Photonic Curing: Activation and Stabilization of Metal Membrane Catalysts (MMCs) for the Electrochemical Reduction of CO₂

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Abstract

Photonic curing, an exposure of matter to intense and short (μ s) light pulses, is herein demonstrated as an effective and versatile method to activate and stabilize electrocatalysts for the electrochemical reduction of CO₂. Catalyst preparation by colloidal synthesis often makes use of surfactants (capping agents) that control the size and morphology of target nano-objects during and after their synthesis. However, this approach can severely compromise the catalytic properties of the as-synthesized nanomaterials. Photonic curing is suitable to gently remove surfactants from the catalyst surface without severely altering its overall structural properties (e.g., surface faceting), thereby increasing the abundance of those surface active sites that can participate in the desired (electro)catalytic reaction. This catalyst activation is exemplarily demonstrated on the basis of Cu nanowire (Cu-NW) catalysts synthesized by an oleylamine route and transferred to a glassy carbon (GC) support electrode. Whereas the 3D-networks of the as-synthesized Cu-NW catalysts predominantly produce hydrogen as product of the electrolysis reaction photonicallly cured Cu-NWs, denoted hereinafter as Cu metal membrane catalysts (MMCs), show a high selectivity towards ethylene formation reaching a Faradaic efficiency of $FE_{C_2H_4} = 42.4\%$ ($J_{C_2H_4} = -7.8$ mA cm⁻², $E = -1.1$ V vs RHE). This high ethylene yield can even be maintained during prolonged electrolysis of 110 h. A further beneficial effect of the photonic curing treatment is related to the substantially increased mechanical stabilization of the Cu-NW film on the support electrode induced by a ‘mild’ sintering of Cu-NWs which remains locally confined to their points of contact. A loss of catalyst material

or a delamination of the catalyst film from the support electrode during massive gas evolution can thus be prevented.

Introduction

The environmental crisis our society currently faces demands a substantial reduction of greenhouse gas emissions as well as an increase of power generation based on renewable resources.¹ In addition, the CO₂ already released into the atmosphere needs to be captured and, most preferably, transformed back into value-added products.²⁻⁴ Among various concepts proposed, it is the electrochemical CO₂ reduction reaction (hereinafter referred to as CO₂RR) which has the potential to become a technologically and economically feasible approach towards the conversion of CO₂ into chemical feedstock, fine chemicals or high energy density fuels⁵ thereby contributing to the future closing of the anthropogenic carbon cycle.⁶⁻⁷ This so-called power-to-value concept becomes particularly appealing when the surplus of renewable electricity from wind, solar and hydro sources is exploited.²⁻³ However, the CO₂RR kinetics and the selectivity towards specific products still needs to be improved to bring the CO₂RR into an economically feasible industrial application. Substantial efforts have already been made in the development of new CO₂RR electrocatalysts with tunable particle size⁸⁻⁹, morphology¹⁰⁻¹¹, grain-boundary and defect densities¹²⁻¹³, to either directly produce value-added products from CO₂ (e.g., C₁-C_n alcohols¹⁴⁻¹⁸) or to obtain reaction intermediates (e.g., CO¹⁹⁻²³) which can be further converted into hydrocarbons or alcohols in the course of subsequent non-electrochemical reactions (e.g., by Fischer-Tropsch synthesis²⁴ or fermentation²⁵) following the primary CO₂RR.

Not only is the availability of specific active sites (e.g., surface facets or defects) of importance for the resulting CO₂RR catalyst but also its morphology on various length scales.¹⁰⁻¹¹ The particular morphology of the three-dimensional porous catalyst architecture determines the transport characteristics of the reactants into the electroactive material and influences therefore the mean residence time of reaction intermediates (e.g., alkenes¹⁰) inside its porous structure. Note that the probability for reaction intermediates to undergo consecutive reactions (e.g., hydrogenation of unsaturated hydrocarbons) also depends on the catalyst porosity.¹⁰⁻¹¹ Further, the three-dimensional structure of the catalyst material needs to be taken into account with regard to the chemical and mechanical stability of the electrode, in particular when high electrolysis current densities (> 200 mA cm⁻²) are targeted. Massive gas evolution, e.g. caused by the parasitic hydrogen evolution reaction (HER) superimposed to the CO₂RR in aqueous reaction media, can induce mechanical stress on the catalyst layer which might lead to its degradation, e.g. by the loss of catalyst material into the electrolyte²⁶ or even the complete delamination of the active layer. A bottom-up design of CO₂RR catalysts controlling the hierarchy of individual structural elements is suited to tackle these challenges. Among others, colloid chemistry can be considered as one promising approach to produce high-surface area electrode materials having a well-defined morphology and

electrocatalytic properties in terms of an engineering of active sites.²⁷ Nonetheless, this colloidal synthesis approach often makes use of organic surfactants controlling nucleation and growth of the desired nano-objects (e.g., particles, wires etc.), stabilizing thus their shape and preventing undesired precipitation and aggregation during and after their synthesis.²⁸⁻³⁰ However, when left on the catalyst surface these surfactants might compromise the performance of the material by sterically blocking the catalytic active sites. This is why several post-synthesis treatments have been proposed for the surfactant removal, e.g. chemical washing²⁸⁻²⁹, thermal annealing under reductive or inert conditions³⁰, exposure to oxidative environments (e.g., O₂ plasma or ozone)^{9, 31}. However, these approaches often require a non-satisfying long treatment time (e.g., thermal annealing), produce huge amounts of organic waste (chemical washing) or can further alter the surface properties of the catalyst (e.g., plasma treatment)³²⁻³³. The post-synthesis activation of surfactant-stabilized nanocatalysts remains therefore a challenge for the electrode fabrication process.

