

as a result of the three distinct cations, complicating the determination of the chemical state according to the pure oxide reference spectra. Importantly, an increased binding energy of both Zr and La following voltammetric treatment was found, which might have arisen from the inclusion of additional Li ions. (Reported by Ru-Shi Liu, National Taiwan University)

This report features the work of Ru-Shi Liu and his co-workers published in J. Phys. Chem. C **121**, 15565 (2017).

ANSTO-TG1 ECHINDA – High-resolution Powder Diffractometer

TLS 01C1 SWLS – EXAFS

TLS 17C1 W200 – EXAFS

- XANES, Oxidation State
- Neutron Powder Diffraction, Crystal Structure, Materials Chemistry

References

1. S. Yu, R. D. Schmidt, R. Garcia-Mendez, E. Herbert, N. J. Dudney, and J. B. Wolfenstine, J. Sakamoto, and D. J. Siegel, *Chem. Mater.* **28**, 197 (2016).
2. S. Song, B. Yan, F. Zheng, H. M. Duong, and L. Lu, *Solid State Ionics* **268**, 135 (2014.)
3. J. Awaka, A. Takashima, K. Kataoka, N. Kijima, Y. Idemoto, and J. Akimoto, *Chem. Lett.* **40**, 60 (2011).
4. Y. T. Chen, A. Jena, W. K. Pang, V. K. Peterson, H. S. Sheu, H. Chang, and R. S. Liu, *J. Phys. Chem. C* **121**, 15565 (2017).

Molecular Design Drives Solar-Hydrogen Conversion

A rational molecular design of polymer heterojunctions is an effective strategy to benefit the exciton dissociation or light-harvesting ability for efficient conversion of solar energy.

The key to solar-hydrogen conversion (SHC) is to develop an ideal photocatalyst with not only an efficient and stable ability for hydrogen production driven with visible light but also a nontoxic and terrestrially abundant elemental composition for promising industrial application. The photocatalysts developed so far are mainly inorganic semiconductors, but the necessity of noble or toxic metals might be a serious hindrance to a large-scale industrial application of those inorganic semiconductors. In contrast, organic semiconductors are more intriguing for photocatalytic applications in terms of terrestrial abundance and environmental benignity, but most organic semiconductors have shown poor photocatalytic SHC efficiencies for three well known reasons: first, the large band gaps limit their harvest to a small portion of visible light; second, unlike free Wannier excitons photogenerated in inorganic semiconductors, photoexcitation of an organic semiconductor typically generates Frenkel excitons with a large exciton binding energy, hence small dissociation probability, resulting in serious charge recombination; third, because of a lack of catalytic reaction sites on the surface of the semiconductor, even if the charge carriers survive recombination, they can contribute only to surface water reduction with a small probability. The further design of organic photocatalysts toward a highly efficient photocatalytic SHC is hence crucial.

In this work, Shaohua Shen and his collaborators reported polymer heterojunction (PHJ) photocatalysts consisting of polymers in the polyfluorene family (PF) and graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) for an efficient SHC.¹ A strategy of molecular design was executed to achieve an improved exciton dissociation and extended light absorption of PHJ photocatalysts for highly efficient photocatalytic SHC. The authors applied synchrotron-based X-ray adsorption techniques at **TLS 20A1** and **TLS 16A1** to clarify the intermolecular interactions between electron-rich aromatic rings of the PF and electron-deficient heptazine rings of $g\text{-C}_3\text{N}_4$.

To acquire profound insight into the electron transfer processes in these PHJ, X-ray absorption near-edge structure (XANES) spectra of the C-, N- and S-edges of the samples as prepared were recorded both in darkness and under illumination. The S K-edge spectra, which probes S 3p unoccupied states, is displayed in **Fig. 1(a)**. It can be observed that there is no spectral difference in pure PFBT with or without illumination, whereas the peak intensity of PFBT/CN decreases under illumination. Specifically, the electron transfer in PFBT/CN differs from that in PFO/CN or PCzF/CN, because of the introduction of the benzothiadiazole unit containing a S atom. Note that the N–C=N bonds exist only in $g\text{-C}_3\text{N}_4$; the C and N K-edge XANES spec-

