Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Molecular engineering for constructing D-A system and enhancing delocalization in g-C_3N_4 with superior photocatalytic activity

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Photoelectrochemical property

The photocurrent was measured on a CHI 660C electrochemical workstation (Shanghai, China) using a conventional three-electrode cell, a Pt plate and an Ag/AgCl electrode as counter electrode and reference electrode, respectively. Na_2SO_4 (0.5 mol/L) was used as the electrolyte solution. The working electrode was prepared according to the following process; FTO glass substrate was cleaned by sonication successively with distilled water, acetone and ethanol for 60 min. Meanwhile, 0.10 g of ethocel (EC) was dissolved in 25 mL of ethanol by ultrasonic dispersion. Then, 5 mg of sample (UCN and UCN-*x*TDA (*x* = 3, 4, 5 and 6 mg)) was ultrasonically dispersed in the aforementioned ethanol of 0.5 mL with EC solution. The resulting dispersion was applied dropwise onto the FTO substrate. The electrodes were sealed with epoxy resin except for the 1 cm^2 sample area used for photoexcitation experiment. The sample electrodes were dried in air before test. The Electrochemical impedance spectroscopy (EIS) was tested at a bias voltage of 0.2 V vs Ag/ AgCl with an AC voltage of 5 mV in the dark. The frequency range were set between 1×10^{-2} and 1×10^{5} Hz. The photocurrent was operated using a 300 W Xe lamp (PLS-FX300HU, Beijing Perfectlight Technology Co. Ltd, China) equipped with a 420 nm cutoff filter.

