In spite of the enormous promise that polymeric carbon nitride (PCN) materials hold for various applications, the fabrication of high-quality, binder-free PCN films and electrodes has been a largely elusive goal to date. Here we tackle this challenge by devising, for the first time, a sol–gel approach that enables facile preparation of thin films based on poly(heptazine imide) (PHI), a polymer belonging to the PCN family. The sol–gel process capitalizes on the use of a water-soluble PHI precursor that allows formation of a non-covalent hydrogel. The hydrogel can be deposited on conductive substrates resulting in formation of mechanically stable polymeric thin layers. The resulting photoanodes exhibit unprecedented PEC performance in alcohol reforming and selective (~100%) conversions with very high photocurrents down to ~0 V vs. RHE, which enables even effective operation under bias-free conditions. The robust binder-free films derived from sol–gel processing of water-soluble PCN thus represent a new paradigm for high-performance ‘soft-matter’ photoelectrocatalytic systems, and pave the way for further applications in which high-quality PCN films are required.
Sol–Gel Processing of Water-Soluble Carbon Nitride Enables High-Performance Photoanodes

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Abstract

In spite of the enormous promise that polymeric carbon nitride (PCN) materials hold for various applications, the fabrication of high-quality, binder-free PCN films and electrodes has been a largely elusive goal to date. Here we tackle this challenge by devising, for the first time, a sol–gel approach that enables facile preparation of thin films based on poly(heptazine imide) (PHI), a polymer belonging to the PCN family. The sol–gel process capitalizes on the use of a water-soluble PHI precursor that allows formation of a non-covalent hydrogel. The hydrogel can be deposited on conductive substrates resulting in formation of mechanically stable polymeric thin layers. The resulting photoanodes exhibit unprecedented PEC performance in alcohol reforming and selective (~100%) conversions with very high photocurrents down to ~0 V vs. RHE, which enables even effective operation under bias-free conditions. The robust binder-free films derived from sol–gel processing of water-soluble PCN thus represent a new paradigm for high-performance ‘soft-matter’ photoelectrocatalytic systems, and pave the way for further applications in which high-quality PCN films are required.
1. Introduction

It has been a little more than a decade since polymeric carbon nitride (PCN, otherwise known as melon, C$_3$N$_4$ polymer or g-C$_3$N$_4$ polymer or g-C$_3$N$_4$) was introduced as a novel type of solid photocatalyst.$^{[1]}$ Its chemical and thermal stability, low cost, non-toxicity and exceptional photocatalytic performance have made it an object of studies of light-driven selective redox transformations$^{[2]}$ and pollutant degradation,$^{[3]}$ solar cells research$^{[4]}$ and, owing to its suitable valence (VB) and conduction (CB) bands positions,$^{[1]}$ especially of photocatalytic H$_2$ production from aqueous suspensions.$^{[1, 5c, 6]}$ However, many of these applications, in particular the generation of solar fuels and other high-value compounds,$^{[7]}$ would profit from operating the PCN within a proper photoelectrochemical (PEC) cell setup, affording thus more efficient charge separation and product isolation. However, this remains a great challenge in view of poor adhesion/cohesion properties of PCN, its unsatisfactory mechanical stability, inhomogeneity and low conductivity of the resulting coatings.$^{[8]}$ In this context, Antonietti et al. recently concluded that “…up to now, broader applications [of PCN] as electronic semiconductors were restricted by the limited processability, as the product is neither soluble nor malleable.”$^{[9]}$ Indeed, the deposition of pre-synthesized PCN materials on conductive and transparent substrates by doctor-blading or drop-casting methods mostly produced loosely assembled particulate PCN films exhibiting poor mechanical stability owing to a large size of the PCN particles, making thus the use of binders mandatory.$^{[8a, 10]}$ Though chemical vapor deposition routes utilizing conventional PCN precursors$^{[11]}$ or their modified analogues$^{[12]}$ produced more uniform coatings, they could not solve the problem of poor adhesion of PCN to the substrate and often resulted in the appearance of high dark currents indicating a low electrochemical stability of the films.$^{[11b, 12a]}$ This drawback could only be amended by applying an intermediate underlying mesoporous layer such as TiO$_2$ acting as binder and electron collector, thus forming a hybrid electrode with improved PEC performance.$^{[11d, 11e, 11g, 13]}$ As an alternative approach, the direct PCN growth on conductive substrates was also proposed.$^{[8c, 14]}$ Since PCN itself was not soluble in any of the tested organic solvents, its precursors were used to grow a layer on the substrate via high-temperature condensation, a notoriously uncontrollable process, leading to the tens of micrometers thick films composed of large loose particles. Such films
typically exhibited suboptimal mechanical and photo-operational stability, which was demonstrated by the detachment of PCN particles from the film under sonication and pronounced self-photooxidation revealed by low Faradaic efficiencies towards the reaction products.\cite{14b, 14d} In order to produce processable solutions or suspensions of PCN, ultrasonication-assisted, thermal or chemical exfoliation has been suggested.\cite{15} Wang et al. achieved processable suspensions composed of ca. 310 nm PCN particles by the exfoliation and oxidation of the bulk carbon nitride with HNO\textsubscript{3}.\cite{8b} The sol-processing followed by thermal stabilization yielded thin PCN films that showed cathodic photocurrents of only few \(\mu\)A cm\(^{-2}\), likely due to a partial decomposition of the PCN structure by the action of the strong oxidizing agent.

We have recently developed a novel synthetic procedure yielding fully water-soluble and stable nanoparticles (~10 nm size) of alkali metal poly(heptazine imide) (PHI),\cite{16} a promising member of the PCN family.\cite{17} As our synthetic strategy avoids the use of aggressive exfoliating or oxidizing agents that might impair the material's structural integrity, the water-soluble PHI exhibited excellent photocatalytic activity in alcohol oxidation and concurrent H\textsubscript{2}O\textsubscript{2} production without any apparent deactivation.\cite{16} Notably, as the presence of hydrophilic oxygenated (mainly cyamelurate) moieties on the nanoparticle surface is highly beneficial in view of effective attachment to the surface of conductive substrates, such as fluorine-doped tin oxide (FTO), and since the water-soluble PHI can be gelled,\cite{16} we anticipated that our water-soluble carbon nitride might be a promising candidate for fabrication of high-quality photoelectrode via sol–gel processing (Figure 1). Herein, we demonstrate, for the first time, the fabrication of binder-free, mechanically robust and photoelectrochemically stable PCN photoanodes via an aqueous sol–gel technique with water-soluble PHI using various and versatile protocols based on electrodeposition, doctor-blading, and spray pyrolysis. The excellent photoelectrocatalytic performance of the resulting photoanodes is demonstrated in alcohol reforming and highly selective (~100 \%) photooxidations in neutral electrolytes under exceptionally low onset potentials, enabling even operation without any external electric bias. Finally, we provide comprehensive mechanistic insights that elucidate the key factors (e.g., porosity and charge
transport properties) governing the photoanode activity and stability, which should drive further optimization of this type of PCN-based photoelectrodes.

2. Experimental

For the details on synthesis, characterization, experimental setup and conditions for PEC measurements see Supporting Information. Briefly, the PHI solution was synthesized followed the methodology reported by Krivtsov et al.[16] The mixture of 0.2 g of NaOH, 0.56 g of KOH and 1.5 g of melamine was treated for 2 h at 330 °C in a lid-covered crucible. The solid reaction product was dissolved and dialyzed to obtain the PHI solution.

The photoelectrodes were prepared on FTO substrates using different methods: i) The electrochemical deposition technique by applying a potential of 2V vs. Ag/AgCl resulting in the formation of a thin PHI layer, which subsequently underwent gelation induced by 37% HCl (PHI-ED). ii) The doctor-blade method was used to produce PHI-DB/HX and PHI-DB/SX electrodes (where X stands for the heat treatment temperature applied subsequently) by deposition on FTO substrates of the PHI gels produced by HCl and ethanol-induced gelation of the PHI solution, respectively; iii) The spray pyrolyzed films (PHI-SP/X, where X stands for the volume of the PHI solution of 4.5 gL⁻¹ applied for pyrolysis) were obtained by spraying the aqueous PHI sol on FTO substrates, which were heated at 200 °C and continuously moved through the nozzle of the spray to obtain homogeneous films.

Photocurrent measurements under simulated sunlight were carried out at least in triplicate. Representative average photocurrent data is plotted, and the uncertainty of photocurrent values is expressed as ± 2σ (σ is the standard deviation).
3. Results and discussion

3.1 Fabrication and Characterization of the Photoanodes

Recently, we introduced a bottom-up approach for the synthesis of water-soluble PHI in the form of colloidal nanoparticles (size ~10 nm), owing their solubility to the surface cyamelurate groups.\[16\] Since smaller heptazine-derived species such as cyameluric acid or its salts, although being catalytically relevant sites in PHI materials, do not show any significant photocatalytic activity on their own,\[17c\] the prepared water-soluble PHI colloids might be considered as the dimensionally smallest photocatalytically active PCN units reported so far. This is one of the key prerequisites for their successful use as a precursor for fabrication of homogeneous, stable and highly photoactive layers on conductive FTO surfaces, in contrast to conventional approaches (Figure 1).

Figure 1. Schematic illustration of conventional approaches and our proposed method for fabrication of PCN photoelectrodes. The PEC performance of the photoanodes derived from water-soluble PCN depends strongly on the processing method and increases in the order: electrodeposition < doctor-blading of gels formed with HCl < doctor-blading of gels formed with ethanol.

Owing to insolubility of the PHI colloids in most of the tested organic solvents, the addition of ethanol allowed us obtaining a PHI hydrogel that could be deposited onto FTO by the doctor blade method (PHI-DB/S). Due to high dispersibility of the K⁺ and Na⁺ containing PHI in water, the electrodes were stabilized by heating at various temperatures under N₂, showing the best PEC performance when treated at 450 °C (Figure S3a, Figure S4a). The obtained films are mechanically highly robust as
demonstrated by a scotch tape test (Figure S5, video). The SEM images evidence the presence of variously sized pores in this electrode with a thickness of ~400 nm (Figure 2a, Figure S6b). The pores are also visible in the atomic force microscopy (AFM) topography images showing a rough surface of the PHI-DB/S450 electrode (Figure S7). An alternative sol–gel preparation procedure consisted in gelation of the PHI solution with HCl causing exchange of K⁺ and Na⁺ present in PHI[16] for H⁺ and leading to the formation of strong H-bonding within the polymer, reducing thus its solubility. The deposition of the gel on FTO by the doctor-blading and subsequent thermal treatment at various temperatures produced PHI-DB/H films. The optimized PHI-DB/H400 samples (Figure S3b, Figure S4b) feature a uniform ~500 nm thick compact layer formed out of intertwined fiber-like particles (Figure 2b). Apparently, the protonation of PHI does not only induce ion-exchange, but it also promotes the H-bonding within the material leading to formation of a more compact layer than in case of the gelation using ethanol.

