Hydroxyl group modified polymeric carbon nitride with highly selective hydrogenation of nitrobenzene to *N*-phenylhydroxylamine under visible light

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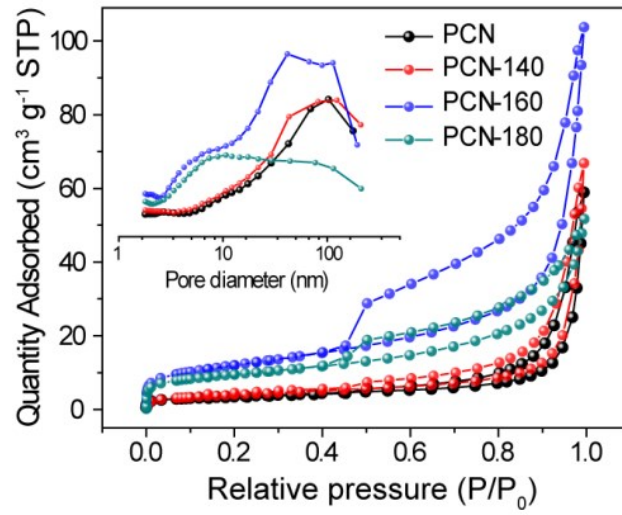
Fig. S1 N$_2$ absorption-desorption isotherms and the corresponding pore size distribution curves (inset).
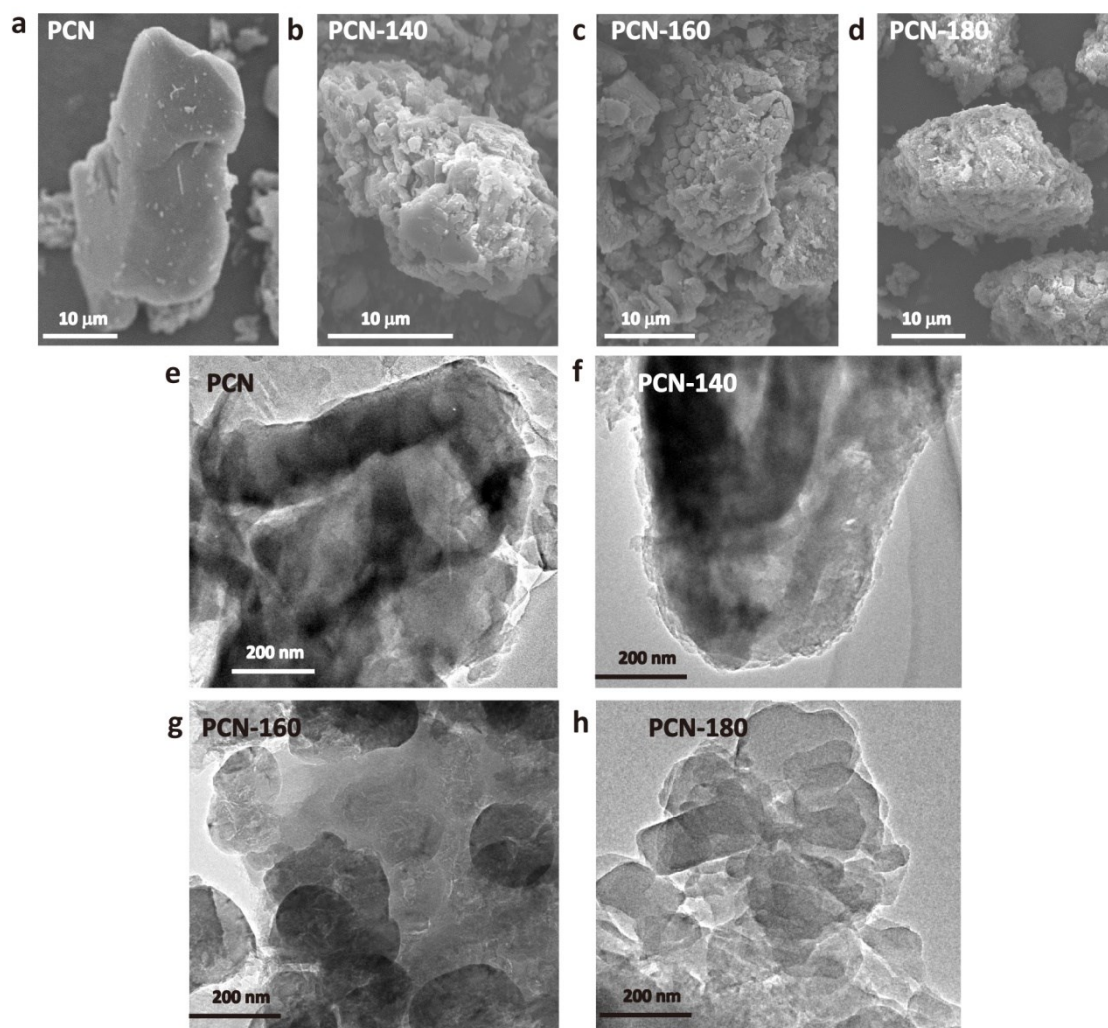
Fig. S2 (a-d) SEM and (e-h) TEM images of PCN before and after hydrothermal treatment.
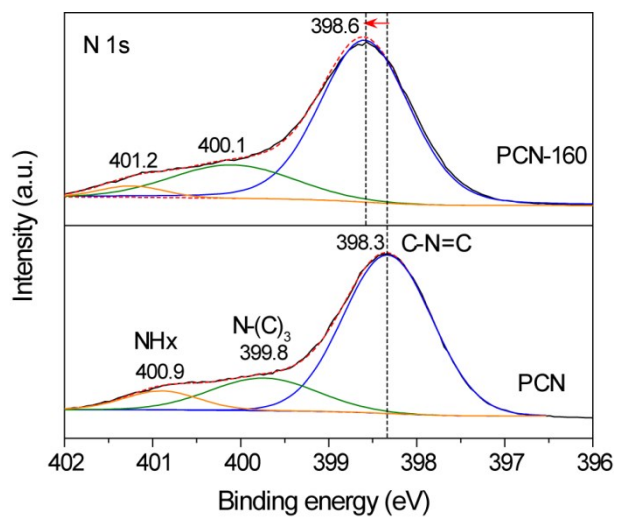
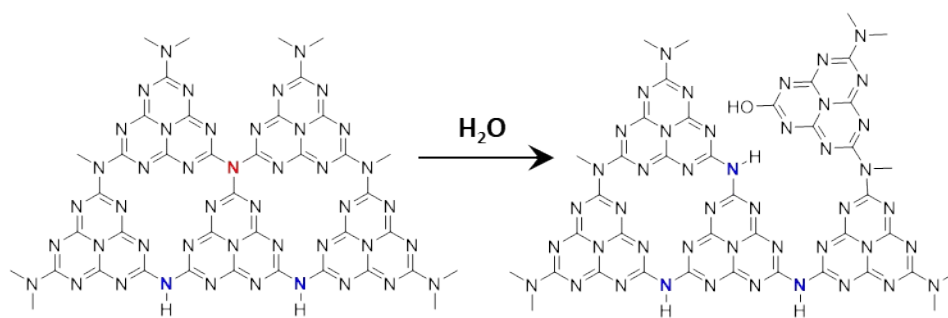**Fig. S3** N 1s XPS spectra of PCN and PCN-160 samples.

