

Supporting information for

Facile fabrication of triphenylamine-based conjugated porous polymers and their application for organic degradation under visible light

Lidan Lan, Fei Liu, Yi Dan* and Long Jiang*

State Key Laboratory of Polymer Materials Engineering of China (Sichuan University), Polymer Research Institute of Sichuan University, Chengdu 610065, China. E-mail: danyi@scu.edu.cn, jianglong@scu.edu.cn; Fax: +86 28 85402465; Tel: +86 28 85407286

Table S1 Elemental composition of TFB-TPA and TA-TPA

Sample		C%	H%	N%
TFB-TPA	Calculated	82.02	3.79	14.18
	Found	77.79	4.86	13.29
TA-TPA	Calculated	82.38	4.81	12.81
	Found	80.33	5.02	12.81

To show the successful Schiff-base chemistry, benzaldehyde (BA), a mono-aldehyde functionalized benzene, is selected as polymer monomer to react with 4,4'4"-triaminotriphenylamine (TPA) in a similar manner with the synthesis of bifunctional TA-TPA and trifunctional TFB-TPA. In a typical synthesis of BA-TPA, BA (64mg, 0.6mmol) and TPA (58mg, 0.2mmol) were weighed into a 20 mL glass vial and dissolved in 2.0 mL of 1,4-dioxane. The mixture was sonicated for 10 min. After adding the acetic acid (6M, 0.3 mL), the solution became dark brown in color which we ascribe to the formation of a low molecular BA-TPA. The vial was sealed and kept still for 3 days under ambient conditions. The product was precipitated with n-hexane and then collected by filtration. Finally, the product was dried in vacuum at 80 °C for 12h to give a dark brown powder. The formation of BA-TPA was further confirmed by FT-IR analysis (Fig. S1). The disappearance of amino group stretch at 3405cm⁻¹, 3335cm⁻¹, the attenuation of the aldehyde group stretch at 1702 cm⁻¹ as well as the appearance of prominent C=N stretching vibration at 1622 cm⁻¹ in the FT-IR spectrum of TA-TPA indicate that starting material TPA had fully reacted with BA

to form imine-linked BA-TPA.

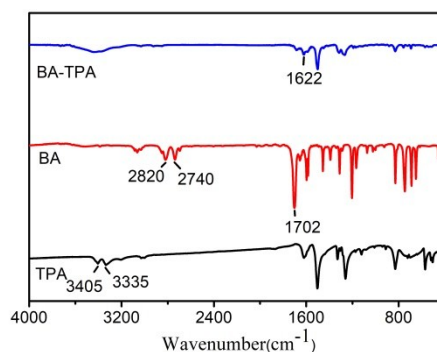


Fig. S1 FT-IR spectra of BA, TPA and BA-TPA.

Fig. S2 presents the N₂ adsorption and desorption isotherms of g-C₃N₄. By using a multipoint Brunauer-Emmett-Teller (BET) method, the surface area of g-C₃N₄ is calculated to be **18 m²/g**.

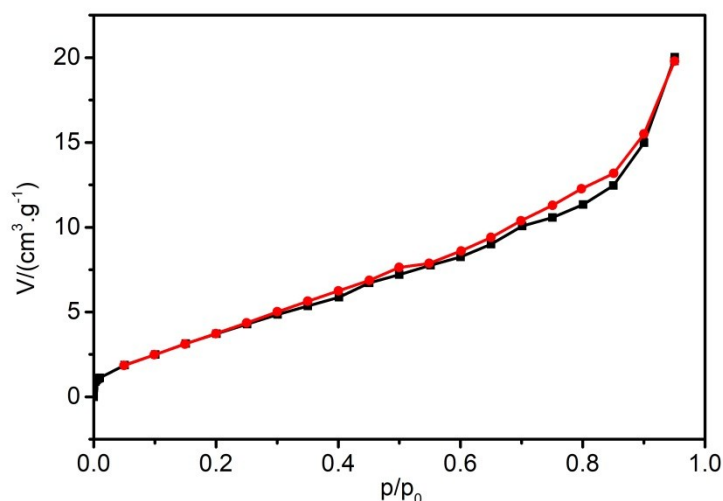


Fig.S2 N₂ adsorption-desorption isotherms for g-C₃N₄.

