

A Graphitic-C₃N₄ “Seaweed” Architecture for Enhanced Hydrogen Evolution**

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Abstract: A seaweed-like graphitic-C₃N₄ (g-C₃N₄ “seaweed”) architecture has been prepared by direct calcination of the freeze-drying-assembled, hydrothermally treated dicyandiamide fiber network. The seaweed network of mesoporous g-C₃N₄ nanofibers is favorable for light harvesting, charge separation and utilization of active sites, and has highly efficient photocatalytic behavior for water splitting. It exhibits a high hydrogen-evolution rate of 9900 $\mu\text{mol h}^{-1} \text{g}^{-1}$ (thirty times higher than that of its g-C₃N₄ bulk counterpart), and a remarkable apparent quantum efficiency of 7.8 % at 420 nm, better than most of the g-C₃N₄ nanostructures reported. This work presents a very simple method for designing and developing high-performance catalysts for hydrogen evolution.

Energy deficiency and environmental pollution are an urgent problem all over the world. Clean hydrogen energy is one of the most promising replacement energy resources owing to its environmental benignity and recyclability. Photochemical water splitting to generate hydrogen by utilizing a photocatalyst, only consuming solar energy, has become the main trend for hydrogen-energy production. Hence, the research and development of new highly effective photocatalysts that can make full use of solar energy by transforming it to hydrogen energy has been a research focus in photocatalysis field.^[1,2]

Graphitic carbon nitride (g-C₃N₄) which has suitable conduction-band and valence-band levels for generating hydrogen and oxygen has attracted considerable interest.^[3] It has been considered one of the most promising photocatalysts for hydrogen production owing to its good chemical stability, anti-photocorrosion, visible-light response, and easily adjustable electronic-band structure. Unfortunately, the catalytic activity of pristine g-C₃N₄ for hydrogen evolution is quite low. In this regard, various strategies have been proposed to improve the performance including the doping with metal/non-metal, creation of heterojunctions, composition, and formation of nanoarchitectures.^[4] Among them, nanostructuring g-C₃N₄ with controllable morphologies is an

efficient way to enhance the photocatalytic activity. To date, the nanostructured g-C₃N₄ including nanobelts,^[5] nanosheets,^[6] and nanospheres^[7] have emerged, but the assembly of low-dimensional g-C₃N₄ nanostructures into macroscopic architectures for hydrogen evolution is rarely reported probably because of the rigorous reaction conditions and complicated preparation process and associated high cost.^[8a]

Generally, there are two approaches to manufacture nanostructured g-C₃N₄. One way is with the aid of organic reagents^[5,8] or catalysts^[9] to form a desired size and shape. However, this type of method often involves tedious purification procedures to separate the desirable nanoparticles from complex reactant mixtures. An alternative is to use silica as a template, however this approach inevitably requires the removal of the template by environmentally hazardous reagents.^[10] As a result, a simple, environmentally friendly and low-cost method for large-scale production of nanostructured g-C₃N₄ photocatalysts with dramatically enhanced photocatalytic activity is needed.

Herein, we present a straightforward, but effective template-free methodology for the large-scale production of g-C₃N₄ “seaweed” which consists of porous fiber structures. Dicyandiamide was used as the starting material undergoing the hydrothermal treatment and vacuum freeze-drying technology was exploited to activate the self-assembly for the formation of the macroscopic network of fiber-like structures. Subsequently, the calcination of the precursor generated the network architectures of g-C₃N₄ “seaweed” which is rich in mesopores. The g-C₃N₄ “seaweed” exhibits a very high rate of hydrogen production, as high as 9900 $\mu\text{mol h}^{-1} \text{g}^{-1}$ under $\lambda > 420$ nm irradiation, which leads to a high turnover number of 385 after 6 h and results in an outstanding quantum efficiency of 7.8 % at 420 nm.