Fig. S4 The schematic presentation for the evolution of carbon environment. The N atom in red represents the N–(C)$_3$ and the N atom in blue represents the N atom in C$_{2N-NH}$.
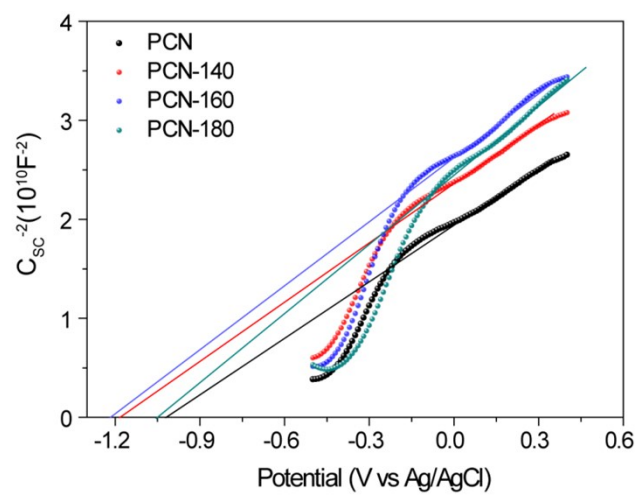
Fig. S5 Mott–Schottky plots measured in 0.1 M Na_2SO_4 aqueous solutionat pH = 5.95 with a fixed frequency of 1000 Hz.
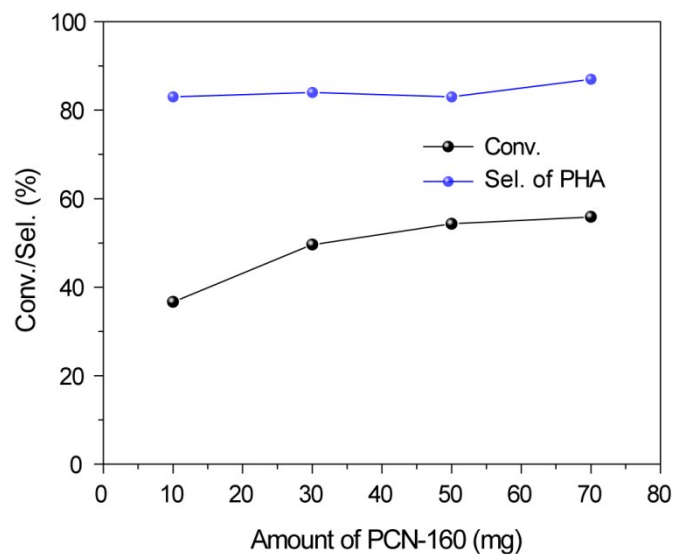
Fig. S6 The relation between catalyst dosage and conversion/selectivity of the reaction. Reaction conditions: nitrobenzene (30 µmol), IPA (1.5 mL), Ar (1 atm), 100 W white LED lamp (0.6 W cm^{-2}), 60 °C, 6 h.