In this present study we introduce *photonic curing* as a novel, fast, and versatile alternative to common catalyst activation methods. Note that, in this context, the term catalyst activation primarily refers to the selective removal of the surfactant (capping agent) from the catalyst surface and not to any further structural or compositional alteration of the as-synthesized catalyst material itself. The latter is well known, for instance, from copper-based CO₂RR catalysts that perform particularly well after being chemically activated by the electroreduction of cupric or cuprous precursor materials.^{18, 34-35}

Photonic curing, which is often called intense pulse light (IPL)³⁶ or flash lamp annealing (FLA)³⁷, is based on the exposure of matter to intense light from a xenon flash lamp thereby inducing an ultra-fast local heating of the surface area exposed to these light pulses. This rapidly emerging technology already finds applications in various industrial fields, e.g. in the manufacturing of printed electronic devices as it allows the replacement of glass or ceramic substrates by less expensive and more flexible materials such as polymer sheets or paper.³⁸⁻³⁹ More importantly, photonic curing substantially reduces process times from hours or minutes down to sub-milliseconds.⁴⁰

In this present study, we exemplarily demonstrate the usability of photonic curing for the effective activation of CO₂RR electrocatalysts by selective surfactant removal. As model system we have chosen highly anisotropic copper nanowires (denoted hereinafter as Cu-NWs) which show preferential (100) texturing on their sidewalls. Early studies on single crystalline Cu catalysts have claimed that the C-C coupling (C2 pathway) is more efficient on (100) textured catalyst, whereas the C1 hydrocarbon pathway was demonstrated to be preferred on (111) facets.⁴¹⁻⁴³ More recent studies utilizing Cu nanocube-type of catalysts with preferential (100) texturing emphasize the need for an optimized ratio of (100) surface sites and certain edge sites in particular for the formation of ethylene from CO₂.⁸

For the colloidal synthesis of Cu-NWs, oleylamine (IUPAC name: (Z)-octadec-9-enylamine, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{NH}_2$, denoted in the following as OAm) is often used as organic reaction medium and reducing agent. At the same time it serves as surfactant which selectively stabilizes (100) facets during the anisotropic nanowire growth in solution.⁴⁴⁻⁴⁵ The primary amine functionality thereby serves as an anchor group to the Cu surface.

In what follows, we will demonstrate that photonic curing enables the removal of the OAm surfactant from the catalyst surface without altering the structure of the Cu-NWs. The performance of the photonic curing approach is compared to other surfactant removal methods, such as thermal annealing, ozone treatment, plasma treatment, and deep UV annealing. To further demonstrate the versatility of photonic curing we will show that this catalyst activation approach is transferable (i) to other catalyst morphologies (e.g. Cu nanoparticles (Cu-NPs)), (ii) to alternative catalyst materials (e.g. Ag-NWs) and (iii) to other organic surfactants (e.g. polyvinylpyrrolidone). Of equal importance is that photonic curing provides means of mechanically stabilizing the three-dimensional network of Cu-NWs which is of particular importance for those electrode processes that involve massive gas evolution (e.g., HER and CO_2RR from aqueous electrolytes). Li et al. recently described a loss of Cu-NW material into the electrolyte under CO_2RR conditions when drop-casted on a glassy carbon support electrode without any further treatment.²⁶ One approach to prevent such mechanical catalyst degradation, proposed by the same authors, is the embedment of Cu-NWs into a carbon black (Ketjen) matrix (catalyst loading 20 wt%) that provides sufficient mechanical stability and prevents Cu-NW detachment from the electrode.²⁶ It should be noted, that the presence of a carbon support exposed to the electrolyte will inevitably affect the resulting Faradaic efficiencies of the electrolysis products. In the latter case, the resulting product distribution originates from superposition of the inherent catalysts characteristics and the contribution of the surrounding carbon matrix (see also supporting information file). On the other hand, photonic curing provides mechanical stability of the three-dimensional network of Cu-NWs without the need of a stabilizing carbon matrix. The resulting layer of the activated and stabilized Cu-NWs assembly is denoted hereinafter as Cu metal membrane catalyst (Cu-MMC).

Experimental

Cu-NW synthesis – Cu nanowires (Cu-NWs) were synthesized according to a modified protocol introduced by Guo et al.⁴⁶ 0.4 mmol of nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$, Aldrich, assay 95%) and 0.8 mmol of copper(II) chloride mono-hydrate ($\text{CuCl}_2 \cdot \text{H}_2\text{O}$, Aldrich, assay > 99.99%) were dissolved in 9 mL of oleylamine (OAm, Aldrich, assay 70%) in a three-necked flask. The solution was kept for 10 min at 100 °C under strong magnetic stirring conditions and continuous flow of high-purity nitrogen gas (99.995%, Carbagas, Switzerland). Subsequently, the solution was rapidly heated up to 180 °C and kept for 3 h at this temperature. After cooling down to room temperature, an excess of hexane was added to the

aforementioned solution thus leading to the appearance of a black precipitate which could be isolated by 6 min centrifugation at 4000 rpm. The precipitate was thoroughly washed in a mixture of hexane and toluene and subsequently dried in a vacuum oven at 50 °C for 1 h yielding a dry powder sample. Afterwards 9 mg of the as-synthesized Cu nanowires were dispersed in 30 mL toluene by ultra-sonication. For comparison purposes (see supporting information file) Ag-NWs and Cu nano-cubes (Cu-NCs) were synthesized also following a colloidal synthesis approach.

