

Cite this: *Chem. Sci.*, 2024, 15, 13381

All publication charges for this article have been paid for by the Royal Society of Chemistry

A scalable approach using a gC_3N_4 -covalent organic framework hybrid catalyst towards sustainable hydrogen production from seawater and wastewater†

Kiran Asokan,^{ab} T. M. Bhagyasree,^{ab} George Devasia,^{bc} Sailaja Krishnamurthy,^{bc} Sabah Solim,^d Lina Rueda,^d Dhabia M. Al-Mohannadi,^e Mohammed Al-Hashimi,^{id e} Konstantinos Kakosimos^e and Sukumaran Santhosh Babu^{id *ab}

The photocatalytic generation of H_2 using covalent organic frameworks (COFs) is gaining more interest. While numerous reports have focused on the production of H_2 from deionized water using COFs, the inability to produce H_2 from industrial wastewater or seawater is a common limitation in many reported catalysts. Additionally, many of these reports lack a clear path to scale up the catalyst synthesis. In this study, we explore the prospect of hybridizing a COF with gC_3N_4 to create a robust photocatalyst for efficient H_2 generation. This hybrid exhibits outstanding performance not only in deionized water, but also in wastewater, and simulated seawater. Furthermore, we explore the feasibility of the bulk-scale synthesis and successfully produce a 20 g hybrid catalyst in a single batch, and the synthesis method is scalable to achieve the commercial target. Remarkably, a maximum HER rate of $94\,873\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ and $109\,125\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ was obtained for the hybrid catalyst from industrial wastewater and simulated seawater, respectively. The performance of bulk-scale batches closely matches that of the small-scale ones. This research paves the way for the utilization of organic photocatalysts on a commercial scale, offering a promising solution for sustainable large-scale H_2 production.

Received 28th February 2024
Accepted 5th July 2024

DOI: 10.1039/d4sc01387e

rsc.li/chemical-science

Introduction

The incorporation of renewable resources in energy generation is an essential pillar for a sustainable future. Among the potential alternatives, hydrogen (H_2), the most prevalent molecule in the universe, stands out as a clean fuel with the potential to supplant conventional fossil fuels. This transition to H_2 is driven by advantages including abundance, emission-free combustion, high energy efficiency, and inherent renewability.¹ Nevertheless, the practical adoption of H_2 encounters certain constraints, particularly concerning long-distance transport and extended-term storage. Issues such as flammability pose challenges in the entire supply and demand chain,

and the production of green H_2 at a large scale may entail elevated costs.¹ The conventional methods for H_2 production involve sources such as natural gases, naphtha, heavy oil, coal, and electrolysis, and industrial-scale production primarily relies on the Bosch process.² However, when exploring sustainable avenues for producing green H_2 , one cannot overlook the fact that 71% of our planet is covered with water, making it an abundant source of H_2 . By harnessing solar energy and employing catalytic processes to extract H_2 from water, we have the opportunity to create a bountiful, clean energy source that aligns with the goals of decarbonization.

Over the past decade, organic photocatalysts have gained increasing prominence in the field of water splitting.^{3–5} In 2014, Lotsch and co-workers reported, for the first time, photocatalytic generation of H_2 ($1970\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$) from water using a hydrazone-based covalent organic framework (COF) as the photosensitizer.⁶ Subsequently, numerous research groups have explored the use of various COFs for the photocatalytic generation of H_2 from water.^{7,8} Over time, several strategies have been employed to enhance the stability of photocatalysts and improve H_2 evolution efficiency. They include molecular engineering,^{9,10} multivariate synthesis,¹¹ defect engineering,¹² dye sensitization,¹³ electron transfer mediators,¹⁴ hybridizations,^{15–23} etc. These efforts have led to significant

^aOrganic Chemistry Division, National Chemical Laboratory (CSIR-NCL), Dr Homi Bhabha Road, Pune 411008, India. E-mail: sb.sukumaran@ncl.res.in

^bAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad 201 002, India

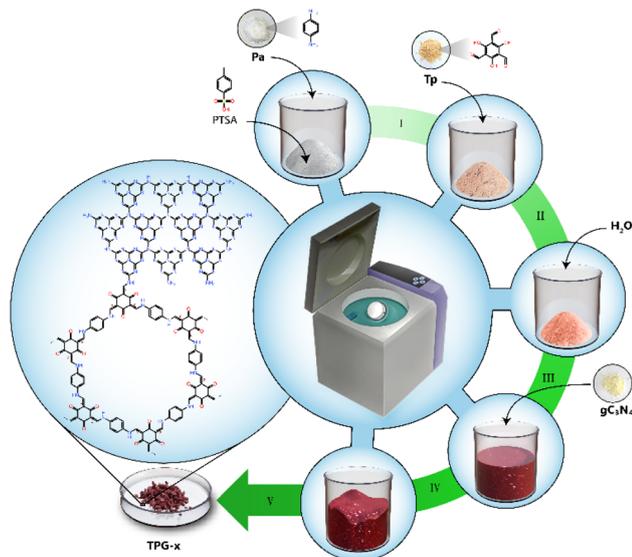
^cPhysical and Materials Chemistry Division, National Chemical Laboratory (CSIR-NCL), Dr Homi Bhabha Road, Pune 411008, India

^dQatar Shell Research & Technology Centre, Qatar Science & Technology Park, Education City, Doha, Qatar

^eChemical Engineering Department, Texas A&M University at Qatar, Doha, Qatar

† Electronic supplementary information (ESI) available: Details of synthesis, characterization of the photocatalysts and HER experiments. See DOI: <https://doi.org/10.1039/d4sc01387e>





Scheme 1 Bulk scale synthesis strategy adopted for the preparation of TPG-*x* photocatalysts. Step I: mix PTSA and Pa in a planetary mixer. Step II: add Tp and mix again. Step III: add an adequate amount of H₂O to the reaction mixture and mix. Step IV: add gC₃N₄ to the reaction mixture and mix. Step V: heat the reaction mixture in an oven at 90 °C, followed by washing and drying to yield the final catalyst in powder form.

