1. INTRODUCTION

As a consequence of the growing demand for clean energy, there has been extensive research in recent decades aimed at replacing conventional fuels with carbon-free energy sources. A higher energy density $\text{H}_2\text{O}_2$ (3.0 MJ L$^{-1}$) has been projected as a potential energy carrier that is relatively free from storage and transport issues. Furthermore, $\text{H}_2\text{O}_2$ has generated substantial interest as a potential, sustainable route. However, even with significant advances in metallic and nonmetallic photocatalysts (PCs), existing photocatalytic systems can only generate low yields of $\text{H}_2\text{O}_2$.

Among nonmetallic photocatalysts, carbon–nitrogen (C–N)-based materials have attracted much attention, as they have a suitable conduction-band edge to carry out the two-electron transfer photochemical $\text{O}_2$ reduction reactions (PCORR) for $\text{H}_2\text{O}_2$ generation. It is also possible to improve their catalytic efficiency by simple structural modifications, where various strategies including alkali metal doping, cocatalyst loading, structural/heterostructural engineering, band alignment, structural defects/vacancy center creation, and surface shielding have been adopted.

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Hirai and co-workers reported the synthesis of a metal-free pyromellitic diimide-doped carbon nitride (g-C$_3$N$_4$/PDI) photocatalyst hybridized with reduced graphene oxide (rGO) for photochemical production of H$_2$O$_2$. They successfully generated nearly 20 mM H$_2$O$_2$ by O$_2$ reduction in 90% (v) 2-propanol/water using a 1.7 g L$^{-1}$ photocatalyst suspension for 9 h irradiation, which is the highest reported solar H$_2$O$_2$ production yet obtained via O$_2$ reduction in the presence of a sacrificial agent. Recently, Quan et al. reported that the synergistic effect of Na$^+$, K$^+$ dopants and N vacancies on C$_3$N$_4$ resulted in a H$_2$O$_2$ production rate of 10.2 mM h$^{-1}$, which is 89.5-fold higher than that of pristine C$_3$N$_4$. Unfortunately, despite the extensive efforts toward a polymeric structured g-C$_3$N$_4$ (triazine $\rightarrow$ tri-s-triazine) synthesis, including doping and defect and structural engineering, the highest values obtained for H$_2$O$_2$ production on the g-C$_3$N$_4$ based photocatalysts such as g-C$_3$N$_4$/PDI/rGO and Na$^+$, K$^+$/g-C$_3$N$_4$ are similar to those reported earlier for metal oxides, sulfides, and molecular photocatalysts. Indeed, in all reported studies, the main obstacle for developing solar-driven H$_2$O$_2$ production as a suitable alternative is the low yield of H$_2$O$_2$ generated.

There is, therefore, a pressing need for the development of an effective photocatalyst that could greatly increase photocatalytic H$_2$O$_2$ production. Stimulated by the earlier reported strategies, we have synthesized a new photocatalyst that combines properties including a higher intrinsic surface area, modified electronic structure, reduced band gap, and defect sites for enhanced H$_2$O$_2$ production. To this end, we have successfully synthesized an alkali metal-halide (MX, M = K$^+$; Li$^+$, X = Cl$^-$) modulated C-N based poly(heptazine imide) (PHI) molecular photocatalyst, MX $\rightarrow$ PHI for PCORR to produce a much higher yield of H$_2$O$_2$ (73.4 mM h$^{-1}$) than obtained previously. The present structurally modulated MX $\rightarrow$ PHI photocatalyst was synthesized by facile polymerization of an environmentally benign precursor, urea, in the presence of alkali metal halides. A combination of microscopic, spectroscopic, and optoelectronic techniques verified the successful intercalation of MXs, found that the 3D-hollow fibers had a lamellar structure, and verified a broadening of the light absorption range and an enhanced light absorption ability of the synthesized catalyst, leading to substantially increased H$_2$O$_2$ production rates. Our work clearly demonstrates the potential of MX $\rightarrow$ PHI for PCORR generating high yields of H$_2$O$_2$.

