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**Cu₂O/TiO₂ Nanowire Assemblies as
Photocathodes for Solar Hydrogen Evolution:
Influence of Diameter, Length and Number
Density of Wires**

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Abstract: The performance of free-standing parallel-aligned nanowire arrays and interconnected networks of single-crystalline cuprous oxide (Cu₂O) coated with titanium oxide (TiO₂) as photocathodes for solar energy harvesting was analyzed. The nanostructures were synthesized by electrodeposition in polymer membranes prepared by ion-track technology. To enhance the photoelectrochemical stability of the nanowires in aqueous solution, they were conformally coated with a 10 nm thick TiO₂ layer by atomic layer deposition. The diameter, size, geometry and number density of the parallel nanowires were systematically varied. The generated photocurrents show a clear increase as a function of wire diameter and wire number. In turn, the photocurrent does not get larger with increasing wire length. Highly interconnected networks of nanowires under 45° from various

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directions enabled further increase of wire density number and exhibited higher photocurrent densities compared to parallel arrays.

Keywords: Cu_2O ; electrodeposition; ion-track technology; nanowires; nanowire networks; photocathode; size effect; solar-to-hydrogen.

1 Introduction

The efficient photoelectrolysis of water to form molecular hydrogen and oxygen is being intensively investigated as a direct way to store solar energy as chemical fuel [1]. This would open up new possibilities such as powering vehicles with hydrogen using fuel cells, thereby producing only water vapor as exhaust product, and decreasing CO_2 emissions [2]. First demonstrations of solar water splitting were made by Fujishima and Honda in the early 1970s using bulk TiO_2 electrodes [3]. Since then, many other water splitting systems have been investigated using various combinations of semiconductor materials, and different electrocatalysts and cell configurations [4]. However, in all cases, the overall reported efficiency remained well below the limit that experts estimate minimum for the commercial viability of photoelectrochemical (PEC) water splitting device applications [2]. Encouraging results have been obtained by combining photovoltaics and PEC water splitting [5, 6].

It is well known that the way to efficient solar water splitting is challenging and that, in spite of the intensive and productive research efforts in recent years, numerous aspects still need to be optimized. This includes: (i) the synthesis of high quality semiconductor materials at moderate costs. Alone or in combination, the applied materials have to absorb sunlight over a large range of the solar spectrum and enable efficient carrier generation and transport. (ii) The design of novel electrode geometries with large surface areas to improve sunlight absorption and provide high reaction rates at the electrolyte-semiconductor interface. (iii) The integration of all components involved in the photoelectrochemical process into an efficient device.

The challenge to solve these three aspects brought nanowire photoelectrodes into the focus of more recent research [7–12]. In particular, nanowires with reduced diameter were shown to favor efficient charge separation and diffusion of photogenerated carriers to the wire surface leading to lower recombination rates [13–17]. It was also considered that nanowire arrays can potentially enhance light absorption over a large range of wavelengths and incidence angles due to suppressed reflection [11]. Another advantage of nanowire arrays is their enormous

surface area yielding a significant increase of the semiconductor-electrolyte interface compared to flat electrodes. As bulk systems, nanowire surfaces can also be decorated with catalysts to improve the desired reaction rates. Many research groups are therefore putting great effort into the development of single-crystalline nanowire assemblies that are mechanically stable and provide large electrolyte accessible surface areas [18, 19].

In PEC water splitting with nanostructured photoelectrodes, different parameters play an important role. For systematic investigations, mechanically stable assemblies of free-standing nanowires with well-defined geometry are mandatory. To disentangle the influence of size-related nanowire parameters on relevant physical characteristics such as light absorption, electrical properties, and morphological and chemical stability requires systematic variation of the diameter, length, orientation, and interconnectivity of the wires [19–23]. Zhu et al. reported, for example, enhanced optical absorption of arrays of Si nanowires and nanocones compared to planar surfaces [24], while Maijenburg et al. demonstrated a significant photocurrent increase for a p-type Cu₂O nanocube system compared to p-type Cu₂O films synthesized under the same conditions [25]. Movsesyan et al. reported a significant increase in photocurrent densities for photoanodes of ZnO/TiO₂ in the form of nanowire networks compared to planar films [19].

In addition, advantages and disadvantages of each photoelectrode material should be weighted. In the case of Cu₂O the advantages include nontoxicity, abundance, scalability, and compatibility with simple and low-cost fabrication processes [26–28]. For PEC applications, in particular, Cu₂O profits from its direct band gap of 1.9–2.2 eV [29, 30], its p-type character caused by intrinsic Cu vacancies in the Cu₂O lattice [31], the favorable position of the conduction band located above the reduction potential of water, and the high absorption coefficient in the visible range [26]. Nevertheless, the stability of Cu₂O in aqueous solution is, unfortunately, limited to a very narrow pH range [32]. Recently, several publications reported that corrosion was prevented by passivating layers fabricated, for example, by atomic layer deposition (ALD) [26, 33, 34]. In particular, several authors have reported a higher stability of Cu₂O photocathodes coated with TiO₂ [35]. The formation of a p–n junction between the Cu₂O and the TiO₂ should also increase the efficiency of the photocathode [35].

