Supporting Information

Conjugated Polymers with Defined Chemical Structure as Model Carbon Catalysts for Nitro Reduction**

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S.1. Sources and purification of the raw materials:

The raw materials and instruments used in the polymerization should be pretreated to remove water and impurities. 2,2'-bipyridine and 3,6-dibromo-phenanthrenequinone (DBPQ) were recrystallized from n-hexane and aceticanhydride respectively, followed by a vacuum drying at 40/50°C for 24h. 1,5-cyclooctadiene (COD), Anhydrous N,N-dimethyl formamide (DMF) and bis-(1,5-cyclooctadiene)-nickel(0) (Ni(COD)$_2$) (Alfa Aesar) were directly used without any pretreatment.

S.2. Preparation of YBN and YPQ:

For YBN, 1.980 g Ni(COD)$_2$ (7.2 mmol), 1.124 g 2,2'-bipyridine (7.2 mmol), 884 μL COD (7.2 mmol) and 45 mL anhydrous DMF were used. After that, 20 mL of anhydrous DMF solution containing 0.630 g TB (2 mmol) was dropwise added into the catalyst solution, and the mixture was stirred at 75 °C for 24 h to produce YBN. Moreover, 0.660 g Ni(COD)$_2$ (2.4 mmol), 0.376 g 2,2'-bipyridine (2.4 mmol), 334 μL COD (2.4 mmol) and 0.366 g DBPQ (1 mmol) were used to produce YPQ with the same strategies as YPB-x and YBN.

S.3. Calculation of the kinetic parameters:

The yield of YPB-6 (0.05 g), YPQ (0.07 g) and YBN (0.15 g) are 78.2 %, 34.3 % and 99 %, respectively. All the other YPB-x products share a >90% yield. The yields are all below 100 % because that some product was lost during the washing and filtrating process and low polymerization degree products dissolved in the solvent.

The yield of the polymerization reaction (Y) is determined by the following equation:

$$Y = \frac{P_{cp} \times W_p}{P_{cm} \times W_m} \times 100\% \qquad (1)$$

Where P_{cp} represents the carbon content (weight percent) in the polymer; W_p represents the weight of the obtained polymer (g); P_{cm} represents the carbon content (weight percent) in the monomer; W_m represents the weight of the monomer (g).

The theoretical oxygen content of the synthesized materials (C) is determined by the feeding ratio x (the molar ratio of TB and DBPQ), and which could be calculated as the following equation：

$$C = \frac{W_O}{x W_T + W_D} \times 100\% \qquad (2)$$

Where W_O represents the weight of oxygen in one unit (x TB and one DBPQ); $x W_T$ and W_D represent the total weight of the skeleton made up of TB and DBPQ with Br removed.

The active oxygen content of YPB-x which represents the oxygen content that could be possibly contacted by the reactant nitrobenzene (NB). Ketonic carbonyl groups exist at the opposite side of C-Br bonds (polymerization reactive sites), which results in a big enough space between C=O bonds and the polymer skeleton. It means that few oxygen atoms are in the bulk from the viewpoint of the chemical structure of the precursors. We make an assumption here that the ketonic carbonyl groups mainly locate at the porous region in the synthesized polymer. Thus the active oxygen content

could be calculated as the following equation：

$$O_{act.}\% = \frac{S_{eff.} \times N}{S_{total} \times N} \times 100\% = \frac{S_{eff.}}{S_{total}} \times 100\% \qquad (3)$$

$S_{eff.}$ means the surface area of the pores larger than 0.59 nm (the dynamic diameter of NB); $S_{total.}$ represents the BET surface area of the given polymer; N represents the surface concentration of oxygen atoms.

The amount of active oxygen involved in one reaction can be calculated as the following equation:

$$n_{act.0} = n_{ox} \times O_{act.}\% \qquad (4)$$

Where n_{ox} represents the amount of oxygen contained in the corresponding polymer and $O_{act.}\%$ represents the active oxygen content of YPB-x.

$$TOF = \frac{n_0 \cdot C\%}{n_{act.0} \cdot t} \qquad (5)$$

Where n_o represents the addition amount of nitrobenzene; t is the reaction time; $C\%$ is the conversion of nitrobenzene during the reaction time.

$$1 - X = 1 - \frac{C_0 - C}{C_0} = exp(-kt)$$

$$R = -\frac{dM_1}{dt}/m_{cat} = -\frac{d(C_0 V(1 - X_1))}{dt}/m_{cat} \qquad (6)$$

Where X represents the conversion of nitrobenzene; t is the reaction time; C_o is the initial concentration of nitrobenzene; C is the current concentration of nitrobenzene at t; R is the reaction rate at 15 % conversion, M_1 represents the residual amount of nitrobenzene; m_{cat} is the mass of catalyst; X_1 is the conversion at t (15 %).

S.4. Structure characterization:

