We report a facile alkali-assisted salt molten method to construct crystalline carbon nitride with rich nitrogen vacancies. Experimental and computational results show that the crystalline structure allows efficient charge transfer and the nitrogen vacancies provide more active sites, resulting in the enhanced photocatalytic hydrogen production.

Semiconductor-enabled photocatalytic water splitting for hydrogen production has been considered a promising pathway for effectively utilizing solar energy. Photocatalytic performance depends largely on the physicochemical properties of the semiconductor materials, including the band gap, band position, photogenerated charge carrier separation efficiency, surface area, crystallinity. Among many promising semiconductor materials, polymeric carbon nitride (CN) has recently been broadly employed in photocatalysis due to its abundance, relatively small bandgap ($\sim 2.7$ eV) allowing for visible light absorption, polymerization-adjustable electronic properties and photochemical stability. However, like other semiconductors suffering from the intrinsic attractive Coulomb interactions leading to bound electron–hole pairs and the strong interactions among excitons, such as exciton–exciton annihilation, pristine CNs also exhibit sluggish exciton dissociation, resulting in moderate photocatalytic activity.

Improving the crystallinity of the semiconductor materials has been proven to be a promising pathway toward accelerating the exciton dissociation process. However, the traditional CN derived from the thermally induced polymerization of $N$-containing precursors presents amorphous structure. Specifically, the heptazine (tri-s-triazine) units are bridged by imide units to generate the one-dimensional chains, interconnecting by hydrogen bonds to form the typical two-dimensional structure (Scheme 1a). Such non-crystalline structure is not beneficial for charge carrier mobility. The widely used ionothermal method involves the molten inorganic salts ($\text{LiCl}$, $\text{KCl}$, etc.) to guide the polymerization process and further tailor the structure of the polymeric CN. The resulting CN possesses an extended $\pi$-conjugated system which favors the light harvesting ability and the charge carrier mobility (Scheme 1b). As expected, the crystalline CN (CN-CTe) exhibited enhanced visible-light-driven photocatalytic activity towards hydrogen evolution with respect to the pristine CN. \footnote{Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cc00280a}

Given that catalytic reactions occur at the surface of a material, catalytic activity is largely dependent upon surface properties.
Recent studies have demonstrated that rationally generating surface vacancies can cause the lattice disorder, thus significantly increasing the surface energy. As a result, the vacancies can serve as additional active sites to more efficiently catalyze photo-reactions (Scheme 1c). Additionally, exciton dissociation can be accelerated by generating surface defects due to distorting the localization of the band-edge states around the defective sites. Remarkable improvements in the photocatalytic hydrogen production activity have also been observed in CN with nitrogen vacancies (CN-NVs) in many recent reports. In addition, the optimized nitrogen vacancies can create intermediate energy levels to narrow down the bandgap of CN for harvesting more visible light.

As described above, enhancing the crystallinity and generating vacancies are two effective approaches to improve CN-based photocatalytic activity. However, those two approaches are essentially contradicting. Improving the crystallinity would reduce the number of vacancies, including surface and bulk vacancies, while generating vacancies can somehow destroy the crystallinity of the materials. Therefore, it is difficult to synergistically combine these two advantages. Very recently, some studies focusing on generating crystalline CN with defective structures have been reported. However, the obtained materials are essentially crystalline CN modified with different functional groups. In this work, we report a facile approach to generate nitrogen vacancies in a crystalline CN system (CN-NVs-CTe). The pristine CN was calcined in the presence of LiCl/KCl/KOH. As a result, CN was recrystallized by LiCl/KCl for enhanced crystallinity, and some of the nitrogen atoms were removed in situ by KOH to generate nitrogen vacancies. As shown in Scheme 1d, the obtained CN-NVs-CTe presents the advantages associated with both crystalline CN and CN-NVs, resulting in enhanced photocatalytic hydrogen production efficiency.

Transmission electron microscopy (TEM) images of CN-NVs-CTe are presented in Fig. S1 (ESI†). Grain boundaries can be clearly observed, which is characteristic of polycrystallinity. And the clear lattice fringes shown in the high-resolution TEM (HRTEM, Fig. 1a and Fig. S1c, ESI†) image further indicates the high crystallinity of CN-NVs-CTe. The measured lattice spacing of 0.96 nm matches that of the (100) plane, representing the distance between in-plane nitride moieties within nitrogen-linked heptazine units. More TEM images of pristine CN and CN-CTe are shown in Fig. S2 and S3 (ESI†). In the X-ray diffraction (XRD) patterns (Fig. 1b), the two characteristic peaks of pristine CN at 13.0° and 27.4° are assigned to the (100) and (002) crystal planes of carbon nitride, representing in-plane packing and interfacial stacking of the carbon nitride sheets, respectively. The broad peaks at approximately 22° observed for CN-NVs and CN-NVs-CTe correspond to the amorphous CN structure, indicating the loss of ordered CN structures caused by the interaction between KOH and carbon nitride. The crystalline CN displays an extended interplanar packing distance compared with pristine CN, resulting in the presence of a new diffraction peak at approximately 8°. Therefore, the highly crystalline structures of CN-CTe and CN-NVs-CTe are confirmed.