The electrodeposition of negatively charged[16] PHI colloids onto FTO (PHI-ED), whose stability towards dissolution was ensured by subsequent HCl-induced gelation, produced a highly inhomogeneous film on FTO consisting of islands of PHI, complicating the estimation of its thickness from the cross-section SEM image (Figure 2c). The intention to produce thicker films by either using higher voltages or longer electrodeposition time only led to mechanically unstable layers of PHI.
Figure 2. Photographs and SEM images of a) PHI-DB/S450, b) PHI-DB/H400 and c) as-prepared PHI-ED. Scale bar is 500 nm.

Due to the thickness of 400-500 nm and inherently low crystallinity of the PHI material, no visible peaks that could be assigned to PCN phases are observed in the XRD patterns of the fabricated electrodes (Figure S9a). Nonetheless, FTIR spectra show the typical fingerprint of the PCN-based materials in the range of 1200 to 1700 cm\(^{-1}\) and at 800 cm\(^{-1}\) corresponding to the \(\nu(C-NH-C)\) and \(\nu(C=\text{N})\) stretching vibrations, and the triazine ring breathing mode, respectively (for a detailed discussion see Supporting Information, Figure S9b).\(^{[16]}\) X-ray photoelectron spectroscopy (XPS) analysis evidences the presence of the elements C, N, K, Na and O in the structure of the PHI films (Figures S10-14, Table S1), which is in agreement with the data obtained for the precursor.\(^{[16]}\) N1s
XP spectra are typical for the PHI materials, having major contributions attributed to the sum of C-N=C and -C≡N species (398.4-398.5 eV), to the N-C₃ groups [19] (399-400 eV) and NHₓ functions (400.9 eV) (for the details on XPS analysis see Supporting Information, Table S2).

While the optical absorption edge of the PHI-DB/S450 sample is only slightly in the visible range (~435 nm) and the protonation blue shifted [10b, 20] this value to 415 nm and 395 nm in PHI-DB/H400 and PHI-ED samples, respectively (Figure S15-17, Table S1), the materials do not demonstrate any significant visible-light PEC activity (Figure 3d, S18). In spite of the low thickness (~400 nm) of the most active PHI-DB/S450 films, the light absorption is strong with absorption coefficients high enough to absorb ~85% of incoming photons at photon energy of 3.3 eV (~376 nm) (for the details on optical properties see the Supporting Information, Figures S15-17, Table S1). This makes our films promising for photocatalytic applications utilizing, for example, low-cost operating LEDs as light sources, which allow for optimal control of the process operation and in which the production cost of UV and visible photons is comparable.[21]

### 3.2 Photoelectrocatalysis

The PEC performance of the films was first investigated by potential dependent (cathodic scan) photocurrent measurements under intermittent irradiation. Although PCN-related materials are known for their high chemical stability among polymers,[1, 22] special care has to be taken with respect to experimental conditions since the decomposition of PCN cannot be ruled out, especially in aggressive electrolytes. Herein, we avoided the use of some commonly applied electrolytes such as H₂SO₄, KOH or NaOH due to the fact that PCN materials were proven to be soluble in these media.[15d, 23] We have also confirmed the instability of the PHI-DB/S450 electrode and some of other PCN-based photoelectrodes reported in literature in basic electrolytes by carrying out experiments in 0.1 M KOH (Figures S19, S20). Therefore, all PEC measurements were performed using 0.1 M Na₂SO₄ electrolyte with pH adjusted to 7.
Figure 3. LSV curves (scanned in cathodic direction with a sweep-rate of 5 mV s\(^{-1}\)) of a) PHI-DB/S450, b) PHI-DB/H400 and c) PHI-ED in 0.1 M \(\text{Na}_2\text{SO}_4\) with and without 10 %v/v methanol (pH 7.0) upon on/off illumination (2 sun, 5 s light/5 s dark) from back side (BS), if not stated otherwise. d) Photoaction spectra (IPCE vs. wavelength plots) of the thin films measured at 1.12 V vs. RHE in 0.1 M \(\text{Na}_2\text{SO}_4\) with 10 %v/v methanol (pH 7.0) under intermittent monochromatic irradiation from the frontside (FS) and from the backside (BS).

The best-performing photoanodes were obtained using the doctor-blading with ethanol as a gelating agent and the heat treatment at 450 °C (PHI-DB/S450). These films exhibited the highest photocurrents in the presence of both methanol (Figure 3a) and glycerol (Figure S21a) as electron donors, with the latter being tested to demonstrate the applicability of our photoanodes for the conversion of biomass-derived feedstock. In the presence of methanol the photocurrents at PHI-DB/S450 photoanodes reached the mean value of 320±40 µA cm\(^{-2}\) at 1.23 V vs. RHE under 2 sun backside (BS) illumination (Figure 3a). For a direct comparison with benchmark data from the literature\citep{10b, 11a, 11b, 11f, 12, 14b, 14c} the same experiments were carried out also under 1 sun irradiation,
resulting in photocurrents of $177\pm27 \, \mu\text{A cm}^{-2}$ at 1.23 V vs. RHE, which is, to the best of our knowledge, the highest value reported so far for photoreforming of alcohols at PCN-based electrodes in neutral electrolytes without showing apparent photocorrosion (Figure S22). Importantly, the photoanodes exhibited a very negative photocurrent onset potential ($<0$ V vs. RHE), so that even at 0 V vs. RHE photocurrent densities of $253\pm12 \, \mu\text{A cm}^{-2}$ (under 2 sun) could be observed. Notably, the photocurrents at the best performing PHI-DB/S450 films do not significantly depend on the applied potential in the range of 0 to 1.6 V vs RHE (Figure 3a). This is reminiscent of the typical behavior of mesoporous and nanocrystalline TiO$_2$ photoanodes,[24] in which the charge separation is not – in contrast to conventional compact semiconductors – controlled by the potential gradient over the space charge region, but the photocurrent generation is governed by the efficiency of the photogenerated electron/hole transfers at the semiconductor/electrolyte and semiconductor/FTO interface and by the transport of electrons through the film.[24] The increase of the PHI film thickness by using more scotch-tape layers during the doctor-blade preparation of the electrodes did not improve the PEC performance (Figure S23a). Under frontside (FS) illumination of PHI-DB/S450, the photocurrents were $\sim185 \, \mu\text{A cm}^{-2}$ at 1.23 V vs. RHE under 2 sun (Figure S24a), which is lower by $\sim40\%$ as compared to the backside (BS) illumination. This indicates that, under high intensity illumination, the photocurrent generation in PHI-DB/S450 is mainly limited by the transport of electrons across the film since the transfer of photogenerated holes to species in the electrolyte can be expected to occur readily within the porous structure of the PHI-DB/S450 photoanodes (cf. Figure 2a). Intriguingly, in contrast to the results obtained under high intensity polychromatic irradiation where BS illumination was optimal, under low intensity monochromatic irradiation the incident (IPCE, Figure 3d) and absorbed (APCE, Figure S18a) photon-to-current efficiencies show higher values for the FS measurements. We speculate that this apparent contradiction might be related to the much lower intensity of the monochromatic light used (without bias light) for the electrode irradiation during these experiments as compared to measurements done under high intensity polychromatic irradiation. This also suggests that the electron transport properties of porous PHI-DB/S450 are negatively influenced by excessive electron accumulation in the film (see the discussion of stability, section 3.4 below), an effect that is presumably pronounced under high intensity illumination.
The oxidation of different electron donors at the PHI-DB/S450 photoanodes was also investigated and resulted in similar photocurrents in the presence of secondary alcohol (isopropanol), lower photocurrents (ca. 200 µA cm\(^{-2}\)) for the oxidation of an aromatic alcohol 4-methoxybenzyl alcohol (4-MBA), and almost no photocurrents were registered when using tertiary alcohol (\(t\)-butanol) or ethylenediaminetetraacetic acid (EDTA) (Figure S25). These results can be well rationalized by the moderate oxidative potential of the PHI’s HOMO level, thus rendering it high selectivity in partial oxidation reactions.\(^{[16, 25]}\)

In addition, we also explored the PEC properties of films obtained from alternative methods of sol–gel fabrication. Firstly, the HCl-protonated PHI films (PHI-DB/H400) prepared using HCl as gelating agent showed photocurrents of \(~50\) µA cm\(^{-2}\) at 1.23 V vs. RHE for the FS and around 20 µA cm\(^{-2}\) for the BS illumination in the presence of methanol (Figure 3b). Notably, apart from lower photocurrents these electrodes differ significantly also in other respects from the previously described optimal PHI-DB/S450 photoanodes obtained by gelation using ethanol. Higher photocurrents under the FS (as compared to the BS) illumination reflect the more compact morphology of these photoanodes, rendering now the hole transfer into the solution as the limiting factor. Furthermore, the electrodes exhibit a much stronger potential dependence and the sign of photocurrents switches from anodic to cathodic at \(\sim-0.2\) V vs. RHE (Figure 3b, Figure S21b). Such effects are known for PCN\(^{[11e, 26]}\) and indicate that the behavior of these materials resembles that of wide-bandgap intrinsic semiconductors with low conductivity, without any pronounced n-type nor p-type character.\(^{[11e]}\) Secondly, the film formation from water soluble PCN could also be initiated electrochemically. However, the resulting PHI-ED films exhibited low photocurrents of ca. 1 µA cm\(^{-2}\) and 4 µA cm\(^{-2}\) at 1.23 V vs. RHE in the absence and the presence of the electron donors, respectively (Figure 3c, Figure S21c). Finally, as an alternative to the applied sol–gel technique for the electrode fabrication, the applicability of a potentially high-throughput spray-pyrolysis method for the PHI photoanodes preparation was tested. High quality of the obtained coatings (PHI-SP) is evident from the SEM images showing a comparable film thickness in the range of 400-500 nm to those obtained by the sol–gel technique (Figure S26). Comparing to the sol–gel procedures, the
samples prepared by spray-pyrolysis showed moderate activity with photocurrents reaching ca. 80 µA cm\(^{-2}\) at 1.23 V vs. RHE (at 2 sun illumination) for the best sample (Figure S27a).