Ag-NWs were synthesized according to a modified protocol introduced by da Silva et al.⁴⁷ 100 mM AgNO₃ (Sigma-Aldrich, 99%) and 50 mM NaBr (Sigma-Aldrich, 99.99%) solutions were prepared using ethylene glycol (EG, Acros Organics, 99.5%) as a solvent. 125 mg poly(vinylpyrrolidone) (PVP, $M_r \approx 1300000 \text{ g mol}^{-1}$, Acros Organics) were dissolved in 20 mL of EG, subsequently heated up to a temperature of 160 °C and continuously stirred (320 rpm) for 1 h at this temperature. Subsequently, 250 μL of the NaBr solution were injected into the reaction vessel. After 15 min, 7.5 mL AgNO₃ were dropwise added to the solution at a rate of 0.15 mL min^{-1} . After the complete addition of the AgNO₃ solution, the reaction mixture was thermally quenched by immersing the reaction vessel into an ice-water bath. After addition of 75 mL of acetone, the obtained suspension of Ag-NWs was centrifuged. Subsequently, the Ag-NWs were carefully washed with H₂O.

Cu-NCs were synthesized according to a modified protocol introduced by Guo et al.⁴⁸ 0.3 mmol CuBr (Acros Organics, 98%) and 0.5 mmol TOPO (Acros Organics, 99%) were dissolved at 80° C under continuous stirring (15 min at 250 rpm) in 7 mL OAm (Sigma-Aldrich, 70%). This solution was then further heated up to 260 °C and kept at this temperature under reflux for 2.5 h. After cooling down to room temperature, an excess of toluene was added to the resulting reddish solution. The obtained suspension of Cu-NCs was centrifuged at 4000 rpm for 10 min. (Hettich Universal 16). The reddish Cu-NCs were further purified by five cycles of re-dispersion/centrifugation in a solvent mixture of toluene (10 mL) and hexane (1 mL).

Electrode preparation – A standard assembly of Cu-NWs was formed by vacuum filtration of 1 mL of the prepared Cu-NW suspension (0.3 mg Cu-NWs/mL) using a Nylon cloth (pore size 0.22 μm , Fisher Scientific). The resulting Cu-NW assembly (1.2 cm in diameter) was lifted off from the Nylon cloth in a glass beaker filled with Milli-Q water. While the Nylon cloth membrane dropped down to the bottom of the glass beaker, the lighter and free-standing assembly of Cu-NWs remained floating on the surface of the Milli-Q water. With the help of a supporting substrate (e.g., Cu foil, glassy carbon, carbon cloth, carbon paper, etc.) the Cu-NW assembly could be picked up, dried and then further subjected to catalyst activation procedures (e.g., photonic curing, thermal annealing, etc.). Individual steps of the Cu-MMC preparation are shown in Fig. 1.

For comparison purposes Cu-NWs were dispersed also on a technical carbon support (see supporting information file). For the preparation of such carbon-supported Cu-NW film, 7.0 mg of the as-prepared Cu-NWs were dispersed in 15 mL of hexane by 1 h sonication. Further, 3.0 mg of carbon powder (Vulcan XC 72r, Cabot, USA) were dispersed in 15 mL of isopropanol by 1 h sonication. Both suspensions were then intermixed, homogenized by sonication and subsequently dried overnight in vacuum. The thus obtained carbon-supported Cu-NWs were re-dispersed in 1.9 mL of isopropanol (Sigma, assay $\geq 99.5\%$) containing 100 μL of Nafion solution (Aldrich, 5 wt% in lower aliphatic alcohols and water). This suspension was subjected to sonication (probe sonicator, Sonics, probe diameter: 3.2mm, frequency: 10 kHz) for 30 min thus yielding a homogeneous catalyst ink. 50 μL of this ink were then drop-casted and dried on a glassy carbon plate ($A = 0.8 \text{ cm}^2$, Alfa Aesar, 2 mm thickness, type1). The GC plate had been mirror polished (0.5 μm , alumina suspension, Buehler, USA) prior to the drop-casting of the catalyst ink. Activated carbon-supported Cu-NWs samples were prepared in the same way. The Cu-NWs were, however, subjected to various activation treatments (i.e., thermal annealing, photonic curing, etc.) prior to their dispersion in the hexane solvent.

Catalyst activation - For the photonic curing treatment a PulseForge 1300 system from NovaCentrix was used (xenon flash lamp, optimized conditions: irradiance 5.9 kW cm^{-2} , 50 μs pulse duration). Light pulses of variable duration in the range from 20 μs to 150 μs were applied to the Cu-NW assemblies in an inert N_2 gas atmosphere thus preventing surface oxidation during the photonic curing. For comparison purposes, the Cu-NW assemblies were also subjected to the thermal annealing under protective N_2 gas atmosphere using a Nabertherm tube furnace. For the ozone treatment a UV ozone system (PSD Series, Novascan) was used. The total duration of the ozone treatment was 2 h. The ozone chamber was, however, opened every 30 min to refresh the atmosphere as the oxygen gets consumed during the treatment. For the N_2 -plasma treatment, the Cu-NWs assemblies were activated for 10 min in a plasma etcher (Plasma Prep III, SPI supplies) at a gas pressure of 300 mT of N_2 and a power of 20 W. For the deep UV treatment, the Cu-NWs assemblies were exposed to UV light in the deep UV chamber (UV253HR from Filgen) for 1 h under N_2 atmosphere.