advancements in the field, demonstrating the versatility and potential of COFs in sustainable H₂ production. Hybridization of COFs using metallic conductors, MOFs, inorganic semiconductors, and polymers to form heterojunctions within COFs has recently emerged as a strategy for photocatalytic H₂ evolution (PHE).²⁴ Even though COF hybridization with gC₃N₄ was reported earlier, the synthesis procedure follows the solvothermal method which limits the opportunity for bulk-scale synthesis.^{25,26} Moreover, the photocatalytic performance was not up to the mark. Ming *et al.* reported a metal-insulator-semiconductor-based photosystem comprising Tp-COF with polyvinylpyrrolidone (PVP) coated Pt nanoparticles (NPs) for the photocatalytic production of H₂.²⁷ Unlike bare Pt NPs, here the photoexcited π -electrons in the n-type Tp-COF semiconductor were effectively extracted and tunnelled towards Pt NPs through an ultrathin PVP insulating layer which further enhanced the activity. While significant progress has been made in PHE, most high-performing photocatalysts have been tested using deionized water for H₂ production.^{28–45} It's important to note that only a small fraction of Earth's water resources, about 1%, is fresh water. Therefore, exploring PHE from alternative sources such as seawater, industrial wastewater, or non-potable water is of great importance. However, there are limited reports on H₂ generation from seawater using COFs due to the challenges posed by side reactions occurring on the catalyst surface and thereby reducing the efficiency of photogenerated charge carriers in photocatalytic processes.^{46–48}

However, in 2023, Yue *et al.* reported a significant breakthrough with a reasonably high-performance H₂ production

rate of 41 300 $\mu\text{mol g}^{-1} \text{h}^{-1}$ using **Tp-Pa**, outperforming many other organic, inorganic, and hybrid materials employed for PHE from seawater under visible light irradiation.⁴⁹ However, the absence of reports addressing sustainable H₂ production using scalable photocatalysts, despite numerous studies demonstrating high rates of H₂ evolution using various synthetic methodologies, is a significant gap in the research field. Herein, we introduce a hybrid catalyst comprising **Tp-Pa** and gC₃N₄ capable of reasonably high H₂ evolution from both seawater and industrial wastewater. In this work, we aim to tackle two major challenges: (1) H₂ production from industrial wastewater and seawater, and (2) bulk-scale synthesis of the photocatalyst (Scheme 1). These efforts not only expand the application of COFs in environmentally significant areas but also make the technology more accessible for practical, large-scale use.

Results and discussion

All the COFs including hybrid COFs **Tp-Pa-gC₃N₄-*x*s** (TPG-*x*, *x* is the percentage of gC₃N₄ to the total quantity of Tp and Pa and it varies as 10, 25, 50, 75, and 100) were prepared using mechanochemical synthesis on a 2 g scale (Schemes S1† and 1, and Table S1†).⁵⁰ A representative chemical structure of **TPG-*x*** is shown in Scheme 1. All the COFs were characterized by FT-IR and intense peaks at around $\sim 1226 \text{ cm}^{-1}$ (–C–N) and $\sim 1551 \text{ cm}^{-1}$ (–C=C) revealed the formation of a β -ketoenamine linked framework for both **Tp-Pa** and **TPG-*x*s** (Fig. 1 and S1†).

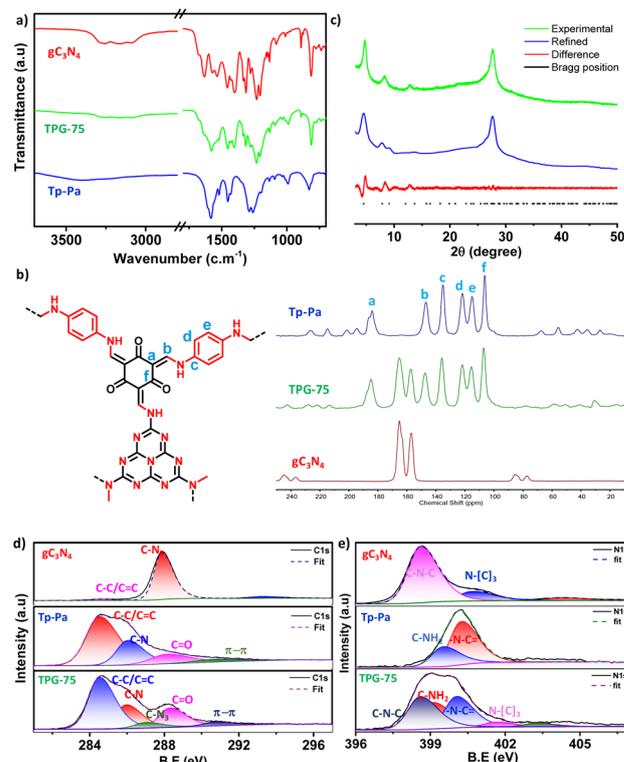


Fig. 1 Comparison of (a) FT-IR, (b) ¹³C CP MAS NMR, (c) PXRD and XPS for (d) C 1s, and (e) N 1s of **Tp-Pa**, gC₃N₄ and **TPG-75**.



Also, the stretching frequencies of nitrogen-containing heterocycles were evident on both gC_3N_4 and TPG-*x*s. A broad peak at around $\sim 3250\text{ cm}^{-1}$ was obtained for gC_3N_4 , which corresponds to the stretching frequency of N-H bonds. Furthermore, the intensity of N-H stretching frequency was reduced for TPG-*x*s, thereby confirming the bond formation between the free aldehyde group of Tp-Pa and NH_2 of gC_3N_4 , which is in line with the previous literature report.^{27,51} Solid-state ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy was utilized to provide evidence of hybrid COF formation. The peaks at around 104.6 and 182 ppm for Tp-Pa and TPG-*x* correspond to $-C=O$ and $-C=C-$ bond formation, respectively; this provided critical insights into the composition and structural characteristics of the synthesized materials, further validating hybrid COF formation and enhancing our understanding of these novel materials. At the same time, pristine gC_3N_4 shows sharp peaks at around 156 and 165 ppm, corresponding to the C-N and C-C bonds of heptazine units. As evident from the graph, hybrid COFs show a gradual increase in the intensity of peaks (heptazine unit) from 0 to 100% of gC_3N_4 in TPG-*x* (Fig. 1 and S2[†]). The crystallinity of the samples was analyzed using powder X-ray diffraction (PXRD). All TPG-*x*s show a sharp crystalline peak around 2θ of 4.8, corresponding to reflection from the (100) plane (Fig. 1 and S3[†]). Similarly, small intense peaks at around 8.07 and 12.9 were also observed, indicating reflection from the (200), and (210) planes, respectively. Apart from this, another peak at 27.5 corresponding to reflection from the (001) plane is also visible, which confirms the π - π stacking arising in the COF. gC_3N_4 shows one sharp intense peak at around $2\theta \approx 27.6$ arising from the stacking of the conjugated heptazine ring.⁵² Notably, the intensity of the peak from the (001) plane increases gradually as the ratio of gC_3N_4 increases because of its overlap with the peak from the (001) plane of Tp-Pa.⁵³ Thermogravimetric analysis (TGA) of COFs shows thermal stability up to 400 °C corresponding to a robust framework. All samples of TPG-*x* showed two major degradation peaks, at around 400 °C corresponding to Tp-Pa and at around 600 °C corresponding to gC_3N_4 (Fig. 1 and S4[†]). The decomposition of all the samples in air points to the composition of the samples.