Although there is a considerable number of publications on the photoelectrochemical performance of both simple and more complex (e.g. multimaterial, core-shell, etc.) nanowire-based systems, most studies deal with only one given set of parameters (wire diameter, material, crystallinity, coating thickness, or wire density) [7, 12, 36–38]. Systematic photoelectrochemical measurements with controlled variation of the relevant wire dimensions have not been yet reported,

although they are essential to understand and optimize the physical processes accompanying the water splitting reaction. In most cases this is due to limited control and lack of flexibility of the applied synthesis techniques.

In this paper we focus on the synthesis and characterization of nanowire-based $\text{Cu}_2\text{O}/\text{TiO}_2$ photocathodes obtained by ion-track technology combined with electrodeposition. Parallel arrays and interconnected networks of single-crystalline Cu_2O nanowires were fabricated and the geometrical parameters such as wire diameter, length and number density were systematically varied one at a time. The nanowire assemblies were conformally coated with a 10 nm thick TiO_2 layer by means of atomic layer deposition (ALD). The photocurrent generated during photoelectrochemical measurements is analyzed as a function of the geometrical wire parameters.

2 Results and discussion

Figure 1 provides information regarding the nanowire fabrication: (a) shows a representative chronoamperometric current vs. time ($I-t$) curve recorded during the electrodeposition of Cu_2O inside the channels of a polycarbonate etched ion-track membrane. The electrodeposition process during the potentiostatic growth of the Cu_2O nanowires is characterized by four different regimes: (1) nucleation and subsequent creation of a diffusion layer, indicated by the sharp initial current peak; (2) nanowire growth inside the nanochannels at nearly constant current; (3) start of cap growth identified by pronounced current increase when Cu_2O reaches the top end of the channels and forms caps on the surface of the membrane; and (4) merging of neighboring caps finally resulting in a closed film if the process is continued [39]. Current-time characteristics displaying these four typical regimes have been already reported in the literature for the growth of nanowires of numerous materials including Cu [40], Au [41], or $\text{Bi}_{1-x}\text{Sb}_x$ [42]. Regardless of material, the four $I-t$ regimes are very similar, although the electrodeposition processes are different. The electrodeposition of metals and semimetals is typically based on a direct reduction process (e.g. $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$) in an acidic electrolyte, while the electrodeposition of Cu_2O occurs in two steps, namely the reduction of Cu^{2+} to Cu^+ , followed by precipitation to Cu_2O in the presence of OH^- ions. The total charge Q_{exp} applied during the deposition can be determined by the integral of the $I-t$ curve up to the time the caps start to grow. Figure 1b presents the length of the Cu_2O nanowires, determined by SEM imaging, as a function of Q_{exp} . The linear correlation clearly reveals that the length of 200 nm diameter Cu_2O wires was adjusted in this case to a growth rate of $\sim 0.8 \mu\text{m}$ per 0.1 C. For the electrodeposition of wires longer than $\sim 4 \mu\text{m}$ it was necessary to improve the

Fig. 1: (a) Representative chronoamperometric curve for the electrodeposition of Cu₂O in etched ion-track channels and schematics displaying four different deposition regimes. (b) Nanowire length, determined by SEM, as a function of charge flow during electrodeposition of a nanowire array with 10^9 wires cm^{-2} and wire diameter ~ 200 nm. (c) Representative top view SEM image of a filled track-etched polycarbonate membrane (wire diameter ~ 200 nm) with overlapping caps on top forming an almost closed layer. The inset shows a higher magnification of caps exhibiting triangular shaped $\langle 111 \rangle$ planes oriented parallel to the membrane surface.

wettability of the 30 μm long channels by adding an anionic surfactant to the alkaline copper sulfate-based electrolyte (see Experimental Section). For longer deposition times, the channels were homogeneously filled, forming caps outside the polymer membrane. Overlapping caps finally form a highly faceted layer (Figure 1c). The morphology of the triangular shaped Cu₂O caps indicates that the electrodeposited nanowires grew along the $\langle 111 \rangle$ direction (Figure 1c, inset). A similar effect was observed for the electrodeposition of smaller nanowires with a diameter ≤ 150 nm. Complete filling of the smaller nanochannels with Cu₂O also required the addition of surfactant. The different steps performed for the synthesis of Cu₂O nanostructures using ion-track nanotechnology and electrodeposition are schematically illustrated in Figure S1.

To protect the Cu_2O nanowires in aqueous solution, the nanowire arrays were finally coated with a 10 nm thick TiO_2 layer using atomic layer deposition (ALD) at 110 °C (see details in Experimental Section). The $\text{Cu}_2\text{O}/\text{TiO}_2$ core-shell nanowires were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) as well as scanning transmission electron microscopy (STEM) to determine their crystal structure and their morphology after the ALD process.

