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Amorphous NiCu Thin Films Sputtered on TiO$_2$ Nanotube Arrays: A Noble-Metal Free Photocatalyst for Hydrogen Evolution

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In this work, NiCu co-catalysts on TiO$_2$ are studied for photocatalytic hydrogen evolution. NiCu co-catalyst films are deposited at room temperature by argon plasma sputtering on high aspect-ratio anodic TiO$_2$ nanotubes. To tune the Ni:Cu atomic ratio, alloys of various compositions were used as sputtering targets. Such co-catalyst films are found to be amorphous with small nanocrystalline domains. A series of parameters is investigated, i.e., i) Ni:Cu relative ratio in the sputtered films, ii) NiCu film thickness, and iii) thickness of the TiO$_2$ nanotube layers. The highest photocatalytic activity is obtained with 8 μm long TiO$_2$ nanotubes, sputter-coated with a 10 nm-thick NiCu films with a 1:1 Ni:Cu atomic ratio. This photocatalyst reaches a stable hydrogen evolution rate of 186 μmol h$^{-1}$ cm$^{-2}$, 4.6 and 3 times higher than that of Ni- and Cu-TiO$_2$, respectively, demonstrating a synergistic co-catalytic effect of Ni and Cu in the alloy co-catalyst film.

Introduction

Since Fujishima and Honda’s discovery dating back to 1972 of water splitting using TiO$_2$ under UV irradiation,$^{[1]}$ hydrogen evolution has been the most studied photocatalytic reaction. Several semiconductors have been developed in the last decades for this purpose, but TiO$_2$ still remains the most used and investigated photocatalyst owing to its cost-effectiveness, availability, non-toxicity, stability against (photo)corrosion and suitable conduction band edge position for water reduction.$^{[2,3]}$ Thermodynamically, photogenerated electrons in TiO$_2$ can drive photocatalytic evolution of H$_2$. This reaction, however, is kinetically limited by the sluggish electron transfer to reactants and high charge carrier recombination in the oxide bulk. These critical features have been addressed with various strategies aimed at enhancing the photocatalytic activity of TiO$_2$. The use of nanostructured materials can limit charge carrier recombination.$^{[3,4]}$ In addition, improved charge carrier transfer can be achieved by decorating the surface of the photocatalyst with appropriate co-catalysts. Noble metals$^{[5–7]}$ and carbonaceous materials$^{[11,12]}$ were shown to enhance the photocatalytic activity of nanostructured TiO$_2$ systems. Noble metals (e.g., Pt, Au), generally, are the most efficient co-catalysts for hydrogen evolution.$^{[13–16]}$ Their cost, however, has led researchers to explore cheaper alternatives with the aim of achieving comparable performance.$^{[17–19]}$ Earth abundant metals...
such as Co,[20] Cu,[18] Ni,[21] and Zn[22] have been in the spotlight. Non-noble metals, their oxides[23,24] or sulphides[25,26] were studied in combination with TiO$_2$, or other semiconductors and showed in some cases promising performance, while on average the performance of noble metals still remains higher. Bimetallic systems based on non-noble metals, such as BiCu,[27] NiFe,[27] NiCu$_2$[28] and NiCu[29–34] were investigated owing to their intriguing optical or electronic properties compared to pure counterparts. It was shown that the enhancement in photocatalytic activity when using bimetallic systems can be significantly higher than the activity reached using single co-catalysts. This suggests that synergistic effects arise that can improve significantly the performance of earth-abundant co-catalysts.[17–26] Such effects have been observed particularly for NiCu systems.[33,34,36] Typically, NiCu co-catalysts can be prepared using various techniques such as wet impregnation,[32] hydrothermal deposition,[33] chemical reduction,[30] laser ablation[29] or electrodeposition.[35] In recent own work,[33] we reported on an alternative approach for the formation of bimetallic NiCu nanoparticles. This method is based on sequential sputtering of Ni and Cu films on TiO$_2$ surfaces, followed by a thermal treatment in Ar atmosphere that induces solid-state dewetting-alloying,[33,34] i.e., the agglomeration of Ni and Cu layers forming NiCu bimetallic nanoparticles at the semiconductor surface. The particles were found to be crystalline, and featured Ni and Cu rich domains.[33] Such NiCu-TiO$_2$ systems (optimized in terms of composition and morphology) exhibited a significantly higher activity compared to the monometallic constituents (Ni-TiO$_2$ and Cu-TiO$_2$).

