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# PHASE TRANSITION INDUCED BAND STRUCTURE ENGINEERING OF BIVO<sub>4</sub> FOR SOLAR FUEL PRODUCTION

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Cost-effective solar water splitting requires earth abundant photocatalytic materials converting photons to working electrons in a highly efficient manner. To develop such suitable photocatalysts, their atomic structure control is of primary importance since their intrinsic attributes (e.g., electronic band structure, electric properties, catalytic activity, etc.) are governed by their atomic configuration. In this regard, BiVO<sub>4</sub>'s atomic structure has been engineered via P5+ doping and In<sup>3+</sup>/Mo<sup>6+</sup> dual doping. The significantly enhanced photo-responsive characteristics of the doping-treated BiVO<sub>4</sub> have been systematically studied within experimental and theoretical domains. Specifically, VO<sub>4</sub> and PO<sub>4</sub> oxoanion exchange in monoclinic BiVO<sub>4</sub> significantly reduces its charge-transfer resistance by increasing charge-carrier density, and thus enhances solar-to-hydrogen efficiency up to 29.3 times, as Fig. 1 shows. Notably, this brand-new oxoanion exchange technique can be applied to other various VO<sub>4</sub>-based semiconductors to improve their electronic, catalytic and photochemical properties. To upgrade the photocatalytic performance of BiVO<sub>4</sub> further, its electronic band structure was engineered by simultaneously substituting In<sup>3+</sup> for Bi<sup>3+</sup> and Mo<sup>6+</sup> for V<sup>5+</sup>, which induced partial phase transformation from pure monoclinic BiVO<sub>4</sub> to a mixture of monoclinic and tetragonal BiVO<sub>4</sub>. This In<sup>3+</sup>/Mo<sup>6+</sup> doped BiVO<sub>4</sub> has a slightly larger band-gap energy (E<sub>g</sub> ~2.5 eV) than usual 'yellow' monoclinic BiVO<sub>4</sub> (E<sub>g</sub> ~2.4 eV) and higher (more negative) conduction band edge (-0.1 VRHE at pH 7) than H<sup>+</sup>/H<sub>2</sub> potential (0 VRHE at pH 7). Consequently, as Fig. 2 displays, the In<sup>3+</sup>/Mo<sup>6+</sup> doped BiVO<sub>4</sub> is able to split water into H<sub>2</sub> and O<sub>2</sub> under visible-light irradiation without using any sacrificial reagents (e.g. CH<sub>3</sub>OH or AgNO<sub>3</sub>). This outcome is the first example of a pure water-splitting photocatalyst responding to visible light without any noble-metal co-catalyst.

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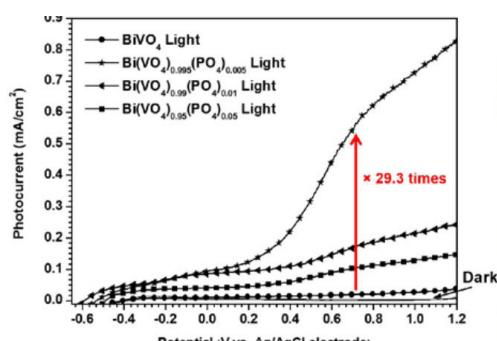


Fig 1: Enhanced photocurrent by PO<sub>4</sub> doping into BiVO<sub>4</sub>

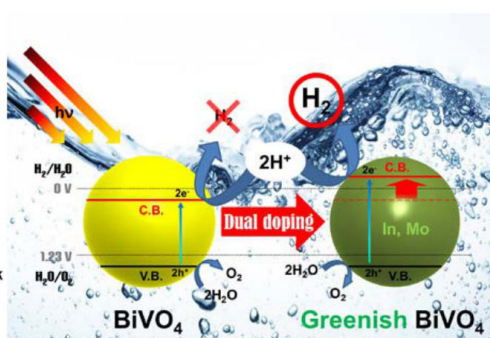


Fig 2: Overall water splitting reaction by In<sup>3+</sup>/Mo<sup>6+</sup> doped BiVO<sub>4</sub>