Figure 2a displays the XRD pattern measured on a representative array of TiO_2 -coated Cu_2O nanowires free-standing on a Au back electrode. The nanowire density is 10^8 wires cm^{-2} , the length $L \sim 3$ μm and the diameter $d \sim 200$ nm. The insets show a photograph of the sample and the corresponding SEM image. The brownish color of the sample indicates a homogeneous growth of the nanowires over the whole sample area of 8 mm in diameter. The XRD pattern shows seven different reflections, four attributed to the polycrystalline Au electrode and the reflections at $2\theta = 36.5^\circ$, 42.5° and 61.6° assigned to the (111), (200) and (220) planes of cubic Cu_2O , respectively. As expected for the ALD conditions applied, the TiO_2 coating is amorphous, and thus no TiO_2 reflections neither from the rutile nor anatase phase could be detected. The reflections corresponding to reference samples of polycrystalline Au powder (PDF-2, card 4-784), cubic Cu_2O (PDF-2, card 78-2076), anatase TiO_2 (PDF-2, card 80-1157) as well as their relative intensities are represented by vertical lines at the bottom of the XRD pattern. The XRD pattern of our array sample reveals that the electrodeposited material is pure Cu_2O without

Fig. 2: Cu_2O nanowires ALD-coated with 10 nm TiO_2 : (a) X-ray diffractogram and (inset) SEM image of a free-standing nanowire array on a gold back electrode ($L \sim 3$ μm , $d \sim 200$ nm, 10^8 wires cm^{-2}) and its photograph (small inset) where the continuous brownish color indicates homogeneous coverage with nanowires. (b) HAADF image of a single $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowire together with a magnified annular bright field (ABF) image showing the (111) orientation of the Cu_2O nanowire ($L \sim 1.5$ μm , $d \sim 110$ nm).

the presence of any Cu and CuO. The Cu₂O nanowires are highly textured with (111) planes oriented perpendicular to the wire axis.

A high-angle annular dark-field (HAADF) STEM image of a representative single cylindrical Cu₂O nanowire coated with a 10 nm TiO₂ film is shown in Figure 2b. The brighter short segment at the bottom of the image corresponds to Au (deposited at the channel openings during the preparation of the conductive Au back electrode, see Experimental section). The homogeneous and conformal ~ 10 nm thick TiO₂ ALD film surrounding the nanowire is also visible. To enable high resolution STEM imaging, a small wire diameter of $d_{\text{Cu}_2\text{O}} \sim 110$ nm was selected. The higher magnification image of the Cu₂O core part clearly reveals a preferential crystallographic orientation of the Cu₂O nanowires along the $\langle 111 \rangle$ direction with fringe distances of 0.25 nm, in agreement with XRD and with the (111) facets observed by SEM on the caps. Additional EELS characterizations of these core-shell structures also confirmed that the electrodeposition leads to pure Cu₂O nanowires of single-crystalline structure along the entire length.

The PEC performance of the Cu₂O/TiO₂ nanowire arrays as photocathodes with wire densities of 10^8 and 10^9 cm⁻² is shown in Figure 3. Linear sweep voltammetry curves under chopped light illumination (100 mW cm⁻²) are depicted in Figure 3a. The light was turned on and off every 5 s during the cathodic scan from 0.6 to -0.27 V_{RHE} (RHE stands for reversible hydrogen electrode) with a scan rate of 10 mV s⁻¹. The increase of the current response when the light is turned on indicates, as expected, the photogeneration of electron-hole pairs by

Fig. 3: (a) Linear sweep voltammetry under chopped AM 1.5 illumination in 0.1 M K₂SO₄ (pH 5.7) solution for Cu₂O/TiO₂ nanowire array photocathodes with a density of 10^8 and 10^9 wires cm⁻². (b) Top view SEM images of free-standing Cu₂O/TiO₂ nanowire arrays on Au back electrode with two different wire densities (wire length $L \sim 3$ μm and diameter $d \sim 200$ nm).

the absorption of light. The large and fast cathodic spikes recorded are tentatively attributed to electron accumulation at the interface. In the future, we will study how the cathodic spikes depend on the quality of the TiO_2 layer, as well as on the presence of additional ALD layers that might improve the band alignment between Cu_2O and TiO_2 .

The TiO_2 layer covering the Cu_2O nanowires significantly improves the overall PEC performances compared to the bare Cu_2O nanowire electrodes, due to the formation of a p–n junction, which favors the separation of the photo-generated charge carriers and consequently lowers the charge carrier recombination probability [35].