We follow up in the present work, adopting a more straightforward method based on direct sputtering of bimetallic alloys, from NiCu targets, for the preparation of NiCu-coated mesoporous TiO$_2$ layers. As mesoporous TiO$_2$ substrates, we use anodic TiO$_2$ nanotube (NT) layers. This strategy allows to form co-catalyst layers where Ni and Cu are already intermixed, without the need for further thermal treatments. The use of alloys as sputter targets allows also for an easy tuning of the co-catalyst composition by using a sputter target with the proper Ni and Cu ratio. Alloy targets of desired composition can in fact be easily produced since the NiCu system is fully miscible. We optimized key factors, i.e., i) NiCu relative ratio, ii) thickness of NiCu layer and iii) thickness of TiO$_2$ NTs, to maximize the photocatalytic H$_2$ evolution performance. The highest hydrogen evolution rate (186 μL·h$^{-1}$·cm$^{-2}$) was obtained using ~8 μm-long TiO$_2$ NTs decorated with a 10 nm-thick NiCu co-catalyst layer with 1:1 at.% NiCu composition. Our results confirm that bimetallic systems such as NiCu layers can provide a synergistic co-catalytic effect for H$_2$ evolution. Moreover, the NiCu co-catalyst is not required to be crystalline to provide a photocatalytic improvement, as the NiCu sputtered films used in this work are of amorphous nature. This simple methodology opens for the screening of new earth abundant co-catalysts, for example by depositing multinary systems on mesoporous photocatalytic surfaces.

**Results and Discussion**

In the present work, high aspect-ratio titanium dioxide nanotube arrays were used as photocatalytic active layers. TiO$_2$ NTs were grown by anodizing a Ti foil in an ethylene glycol solution to produce several micrometer-thick layers. In Figure 1a–b it is possible to observe the morphological features of the formed tubes, namely, a pore top opening of ~70 nm and a tube length of ~6.5 μm. This NT length was chosen for preliminary experiments as it is reported in literature that it provides the highest photocatalytic activity due to optimized light absorption and charge carrier separation.[34]

After anodization, the materials were annealed at 450 °C for 1 h to crystallize the amorphous TiO$_2$. Diffraction peaks were attributed to either anatase TiO$_2$ or Ti metal (substrate) as reported in Figure 1c and Table S1 (Supporting Information). No rutile peaks were detected meaning that annealing under these conditions converts amorphous TiO$_2$ to pure anatase.

The crystalline TiO$_2$ NTs were subsequently coated by plasma sputtering with 10 nm-thick metal films using pure nickel, pure copper, and their alloys with three different NiCu ratios (25:75, 50:50 and 75:25) as sputter target materials. A scheme of the photocatalyst preparation is provided in Figure S1. The alloys are named as 25Ni75Cu, 50Ni50Cu and 75Ni25Cu according to their nominal composition. The morphology of NiCu-decorated systems are shown in Figure 2a–f.

The morphology of the co-catalyst layers varies depending on the composition. Co-catalysts formed by sputtering from Cu-rich targets are characterized by the presence of isolated particles with an estimated size of ~20–35 nm, whereas Ni-rich coatings appear as dense films featuring a nanoparticulate
texture (diameter of the nanoparticles < 10 nm). Besides, at the surface of the photocatalysts it is possible to notice the penetration of the sputtered layers inside the nanotubular structure to a depth of a few hundred nanometers (Figure 2d). Thus, only the outermost part of the NTs is coated by the sputtered co-catalyst.

Although clearly visible by SEM observations, the presence of Ni and Cu species was not detected by X-ray diffraction measurements (Figure S2). The absence of Ni and Cu signals in the XRD patterns may be due to the low co-catalyst loading (10 nm-thick NiCu layer), or to the nature of such layers (sputtered at room temperature) which were found to be nanocrystalline, as discussed along with TEM results below.