Figure 1. Alkali metal halide incorporated lamellar fiber structured PHI molecular photocatalyst. (a) Schematic illustration highlighting the growth mechanism of hollow fiber MX $\rightarrow$ PHI particles/rods. The conceptual graphic shows the deep penetration of solar light, light radiation trapping, and O$_2$ gas molecule absorbance/confine resulting in photochemical performance enhancement. (b) HAADF-STEM image of agglomerated MX $\rightarrow$ PHI. (c) HRTEM image of individual MX $\rightarrow$ PHI particles with associated fast Fourier transform (FFT) (d). (e) HRTEM image of MX $\rightarrow$ PHI particles with superimposed structure (C, N, and embedded alkali metal halides atoms colored in gray, blue, and red, respectively). (f) HAADF-STEM image and corresponding XEDS maps for carbon, nitrogen, potassium, chlorine, and oxygen. All elements appear to be distributed homogeneously within an agglomerated region.
2. RESULTS AND DISCUSSION

2.1. MX → PHI Growth and Characteristics Evaluation. Solid-state polymerization of tri-s-triazine structured metal-doped g-C₃N₄ typically involves two steps: thermal condensation of nitrogen-rich precursors (urea, melamine, etc.) followed by ionothermal polymerization of the C−N based polymer. The present highly photoactive MX → PHI photocatalyst was, however, directly synthesized from urea using a single-step ionothermal polymerization. To analyze the growth of the MX → PHI photocatalyst, two separate sets of experiments were performed. The samples collected at 350 and 500 °C during ionothermal polymerization of urea were denoted as MX → PHI₃₅₀ and MX → PHI₅₀₀, respectively, and the growth process is illustrated schematically in Figure 1a.

The morphologies of MX → PHI₃₅₀, MX → PHI₅₀₀, and MX → PHI (the final product after 5 h polymerization at 550 °C) were characterized by scanning electron microscopy (SEM) to substantiate the growth mechanism (Figures S1–S6). The SEM micrographs of solidified MX → PHI₃₅₀ (Figure S1) revealed coiling of thin polymeric sheets of basic carbon nitride (BCN) to form swirled polymeric hollow fibers/rods at the initial stage of polymerization, which later transformed into highly crystalline hollow fibers/rods (Figures S3 and S5). Furthermore, the presence of alkali metal-halide ions results in the polymeric sheets folding to achieve energetically favorable hollow fibers, with a self-shaping crystal growth mechanism. MX → PHI therefore has a 3D-hollow fiber morphology which consists of macroporous lamellar walls with a higher thickness compared to triazine structured BCN, which has an aggregated sheetlike morphology (Figures S7 and S8).

High-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images (Figure 1b) revealed that the MX → PHI materials have aggregates of nanosized particles and rods. High-resolution TEM images of an MX → PHI particle (Figure 1c,d, and Figure S9) confirm the crystalline nature of MX → PHI. Characteristic distances of 10.57 Å, corresponding to the (110) plane in poly(heptazine imide), and 3.25 Å, corresponding to the (001) plane were found. The poly(heptazine imide) structure can be matched to features in the HRTEM images (Figure 1e) and the Fourier transform of a simulated HRTEM image contains low-frequency peaks that match those in the Fourier transform of the experimental images (Figure S10).

The insertion of alkali metal halides was confirmed by X-ray energy dispersive spectroscopy (XEDS) in the STEM. The HAADF-STEM image and corresponding XEDS maps of individual elements (carbon, nitrogen, oxygen, potassium, and chlorine) (Figure 1f) reveal successful and uniform distributions of each element into MX → PHI, which is consistent with the SEM-XEDS data (Figures S2, S4, and S6). The homogeneous distribution of K and Cl throughout the sample demonstrates that ionothermal polymerization of urea results in the diffusion of the alkali metal halide into the growing polymeric unit of the heptazine imide.

