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Comparative study of the photocatalytic effects of pulsed laser deposited CoO and NiO nanoparticles onto TiO₂ nanotubes for the photoelectrochemical water splitting

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ABSTRACT

Hybrid structures combining a photo-active material and non noble metal oxide co-catalyst nanoparticles are of strong interest to produce efficient photoelectrodes for hydrogen production while limiting the cost due to noble metals (Pt, Ru ...). In order to get some insight on the mechanism change induced by such co-catalyst nanoparticles (NPs), we conducted a comparative study between cobalt and nickel oxide nanoparticles deposited onto TiO₂ nanotubes (NTs) prepared through anodization. The TiO₂-NTs were decorated with CoO and NiO nanoparticles using the reactive pulsed laser deposition (PLD) method. The oxygen atmosphere used during the PLD process, ensures the *in-situ* oxidation of the metal nanoparticles into CoO and NiO. The surface loadings of CoO or NiO NPs were controlled by the number of laser ablation pulses (N_{LP}). The efficiency of CoO and NiO NPs as co-catalysts for photo-electrochemical water splitting was studied by cyclic voltammetry, as a function of N_{LP} , under both simulated sunlight and visible light illuminations and by external quantum efficiency (EQE) measurements. We determined an optimal catalyst loading at $N_{LP} = 2000$, allowing to almost triple the photoconversion efficiency (PCE) for both TiO₂-NTs/CoO-NPs and TiO₂-NTs/NiO-NPs nanohybrid photoanodes, in comparison with bare TiO₂-NTs. Moreover, CoO-NPs were found to be the best co-catalyst under visible light illumination, with a PCE almost 10 times higher than for TiO₂. This significant enhancement of the visible light activity is ascribed to the narrower band gap of CoO and to the formation of a heterojunction with TiO₂ that is more favorable for charge transfer than in the case of NiO co-catalyst.

1. Introduction

With the increasing energy demand and a strong will to find an alternative to fossil fuels, there is an urgent need to find a renewable energy source, which can be stored and used on demand. Hydrogen is a highly promising alternative energy carrier that already present encouraging large scale applications such as cars and trains powered by fuel cells [1]. In addition to the versatility of its uses, hydrogen is a non-carbonaceous storable fuel, with water as the only reaction product, making it particularly attractive as an energy carrier. However, hydrogen is nowadays mainly produced from fossil resources [2]. A promising approach for a clean and sustainable hydrogen production is solar driven photoelectrochemical (PEC) water-splitting. Succinctly, a

PEC cell is composed of a working photoelectrode and a counter-electrode; the photoelectrode consists of a semi-conductor material with an appropriate bandgap to absorb solar light and generate electron/hole (e^-/h^+) pairs; the photo-generated charges are responsible for the oxidation of water into oxygen, and its reduction into hydrogen. These two reactions are commonly referred to as oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).

One of the biggest challenges is to overcome the slow kinetic of the oxidation reaction, which consequently requires high overpotential. Water electrolysis is therefore mostly restricted by the complex OER reaction that involves the transfer of $4e^-$, according to the following sequence (in alkaline electrolyte) [3]:

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As seen above, this four electrons reaction involves the formation of at least three intermediates before turning water into oxygen. It has already been established that binding energies of these intermediates with the surface of the catalyst play a crucial role. Based on experimental and computational work, an OER volcano plot has been proposed, relying on standard free energies of OH_{ads} and O_{ads} intermediates to assess the efficiencies of diverse catalysts toward the OER [4]. TiO_2 is a well known material that can be used as photoanode for water splitting both in alkaline and acidic medium. Nevertheless, according to the volcano plot mentioned above, its catalytic efficiency over the OER is limited and is expected to be improved by depositing co-catalysts on its surface. Recent efforts have been particularly targeting the deposition, on TiO_2 structures, of efficient catalyst for OER. If IrO_2 and RuO_2 are considered as state-of-the-art [5], their high costs limit their usage. As an alternative, investigations on chalcogenides [6], transition metal nitrides [7], transition metal oxides [8,9], hydroxides [10], or oxy-hydroxides [11] were conducted. While some transition metal nitrides displayed promising catalytic activity and better electrical conductivity than metal oxides, they however suffer of a poor stability [7]. Interestingly, cobalt and nickel oxides are found to be at the top part of the volcano plot based on Calle-Vallejo et al. DFT calculations [12], and therefore can be used as co-catalysts to enhance the catalytic efficiency of TiO_2 for OER. As a matter of fact, Qarechalloo et al. have decorated TiO_2 nanotubes (NTs) with CoO_x with an electrodeposition method [13]. By varying the electrodeposition current densities and time, they obtained different catalysts shapes and loadings. They have decorated TiO_2 -NTs with well distributed CoO_x nanoparticles with an average size of 35 nm, that exhibit a photocurrent twice better than that produced by bare TiO_2 -NTs. On the other hand, Uddin et al. have prepared a NiO/TiO_2 heterostructure by a one-pot sol-gel synthesis [14]. The performance of their material was measured with hydrogen photocatalytic production by methanol photoreforming, where TiO_2 with 1 wt % of NiO has led to a H_2 production rate almost four times more important than P25 TiO_2 used as a reference, pointing out the efficiency of the NiO catalyst. In addition, Deng et al. have used an electrodeposition method to decorate TiO_2 nanotubes with NiO nanoparticles [15]. They have studied the efficiency of their material by a photocatalytic degradation of 4-chlorophenol, which was found to be twice more efficient than bare TiO_2 . They ascribed their enhanced activity to a better charge separation due to the formation of a heterojunction between the two semi-conductors. The improvement of charge separation by creating heterojunction that can modify the bands bending at the surface of the semi-conductor is a strategy of great importance for development of efficient photocatalysts at lower cost [16,17]. If these experimental studies are in line with the theoretical predictions that CoO and NiO are good co-catalyst materials, the mechanism improving the performance of the heterostructure still need to be investigated. Recent studies over the world present original approach to characterize the mechanisms involved in photo-electrochemical materials under irradiation [18–21], but only few of them investigated the influence of a co-catalyst deposition on semiconducting nanostructure on these mechanisms.