Electrode characterization - The Cu-NW assemblies were characterized by means of Scanning Electron Microscopy (Zeiss DSM 982). The identical location transmission electron microscopy (IL-TEM) was carried out using a FEI Titan Themis system operated at 300 kV. The thickness of the Cu-NW assemblies was determined on the basis of white-light interferometry (ContourGT profilometer, Bruker). The crystallinity of the catalysts was characterized by means of powder X-ray diffraction (XRD) techniques. An STOE Stadi P system with a Cu $K\alpha$ radiation source ($\lambda = 0.1540 \text{ nm}$, 40 mA) generated at 40 keV was used. XRD spectra were recorded in reflection mode (Bragg-Brentano geometry) with 2θ values ranging between 30 and 80 degrees in steps of 1° min^{-1} . The obtained XRD patterns were analyzed and compared

to PDF (Powder Diffraction File) standards for Cu. Fourier transform infrared (FTIR) spectra were acquired between 4000 and 400 cm^{-1} using a FT/IR 4700 spectrometer (Jasco, Germany) in air in an attenuated total reflection (ATR) mode. For this latter measurement, the Cu-MMCs were deposited on glass slides (see Fig. S1).

XPS spectra were acquired on a Physical Electronics (PHI) Quantum 2000 Scanning ESCA Microprobe System using monochromated Al K α radiation ($h\nu = 1486.7$ eV) and a hemispherical capacitor electron-energy analyzer equipped with a channel plate and a position-sensitive detector. The electron take-off angle was 45° and the analyzer was operated in the constant pass energy mode at 23.5 eV for the detailed spectra of the Cu2 $p_{3/2}$, O1s, C1s and N1s peaks with a step size of 0.20 eV. The beam diameter was typically 150 μm . The binding energy was calibrated using Cu2 $p_{3/2}$, Ag3 $d_{5/2}$ and Au4 $f_{7/2}$ emissions at 932.62 eV, 368.21 eV, and 83.96 eV, respectively to within ± 0.1 eV. To compensate for eventual surface charging, built-in electron and argon ion neutralizers were used. The base pressure of the system was below 5×10^{-7} Pa. The spectra were analyzed using the software MultiPak 8.2B and peaks are shown after a Shirley background subtraction. The atomic concentrations were calculated using the corrected relative sensitivity factors as given by the manufacturer and normalized to 100 at%. The uncertainty is around 10 % relative.

Electrochemical characterization - CO₂ electrolysis experiments were performed using a potentiostat/galvanostat (Metrohm Autolab 302N, The Netherlands) attached to a custom-built, air-tight glass-cell (H-type) which has been described elsewhere.¹⁰ The current interrupt approach (Autolab Nova, Metrohm) was used to determine the iR drop (cell resistance). All potentials given herein are iR-compensated. The three-electrode arrangement used consisted of a leakless Ag/AgCl_{3M} reference electrode (EDAQ), a bright Pt-foil (15mm $\times$ 5mm) serving as counter electrode and the glassy carbon-supported Cu-MMC catalysts serving as working electrodes. For the sake of comparability, all potentials measured versus Ag/AgCl_{3M} were referenced with respect to the RHE (reversible hydrogen electrode). Technical details of the CO₂RR product analysis based on online gas-chromatography (GC) and ion exchange chromatography (IC) have been described elsewhere.¹⁰ Electrolysis experiments were carried out in 0.5M KHCO₃ (ACS grade, Sigma-Aldrich) electrolyte solutions saturated with Ar or CO₂ gas (99.999%, Carbagas, Switzerland). Note that, unless otherwise mentioned, a newly prepared catalyst electrode has been used for each CO₂ electrolysis experiment.

Results and discussion

Catalyst activation (surfactant removal) – Fig. 2a-b depicts representative white light interferometric images of the catalyst material that has been transferred after its filtration to a glassy carbon support (see also Fig. 1). This microscopic inspection reveals a rather homogeneous but highly porous catalyst film

with a root-mean-squared (RMS) roughness of $R_q \approx 340$ nm (see also Fig. S2). From the corresponding interferometric analysis of the catalyst film edge, a mean layer thickness of ~ 400 nm could be determined (panel c and d in Fig. 2). Note that the electrode was masked by insulating Teflon tape prior to the CO_2 electrolysis so that a defined geometric surface area of 0.8 cm^2 was exposed to the electrolyte (Fig. S3).

The analysis of the catalyst film by scanning electron microscopy (SEM) shows a three-dimensional network of randomly distributed Cu-NWs (Fig. 3a). Their length can exceed tens of micrometers whereas the nanowire diameter is typically in the range of $50 \text{ nm} - 70 \text{ nm}$ (see representative HR-TEM in Fig. 3b). Selective area electron diffraction (SAED) analysis obtained from an individual Cu-NW (Fig. 3c) confirms, in full accordance with the literature, the five-fold twinned face centered cubic (fcc) structure of the Cu-NWs and their preferential orientation along the $[110]$ crystallographic direction.⁴⁹ The sidewalls of the Cu-NWs consist of 5 (100) textured facets whereas the pentagonal apex of the Cu-NW is (111) terminated (Fig. 3d). These (111) facets represent the actual growth front where precursor ions get preferentially reduced and added to the developing nanowire. Earlier studies⁵⁰ suggest a preferential and stronger adsorption of the organic surfactants on the (100) facets thereby sterically blocking these sites for further addition of metal atoms. The anisotropy of the metal growth originates, at least in this scenario, from the weaker surfactant adsorption on the (111) facets thus allowing for the continuous unidirectional addition of metal atoms. More recent studies emphasize, however, the important role of chloride anions for this highly anisotropic growth of Cu-NWs in particular when carried out in aqueous solutions.⁵¹ Note that cupric chloride is typically used as copper source for the Cu-NWs growth. Chloride anions tend to strongly chemisorb on Cu surfaces.⁵²⁻⁵⁸ Wiley et al. discussed the competitive adsorption of chloride and alkylamine-based surfactants as origin of the anisotropic Cu growth. Chloride anions were demonstrated to remove the surfactant more effectively from the (111) oriented facets, thereby keeping them active for the metal growth.⁵¹

