

Metal-free Synthesis of Pyridyl Conjugated Microporous Polymers for Photocatalytic Hydrogen Evolution

Qin-Ruo Zeng^a, Zhong-Hua Cheng^a, Chen Yang^a, Yan He^a, Nan Meng^a, Charl F. J. Faul^b, and Yao-Zu Liao^{a*}

^a State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

^b School of Chemistry, University of Bristol, BS8 1TS Bristol, U.K.

Abstract Developing efficient, stable and sustainable photocatalysts for water splitting is one of the most significant methods for generating hydrogen. Conjugated microporous polymers, as a new type of organic semiconductor photocatalyst, have adjustable bandgaps and high specific surface areas, and can be synthesized using diverse methods. In this work, we report the design and synthesis of a series of pyridyl conjugated microporous polymers (PCMPs) utilizing polycondensation of aromatic aldehydes and aromatic ketones in the presence of ammonium acetate. PCMPs with different chemical structures were synthesized *via* adjusting monomers with different geometries and contents of nitrogen element, which could adjust the bandgap and photocatalytic performance. Photocatalytic hydrogen evolution rate (HER) up to 1198.9 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ was achieved on the optimized polymer with a specific surface area of 312 $\text{m}^2\cdot\text{g}^{-1}$ under UV-Vis light irradiation ($\lambda > 320\text{ nm}$). This metal-free synthetic method provides a new avenue to preparing an efficient photocatalyst for hydrogen evolution.

Keywords Pyridyl conjugated microporous polymer; Metal-free synthesis; Adjustable bandgaps; Photocatalytic hydrogen evolution

Citation: Zeng, Q. R.; Cheng, Z. H.; Yang, C.; He, Y.; Meng, N.; Faul, C. F. J.; Liao, Y. Z. Metal-free synthesis of pyridyl conjugated microporous polymers for photocatalytic hydrogen evolution. *Chinese J. Polym. Sci.* 2021, 39, 1004–1012.

INTRODUCTION

To mitigate the serious environmental problems and energy crisis, it is urgent and essential to develop green and sustainable sources of energy.^[1–4] Hydrogen energy with the characteristics of high combustion calorific value and pollution-free is considered to be one of the most ideal energy sources for the future.^[5–7] Water splitting *via* photocatalysis represents a valuable approach to generating hydrogen energy.^[8] Inorganic semiconductor photocatalysts have been extensively studied because of their capabilities to generate electrons and holes while absorbing ultraviolet (UV) or visible light. However, most of them have narrow absorption range of light due to their large bandgaps.^[9–12] In comparison, organic semiconductor photocatalysts have received increasing attention owing to their versatile synthesis and designability of monomers. Moreover, the electronic properties and the ability to access a range of functions of organic semiconductors could be controlled *via* simply adjusting their chemical structures,^[13,14] which exhibits a great potential for photocatalytic hydrogen evolution applications. For example, as a typical organic semiconductor, linear conjugated polymer *e.g.* poly(*p*-phenylene),^[15] has been widely applied in photocatalytic hydrogen production. Even though some of them showed a weak response and poor

stability, which could be overcome *via* loading active materials with precious metals and forming metal coordination bonds. Thereby, the organic semiconductors could narrow the bandgap to absorb more visible light and promote the separation of photogenerated electrons and holes.^[16] As another typical organic semiconductor, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) with a highly delocalized conjugated 2-dimension (2D) structure, has also been used for photocatalytic hydrogen evolution. Various syntheses and designable strategies for $\text{g-C}_3\text{N}_4$ have been reported to enhance the photocatalytic efficiencies;^[17–19] however, the difficulty of reproducible synthesis and low yield limit its practical applications. Meanwhile, ultrafast charge carrier recombination and narrow light response range restrain the efficiency of hydrogen evolution using $\text{g-C}_3\text{N}_4$.^[20–22]

Conjugated microporous polymers (CMPs) possess a microporous structure that provides a high surface area, which could expose more active sites. Meanwhile, CMPs can be synthesized using a range of approaches, and their band structures can be readily adjusted to increase the wavelength of light absorption of visible light.^[23–26] Over the past decade, the studies of CMPs revealed that choosing monomers with various structures could adjust the structure frame to increase hydrogen evolution rate.^[27–30] However, most syntheses of CMPs utilized metal-catalyzed coupling reactions, including Suzuki-Miyaura coupling, Yamamoto coupling, and Sonogashira-Hagihara coupling reactions,^[31–35] which have limitations of high cost, harsh reaction conditions, and complex purification. Hence, the development of an effective and

* Corresponding author, E-mail: yzliao@dhu.edu.cn

Received December 26, 2020; Accepted February 25, 2021; Published online May 25, 2021

metal-free method for synthesizing CMPs with suitable functionalities and optoelectronic structures for photocatalytic hydrogen evolution is highly desired.

The Chichibabin reaction,^[36] is a metal-free organic synthesis method using aromatic aldehyde and aromatic ketone *via* cross-coupling to generate the pyridine ring, of which the nitrogen resource is ammonium acetate. The existence of the pyridine ring provides sites for the preparation of N-doped CMPs. This synthetic method with no participation of any metal catalysts and the reaction conditions are mild with the reaction completed within a few minutes.^[37] With the initially suggested feasibility of the Chichibabin reaction, this approach can be further developed for the production of CMPs, whose molecular structure can be rationally designed for the applications of hydrogen evolution.

In this study, we chose two aromatic ketones and three aromatic aldehydes as monomers to synthesize a series of pyridyl conjugated microporous polymers (PCMPs) using Chichibabin reaction for photocatalytic hydrogen evolution. The molecular structures and the bandgaps of PCMPs were regulated using different monomers. All the PCMPs display high specific surface areas and high microporous volumes. PCMPs with triazine structures show high photocatalytic property for hydrogen evolution.

EXPERIMENTAL

Materials

1,3,5-Tri(*p*-formylphenyl)benzene (TFPB, AR), 2,4,6-tris(4-alde-

hyde phenyl)-1,3,5-triazine (TAPT, AR) and tri(4-formylphenyl)amine (TFPA, AR) were purchased from Shanghai Kaiyulin Pharmaceutical Technology. 1,4-Diacetyl benzene (DAB, AR) and 1,3,5-triacetyl benzene (TAB, AR) were purchased from Chemical Industrial Development Co., Ltd. Ammonium acetate (AR) and pyridine (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Triethanolamine (AR, 98%) was purchased from MACKLIN. Chloroplatinic acid hexahydrate was provided by Sigma-Aldrich.

