1. Introduction

The artificial photocatalytic production of hydrogen fuel by water splitting has been an active research topic in the past decades. Different kinds of semiconductors, such as metal-based oxide, nitrides, phosphides, and sulfides were developed for efficient hydrogen evolution,[1] among which, the graphite carbon nitride (CN) has attracted intensive research interest since the pioneering work by Wang et al.[2] Although this metal-free, visible light response 2D conjugated semiconductor is chemically stable and easy for preparation, it still has some disadvantages, such as low absorbance in visible light, low specific surface area (SSA), and low charge carriers separation. To overcome these drawbacks, many researches have been focused on the heteroatom doping,[3] morphology, and nanostructure control of C₃N₄.[4] However, many of these modified carbon nitride still showed poor activities,[3e,5] and the intrinsic drawbacks, i.e., the poor charge carrier transport and separation, are not fully addressed.[3e,4a,5e,6]

Theoretically, the atomic order degree in solid-state semiconductor is crucial for the efficient separation of photogenerated charge carriers. For the polymeric π-conjugated framework, the charge transport along the in-plane direction is considered important to the migration of photogenerated charge carriers.[4b,7] However, up to now, it still remains a challenge to fabricate carbon nitride with well-ordered in-plane structure, which attributes to two reasons: (1) the precursors used to prepare carbon nitride, such as melamine, dicyandiamide, undergo melting before polycondensation reaction,
which results in the disordered condensation and the tangled CN chains; (2) it is too difficult to ensure that the uniform unit is heptazine in the prepared carbon nitride, usually triazine remaining in the scaffold during the thermal polymerization, which makes the in-plane less unified. Schwinghammer et al. synthesized crystalline PTI (polytriazine imide)/Li$^+$Cl$^-$ in a two-step ionothermal synthesis. Exfoliation of bulk crystalline PTI resulted in carbon nitride nanosheet with significantly enhanced hydrogen evolution. However, the ionothermal synthesis is hard to operate and difficult for wide application. Herein, we first report a simple preparation of a low-dimensional carbon nitride with enhanced in-plane ordering by calcinating the self-assembled heptazine precursors (SAHEP). The highly ordered heptazine can be transformed into poly(tri-s-triazine) with improved in-plane ordering, which showed a high hydrogen evolution rate (HER) of 420 $\mu$mol h$^{-1}$ and a remarkable apparent quantum efficiency (AQE) of 8.9% at 420 nm.

2. Results and Discussion

The SAHEP was obtained by refluxing heptazine in hot water-containing solutions. In Makowski et al.’s work, it is reported that the self-assembly of heptazine in hot aqueous solution resulted in the formation of hydrogen-bonded, hexagonal rosettes of heptazine units surrounding infinite channels with a diameter of 8.9 Å. In our case, when heptazine was refluxed in pure water at 80 °C for 10 h, micrometer-scaled rod of melem hydrate can be formed, as shown in Figure 1a. It is further found that by adding different amounts of isopropyl alcohol (IPA), the size of these assembled heptazine can be tuned into submicrometer scale (Figure 1c,d). 10% of water in IPA resulted in the assembled heptazine rods with diameters about 300–600 nm and a length about 10 $\mu$m, while 20% of water in IPA induced the assembly of heptazine into rods with a larger diameter (about 0.5–1 $\mu$m).

However, no assembled rods can be found with 5% of water in IPA (Figure 1b), which may be due to the kinetic resistance in the presence of such a low content of water. X-ray diffraction (XRD) patterns (Figure 2) of the assembled heptazine in pure water or 10% water/IPA coincide well with that of melem hydrate formed in Makowski et al.’s work, reflecting its R3c space group, while melamine and the as-prepared heptazine showed unindexed patterns. It is also shown that the resulted heptazine refluxed in pure IPA or 5% water/IPA exhibits quite different XRD patterns, indicating heptazine assembly can be only formed with the existence of enough water molecules.

SAHEP refluxed in 10% water/IPA was calcinated under Ar at 550 °C for 4 h at different temperature-rise rates,
leading to series of CNs noted as SAHEP-CNs-x, where x represents the temperature-rise rate in the calcination process. The submicrometer rod-like morphology of the precursor was well maintained during the poly-condensation without volumetric shrinkage in spite of different temperature-rise rates in the calcination process (Figure S1, Supporting Information).

