Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Functions of Hydroxyapatite in Fabricating N-doped Carbon for Excellent Catalyst and Supercapacitor

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Experimental

Chemicals

Hydroxylapatite (≥ 97 %), ammonium phosphate dibasic (AR. 99 %) and benzylamine (AR. 99 %) were purchased from Shanghai Macklin Biochemical Corporation. 4-（Trifluoromethyl）benzylamine (98 %) and M-tolylmethanamine (98 %) were purchased from LeYan factory. 1, 10-Phenantthroline (AR. 99 %) was purchased from Shanghai Macklin Chemical Technology Factory. Phenyl hydrazine (AR.), 4-Bramabenzylamine (97 %) and 2-Thiophenrmthylamine (97 %) were purchased from Shanghai Energy Chemical Technology Factory. 4-Methoxybenzylamine (95 %) was purchased from Shanghai Shuya factory. Glucose (AR.) was purchased from Tianjin Kermol Corporation. 4-Chlorobenzylamine (98 %) and 4-Fluorobenzylamine (99 %) were purchased from Aladdin Industrial Corporation. 3, 3', 5, 5'-Tetramethylbenzidine (AR. ≥99 %) was purchased from Sigma-Aldrich (Shanghai) Trading Corporation. Benzoic Acid (AR. ≥99 %) and dichloromethane (AR. ≥99 %) were purchased Tianjin chemical reagent factory. Sodium hydroxide was Tianjin Beichen regent factory. Benzoquinone (AR. ≥99 %) was purchased from J&K Scientific LTD. Phenol was purchased from Tianjin Fuchen chemical reagents factory. Tertiary butanol (GR. 98 %) was purchased from Tianjin Guangfu fine chemical research institute. All chemicals were used without further purification.

Characterizations

Transmission electronic microscopy (TEM, Tecnai G2 F20) was used to research the morphology of NC(HAP). X-ray diffractometer (XRD, Bruker D8 ADVANCE) with Cu Ka (λ = 1.5418 Å) recorded the diffraction (XRD) patterns of all samples. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) was applied to research the valence states of all elements in samples. Laser Confocal Micro-Raman Spectroscope (LabRAM HR800, Horiba Jobin Yvon, France) was utilized to present Raman spectra of all samples with 532 nm of laser wavelength. The annealing process of HAP, HAP+phen and phen were researched on Thermogravimetric analyzer (TGA NETZSCH STA 449C). The material was pretreated in vacuum at 150 ° C for 4 hours and the nitrogen adsorption-desorption experiment was carried out on an automated specific surface (JWGB SCI. & TECH. , Beijing).