The $\text{Cu}_2\text{O}/\text{TiO}_2$ nanowire arrays based photocathodes show photocurrent densities of ~ 0.07 and $\sim 0.25 \text{ mA cm}^{-2}$ at $-0.17 \text{ V}_{\text{RHE}}$ for a density of 10^8 and $10^9 \text{ wires cm}^{-2}$, respectively. Thus, increasing the wire density by a factor of 10 results only in a photocurrent increase by a factor of only 3–4. We attribute this effect to the increased nanowire packing (see Figure 3b). Electrodeposition in overlapped nanochannels (which occurs at high nanochannel densities due to their random spatial distribution) results in nanowires of effectively larger diameter, reducing the effective semiconductor volume (i.e. mass) as well as the effective wire surface accessible to the electrolyte. For the larger wire density, the dark current is higher, probably due to the larger number of shunting pathways at the interface between the Cu_2O nanowire, the Au back electrode and the TiO_2 coating layer [43]. When chopping the light on/off, large current spikes appear which are commonly attributed to the recombination of the photogenerated electrons and holes, and indicate the presence of surface states and/or active recombination active centers at the surface of the photoelectrode [44]. For our Cu_2O nanowire photocathodes, such surface centers are expected because our nanowire arrays were applied as-grown without post-annealing or other surface treatments usually applied to improve the quality of the photocathode material [26, 33, 34, 45]. We refrained from applying post-treatments to focus on the geometrical influence on the PEC performance and avoid differences in material quality originating from possible size-dependent post-treatment effects [22]. In principle, the performance of our photoelectrodes should be significantly better once the amount of defects is reduced by suitable sample annealing [32–35]. Grätzel et al. demonstrated that a post-annealing treatment significantly increases the PEC performance and the stability of the photocathode [34].

Figure 4 shows the PEC measurements and representative SEM images of arrays of TiO_2 coated Cu_2O nanowires with average length 2.1 (blue), 3.3 (green), and $5.9 \mu\text{m}$ (red), wire diameter $\sim 150 \text{ nm}$, and density $10^9 \text{ wires cm}^{-2}$. The linear sweep voltammetry curves of these samples under chopped AM 1.5 light illumination are depicted in Figure 4a. The photocurrent response along the potential scan

Fig. 4: PEC measurements of Cu₂O/TiO₂ core/shell nanowire arrays of fixed wire diameter $d \sim 150 \text{ nm}$ and different wire lengths (density $10^9 \text{ wires cm}^{-2}$): (a) Linear sweep voltammograms, (b) photocurrent responses recorded at $-0.17 \text{ V}_{\text{RHE}}$ as a function of the wire length, and (c) Top-view SEM images of arrays with three different wire lengths.

from 0.6 to $-0.27 \text{ V}_{\text{RHE}}$ is very similar, while the dark current varies from sample to sample. The corresponding top view SEM images in Figure 4c show that the longer wires start to bend and touch each other at the tips. This should be considered, because processes such as light absorption and gas bubble management are probably influenced by the geometrical arrangement of the nanowires. The fact that the photocurrent does not increase with increasing wire length limits the advantages of nanostructured photoelectrodes compared to planar films. If the nanowire length is also limited to a few μm due to the absorption coefficient of light, for a given thickness, the nanowire array sacrifices Cu₂O volume at the expenses of increasing the available semiconductor-electrolyte interface. For example, a Cu₂O nanowire array (density: $10^9 \text{ wires cm}^{-2}$, diameter: 150 nm, length: 2 μm) provides $7 \cdot 10^{-6} \text{ cm}^3$ (i.e. 42 μg) compared to $40 \cdot 10^{-6} \text{ cm}^3$ (i.e. $\sim 240 \mu\text{g}$) for a 2 μm thick Cu₂O film of the same geometrical surface area ($\sim 0.2 \text{ cm}^2$).

To study the influence of the nanowire diameter, we synthesized new series of arrays of nanowires systematically by varying the diameter between ~ 80 and ~ 250 nm for a given wire density. Figure 5 displays the photocurrent values measured at -0.17 V_{RHE} as a function of the wire diameter for a density of 10^8 and 10^9 wires cm^{-2} . In both cases, a clear increase of the photocurrent value with increasing nanowire diameter is observed. The rising photocurrent values are attributed to the associated increase in semiconductor volume and semiconductor-electrolyte interface. To elucidate the relative contribution of these two parameters, further systematic experiments are necessary. For all nanowire diameters, a 10 times increase in wire number results in an increase in photocurrent density clearly smaller than 10, as discussed already above.

This limitation, already mentioned for 200 nm diameter wires (Figure 3), is attributed to the formation of wire twins, triplets, etc. at higher parallel wire densities caused by the random spatial wire distribution. This, in turn, effectively decreases the nominal increase in semiconductor/electrolyte interface. In addition, in twins, triplets, etc. the generated minority charge carriers must travel longer distances to reach the electrolyte interface, which results in an increase in carriers recombination and lower photocurrent densities. An increase in wire overlapping results, in turn, in an increase in effective wire diameter and a decrease in semiconductor-electrolyte interface.

To overcome this limitation, we additionally prepared and characterized 3D interconnected Cu_2O nanowire networks. In this case, the ion irradiation of the

Fig. 5: Photocurrent density (at -0.17 V vs. RHE) as a function of nanowire diameter for photocathode nanowire arrays with density 10^8 wires cm^{-2} (blue) and 10^9 wires cm^{-2} (red), measured in 0.1 M K_2SO_4 (pH 5.7) solution under AM 1.5 illumination.

polymeric membrane is performed under 45° beam incidence with respect to the surface normal entering from four different directions. Chemical etching leads to an interconnected channel system that can be filled by electrodeposition in a similar manner as parallel channels. Such networks were previously fabricated from Pt [46], Sb [47], and ZnO [19]. The Cu₂O network samples were also coated by TiO₂ using the same ALD conditions as for the parallel nanowire arrays.