The Ni:Cu composition ratio and oxidation state of Ni and Cu were investigated by XPS. This study was carried out using Ni-, Cu- and NiCu-sputtered layers (10 nm-thick) on Si wafers. For simplicity, we used Si substrates to avoid the undefined top morphology of nanotubes and their large oxygen content. On the contrary, Si wafers are atomically flat and carry only a very thin (ca. 1–2 nm thick) native surface oxide layer. Figure 3a shows that the surface composition of the sputtered co-catalyst layers changes accordingly to the target used for deposition. Only minor deviations from the nominal target compositions were observed. These small discrepancies may be ascribed to the different sputter yield of Ni and Cu.

The XPS depth profile analysis for the 50Ni50Cu layer (Figure 3b and Table S2) reveals that the outermost NiCu region features a higher oxygen content and a higher Cu concentration than in depth. Sputtering to a depth of 3 or 6 nm, instead, shows i) an almost 1:1 Ni:Cu atomic ratio, that is in line with the sputter target composition, and ii) a much lower oxygen content (ca. a half of that found at the surface). The large content of oxygen in the surface can be explained assuming surface oxidation of the NiCu layers when exposed to air. The presence of oxygen in depth may not be due to sample exposure to the environment but suggests some oxygen incorporation during sputtering (discussed below). As for the variation of the Ni:Cu ratio, the different sputter yield for Ni and Cu can be the cause of the inhomogeneity along the depth of the layer.

High resolution XPS spectra (reported in Figures 4 and 5) were recorded for Cu2p, Ni2p and O1s, and were analyzed to determine the oxidation state of Cu and Ni in the sputtered layers. Regarding Cu, it is possible to observe for all Cu-containing samples (Figures 4a–d) the presence of both metallic Cu (932.6 eV), and oxidized Cu species (see CuO and Cu(OH)2).

Figure 2. SEM top views of TiO2 NTs after the deposition of a) pure Cu, f) pure Ni and b), c), e) NiCu alloys with different compositions (nominal thickness of 10 nm for all the samples). d) SEM cross section view of 50Ni50Cu–TiO2 revealing the alloy penetration in the nanostructures.

Figure 3. a) Ni and Cu relative content obtained by XPS analysis at a sampling depth of 3 nm for Ni, Cu and NiCu alloys (10 nm-thick layer) sputtered on Si wafer. b) XPS depth profile analysis for 50Ni50Cu alloy (10 nm-thick layer) sputtered on Si wafer.
peaks at higher binding energies). These species differ in their relative content when varying the composition of the sputtered layer: the fraction of metallic Cu phase decreases as the Ni amount in the alloy increases, i.e., leading to the presence of larger amounts of oxidized Cu species in Ni-rich alloys. The relative content of Cu(0) ranges from 63.3 % in 100Cu to 29.2 % in 75Ni25Cu (see Figure 4e and Table S3). Analogously, also the speciation of Ni is affected by the composition of the alloy: the peak of Ni(0) at 852.6 eV is visible only for Cu-rich alloys, i.e., 25Ni75Cu and 50Ni50Cu (see Figures 5b and 5c). Such peak is not observed for other Ni-rich samples (100Ni and 75Ni25Cu, see Figures 5a and 5d). In the case of Ni, the relative content of metallic phase is much lower than that of oxidized Ni species. The content of oxidized Ni species (sum of NiO (853.9 eV) and Ni(OH)$_2$ (855.7 eV)) ranges from 2.3 % in 25Ni75Cu to 0 % in 100Ni and 75NiCu (Figure 5e and Table S3). The presence of oxidized Ni and Cu species is also confirmed by O1s signals (Figure S3): the peak at 529.5 eV (present only in Ni-rich samples) is associated to the presence of NiO$^{[46]}$ whereas the peak at 530.3 eV (present only in Cu-rich samples) is related to the presence of CuO.$^{[41]}$ A second peak at 531.3-531.6 eV is present in all the samples and may be ascribed to the presence of defects in the metal oxide layer.$^{[42]}$ Finally, high resolution XPS measurements taken for Cu2p and Ni2p (Figure S4) at different depths (by Ar sputter-etching) indicate that not only the surface, but the entire layer is partially oxidized as practically no Cu and Ni metal phases are present in the inner regions of the layer. These results are well in line with data shown in Figure 3b and can be explained by considering the relatively high background pressure used during sputtering ($10^{-2}$ mbar), i.e., traces of oxygen may be incorporated during film deposition. The incorporation of oxygen during deposition may also account for the fact that Cu-rich layers contain lower amounts of oxidized phases for both Cu and Ni (Figure S3). In general, the larger the Cu content, the lower the amount of oxygen incorporated in the sputtered layer. Conversely, the content of oxidized phases increases with increasing the atomic fraction of Ni in the NiCu layer.

