Supporting Information

Facile green synthesis of crystalline polyimide photocatalyst for hydrogen generation from water

Sheng Chu,[a,b] Ying Wang,*[a,b] Yong Guo,[a] Peng Zhou,[a] He Yu,[a] Leilei Luo,[a,b] Fei Kong[a,b] and Zhigang Zou*[a]

[a] *Eco-materials and Renewable Energy Research Center (ERERC), National Laboratory of Solid State Microstructure, Nanjing University, Nanjing, 210093, People's Republic of China*

[b] *School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, People's Republic of China*

Experimental Section

Sample Preparation:

PI was synthesized in the following procedure: Melamine (MA) and pyromellitic dianhydride (PMDA) with equal molar ratio (10 mmol) were mixed uniformly in an agate mortar. Then the mixture was put into a porcelain crucible loosed covered with a lid and heated at 7 ^{o}C /min up to 325 ^{o}C for 4 h. The resultant block solid was ground well into powder and washed with water at 50 ^{o}C to remove any residual MA monomer if exists. Finally, the solid was filtered and dried at 100 ^{o}C overnight. The yield was 95%. Elemental analysis calculated for PI product $C_{13}H_4N_6O_4$: C, 50.66; H, 1.31; N, 27.27; O, 20.76%. Found: C, 49.52; H, 2.20; N, 28.70; O, 19.58%.

g-C_3N_4 was synthesized by heating 5g cyanamide at 2.2 ^{o}C /min up to 550 ^{o}C for 4 h according to the previous report.[1] The as-obtained solid was then ground well into powder with an agate mortar. The yield was about 50%.

PI-solution was synthesized by a conventional solution process similar to the reported procedure.[2] Simply, MA (10 mmol), PMDA (10 mmol) and DMSO (30 ml) were added to 50 mL three-neck flask. The mixture was stirred 0.5 h at room temperature under N_2 flow. Then, 2 mL of toluene was added, and the mixture was

heated to 180 ^{o}C for 24 h with a Dean-Stark apparatus. After cooling, the insoluble solid was isolated from the system by filtration, and washed with acetone, tetrahydrofurane and water several times. Finally, the solid was dried at 100 ^{o}C overnight in 35% yield.

Characterization:

FTIR spectra were recorded on a Nicolet NEXUS870 spectrometer. Solid-state ^{13}C NMR experiments were performed on a Bruker AdvanceIII 400WB spectrometer equipped with a 9.4 T magnet. The chemical shift was referenced to adamantane. Elemental analysis was determined by Elementar vario EL analyzer. TG analysis was carried out using Netzsch STA 449C equipment with a heating rate of 10 °C/min under a nitrogen atmosphere. XRD measurements were performed on a Rigaku Ultima III X-ray diffractometer using CuKα radiation. Specific surface area was measured using Micromeritics Tristar-3000 equipment. Transmission electron microscopy (TEM) image was recorded on a JEM-2100 electron microscope. SEM image was obtained on a Hitachi S4800 FE-SEM system. UV-Vis spectra were collected by Shimadzu UV-2550 spectrometer.

Photocatalytic tests:

Reactions were carried out in a closed gas-circulation system. A 300 W Xenon lamp was used as the light source, and visible light irradiation was realized by attaching a 420 nm cutoff filter. 0.2 g catalyst was dispersed in an aqueous solution (400 mL) containing methanol (10 vol%) as the sacrificial electron donor and 1 wt % Pt as the cocatalyst. Pt was photodeposited on the catalyst by using H_2PtCl_6 dissolved in the reactant solution. The reactant solution was first irradiated under full arc light (λ>300 nm) for 1 h to facilitate the deposition of Pt. Then, the system was evacuated several times prior to irradiation. The evolved H_2 was analyzed by an online gas chromatography (GC-14C, Shimadzu, TCD, Ar carrier).

Theoretical calculation:

All calculations were performed with Gaussian 03 program. B3LYP/6-31g method was used to optimize PI model. HOMO and LUMO orbitals of PI model were constructed with Gview program based on the B3LYP/6-31g-optimized results.