The above results clearly show that the PEC properties and performance of the photoanodes depends strongly on the sol–gel deposition protocol used. The photocurrents at the best-performing photoanodes (PHI-DB/S450) were higher by the factors of 6 and 64 as compared to the photocurrents recorded at PHI-DB/H400 and PHI-ED, respectively. We assume that the superior PEC performance of PHI-DB/S450 is mainly due its enhanced porosity (Figures 2a,b, S7), allowing thus more efficient hole transfer from the excited PHI into the electrolyte (Figure S28). In addition to that, within the porous structure of PHI-DB/S450 the detrimental effects of electron accumulation in the films can be partially mitigated by effective screening of the accumulated negative charge by ions in the electrolyte. The fact that the PHI-DB/S450 film can be easily permeated by the electrolyte is also confirmed by the presence of reduction and oxidation peaks during the cycling voltammetry in the presence of the hexacyanoferrate redox pair,\(^{[27]}\) whereby at much more compact (non-porous) PHI-DB/H400 and PHI-SP films the hexacyanoferrate redox waves are completely absent (Figures S28 and S27b). Notably, the higher porosity of PHI-DB/S450 accounts for more efficient hole extraction and less pronounced PHI self-oxidation, increasing thus also its stability. These superior properties of the porous PHI-DB/S450 films are further corroborated by electrochemical impedance spectroscopic (EIS) study carried out in the presence of the hexacyanoferrate redox couple, which shows that both the film resistance (characterizing the charge transport through the PHI layer) and the interfacial charge transfer resistance are more than 200 times lower for PHI-DB/S450 than for the compact PHI-DB/H400 sample (Figure S29, Table S3). The possible contribution of K\(^+\) and Na\(^+\) ions in PHI-DB/S450 to its increased activity was ruled-out by rinsing it in 2M HCl solution leading to an almost complete loss of alkali-metal cations (Figure S11, Table S1), while the PEC performance remained unchanged (Figure S30a). On the other hand, the attempt to activate the PHI-DB/H400 electrode by its treatment in KOH/NaOH solution only yielded a moderate improvement of its activity (Figure S30b), which was likely due to the film etching and the enhanced porosity rather than to ion-exchange, since no increase of the alkali metals content was observed (Figure S13, Table S1).
3.3 Photoelectrocatalytic Reforming and Conversion of Alcohols under Zero External Bias

Although complete PEC water splitting is an attractive technology, the sluggish kinetics of oxygen evolution and correspondingly high overpotentials and stability issues of the photoanode still impede its broad implementation. On the other hand, the photoreforming of biomass-derived molecules usually treated as waste or byproducts represents a viable alternative route for photocatalytic hydrogen fuel production.\cite{28} We anticipated that the exceptionally low photocurrent onset potential (< 0 V vs. RHE, Figure 3a) during alcohol oxidation at our PHI-DB/S450 photoanodes should enable H₂ evolution even without any external electric bias.

![Figure 4](image-url)

**Figure 4.** Photocurrents (black) and area of the peak assigned to H₂ (red) detected by the GC-BID for PHI-DB/S450 in 0.1 M Na₂SO₄ with 10 v/v% methanol under 2 sun irradiation in argon in a two electrode setup at a) 0 V vs. Pt and b) 0.5 V vs. Pt.

Indeed, we observed H₂ evolution at a Pt counter electrode under bias-free conditions in a two-electrode setup (0 V vs. Pt) in a neutral pH electrolyte (Figures 4a, S31a). The H₂ evolution is clearly light-initiated as no hydrogen was detected during the first 30 min of the experiment under dark conditions. The increase of the GC signal corresponding to H₂ after the light is switched off is attributed to the diffusion of the produced H₂ gas from the solution and from the surface of the Pt electrode into the headspace. After the equilibrium is reached and the irradiation started again, a clear increase in the H₂ production is observed again (Figure 4a). Similar performance is demonstrated under relatively low applied potential (0.5 V vs. Pt), whereby much higher
photocurrents and amounts of the evolved hydrogen are observed (Figure 4b, Figure S31b). The applicability of the prepared photoanodes was also tested in conversion of other biomass-derived model substrates such as glycerol (Figure S32) and 4-MBA (Figure S33), with photocurrents and H₂ evolution rates in the same range as those obtained with methanol.

In order to demonstrate the applicability of our photoanodes for selective photoelectrocatalytic conversions and to prove unambiguously that the generated photocurrents and H₂ evolution at the counter-electrode are accompanied by the substrate oxidation at the photoanode rather than by its photocorrosion, we tested also the selective conversion of 4-MBA, a lignin model molecule, to 4-anisaldehyde. This reaction is known to proceed with very high selectivity in irradiated PHI suspensions.⁶ Only minor quantities of 4-anisaldehyde were formed in blank experiments using FTO and Ti as working and counter electrodes, respectively (Figure S34). In contrast, at the PHI-DB/S450 photoanodes the PEC conversion of 4-MBA to 4-anisaldehyde proceeded with excellent selectivity (~100 %) even under zero-bias conditions in a two-electrode setup (Figure 5a, S35a). The very high selectivity of ~100% over the whole extent of the reaction was confirmed under applied bias (1.1 V vs. RHE) in a three-electrode cell, which enabled higher yields and thus a more accurate quantification of the Faradaic efficiency towards 4-anisaldehyde (Figure 5b, S35b).

Figure 5. Photocurrent density (black) and experimental (red) and theoretical (blue) 4-anisaldehyde concentration registered for PEC oxidation of 4-MBA (20 mM) in 0.1 M Na₂SO₄ over PHI-DB/S450 under 2 sun irradiation in Ar atmosphere at a) 0 V vs. Ti (two-electrode setup) and b) 1.1 V vs. RHE (three-electrode setup). A Ti foil was used as a counter electrode in order to avoid thermal catalytic oxidation of 4-MBA at Pt. The experimental Faradaic efficiencies slightly exceeding the theoretical values are due to analytical limitations related to water evaporation from the reaction cell caused by continuous purging with Argon.
3.4 Operational Stability

The operational stability remains one of the critical issues hindering the application of soft-matter photoanode materials. The very good electrochemical stability of the PHI-DB/S450 film is supported by practically absent dark currents at potentials of around 1.6 V vs RHE (Figure 3a), which is in stark contrast to what is frequently reported for PCN-based photoanodes, especially when tested in aggressive electrolytes.\cite{14b, 29} Moreover, the photocurrents measured in the absence of additional electron donors are ca. 20 times lower than those obtained using methanol (Figure 3a) or glycerol (Figure S21a). Such a drastic difference in the photocurrents with and without additional reducing agents is in line with reports that PCN-based systems are incapable of four-electron water oxidation to dioxygen without assistance of a co-catalyst.\cite{11e, 30} Although PCN-promoted water photooxidation was sometimes suggested, solely on the basis of recorded photocurrents, to occur in some studies, it has typically not been supported by direct experimental evidence of oxygen evolution.\cite{14b, 14c, 31} In addition, it has been shown that it was primarily the photocorrosion that was responsible for high photocurrents as only small amount of oxygen could be detected in the absence of electron donors and/or the Faradaic efficiency for oxygen formation was that low to suggest that other PEC reactions, such as oxidation of PCN itself, were occurring.\cite{14e, 32} Therefore, we assume that photocurrents observed at PCN-based photoanodes in aqueous electrolytes in the absence of any additional electron donors are mostly due to photocorrosion, leading to the formation of nitrates\cite{33} or partially oxidized heptazine or triazine species. In this context, the very low photocurrents obtained for PHI-DB/S450 under such conditions (black curve in Figure 3a) are significant and indicate a very good inherent PEC stability of our photoanodes. Indeed, the PHI-DB/S450 photoanodes operated in the presence of additional electron donors demonstrate stable photocurrents for up to 8 h of irradiation both with applied external potential and under zero bias (Figure 5, Figure S 35). The rapid decay of the initially very high photocurrents to more stable values observed during the first hour of irradiation (Figure 4a, Figure 5a) can be most likely ascribed to excessive electron accumulation in the PHI film, which is a known bottleneck of PCN-based photocatalysts.\cite{15b} Especially under zero external electric bias, the accumulated electrons are less efficiently extracted from the film into the underlying
FTO, making thus the initial photocurrent decay more pronounced. Further long-term stability tests were carried out at 1.1 V vs. RHE under 2 sun illumination. It should be noted that typical stability tests reported in the literature so far were done for much shorter times (~1 h of irradiation), whereby at longer times a drastic drop of activity (by 93 % within 10 hours) has been usually observed. In contrast, the activity of our PHI-DB/S450 photoanode is maintained at nearly the same level for the first hour of irradiation, followed by a drop to 61 % after 5 h, and eventually decreasing to 35 % of initial photocurrents after 16 h of irradiation (Figure S36). Notably, in spite of the decreased photocurrent, the mechanical integrity of the film is preserved (Figure S37). The deactivation kinetics of the PHI-DB/S450 electrode increases upon increasing the irradiation power, which again suggests the effect of electron accumulation on the material stability (Figure S36). EIS measurements after the long-term stability test indicate a higher internal resistance of the film (lower $n$ values of the constant phase element, CPE2, parameter) which might be responsible for the decrease in photocurrent density (Table S4, Figure S38). A more detailed investigation of deactivation (for the discussion see Supplementary Information) revealed that the performance of the PHI-DB/S450 films is stable in the potential range of 0 to 1.6 V vs RHE (Figure S39). However, applying excessive negative potentials (below 0 V vs. RHE) to the photoanode causes a dramatic reduction of the photocurrent density during the subsequent PEC cycles (Figure S40), although the film stays mechanically stable (Figure S41). Intriguingly, this deactivation occurs also without irradiation, but does not occur if the measurement is carried out in the absence of organic electron donors (Figure S2). The EIS measurements have again shown that the $n$ values for CPE2 being initially typical for the capacitor ($n = 1$) changed to $n = 0.3$ (for a pure resistor $n = 0$), indicating a higher internal resistance of the PHI-DB/S450 film upon deactivation (Table S4, Figure S38). We have developed several hypotheses with respect to the nature of the PHI deactivation such as (i) deterioration of the interfacial contact of the film with FTO, in which tin is reduced in this potential range (Figure S42, Figure S43); (ii) the effect of a possible exchange of K$^+$ for Na$^+$ or H$^+$ in the PHI structure, and (iii) generation of a PHI$^-$ radical followed by irreversible reaction with the organic substrate or the products of its oxidation. While the first two hypotheses could be effectively ruled out (for a detailed discussion see Supplementary Information, Figure S43, Figure S44), the last
one is most likely correct, as corroborated by the fact that an addition of a good electron acceptor (H₂O₂) to the methanol-containing electrolyte completely mitigated the deactivation of the photoelectrode (Figure S43f). Based on this, we assume that the partial deactivation observed either after prolonged operation or occurring upon applying excessively negative potential has a similar reason in both cases: it is related not to the deterioration of the molecular structure of the PHI material as the typical fingerprint IR bands are almost unchanged upon deactivation (Figure S45), but rather to irreversible chemical reactions with organic substrates induced by the negatively charged PHI, such as condensation reactions between the organic substrates or the products of their oxidation and the PHI surface sites. In turn, these chemical changes within the porous structure of PHI-DB/S450 influence negatively both the interfacial charge transfer and electron transport properties within the film, in line with the above mentioned EIS results. The AFM study confirms the integrity of the film after the long-term PEC reactions as well as after applying negative potential to the film, however it also indicates an increased roughness of the electrode surface after prolonged operation suggesting that the morphological changes might be a relevant factor contributing to the material deactivation (Figures S46, S47, Table 5). It follows that further efforts in developing this new type of PCN photoanodes must take into account the peculiar photoinduced chemistry of PHI materials, and further studies aimed at understanding and optimizing the effect of operational conditions on activity and stability are mandatory.

