Decoration of ultra-long carbon nanotubes with Cu$_2$O nanocrystals: a hybrid platform for enhanced photoelectrochemical CO$_2$ reduction

E. Kecsenovity, B. Endrődi, Zs. Pápa, K. Hernádi, K. Rajeshwar* and C. Janáky*

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Paper: c5ta10457b
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Decoration of ultra-long carbon nanotubes with Cu$_2$O nanocrystals: a hybrid platform for enhanced photoelectrochemical CO$_2$ reduction†

E. Kecsenovity,ab B. Endrödi,ab Zs. Pápa, K. Hernádi,d K. Rajeshwar*c and C. Janáky*ab

Photoelectrochemical reduction of CO$_2$ to form useful chemicals is an increasingly studied avenue for harnessing and storing solar energy. In the quest for efficient and stable photocathode materials, nanostructured hybrid assemblies are eminently attractive candidates, because they exhibit multiple favorable properties that cannot be expected from a single material. One possible direction is to combine p-type inorganic semiconductors with highly conductive large surface area electrodes such as carbon nanotube networks. In this work, the controlled synthesis photoelectrochemical behavior of CNT/Cu$_2$O films was reported for the first time for CO$_2$ reduction applications. A carefully designed, multiple-step electrodeposition protocol was developed that ensured homogeneous coating of CNTs with Cu$_2$O nanocrystals. The hybrid materials were characterized by electron microscopy, X-ray diffraction, Raman spectroscopy, electrochemical impedance spectroscopy, and photoelectrochemical methods. The hybrid films had five-fold higher electrical conductivity compared to their pure Cu$_2$O counterparts. This enhanced charge transport property resulted in a drastic increase in the photocurrents measured for CO$_2$ reduction. In addition to this superior performance, long term photoelectrolysis measurements proved that the CNT/Cu$_2$O hybrids were more stable than the oxide alone. These observations, together with the established structure/property relationships, may contribute to the rational design of nanocarbon/inorganic semiconductor hybrid photocathodes for deployment in photoelectrochemical cells.

Introduction

Semiconductor photoelectrochemistry is an intensely studied approach for solar fuel generation.$^{1,2}$ Photoelectrochemical (PEC) water splitting,$^3$ and more recently, CO$_2$ reduction,$^4$ have been at the forefront of research because of their promise to simultaneously remove a greenhouse gas, and to harness and store the energy of sunlight in the form of useful fuels. In the simplest case, the semiconductor itself acts as the light absorber as well as the catalyst as was first shown for p-GaP as an example.$^5$ To efficiently drive a thermodynamically uphill reaction at the semiconductor/electrolyte interface, however, the employed photoelectrode needs to fulfil multiple criteria at the same time.$^6$ Light absorption, charge carrier transport, surface chemical properties, chemical/electrochemical/photostability, and cost: these are only some of the factors that need to be optimized. Perhaps this is the reason that although several different semiconductors were tested since the first reports,$^7$ much remains to be done to achieve similar progress to what the solar cell photovoltaics community has witnessed for electricity generation.$^8$

Since our proof-of-concept studies on the solar photocatalytic methanol synthesis using hybrid CuO/Cu$_2$O nanorod arrays,$^9$ different laboratories have employed Cu$_2$O as a photocathode material in CO$_2$ reduction.$^{10,11}$ In addition, further progress has been achieved in terms of (i) analyzing the potential dependent product distribution,$^{12}$ (ii) realizing the reaction in a continuous flow reactor,$^{13}$ and (iii) gaining mechanistic understanding of CO$_2$ adsorption using quantum chemical calculations.$^{14}$ The instability of Cu$_2$O towards photoelectrochemical corrosion (i.e., metallic copper formation) was already found to be a major problem in earlier reports on PEC water splitting using this material.$^{15,16}$ Application of surface coating was demonstrated as a possible strategy to increase the photoelectrode lifetime, either by employing a carbon coating$^{17}$ or other via atomic
layer deposition of Al-doped zinc oxide and titanium oxide nanolayers.\textsuperscript{28,29} Employing a surface coating on the Cu$_2$O surface, however, is not necessarily useful in CO$_2$ reduction, where Cu surface clusters play a specific catalytic role in the reaction as was shown in different electrocatalytic reaction schemes.\textsuperscript{29}