As a representative example, the detailed characterization of TPG-75 is provided in Fig. 1 and 2. X-ray photoelectron spectroscopy (XPS) revealed the presence of C 1s, N 1s, and O 1s in both pristine and hybrid COFs (Fig. 1 and S5[†]). Furthermore, the C 1s spectrum of gC_3N_4 , Tp-Pa, and TPG-75 was deconvoluted into different peaks.^{27,51} As shown in Fig. 1d, the C 1s spectrum of pristine gC_3N_4 can be deconvoluted into one major individual peak at 287.9 eV corresponding to the C-N bond along with an adventitious carbon peak at 284.6 eV. At the same time, the spectrum of the hybrid COF can be deconvoluted into 4 individual peaks at 284.6, 285.9, 288.3, and 290.7 corresponding to C-C/C=C, C-N, C=O, and π - π interaction, respectively. Similarly, a full survey of the N 1s spectrum reveals the individual N1s peaks of both gC_3N_4 and Tp-Pa in TPG-75 (Fig. 1e). Hence XPS of TPG-75 shows a combination of gC_3N_4 and Tp-Pa. The morphology of the samples was analyzed using Field Emission Scanning Electron Microscopy (FE-SEM) and High-Resolution Transmission Electron Microscopy (HR-TEM)

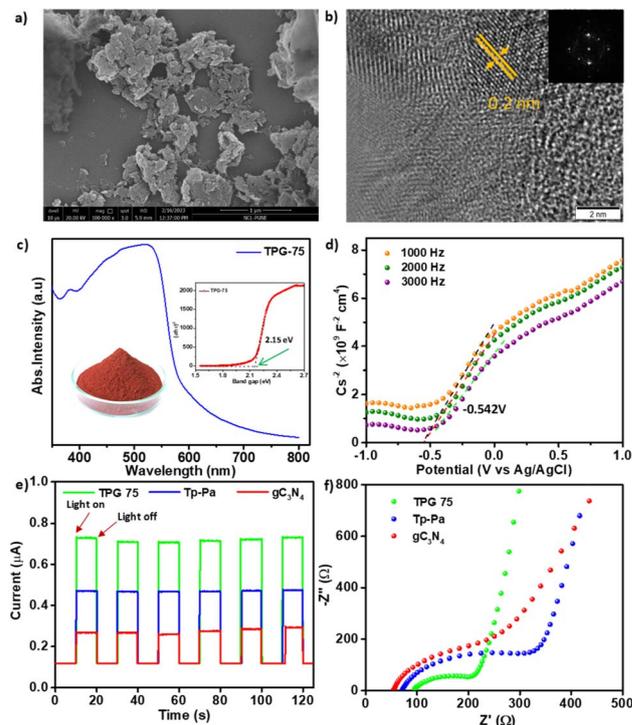


Fig. 2 (a) FE-SEM image of TPG-75. (b) HR-TEM image of TPG-75 showing lattice fringes and d -spacing; SAED pattern is shown as an inset. (c) UV-vis DRS pattern of TPG-75 (inset shows the corresponding Tauc plot). (d) Mott-Schottky measurement of TPG-75. (e) Photocurrent measurements of TPG-75, Tp-Pa, and gC_3N_4 under visible light irradiation on and off conditions with a time interval of 20 seconds. (f) EIS of TPG-75, Tp-Pa, and gC_3N_4 .

(Fig. 2a, b and S6–S12[†]). gC_3N_4 showed a sheet-like morphology with a thickness of around 20–30 nm and stacking of sheets to form a layered structure (Fig. S7[†]). HR-TEM images also confirmed the sheet-like morphology of TPG-75 having crystalline fringes with a d -spacing of 0.2 nm (Fig. 2b). The selected area electron diffraction (SAED) pattern also confirmed the crystallinity of the samples at a lower amount of gC_3N_4 . As the percentage increased, the fringes were not visible, especially for TPG-100 (Fig. S12[†]). At the same time, the characteristic morphology of gC_3N_4 was more evident in TPG-75 and TPG-100 (Fig. S11 and S12[†]). Elemental mapping using Scanning Tunneling Electron Microscopy (STEM) was also carried out and it confirmed the presence of C (81%), N (15%), and O (4%) in TPG-75 (Fig. S13[†]).

The permanent porosity and surface area of the samples were analyzed using Brunauer–Emmett–Teller (BET) and Density Functional Theory (DFT) pore size distribution methods. TPG-*x*s showed a lower surface area compared to pristine Tp-Pa due to the incorporation of gC_3N_4 . A BET surface area of $652\text{ m}^2\text{ g}^{-1}$ was obtained for TPG-75 which is less compared to the surface area of Tp-Pa ($1171\text{ m}^2\text{ g}^{-1}$). It is to be noted that gC_3N_4 exhibited a very low surface area of $87\text{ m}^2\text{ g}^{-1}$ and increasing gC_3N_4 content gradually decreased the surface area of TPG-*x*s (Fig. S14–S20[†]). Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was used to measure the



absorption features and all COFs exhibited a broad absorption ranging from 300 to 750 nm whereas the absorption of gC_3N_4 is limited to 300 to 400 nm (Fig. S21[†]). The optical energy band gaps were calculated from the Tauc plot for all catalysts and it was found that gC_3N_4 has a broader band gap of 3.1 eV whereas **Tp-Pa** exhibits a narrow band gap of 2.14 eV (Fig. 2c). The obtained band gap values are comparable with previously reported values.^{27,51} The band gap of **TPG-75** was 2.15 eV, which is similar to the band gap of **Tp-Pa** (Fig. S22[†]). At the same time, the Mott-Schottky measurements exhibit a positive slope denoting n-type semiconductor characteristics for the hybrid catalyst (Fig. 2d), pristine gC_3N_4 , and **Tp-Pa** (Fig. S23[†]). In order to understand the light responses, the photocurrent measurement of **TPG-75** was conducted and compared with that of **Tp-Pa** and gC_3N_4 (Fig. 2e). **TPG-75** shows a higher photocurrent response compared to **Tp-Pa** and gC_3N_4 during several on-off photoirradiation cycles under identical experimental conditions. A sequential increment in photoresponse was noticed from **Tp-Pa** to gC_3N_4 and further to **TPG-75**. Furthermore, the results from the electrochemical impedance spectra (EIS) reveal a notable reduction in charge transfer resistance for charge separation in **TPG-75** compared to that of **Tp-Pa** and gC_3N_4 (Fig. 2f). These findings collectively affirm that the hybridization process has brought about a substantial enhancement in charge separation within the COF platform.