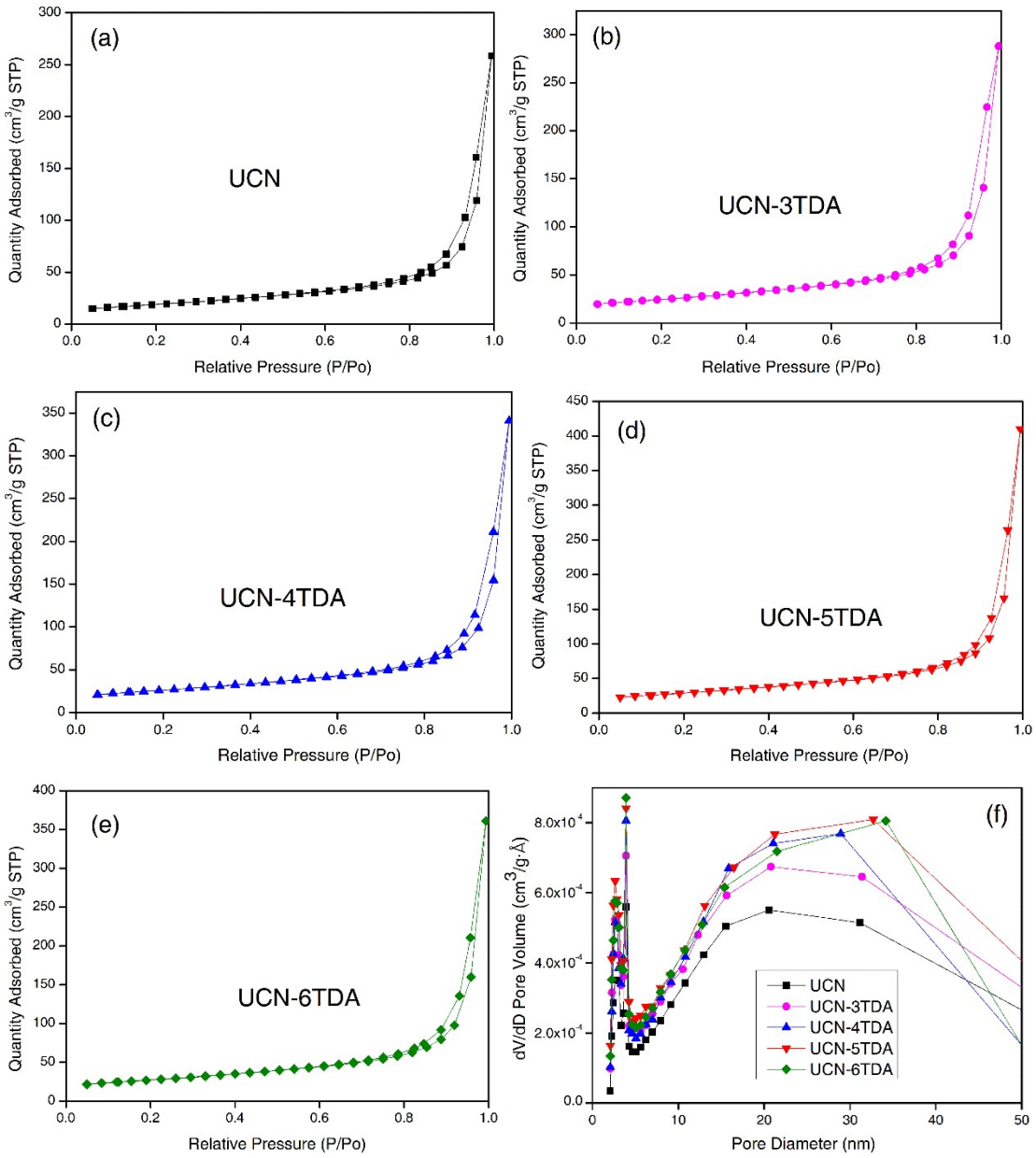


Figure S1 N_2 adsorption/desorption isotherms and pore size distribution of UCN and UCN-*x*TDA.

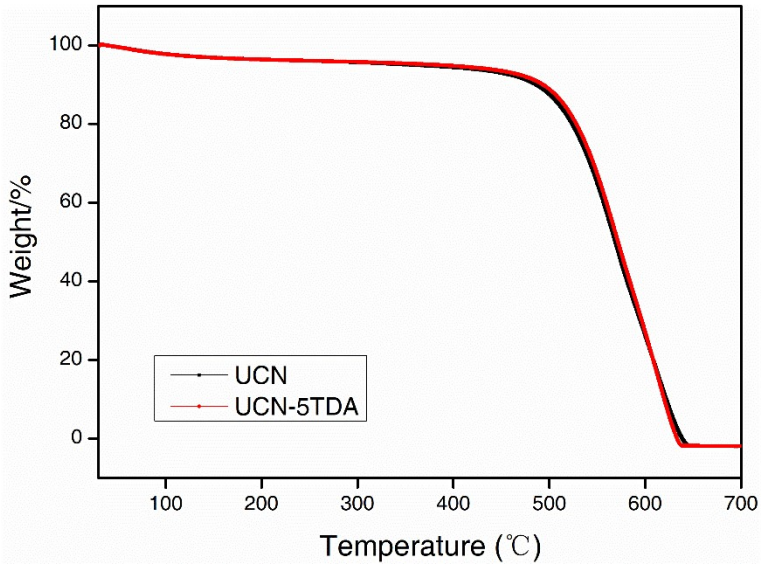


Figure S2 TG of UCN and UCN-5TDA in N_2 flow.

