

Electronic Supporting Information

Rapid Microwave-assisted Green Production of Crystalline Polyimide for Enhanced Visible-Light-Induced Photocatalytic Hydrogen Production

Li Lin,^a Ping Ye,^a Chang Cao,^a Qi Jin,^a Geng-Sheng Xu,^a Yu-Hua Shen,^{a, b} and Yu-Peng Yuan*^{a, b}

^a Laboratory of Advanced Porous Materials, School of Chemistry and Chemical Engineering, Anhui University, Hefei 230036, P. R. China

^b Innovation Lab for Clean Energy & Green Catalysis, Anhui University, Hefei 230601, P. R. China

Corresponding Author:

E-mail: yupengyuan@ahu.edu.cn (Y. Yuan)

Experimental Section

Synthesis of MPI samples

In a typical process for preparing MPI samples through MW-assisted heating synthesis, equal molar of melamine (10 mmol) and pyromellitic dianhydride (PMDA) (Sinopharm Chemical Reagent Co. Ltd, China) were grounded uniformly using an agate mortar. Then the mixture was transferred to an alumina crucible (25 mL) covered with another crucible (50 mL) and then sealed with aluminum silicate. The crucibles containing starting materials were then put into a big alumina crucible (200 mL) and buried with the CuO powder ($\geq 98.0\%$, Sinopharm Chemical Reagent Co. Ltd, China). The prepared crucibles were then irradiated by microwave for desired time in a domestic microwave oven (M721NH1-PW, Meiling) at 700 W MW power. For comparison purpose, The PI was also heated to 325 °C for 2 h in Air (labeled as PI325).

Characterizations

The crystal structure of UG-x hybrids were analyzed by X-ray powder diffraction on a DX-2700 X-ray diffractometer with Cu K α 1 radiation. The acceleration voltage and the applied current were 40 kV and 40 mA, respectively. Morphology was observed by field emission scanning electron microscopy (SEM: Hitachi S-4800) and transmission electron microscopy (TEM: JEOL JEM-2100F). UV-vis diffuse reflectance spectra (DRS) were collected over the spectral range 320-800 nm on a HITACHI U-3900 UV-Vis spectrophotometer. BaSO $_4$ was used as a reflectance standard. FT-IR measurements were performed using a Fourier transform infrared (FT-IR) spectrometer (IRPrestige-21, Shimadzu) with the samples dispersed

in KBr pellets. Photoluminescence spectra (PL) were recorded on a HITACHI F-4600 fluorometer (Japan). Time-resolved PL spectra were collected on a HORIB FluoroMax-4P spectrometer at room temperature. The surface area of the obtained samples was determined by the BET method from N₂ adsorption isotherms at 77 K (ASAP-2020, Micromeritics).

Photocatalytic measurements

Photocatalytic H₂ production reactions were carried out in a closed circulation system consisting of a gas circulation pump, a pressure sensor, and gas sampling valves. Typically, 50 mg of the prepared PI samples was dispersed in 100 mL aqueous solution of triethanolamine (TEOA, 15 vol. %). Pt (0.5 wt %) as co-catalyst for H₂ production was *in-situ* photo-deposited upon PI surface through injecting small amount of H₂PtCl₆ solution into the reactor. The reactor was purged with argon to drive away the residual air. The photocatalytic hydrogen evolution was initiated by irradiating the suspension with a 300-W xenon lamp coupled with a UV cut-off filter ($\lambda > 420$ nm). The gas product were analyzed periodically through a gas chromatograph (GC-1690, Kexiao, China) with a TCD detector.

