Local spatial charge separation and proton activation induced by surface hydroxylation promoting photocatalytic hydrogen evolution of polymeric carbon nitride

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**ABSTRACT**

Polymeric carbon nitride as an intriguing earth-abundant visible light photocatalyst for H\textsubscript{2} evolution has projected huge potentials. A high-performance polymeric carbon nitride photocatalyst system always requires fabrication of nanostructure or assistance of other semiconductors for ample reactive sites or rapid carrier migration/charge separation. Here, we disclose that hydroxylation as an efficient surface polarization decoration tactic without involving nanostructure or other semiconductors can substantially promote local spatial charge separation and proton activation of polymeric carbon nitride, thus achieving high photocatalytic H\textsubscript{2} evolution. The post-hydrothermal treatment allows polymeric carbon nitride surface controllable grafting of abundant hydroxyls (–OH) on the C≡N sites, which not only extends the 2D conjugate electron system of polymeric carbon nitride to 3D space to realize local spatial charge separation, but also polarizes the neighboring N atoms (C–N=C) to promote the proton adsorption and activation on them, further contributing to the high H\textsubscript{2} evolution performance. The deep hydroxylation offered by introduction of basic ammonium salts discloses a pH-dependent hydroxylation-level mechanism and renders a ~11-fold enhancement in H\textsubscript{2} generation rate with an AQY of 9.1% at 420 ± 15 nm. The finding may bring a new opportunity for developing highly-efficient HER materials base on surface polarization of functional groups.

1. Introduction

Converting low density solar energy directly into high energy density fuel hydrogen (H\textsubscript{2}) via semiconductor photocatalysis is an intriguing strategy, and polymeric carbon nitride as an earth-abundant visible light photocatalyst for H\textsubscript{2} evolution obtains extensive interest [1–4]. Polymeric carbon nitride, as an intriguing earth-abundant visible light photocatalyst for H\textsubscript{2} evolution, has attracted extensive attention due to the two-dimensional configuration and unique electronic band structure [5–9]. For the purpose of advancing the hydrogen evolution ability of polymeric carbon nitride for practical applications, considerable efforts have been made toward conquering the inherent shortcomings of polymeric carbon nitride in recent years. Generally, a high-performance polymeric carbon nitride photocatalyst system always requires fabrication of nanostructure, creating defects or assistance of other semiconductors. Constructing nanoscaled/porous/ultra-thin/special structure aims to shorten the diffusion path of charge carriers, allowing carriers rapid migration onto the surface of catalysts to participate in the redox reactions [10–12]. Hetero/homojunction fabrication holds the merits of spatial charge separation between phases and thus inhibits recombination of electrons and holes [13–15]. Atomic doping and vacancies formation serve as the primary means for creating defects, which regulate the electronic structure for more efficient light harvesting as well as charge separation [16–23]. Namely, the current modifications on polymeric carbon nitride basically focus on its inherent characteristics, e.g. structure, photobabsorption and charge separation efficiency.

Another pivotal influential factor for hydrogen evolution is proton (H\textsuperscript{+}) adsorption and activation over reactive sites, which is also the primary step before the following proton reduction. Nevertheless, this
aspect has seldom been considered for polymeric carbon nitride so far. Lately, a pioneering work unearthed that introduction of Co$_3$P$_4$ onto polymeric carbon nitride nanosheets as a single reactive site not only prolongs carriers’ lifetime by ~20 times relative to pristine polymeric carbon nitride, but also promotes water molecular adsorption and activation, realizing overall water splitting. Though a large progress has been made in this work, the efficient water splitting process needs the assistance of enethic Co$_3$P$_4$ species, which complicates the synthetic procedure and hampers practical applications [24]. Decoration based on polymeric carbon nitride itself without introducing alien catalyst for achieving efficient charge separation and meanwhile H$_2$O/H$^+$ activation is thus a meaningful and highly challenging subject.