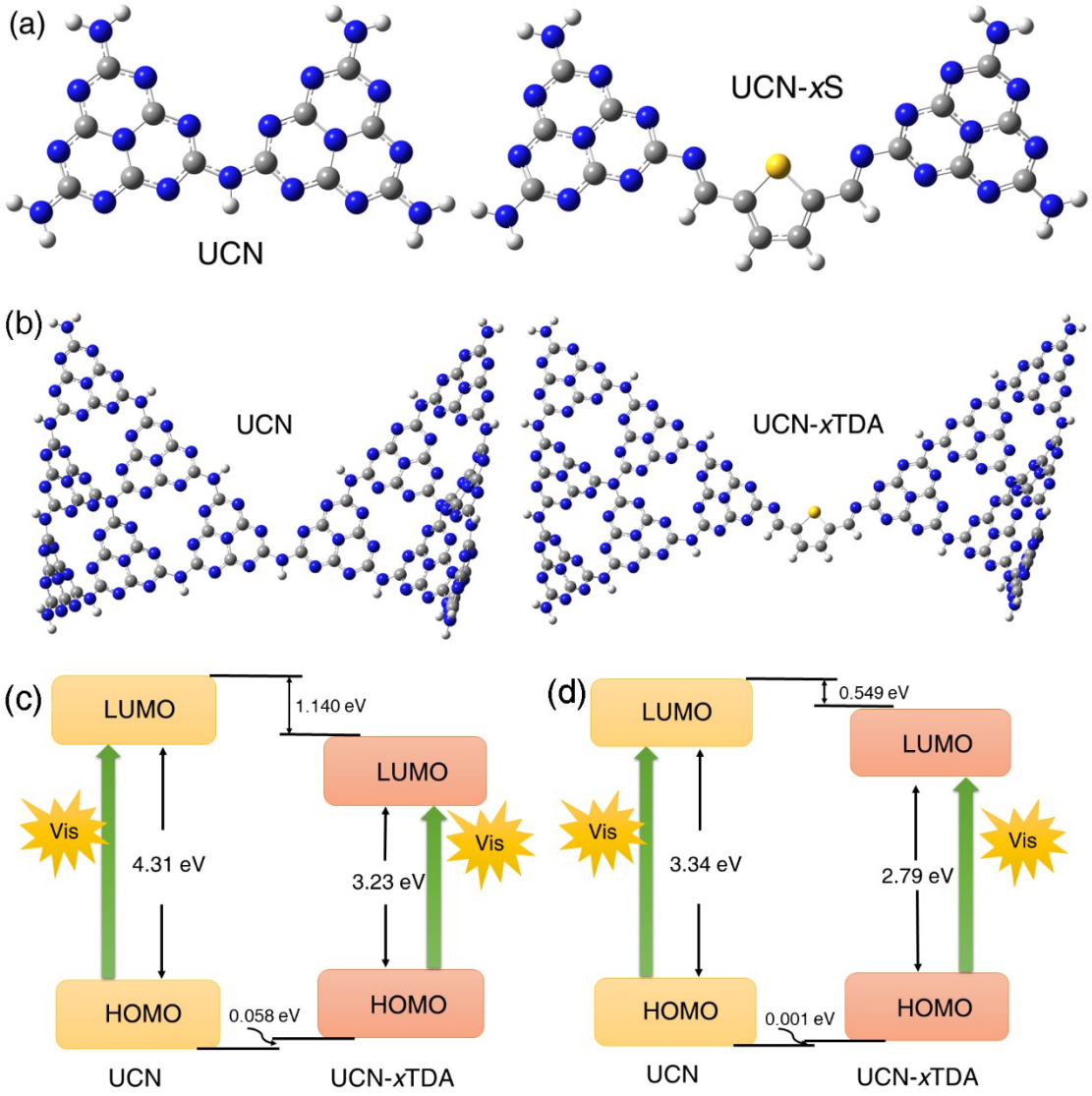


Figure S3 the Optimized polymeric (a) monomer and (b) hexamer models and their corresponding (c, d) schematic diagram of the HOMO and LUMO for UCN and UCN-*x*TDA.