4. Conclusion

In this work, we have established a novel and versatile sol–gel route for fabrication of robust and binder-free PCN films, and demonstrated their use as high-performance photoanodes. We employed a water-soluble PCN precursor composed of small (~10 nm) nanoparticles that enabled us to form a non-covalent hydrogel that can be deposited on a conductive substrate resulting in formation of mechanically stable PCN thin layers, in contrast to the commonly obtained loosely attached thick particulate coatings. The optimized process yields porous PCN photoanodes that exhibit unprecedented PEC performance in terms of both activity and operational stability, with respect to
conventional PCN-based photoanodes reported so far. The photoanodes excel, in particular, by their very low photocurrent onset potential, which allows to carry out various useful photoelectrocatalytic conversions of organic compounds even without any external electric bias (bias-free conditions), as demonstrated by effective light-driven reforming of methanol and glycerol to hydrogen, and by highly selective (~100%) photooxidation of 4-MBA. Notably, the latter two compounds represent biomass-derived molecules, which highlights the applicability of our photoanodes for light-driven valorization of low-value chemical feedstock to value-added compounds.[7,36] The robust binder-free films derived from sol–gel processing of water-soluble PCN thus represent a new paradigm for high-performance ‘soft-matter’ photoelectrocatalytic systems, and pave the way for further applications in which high-quality PCN films are required, such as electrochemical sensors[37] or (photo)batteries.[34b]

Supporting Information. Experimental details; additional characterization results (XRD, XPS, FTIR, AFM, EIS, photoelectrocatalysis, stability tests); video of the scotch-tape test (Scotch_tape_test.mp4).

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Robust binder-free films derived from sol–gel processing of a water-soluble polymeric carbon nitride precursor exhibit unprecedented performance in photoelectrocatalytic reforming of alcohols, including effective operation under bias-free conditions.
Supporting Information

Sol–Gel Processing of Water-Soluble Carbon Nitride Enables High-Performance Photoanodes

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**Figure S8.** Photographs of the PHI-ED electrodes prepared by applying 2 V vs. Ag/AgCl for 5 min (left) and for 30 min (right). The latter was not stable in contact with electrolyte.

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**Figure S16.** Absorption coefficient (solid line) and light penetration length (1/α, dashed line) of the PHI films. Grey column shows approximate indirect bandgaps. Solid line: α.

**Figure S17.** (a) Determination of the bandgap energies from Tauc plots by employing absorption coefficients of the PHI films. Solid line: indirect. b) Determination of the bandgap energies from Tauc plots by employing IPCE values obtained for the PHI films. Solid line: indirect bandgap. c) Determination of the bandgap energies from Tauc plots by employing APCE values obtained for the PHI films. Solid line: indirect.

**Figure S18.** a) Photoaction spectra (APCE vs. wavelength plots) of the thin films measured at 1.12 V vs. RHE in Na₂SO₄ (0.1 M, pH 7.0) under intermittent monochromatic irradiation from the frontside (FS) and from the backside (BS). Photocurrent transients measured at thin electrodes in 0.1 M
Na$_2$SO$_4$ with 10 %v/v methanol aqueous solution at 1.12 V vs. RHE under intermittent monochromatic irradiation (30 s idle at beginning, next 25 s light / 15 s dark) from 330 to 500 nm with interval of 10 nm from b) BS and c) FS.

**Figure S19.** LSV of PHI-DB/S450 in 0.1 M KOH with 10 v/v% methanol recorded under intermittent irradiation (2 sun) with sweep rate of 5 mV s$^{-1}$. A photograph of the electrode after an LSV measurement in KOH is shown as inset.

**Figure S20.** Stability test of the carbon nitride electrode prepared following the method proposed in Ref.$^{[9]}$ in 0.1 M KOH with 10 v/v% methanol for 16.5 h under 1 sun irradiation with AM 1.5G filter. A picture of the electrode after stability test is shown as inset.

**Figure S21.** LSV curves of (a) PHI-DB/S450, (b) PHI-DB/H400 and (c) PHI-EB in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol or 10 %v/v glycerol (pH 7.0) upon on/off 2 sun illumination. BS and FS stand for backside and frontside illumination. PEPS stands for "photoelectrochemical photocurrent switching" effect.$^{[10]}$

**Figure S22.** LSV of PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol (pH 7.0) under 1 sun and 2 sun backside irradiation.

**Figure S23.** LSV curves registered in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol (pH 7.0) upon on/off 2 sun illumination from backside for PHI-DB/S450 prepared using (a) two and (b) three scotch tape layers. (c) PHI-DB/H400 prepared using two scotch-tape layers.

**Figure S24.** LSV curves of (a) PHI-DB/S450 and (b) PHI-DB/H400 in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol upon on/off two-sun backside illumination.

**Figure S25.** LSV of PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 10 %v/v isopropyl alcohol, 10 %v/v methanol, 20 mM 4-MBA, 10 %v/v tert-butyl alcohol or 0.1 M EDTA (pH 7.0) under 2 sun backside irradiation.

**Figure S26.** Photographs and SEM images of (a) PHI-SP/2, (b) PHI-SP/5 and (c) PHI-SP/10.

**Figure S27.** (a) LSV of the spray-pyrolyzed PHI samples in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol upon on/off two sun illumination and (b) Porosity test of the PHI-SP samples in 0.1 M Na$_2$SO$_4$, 0.5 mM K$_3$[Fe(CN)$_6$] and 0.5 mM K$_4$[Fe(CN)$_6$] in the dark.

**Figure S28.** Porosity test of PHI-DB/H400 and PHI-DB/S450 in 0.1 M Na$_2$SO$_4$, 0.5 mM K$_3$[Fe(CN)$_6$] and 0.5 mM K$_4$[Fe(CN)$_6$] in the dark.
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Figure S30. LSV in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol upon on/off 2 sun illumination of (a) PHI-DB/S450 before and after treatment with 2M HCl and (b) PHI-DB/H400 before and after treatment with a mixture of 0.1 M NaOH and 0.1 M KOH.

Figure S31. Photocurrent density (red) and GC signal area of H$_2$ peak (black) registered for PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 10 v/v% methanol under two sun irradiation in Ar atmosphere at a) 0 V vs. Pt and b) 0.5 V vs. Pt. The respective GC chromatograms for the methanol photoreforming.

Figure S32. Photocurrent density (red) and GC signal area of H$_2$ peak (black) registered for PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 10 v/v% glycerol under two sun irradiation in Ar atmosphere at a) 0 V vs. Pt and b) 0.5 V vs. Pt. The respective GC chromatograms for the glycerol photoreforming.

Figure S33. Photocurrent density (red) and GC signal area of H$_2$ peak (black) registered for PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 20 mM 4-MBA under two sun irradiation in Ar atmosphere at a) 0 V vs. Pt and b) 0.5 V vs. Pt. The respective GC chromatograms for the 4-MBA photoreforming.

Figure S34. HPLC chromatograms of the 4-MBA PEC conversion products obtained in the absence of PHI. Pure FTO and Ti used as anode and cathode, respectively. Conditions: 0.1 M Na$_2$SO$_4$, 20 mM 4-MBA under two sun irradiation in Ar atmosphere at 1.1 V vs RHE.

Figure S35. HPLC chromatograms of the 4-MBA PEC conversion products obtained using PHI-DB/S450 as photoanode and Ti foil as photocathode. Conditions: 0.1 M Na$_2$SO$_4$, 20 mM 4-MBA under two sun irradiation in Ar atmosphere in a) two-electrode cell at 0 V vs Ti and b) three-electrode cell at 1.1 V vs RHE.

Figure S36. Stability test of PHI-DB/S450 and PHI-DB/H400 in air, at 1.12 V vs. RHE in 0.1 M Na$_2$SO$_4$ and 10 v/v% methanol under LED (365 nm, 20 mW cm$^{-2}$) or under solar simulator with different intensities. The values in mW cm$^{-2}$ indicate the light intensity in the UV range (<400 nm) obtained by the integration of the AM1.5 spectrum.
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Figure S47. AFM topography images of a) the PHI-DB/S450 film and c) PHI-DB/H400 film; b) and d) the respective films after applying negative potentials from 0 to -0.4 V vs RHE in 10 v/v% of MeOH in 0.1 M Na₂SO₄, under 2 sun irradiation........................................................................................................................................................................................................................................................................ 51
Experimental

Materials
Melamine (99%), 4-methoxybenzyl alcohol (4-MBA) (98%), 4-anisaldehyde (98%) and 4-methoxybenzoic acid (98%) were provided by Sigma Aldrich, KOH (99%), NaOH (99%), HCl (37%), Na₂SO₄ (99.99%), methanol (99.9%) and isopropyl alcohol (99.8%) by Merck and Titanium foil (99.6+% by Advent Research Materials. Glycerol (99.5%), ethanol (99.8%), ethylenediaminetetraacetic acid disodium salt dehydrate (EDTA) (99.9%) and KCl (100.1%) were purchased by VWR, FTO Pilkington TEC 15 by Xop Fisica SL and tert-butyl alcohol by Honeywell Chemicals (99.7%).

Synthesis

Synthesis of the PHI solution: PHI solution was synthesized following the methodology reported by Krivtsov et al. Briefly, 0.2 g of NaOH, 0.56 g of KOH and 1.5 g of melamine were ground and transferred into a ceramic crucible. The lid-covered crucible was heated in a muffle furnace for 2 h at 330 °C with a heating rate of 5 °C min⁻¹. After cooling down to room temperature, the orange solid was dissolved in deionized water, the insoluble part was filtered out with a paper filter, while the solution was filtered through a 0.2 µm PTFE syringe filter. The filtered liquid was filled inside a cellulose membrane sack with a pore size of 3.5 kDa and dialyzed against deionized water for 5 days. The dialyzed solution of the PHI nanoparticles was concentrated by evaporation at 70 °C until the desired concentration of PHI was achieved. The concentration of the PHI in the solutions was determined gravimetrically.

Preparation of FTO substrate: The FTO substrates were cleaned by sonication in acetone for 20 min and washing with deionized water. Afterwards, the FTOs were boiled for 10 min in 0.1 M NaOH followed by washing again with deionized water and drying.

Preparation of the PHI-DB/S electrodes: 12.5 mL of the PHI solution (4.5 g L⁻¹, pH ~8.5) was gelled by the addition of 32.5 mL of ethanol and centrifuged for 10 min at 8000 r.p.m. The obtained gel-like
solid was washed three times with ethanol and then the gel was liquified by vortexing. Then, 200 µL of the liquified gel was smeared on two FTO glasses (or two Ti-foil pieces of a similar size) by the doctor blade technique using a scotch tape as a frame and spacer. The electrodes were dried in air at room temperature and heated at different temperatures under N₂ flow in a tube furnace with a heating rate of 5 °C min⁻¹.