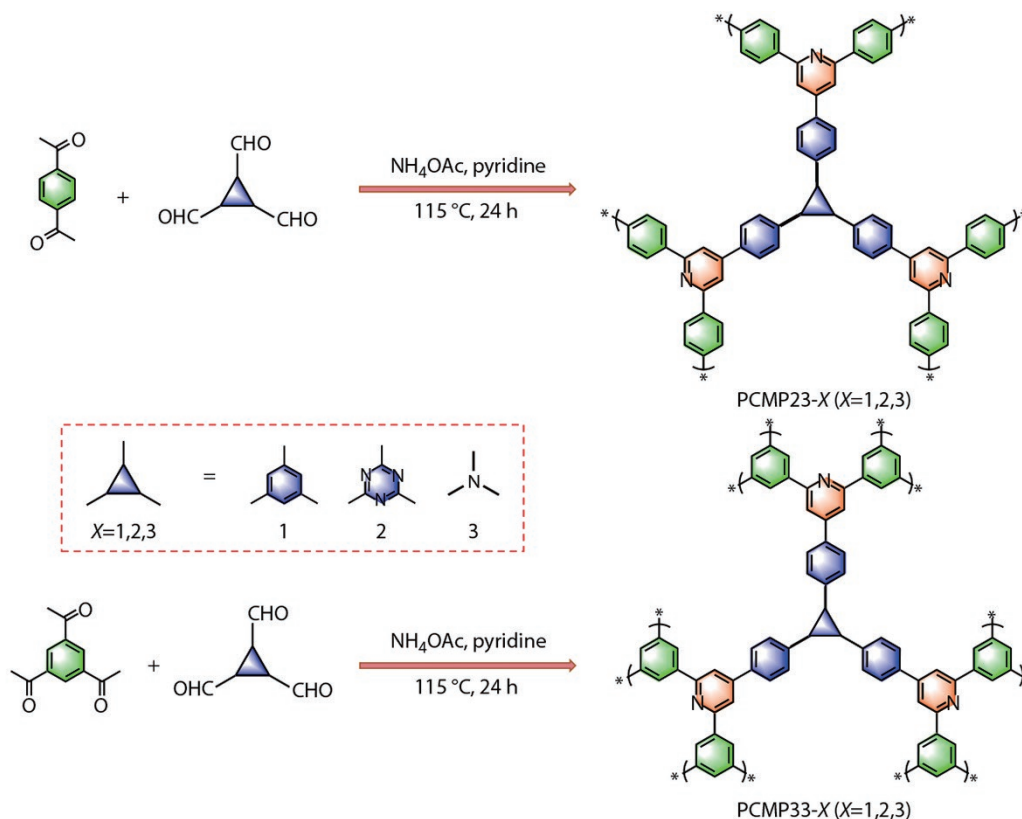
Synthesis of PCMPs

Synthesis of PCMP23-*X* (*X*=1,2,3)

A typical synthetic route (Scheme 1) to PCMP23-1 is given as an example. DAB (243.3 mg, 1.5 mmol), TFPB (195.2 mg, 0.5 mmol) and ammonium acetate (1.542 g, 20 mmol) were added to a 250 mL round-bottom flask with 100 mL of pyridine. The mixture was heated to 115 °C, stirred for 24 h, and then filtrated to collect the precipitate. The precipitate was washed with deionized water (100 mL, 60 °C), methanol (100 mL, 60 °C) and chloroform (100 mL, 60 °C), and then dried in a vacuum oven at 60 °C for 24 h. PCMP23-2 and PCMP23-3 were produced using the same synthetic procedure, but replacing TFPB with TAPT (196.6 mg, 1.5 mmol) and TFPA (164.7 mg, 1.5 mmol), respectively.

Synthesis of PCMP33-*X* (*X*=1,2,3)

A typical synthetic route (Scheme 1) to PCMP33-1 is given as an example. TAB (204.2 mg, 1 mmol), TFPB (195.2 mg, 0.5 mmol) and ammonium acetate (1.155 g, 15 mmol) were added to a



Scheme 1 Synthetic routes to PCMPs. (PCMPs synthesized using DAB with aldehyde group monomers were denoted as PCMP23-*X*; PCMPs synthesized using TAB with aldehyde group monomers were denoted as PCMP33-*X*).

250 mL round-bottom flask with the addition of 100 mL of pyridine. The mixture was heated to 115 °C and stirred for 24 h, which was then filtrated to collect the precipitate. The precipitate was washed with deionized water (100 mL, 60 °C), methanol (100 mL, 60 °C) and chloroform (100 mL, 60 °C), and then dried in a vacuum oven at 60 °C for 24 h. PCMP33-2 and PCMP33-3 were produced using the same synthetic route, but replacing TFPB with TAPT (196.6 mg, 1.5 mmol) and TFPA (164.7 mg, 1.5 mmol), respectively.

Characterization

Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 6700 FTIR spectrometer (Thermo Fisher) at room temperature. Solid-state ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker Advance-400 spectrometer (400 MHz). X-ray diffraction (XRD) patterns (Cu-K α radiation, 2θ : 5°–90°, step size: 0.03°) were obtained on a D/max-2550VB+/PC (18 kW) X-ray diffractometer (Bruker-AXS, Germany). Thermogravimetric analysis (TGA) was conducted on a Netzsch TG 209 F1Libra in a N_2 environment (40 °C to 900 °C, 10 °C·min $^{-1}$). Scanning electron microscopy (SEM) observation of the polymer networks was performed on SU8010. The Brunauer-Emmett-Teller (BET) surface areas were calculated from N_2 adsorption/desorption isotherms at 77.4 K after degassing the samples under a high vacuum at 120 °C for 12 h, which were acquired on a Micromeritics ASAP 2460 surface area analyzer. The nonlocal density functional theory (NLDF) model was used to calculate the distribution of pore size. UV-Vis absorption spectra were obtained on a spectrophotometer (Lambda-35, US) using BaSO_4 as a reflectance sample.

Electrochemical Measurements

Cyclic voltammetry (CV) measurements were carried out on an Interface 1000E (GAMRY) electrochemical workstation in a three-electrode-cell system: glassy carbon electrode as the working electrode, Ag/AgCl electrode as the reference electrode, platinum wire as the counter electrode. The sample (4 mg) was dispersed in 1 mL of methanol with 80 μL of Nafion. Then the mixture was drop-casted on top of a glassy carbon working electrode and enabled the solvent to evaporate in a vacuum chamber for 1 h. The measurement was carried out in a 0.1 mol·L $^{-1}$ of tetrabutylammonium hexafluorophosphate solution as supporting electrolyte in acetonitrile with a scan rate of 50 mV·s $^{-1}$ in the range of −1.5 V to 0 V. For the conversion from Ag/AgCl redox couple to the normal hydrogen electrode (NHE), the equation $E_{\text{NHE}} = E_{\text{SCE}} - 0.22$ V was applied.

Photocatalytic Hydrogen Production Test

The hydrogen evolution reaction was carried out on Labsolar 6A (Beijing Perfect Light Technology Co., Ltd.) system. Catalyst powders (10 mg) were dispersed in deionized water (45 mL), triethanolamine (TEOA, 5 mL), and H_2PtCl_6 (Pt, 3 wt%, 50 μL), which were then sonicated for 30 min to ensure an even dispersion. The dispersed catalyst powders were poured into a 500 mL quartz glass reactor and cooled using circulating water (5 °C). For photocatalysis, a 300 W Xe lamp (PLS-SXE300/300UV) was used for top illumination. TEOA was used as a sacrificial agent, and H_2PtCl_6 as a promoter. To measure the production of H_2 , evolved gas was measured using a Gas Chromatograph 9790II from Zhejiang Fuli Analytical Instrument Co., Ltd.