Recently, surface hydroxylation was reported as a facile and efficacious strategy to promote the photocatalytic activity of polymeric carbon nitride. Li et al. [25] prepared porous carbon nitride with hydroxylation through a hydrothermal process in the presence of ammonium hydroxide. The modified carbon nitride shows enhanced specific surface area and hydrogen evolution efficiency. Zheng et al. [26] reported ultrasonic treatment with hydrogen peroxide to realize hydroxylation of carbon nitride, which improves the visible light absorption and RhB degradation rate. However, hydroxylation in the previous reports also results in improvement on other properties simultaneously, such as enhanced specific surface area or photoabsorption, which is prejudicial to identify the positive effect of surface hydroxylation. It is very necessary to clarify the action of surface hydroxylation on photocatalysis, particularly H$^+$ activation, by developing a controllable modification strategy. More importantly, it is critical for understanding the essence of surface-functional-group decoration, which is helpful for smartly designing high-performance photocatalyst.

Herein, we disclose that surface hydroxylation can substantially promote local spatial charge separation and proton activation of polymeric carbon nitride, achieving high-efficiency H$_2$ production. We utilized a plain hydrothermal process to precisely construct a series of surface hydroxyln polymeric carbon nitride through temperature control with keeping the specific surface area and photoabsorption unchanged. Hydroxylation results in a photocatalytic H$_2$ evolution activity increase by ~5 times. Then, a pH-adjusted deep hydroxylation level was developed with introducing a series of ammonium salts in the post-treatment process, and the optimal H$_2$ evolution rate achieves ~11 times enhancement with a AQY of 9.1% at 420 ± 15 nm. Based on experimental and DFT calculation results, the grafted surface hydroxyls not only facilitate the local spatial charge separation, but also can realize the polarization of N atoms (C–N–C) with lone pairs of electrons, promoting proton adsorption and activation, co-benefiting the H$_2$ evolution reaction, which was further substantiated by sacrificial-agents controlled test.

2. Experimental details

2.1. Synthesis

The pristine polymeric carbon nitride was fabricated by a thermal polymerization method using melanine (Sinopharm Chemical Reagent Co., Ltd.) as precursor, which was calcined in a corundum crucible with a cover at 520 °C for 4 h [27]. The obtained solid was fully grinded by agate mortar, washed with distilled water and dried at 80 °C for 12 h. The pristine polymeric carbon nitride sample obtained was named as CN. To synthesize the hydroxy surface-grafted polymeric carbon nitride, CN samples were treated by a hydrothermal route. 0.4 g CN powder and 20 ml deionized water were transferred into a 30 ml quartz-tesfon-lined stainless autoclave (Fig. S11) and heated at different temperatures for 6 h in an electric heat oven. The samples treated at 100 °C, 120 °C, 140 °C and 180 °C were named as OH-CN1, OH-CN2, OH-CN3, and OH-CN4, respectively (the picture of all the samples were shown in Fig. S12). After hydrothermal treatment, the powders were washed with distilled water and dried at 80 °C for 12 h.

To explore the hydroxylation mechanism, another series of hydroxyl grafted polymeric carbon nitride samples were prepared by adding various ammonium salts (3 mmol), including (NH$_4$)$_2$CO$_3$, (NH$_4$)$_3$PO$_4$, CH$_3$COONH$_4$, (NH$_4$)$_2$SO$_4$ and NH$_4$Cl (all from Beijing Chemical Industry Group Co., Ltd.), in the same post-hydrothermal process, and the following procedures were same with the above process. CN treated by plasma cleaner was carried on an instrument (CPC-A, CIF International Group Co., Ltd., America) for 5 min, and named as CN-Plasma cleaner.