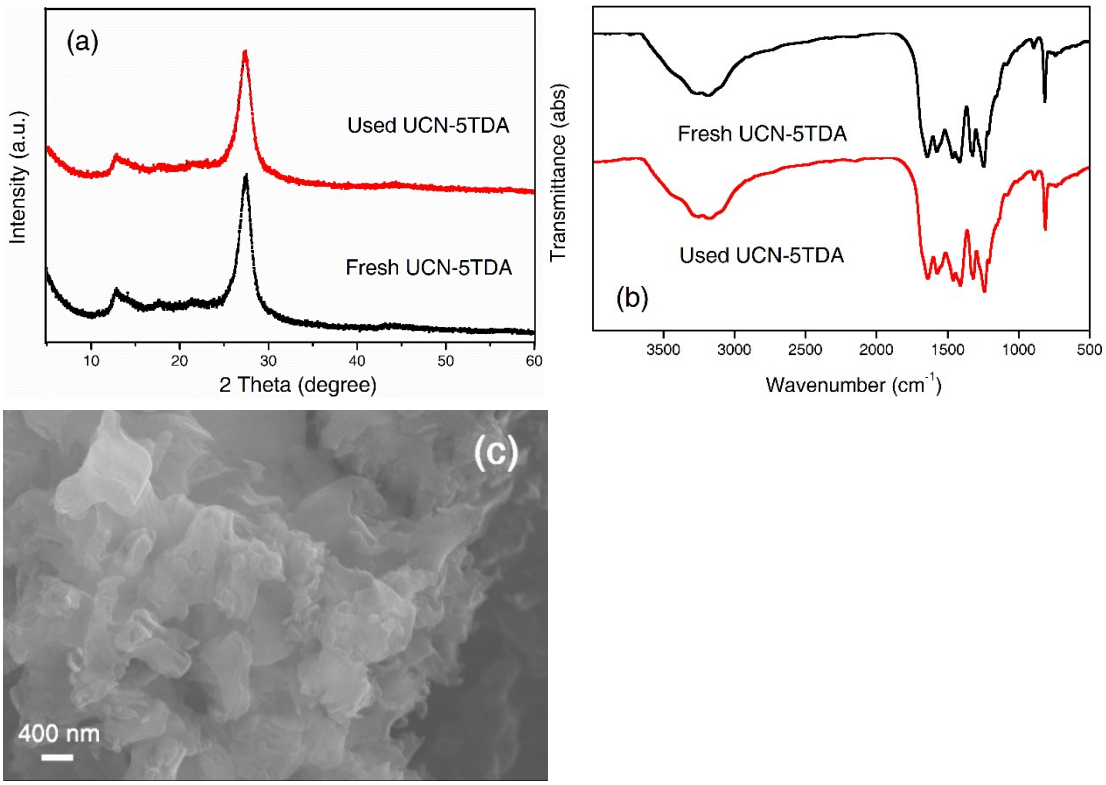