RESULTS AND DISCUSSION

Fig. 1(a) shows the XRD patterns of the synthesized PCMPs. All the samples display highly broad diffraction peaks, which indicates their amorphous structures. Fig. 1(b) shows the TGA of PCMPs, and all the polymers show high thermal stability (decomposition temperature $T_d > 400$ °C). FTIR spectra confirm the structures of polymer chains (Figs. 1c and 1d). The three aldehyde monomers have characteristic bands of —CHO at 2750 cm $^{-1}$ which disappear in PCMPs. Moreover, the characteristic bands of C=O (aldehyde group) and C=O (ketone group) at 1730 and 1680 cm $^{-1}$, respectively, were significantly reduced in PCMPs, indicating the reaction of aldehyde and ketone monomers. The characteristic band of the triazine ring C—N (1360 cm $^{-1}$) retained in PCMP23-2 and PCMP33-2, and the characteristic band of C—N in TFPA (1259 cm $^{-1}$) can also be found in PCMP23-3 and PCMP33-3. The solid-state ^{13}C -NMR spectra are shown in Fig. 2(a). The characteristic carbon signals of the benzene ring could be observed at 127 and 136 ppm. There are weak signals in PCMP23-1 and PCMP33-1 at 140 ppm, which could be derived from C—N (pyridine nitrogen). In PCMP23-2 and PCMP33-2, the signal at 169 ppm is derived from the triazine ring. The signal at 146 ppm is contributed to C—N due to the used monomer of TFPA in PCMP23-3 and PCMP33-3. Various element species in polymers can be determined using XPS. Fig. 2(b) shows the full XPS spectra of polymers, which confirms the existence of C and N elements. As shown in Fig. 2(c), the main C 1s peaks at 284.8 and 284.6 eV can be ascribed to the C=C and C—C, and a new peak at 285.6 eV indicates the existence of C=N. In the N 1s spectrum (Fig. 2d), there is one main N 1s peak with a binding energy of 398.8 eV in TAPT, the same with a binding energy of 399.8 eV in TFPA. After the Chichibabin reaction, an additional N 1s peak at 398.5 eV was generated (Fig. 2d), which can be identified as pyridine nitrogen. The existence of pyridine nitrogen indicates that the pyridyl polymers were successfully synthesized.

Fig. 3 shows the morphologies of PCMPs which are irregular particles with various sizes. The choice of DAB or TAB had no influence on the morphologies of PCMPs. The porosity of PCMPs was investigated via nitrogen adsorption analyses (Figs. 4a and 4b). The curves of N_2 adsorption and desorption of PCMPs rose rapidly at a relative low-pressure region ($p/p_0 < 0.001$), which means rapid gas adsorption linked to their abundant micropores in the polymer networks. At relative medium- and high-pressure region ($p/p_0 = 0.1–1.0$), the curves rose at a slow rate, indicating the presence of macropores in PCMPs, which might be caused by the porosity or void of the interparticle.^[38] The existence of “hysteresis loop” is consistent with elastic deformations or swelling as a result of gas sorption.^[39,40] Figs. 4(c) and 4(d) show the pore size distribution (PSD) curves for the polymer networks calculated by non-local density functional theory (NLDF). Most of the pore widths are smaller than 2 nm, which indicates their abundant micropores in the polymer networks. Especially for PCMP23-2 and PCMP33-2, the pores are all microporous. Table 1 shows the BET specific surface areas. The specific surface areas of PCMP23-X and PCMP33-X are roughly 300–600 m ^{2} ·g $^{-1}$. The specific surface area affects the photocatalytic efficiency, and it is proposed that the existence of pores can accelerate the transport of substances and expose more active sites to

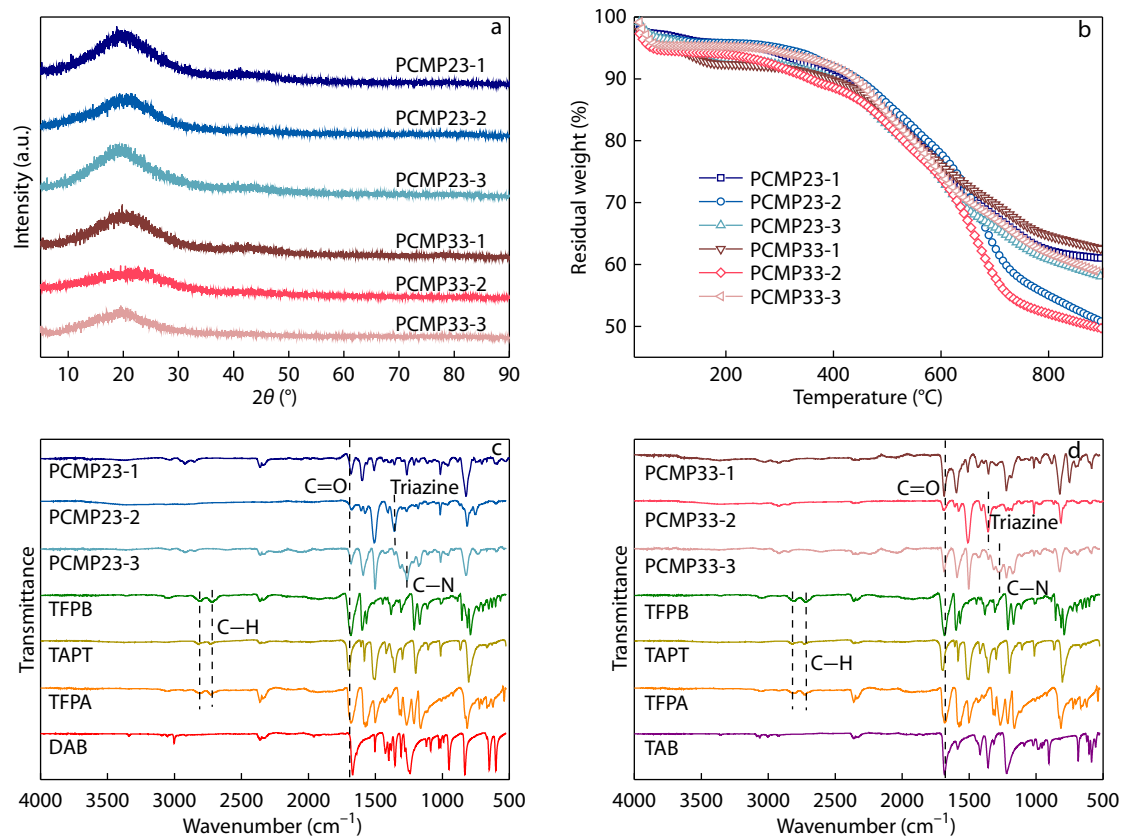


Fig. 1 (a) XRD patterns of PCMPs; (b) TGA curves of PCMPs; FTIR spectra of (c) monomers and PCMP23-X, and (d) monomers and PCMP33-X.