Characterizations and Results

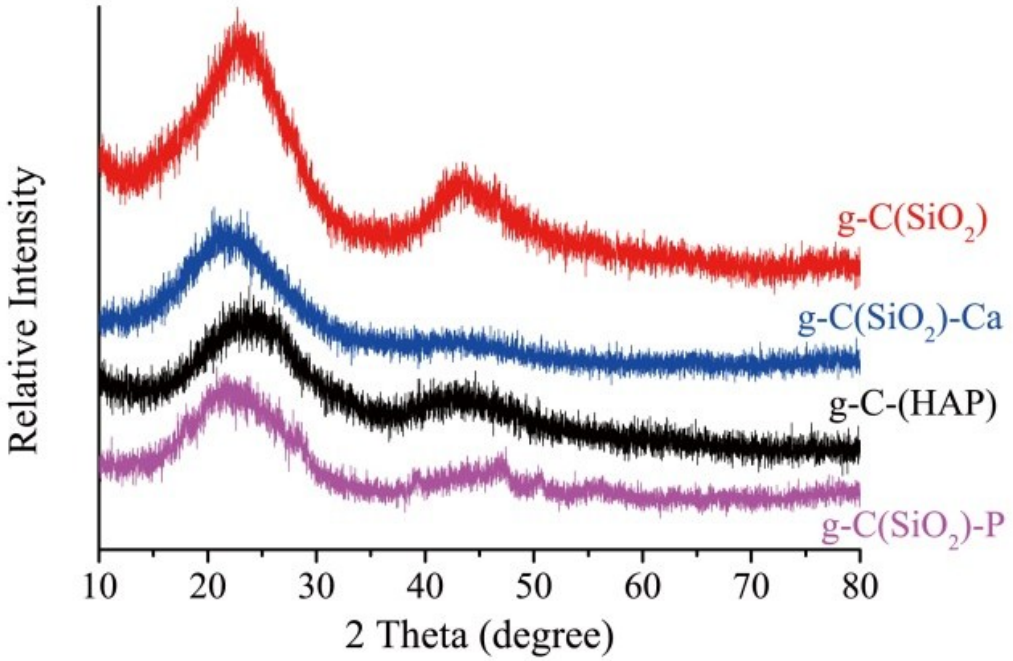

Fig. S1 The XRD of different carbon materials.

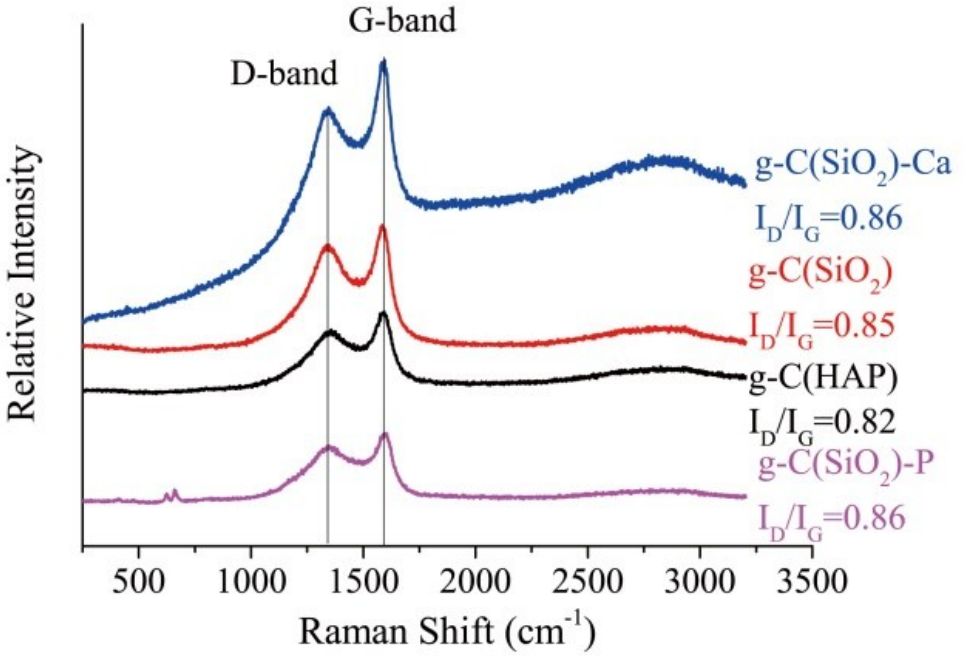

Fig. S2 Raman spectra of g-C(HAP), g-C(SiO_2), g-C(SiO_2)-Ca and g-C(SiO_2)-P.

