

# Highly Efficient Photo Rechargeable Supercapacitor based on Ambipolar Interface of Graphitic Carbon Nitride and MXene

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Dual-functional materials for both the optically and the electrochemically active electrode enable efficient direct storage of solar energy into electrical energy. A photo rechargeable supercapacitor is developed using an ambipolar interface of MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ) and protonated graphitic carbon nitride under light illumination. An extraordinarily large increase of 1960% in the electrochemical capacitance is measured under the light illumination (420 nm) compared to its dark capacitance.

Ambipolar interface induces an anomalous increase in the capacitance at an ultra-high scan rate of  $1.5 \times 10^5$  mV/s under the light illumination. Moreover, the photo-assisted, voltage of ~270 mV is generated in the rechargeable supercapacitor. The extraordinary results are attributed to the attractive interface of oppositely charged MXene and protonated graphitic carbon nitride.

## Introduction

The demand for energy storage devices with high power density and enhanced energy capacity at high scan rate is increasing day-by-day due to the ever-inflating uses of portable electronic devices.<sup>[1–3]</sup> Supercapacitors have become an important class of energy storage devices because of their potential in electric vehicles and consumer electronics. The steep rise in popularity of supercapacitor is attributed to the traits such as longer life cycles, fast charge-discharge capability and high-power density. So far, considerable research has been reported to improve the performance of supercapacitors by developing high-performing electrode materials such as carbon in refined forms,<sup>[4,5]</sup> transition metal oxides [ $\text{Co}(\text{OH})_2$ ,  $\text{MnO}_2$  and  $\text{CuO}$ ]<sup>[6–8]</sup> and conducting polymer films<sup>[9]</sup> for long life cycles and high power density.<sup>[10]</sup> An additional functionality of photo rechargeable energy storage capability in supercapacitors is a novel concept for enabling efficient direct storage of solar energy into electrical energy. Thus, photo rechargeable energy storage is a promising development for the sustainable and eco-friendly use of electrical power for advanced power sources.<sup>[11,12]</sup>

Until now, energy storage devices are coupled with the energy conversion systems like solar cells,<sup>[13–15]</sup> which involve low level of integration, complexity of circuits, large size,

external wiring, inflexibility, ohmic losses and overall less efficiency. Therefore, to overcome such disadvantages, various functional units should be integrated into a single device.<sup>[16–21]</sup> Several modified designs are reported to develop photo rechargeable devices consisting of supercapacitors and solar cells, integrated in a single unit.<sup>[22–24]</sup> In one of the reports, an integrated all-inorganic perovskite solar capacitor has been constructed by combining a  $\text{CsPbBr}_3$  perovskite solar cell and a silica gel supercapacitor unit<sup>[22]</sup> for a high operating potential window of 1.2 V, fast rate of photocharging and good stability during charge/discharge cycles. However, the disadvantage of such an architecture is the need for manual switching of electrodes for charging and discharging.

Devices with dual-functional materials, *i.e.*, with both the capabilities of energy conversion and storage will be the way forward to autonomous, self-powered energy storage devices.<sup>[25–28]</sup> Optical charging in such devices can be achieved by incorporating a photoactive electrode, which can produce electrical energy from the generation of electron-hole pairs under light illumination. Thus, semiconducting materials that have both photoresponsive properties and capacitive behaviour are reported.<sup>[29–31]</sup> However, these devices suffer from lack of spontaneous generation of photovoltage, which predominantly pertains to optimization of the device structure by energy-level alignment.

So far, graphitic materials find a special place in fabrication of highly efficient supercapacitors due to high electrical conductivity, functional surfaces and high surface area. Among these, graphitic carbon nitride ( $\text{C}_3\text{N}_4$ ) is an optically active material with a bandgap of 2.75 eV. We developed a photo rechargeable energy storage device using an intimate interfacial contact between oppositely charged semiconducting protonated  $\text{C}_3\text{N}_4$  ( $\text{pC}_3\text{N}_4$ ) and MXene ( $\text{Ti}_3\text{C}_2\text{T}_x$ ). The positively charged surface of  $\text{pC}_3\text{N}_4$  allows strong mutual electrostatic attraction with MXene (negatively charged

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surface).<sup>[32,33]</sup> The resulting pC<sub>3</sub>N<sub>4</sub>/MXene heterointerface is successfully obtained by the  $\pi$ - $\pi$  stacking and electrostatic attraction. Thus, the resulting nanostructure with high surface area results in much improved and efficient transport of charges across the heterointerfaces. The pC<sub>3</sub>N<sub>4</sub> as an electrode material showed self-optical charging capability with a maximum generated voltage of 420 mV<sub>Ag/AgCl</sub> after exposure to an illumination of 420 nm radiation, which is higher than the voltage obtained without protonated C<sub>3</sub>N<sub>4</sub> (300 mV<sub>Ag/AgCl</sub>). A photo rechargeable pC<sub>3</sub>N<sub>4</sub>/MXene based solid-state energy storage device demonstrated an areal electrochemical capacitance of 3037.5  $\mu$ F/cm<sup>2</sup> at a scan rate of 1 mV/s and a capacitance enhancement of 1960% is observed under light illumination (420 nm). Moreover, device showed a stable response at an ultra-high scan rate of 150000 mV/s with a significant enhancement in capacitance (214%) under illumination caused by ambipolar transport. Another important attribute of the resulting device is that the light illumination of 420 nm induces a photovoltage of 270 mV without applying any external current or voltage. Thus, photo rechargeable pC<sub>3</sub>N<sub>4</sub>/MXene based solid-state energy storage device is a novel highly efficient solid-state supercapacitor.