Electron microscopy in combination with energy dispersive X-ray spectroscopy (EDXS) was employed to shed light on the formation of the metal oxide layer. Figures 4a-d illustrate the high resolution XPS spectra in the Cu2p region for all Cu-containing NiCu layers. Figure 4e shows the relative content of metal and oxidized Cu (sum of CuO and Cu(OH)$_2$ species) by varying the composition of the NiCu layer.
composition, structure, and morphology of a 50Ni50Cu atop the TiO$_2$ nanotubes. An EDXS map of the nanotube top is shown in Figure 6a. The corresponding line profiles (Figure 6b) along the arrow indicated in Figure 6a confirm the nominal composition in line with the XPS data of Figure 3. In addition, the NiCu signal decreases towards the bulk within the outermost ~0.6 μm. Scanning transmission electron microscopy (STEM) of the film as compiled in Figure 6c-d reveal NiCu island with lateral as well as vertical dimensions of a few ten nm, confirming what observed in the SEM images. Moreover, nanocrystalline domains are visible in high-resolution STEM bright field (BF) images (Figure 6d).

To confirm the nanocrystalline nature of the film and the anatase phase of the nanotubes, selected area electron diffraction (SAED) is performed on the bulk and on the top part (Figure 6e) of a nanotube in cross-section. The corresponding diffraction patterns are radially integrated and compared with the theoretical peak positions of anatase and Cu. The compiled data in Figure 6f confirm i) the presence of crystalline Cu(Ni) species and ii) the nanocrystalline character of the films. Note that peak broadening can originate from both a finite crystalline domain size and local variations in the NiCu composition.

The NiCu-coated photocatalyst layers were characterized in view of their photocatalytic performance. Preliminary photocatalytic hydrogen evolution tests were conducted under UV light (365 nm) for a total illumination time of 4 hours in a 20 % EtOH–H$_2$O using NiCu–TiO$_2$ systems. Coating the NiCu co-catalyst only on the top of the nanotube structure leaves free TiO$_2$ surface inside the nanotubes where the hole mediated oxidation of ethanol likely takes place, while hydrogen evolution takes place at the NiCu surface. A sketch of the proposed H$_2$ evolution mechanism by ethanol photocatalytic reforming on NiCu–TiO$_2$ is provided in the SI, Figure S5.

We tested first TiO$_2$ nanotubes sputter-coated with 10 nm-thick co-catalyst layers of different composition (samples shown...
The results of these experiments are summarized in Figure 7. The data reveal that undecorated TiO$_2$ NTs, as expected, show a negligible photocatalytic H$_2$ generation (0.9 μL.h$^{-1}$.cm$^{-2}$). Differently, TiO$_2$ NTs coated with pure Cu and Ni layers exhibit an improved H$_2$ production rate (64.3 μL.h$^{-1}$.cm$^{-2}$ and 40.3 μL.h$^{-1}$.cm$^{-2}$, respectively). However, highest photocatalytic H$_2$ evolution rates are always obtained when using NiCu-decorated TiO$_2$ NTs, regardless of the NiCu relative composition. The samples 25Ni75Cu-, 50Ni50Cu- and 75Ni25Cu-TiO$_2$ provide a clearly higher photocatalytic efficiency compared to pure Ni- or Cu-modified TiO$_2$ (using the same total metal loading). 50Ni50Cu-TiO$_2$ is the most performing photocatalyst, showing an H$_2$ generation rate of 169.4 μL.h$^{-1}$.cm$^{-2}$, i.e., around 190 times higher than pristine TiO$_2$, and ~2.6 and ~4.2 times higher than that of 100Cu- and 100Ni-TiO$_2$, respectively. It is interesting to note that the activity observed for any bimetallic NiCu system is substantially higher than the sum of the activity of pure Ni and Cu co-catalysts layers. This suggests that the bimetallic systems provide synergistic effects, as also proposed in previous work.[31,43,44] Electronic interactions of Ni atoms with neighboring Cu atoms allow to modulate (reduce) the binding energy of protons on active sites, which may enhance the kinetics of H$_2$ evolution.\[44,45,46\] We performed linear sweep voltammetry (LSV) experiments to characterize the electrochemical hydrogen evolution reaction (HER) activity of bimetallic NiCu films vs. monometallic Ni or Cu films. For this, Ni, Cu and NiCu films (50 nm-thick) were sputter-coated on electrically conductive fluorine-doped tin oxide (FTO) slides and tested as working electrodes for HER in a 3-electrode electrochemical cell. Results (Figure S6) are discussed in the SI. Briefly, the electrochemical HER trend (Ni > NiCu > Cu), in terms of overpotential required to drive HER at -10 mA cm$^{-2}$, differs from that observed in the photocatalytic H$_2$ evolution experiments, i.e., NiCu > Cu > Ni (Figure 7). However, when comparing (“open circuit”) photocatalytic results with electrochemical HER data (polarization curves) one should carefully consider the different “exit energy” of TiO$_2$ conduction band electrons (i.e., the potential of the CB minimum) vs. the applied external electrical bias.