X-ray photoelectron spectroscopy (XPS) was used to characterize the surface composition and inductively coupled
plasma-mass spectrometry (ICP-MS) was used to analyze bulk composition of the catalysts and to demonstrate the insertion of alkali metal halides in the PHI framework. The spectra confirm the presence of C, N, O, K, Cl, and Li elements in MX→PHI while only C, N, and O were present in BCN, clearly indicating the doping of MX into MX→PHI (Figure S11). The high resolution C 1s spectrum in MX→PHI showed three peaks at 288.3, 286.4, and 284.9 eV (Figure 2a C 1s). The peaks at 288.3 and 284.9 eV are attributed to C atoms in aromatic N=C=N structures and graphitic C−C, respectively, and are present in both MX→PHI and BCN (Figure S12). However, the peak at 286.4 eV (Figure 2a C 1s) in MX→PHI originates from the C≡N species, as was later corroborated by FTIR analysis. The N 1s XPS spectra (Figure 2a N 1s) display 4 peaks: the peaks at 398.5 and 399.9 eV are assigned to the N atoms within C−N≡C and N−(C)3 in heptazine units; the peak at 401.1 eV belongs to the N atoms in C≡N species or bridging −NHx. Thus, XPS results also confirmed the existence of heptazine frameworks in MX→PHI. Two peaks (293.0 and 295.8 eV) with a doublet separation value of 2.8 eV of K 2p showed the presence of K in MX→PHI framework. The XPS spectra of Cl 2p and Li 1s were measured and the peak assignments confirmed the presence of Cl and Li (Figure 2a). Overall, these results from XPS, STEM-XEDS, and ICP-MS (Table S1) showed the uniform and successful insertion of MX into the PHI framework.

The crystal structure of MX→PHI was characterized by powder XRD measurements. A comparison of XRD patterns of MX→PHI350, MX→PHI500, and MX→PHI showed the appearance of additional diffraction peaks and peak shifts in MX→PHI, while some peaks, initially observed in MX→PHI350, disappeared with increased temperature. The high-intensity diffraction peaks at 8.3° (10.57 Å) and 27.5° (3.25 Å) in the XRD pattern of MX→PHI confirmed the poly(heptazine imide) structure of MX→PHI (Figure 2b−d). The XRD patterns demonstrated that, relative to the 3.20 Å interplanar stacking in the triazine structured BCN (Figure S13b), there is a slightly wider interplanar stacking (3.25 Å) of poly(heptazine imide) units in the perpendicular direction and heptazine unit stacking with about 10.57 Å in-plane periodicity, which are driven by the insertion of MX. The results show that the triazine phase is further polymerized into the polyheptazine phase through a controlled ionothermal polymerization process in the presence of MX under an Ar atmosphere. Thus, the potential changes in interplanar stacking, together with the possible adjustments in the electron-rich π conjugated framework, the in-plane lattice packing, and the edge defects resulting in −C≡N and −NOx functionalization are affirmed upon intercalation of alkali metals and halide ions.40−42

Attenuated total reflectance coupled Fourier transform infrared (ATR-FTIR) (Figure 3a and Figure S14), and Raman (Figure 3b and Figure S15) spectroscopic techniques were used for the characterization of BCN, MX→PHI350, MX→PHI500, and MX→PHI, so that the thermal transformation of urea to MX→PHI in the presence of alkali metals halides could be confirmed (as discussed in Supporting Note S1).
To explore further the textural properties and to provide confirmation of the porous geometry of the 3D hollow fibers/rods in MX → PHI particles, as sketched in Figure 1, N₂ adsorption–desorption measurements were performed at 77 K and isotherms have been reported and discussed in Figure 3c and Figure S16 and Supporting Note S2. The results of SEM, TEM, XPS, XRD, FTIR, and N₂ adsorption–desorption together demonstrate the successful preparation of an alkali metal halide incorporated poly(-heptazine imide) photocatalyst. To test further the suitability of MX → PHI as an efficient photocatalyst for increased photocatalytic H₂O₂ production, the optical properties and charge separation ability of the material were analyzed.