In this work, we report on the use of the reactive pulsed laser deposition technique (PLD) under a low pressure oxygen atmosphere to deposit CoO or NiO nanoparticles (NPs) onto TiO_2 nanotubes arrays. The aim of this study is to achieve a comparative assessment of the catalytic efficiency of these CoO and NiO NPs decorated TiO_2 -NTs as photoanodes for the PEC water-splitting and of their behavior under different irradiation conditions. The PLD is a non-equilibrium physical vapor

deposition technique that has been shown to be very effective for the *in-situ* deposition of different nanoparticles onto various nanomaterials, including carbon nanotubes or TiO_2 nanorods [22–24]. In addition, the PLD technique is well known for its ability to deposit nanoparticles with high-purity (no residual precursors) which is particularly important for such type of mechanistic studies. Furthermore, the obtained deposits show good crystallinity and strong adhesion to the underlying substrate because of the energetic ablated species involved in laser deposition process. All these unique PLD features should contribute to improve the photoelectrochemical performance of the NPs decorated NTs through an efficient charge transfer thanks to a strong adhesion between the deposited co-catalyst NPs and the TiO_2 -NTs, as this has been demonstrated in the case of PbS -NPs and carbon nanotubes [25]. Thus, by achieving a systematic investigation of both CoO -NPs and NiO -NPs decorated TiO_2 -NTs based photoanodes, we have demonstrated that their photoconversion efficiency, under sunlight illumination, can be tripled in comparison with bare TiO_2 -NTs photoanodes. More interestingly, under visible light illumination conditions, the PLD deposited CoO -NPs were found to perform even better by exhibiting a photo-conversion efficiency almost one order of magnitude higher than that of bare TiO_2 -NTs photoanodes. By combining, different spectroscopic and photo-electrochemical experiment, we proposed a model that explains the difference of performance between the two co-catalysts by the involvement of different mechanisms.

2. Experimental

Titanium dioxide nanotubes were synthesized using anodization of a titanium foil (2.0cm x 1.5cm x 50μm; 99.6% MaTeck), in an ethylene glycol (>99.5%; Sigma-Aldrich) based electrolyte with 0.3%_{w/w} of NH_4F (98.0%, Sigma-Aldrich) and 1%_{v/v} of Milli-Q water. Prior to the anodization, Ti foils were consecutively degreased by ultrasonication in acetone, ethanol and rinsed by Milli-Q water. A two electrode Teflon electrochemical cell (diameter 7 cm) filled with 125 mL of electrolyte was used to carry out the synthesis using a Pt plate (2.0 x 2.0 cm, Mateck GmbH) as a counter-electrode. A biologic SP300 potentiostat with booster was used to apply an anodization voltage of 45 V between the counter-electrode and the Ti foil, allowing growth of a highly ordered TiO_2 nanotubes array. Adhesion between NTs and Ti foil was increased with a pre-anodization step (45 V, 1h30), followed by removal of the initially formed arrays of NTs using a scotch tape. To control the length of nanotubes, anodization was systematically stopped when a charge density of 5 C cm⁻² was transferred during the synthesis. The resulting amorphous samples were then carefully rinsed with Milli-Q water, and dried under nitrogen flow, before being annealed at 500 °C (5 °C.min⁻¹ heating and cooling ramps) during 4 h under air flow (100 mL min⁻¹).

Deposition of CoO or NiO NPs was achieved through the reactive pulsed laser ablation of metallic cobalt or nickel targets under an oxygen background atmosphere. The PLD was carried out by focusing an KrF excimer laser ($\lambda = 248$ nm; pulse duration = 15 ns; Pulse frequency = 20 Hz) onto the target (2" metallic disk of Cobalt or Nickel, Kurt J. Lesker, 99.9%), at an incidence angle of 45°. Both TiO_2 -NTs and quartz substrates were placed on the same substrate holder, which is placed parallel to the target at a distance of 7cm. The PLD chamber was first turbo-pumped down to a pressure of $2.5 \cdot 10^{-5}$ torr, and then it was filled with oxygen gas until it reaches a partial pressure of 300 mTorr which is maintained during the whole deposition process. Prior to the NPs deposition, the target was systematically cleaned by laser ablating its surface during 5 min while the substrates to be decorated are isolated by a mechanical shutter from the laser ablation plume. To ensure a uniform coverage of the samples by nanoparticles, the substrate holder was rotated at 5 rpm, while the focused laser beam is being swept on the target rotating in opposite direction with respect to the substrate holder. The laser energy density on the target was kept at 4 J cm⁻² during NPs deposition. In this work, the number of laser ablation pulses, N_{LP} , was varied ($N_{LP} = 500; 2000; 5000; 10,000$) for each target (cobalt or

Fig. 1. Typical SEM images of (a) TiO₂ nanotubes array at 45°; Top view of TiO₂ nanotubes before (b) and after (c) their decoration with nickel NPs at $N_{LP} = 2000$ and with (d) cobalt NPs ($N_{LP} = 10,000$).

nickel).