There is an increase in the conversion rate of nitrobenzene as the amount of catalyst increased from 10 mg to 50 mg, which almost has no effect on the selectivity toward *N*-phenylhydroxylamine. Excess amount catalyst (> 50 mg) almost provides no contribution to the photocatalytic reaction. Therefore, 50 mg is the optimal amount in the reaction system.
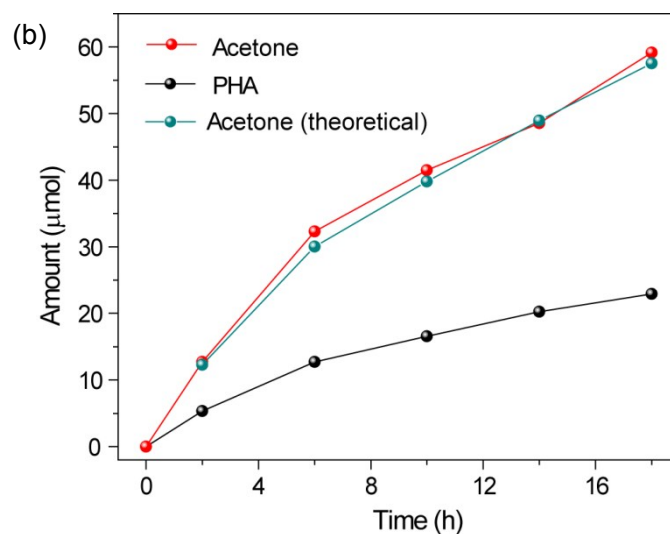
(a)

$$\text{PhNO}_2 + 2\text{H}_3\text{C}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{O}\textcolor{red}{\text{H}}}{|}}{\text{C}}}-\text{CH}_3 \xrightarrow[\text{Cat.}]{h\nu} \text{PhN}\textcolor{red}{\text{H}}\text{O}\textcolor{red}{\text{H}} + 2\text{H}_3\text{C}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{CH}_3 + \textcolor{red}{\text{H}_2}\text{O}$$
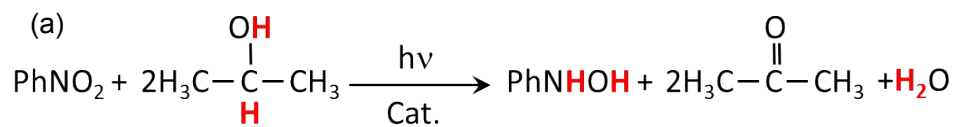
(b)