2.2. Optical Properties and Electronic Band Structure.

The high light absorption efficiency of MX → PHI was confirmed by diffuse reflectance UV–visible (DR-UV vis) absorption spectroscopy, reported in Figure 3d. Compared with BCN, the MX → PHI hollow fibers/rods show significantly higher light absorption, both in the UV and visible regions (Figure 3d) as well as a red-shift (Figure 3d, highlighted by the red arrow). The red-shift in the absorption spectrum of the MX → PHI photocatalyst suggests extended π conjugation, and a delocalized aromatic π conjugated system.43,44 The high light absorption efficiency of MX → PHI is probably due to multiple diffuse reflectance inside the nanoarchitecture, leading to trapping and deep penetration of solar radiation. (Figure 1 and Figure S5).

The inset digital images (Figure 3d) of BCN and MX → PHI samples show an apparent color change from white to greenish yellow, which suggests that the bandgap is altered in MX → PHI resulting in extended solar spectrum absorption efficacy. The UV–vis absorption spectra also highlighted an intense band between 350 and 450 nm assigned to a π → π* transition in the s-triazine unit of the C–N based polymers.38,45 The visible region absorption edge and steep visible region absorption edge as well as a red-shift (Figure 3d, inset) for both the materials exhibit two distinctive peaks in Figure 3f and Figure S19, respectively. The O₂ TPD profiles (Figure 3f) for both the materials exhibit two distinctive peaks in the temperature range of 150–550 °C and 650–800 °C. The release of chemisorbed and surface lattice O₂ molecules resulted in deoxygenation peaks with maxima at 295 and 445 °C for BCN and MX → PHI (Figure 3f, inset), respectively. As well as a significant peak shift to higher temperature for MX → PHI photocatalyst, the amount of desorbed O₂ based on the peak area, is also ∼4 times higher than for the reference BCN photocatalyst. The positively charged alkali metal encapsulated into the C–N based PHI framework can play a key role in the interaction of O₂ with the surface of the molecular photocatalyst. The TGA thermograms (Figure S19) further complemented the O₂ TPD results, as a steady weight loss in the temperature range of 25–550 °C was observed for MX → PHI, possibly because of adsorbed water molecules and atmospheric gases.

Since light harvesting, energy band structure, surface area, and charge carrier separation efficiency are the main factors affecting the performance of photocatalysts, from the factors discussed above, we would expect a significantly enhanced solar H₂O₂ production for MX → PHI. The mesoporous character, higher surface area, lamellar hollow fiber structure of MX → PHI, and the presence of alkali metal halides contributed to improving the light absorbance efficiency, the charge carrier separation, and the O₂ gas molecule confinement, which in turn should improve the photochemical performance of MX → PHI for the O₂ reduction reaction.

2.3. Solar H₂O₂ Production.

The photochemical H₂O₂ production performance of the visible light absorber MX → PHI (E_{BG} = 2.67 eV) has been comprehensively investigated under UV–visible light. First, to optimize the reaction conditions of the particulate photocatalytic system for...
maximized solar H₂O₂ production on MX → PHI, a variation in reaction solvent was examined. The solar H₂O₂ production profiles for three different electron and proton donor aliphatic alcohols at a fixed concentration of 10 M are reported in Figure 4a, demonstrating that ethanol is an optimal solvent for solar H₂O₂ production. The highest solar H₂O₂ production of 146.8 mM was achieved for 2 h irradiation of MX → PHI in 10 M ethanol.