The surface morphology of our samples was examined by means of scanning electron microscopy (SEM) using a GeminiSEM 500 (Zeiss) microscope, equipped with a field emission gun as an electron source. The chemical bonding states of the CoO and NiO nanoparticles were characterized by X-ray Photoelectron Spectroscopy (XPS). The XPS spectra were acquired by using a Thermo VG Scientific spectrophotometer (Al anode, $h\nu = 1486.6$ eV, Pass Energy 20 eV), and analyzed by the CasaXPS software. The XPS spectra positions were corrected with the adventitious carbon peak (285.0 V) as an internal reference. The optical absorbance of the CoO and NiO nanoparticles (deposited purposely on quartz substrates) were recorded with a PerkinElmer UV-vis spectrophotometer over the 200–800 nm wavelength range.

Cyclic voltammetry (CV) was performed with a Biologic SP-300 potentiostat, with an applied potential ranging from -1.5 V to -0.3 V vs MSE ($0.64 + 0.059$ pH V vs RHE), at a 10 mV s⁻¹ scan rate. A homemade 3 electrodes PEC cell was filled with 100 mL of alkaline electrolyte (0.01 M NaOH + 0.1 M Na₂SO₄), with a platinum mesh being the counter-electrode. A surface of 0.44 cm² (delimited by an O-ring) of the samples (i.e. TiO₂-NTs photoanode subsequently PLD-decorated with CoO or NiO NPs) were illuminated with a Xe arc lamp (Newport; 300W) under two spectral configurations: (i) with an AM1.5G filter, in order to simulate the solar spectrum (total irradiance 100 mW cm⁻²), and (ii) with the combination of an AM1.5G and a 400 nm long pass filter (total irradiance 70 mW cm⁻²), in order to measure their performance under the solar visible light illumination condition. Prior to the PEC experiments, the electrolyte was deoxygenated with a nitrogen flow. The External Quantum Efficiency (EQE) of our photoanodes was systematically measured with the same homemade cell illuminated with a Xe arc lamp (Newport; 150W), passing through a Newport Oriel 1/8 m Cornerstone Monochromator. A 1.05 V vs RHE potential was applied to our samples, and EQE was measured from over the 280–800 nm wavelength range with 8 nm steps. Electrochemical impedance spectroscopy (EIS) measurement were carried out with frequency range from 0.05 Hz to 100 kHz at a potential of 1.05 V vs RHE, (amplitude modulation equal to 10 mV) under visible light with a LED at $\lambda = 420$ nm (Thorlabs).

3. Results and discussion

The morphology of the TiO₂-NTs before and after their decoration

Fig. 2. a) TEM picture of TiO₂ NTS decorated with CoO NPs ($N_{LP} = 10000$). Red circles represent areas analyzed with EDX b) atomic concentration of Co for these area. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 3. XPS Core level spectra of (a) Ti 2p, (b) O 1s, (c) Co 2p and (d) Ni 2p spectral regions acquired from TiO_2 -NTs samples decorated with CoO or NiO at $N_{LP} = 10000$.

with catalyst nanoparticles was investigated with SEM observations. Fig. 1a shows a typical image of the vertically aligned TiO_2 -NTs array obtained after anodization, with an average NTs' length of $3.55 \pm 0.05 \mu\text{m}$, an external diameter of $112 \pm 2 \text{ nm}$ and an internal diameter of $50 \pm 2 \text{ nm}$. One can notice the pre-anodization step left a hexagonal initiation layer on top of the nanotubes (Fig. 1b). The comparison of the top-view SEM images of TiO_2 -NTs nanotubes before (Fig. 1b) and after their decoration with CoO (or NiO) nanoparticles (Fig. 1c/or 1d) clearly shows the presence of the PLD-deposited co-catalysts nanoparticles. The CoO or NiO nanoparticles are seen more easily on the top or edge of the nanotubes walls, where they tend to agglomerate. From the SEM observations, CoO/NiO NPs have a size $\leq 20 \text{ nm}$ (Fig. 1c).

The presence of NPs inside the nanotubes has been confirmed by local EDX-TEM measurements, where the average Co relative concentration is found to be higher at the top ($[\text{Co}] = 2.7\%_{\text{at}}$) of the NTs (the firstly exposed part to the laser ablation plume) than inside ($[\text{Co}] = 1.0\%_{\text{at}}$) of the NTs (see Fig. 2, analysis in red circles area). The presence of NPs inside the nanotubes is not surprising as their average size ($< 20 \text{ nm}$) is much smaller than the measured inner diameter of TiO_2 -NTs (50 nm).