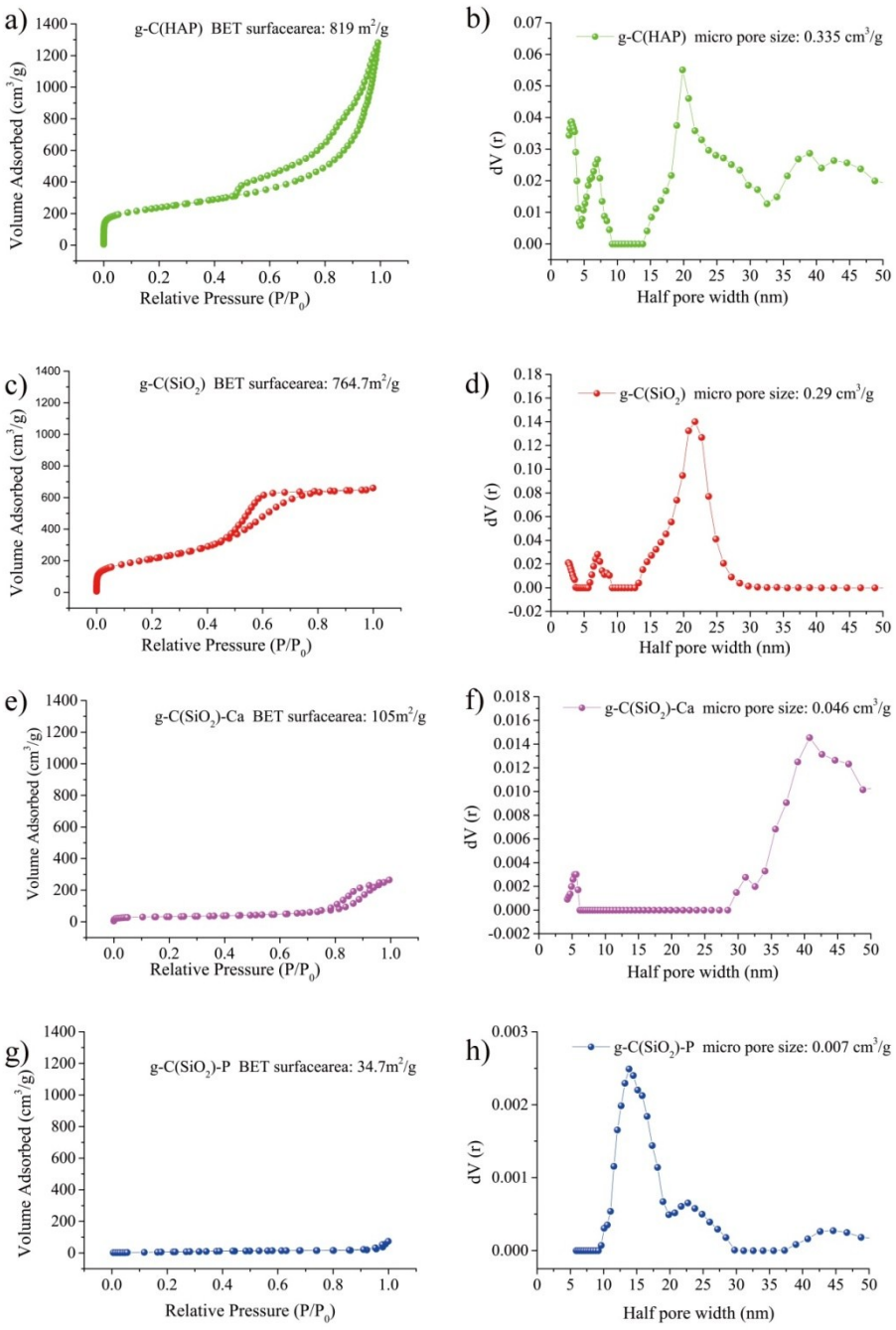

Fig. S3 a), c), e) and g) N_2 absorption-desorption isotherms of g-C(HAP), g-C(SiO_2), g-C(SiO_2)-P and g-C(SiO_2)-Ca; b), d), f) and h) pore size distributions of g-C(HAP), g-C(SiO_2), g-C(SiO_2)-P and g-C(SiO_2)-Ca based on NLDFT model of adsorption isotherms.

Table S1. The textural properties of all samples.

Sample	S_{BET} [a] (m^2/g)	V_{total} [b] (cm^3/g)	V_{micro} [c] (cm^3/g)	$P_{micropore}$ [d] (nm)	$P_{mesopore}$ [e] (nm)
NC(HAP)-600	66	0.037	0.007	1.16	2.185
NC(HAP)	115	0.106	0.04	0.598	2.386
NC(HAP)-800	162	0.610	0.071	0.634	-
NC(SiO_2)	518	0.315	0.226	0.599	2.069
g-C(SiO_2)-P	34.7	0.061	0.007	1.503	2.187
g-C(SiO_2)- Ca	105	0.371	0.046	0.64	16.85
g-C(HAP)	819	1.698	0.335	0.620	2.078
g-C(SiO_2)	764.7	0.947	0.29	0.645	4.799

[a] Specific BET surface area.