Figure 6 presents SEM images of 3D networks of different wire density and PEC measurements comparing parallel nanowire arrays and networks with a fixed wire diameter of ~ 100 nm. The wire density of the parallel array was $\sim 1 \cdot 10^9$ wires cm^{-2} and for the networks $\sim 4 \cdot 5 \cdot 10^8$ (top) and $\sim 4 \cdot 1 \cdot 10^9$ wires cm^{-2} (bottom), i.e. in total $\sim 2 \cdot 10^9$ and $\sim 4 \cdot 10^9$ wires cm^{-2} , respectively. This approach enabled attaining effectively higher nanowire densities without additional wire overlapping, i.e. increasing the volume of Cu₂O and the semiconductor/electrolyte interface area without influencing the effective nanowire diameter. A low magnification SEM image of a large area of the photocathode is shown in the Supplementary Information (Figure S2). The linear sweep voltammetry curves were all recorded in 0.1 M K₂SO₄ solution (pH 5.7) under chopped light illumination (100 mW cm^{-2}). The photocurrent values for both nanowire networks are higher than for the array. The increase factor is 2 and 4, respectively, which is in good agreement with the higher wire density of the networks. Assuming that the length

Fig. 6: (a) Linear sweep voltammetry under chopped AM 1.5 illumination in 0.1 M K₂SO₄ (pH 5.7) solution for photocathodes made of TiO₂-coated Cu₂O nanowire arrays [$L_{\text{arrays}} \sim 1.6 \mu\text{m}$, $1 \cdot 10^9$ wires cm^{-2} (orange)] and networks ($L_{\text{networks}} \sim 5 \mu\text{m}$) with two different wire densities, namely, $2 \cdot 10^9$ (green), and $4 \cdot 10^9$ wires cm^{-2} (blue). (b) SEM top-view images of coated 3D Cu₂O nanowire networks. The wire diameter in all cases is ~ 100 nm.

does not play a role as in the other examples shown earlier, this would imply that both, an increase in Cu_2O volume in the form of a higher number of 100 nm diameter wires, and/or an increase in surface-electrolyte interface caused by the increase in wire density can be responsible for the higher generated photocurrent densities. The relative inclination of the Cu_2O nanowires within the network may also contribute to enhancing its photocathodic activity by improving light trapping due to effective light scattering within the network.

Networks with high wire densities are characterized by multiple intersections between adjacent inclined wires and small inter-wire spacings (Figure 6b). This could explain that the photocurrent spikes appearing during on/off switching of the light are more pronounced for the network with the higher nanowire density (Figure 6a). The densest nanowire network exhibits also a higher dark current, indicating again that the presence of a higher amount of wires connected with Au back electrode and the TiO_2 layer may result in a larger density of shunting pathways. Consistently, the stability of the nanostructured photoelectrodes was limited, as revealed during chronoamperometric measurements (Figure S3). In the future, the addition of a second electrodeposited Cu_2O layer prior to TiO_2 ALD coating should contribute to decreasing the dark current and increasing the photocurrent stability by avoiding such shunting paths [43]. An optimization of the TiO_2 ALD deposition conditions, for example, by increasing the process temperature and/or by using different precursors as well as by testing thicker layers, should also yield more stable photocathodes.

3 Conclusions

Photocathodes consisting of diameter and length-tailored assemblies of $\langle 111 \rangle$ oriented single-crystalline Cu_2O nanowires arrays and networks were synthesized by electrodeposition in etched ion-track polycarbonate membranes and conformally ALD-coated with TiO_2 . The photoelectrochemical performance was tested for a variety of length, diameter, and density of the wires. For wire arrays, the photocurrent does not vary as a function of the nanowire length, but clearly increases for larger nanowire diameters and nanowire densities. The suitability of arrays with free-standing parallel oriented nanowires is limited due to the additional growth of wire twins, triplets, etc. at high densities, which decreases the effective semiconductor/electrolyte interface and increases the minority charge carrier paths to the electrolyte. In addition, the nanostructured arrays provide less volume/mass of Cu_2O photoabsorber material than a film with the same thickness and sample area. We showed that 3D Cu_2O interconnected nanowire networks provided stable photocathodes of higher wire densities and higher surface areas, thus

yielding higher light-induced photocurrent densities than the parallel nanowire arrays. These results evidence that systematic investigations on the influence of the geometrical parameters of nanostructured photoelectrodes using model systems are important and necessary to discuss the advantages and disadvantages of nanostructured solar water splitting systems, and to optimize future electrode geometries.