Fig. S7 The equation of the hydrogen transfer process from nitrobenzene to PHA (a) and the production of acetone during the hydrogenation (b). The line in dark cyan represent the sum of theoretical acetone output calculated base on all products.
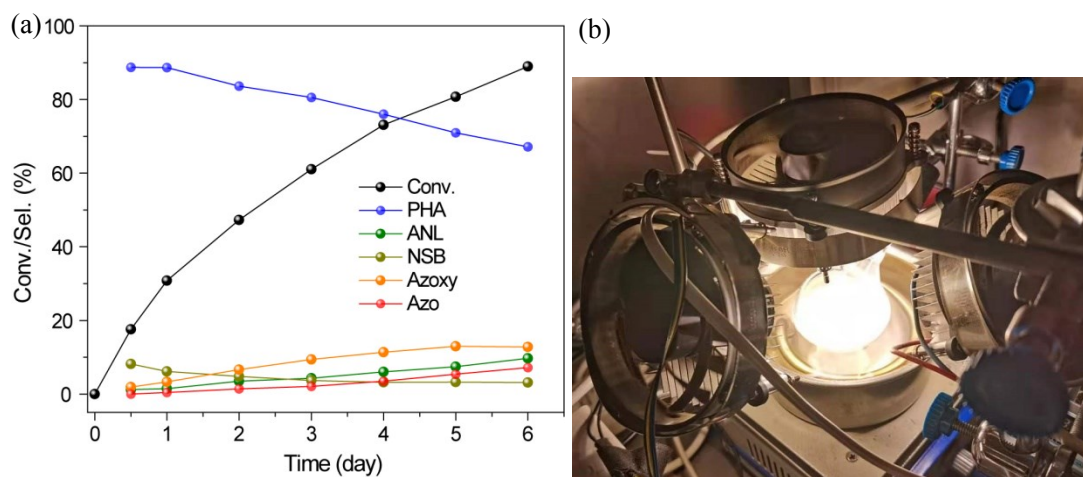
Fig. S8 Time dependent profiles of the scale-up experiment showing the conversion of nitrobenzene and the product selectivity (a) and the photograph of the equipment during the scale up reaction (b). Reaction conditions: PCN-160 (500 mg), nitrobenzene (1 mmol), IPA (50 mL), Ar (1 atm), 60 °C, three 100 W white LED lamp. The optical power of each lamp was 1 W. Three lamps shined on the reaction flask from the top and the side simultaneously.
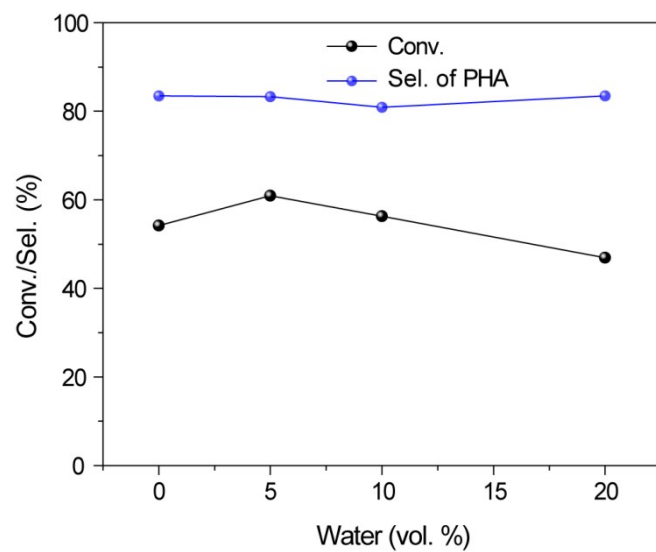
Fig. S9 The effect of water on selective hydrogenation of nitrobenzene. Reaction conditions: nitrobenzene (30 μmol), IPA+Water (1.5 mL), photocatalyst (50 mg), Ar (1 atm), 100 W white LED lamp (0.6 W cm^{-2}), 60 °C,6 h.
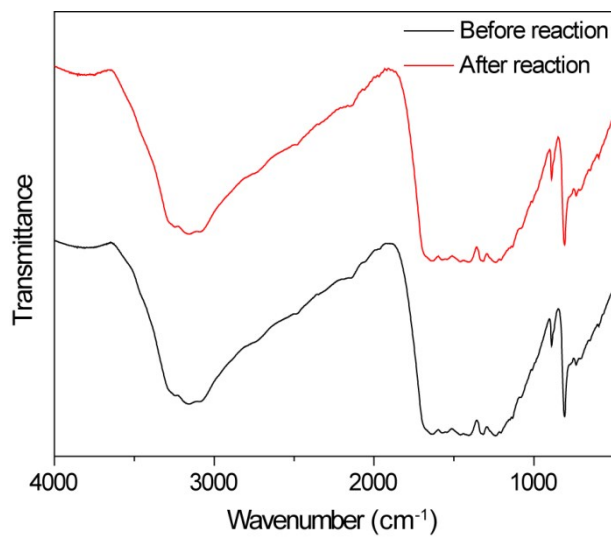
Fig. S10 FT-IR spectra of PCN-160 before and after the photocatalytic reaction.
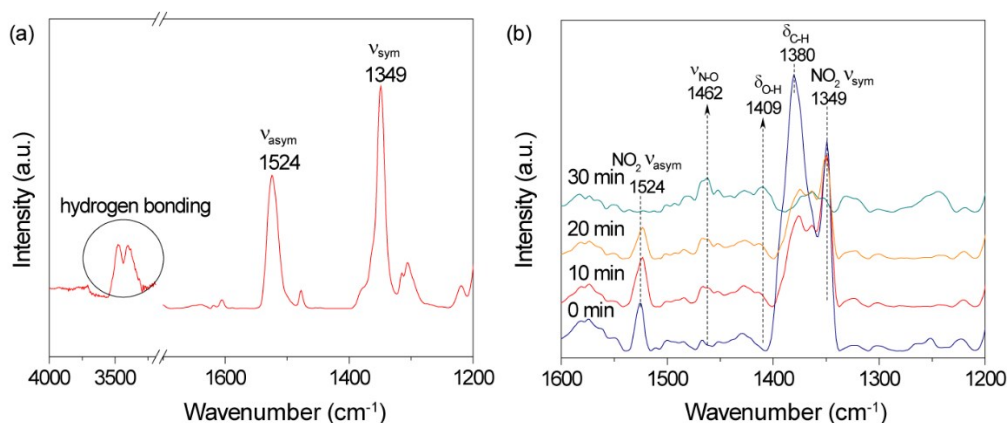
Fig. S11 (a) The adsorption of nitrobenzene over PCN-160. (b) The time dependent *in situ* DRIFTS spectra of the conversion of nitrobenzene over PCN-160 under white LED light irradiation.