PHE of all hybrid COFs, **Tp-Pa**, and gC_3N_4 was carried out in a quartz round bottom flask of 50 mL capacity under visible light irradiation in the presence of SED and a cocatalyst. In a typical experiment, 5 mg of catalyst was dispersed in an aqueous solution of 0.056 M (200 mg) ascorbic acid (AA) in 20 mL H_2O . PVP-coated Pt NPs were synthesized according to the reported literature⁵⁴ and used as such as the cocatalyst. The HER rate of **Tp-Pa** was found to be $26\ 126\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$, which is comparable with that in the previous report (Fig. 3a).⁴⁹ It has to be noted that gC_3N_4 showed no activity with AA as SED under

identical experimental conditions (Fig. 3a). Surprisingly, hybrid catalysts with different percentages of gC_3N_4 performed much better than **Tp-Pa**, delivering a nearly three-fold increase in activity. For instance, **TPG-75** showed a remarkably high catalytic activity of $85\ 617$ and $179\ 064\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ under visible light and simulated solar light illumination, respectively (Fig. 3b). An increase in activity under simulated solar light can be attributed to the high light absorption and generation of more electron-hole pairs by the hybrid catalyst. An increase in gC_3N_4 content resulted in high photocatalytic activity up to 75 wt% gC_3N_4 ; however, **TPG-100** showed lower performance than **TPG-75** (Fig. 3a).

Optimizations in PHE was performed by varying quantities of the catalyst, SED, and cocatalyst. The effect of the photocatalyst amount was evaluated with **TPG-75** under standard conditions. With 2 mg and 10 mg catalyst loading under the same optimized conditions, a maximum of $129\ 416\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ and $38\ 717\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ of HER rate was obtained, respectively (Fig. S24[†]). Although the rate is high for 2 mg of **TPG-75**, the cumulative production of H_2 was only $1294\ \mu\text{mol}$ compared to $2030\ \mu\text{mol}$ with a 5 mg catalyst and $1770\ \mu\text{mol}$ with a 10 mg catalyst. At the same time, a reduction in production was observed with 10 mg of the **TPG-75** catalyst because more catalyst concentration can hinder light absorption. After confirming the optimum catalyst amount, the quantity of SED used was optimized. Initially, 100 mg SED was used by keeping other conditions the same and tested for PHE. It was noted that by increasing the AA quantity from 100 to 200 mg, a drastic increase in the HER rate was observed. Furthermore, an increase in AA from 200 to 300 and 400 mg yielded nearly the same HER rate (Fig. S25[†]). Later, the quantity of PVP-Pt NPs was optimized with 5 mg of **TPG-75**, and upon increasing the loading of PVP-Pt NPs from 100 to 400 μL , a decrease in H_2 evolution was observed (Fig. S26[†]). The optimization experiments concluded that a combination of 5 mg of **TPG-75**, 20 mL H_2O , 200 mg of AA, and 100 μL of PVP-Pt NPs is the optimum condition for the HER. Different sacrificial agents were screened for the PHE studies of **TPG-75**. Besides AA, triethanolamine, sodium ascorbate (SA), lactic acid, and citric acid were used for PHE. Interestingly, **TPG-75** showed a steady performance of $26\ 433\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ with SA as SED. At the same time, the hybrid catalyst did not show any H_2 evolution with other SEDs (Fig. S27[†]). **TPG-75** exhibits a more remarkable performance than many of the reported COF catalysts in terms of PHE from deionized water (Table S2[†]). The enhanced HER activity has arisen from the synergistic effect of **Tp-Pa** and gC_3N_4 parts in the **TPGs**.

As an extensive study, we employed our catalyst in the photocatalytic HER from water sources other than deionized water (Table S3[†]). First, the performance of **TPG-75** was studied in industrial wastewater containing 0.1% formic acid, propionic acid, and butyric acid. **TPG-75** could give a $109\ 432\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ HER rate under visible light irradiation and optimized conditions (Fig. 3c). This is the highest value reported for any organic photocatalyst from industrial wastewater.⁵⁵ Also, the performance of the same catalyst with processed seawater was $90\ 602\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ which is also the best performance, higher than

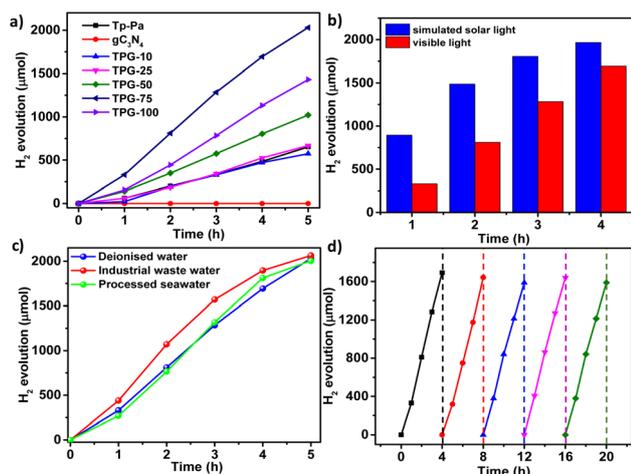


Fig. 3 (a) Comparison of the HER rate of **TPG**-xs with **Tp-Pa** and gC_3N_4 . (b) Comparison of the HER rate of **TPG-75** with visible light and simulated solar light. (c) Comparison of the HER rate of **TPG-75** with different water sources. (d) Cycling stability of the PHE of **TPG-75** with deionized water up to 5 cycles.