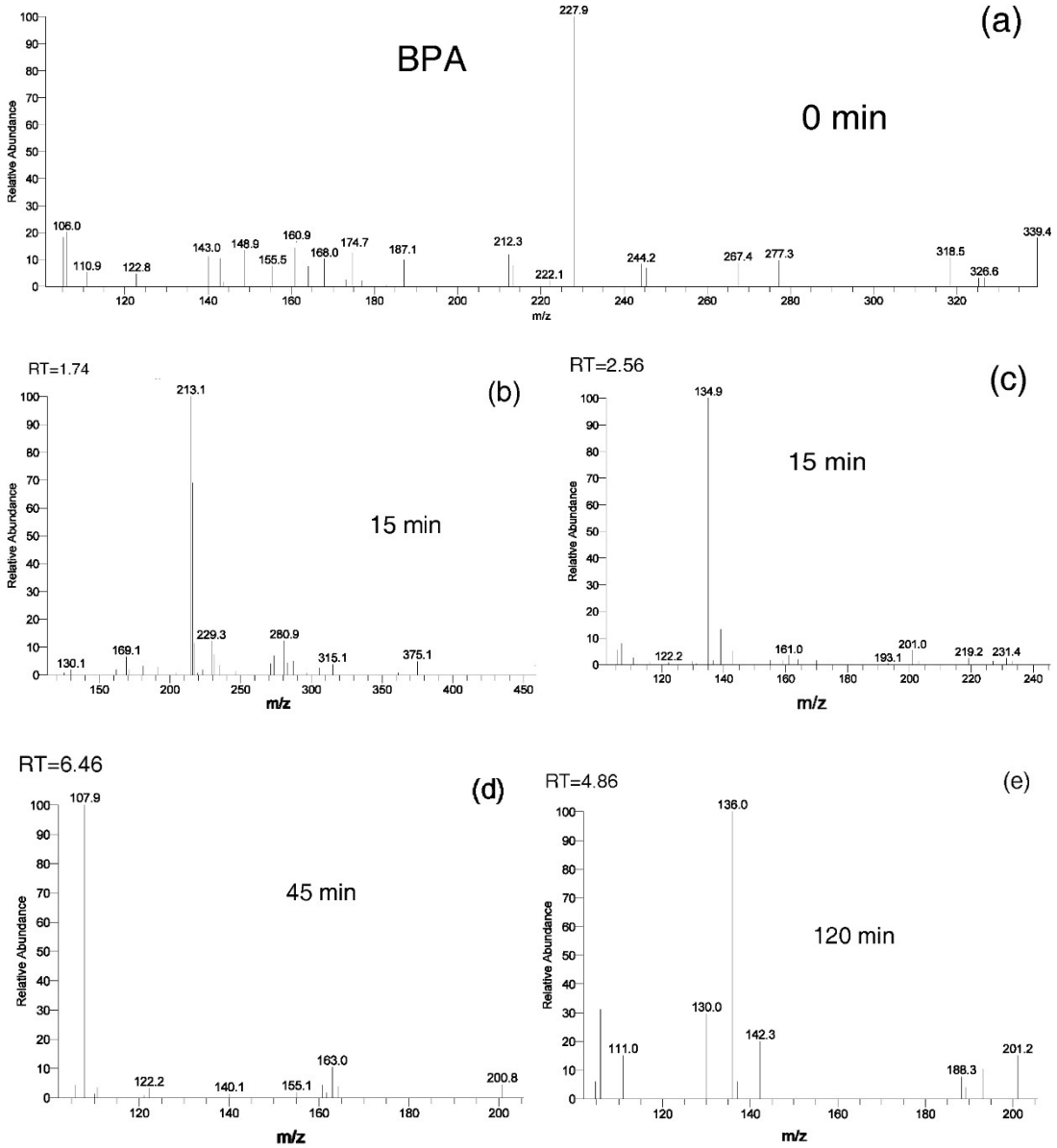