The pristine dicyandiamide has a square crystal grain size of approximately 1.5 μm (Figure S1 a,b in the Supporting Information) and its morphology was dramatically altered to a white macroscopic monolith consisted of interconnected network of fiber-like structures (Figure 1 a,b) after freeze-drying the hydrothermally treated dicyandiamide (HTD) solution. As shown in Figure 1 c,d, the assembled sample shows drastically reduced grain size compared to pristine dicyandiamide. Typically, a large piece of g-C₃N₄ was obtained by calcining the freeze-drying-assembled HTD at 550 °C (Figure 1 e), which was composed of interlocking fibers of hundreds of nanometers in width and tens of microns in length resembling “seaweed” (Figure 1 f,g) and designated as g-C₃N₄ (550) “seaweed”. The TEM image revealed that the microfibers were enriched with mesopores of less than 20 nm (Figure 1 h and its inset). Compared to g-C₃N₄ bulk (Figure S2 a,b), g-C₃N₄ (550) “seaweed” features a morphology of

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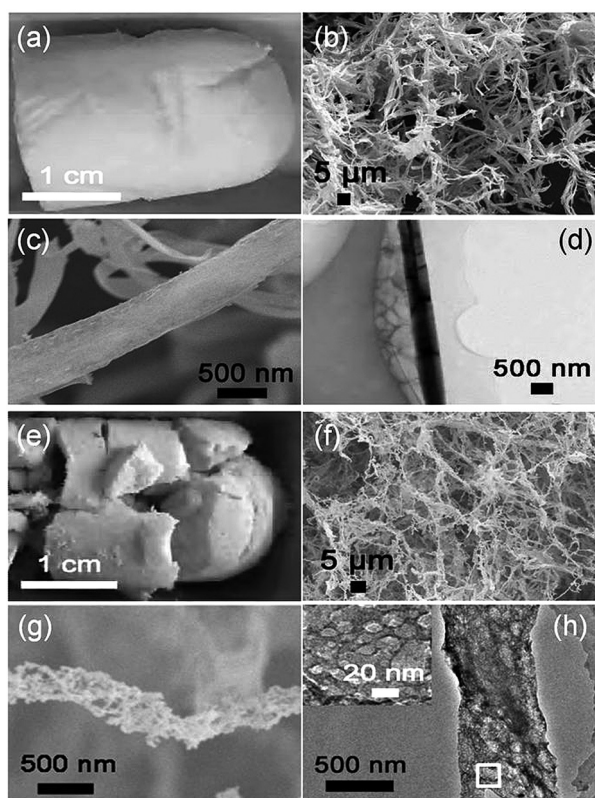


Figure 1. a) Photograph and b) low-, c) high-magnification SEM images of the freeze-dried, hydrothermally treated dicyandiamide (HTD); d) TEM image of a single fiber of the freeze-dried HTD; e) Photograph and f) low-, h) high-magnification SEM images of g-C₃N₄ (550) "seaweed"; h) TEM image of a fiber of g-C₃N₄ (550) "seaweed" (Inset: the enlarged view of the rectangle area).