[b] Total pore volume, calculated according to nonlocal density functional theory (NLDFT) method.

[c] Micropore volume, calculated according to Horvaih-Kawazoe (HK) method.

[d] Micropore size, calculated according to Horvaih-Kawazoe (HK) method.

[e] Mesopore size, calculated by the Barret–Joyner–Halenda (BJH) method.

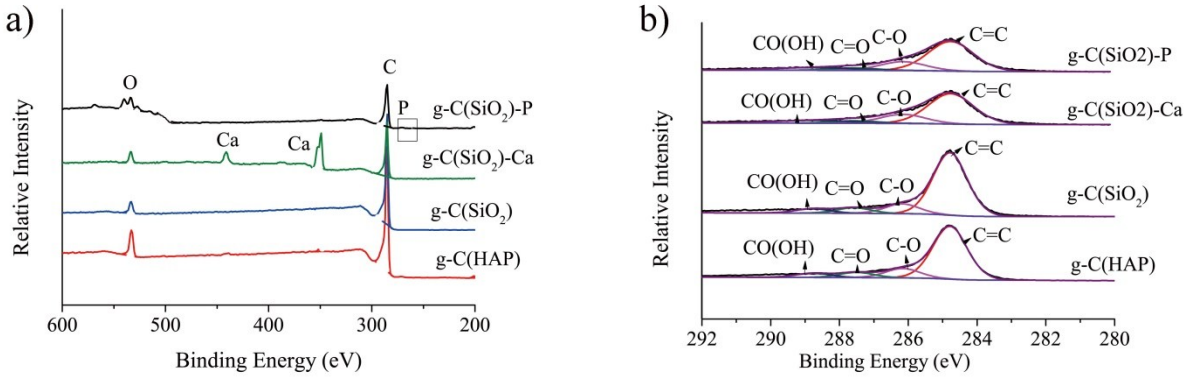

Fig. S4 a) Full XPS spectrum of g-C(HAP), g-C(SiO_2), g-C(SiO_2)-P and g-C(SiO_2)-Ca, b) XPS C1s spectrum of g-C(HAP), g-C(SiO_2), g-C(SiO_2)-P and g-C(SiO_2)-Ca.