The recycling tests for the degradation of TC under visible light were performed to evaluate the stability of synthesized TFB-TPA. As revealed by Fig. S3, the photocatalytic activity of TFB-TPA decreased with the increasing repetitions. In order to find out the reason for the decreasing photocatalytic activity, fourier transform infrared test, solid UV-vis diffused reflection experiment, N₂ adsorption and desorption analysis and PXRD patterns measurement were carried out on the original TFB-TPA and the cycle-used TFB-TPA. As can be seen from the comparative UV-vis absorption spectrum of original TFB-TPA and cycle-used TFB-TPA (Fig. S4(a)), in the wave number range from 500 nm to 800 nm, the cycle-used TFB-TPA exhibits

higher light absorption ability. This result may suggest some structure transformation of TFB-TPA. However, it is probably due to the precision of the testing instrument that there is no obvious change in the infrared spectra of the catalyst before and after use (Fig. S4(b)). N₂ adsorption and desorption analysis and PXRD patterns measurements were performed to investigate the texture stabilization of TFB-TPA during the photocatalytic process. As presented in Fig. S4(c), the PXRD pattern of cycle-used TFB-TPA shows relatively weak peaks at 7.07° and 11.64° in comparison with the original TFB-TPA. The Brunauer-Emmett-Teller (BET) surface area of original TFB-TPA is calculated to be **372 m²/g** whereas the cycle-used TFB-TPA possesses a lower BET surface area of and **187 m²/g**. The total pore volume (P/P₀ = 0.950) is estimated as **0.589 cm³/g** for original TFB-TPA and **0.333 cm³/g** for cycle-used TFB-TPA (Table S2). These experimental results clearly indicate the decrease of crystallinity and porosity during photocatalytic process. The crystallization process of these organic porous structures via Schiff-base reaction requires dynamic reversible bond formation. The dynamic repairing nature of these chemical bonds limits their crystallinity and porosity stability under the photocatalytic condition. On the other hand, the rich porous structure is helpful for the adsorption and enrichment of pollutants on the surface of the catalyst, which provides more reaction sites for the catalyst and thus improves the catalytic activity. Therefore, the decrease of crystallinity and porosity might be a main reason for the decrease of catalytic performance.

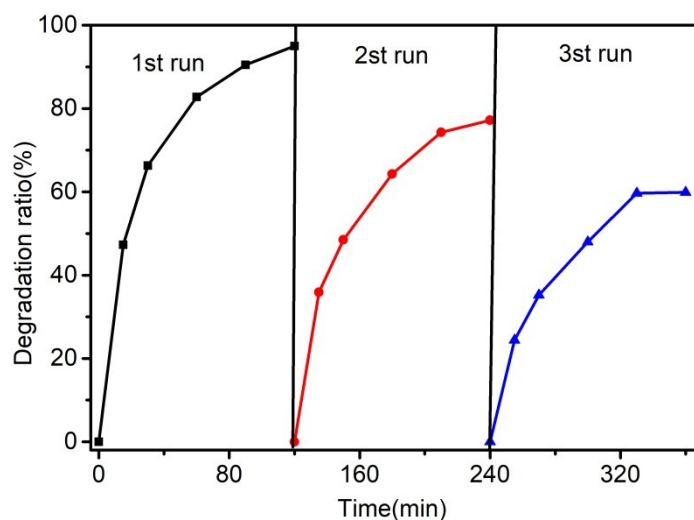


Fig.S3 The degradation of TC by TFB-TPA over repeated experiments.