In addition to instability, two other factors, namely, surface area and charge carrier mobility, are also critical issues limiting the performance of photocathodes. To address the above challenges together as a whole, nanostructuring of the electrode may offer a viable avenue of attack.\textsuperscript{31} In addition, nanocarbon/inorganic semiconductor hybrids offer a promising platform in different solar energy application schemes, by uniting the high electrical conductivity of the carbon component with the photocactive behavior of the inorganic material.\textsuperscript{32} There are different studies in the literature, proving the above concept in both binary\textsuperscript{22,24} and ternary hybrid configurations.\textsuperscript{22,26} As for Cu$_2$O specifically, it has been combined with both carbon quantum dots\textsuperscript{33} and reduced graphene oxide sheets\textsuperscript{34} recently to perform the photo-driven reduction of CO$_2$ to fuels. These studies used a slurry of the composite material. To the best of our knowledge, however, there is no precedence in the literature, where such hybrids were employed as photocathodes in a photoelectrochemical cell.

To efficiently exploit these possible synergies in a PEC configuration, however, carefully designed synthetic protocols are required, which allow us to tailor the composition and morphology of the hybrid material toward the targeted reaction. Electrochemical deposition of inorganic semiconductors on carbon nanostructures is an emerging topic with high applicability in various application avenues.\textsuperscript{35} This preparation method can be particularly useful for PEC applications, where electronic communication between the components is a prerequisite. In this study we accordingly present the tailored electrodeposition of Cu$_2$O nanocrystals on high quality ultra-long carbon nanotubes (CNTs). To the best of our knowledge, this is the first time when photoelectrochemical CO$_2$-reduction was driven at a nanocarbon/inorganic semiconductor hybrid electrode material. It is demonstrated that efficient charge carrier transport and rapid charge carrier extraction contribute to both remarkably higher photocurrents and higher stability. The effects of the composition and morphology on the PEC performance are also discussed and structure–property relationships are established.

### Experimental

#### CVD synthesis of CNT arrays

High quality, ultra-long (1–1.5 mm) carbon nanotube arrays were grown following a previously optimized chemical vapor deposition (CVD) process, detailed elsewhere.\textsuperscript{9} The Al$_2$O$_3$ support layer and the mixed Fe–Co catalyst layer were deposited subsequently on silicon substrates using a pulsed laser deposition method, by focusing the laser beam (LLG TWINAMP ArF excimer laser, $\lambda = 193$ nm, pulse length 18 ns, and repetition rate 10 Hz) on pressed Al$_2$O$_3$ and Fe–Co (1 : 1 molar ratio) targets, respectively.

The catalyst-coated silicon wafers were placed in a fixed-bed flow quartz tube reactor (20 mm diameter, 800 mm length). The reaction chamber was heated to 750 °C under nitrogen purging (100 mL min$^{-1}$). After 5 min, hydrogen gas (with a flow rate of 80 mL min$^{-1}$) was added to the nitrogen, and the catalysts were activated for 5 min in this mixture. Subsequently, an ethylene carbon source (100 mL min$^{-1}$) and moisturized nitrogen (25 mL min$^{-1}$, bubbled through 25 °C water to achieve ~2 ppm water content in the reaction chamber) were also introduced into the quartz tube for the 30 min CVD process.

#### Electrode preparation

Arrays of CNTs were dispersed in ethanol by ultrasonic treatment. The formed dispersion ($c \approx 10 \mu\text{g mL}^{-1}$) was spray-coated on preheated indium doped tin oxide covered glass (ITO) electrodes, using an Alder AD320 type airbrush, operated with 1 bar compressed air. To remove traces of the solvent and to enhance adhesion of the CNTs, the thin layers were kept in an oven (180 °C) for 1 h. Carbon nanotube loading of the electrodes was controlled with the number of spray steps (5–100 µg cm$^{-2}$, denoted as CNT5, CNT10, etc.), and quantified by quartz crystal microbalance (QCM) measurements using a Stanford Research System QCM-200 type instrument.

#### Cu$_2$O electrodeposition

Cu$_2$O was electrodeposited from an alkaline solution of lactate-stabilized copper sulfate, containing 0.4 mol dm$^{-3}$ cupric sulfate and 3 mol dm$^{-3}$ lactic acid in deionized water (Millipore Direct Q3-UV, 18.2 MΩ cm). The bath pH was adjusted to 9 with concentrated sodium hydroxide solution. The temperature of the solution was maintained at 60 °C, and it was constantly stirred by using a magnetic stirrer during the electrodeposition.