Figure S2a,b in the Supporting Information show the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of SAHEP-CNs-1. The layered sheet-like structure was clearly observed in TEM (Figure S2b,c, Supporting Information). Due to the in-plane shrinkage in the poly-condensation, micropore–mesopore structure was formed within the CNs sheet. Compared with CNs prepared by calcinating melamine directly in Ar (short as MP-CN), the resulted SAHEP-CN exhibits a different XRD pattern as shown in Figure 3a,b. The diffraction peak at $2\theta = 13.2^\circ$ is much sharper and more symmetric, and at the same time, the peak at $2\theta = 27.2^\circ$ is broadened, especially for SAHEP-CN calcinated by low temperature-rise rate. The fresh heptazine prepared by calcinating melamine at 420 °C was used as another controlled precursor, i.e., the non-assembled heptazine (NAHEP). In the XRD of CNs (NAHEP-CN) resulted from the calcination of NAHEP, the feature of peaks at $2\theta = 13.2^\circ$ and $27.2^\circ$ is similar to that of MP-CN. For clear comparison, the full-width at half maximum (FWHM) and the relative intensity ratio of peak (100) and peak (002) for the different CNs were listed in Table 1.

It is obviously noted that through assembly of heptazine precursor, the resulted CNs showed a much narrowed FWHM of peak (100), broadened FWHM of peak (002) and increased relative intensity ratio of peak (100) and peak (002), suggesting an enhanced in-plane ordering and decreased stack along the c-axis, especially when the assembled precursors were calcinated with a low temperature-rise rate.[10,11] The selected area electron diffraction pattern in Figure S2b in the Supporting Information showing two diffuse diffraction rings also confirmed the enhanced in-plane ordering. It is also implied that in the calcination process, temperature-rising rate plays an important role to the microstructure of the resulted SAHEP-CN, which is also reported by Li et al.[12]

According to the report by Makowski et al., the assembled melem hydrate can be presented by an average formula of $C_6N_7(NH_2)_3 \cdot 2.3H_2O$ (water mass ratio: 16.2%). Even dehydrated under vacuum at 150 °C overnight, the resulted product is formulated as $C_6N_7(NH_2)_3 \cdot 0.3H_2O$ by element analysis,[9] implying that strong interaction maintains between heptazine and H$_2$O even at high temperature. In our case, it is also indicated by the thermogravimetry (TG) curves (Figure S3, Supporting Information) that the structural water in SAHEP only lost partially (about 12 mass%) before 450 °C, even less weight loss with lower temperature-rising rate (Figure S3a, Supporting Information). There is no such evident endothermic peak in DTG curve of SAHEP-10% as in that of raw heptazine (Figure S3, Supporting Information). Since the detailed mechanism inside the calcination of the assembled heptazine is not clear and we can only speculate the possibility from the chemistry and material viewpoint based on the conclusion from Makowski’s work. It is speculated that since the heptazine units are confined by the water molecules through hydrogen bonding, the dehydration during calcination would induce an alternative metastable structure to form some interaction between the incomplete dehydrated

Table 1. The full-width at half maximum (FWHM) and the relative intensity ratio of peak (100) and peak (002) for the different CNs and the corresponding atom ratio of N/C.

<table>
<thead>
<tr>
<th></th>
<th>SAHEP-CN-1</th>
<th>SAHEP-CN-4</th>
<th>SAHEP-CN-15</th>
<th>NAHEP-CN</th>
<th>MP-CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM of peak (100)</td>
<td>1.04</td>
<td>1.04</td>
<td>1.16</td>
<td>2.02</td>
<td>2.34</td>
</tr>
<tr>
<td>FWHM of peak (002)</td>
<td>2.91</td>
<td>2.69</td>
<td>2.37</td>
<td>1.09</td>
<td>0.95</td>
</tr>
<tr>
<td>Intensity ratio of peak (100) to (002)</td>
<td>0.518</td>
<td>0.371</td>
<td>0.289</td>
<td>0.11</td>
<td>0.075</td>
</tr>
<tr>
<td>Atom ratio of N/C</td>
<td>1.50</td>
<td>1.50</td>
<td>1.51</td>
<td>1.36</td>
<td>1.34</td>
</tr>
</tbody>
</table>
water and heptazine or there may be partial hydrolysis to form \((C_6N_7(NH_2)_{2.7}(OH)_{0.3})\) as inferred by Makowski et al.,\[9\] in both of which case, the disordered and intense condensation of heptazine will be definitely hindered, especially when calcinated with lower temperature-rising rate. Thus, the endothermic condensation is not as intense as that in the raw condensed heptazine by comparing the endothermic peak at around 520 °C in the differential thermal analyzer (DTA) curve (Figure S3b, Supporting Information).