## Results and Discussion

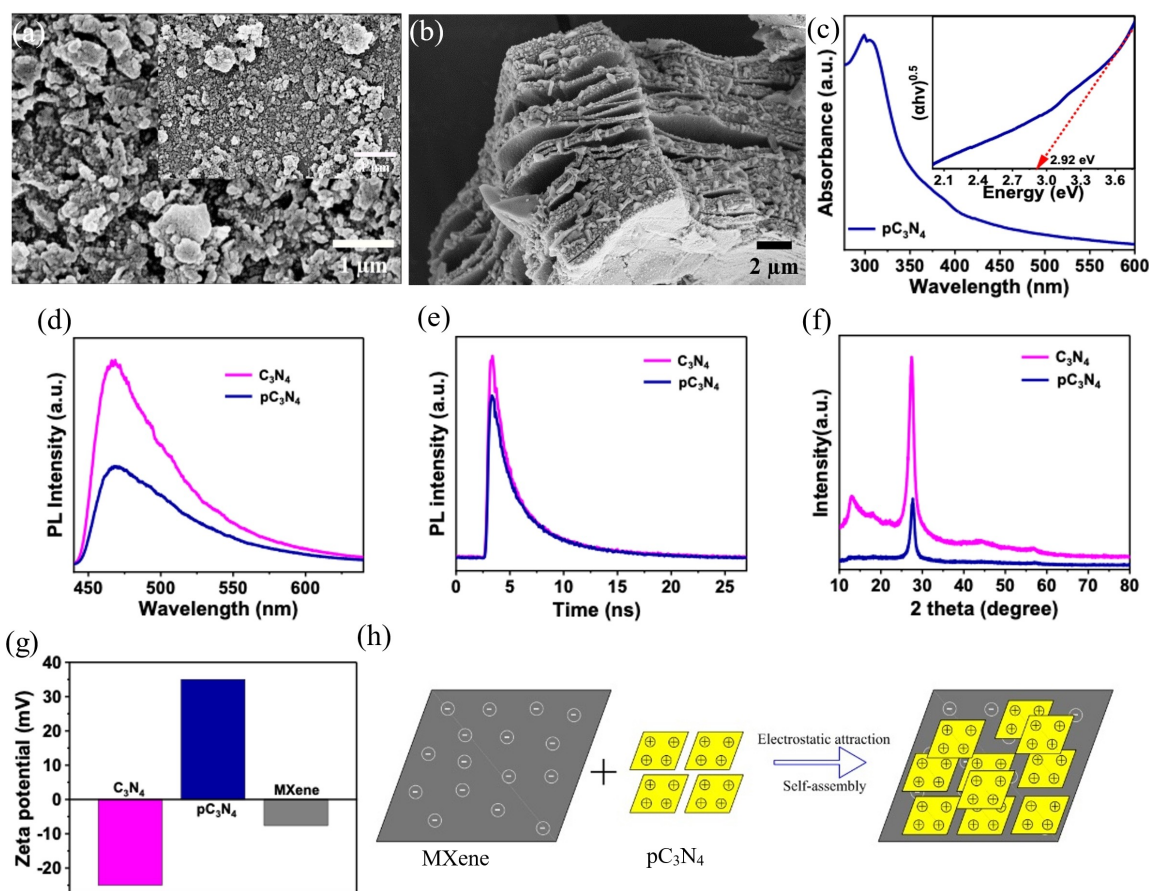
### Material characterizations

Surface morphologies of both C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub> are shown in scanning electron microscopy (SEM) images (Figure 1a and inset image, respectively). The protonation of C<sub>3</sub>N<sub>4</sub> induces exfoliation and reduction in flake size as shown in the inset figure. Figure 1(b) is an SEM image of as-procured MXene. Energy bandgap ( $E_g$ ) of both the C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub> was measured via UV-vis (ultraviolet-visible) absorption spectra in Figure S1, Figure 1(c) using the tauc approach (inset of Figure S1 and Figure 1(c)) from the Kubelka-Munk relation.<sup>[34,35]</sup>

$$\alpha E_{\text{photon}} = K(E_{\text{photon}} - E_g)^{n/2} \quad (1)$$

where,  $\alpha$ =absorption coefficient,  $K$ =constant,  $h\nu = E_{\text{photon}}$ , and  $n=4$  for C<sub>3</sub>N<sub>4</sub>. The measured  $E_g$  values of C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub> are 2.75 and 2.92 eV (inset), respectively. The observed blue-shift in  $E_g$  can be attributed to the  $\pi$ -conjugated system weakening as a consequence of the decreased condensation.<sup>[36]</sup>

Photoluminescence (PL) spectra of pristine C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub> in a broad range (440–600 nm) is shown in Figure 1(d) demonstrating emissions from the multiple photoactive energy



**Figure 1.** SEM images of a) C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub> (inset). b) SEM image of as-procured MXene. c) UV-vis absorption spectrum and tauc plot (inset) to determine the optical band gap of pC<sub>3</sub>N<sub>4</sub>. d) PL spectrum and e) time-resolved PL spectrum of C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub> under an excitation by a radiation of wavelength 405 nm. f) XRD patterns of C<sub>3</sub>N<sub>4</sub> and pC<sub>3</sub>N<sub>4</sub>. g) Zeta potentials of C<sub>3</sub>N<sub>4</sub>, pC<sub>3</sub>N<sub>4</sub> and MXene. h) Schematic illustration of electrostatic self-assembling of pC<sub>3</sub>N<sub>4</sub> and MXene.

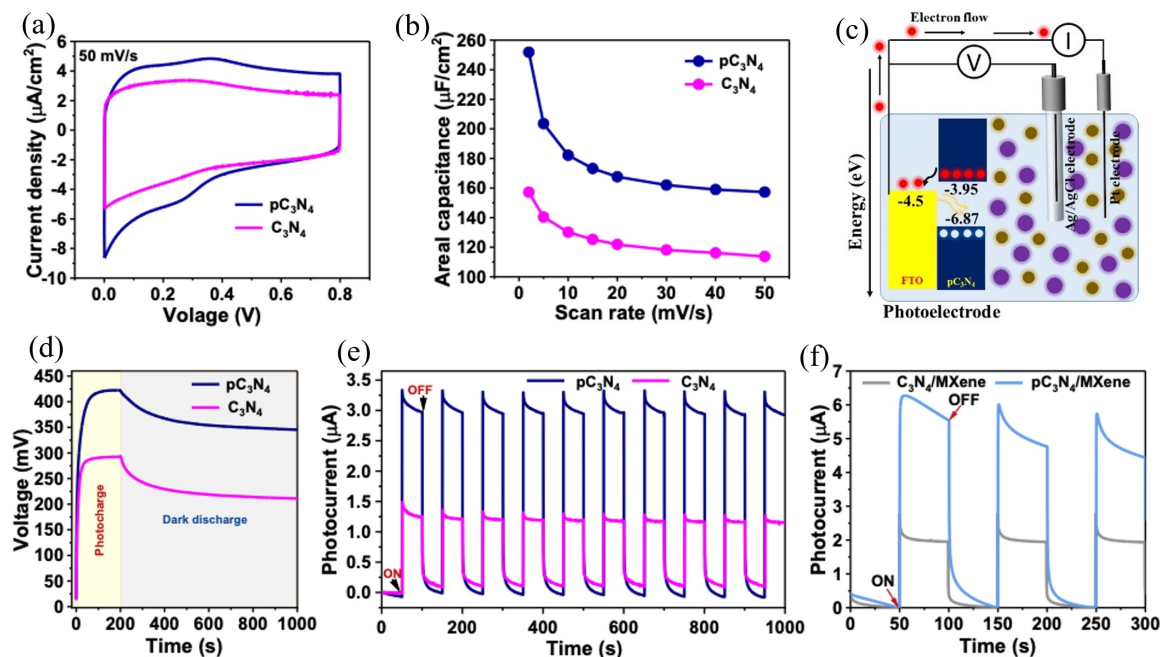
levels of the material. PL intensity of  $\text{pC}_3\text{N}_4$  is lower compared to  $\text{C}_3\text{N}_4$ , indicating that the radiative recombination in  $\text{pC}_3\text{N}_4$  is greatly suppressed. The time-resolved spectra investigated the kinetics of PL decay. The lifetimes of photoexcited charge carriers in  $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$  are shown in Figure 1(e). Average lifetimes are obtained using bi-exponential fitting of the PL decay. The calculated average lifetimes for the  $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$  are  $2.47 \pm 0.02$  ns and  $2.84 \pm 0.02$  ns, respectively. After protonation, the charge carrier lifetime increased by 15% that indicates an increase in the separation efficiency of photo-generated charge carriers and hence, effectively reduced charge recombination. The decreased PL intensity and extended lifetime are associated with the improved localization of charge on the carbon nitride matrix. The improved localization of charge in protonated  $\text{C}_3\text{N}_4$  ( $\text{pC}_3\text{N}_4$ ) is often observed in various experimental and theoretical studies. Protonation introduces localized positively charged sites ( $\text{N}-\text{H}^+$ ) in heterocycles and the cyano group of the exfoliated  $\text{C}_3\text{N}_4$ .<sup>[37,38]</sup> Further, density functional theory (DFT) calculations have demonstrated the formation of  $\text{N}-\text{H}^+$  sites and the alteration of the electronic band structure by Yu. et al and Martin et al.<sup>[39,40]</sup> Yang et al. and Du et al. provided X-ray photoelectron spectroscopy (XPS) measurements for evidence of changes in the electronic structure of  $\text{pC}_3\text{N}_4$  due to protonation.<sup>[37,38]</sup> Shifts in binding energies of N and H peaks revealed the formation of  $\text{N}-\text{H}^+$  sites. The localized charge carriers at protonation sites act as non-radiative recombination centres. This means that instead of recombining and emitting photons as in PL, charge carriers recombine non-radiatively, leading to a reduction in PL intensity. The effect is consistent with the concept of trap-assisted recombination. Because the trapped charge carriers have a longer lifetime due to their localized nature and hence persist in the material for a longer duration before recombining, resulting in an extended PL lifetime.

