Sunlight Selective Photodeposition of $\text{CoOx}(\text{OH})_y$ and $\text{NiOx}(\text{OH})_y$ on Truncated Bipyramidal BiVO_4 for Highly Efficient Photocatalysis

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Sun Light Selective Photodeposition of $\text{CoO}_x(\text{OH})_y$ and $\text{NiO}_x(\text{OH})_y$ on Truncated Bipyramidal BiVO_4 for Highly Efficient Photocatalysis

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ABSTRACT

Facet-engineered monoclinic scheelite BiVO_4 particles decorated with various co-catalysts were successfully synthesized by selective sun light photodeposition of metal or metal oxy(hydroxide) nanoparticles onto the facets of truncated bipyramidal BiVO_4 monoclinic crystals co-exposing $\{010\}$ and $\{110\}$ facets. X-ray photoelectron spectroscopy, scanning electron microscopy and scanning Auger microscopy revealed that metallic silver (Ag) and cobalt (oxy)hydroxide ($\text{CoO}_x(\text{OH})_y$) particles were selectively deposited onto the $\{010\}$ and $\{110\}$ facets, respectively, regardless of the co-catalyst amount. By contrast, the nickel (oxy)hydroxide ($\text{NiO}_x(\text{OH})_y$) photodeposition depends on the nickel precursor amount with an unprecedented selectivity for 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ with a preferential deposition onto the $\{010\}$ facets and the edges between the $\{110\}$ facets. Moreover, these noble metal-free heterostructures led to remarkable photocatalytic properties for rhodamine B photodecomposition and sacrificial water oxidation reactions. For instance, 0.2 wt% $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ led to one of the highest oxygen evolution rate, i.e. $1538 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, ever described which is ten times higher than that found for bare BiVO_4 . The selective deposition of cobalt (oxy)hydroxide species onto the more electron-deficient facet of truncated bipyramidal monoclinic BiVO_4 particles favors photogenerated charge carrier separation and therefore plays a key role for efficient photochemical oxygen evolution.

1. INTRODUCTION

In the broad context of increasing energy demand and the various environmental issues related to the intensive use of fossil energy resources, water photolysis from solar light is one of the most attractive approaches to produce clean hydrogen fuel.¹ Photoelectrochemical (PEC) and powdered photocatalytic water splitting are the two main technologies which have been implemented to achieve the splitting of water into hydrogen (H_2) and oxygen (O_2) through a photocatalytic process.^{2,3} First of all, in a PEC design a photoelectrode drives the reduction or oxidation reaction, while, the other charge carrier is shuttled through a wire towards another electrode which catalyzes the opposite reaction with or without light.^{4,5} Conversely, particulate photocatalysts are dispersed as a colloid or anchored onto a substrate whereby photoreduction and photooxidation are catalysed by one photocatalyst or through a Z-scheme where a shuttle redox mediator transfers charge carriers between two different photocatalysts.⁶⁻¹⁰ Whereas the photoelectrochemical method requires a sophisticated cell set-up with noble metal counter-electrodes, necessitates an external potential bias, and leads to scale-up issues, particulate photocatalysis in principle only requires a suspension of photocatalyst powders in a water basin. For instance, a thorough technoeconomic study on both designs for water splitting has shown that particulate water splitting based on baggies including particle slurries is expected to be economically viable considering 5% solar-to- H_2 conversion efficiencies and five years lifetime.¹¹ However, particulate based systems still lag behind in efficiency.^{8,10} To improve the efficiency of particulate photocatalysts to promote H_2 or O_2 evolution reactions, materials with suitable band gaps need to be combined to optimize light absorption, particle sizes need to be adapted so that diffusion length and absorption length are both accommodated and additional

contact materials should be applied to overcome intrinsic drawbacks of the main photoabsorber to create appropriate heterostructures.^{6,12,13}

Bismuth vanadate (BiVO_4) is a non-toxic and medium band-gap (2.4 eV) n-type semiconductor which has attracted worldwide attention as a visible-light active photocatalyst.^{14,15} Particularly, scheelite monoclinic BiVO_4 is one of the most active polymorphs in photocatalytic oxygen evolution,¹⁶ having reached near to maximum efficiencies when implemented as a photoanode material in PEC devices.^{17,18} However, the oxidation capability of bare BiVO_4 is hindered by weak charge carrier mobilities, short charge carrier diffusion lengths and a high charge recombination rate at the surface.¹⁹ To circumvent these inconveniences, heterostructuring by contacting BiVO_4 with other materials such as TiO_2 ,²⁰ WO_3 ,^{21,22} RuO_x ,²³ or (oxy)(hydr)oxides of first row transition metals (Co, Fe, Ni)^{24,25} has been proposed. Thus, several studies have shown that BiVO_4 photoanodes modified with $\text{NiO}_x(\text{OH})_y$ in combination with FeO_xOH_y yielded enhanced photocurrent densities in photoelectrochemical cells.²⁶⁻²⁹ In addition, Domen *et al.* found that a 6 nm thick conformal layer of NiOOH on a $\text{CoO}_x/\text{BiVO}_4$ anode led to a threefold increase in photocurrent, reaching 2.5 mA/cm^2 at 0.6 V vs RHE.³⁰ On the other hand, various spinel-type Co_3O_4 or $\text{CoO}_x/\text{BiVO}_4$ -based heterostructures showed enhanced photocatalytic properties for water oxidation³¹ or pollutant decomposition.^{32,33} The exact advantages of the first row transition metal oxides is still under debate, as some authors relate the increased water oxidation efficiencies to enhanced charge carrier separation,³⁴ surface passivation³⁵ or catalytic effects.³⁶

