Exploring the Mechanisms of Nitrogen Adsorption and Activation on the 2H/1T Mixed-phase Ultrathin $Mo_{1-x}W_xS_2$ Nanosheets for Boosting Nitrogen Photosynthesis

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Solar-driven conversion of nitrogen (N_2) to ammonia (NH_3) is highly appealing yet still in its infancy as low photocatalytic efficiency, and unclear adsorption and activation mechanisms of N_2. Based on the two key points, an ultrathin alloyed $Mo_{1-x}W_xS_2$ nanosheets with tunable 2H/1T phase ratios was proposed to boost photoreduction N_2 efficiency by simultaneously promoting N_2 adsorption and activation, and moreover, the alloyed $Mo_{1-x}W_xS_2$ nanosheets for the ratio of 2H/1T = 1:1 can reach about 111 μmol g_{cat}^{-1} h^{-1} under visible light, displaying 3.7 (or 3)-fold higher than that of pristine MoS_2 (or WS_2). With the aid of density functional theory (DFT) calculations and X-ray absorption near-edge fine structure (XANES) techniques, the coordination chemistry and adsorption behavior of N_2 over the crystal interface were investigated during the N_2 fixation process. The results show that the interface distortion with W doping leads to the largest adsorption energy (-2.05 eV) and higher electron density state in W 5d orbitals, which can not only polarize the adsorbed N_2 molecules for better activation but also promote the electron transfer to them for greatly enhancing photocatalytic efficiency. This work proposes a new insight into the adsorption and activation mechanism of N_2 on ammonia synthesis.