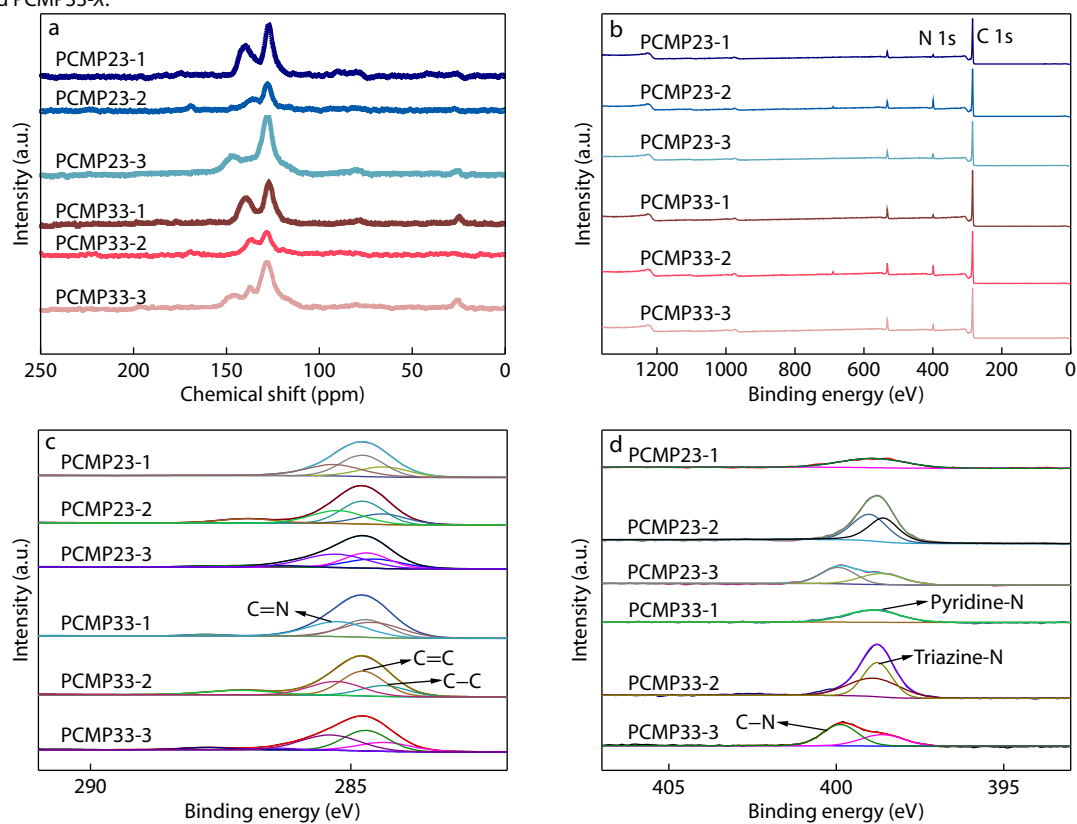


Fig. 2 (a) Solid state ^{13}C CP/MAS NMR spectra of PCMPs; XPS spectra of PCMPs: (b) full spectra, (c) C 1s, (d) N 1s.

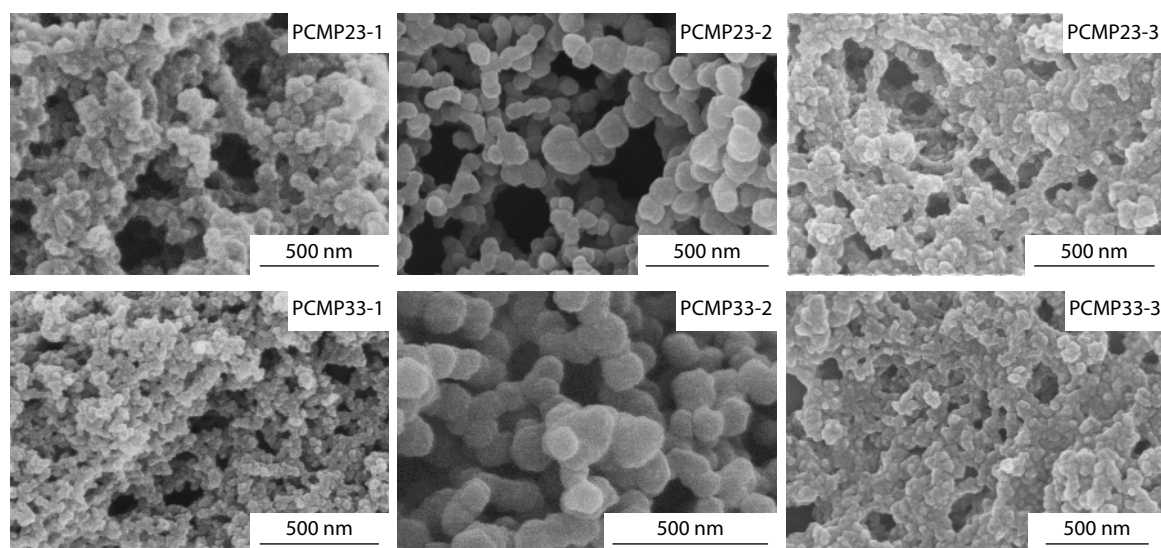


Fig. 3 SEM images of PCMPs.

