Tailored 2D g-C_3N_4 Photocathodes with NiMoBW Sites for Efficient Furan Conversion

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Abstract:

Electrocatalytic and photoelectro-electrocatalytic hydrogenation offer sustainable routes for upgrading biomass-derived furans, yet the reliance on noble metals and limited visible-light utilisation constrain industrial deployment. We will present and discuss results concerning a quadruple-doped 2D graphitic carbon nitride, NiMoBW@g-C_3N_4 (in different molar ratios), which has been synthesized to overcome these challenges. Synthesis via hydrothermal and impregnation–reduction yields a hierarchically porous photocatalyst (BET surface area ≈ 80 $m^2\ g^{-1}$) in which atomically dispersed Ni and Mo sites cooperate with sub-nanometric B- and W-induced defect domains to accelerate proton–electron transfer while suppressing competing H_2 evolution.

In electrochemical hydrogenation (0.1 M NaOH, −0.70 V vs RHE, 25 °C), the material converts furfural to furfuryl alcohol with 85 % conversion and 80 % Faradaic efficiency; under identical conditions 5-hydroxymethylfurfural is reduced to 2,5-bis(hydroxymethyl)furan with 78 % conversion and 75 % Faradaic efficiency. Visible-light illumination (AM 1.5 G, 100 mW cm^{-2}) lowers the required bias and maintains conversions of 80 % and 75 % for the respective substrates while preserving Faradaic efficiencies above 75%. Impedance and transient-photocurrent analyses attribute the performance to rapid charge separation across B,N-modulated band states and to Ni–Mo dual single-atom centres that favour C═O hydrogenation over ring hydrogenation. The photocathode retains >95 % activity after 20 h continuous operation and exhibits negligible metal leaching. These results position NiMoBW@g-C_3N_4 as a noble-metal-free, dual-mode 2D material for solar-assisted bio-oil refining, achieving high (75–85 %) conversion and Faradaic efficiency in aqueous media.

Additionally, Density Functional Theory (DFT) calculations were performed to gain insight into the electronic modifications induced by Ni, Mo, B, and W co-doping in the 2D g-C_3N_4 matrix. Projected density of states (PDOS) analyses show that B and W doping introduced localized states near the Fermi level, reducing the bandgap and promoting visible-light responsiveness. Charge density difference maps reveal effective charge delocalization between the g-C_3N_4 framework and the Ni–Mo dual single-atom sites, while B and W atoms contributed to electronic asymmetry and defect formation, further enhancing carrier mobility. Bader charge analysis confirmed redistribution of electron density across doped regions, supporting improved charge separation and retention. These theoretical insights are consistent with the observed photocatalytic efficiency, stability, and suppressed recombination behavior of NiMoBW@g-C_3N_4.

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Figures

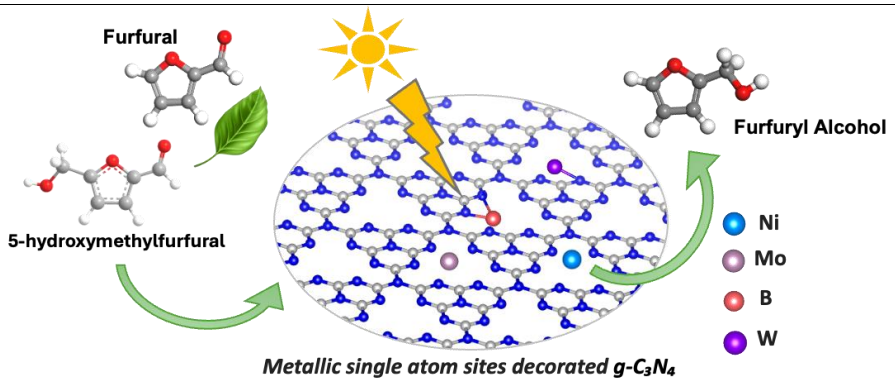

Figure 1: Biomass-Derived Furans upgrading on NiMoBW@g-C_3N_4 towards furfuryl alcohol production.