2.2. Characterization

The phase structures of the as-prepared samples were recorded with a powder X-ray diffraction (XRD) detection using a diffractometer with Cu K$_\alpha$ radiation source (D8 Advance, Bruker, Germany). The Fourier-transform infrared (FTIR) spectra were measured by a spectrometer (TENSOR 27, Bruker, Germany) in the frequency range from 400 to 2000 cm$^{-1}$. UV-visible diffuse reflectance spectra (DRS) were collected on a UV-visible spectrophotometer ( Cary 5000, Varian, America). Specific surface areas were measured via the Brunauer–Emmett–Teller (BET) method by nitrogen adsorption-desorption at 77 K (ASAP 2460, Micromeritics, America). The X-ray photoelectron spectroscopy (XPS) measurements were implemented on XPS apparatus (ESCALAB 250 Xi ThermoFishier, America). The particular peak of C-C at 284.73 eV in C 1s graph was used as the calibration standard. The elemental analysis measurement was depended on Vario MACRO cube element analyzer and EuroVector EA3000 elemental Analyzer. Thermogravimetry analysis (TGA) was carried out by Q5000IR TGA (TA Instruments, America). Zeta potential data were obtained by Zetasizer Nano (Malvern Panalytical, UK). The microstructure and morphology of the samples were researched with a transmission electron microscope (TEM, Tecnai G2 F20, FEI, Czech Republic). Surface photovoltage (SPV) measurement system included a source of monochromatic light which provided by a 300 W Xe lamp and a double-prism monochromator (Zolix SBP500), a lock-in amplifier (SR830-DSP) with a light chopper (SRS40) and a photovoltaic cell. Photocatalyst powder was placed between ITO electrode and a copper electrode.

2.3. Photoelectrochemical measurements

The photoelectrochemical properties, including photocurrent response, electrochemical impedance spectrum (EIS), voltammmograms (I-V) and Mott-Schottky curves, were measured via a standard three-electrode system with an electrochemical workstation (CHI660E, Chenhua Instruments Co., China). Saturated calomel electrode (SCE) and platinum wire were utilized as the reference electrode and counter electrode. The working electrode was samples film coated on indium-tin oxide (ITO) sheet glass. The electrolyte solution was 0.1 mol/l Na$_2$SO$_4$ solution. A 300 W Xe lamp with a 420 nm cutoff filter was the visible light source.

2.4. Photocatalytic activity evaluation

Hydrogen generation experiments were conducted with a 300 W Xe lamp (with a 420 nm cutoff filter) as the light source and a 0.81 sealed quartz glass reactor (φ10 cm×10 cm) (Fig. S13). A circulating conditioned water system kept the reactor system at 25 °C. Before the experiment, samples were loaded 1 wt% Pt as the co-catalyst by photodeposition method. 50 mg as-prepared photocatalyst was spread evenly on the reactor with 100 ml sacrificial agent solution (10 vol% lactic acid solution). Then the air in the reactor was removed by Ar stream. During the experiment, the light was taken from the top of the reactor and 1 ml gas sample was collected every hour. A gas chromatograph (GC-7900, Techcomp limited, China) equipped with a thermal conductivity detector was used to analyzed the concentrations of H$_2$. 

2.5. DFT calculations

Spin-polarized DFT-D2 calculations [28] were conducted using the “Vienna ab initio simulation package” (VASP5.4) [29,30] applying a generalized gradient correlation functional [31]. A plane-wave basis set with cut-off energy 450 eV within the framework of the projector-augmented wave method was employed [32,33]. The Gaussian smearing width was set to 0.2 eV. The Brillouin zone was sampled with a 3 × 3 × 1 Monkhorst Pack grid. All atoms were converged to 0.01 eV Å⁻¹. A 3 × 3 × 1 supercell of monolayer polymeric carbon nitride was first relaxed; the calculated N–C bond length is consistent with the published values [34].

The doping energy (\(E_D\)) is defined as

\[
E_D = E_{\text{doped CN}} - (E_{\text{pure CN}} + E_{\text{O/OH}})
\]

where \(E_{\text{O/OH}}\) refers to the total energy of O and OH species, which is calculated from the isolated O₂ and H₂O molecules, respectively.

The adsorption energy (\(E_{\text{ads}}\)) is defined as

\[
E_{\text{ads}} = E_{\text{tot}} - (E_{\text{CN}} + E_{\text{H}})
\]

where \(E_{\text{tot}}\), \(E_{\text{CN}}\) and \(E_{\text{H}}\) depict the total energy of the adsorption complex, the pure CN and the isolated H element, respectively.