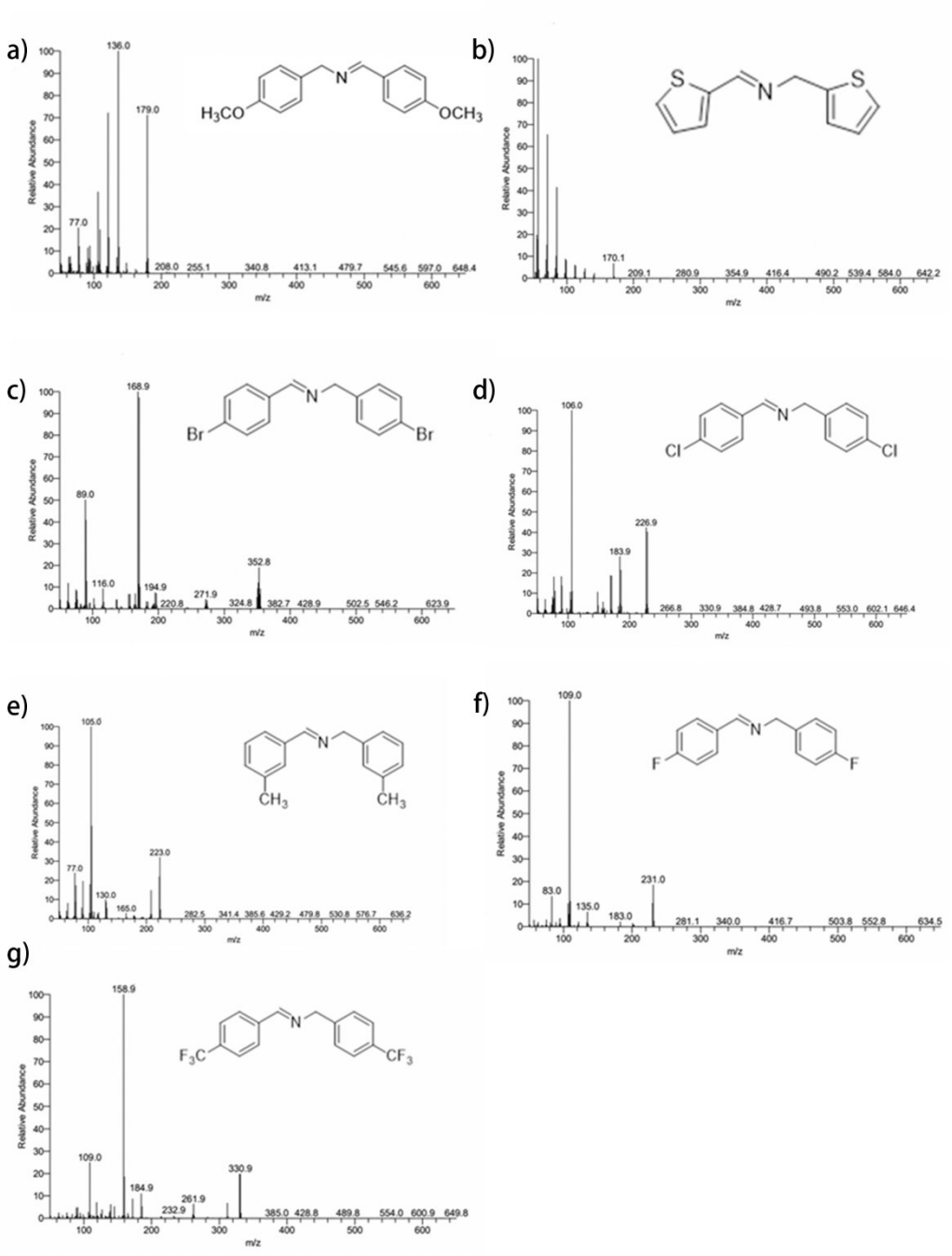

Fig. S5 The structures of imines were all confirmed by GC-MS.

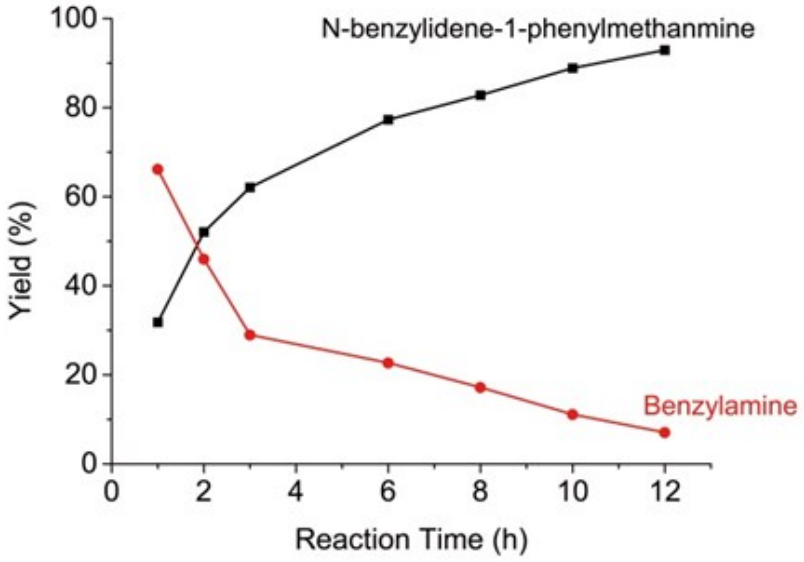

Fig. S6 The conversion of benzylamine and the yield profile of the product imine at different reaction times. Reaction conditions: benzylamine (1 mmol), solvent (3 mL), NC(HAP) (0.01 g), O_2 balloon, 50 °C.