Element analysis (EA, Table S1, ESI†) were performed to investigate the chemical compositions of the as-prepared samples. The bulk CN presents a C/N ratio of 0.6093. As expected, the ratio increases to 0.6478 for CN-NVs due to the nitrogen removal by KOH, and 0.6602 for CN-CTe because of the formation of extended conjugated system. Therefore, the CN-CTe yields the highest C/N ratio of 0.6796. X-ray photoelectron spectroscopy (XPS) was further employed to probe the nitrogen vacancies. As shown in the high-resolution XPS spectra (Fig. 1c), the three main peaks observed at 398.8, 400.4 and 401.3 eV correspond to the sp2-carbon nitride, representing in-plane packing and interfacial stacking of the carbon nitride sheets, respectively.20 The (C–N–H), and bridged or terminal amino group (C–N–H), respectively. The (C–N–C)/(N–(C)3) ratio is determined to be 3.92 in the bulk CN. Upon the generation of nitrogen vacancies, the ratio in CN-NVs drops to 3.32. Due to the formation of more N-(C)3 units in the structure, crystalline CN presents a smaller ratio at 3.10. With the synergistic effect, CN-NVs-CTe exhibits the smallest ratio at 2.30. C 1s XPS spectrum (Fig. S4, ESI†) of CN, CN-NVs and CN-NVs-CTe was also conducted to verify the existence of nitrogen vacancies. The XPS and EA analysis are in great agreement, confirming the abundant nitrogen vacancies in CN-NVs-CTe. And the results are supported by FTIR spectra (Fig. S5, ESI†).

Low-temperature electron paramagnetic resonance (EPR) spectroscopy was performed to further verify the nitrogen vacancies. EPR spectra can provide insights about the unpaired electrons in the photoreaction process. As shown in Fig. 1d, a visible absorption signal with a g value of 2.064 is observed, which can be ascribed to the unpaired electrons on the sp2-carbon atoms in conjugated aromatic rings. Compared with bulk CN, the paramagnetic signal of CN-NVs is much stronger due to the redistribution of π-electrons caused by nitrogen vacancies in the structure. Surprisingly, CN-CTe yields a higher paramagnetic signal than CN-NVs. EPR intensity is dependent on the amount of unpaired electrons and the electron mobility.22,24 Despite less unpaired electrons, the CN-CTe exhibits an enhanced conductivity due to its highly ordered structure allowing for the improved delocalization of electrons. Driven by the synergistic effect of nitrogen vacancies and high crystallinity, CN-NVs-CTe shows the highest EPR signal.
The light-harvesting ability of different samples was tested by UV-vis diffuse reflectance spectroscopy (DRS, Fig. 2a). The corresponding bandgaps (bg) and LUMO energy levels determined from Kubelka–Munk function (Fig. S6, ESI†) and Mott–Schottky plot (Fig. S7, ESI†) are summarized in Fig. 2b. The band structure measured by Mott–Schottky plot is in good agreement with the results calculated from the DRS and valence band XPS (VBXPS, Fig. S8 and Table S2, ESI†). Compared with the bulk CN, the CN-NVs exhibits an extended photoresponse due to the formation of surface intermediate states induced by nitrogen vacancies, 10 and the CN-CTe presents an increased absorbance because of the enhanced structural rigidity. 25 Driven by the synergistic effects, the CN-NVs-CTe possess both extended photoresponse and enhanced absorbance, indicating the improved light absorption ability. Also, the CN-NVs-CTe displays a very positive HOMO level, which will facilitate the water oxidation process, and eventually accelerate the photocatalytic hydrogen production reaction.

Steady-state (Fig. 2c) and time-resolved (Fig. 2d) photoluminescence (PL) spectra were used to investigate the thermodynamics of the photoexcited charge carriers. As seen in Fig. 2c, bulk CN exhibits a strong and broad PL emission peak centered at approximately 470 nm (λex = 408 nm). With nitrogen vacancies serving as electron traps, CN-NVs generates a significantly decreased PL intensity compared with bulk CN. The emission intensity is further decreased in the case of CN-CTe, which is due to an increased π state and stronger orbital overlap resulting from the extended π-conjugated system. 5 It indicates that the charge separation process in CN-NVs and CN-CTe is much more efficient than in bulk CN. 9 Because of the presence of crystalline/ vacancies structure, the charge separation efficiency of CN-NVs-CTe is better than CN-NVs and CN-CTe. The lifetimes of the charge-separated state were determined from fitting the time-resolved PL spectra, and the results are summarized in Table S3 (ESI†). The corresponding lifetimes of CN, CN-NVs, CN-CTe and CN-NVs-CTe are 2.685, 2.191, 2.089 and 1.675 ns, following the similar trend to the change of steady-state PL emission intensity.