that from deionized water under similar conditions of PHE. From these studies, we found that the performance of the catalyst is not degrading in wastewater and processed seawater and is stable in both cases to deliver a good HER. The reusability and cycling studies of the hybrid photocatalyst under the optimized conditions under visible light irradiation were conducted, and it was found that the photocatalyst is stable with similar performance for more than 5 cycles (Fig. 3d). The recycled sample was filtered again, recovered fully, and tested for chemical and morphological changes, if any. It is worth noting that even after repeated cycles, the catalyst remained the same without any considerable physical or chemical degradation. HR-TEM images show layered sheet-like morphology with Pt NPs of size 2–4 nm embedded in the sheet (Fig. S28†). STEM analysis and elemental mapping of the sample were also conducted which proved the incorporation of Pt NPs all over the surface and between layers of TPG-75 (Fig. S29†). In addition, Pt NPs were distributed in a segregated way all over the catalyst surface owing to the affinity of NPs to the heteroatoms of the hybrid catalyst. The FT-IR spectrum of the recycled catalyst shows no extra peak confirming the stability of the catalyst (Fig. S30†). To understand this further, the HER was performed by physically mixing **Tp-Pa** and **gC₃N₄** in the same ratio as that adopted for TPG-75 before irradiation. Interestingly, we could observe a decline in the HER compared to TPG-75 (Fig. S31†). This indicates the need to physically connect the two components to boost HER performance. The apparent quantum yield (AQY) of the best-performing sample TPG-75 was investigated at different wavelengths. For this, monochromatic wavelength filters ranging from 450, 500, and 550 nm were chosen for irradiation. Interestingly, an AQY of 10.4% was obtained for TPG-75 in deionized water at 450 nm whereas 8.34% and 4% AQY were obtained at 500 nm and 550 nm, respectively. The performance of TPG-75 was also studied under direct sunlight. In a typical experiment with the same optimized conditions, the performance of TPG-75 under direct sunlight was nearly comparable with the H₂ evolution using a solar simulator (Fig. S32†). However, the intensity of light irradiation controls the H₂ evolution in direct sunlight experiments (Fig. S32†). It is clearly understood that a similar performance of TPG-75 under a solar simulator was retained with half the light intensity under direct sunlight. The intensity of the light used from the solar simulator was 300 mW cm⁻² whereas the average intensity from sunlight was nearly 152 mW cm⁻².

To understand the synergistic effect between pristine COF and **gC₃N₄** in hybrid TPG-*x*, different experiments were conducted. The steady-state emission spectrum of the hybrid photocatalyst was measured and compared with that of **Tp-Pa** and **gC₃N₄** (Fig. S33†). Accordingly, **gC₃N₄** shows an emission peak at around 445 nm; however, **Tp-Pa** and TPG-*x* were not emissive. In fact, the emission of the **gC₃N₄** counterpart in TPG-*x* was quenched due to the charge transfer (CT) between **Tp-Pa** and **gC₃N₄** and this was supported by a decrease in emission lifetime of **gC₃N₄** in the presence of **Tp-Pa** (Fig. S34 and Table S4†). To elucidate this assumption, we performed additional experiments by preparing control samples. Pristine **gC₃N₄** was ground with different ratios of **Tp-Pa** (100 : 0.01, 100 : 0.05, 100 :

1, and 100 : 5), and the corresponding emission spectra were recorded (Fig. S35†). We could observe a gradual quenching of the emission intensity of **gC₃N₄** upon mixing with **Tp-Pa** (Fig. S36†). The intensity of emission maxima decreased as the amount of **Tp-Pa** increased, along with a slight blue shift in emission maxima. This could point out the CT between **Tp-Pa** and **gC₃N₄**.^{44,56} Correspondingly, the emission lifetime of control samples was also measured (Fig. S37 and Table S5†). The band structure of **Tp-Pa** and **gC₃N₄** was confirmed by ultraviolet photoelectron spectroscopy (UPS) experiments.⁵⁷ From UPS studies, the energy of the valence band maximum (E_{VBM}) was calculated by subtracting the width of the UPS spectrum from the excitation energy of the He I source (21.22 eV). E_{VBM} of **Tp-Pa** and **gC₃N₄** was found to be -7.45 and -6.73 eV, respectively (Fig. S38†). Similarly, the energy of the conduction band minimum (E_{CBM}) was calculated from the Tauc plot and E_{VBM} and was found to be -5.31 and -3.63 eV, respectively.

DFT calculations were used to understand the charge distribution between **gC₃N₄** (001) and **Tp-Pa** (001) surfaces. First, the slab structures of **gC₃N₄** and **Tp-Pa** were optimized for further calculations (Fig. 4a and b). Fig. 4c and d show the electrostatic potential of **gC₃N₄** and **Tp-Pa** where it is observed that the work functions of **gC₃N₄** and **Tp-Pa** are 4.58 eV and 4.71 eV, respectively. Work function differences between the heterojunction integrant give us an idea about charge distribution and hence induce electric field formation. This in turn affects the CT process and separates photogenerated electrons and holes.⁵⁸ As the work function of **gC₃N₄** is smaller than that of **Tp-Pa**, charges will move from **gC₃N₄** to the COF until the

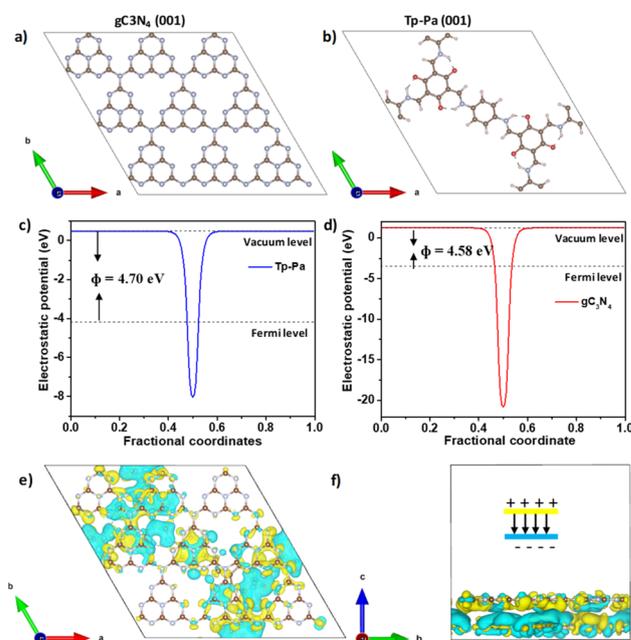


Fig. 4 Optimized slab structure of (a) **gC₃N₄** and (b) **Tp-Pa** COF. Theoretical electrostatic potential of (c) **Tp-Pa** (001) and (d) **gC₃N₄** (001). Three-dimensional calculated charge density difference of the **Tp-Pa/gC₃N₄** heterostructure from the (e) top view and (f) side view.