It is discovered that although in FT-IR spectra (Figure S4, Supporting Information), most of absorbance bands are similar, absorbance bands at 3400–3500 cm\(^{-1}\) of SAHEP-CNs is stronger than that of MP-CNs and NAHEP-CNs, suggesting a higher content of NH\(_2\)/NH group in SAHEP-CNs. The XPS analysis was further used to define the carbon (C) and nitrogen (N) elements. As shown in Figure S5 in the Supporting Information, the C 1s spectra of all the CNs contain two peaks, located at 284.6 and 288.0 eV, respectively, which can be ascribed to graphite sp\(^2\) C–C bond from carbon pollutions and the sp\(^3\) hybridized carbon bonded to N in the C-N-C coordination, respectively. The deconvolution of the N 1s spectra shows three peaks located at 398.7, 400.0, and 401.1 eV, ascribed to sp\(^2\) N atoms in triazine rings, sp\(^3\) N atoms in H–N–(C)\(_3\) and the amino groups in C–NH\(_x\), respectively. The proportion distribution of these three peaks according to the deconvolution results was summarized in Table S1 in the Supporting Information. It shows that the sum of H–N–(C)\(_3\) and C–NH\(_x\) proportion for SAHEP-CNs is higher than that for MP-CNs or NAHEP-CNs, which is in agreement with the element analysis results listed in Table 1. Therefore, it is fully concluded that CNs from the assembled heptazine may contain more structured carbon nitride chain by hydrogen bonding through NH/NH\(_2\) groups.\[13\]

It is important to note that the symmetric electron spin resonance (ESR) spectrum (Figure S6a, Supporting Information) with g value of 2.003 of SAHEP-CNs-1 was stronger than that of MP-CNs and NAHEP-CNs, which may be related with the increased delocalization of single electrons in the CNx framework.\[4\] This speculation is also confirmed by the slight red-shift photoluminescence (PL) resulted from the higher conjugated carbon–nitrogen structure (Figure S6b, Supporting Information). It is suspected that the enhanced long-range ordering and conjugation would contribute to an improved charge carrier transport and electron–hole separation when this semiconductor was irradiated.

In brief for above analysis and the crystal structure of SAHEP, water molecules were functioned as a spatial template for the self-assembly of heptazine units into SAHEP, in which (110) facet was extended in micrometer scale while (001) facet extended in hundreds of nanometers as shown in Figure 4a,b. All atoms aligned within 0.36 nm in c-axis are shown in Figure 4c. The micrometer-scaled confined heptazine would undergo poly-condensation into carbon nitride with enhanced in-plane ordering, while extension of hundreds of nanometers in c-axis of SAHEP-CNs induces less stacking along c-axis in the resulted SAHEP-CNs. Since low temperature-rising rate is benefit for the metastable state before condensation, the spatial confinement is more evident when calcination with a lower temperature-rising rate. Although the resulted carbon nitride is actually not crystalline in long range due to the uncontrollable thermal motion of heptazine, the in-plane ordering can be largely improved as compared with the non-assembled precursors.

In the UV–vis optical absorption spectra (Figure S7a, Supporting Information), SAHEP-CNs showed a similar
absorption compared with MP-CNs or NAHEP-CNs. By the transformed Kubelka–Munk function calculation, the corresponding bandgap energy of SAHEP-CNs turn out to be close to that of MP-CNs or NAHEP-CNs.\textsuperscript{[14]} The conduction band (CB) edges of the as-prepared CNs were investigated by means of Mott–Schottky measurements (Figure S7b, Supporting Information). Combined with the bandgap value obtained from Kubelka–Munk function calculation, the corresponding valence band (VB) edges of the different CNs were calculated. It is shown in Figure S7c in the Supporting Information that both CB and VB edges of SAHEP-CNs were very similar to those of MP-CNs or NAHEP-CNs. It is noted in Figure S8 in the Supporting Information that SAHEP shows a similar UV–vis absorption feature to the as-prepared heptazine and the onset of optical absorption is far from that of CNs mentioned above. Therefore, we can conclude that the no carbon nitride was formed after the heptazine refluxed.