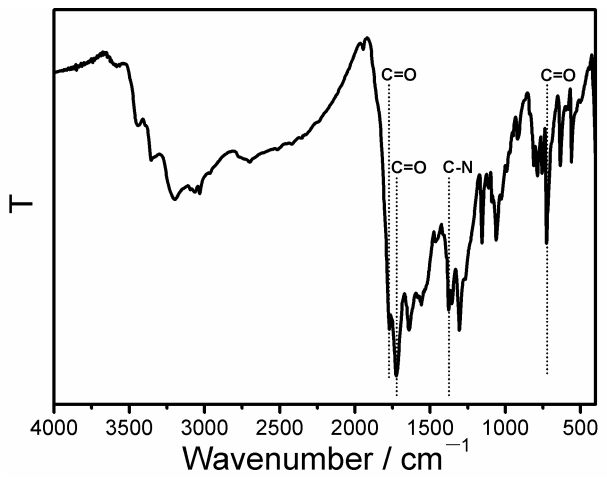

Fig. S1 FTIR spectrum of PI.

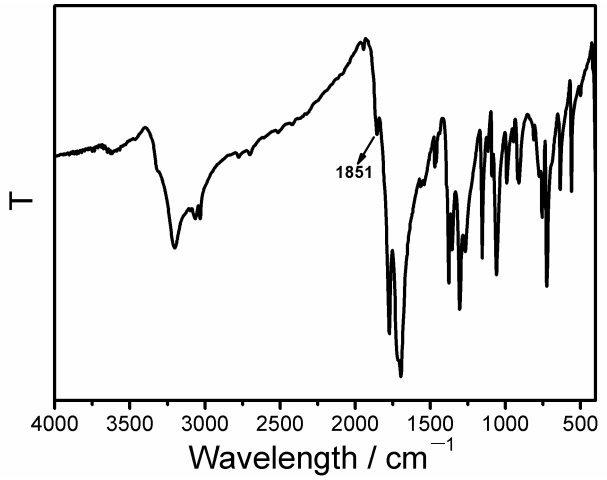

Fig. S2 FTIR spectrum of anhydride-terminated PI. The molar ratio of MA to PMDA is 1:3 to prepare anhydride-terminated PI.

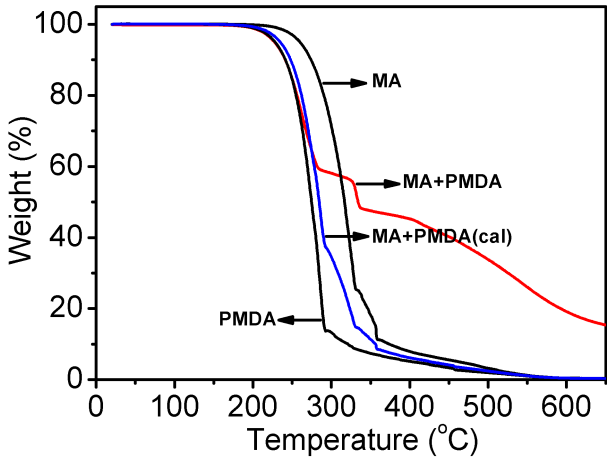

Fig. S3 TG analysis of MA, PMDA and MA+PMDA under N_2 atmosphere. MA+PMDA sample is prepared by mixing MA and PMDA with equal molar ratio. MA+PMDA (cal) is calculated by adding MA data with PMDA data assumed that no reaction occurs. The bifurcation point of MA+PMDA and MA+PMDA (cal) data (about 285 °C) is identified as the starting reaction temperature. Above this temperature, polyimide product is formed between MA and PMDA and thus leads to a higher decomposition temperature than the two comonomers.