*Preparation of the PHI-DB/H electrodes:* 25 mL of PHI solution (4.5 g L⁻¹, pH ~8.5) was gelled by the addition of 0.5 mL of 37% HCl and centrifuged for 10 min at 8000 r.p.m. The remaining solid was liquified by vortexing. Then, 200 µL of the liquified gel was smeared on two FTO glasses by the doctor blade technique using a scotch-tape as a frame and spacer. The electrodes were dried in air at room temperature and heated at different temperatures under N₂ flow in a tube furnace with a heating rate of 5 °C min⁻¹.

*Preparation of the PHI-ED electrodes:* A three-electrode setup with FTO glass as working electrode, a Pt counter electrode, and a Ag/AgCl (3.5 M KCl) reference electrode was used for electrochemical deposition of PHI on FTO substrate. 5mL of PCN (3 g L⁻¹) at pH in the range of 7.5-8.5 was filled in the electrochemical cell. A potential of 2 V vs. Ag/AgCl was applied for 5 min using a SP-300 Biologic potentiostat, resulting in the formation of a thin PHI layer on the FTO substrate. Subsequently, after the electrochemical deposition, the obtained layer was gelled with 20 µL of 37% HCl producing a water-insoluble film.

The spray pyrolyzed films (PHI-SP/X, where X stands for the volume of the PHI solution of 4.5 gL⁻¹ applied for pyrolysis) were obtained by spraying the aqueous PHI sol on FTO substrates, which were heated at 200 °C and continuously moved through the nozzle of the spray to obtain homogeneous films. The solution flow rate, the nozzle-substrate distance and the compressed air employed to atomize the solution were 20 ml min⁻¹, 25 cm and 2 bars, respectively. After deposition, the films were heated at 450 °C for 1 h under N₂ atmosphere.
Materials characterization

The morphology, cross sections and elemental composition of the samples were analyzed with a scanning electron microscope (Supra 55VP, SmartSEM™, Zeiss) with a field emission electron gun using an Inlens detector and 10 kV as electron accelerating potential also equipped with an Oxford Instruments EDX analyzer. The microstructure and the thickness of the films obtained by spray-pyrolysis was analyzed by a Field Emission scanning electron microscope (FEI, Helios Nanolab 650, Hillsboro, OR, USA), equipped with a Tomohawk focused ion beam (FIB).

XRD patterns were obtained using a Pananalytical X’pert PRO diffractometer operating at Cu Kα radiation.

FTIR spectra were recorded by means of a Shimadzu IRTracer-100 spectrometer at a resolution of 4 cm⁻¹ from the samples powdered and pressed into KBr pellets. Owing to a high mechanical stability of the films and their low thickness, the PHI-DB/H and PHI-DB/S films were prepared using two scotch tape layers and thermally treated under the same conditions, then the films were scratched with a spatula to prepare the pellets for the FTIR study. For the case of the PHI-ED film, the necessary amount of the sample for the measurements was obtained by a prolonged deposition time (30 min at 2V vs. Ag/AgCl).

X-ray photoelectron spectroscopy (XPS) was performed using a UHV Multiprobe system (Scienta Omicron, Germany) with a monochromatic X-ray source (Al Kα) and an electron analyzer (Argus CU) with 0.6 eV energy resolution. For individual samples, charge compensation during data acquisition was realized by an electron flood gun (NEK 150, Staib, Germany) at 6 eV and 50 μA. The background was subtracted, and spectra were calibrated using the C 1s peak (284.6 eV) before undergoing fitting using Voigt functions (30:70). For cation exchange investigations, the PHI-DB/S450 or PHI-DB/H400 film was treated with 2 M HCl or a mixture of 0.1 M KOH/NaOH, respectively, and afterwards rinsed with deionized water. Before measurements, all samples were again rinsed with ultrapure water (0.056 μS, MembraPure Aquinity2 E35) for 20 sec and afterwards immediately dried in a stream of nitrogen gas (N2 Linde, Germany, purity 5.0).
The optical properties of the thin films were evaluated by UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS, UV2600 Shimadzu). Absorptance $A$ was calculated according to the equation $A(\%) = 100\% - T(\%) - R(\%)$, where $T$ and $R$ are transmittance and reflectance, respectively. Absorption coefficient was calculated from $\alpha = -\ln(A - 1) \cdot d^{-1}$, where $d$ is a thickness of the film obtained from the cross-section SEM measurements. Tauc plots based on the UV/Vis data were used to determine the optical bandgap.\textsuperscript{[2]}

Infrared attenuated total reflection (IR- ATR) spectra were recorded using a Bruker Vertex 70 FT-IR spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a liquid nitrogen-cooled wide-band mercury–cadmium–telluride (MCT) detector (Infrared Associates, FL, USA). A single-bounce IR- ATR assembly (GladiATR, PIKE Technologies, WI, USA) with a diamond ATR waveguide (3 mm in diameter) was used. IR spectra were recorded for each sample three times with a spectral resolution of 2 cm\(^{-1}\) averaging 64 spectra within a spectral window of 4000 – 400 cm\(^{-1}\). The FTO substrate was used as background spectra. An adjustable pressure clamp facilitated determining the optimum contact pressure and ensured that all samples were reproducibly pressed against the ATR unit. Data acquisition was performed with the Bruker OPUS 8.1 software package. Savitzky-Golay filter was used to smooth the spectra using Essential FTIR software (Operant LLC, WI, USA).

A 5500 AFM/SPM was used for all AFM measurements using PicoView 1.20 software (Keysight Technologies, AZ, USA). All measurements were performed in contact mode with silicon nitride probes (ORC-8, Bruker AFM probes, CA, USA) to determine the film roughness and porosity. Images were recorded with a scan speed of 0.7 lines s\(^{-1}\). The surface arithmetic roughness ($S_a$) was determined at each sample at 8 different areas (10 x 10 µm).

**Electrochemical measurements**

If not denoted otherwise, all photoelectrochemical measurements were performed in 0.1 M Na\(_2\)SO\(_4\) electrolyte at pH 7.0 (adjusted by addition of NaOH) using a three-electrode setup with a Pt counter electrode, a Ag/AgCl (3.5 M KCl) reference electrode and the respective PCN-coated FTO electrode.
as working electrode using a SP-300 Biologic potentiostat and a scan rate of 5 mV s\(^{-1}\) if not stated otherwise. The photoelectrodes were pressed against an O-ring of the cell, leaving an irradiated area of 0.5 cm\(^2\). If not stated otherwise, the electrodes were irradiated from backside, with an Ushio 150 W Xe lamp in a light-condensing lamp housing (LOT-Oriel GmbH). The value of photocurrent density was taken as a difference between current density under irradiation and in the dark. The dependence of the electrodes’ performance on the irradiation intensity under a 365 nm LED in the range of 5-30 mW cm\(^{-2}\) was carried out for the PHI-DB/S450 electrode, and showed the linear increase of the photocurrent up to 10 mW cm\(^{-2}\), which is equivalent to the UV contribution in the two-sun irradiation of the solar-simulator. Henceforth, the PEC measurements were performed under Xenon two-sun irradiation (200 mW cm\(^{-2}\)) with an air mass 1.5G filter for all prepared electrodes, if not stated otherwise (Figure S 1). Prior to the PEC experiments, the PHI-DB/S450 electrodes were activated by applying the potentials from 1.6 to −0.4 V vs. RHE under two-sun irradiation in 0.1 M Na\(_2\)SO\(_4\) electrolyte at pH 7.0 (Figure S 2). The activation procedure permitted to eliminate impurities and attain a stable PEC performance of the electrodes. For photocurrent measurements in the presence of additional reducing agents, 10 v/v% of methanol, glycerol, isopropanol, tert-butanol, 20 mM 4-methoxybenzyl alcohol (4-MBA) or 0.1 M of EDTA was added to the electrolyte solution. Photoaction spectra were recorded using a photoelectric spectrometer (Instytut Fotonowy) equipped with a tunable monochromatic light source provided with a 150W Xenon lamp and a grating monochromator with a bandwidth of ∼10 nm. The incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the photoanodes were measured at 1.12 V vs. RHE. The value of photocurrent density was taken as a difference between the current density under irradiation and in the dark with a wavelength sampling interval of 10 nm from 330 nm to 500 nm. The IPCE value for each wavelength was calculated according to the equation IPCE (%) = \((i_{\text{ph}}hc)/(\lambda Pq)\)100%, where \(i_{\text{ph}}\) is the photocurrent density, \(h\) is the Planck’s constant, \(c\) is the velocity of light, \(P\) is the light power density, \(\lambda\) is the irradiation wavelength, and \(q\) is the elementary charge. The absorbed monochromatic photon-to-current conversion efficiency (APCE) spectra were obtained by dividing the IPCE spectra by the absorptance values. Impedance measurements were performed in a mixture of 0.1 M Na\(_2\)SO\(_4\), 0.1 M K\(_3\)[Fe(CN)\(_6\)] and 0.1 M K\(_4\)[Fe(CN)\(_6\)] at pH 7.0 in a frequency range of 100
kHz to 100 mHz in dark at 0.73 V vs. RHE. In order to avoid artefacts at high frequencies, a capacitor of 100 nF was used as a bridge between the CE and RE.\textsuperscript{[3]} The use of the $K_3[\text{Fe(CN)}_6] / K_4[\text{Fe(CN)}_6]$ redox pair was beneficial in terms of improving the linearity and invariance of the system’s response and increasing thus the quality of the recorded spectra, as checked by Kramers-Kronig analysis during the fitting procedure (EIS Spectrum Analyser 1.0 software).\textsuperscript{[4]}

The photoreforming of alcohols was studied in 0.1 M Na$_2$SO$_4$ at pH 7 using a two-electrode setup with a cathodic compartment containing Pt counter electrode, equipped with a rubber septum and separated from the anodic compartment by the Nafion-impregnated glass frit. The anodic compartment contained 0.1 M Na$_2$SO$_4$ with either 10 v/v% methanol, 10 v/v% glycerol or 20 mM MBA at pH 7.0. Before the measurement, the electrolyte in both compartments was purged for 30 min with Ar and then the system was left in dark under applied potential (or under zero bias) for another 30 min before irradiation started. After the irradiation for 2 h, the system was monitored in the dark for 2 h before the light was switched on again for additional 2 h. Hydrogen evolution was tracked using a Shimadzu GC-2010 Plus equipped with a BID detector and a ShinCarbon ST column. The discharge He gas flow was 70 mL min$^{-1}$ and the column temperature was 35 °C for 2.5 min followed by 20 °C min$^{-1}$ heating up to 180 °C for 0.5 min. For the H$_2$ detection, the samples of 50 µL taken from the head space of the cathodic compartment were directly injected into the GC column. Only semi-quantitative tests for H$_2$ evolution have been carried out, since the equilibrium between the hydrogen dissolved in the electrolyte, adsorbed on the Pt electrode and in the headspace significantly affected the measured concentrations, thus not permitting accurate quantitative estimation.