The presence of surfactants on the surface of the Cu-NWs after the wet chemical synthesis represents a severe drawback for their application as catalysts, due to the active reaction sites being sterically blocked by the surfactants. A mild catalyst activation process is therefore required that selectively removes the surfactant molecules from the NW surfaces while preserving their unique structural properties. In order to identify optimum experimental conditions for the surfactant removal and catalyst activation, Cu-NW assemblies were subjected to photonic curing at constant irradiance (5.9 kW cm^{-2}) but variable pulse lengths (single pulse approach). The photonic curing was carried out in a nitrogen gas atmosphere to avoid any extra compositional or structural change of the Cu-NWs that might go along with oxidation of the nano-material when exposed to oxygen during the photonic treatment. After activation, the resulting catalytic performance was studied by means of CO_2RR product analysis following one hour potentiostatic electrolysis of a CO_2 -saturated 0.5 M KHCO_3 solution at -1.1 V vs. RHE. Results of this pre-screening

step are presented in Fig. 4a (note that the irradiance dependence was already screened beforehand, see Fig. S4). As expected, the as-prepared Cu-NW assemblies show only a minor activity towards CO₂RR. H₂, originating from the parasitic HER, is the predominant product of the electrolysis reaction reaching a Faradaic efficiency of FE_{H₂} = 73.3% (J_{H₂} = -13.9 mA cm⁻²). Formate is clearly the main CO₂RR product with a Faradaic yield of 12.0% (J_{formate} = -2.3 mA cm⁻²), followed by minor yields of ethylene (FE_{C₂H₄} = 5.1%, J_{C₂H₄} = -0.97 mA cm⁻²). Also traces of CO could be detected (FE_{CO} = 1.9%, J_{CO} = -0.36 mA cm⁻²). Note that formate is the least demanding CO₂RR product with regard to the Cu catalyst (Cu-O binding) whereas formation of ethylene requires a high abundance of next neighbor adsorption sites that can strongly bind CO (Cu-C binding) thus being a mechanistic prerequisite for subsequent C-C coupling reactions.⁵⁹⁻⁶⁰ CO forms as key intermediate in the course of the CO₂ electroreduction. In particular the (100) facets, key structural motifs of the NW sidewalls, have been discussed in the literature as active for the C-C coupling reaction.^{43, 60-61} The hydrocarbon pathways remain, however, largely suppressed on the non-activated Cu-NW electrocatalyst when the OAm surfactant is still present (Fig. 4a).

When considering ethylene as the most valuable CO₂RR product there is a clear optimum at 50 μs pulse duration (Fig. 4a) resulting in a maximum ethylene efficiency of FE_{C₂H₄} = 42.4% (J_{C₂H₄} = -7.8 mA cm⁻²), thus being indicative for an effective OAm surfactant removal (for details see Tab. S1). Note that the SEM and HR-TEM analyses in Fig. 3 were carried out after the photonic curing proving that, at least under the given experimental conditions, this activation treatment does not severely affect the structural characteristics of the Cu-NWs. After applying optimum curing conditions, the Faradaic efficiency for H₂ production is substantially reduced to FE_{H₂} = 32% (J_{H₂} = -5.9 mA cm⁻²), whereas the total CO₂RR efficiency reaches FE_{CO₂RR} = 69% (J_{CO₂RR} = -12.8 mA cm⁻²). More extended photonic curing leads, however, to the gradual drop down of the total CO₂RR efficiencies, e.g. FE_{CO₂RR} = 34% (J_{CO₂RR} = -5.8 mA cm⁻²) when pulses of 150 μs duration are applied (Fig. 4a). This trend can be regarded as an experimental hint for an undesired structural degradation of the Cu-NW catalyst taking place upon prolonged photonic curing times at the given irradiance of 5.9 kW cm⁻². This conclusion is consistent with an SEM inspection of the photonicallly cured Cu-MMCs demonstrating that the 50 μs photonic curing at 5.9 kW cm⁻² does not induces structural changes of the Cu-NW assembly on larger macroscopic length scales or on the length scale of individual Cu-NWs (Fig. S5). By contrast, prolonged photonic curing times lead to severe structural alterations of the Cu-NWs (Fig. S6a). As a result, semi-hemispheric droplets appear on the NW sidewalls. Similar morphological and structural changes were observed after thermal annealing at temperatures ≥ 300°C (Fig. S6b). One might assume that these substantial structural changes also involve a decrease in the relative abundance of those specific surface sites needed for the C-C coupling.

Fig. 4b displays the complete potential dependent CO₂RR product analysis for the optimum photonic curing conditions (50 μ s, 5.9 kW cm⁻²). A maximum of FE_{C₂H₄} = 42.4% (J_{C₂H₄} = -7.8 mA cm⁻²) is observed for an electrolysis potential of -1.1 V vs RHE that is anti-correlated with the minimum in the Faradaic efficiency for hydrogen production (FE_{H₂} = 32.0%, J_{H₂} = -5.9 mA cm⁻²). At higher overpotentials, e.g. at -1.2 vs RHE, the hydrogen efficiency starts to increase (FE_{H₂} = 41.3%, J_{H₂} = -10.2 mA cm⁻²) at the expense of the ethylene yield (FE_{C₂H₄} = 35.6%, J_{C₂H₄} = -8.8 mA cm⁻²). Note that this trend does not necessarily point to the loss of catalytic performance of the Cu-MMC at higher overpotentials but might, instead, be ascribed to the onset of CO₂ mass transport limitations in quiescent aqueous electrolytes where the CO₂ solubility is limited to ~35 mM.^{3, 6} The high reproducibility of the electrode preparation and catalyst activation procedure is demonstrated in Fig. S7 showing the CO₂RR product distribution of five independent electrolysis experiments performed at -1.1 V vs RHE.