Fermi level equilibrium is reached. Also, the Fermi level position of Tp-Pa (-4.23 eV) being lower than that of gC_3N_4 (-3.37 eV) will accelerate the CT from gC_3N_4 to **Tp-Pa**. Furthermore, to understand the CT process, the charge density difference between **Tp-Pa** and gC_3N_4 was calculated. For this calculation, a heterostructure model consisting of a 3×3 cell of gC_3N_4 (001) and one unit cell of **Tp-Pa** (001) was taken. We could see that after optimizing, there is a pronounced distortion in the surfaces resulting from the interaction between gC_3N_4 and **Tp-Pa** (Fig. S39[†]). Also, a three-dimensional (3D) charge density differential for the **Tp-Pa/gC₃N₄** heterostructure was obtained to understand the CT process (Fig. 4e and f). The yellow and cyan regions show positive and negative charges on the heterostructure. It is evident from the calculation that **Tp-Pa** is mostly dominated by the cyan region (negative) and gC_3N_4 is mostly dominated by the yellow region (positive) indicating a good amount of charge accumulation and reduction on **Tp-Pa** and gC_3N_4 , respectively. When in contact, the charge accumulation and reduction occur and ultimately cause a band edge bending phenomenon on gC_3N_4 and **Tp-Pa**, respectively. The band bending phenomenon causes the band edge of **Tp-Pa** to move downwards whereas the band edge of gC_3N_4 moves upwards and the PHE of **TPG-xS** can be explained based on these conclusions (Fig. 5). Upon irradiating with light, the electrons of gC_3N_4 and **Tp-Pa** will get excited to higher energy levels. Due to the band bending up/downward phenomenon, the excited electrons of **Tp-Pa** will recombine with the holes of gC_3N_4 , hence decreasing the charge recombination process within gC_3N_4 . Furthermore, the excited state electrons of gC_3N_4 will be transferred to Pt NPs. At the same time, the holes generated in **Tp-Pa** will be carried forward by AA and oxidized to dehydroascorbic acid. The above observation was further confirmed by PHE studies and emission studies of control samples (Fig. S36[†]). It must be remembered that gC_3N_4 is not performing well with AA suggesting that whatever holes were generated in gC_3N_4 could not be transferred to AA and oxidized. Also, from emission, it was evident that due to CT between gC_3N_4 and **Tp-Pa**, the emission of gC_3N_4 was quenched by adding **Tp-Pa**.

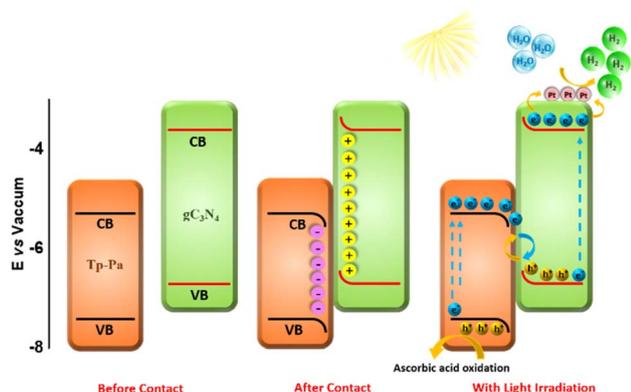


Fig. 5 Band structure of **Tp-Pa** and gC_3N_4 with a plausible PHE mechanism upon irradiating with light.

We prepared **TPG-75** on a 20 g scale using a planetary mixer and the detailed procedure is provided in the experimental section. After extensive washing and purification, **TPG-75-20G** was characterized by ^{13}C NMR, FT-IR, XPS, BET, HR-TEM, PXRD (Fig. S40[†]), FE-SEM, and STEM elemental mapping (Fig. S41[†]). All the experimental results are in line with the small-scale synthesis (2 g) and confirm the suitability of the synthesis protocol for the large-scale production of **TPGs**. PHE of **TPG-75-20G** exhibited a comparable performance of $84\,383\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ with deionized water and no significant reduction in the H_2 evolution rate upon scale-up synthesis (Fig. 6a and b, and Video S1[†]). Similarly, comparable performance to that of **TPG-75** was noticed with processed seawater ($90\,371\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$) and industrial wastewater ($94\,873\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$) (Fig. 6b). To further extend the scope of using the catalyst for the production of H_2 from seawater, we prepared simulated seawater using a standard protocol⁵⁹ and examined it for PHE studies. Using optimized PHE conditions, the performance of **TPG-75-20G** from simulated seawater was found to be $109\,125\ \mu\text{mol g}^{-1}\ \text{h}^{-1}$ which is one of the highest reported values among different photocatalysts studied to date (Fig. 6a). The exceptional increment in the HER rate from simulated seawater can be attributed to the *in situ* polarization of the framework arising from the adsorption of metal salts. The polarization effect plays a crucial role in amplifying the dielectric constant of the organic semiconductor. This, in turn, reduces the exciton dissociation energy, enhancing the charge separation and transfer. Consequently, it facilitates the promotion of H_2 production from seawater.⁴⁹ We compared these results with reported literature on the photocatalytic HER from seawater and found that our sample is one of the best-performing catalysts among organic, inorganic, and hybrid materials (Fig. 6c and Table S6[†]). The cycling stability of **TPG-75-20G** was also investigated, revealing stability for more than 5 cycles with minimal degradation observed in hydrogen evolution using deionized water (Fig. S42[†]).

To further support the results, we have obtained photocurrent responses and conducted EIS studies of **TPG-75-20G** in different water sources. From photocurrent responses, we could

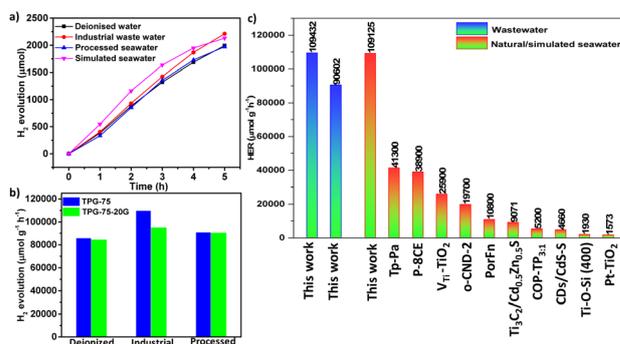


Fig. 6 (a) HER performance of **TPG-75-20G** with different water sources and (b) comparison of HER performance of **TPG-75** and **TPG-75-20G** with different water sources. (c) Comparison of the HER rate of **TPG-75** with that of different hybrid materials reported so far from wastewater and simulated or natural seawater.



see that the light responses of **TPG-75-20G** were more prominent in industrial wastewater and simulated seawater compared to deionized water (Fig. S43†) proving the higher H₂ evolution from industrial wastewater and simulated seawater. The EIS studies also revealed small charge transfer resistance for **TPG-75-20G** with different water sources (Fig. S43†). In short, all the supporting experiments point to the merit of our work to achieve scalable synthesis and remarkable H₂ production from seawater and industrial wastewater.