In order to quantitatively estimate the efficiency of the alcohol photoconversion, the 4-MBA photoelectrochemical oxidation at 0 V vs. Ti foil counter-electrode (in a two-electrode setup) and at 1.1 V vs RHE (in a three-electrode setup) was carried out. A Ti counter-electrode was used instead of the Pt one since thermal catalytic oxidation of 4-MBA to 4-anisaldehyde was found to take place on the Pt surface in the dark. Before the irradiation was started, the electrolyte was purged with Ar and the photoconversion experiment was carried out under continuous Ar flow into the headspace.
For the analysis of the PEC liquid phase reaction products an HPLC Shimadzu LC-10ADvp equipped with a UV detector SPD-20A and a reversed phase C18 Nucleosil column was used. Acetonitrile/trifluoroacetic acid (30/70 vol.) was used as a mobile phase at a flow of 1.2 mL min\(^{-1}\) and a column temperature of 60 °C. 4-MBA, 4-methoxybenzoic acid and 4-anisaldehyde were detected and quantified at wavelength of 240 nm. The theoretical quantity of 4-anisaldehyde produced during the reaction was estimated using the Faraday law (1) on the basis of the observed currents.

\[
n = \frac{Q}{Fz}
\]  

where \(z\) is the number of electrons transferred to complete the reaction, \(n\) is the number of moles of 4-anisaldehyde, \(F\) is the Faraday constant and \(Q\) is the total charge passed through the PEC system.

![Figure S1](image.png)

**Figure S1.** Photocurrent density of PHI-DBI/S450 vs. light intensity of a 365 nm LED in 0.1 M Na\(_2\)SO\(_4\) with 10 %v/v methanol (pH 7.0) at 0.63 V vs. RHE.
Figure S2. Activation of the PHI-DB/S450 electrode in 0.1 M Na$_2$SO$_4$ (pH 7.0) under 2 sun irradiation.

Results and Discussion

Morphology and stability of the prepared electrodes

Figure S3. Photographs of the (a) PHI-DB/S and (b) PHI-DB/H electrodes calcined under N$_2$ at 200 °C and 300 °C taken after the contact with the electrolyte.
Figure S4. Linear sweep voltammetry of (a) PHI-DB/S400, (b) PHI-DB/H300 and PHI-DB/H450 in 0.1 M Na$_2$SO$_4$ with 10 v/v% methanol, recorded under intermittent irradiation (2 sun) with a sweep rate of 5 mV s$^{-1}$.

Figure S5. Photograph of PHI-DB/S450 after the scotch tape test (using Tesafilm Adhesive Tape), which also can be seen in video Scotch_tape_test.mp4.
**Figure S6.** SEM images of the as-prepared and calcined (a) PHI-DB/H and (b) PHI-DB/S films.
Figure S7. AFM topography images of the as-prepared a) PHI-DB/S450 film; b) corresponding zoomed view; c) 3D-image: zoomed view; d) cross-section of a pore of the PHI-DB/S450 film (pore depth = 82.8 ± 6.5 nm; n = 5). Images were recorded in contact mode with 0.7 lines s\(^{-1}\).

Figure S8. Photographs of the PHI-ED electrodes prepared by applying 2 V vs. Ag/AgCl for 5 min (left) and for 30 min (right). The latter was not stable in contact with electrolyte.
XRD and FTIR characterization of the prepared films

FTIR spectra confirm the poly(heptazine imide) (PHI) nature of the as-prepared as well as calcined films showing the typical fingerprint of PCN-based materials in the range of 1200 to 1700 cm\(^{-1}\) corresponding to the \(\nu(C-NH-C)\) and \(\nu(C=N)\) stretching vibrations, and the triazine ring breathing mode at 800 cm\(^{-1}\) (Figure S9b).\(^5\) Furthermore, (C=N) vibrations in the range of 2150-2175 cm\(^{-1}\) and the stretching vibrations of NH\(_x\)- or OH-groups at 3450 cm\(^{-1}\) are present.\(^1\) The reduced intensity corresponding to the -C≡N functions observed for the PHI-DB/H400 sample with respect to PHI-DB/S450 (Figure S9b) can be most likely assigned to the hydrolysis of these groups induced by the HCl treatment and resulting in the formation of the terminal NH\(_2\) moieties. Additionally, EDX measurements demonstrate that the K\(^+\) and Na\(^+\) content in the protonated PHI films is significantly lower than in the one gelled with ethanol (Table S1).

Figure S9. (a) XRD patterns of the thin films and FTO, (b) FTIR spectra of calcined and as prepared PHI-DB/S, PHI-DB/H and PHI-DB/ED.

XPS analysis of the prepared films

XPS analysis confirms the presence of the elements C, N, K, Na and O in the structure of the PHI films (Figures S10 – S14), which is in agreement with the data obtained for the precursor.\(^1\) The chlorine is also found for the case of the protonated samples (Figure S12, S14). Four different contributions can be identified in the deconvoluted N1s XP spectra of the prepared films, the major one being attributed to the sum of C-N=C and -C≡N species (398.4-398.5 eV) (Figures S10 – S14,
The signals centred at ca. 404 eV and 401 eV are assigned to a shake-up peak due N-N \( \pi \)-excitation and to NH\textsubscript{x}-groups, respectively. Conventionally, the peak in the range of 399-400 eV is attributed to N-C\textsubscript{3} species\textsuperscript{[6]}, which in this case, however, is improbable due to the ratio between the areas of the maxima at 398.4 eV to that of 399.8 eV resulting in the relationships 1 : 3.9 and 1 : 3.1 for PHI-ED and PHI-DB/H400 (Figure S12 – S14, Table S2), respectively, being very far from what should be ideally found for the heptazine based PCN, \textit{i.e.}, 1 : 6. The same relationship determined for the PHI-DB/S450 sample is 1 : 9.9, which is more realistic considering the fact that the peak at 398.4 eV represents a sum of the C-N=C and -C≡N species (Figure S10, S11, Table S2). Thus, the enhanced intensity of the maximum at 399.8 eV observed for the protonated PHI electrodes might be attributed to the protonation of the heptazine N-atoms by HCl according to the model proposed by Zhang et al.\textsuperscript{[7]}

\textbf{Table S1.} Comparison of absorption edge, EDX- and XPS elemental compositions and C:N ratio obtained by EDX of PHI-ED, PHI-DB/H400, PHI-DB/S450 and PHI-DB/S450 deactivated (after applying negative potential).

| Sample name         | Absorption edge | EDX Elemental composition / at\% | C:N ratio EDX | XPS Elemental composition / at\% |
|---------------------|----------------|---------------------------------|---------------|----------------------------------|
| PHI-ED              | 395 nm         | C\textsubscript{29.2}N\textsubscript{40.4}O\textsubscript{18.7}Na\textsubscript{1.3}K\textsubscript{1.5}Cl\textsubscript{2.1}Sn\textsubscript{6.6}Si\textsubscript{0.3} | 0.72          | C\textsubscript{47.8}N\textsubscript{38.1}O\textsubscript{8.9}Na\textsubscript{0.6}K\textsubscript{2.4}Cl\textsubscript{2.6} |
| PHI-DB/H400         | 415 nm         | C\textsubscript{23.4}N\textsubscript{29.8}O\textsubscript{25.5}Na\textsubscript{1.9}K\textsubscript{1.0}Cl\textsubscript{2.2}Sn\textsubscript{18.8}Si\textsubscript{0.5} | 0.79          | C\textsubscript{48.5}N\textsubscript{39.5}O\textsubscript{7.5}Na\textsubscript{0.1}K\textsubscript{3.5}Cl\textsubscript{0.3} |
| PHI-DB/S450         | 435 nm         | C\textsubscript{19.4}N\textsubscript{21.6}O\textsubscript{36.7}Na\textsubscript{2.0}K\textsubscript{2.6}Sn\textsubscript{17.7}Si\textsubscript{0.8} | 0.92          | C\textsubscript{46.1}N\textsubscript{38.2}O\textsubscript{9.0}Na\textsubscript{1.1}K\textsubscript{7.4}Cl\textsubscript{0.2} |
| PHI-DB/S450 deactivated | -              | C\textsubscript{23.7}Na\textsubscript{26.3}N\textsubscript{2.0}K\textsubscript{3.0}Sn\textsubscript{10.8}Si\textsubscript{0.4} | 0.7           | -                                |
| PHI-DB/S450 washed with 2M HCl | -              | -                                | -             | C\textsubscript{50.3}N\textsubscript{41.9}O\textsubscript{7.4}K\textsubscript{0.3} |
| PHI-DB/H400 washed with 0.1M KOH/NaOH | -              | -                                | -             | C\textsubscript{52.2}Na\textsubscript{38.8}O\textsubscript{7.1}K\textsubscript{1.7}Na\textsubscript{0.2} |
| PHI-ED washed with water | -              | -                                | -             | C\textsubscript{47.8}Na\textsubscript{41.0}O\textsubscript{8.7}Na\textsubscript{0.2}K\textsubscript{1.5}Cl\textsubscript{0.8} |
| PHI-DB/H400 washed with water | -              | -                                | -             | C\textsubscript{50.9}Na\textsubscript{40.1}O\textsubscript{7.0}Na\textsubscript{0.2}K\textsubscript{1.8}Cl\textsubscript{0.1} |
| PHI-DB/S450 washed with water | -              | -                                | -             | C\textsubscript{47.8}Na\textsubscript{38.7}O\textsubscript{7.4}Na\textsubscript{0.2}K\textsubscript{5.6} |
Figure S10. High resolution XPS of C 1s, K 2p, N 1s, Na 1s, O 1s and Cl 2p of PHI-DB/S450 rinsed with water.
Figure S11. High resolution XPS of C 1s, K 2p, N 1s, Na 1s, O 1s and Cl 2p of PHI-DB/S450 washed with 2M HCl and rinsed in water afterwards.
Figure S12. High resolution XPS of C 1s, K 2p, N 1s, Na 1s, O 1s and Cl 2p of PHI-DB/H400 rinsed with water.
Figure S13. High resolution XPS of C 1s, N 1s, Na 1s, O 1s and Cl 2p of PHI-DB/H400 washed with a mixture of 0.1M KOH/NaOH and rinsed in water afterwards.
Figure S14. High resolution XPS of C 1s, K 2p, N 1s, Na 1s, O 1s and Cl 2p of PHI-DB/ED rinsed with water.
Table S2. Ratio between the peaks in N 1s XPS compared with the sum of C-N=C and C≡N.