Furthermore, six different concentrations of ethanol in solution were analyzed for maximized solar H₂O₂ production (Figure 4b). As expected, a steady increase in solar H₂O₂ production rate was observed with an increase in the concentration of ethanol. After 2 h of the photochemical reaction, the recorded solar H₂O₂ production rate in 2 M ethanol solution was 24.0 mM h⁻¹, which further increased to 30.4 mM h⁻¹ for 4 M, 38.7 mM h⁻¹ for 6 M, 51.2 mM h⁻¹ for 8 M, and finally reached a maximum of 73.4 mM h⁻¹ for the 10 M ethanol solution. For higher concentrations, no significant increases in the solar H₂O₂ production rate was observed and a nearly constant value of 71.46 mM h⁻¹ for 12 M ethanol was recorded. These results show that a proper balance can be achieved between the generated ions (H⁺ and O₂⁻) and their mobilities in the liquid phase to perform the proton and electron transfer for the solar H₂O₂ production reaction (O₂⁻ + 2H⁺ + e⁻ → H₂O₂), using a 10 M ethanol solution. An excess of electron and proton donors may impede the surface reaction at the solid−liquid interface, preventing the accessibility of reactants and the mobility of charged reaction intermediates. An additional experiment with different aliphatic alcohols having a fixed water content (50 vol %) was also performed (Figure 4c and Supporting Note S3). Furthermore, to identify the optimized photocatalyst concentration in the reaction solution, three different suspension concentrations of MX → PHI (0.5, 1.0, and 1.5 g L⁻¹) in 10 M ethanol were investigated and reported in Figure S20.

The time-dependent solar H₂O₂ production profiles for triazine-based BCN and heptazine imide-based MX → PHI in 10 M ethanol solution (Figure 4d) provide a comparison of their PCORR capabilities. Clearly, triazine-structured BCN displayed a poor efficiency toward 2e⁻ PCORR pathway for solar H₂O₂ production and only generated 0.98 mM H₂O₂ after 2 h of UV−vis irradiation (Figure S21). In contrast, the alkali metal halide-structure modulated, surface-functionalized MX → PHI demonstrated a significantly higher solar H₂O₂ production (146.8 mM) at a rate of 73.4 mM h⁻¹. The latter is the highest reported value for solar H₂O₂ production that we have found among other particulate photochemical systems, irrespective of photocatalyst type (carbon nitride, metal oxide, metal sulfi de, metal organic-based, hybrid, etc.). Addition-ally, the effectiveness of MX → PHI under the visible light spectrum was also analyzed. For this, solar H₂O₂ production was carried out in O₂ saturated 10 M ethanol solution under visible light irradiation (≥400 nm), while keeping all other conditions the same. Even under visible light irradiation (Figure 4d), MX → PHI gave a high yield of solar H₂O₂ (77.3 mM), which is also the highest among those reported using particulate photochemical systems, so far.
Thus, MX → PHI resulted in nearly 150 times higher solar H2O2 production than that of BCN under UV−visible irradiation and >4250 times higher solar H2O2 production as compared to BCN under visible light irradiation. As discussed earlier (Figure 1), the significantly enhanced photocatalytic performance of MX → PHI is a consequence of a combination of factors: the synergistic effect of the morphology and optical and electronic properties induced by the structure-modulation of poly(heptazine imide) with alkali metal halides through controlled ionothermal polymerization.

The pH of the reaction solution may also have a significant effect on the proton-coupled electron transfer-assisted solar H2O2 production. Therefore, the photocatalytic production of solar H2O2 was also carried out at pH 4 and pH 10 (Figure 4e). The MX → PHI showed a significant decrease in solar H2O2 production with increased pH (pH 10) whereas an insignificant difference was observed in the H2O2 production profile for PCORR carried out at pH 4 and neutral pH solution (without maintaining the pH using acid or base). The results show that no additional pH adjustment steps are required to maximize the performance.

The photocatalytic performance of the as-synthesized MX → PHI for reductive solar H2O2 generation from O2 saturated deionized water (DIW) without using any electron and proton donor sacrificial agent was also evaluated to corroborate the greater possibilities and high potential of MX → PHI for unassisted solar fuel production. A significant amount of solar H2O2 production (74.0 μM) in the initial 15 min of light irradiation over bare MX → PHI was observed under UV−visible light irradiation (Figure 4f), which is also comparable to some of the most recently reported photocatalytic systems.15,18,32 A relatively low solar H2O2 production and SCC efficiency in the absence of a sacrificial agent is probably due to the consecutive decomposition of photogenerated H2O2 on the MX → PHI surfaces during the photochemical reaction, which explains why the self-oxidation of photogenerated H2O2 resulted in the saturation of the H2O2 production after 30 min of irradiation (Figure 4f).