The X-ray diffraction (XRD) patterns of  $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$  show a hexagonal carbon nitride structure (JCPDS card no. 87-1526) (Figure 1f). The intense peak at  $27.38^\circ$  ( $d = 0.325$  nm) of  $\text{C}_3\text{N}_4$  is a characteristic of interlayer stacking reflection of conjugated aromatic systems, corresponding to the (002) plane for the graphitic materials.<sup>[41]</sup> The low angle peak of  $\text{C}_3\text{N}_4$  is located at  $13.1^\circ$  indexed for (100) plane corresponding to in-plane structure packing of aromatic systems.<sup>[41]</sup> The decrease in crystallinity after protonation causes shifting of (002) peak positions to  $27.7^\circ$  with a lower peak intensity. The change in interplanar distance from 0.325 nm to 0.321 nm demonstrates the tighter packing in the aggregates of protonated  $\text{gC}_3\text{N}_4$  nanosheets. In case of protonated carbon nitride this reduction in interlayer spacing after protonation can be attributed to the electrostatic attraction between the positively charged protons ( $\text{H}^+$ ) introduced during protonation and the negatively charged nitrogen sites in the  $\text{C}_3\text{N}_4$  structure. The reduction in interlayer spacing after protonation is quite evident and is reported by others as well.<sup>[42,43]</sup> Moreover, the Brunauer, Emmett and Teller (BET) surface area of  $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$  are  $10.4 \text{ m}^2/\text{g}$  and  $25.7 \text{ m}^2/\text{g}$ , respectively, thus indicating effective exfoliation of  $\text{C}_3\text{N}_4$  in agreement with the XRD results.<sup>[44]</sup>

The  $-\text{C}-\text{N}-$  motifs present in  $\text{C}_3\text{N}_4$  help in an easy protonation using hydrochloric acid. The process of protonation induces surface charge modification from a negatively charged surface to a positively charged surface. Structural modification in  $\text{C}_3\text{N}_4$  before and after protonation is shown in Figure S2. The measured zeta potential value of  $\text{pC}_3\text{N}_4$  is  $+35$  mV when dispersed in ethanol at pH 7.3 (Figure 1g). The value of zeta potential for  $\text{C}_3\text{N}_4$  is  $-25$  mV. Therefore, as a marker for successful protonation, zeta potential of  $\text{C}_3\text{N}_4$  dispersed in ethanol was shifted from  $-25$  to  $+35$  mV after protonation. The  $\text{pC}_3\text{N}_4$  was further modified with the MXene using a self-assembly mechanism operating between  $\text{pC}_3\text{N}_4$  and MXene due to electrostatic interaction. MXene has a negatively charged surface with a zeta potential value of  $-7$  mV. Hence, self-assembly between negatively charged MXene and positively charged  $\text{pC}_3\text{N}_4$  was spontaneous as shown by the schematic (Figure 1h). This is driven by electrostatic interactions and  $\pi-\pi$  stacking between the two materials. The detailed characterizations of  $\text{C}_3\text{N}_4/\text{MXene}$  and  $\text{pC}_3\text{N}_4/\text{MXene}$  are described in supplementary information, Figures S3–S7.

### Electrochemical characterizations

The electrochemical performance of both the  $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$  was evaluated in a three-electrode configuration by cyclic voltammetry (CV), galvanostatic charge-discharge (CD) and electrochemical impedance spectroscopy (EIS) measurements. Fluorine-doped tin oxide (FTO) coated glass substrates were used for the working electrode. Figure 2(a) shows CV curves of  $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$  at a scan rate of  $50 \text{ mV/s}$  in the potential (V vs. Ag/AgCl) range of  $0-0.8 \text{ V}$  using  $1 \text{ M H}_3\text{PO}_4$  (phosphoric acid) as electrolyte. The CV profile of  $\text{C}_3\text{N}_4$  depicts a rectangular profile, demonstrating charge storage via the formation of an electric double layer (EDL) at the electrode-electrolyte interface. However,  $\text{pC}_3\text{N}_4$  shows a slight deviation from the rectangular shape of the CV curve, indicating pseudocapacitive nature. When  $\text{pC}_3\text{N}_4$  is protonated, some of the nitrogen atoms in the  $\text{C}_3\text{N}_4$  lattice become protonated, leading to the formation of  $\text{N}-\text{H}^+$  bonds to introduce localized positive charge centers in the material. The redox peaks observed in CV curves are associated with the transfer of electrons to or from the protonation sites ( $\text{N}-\text{H}^+$  bonds) within the  $\text{pC}_3\text{N}_4$  structure. These redox reactions involve the protons gaining or losing electrons, leading to changes in their oxidation states. Redox reaction that can occur at protonation sites is the reversible exchange of electrons and protons, which can be represented as:  $\text{N}-\text{H}^+ + \text{e}^- \rightleftharpoons \text{N}-\text{H}$ . In this reaction, the  $\text{N}-\text{H}^+$  site gains an electron to form a neutral  $\text{N}-\text{H}$  site. This electron transfer leads to a reduction process (the gain of electrons), which is typically observed as a cathodic peak in the CV curve. Redox reaction can also be attributed to surface functional groups that attached during protonation.<sup>[45]</sup> Functional groups like amine groups ( $\text{NH}_2$ ) and other nitrogen-containing moieties can undergo reversible redox reactions by accepting or donating electrons and participating in proton-coupled electron transfer reactions. The charge storage mecha-