an interlayer stacking reflection of conjugated aromatic segments, respectively.^[4d,5-7] Compared to g-C₃N₄ bulk, g-C₃N₄ (550) "seaweed" shows a shift and widened diffraction peak appears at about 26.8°, indicating a slightly enlarged interlayer spacing.^[4,7] The peak located at 13.3° was absent for g-C₃N₄ (550) "seaweed", suggesting a smaller planar size,^[4,7] as observed in TEM image (Figure 1h). As g-C₃N₄ (550) "seaweed" has a mesoporous structure and exhibits much smaller and thinner particles/sheets than g-C₃N₄ bulk (Figure S2), it can be homogeneously dispersed in water with concentrations of 1 mg mL⁻¹ without precipitation even after storage for two weeks under ambient conditions, in sharp contrast to the poor dispersibility observed for g-C₃N₄ bulk (Figure S3), which thus favors a maximized exposure of catalytic species to water. FT-IR spectrum of g-C₃N₄ (550) "seaweed" exhibits several strong bands in the region 1200–1700 cm⁻¹ (Figure 2c), which belong to the typical stretching modes of CN heterocycles. The peak at approximately 810 cm⁻¹ originates from the characteristic breathing mode of tri-s-triazine units.^[4d,5-7] There is an enhanced absorption for g-C₃N₄ "seaweed" in the 2900–3600 cm⁻¹ range corresponding to the surface-bonded H₂O molecules and amino groups, which indicate the enlarged open-up surfaces.^[7] X-ray photoelectron spectroscopy (XPS) shows g-C₃N₄ "seaweed" has a similar chemical composition to that of g-C₃N₄ bulk (Figure S4a). High resolution N1s spectrum of g-C₃N₄ (550) "seaweed" (Figure 2d) reveals the existence of sp²-hybridized nitrogen (N1) at 398.8 eV, the tertiary nitrogen (N(C)₃, N2) at 399.7 eV and the amino functional groups (N3) at 400.8 eV.^[4-7] Accordingly, C1s spectrum (Figure S4b) shows the C–C, N–C=N, and C–O bands,^[4-7] which match with the energy dispersive X-ray (EDX) spectrum (Figure S5). Overall, g-

thin and porous fibers (detailed discussion in Supporting Information). Nitrogen adsorption–desorption isotherms (Figure 2a) show that the nitrogen uptake of g-C₃N₄ (550) "seaweed" is significantly greater in the high-pressure range than for g-C₃N₄ bulk, indicating the existence of mesopores. The Brunauer–Emmett–Teller (BET) surface area of g-C₃N₄ (550) "seaweed" is approximately 130 m² g⁻¹, which is over 10-times higher than that of g-C₃N₄ bulk (ca. 12 m² g⁻¹). The pore size is mainly less than 20 nm (inset in Figure 2a), consistent with the TEM observation (Figure 1h and its inset). Such a 10-fold increase in the specific surface area of g-C₃N₄ (550) "seaweed" should be beneficial for its application as a photocatalyst as a more exposed interfacial contact to the reactant would be highly demanded.

For X-ray diffraction (XRD) analysis, g-C₃N₄ bulk features two peaks (Figure 2b) at 13.3° and 27.4° arising from an in-plane structural packing motif and

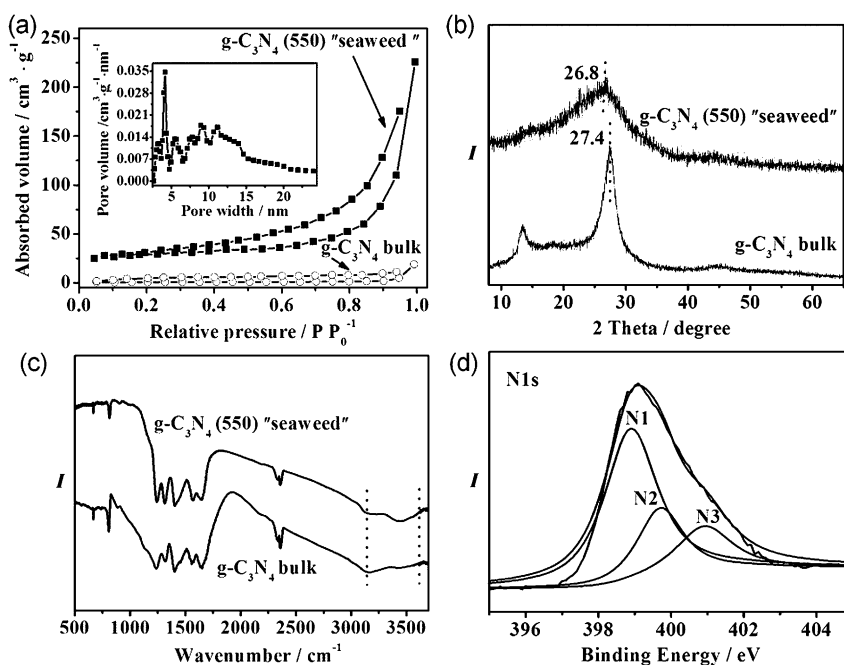


Figure 2. a) N₂ adsorption isotherms of g-C₃N₄ (550) "seaweed" and g-C₃N₄ bulk. Inset: pore size distribution of g-C₃N₄ (550) "seaweed"; b) XRD patterns and c) FT-IR spectrum of g-C₃N₄ (550) "seaweed" and g-C₃N₄ bulk; d) The high-resolution N1s XPS spectrum of g-C₃N₄ (550) "seaweed".