All the electrochemical measurements were performed on a Metrohm Autolab PGSTAT302N type potentiostat/galvanostat. The electrodeposition was performed in a classic three electrode cell, using Pt sheet and Ag/AgCl/3 M NaCl counter and reference electrodes, respectively. For Cu$_2$O electrodeposition, after carefully studying the linear sweep voltammetry curves, a potentiostatic method was applied by adjusting previous procedures.\textsuperscript{31,32} To ensure complete coverage of the CNTs, nuclei formation was initialized by introducing a seed nucleation step at more negative potential ($\approx 0.35$ V) until the first 50 mC cm$^{-2}$ charge was passed (~15 s) (Fig. 1b). The deposition was then continued at a less negative potential ($E = 0.25$ V, ~20 s each step) to achieve uniform and homogenous crystal growth. After each 50 mC of passed charge, the deposition was interrupted for 60 s to avoid depletion of the solution.

#### Electrochemical impedance spectroscopy (EIS) and Mott–Schottky analysis

Impedance spectra of the Cu$_2$O and CNT/Cu$_2$O layers were recorded in a 0.1 mol dm$^{-3}$ sodium acetate solution at open circuit potential, in the 0.1 Hz to 1 MHz frequency range, using a sinusoidal excitation signal (10 mV RMS amplitude). For Mott–Schottky analysis, impedance spectra of the electrodes
were recorded at 6 frequencies (1 kHz–75 kHz) between $E = 0.10$ and 0.42 V potentials.

**Photoelectrochemical measurements**

Photovoltammograms were recorded in a two-compartment, sealed electrochemical cell in a 1 mol dm$^{-3}$ Na$_2$SO$_4$ solution. The solution was saturated with N$_2$ or CO$_2$ by bubbling the gases through the cell for 30 min before, and forming gas pillows above the solutions during the measurements. The photovoltammograms were recorded under periodically interrupted (0.2 Hz, with an automated chopper) solar irradiation, using a Newport LCS-100 type solar simulator (100 W), operated at full output with a UV-cutoff filter ($<400$ nm).

Long-term carbon dioxide photoelectrolysis (and consequently constant potential stability) tests were performed using the same arrangement. The electrode potential was kept at +0.05 V (vs. Ag/AgCl/3 M NaCl), and was irradiated with the above described light source (periodically interrupted at 0.033 Hz). Liquid aliquots were taken at the end of photoelectrolysis to be analyzed in a gas chromatograph equipped with a mass spectrometer as the detector (GC-MS). The aliquots were injected into the Shimadzu GC-MS 2010SE chromatograph coupled with a MS QP2010 detector. The chromatographic column was a Stabilwax-DA (30 m length and 0.32 mm inner diameter) set at 40 °C, and the injection port temperature was 220 °C. The MS detector was set at 200 °C, and helium was used as the carrier gas. Product detection was afforded by selective ion monitoring (SIM)-MS, while the total ion chromatogram was used for the quantification of methanol, ethanol, and formic acid.

**Structural characterization**

Raman spectroscopic studies were performed on a DXR Raman Microscope using a green laser ($\lambda = 532$ nm), operating at 1 mW laser power. A FEI Tecnai G2 20 X-Twin type instrument, operating at an acceleration voltage of 200 kV, was used for transmission electron microscopy (TEM) investigations. Scanning electron microscopy (SEM) images were recorded by using a Hitachi S-4700 field emission scanning electron microscope (coupled with a Röntec EDX detector), operating at an acceleration voltage of 10 kV. X-Ray diffraction (XRD) data were recorded in the range, $2\Theta = 20–60^\circ$, at 1° minute$^{-1}$ scan rate by using a Rigaku Miniflex II instrument, operating with a Cu K$_{\alpha,1}$ radiation source ($\lambda = 0.1541$ nm).

**Results and discussion**

As the first step, ordered arrays of ultra-long CNTs were synthesized by the CVD method (Fig. S1†). These nanostuctures can be used as electrode materials without any additional treatment, and we performed electrodeposition of Cu$_2$O on these carbon nanotubes.$^{29}$ For PEC applications however, the large thickness of the electrode (∼1 mm) is not suitable, considering the penetration depth of solar irradiation. Therefore, the synthesized nanocarbon arrays were sonicated, and the obtained suspension was spray-coated on ITO electrodes. Via this method, an interconnected nanonet structure was reproducibly obtained (see, for example, Fig. 2a below), where the thickness was controlled by the number of the spray-coat cycles.