**Figure 2.** The electrochemical performance of  $C_3N_4$  and  $pC_3N_4$  electrodes in 1 M  $H_3PO_4$  aqueous electrolyte in a three-electrode configuration. a) CV responses at a scan rate of 50 mV/s. b) Areal capacitance of  $C_3N_4$  and  $pC_3N_4$  for a range of scan rates. c) Schematic illustration of photocharging mechanism in a three-electrode configuration of  $pC_3N_4$ /FTO electrodes. d) Photo-voltage of  $pC_3N_4$  and  $C_3N_4$  electrodes using light ( $\lambda \sim 420$  nm) and discharge in dark condition. e) Cyclic photocurrent of  $pC_3N_4$  and  $C_3N_4$  electrodes at zero bias voltage under dark and illuminated conditions. f) Photocurrent of  $C_3N_4$ /MXene and  $pC_3N_4$ /MXene electrodes at zero applied voltage under cyclic dark/illuminated conditions.

nism of the electrode was further investigated by Dunn's method for quantitative separation of two components, namely:<sup>[46,47]</sup> (more details are provided in the Supporting Information, Figure S8)

- (i) Diffusion independent capacitive contribution from EDL at the electrode-electrolyte interface and/or faradaic charge transfer at the surface-bound atoms (pseudocapacitance).
- (ii) Diffusion-controlled faradaic contribution (intercalated pseudocapacitance).

As shown in Figure S8(a and b), the surface capacitive process contributes 85% and 90% of the total charge storage at 5 mV/s in the  $pC_3N_4$  and  $C_3N_4$  electrodes, respectively, suggesting a dominated surface capacitive contribution. A higher diffusion-controlled contribution in the  $pC_3N_4$  may be due the presence of terminal groups attached during the protonation and localized positive charge centers.<sup>[45]</sup> Figure 2(b) shows the measured areal capacitance with the scan rate. The capacitance of  $pC_3N_4$  is 251, 203, 182, 173, 157 μF/cm² at the scan rates of 2, 5, 10, 15 and 50 mV/s, respectively, revealing a maximum of 60% increase in the capacitance at a scan rate of 2 mV/s than that obtained from  $C_3N_4$  based electrode (157, 140, 130, 125, 113 μF/cm²).

The electrochemical measurements were performed on both the  $pC_3N_4$  and  $C_3N_4$  as photo-electrodes in the presence of light illumination. The photo charging capabilities of the electrodes are obtained under light illumination of wavelength 420 nm in the absence of any external electrical bias and discharging in the dark condition (no illumination) in an

open circuit. Photo charging principle of the working electrode is depicted using the energy level diagrams of the material and FTO, as shown in Figures 2(c) and S9. A maximum photo-voltage in  $pC_3N_4$  is measured 420 mV<sub>Ag/AgCl</sub> after light illumination for 180 s, which is higher than  $C_3N_4$  (300 mV<sub>Ag/AgCl</sub>) (Figure 2d). The achieved photo-voltage is lesser than the potential window of galvanostatic charging, which can be attributed to the difference in bias condition for the charging. Light illumination on the electrodes causes a spontaneous photo charging process, whereas galvanostatic charging is obtained upon application of an external current. Moreover, the working electrode is photo charged using light illumination and discharged over a load. The discharging was performed for a total time of 550 s where first it was discharged in the presence of light and later in the dark condition. Once the electrode is continuously exposed to the light, while discharging the output voltage drops to 70% and approaches to a constant value due to the charge balancing between the photo charging and discharging process (Figure S10). After the light is turned off, output voltage of the electrode further drops to 80 mV. During photo charging process, photogenerated electrons in electrode are transported to the counter electrode and the photogenerated accumulated holes attract oppositely charged anions ( $PO_4^{3-}$ ) in the electrolyte at the electrode to form an EDL. Further, the transfer of electrons in the external circuit or photo charging was confirmed using current time measurement in presence of illumination at zero applied voltage. The result in Figure 2(e) shows that current increases from 0 to 3.2 μA for  $pC_3N_4$  (0 to 1.5 μA for  $C_3N_4$ ) upon

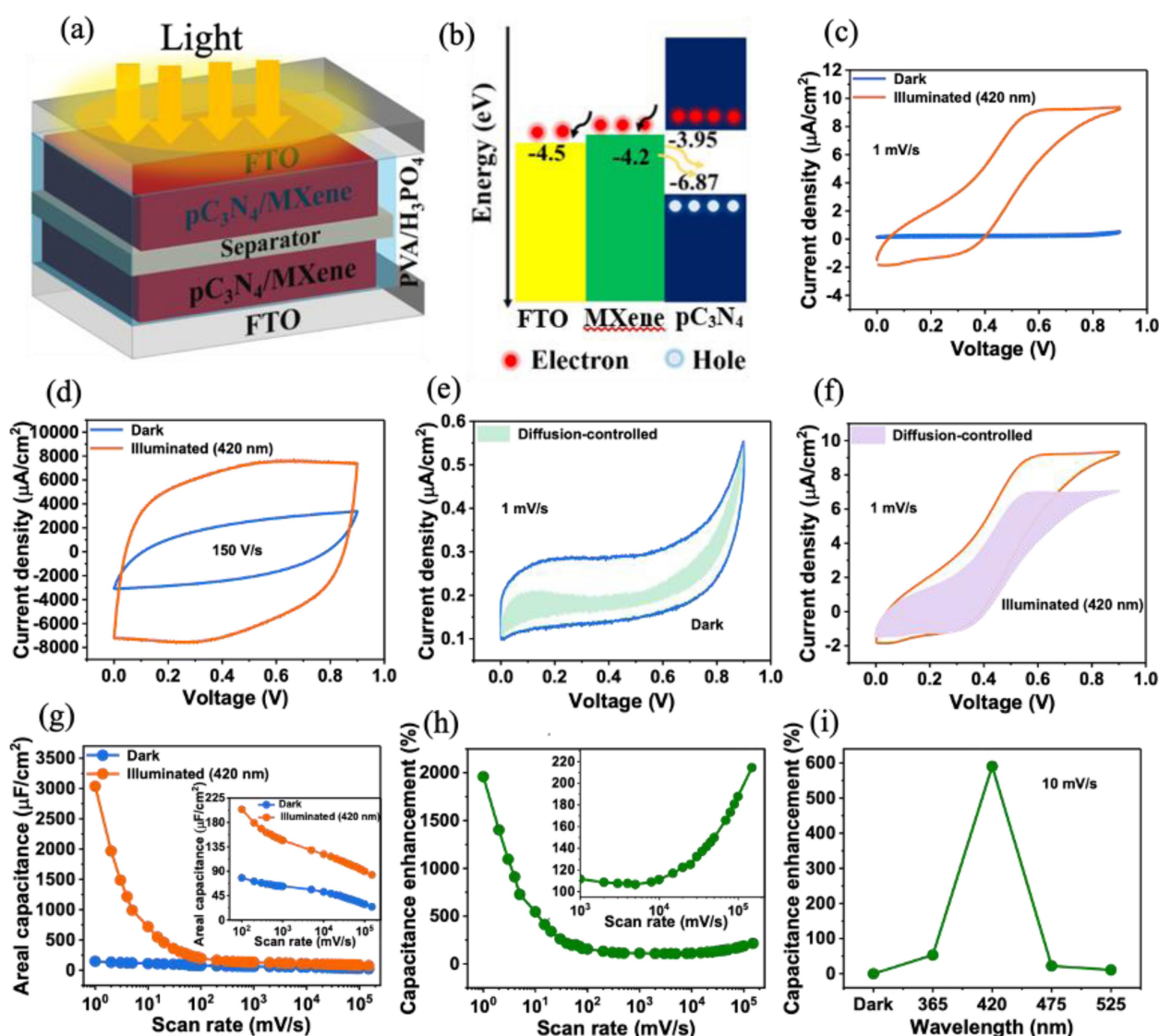


illumination for 50 s and approaches to 0  $\mu\text{A}$  in the dark conditions. In addition to a high electrochemical capacitance,  $\text{pC}_3\text{N}_4$  also exhibits higher photo-electrochemical performance, *i.e.*, generation of higher photocurrent and voltage.

