

XAFS study on the structure and photocatalytic activity of g-C₃N₄-based in-plane heterostructure

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Abstract

Direct and efficient photocatalytic water splitting is critical for sustainable conversion and storage of renewable solar energy. We have synthesized a two-dimensional C₃N₄-based in-plane heterostructure (C_{ring}-C₃N₄) that achieves fast spatial transfer of photoexcited electrons for realizing highly efficient and spontaneous overall water splitting.[1-2] Herein, we have applied X-ray absorption spectroscopy to study the atomic and electronic structure of the local environment in the two-dimensional in-plane heterostructure.

The synthesis of C_{ring}-C₃N₄ undergoes three steps: melem forming, triazine-carbon ring unit constructing, and final polymerization. In detail, the mixed resultants went through three stages of heating: 300 °C for 1h, 400 °C for 1h and 550 °C for 4 h. The purification process is as follows: 1) DI purification to remove residual water-soluble species; 2) HNO₃ purification to remove amide impurity; 3) ethanol and DI purification. The XAFS spectra were measured at BL12B-a beamline of National Synchrotron Radiation Laboratory (NSRL, China). Theoretical C K-edge XANES spectra calculated using FEFF8.2 code.

To understand the origin of the prominent photocatalytic activity of C_{ring}-C₃N₄, we performed various atomic and electronic structural characterizations on the samples. The XANES spectrum of C_{ring}-C₃N₄ displays sp² hybridization of C–C and C=C bonds for graphitic carbon-ring. To further support this deduction, theoretical C K-edge XANES spectra for several structure models calculated using FEFF8.2 code. Apparently, the calculations based on C_{ring}-C₃N₄ models could reproduce the main spectral features of the corresponding experimental spectra of C_{ring}-C₃N₄, providing theoretical evidence for the formation of sp² π-conjugated heterointerface in C_{ring}-C₃N₄. This π-conjugate connection will significantly modify the electronic structure of in-plane heterostructure. The high electron state density around the Fermi level introduced by carbon ring incorporation could synergistically prolong the photocarrier diffusion length and lifetime by 10 times relative to pristine g-C₃N₄.

In summary, we have used synchronous radiation X-ray absorption spectroscopy to reveal the internal mechanism of the rapid separation and migration in the two-dimensional planar heterostructure. Our results may open up opportunities for the understanding of the structure-performance correlations of the efficient and cost-effective photocatalysts for the production of clean energy.

References

- [1] **Wei Che**[†], Weiren Cheng[†], Qinghua Liu, and Shiqiang Wei* et al, *J. Am. Chem. Soc.* 2017, 139 (8), 3021–3026.
- [2] Weiren Cheng, **Wei Che**, Qinghua Liu, and Shiqiang Wei* et al, *J. Mater. Chem. A*, 2017, 5, 19649-19655.