Usually, contact materials are deposited in a random manner on particulate BiVO_4 -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 of Ohno *et al.* on anatase and rutile TiO₂ particles³⁷ which have revealed the key role of exposed facets in the separation of photoinduced electron-hole pairs,^{38,39} photodeposition is now considered as a sort of general route for synthesizing heterostructures.^{40,41} 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.⁴²

Anisotropic photodeposition on BiVO₄ microcrystals has been extensively studied by Can Li *et al.* They have first shown using field emission secondary electron microscopy (FESEM) 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.⁴³ 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, with Pt/BiVO₄/CoO_x reaching an oxygen evolution rate of 1070 $\mu\text{mol.h}^{-1}.\text{g}^{-1}$ compared to only 7 $\mu\text{mol.h}^{-1}.\text{g}^{-1}$ for bare BiVO₄.⁴⁴ However, the dependence of the photodeposition as a function of the cocatalyst amount has not been studied in detail in particular due to the fact of the limitations of FESEM coupled to energy dispersive X-ray spectroscopy (EDS) analyses. Moreover, even though the photodeposition of nickel based compounds has been successfully achieved onto different semiconductors such as CdS,⁴⁵ TiO₂,⁴⁶

or even BiVO₄ films,⁴⁷ the regioselective deposition of nickel based oxides onto faceted BiVO₄ crystals has not been envisaged so far, despite the interest of this co-catalyst for photocatalytic purposes.^{26,47}

We have recently reported interface experiments showing that strong upwards band bending was observed for CoO_x/BiVO₄ and NiO/BiVO₄ interfaces indicating that this kind of heterostructures should favor charge carrier separation.³⁴ In this context, we herein report the photodeposition of CoO_x(OH)_y and NiO_x(OH)_y cocatalyst, via the original use of simulated sun light, on BiVO₄ microcrystals exposing well-defined {010} and {110} facets. 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 heterostructures prepared were tested for rhodamine B photodecomposition and water oxidation reactions, and were compared with previously studied Ag/BiVO₄ systems.

2. EXPERIMENTAL SECTION

2.1. Photocatalysts preparation

All reagents were bought in analytical grade and employed as received. Aqueous solutions were prepared using deionized water. Truncated bipyramidal BiVO₄ microparticles exposing well-defined facets were synthesized by optimizing and up-scaling a literature procedure.⁴⁸ The detailed synthesis procedure is described in the ESI. Cobalt (II) and nickel (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O) and silver nitrate (Ag(NO₃)) were used as reagents to photo-deposit CoO_x(OH)_y, NiO_x(OH)_y, and Ag onto the microcrystalline BiVO₄ particles in the 0.1-10 wt% range. Sodium iodate was used as a sacrificial agent for the CoO_x(OH)_y photo-deposition. A KBi buffer was used to maintain the pH at 9.2 for the NiO_x(OH)_y photo-deposition.⁴⁷ It is also worth mentioning that nickel amount of about 10 wt%,

precipitation of nickel dihydroxide ($\text{Ni}(\text{OH})_2$) was observed which has required the elimination of the precipitate before putting the solution in contact with the BiVO_4 microcrystals. In a typical procedure, a 100 mL aqueous solution of metal salts and additional agents was first prepared. Subsequently, 500 mg BiVO_4 powder was added and then sonicated for 10 min to obtain a good dispersion. The sides of the glass reaction vessel were then covered by aluminum foil so that the light source only illuminates the dispersion from the top. The suspension was then stirred during 1 h in the dark to reach adsorption equilibrium of the metal salts on the BiVO_4 particle surfaces. Next, the photodeposition of the metallic precursor on the BiVO_4 particles was initiated by switching on the solar simulator, which was used as a light source. After stirring under static air for 1-5 h, the solar simulator was switched off and the heterostructured powder was washed at least 5 times with distilled water through cycles of centrifugation and redispersion in water via sonication. Finally, drying at 70 °C for 8 h yielded about 0.45 g of the desired heterostructured photocatalyst. The precise parameters used for each system are detailed in Table S1. The solar simulator was a class AAA Newport Oriel Sol3A, using a 450 W Xenon lamp as light source, an AM 1.5G filter. It was calibrated with a certified Si-based solar cell (Newport Oriel, 91150V) to provide an incident flux of 100 mW.cm^{-2} (1 sun) (Figure S1).