The PL results confirm that the CN-NVs-CTe exhibits an enhanced charge separation efficiency over CN, CN-NVs and CN-CTe.

The photocatalytic hydrogen evolution activities of the prepared samples were evaluated using full-spectrum and visible light (λ > 420 nm) in methanol (MeOH)/H2O systems with Pd as a cocatalyst at room temperature (Fig. 3a). Under visible light irradiation, CN exhibits a hydrogen evolution rate of 29.9 μmol g⁻¹ h⁻¹, while CN-NVs and CN-CTe improve the performance to 230.0 and 249.6 μmol g⁻¹ h⁻¹, respectively. As expected, CN-NVs-CTe shows the highest hydrogen evolution activity, with a remarkable rate of 552.7 μmol g⁻¹ h⁻¹, which is 18.48 times than that of CN. In addition, the photocatalytic hydrogen production driven by the full-spectrum light was further carried out with other conditions unchanged. Also, CN-NVs-CTe presents the highest hydrogen production rate of 8723.8 μmol h⁻¹ g⁻¹, which is much higher than CN (2714.3 μmol h⁻¹ g⁻¹), CN-NVs (4906.0 μmol h⁻¹ g⁻¹) and CN-CTe (6156.0 μmol g⁻¹ h⁻¹). Additionally, the optimization of sample defect concentration was achieved by adjusting the amount of KOH added, and the corresponding performance was shown in Fig. S9 (ESI†). The cycling stability of CN-NVs-CTe was studied. As displayed in Fig. 3b, no significant decrease in hydrogen evolution activity was observed after five cycles. The excellent activity of CN-NVs-CTe confirms the synergistic effect of crystalline structure and nitrogen vacancies towards enhancing the photocatalytic hydrogen production activities.

The mechanism for the improved photocatalytic activity was then investigated using electrochemical impedance spectroscopy (EIS, Fig. 3c) and surface photovoltage (SPV, Fig. 3d) spectra. As shown in Fig. 3c, under dark conditions, CN and CN-NVs are identically conductive due to the presence of defects in the materials. The conductivity of CN-CTe is improved because of the high crystallinity for enhanced electron mobility. CN-NVs-CTe shows the smallest radius determined from the Nyquist plots, suggesting the best electron transfer ability to enable the
improved charge mobility.\textsuperscript{4} Furthermore, upon illumination with the light, CN-NVs exhibits a significantly improved electron transfer ability, indicating that the defects can significantly enhance the capture of photons and the conversion of photoelectricity.\textsuperscript{21,26} Due to the synergistic effect of high crystallinity and nitrogen vacancies, CN-NVs-CTe shows the best electron transfer ability under both dark and light conditions. The charge separation and transfer abilities were further investigated using surface photovoltage (SPV) technique.\textsuperscript{26} As shown in Fig. 3d, due to the presence of nitrogen vacancies, the photoresponse wavelength of CN-NVs and CN-NVs-CTe is extended to 550 nm. Although the photoresponse of CN-CTe is narrower, its photovoltage is much larger than those of CN and CN-NVs due to the enhanced crystallinity. Because of the synergistic effect of nitrogen vacancies and high crystallinity, CN-NVs-CTe shows a highly enhanced photovoltage and extended photoresponse. As a result, under the light irradiation, CN-NVs-CTe generates the highest photocurrent intensity (Fig. S10, ESI†).

Finally, density functional theory (DFT) calculations were performed to reveal the nature of enhanced photocatalytic activities of CN-NVs-CTe. Fig. S11 (ESI†) presents the optimized structures of CN-CTe and CN-NVs-CTe, respectively. Fig. S12 (ESI†) shows the images of electron density difference and population analysis about CN-CTe (Fig. S12a, ESI†) and CN-NVs-CTe (Fig. S12b, ESI†). Fig. S12c and d (ESI†) are the detailed population charge in the green dot circle from Fig. S12a and b (ESI†). Apparently, the electron density of CN-CTe is uniformly distributed on the framework, while the nitrogen vacancies in CN-NVs-CTe cause the electrons to be unevenly distributed. And the amount of charge near the nitrogen vacancies changes from Fig. S12c and d (ESI†). As a result, the change in charge distribution may increase the gain and loss of electrons, thus improving the chemical activity near the nitrogen vacancies.

In summary, a synergistic effect of engineering surface nitrogen vacancies and improving the crystallinity of carbon nitride-based materials to enhance the photocatalytic hydrogen evolution activities has been successfully achieved. The CN-NVs-CTe exhibits an extended photoresponse towards visible light, enhanced charge separation efficiency, and improved charge mobility. Our findings could open a new avenue for the preparation of photocatalysts with unique crystalline/vacancy structures for various applications.

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Conflicts of interest
There are no conflicts to declare.

Notes and references