Prior to electrodeposition of the Cu$_2$O crystals, an electrochemical conditioning step was carried out in the Cu–lactate solution, to remove any entrapped gas and to ensure proper wetting of the CNT film. This step consisted of multiple cyclic voltammetry scans in a potential window ($E = 0.0$ V–0.5 V), where the lower vertex potential was more positive than the potential required for the reduction of Cu$^{2+}$. During these cycles we observed that the evolution of the capacitance dominated the electrochemical behavior of the CNTs (Fig. S2†), with parallel desorption of the entrapped gases (N$_2$ and O$_2$). In the case of thicker CNT films, we found this step to be essential for achieving high Cu$_2$O loadings in the subsequent electrodeposition process.

Based on earlier literature studies,$^{8,11,32}$ we aimed to employ slow potentiostatic deposition, to minimize the metallic Cu content of the deposited oxide phase. To determine the deposition potential, linear sweep voltammograms (LSVs) were recorded. As seen in Fig. 1a, the two curves have a very similar pattern, but the cathodic currents start to develop at markedly less negative potential values ($E \approx -0.2$ V) on the CNTs than at the bare ITO coated glass electrode. This shift indicates that
oxide formation is favored on the CNTs, and by appropriately selecting the potential value, Cu$_2$O crystals could be exclusively deposited on the CNTs (this was also confirmed by the SEM images, see below). The composition and morphology of the CNT/Cu$_2$O hybrid greatly affect its electrical- and photoelectrochemical properties (for example, a complete filling of the nanocarbon template may hinder the accessibility of Cu$_2$O in the deeper regions). To establish structure–property relationships, and to find the best performing material in PEC CO$_2$ reduction, the thickness of the CNT film (5–100 mC/cm$^2$), as well as the amount of the electrodeposited Cu$_2$O, was systematically varied (50–2000 mC/cm$^2$).

It was found that simple potentiostatic growth results in homogeneous films without, or with very small amounts of CNTs. On the other hand, for thicker CNT films, more sophisticated methods are indeed required. Therefore, we developed an approach consisting of multiple potentiostatic deposition steps, as well as rest periods interspersed among them, to allow for continuous supply of the copper ions from the bulk solution (Fig. 1b). An initial nucleation step at a more negative potential (−0.35 V) was also found to be beneficial for achieving homogeneous coating on the ITO/CNT electrode. The length of this nucleation step, however, cannot be too long, because formation of metallic copper also occurs at this potential. Accordingly, the subsequent Cu$_2$O growth was performed at less negative potential (−0.25 V). This protocol is summarized in Fig. 1b, whereas the observed response is shown in Fig. 1c. As seen in Fig. 1c, the rapid nucleation occurs during the first step (as deduced from the high currents), while a steady growth is indicated during the subsequent phase.

The above observations were also confirmed at the submicroscopic level. Scanning electron microscopic studies showed the bare CNT nanonet (Fig. 2a) and the formation of typical octahedral Cu$_2$O crystals on the CNT surface (Fig. 2b and c). Importantly, while some bare carbon nanotubes can be spotted on the sample synthesized without the pre-nucleation step (Fig. 2b), perfect coverage is seen when the optimized protocol was employed (Fig. 2c). This better homogeneity was a general trend, observed in all the cases when the pre-nucleation step was applied. In addition, a striking difference can be seen in the size of the Cu$_2$O particles deposited, namely they are much smaller in the latter case. This is not a surprise considering the equal amount of deposition charge (200 mC), and the larger number of nuclei formed during the nucleation step at a more negative potential. This difference was also quantified by obtaining the particle size distribution. As shown in the histograms in Fig. 2d, the particles are massively larger in the first case ($d_{av}$ = 200 nm vs. 60 nm). We note here that these particle sizes serve only for comparative purposes, since they can be widely tuned by the deposition charge. TEM images (Fig. 2e and f) confirmed the above conclusions, and very similar particle sizes were obtained.