3. Results and discussions

The hydroxyl grafted polymeric carbon nitride samples (OH-CN1, OH-CN2, OH-CN3 and OH-CN4) were prepared by hydrothermally post-treating the melamine-polymerization yielded bulk polymeric carbon nitride (CN) with controlling the different synthetic parameters [6]. First, elemental analysis was carried out to reveal the composition difference among the as-obtained samples. As listed in Table 1, the C/N ratio for all the samples was kept at 0.56, indicating that the CN₇ tri-s-triazines skeleton was well maintained after the above treatment. All the modified samples have a larger amount of O and H than CN, and OH-CN3 has the largest one, which suggests that the post-hydrothermal strategy gives rise to generation of more hydroxyls on polymeric carbon nitride, and they are not doped into the CN₇ tri-s-triazines by replacing C or N. Namely, hydroxyls are more likely grafted onto the surface of polymeric carbon nitride, which is further substantiated by the following XPS tests.

X-ray diffraction (XRD) patterns (Fig. S1a) of all the samples display two diffraction peaks at around 13° and 27.5°, which are the typical diffraction signals of (100) and (002) of polymeric carbon nitride [5]. No variation occurs for peak position width or intensity, revealing that the modiﬁed samples have a larger amount of O and H than CN, and OH-CN3 has the largest one, which suggests that the post-hydrothermal strategy gives rise to generation of more hydroxyls on polymeric carbon nitride, and they are not doped into the CN₇ tri-s-triazines by replacing lattice C or N. Namely, hydroxyls are more likely grafted onto the surface of polymeric carbon nitride, which is further substantiated by the following XPS tests.

The morphology and element distribution of CN and OH-CN3 were surveyed by transmission electron microscope (TEM). CN and OH-CN3 were all irregular plates, which are caused by the diﬀerent number n value of polymeric carbon nitride is 1 because it's direct-allowed transition [17,18,37]. The band gap value of all the as-prepared samples is 2.73 eV (Fig. S4). These results also rule out the possibility of O doping of modified samples, because the O doping would lead to an obvious shift of absorption edge and band gap change.
Fig. 1. Optimized structures of (a1) polymeric carbon nitride, (a2) O-CN and (a3) OH-CN (Eb stands for binding energy); XPS spectra of (b) C 1s, (c) N 1s, (d) O 1s of CN and OH-CN3 and (e) O 1s spectra of CN, OH-CN3 and OH-CN3 after Ar⁺ etching for 20 nm.

Fig. 2. TEM images and element mapping for (a) CN and (b) OH-CN3.
Then, the band structure was solved via Mott-Schottky curves and VB-XPS. The Mott-Schottky plots (Fig. 3b) of CN and OH-CNx (x = 1, 2, 3, 4) manifest that they own the same conduction band (CB) position assuming that the flat potential value is approximately equal to the Fermi level [38,39]. The VB-XPS (Fig. S5) reveals the same valance band (VB) position of OH-CN3 and CN. Thus, the surface hydroxyl modification did not change the band gap and band energy levels of polymeric carbon nitride.

We proceed to explore the primary factors that are closely associated with photocatalytic performance are considered. Specific surface area, crystallinity, photoabsorption and band energy levels are all ruled out based on the above results, which would not contribute to the photo-reactivity enhancement. Herein, the contact angles of CN and OH-CN3 were also measured, which are 20.8° and 21.0°, respectively, indicative of no hydrophilicity difference for both polymeric carbon nitride samples (Fig. S6).