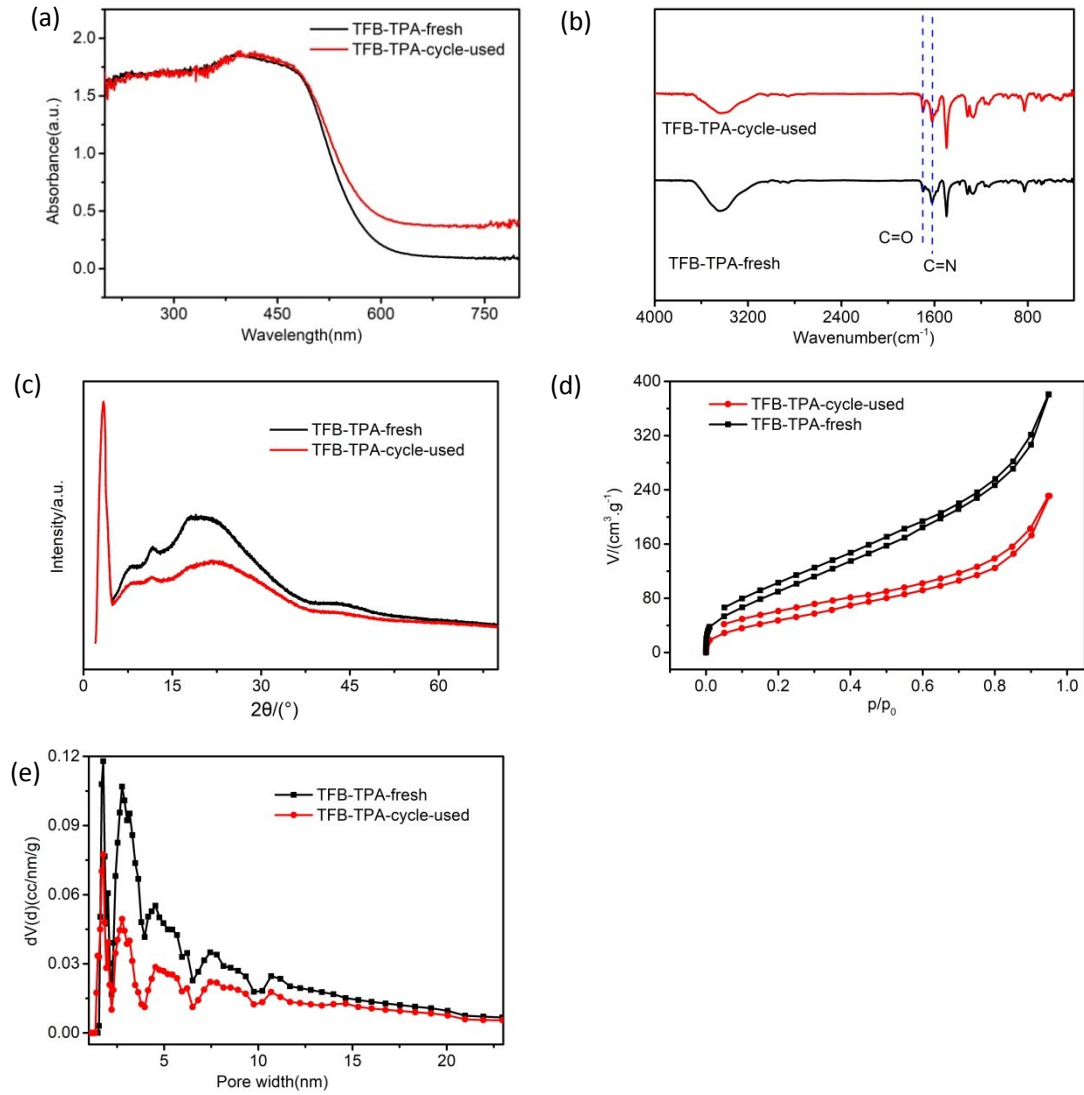


Fig.S4 (a) UV-vis absorption spectrum (b) FT-IR spectra (c) PXRD patterns (d) N₂ sorption isotherm(e) pore size distribution of original TFB-TPA and cycle-used TFB-TPA

Table S2 Specific surface area and total pore volume of original TFB-TPA and cycle-used TFB-TPA

Sample	S_{BET}^a (m ² /g)	V_{total}^b (cm ³ /g)
Original TFB-TPA	372	0.589
Cycle-used TFB-TPA	187	0.333