Regarding the presence of oxidized Ni and Cu species in the co-catalyst film as shown by XPS results (above, Figures 4 and 5); it is worth to point out that in previous own work\[34\] on Ni-, Cu-, and NiCu nanoparticle-modified TiO$_2$ we demonstrated that, under illumination, oxidized Ni and Cu species such as native oxides at the co-catalyst surface are promptly reduced to a metallic phase. Reduction of such oxidized Ni and Cu species can be driven by photo-promoted CB electrons. Thus, it is possible that also the oxidized Ni and Cu species present in the herein studied NiCu films undergo reduction to a NiCu metal phase under illumination and in the presence of ethanol as hole-scavenger. Additionally, theoretical calculations shows that the work function of NiCu increases from 4.65 eV (pure Cu) up to 5.11 (pure Ni) as nickel content increases, and this provides a higher Schottky barrier that may grant a better charge carrier separation at the semiconductor/metal interface.\[47–50\]

Finally, the NiCu co-catalyst films provide a significant H$_2$ evolution enhancement despite being mainly amorphous with nm-sized crystalline domains. This indicates that a high degree of crystallinity of the co-catalyst is not a strict requirement to
mediate electron transfer and proton reduction. Similar observations were made in a few recent articles studying amorphous metal, oxide, or sulfide co-catalysts.\cite{31-34}

After determining the optimal Ni:Cu ratio, parameters such as the co-catalyst layer thickness and the length of the TiO\textsubscript{2} NTs were investigated. Firstly, 6.5 \( \mu \)m long TiO\textsubscript{2} NTs were coated with 50Ni50Cu alloy layers of different nominal thickness obtained by varying the sputtering time. The morphologies of the resulting materials are shown in Figures 8a-f. When depositing NiCu layers with nominal thickness < 5 nm, no structural change of the NT top surface can be appreciated by SEM (Figures 8a-c). Thicker layers (10, 15 and 20 nm) are instead clearly visible and feature a less smooth and uniform appearance with increasing the layer thickness (Figures 8d-f). Interestingly, the samples decorated with 15 and 20 nm thick layers are characterized by the presence of cubic shaped nanoparticles. This might be due to the formation of CuO crystals.\cite{35,36}

Moreover, thick NiCu films partially clog the top opening of the NTs.

These samples were tested in view of their photocatalytic activity towards hydrogen evolution. The results are shown in Figure 9a. A marked increase in photocatalytic performance was observed for all NiCu-decorated samples reaching an optimal performance with the 10 nm-thick layer. This can be considered the best compromise in terms of activity versus amount of co-catalyst. Thicker layers (15 and 20 nm) resulted in a decreased photocatalytic activity probably due to the excessive coverage of the TiO\textsubscript{2} surface which may cause i) a reduction of the available surface area for photocatalysis due to the clogging of the tube opening and ii) shadowing effects leading to a lower photon flux reaching the TiO\textsubscript{2} layer.