Photocurrents from  $\text{pC}_3\text{N}_4$  and  $\text{C}_3\text{N}_4$  composites with MXene were measured using a three-electrode setup, with  $\text{C}_3\text{N}_4/\text{MXene}$  and  $\text{pC}_3\text{N}_4/\text{MXene}$  as electrodes. These measurements were conducted under light ( $\lambda \sim 420 \text{ nm}$ ) illumination using 1 M  $\text{H}_3\text{PO}_4$  electrolyte. As shown in Figure 2(f), the photocurrent intensity for  $\text{pC}_3\text{N}_4/\text{MXene}$  is three times higher than that of  $\text{C}_3\text{N}_4/\text{MXene}$ , indicating efficient charge transfer efficiency at the  $\text{pC}_3\text{N}_4/\text{MXene}$  interfaces. The MXene, due to its good electrical conductivity, provides transportation of the photoelectrons generated by the  $\text{pC}_3\text{N}_4$ , which reduces

the recombination of the photoinduced charge carriers. Therefore, both the SEM and photocurrent responses confirm the formation of advantageous interfacial interaction in the  $\text{pC}_3\text{N}_4/\text{MXene}$  composites *via* electrostatic attractive forces.

In view of practical uses of  $\text{pC}_3\text{N}_4/\text{MXene}$ , the performance of  $\text{pC}_3\text{N}_4/\text{MXene}$  was further evaluated in a device configuration, fabricated using a method described experimental section. The photo-electrochemical properties of  $\text{pC}_3\text{N}_4/\text{MXene}$  were evaluated using sandwich device configuration of symmetric supercapacitor with PVA/ $\text{H}_3\text{PO}_4$  (poly(vinyl alcohol)/phosphoric acid) electrolyte as shown schematically in Figure 3(a). The energy band diagram of  $\text{pC}_3\text{N}_4/\text{MXene}$  with the FTO is shown in the schematic (Figure 3b). CV measurements were conducted to measure photo-assisted changes in the  $\text{pC}_3\text{N}_4/\text{MXene}/\text{FTO}$  device at a scan



**Figure 3.** Electrochemical performance of  $\text{pC}_3\text{N}_4/\text{MXene}$  device under dark and illuminated conditions. a) Schematic of  $\text{pC}_3\text{N}_4/\text{MXene}$  fabricated supercapacitor device. b) Energy band diagram of electrode material with FTO current collector. CV curves in dark and under illumination ( $\lambda \sim 420 \text{ nm}$ ) at a scan rate of c) 1 mV/s and d) 150 V/s. Quantification of diffusion-controlled contribution to charge storage in e) dark and f) illuminated conditions at 1 mV/s (shaded region). g) Areal capacitance comparison under dark and illuminated conditions (420 nm) for a range of scan rates; Inset: Areal capacitance comparison at high scan rates. h) Capacitance enhancement under illumination (420 nm) compared to dark condition for a range of scan rates. Inset: Capacitance enhancement at high scan rates. i) Capacitance enhancement under illumination with the variation in light wavelength.

rate from 1 to 150000 mV/s under both dark and illuminated conditions ( $\lambda \sim 420$  nm) (Figure S11 and S12). The  $\text{pC}_3\text{N}_4/\text{MXene}$  device in dark condition presents nearly rectangular CV response up to a maximum scan rate of 1 V/s, which is a typical of EDL capacitor. At higher scan rates of 50–150 V/s, the CV responses slightly deviate from rectangular shape indicating the presence of resistive behaviour. Thus, the device capability of providing nearly rectangular CV response up to ultra-high scan rate indicates high-power handling capabilities. In presence of light illumination, the device exhibits a surge in the current as well as possess larger area of the CV curve at all the scan rates compared to the dark condition (Figures 3c and d, S13).

Figure 3(c and d) exhibits the enhanced CV responses under radiation illumination condition ( $\lambda \sim 420$  nm) at a scan rate of 1 mV/s and 150 V/s, respectively. The illumination induced CV curves at lower scan rates up to 1 V/s show non-rectangular shape and at higher scan rates the CV curves show again a rectangular shape. The occurrence of redox peaks at low scan rates in the cyclic voltammetry (CV) curves of the  $\text{pC}_3\text{N}_4/\text{MXene}$  composite electrode under illumination suggests that the redox reactions between the electrode materials and electrolyte ions primarily occur under light illumination. This behavior indicates that light plays a significant role in triggering electrochemical processes in the composite electrode. Under illumination photons from the light source are absorbed by the  $\text{pC}_3\text{N}_4$  component of the composite electrode, creating electron-hole pairs ( $\text{e}^-$  and  $\text{h}^+$ ). Electrons ( $\text{e}^-$ ) are transferred to the MXene component due to its excellent electron conductivity, while the holes ( $\text{h}^+$ ) remain in the  $\text{pC}_3\text{N}_4$ . Electrons ( $\text{e}^-$ ) generated by the photo-excitation process can participate in cathodic reactions at the electrode surface, leading to reduction reactions. Holes ( $\text{h}^+$ ) generated during photoexcitation can participate in anodic reactions, leading to oxidation reactions. Moreover, the  $\text{pC}_3\text{N}_4/\text{MXene}$  device is capable of providing significant photo-electrochemical charge storage for an ultra-long range of scan rates from 1 to 150000 mV/s. Again, Dunn's method<sup>[46,47]</sup> is used for understanding the charge storage mechanism in  $\text{pC}_3\text{N}_4/\text{MXene}$  device in both the dark and illuminated conditions. Figure 3(e and f) shows diffusion-controlled contribution of the device in a shaded area at 1 mV/s scan rate in dark and illumination conditions, respectively. Figure S14 exhibits contribution ratios for a range of scan rates. At very low scan rates (1 to 5 mV/s), significant surface capacitive-controlled capacitance is obtained in dark condition, whereas under illumination at lower scan rate, the diffusion-controlled capacitance predominantly increases as presented in Figure S14. However, at higher scan rate, the device shows a dominated surface capacitive response in both dark and illuminated conditions (Figure S15a–d). Figure S15(a and b) shows diffusive contribution of the device by the shaded area at a scan rate of 500 mV/s in dark and illuminated conditions, respectively. Figure S15(c and d) shows the contribution ratios for a range of high scan rates in dark and illuminated conditions, respectively. The calculated areal capacitance of  $\text{pC}_3\text{N}_4/\text{MXene}$  device in the