\textbf{N}_2-\text{adsorption measurement} at 77 K indicated that all these different CNs are featured as mesoporous network (see the adsorption isotherm in Figure S9 in the Supporting Information). The BET SSA of MP-CNs, NAHEP-CNs, SAHEP-CNs-15, and SAHEP-CNs-4 are around 11.4, 14.5, 17.9, and 23.9 m\textsuperscript{2} g\textsuperscript{-1}, respectively, while SAHEP-CNs-1 showed a higher SSA of 40.8 m\textsuperscript{2} g\textsuperscript{-1}, which is in agreement with the highest intensity ratio of peak (100) to (002) in the XRD pattern and the least stacking along the c-axis as mentioned above.

The photocatalytic activity of the different CNs was evaluated under visible light (λ > 420 nm) irradiation with photodeposited Pt particles as co-catalysts and triethanolamine (TEOA) as a sacrificial reagent. As shown in Figure 5a, MP-CNs and NAHEP-CNs showed a HER of 80 and 115 μmol h\textsuperscript{-1}, respectively, which were higher than that of CNs prepared by heating melamine in air as shown in Figure S10 in the Supporting Information (HER of 29 μmol h\textsuperscript{-1}). Obviously, SAHEP-CNs exhibit much improved activity especially for those calcinated at lower temperature-rising rate. Specifically, SAHEP-CNs-4 and SAHEP-CNs-15 show high HER of 360 and 290 μmol h\textsuperscript{-1}, respectively. SAHEP-CNs-1 has the highest HER of 420 μmol h\textsuperscript{-1} without noticeable deactivation after 12 h irradiation (Figure 6b), which is nearly 14.6 times as high as that of CNs prepared by calcinating melamine in air.

The AQE for H\textsubscript{2} evolution of SAHEP-CNs-1 was measured with various monochromatic light irradiations. As expected, the SAHEP-CNs-1 gave high AQE in wavelength range of 370–520 nm and the AQE at 420 nm is as high as 8.9% (Figure 5c). The wavelength-dependent HER activity matched well with the UV–vis spectra, suggesting that the hydrogen evolution was resulted from the photogenerated electrons in the excited CNs. The rod-like morphology (in Figure S11a in the Supporting Information) is rather stable even after 12 h irradiation. The Pt co-catalysts are photodeposited on the surface homogeneously, as shown in the EDS mapping in Figure S11b–d in the Supporting Information.

To further confirm the uniformly enhanced performance of these CNs derived from assembled heptazine precursors, assembled heptazine from 20% water/IPA solvent was used...
as precursors to prepare CNs (SAHEP-20%-CNs-1) by calcination at 550 °C under argon with a mild temperature-rising rate of 1 K min⁻¹. The SEM image in Figure S12b in the Supporting Information showed that the rod-like morphology of CNs has been inherited from the assembled precursors as shown in Figure 1d. The BET measurement indicates a SSA of 34.1 m² g⁻¹ from the isotherm shown in Figure S12c in the Supporting Information. SAHEP-20%-CNs-1 exhibits similar XRD pattern with SAHEP-CNns (Figure S12a, Supporting Information) and high H₂ evolution rate of about 300 μmol h⁻¹ (Figure S12d, Supporting Information).

As compared in Table S2 in Supporting Information, the resulted hydrogen generation rate and AQE value is among the highest reported values for C₃N₄-based photocatalysts. Based on the similar UV–vis light absorption characteristic, SSA is an important factor to the photocatalytic performance. As reported, low-dimensional carbon nitrides, such as nanosheets,[4c,15] nanosphere,[4a] usually possess more surface-active sites for photocatalysis due to the large surface area.[16,17] However, in our case, the SAHEP-CNns exhibit neither nanostructured architecture nor high surface area, but the photocatalytic performance is still very satisfied for bulk carbon nitride without doping and heterostructure. It is reasonable to suspect that the enhanced activity may be related to the improved charge carrier transport inside the carbon nitride polymer. Merschjann et al. ever suggested the possible interplanar transport, intrachain, and intraplanar transitions although there is not well-founded transport model.[7] The enhanced photocurrent (Figure 5d) and the decreased arc radius in the electrochemical impedance spectrum (EIS; Figure S13, Supporting Information) of SAHEP-CNns compared with MP-CNns or NAHEP-CNns further confirmed the improved charge transport and electronic conductivity within the inner planar of CNs.