The photocatalytic hydrogen generation performance of all the samples was investigated with visible light irradiation (λ > 420 nm) via controlling the different conditions. First, the H2 evolution experiments were conducted under visible light irradiation with 1 wt% Pt as co-catalyst and 10 vol% lactic acids as sacrificial agent. All the polymeric carbon nitride grafted with surface hydroxyl exhibited largely strengthened H2 generation activity (Fig. 4a), and OH-CN3 shows the optimal performance, which can generate 1.6 mmol/g H2 in 5 h with a linear growth. The H2 production rate (0.310 mmol/g/h) is approximately 4.7 times higher than that of CN (0.066 mmol/g/h) (Fig. 4b). The linear growth of each H2 generation plots certifies the high stable photocatalytic efficiency. To exclude the influence of co-catalyst on photoactivity improvement, the photocatalytic H2 generation test in the absence of Pt was conducted. As shown in Fig. S7, without Pt as co-catalyst, all the C3N4 samples modified with surface hydroxylation show higher photocatalytic hydrogen generation activity than CN, and OH-CN3 still displays the optimal performance. This result confirms that the improvement on H2 production activity comes from the surface hydroxylation instead of Pt co-catalyst. The cycling H2 generation experiment tests show that no activity loss occurs for OH-CN3 after four cycles (Fig. 4c), demonstrating a high photochemical stability. The surface chemical structure of OH-CN3 after H2 generation reaction in acidic condition was investigated by XPS (Fig. S8). The O 1s and C 1s high resolution XPS peaks of OH-CN3 remained unchanged without any peak shift before and after H2 generation, which indicates the high stability of surface hydroxyl during the photocatalytic process. It is well known that plasma treatment can make materials hydrophilic by surface hydroxylation. In order to confirm the high photocatalytic H2 generation activity caused by the hydroxyl surface grafting, the plasma cleaner was introduced as another approach to hydroxyl grafting on polymeric carbon nitride. As displayed in Fig. 4d, CN-Plasma cleaner (CN treated by plasma cleaner) also displayed a stronger ability in H2 generation than CN, corroborating the positive role of surface hydroxylation in promoting the H2 evolution activity.

It is found that the pressure in hydrothermal reactor during the post-hydrothermal treatment process gradually increased with raising the heating temperature from 100 to 180 °C (Table S1), corresponding the as-yielded samples from OH-CN1 to OH-CN4. Considering that OH-CN3 has the largest amount of –OH, it is speculated that an appropriate hydrothermal environment with moderate temperature and pressure results in the sufficient hydroxyl grafted on the surface of polymeric carbon nitride. Besides, the pH value in the post-hydrothermal process plays a prominent role in determining the hydroxylation level. In view of that polymeric carbon nitride could be protonated in strong acid and decompose in strong base [20], the pH value was modestly adjusted by introducing a series of ammonium salts. It is obvious that polymeric carbon nitride treated by different ammonium salts showed very distinct H2 generation efficiency (Fig. 4e). The H2 production efficiencies of the polymeric carbon nitride samples treated by CH3COONH4, (NH4)2SO4 and NH4Cl (pH ≤ 7) solution were similar to OH-CN3 (H2O). Whereas the samples treated by (NH4)2CO3 or (NH4)3PO4 where the aqueous solutions were basic (pH > 7) exhibited a dramatic enhancement on H2 generation. The highest H2 evolution rate of polymeric carbon nitride achieved with treatment of (NH4)2CO3 increases as high as 11-fold with an apparent quantum yield (AQY) of 9.1% under λ = 420 nm [40]. It may imply that the basic ammonium salts possess supplementary function of aggrandizing the hydroxyl surface grafting. On account of being capable of serving as the alkaline buffer in the post-hydrothermal reaction, the alkaline ammonium salts can continually provide enough -OH for hydroxylation, and the more hydroxys caused a higher photocatalytic H2 generation. But this function cannot be realized by acidic or neutral ammonium salts. For further confirmation, the O 1s XPS spectra of OH-CN3 with and without treating by (NH4)3PO4 were compared (Fig. 4f), and addition of (NH4)3PO4 greatly increases the peak intensity for the O 1s of OH-CN3, uncovering the presence of a much larger amount of O species (lattice C-O and surface C=O–H bonds). After Ar⁺ etching for 20 nm, the O 1s peak intensity for both OH-CN3 with and without addition of (NH4)3PO4 decline to the same level. It substantiates that introduction of basic ammonium salts can supply more abundant -OH for hydroxylation. Besides, no P 2p or S 2p signal can be detected in the XPS spectra of OH-CN3 with addition of (NH4)2PO4 or (NH4)2SO4 (Fig. S9), which excludes the interference by elements doping or surface decoration by other anions/anionic groups.

