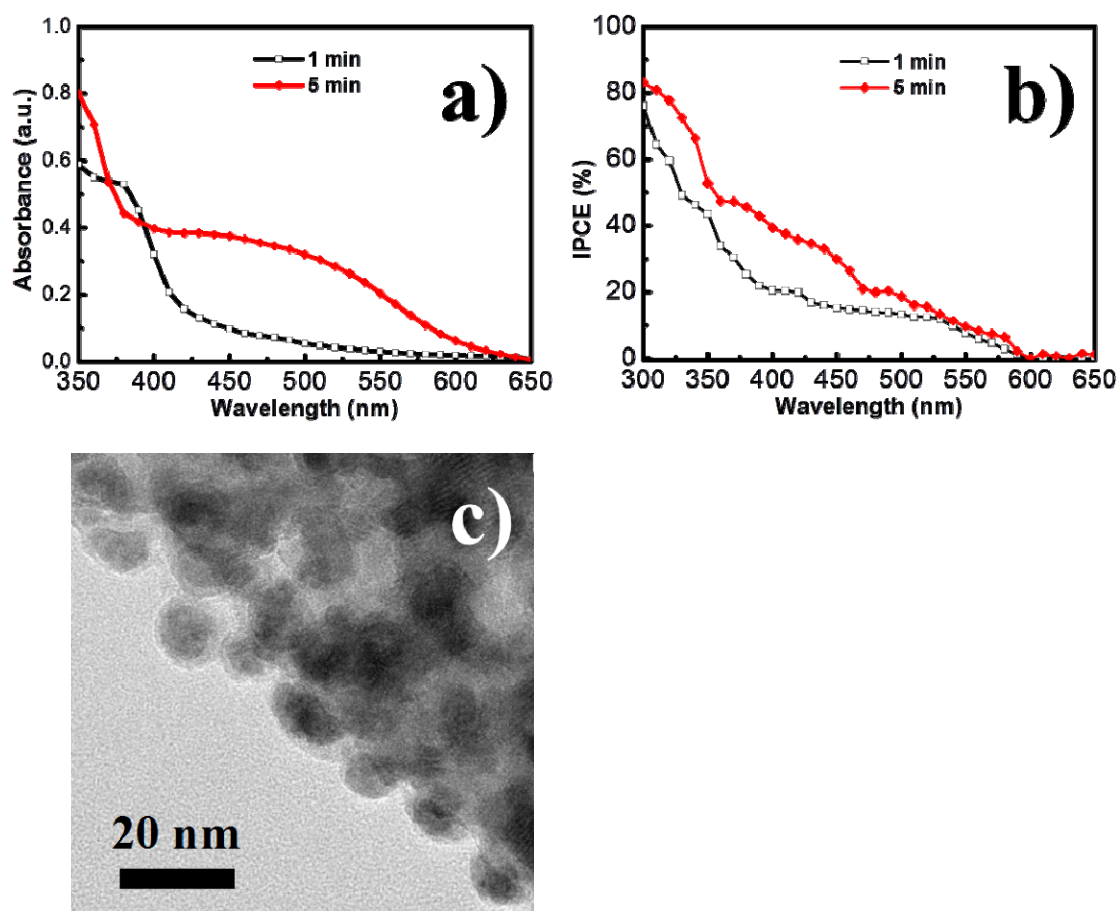
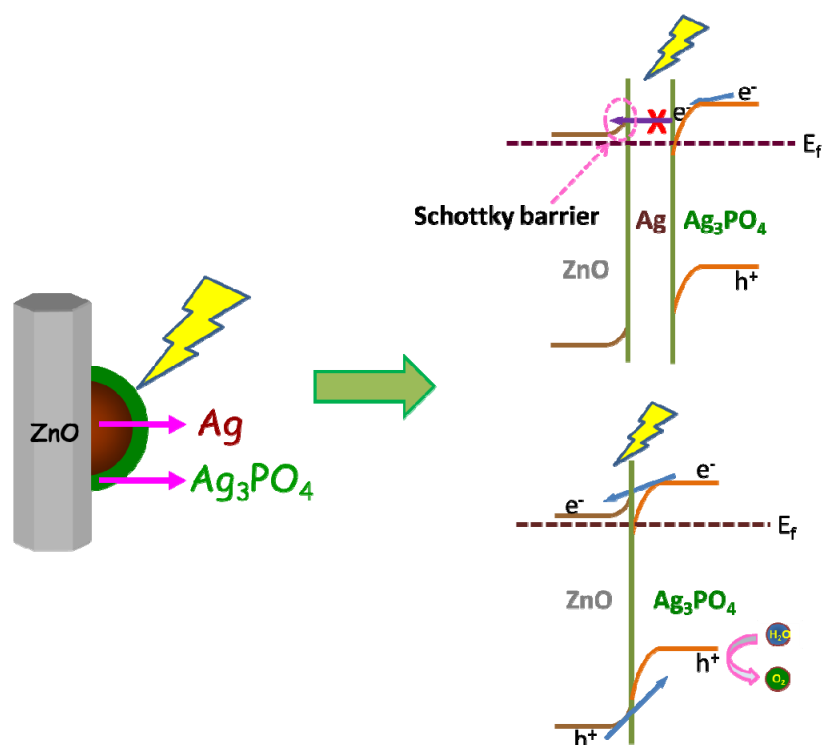