Structural properties of the hybrid assemblies were investigated using Raman spectroscopy and X-ray diffraction (XRD), and both techniques confirmed the formation of Cu$_2$O nanocrystals on the CNTs (Fig. 3a and b, respectively). The spectrum of the CNT film shows the typical D and G-bands at 1346 and 1588 cm$^{-1}$, respectively. The bands at 150, 212, and 630 cm$^{-1}$ all confirm the formation of cuprite (Cu$_2$O) crystals. Importantly, the absence of the phonon peak around 300 cm$^{-1}$ proves the
absence of CuO in the film. On the spectrum of the hybrid sample, beyond the obvious appearance of the bands of its constituents, an interesting phenomenon can be spotted. The decrease in the D/G band ratio after the cathodic synthesis indicates an improved quality (most likely because of the electrochemical reduction of certain oxygen-functional groups). XRD data furnished further evidence for the formation of Cu2O. Comparison of the XRD patterns of two CNT/Cu2O samples (with and without a nucleation step) is provided in Fig. 3b. Both patterns are consistent with the presence of a Cu2O phase, except two minor diffractions (marked with asterisks) which originate from the presence of metallic copper traces. The Scherrer equation was employed to estimate the size of the crystalline domains using the most intensive reflection (111). As seen in Fig. 3b, in line with the electron microscopic observations (see above), a markedly smaller value was obtained for the sample obtained with a pre-nucleation step (21 nm vs. 30 nm).

Electrochemical impedance spectroscopy was employed to probe the electrical properties of the bare Cu2O and the CNT/Cu2O electrodes deposited with identical charge density (1C). Nyquist plots are presented in Fig. 4, together with the fit obtained using the equivalent circuit shown in Fig. S3.† The most important point from the analysis of these EIS data was that the Cu2O/CNT electrode shows a 4–5 times lower charge transfer resistance compared to the bare Cu2O electrode (440 Ω vs. 1.9 kΩ), while the other circuit parameters were practically the same. This massive decrease can be attributed to the presence of a well-connected, highly conductive pathway under and between the Cu2O nanocrystallites.22,23 Importantly, this architecture may lead to suppressed charge carrier recombination, and rapid charge carrier extraction, and therefore to better catalytic activity and longer lifetime of the catalyst. The flat-band potentials were determined for both samples using Mott–Schottky analyses. For the bare Cu2O, this was found to be 0.29 V (0.5 V vs. SHE), which agrees well with previously reported values.11 Upon introducing the CNT network, only a slight positive shift can be witnessed, which means that the deposited Cu2O has a very similar flat-band potential in both cases (~0.55 V vs. SHE).

Fig. 5a compares linear sweep photovoltammetry data of the CNT/Cu2O hybrid material (CNT10, 200 mC Cu2O), both in the presence and absence of dissolved CO2. This voltammetry technique consists of a slow scan of the potential (2 mV s−1) while the film irradiation is periodically chopped. In this manner, both the dark and light-induced photoresponses of the hybrid samples can be assessed in a single experiment. As seen in Fig. 5, cathodic photocurrents can be detected for all the samples, diagnostic of the p-type semiconductor behavior of the

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**Fig. 3** (a) Raman spectra of a CNT film, an electrodeposited Cu2O film, and a hybrid CNT/Cu2O sample. (b) XRD patterns of two different CNT/Cu2O samples synthesized with and without a pre-nucleation step respectively. * indicates the reflection from the metallic Cu phase.

**Fig. 4** Measured (points) and simulated (solid lines) Nyquist plots of (a) Cu2O and (b) CNT/Cu2O, recorded in 0.1 mol dm−3 sodium acetate solution at open circuit potential, in the 0.1 Hz to 1 MHz frequency range.
electrodeposited Cu2O. This observation is entirely consistent with the negative slope of the Mott–Schottky plots, obtained from EIS measurements (Fig. S4†). The photocurrent flow is sustained by the reduction of either H+ ions (H2-evolution), or dissolved CO2, as was demonstrated for the CuO/Cu2O hybrids earlier.4,10 As seen in Fig. 5a, much higher currents were measured in the presence of CO2, indicating that the latter process is favored on this photocathode. To deconvolute the effect of the more acidic environment (and thus the enhanced H2-evolution) in the CO2 saturated case, a photovoltammogram recorded in a N2 atmosphere, but at pH 4, is also included. As seen in Fig. 5a, there was an increase compared to the neutral solution, but the photocurrents were still much smaller than those in the CO2 case.