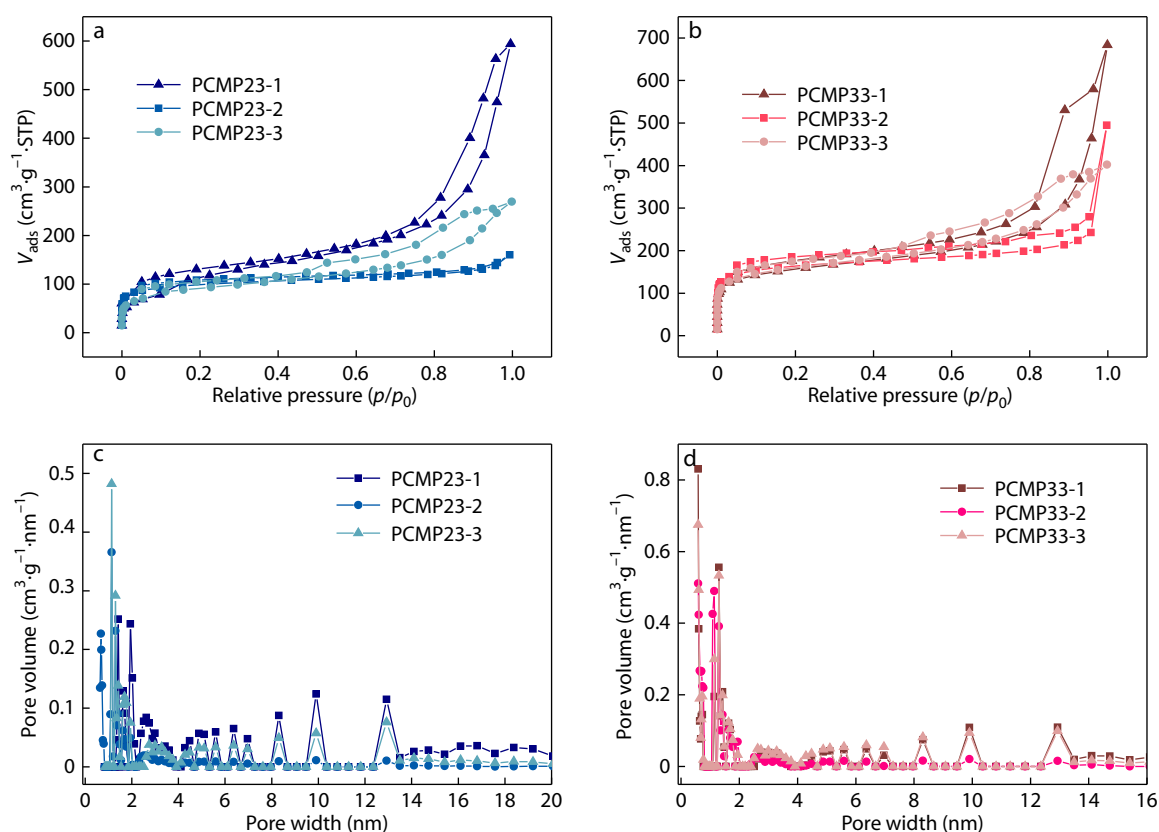


Fig. 4 N_2 adsorption/desorption isotherms for PCMPs collected at 77.3 K; (a) PCMP23-X; (b) PCMP33-X; pore size distribution curves calculated using the model of NLDFT; (c) PCMP23-X; (d) PCMP33-X.

provide conditions for efficient hydrogen evolution property in the photocatalytic process.

To study the optical characteristics of polymeric photocatalysts, the UV-Vis absorption spectra of PCMPs were measured using solid-state powders. PCMPs have broad light absorption in the range of 200–600 nm (Figs. 5a and 5b). PCMP23-3 and PCMP33-3 have wider absorption in the range of

500–600 nm compared with other four PCMPs. The band gaps of PCMPs are above 1.23 eV, which meets the requirement for photolysis of water to produce hydrogen. The bandgap is narrow with a theoretically wide range of sunlight absorption, which indicates that PCMPs have excellent potential in photocatalysis. Table 2 shows the band positions of the highest occupied molecular orbital (HOMO), the low-

Table 1 Summary of pore properties for PCMPs.

Sample	Surface area ($\text{m}^2\cdot\text{g}^{-1}$)		Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	
	BET method ^a	Langmuir method ^b	Micro-pore ^c	Total pore ^d
PCMP23-1	434.8	1292.3	0.078	0.680
PCMP23-2	312.3	573.2	0.099	0.209
PCMP23-3	304.4	793.4	0.066	0.369
PCMP33-1	511.9	1257.6	0.120	0.660
PCMP33-2	515.2	915.8	0.172	0.346
PCMP33-3	523.1	1219.0	0.120	0.563

^a Surface area calculated from N_2 adsorption isotherm in the relative pressure (p/p_0) ranging from 0.05 to 0.20; ^b Surface area of micropores calculated from the N_2 adsorption isotherm using Langmuir method; ^c The micropore volume derived from the t -plot method; ^d The total pore volume at $p/p_0=0.95$.

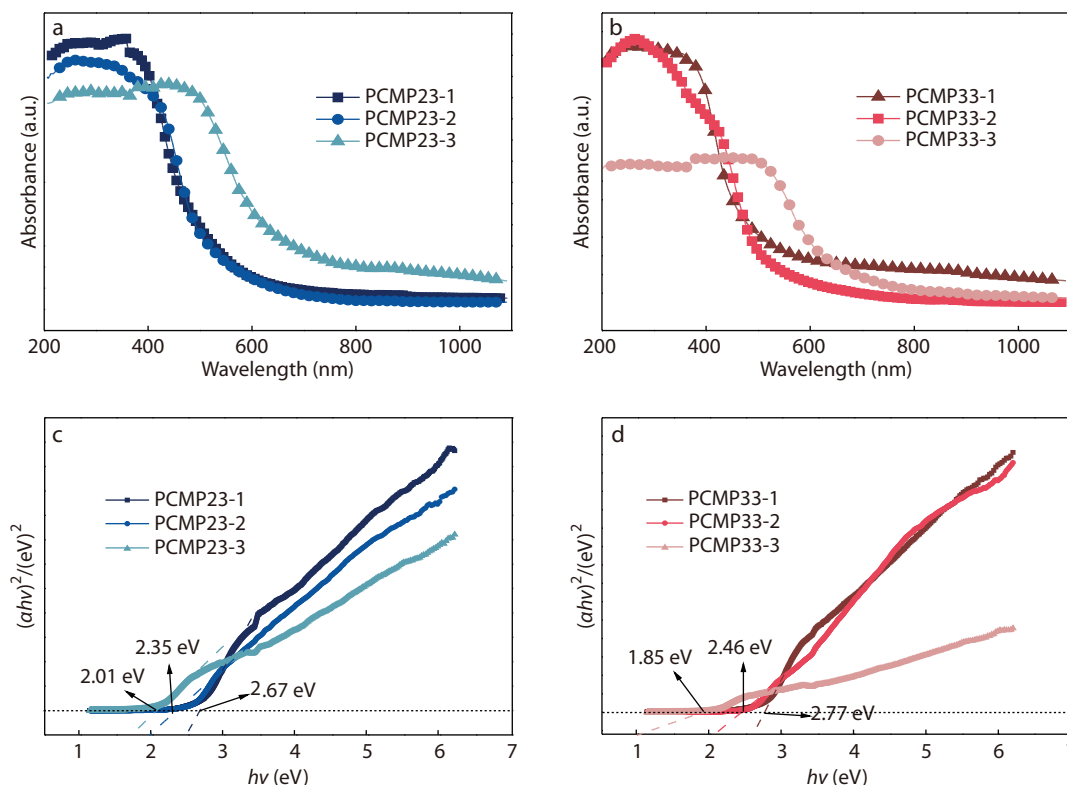


Fig. 5 UV-Vis absorption spectra of (a) PCMP23-X; (b) PCMP33-X; the estimated optical bandgaps of (c) PCMP23-X; (d) PCMP33-X based on the Tauc plot method.

Table 2 HOMO and LUMO band positions and energy gaps (E_g) of polymers.