Fig. SI 2 XRD pattern of the ZnO NRs loaded with Ag@Ag<sub>3</sub>(PO<sub>4</sub>)<sub>1-x</sub> NPs.



**Fig. SI 3** (a) Absorption spectra and (b) IPCE spectra of ZnO NRs loaded with  $\text{Ag@Ag}_3(\text{PO}_4)_{1-x}$  NPs at Ag deposition time of 1 and 5 min, respectively. (c) Typical TEM image of the ZnO NRs loaded with  $\text{Ag@Ag}_3(\text{PO}_4)_{1-x}$  NPs at Ag deposition time of 5 min. As can be seen, the particle size of  $\text{Ag@Ag}_3(\text{PO}_4)_{1-x}$  increases as the deposition time increases from 3 to 5 min. Although a slightly redshift in the band position of Ag LSPR for larger particles deposited at longer deposition time is observed (via absorption data), large amounts of  $\text{Ag@Ag}_3(\text{PO}_4)_{1-x}$  NPs aggregated and became a continuous film which covered upon the surface of ZnO NRs. The lower dispersity and uniformity of  $\text{Ag@Ag}_3(\text{PO}_4)_{1-x}$  NPs resulted in poor photoresponse (via IPCE data).



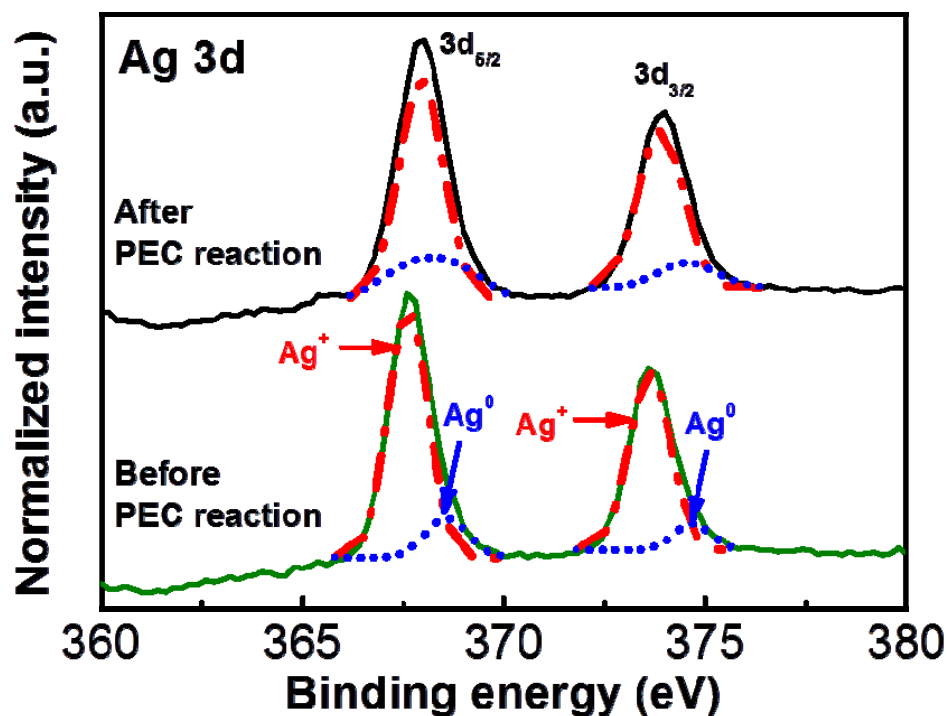
**Fig. SI 4** Schematic band diagram of electron transfer pathways in this hybrid during PEC reactions. Upon illumination, it is significantly that the energy band alignment of ZnO with respect to the work function of Ag is energetically unfavorable for the direct transfer of electron from Ag to ZnO. While electron transport at metal-semiconductor interfaces is well-known among the electrical engineering community (i.e., the Schottky diode), no rigorous model for this process has been put forth in the context of plasmonic catalysis. Here, we demonstrate enhanced PEC performance under illumination in ZnO NRs by exploiting the large plasmon resonance of Ag@Ag<sub>3</sub>(PO<sub>4</sub>)<sub>1-x</sub> NPs. Electromagnetic simulations of this hybrid provide a quantitative basis for determining the underlying photocatalytic enhancement mechanism. This model is based on the near-field optical enhancement of Ag@Ag<sub>3</sub>(PO<sub>4</sub>)<sub>1-x</sub> NPs. Enhanced light absorption and photocurrents in photocatalytic chemistry have also been reported by using a similar plasmonic enhancement mechanism.