A Triad Photoanode for Visible Light-Driven Water Oxidation via Immobilization of Molecular Polyoxometalate on Polymeric Carbon Nitride

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Due to their availability, low cost, nontoxicity, and tunability, polymeric carbon nitrides (CN\textsubscript{x}) represent one of the most attractive materials classes for the development of fully sustainable photo(electro)catalytic systems for solar-driven water splitting. However, the development of CN\textsubscript{x}-based photoanodes for visible light-driven water oxidation to dioxygen is rather challenging, particularly due to issues related to photoelectrode stability and effective coupling of the light absorber with water oxidation catalysts. Herein, a triadic photoanode comprising a porous TiO\textsubscript{2} electron collector scaffold sensitized by CN\textsubscript{x} coupled to a molecular cobalt polyoxometalate (CoPOM = [Co\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2}(PW\textsubscript{9}O\textsubscript{34})\textsubscript{2}]\textsuperscript{10\textsuperscript{-}}) catalyst is reported. Complete water oxidation to dioxygen under visible (λ > 420 nm) light irradiation is demonstrated, with photocurrents down to relatively low bias potentials (0.2 V vs RHE). Furthermore, polyethyleneimine (PEI), a cationic polymer is shown to act as an effective and non-sacrificial electrostatic linker for immobilization of the anionic CoPOM onto the negatively charged surface of CN\textsubscript{x}. The optimized deposition of CoPOM using the PEI linker translates directly into improved efficiency of the transfer of photogenerated holes to water molecules and to enhanced oxygen evolution. This work thus provides important design rules for effective immobilization of POM-based catalysts into soft-matter photoelectrocatalytic architectures for light-driven water oxidation.

1. Introduction

Solar-driven water splitting utilizing photo(electro)catalytic systems is a possible strategy to secure the future supply of low-entropy energy in form of storable high-energy molecular fuels, such as hydrogen, alcohols, or hydrocarbons.[1–5] However, practically viable and sustainable systems required for large-scale applications should be preferably based on highly abundant and low-cost materials with non-critical availability, i.e., without any possible supply restrictions due to various political, economic or environmental concerns. In terms of sustainability, low cost, and nontoxicity, one of the most attractive materials for photo(electro)catalytic applications are polymeric carbon nitrides (CN\textsubscript{x}).[6–9] Carbon nitrides are readily available, tunable and chemically robust polymers,[10] that have been widely utilized in a variety of light-driven chemical processes such as hydrogen evolution,[11–14] CO\textsubscript{2} reduction,[15,16] selective chemical syntheses,[17–20] or organic pollutants degradation.[21,22]

However, the studies demonstrating visible light-driven water oxidation to dioxygen using CN\textsubscript{x}-based photoelectrocatalytic systems are still rather rare.[23,24] This is, on the one hand, due to the notoriously slow kinetics of the oxygen evolution reaction (OER).[25] which typically results in accumulation of oxidizing equivalents that translates into enhanced photocorrosion of CN\textsubscript{x}.[26] On the other hand, the very fabrication of mechanically robust CN\textsubscript{x}-based photoelectrodes is challenging,[27,28] in particular due to the poor adhesion of CN\textsubscript{x} to conductive substrates.[29–32] and the very low conductivity of CN\textsubscript{x} films, hindering efficient charge transport to the external circuit.[33]

In our own work, we have been developing a distinct type of hybrid CN\textsubscript{x}-based photoanodes in which a thin layer of CN\textsubscript{x} is deposited onto a porous TiO\textsubscript{2} layer that acts as an electron-collecting scaffold, overcoming thus at the same time both the problems of low adhesion and low electronic conductivity of CN\textsubscript{x}. Such photoanodes are capable of visible light-driven oxygen evolution upon deposition of a suitable cocatalyst for water oxidation, typically in form of metal oxide (IrO\textsubscript{x}, CoO\textsubscript{x}, NiO\textsubscript{x}) nanoparticles.[36,34–41] Notably, we found out that one of the crucial problems of the metal oxide nanoparticles as cocatalysts is their parasitic absorption of visible light, blocking thus the light
absorption by the light absorber. This problem could be only partially overcome by using, for example, ultrasmall (1–2 nm) CoO(OH)x nanoparticles that exhibit a larger bandgap and correspondingly better transparency in the visible range due to quantum size effects.[26] This led us to hypothesize that, in contrast to conventional bulk metal oxide-based water oxidation catalysts, a molecular-scale catalyst might be favorable for preventing the undesired light absorption by the catalyst and enabling also more controllable cocatalyst deposition. With this motivation in mind, we turned our attention to water oxidation catalysts based on well-defined molecular polyoxometalates (POMs), such as [Co4(H2O)2(PW9O34)2]10− = CoPOM, a tetra-cobalt-doped polyoxometalate, that have attracted much attention with regards to catalytic applications,[42–46] and have been previously utilized as cocatalysts on various semiconducting metal oxides (e.g., TiO2, Fe2O3) to fabricate photoanodes for light-driven water splitting.[47,48] However, to the best of our knowledge, no studies on CNx-based photoanodes comprising molecular POMs cocatalysts for photoelectrocatalytic water-splitting have been reported so far.