C_3N_4 (550) “seaweed” has the intrinsic structure of typical $\text{g-C}_3\text{N}_4$ but with a hierarchical nanostructured high surface area that could potentially lead to a largely improved evolution rate of water splitting.

The hierarchical nanostructured architectures greatly altered the optical properties of $\text{g-C}_3\text{N}_4$ (550) “seaweed” compared to $\text{g-C}_3\text{N}_4$ bulk. In Figure 3a, the photoabsorption

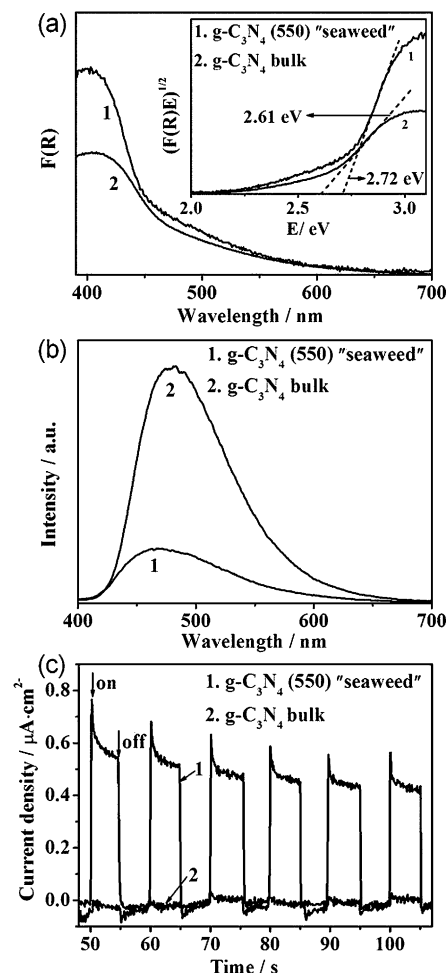


Figure 3. a) UV/Vis diffuse reflectance spectra of 1) $\text{g-C}_3\text{N}_4$ (550) “seaweed” and 2) $\text{g-C}_3\text{N}_4$ bulk (Inset: bandgap energies); b) PL spectra of 1) $\text{g-C}_3\text{N}_4$ (550) “seaweed” and 2) $\text{g-C}_3\text{N}_4$ bulk with the excitation wavelength of 400 nm; c) Transient photocurrents under visible light illumination ($\lambda > 420$ nm) of 1) $\text{g-C}_3\text{N}_4$ (550) “seaweed” and 2) $\text{g-C}_3\text{N}_4$ bulk obtained at 0.1 V vs. Ag/AgCl in a 0.2 M Na_2SO_4 aqueous solution (pH 6.8).

edge of $\text{g-C}_3\text{N}_4$ (550) “seaweed” displays a hypochromic shift from 475 nm to 455 nm. The corresponding bandgap energy increases from 2.61 eV to 2.72 eV, indicating the quantum confinement effect in $\text{g-C}_3\text{N}_4$ (550) “seaweed” (Figure 3a inset).^[4d,e] Furthermore, a remarkably enhanced light-harvesting ability is also discovered for $\text{g-C}_3\text{N}_4$ (550) “seaweed” across the whole optical spectrum, mainly arising from multiple scattering effects and the existence of large numbers of defect sites associated with the mesoporous surfaces.^[7,10a] The structure-induced property change can also be observed