To investigate the chemical bonding states of CoO and NiO nanoparticles deposited on TiO_2 nanotubes, XPS measurements were carried out. Fig. 3a presents the Ti 2p core level spectra of the TiO_2 nanotubes decorated with CoO (at $N_{LP} = 10000$) and NiO (at $N_{LP} = 10000$). Both spectra consist of two lines at 458.7 and 464.6 eV, which correspond to the $\text{Ti } 2p_{3/2}$ and $\text{Ti } 2p_{1/2}$ states, respectively, of Ti in TiO_2 [26]. Fig. 3b

shows the O 1s spectra of the TiO_2 -NTs decorated with NiO or CoO nanoparticles (at $N_{LP} = 10000$). The O 1s envelope can be decomposed into three Gaussian-Lorentzian, centered at $528.4 \pm 0.2 \text{ eV}$ (O 1s A in green), $530.0 \pm 0.2 \text{ eV}$ (O 1s B in red) and $531.4 \pm 0.2 \text{ eV}$ (O 1s C in blue). The O 1s A peak energy position is in good accordance with that of O in either Co-O [27] or Ni-O [28]. The O 1s B peak is attributed to Ti-O bonds in TiO_2 [29], whereas the broad O 1s C peak can correspond to C=O organic contamination as well as to OH surface hydroxyl bonds [30]. Fig. 3c shows the Co 2p core level spectrum of TiO_2 nanotubes decorated with CoO-NPs (at $N_{LP} = 10000$).

The main observed line is a doublet of Co $2p_{3/2}$ and Co $2p_{1/2}$, with binding energies of 780.4 eV and 795.7 eV respectively, which correspond to that of Co-O bonds in CoO [31]. The presence of strong shakeup satellite peaks (at 786.5 eV and 803.5 eV binding energies) is characteristics of Co^{2+} [32]. Similarly, Fig. 3d displays the Ni 2p XPS spectrum, where two main peaks Ni $2p_{3/2}$ and Ni $2p_{1/2}$ (located at 855.2 eV and 872.7 eV, respectively) are characteristic of NiO [33]. The Ni 2p spectrum also presents two satellite peaks (at 860.5 and 855.1 eV), confirming the oxidation of nickel into NiO [34]. Therefore, these XPS results confirm that the reactive laser ablation of cobalt (or nickel) under a background oxygen atmosphere is very effective in producing cobalt oxide (or nickel oxide) nanoparticles, with a Co^{2+} (or Ni^{2+}) oxidation states.

To compare the PEC activity of NiO and CoO nanoparticles as co-catalysts for hydrogen production via water-splitting, the cyclic voltammetry technique was carried out, as shown on Fig. 4. Measurements were performed beforehand in the dark (black curves in Fig. 4a and b) to obtain the residual current density of our samples. The PEC responses under both AM1.5 illuminations (100 mW cm^{-2}) and visible solar light ($\lambda > 400 \text{ nm}$; 70 mW cm^{-2}) were systematically measured with (solid blue and red lines in Fig. 4) and without CoO (or NiO) nanoparticles decoration (solid black lines in Fig. 4).

Under illumination, the photocurrent rises at positive potentials ($E > 0.3 \text{ V vs. RHE}$) due to electron-hole pairs separation under the electric field at the TiO_2 -NTs/electrolyte interface. It is worth noting that the generated photocurrent is significantly higher for the TiO_2 -NTs decorated samples with either CoO or NiO nanoparticles, in comparison with bare TiO_2 -NTs. This clearly points out the catalytic enhancement brought by of both co-catalysts under either solar or visible illumination. To correlate this increased photocurrent with O_2 and H_2 production, we have also calculated the Faradic (η_F) efficiency from H_2 and O_2 production determined by gas chromatography (details can be found in ESI figure S1). All samples (with and without co-catalyst) have a similar faradic efficiency of about $87 \pm 5\%$ for the OER, and 100% for the HER. Cyclic voltammetry also shows reduction peak at $\sim 0.5 \text{ V vs. RHE}$ under visible light (Fig. 4b and d), that might be associated with the filling of trap states [35]. Another reduction peaks is found at $\sim 0.2 \text{ V vs. RHE}$ for TiO_2 -NTs decorated with both co-catalysts when illuminated with simulated sunlight (Fig. 4a and c). To have a better understanding of the origin of this peak, cyclic voltammetry of bare TiO_2 -NTs was recorded in an electrolyte with (O_2 flow) and without (N_2 flow) dissolved oxygen. The obtained voltammograms (presented on Fig. 5) revealed that the same reduction peak ($\sim 0.2 \text{ V vs. RHE}$) was only observed when measurements were performed with an oxygen saturated electrolyte, pointing out that this peak is associated with reduction of oxygen species. The higher photocurrent observed on the cyclic voltammograms of TiO_2 -NTs decorated with either CoO or NiO nanoparticles is indicative of a higher production of oxygen on the photoanode resulting from the water-splitting reaction. Thus, this catalytically produced oxygen is afterwards reduced, explaining thereby the presence of a cathodic peak on the voltammograms. However, one cannot exclude that this cathodic peak could also be associated with some reduction of the CoO (or NiO) nanoparticles.