·OH radicals measurement

It has been reported that ·OH radicals could react with terephthalic acid (TA) in basic solution to form 2-hydroxy-terephthalic acid (TAOH) that can emit fluorescence signal with a peak centered at 426 nm. Accordingly, the fluorescence signal intensity of TAOH can be used to qualitatively identify the formation rate of ·OH radicals which is associated with the charge separation efficiency on the photocatalyst.¹⁻³ The

·OH radical reactions were performed as follows. 10 mg of each sample (g-C₃N₄ and PCN-5) was suspended in 10 mL solution containing 10 mM of NaOH and 5 mM of terephthalic acid (TA, Sigma-Aldrich), respectively. Prior to irradiation by visible light, the suspension was stirred in dark for 10 min. After 10 min visible light irradiation, the solution was centrifuged (14000 rpm for 10 min) and then measured the fluorescence of the TAOH by a fluorescence spectrophotometer (Shimazu RF-5310PC). The excitation wavelength was 320 nm.

1. T. Hirakawa and Y. Nosaka, *Langmuir*, 2002, **18**, 3247-3254.
2. Y. Liu, Y. Hu, M. Zhou, H. Qian and X. Hu, *Appl. Catal. B: Environ.*, 2012, **125**, 425-431.
3. Y. P. Yuan, S. W. Cao, Y. S. Liao, L. S. Yin and C. Xue, *Appl. Catal. B-Environ.*, 2013, **140-141**, 164-168.

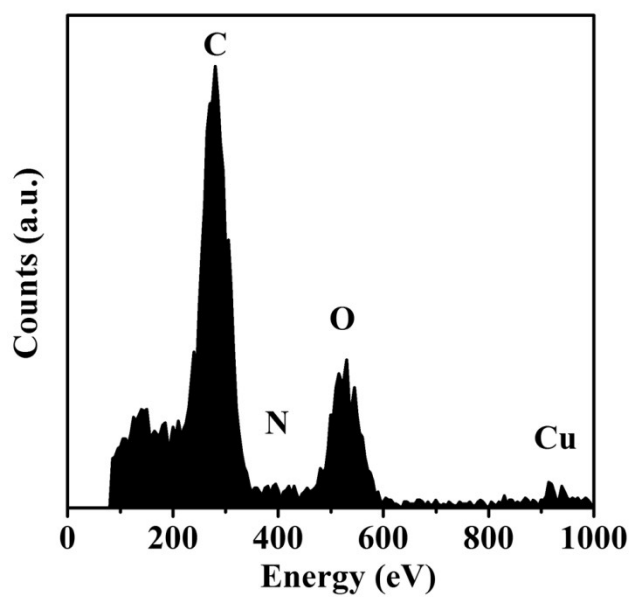


Fig. S1 EDX spectrum of MPI₇.

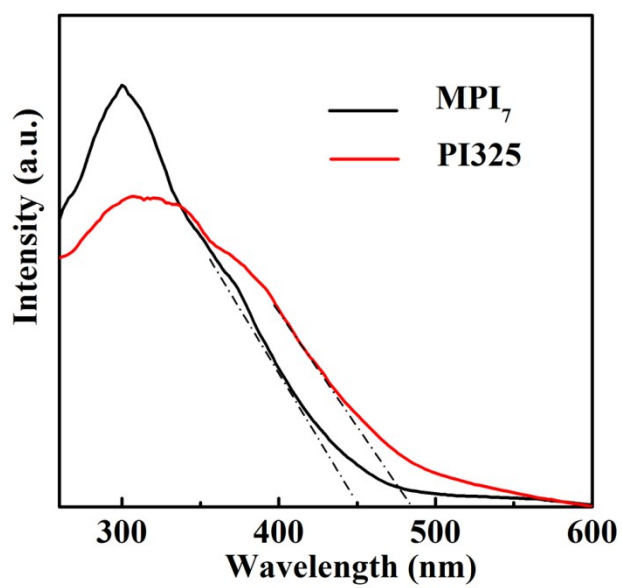


Fig. S2 The UV-Vis diffuse reflection spectra of MPI₇ and PI325.