in the photoluminescence spectra. As shown in Figure 3b and Figure S6, the otherwise strong photoluminescence is quenched, suggesting that the energy-wasteful charge recombination is substantially suppressed, and thus improving charge separation.^[10a,b] The property change should be attributed to the structural benefits of $\text{g-C}_3\text{N}_4$ (550) “seaweed” because its open-framework construction can create new surface states for charge traps. Furthermore, and $\text{g-C}_3\text{N}_4$ (550) “seaweed” featuring 1D thin fibers might facilitate photo-generated electron transfer onto its surfaces for reacting with water molecules, which could in return inhibit the charge recombination. The clear enhancement of photocurrent (Figure 3c) for $\text{g-C}_3\text{N}_4$ (550) “seaweed” indicates an improved charge separation, and therefore an enhancement of the photocatalytic performance.^[5,6]

The photocatalytic activities of $\text{g-C}_3\text{N}_4$ (550) “seaweed” was examined for hydrogen evolution from water by using 3 wt % Pt as a co-catalyst and 10 vol % triethanolamine as an electron donor under visible light irradiation ($\lambda > 420$ nm). As shown in Figure 4a, 1.2 mmol H_2 gas (26.9 mL) was produced

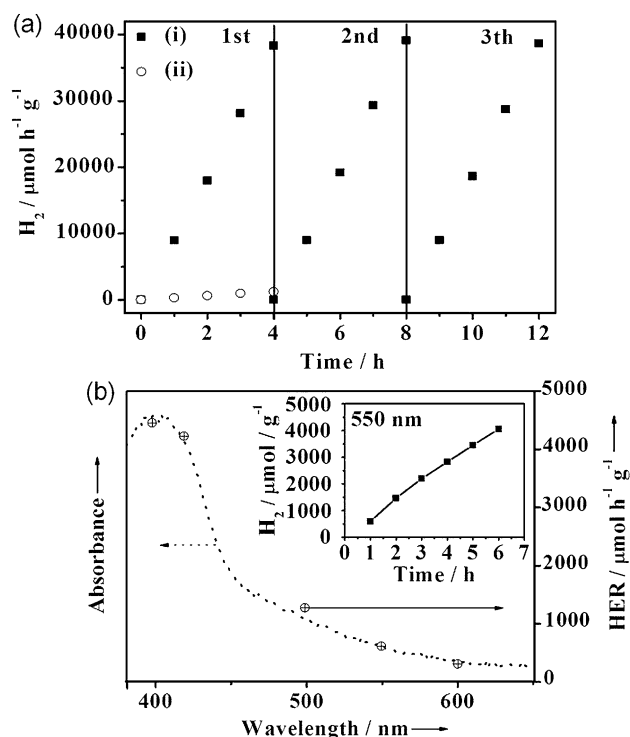


Figure 4. a) Photocatalytic activities of $\text{g-C}_3\text{N}_4$ (550) “seaweed” (i) and $\text{g-C}_3\text{N}_4$ bulk (ii) under irradiation with visible light ($\lambda > 420$); b) Wavelength dependence of H_2 evolution rate on $\text{g-C}_3\text{N}_4$ (550) “seaweed” (inset: the H_2 evolution under 550 nm light irradiation).

without noticeable deactivation after 12 h. The hydrogen evolution rate (HER) of $\text{g-C}_3\text{N}_4$ (550) “seaweed” steadily reaches to $9900 \mu\text{mol h}^{-1} \text{g}^{-1}$, over thirty times that of $\text{g-C}_3\text{N}_4$ bulk ($300 \mu\text{mol h}^{-1} \text{g}^{-1}$). In addition it has a turnover number (TON) of 385 in 6 h, much higher than that of $\text{g-C}_3\text{N}_4$ bulk (2.3) (Figure S7). Wavelength dependence of H_2 evolution reveals the activity of $\text{g-C}_3\text{N}_4$ (550) “seaweed” corresponds to its optical absorption spectrum, suggesting that the H_2

production is primarily driven by photo-induced electrons in carbon nitride polymer (Figure 4b).^[7] The calculated apparent quantum efficiency of g-C₃N₄ (550) “seaweed” is 7.8 % under irradiation at 420 nm. In addition, g-C₃N₄ (550) “seaweed” still shows a nearly linear profile of photocatalytic activity (HER = 614 $\mu\text{mol h}^{-1} \text{g}^{-1}$) for 6 h at 550 nm monochromatic illumination (Figure 4b inset).

