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## **Laser-Driven Selective Photodeposition of Metals and Metal Oxides on BiVO4 Nanoplates with Controlled Size for Highly Efficient Photocatalysis**

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Bismuth vanadate (BiVO<sub>4</sub>) is a nontoxic and medium band gap (2.4 eV) n-type semiconductor which has attracted worldwide attention as a visible-light active photocatalyst. Particularly, scheelite monoclinic BiVO<sub>4</sub> is one of the most active polymorphs in photocatalytic oxygen evolution. However, the oxidation capability of bare  $\rm BiVO_4$  is hindered by weak charge carrier mobilities, short charge carrier diffusion lengths, and a high charge recombination rate at the surface. To circumvent these inconveniences, heterostructuring by contacting  $B\dot{N}O_4$  with other materials such as noble metals and metal oxides has been proposed.

Usually, contact materials are deposited in a random manner on particulate  $BiVO<sub>4</sub>$ -based photocatalysts. In this case no distinct flow path for photogenerated holes and electrons can exist which makes bulk and surface recombination still prominent due to insufficient charge carrier separation. Since the pioneer works on anatase and rutile  $TiO<sub>2</sub>$  particles which have revealed the key role of exposed facets in the separation of photoinduced electron–hole pairs, photodeposition is now considered as a sort of general route for synthesizing heterostructures. Indeed, photogenerated electrons and holes preferentially accumulate on different crystalline facets which renders cocatalyst deposition regioselective depending on whether the process involves an oxidation or reduction reaction. Systematic studies on single crystalline  $TiO<sub>2</sub>$  (anatase) exposing different facets have shown that the different surfaces (100) vs (110) provide indeed different electronic surface properties including different work functions which promote charge carrier separation into different directions.

Anisotropic photodeposition on BiVO<sub>4</sub> microcrystals has been extensively studied. It has been shown that metallic deposits were preferentially found on {010} facets after metal ion photoreduction, while metal oxide deposits were found on the {110} facets after metal ion photo-oxidation, evidencing that electrons and holes accumulate on different sites on anisotropic  $\angle Bivo_4$  crystals. Besides providing proof of enhanced charge carrier separation, the preferential photodeposition was used to construct  $B\dot{N}O_4$  photocatalysts with even better photocatalytic oxygen evolution efficiencies by depositing reduction cocatalysts on the more reducing {010} facets and oxidation cocatalysts on the more oxidative {110} facets.

On the other hand,  $\rm BiVO_4$  microcrystals generally reported in the literature present compromised colloidal stability and low surface activity due to size effects. Thus, dedicated experiments need to be tackled to control and decrease the size.

In this context, we herein report for the first time a universal photodeposition of noble metal [Au, Ag, Pd] and/or metal oxide  $[CoO<sub>x</sub>, MnO<sub>x</sub>, FeO<sub>x</sub>]$  cocatalysts, via the original use of laser light, on BiVO<sub>4</sub> nanocrystals exposing well-defined {010} and {110} facets, being the main advantage of laser photodeposition the shorter procedure times due to high intensity effects. The monoclinic  $\rm BiVO_4$ nanocrystals here exhibited are one of the smaller reported ever, showing more than an 8-fold edge length and 4-fold thickness reduction compared to the common microcrystals generally reported in the literature. Both chemistry and regioselectivity of the deposition was investigated employing Xray photoelectron spectroscopy and various electron microscopy techniques. Then, the photocatalytic efficiencies of the structures prepared were tested for water oxidation reactions and were compared with previously studied systems.

**Keywords:** Laser photodeposition, Facet-engineered metal and metal oxides monoclinic scheelite BiVO4 crystals, Size control, Photocatalysis, Sacrificial water oxidation, Hydrogen production