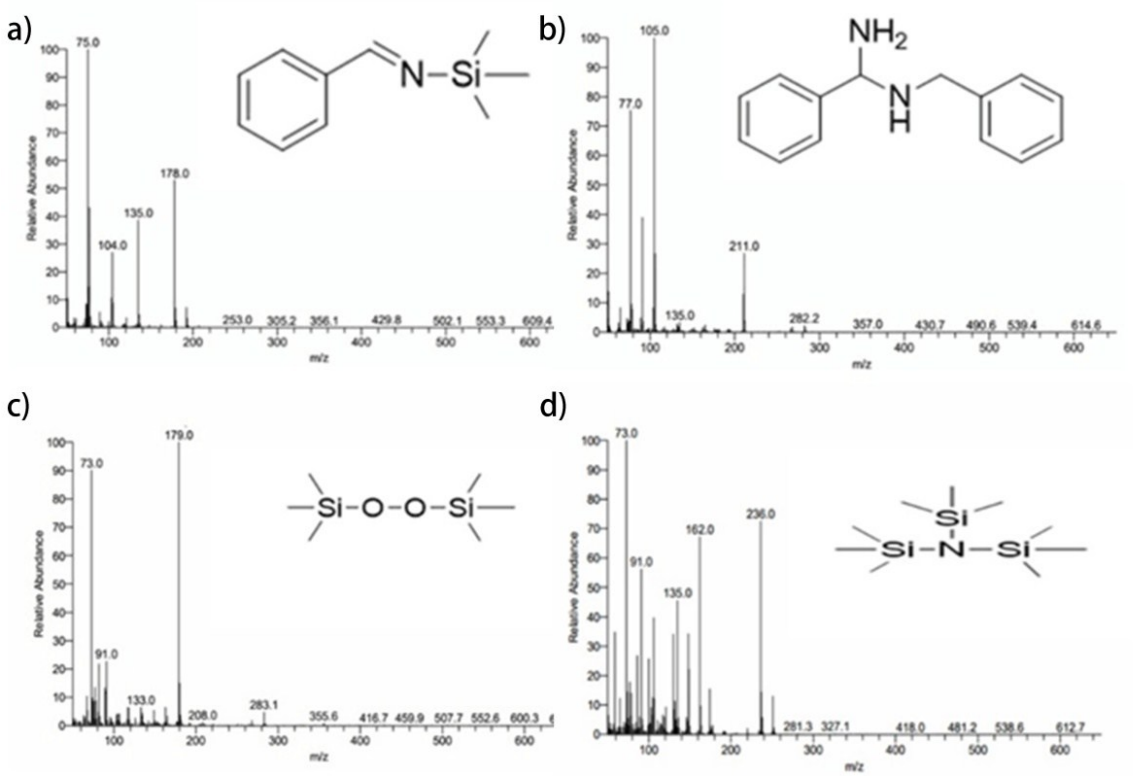

Fig. S7 The experiment of silanization to capture intermediate which confirmed by GC-MS. a) phenylmethanimine, b) N-benzyl-1-phenylmethanediamine, c) hydroperoxide, d) ammonia.