<sup>1-3</sup> Therefore, in the entire PEC photoanode configuration, the Ag<sub>3</sub>(PO<sub>4</sub>)<sub>1-x</sub> absorbs mainly visible light enhanced by LSPR of Ag core, and the photo-generated electrons are transferred to ZnO/ITO to contribute photocurrent.

Another possible mechanism in the enhancement of photocurrent is to generate hot electron-hole pairs by plasmon decay. Landau damping is known to convert plasmons into hot electrons. While the absorption initially creates a plasmon, this plasmon only persists for femtoseconds before it begins degrading and being converted into other types of excited states.<sup>4,5</sup> Once the hot electron is produced, the barrier for electron transfer from Ag to ZnO is gone. This clearly shows that a plasmon-to-hot electron transfer occurs readily. Therefore, the generated hot electrons will probably contribute to the photocurrent.

*Energy Environ. Sci. (Communications)*

## References

- 1 Z. Liu, W. Hou, P. Pavaskar, M. Aykol and S. B. Cronin, *Nano Lett.*, 2011, **11**, 1111.
- 2 I. Thomann, B. A. Pinaud, Z. Chen, B. M. Clemens, T. F. Jaramillo and M. L. Brongersma, *Nano Lett.*, 2011, **11**, 3440.
- 3 D. B. Ingram and S. Linic, *J. Am. Chem. Soc.*, 2011, **133**, 5202.
- 4 M. W. Knight, H. Sobhani, P. Nordlander and N. J. Halas, *Science*, 2011, **332**, 702.
- 5 Y. K. Lee, C. H. Jung, J. Park, H. Seo, G. A. Somorjai and J. Y. Park, *Nano Lett.*, 2011, **11**, 4251.



**Fig. SI 5** Ag 3d XPS spectra of  $Ag@Ag_3(PO_4)_{1-x}$ -photosensitized ZnO photoanodes before and after photocatalytic reactions. Two bands at ca. 367.7 and 373.7 eV are ascribed to Ag  $3d_{5/2}$  and Ag  $3d_{3/2}$  binding energies. These bands could be further deconvoluted into two peaks, where the bands at 367.5 and 373.8 eV are ascribed to the  $Ag^+$  of  $Ag_3PO_4$ , and those at 368.4 and 374.2 eV are ascribed to the metallic  $Ag^0$ . It clearly shows that the intensity of  $Ag^+$  decreased while that of  $Ag^0$  increased during the photocatalytic process, which indicates that slightly partial  $Ag^+$  gradually transformed to be metallic  $Ag^0$  under the sustaining irradiation.