In this report, we describe for the first time a triadic design of a photoanode consisting of porous TiO2 as an electron collector, CNx as a sensitizer for visible light, and CoPOM as a molecular water oxidation catalyst. The triad photoanode enables visible (λ > 420 nm) light-driven oxidation of water to dioxygen at moderate bias potentials (>0.2 V vs RHE). Notably, we show that effective immobilization of CoPOM into the porous structure of the photoanode plays a crucial role in photoanode performance and can be significantly improved using polyethyleneimine (PEI), a cationic polymer that can act as a non-sacrificial, electrostatic linker between the surface of CNx and the CoPOM that are both charged negatively (Scheme 1). The thus achieved optimized immobilization of CoPOM is demonstrated to result in a more efficient transfer of photogenerated holes to water molecules and enhanced oxygen evolution.

2. Experimental Section

2.1. Materials

Fluorine-doped tin oxide (FTO) Pilkington TEC glass was purchased from the XOP company (XOP Glass, Castellón Spain). Deionized water was used for rinsing samples. TiO2 powder (Hombikat UV 100, Sachtleben, Germany, anatase, specific surface area (BET) = 300 m2 g−1, crystallite size < 10 nm) was used to prepare the substrate for CNx deposition. Urea, PEI (50 wt%, dissolved in water), anhydrous ethanol, 2-propanol, acetone, sodium hydroxide, boric acid (99.5%), sodium sulfate, and hydrochloric acid (37%) were purchased from Sigma–Aldrich, Na2WO4·2H2O, Na2HPO4·7H2O, NaCl, and Co(NO3)2·6H2O were provided by Merck.

2.2. Synthesis of CoPOM

The CoPOM complex was synthesized according to literature.[42] Briefly, Na2WO4·2H2O (50.89 g), Na2HPO4·7H2O (4.60 g) and Co(NO3)2·6H2O (9.98 g) were dissolved in 50 mL deionized water in a 200 mL round-bottom flask. The pH was adjusted to 7 by HCl under magnetic stirring. The solution was then stirred and refluxed at 100 °C for 2 h and cooled down to room temperature. CoPOM was finally obtained by recrystallization and washed by deionized water. The purity of CoPOM is confirmed by Attenuated total reflection Fourier transform infrared (ATR-IR) spectroscopy.

2.3. Preparation of FTO/TiO2 Substrates

TiO2 layers on FTO were prepared using an established doctor-blading protocol.[26] Briefly, 0.25 g TiO2 powder (Hombikat UV-100, pure anatase) was added to 1.25 mL anhydrous ethanol. The mixture was treated in ultrasonic bath for 10 min to produce a well-dispersed suspension. The FTO glass substrates with a size of 1.5 × 2.5 cm were first cleaned by acetone for removing residual organic contaminants by ultrasonication for 20 min. The cleaned FTO glass was then etched in 0.1 M NaOH and rinsed with deionized water. Two FTO glass pieces were placed between microscope glasses and fixed using a 3M scotch tape as frame. The FTO/TiO2 substrates were abbreviated as TiO2 in this report.

2.4. Deposition of CNx

CNx was deposited by chemical vapor deposition of urea pyrolysis products according to the previous report.[26] Two pieces of TiO2 electrodes were placed in a Schlenk tube connected to a round-bottom flask containing 1 g of urea. Before the CNx deposition was started, the muffle oven (Carbolite, Germany) was preheated to 425 °C. Then, the reactor was directly placed into the muffle oven and heated at 425 °C for 30 min. Finally, the reactor was cooled down to room temperature in air. The resulting electrodes are denoted as CNx-TiO2.