Charge movement behaviors, as important factors that take crucial part in photocatalytic process, are monitored by conducting a series of photoelectrochemical tests. The transient photocurrent responses (Fig. 5a) of OH-CNx (x = 1, 2, 3, 4) are profoundly strengthened in comparison with that of CN under visible light illumination, and the photocurrent intensity of OH-CN3 was almost 4.7 times that of CN, demonstrating that the photon-generated charge carriers of polymeric carbon nitride are efficiently separated through hydroxyl grafting [41]. Electrochemical impedance spectrum (EIS) can reflect the charge transfer efficiency between interface of photocatalysts and electrolyte, and a smaller arc radius in EIS plot indicates more efficient charge transfer. OH-CN3 shows the smallest arc radius in EIS plot among the following materials.
samples (Fig. 5b), evidencing the greatly advanced interfacial charge transfer efficiency [42]. Density of charge carriers is a significant parameter for photocatalysis. The photocurrent onset potential in I-V curve reveals the quasi Fermi level of majority carriers with the presence of fast electron acceptor (e.g. MVCl2) [41]. The open-circuit potentials of OH-CN3 (−0.14 V) were all positive than CN (−0.24 V) and are closer to 0 V, signifying the enlarged carrier density of OH-CN3 (Fig. 5c). In the quasi Fermi level, the carrier density difference between CN and OH-CN3 can be calculated by Nernst equation [41],

$$E_0 - E_2 = kT\ln\left(\frac{N_2}{N_1}\right)$$

$$= \frac{-e}{T}$$

$$\frac{N_2}{N_1}$$

wherein, $E_0$, $N_0$, $N_2$, $k$, $T$ and $e$ are the quasi Fermi level, carrier density, the Boltzmann constant, temperature and elementary charge. Based on the equation, the carrier densities of OH-CN3 were determined to be 47.8 times larger than that of CN. Besides, the photo-generated carrier separation efficiency in bulk was investigated by surface photovoltage (SPV). The SPV spectra (Fig. 5d) of CN and OH-CNx ($x = 1, 2, 3, 4$) exhibited the same variation tendency with H$_2$ generation activity (Fig. 3a). All the hydroxyl grafted samples displayed stronger photovoltage signal than CN, demonstrating more efficient bulk charge separation occurs with hydroxyl grafting, and OH-CN3 shows the highest efficiency. Based on the above results, the bulk charge separation, interfacial charge migration and charge carriers' density of polymeric carbon nitride are all profoundly promoted through surface hydroxylation.

To get in-depth insight into charge action, DFT calculations were conducted. Fig. 6a illustrated the electronic localization function for the bonding effect between -OH and polymeric carbon nitride layer. It is evident that there was a stable covalent bond (H–O–C≡N) formed between -OH and -C≡N, as observed in the consecutive area in red, and the ELF value of C–O was 0.38. As the essence of covalent bond is the electron transport between atoms, herein the carried charge ($\Delta q$) of -OH and polymeric carbon nitride was calculated with Bader method to estimate the electron transport direction [43–45]. One can observe from (Fig. 6b) that the charges are mainly depleted from C atoms (yellow sphere), and accumulated around O atoms (blue sphere). Namely, the electrons are more prone to transfer from the polymeric carbon nitride lattice skeleton to the surface -OH, which efficaciously extends conjugate electron system of polymeric carbon nitride from the two-dimensional (2D) plane to three-dimensional (3D) space. Therefore, the surface hydroxylation allows polymeric carbon nitride to realize local spatial charge separation, accounting for the excellent charge transfer.

As surface defect modification was demonstrated capable of promoting oxygen adsorption [46,47], here surface hydroxylation was
investigated to see if it has impact on the proton action in the hydrogen evolution process. Fig. 6c illustrated the charge difference of proton adsorbed on CN and OH-CN. In comparison with CN, H\(^+\) was more inclined to adsorb on OH-CN with a larger adsorption energy \(\Delta q = -0.68\) eV vs. \(\Delta q = -0.41\) eV for CN, which gives rise to a greater conversion possibility for activating H\(^+\) to H\(^2\). It is found that H\(^+\) prefers to adsorb on the two-coordinated N atoms that possessed additional lone pairs of electrons, because the lone pairs of electrons are more prone to be polarized and thus serve as active sites for H\(^+\) adsorption [19]. For confirmation, the Zeta potential of CN and OH-CN\(x\) (\(x = 1, 2, 3, 4\)) samples were measured. It is obvious that the carbon nitride samples with surface hydroxylation all reveal a less negative Zeta potential than CN (Fig. S10), which provides a good evidence for proton adsorption process. The hydroxyls grafted on the surface of polymeric carbon nitride could induce the redistribution of local charge between OH and polymeric carbon nitride plane, which polarizes the lone pair of electrons of two-coordinated N atoms to allow them deviation from the original orbit, enhancing the activation of H\(^+\) to H\(^2\) and to H\(^2\). For further comparison and disclosing the merit of surface OH, O doped polymeric carbon nitride was also compared. O atom was found doped