In order to quantify the PEC activity enhancement brought by CoO and NiO nanoparticles, the net photocurrent densities under both AM1.5 (J_{ph}) and visible light ($J_{ph,vis}$) were calculated by subtracting the dark-

Fig. 4. Typical cyclic voltammograms of TiO₂-NTs without (solid black lines) and with (solid blue or red lines) CoO and NiO nanoparticles decoration (at $N_{LP} = 2000$) under both AM1.5 illumination [(a) and (c)] and visible illumination (AM1.5 + 400nm high-pass filter) [(b) and (d)]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. Cyclic voltammograms of TiO₂ nanotubes measured in a basic electrolyte depleted or saturated with oxygen.

current density from the one measured under illumination, at $E = 1.05$ V vs RHE. To be able to compare both sunlight and visible light illuminations, the J_{ph} and $J_{ph,vis}$ values were normalized with the irrespective incident light power densities (P and P_{vis}), providing thereby the photoconversion efficiency α and α_{vis} of our samples. The PEC improvement brought by the metal oxide (MO) nanoparticles, namely CoO and NiO NPs, under sunlight (ϵ) and visible solar light (ϵ_{vis}) in comparison with bare TiO₂-NTs was calculated as followed:

$$\epsilon = \frac{\alpha_{(TiO_2+MO)} - \alpha_{(TiO_2)}}{\alpha_{(TiO_2)}} \times 100 \quad (5)$$

$$\epsilon_{vis} = \frac{\alpha_{vis(TiO_2+MO)} - \alpha_{vis(TiO_2)}}{\alpha_{vis(TiO_2)}} \times 100 \quad (6)$$

Fig. 6. Variations of ϵ and ϵ_{vis} with N_{LP} for TiO₂-NTs decorated with CoO or NiO nanoparticles.

where $M = \text{Co or Ni}$, $\alpha = \frac{J_{ph}}{P}$, and $\alpha_{vis} = \frac{J_{ph,vis}}{P_{vis}}$. Fig. 6 shows the variations of both ϵ and ϵ_{vis} as a function of N_{LP} (which mainly translates here the catalyst loading or the amount of deposited MO-NPs) for both CoO and NiO nanoparticles. Under sunlight, the smallest amount of deposited nanoparticles ($N_{LP} = 500$) is already found to lead to an enhancement of PEC activity by $\sim 58\%$ for both CoO and NiO NPs catalysts. A maximum of enhancement is reached at $N_{LP} = 2000$, where ϵ was found to reach a maximum value of 163% and 148% for TiO₂-CoO and TiO₂-NiO, respectively. At higher catalyst loadings ($N_{LP} \geq 5000$), ϵ quickly

Fig. 7. EQE spectra of TiO_2 -NTs photoanodes before and after their decoration with CoO or NiO nanoparticles (at $N_{LP} = 5000$) with their Y-axis presented in both (a) linear and (b) log scales. (c) EQE of TiO_2 -CoO and TiO_2 -NiO samples divided by the EQE of their bare TiO_2 -NTs counterpart.

decreases for the TiO_2 -NTs photoanodes decorated with NiO-NPs, pointing out that the beneficial effect brought by NiO-NPs is somehow counteracted by a lesser light absorption by the TiO_2 as their surface is getting covered progressively by the NiO-NPs that might diffuse the light before it reaches the nanotubes.

This phenomenon is less present for TiO_2 -NTs decorated with CoO-NPs, as ϵ is seen to still display a significant improvement of PEC activity at the highest catalyst loading ($N_{LP} = 10000$), with a value of 112%. This suggests that even if the TiO_2 -NTs' surface is getting progressively covered by CoO-NPs, the latter still contribute to the improvement of the overall PEC activity of the photoanode (this will be discussed hereafter) contrary to the NiO-NPs. Fig. 6b shows the variation of PEC activity of TiO_2 -NTs decorated with both CoO and NiO NPs under visible solar light (ϵ_{vis}). The N_{LP} dependence of the PEC activity for the NiO-NPs decorated TiO_2 -NTs is found to be quite similar under sunlight or under visible light, in the sense that ϵ_{vis} reaches its maximum value of 382% at $N_{LP} = 2000$ and then decreases at higher NiO-NPs loading ($N_{LP} \geq 5000$). In contrast, the decoration of TiO_2 -NTs with CoO-NPs leads to an almost linear and continuous increase of ϵ_{vis} as a function

of N_{LP} , with a maximum value of 834% at the highest loading of $N_{LP} = 10000$. Note that these values are much higher than the ones under sunlight, simply because ϵ_{vis} is normalized with respect to the photocurrent of TiO_2 under visible light which stays low.

While our results clearly show that both co-catalysts are effective for significantly improving the PEC activity of the TiO_2 -NTs photoanodes under solar and visible irradiation, they nevertheless behave differently (the N_{LP} dependences of ϵ and particularly ϵ_{vis} are different for CoO and NiO NPs). To gain more insights on the role of each MO-NPs catalyst, we have systematically measured the EQE spectra of TiO_2 -NTs photoanodes decorated with either CoO or NiO nanoparticles. The EQE value at a given wavelength (λ) is based on the photocurrent measured ($J_{ph}(\lambda)$) and normalized to the incident power ($P(\lambda)$) at this wavelength, according to the following equation:

$$EQE(\lambda) = \frac{hc}{e} \left(\frac{J_{ph}(\lambda)}{P(\lambda) \cdot \lambda} \right) \quad (7)$$

with h the Planck constant, c the speed of light in vacuum and e the charge of the electron. Fig. 7a shows the EQE spectra for TiO_2 -NTs photoanodes before (dark curve) and after their decoration with NiO-NPs (red curve) and CoO-NPs (blue curve) at $N_{LP} = 5000$. For the whole UV spectral region, both NiO and CoO nanoparticles are seen to induce a clear increase of the EQE, in good agreement with the above-discussed ϵ results. Indeed, at the shortest wavelength ($\lambda = 280$ nm), the EQE is improved by a factor ~ 2 for the NiO-NPs decorated TiO_2 -NTs photoanodes ($\epsilon = 118\%$), and by a factor ~ 2.5 for the CoO-NPs decorated ones ($\epsilon = 153\%$). The NiO-NPs are seen to be relatively less efficient as co-catalyst than the CoO-NPs, suggesting that they might absorb less photon and/or are less efficient in transferring photocharges to their underlying TiO_2 -NTs (this will be clarified hereafter).

