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

Miquel Torras ^{1,2,3}, Thierry Toupance ¹, Marie-Helene Delville ² and Jean-Pierre Delville ³

¹Institut des Sciences Moléculaires (ISM), Université de Bordeaux, UMR 5255 CNRS, Bordeaux INP, 351 Cours de la Libération, 33405 Talence, France

²Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB), UMR 5026 CNRS, Université de Bordeaux, Bordeaux INP, 87 Avenue du Dr. A. Schweitzer, 33608 Pessac, France

³Laboratoire Ondes et Matière d'Aquitaine (LOMA), UMR 5798 CNRS, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence, France

Presenting author e-mail: miquel.torras@u-bordeaux.fr

Bismuth vanadate (BiVO₄) 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 BiVO₄ is one of the most active polymorphs in photocatalytic oxygen evolution. However, the oxidation capability of bare BiVO₄ 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 BiVO₄ with other materials such as noble metals and metal oxides has been proposed.

Usually, contact materials are deposited in a random manner on particulate BiVO₄-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 TiO₂ 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 TiO₂ (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.

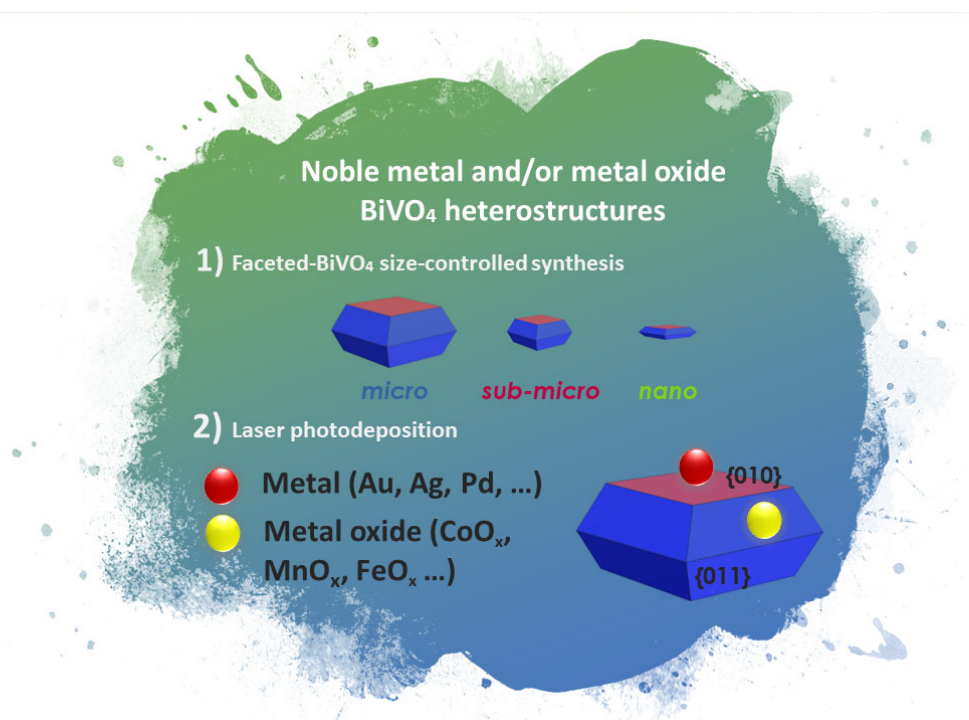
Anisotropic photodeposition on BiVO₄ microcrystals has been extensively studied. It has been shown that metallic deposits were preferentially found on {010} facets after metal ion photoreduction, while metal oxide deposits were found on the {110} facets after metal ion photo-oxidation, evidencing that electrons and holes accumulate on different sites on anisotropic BiVO₄ crystals. Besides providing proof of enhanced charge carrier separation, the preferential photodeposition was used to construct BiVO₄ 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, BiVO₄ 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_x, MnO_x, FeO_x] cocatalysts, via the original use of laser light, on

BiVO_4 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 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 X-ray 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 BiVO_4 crystals, Size control, Photocatalysis, Sacrificial water oxidation, Hydrogen production



TOC Graphic