For comparison, a series of g-C₃N₄ “seaweed” samples were obtained by calcining the precursors of the freeze-drying assembled HTD under controlled temperatures. The g-C₃N₄ “seaweed” samples obtained by calcination at 500 °C, 600 °C, and 650 °C were designated as g-C₃N₄ (500), (600), and (650) “seaweed”, respectively. All the g-C₃N₄ “seaweed” samples are mesoporous fiber networks (Figure S8) and show similar XRD patterns and IR spectra (Figure S9 and S10) to g-C₃N₄ (550) “seaweed”. BET surface areas of g-C₃N₄ (500), (600), and (650) “seaweed” are around 103 cm² g⁻¹, 135 cm² g⁻¹ and 147 cm² g⁻¹, respectively, closely to that of g-C₃N₄ (550) “seaweed” and much larger than that of g-C₃N₄ bulk. Note that the HER of g-C₃N₄ (550) “seaweed” is the highest versus other samples (Figure 5a). This performance variation may be directly associated with the effect of the nitrogen species according to previous reports.^[11] As shown in Figure S11 and

Table S1, the ratio of sp² C=N=C bonds to the sum of sp³ N=[C]₃ and C-NH_x bonds for g-C₃N₄ (550) “seaweed” was 1.48, higher than those samples treated at 500 °C, 600 °C, and 650 °C (1.24, 1.30, and 1.27, respectively), indicating that the sp²-bonded nitrogen atom contributes more to the bandgap absorption than other nitrogen species,^[11] thus inducing a larger enhancement in photocatalytic activity. The optimal g-C₃N₄ (550) “seaweed” with the excellent HER of 9900 $\mu\text{mol h}^{-1} \text{g}^{-1}$ and apparent quantum efficiency of 7.8 % at 420 nm is greater than most of the nanostructured g-C₃N₄ photocatalysts reported (Figure 5b and Table S2), except g-C₃N₄ nanospheres.^[7] However, for the preparation of g-C₃N₄ nanospheres, silica spheres were usually used as sacrificial templates, a large amount of organic solvents (e.g., tetraethyl orthosilicate, cyclohexane, cetylpyridinium bromide), and a tedious multistep process were involved, that is challenging to scale up into large quantity production.

In summary, we have successfully assembled 1D nanofibers of g-C₃N₄ with mesoporous structure into a “seaweed” architecture by using a simple method of freeze-drying self-assembly approach. The product has improved electron-transfer ability, enhanced light harvesting, and increased active sites, it exhibits highly efficient photocatalytic activity, better than most nanostructured g-C₃N₄ catalysts. This work provides a simple method for large-scale constructing the new type of g-C₃N₄ nanostructured materials for a large variety of optoelectronic devices and biological applications.

Experimental Section

Synthesis: Dicyandiamide (0.50 g) was added into deionized water (12.5 mL), and the mixture was placed into a sonic bath for 30 min to obtain a homogeneous solution. The solution was sealed in a Teflon-lined autoclave at 200 °C for 4 h, and then kept in liquid nitrogen to induce the freezing assisted assembly. The final sample was collected by thermal treatment of the freeze-dried HTD at different temperatures (500 °C to 650 °C) with a ramp rate of 1 °C min⁻¹ in Ar flow. The hydrothermal pretreatment prior to the vacuum freeze-drying process has a significant effect on the morphology and performance of the final g-C₃N₄ “seaweed” products, which has been discussed in detail in Figure S12–S17 in Supporting Information). For comparison, the g-C₃N₄ bulk was synthesized by directly heating dicyandiamide from room temperature to 550 °C in Ar with a ramp rate of 1 °C min⁻¹ and stabilized for 4 h, then cooled to room temperature.