2.2. Photocatalysts characterization

X-ray diffractograms were recorded with a Bruker AXS diffractometer (D2 PHASER) using a Cu anode ($\text{K}\alpha$ radiation). 2θ data were collected through continuous scanning from 10° to 70° with a 0.01° sampling pitch and a 6° min^{-1} scan rate. UV-Vis diffuse reflectance spectra of the powder samples were recorded using an UV-Vis-NIR spectrometer (Lambda 900) in the wavelength range of 300 to 800 nm. A JEOL JEM 2100F, equipped with a Schottky-type FEG and operated at an acceleration voltage of 200 kV, was used to perform high resolution

transmission electron microscopy (HRTEM) and energy dispersive spectroscopy (EDS). The BiVO₄ morphology was roughly determined through secondary electron imaging (SEI, up to 10.000X magnification) using a Hitachi TM 1000 microscope. To confirm the BiVO₄ morphology and analyze the spatial distribution of the metal(oxide) deposits on BiVO₄ high resolution secondary scanning electron microscopy (SEM) was performed with a JEOL 6700F or a JEOL 7600F, both equipped with a field emission gun and detectors for secondary electron imaging (SEI), back scattered electron imaging (BSE) and EDS. Scanning Auger microscopy (SAM) was performed with a PHI 710 scanning Auger nanoprobe, having a maximal lateral resolution of 10 nm and a maximal SEI resolution of 3 nm, to elucidate how the contact materials of the heterostructured powder samples were distributed along the particulate photoabsorbers. Different types of measuring modes were used, including point measurements (Auger spectra acquisition on a certain point), zone measurements (Auger spectra acquisition on a certain area) and mapping (Auger intensity acquisition of a certain area by scanning the area in a raster like pattern). Also SAM depth profiling, was occasionally tried, whereby an Argon ion gun (sputter rate 10 nm/min) was used to gradually sputter a sample and Auger spectra were measured after each sputter step. The oxidation state of the metal(oxide) deposits was analyzed at the Darmstadt Integrated System for MATerials research (DAISY-MAT) through X-ray photoelectron spectroscopy (XPS), using a Physical Electronics PHI 5700 multi-technique surface analysis system. XPS powder samples were prepared by applying a bit of heterostructured BiVO₄ powder on a thin piece of conductive indium foil placed onto a stainless steel holder. Details on the DAISY-MAT setup and handling of data are given elsewhere.^{49,50}

2.3. Photocatalytic tests

Photocatalytic behaviors of the prepared photocatalysts were first evaluated by decomposition of rhodamine B (RhB, Aldrich) under simulated sun light illumination using the solar simulator described above. All experiments were performed at neutral pH, under ambient pressure and temperature. In a typical dye degradation experiment, 50 mg of the photocatalyst powder was loaded into a glass beaker together with 100 mL of a RhB aqueous solution (10 mg.L⁻¹ in distilled water). After sonication for 10 min to disperse the photocatalyst powder, the dispersion was stirred at 750 RPM in the dark for 30 min. At that point the shutter of the solar simulator was opened and the dispersion was illuminated. Then at time intervals of 30 min, 1.2 mL aliquots were taken from the dispersion during a period of 2 h. Next, all recuperated aliquots (normally 6 in total) were centrifuged to separate the photocatalyst powder from the RhB solution. For each aliquot, 1 mL was taken, diluted to 3 mL with distilled water, and loaded into a quartz cuvette with a 1 cm path length. The remaining RhB amount was followed by UV-visible spectroscopy monitoring the change in absorption at $\lambda_{\text{max}} = 554$ nm using a Shimadzu, UV-1650 pc spectrophotometer. Blank experiments were also conducted with catalysts in the dark and without catalysts under light irradiation. All experiments were at least repeated twice to assess the reproducibility of the experiments, and the average data for two experiments are discussed in the following. Furthermore, free radical trap experiments were conducted using a previously reported procedure (see ESI).⁴⁶

The sacrificial photochemical water oxidation tests were carried out under an argon atmosphere with exclusion of air. Solvents were distilled under an argon atmosphere, or degassed via standard procedures prior to use and stored under argon. Each experiment was conducted in a double-walled thermostatically controlled reaction vessel (at a constant

temperature of 25 °C) which was connected via a condenser to an automatic gas burette, operated at a constant pressure (1 ± 0.05 bar). In a typical reaction, this setup was evacuated and flushed with argon three times to remove any other gases. The photocatalysts were introduced as a powder (50 mg) in the presence of sodium periodate (NaIO_4 , 1 mmol) as sacrificial agent and using a 10 mL phosphate (10 mmol.L^{-1} , pH 7.0) buffered solution as reaction medium. After stirring (300 rpm) for 5 min to reach thermal equilibrium, the photochemical oxygen evolution reaction was started by illuminating the reaction vessel with a 300 W Xe lamp (LOT-QuantumDesign GmbH) with an output power of 1.5 W and equipped with a 420 nm cut-off filter. The volume of evolved gases was continuously measured by the automatic gas burette, connected to a pressure sensor. After stopping the reaction, a 1 mL gas sample was taken and analysed with a GC (Agilent GC HP 6890N) equipped with a carboxen 1000 column and a thermal conductivity detector (TCD), having argon as carrier gas. Each catalytic test ran for 20 h.

3. RESULT AND DISCUSSION

3.1 Faceted BiVO_4 microcrystals

Reproducible BiVO_4 microcrystals were synthesized using a conventional hydrothermal route by fixing the pH value at 1.5. SEM images depicted in Figure 1a indicate that the synthesized BiVO_4 powders exhibit truncated bipyramidal morphology. The large top faces of the microcrystals correspond to the $\{010\}$ crystalline facets whereas the lateral sides can be assigned to the $\{110\}$ crystalline facets. Moreover, XRD patterns reveal the formation of monoclinic scheelite BiVO_4 microcrystals with no signal corresponding to tetragonal BiVO_4 (Figure S2). These monoclinic BiVO_4 microcrystals were then used as substrate to photodeposit regioselectively various co-catalysts using simulated sun light.