Comparable or even higher ethylene efficiencies than the one achieved in this present study were already reported in the literature.^{8, 34, 61-63} E.g., Mistry et al. obtained an ethylene selectivity of FE_{C₂H₄} $\approx$ 60% at comparably low overpotentials of -0.9 V vs RHE. These extraordinarily high C₂H₄ yields are typically observed only when using so-called oxide-derived (OD) Cu catalysts. Facile approaches to activate Cu based CO₂RR catalysts by oxidation are the exposure to oxygen plasma, thermal annealing in air⁶⁴⁻⁶⁵, or electrode anodization³⁵. These formed cupric and cuprous oxides typically get reduced under CO₂RR conditions thereby creating those low-coordinated sites and grain boundaries which are particularly active for hydrocarbon or alcohol formation¹⁵. An extra activation of the Cu-NW catalyst, e.g., by surface oxidation, was excluded herein as the photonic curing was carried out in inert N₂ atmosphere (see experimental section). Further chemical activation of the Cu-MMCs will be treated separately in a forthcoming study.

It is interesting to note that no substantial ethane formation is observed for the Cu-MMC catalyst (Fig. 4b). From porous Cu foam catalysts it is known that, due to the prolonged residence time of the intermediates inside the three-dimensional catalyst, formed ethylene gets, to some extent, further reduced to ethane as consequence of re-adsorption and subsequent reduction steps. The Cu foam catalysts, studied by Dutta et al.¹⁰, show a primary macro-porosity with pore sizes on the micrometer length scale and a secondary porosity of their dendritic sidewalls on the nm length scale. These previous studies indicate that the electrolyte can penetrate into the μ m-sized macro-pores of the Cu foams giving rise to a pronounced pore-size dependence of the resulting CO₂RR product distribution.¹⁰

The absence of ethane in the present case (Fig. 4b) can be regarded as first experimental hint for an electrolyte which does not completely penetrate the entire three-dimensional network of the Cu-NWs. Apparently, the wetting of the Cu-MMC remains confined to the outermost volume of the 3D network of Cu-NWs. To support this hypothesis we carried out two extra control experiments. The first one was

based on a thickness variation of the Cu-MMC (see Fig. S2, S8 and S9). The CO₂RR product distribution is found to be largely insensitive to the further increase of the Cu-NW layer thickness (Fig. S8a). A slight increase of the H₂ efficiency was, however, observed when the Cu-MMC thickness was further reduced (Fig. S8a). This latter observation might point to a certain contribution of the glassy carbon substrate to the resulting CO₂RR product distribution when the MMC thickness falls below a critical value (Fig. S8b). Exchanging the glassy carbon support of the Cu-MMC by an Ag foil does not lead to a substantial alteration of the CO₂RR product distribution provided the Cu-MMC layer thickness is sufficiently high (Fig. S10a). These control experiments are indicative for an electrolysis reaction that takes place within a spatially confined and constant volume of the three-dimensional Cu-MMC as illustrated in Fig. S8b and S10b.

For comparison purposes, we present in Fig. S11 a similar potential-dependent product analysis for Cu-MMC samples treated by thermal annealing in an inert nitrogen gas atmosphere at 200 °C. Also this approach leads to certain catalyst activation but on a significantly lower level as compared to the photonic curing (Fig. 4a-b). A maximum of FE_{C₂H₄} = 15.5% (J_{C₂H₄} = -2.5 mA cm⁻²) is yielded after the 2 h annealing at 200 °C. Obviously, there is no clear preference for C-C coupled hydrocarbons after the thermal annealing, no matter what annealing times have been applied. Methane efficiencies are, however, comparably high after the thermal treatment, e.g. FE_{CH₄} = 9.2% at -1.1 V vs RHE (Fig. S11). A C₂/C₁ hydrocarbon ratio of ~1.7 clearly points to poor product selectivity towards ethylene. In case of the catalyst activated by photonic curing the respective C₂/C₁ hydrocarbon ratio at -1.1 V vs RHE electrolysis potentials is 12.1 (Fig. 4b). Annealing temperatures above 200 °C lead to a further decrease of the CO₂RR performance most likely due to structural catalyst degradation as observed in the SEM analysis (Fig. S6b).

A more complete overview over the performance of different surfactant removal approaches is provided in Fig. 5 that includes thermal annealing, the exposure of the catalyst to ozone, deep UV treatment and plasma activation. Among these, it is indeed the photonic curing which demonstrates the most promising results, in particular when ethylene is targeted as CO₂RR product. It can be hypothesized that the observed differences in the CO₂RR performance are due to different efficiencies in the OAm surfactant removal. To support this hypothesis surface-sensitive XPS analyses were carried out after applying the activation treatments to the Cu-NW catalyst films (Fig. 6). The ratio of the integrated N1s and Cu2p_{3/2} intensities can be considered as a measure for the effectiveness of the respective surfactant removal. As expected, the as prepared sample shows the highest N1s:Cu2p_{3/2} ratio followed by the thermally annealed one. This observation is fully consistent with the non-satisfying CO₂RR performance of the as-prepared and annealed catalyst samples (Fig. 5 and S11). A more efficient surfactant removal is observed for the plasma and ozone treatments. Obviously, the photonic curing and the deep UV treatment lead to an

almost complete surfactant removal (Fig. 6b). The comparison of Fig. 4 and 5 demonstrates a qualitatively reasonable correlation between the surfactant removal, probed by XPS via the $N1s:Cu2p_{3/2}$ ratio, and the resulting CO_2RR performance. An effective surfactant removal is further confirmed by the IR inspection of the photonicallly cured Cu-MMC sample (Fig. S12).