The *in situ* DRIFTS was recorded by a Bruker TENSOR Ⅱ spectrometer equipped with a Praying Mantis diffuse reflectance accessory (Harrick Scientific Products Inc.) and a MCT detector cooled by liquid N_2. PCN-160 was loaded in the reaction cell and was set as the background. 10 μL of nitrobenzene was dropped on the surface of the PCN-160. The spectrum was recorded under Ar flow (30 mL min^{-1}) for 30 min until the signals stable (Fig. S11a). Then 30 μL of isopropanol was introduced into the system. The spectrum was scanned every 10 min of illumination with the white LED light after 10 min of Ar flow to remove the oxygen in the reaction cell (Fig. S11b).
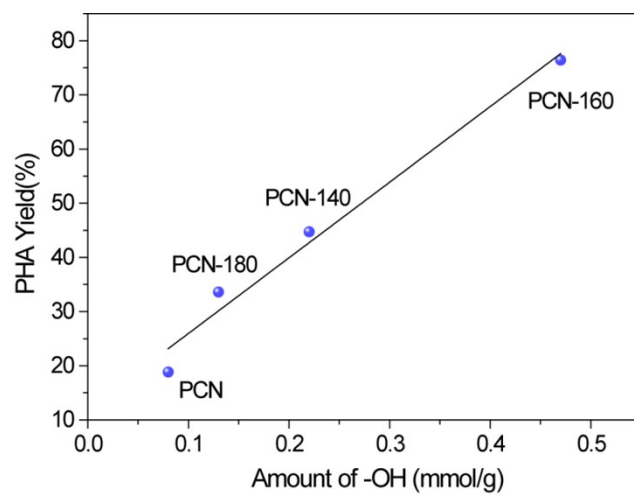
Fig. S12 The amount of –OH quantitative analysed by Boehm titration *vs*. PHA yield at 18 h.
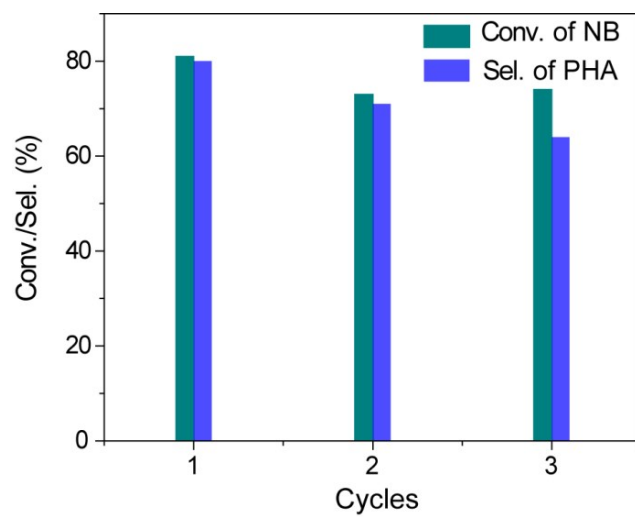
Fig. S13 The reusability of PCN-160 photocatalyst.
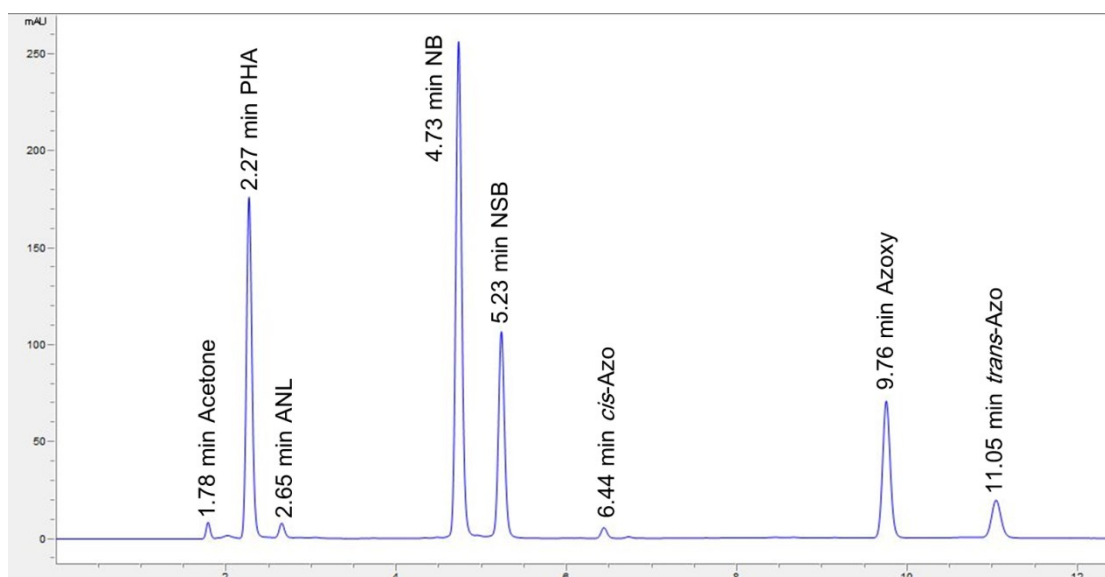
Fig. S14 The HPLC chromatogram of the reaction mixture at 14 h over PCN-160