Conclusions

We present, for the first time, the large-scale synthesis of an organic photocatalyst with outstanding HER efficiency. We successfully synthesized a hybrid photocatalyst based on **Tp-Pa** and **gC₃N₄** through a scalable mechanochemical method and comprehensively characterized it using various experimental techniques. The hybrid photocatalyst exhibited high crystallinity and surface area. Our comprehensive research, incorporating electrochemical methods and theoretical calculation, suggests that the presence of both **Tp-Pa** and **gC₃N₄** components results in synergistic effects. Consequently, the semi-conducting properties of the hybrid catalyst can be finely tuned, making it a promising photocatalyst for H₂ evolution from water. The improved photocatalytic HER rate can be attributed to the enhanced charge dissociation and exciton formation within the hybrid catalyst. Notably, the hybrid catalyst achieves a remarkable photocatalytic HER rate of 85 617 and 179 064 μmol g⁻¹ h⁻¹ under visible light and simulated solar light, respectively. It also performs exceptionally well with different water sources, demonstrating rates of 109 432 μmol g⁻¹ h⁻¹ for industrial wastewater and 90 602 μmol g⁻¹ h⁻¹ for processed seawater. This represents the highest reported rate for a photocatalyst that is effective in deionized water, wastewater, and seawater.

Furthermore, we have explored the bulk synthesis of these photocatalysts, a critical step toward potential industrial applications. A facile mechanochemical synthesis procedure using a planetary mixer enabled us to successfully synthesize 20 g of photocatalyst in a single batch while retaining crystallinity, surface area, and nearly the same H₂ evolution. Remarkable HER rates of 84 383, 90 371, 94 873, and 109 125 μmol g⁻¹ h⁻¹ were obtained for deionized water, processed seawater, industrial wastewater, and simulated seawater, respectively. Our work contributes valuable insights into the development of organic semiconductors for industrial applications, emphasizing scalability and mass production targeting potential commercialization.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

S. S. B. conceived the research idea. K. A. synthesized and characterized COFs and conducted all photocatalytic HER

experiments. B. T. M. designed and performed all the electrochemistry experiments. G. D. and S. K. carried out the DFT calculation and provided the corresponding write-up. The results were regularly discussed and all the contributing authors commented and provided significant suggestions. K. A. and S. S. B. wrote the manuscript with contributions from all authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge the support of this work from the Qatar National Research Fund (QNRF), project number NPRP12S-0228-190188, led and co-funded by the Qatar Shell Research and Technology Center (QSRTC). We thank Flavia Cassiola, Product Quality Lead, Renewable Feedstocks, Shell, for the inputs and feedback on the manuscript.

References

- 1 N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15729–15735.
- 2 K. C. Christoforidis and P. Fornasiero, *ChemCatChem*, 2017, **9**, 1523.
- 3 Y. Li, X. Song, G. Zhang, L. Wang, Y. Liu, W. Chen and L. Chen, *ChemSusChem*, 2022, **15**, e202200901.
- 4 K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang and D. Jiang, *Chem. Rev.*, 2020, **120**, 8814.
- 5 A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166.
- 6 L. Stegbauer, K. Schwinghammer and B. V. Lotsch, *Chem. Sci.*, 2014, **5**, 2789.
- 7 T. He and Y. Zhao, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303086.
- 8 C.-C. Gu, F.-H. Xu, W.-K. Zhu, R.-J. Wu, L. Deng, J. Zou, B.-C. Weng and R.-L. Zhu, *Chem. Commun.*, 2023, **59**, 7302.
- 9 W. Chen, L. Wang, D. Mo, F. He, Z. Wen, X. Wu, H. Xu and L. Chen, *Angew. Chem., Int. Ed.*, 2020, **59**, 16902.
- 10 J. Yang, A. Acharjya, M. Ye, J. Rabeah, S. Li, Z. Kochovski, S. Youk, J. Roeser, J. Grüneberg, C. Penschke, M. Schwarze, T. Wang, Y. Lu, R. Van De Krol, M. Oschatz, R. Schomäcker, P. Saalfrank and A. Thomas, *Angew. Chem., Int. Ed.*, 2021, **60**, 19797.
- 11 T. Zhou, X. Huang, Z. Mi, Y. Zhu, R. Wang, C. Wang and J. Guo, *Polym. Chem.*, 2021, **12**, 3250.
- 12 J. Wang, X.-X. Tian, L. Yu, D. J. Young, W.-B. Wang, H.-Y. Li and H.-X. Li, *J. Mater. Chem. A*, 2021, **9**, 25474.
- 13 Y. Luo, B. Zhang, C. Liu, D. Xia, X. Ou, Y. Cai, Y. Zhou, J. Jiang and B. Han, *Angew. Chem., Int. Ed.*, 2023, e202305355.
- 14 Z. Mi, T. Zhou, W. Weng, J. Unruangsri, K. Hu, W. Yang, C. Wang, K. A. I. Zhang and J. Guo, *Angew. Chem., Int. Ed.*, 2021, **60**, 9642.