3.2 Regioselective metal photodeposition under simulated solar light

The use of simulated sun light to achieve the photodeposition of co-catalysts onto BiVO₄ microcrystals was first investigated in the case of metallic silver by adapting the procedure of Li *et al.*⁴³ FESEM images shown in Figure S3a suggest that the silver deposition occurs on the {010} facets of the BiVO₄ microcrystals, whereby the size of the deposits ranges from a hundred to a few hundred nanometers. Moreover, EDS elemental maps (Figure S3b-e) show clearly well-defined silver-containing particles which therefore confirm the preparation of a heterostructured Ag/BiVO₄ powder. The oxidation state of the silver deposit was then closely examined by XPS (Figure S4). Only, emissions characteristic of bismuth, vanadium, silver and oxygen were detected in the survey spectrum. The line shapes of the Bi 4f and V 2p_{3/2} core level spectra are symmetric and the corresponding features can be attributed to Bi³⁺ and V⁵⁺ species.^{51,52} The Ag 3d region exhibits two signals with binding energy maxima located at 368.3 eV and 374.3 eV which can be assigned to the Ag 3d_{5/2} and Ag 3d_{3/2} core levels arising from spin-orbit coupling. These energy values along with the splitting between the Ag 3d doublet, i.e. 6 eV, are consistent with the formation of metallic silver.^{53,54} Those results therefore indicate that, after solar light absorption, silver cations are preferentially reduced on the {010} facets after sun light absorption probably due to the preferential accumulation of electrons onto the {010} facets as previously shown.^{43,55}

3.3 Regioselective metal oxy(hydroxide) photodeposition under simulated solar light

Once the photoreduction was demonstrated, the photo-oxidation of cobalt nitrate onto BiVO₄ microcrystals using simulated solar light was studied. FESEM micrographs showed an increased roughness of the {110} facets which can be attributed to the regioselective deposition of cobalt-based particles (Figure 1b).⁴⁴

Figure 1. FESEM image of BiVO_4 (a) and 2 wt% $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ (b).

SAM mapping confirms more clearly that cobalt is almost restricted to the $\{110\}$ facets while the $\{010\}$ facets remain largely uncovered (Figure 2). Another important finding inferred from the SAM maps is that bismuth and vanadium signal intensity varies for the different facets. Thus, the $\{110\}$ facets seem to be more bismuth rich while vanadium seems to be more abundant on the $\{010\}$ facets. So far, anisotropic charge carrier mobilities⁵⁶ or higher upwards bend bending for the $\{110\}$ facets^{55,57} have been mainly proposed to rationalize the stronger hole accumulation on these facets. The facet specificity of the V/Bi surface stoichiometry could also play a role in the charge carrier separation. Furthermore, XPS analyses provide further insight in the oxidation state of the cobalt species. Along with the expected features for Bi^{3+} and V^{5+} species, the XPS spectra show quite complicated signals in the Co $2p_{3/2}$ region consisting of an asymmetric main line and several satellites due to plasmon loss features, electron correlations and final-state processes.^{58,59} The Co $2p_{3/2}$ spectrum is similar to the one reported for CoO and $\text{Co}(\text{OH})_2$ with a broad main line at a binding energy around 780 eV and a shoulder at 786 eV.^{58,60} By contrast, the Co $2p_{3/2}$ satellite structure reported for CoOOH and Co_3O_4 species show a much smaller shoulder at 786 eV and an additional bump at a binding energy of 790 eV,^{58,61} which some authors explain

Figure 2. SAM and XPS analyses for 2 wt% $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$. SAM elemental maps: Bi, V, O, Co and C (a); Core level XP spectra: $\text{Co}2p_{3/2}$, $\text{Bi}4f$, $\text{V}2p_{3/2}$ and $\text{O}1s$ core level XP spectra (b). Dark areas in (a) correspond to regions where mapped element is not present.

by the (partial) cobalt oxidation state change from Co^{2+} to Co^{3+} for CoOOH and Co_3O_4 .^{60,62} Thus, the samples prepared in this study contain seemingly more Co^{2+} , indicating that cobalt is most likely only partly oxidized during the photodeposition process. The cobalt species should be therefore denoted as $\text{CoO}_x(\text{OH})_y$ which is more accurate than Co_3O_4 usually proposed in the literature with similar XPS spectra.⁴⁴ At this stage, it is also worthwhile to mention that the cobalt species has been found to change during the photo-oxidation of water which makes it difficult to propose an exact composition for the cobalt co-catalyst.^{60,63}