One can notice that the EQE in the UV spectral domain reaches its maximum at $\lambda = 350$ nm for TiO_2 -NTs decorated with either CoO or NiO nanoparticles unlike the bare TiO_2 -NTs where the maximum EQE occurs at the shortest wavelength of 280 nm. The occurrence of such maximum can be explained by certain competition between light absorption from TiO_2 -NTs/NPs, and diffusion length of photogenerated electrons in the nanotubes [36]. In fact, while short wavelength photons ($\lambda < 320$ nm) are mainly absorbed in the very top of the TiO_2 -NTs, incident photons with longer wavelengths ($\lambda > 320$ nm) penetrate deeper in the nanotubes. The photogenerated e^- at the top of the NPs/NTs (for shorter wavelength) have a much longer pathway to go before they can be collected at the underlying titanium foil, increasing thereby their chance to recombine or be trapped and limiting thus the photoconversion efficiency process (lower EQE). In contrast, e^- photogenerated deeper inside the nanotubes (for higher λ) have a shorter pathway, which makes their collection more efficient, resulting in a relatively higher EQE value.

To achieve a neater comparison of the EQE spectra in the visible range, the EQE data of Fig. 7a were plotted while using a log scale for the EQE Y-axis, as shown in Fig. 7b. Thus, the TiO_2 -NTs decorated with CoO-NPs are clearly seen to exhibit the highest EQE values over the 400–530 nm visible light range. Nonetheless, the EQE of the NiO-NPs decorated TiO_2 -NTs photoanodes is shown to be significantly higher than that of bare TiO_2 NTs, in the same 400–530 nm visible range. In order to have a quantitative appreciation of the relative EQE improvements strictly brought by the MO-NPs decoration, the EQE values of CoO-NPs/ TiO_2 and NiO-NPs/ TiO_2 photoanodes were normalized with respect to their corresponding EQE values of bare TiO_2 -NTs as follows:

$$EQE_{Ratio} = \frac{EQE(\lambda)_{\text{TiO}_2\text{-MO}} - EQE(\lambda)_{\text{TiO}_2}}{EQE(\lambda)_{\text{TiO}_2}} \times 100 \quad (\text{with } M \equiv \text{Co or Ni}) \quad (8)$$

Fig. 7c shows the variation of the EQE_{Ratio} as a function of the wavelength where the relative improvement brought by CoO-NPs and NiO-NPs is clearly reflected. Three spectral ranges can be clearly distinguished: (i) in the UV domain ($\lambda \leq 380$ nm), both CoO-NPs and NiO-NPs lead to an almost flat improvement of the EQE_{Ratio} , with the

Fig. 8. UV-Vis absorption spectra of CoO and NiO nanoparticles deposited on quartz substrates at selected N_{LP} values of 5000 and 10000. The inset shows the Tauc plots derived from the UV-Vis for the CoO and NiO nanoparticles deposited at $N_{LP} = 10000$.

CoO-NPs being more efficient than the NiO-NPs ones (the small bump observed at ~ 350 nm for both samples is just a replication of the maximum EQE discussed in the results of Fig. 7a); (ii) in the visible domain ($400 \leq \lambda \leq 500$ nm), the CoO-NPs are clearly seen to outperform the NiO-NPs ones with a significant maximum EQE_{Ratio} of 1400% at 425 nm (vs. $\sim 300\%$ for NiO-NPs at the same wavelength and for the same N_{LP}) and (iii) for wavelength higher than 500 nm, the EQE_{Ratio} of CoO-NPs ($\sim 500\%$) and NiO-NPs ($\sim 200\%$) remains flat but are less significant since the photocurrents are low in this spectral range. These results highlight the fact that NiO-NPs show a clear improvement of the photoconversion efficiency (with an EQE_{Ratio} oscillating between 100% and 300%) all over the 280–530 nm range. In the UV range, CoO-NPs show an EQE_{Ratio} twice better than NiO-NPs, translating a better catalytic

effect. In addition, CoO-NPs perform even better in the visible range, by exhibiting an EQE_{Ratio} with a tremendous increase peaking at $\sim 1400\%$ around 425 nm. In other words, NiO-NPs seem to strictly improve the catalytic efficiency of TiO_2 -NTs towards water-splitting reaction, whereas CoO-NPs additionally present a photo-effect particularly in the visible range.

From EQE data, the theoretical solar to hydrogen (STH) conversion efficiency under standard AM1.5G illumination condition can be calculated according to Ref. [37]:

$$STH = \frac{n_{H_2} \times \Delta G^0}{P_{AM1.5}} \times 100 = \frac{j_{EQE} \times 1.23V \times \eta_{FH_2}}{P_{AM1.5}} \times 100 \quad (9)$$

With n_{H_2} the amount of H_2 produced ($mol.s^{-1}.m^{-2}$) ($= j_{EQE}/(2F)$), ΔG^0 is the free energy in standard conditions ($237 kJ mol^{-1}$) and $P_{AM1.5}$ the power density of the AM1.5G spectra ($1000 W m^{-2}$). The current j_{EQE} is determined by integrating the EQE convoluted with the AM1.5G spectral distribution according to:

$$j_{EQE} = \frac{e}{hc} \int EQE(\lambda) \times P_{AM1.5}(\lambda) \times \lambda \cdot d\lambda \quad (10)$$

The calculated STH value confirmed the tendency observed for TiO_2 -NTs, STH is limited to 0.20% while it increase to 0.51% and 0.73% for the samples modified with NiO-NPs and CoO-NPs respectively. It should also be noticed that the contribution to j_{EQE} coming from visible light photons ($\lambda > 400$ nm) is two times higher for CoO modified TiO_2 -NTs than for the other samples (details in ESI).