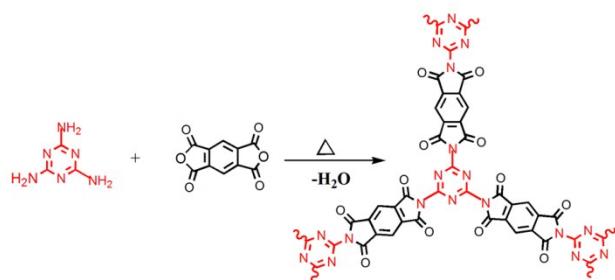


Fig. S3 Schematic illustration of PI synthesis. The theoretic formula of PI can be written as C₁₂N₄O₄H₂.

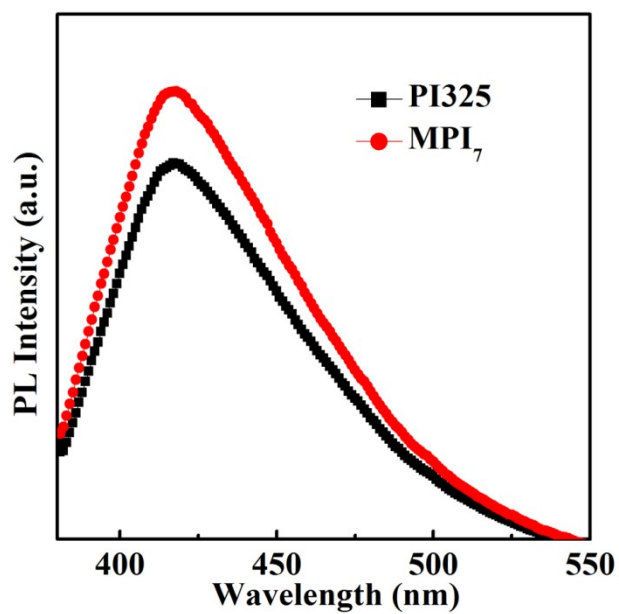


Fig. S4 Photoluminescence spectra of TAOH formed by the reaction of TA with ·OH radicals generated from different samples under visible light irradiation for 10 min.

Table S1. Fitted lifetimes of the fluorescence decay profiles

Samples	A ₁ [%]	T ₁ [ns]	A ₂ [%]	T ₂ [ns]	A ₃ [%]	T ₃ [ns]
PI325	4	2.32	0	12.94	96	0.21
MPI ₇	3	2.80	2	12.50	95	0.24

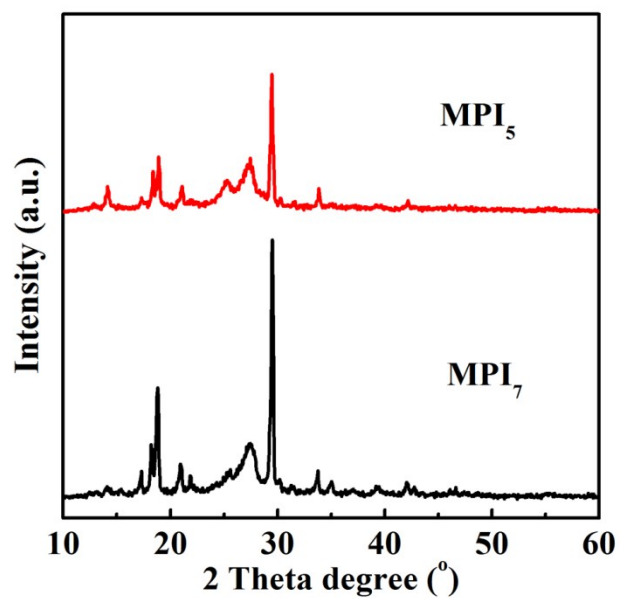


Fig. S5 The XRD patterns of MPI₅ and MPI₇ samples.