The effect of the hybrid architecture was studied by comparing and contrasting photoelectrochemical (PEC) data gathered with and without the presence of CNTs. Fig. 5b shows the photovoltammograms of the bare Cu2O, and two hybrid films with different CNT-contents. The most obvious difference was the striking increase of the photocurrent values in the case of CO2, indicating that the latter process is favored on this photocathode. To deconvolute the effect of the increased surface area on the photocurrent magnitude, the surface roughness of the hybrid samples was compared (Fig. S6†). It can be seen that both films are built up from nanoparticles of a similar size. This suggests that introduction of the CNT film does not alter the overall morphology.

As deduced from these studies, there was a slight increase in the overall charge capacitance that mostly stemmed from the contribution of the uncoated CNTs. This conclusion is supported by the observation that the capacitance value related to the Cu2O surface remained unchanged in the hybrid configuration. In addition, careful examination of the shape of the photocurrent transients in Fig. 5 revealed another significant change, confirming that something else beyond the surface area contributed to the increased photocurrents. Namely, the spike/plateau ratio showed a decrease with increasing CNT-content. This is diagnostic of the charged carriers being effectively separated in the composite structure before they undergo recombination.

In Fig. 6a, the plateau current is plotted vs. the thickness of the CNT film for various hybrid samples, containing relatively little Cu2O (0.2C deposition charge). Clearly, there was a steep increase in the currents until a certain thickness; however, further increase had only a moderate effect. If the CNT film thickness was kept fixed (10 mg cm−2), and the amount of electrodeposited Cu2O was varied, similar interesting trends could be seen. In Fig. 6b, the ratio of the stationary photocurrent values (measured at E = 0.1 V) between the bare and CNT-containing Cu2O is compared as a function of Cu2O amount. The trend is clear, the largest effect occurred when the Cu2O content was small. This is not surprising, since the gradually increasing amounts of Cu2O covered the thin CNT film, and the

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**Fig. 5** (a) LSV curves of a CNT10/Cu2O hybrid sample registered at 2 mV s−1, in 0.1 M Na2SO4 solution under N2 (both at pH = 4.0 and 7.0) and CO2 (pH = 4.0) atmospheres, with the full output of a 100 W solar simulator, employing a UV cut-off filter (−400 nm); (b) comparison of the photovoltammograms registered for hybrid samples with different CNT-contents (1C Cu2O in all the cases) in CO2 saturated 0.1 M Na2SO4 solution; (c) enlarged view of a photocurrent transient from (b).
sample behaved more and more similarly to the bulk film. Taking all these observations into consideration as a whole, we conclude that parallel optimization of the CNT thickness and Cu2O amount is necessary to obtain high performance photocathodes.

Long term PEC measurements were performed for both a bare Cu2O and a CNT/Cu2O film (Fig. 7). Chronoamperometric curves were registered at $E = 0.05$ V under periodically chopped solar irradiation, for 15 000 s (over 4 h, note the logarithmic scale in the figure). While the shape of the curves is very similar, important differences can be spotted. While the bare Cu2O, consistently with earlier reports, retains only 25% of its initial photoactivity (60 $\mu$A vs. 240 $\mu$A), this ratio is 60% for the CNT/Cu2O hybrid sample (260 $\mu$A vs. 450 $\mu$A). This is a key observation of this study, because it proves that by introducing a highly conductive nanostructured scaffold into the Cu2O film, the stability of the photocathode can be increased. At this juncture, it is important to emphasize that the choice of the potential to drive the photoelectrolysis was deliberate. At this potential (see again the Pourbaix-diagram in Fig. S5†), the eventually forming metallic Cu moieties can be electrochemically re-oxidized to Cu2O (self-healing). In fact, the slow development of small anodic dark currents in Fig. 7 supports this hypothesis. Finally, we note that a similar stability increase was witnessed in a sensing application when Cu2O nanocubes were immobilized on graphene.35

The liquid products formed during the long term photoelectrolysis were monitored using GC-MS. A typical chromatogram recorded for the CNT/Cu2O electrode is shown in Fig. 8, along with that of the calibration standard. As seen in the figure, methanol, ethanol, and formaldehyde were detected in the solution for CO2-saturated samples. Semi-quantitative analysis of the products afforded faradaic efficiencies of 9%, 24% and 18%, respectively. The rest of the charge was related to H2 formation (this was the only product detected in the gas phase), and the reduction of Cu2O to Cu as discussed above. We also note that no such products (except H2) could be detected for

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**Fig. 6** Comparison of the photoelectrochemical performance of different CNT/Cu2O electrodes. (a) Maximum of the stationary photocurrents measured at $E = 0.1$ V, and (b) the ratio of the maximum photocurrents measured with and without CNTs.