2.5. Immobilization of CoPOM on CNx-TiO2

First, CoPOM (5 × 10−3 m) and PEI (6 × 10−3 m, based on monomer) solutions in an aqueous solution of sodium phosphate
(80 × 10⁻³ m, pH 5) and NaCl (137 × 10⁻³ m) were prepared. Then, CNₓ-TiO₂ electrode was first dipped into the PEI solution for 5 min, then rinsed with distilled water and dried in air, followed by dipping in the CoPOM solution for another 5 min. The dipping processes in PEI and CoPOM were alternately repeated for five times to acquire desired amount of CoPOM and the sample was named as CoPOM-PEI-CNₓ-TiO₂. The reference sample without PEI was prepared by dipping CNₓ-TiO₂ only into the CoPOM solution for five times and named as CoPOM-CNₓ-TiO₂.

**2.6. Material Characterization**

The electronic absorption spectra were measured using a UV–vis spectrophotometer (UV-2600, Shimadzu, Japan) equipped with the integrating sphere and the absorptance (Abs.) was calculated by the equation:

\[
\text{Absorptance(%) = 100\% – Reflectance(%) – Transmittance(%) (1)}
\]

The baselines were recorded using an FTO glass and a BaSO₄ plate as references for transmittance and reflectance, respectively. Scanning electron microscopy (SEM) and focused Ga ion beam (FIB) cross sections were performed using a NVision 40 Ar (Carl Zeiss Microscopy, Germany) SEM/FIB crossbeam machine. energy-dispersive X-ray spectroscopy (EDX) investigations were done with the attached Octane Elite (AMETEK EDAX, USA) EDX system. Photoluminescence (PL) spectra were recorded on an RF-6000 spectrofluorophotometer (Shimadzu, Japan) using excitation wavelength of 360 nm with a 400 nm cut-off filter placed in front of the emission detector. ATR-FTIR spectroscopy was performed using a PHI Quantera SXM system (ULVAC-PHI, Japan). The binding energies were calibrated based on C 1s peak of adventitious carbon (284.8 eV).

**2.7. Photoelectrocatalytic Measurements**

The photoelectrochemical measurements were conducted using an SP-300 BioLogic potentiostat and a typical 3-electrode system consisting of a Pt wire counter electrode, a Ag/AgCl (3.5 m KCl, 0.207 V vs SHE) reference electrode and tested photoanodes as working electrodes with geometric irradiation area of 0.5 cm². Photoanodes were irradiated by visible light (λ > 420 nm) using a 150 W Xe lamp (LOT-Oriel) with light power density of ~150 mW cm⁻², equipped with a KG-3 (LOT-Quantum Design) heat-absorbing filter and a 420 nm longpass optical filter. All electrodes were illuminated from backside (through FTO glass). All photoelectrochemical measurements at hybrid photoanodes were carried out at least in triplicate (at three different electrodes), and representative average data is shown.

The charge separation efficiency (ηsep) and the hole transfer efficiency (ηtr) were evaluated using the approach reported by Dotan et al.,[49] and utilizing sodium sulfite as a readily oxidizable reducing agent.[50] The hole transfer efficiency (ηtr) was determined using the equation:

\[
\eta_{\text{tr}} = \frac{J_{\text{HO}}}{J_{\text{NaSO}_2}}
\]

where \(J_{\text{HO}}\) and \(J_{\text{NaSO}_2}\) are the photocurrents measured in the absence and presence of additional hole scavenger (Na₂SO₃), respectively. The charge separation efficiency (ηsep) was estimated by the equation:

\[
\eta_{\text{sep}} = \frac{J_{\text{max}}}{J_{\text{NaSO}_2}}
\]

where \(J_{\text{max}}\) is the maximal photocurrent obtained by integrating the Abs spectrum (Figure 1b) over the AM1.5G solar spectrum (ASTM G-173;[51] 1.5 sun intensity) from 420 to 600 nm with Abs at 600 nm as a baseline.

