

# XAFS Study on Single-site Active Cobalt-based Photocatalyst

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Solar-driven water splitting represents “Holy Grail” technique and the ultimate goal of solar energy storage. Rational design and synthesis of efficient photocatalysts are of crucial significance but have so far been plagued by the lack of definite correlations between structure and catalytic performance. Here, taking single-site Co-based photocatalysts as prototype, the formation process and well-defined structure were thoroughly investigated in combination of X-ray absorption spectroscopy and electron microscopy. The single Co site was revealed to effectively prolong carrier lifetime, and boost surface catalytic activity for achieving robust overall water splitting.

The Co *K*-edge XAFS spectra were recorded at the 1W1B beamline of Beijing Synchrotron Radiation Facility, China. The hard X-ray was monochromatized with Si(111) double-crystal monochromator and the detuning was done by 30% to remove harmonics. XAFS data were collected in fluorescence mode.

The HAADF-STEM measurement results clearly identify the atomic dispersion of Co species. Further, the formation process was monitored by the Co *K*-edge X-ray absorption spectroscopy. For Co<sub>1</sub>-oxo/C<sub>3</sub>N<sub>4</sub>, the XANES spectrum as well as the single prominent Co<sup>2+</sup>-O coordination peak in Fourier transforms (FT) spectrum indicate that Co are preserved in an octahedral coordination [CoO<sub>6</sub>], while confined in an atomically dispersed distribution. Upon phosphidation, the XANES spectrum and the FT curve unambiguously revealed that the coordination atoms around Co are totally changed to P after phosphidation. Combing the microscopy analyses, we demonstrated the primary existence of atomically dispersed Co, and EXAFS fitting indicates the Co-P coordination number was 4.0.

The single-site photocatalyst exhibited H<sub>2</sub> quantum efficiency of 2.2% at 500 nm. The remarkable activity was ascribed to the following factors:(i) The Co<sub>1</sub>-P<sub>4</sub> site induced new mid-gap states, which not only enhance the light-harvesting capability, but serve as separation centers to inhibit electron-hole recombination. (ii) The heteroatom P doping significantly promotes the charge transfer. (iii) The Co<sub>1</sub>-P<sub>4</sub> structure with low-coordination Co<sub>1</sub> site is beneficial for H<sub>2</sub>O adsorption and activation.

In summary, X-ray absorption spectroscopy and electron microscopy are combined to probe the formation process of single-site Co<sub>1</sub>-P<sub>4</sub> on g-C<sub>3</sub>N<sub>4</sub>. The single-site configuration allows the efficient charge separation and transfer and boosting of two half-reactions. These findings enrich our understanding on the great potential of single-site structure as a valuable component for future optimization of high-performance photocatalysts.

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