**Fig. 7** Long-term chronoamperometry data of a Cu2O and a CNT100/Cu2O film with an identical Cu2O content (1C), registered at 0.05 V potential (vs. Ag/AgCl/3 M NaCl), in CO2 saturated 0.1 M Na2SO4 solution.

**Fig. 8** GC-MS profiles registered using selective ion monitoring (SIM) for the sample after 7 h photoelectrolysis (similarly to Fig. 7), as well as for a standard solution containing 2.0 ppm methanol, ethanol, and formic acid respectively.
samples obtained from the experiments under N$_2$-saturation. As for the comparison with the bare Cu$_2$O photoelectrodes, we can conclude that the formation of the same products was observed with a similar overall faradaic efficiency, although their relative ratio was slightly different.

Conclusions

An interconnected network (nanonet) of ultra-long CNTs was employed as a highly conductive template for the controlled electrodeposition of Cu$_2$O nanoparticles. The homogeneous coating (together with control over the particle size) was ensured by a first nucleation step, followed by several growth steps that were interspersed by rest periods. SEM and TEM images demonstrated that by employing the optimized protocol, the oxide nanoparticles were exclusively deposited on the CNTs, resulting in complete coverage of the conductive scaffold. Raman spectroscopy and XRD showed the formation of Cu$_2$O, with the presence of minor traces of metallic Cu. Beyond corroborating the p-type behavior of the photoelectrodes, EIS indicated a fivefold increase in the electrical conductivity of the CNT/Cu$_2$O hybrid, compared to that of the bare oxide. This enhancement is indeed very beneficial for all photoelectrochemical applications, where transport and recombination of the photogenerated charge carriers is a limiting factor.

By comparing photovoltammetry curves registered under N$_2$ and CO$_2$ atmospheres, the drastically enhanced photocurrents in the latter case proved the activity of the photocathode towards the reduction of CO$_2$. To understand the contribution of both components to the photoelectrochemical performance of the hybrid material, and maximize the possible synergies, both the CNT film thickness and the electrodeposited Cu$_2$O amount were varied systematically. Under optimal conditions, an almost threefold increase was achieved in the maximum photocurrents, compared to the bare oxide film. What is equally important, the hybrid electrodes showed a markedly improved stability during long term (over 4 h) photoelectrolysis. We note here that careful analysis of the Pourbaix-diagram for Cu enabled selection of an optimal potential, where electrochemical self-healing also contributed to the observed stability. All these beneficial properties can be explained by the introduction of the nanostructured conductive framework (the CNT nanonet) into the photoelectrode.

Firstly, the faster transport of photogenerated electrons to the Cu$_2$O/electrolyte interface is ensured by the fact that instead of having a bulk Cu$_2$O layer, Cu$_2$O nanoparticles are present in the system. Secondly, transport of the photogenerated holes from the Cu$_2$O crystals to the supporting electrode is facilitated by the highly conductive carbon nanotube network. These factors reduce charge carrier recombination, as diagnosed from the change in the photocurrent transient profiles, resulting in better photoelectrochemical performance. GC-MS analysis proved unambiguously that the cathodic photocurrents led to the formation of liquid fuels such as methanol, ethanol, and formic acid.

Finally, we note that the demonstrated concept (i.e., electrodeposition of semiconductors on nanostructured carbon electrodes for solar fuel generation) points well beyond the studied system. There is a wealth of possible combinations, where precise control over the composition and morphology of these hybrid photoelectrodes may lead to major breakthroughs in the future.

Acknowledgements

C. J. gratefully acknowledges the support from the Hungarian Academy of Science, through its “Momentum” Excellence Program (LP2014-3). E. K., Zs. P., and K. H. appreciate the financial support of NKFI under the NN 114463 grant. K. R. acknowledges partial funding support for this work from the National Science Foundation (CHE-1303803). The authors thank Dr. B. Knellner (Simkon Ltd) for assistance with the GC-MS measurements. We thank the three anonymous reviewers for constructive criticisms on an earlier version of this manuscript.

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