	PCMP23-1	PCMP23-2	PCMP23-3	PCMP33-1	PCMP33-2	PCMP33-3
LUMO	-0.98	-1.02	-0.96	-0.96	-0.94	-0.94
HOMO	1.69	1.54	1.05	1.81	1.52	0.91
E_g	2.67	2.56	2.01	2.77	2.46	1.85

est unoccupied molecular orbital (LUMO) and the bandgap of the polymers, which were obtained through the estimation from Tauc plots (Figs. 5c and 5d) and CV curves (Fig. 6). The position of LUMO of PCMP23-2 is in the most negative position, which could contribute to an excellent photocatalysis hydrogen evolution *via* strong reducibility.

The photocatalytic hydrogen evolution performance of PCMPs was tested *via* employing polymer powders as photocatalysts in deionized water with the sacrificial TEOA (10 vol%). The hydrogen production rate is shown in Figs. 7(a) and 7(b). The hydrogen production rates of PCMP23-1

and PCMP33-1 are significantly different, 126.4 and 887.9 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, respectively. This difference may be due to the different steric hindrance induced by the different aromatic ketones of these two polymers, which affects the contact between the co-catalyst and active sites. The hydrogen production rates of PCMP23-2 and PCMP33-2 show similar rates of hydrogen production, 1198.9 and 1012.7 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, respectively. This may be due to the existence of the triazine ring. The force between carbon and nitrogen should be greater than that of forming space steric hindrance, and thus the aromatic ketones have little effect on

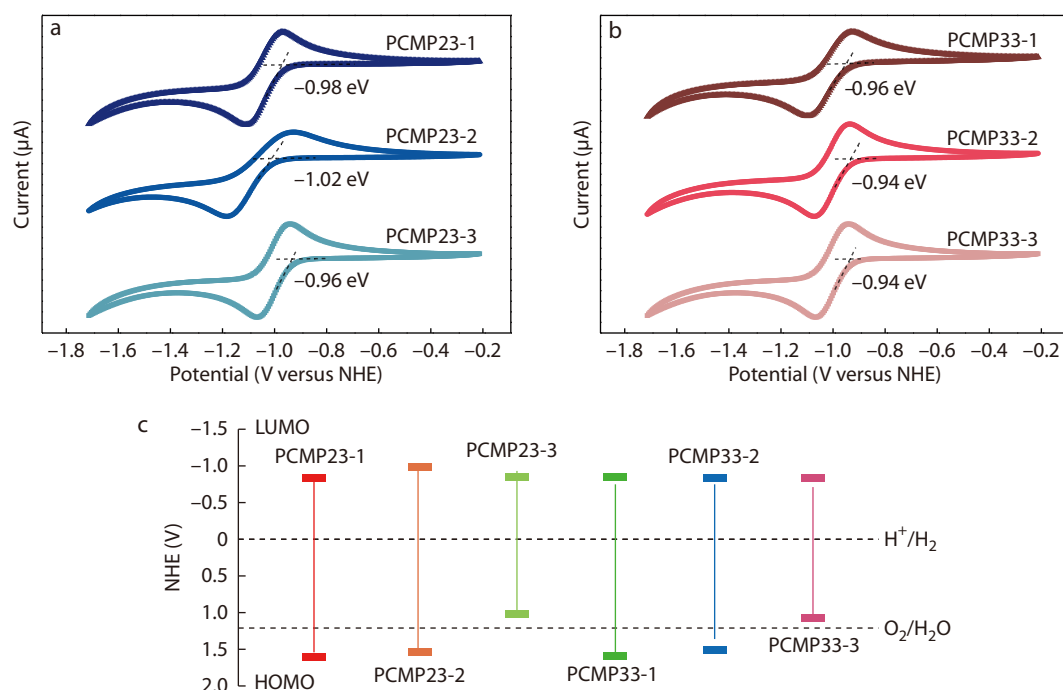


Fig. 6 Cyclic voltammetry measurements of (a) PCMP23-X and (b) PCMP33-X; (c) HOMO and LUMO band positions of PCMPs;

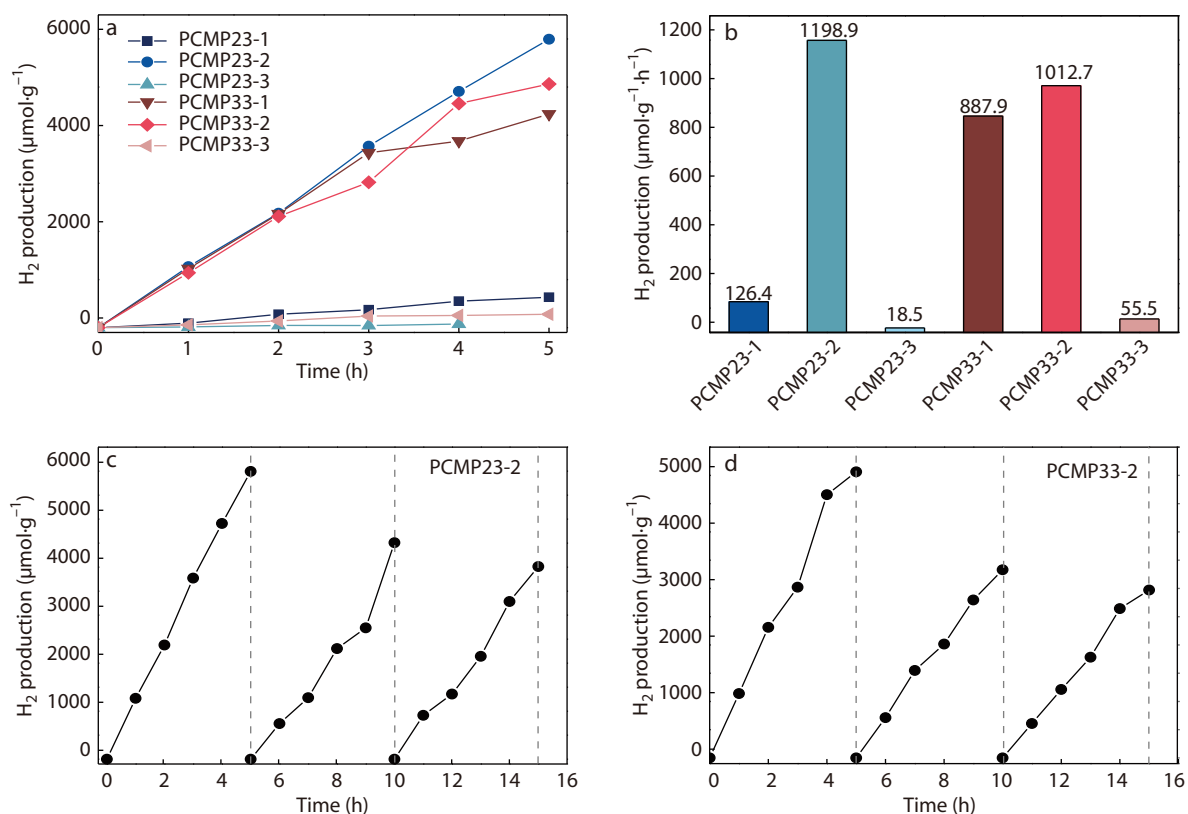


Fig. 7 (a) Time course of hydrogen evolution of the polymers ($\lambda > 320$ nm); (b) The hydrogen evolution of PCMPs ($\lambda > 320$ nm); (c, d) The stability tested using PCMP23-2/PCMP33-2 over a time period of 15 h.