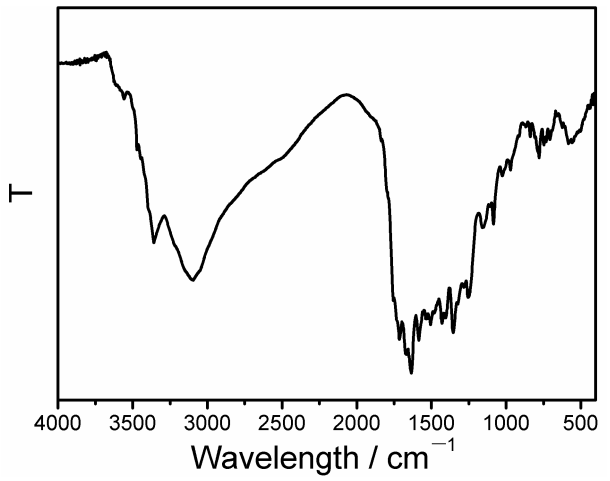

Fig. S4 FTIR spectrum of PI condensed at 250 °C.

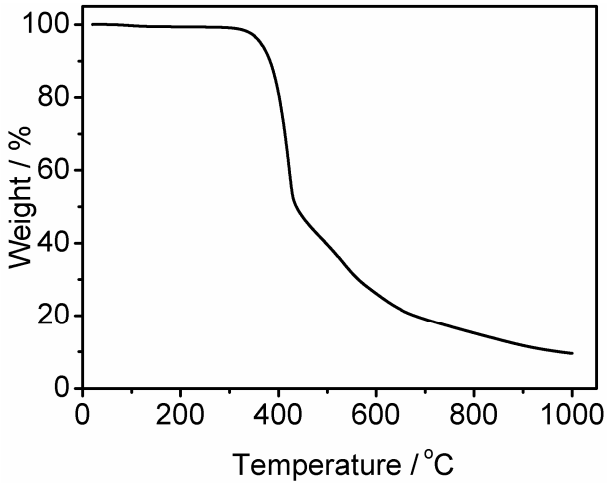

Fig. S5 TG analysis of PI under N_2 atmosphere.

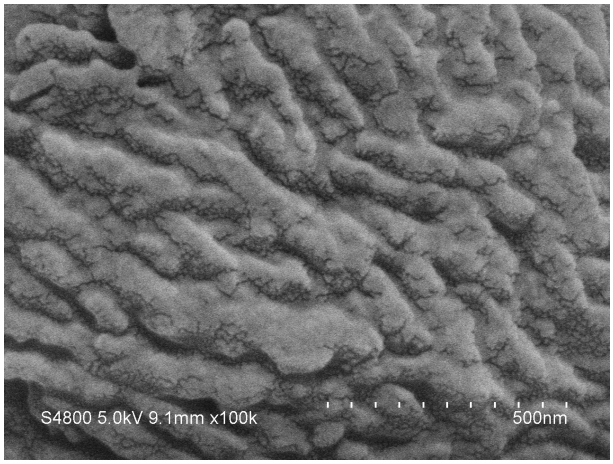

Fig. S6 SEM image of PI.

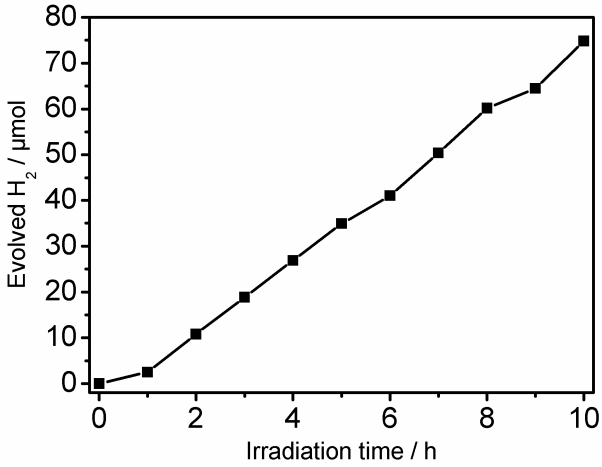

Fig. S7 Time course of H_2 evolution from a 10 vol % aqueous methanol solution by Pt-deposited g-C_3N_4 under visible light irradiation (λ□> 420 nm).