4 Experimental

4.1 Polycarbonate etched ion-track membranes

Polycarbonate foils (30 μm thick, Makrofol M, Bayer AG) were irradiated by ~ 2 GeV Au ions at the universal linear accelerator (UNILAC) of the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany. For the arrays, the irradiation was performed under normal incidence applying a fluence of 10^8 and 10^9 ions cm^{-2} . In contrast, for the networks the polymer foils were exposed under an angle of 45° sequentially from four different directions with $5 \cdot 10^8$ and 10^9 ions cm^{-2} at each step summing up in total to $2 \cdot 10^9$ and $4 \cdot 10^9$ ions cm^{-2} . Each individual ion creates a so-called ion-track, which is subsequently selectively removed in a wet-etching process in 6 M NaOH (NaOH pellets $\geq 99\%$ p.a., Carl Roth GmbH & Co. KG) at 50°C , resulting into a cylindrical nanochannel. After etching, polycarbonate etched ion-track membranes with parallel oriented channel arrays and interconnected tilted nanochannels are obtained. Prior to etching, the irradiated polymer foils were exposed to UV light (30 W, 312 nm, T-30M, Vilber Lourmat) for 1 h (both sides) to improve the etching selectivity and the homogeneity of the distribution of nanochannel diameters [48].

4.2 Au substrate working electrode

After rinsing and drying the polycarbonate membrane, a 30 nm thin Au layer was sputtered on one side to act as a conductive contact. The DC sputtering was performed at room temperature with a Edwards Sputter Coater S150B system. The average growth rate of the layer was 0.05 nm s^{-1} . This Au layer was reinforced by electrodeposition of a $\sim 7 \text{ }\mu\text{m}$ Au film, synthesized potentiostatically using a commercial ammonium gold (I) sulfite (AuSF , 15 g Au L^{-1} , 99.9%, METAKEM GmbH) solution at a constant bias voltage of $U = -0.7 \text{ V}$ vs. a Au spiral anode. The resulting Au film served as working electrode for the electrodeposition of p-type Cu_2O single crystals into the nanochannels and provided a stable planar substrate for further handling of the sample.

4.3 Cu₂O nanowire electrodeposition

Single crystalline Cu₂O was electrodeposited from an alkaline electrolyte of lactate stabilized copper sulfate electrolyte consisting of 0.02 M CuSO₄ (CuSO₄ · 5 H₂O, ACS reagent ≥98%, Sigma Aldrich) and 0.4 M lactic acid (CH₃CH(OH)CO₂H, Carl Roth GmbH & Co. KG). The pH of the electrolyte was adjusted to 12 by adding NaOH pellets. The basic environment of the solution ensures the electrodeposition of p-type Cu₂O crystals [49]. For the electrodeposition of Cu₂O into the interconnected nanochannel membranes, membranes and some of the parallel nanochannel array membranes, a 0.5%₀₀ DOWFAXTM 2A1 anionic surfactant solution (Dow Chemical Company) was added to the copper sulfate electrolyte to ensure a good wettability of the membrane [50]. Before starting the electrodeposition, both membrane and electrolyte were maintained at 60 °C for 1 h. During this time, the electrolyte wets all the high aspect ratio nanochannels and a homogeneous temperature distribution of the electrolyte is obtained. Cu₂O was then electrodeposited inside the channels at $T = 60\text{ °C}$ and a constant potential of $U = -0.4\text{ V}$ vs. Ag/AgCl using a potentiostat 1000 from Gamry Instruments, Inc. The Au back electrode and a Pt spiral served as working and counter electrodes, respectively. As reference electrode a Ag/AgCl (sat. KCl) electrode was used. After electrodeposition, the samples were thoroughly rinsed with deionized water (resistivity ≥18.2 MΩ cm, Milli-Q[®] purification system), and gently dried with N₂ gas. To dissolve the polymer matrix, the samples were fixed to a modified SEM holder and immersed in dichloromethane (CH₂Cl₂, purity >99.5%, Carl Roth GmbH & Co. KG). The resulting free-standing Cu₂O nanowire assemblies were further characterized by SEM. For TEM measurements, the Cu₂O nanowires were detached from the Au support layer in an ultrasonic bath, and dropped on Au TEM grids using a micropipette.

4.4 TiO₂ atomic layer deposition

TiO₂ coating of the wire assemblies was performed by atomic layer deposition (ALD) using a PICOSUNTM R-200 system. TiO₂ was deposited at 110 °C using titanium tetrakisopropoxide (TTIP, Pegasus Chemicals Limited) and deionized water as Ti and O precursors, respectively, with N₂ gas (high purity grade 5N, Air Liquide) as carrier gas. TTIP was heated to 70 °C to ensure sufficient vapor pressure. TTIP and H₂O were held in the chamber for 5.2 and 0.4 s, respectively, followed by a 50 s N₂ purge. The growth per cycle (GPC) was measured by ellipsometry on films deposited on optically polished silicon wafers with a thermally grown oxide layer. The GPC for TiO₂ was 0.11 Å/cycle. A TiO₂ film of approximately 10 nm in thickness typically required 980 deposition cycles (~28 h).

4.5 Material characterization

X-ray diffraction (XRD) patterns were acquired with a Bruker D2 PHASER diffractometer (Billerica, MA, USA) in Bragg-Brentano mode, using monochromatic Cu K α excitation (1.540598 Å) to determine the crystal phase of the nanowires. Diffractograms were acquired from $2\theta = 20^\circ$ – 65° at a scan rate of 1° min^{-1} and with a step width of 0.02° . The morphology of the nanowire arrays was characterized using a high-resolution scanning electron microscope (HRSEM, Philips XL30 FEG) operated at an accelerating voltage of 10 kV. For SEM inspection, the samples were typically tilted by 30° .