Characterization: The morphology of the samples was investigated by scanning (SEM, JSM-7500) and transmission (TEM, 7650B, Hitachi) electron microscopy. XRD patterns were obtained by using a Netherlands 1,710 diffractometer with a Cu K α irradiation source ($\lambda = 1.54 \text{ \AA}$). FTIR spectra were recorded on a Bruker spectrometer (Equinox 55/S) using KBr pellets. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al K α radiation. The UV/Vis absorption and the photoluminescence spectra were measured with a 5300pc spectrophotometer and a SPEX fluorolog-3 fluorimeter. BET specific surface area was determined by nitrogen adsorption-desorption isotherm measurements at 77 K (NOVA 2200e).

Photocatalytic tests: Photocatalytic water splitting was carried out in a top-irradiation vessel connected to a gas-closed glass system. Photocatalyst powder (10 mg) was dispersed in aqueous solution (100 mL) containing 10 vol % triethanolamine scavenger and 3 wt % (respect to Pt, acting as co-catalysts) H₂PtCl₆·6H₂O. The temperature of the reaction solution was carefully maintained below 6 °C during the whole experiment. The reactor was then sealed and evacuated

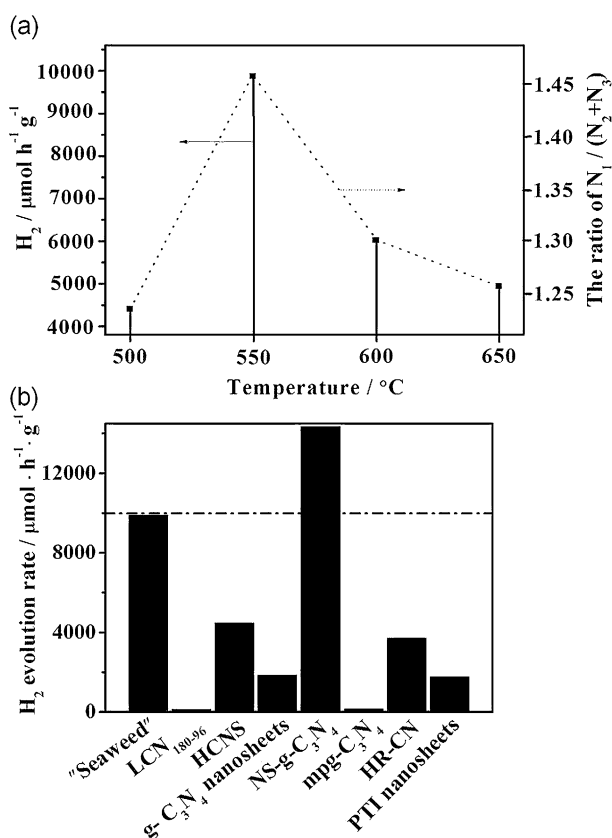


Figure 5. a) Hydrogen-evolution rate of g-C₃N₄ (500), (550), (600), and (650) “seaweed” samples prepared at the indicated temperatures (dotted line is to guide the eye); b) The Hydrogen-evolution rate for various nanostructured g-C₃N₄ photocatalysts (“seaweed” representing g-C₃N₄ (550) “seaweed” in this work, LCN₁₈₀₋₉₆ Ref. [5], HCNS Ref. [8b], g-C₃N₄ nanosheets Ref. [6a], NS-G-C₃N₄ Ref. [7], mpg-C₃N₄ Ref. [10a], HR-CN Ref. [8c], PTI-nanosheets Ref. [8d]).

several times to remove air before irradiated under a 300 W Xe lamp equipped with a 420 nm cutoff filter. The amount of evolved H₂ was analyzed by gas chromatography (GC-7920) with high-purity nitrogen carrier gas.