To better understand the above-discussed wavelength dependence of the EQE of the photoanodes, the optical properties of NiO-NPs and CoO-NPs were investigated by means of UV-vis absorption spectroscopy. For this purpose, CoO-NPs and NiO-NPs were also deposited onto quartz substrates concomitantly with their deposition on the TiO_2 -NTs (i.e. during the same PLD deposition).

Fig. 8 shows the absorbance spectra of both CoO and NiO nanoparticles deposited on quartz, at selected N_{LP} values, namely 5000 and 10000. Expectedly, higher N_{LP} (i.e., higher loading) leads to a higher absorbance of the NPs all over the UV-Vis investigated range. Interestingly, the CoO-NPs are seen to exhibit a higher absorption than the NiO-NPs ones. Moreover, the CoO-NPs absorption spectra show an absorption band around 430 nm (not present in the case of NiO-NPs). This feature is reminiscent of the EQE_{Ratio} peak also observed around 425 nm (see Fig. 7c). The UV-Vis spectra of the CoO and NiO NPs were analyzed and their corresponding Tauc plots are presented on the inset of Fig. 8. The Tauc plots of CoO-NPs and NiO-NPs (deposited at $N_{LP} = 10000$) yielded bandgap values of ~ 2.5 eV and ~ 4.0 eV, respectively, and are consistent with literature values [38,39]. These results clearly establish

Fig. 9. Bode plot of EIS measurement carried out under visible light with (a) TiO_2 nanotubes before and after their decoration with CoO at various N_{LP} , and (b) TiO_2 nanotubes before and after their decoration with CoO and NiO at $N_{LP} = 10,000$. The variation of the modulus of impedance is represented with the straight lines, whereas the phase variation is displayed with empty circles.

Fig. 10. Schematic representation of the energy band diagrams of the heterojunctions formed between n-TiO₂ and p-CoO or p-NiO nanoparticles.

the enhanced absorbance of CoO-NPs in the visible range in comparison to the NiO-NPs, correlating thereby with their observed higher photo-conversion efficiency.

To assess the influence of CoO and NiO NPs on charge transfer behavior, electrochemical impedance spectroscopy measurements under visible light were conducted. The impedance modulus of TiO₂ nanotubes decorated with CoO or NiO NPs is systematically lower than pristine nanotubes, as seen on Bode plots shown on Fig. 9. This indicates a reduced transfer resistance, in favor of the increased photocurrent produced by these samples, as seen previously. In addition, the phase angle clearly shows two separated time constants for all the samples, underlined with dash lines on Fig. 9. In the high frequency range, this contribution is ascribed to the charge transfers occurring at the photoanode/electrolyte interface. Interestingly, increasing the CoO NPs loading (i.e., N_{LP}) on TiO₂ nanotubes leads to a shift at higher frequencies, which points out faster charge transfer processes. This reveals a better charge separation brought by the catalytic effect of the deposited nanoparticles. This is in good agreement with the increasing values of ε_{vis} with N_{LP} observed previously with these samples. The time constant of nanotubes decorated with NiO NPs ($N_{LP} = 10,000$) is found in between the ones of bare TiO₂ and TiO₂-CoO ($N_{LP} = 10,000$), revealing faster charge transfer than pristine TiO₂, that remains slower than the other studied co-catalyst. In fact, absorption of photons in the visible from CoO NPs should allow a decrease of the charge transfer resistance, which translates into a significant shift at higher frequency, in comparison with NiO NPs. In the lower frequency range, the observed time constant is once again systematically faster for samples decorated with CoO or NiO than raw TiO₂ nanotubes. The beneficial catalytic effect brought by the NPs leads to a higher photocurrent, therefore a larger amount of oxygen should be produced at the photoanode. Consequently, the diffusion gradient at the photoanode/electrolyte interface becomes more important, allowing O₂ to diffuse faster in the bulk of the

electrolyte. This phenomenon could be translated into these higher frequencies observed with samples decorated with the co-catalysts.