Finally, we explored the effect of the length of TiO\textsubscript{2} NTs on the photocatalytic H\textsubscript{2} evolution performance of (10 nm) 50Ni50Cu-TiO\textsubscript{2} (Figure 9b). Nanotubes with different thicknesses were synthesized by varying the anodization time. The results, summarized in Figure 9b, clearly show that an increase in nanotubes length up to 6.5 \( \mu \)m results in an enhanced photocatalytic activity. This is because thicker nanotubes layers offer improved light absorption.\cite{37} In line with literature data, increasing the length of nanotubes above 6–8 \( \mu \)m does not improve the photocatalytic activity further. Hence, one can conclude that thicker nanotube layers do not offer improved optical absorption and charge collection efficiency.\cite{38} The optimal nanotube length is thus be 8.5 \( \mu \)m, providing a hydrogen evolution rate of 186.3 \( \mu \)L h\textsuperscript{-1} cm\textsuperscript{-2}, which corresponds to an estimated apparent quantum yield of 1.39% (see details on AQY estimation in the SI).

Once identified the most active photocatalyst by tuning the composition of the sputtered co-catalyst layer (Ni:Cu ratio ∼ 1), its thickness (10 nm) and the thickness of the TiO\textsubscript{2} NT layer (8.5 \( \mu \)m), repeated tests were conducted using the same sample (Figure 9c). In these consecutive tests, only minor variations in the generated H\textsubscript{2} amount were observed (with no clear trend), indicating an average H\textsubscript{2} evolution rate of 203 ± 19 \( \mu \)L h\textsuperscript{-1} cm\textsuperscript{-2} with no significant activity decay taking place after five photocatalytic tests.

Conclusions

We demonstrated the preparation of a noble metal-free photocatalyst for hydrogen evolution by sputtering NiCu alloy films on the surface of mesoporous TiO\textsubscript{2} layers (high aspect ratio TiO\textsubscript{2} nanotube layers). We investigated the photocatalyst activity towards hydrogen evolution by screening the effect of i) the Ni:Cu relative ratio, ii) the NiCu film thickness and iii) the TiO\textsubscript{2} nanotube length. We found that 10 nm-thick NiCu layers sputtered from 50Cu:50Ni targets on ~ 8.5 \( \mu \)m-thick TiO\textsubscript{2} nanotube layers provide a highest efficiency for hydrogen evolution, i.e., 186.3 \( \mu \)L h\textsuperscript{-1} cm\textsuperscript{-2}, which is 200 times higher than pristine TiO\textsubscript{2} nanotubes (0.6 \( \mu \)L h\textsuperscript{-1} cm\textsuperscript{-2}), and 4.6 (40.3 \( \mu \)L h\textsuperscript{-1} cm\textsuperscript{-2}) and 3 (64.3 \( \mu \)L h\textsuperscript{-1} cm\textsuperscript{-2}) times higher than pure Ni- and Cu-TiO\textsubscript{2}, respectively. The activity enhancement observed for bimetallic NiCu co-catalysts is substantially higher than the sum of the activity of pure Ni and Cu co-catalysts. This suggests that the bimetallic layers provide a synergistic effects, i.e., electronic interactions of Ni atoms with neighboring Cu atoms allow to modulate (reduce) the binding energy of protons on active sites which favors hydrogen evolution.

![Figure 8. SEM top view images of 50Ni50Cu-TiO\textsubscript{2} samples (6.5 \( \mu \)m long TiO\textsubscript{2} nanotubes) coated with alloy layers of different thickness.](image-url)
sites, which may enhance the kinetics of H₂ evolution. In future work, we will address the stability of Ni and Cu species under intermittent illumination (light on-off cycles).

**Experimental**

**Fabrication of the TiO₂ nanotubes array and thermal treatment**

Ti foils (Advent Research Materials, 0.125 mm thickness, 99.6+ purity) were degreased by sonication in acetone, ethanol, ultrapure water and were then dried under a N₂ stream. Then, the cleaned Ti foils were anodized in an ethylene glycol electrolyte with a NH₄F concentration of 0.15 M and 3 vol.% H₂O content. For the anodic growth, a two-electrode configuration was used, where the Ti foil (15 mm × 15 mm) and a Pt sheet were used as working and counter electrode, respectively. We used a bottom mount electrochemical cell with an O-ring diameter of 1 cm. The choice of using anodic TiO₂ nanotube layers was made as their morphology can be tuned by controlling simple experimental parameters and because of their high surface area. The anodization experiments were carried out by applying a potential of 60 V using a DC power supply (VLP 2403 Volcraft). Anodization time was varied to tune the thickness of the nanotube layers. To obtain 6.5 μm-long nanotubes, a time of 17 minutes was used. Additional information on times used for anodization can be found in Table S4 (Supporting Information).