The oxygen evolution was recorded by the FireSting optical fiber oxygen meter (PyroScience, GmbH) in a home-made air-tight two-compartment cell with the oxygen collection efficiency as ≈75%, which was estimated by a direct electrolysis using a Pt working electrode. The volume of the photoanode compartment was 5 mL. The oxygen concentrations were not corrected for the losses in the gaseous headspace. The electrolyte was purged with argon before the electrodes were illuminated under applied potential of 1.12 V versus RHE. The incident monochromatic photon-to-current conversion efficiency (IPCE) was recorded using a photoelectric spectrometer.
(Instytut Fotonowy Sp. z o.o.) equipped with a tunable monochromatic light source provided with a 150 W Xenon lamp and a grating monochromator with a bandwidth of ≈10 nm. The value of photocurrent density was the difference between current density under irradiation and in the dark in steady-state conditions with a wavelength sampling interval of 10 nm. The IPCE value for each wavelength was calculated according to equation:

$$IPCE(\%) = \left( \frac{i_{ph}}{\lambda P q} \right) \times 100\%$$  \hspace{1cm} (4)$$

where $i_{ph}$ is the photocurrent density, $h$ is 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 electrolyte for all photoelectrochemical measurements was 0.1 M sodium borate electrolyte with pH value of 8.0. Na$_2$SO$_4$ (0.1 M) was dissolved in the electrolyte when photocurrents were measured in the presence of sacrificial electron donor. All potentials are recalculated and reported versus RHE.

3. Results and Discussion

The immobilization of the negatively charged $[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ (CoPOM) water oxidation catalyst onto polymeric carbon nitride is challenging since the surface of carbon nitride is known to be negatively charged due to large amount of unprotonated surface Brønsted base moieties that can be protonated only by highly concentrated strong acids.$^{[52,53]}$ In order to effectively immobilize the anionic CoPOM cocatalyst onto the internal surface of our porous CN$_x$-TiO$_2$ photoelectrodes, we therefore utilized the layer-by-layer technique demonstrated by Jeon et al. for immobilization of CoPOM onto various metal oxides.$^{[47]}$ The CN$_x$-TiO$_2$ electrodes carrying a negative surface net charge were sequentially immersed into a solution of the cationic PEI linker and a solution of molecular CoPOM as compared to, for example, cobalt oxide catalysts that typically show significant light absorption in the visible range due to their fully developed band structure and correspondingly low bandgap, blocking thus partially the visible light absorption by the light absorber.$^{[35]}$

The photoelectrocatalytic properties of our photoanodes were investigated under visible light ($\lambda > 420$ nm) using an appropriate cutoff-filter, in order to effectively shut off the intrinsic UV light absorption of TiO$_2$. The porous TiO$_2$ layer thus serves as an electron-collecting scaffold that transports electrons injected under visible light irradiation from CN$_x$ into TiO$_2$ to the underlying FTO glass support, whereas the oxidizing equivalents (i.e., photoholes) photogenerated in CN$_x$ should be ideally channeled to the water-oxidizing CoPOM catalyst to drive dioxygen evolution from water. First, potential-dependent photocurrents (Figure 2a) were measured for all electrodes utilizing illumination by chopped visible light ($\lambda > 420$ nm, 150 mW cm$^{-2}$) in borate electrolyte (pH 8). As expected, no photocurrents could be detected at the pristine TiO$_2$ substrate since anatase TiO$_2$ cannot be excited by visible light. The photocurrents recorded for the CN$_x$-TiO$_2$ electrode without any CoPOM catalyst are attributed to the photocorrosion processes presumably at the CN$_x$/TiO$_2$ interface as no oxygen evolution was detected at this electrode under identical experimental conditions (see Figure 3). In contrast, the photocurrent values significantly
increased in the presence of both CN$_x$ sensitizer and CoPOM cocatalyst. Importantly, the polymeric PEI linker-containing CoPOM-PEI-CN$_x$-TiO$_2$ photoanode showed the highest photocurrents within the whole potential range and also the highest monochromatic quantum efficiencies (IPCE) measured at a constant bias potential of 1.12 V versus RHE (Figure 2b). Importantly, the CoPOM-PEI-CN$_x$-TiO$_2$ photoanode exhibited also the most negative photocurrent onset potential of 0.2 V versus RHE, which clearly indicates an improved rectifying behavior due to more effective extraction of photogenerated holes from CN$_x$. Figure 2c shows photocurrent transients under the same visible light irradiation conditions at a constant potential of 0.78 V versus RHE, and indicates a relatively good short-term stability of the photocurrent response. Interestingly, for the CoPOM-free electrode (black line), the current spikes after switching on the light and negative current overshoots appearing after the light is switched off become significantly more pronounced. Such spikes and overshoots are a typical fingerprint of intense surface recombination processes,\cite{58} indicating that, in the absence of water oxidation catalyst, the photoholes in CN$_x$ do not undergo the desired interfacial transfer, but instead accumulate in the CN$_x$ layer and subsequently either recombine or induce photocorrosion. In contrast, the current spikes are less pronounced and the overshoots are nearly absent in both CoPOM-containing electrodes, which again indicates that the CoPOM cocatalyst can extract holes generated in the CN$_x$ layer and trigger the desired water oxidation reaction.