While both co-catalysts improve the overall efficiency, there is a clear outperformance of CoO-NPs over the NiO-NPs ones, as clearly apparent from our data. It can be explained by the following hypothesis: the formation of local heterojunctions between the p-type semi-conducting CoO and NiO nanoparticles and the n-type underlying TiO₂-NTs [13,40]. At the equilibrium, once the junctions are formed, the Fermi levels (E_F) of co-catalyst NPs and TiO₂ equalized. The built-in electric field at the interface improves the electron/hole pair separation, and acts as a driving force for the migration of electrons from MO-NPs to TiO₂-NTs and for holes in the opposite direction, as depicted in the energy band diagrams of Fig. 10. The built-in potential is directly related to the difference between the Fermi levels of MO and TiO₂ and thereby to their associated work functions. With $\Phi(TiO_2)$, $\Phi(CoO)$ and $\Phi(NiO)$ values of 4.23 [41, p. 2], 5.03 [42] and 4.6 eV [43] respectively, the built-in potential is higher in the case of CoO/TiO₂ than in the case of NiO/TiO₂, (cf. Fig. 10). This should result in an increased separation of charges for CoO/TiO₂ structure, which can be put in relation with the faster charge transfer observed for this sample by EIS. This improved charge transfer translates into increased photoconversion efficiency, as observed on our samples both by CV and EQE measurement. In addition, the smaller bandgap of the CoO-NPs implies a better harvest of visible light photon, particularly in the (400–480) nm range where the EQE_{Ratio} reaches its maximum. Consequently CoO-NPs, will act not only as co-catalyst, but also actively participate as a photo-electrocatalyst as evidenced by the EQE measurements. This smaller bandgap of CoO can also explain why CoO-NPs modified photoanode performs better at high deposited quantity in comparison to NiO: while NiO accumulation at the top might result in increase light screening (via diffusion) for the underlying TiO₂, CoO will absorb a part of this light and directly participate to the overall photoelectrochemical process.

Fig. 11. Alternation of cyclic voltammetry and chronoamperometry ($E = 1.05$ V vs RHE) of TiO₂-NTs photoanodes before and after their decoration with CoO and NiO nanoparticles (at $N_{LP} = 500$).

Finally, the stability of our photoanodes has also been investigated, for a minimum of 35 h under intense UV irradiation (20 mW cm^{-2}), as shown in Fig. 11. For this purpose, an alternation of cyclic voltammetry (CV; from -0.15 to 1.05 V vs RHE; 3 cycles) and chronoamperometry (CA; $E = 1.05$ V vs RHE) measurements under UV light (LED $\lambda = 365$ nm) were carried out. The tested samples are as prepared TiO₂-NTs and TiO₂ nanotubes after their decoration with CoO-NPs and NiO-NPs ($N_{LP} = 500$).

The spikes observed every 2 h in Fig. 11a) are the consequence of an open circuit voltage step between CV and CA experiment, this peak of current is systematically observed at the beginning of each CA measurement due to the polarization of the electrode, as illustrated in Fig. 11b). While the beneficial effect of the PLD-based MO-NPs decoration is clearly confirmed, as their associated current densities are higher than that of bare TiO₂-NTs, the CoO-NPs modified photoanode expectedly performed better than the NiO-NPs one. Regardless of the MO-NPs nature, the current density is found to increase slightly (ca. 15%) during the first 20 h. After 35 h of measurements, the photocurrent density does not show any degradation, illustrating the excellent stability of our photoanodes, with or without MO-NPs.

4. Conclusion

The reactive pulsed laser deposition has been successfully used to decorate TiO₂-NTs with CoO and NiO nanoparticles at various nanoparticles loadings through the adjustment of N_{LP} . The oxygen background atmosphere used during the reactive PLD process is essential to synthesize CoO and NiO nanoparticles from the ablation of Co and Ni metallic targets. The MO-NPs (with a diameter ≤ 20 nm) were deposited on TiO₂-NTs with an inner diameter of ~ 50 nm, permitting both outer and inner decoration of the nanotubes. Cyclic voltammetry measurements were carried out to assess the photoconversion efficiency of our nanohybrid photoanodes (namely CoO/NiO NPs decorated TiO₂-NTs). Under solar illumination, $N_{LP} = 2000$ has been identified as the optimal decoration condition, for both catalyst nanoparticles, that increases the photo-electrochemical activity of the decorated photoanodes by $\sim 150\%$ in comparison with bare TiO₂-NTs. This enhanced photoconversion efficiency is believed to be due to the formation of local p-n heterojunctions between the p-type CoO (/NiO) NPs and n-TiO₂-NTs. The band structure of the different semiconductors results in higher potential difference, and consequently improved charge separation, for CoO/TiO₂ heterojunction than for NiO/TiO₂. This could explain the higher performances observed for CoO NPs deposition over NiO NPs.

The performance of CoO-NPs was particularly enhanced in the visible spectral region ($\lambda > 400$ nm), as their associated photoconversion efficiency is found to increase continuously with the amount of deposited CoO-nanoparticles. The improvement in visible reaches a maximum value of 834% at $N_{LP} = 10000$, this points out that the CoO-NPs/TiO₂-

NTs photoanode is ~ 9 times more efficient under visible light than the bare TiO₂-NTs one. The additional photocatalytic effect exhibited by the CoO-NPs in the visible is believed to be a consequence of their visible bandgap (of ~ 2.5 eV as derived here from UV-vis measurements), enabling them to harvest more photons in the 400–500 nm range and transferring efficiently the photogenerated electrons to the TiO₂-NTs. This study demonstrates that the CoO-NPs are definitely excellent photocatalyst candidates for improved photoelectrochemical conversion of both UV and visible light photons. The NPs deposition by the energetic PLD technique ensures their strong anchoring to the underlying TiO₂-NTs, contributing thereby to the observed stability of the photoanodes.

CRediT authorship contribution statement

Thomas Favet: Investigation, Data curation, Visualization, Writing - original draft. **Thomas Cottineau:** Supervision, Investigation, Data curation, Writing - original draft, Writing - review & editing, Resources. **Valérie Keller:** Funding acquisition. **My Ali El Khakani:** Supervision, Writing - review & editing, Funding acquisition, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solmat.2020.110703>.

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