The photodeposition of nickel oxide species onto BiVO₄ microcrystals was then investigated for three different nominal nickel contents, i. e. 0.1, 1 and 10 wt% Ni. FESEM images suggest that the regioselectivity of the nickel-based deposit depends on the weight percentage of nickel (Figure 3). Thus, for the samples containing 1 and 10 wt% Ni, nickel seems to be unselectively deposited over the entirety of the BiVO₄ particle surface. This was confirmed by EDS mapping of the nickel element which showed that nickel is present on the whole surface of the BiVO₄ particles for the 10 wt% Ni sample (Figure 3c). By contrast, a certain regioselectivity was observed in the 0.1 wt% Ni heterostructure with a preferential nickel deposition on the edge between two {110} facets according to FESEM images (Figures 3e-f). These trends were then confirmed by SAM studies. SAM sputter profiles were run measuring the Ni L3VV Auger lines on zones corresponding to BiVO₄ {010} facets and {110} facets defined by SEM images (Figure g-h). An intense Ni L3VV Auger signal was detected for each zone of the microcrystals for the 1 wt% Ni sample confirming the absence of regioselectivity for a high amount of nickel (Figure 3i). After each sputter step the Ni L3VV Auger signal intensity decreases, confirming that Ni is predominantly located at the BiVO₄ particle surface. Contrarily, for the 0.1 wt% Ni sample a Ni L3VV Auger signal is only visible when zones on the {010} facets were measured (Figure 3j). In addition, bright-field and dark-field STEM images on the edge of the {110} facets for the 0.1 wt% Ni sample reveal the presence of small particles which can be attributed to nickel oxide species according to EDS analyses (Figure S5). As a consequence, the nickel deposit appears to be limited to the {010} facets and the edges between the {110} facets in the 0.1 wt% Ni heterostructure.

Figure 3. SEM images for bare BiVO_4 (a), 10 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (b), 10 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ with Ni EDS mapping (c), 1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (d) and 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (e-f). SEM images for 1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (g) and 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (h) indicating on which zones Ni L_3VV SAM sputter profiles were measured. Ni L_3VV SAM sputter profiles for 1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (i) and 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ (j) Areas 1 and 2 correspond to $\{110\}$ facets while areas 3 and 4 stands for $\{010\}$ facets.

Further insights in the surface composition of the 0.1 wt% and 1 wt% Ni samples were inferred from XP core level spectra of Ni 2p, O 1s, V $2p_{3/2}$ and Bi 4f (Figure 4). As for the other heterostructures, the core level binding energies found for V $2p_{3/2}$ and Bi 4f are characteristic of V^{5+} and Bi^{3+} chemical states in BiVO_4 .^{51,52} As expected, the Ni 2p-to-Bi 4f intensity ratio is higher for the 1 wt% Ni sample compared to the 0.1 wt% Ni one. Furthermore, two main features are detected in the O 1s core level spectrum at 530.3 eV and 532.2 eV, respectively. The former can be assigned to metal oxides, i.e. O^{2-} sites, while the latter is typical for hydroxyl groups and organic carbon-oxygen bonds, commonly present in ex situ prepared samples due to adherence of water and organic compounds onto the sample surface.⁵² It is also worth underlining that the

hydroxyl feature is considerably more intense than usual, even higher than the O^{2-} signal, for the 1 wt% Ni sample which suggests a large amount of hydroxide species. Finally, the Ni 2p core level region is complex with four main features at 856.6 eV belonging to Ni 2p_{3/2}, 861.5 eV belonging to a Ni 2p_{3/2} satellite, 874.3 eV belonging to Ni 2p_{1/2} and 880.7 eV corresponding to a Ni 2p_{1/2} satellite. The presence of pure NiO and metallic nickel can be excluded, since that would give rise to a noticeable peak splitting of the main Ni 2p_{3/2} line at 856.5 eV for NiO⁶⁴ and a characteristic Ni 2p_{3/2} feature at 852.6 eV for Ni⁶⁵ which are not observed here. Instead, the Ni 2p line shape resembles more to that reported for a mixed nickel oxyhydroxide.^{64,66} As a result, the nickel species should be designated as NiO_x(OH)_y.

Figure 4. Core level XP spectra for 0.1 wt% and 1 wt% NiO_x(OH)_y/BiVO₄: Ni 2p (a), O 1s (b), V 2p_{3/2} (c) and Bi 4f (d) core level XP spectra.

3.4 Photocatalytic properties

First of all, the optical band gaps of the different heterostructures prepared were determined by UV-visible diffuse reflectance spectroscopy (Figure S6a). It is generally admitted that BiVO₄ is an indirect band gap semiconductor,⁶⁷ whereas light absorption involves direct transition. Thus, Tauc plots of $[F(R)hv]^2$ vs. hv led to direct optical band gap in the range of 2.48-2.52 eV while

Tauc plots of $[F(R)hv]^{1/2}$ vs. $h\nu$ yielded indirect optical band gap of about 2.41-2.43 eV (Figure S6b-c). This shows that the deposited contact materials do not have a strong influence on the light absorption properties of the heterophotocatalysts.