- 15 Y.-H. Yao, J. Li, H. Zhang, H.-L. Tang, L. Fang, G.-D. Niu, X.-J. Sun and F.-M. Zhang, *J. Mater. Chem. A*, 2020, **8**, 8949.
- 16 Y.-J. Cheng, R. Wang, S. Wang, X.-J. Xi, L.-F. Ma and S.-Q. Zang, *Chem. Commun.*, 2018, **54**, 13563.
- 17 Y.-H. Yao, Y. Yang, Y. Wang, H. Zhang, H.-L. Tang, H.-Y. Zhang, G. Zhang, Y. Wang, F.-M. Zhang and H. Yan, *J. Colloid Interface Sci.*, 2022, **608**, 2613.
- 18 F.-M. Zhang, J.-L. Sheng, Z.-D. Yang, X.-J. Sun, H.-L. Tang, M. Lu, H. Dong, F.-C. Shen, J. Liu and Y.-Q. Lan, *Angew. Chem., Int. Ed.*, 2018, **57**, 12106.
- 19 H.-Y. Zhang, Y. Yang, C.-C. Li, H.-L. Tang, F.-M. Zhang, G.-L. Zhang and H. Yan, *J. Mater. Chem. A*, 2021, **9**, 16743.
- 20 C.-C. Li, M.-Y. Gao, X.-J. Sun, H.-L. Tang, H. Dong and F.-M. Zhang, *Appl. Catal., B*, 2020, **266**, 118586.
- 21 H. Yan, Y.-H. Liu, Y. Yang, H.-Y. Zhang, X.-R. Liu, J.-Z. Wei, L.-L. Bai, Y. Wang and F.-M. Zhang, *Chem. Eng. J.*, 2022, **431**, 133404.
- 22 Y. Chen, D. Yang, Y. Gao, R. Li, K. An, W. Wang, Z. Zhao, X. Xin, H. Ren and Z. Jiang, *Research*, 2021, **2021**, 9798564.
- 23 M. Luo, Q. Yang, W. Yang, J. Wang, F. He, K. Liu, H. Cao and H. Yan, *Small*, 2020, **16**, 2001100.
- 24 S. Navalón, A. Dhakshinamoorthy, M. Álvaro, B. Ferrer and H. García, *Chem. Rev.*, 2023, **123**, 445.
- 25 P. Dong, A. Zhang, T. Cheng, J. Pan, J. Song, L. Zhang, R. Guan, X. Xi and J. Zhang, *Chin. J. Catal.*, 2022, **43**, 2592.
- 26 M. Luo, Q. Yang, K. Liu, H. Cao and H. Yan, *Chem. Commun.*, 2019, **55**, 5829–5832.
- 27 J. Ming, A. Liu, J. Zhao, P. Zhang, H. Huang, H. Lin, Z. Xu, X. Zhang, X. Wang, J. Hofkens, M. B. J. Roeflaers and J. Long, *Angew. Chem., Int. Ed.*, 2019, **58**, 18290.
- 28 X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W.-H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Nat. Chem.*, 2018, **10**, 1180.
- 29 T. Banerjee, F. Haase, G. Savasci, K. Gottschling, C. Ochsenfeld and B. V. Lotsch, *J. Am. Chem. Soc.*, 2017, **139**, 16228.
- 30 J. Xu, C. Yang, S. Bi, W. Wang, Y. He, D. Wu, Q. Liang, X. Wang and F. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 23845.
- 31 H. Wang, C. Qian, J. Liu, Y. Zeng, D. Wang, W. Zhou, L. Gu, H. Wu, G. Liu and Y. Zhao, *J. Am. Chem. Soc.*, 2020, **142**, 4862.
- 32 K. Gottschling, G. Savasci, H. Vignolo-González, S. Schmidt, P. Mauker, T. Banerjee, P. Rovó, C. Ochsenfeld and B. V. Lotsch, *J. Am. Chem. Soc.*, 2020, **142**, 12146.
- 33 Y.-P. Zhang, H.-L. Tang, H. Dong, M.-Y. Gao, C.-C. Li, X.-J. Sun, J.-Z. Wei, Y. Qu, Z.-J. Li and F.-M. Zhang, *J. Mater. Chem. A*, 2020, **8**, 4334.
- 34 Y. Bai, Y. Liu, M. Liu, X. Wang, S. Shang, W. Gao, C. Du, Y. Qiao, J. Chen, J. Dong and Y. Liu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202113067.
- 35 Y. Yang, N. Luo, S. Lin, H. Yao and Y. Cai, *ACS Catal.*, 2022, **12**, 10718.
- 36 W. Dong, Z. Qin, K. Wang, Y. Xiao, X. Liu, S. Ren and L. Li, *Angew. Chem., Int. Ed.*, 2023, **62**, e202216073.
- 37 S. Ma, T. Deng, Z. Li, Z. Zhang, J. Jia, Q. Li, G. Wu, H. Xia, S. Yang and X. Liu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202208919.
- 38 W. Zhou, Q. Deng, H. He, L. Yang, T. Liu, X. Wang, D. Zheng, Z. Dai, L. Sun, C. Liu, H. Wu, Z. Li and W. Deng, *Angew. Chem., Int. Ed.*, 2023, **62**, e202214143.
- 39 L. Sun, W. Wang, T. Kong, H. Jiang, H. Tang and Q. Liu, *J. Mater. Chem. A*, 2022, **10**, 22531.
- 40 G. Yan, X. Sun, K. Zhang, Y. Zhang, H. Li, Y. Dou, D. Yuan, H. Huang, B. Jia, H. Li and T. Ma, *Small*, 2022, **18**, 2201340.
- 41 B. Cai, L. Cao, R. Zhang, N. Xu, J. Tang, K. Wang, Q. Li, B. Xu, Y. Liu and Y. Fan, *ACS Appl. Energy Mater.*, 2023, **6**, 930.
- 42 L. Dai, A. Dong, X. Meng, H. Liu, Y. Li, P. Li and B. Wang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202300224.
- 43 Z. Li, T. Deng, S. Ma, Z. Zhang, G. Wu, J. Wang, Q. Li, H. Xia, S.-W. Yang and X. Liu, *J. Am. Chem. Soc.*, 2023, **145**(15), 8364–8374.
- 44 H. Zhang, Z. Lin, P. Kidkhunthod and J. Guo, *Angew. Chem., Int. Ed.*, 2023, **62**, e202217527.
- 45 R. Shen, G. Liang, L. Hao, P. Zhang and X. Li, *Adv. Mater.*, 2023, 2303649.
- 46 S. Fukuzumi, Y.-M. Lee and W. Nam, *ChemSusChem*, 2017, **10**, 4264.
- 47 K. C. Ranjeesh, L. George, A. Maibam, S. Krishnamurthy and S. S. Babu, *ChemCatChem*, 2021, **13**, 1717.
- 48 Y. Lu, Y.-X. Liu, S. Cao and X.-Y. Yang, *Photo-Driven Seawater Splitting for Hydrogen Production*, ed. X.-Y. Yang, Springer Nature Singapore, Singapore, 2023, pp. 99–164.
- 49 Q. Yue, G. Li, P. Fu, B. Meng, F. Ma, Y. Zhou and J. Wang, *Nano Res.*, 2023, **16**, 6251.
- 50 K. Asokan, M. K. Patil, S. P. Mukherjee, S. B. Sukumaran and T. Nandakumar, *Chem.–Asian J.*, 2022, **17**, e202201012.
- 51 D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo and J. Tang, *Angew. Chem., Int. Ed.*, 2014, **53**, 9240.
- 52 H. Ou, L. Lin, Y. Zheng, P. Yang, Y. Fang and X. Wang, *Adv. Mater.*, 2017, **29**, 1700008.
- 53 S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524–19527.
- 54 Z. Tang, D. Geng and G. Lu, *J. Colloid Interface Sci.*, 2005, **287**, 159–166.
- 55 S. S. Tak, O. Shetye, O. Muley, H. Jaiswal and S. N. Malik, *Int. J. Hydrogen Energy*, 2022, **47**, 37282.
- 56 K. Wang, Y. Zhong, W. Dong, Y. Xiao, S. Ren and L. Li, *Angew. Chem., Int. Ed.*, 2023, **62**, e202304611.
- 57 J. Xu, C. Yang, S. Bi, W. Wang, Y. He, D. Wu, Q. Liang, X. Wang and F. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 23845–23853.
- 58 Q. Xu, L. Zhang, J. Yu, S. Wageh, A. A. Al-Ghamdi and M. Jaroniec, *Mater. Today*, 2018, **21**, 1042.
- 59 J. Lyman and R. H. Fleming, *J. Mar. Res.*, 2018, **3**, 134–146.