External standard method was used to analyze all products quantitatively. The mobile phase was methanol and water with a gradient ratio and the detection wavelength was 280 nm. The gradient ratio of the mobile phase of HPLC was shown as follows.

Time (min)	Water (%)	Methanol (%)	Rate of flow (mL/min)
0	50	50	1
6	20	80	1
12	20	80	1
14	50	50	1
16	50	50	1

Table S1 Summary of the physical and optical properties of all samples.

Samples	S_{BET} (m^2 g^{-1})	E_g (eV)	CB (V *vs*. NHE)[a]	VB (V *vs*. NHE)[b]
PCN	12.2	2.61	−0.82	1.79
PCN-140	14.3	2.63	−0.98	1.65
PCN-160	42.6	2.65	−1.0	1.65
PCN-180	32.8	2.67	−0.85	1.82

[a] The position of conduction band (CB) was acquired from the Mott-Schottky plots shown in Fig. S5. The potential conversion was based on the formula E (V *vs*. NHE) = E (V *vs*. Ag/AgCl) + 0.197. [b] The valance band position was obtained by summing band gap energy (E_g) and the potential of conduction band.

Table S2 Surface atomic ratio of all samples determined by XPS spectra.

Samples	N (atom %)	C (atom %)	O (atom %)	C/N	N/O
PCN	58.41	40.74	0.86	0.697	67.9
PCN-140	57.69	40.66	1.65	0.705	34.9
PCN-160	56.50	41.54	1.96	0.735	28.8
PCN-180	54.23	36.97	8.80	0.682	6.2

Table S3 Elemental analysis results of all samples measured by elemental analyser.