The time-resolved PL spectra are further investigated and PL lifetimes are calculated by fitting the decay curve with a tri-exponential function as shown in Figure 6 and Table S3 in the Supporting Information. In an obvious contrast, SAHEP-CNns-1 exhibits the longest average lifetime (23.378 ns), which is three times and more than twice as long as those of MP-CNns (7.707 ns) and NAHEP-CNns (10.061 ns), respectively. The ordered planar structure of polymeric CN framework with enhanced conjugation is definitely considered beneficial to the intraplanar diffusion of charge carriers, resulting the prolonged average lifetime and the tremendously improved photoactivity.

3. Conclusion

In conclusion, through the preformed assembly of heptazine precursors, the resulted micro-nanostructured carbon nitrides showed enhanced ordering within the graphitic planar and decreased interlayer stacking due to the refinement of water molecules, especially in the mild calcination process with low temperature-rising rate. Attributed to the excellent charge separation by the intraplanar transport, a tremendously improved H₂ evolution rate of 420 μmol h⁻¹ under visible light (λ > 420 nm) with an apparent quantum efficiency of 8.9% at 420 nm was obtained, which is among the highest value for C₃N₄-related photocatalyst in the literature. This work disclosed that enhanced in-plane ordering is one critical factor for the improved photocatalytic H₂ evolution of carbon nitride, attributed to the prolonged lifetime of charge carriers by accelerating the charge transport and separation within the graphitic planar. Considering the relative facile fabrication without use of template and harsh condition, our finding can be envisaged to be more promising for efficient applications in the fields of pollutant degradation, CO₂ reduction and overall water splitting.

4. Experimental Section

Material Preparation: Raw heptazine was obtained by heating melamine in a porcelain crucible covered by a tin foil paper in a muffle furnace at 420 °C for 4 h. The resulted white heptazine was then placed in a dried flask, to which different solvents with various volume ratios of water (i.e., pure water, 5% water in IPA, 10% water in IPA, 20% water in IPA, pure IPA) was added before refluxing at 80 °C for 10 h. The resulted heptazine was collected and dried at room temperature. CNs were synthesized by calcinating the different precursors under argon with different temperature-rising rates to 550 °C and kept at 550 °C. The default temperature-rising rate for precursors such as melamine, non-assembled heptazine is 4 K min⁻¹.

Characterization: Powder XRD was carried out on an X-ray diffractometer (Rint 2000, Altima III, Rigaku Co. Japan) with a Cu Kα source. The morphologies were investigated by scanning electron microscopy (Field Emission Scanning Electron Microscope, JSM-6701F). TEM images, combined with energy dispersive X-ray spectroscopy (EDX) mapping were recorded with a field emission transmission electron microscope (2100F, JEOL Co., Japan) operating at 200 kV. The UV–vis absorption was measured with a UV–visible spectrophotometer (Shimadzu, UV-2600) using BaSO₄ as the reflectance standard reference. XPS measurement was carried out with electron spectrometer (PHI Quantera SXM, ULVAC-PHI Inc., Japan). PL spectra were recorded by a JASCO FP-6500 spectrofluorometer.
BET N$_2$-adsorption measurement was processed with Autosorb-IQ2 Quantachrome Instrument at 77 K after the samples were degassed at 100 °C overnight. FT-IR spectra were recorded by Nicolet 4700 spectrometer. Thermogravimetric measurements were conducted on a Seiko Instrument TG-DTA 6200. ESR measurements were carried out at room temperature on a JEOL JES-FA-200.

**Photocatalytic Measurements**: Photocatalytic activities were evaluated by the hydrogen evolution from water under visible light irradiation with TEOA as electron donor. Typically, 100 mg catalyst was suspended in a Pyrex glass reaction cell containing 260 mL 10 vol% of TEOA aqueous solution. 3 wt% Pt was added for the in-situ photodeposition and used as co-catalyst. Before the irradiation, the reaction cell was evacuated to remove the air completely. The produced H$_2$ was analyzed by an online gas chromatograph (GC-8A, Shimadzu Corp., Japan). The AQE was measured at various monochromatic lights which were obtained by using a series of bandpass filters (Optical Coating Japan). A water filter was used to avoid the overwhelmed heating. The light intensity was measured at nine different points to obtain an average intensity with a spectroradiometer (Ushio, USR-40, Japan). The AQE at each monochromatic wavelength was calculated by the following equation:

\[
\text{AQE} = \frac{2 \times \text{amount of } H_2 \text{ molecules evolved in unit time}}{\text{incident photons in unit time}} \times 100\%.
\]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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