The cyclic photocatalytic performance of MX → PHI was examined under the same reaction conditions for three repeated runs (Figure 5a). The linear increase in solar H2O2 production for each run demonstrated a sustained photocatalytic activity of MX → PHI. To substantiate further the unchanged surface structure and intact optical properties of MX → PHI during the PCORR recyclability tests, the samples collected after each run were analyzed by DR-UV−vis (Figure 5b) and FTIR (Figure 5c) spectroscopy. The FTIR spectra for each collected sample at the end of PCORR did not show any significant change in the vibration peak positioning and their intensities (Figure 5c). However, relative to the original MX → PHI sample, the absorption spectra for MX → PHI collected after the first and second runs displayed a slight improvement in light absorption, with a red-shift and extended tailing (Figure 5b). The extended tail may correspond to minor changes in the surface functionality of the polymeric structure of MX → PHI, as a result of photoactivation during PCORR.

The cyclic photochemical performance (Figure 5a), spectroscopic examinations (Figure 5b,c) and N2 adsorption−
desorption studies (Figure S22) showed that the photoactivity, chemical structure, and texture properties of the MX → PHI photocatalyst remained largely unchanged during the repeated experiments.

The apparent quantum yield (AQY) of MX → PHI for solar H2O2 production was also measured using 365 and 450 nm light irradiation. The AQY values obtained for H2O2 production at 365 nm (UV light) and 450 nm (visible light) are ~96% and 21%, respectively, for MX → PHI with a catalyst dosage of 1 g L⁻¹ in 10 M ethanol (Figure S23). These values are higher than those reported for previous photocatalysts for peroxide production, indicating that MX → PHI is a highly efficient molecular photocatalyst for sustainable solar H2O2 production via a 2e⁻ pathway. AQY values for PCORR to H2O2 matched well with the DR-UV visible spectrum of MX → PHI proving that the PCORR is via a 2e⁻ process.

The reaction kinetics of 2e⁻ PCORR to H2O2 over the surface of irradiated BCN and MX → PHI photocatalysts was investigated using the kinetic model of photochemical H2O2 generation at the initial phase of reaction reported by Hoffmann and co-workers as follows: [H2O2] = (k_f/k_d)(1 − e⁻k_dτ) + [H2O2]_0 e⁻k_fτ. Here, k_f and k_d are the rate constants for photochemical H2O2 formation and decomposition reactions, respectively. Following the reaction kinetics, the H2O2 formation rate is determined by zero-order kinetics because the reaction solution is continuously purged with O2, while the decomposition reaction rate with fixed initial H2O2 concentration follows first order kinetics. The k_d value for MX → PHI (0.00208 min⁻¹) (Figure 5d, inset), obtained after fitting the H2O2 photodecomposition profile (Figure 5d) to first-order reaction kinetics, was slightly greater than that of triazine structured BCN (0.00183 min⁻¹). However, a large difference between k_f values of MX → PHI (1.2233 mM min⁻¹) and BCN (0.0085 mM min⁻¹) was observed. The kinetic data demonstrate that solar H2O2 production is primarily governed by the formation kinetics. Furthermore, electrochemical rotating disc electrode (RDE) analysis confirms the 2e⁻ O₂ reduction pathway to H2O2 generation rather than 4e⁻ (H₂O formation) over MX → PHI (Figure 5e,f). The calculated electron transfer number from the slopes of the linearly fitted Koutecky–Levich (K–L) plots at the different potentials (Figure Sf) was around 2.06.

Furthermore, to validate the generation of O₂^•⁻ (superoxide anion radical) intermediate reaction species during photochemical H2O2 production over the MX → PHI surface, the in situ coloration of XTT (2,3-bis-(2-methoxy-4-nitro-5-sulfo-phenyl)-2H-tetrazolium-5-carboxanilide) when reacted with photogenerated O₂^•⁻ into orange colored XTT-formazan (Figure S24a) has been used. The appearance of the dark orange color (Figure S24b) and absorbance λ_{max} around 481 nm (Figure S24c) illustrated the generation of the O₂^•⁻ reaction intermediate during PCORR over MX → PHI.