the performance of the hydrogen production of polymers. Meanwhile, the existence of the triazine ring brings more active sites to PCMP23-2 and PCMP33-2 to contact with cocata-

lyst, thus getting high catalytic performance. Both PCMP23-3 and PCMP33-3 show good resistance to visible light under the ultraviolet absorption spectrum, and however, the rates

of hydrogen production are extremely low, 18.5 and 55.5 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, respectively. The cycling stabilities of PCMP23-2 and PCMP33-2 were evaluated in a continuous photocatalytic reaction for 15 h with intermittent evacuation every 5 h under the irradiation of UV-Vis light. As shown in Figs. 7(c) and 7(d), a linear relationship between the amount of produced hydrogen and the reaction time can be observed for each photocatalytic cycle. However, a decrease in photocatalytic activity can be observed for PCMP23-2 and PCMP33-2, which indicates that PCMPs are not stable in photocatalysis under UV-Vis light irradiation.

CONCLUSIONS

In this study, we successfully synthesized a series of pyridyl conjugated microporous polymers (PCMPs) via a green metal-free synthetic route for photocatalytic hydrogen evolution. The bandgap of polymers can be adjusted by changing the structures of monomers. Using ketone group monomer of TAB could obtain high special surface areas (up to 523 $\text{m}^2\cdot\text{g}^{-1}$) compared to DAB (up to 435 $\text{m}^2\cdot\text{g}^{-1}$). The PCMPs containing triazine ring in the monomer show an excellent rate of hydrogen production (1198.9 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). The TFPA as the monomer-reacted polymer exhibits broad visible light absorption in the UV-Vis spectrum. This metal-free synthetic method provides a new avenue to preparing efficient photocatalysts for hydrogen evolution.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 52073046, 51873036 and 51673039), the Chang Jiang Scholars Program (No. Q2019152), the Fundamental Research Funds for the Central Universities (No. 2232019A3-01), the Shanghai Shuguang Program (No. 19SG28), the Shanghai Natural Science Foundation (No. 19D3859), the Shanghai Pujiang Talent Program (No. 20PJ1400600) and the International Joint Laboratory for Advanced Fiber and Low-Dimension Materials (No. 18520750400).

REFERENCES

- Nazir, M. S.; Mahdi, A. J.; Bilal, M.; Sohail, H. M.; Ali, N.; Iqbal, H. M. N. Environmental impact and pollution-related challenges of renewable wind energy paradigm—a review. *Sci. Total. Environ.* **2019**, 683, 436–444.
- Wang, W. J.; Chen, M.; Huang, D. L.; Zeng, G. M.; Zhang, C.; Lai, C.; Zhou, C. Y.; Yang, Y.; Cheng, M.; Hu, L.; Xiong, W. P.; Li, Z. H.; Wang, Z. W. An overview on nitride and nitrogen-doped photocatalysts for energy and environmental applications. *Compos. B. Eng.* **2019**, 172, 704–723.
- Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **2012**, 488, 294–303.
- Meng, N.; Ren, X.; Santagiuliana, G.; Ventura, L.; Zhang, H.; Wu, J.; Yan, H.; Reece, M. J.; Bilotti, E. Ultrahigh β -phase content poly(vinylidene fluoride) with relaxor-like ferroelectricity for high energy density capacitors. *Nat. Commun.* **2019**, 10, 4535.
- Turner, J.; Sverdrup, G.; Mann, M. K.; Maness, P. C.; Kroposki, B.; Ghirardi, M.; Evans, R. J.; Blake, D. Renewable hydrogen production. *Int. J. Energy Res.* **2008**, 32, 379–407.
- Zhang, J. H.; Wei, M. J.; Wei, Z. W.; Pan, M.; Su, C. Y. Ultrathin graphitic carbon nitride nanosheets for photocatalytic hydrogen evolution. *ACS Appl. Nano Mater.* **2020**, 3, 1010–1018.
- Hosseini, S. E.; Wahid, M. A. Hydrogen production from renewable and sustainable energy resources: promising green energy carrier for clean development. *Renew. Sust. Energ. Rev.* **2016**, 57, 850–866.
- Islam, A.; Teo, S. H.; Awual, M. R.; Taufiq Yap, Y. H. Ultrathin assemblies of porous array for enhanced H_2 evolution. *Sci. Rep.* **2020**, 10, 2324.
- Huo, J. W.; Yuan, C.; Wang, Y. , Nanocomposites of three-dimensionally ordered porous TiO_2 decorated with Pt and reduced graphene oxide for the visible-light photocatalytic degradation of waterborne pollutants. *ACS Appl. Nano Mater.* **2019**, 2, 2713–2724.
- Wu, T. T.; Niu, P.; Yang, Y. Q.; Yin, L. C.; Tan, J.; Zhu, H. Z.; Irvine, J. T. S.; Wang, L. Z.; Liu, G.; Cheng, H. M. Homogeneous doping of substitutional nitrogen/carbon in TiO_2 plates for visible light photocatalytic water oxidation. *Adv. Funct. Mater.* **2019**, 29, 1901943.
- Meng, A. Y.; Zhang, L. Y.; Cheng, B.; Yu, J. G. Dual cocatalysts in TiO_2 photocatalysis. *Adv. Mater.* **2019**, 31, 1807660.
- Guo, Q.; Zhou, C. Y.; Ma, Z. B.; Yang, X. M. Fundamentals of TiO_2 photocatalysis: concepts, mechanisms, and challenges. *Adv. Mater.* **2019**, 31, 1901997.
- Wang, M. Y.; Zhang, Q. J.; Shen, Q. Q.; Li, Q. Y.; Ren, S. J. Truxene-based conjugated microporous polymers via different synthetic methods. *Chinese J. Polym. Sci.* **2020**, 38, 151–157.
- Hu, X. L.; Li, H. G.; Tan, B. E. , COFs-based porous materials for photocatalytic applications. *Chinese J. Polym. Sci.* **2020**, 38, 673–684.
- Yanagida, S.; Kabumoto, A.; Mizumoto, K.; Pac, C.; Yoshino, K. Poly(*p*-phenylene)-catalysed photoreduction of water to hydrogen. *J. Chem. Soc., Chem. Commun.* **1985**, 8, 474–475.
- Maruyama, T.; Yamamoto, T. Effective photocatalytic system based on chelating π -conjugated poly(2,2'-bipyridine-5,5'-diyl) and platinum for photoevolution of H_2 from aqueous media and spectroscopic analysis of the catalyst. *J. Phys. Chem. B* **1997**, 101, 3806–3810.
- Wang, X. C.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J. M.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* **2009**, 8, 76–80.
- Wang, X. C.; Maeda, K.; Chen, X. F.; Takanabe, K.; Domen, K.; Hou, Y. D.; Fu, X. Z.; Antonietti, M. Polymer semiconductors for artificial photosynthesis: hydrogen evolution by mesoporous graphitic carbon nitride with visible light. *J. Am. Chem. Soc.* **2009**, 131, 1680–1681.
- Bhunia, M. K.; Yamauchi, K.; Takanabe, K. Harvesting solar light with crystalline carbon nitrides for efficient photocatalytic hydrogen evolution. *Angew. Chem. Int. Ed.* **2014**, 53, 11001–11005.
- Rawool, S. A.; Samanta, A.; Ajithkumar, T. G.; Kar, Y.; Polshettiwar, V. Photocatalytic hydrogen generation and CO_2 conversion using g- C_3N_4 decorated dendritic fibrous nanosilica: role of interfaces between silica and g- C_3N_4 . *ACS Appl. Energy Mater.* **2020**, 3, 8150–8158.
- Wang, W. C.; Tao, Y.; Du, L. L.; Wei, Z.; Yan, Z. P.; Chan, W. K.; Lian, Z. C.; Zhu, R. X.; Phillips, D. L.; Li, G. S. Femtosecond time-resolved spectroscopic observation of long-lived charge separation in bimetallic sulfide/g- C_3N_4 for boosting photocatalytic H_2 evolution. *Appl. Catal. B* **2021**, 282, 119568.
- Godin, R.; Wang, Y.; Zwijnenburg, M. A.; Tang, J.; Durrant, J. R. Time-resolved spectroscopic investigation of charge trapping in carbon nitrides photocatalysts for hydrogen generation. *J. Am.*