In order to shed more light on the factors governing the photosresponse of CoPOM-containing photoanodes, we performed an analysis of charge separation ($\eta_{sep}$) and hole transfer ($\eta_{tr}$) efficiencies according to established protocols.\cite{49,50,59} This analysis is based on the assumption that the measured photocurrent density in water oxidation can be calculated by multiplying the maximum possible photocurrent (obtained from the absorbed photon flux) by $\eta_{sep}$ and $\eta_{tr}$, whereby the hole transfer efficiency $\eta_{tr}$ in the presence of a readily oxidizable reducing agent (here Na$_2$SO$_3$) is taken as 100%; for details see the experimental section. The calculated $\eta_{tr}$ and $\eta_{sep}$ values for the both CoPOM-containing electrodes are depicted in Figure 2d, calculated from data in Figure 2a and Figure S8 (Supporting Information). As expected, both efficiencies show clear dependence on the applied potential as stronger positive applied bias is beneficial for both charge separation and hole transfer. Notably, the charge separation efficiency $\eta_{sep}$ is very similar for both PEI linker-free CoPOM-CN$_x$-TiO$_2$ and PEI-containing CoPOM-PEI-CN$_x$-TiO$_2$, which is also in line with only minor differences in PL spectra of the corresponding photoanodes that are possibly related to slightly more efficient quenching of emissive states in CN$_x$ (Figure S9, Supporting Information). In stark contrast, the CoPOM-PEI-CN$_x$-TiO$_2$ exhibits significantly higher charge transfer efficiencies than CoPOM-CN$_x$-TiO$_2$ in the whole potential range. In other words, these data suggest that the superior photoelectrocatalytic behavior of the PEI linker-containing CoPOM-PEI-CN$_x$-TiO$_2$ photoanode arises from a more efficient
transfer of photogenerated holes from CNx to water, which can be attributed to the higher CoPOM loading due to the beneficial effect of the cationic PEI polymer linker. However, in addition to its beneficial effect on the CoPOM immobilization, a question arises whether the cationic PEI polymer could potentially also act as a sacrificial electron donor that can be simply more easily oxidized than water by holes from CNx. In order to directly address this issue, we measured the photocurrents from the CNx-TiO2 electrode modified with PEI polymer only (dipped in PEI solution five times), and the measurements at PEI-CNx-TiO2 photoanodes were subsequently in four cycles. The deposition of PEI enhanced photocurrents, but a gradual decrease of photocurrents was observed, ending up at the same values as those for the CNx-TiO2 photoanode (Figure 3a). Hence, in the absence of the CoPOM catalyst, the PEI does effectively extract the holes from CNx, but is thereby oxidatively degraded. As a next step, the same protocol was also applied to the CoPOM-PEI-CNx-TiO2 photoanode. Contrary to the gradual decline of photocurrents observed for PEI-CNx-TiO2, the photocurrents at CoPOM-PEI-CNx-TiO2 remain completely stable over all four cycles (Figure 3b). This is also in line with the chronoamperometric photocurrent measurements of the three electrodes (Figure 3c), which show that PEI-CNx-TiO2 exhibits a fast decline in photocurrent due to degradation of PEI in the absence of CoPOM, whereby the photocurrent at CoPOM-PEI-CNx-TiO2 is practically stable. Therefore, we conclude that in the presence of CoPOM, the holes are efficiently transferred from PEI to the CoPOM catalyst where they drive water oxidation, and the cationic PEI linker is thereby effectively stabilized.

Figure 3. Photocurrent stability test recorded under intermittent polychromatic irradiation (λ > 420 nm, 150 mW cm−2) in a borate electrolyte (0.1 M, pH 8) at cathodic sweep of 5 mV s−1 for photoanode with a) and without b) the CoPOM cocatalyst; chronoamperometric curves under illumination showing the degradation of PEI in the absence of CoPOM c).