Considering the exceptional solar H₂O₂ production performance of MX → PHI via the 2e⁻ PCORR pathway in an organic solvent, a comparison was drawn with previously reported photocatalysts for similar reaction systems. The present MX → PHI photocatalyst exhibited a higher solar H₂O₂ production rate than that of most of the carbon nitride, metal oxide, metal sulfide, and metal organic-based photocatalysts, respectively (Table S2).

3. SUMMARY AND CONCLUSIONS

We successfully achieved the highest ever solar H₂O₂ production rate (73.4 mM h⁻¹) via the 2e⁻ PCORR pathway on an alkali metal-halide modulated poly(heptazine imide) (MX → PHI). Compared to the triazine structured pristine carbon nitride, there is an increase of nearly 150 and >4250 times in H₂O₂ production on MX → PHI under UV-visible and visible light (≥400 nm) irradiation, respectively, which reflects the effect of the basic structure of poly(heptazine imide) and the engineering of its morphological, optical, and electronic properties via alkali metal-halides. In particular, combining effective light absorption, charge separation, and O₂ trapping in MX → PHI makes it an exceptionally highly photocatalytic molecular catalyst. Our study provides insight for potential materials based on poly(heptazine imide) for sustainable H₂O₂ production by utilizing natural resources (sun, water, and air).

4. EXPERIMENTAL SECTION

4.1. Synthesis of Bulk Triazine Structured Carbon Nitride (BCN). The BCN was synthesized via thermal pyrolysis of urea at 550 °C for 3 h in a muffle furnace. After the completion of thermal polymerization of urea to triazine structured g-C₃N₄, the product was washed with deionized water and collected by filtration followed by vacuum drying. The dried white product (4.6% yield with respect to urea precursor) was further ground to a fine powder and stored as such for photocatalytic performance characterization.

4.2. Synthesis of Alkali Metal-Halides (MX) Modulated PHI (MX → PHI). The MX → PHI was synthesized by controlled ionothermal polymerization processes. The distinctly structured MX → PHI was obtained by mixing a fixed ratio of urea to KCl−LiCl eutectic mixture (5:3) to carry out the polymerization in a tube furnace under a continuous flow of Ar gas at 550 °C at a ramp rate of 3 °C min⁻¹ for 5 h. The synthesis is sensitive to atmospheric conditions, therefore, Ar gas was continuously purged into the reaction mixture to minimize the O₂ and water content. The greenish-yellow colored product, obtained from the cooled polymerized sample, was washed with DI water and collected by filtration followed by vacuum drying. The dried product was ground into a fine powder with an agate mortar and stored as such in an amber vial for photocatalytic studies and characterization. The final yield of MX → PHI (7.5% with respect to urea precursor) was higher than BCN. Ionothermal polymerization facilitates more uniform doping in the basic framework of the PHI molecular photocatalyst and simultaneously might introduce surface functionality and performance-enhancing structural defects. Moreover, ordering and stabilization of the intermediates result in the synthesis of a highly efficient MX → PHI molecular photocatalyst.

4.3. Photochemical H₂O₂ Production. For particular photochemical experiments, a fixed concentration of 7.5 mL of alcohol solution (C₂H₅–C₃H₇) was placed in the Pyrex glass test tube, followed by the addition of 7.5 mg of photocatalyst (except an experiment including photocatalyst concentration variation). The reaction suspension was subjected to light irradiation with continuous O₂ gas bubbling (~100 cc) throughout the experiment for PCORR. The photochemical performance of BCN and MX → PHI molecular photocatalysts were examined and compared under UV-visible as well as visible light only (≥400 nm) using a 150 W xenon lamp (optical irradiance 175 mW cm⁻²) coupled with an air mass filter (AM1.5G). During the photochemical reaction, 0.5–1.0 mL aliquots were collected at certain time intervals by a syringe and the clear sample was obtained by using a 0.20 μM pore, 15 mm Minisart RC, syringe filter. For the cyclic performance of photocatalysts, 50 mg of photocatalyst suspension (1 g L⁻¹) in 10 M ethanol solution was used so that after each run enough material could be collected. After 2 h of irradiation, photocatalysts were filtered out from the reaction mixture,
washed with DIW, vacuum-dried, and dispersed in 10 M ethanol solution by keeping the same catalyst concentration (1 g L$^{-1}$).