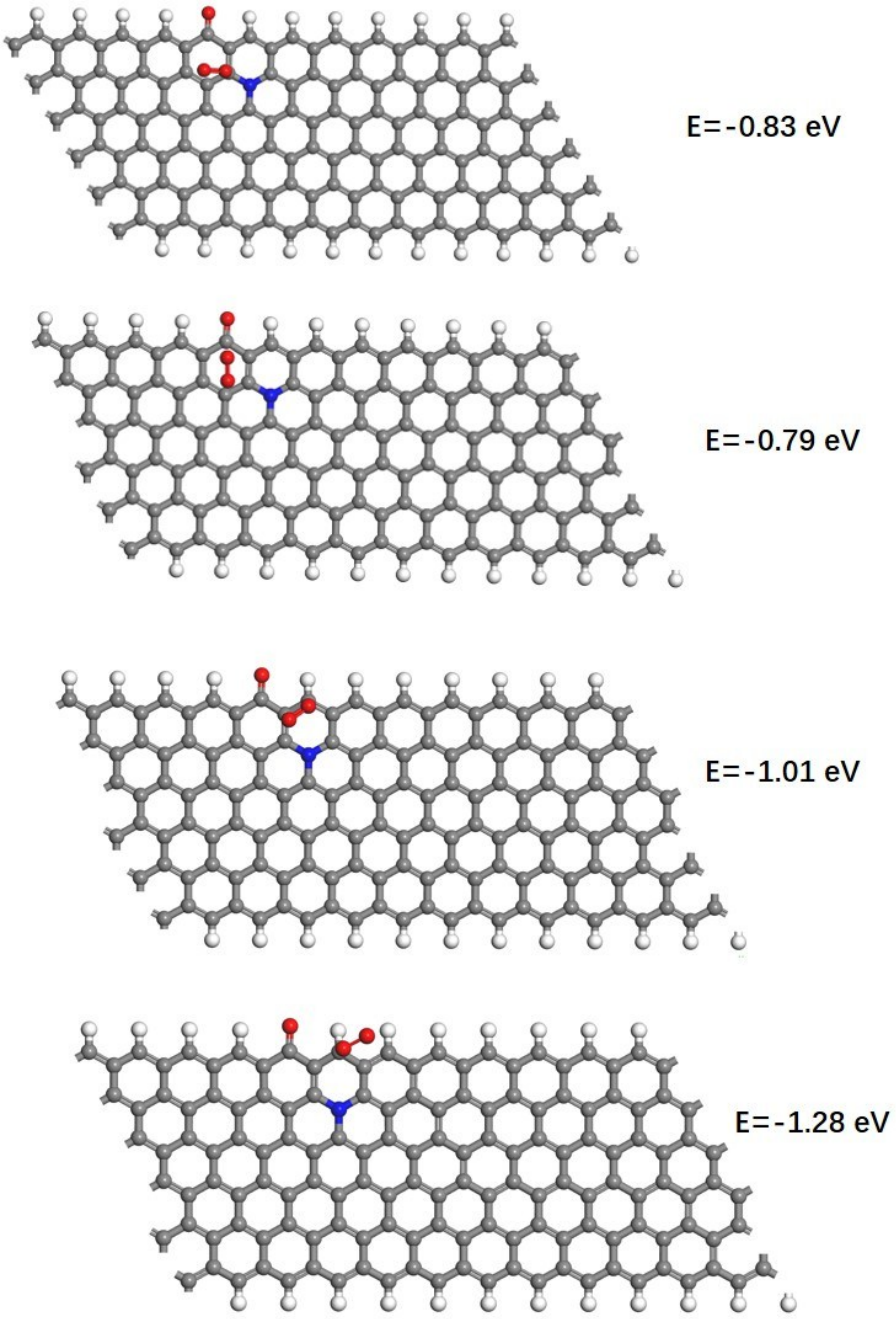

Fig. S8 The configurations and energy of the oxygen adsorbed on model catalyst.