It should be emphasized at this point that the catalyst activation by photonic curing is highly versatile and not limited to Cu-based materials. Photonic curing can be applied to other colloidal systems prepared by various surfactant-assisted synthesis routes. As an example we present in the supporting information file analogous investigations on Ag-NWs synthesized by the assistance of polyvinylpyrrolidone (PVP). Their selectivity towards CO formation can substantially be improved by applying the novel photonic curing activation method (see Fig. S13). These supporting experiments further demonstrate that the surfactant removal is not only limited to monomeric OAm surfactants but can be successfully applied also to polymeric capping agents (e.g., PVPs). Furthermore, the catalyst activation by photonic curing is also transferable to other catalyst morphologies, e.g. shaped nanoparticles (see Fig. S14).

Catalyst stability – Not only are the product selectivity and the achieved partial CO_2RR current densities of importance for the evaluation of the overall catalyst performance but also the mechanical robustness and the long-term chemical stability of the electrode assembly.

In order to demonstrate the superior mechanical stability of the photonicallly cured Cu-MMCs optical micrographs were taken before and after 1 h CO_2RR at -1.1V vs RHE (Fig. 7). Gas evolution reactions (e.g., HER and CO_2RR) can induce substantial mechanical stress to the electrode assembly particularly when exposed to an aqueous environment. This stress often leads to a loss of active catalyst material into the solution phase during the electrolysis reaction²⁶ or even to a partial or complete delamination of the catalyst layer from the support electrode. Delamination phenomena upon CO_2RR are observed in particular for the as-prepared Cu-NW sample and the thermally annealed one whereas substantial losses of catalyst material into the solution phase become apparent from the optical micrographs of those samples treated by deep UV light and by ozone exposure (Fig. 7). The only catalyst sample which obviously remains unaffected by the CO_2RR at -1.1 V vs RHE is the photonicallly cured one (repective repetition experiments are shown in Fig. S15). This observation is also consistent with an identical location microscopic inspection of the photonicallly cured Cu-MMC prior to and after the CO_2RR not showing any severe morphological alterations after the electrolysis reaction at -1.1 V vs RHE (Fig. S16). Such mechanical stabilization is most likely achieved by the ‘mild’ sintering of the Cu-NWs upon photonic curing which remains locally confined to their points of contact, at least for the given curing conditions (50 μs , 5.9 kW cm^{-2}). Further, the photonic curing not only improves the rigidity of the 3D Cu-NW assembly itself. It also improves the adhesion to the underlying support material (e.g., to the glassy carbon electrode).

Massive losses of Cu-NW material into the electrolyte during the electrolysis, as reported by Li et al.²⁶, can thus be prevented even without using a stabilizing carbon matrix (e.g., Vulcan, Ketjn; Nafion) .

With regard to the structural stability on a nanometer scale, nanowire-based catalysts seem to be superior over nanoparticles of the same catalyst material (see Fig. S17). Cube-shaped Cu-NPs of similar diameter as the Cu-NWs studied herein undergo comparably fast structural degradation involving the loss of the extended and preferential (100) texturing upon CO₂RR (Fig. S17).⁶⁶ This might be an important finding for the application of CO₂RR catalysts under industrial conditions where their reliability is key.

At this point the question arises whether the observed trend in the CO₂RR performance (Fig. 5) can solely be ascribed to differences in the OAm removal efficiency as concluded from Fig. 6 or whether extra effects due to the observed degradation phenomena (Fig. 7) also contribute, at least to some extent, to the resulting CO₂RR product distribution. In particular the delamination of the Cu-NW films from the glassy carbon support will necessarily lead to a certain contribution of the support material to the overall electrolysis reaction. As the glassy carbon support electrode is active only towards the HER an increase of the FE_{H₂} is indeed expected. However, cyclic voltammetric control experiments carried out in the Ar-saturated and CO₂-saturated 0.5 M KHCO₃ solution (Fig. S18) clearly demonstrate a comparably low activity of the glassy carbon electrode towards the HER at the relevant electrolysis potential of -1.1 V vs RHE. From this control experiment we therefore conclude that the main contribution to the FE_{H₂} in case of the as-prepared and thermally annealed samples (Fig. 5) originates from the inefficient removal of surfactants from the Cu catalyst surface with only minor contributions from the glassy carbon support after the partial delamination of the catalyst film.

Further, to avoid the undesired structural degradation processes at elevated current densities (Fig. 7) selected CO₂ electrolysis experiments were carried out also at -0.8 V vs RHE. Due to the reduced overall current densities at -0.8 V vs RHE in the order of $\sim 2.5 \text{ mA cm}^{-2}$ all the pretreated catalyst films remain structurally intact as evidenced by the optical inspection shown in Fig. S19a. Important to note is that also at these lower overpotentials the same trend of an improved CO₂RR performance is observed after the photonic curing treatment (Fig. S19b) as already seen for the electrolysis at -1.1 V vs RHE (Fig. 5). The comparably higher Faradaic efficiency towards hydrogen in case of the thermally annealed sample can solely be ascribed to an insufficient surfactant removal whereas undesired side effects originating from the glassy carbon support after partial delamination of the catalyst layer can be excluded in this case (Fig. S19b) .

An alternative route to avoid losses of catalyst material into the aqueous electrolyte phase during the electrolysis reaction is the embedment of Cu-NWs into a carbon support matrix as recently discussed by Li et al.²⁶ Also in this case the photonic curing of the Cu-NWs, carried out prior to the catalyst ink preparation, leads to a further improvement of the CO₂RR performance (Fig. S20). It should be

however, noted that catalyst films based on C-supported Cu-NWs predominantly yield methane as major hydrocarbon product of the CO₂RR in full agreement with the recent work by Li et al.²⁶ This observation again points to the fact that the resulting CO₂RR product distribution is not solely governed by the intrinsic structural properties of the catalyst material on the atomic scale (e.g., (100) versus (111) surface faceting) but, as already pointed out by Dutta et al.¹⁰, results from the complex convolution of several effects involving also the catalyst film morphology on various length scales which affects the local reaction environment (e.g., local pH) and the reactant/product transport characteristics inside the three-dimensional catalyst material.