| Sample name                  | Ratio C-N=C+ C≡N to N-C₃ | Ratio C-N=C+ C≡N to C-NHₓ | Ratio C-N=C+ C≡N to N-N |
|------------------------------|---------------------------|---------------------------|-------------------------|
| PHI-ED                       | 3.9                       | 3.0                       | 20.3                    |
| PHI-DB/H400                  | 3.1                       | 5.2                       | 25.8                    |
| PHI-DB/S450                  | 9.9                       | 6.1                       | 38.8                    |
| PHI-DB/S450 washed with 2M HCl | 11.9                      | 3.0                       | 46.2                    |
| PHI-DB/H400 washed with 1M KOH/NaOH | 3.8                      | 4.8                       | 31.7                    |

Photon-to-Current Conversion

Absorption coefficient (Figure S16) of the films was calculated using the film thickness obtained by SEM being 400 nm and 500 nm for PHI-DB/S450 and PHI-DB/H400, respectively (see experimental). At the absorption edge of both materials of ~2.9 eV the absorption coefficient is enhanced from 1.4 × 10³ for PHI-DB/H400 to 4.1 × 10³ cm⁻¹ for PHI-DB/S450. It reaches the maximum value of 3.6 × 10⁴ cm⁻¹ for PHI-DB/S450 starting already at 3.3 eV, which corresponds to a penetration depth (~63 % of photons absorbed) of α⁻¹ = 277 nm. This translates to an overall absorption of ~85 % of photons at 3.3 eV (~376 nm) for a film with a thickness of only ~400 nm. Longer penetration depths are obtained for PHI-DB/H400 as the comparable absorption coefficient (3.6 × 10⁴ cm⁻¹) are observed at ~3.7 eV indicating the inferior absorption properties of this sample. Tauc plots are calculated using the absorption coefficients and considering the indirect bandgaps of 2.9 eV for both samples, whereas direct bandgaps are wider and are 3.1 eV and 3.2 eV for PHI-DB/S450 and PHI-DB/H400, respectively (Figure S16, Figure S17). These slight differences could have arisen from the structural differences between protonated and non-protonated materials and different alkali metal content. Notably, very similar results were obtained using the data from the photoaction spectra (IPCE and APCE values) instead of the absorption coefficient (Figure S18b,c).

The photocurrent action spectra evidence a slight blue-shift of the PHI response compared to conventional[8] PCN materials (Figure S18), possibly owing to the small thickness of the films. The
measurements of the incident (IPCE, Figure 3d) and absorbed (APCE) photon-to-current efficiency were conducted in the presence of methanol at 1.12 V vs. RHE showing higher values for the PHI-DB/S450 sample compared to the PHI-DB/H400 one, independently on the irradiation side (Figure S18).

Figure S15. Absorptance of PHI-ED, PHI-DB/H400 and PHI-DB/S450.

Figure S16. Absorption coefficient (solid line) and light penetration length ($1/\alpha$, dashed line) of the PHI films. Grey column shows approximate indirect bandgaps. Solid line: $\alpha$. 

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Figure S17. (a) Determination of the bandgap energies from Tauc plots by employing absorption coefficients of the PHI films. Solid line: indirect. b) Determination of the bandgap energies from Tauc plots by employing IPCE values obtained for the PHI films. Solid line: indirect bandgap. c) Determination of the bandgap energies from Tauc plots by employing APCE values obtained for the PHI films. Solid line: indirect.
Figure S18. a) Photoaction spectra (APCE vs. wavelength plots) of the thin films measured at 1.12 V vs. RHE in Na₂SO₄ (0.1 M, pH 7.0) under intermittent monochromatic irradiation from the frontside (FS) and from the backside (BS). Photocurrent transients measured at thin electrodes in 0.1 M Na₂SO₄ with 10 %v/v methanol aqueous solution at 1.12 V vs. RHE under intermittent monochromatic irradiation (30 s idle at beginning, next 25 s light / 15 s dark) from 330 to 500 nm with interval of 10 nm from b) BS and c) FS.
**Photoelectrochemical studies of the PHI films**

**Figure S19.** LSV of PHI-DB/S450 in 0.1 M KOH with 10 v/v% methanol recorded under intermittent irradiation (2 sun) with sweep rate of 5 mV s$^{-1}$. A photograph of the electrode after an LSV measurement in KOH is shown as inset.

**Figure S20.** Stability test of the carbon nitride electrode prepared following the method proposed in Ref.[9] in 0.1 M KOH with 10 v/v% methanol for 16.5 h under 1 sun irradiation with AM 1.5G filter. A picture of the electrode after stability test is shown as inset.
Figure S21. LSV curves of (a) PHI-DB/S450, (b) PHI-DB/H400 and (c) PHI-EB in 0.1 M Na₂SO₄ with 10 %v/v methanol or 10 %v/v glycerol (pH 7.0) upon on/off 2 sun illumination. BS and FS stand for backside and frontside illumination. PEPS stands for "photoelectrochemical photocurrent switching" effect.[10]
Figure S22. LSV of PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol (pH 7.0) under 1 sun and 2 sun backside irradiation.
Figure S23. LSV curves registered in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol (pH 7.0) upon on/off 2 sun illumination from backside for PHI-DB/S450 prepared using (a) two and (b) three scotch tape layers. (c) PHI-DB/H400 prepared using two scotch-tape layers.
Figure S24. LSV curves of (a) PHI-DB/S450 and (b) PHI-DB/H400 in 0.1 M Na₂SO₄ with 10 %v/v methanol upon on/off two-sun backside illumination.

Figure S25. LSV of PHI-DB/S450 in 0.1 M Na₂SO₄ with 10 %v/v isopropyl alcohol, 10 %v/v methanol, 20 mM 4-MBA, 10 %v/v tert-butyl alcohol or 0.1 M EDTA (pH 7.0) under 2 sun backside irradiation.
Figure S26. Photographs and SEM images of (a) PHI-SP/2, (b) PHI-SP/5 and (c) PHI-SP/10.
Figure S27. (a) LSV of the spray-pyrolyzed PHI samples in 0.1 M Na$_2$SO$_4$ with 10 %v/v methanol upon on/off two sun illumination and (b) Porosity test of the PHI-SP samples in 0.1 M Na$_2$SO$_4$, 0.5 mM K$_3$[Fe(CN)$_6$] and 0.5 mM K$_4$[Fe(CN)$_6$] in the dark.

Figure S28. Porosity test of PHI-DB/H400 and PHI-DB/S450 in 0.1 M Na$_2$SO$_4$, 0.5 mM K$_3$[Fe(CN)$_6$] and 0.5 mM K$_4$[Fe(CN)$_6$] in the dark.
Figure S29. a) Bode impedance plot and b) Nyquist impedance plot of PHI-DB/S450 and PHI-DB/H400 in 0.1 M Na$_2$SO$_4$, 0.1 M K$_3$[Fe(CN)$_6$] and 0.1 M K$_4$[Fe(CN)$_6$] (pH 7.0) in dark at 0.73 V vs. RHE in a frequency range from 100 kHz to 100 mHz. Raw data is shown as dots and fit obtained with the equivalent circuit (c) is shown as line. The R1, R2 and R3 elements represent the uncompensated resistance (e.g. electrolyte, electrical contact, FTO), film resistance, and charge transfer resistance, respectively. Constant phase element (CPE) and Warburg element (W) were chosen to account for the porosity of the films.

Table S3. Parameter values obtained from the fit with the equivalent circuit (Figure S29c) in 0.1 M Na$_2$SO$_4$, 0.1 M K$_3$[Fe(CN)$_6$] and 0.1 M K$_4$[Fe(CN)$_6$] (pH 7.0) at 0.73 V vs. RHE with a frequency range from 100 kHz to 100 mHz.

| Parameters   | PHI-DB/H400 | PHI-DB/S450 |
|--------------|-------------|-------------|
| R1 / Ω       | 26.8        | 2.8E-15     |
| R2 / Ω       | 11776       | 55.2        |
| R3 / Ω       | 33556       | 149.8       |
| W / Ω s$^{-1/2}$ | 2.3E-12    | 14.2        |
| P1 / Ω$^{-1}$ s$^{n1}$ | 1.3E-7     | 8.9E-11     |
| n1           | 0.9         | 1.0         |
| P2 / Ω$^{-1}$ s$^{n2}$ | 2.9E-6     | 2.6E-5      |
| n2           | 0.7         | 0.9         |
Figure S30. LSV in 0.1 M Na₂SO₄ with 10 %v/v methanol upon on/off 2 sun illumination of (a) PHI-DB/S450 before and after treatment with 2M HCl and (b) PHI-DB/H400 before and after treatment with a mixture of 0.1 M NaOH and 0.1 M KOH.

**Photoelectrocatalytic reforming and selective conversion of alcohols**

Figure S31. Photocurrent density (red) and GC signal area of H₂ peak (black) registered for PHI-DB/S450 in 0.1 M Na₂SO₄ with 10 %v/v% methanol under two sun irradiation in Ar atmosphere at a) 0 V vs. Pt and b) 0.5 V vs. Pt. The respective GC chromatograms for the methanol photoreforming.
Figure S32. Photocurrent density (red) and GC signal area of H$_2$ peak (black) registered for PHI-DB/S450 in 0.1 M Na$_2$SO$_4$ with 10 v/v% glycerol under two sun irradiation in Ar atmosphere at a) 0 V vs. Pt and b) 0.5 V vs. Pt. The respective GC chromatograms for the glycerol photoreforming.
Figure S33. Photocurrent density (red) and GC signal area of H₂ peak (black) registered for PHI-DB/S450 in 0.1 M Na₂SO₄ with 20 mM 4-MBA under two sun irradiation in Ar atmosphere at a) 0 V vs. Pt and b) 0.5 V vs. Pt. The respective GC chromatograms for the 4-MBA photoreforming.
Figure S34. HPLC chromatograms of the 4-MBA PEC conversion products obtained in the absence of PHI. Pure FTO and Ti used as anode and cathode, respectively. Conditions: 0.1 M Na$_2$SO$_4$, 20 mM 4-MBA under two sun irradiation in Ar atmosphere at 1.1 V vs RHE.
Figure S35. HPLC chromatograms of the 4-MBA PEC conversion products obtained using PHI-DB/S450 as photoanode and Ti foil as photocathode. Conditions: 0.1 M Na₂SO₄, 20 mM 4-MBA under two sun irradiation in Ar atmosphere in a) two-electrode cell at 0 V vs Ti and b) three-electrode cell at 1.1 V vs RHE.
Stability of the photoanodes