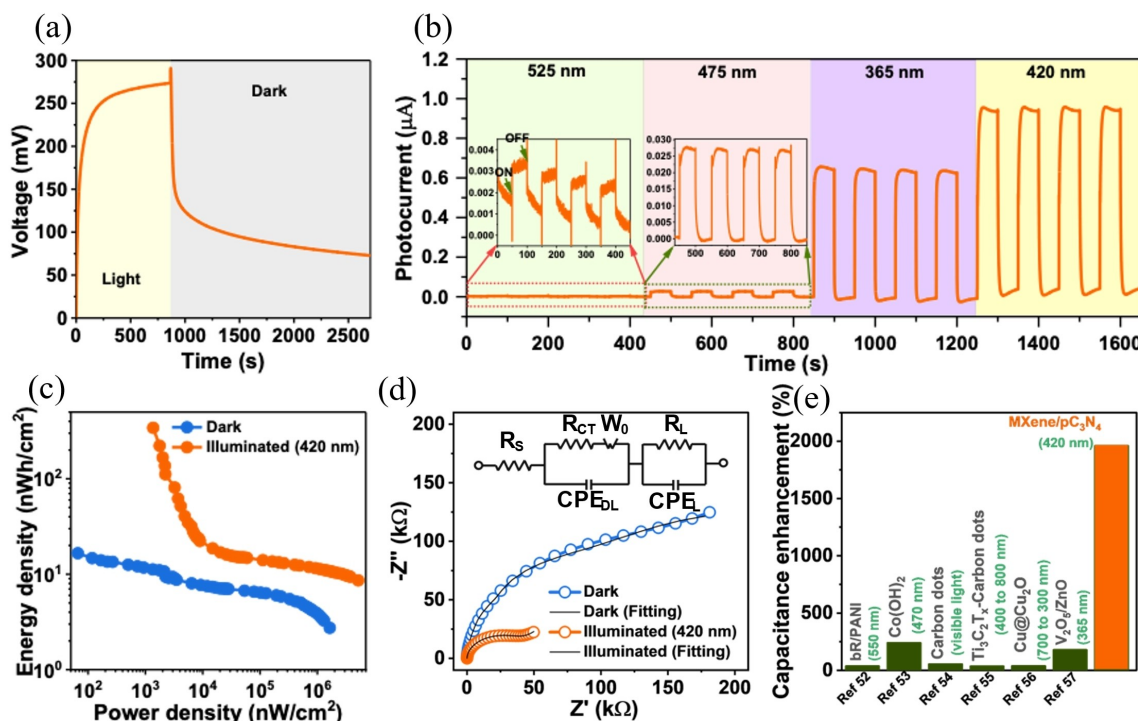
dark and illuminated conditions for a range of scan rates (1–150000 mV/s) is shown in Figure 3(g). A significant enhancement in electrochemical capacitance is observed in the presence of light illumination. The  $\text{pC}_3\text{N}_4/\text{MXene}$  device in dark condition exhibited an areal capacitance of about  $147.5 \mu\text{F}/\text{cm}^2$  at a scan rate of 1 mV/s, which is dropped to  $94.9 \mu\text{F}/\text{cm}^2$ ,  $77.7 \mu\text{F}/\text{cm}^2$ ,  $65.5 \mu\text{F}/\text{cm}^2$ ,  $62.3 \mu\text{F}/\text{cm}^2$  at a scan rate of 50 mV/s, 100 mV/s, 500 mV/ and 1000 mV/s, respectively, which is about 64.3%, 52.6%, 44.4% and 42.3%, respectively higher of its initial capacitance at a scan rate of 1 mV/s. Moreover, capacitance was further reduced to  $46.2 \mu\text{F}/\text{cm}^2$ ,  $36.96 \mu\text{F}/\text{cm}^2$ ,  $29.03 \mu\text{F}/\text{cm}^2$  and  $24.35 \mu\text{F}/\text{cm}^2$  at an ultra-high scan rate of 20000, 50000, 100000, and 150000 mV/s, respectively (Figure 3g). The areal capacitance value at a scan rate of 150000 is about 16.5% of the initial capacitance recorded at a 1 mV/s scan rate. The  $\text{pC}_3\text{N}_4/\text{MXene}$  device under illumination (420 nm) exhibits areal capacitance of  $3037.5 \mu\text{F}/\text{cm}^2$  at a scan rate of 1 mV/s, which dropped to  $281.9 \mu\text{F}/\text{cm}^2$ ,  $198 \mu\text{F}/\text{cm}^2$ ,  $139 \mu\text{F}/\text{cm}^2$ ,  $131.8 \mu\text{F}/\text{cm}^2$  at a scan rate of 50 mV/s, 100 mV/s, 500 mV/ and 1000 mV/s, respectively. Moreover, the device shows areal capacitance of  $102.8 \mu\text{F}/\text{cm}^2$ ,  $92.4 \mu\text{F}/\text{cm}^2$ ,  $83.59 \mu\text{F}/\text{cm}^2$  and  $76.6 \mu\text{F}/\text{cm}^2$  under illumination at an ultra-high scan rate of 20000, 50000, 100000, and 150000 mV/s, respectively (Figure 3g). Figure 3(h) exhibits significant enhancement in capacitance under illumination of visible light for a wide range of scan rates (1 mV/s–150 V/s). Upon illumination, an anomalously high areal capacitance of 1960% is observed under 420 nm light illumination compared to dark condition (Figure 3h). Interestingly, the device under illumination showed a decreasing trend in percentage enhancement in capacitance up to 1000 mV/s and then increased, as shown in inset of Figure 3(h). A decrease in percentage enhancement in capacitance is due to the insufficient time for charge interaction causing lesser charges to be stored in the system. Moreover, an increase in percentage enhancement in capacitance could be attributed to the light enhanced ambipolar transport at higher scan rates.<sup>[48]</sup> At higher scan rate light illumination lead to the development of space charge due to the reduced activation energy of ions for the migration as was observed earlier by Zhao et al.<sup>[49]</sup> More accumulation of ions in EDL under light illumination increases EDL capacitance. The device was also tested in the presence of other wavelengths, e.g., 365 nm, 475 nm, 525 nm to evaluate optical charging capabilities, as shown in Figure 3(i). The obtained results suggested a negligible increase in the photo-assisted changes in the electrochemical capacitance for other wavelengths compared to 420 nm which can be attributed to the near band-gap energy of 2.95 eV for the  $\text{pC}_3\text{N}_4$  ( $\sim 2.92$  eV). Furthermore, the  $\text{pC}_3\text{N}_4/\text{MXene}$  device capacitance response is observed with different intensity of light (420 nm). The photo-assisted electrochemical capacitance enhanced from  $\sim 100\%$  to  $200\%$  with increasing light intensity from  $\sim 5$  to  $20 \text{ mW}/\text{cm}^2$  (Figure S16).