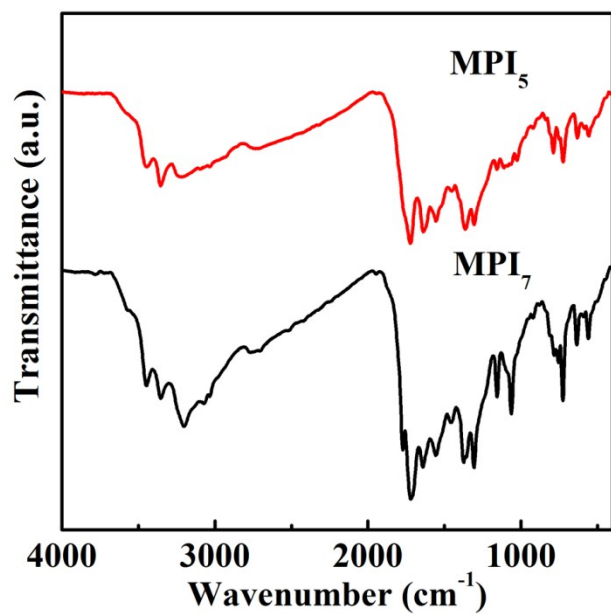


Fig. S6 The FT-IR spectra of MPI₅ and MPI₇.

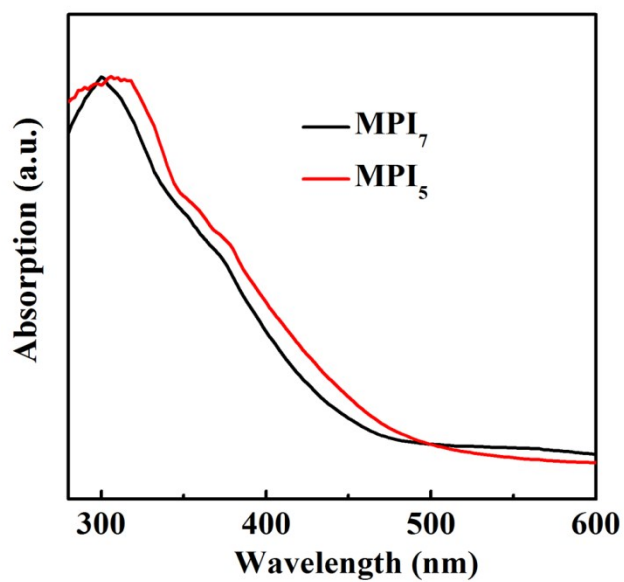


Fig. S7 The UV-Vis diffuse reflection spectra of MPI₅ and MPI₇.

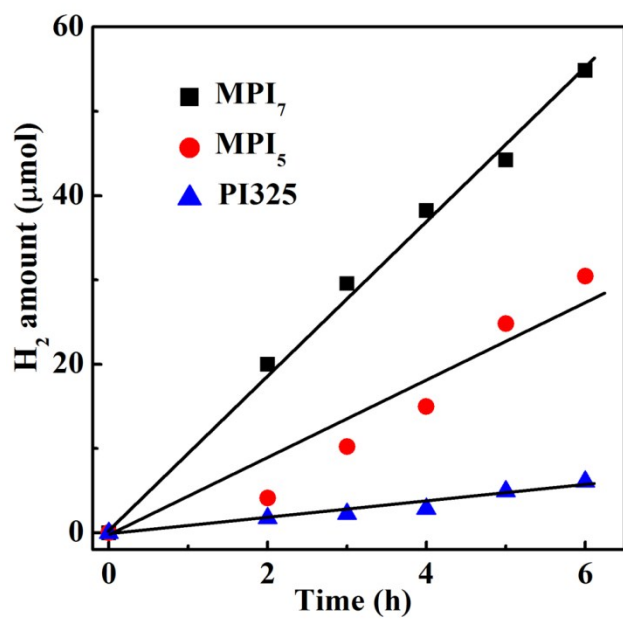


Fig. S8 Photocatalytic H₂ production over MPI₅ (red), MPI₇ (black) and PI325 (blue) samples.