4.6 Photoelectrochemical measurements

All PEC measurements were conducted in an aqueous electrolyte containing 0.1 M K₂SO₄ (ACS reagent $\geq 99\%$, Fluka) with a pH of 5.7 using a three-electrode configuration with a synthesized photocathode as working electrode, a Pt wire as counter electrode and Ag/AgCl (sat. KCl) as reference electrode. The PEC performance of the photocathodes was studied using a Gamry Reference 600 (Gamry Instruments, Inc.). The working electrodes were fixed in a commercial photoelectrochemical system (PECC-2 cell, Zahner) and exposed to AM 1.5 light illumination (100 mW cm^{-2}) from a solar simulator equipped with a 150 W Xenon arc lamp (LOT QuantumDesign GmbH) calibrated with a silicon diode (Newport Oriel, P/N 91150V). The light illumination was chopped with an electrical shutter (frequency = 0.2 Hz). Linear sweep voltammetry (LSV) was carried out under dark, constant illumination, and chopped light (on/off, 5 s) with a scan rate of 10 mV s^{-1} in the cathodic direction. All potentials reported are referenced to the reversible hydrogen electrode (RHE) by:

$$U_{\text{RHE}} = U_{\text{Ag/AgCl}} + U_{\text{Ag/AgCl}}^0 + 0.059 \text{ pH},$$

where U_{RHE} is the potential converted vs. RHE, $V_{\text{Ag/AgCl}}$ is the potential applied vs. Ag/AgCl reference electrode ($U_{\text{Ag/AgCl}}^0 = 0.199 \text{ V}$), and pH = 5.7.

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employed for this work is based on an UMAT irradiation experiment, which was performed at the beamline XO at the GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt (Germany) in the frame of FAIR-Phase 0.

References

1. C. A. Grimes, O. K. Varghese, S. Ranjan, *Light, Water, Hydrogen: The Solar Generation of Hydrogen by Water Photoelectrolysis*, Springer, New York (2008).
2. H. J. Lewerenz, L. Peter, L. M. Peter, R. S. O. Chemistry, *Photoelectrochemical Water Splitting: Materials, Processes and Architectures*, RSC Publishing, Cambridge, UK (2013).
3. A. Fujishima, K. Honda, *Nature* **238** (1972) 37.
4. M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, *Chem. Rev.* **110** (2010) 6446.
5. O. Khaselev, J. A. Turner, *Science* **280** (1998) 425.
6. F. Urbain, V. Smirnov, J.-P. Becker, U. Rau, J. Ziegler, B. Kaiser, W. Jaegermann, F. Finger, *Sol. Energy Mater. Sol. Cells* **140** (2015) 275.
7. R. van de Krol, Y. Liang, J. Schoonman, J. Mater. Chem. **18** (2008) 2311.
8. S. W. Boettcher, J. M. Spurgeon, M. C. Putnam, E. L. Warren, D. B. Turner-Evans, M. D. Kelzenberg, J. R. Maiolo, H. A. Atwater, N. S. Lewis, *Science* **327** (2010) 185.
9. N. Tétreault, M. Grätzel, *Energy Environ. Sci.* **5** (2012) 8506.
10. J. M. Foley, M. J. Price, J. I. Feldblyum, S. Maldonado, *Energy Environ. Sci.* **5** (2012) 5203.
11. F. E. Osterloh, *Chem. Soc. Rev.* **42** (2013) 2294.
12. S. C. Warren, K. Voitchovsky, H. Dotan, C. M. Leroy, M. Cornuz, F. Stellacci, C. Hébert, A. Rothschild, M. Grätzel, *Nat. Mater.* **12** (2013) 842.
13. A. I. Hochbaum, P. Yang, *Chem. Rev.* **110** (2010) 527.
14. X. Yang, A. Wolcott, G. Wang, A. Sobo, R. C. Fitzmorris, F. Qian, J. Z. Zhang, Y. Li, *Nano Lett.* **9** (2009) 2331.
15. S. Hoang, S. Guo, N. T. Hahn, A. J. Bard, C. B. Mullins, *Nano Lett.* **12** (2012) 26.
16. M. Liu, N. de Leon Snapp, H. Park, *Chem. Sci.* **2** (2011) 80.
17. I. Oh, J. Kye, S. Hwang, *Nano Lett.* **12** (2012) 298.
18. S. Kment, F. Riboni, S. Pausova, L. Wang, L. Wang, H. Han, Z. Hubicka, J. Krysa, P. Schmuki, R. Zboril, *Chem. Soc. Rev.* **46** (2017) 3716.
19. L. Movsesyan, A. W. Maijenburg, N. Goethals, W. Sigle, A. Spende, F. Yang, B. Kaiser, W. Jaegermann, S.-Y. Park, G. Mul, C. Trautmann, M. E. Toimil-Molares, *Nanomater. (Basel, Switzerland)* **8** (2018) 693.
20. F. Neubrech, T. Kolb, R. Lovrincic, G. Fahsold, A. Pucci, J. Aizpurua, T. W. Cornelius, M. E. Toimil-Molares, R. Neumann, S. Karim, *Appl. Phys. Lett.* **89** (2006) 253104.
21. V. Giannini, A. I. Fernández-Domínguez, S. C. Heck, S. A. Maier, *Chem. Rev.* **111** (2011) 3888.
22. M. E. Toimil-Molares, A. G. Balogh, T. W. Cornelius, R. Neumann, C. Trautmann, *Appl. Phys. Lett.* **85** (2004) 5337.
23. M. Liu, C.-Y. Nam, C. T. Black, J. Kamcev, L. Zhang, *J. Phys. Chem. C* **117** (2013) 13396.
24. J. Zhu, Z. Yu, G. F. Burkhard, C.-M. Hsu, S. T. Connor, Y. Xu, Q. Wang, M. McGehee, S. Fan, Y. Cui, *Nano Lett.* **9** (2009) 279.