Figure S4 (a) XRD patterns and (b) FTIR of UCN-5TDA before and after repeated irradiation; (c) SEM images of UCN-5TDA after repeated irradiation.


(a)
BPA
0 min
Relative Abundance
m/z
227.9
106.0
110.9
122.8
143.0
148.9
155.5
160.9
168.0
174.7
187.1
212.3
222.1
244.2
267.4
277.3
318.5
326.6
339.4
(b)
RT=1.74
15 min
213.1
130.1
169.1
229.3
260.9
315.1
375.1
(c)
RT=2.56
15 min
134.9
122.2
161.0
193.1
201.0
219.2
231.4
(d)
RT=6.46
45 min
107.9
122.2
140.1
155.1
163.0
200.8
(e)
RT=4.86
120 min
136.0
111.0
130.0
142.3
188.3
201.2

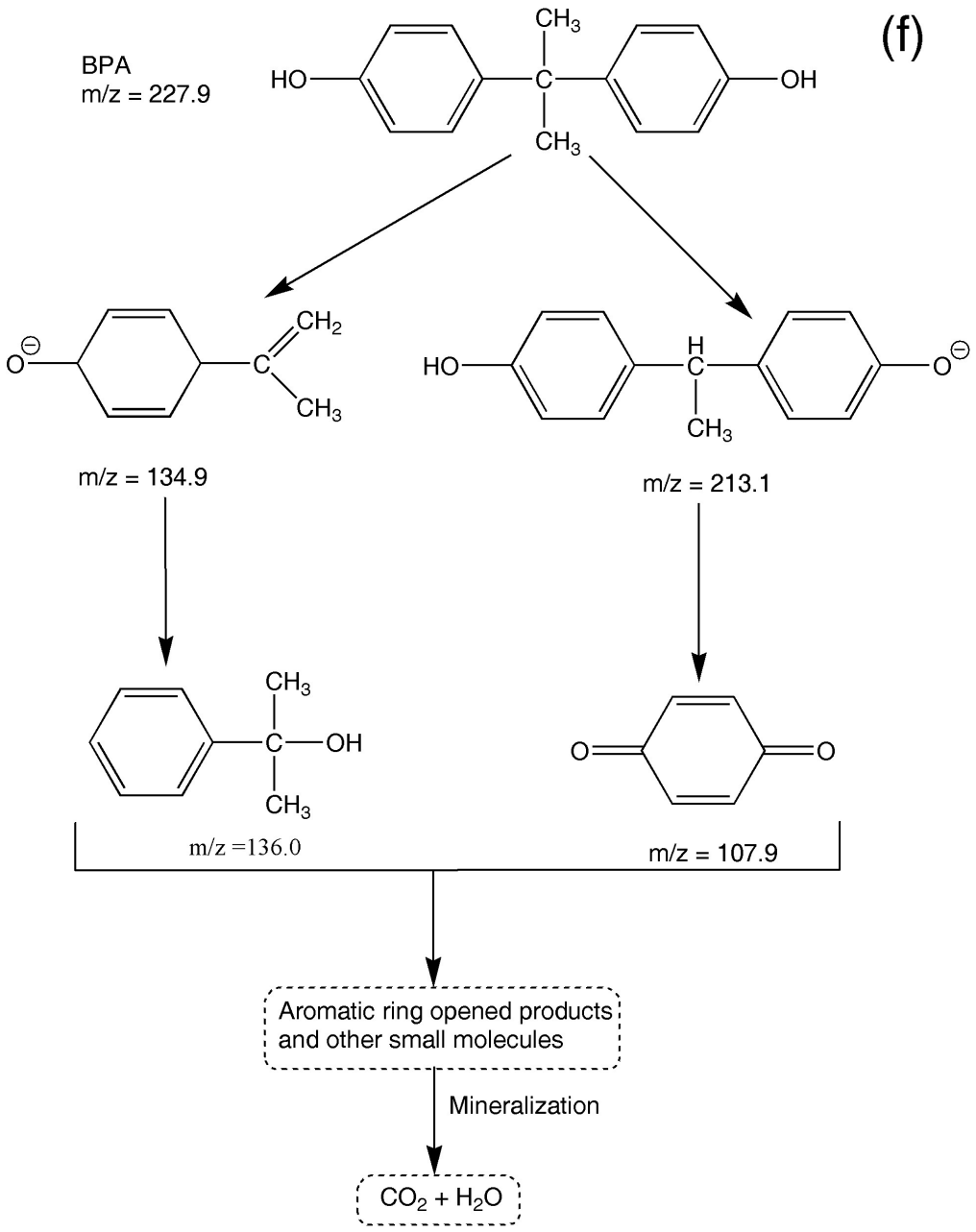


Figure S5 (a-e) Mass spectra of by-products generated during the photodegradation of BPA after 0, 15, 45 and 120 min of irradiation; (f) Proposed degradation pathway for BPA using UCN-5TDA.