After anodization, the samples were rinsed and soaked in ethanol overnight (to remove the residual adsorbed electrolyte), subsequently they were dried in a N₂ stream. Finally, the amorphous TiO₂ nanotubes were annealed at 450 °C for 1 h in air to crystallize the oxide into anatase phase.

**Sputter deposition of Ni, Cu and NiCu**

In order to coat the outermost surface of the nanotubes arrays, a plasma sputter-coater (EM SCD 500, Leica) was used to sputter Cu, Ni and NiCu alloy layers using the following targets: Cu (99.60 at.% pure, Baltic praeparation e.K), Ni (99.98 at.% pure), 25Ni75Cu (25 % Ni-75 %Cu, at.%), 50Ni50Cu (50 %Ni-50 %Cu, at.%), and 75Ni25Cu (75 %Ni-25 %Cu, at.%). Besides Cu, all sputter targets were provided by Hauner Metallische Werkstoffe, Germany. In any case the applied sputtering current was set to 16 mA and the pressure of the sputtering chamber was set at 10⁻² mbar of Ar. The amount of sputtered metal, i.e., the nominal thickness of the co-catalyst film, was in situ determined by an automated quartz crystal film-thickness sensor.

**Characterization of materials**

To examine the crystallographic properties of the materials, X-ray diffraction (XRD) was performed using a X’pert Philips MPD (equipped with a Panalytical X’celerator detector), using graphite monochromized Cu Kα radiation (wavelength 1.54056 Å). The measurements were carried out with the following parameters: step size 0.03°; time per step 2 s; scan rate (continuous) 0.015° s⁻¹. A field-emission scanning electron microscope (FE-SEM, Hitachi S4800) and a transmission electron microscope (TEM TITAN 60–300, FEI, USA) were used to characterize the morphology of the
Electrochemical hydrogen evolution experiments

Experiments were conducted with a three-electrode cell configuration using a Ag/AgCl electrode (3 M KCl) as reference electrode, platinum wire as counter electrode and aqueous 0.5 M Na2SO4 solution as electrolyte (pH ~6.3). Ni, Cu and NiCu films (50 nm-thick) were sputtered-coated on electrically conductive fluorine-doped tin oxide (FTO) slides and tested as working electrodes for the hydrogen evolution reaction (HER). The HER performance of the samples was evaluated in terms of overpotential at geometric area.

Photocatalytic experiments

Photocatalytic measurements for H2 generation were carried out by irradiating the photocatalyst layers in a 20% ethanol-water solution (ethanol was used as a hole-scavenger) in a quartz tube sealed with a gas-tight cap for a total of 4 hours. At light source, we used a LED UV light (Opsytec, 365 nm, beam size 0.785 cm2) with a power of 100 mW cm^-2. The ethanol-water solution and the cell headspace (volume 5.12 ml) was purged with N2 gas for 15 minutes prior to the H2 evolution tests.

The amount of produced H2 was measured by using a gas chromatograph (GCMSQO2010SE, Shimadzu) equipped with a thermal conductivity detector and a Restek micropacked Shin Carbon ST column (2 m x 0.53 mm). Recycling tests were performed as following: at the end of a 4 h photocatalytic test, the photocatalyst was rinsed and placed in the quartz tube in a fresh 20% EtOH-H2O solution and was again irradiated with UV light (365 nm) for 4 h.

Acknowledgements

The authors acknowledge H. Hildebrand, A. Friedrich, A. Knoop, and U. Marten-Jahns for technical help. M.A. acknowledges the financial support from the Emerging Talents Initiative ETI (ETI2018/2_Tech.11) provided by the FAU Friedrich-Alexander University Erlangen-Nuremberg, Germany. J.W. and E.S. acknowledge the DFG for funding via the research training group GRK 1896 “In Situ Microscopy with Electrons, X-rays, and Scanning Probes”. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.
A photocatalyst consisting of an amorphous NiCu thin film sputtered on anodic TiO$_2$ nanotubes is studied for photocatalytic hydrogen evolution. A performance improvement of 4.6 and 3 times compared to photocatalysts modified with pure Ni or pure Cu films is achieved due to synergistic effect of Ni and Cu in the bimetallic co-catalyst layer.

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