Samples	N (mol %)	C (mol %)	H (mol %)	O (mol %)[a]	C/N	N/O
PCN	48.50±0.013	31.99±0.013	19.32±0.001	0.19	0.660	255.5
PCN-140	47.64±0.035	31.17±0.011	20.15±0.043	1.04	0.654	45.9
PCN-160	45.97±0.025	29.83±0.056	22.34±0.036	1.86	0.649	24.7
PCN-180	42.95±0.059	27.83±0.068	25.13±0.119	4.08	0.648	10.5

[a] The oxygen content was acquired by "O % = 100% − C % − N % − H % based on that there were only C, N, O and H elements in the catalysts.

Table S4 TEM-EDS results of all samples.

Samples	C (atom %)	N (atom %)	O (atom %)	N/O
PCN	70.34	29.25	0.41	71.34
PCN-140	61.59	37.70	0.70	53.86
PCN-160	58.59	40.61	0.79	51.40
PCN-180	58.22	40.84	0.95	42.99

Table S5 Relative ratios of C-N=C, N-(C)$_3$ and NH$_x$ determined by N 1s spectra

Samples	C-N=C (%) N2	N-(C)$_3$ (%) N3	NH$_x$ (%) N1	N1/N3
PCN	74.08	18.16	7.75	0.43
PCN-160	77.37	19.91	3.56	0.19

Table S6 The fitting parameters of the time-resolved PL delay curve in Fig. 2d.

Samples	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	B_1	B_2	B_3	A	τ_{ave} (ns)
PCN	6.67	43.87	1.27	1.83×10^{-2}	1.41×10^{-3}	0.11	4.49	2.51
PCN-160	5.20	36.12	1.13	2.03×10^{-2}	1.03×10^{-3}	0.11	3.07	2.01

The data in Fig. 2d was fitted to tri-exponential functions

$$f(t) = A + B_1 e^{-\frac{t}{\tau 1}} + B_2 e^{-\frac{t}{\tau 2}} + B_3 e^{-\frac{t}{\tau 3}}$$

where A, B_i and τ_i represented the background, pre-exponential factors and the characteristic lifetimes.

The average lifetime was expressed as τ_{ave} = $\dfrac{B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3}{B_1 + B_1 + B_1}$

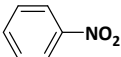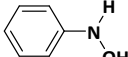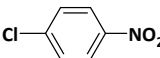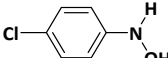**Table S7** The conversion of nitrobenzene in absence of light or PCN-160.
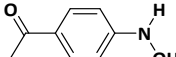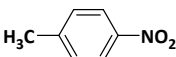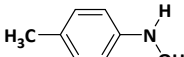
Entry	Catalyst	Light	Conv. (%)	Sel. (%)				
				PHA	ANL	NSB	Azoxy	Azo
1	-	Yes	4.9	70.1	4.2	25.8	n.d.	n.d.
2	PCN-160	No	0	n.d.	n.d.	n.d.	n.d.	n.d.

Reaction conditions: nitrobenzene (30 µmol), IPA (1.5 mL), photocatalyst (50 mg), Ar (1 atm), 100 W white LED lamp (0.6 W cm^{-2}), 60 °C,18 h. n.d. = not detected.

Table S8 Summary of the photocatalytic conversion of nitrobenzene over various catalysts.

Entry	Catalyst	Light	Sel. (%) ANL	Sel. (%)	Reference
1	g-C_3N_4	450 nm 410 nm	- -	95 (Azoxy) 94 (Azo)	*Nat. Commun. 2018, 9, 60*
2	amphiphilic g-C_3N_4	> 420 nm	100	-	*J. Mater. Chem. A 2019, 7, 13071*
3	CdS/g-C_3N_4	> 420 nm	52.8	-	*Chin. J. Chem. 2017, 35, 217 – 225*
4	TiO_2/g-C_3N_4/ graphene	visible light	97	-	*Appl. Catal. B: Environ. 2017, 203, 1 – 8*
5	Ag-rGO /g-C_3N_4	> 400 nm	98	-	*J. Hazard. Mater. 2020, 387, 121700*
6	Ni/P-g-C_3N_4	> 400 nm	98.5	-	*Nanomaterials 2016, 6, 59*
7	TiO_2	> 300 nm	97	-	*ACS Catal. 2013, 3, 2318 – 2326*
8	Fe_2O_3/$BiVO_4$	> 420 nm	98	-	*Ceram. Int. 2020, 46, 24534 – 24543*
9	Graphene/ Ce-UiO-66	> 400 nm	99	-	*Appl. Surf. Sci. 2017, 420, 276 – 285.*
10	Cu/graphene	visible light	-	98.2 (Azo)	*Angew. Chem. Int. Ed. 2014, 53, 1973 – 1977*
11	Au–Cu/ZrO_2	visible light	95	-	*ACS Catal. 2016,6, 1744 – 1753*
12	Ag-Cu/ZrO_2	400–750 nm	-	86 (Azoxy)	*Green Chem. 2016, 18, 817 – 825*
13	Cu_7S_4@Pd	1500 nm	100	-	*Nano Lett. 2015, 15, 6295 – 6301*
14	Eosin Y	green light	99	-	*Green Chem. 2014, 16,1082 – 1086*