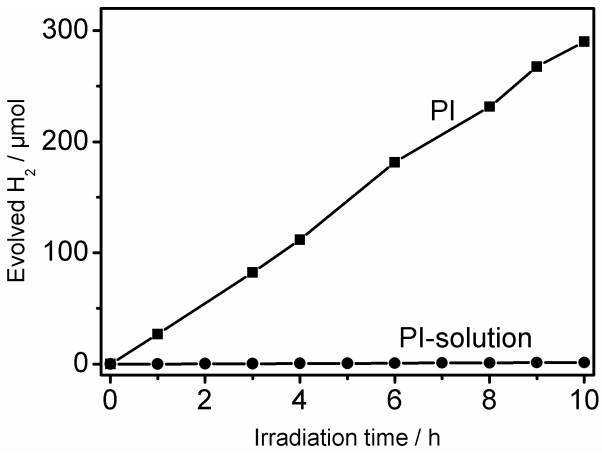

Fig. S8 Time course of H_2 evolution from a 10 vol % aqueous methanol solution by Pt-deposited PI and PI-solution under full arc light irradiation (λ□> 300 nm). The H_2 evolution rates of the two sample in 10 h are 29 and 0.1 μ mol/h, respectively.

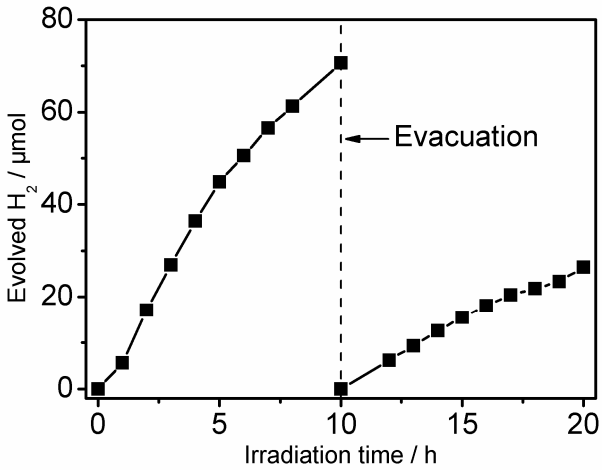

Fig. S9 Stability test of Pt-deposited PI for H_2 evolution from a 10 vol % aqueous methanol solution under prolonged visible light irradiation for 20 h.

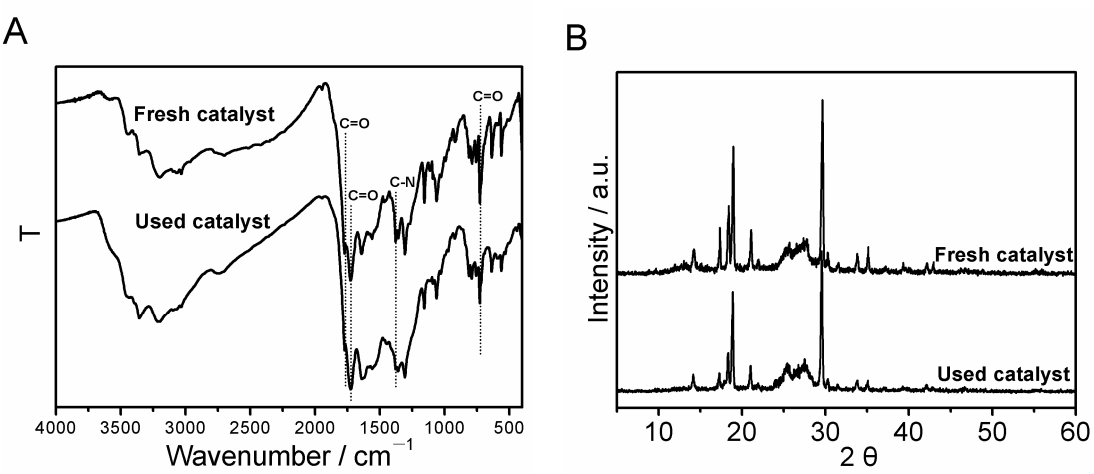

Fig. S10 A) FTIR spectra and B) XRD patterns of PI before and after the photocatalytic reaction.

References:

1 X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* 2009, **8,** 76.

2 Y. L. Luo, B. Y. Li, L. Y. Liang, B. E. Tan, *Chem. Commun.* 2011, **47,** 7704.