25. A. W. Maijenburg, A. N. Hattori, M. De Respinis, C. M. McShane, K.-S. Choi, B. Dam, H. Tanaka, J. E. ten Elshof, *ACS Appl. Mater. Interfaces* **5** (2013) 10938.
26. A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, E. Thimsen, *Nat. Mater.* **10** (2011) 456.
27. R. Wick, S. D. Tilley, *J. Phys. Chem. C* **119** (2015) 26243.
28. H. Qi, J. Wolfe, D. Fichou, Z. Chen, *Sci. Rep.* **6** (2016) 30882.
29. T. D. Golden, M. G. Shumsky, Y. Zhou, R. A. VanderWerf, R. A. Van Leeuwen, J. A. Switzer, *Chem. Mater.* **8** (1996) 2499.
30. P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, *Chem. Mater.* **11** (1999) 3512.
31. H. Raebiger, S. Lany, A. Zunger, *Phys. Rev. B* **76** (2007) 045209.
32. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 1st ed., Pergamon Press, Oxford, UK (1966).
33. S. D. Tilley, M. Schreier, J. Azevedo, M. Stefik, M. Graetzel, *Adv. Funct. Mater.* **24** (2014) 303.
34. A. Paracchino, N. Mathews, T. Hisatomi, M. Stefik, S. D. Tilley, M. Grätzel, *Energy Environ. Sci.* **5** (2012) 8673.
35. W. Siripala, A. Ivanovskaya, T. F. Jaramillo, S.-H. Baeck, E. W. McFarland, *Sol. Energy Mater. Sol. Cells* **77** (2003) 229.
36. J. Resasco, H. Zhang, N. Kornienko, N. Becknell, H. Lee, J. Guo, A. L. Briseno, P. Yang, *ACS Cent. Sci.* **2** (2016) 80.
37. S. Hernández, D. Hidalgo, A. Sacco, A. Chiodoni, A. Lamberti, V. Cauda, E. Tresso, G. Saracco, *Phys. Chem. Chem. Phys.* **17** (2015) 7775.
38. B. D. Alexander, P. J. Kulesza, I. Rutkowska, R. Solarska, J. Augustynski, *J. Mater. Chem.* **18** (2008) 2298.
39. M. E. Toimil-Molares, *Beilstein J. Nanotechnol.* **3** (2012) 860.
40. M. E. Toimil-Molares, V. Buschmann, D. Dobrev, R. Neumann, R. Scholz, I. U. Schuchert, J. Vetter, *Adv. Mater.* **13** (2001) 62.
41. J. Liu, J. L. Duan, M. E. Toimil-Molares, S. Karim, T. W. Cornelius, D. Dobrev, H. J. Yao, Y. M. Sun, M. D. Hou, D. Mo, *Nanotechnology* **17** (2006) 1922.
42. S. Müller, C. Schötz, O. Picht, W. Sigle, P. Kopold, M. Rauber, I. Alber, R. Neumann, M. E. Toimil-Molares, *Crystal Growth Design* **12** (2012) 615.
43. J. Luo, L. Steier, M.-K. Son, M. Schreier, M. T. Mayer, M. Grätzel, *Nano Lett.* **16** (2016) 1848.
44. L. M. Peter, *Chem. Rev.* **90** (1990) 753.
45. C. G. Morales-Guio, S. D. Tilley, H. Vrubel, M. Grätzel, X. Hu, *Nat. Commun.* **5** (2014) 3059.
46. M. Rauber, I. Alber, S. Müller, R. Neumann, O. Picht, C. Roth, A. Schökel, M. E. Toimil-Molares, W. Ensinger, *Nano Lett.* **11** (2011) 2304.
47. M. F. P. Wagner, F. Völklein, H. Reith, C. Trautmann, M. E. Toimil-Molares, *Phys. Status Solidi (a)* **213** (2016) 610.
48. E. Ferain, R. Legras, *Nucl. Instrum. Methods Phys. Res. Sect. B* **82** (1993) 539.
49. L. Wang, M. Tao, *Electrochem. Solid-State Lett.* **10** (2007) H248.
50. Z. Wang, Y. Chen, X. Sun, R. Duddu, S. Lin, *J. Membrane Sci.* **559** (2018) 183.

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