Fig. 5. (a) Transient photocurrent response; (b) EIS plots with 0.1 M Na\(_2\)SO\(_4\) solution under visible light (\(\lambda > 420\) nm); (c) I-V curves with presence of 1 mM MVCl\(_2\) under visible light (\(\lambda > 420\) nm); (d) surface photovoltage (SPV) spectra of CN and OH-CN\(x\) (\(x = 1, 2, 3, 4\)).

Fig. 6. (a) Electronic localization function, (b) charge difference at top view and side view; (c) charge difference of proton adsorbed on CN, O-CN and OH-CN. Charge accumulation is in blue and depletion in yellow. \(E_{\text{ads}}\) and \(\Delta q\) stands for the adsorption energy and carried charge for proton (negative means heat release).
into the lattice by replacing N atom. Noticeably, O doped polymeric carbon nitride shows very similar adsorption energy and carried charge compared to CN, manifesting that O doping has no positive effect on H\(^+\) adsorption and activation. And the mechanism of the whole improved photocatalytic activity process is exhibited in Fig. 7.

Since proton activation makes the major contribution to the H\(_2\) evolution activity enhancement of hydroxyl grafted polymeric carbon nitride, the amount of proton in the reaction solution should be crucial. H\(_2\) generation tests with different sacrificial agents were conducted (Fig. 8). Lactic acid, methanol and triethanolamine as acidic, neutral and basic sacrificial agents were selected, respectively. H\(_2\) generation rate of OH-CN3 is as high as 4.7 times that of CN using acid. However, the H\(_2\) evolution rate merely increased to 2.6 and 2.2 times for OH-CN3 with addition of methanol and triethanolamine, respectively. Presence of large amount of H\(^+\) is more favorable for H\(_2\) production of OH-CN3, which verifies the role of surface hydroxyl in proton activation. And the enhanced H\(_2\) production activity of OH-CN3 with addition of methanol and triethanolamine should be mainly attributed to the improved charge separation.

4. Conclusions

In summary, surface hydroxylation of polymeric carbon nitride was realized by facile post-hydrothermal treatment and plasmonic treatment, which promotes local spatial charge separation and proton activation, substantially boosting the photocatalytic H\(_2\) evolution. All hydroxylation polymeric carbon nitride post-treated in aqueous solution exhibit enhanced photocatalytic H\(_2\) production activity, and the evolution rate increases as high as ~5 times for the one with the most surface hydroxyls. PH-modulated deep hydroxylation of polymeric carbon nitride unfolds that introduction of basic ammonium salts, such as (NH\(_4\))\(_2\)CO\(_3\) and (NH\(_4\))\(_3\)PO\(_4\), in the post-treatment process drastically promote the photocatalytic activity, achieving ~11-fold increase in H\(_2\) generation rate with a AQY of 9.1% at 420 ± 15 nm. The bulk charge separation, interfacial charge transfer and carries densities are all greatly advanced, which attributes to the efficient local spatial charge separation via extending the conjugate electron system from 2D plane to 3D space. More importantly, the surface hydroxyls on -C≡N sites of polymeric carbon nitride polarizes the neighboring N atoms (C-N=C) to promote the proton adsorption and activation, further strengthening the H\(_2\) evolution performance, as verified by sacrificial-agents controlled test. We expect the concept of surface polarization of functional group inspires the property optimization of materials in other fields, such as electrocatalysis, sensors.

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Appendix A. Supplementary material

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material design strategies for electro-
accumulation in the form of surface
ivory of graphitic carbon nitride (melon) photocatalysts by homogeneous self-

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