## Iron Doping Enhanced Photocatalytic Nitrogen Fixation Performance of WO<sub>3</sub> with Three-Dimensionally Orderd Macroporous Structure

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Abstract : Ammonia, as one of the largest-volume industrial chemicals, is mostly produced by century-old Haber-Bosch process with extreme conditions and high-cost. Under the circumstance, researchers are dedicated in finding new ways to replace the Haber-Bosch process. Photocatalytic nitrogen fixation is a promising sustainable, clear and green strategy for ammonia synthesis, butit is still a big challenge due to the high activation energy for nitrogen. It is essential to develop an efficient photocatalyst for making this approach industrial application. Constructing chemisorption active sites through defect engineering can be defined as an effective and reliable means to improve nitrogen activation by forming the extraordinary coordination environment and electronic structure. Besides, the construction of three-dimensionally orderdmacroporous (3DOM) structured photocatalyst is considered to be one of effectivestrategiesto improve the activity due to it canincrease the diffusion rate of reactants in the interior, which isbeneficial to the mass transfer process of nitrogen molecules in photocatalytic nitrogen reduction. Herein, Fe doped 3DOM WO<sub>3</sub>(Fe-3DOM WO<sub>3</sub>) without noble metal cocatalysts is synthesized by a polystyrene-template strategy, which is firstly used for photocatalytic nitrogen fixation. To elucidate the chemical nature of the dopant, the X-ray diffraction (XRD) analysiswas conducted. The pure 3DOM WO<sub>3</sub> has a monoclinic type crystal structure. And no additional peak is observed in Fe doped 3DOM WO<sub>3</sub>, indicating that the incorporation of Fe atoms did not result in a secondary phase formation. In order to confirm the morphologies of Fe-3DOM WO<sub>3</sub>and 3DOM WO<sub>3</sub>, scanning electron microscopy (SEM) was employed. The synthesized Fe-3DOM WO<sub>3</sub> and 3DOM WO<sub>3</sub> both exhibit a highly ordered three dimensional inverse opal structure with interconnected pores. From high-resolution TEM image of Fe-3DOM WO<sub>3</sub>, the ordered lattice fringes with a spacing of 3.84 Å can be assigned to the (001) plane of WO<sub>3</sub>, which is consistent with the XRD results. Finally, the photocatalytic nitrogen reduction performance of 3DOM WO<sub>3</sub> and Fe doped 3DOM WO<sub>3</sub> with various Fe contents were examined. As a result, both Fe-3DOM WO<sub>3</sub> samples achieve higher ammonia production rate than that of pure 3DOM WO<sub>3</sub>, indicating that the doped Fe plays a critical role in the photocatalytic nitrogen fixation performance. To verify the reaction process upon N2 reduction on the Fe-3DOM WO<sub>3</sub>, in-situ diffuse reflectance infrared Fourier-transform spectroscopy was employed to monitor the intermediates. The in-situ DRIFTS spectra of Fe-3DOM WO<sub>3</sub> exhibit the increased signals with the irradiation time from 0-60min in the N2 atmosphere. The above results prove that nitrogen is gradually hydrogenated to produce ammonia over Fe-3DOM WO<sub>3</sub>. Thiswork would enrich our knowledge in designing efficient photocatalystsfor photocatalytic nitrogen reduction.

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