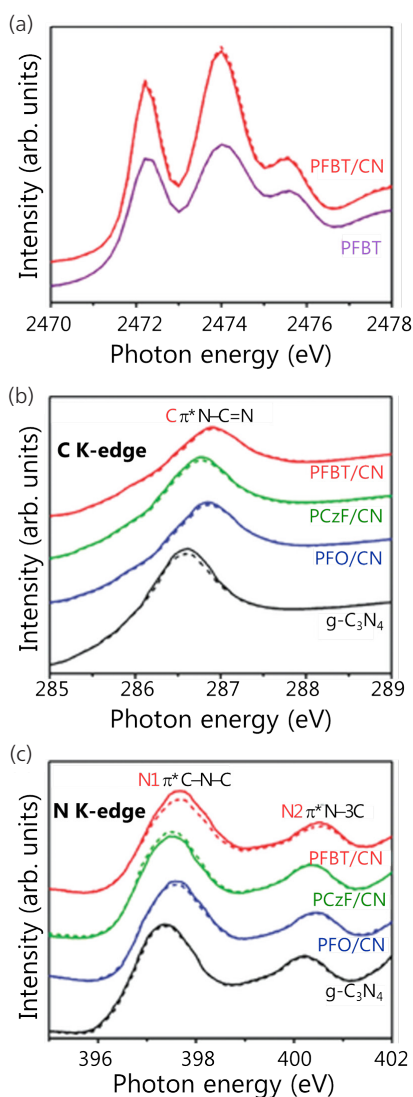


Fig. 1: (a) S K-edge XANES of PFBT and PFBT/CN in darkness and under illumination. (b) C K-edge XANES of PFO/CN, PCzF/CN, PFBT/CN and $g\text{-C}_3\text{N}_4$ in darkness and under illumination. (c) N K-edge XANES of PFO/CN, PCzF/CN, PFBT/CN, and $g\text{-C}_3\text{N}_4$ in darkness and under illumination. (dot-dashed lines: in darkness; solid lines: under illumination). [Reproduced from Ref. 1]

tra of the PHJ in **Figs. 1(b) and 1(c)** are derived from the heptazine rings of $g\text{-C}_3\text{N}_4$. The C K-edge spectra of $g\text{-C}_3\text{N}_4$ and PHJ upon irradiation showed greater intensity than under darkness, indicating that more empty states were created in the LUMO of $g\text{-C}_3\text{N}_4$. Notably, the decreased intensities of the PHJ are due to charge transfer from the LUMO of PF to the C sites in $g\text{-C}_3\text{N}_4$. The N K-edge spectra of both PFO/CN and PFBT/CN show enhanced intensities under illumination, whereas the N K-edge intensity of PCzF/CN decreases under illumination. This fact indicates that electron transfer from PCzF to the N sites in $g\text{-C}_3\text{N}_4$ is more facile, which might account for the charge-transfer dynamics of PCzF/CN more accelerated than of PFO/CN and PFBT/CN. Together with the significantly increased intensity of the N K-edge in PFBT/CN under illumination, it can be deduced that there is an electron migration from the N site of the heptazine rings back to the S site in PFBT.

In summary, PHJ formed via intermolecular $\pi\text{-}\pi$ interactions were developed for stable and efficient photocatalytic SHC. A strategy of molecular design was further proposed toward increased photocatalytic activities, through modification of the polymer molecules for efficient exciton dissociation or extended light absorption. Potentially, through rational molecular design, the band energy levels of the organic semiconductors can be further optimized to attain wide-band optical absorption as well as efficient charge separation, to achieve high photocatalytic SHC efficiency over the entire solar spectrum. (Reported by Yan-Gu Lin)

*This report features the work of Shaohua Shen and his co-workers published in Adv. Mater. **29**, 1606198 (2017).*

TLS 20A1 BM – (H-SGM) XAS

TLS 16A1 BM – Tender X-ray Absorption, Diffraction

- XANES, EXAFS
- Material Science, Chemistry, Condensed Matter Physics, Environmental and Earth Science

Reference

1. J. Chen, C.-L. Dong, D. Zhao, Y.-C. Huang, X. Wang, L. Samad, L. Dang, M. Shearer, S. Shen, and L. Guo, Adv. Mater. **29**, 1606198 (2017).

Probing the Structural Evolution of a Battery with X-rays

Spectra and scattering have given significant insight into battery reactions.

Batteries to store electric energy have attracted intense attention because of the steadily increasing demands of mobile and stationary applications. In principle, the capacity of an electrode to store charge is related to the number of ionic intercalants that is limited by their size, and is also dependent on the structure and morphol-