

Structure-activity correlations of Co single-site photocatalyst studied by XAFS

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Atomically dispersed catalysts comprising mononuclear metal complexes or single metal atoms provide a suitable model for atomic-level insight into reaction kinetics of active site. However, the structure of the single site has remained elusive. In this work, we report an atomic-level analysis of local structure of single Cobalt site photocatalyst by means of X-ray absorption fine structure (XAFS) technique.

Atomically dispersed Co-based composites (noted as “Co₁/PCN”) were fabricated by atomic-layer-deposition technique, which involves exposing cobaltocene precursor to phosphidation-treated g-C₃N₄, followed by O₃ treatment to remove the surface Cp ligand. The Co K-edge XAFS data were recorded in the 1W1B beamline of Beijing Synchrotron Radiation Factory (BSRF) and BL14W1 station of Shanghai Synchrotron Radiation Facility (SSRF). XAFS data for Co₁/PCN was recorded in fluorescence mode, while the XAFS data for reference samples were collected in transmission mode.

The Co coordination environment was investigated by XANES and EXAFS spectroscopies at the Co K-edge. The XANES spectral shape for Co₁/PCN was different from that of CoO and Co₃O₄, which was possibly due to the formation of the Co–N/C coordination. Furthermore, the Fourier-transformed (FT) k³-weighted $\chi(k)$ function of Co₁/PCN showed single peak attributed to the coordination between Co and light C/N elements, with no metal Co-Co contribution can be observed. The experimental EXAFS spectrum can be fitted with high accuracy using “Co₁-N₄” model, giving the average bond length (R) of 2.01 Å, and the coordination number (N) of 4 for Co-N bond. Moreover, the XANES simulations revealed “Co₁-N₄” configuration can reproduce the experimental spectrum well. Therefore, we suggest that the Co atom is isolated located in the cavity bonded with four in-plane porphyrin N atoms, forming a “Co₁-N₄” motif embedded in a g-C₃N₄ sheet. Theoretical investigations revealed that the coordinated donor nitrogen increases the electron density and lowers the formation barrier of key Co hydride intermediate, thereby accelerating H-H coupling to facilitate H₂ generation. Consequently, this noble metal-free composite exhibited enhanced H₂ production activity.

In conclusion, we designed a novel single-site photocatalyst containing the atomically dispersed Co sites anchored on carbon nitrides for efficient solar-driven hydrogen evolution. By using XAFS technique, the structure of single Co sites was demonstrated as Co₁-N₄ geometry, which could facilitate photocatalytic H₂ generation.

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