To further demonstrate the superior chemical stability of the photonicallly cured Cu-MMC an extended 110 h lasting CO₂ electrolysis has been carried out at an applied potential of -1.1 V vs RHE (Fig. 8). Within this period of electrolysis time the ethylene efficiency remains well above > 40%. At least on this time scale there is no noticeable catalyst degradation. The photonicallly cured Cu-MMC also withstands stressing experiments where the electropotential is periodically switched from the OCP to -1.1V vs RHE (Fig. S21).

When using (polycrystalline) Cu catalysts, it is often the coupled C1/2 hydrocarbon pathway (Figure 9) which causes a fast and irreversible catalyst degradation.¹⁵ According to early work by Hori et al.⁶⁷, Akhade et al.⁶⁸ and Dewulf et al.⁶⁹, hydrocarbon formation might involve an irreversible chemisorption of *C surface species on the catalyst surface, which blocks those sterically demanding reactive sites that are required for the *CH₂ dimerization.¹⁵ More recent DFT results by Nie et al.⁷⁰ discuss C1 and C2 pathways that also share key intermediates such as *CO, *COH and *CH₂ but do not involve the formation of poisoning *C species. The long term stability of the photonicallly cured Cu-MMC catalyst suggests that both methane and ethylene formation occur in the present case rather via the *COH route⁷⁰ than via the *C pathway. The latter would lead to an irreversible poisoning of the catalyst surface as shown by Rahaman et al. for dendritic Cu.¹⁵

Conclusions

Photonic curing in an inert gas atmosphere has been introduced as an effective and highly versatile method to remove surfactants (capping agents) from the surface of stabilized nanomaterials (e.g. nanowires, nanoparticles etc.) thereby activating them for electrocatalytic reactions, e.g. the CO₂ electroreduction reaction (CO₂RR). Crucial is the right balance of the energy input, depending on factors such as the irradiance (kW cm⁻²) and the irradiation time (typically in the range of μs), to remove the surfactant from the as-synthesized catalyst without degrading those structural features (e.g., surface sites) of the nanomaterial that are particularly active towards the targeted (electro)catalytic reaction. One prime example, discussed in detail herein, is the activation of oleylamine stabilized Cu-NWs which yield up to 42% ethylene as CO₂RR product at -1.1V vs RHE after applying one single pulse of 50 μs duration at 5.9

kW cm^{-2} irradiance. Optimized curing conditions depend on the chemical nature of the catalyst material, the support electrode and the capping agent used during synthesis. Photonic curing also leads to a substantial mechanical stabilization of the NW assembly (denoted as metal membrane catalyst: MMC) thus being important in particular for electrocatalytic reactions involving massive gas evolution which can induce mechanical stress to the electrode assembly.

Future method development will focus on multi-step catalyst activation steps, e.g. involving reactive gas environments with the aim to direct the CO_2RR product distribution towards alcohol formation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

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Notes

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Figure Captions

- Figure 1: Schematic representations and top-down optical micrographs of individual steps followed for the preparation of the Cu-MMC (copper metal membrane catalyst) on the glassy carbon support.
- Figure 2: White-light interferometric analysis of the Cu-MMC after the photonic curing (5.9 kW cm⁻²; 50μs); a) – b) Representative location in the center of the Cu-MMC; c) Representative location at the edge of the Cu-MMC; d) Cross-sectional line-scan indicated in c).
- Figure 3: a) Top-down SEM inspection of the Cu-MMC after the photonic curing; b) HR-TEM micrograph of an individual Cu-NW; c) Selective area electron diffraction (SAED) analysis obtained from an individual Cu-NW after the photonic curing; d) Schematic drawing showing the Cu-NW before (left panel) and after (right panel) the activation treatment.
- Figure 4: a) CO₂RR product distributions from various Cu-MMCs photonicallly cured using a constant irradiance of 5.9 kW cm⁻² but varying pulse times; the CO₂RRs were carried out for 1 h at -1.1 V vs RHE in each case; b) Potential depending CO₂RR product distributions derived from the optimum catalyst at 50 μs curing time.
- Figure 5: CO₂RR product distribution at -1.1V vs RHE (1 h electrolysis) derived from catalysts treated by various procedures for the removal of the surfactant. For comparison purposes also the results from the as-prepared (AP) sample are shown.
- Figure 6: a) XPS analyses of the Cu-NW assemblies carried out after applying different activation treatments (for details see text). The ratio of the integrated N1s and Cu2p_{3/2} emissions serves as measure for the removal of the surfactants which preferably bind via their nitrogen functionality to the copper surface; b) Enlarged section of a) focusing on the well-performing surfactant removal treatments.
- Figure 7: Optical micrographs of the Cu-NW catalysts prior to and after 1 h CO₂RR at -1.1 V vs RHE. Considered are the as-prepared sample, the one thermally annealed at 200 °C, the ones exposed to ozone and deep UV light, and the photonicallly cured Cu catalyst.
- Figure 8: Long-term (110 h) continuous CO₂ electrolysis experiment carried out over the photonicallly cured Cu-MMC at -1.1 V vs RHE (note that the product detection by online gas-chromatography was not carried out over the full electrolysis time).
- Figure 9: Proposed reaction mechanism of ethylene formation on Cu catalysts.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8