- Chem. Soc.* **2017**, *139*, 5216–5224.
- 23 Lee, J. S. M.; Cooper, A. I. Advances in conjugated microporous polymers. *Chem. Rev.* **2020**, *120*, 2171–2214.
 - 24 Zhi, Y. F.; Yao, Z. J.; Jiang, W. B.; Xia, H.; Shi, Z.; Mu, Y.; Liu, X. Conjugated microporous polymers as heterogeneous photocatalysts for efficient degradation of a mustard-gas simulant. *ACS Appl. Mater. Interfaces* **2019**, *11*, 37578–37585.
 - 25 Sprick, R. S.; Jiang, J. X.; Bonillo, B.; Ren, S.; Ratvijitvech, T.; Guiglion, P.; Zwiijnenburg, M. A.; Adams, D. J.; Cooper, A. I. Tunable organic photocatalysts for visible-light-driven hydrogen evolution. *J. Am. Chem. Soc.* **2015**, *137*, 3265–3270.
 - 26 Liras, M.; Iglesias, M.; Sánchez, F. Conjugated microporous polymers incorporating BODIPY moieties as light-emitting materials and recyclable visible-light photocatalysts. *Macromolecules* **2016**, *49*, 1666–1673.
 - 27 Xu, Y. F.; Mao, N.; Zhang, C.; Wang, X.; Zeng, J. H.; Chen, Y.; Wang, F.; Jiang, J. X. Rational design of donor- π -acceptor conjugated microporous polymers for photocatalytic hydrogen production. *Appl. Catal. B* **2018**, *228*, 1–9.
 - 28 Wang, X. P.; Zhao, X. D.; Dong, W. B.; Zhang, X. H.; Xiang, Y. G.; Huang, Q. Y.; Chen, H. Integrating amino groups within conjugated microporous polymers by versatile thiol-yne coupling for light-driven hydrogen evolution. *J. Mater. Chem. A* **2019**, *7*, 16277–16284.
 - 29 Gao, X. M.; Shu, C.; Zhang, C.; Ma, W. Y.; Ren, S. B.; Wang, F.; Chen, Y.; Zeng, J. H.; Jiang, J. X. Substituent effect of conjugated microporous polymers on the photocatalytic hydrogen evolution activity. *J. Mater. Chem. A* **2020**, *8*, 2404–2411.
 - 30 Zhang, X. L.; Wang, L.; Chen, L.; Ma, X. Y.; Xu, H. X. , Ultrathin 2D conjugated polymer nanosheets for solar fuel generation. *Chinese J. Polym. Sci.* **2019**, *37*, 101–114.
 - 31 Chen, L.; Honsho, Y.; Seki, S.; Jiang, D. Light-harvesting conjugated microporous polymers: rapid and highly efficient flow of light energy with a porous polyphenylene framework as antenna. *J. Am. Chem. Soc.* **2010**, *132*, 6742–6748.
 - 32 Liu, Q.; Tang, Z.; Wu, M.; Zhou, Z. Design, preparation and application of conjugated microporous polymers. *Polym. Int.* **2014**, *63*, 381–392.
 - 33 Schmidt, J.; Werner, M.; Thomas, A. Conjugated microporous polymer networks via yamamoto polymerization. *Macromolecules* **2009**, *42*, 4426–4429.
 - 34 Jiang, J. X.; Trewin, A.; Adams, D. J.; Cooper, A. I. Band gap engineering in fluorescent conjugated microporous polymers. *Chem. Sci.* **2011**, *2*, 1777–1781.
 - 35 Trunk, M.; Herrmann, A.; Bildirir, H.; Yassin, A.; Schmidt, J.; Thomas, A. Copper-free sonogashira coupling for high-surface-area conjugated microporous poly(aryleneethynylene) networks. *Chem. Eur. J.* **2016**, *22*, 7179–7183.
 - 36 Weiss, M. Acetic acid ammonium acetate reactions-an improved Chichibabin pyridine synthesis¹. *J. Am. Chem. Soc.* **1952**, *74*, 200–202.
 - 37 Cheng, Z. H.; Wang, L.; He, Y.; Chen, X. J.; Wu, X. J.; Xu, H. X.; Liao, Y. Z.; Zhu, M. F. Rapid metal-free synthesis of pyridyl-functionalized conjugated microporous polymers for visible-light-driven water splitting. *Polym. Chem.* **2020**, *11*, 3393–3397.
 - 38 Jiang, J. X.; Su, F.; Trewin, A.; Wood, C. D.; Niu, H.; Jones, J. T. A.; Khimyak, Y. Z.; Cooper, A. I. Synthetic control of the pore dimension and surface area in conjugated microporous polymer and copolymer networks. *J. Am. Chem. Soc.* **2008**, *130*, 7710–7720.
 - 39 Zhang, C.; Kong, R.; Wang, X.; Xu, Y.; Wang, F.; Ren, W.; Wang, Y.; Su, F.; Jiang, J. X. Porous carbons derived from hypercrosslinked porous polymers for gas adsorption and energy storage. *Carbon* **2017**, *114*, 608–618.
 - 40 Weber, J.; Antonietti, M.; Thomas, A. Microporous networks of high-performance polymers: elastic deformations and gas sorption properties. *Macromolecules* **2008**, *41*, 2880–2885.