The photocatalytic properties were first examined by the photodecomposition of RhB over different photocatalysts (with a co-catalyst loading of 0.1 wt%) under simulated sun light (1 sun) and static air (Figure S7). A blank experiment in the absence of photocatalyst confirms that photolysis of RhB under sun light can be neglected. Thus, 0.1 wt% Ag/BiVO₄ and 0.1 wt% NiO_x(OH)_y/BiVO₄ photocatalysts appeared to be the most efficient with about 50% dye decomposition after 2h irradiation while 0.1 wt% CoO_x(OH)_y/BiVO₄ showed a lower activity, similar to that of bare BiVO₄. Photodegradation of RhB by these materials can be modeled by using a pseudo first order kinetic law, $\ln(C/C_0) = k_{app}t$ where k_{app} is the pseudo first-order rate constant and, C and C₀ stand for the concentration of the dye in solution at time t and 0. Apparent rate constants were estimated to be $3.3 \times 10^{-3} \text{ min}^{-1}$, $2.7 \times 10^{-3} \text{ min}^{-1}$, $5.5 \times 10^{-3} \text{ min}^{-1}$ and $6.7 \times 10^{-3} \text{ min}^{-1}$ for BiVO₄, 0.1 wt% CoO_x(OH)_y/BiVO₄, 0.1 wt% NiO_x(OH)_y/BiVO₄ and 0.1 wt% Ag/BiVO₄, respectively. While the beneficial effect of metallic silver particles in BiVO₄ based photocatalysis is well-documented,^{68,69} it is the first time that the same trend is reported for NiO_x(OH)_y deposits. For Ag/BiVO₄ system, it has been reported that superoxide radicals (O₂^{•-}) are the main species involved in the degradation of organics.⁶⁹ To get an insight in the radicals involved in the case of the original 0.1 wt% NiO_x(OH)_y/BiVO₄ photocatalyst, propan-2-ol (IPA), 1,4-benzoquinone (BQ) and potassium iodide (KI) were used as hydroxyl radical (OH[•]), superoxide radical (O₂^{•-}) and hole (h⁺) scavengers, respectively for RhB photodecomposition. Figure S8 reports on the kinetic rate constant found in each case normalized by that in the absence of trapping agents. Thus, addition of IPA and KI has strongly diminished the

photocatalytic activity of 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ material while BQ led to a less pronounced decrease. As a result, $\text{O}_2^{\bullet-}$ radicals which are only formed by photogenerated electrons are not the dominant species ruling the photocatalytic activity while holes play an important role in the photocatalytic decomposition of RhB in the presence of the $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ system. This could be due to the combination of a catalytic effect of $\text{NiO}_x(\text{OH})_y$ particles lowering the activation energy with an enhanced hole collection at the $\text{NiO}_x(\text{OH})_y\text{-BiVO}_4\{110\}$ interface.

Then, photochemical sacrificial water splitting experiments were carried out to determine the ability of the different photocatalysts to promote O_2 evolution reaction in the presence of an electron scavenger (sodium periodate). At this stage, it is worth mentioning that the use of sacrificial reagents may lead to undesired phenomena such as side reactions, deactivation and changing driving forces.⁷⁰ Nonetheless, this approach allows for a simplification of the complex system of overall water splitting and hence a more detailed understanding of the basic processes. As depicted in Fig. 5A, no significant amount of O_2 was generated in the absence of light while a volume increase of 1 mL was observed for a blank experiment without photocatalyst (Fig. S9). In contrast irradiation for 6 h of 0.2 wt% $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ suspensions in NaIO_4 /water mixture led to the production of about 12 mL of O_2 evidencing the occurrence of an actual photocatalytic process. Typical plots of the time course of O_2 evolution for the different photocatalysts investigated are shown in Fig. 5B. Regardless of the photocatalyst nature, the amount of evolved O_2 was increasing linearly with time thus revealing the high stability of the photocatalysts to reach a plateau value which corresponds to the total consumption of the scavenger (see ESI). This result evidences that reduction of IO_4^- does not constitute the rate-limiting step.

Figure 5. (A) Photocatalytic evolution of O₂ under different conditions. (B) O₂ evolution over bare BiVO₄ (a, blue), 1 wt% NiO_x(OH)_y/BiVO₄ (b, magenta) and 0.2 wt% CoO_x(OH)_y/BiVO₄ (c, red).

To get a more quantitative insight in the photocatalytic properties, a linear regression was performed on the linear part of the gas evolution curves, i.e. at a reaction time between 2 and 3 h, and the resulting rates are gathered in Table 1. Implementation of CoO_x(OH)_y as co-catalyst boosts the sacrificial water oxidation performance of BiVO₄ by about 10 times, with respect to bare BiVO₄. However, the NiO_x(OH)_y/BiVO₄ heterostructures exhibited only a fair water oxidation rate compared to the other heterostructures, since the O₂ evolution is only twice as high with respect to bare BiVO₄. These results may be related to the highly regioselective deposition of the CoO_x(OH)_y oxidation co-catalyst on the electron-deficient {110} facets of BiVO₄ microcrystals compared to NiO_x(OH)_y which is mainly located on the electron-rich {010} facets of BiVO₄. The CoO_x(OH)_y regioselectivity, the preferential accumulation of holes on the {110} facets^{44,55} and upwards band bending at CoO_x/BiVO₄ contacts³⁴ favors the spatial charge separation of the photogenerated charge carriers which inhibits charge recombination and leads to enhanced photocatalytic O₂ evolution rate.

Table 1: O₂ evolution rates of some photocatalysts prepared in this work in comparison with those reported in literature for state of the art photocatalysts based on BiVO₄. All the literature data have been acquired under visible light ($\lambda > 420$ nm) using a 300 W Xe lamp.