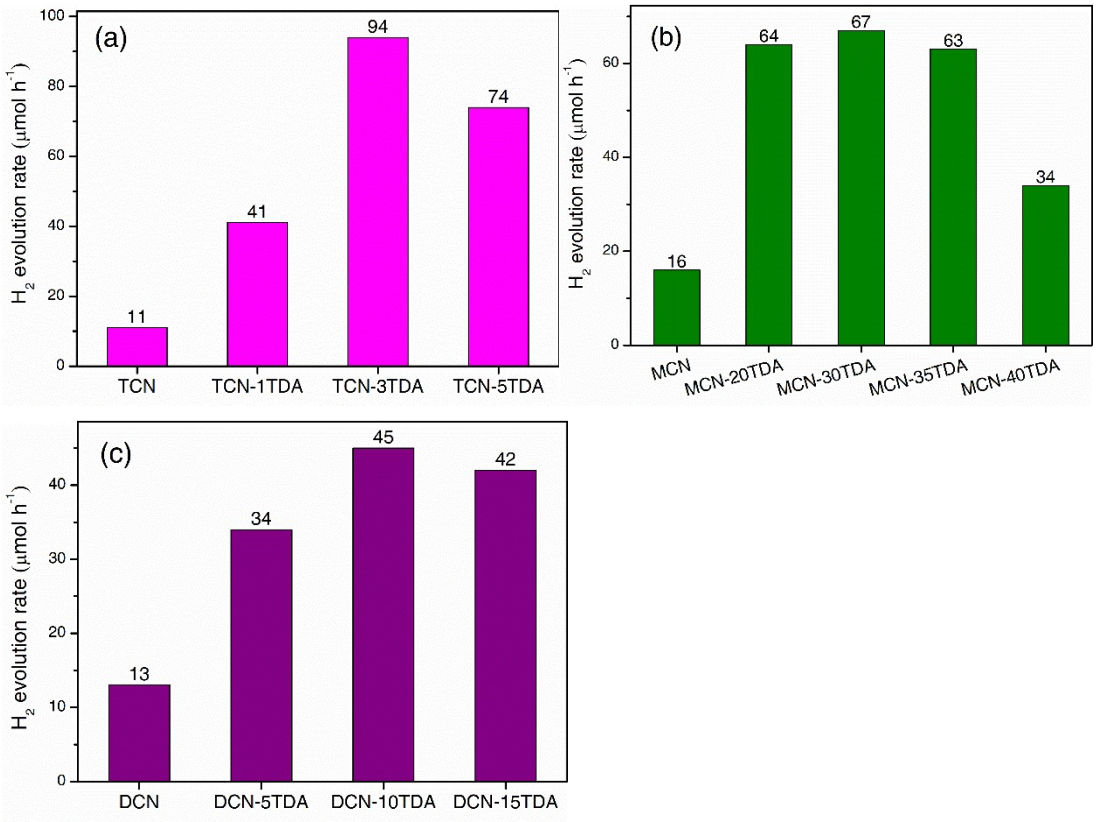


Figure S6 hydrogen evolution rates of the photocatalyst derived from different precursors under visible light ($\lambda > 420$ nm).

Table S1. Comparison of photocatalytic activity of the reported g-C_3N_4.

Catalyst	Light Source	Reaction Conditions	HER (mmol h^{-1} g^{-1})	Apparent quantum efficiency	Ref.
UCN-5TDA	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	12.35	40.5% (400 nm) 13.3% (450 nm) 7.93% (500 nm) 1.25% (550 nm)	This work
UCN-BI_{400}	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(20 vol%)	5.44	23.3% (420 nm) 7% (450 nm) 3% (500 nm) 0.5% (550 nm)	[1]
UCN-4TAPB	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	10.55	40.0% (400 nm) 3.8% (500 nm)	[2]
UCN-BD	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	3.43	12.3% (450 nm)	[3]
PTI-0.13	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	8.16	15% (400 nm) 7.0% (420 nm) 4.6% (450 nm) 0.8% (550 nm)	[4]
O-CN2	300 W Xe lamp, λ > 420 nm	1 wt% of Pt; Aqueous Lactic acid solution (10 vol%)	1.06	13.2% (420 nm) 4.5% (450 nm) 1.5% (500 nm) 1.0% (550 nm)	[5]
UCN-10	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution(10 vol%)	2.33	8.2% (450 nm)	[6]
UM3	300 W Xe lamp, λ > 420 nm	1 wt% of Pt; Aqueous Lactic acid solution (20 vol%)	3.58	27.8% (420 nm) 12% (450 nm) 7% (500 nm)	[7]
g-C_3N_4 (urea)	300 W Xe lamp, λ > 395 nm	3 wt% of Pt; Aqueous TEOA solution(13 vol%)	3.33	26.5% (400 nm) 12.5% (420 nm) 4% (450 nm)	[8]
g-C_3N_4 (urea and thiourea)	300 W Xe lamp, λ> 400 nm	1 wt% of Pt; Aqueous methanol solution (20vol%), pH=13.3 (KOH)	2.23	6.67% (400 nm)	[9]
MCN-1	300 W Xe lamp, λ > 420 nm	3 wt% of Pt; Aqueous TEOA solution (10vol%)	0.60	7.8% (420 nm)	[10]

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