In order to unambiguously prove the dioxygen evolution at CoPOM modified photoanodes, we performed photoelectrocatalytic OER measurements (Figure 4a) in a borate solution (pH 8) under prolonged (1 h) visible light irradiation (λ > 420 nm, 150 mW cm−2). Both CoPOM-containing hybrid photoanodes, CoPOM-CNx-TiO2 and CoPOM-PEI-CNx-TiO2, clearly exhibit OER activity under visible light illumination. This confirms our assumption that charge transfer from CNx to CoPOM is feasible and that the presence of the CoPOM cocatalyst is necessary to trigger the OER. Importantly, at the PEI-containing electrode the oxygen evolution rate was doubled compared to the counterpart photoanode without PEI. Importantly, no oxygen evolution was observed at the CoPOM-free CNx-TiO2 photoanode despite substantial photocurrents that can be ascribed to photocorrosion.[38] This result is also in line with our previous studies that confirmed that the presence of an effective OER catalyst is absolutely necessary to observe oxygen as a product of water oxidation at CNx-TiO2 hybrid photoanodes.[26,34–41] On the other hand,

Figure 4. Dioxygen evolution a) and corresponding photocurrent transients b); measured under polychromatic visible light irradiation (λ > 420 nm, 150 mW cm−2) at 1.12 V versus RHE in a borate electrolyte (0.1 M, pH 8.0). The oxygen evolution was measured at least at three different electrodes (representative curves are shown), and the error is taken as 2σ (σ = standard deviation; 95% confidence interval).
CNx-free pristine TiO2 photoanodes modified with CoPOM exhibited neither photocurrents nor oxygen evolution since pristine TiO2 does not absorb in the visible range. The apparent (based on dissolved O2 and uncorrected for losses in the head-space) Faradaic efficiencies (FE) of oxygen evolution for CoPOM-PEI-CNx-TiO2 (15% ± 4%) and for CoPOM-CNx-TiO2 (12% ± 4%) are rather low, which suggests that even in the best photoanodes the overall utilization of holes generated in CNx for water oxidation is still far from optimum, and a substantial portion of holes does not induce the OER but instead contributes to the photocorrosion of CNx (Figure 4b). The improved photocurrent onset potential, higher oxygen production rate, and FE at the PEI-containing CoPOM-PEI-CNx-TiO2 photoanode clearly confirm the beneficial effect of the cationic PEI polymer that serves as an effective linker by establishing the electrostatic attraction between the CNx sensitizer and CoPOM catalyst that are both negatively charged. This results in a more efficient hole extraction from CNx and more effective utilization of photogenerated holes for water oxidation due to the more effective immobilization (i.e., higher loading) of the CoPOM water oxidation catalyst.

4. Conclusion

For the first time, a triad photoanode comprising a molecular cobalt polyoxometalate (CoPOM) embedded in the porous structure of hybrid photoanodes consisting of polymeric carbon nitride deposited onto an electron collecting porous TiO2 layer is reported. The photoanodes exhibit complete water oxidation to dioxygen under visible (λ > 420 nm) light irradiation, with photocurrents down to relatively low bias potentials of 0.2 V versus RHE. Importantly, it is demonstrated that PEI, a positively charged cationic polymer that has been previously reported to enable improved deposition of CoPOM onto various metal oxides,[47,48,60] can also act as a highly effective electrostatic linker for immobilization of the anionic CoPOM onto the negatively charged surface of carbon nitride. Mechanistic studies revealed that the optimized deposition of CoPOM using the PEI linker translates directly into improved efficiency of the transfer of photogenerated oxidizing equivalents (holes) to water molecules and thus to enhanced oxygen evolution. On the other hand, the charge separation efficiency in triad photoanodes was largely unaffected by the CoPOM loading, and remained rather low (below 10% at moderate bias potentials), suggesting that primary recombination is a key performance bottleneck in triad photoanodes. Importantly, we also show that the PEI linker is effectively stabilized in the presence of the CoPOM catalyst that efficiently extracts the holes from PEI, preventing thus the oxidative degradation that takes place in the absence of CoPOM. This work thus highlights the importance of careful design of multi-component photoelectrocatalytic systems, and provides a simple protocol for effective immobilization of POM-based catalysts into soft matter-based photoelectrocatalytic architectures for light-driven water oxidation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carbon nitride, oxygen evolution, photoelectrochemistry, polyoxometalates, water splitting

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