Keywords: g-C₃N₄ “seaweed” · hydrogen evolution · photocatalysis · self-assembly · template-free

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- [1] K. Maeda, K. Teramura, D. L. Lu, T. Takata, N. Saito, Y. Ioune, K. Domen, *Nature* **2006**, *440*, 295.
- [2] X. B. Chen, S. H. Shen, L. J. Guo, S. S. Mao, *Chem. Rev.* **2010**, *110*, 6503–6570.
- [3] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2008**, *8*, 76–80.
- [4] a) X. Wang, X. Chen, A. Thomas, X. Fu, M. Antonietti, *Adv. Mater.* **2009**, *21*, 1609–1612; b) G. Liu, P. Niu, C. H. Sun, S. C. Smith, Z. G. Chen, G. Q. Lu, H. M. Cheng, *J. Am. Chem. Soc.* **2010**, *132*, 11642–11648; c) Z. Z. Lin, X. C. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 1735–1738; *Angew. Chem.* **2013**, *125*, 1779–1782; d) G. G. Zhang, M. W. Zhang, X. X. Ye, X. Q. Qiu, S. Lin, X. C. Wang, *Adv. Mater.* **2014**, *26*, 805–809; e) Q. Han, C. G. Hu, F. Zhao, Z. P. Zhang, N. Chen, L. T. Qu, *J. Mater. Chem. A* **2015**, *3*, 4612–4619.
- [5] Y. J. Cui, Z. X. Ding, X. Z. Fu, X. C. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 11814–11818; *Angew. Chem.* **2012**, *124*, 11984–11988.
- [6] a) S. B. Yang, Y. J. Gong, J. S. Zhang, L. Zhan, L. L. Ma, Z. Y. Fang, R. Vajtai, X. C. Wang, P. M. Ajayan, *Adv. Mater.* **2013**, *25*, 2452–2457; b) Q. Han, F. Zhao, C. G. Hu, L. X. Lv, Z. P. Zhang, N. Chen, L. T. Qu, *Nano Res.* **2015**, *8*, 1718–1728.
- [7] J. S. Zhang, M. W. Zhang, C. Yang, X. C. Wang, *Adv. Mater.* **2014**, *26*, 4121–4126.
- [8] a) Y. S. Jun, J. Park, S. U. Lee, A. Thomas, W. Hi, G. D. Stucky, *Angew. Chem. Int. Ed.* **2013**, *52*, 11083–11087; *Angew. Chem.* **2013**, *125*, 11289–11293; b) J. H. Sun, J. S. Zhang, M. W. Zhang, M. Antonietti, X. Z. Fu, X. C. Wang, *Nat. Commun.* **2012**, *1139*; c) Y. Zheng, L. H. Lin, X. J. Ye, F. S. Guo, X. C. Wang, *Angew. Chem. Int. Ed.* **2014**, *53*, 11926–11930; *Angew. Chem.* **2014**, *126*, 12120–12124; d) K. Schwinghammer, M. B. Mesch, V. Duppel, C. Ziegler, J. Senker, B. V. Lotsch, *J. Am. Chem. Soc.* **2014**, *136*, 1730–1733.
- [9] a) V. N. Khabashesku, J. L. Zimmerman, J. L. Margrave, *Chem. Mater.* **2000**, *12*, 3264–3270; b) J. L. Zimmerman, R. Williams, V. N. Khabashesku, J. L. Margrave, *Nano Lett.* **2001**, *1*, 731–734.
- [10] a) X. Wang, K. Maeda, X. Chen, K. Takanabe, K. Domen, Y. Hou, X. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, *131*, 1680–1681; b) K. Kailasam, J. D. Epping, A. Thomas, S. Losse, H. Junge, *Energy Environ. Sci.* **2011**, *4*, 4668–4674.
- [11] D. J. Martin, K. P. Qiu, S. A. Shevlin, A. D. Handoko, X. W. Chen, Z. X. Guo, J. W. Tang, *Angew. Chem. Int. Ed.* **2014**, *53*, 9240–9245; *Angew. Chem.* **2014**, *126*, 9394–9399.

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