Table S9 Photocatalytic hydrogenation of nitroarenes to N-arylhydroxylamines over PCN-160.

Substrate	Product	Time (h)	Conv. (%)	Sel. (%)
Benzene–NO$_2$	Benzene–N(H)–OH	14	81.1	80.3
Cl–C$_6$H$_4$–NO$_2$	Cl–C$_6$H$_4$–N(H)–OH	13	83.1	61.2
CH$_3$C(O)–C$_6$H$_4$–NO$_2$	CH$_3$C(O)–C$_6$H$_4$–N(H)–OH	14	79.2	85.8
H$_3$C–C$_6$H$_4$–NO$_2$	H$_3$C–C$_6$H$_4$–N(H)–OH	18	84.9	63.4

Reaction conditions: substrate (30 µmol), IPA (1.5 mL), PCN-160 (50 mg), Ar (1 atm), 100 W white LED lamp (0.6 W cm^{-2}). Conv. = conversion, Sel. = selectivity. The conversion was determined by HPLC using external standard method. The selectivity of N-arylhydroxylamines was determined by the combined analysis of HPLC and ^{1}H NMR. The low selectivity of –Cl and –CH$_3$ substituted *N*-arylhydroxylamines may be caused by its oxidation in air before ^{1}H NMR testing.

Apparent quantum efficiency (AQE) calculation

Reaction conditions: nitrobenzene (30 μmol), isopropanol (1.5 mL), PCN-160 (50 mg), 60±2 °C, 10 h, 1 atm Ar atmosphere, irradiation area (1.5 cm^{-2}). Blue (425-510 nm, peak at 459 nm), green (475-600 nm, peak at 525 nm), and red (585-655 nm, peak at 626 nm) coloured LED lights were used to measure the apparent quantum efficiency (AQE). The light intensity of each single coloured LED was 0.15 W cm^{-2}. Four electrons were needed to obtain one *N*-phenylhydroxylamine (PHA) molecule.

$$Apparent\ quantum\ efficiency\ (\%)$$
$$= \frac{mols\ of\ reacted\ electrons\ (photon\ excited)\ per\ unit\ time}{mols\ of\ incident\ photons\ per\ unit\ time} \times 100$$

$$mols\ of\ reacted\ electrons\ (photon\ excited)\ per\ unit\ time$$
$$= \frac{PHA\ yield \times 30 \times 10^{-6} mol \times 4 \times N_A}{10 \times 3600\ s}$$

where N_A represented the Avogadro's constant (6.02×10^{23} mol^{-1}).

$$mols\ of\ incident\ photons\ per\ unit\ time = \frac{0.15\ W\ cm^{-2} \times 1.5\ cm^2 \times \lambda \times 10^{-9} m}{h \times c}$$

where *λ*, *h* and *c* represented the light wavelength in nanometer, Plank's constant (6.63 × 10^{-34} J s) and the speed of light in vacuum (3 × 10^8 m s^{-1}), respectively.

As for the blue LED light, the yield of PHA at 10 h was 27.6% The AQE can be calculated as:

$$AQE = \frac{0.276 \times 30 \times 10^{-6} mol \times 4 \times 6.02 \times 10^{23} mol^{-1} \times 6.63 \times 10^{-34} J\ s \times 3 \times 10^8 m\ s^{-1}}{10 \times 3600\ s \times 0.15\ W\ cm^{-2} \times 1.5\ cm^2 \times 459 \times 10^{-9} m} \times 100$$

$$= 0.107\%$$