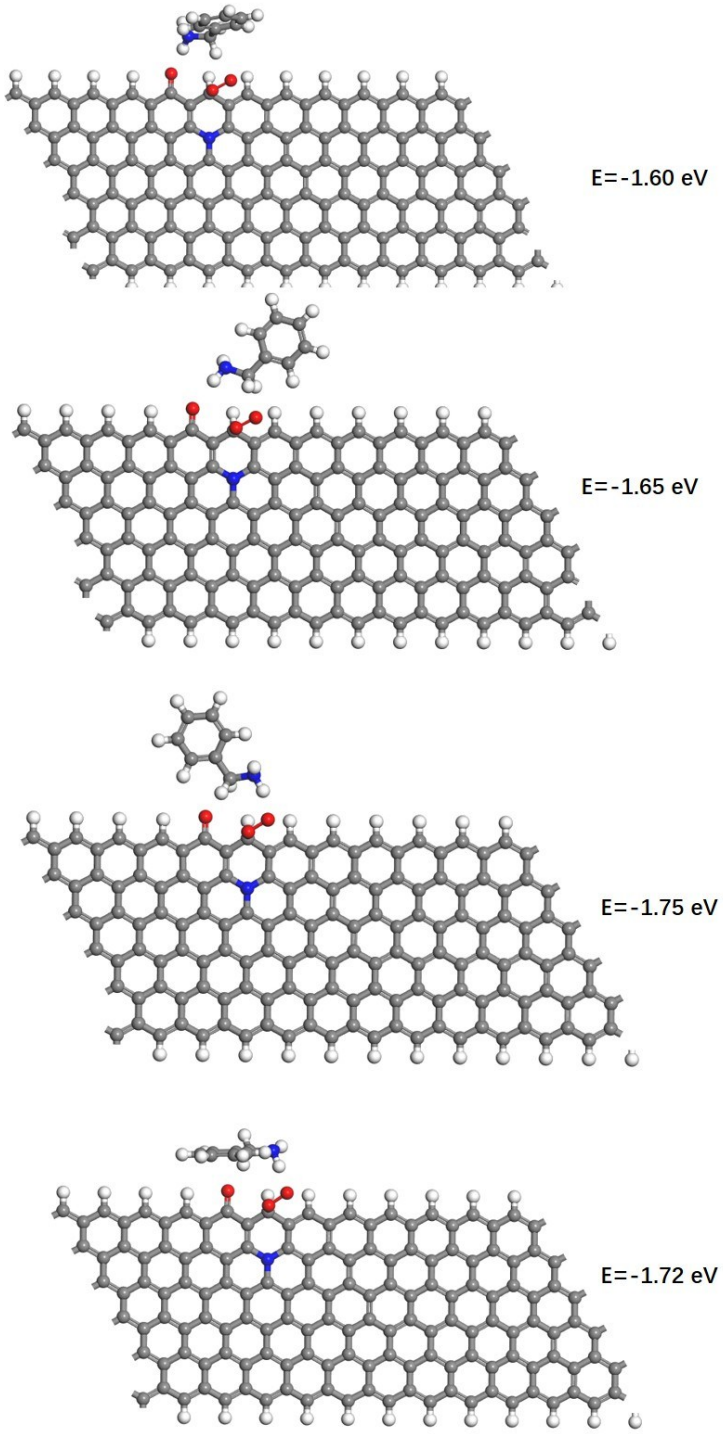

Fig. S9 The configurations and energy of benzylamine adsorbed on model catalyst anchoring oxygen molecule.

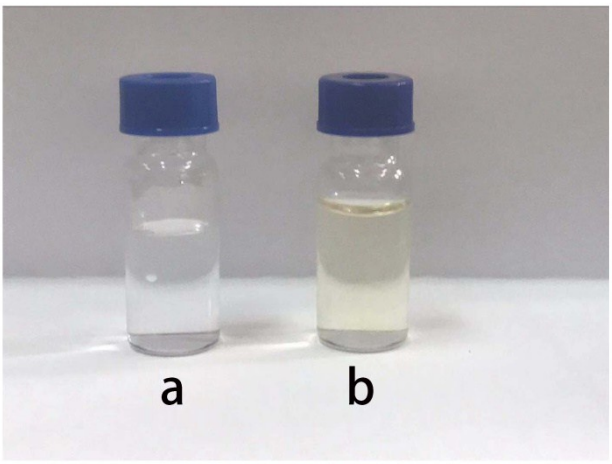

Fig. S10 a) The filtrate was obtained without NC(HAP) catalyst; b) The filtrate was obtained by hydroperoxide oxidized TMB.