The stability test was carried out at 1.12 V vs. RHE under two sun illumination. Low PEC stability of PCN-based electrodes is a well-known problem. Most of stability tests reported in the literature so far were provided only for around 1 h of irradiation,\(^8,^{11}\) whereby at longer times (~10 h) the photocurrents were reported to drop down to ~7% of the initial performance.\(^{12}\) We have studied the electrode stability under irradiation for 16 h. PHI-DB/S450 maintains nearly the same photocurrents for the first hour of two-sun irradiation, and then drops only to ~61% after 5 h. Eventually, after 16 h of irradiation the electrodes show ~35% of the initial photocurrents (Figure S36). In spite of that decrease, the mechanical integrity of the film is preserved (Figure S37). The extent and kinetics of the deactivation depend upon the light intensity. One can suggest that by applying higher light intensity the produced electrons cannot be discharged quickly enough and the formed PHI\(^{•−}\) radical can react with the organic substrate, thus provoking the electrode deactivation (Figure S36). Remarkably, the activity of the PHI-DB/H400, although inferior to that of PHI-DB/S450, does not suffer any significant decrease and remains at ~91% after 24 h of irradiation (Figure S36). This can be explained by higher currents observed for PHI-DB/S450 resulting in more reaction events on its surface. The formation of various reaction products during the PEC measurements might be responsible for the blockage of the PHI active sites. After 16 h of irradiation a minor quantity of H\(_2\)O\(_2\) was detected in the electrolyte, indicating that not all the photo-generated electrons were extracted through the FTO and into the circuit, but that also shows that the reduction of O\(_2\) on the PHI surface also took place to some extent. Such side-reactions could have an impact on the properties of the PHI-based electrodes and the measures of reducing their effect on the electrode performance is the subject of the following research. EIS measurements after the long-term stability test indicate a higher internal resistance of the film (lower \(n\) values of the CPE2 parameter) which might be responsible for the decrease in photocurrent density (Table S4, Figure S38).
Figure S36. Stability test of PHI-DB/S450 and PHI-DB/H400 in air, at 1.12 V vs. RHE in 0.1 M Na$_2$SO$_4$ and 10 v/v% methanol under LED (365 nm, 20 mW cm$^{-2}$) or under solar simulator with different intensities. The values in mW cm$^{-2}$ indicate the light intensity in the UV range (<400 nm) obtained by the integration of the AM1.5 spectrum.

Figure S37. Photograph of PHI-DB/S450 after stability test for 16 h in 0.1 M Na$_2$SO$_4$ and 10 v/v% methanol under two sun irradiation at 1.12 V vs. RHE.
**Figure S38.** Nyquist impedance plot of PHI-DB/S450 (black), PHI-DB/S450 after applying -0.4 V vs. RHE with methanol (blue) and PHI-DB/S450 after 16 h stability test with methanol and applying 1.12 V vs. RHE. Conditions: 0.1 M Na$_2$SO$_4$, 0.1 M K$_3$[Fe(CN)$_6$] and 0.1 M K$_4$[Fe(CN)$_6$] (pH 7.0) in dark at 0.73 V vs. RHE in a frequency range from 100 kHz to 100 mHz. Raw data is shown as dots and fit obtained with the equivalent circuit (Figure S29c) is shown as line.

**Table S4.** Parameter values obtained from the fit with the equivalent circuit (Figure S29c) in 0.1 M Na$_2$SO$_4$, 0.1 M K$_3$[Fe(CN)$_6$] and 0.1 M K$_4$[Fe(CN)$_6$] (pH 7.0) at 0.73 V vs. RHE with a frequency range from 100 kHz to 100 mHz.

| Parameters          | PHI-DB/S450       | PHI-DB/S450 deactivated under negative potentials | PHI-DB/S450 after stability test |
|---------------------|-------------------|--------------------------------------------------|----------------------------------|
| R1 / Ω              | 2.8E-15           | 7.5                                              | 48.6                             |
| R2 / Ω              | 55.2              | 38.3                                             | 50.9                             |
| R3 / Ω              | 149.8             | 770.8                                            | 243.5                            |
| W / Ω s$^{-1/2}$    | 14.2              | 12.6                                             | 13.1                             |
| P1 / Ω$^{-1}$ s$^{n_1}$ | 8.9E-11           | 1.5E-5                                           | 7.0E-5                           |
| n$^1$               | 1.0               | 0.3                                              | 0.6                              |
| P2 / Ω$^{-1}$ s$^{n_2}$ | 2.6E-5           | 1.2E-5                                           | 1.9E-7                           |
| n$^2$               | 0.9               | 0.9                                              | 1                                |

In order to mitigate the photoelectrode deactivation under negative potentials (Figure S40), a systematic study was carried out. Apparently, the mechanical stability of the material is not an issue, since the deactivated film is found stable (Figure S41). A higher extent of deactivation observed under inert atmosphere indicates that the main cause for this process must be related to the
discharge of accumulated electrons from the PHI material (Figure S40). Subjecting the PHI-DB/S450 electrode to negative potentials in the presence of additional organic electron donors in the dark results in the same photocurrents decrease, although of lower magnitude, hence the deactivation is an electrochemical process, promoted even more by light. (Figure S43b). The hypothesis concerning the deterioration of the interfacial contact of the film with FTO, in which tin is reduced in this potential range (Figure S43c, Figure S42), could not be confirmed as the same deactivation occurred for the PHI-DB/S450 film prepared on Ti-foil, despite the prepared film being mechanically stable and showing the photocurrent density equally high as that observed for PHI-DB/S450 prepared on FTO and irradiated from the frontside (Figure S44, Figure S21). We also ruled out the effect of a possible exchange of K⁺ and Na⁺ in PHI structure to H⁺, which might take place while applying negative potential to the electrode as EDX measurements did not show any variation in K⁺ and Na⁺ content before and after applying negative potentials in the presence of the electron donor (Table S1). Furthermore, the tests performed in KCl electrolyte instead of Na₂SO₄, in order to prevent potassium to sodium exchange, resulted in the same deactivation during the second cycle (Figure S43d).

Herein we recall the ability of PHI to store negative charge in the form of PHI⁻ radical formed under light in anaerobic conditions with an appropriate electron donor and at very negative potentials. This long living PHI⁻ radical can transfer its charge to powerful electron acceptors such as methyl viologen and be converted back to the initial PHI. Methyl viologen was added to the electrolyte and negative potentials were applied, resulting, however, again in deactivation (Figure S43e). However, after an alternative electron acceptor, a powerful oxidizing agent (H₂O₂), was added to the electrolyte, after applying negative potentials to the electrode in presence of hydrogen peroxide and electron donor (methanol), the photocurrents remained high, showing no apparent signs of deactivation (Figure S43f).
Figure S39. Stability of PHI-DB/S450 in 0.1 M Na₂SO₄ with 10 %v/v methanol (pH 7.0) applying potential from 1.6 to 0 V vs. RHE for 5 cycles.

Figure S40. Stability of PHI-DB/S450 after applying negative potentials in 0.1 M Na₂SO₄ with 10 %v/v methanol (pH 7.0) with the first LSV in air (black) and the second in Ar (blue) or in air (red).
**Figure S41.** Photograph of PHI-DB/S450 after applying negative potential.

**Figure S42.** LSV of FTO in 0.1M Na$_2$SO$_4$ with and without 10% v/v methanol (pH 7.0) upon on/off two sun illumination.
Figure S43. Comparison of the deactivation processes of PHI-DB/S450 after applying negative potentials. The ratio of photocurrents at 1.23 V vs. RHE before ($j_0$) and after ($j$) LSV from 1.6 to −0.4 V vs. RHE in 0.1 M Na$_2$SO$_4$ with 10 v/v% methanol (a) on FTO under two sun irradiation, (b) on FTO in dark and (c) on Ti-foil under two sun irradiation. d) The ratio of photocurrents at 1.23 V vs. RHE before ($j_0$) and after ($j$) LSV from 1.6 to −0.4 V vs. RHE under two sun irradiation in 0.1 M KCl with 10 v/v% methanol and 0.1 M Na$_2$SO$_4$ with 10 v/v% methanol and addition of (e) methyl viologen (MV) or (f) H$_2$O$_2$.

Figure S44. (a) LSV of the PHI-DB/S450 film on Ti-foil in 0.1 M Na$_2$SO$_4$ with 10 v/v% methanol. Photograph of the film is shown as an inset.
Figure S45. ATR IR spectra of the PHI-DB/S450 films. PHI-DB/S450 pristine film (black), PHI-DB/S450 activated in Na₂SO₄ 0.1M under 2 sun irradiation under LSV conditions from 1.6 to –0.4 V vs RHE in absence of electron donors (red), PHI-DB/S450 after applying negative potential in the range from 0 to –0.4 V vs RHE (green) and PHI-DB/S450 after long-term stability test in 10 v/v% of MeOH in 0.1 M Na₂SO₄, under 2 sun irradiation at applied 1.12 V vs RHE for 16 h. (a) Full spectra, (b) selected region of the wavenumbers.

The activation of the film performed prior to the PEC experiments (Figure S2) results in the shift of the IR band at about 1062 cm⁻¹ and the complete disappearance of the peak at 1000 cm⁻¹ (Figure S44). The absence of these bands in the spectrum of the corresponding precursor of the film[1]
suggests that they must be attributed to some easily oxidizable impurities produced during the heat treatment of the gel deposited on FTO. The IR spectroscopic study evidences that the molecular structure of the PCN films remained mostly unaltered after long-term stability tests or after exposing the film to negative potentials and only minor changes of the spectral features can be observed.

Figure S46. AFM topography images of the a) PHI-DB/S450 film and b) PHI-DB/S450 after long-term stability test in 10 v/v% of MeOH in 0.1 M Na₂SO₄, under 2 sun irradiation at applied 1.12 V vs RHE for 16 h.

Figure S47. AFM topography images of a) the PHI-DB/S450 film and c) PHI-DB/H400 film; b) and d) the respective films after applying negative potentials from 0 to -0.4 V vs RHE in 10 v/v% of MeOH in 0.1 M Na₂SO₄, under 2 sun irradiation.
Table S5. Mean roughness of the photoanodes before and after usage determined by AFM

| Sample                                | Sa (nm)   |
|---------------------------------------|-----------|
| PHI-DB/S450                           | 56.1 ± 10.1 |
| PHI-DB/S450 after long term stability* | 74.2 ± 17.3 |
| PHI-DB/S450                           | 59.9 ± 17.8 |
| PHI-DB/S450 after applying negative potential** | 46.0 ± 13.5 |
| PHI-DB/H400                           | 31.8 ± 8.3  |
| PHI-DB/SH400 after applying negative potential** | 31.3 ± 5.5  |

Mean roughness (Sa) determined on an area of 10 x 10 µm at 2 different spots (ORC-8 Bruker AFM probes, k = 0.15 N/m); (n = 8).

* PHI-DB/S450 after long-term stability test in 10 v/v% of MeOH in 0.1 M Na₂SO₄, under 2 sun irradiation at applied 1.12 V vs RHE for 16 h.

** After applying negative potentials from 0 to -0.4 V vs RHE in 10 v/v% of MeOH in 0.1 M Na₂SO₄, under 2 sun irradiation.
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