The electrochemical performance of  $\text{pC}_3\text{N}_4/\text{MXene}$  device under illumination was evaluated using CD measurements for a range of current densities. The CD curves of the device in dark

conditions show a triangular shape at a current density of  $1.25 \mu\text{A}/\text{cm}^2$ , indicating dominating EDL capacitance behaviour, well-matched with the observation from the CV curves (Figure S17). Under illumination, the device exhibits larger charge-discharge time along with non-linear CD responses due to the presence of pseudocapacitive charge storage along with EDL (Figure S17). The calculated areal capacitances from the CD curves exhibit higher performance in presence of illumination compared to dark at all current densities, as shown in Figure S18. Under illumination, the devices recorded a maximum areal capacitance of  $500 \mu\text{F}/\text{cm}^2$  at a current density of  $10 \mu\text{A}/\text{cm}^2$ . The photo-electrochemical change is verified from CV and CD results in  $\text{pC}_3\text{N}_4/\text{MXene}$  solid-state device. The advantage of  $\text{pC}_3\text{N}_4$  compared to  $\text{C}_3\text{N}_4$  was discussed earlier using electrochemical and photocurrent measurements in three-electrode setup. Moreover, the advantage of adding MXene as electrode material further understood by comparing  $\text{pC}_3\text{N}_4/\text{MXene}$  with the electrochemical response of  $\text{pC}_3\text{N}_4$  device. CV measurements in  $\text{pC}_3\text{N}_4$  device were performed in dark and under illumination using different wavelengths of light. The measured areal capacitances obtained from CV curve in dark and under illumination were compared and shown in Figure S19(a). The  $\text{pC}_3\text{N}_4$  device shows a maximum capacitance value of  $210 \mu\text{F}/\text{cm}^2$  at a scan rate of  $10 \text{ mV}/\text{s}$  under light illumination of  $420 \text{ nm}$  and  $110 \mu\text{F}/\text{cm}^2$  at the same scan rate in dark conditions. The calculated capacitance enhancement under illumination of different wavelengths of light, when compared to dark condition, is shown in Figure S19(b). The maximum

capacitance enhancement of  $\sim 90\%$  obtained under illumination of  $420 \text{ nm}$  light is much lesser than the capacitance enhancement obtained in the  $\text{pC}_3\text{N}_4/\text{MXene}$  device ( $\sim 600\%$ ).

Apart from photo-assisted enhancement in the electrochemical capacitance, the  $\text{pC}_3\text{N}_4/\text{MXene}$  device can be charged in the presence of light without any external electrical bias. Figure 4(a) shows the optical charging of the device with the generated voltage of  $\sim 270 \text{ mV}$  when illuminated for  $250 \text{ s}$  and subsequent discharge in the dark for a prolonged time. Under illumination, the photoexcited electrons travel from the photo-electrode to the counter electrode *via* the external circuit, causing adsorption of cations ( $\text{H}^+$ ) at the electrode-electrolyte interface to form a double-layer at the interface. While the photogenerated holes attract anions towards the photoelectrode for adsorption at the electrode-electrolyte interface. The obtained photovoltage in  $\text{pC}_3\text{N}_4/\text{MXene}$  device due to light exposure is compared with previously reported supercapacitors utilized with photo-assisted measurements (Table S1). The entire process results in optical charging of the device under light exposure. The stability of the device is investigated using repeated optical charging and discharging in dark condition for each cycle of  $100 \text{ s}$ , shown in Figure S20. The charging of  $\text{pC}_3\text{N}_4/\text{MXene}$  under illumination can be further confirmed from the chronoamperometry measurement (i.e., current versus time) measurement in absence of externally applied voltage. Chronoamperometry measurements were performed using different wavelengths of light, e.g.,  $525$ ,  $475$ ,  $365$ , and  $420 \text{ nm}$  as shown in Figure 4(b). The measured photocurrent under the



**Figure 4.** a) Photocharge of  $\text{pC}_3\text{N}_4/\text{MXene}$  device using  $420 \text{ nm}$  light and discharge in dark conditions in absence of external bias condition. b) Photocurrent of  $\text{pC}_3\text{N}_4/\text{MXene}$  device under cyclic dark and illuminated conditions with different wavelength of light at zero applied voltage. c) Ragone plot of  $\text{pC}_3\text{N}_4/\text{MXene}$  device in dark and illuminated conditions. d) Nyquist plot of  $\text{pC}_3\text{N}_4/\text{MXene}$  device in dark and illuminated conditions, Randle's equivalent circuit model depicted in the inset. e) Capacitance enhancement comparison of our  $\text{pC}_3\text{N}_4/\text{MXene}$  device with previously reported photo charge-assisted devices.



illumination of 420 nm is substantially higher than other wavelengths as shown in Figure 4(b), which is attributed to near higher energy of 420 nm ( $\sim 2.95$  eV) light to the band-gap of  $\text{pC}_3\text{N}_4$  ( $\sim 2.92$  eV). Furthermore, the advantage of  $\text{pC}_3\text{N}_4/\text{MXene}$  compared to  $\text{pC}_3\text{N}_4$  device is understood using photocurrent measurement at  $V=0$  condition. The measured photocurrent for  $\text{pC}_3\text{N}_4$  device is much lower than  $\text{pC}_3\text{N}_4/\text{MXene}$  device (Figure S21), indicating a meaningful introduction of MXene for highly photoactive electrode materials.

The areal energy density and power density of  $\text{pC}_3\text{N}_4/\text{MXene}$  device in dark and illumination conditions are shown in Figure 4(c). Our  $\text{pC}_3\text{N}_4/\text{MXene}$  device demonstrated maximum areal energy density of  $341.7 \text{ nWh/cm}^2$  at a power density of  $1366.8 \text{ nW/cm}^2$  under illumination, which is higher than the values obtained for dark condition ( $16.58 \text{ nWh/cm}^2$  at  $66.34 \text{ nW/cm}^2$ ). A 20-fold increase in energy density is obtained for the device under 420 nm light illumination than dark condition. Furthermore,  $\text{pC}_3\text{N}_4/\text{MXene}$  device in illuminated and dark conditions exhibit maximum power density of  $5170 \mu\text{W/cm}^2$  and  $1643 \mu\text{W/cm}^2$ , respectively.

EIS was used for understanding ion transport properties of the  $\text{pC}_3\text{N}_4/\text{MXene}$  device in dark and illuminated condition for a range of frequencies (0.01 Hz to 100 kHz). The Nyquist plot for the device in the two conditions is shown in Figure 4(d). The inset in Figure 4(d) illustrates the equivalent circuit employed to fit the EIS data in this study. The results of the fitting for the various circuit elements can be found in Table S2. The term " $R_s$ " is referred as solution resistance, corresponds to the equivalent series resistance. This component typically characterizes the resistance associated with the electrolyte, in conjunction with the internal resistance of the electrode.<sup>[50]</sup> In this study, the  $R_s$  value was determined to be  $15.18 \Omega$  under dark condition and  $14.73 \Omega$  under illuminated condition. A slight reduction in  $R_s$  suggests a minor decrease in the solution resistance under illumination, indicating a subtle enhancement in ionic conductivity.<sup>[43]</sup> The " $R_{CT}$ " as the charge transfer resistance, signifies the rate at which redox reactions occur at the electrode-electrolyte interface.<sup>[51]</sup> A substantial reduction in  $R_{CT}$  following illumination is indicative of improved charge transfer kinetics. The " $\text{CPE}_{DL}$ " is a constant phase element (CPE) that represents the double layer capacitance. This capacitance arises at interfaces between solids and ionic solutions due to the separation of ionic and/or electronic charges.<sup>[50]</sup> The " $W_o$ " represents the Warburg element, reflecting the diffusion of ions into the electrode, particularly in the intermediate frequency range. This element accounts for the frequency-dependent nature of the diffusion process. The " $R_L$ " denotes the leakage resistance, which is usually very high and can often be disregarded in the circuit analysis.<sup>[51]</sup>  $\text{CPE}_L$  is used to describe pseudocapacitance, which arises due to voltage-dependent Faradaic charge transfer processes.<sup>[50]</sup>