Photocatalyst	Electron scavenger	O ₂ evolution ($\mu\text{mol.h}^{-1}.\text{g}^{-1}$)	Ref
BiVO ₄	0.1 M NaIO ₄	154	This work
0.1 wt% NiO _x (OH) _y /BiVO ₄	0.1 M NaIO ₄	292	This work
1 wt% NiO _x (OH) _y /BiVO ₄	0.1 M NaIO ₄	304	This work
0.08 wt% CoO _x (OH) _y /BiVO ₄	0.1 M NaIO ₄	1330	This work
0.2 wt% CoO _x (OH) _y /BiVO ₄	0.1 M NaIO ₄	1538	This work
BiVO ₄	0.05 M AgNO ₃	835	14
BiVO ₄	0.05 M AgNO ₃	920	72
PO ₄ -doped BiVO ₄	aqueous AgNO ₃	670	73
S-doped-C ₃ N ₄ /BiVO ₄	0.05 M AgNO ₃	750	74
Ru-SrTiO ₃ :Rh-RGO/BiVO ₄	H ₂ SO ₄	167	75
Ru-SrTiO ₃ :Rh/BiVO ₄	H ₂ SO ₄	540	76
Pt/BiVO ₄ /MnO _x	0.02M NaIO ₃	630	43
Pt/BiVO ₄ /Co ₃ O ₄	0.02M NaIO ₃	1070	44
V _o -ZnO/BiVO ₄	0.05 M AgNO ₃	1356	77

3.5 Discussion

The photodeposition of various co-catalysts onto faceted BiVO₄ microcrystals has been successfully achieved using 1 sun illumination with a regioselectivity strongly dependent upon the co-catalyst used. The expected facet-selectivity was actually observed for both silver and cobalt photodeposition carried out at pH 7.^{43,44} Under these pH conditions, the main metallic precursor species are cationic, i.e. Ag⁺ or Co²⁺, and BiVO₄ truncated bipyramidal surfaces are

negatively charged since the isoelectric point of these microparticles has been reported to be about 3.5.⁴³ As a consequence, specific adsorption of the metallic precursor cannot be at the origin in the difference of the regioselectivity observed. On the other hand, as the same counter-ion, i.e. NO_3^- , was used in both cases, preferential chemisorption of anions on specific facets can be ruled out to interpret the facet selectivity. Finally, favored interactions of the neutral, i.e. methanol, or negatively charged, i.e. IO_3^- , hole or electron scavengers with specific facets is unlikely owing to the negative charge of the BiVO_4 surfaces. The regioselectivity for the Ag and $\text{CoO}_x(\text{OH})_y$ deposition can therefore be assigned to the different electrochemical properties of the {010} and {110} facets under light irradiation which favors the reduction of silver cations on the electron-rich {010} facets and the oxidation of the cobalt precursor on the electron-deficient {110} facets of the BiVO_4 microcrystals. These findings obtained at 1 sun are fully consistent with those previously reported with other light sources.^{43,44}

On the other hand, the regioselectivity of the nickel photodeposition strongly depends on the wt% of nickel in the reaction mixture since nickel species was selectively deposited onto the {010} facets and the edges between the {110} facets in the 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ sample whereas no selectivity was detected for nickel amount equal to or higher than 1 wt%. Overall, the difference in regioselectivity of Co and Ni is striking due to their very similar chemistry. The standard oxidation potentials for the oxidation of Co^{2+} to CoOOH (1.76 V) and Ni^{2+} to NiOOH (2.05 V) are close and both allowed according to the BiVO_4 VBM of about 2.8 V vs NHE. Similarly, the standard reduction potentials for the reduction of Co^{2+} to Co(s) (-0.282 V) and Ni^{2+} to Ni(s) (-0.236 V) can thermodynamically not take place at the BiVO_4 surface under light illumination, because of the more positive BiVO_4 CBM.⁷¹ Thus, only oxidation of Ni^{2+} is assumed just as for Co^{2+} . The difference in regioselectivity could have to do with the difference

in pH, as Co^{2+} was deposited at pH 7, while Ni^{2+} was deposited at pH 9.2 using a KBi buffer. The $\{010\}$ facets could be more negatively charged, leading to a preferential adsorption of the Ni^{2+} ions onto these facets. The Ni^{2+} ions could then react with OH^- leading to an impregnation onto the $\{010\}$ facets. Regarding the suitable standard reduction potential (0.52 V) the impregnated $\text{Ni}(\text{OH})_2$ could then further oxidize to NiOOH during light illumination.⁷¹ Additionally, the regioselective adsorption of Ni on the $\{110\}$ edges could be due to even higher hole accumulation on these edges than on the $\{110\}$ facets, so that for low Ni^{2+} concentrations only photodeposition takes place on the $\{110\}$ edges.

As far as the photocatalytic properties are concerned, the rates found for the photodecomposition of RhB in the presence of 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ and 0.1 wt% Ag/BiVO_4 under static air fall within the range of those reported by Li *et al.* for BiVO_4 microcrystals endowed with a single co-catalyst under oxygen bubbling.⁴⁴ As a result, associated with BiVO_4 particles, $\text{NiO}_x(\text{OH})_y$ is a good co-catalyst for the photodegradation of organics. Moreover, comparison with literature indicates that the materials developed in this study compete well with the most efficient photocatalysts for sacrificial water oxidation reaction (Table 1).^{14,43,44,72-77} First of all, our results are on line with those reported by Li *et al.* for similar morphologies,⁴⁴ in the sense that boosted water oxidation performances were obtained for cobalt based materials. In addition, the O_2 evolution reaction rates for BiVO_4 , 0.1 wt% $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ and 0.2 wt% $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ were significantly higher than those described by Li *et al.* for BiVO_4 , $\text{Co}_3\text{O}_4/\text{BiVO}_4$ and Pt/BiVO_4 , i.e. 6.7, 16.7 and 112.0 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.⁴⁴ These data reveal the quality of the faceted BiVO_4 microcrystals and the cobalt oxide deposit obtained under sun light illumination. Finally, the overview provided in Table 1 clearly indicates that the 0.2 wt% $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ led to one of the highest sacrificial O_2 evolution