4.4. Hydrogen Peroxide Detection. The H$_2$O$_2$ amount in the solution was quantified using a colorimetric method. A UV–visible spectrophotometer (UV-1800, Shimadzu). Depending on the H$_2$O$_2$ concentration, the collected samples were diluted multiple times (10–6000) before estimation so that the photogenerated H$_2$O$_2$ concentration lies in the calibrated range. To perform the colorimetric estimation of H$_2$O$_2$ in an aqueous solution, 0.4 mL of 0.1 M sodium phosphate buffer (pH 6) was mixed with 1.12 mL of DIW followed by the addition of 1 mL of sample. To the buffered solution, 0.05 mL of N,N-Diethyl-p-phenylene-diamine sulfate (DPD) solution followed by 0.05 mL of peroxidase (POD) was mixed to catalyze the oxidation of DPD in the phenylene-diamine sulfate (DPD) solution followed by 0.05 mL of DPD solution, 0.05 mL of DIW, and 0.05 mL of 7.5 mg of MX dispersed in 7.5 mL of DIW. The resultant reaction suspension in the Pyrex glass test tube was subjected to side-light irradiation with continuous O$_2$ gas bubbling (rad s$^{-1}$). Here $j$ indicates current density (mA cm$^{-2}$), $j_k$ kinetic current density (mA cm$^{-2}$), $n$ electron transfer number ($n$), $F$ Faradaic constant (96485 C mol$^{-1}$), $D_a$ diffusion coefficient of dissolved oxygen in the 0.1 M KOH at 298 K (1.9 × 10$^{-5}$ cm s$^{-1}$), $v$ kinematic viscosity of the 0.1 M KOH (0.01 cm$^2$ s$^{-1}$), $C_a$ saturation concentration of dissolved oxygen in the 0.1 M KOH (1.2 × 10$^{-5}$ mol L$^{-1}$), and $\omega$ angular velocity of the disk electrode (rad s$^{-1}$). The slope ($B'$) of the plot $j = f(\omega)$ as a function of $\omega^{-1/2}$ is used to calculate the electron transfer number ($n$).

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00528.

Materials details; characterization information; Supporting Note 1, ATR-FTIR and Raman spectroscopy; Supporting Note 52, N$_2$ adsorption–desorption; Supporting Note 53, effect of different aliphatic alcohols having fixed water content (50 vol %) on solar H$_2$O$_2$ production; additional data on the characterization of as-synthesized samples SEM micrographs, XEDS overlay images, TEM/HRTEM images, FFT patterns, XPS survey scan/core level spectra, XRD patterns, FTIR spectra, Raman spectra, N$_2$ adsorption–desorption isotherm, UPS spectra, energy diagram, and TGA thermograms; photochemical H$_2$O$_2$ production plots; absorbance spectra and calibration curve for spectrophotometric quantification of photogenerated H$_2$O$_2$ content in the reaction solution, elemental composition table, and comparison table of photocatalysts for solar H$_2$O$_2$ production from an oxygen saturated solution of electron and proton donor solvents (PDF)

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Author Contributions
P.S. proposed and designed the project. P.S. performed and planned the experiments. T.J.A.S. acquired the electron microscopy images and analyzed these data. M.S. contributed to the XPS and electrochemical analysis. M.B. provide valuable input. C.R.A.C. supervised and guided the project. P.S. and M.S. wrote the manuscript, and M.B., T.J.A.S., and C.R.A.C. extensively modified the manuscript.

Notes
The authors declare no competing financial interest.

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■ ABBREVIATIONS
MX → PHI; alkali metal-halide modulated poly(heptazine imide); BCN; basic carbon nitride; PCORR; photochemical O₂ reduction reaction; DIW; deionized water.

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