The capacitance enhancement in  $\text{pC}_3\text{N}_4/\text{MXene}$  device due to light exposure is compared with previously reported supercapacitors utilized with photo-assisted enhancement e.g., bR/PANI supercapacitor (550 nm, 37.2%),<sup>[52]</sup>  $\text{Co(OH)}_2$  supercapacitor (470 nm, 240%),<sup>[53]</sup> carbon dot supercapacitor (visible light, 54.4%),<sup>[54]</sup>  $\text{Ti}_3\text{C}_2\text{T}_x$ -carbon dots supercapacitors (400 to 800 nm,

35.9%),<sup>[55]</sup> nanoporous  $\text{Cu@Cu}_2\text{O}$  supercapacitor (700 to 300 nm, 37.9%),<sup>[56]</sup>  $\text{V}_2\text{O}_5/\text{ZnO}$ <sup>[57]</sup> (365 nm, 178%) (Figure 4e). We report the considerably high enhancement of capacitance ( $\sim 1960\%$ ) under illumination among the state-of-the-art reported energy storage devices for photo charged enhanced capacitance.

## Conclusion

Charging of supercapacitors rely on external power sources. This work demonstrates a photo rechargeable supercapacitor using a highly photoactive heterojunction of  $\text{pC}_3\text{N}_4/\text{MXene}$  via an electrostatic self-assembly approach for simultaneous storing of energy and charging by light. Photo electrode of  $\text{pC}_3\text{N}_4$  provided higher electrochemical activity (60% enhancement in capacitance), enhancement in photocurrent (113% increase), high photovoltage (420 mV, 40% increase) than bulk  $\text{C}_3\text{N}_4$ . The intimate contact between positively charged  $\text{pC}_3\text{N}_4$  and negatively charged MXene sheets provided accelerated photo-induced electrons transfer from the conduction band of  $\text{pC}_3\text{N}_4$  to the metallic MXene. These reflect in areal capacitance under illumination than dark conditions and photocurrent measurement in the  $\text{pC}_3\text{N}_4/\text{MXene}$  device with an enhancement of  $\sim 567\%$  and  $\sim 480\%$  than pure  $\text{pC}_3\text{N}_4$  device. The photo-rechargeable supercapacitor achieved a capacitance enhancement of 1960% under illumination of 420 nm light than dark conditions and a photo voltage of 270 mV.

## Experimental Section

### Synthesis of graphitic $\text{C}_3\text{N}_4$ and protonation of $\text{C}_3\text{N}_4$

In a typical synthesis procedure, 5 g of melamine ( $\text{C}_3\text{H}_6\text{N}_6$ ) was transferred into a ceramic crucible with 80% volume filling and covered by a lid. The crucible was placed in a muffle furnace to heat at  $550^\circ\text{C}$  for 4 h under ambient air environment, thereafter, the furnace was cooled down to room temperature. The yellow colour solid of  $\text{C}_3\text{N}_4$  was collected and milled into powder for the protonation. The protonation treatment was commenced by stirring of as-obtained  $\text{C}_3\text{N}_4$  (3 g) with hydrochloric acid (37%, 30 mL) for 3 h at  $80^\circ\text{C}$  and using repetitive centrifugal washing with the de-ionized (DI) water until the neutral solution was obtained.<sup>[45]</sup> The product was dried at  $100^\circ\text{C}$  for overnight. The resulting powder was dispersed in 30 mL ethanol and sonicated for 2 h. Furthermore,  $\text{pC}_3\text{N}_4$  was obtained through vacuum filtration of the suspension and drying at  $100^\circ\text{C}$  overnight.

### Preparation of photo-electrode and supercapacitor device

Photo-electrodes for the three-electrode measurements were prepared on FTO coated glass substrate as the working electrode. As-prepared materials ( $\text{C}_3\text{N}_4$  and  $\text{pC}_3\text{N}_4$ ) (90 wt%) were dispersed in ethanol solvent (10 mL) and sonicated for 2 h. Further, polyvinylidene fluoride (PVDF) of 10 wt% was added to the dispersion and stirred for 6 h. The homogeneous solution was spray coated using argon as the carrier gas onto the FTO coated glass substrate at  $120^\circ\text{C}$ . Area of the electrode material deposited on the substrate was  $\sim 1 \times 1.5 \text{ cm}^2$  with a mass loading of  $\sim 2.5 \text{ mg/cm}^2$ .



The device fabrication commenced with dispersing 90 wt% of  $\text{pC}_3\text{N}_4$  and 10 wt% MXene (procured from nanochemazone) together in ethanol solvent (10 ml) and sonicated for 4 h. The homogeneous solution was spray coated using argon as a carrier gas onto the FTO coated glass substrate at  $120^\circ\text{C}$ . A copper strip was attached on the uncoated FTO with silver paste enabling strong electrical contact. The device is assembled using two pieces of material-coated FTO electrodes separated by PVA/ $\text{H}_3\text{PO}_4$  (poly(vinyl alcohol)/phosphoric acid) gel coated filter paper. The gel electrolyte, PVA/ $\text{H}_3\text{PO}_4$ , was prepared by mixing 6 g PVA and 6 g  $\text{H}_3\text{PO}_4$  in 60 mL DI water, followed by vigorous stirring for 2 h at  $85^\circ\text{C}$ . Finally,  $\text{pC}_3\text{N}_4$ /MXene/FTO device was kept in a laminar hood overnight to remove excess water present in the electrolyte. Similarly, a device without MXene ( $\text{pC}_3\text{N}_4$ /FTO) was also prepared using the same procedures as described above.

### Electrochemical characterizations

CV, CD and EIS were carried out in two- and three-electrode configurations using the CHI660E electrochemical workstation at room temperature. Three-electrode measurements were carried out using standard three-electrode cell where material coated FTO electrodes was used as working electrode, Ag/AgCl as reference electrodes and platinum (Pt) wire as a counter electrode. An aqueous solution of 1 M  $\text{H}_3\text{PO}_4$  was used as the electrolyte. EIS was measured using an input ac signal of 5 mV in the frequency range from 0.01 Hz to 100 kHz. Photo-assisted measurements were performed under light illumination using light emitting diodes of wavelengths 365, 420, 475, and 525 nm.

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### Conflict of Interests

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:** photo rechargeable supercapacitor · carbon nitride · MXene · self-powered

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