rate ever reported in the literature. Figure 6 depicts the band alignment of our $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ and $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ heterostructured particles along the [010] and [110] direction based on the differences in band alignment along the [010] and [110] direction for bare truncated bipyramidal BiVO_4 crystals,⁵⁵ the band alignment at the $\text{CoO}_x/\text{BiVO}_4$ and NiO/BiVO_4 contacts³⁴ and the observed regioselectivity. Surface photovoltage measurements on truncated bipyramidal BiVO_4 crystals have demonstrated upwards band bending in the [110] direction, which is almost absent in the [010] direction.⁵⁵ For both $\text{CoO}_x/\text{BiVO}_4$ and NiO/BiVO_4 strong upwards band bending at the heterocontact in BiVO_4 has been observed.³⁴ Because Co cocatalyst could only be detected on the [110] facets of $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ upwards band bending can be expected in the [110] direction but not in the [010] direction. As a consequence of the upward band bending in the [110] direction holes will be driven to the $\text{CoO}_x(\text{OH})_y$ coated [110] facets, whereas the electrons will move to the {010} facets with no/small band bending. This clear and strong difference in band bending along the different crystalline directions allow for clear charge carrier separation and reduced surface charge carrier recombination and could explain why a remarkable water oxidation efficiency was reached with $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$. In contrast, Ni cocatalyst could be found on the edges of the {110} facets and on the {010} facets. Therefore, upwards band bending can be expected in the [110] direction and the [010] direction, giving no clear separation path for light induced electron-hole pairs. Another reason why our heterostructured BiVO_4 photocatalysts exhibited a better water oxidation efficiency than bare BiVO_4 could be due to enhanced surface passivation, since Zachäus *et al.* showed using intensity modulated photocurrent spectroscopy that CoPi effectively passivated the surface of BiVO_4 .³⁵ For a more detailed analysis on the relative contributions of the suggested mechanistic explanations single

crystalline studies with well defined surface facets would be of interest as have been performed on anatase TiO_2 .⁴²

Figure 6. Schematic of the energy band alignment for $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ and $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ along the $[010]$ and $[110]$ direction, showing the potential pathways of light induced charge carriers (a). Schematics of the electrochemical sacrificial oxygen evolution reactions on $\text{CoO}_x(\text{OH})_y/\text{BiVO}_4$ and $\text{NiO}_x(\text{OH})_y/\text{BiVO}_4$ using NaIO_4 as sacrificial agent. The thickness of the arrows corresponds to the efficiency of the reactions.

4. CONCLUSION

In this work, we have demonstrated that Ag/BiVO₄, CoO_x(OH)_y/BiVO₄ and new NiO_x(OH)_y/BiVO₄ heterostructures could be successfully synthesized through an original sun light photodeposition route. Combining scanning electron and Auger microscopy with X-ray photoelectron spectroscopy enabled to unravel the regioselectivity and the chemical nature of the co-catalyst deposits. Metallic silver (Ag) and cobalt (oxy)hydroxide (CoO_x(OH)_y) particles were selectively deposited onto the {010} and {110} facets, respectively, of {010}/{110} dual facet exposed BiVO₄ microcrystals. On the other hand, nickel (oxy)hydroxide (NiO_x(OH)_y) photodeposition shows no facet selectivity for nickel precursor amount higher than 1 wt% while an original selectivity was observed for 0.1 wt% NiO_x(OH)_y/BiVO₄ with a preferential deposition onto the {010} facets and the edges between the {110} facets. In addition, most of the heterostructures prepared showed enhanced photocatalytic properties. Thus, 0.1 wt% Ag/BiVO₄, and 0.1 wt% NiO_x(OH)_y/BiVO₄ led to almost twice higher decomposition rates of RhB than bare BiVO₄ under simulated sun illumination. More interestingly, for sacrificial water oxidation 0.2 wt% CoO_x(OH)_y/BiVO₄ yielded one of the highest oxygen evolution rates, i.e. 1538 μmol.h⁻¹.g⁻¹, ever reported in the literature which represents a tenfold increase compared to bare BiVO₄. Our study therefore emphasizes the key contribution of regioselective deposition of cobalt oxide species onto the more electron-deficient facet of truncated bipyramidal scheelite BiVO₄ microcrystals for efficient oxygen evolution reaction. Finally, this work shed light on the potentialities of solar irradiation instead of conventional lamps to fabricate efficient heterostructured photocatalysts by associating an appropriate co-catalyst and selective deposition onto the specific facet of metal oxide photoabsorbers. The results obtained in our study support the idea to fabricate well defined heterostructures of absorber materials coupled to co-catalysts

working as contact and catalytic center. A challenging but rewardable research direction of nanotechnology would be to form faceted nanocrystals with electronically well defined facets for electron and hole scavenging, the effect of which will be supported by cocatalyst materials with strongly deviating electronic properties. In short, a nano-sized cell arrangement with contact materials providing an adapted electronic contact, but also preferential catalytic properties would be favorable.

ASSOCIATED CONTENT

Supporting Information. XRD patterns, UV-visible spectroscopy data, complementary SEM, SAM and XPS data, RhB photodecomposition data.

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The manuscript was written through contributions of all authors.

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SYNOPSIS