The FT-IR spectra were recorded by KBr disc technique with a Nicolet iS10-iZ10 FT-IR spectroscopy (Thermo Fisher Scientific). Solid-state ^{13}C NMR experiments were carried out on a Varian Infinity plus-300 spectrometer at resonance frequencies of 75.38 MHz and recorded using a 4 mm double-resonance MAS probe at a spinning rate of 12 kHz. Pulse width (π/2) for ^{13}C was measured to be 4.1 μs. A contact time of 6 ms and a recycle delay of 3 s were used for the solid-state ^{13}C cross-polarisation magic-angle spinning nuclear magnetic resonance (CP/MAS) measurement. The chemical shift of ^{13}C was externally referenced to hexamethyl benzene. The scanning electron microscope (SEM) images and energy dispersive spectroscopy (EDS) were taken on a Nova Nano SEM 450 at an acceleration voltage of 10 kV with EDAX detector with Si slices settled on Al plates as sample carriers. The transmission electron microscopy (TEM) images were taken on a Tecnai G2 F20 (FEI) microscope with a 200 kV accelerating voltage. The specific surface area was measured by recording N_2 adsorption/desorption isotherms at 77 K and calculated by the BET method. The pore volume and pore distribution were calculated from the N_2 adsorption/desorption isotherms using NLDFT method with a N_2 @ 77model. The element analysis (EA) was tested on a Verio EL (Elementar) instrument using the CHN-patterns and O-patterns. The x-ray diffraction patterns (XRD) were collected by using a Rigaku X-ray diffractometer (D/MAX-2400) with a Cu Kα source at a scan rate of 2°/min. The thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449 F3 instrument under a mixture flow of argon (20 ml/min) and synthetic air (30 ml/min) with a heating rate of 10 K/min from 35 to 950 °C.

S.5. Performance of the model catalysts:

Ethanol was used as solvent for its good dissolvability of nitrobenzene and hydrazine hydrate and low toxicity which meets the requirement of green chemistry well. After reacted for 6h, the solution was diluted with methanol and deionized water (3:1) to 50

mL, and which was further analyzed and quantified by High Performance Liquid Chromatography (HPLC) (Elite, UV detector, mobile phase: 75/25 (v/v) methanol/water) with a SinoChrom ODS-BP column.
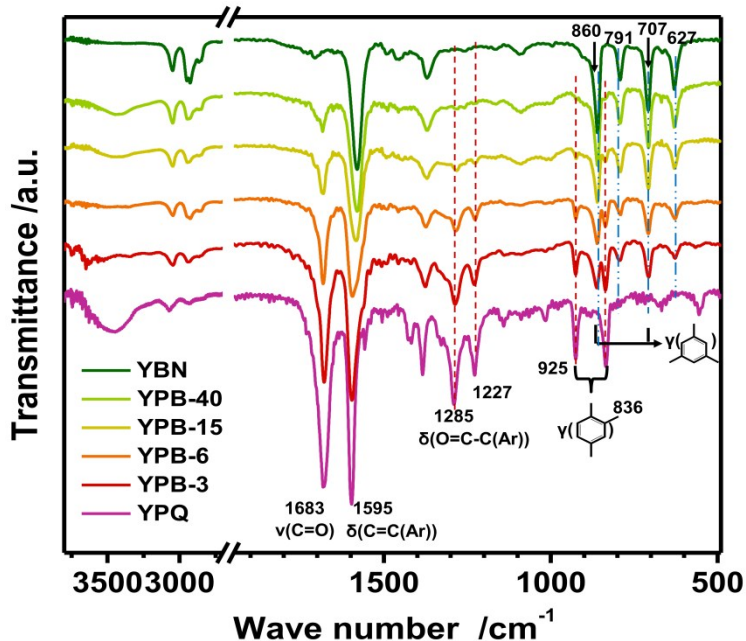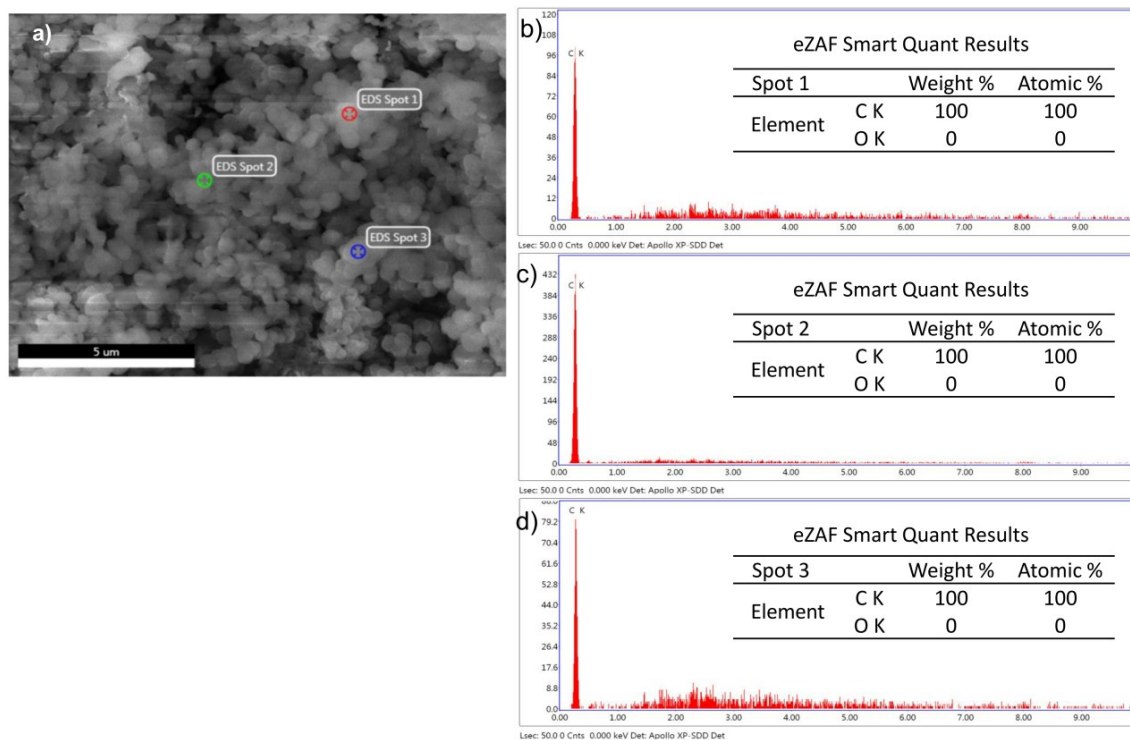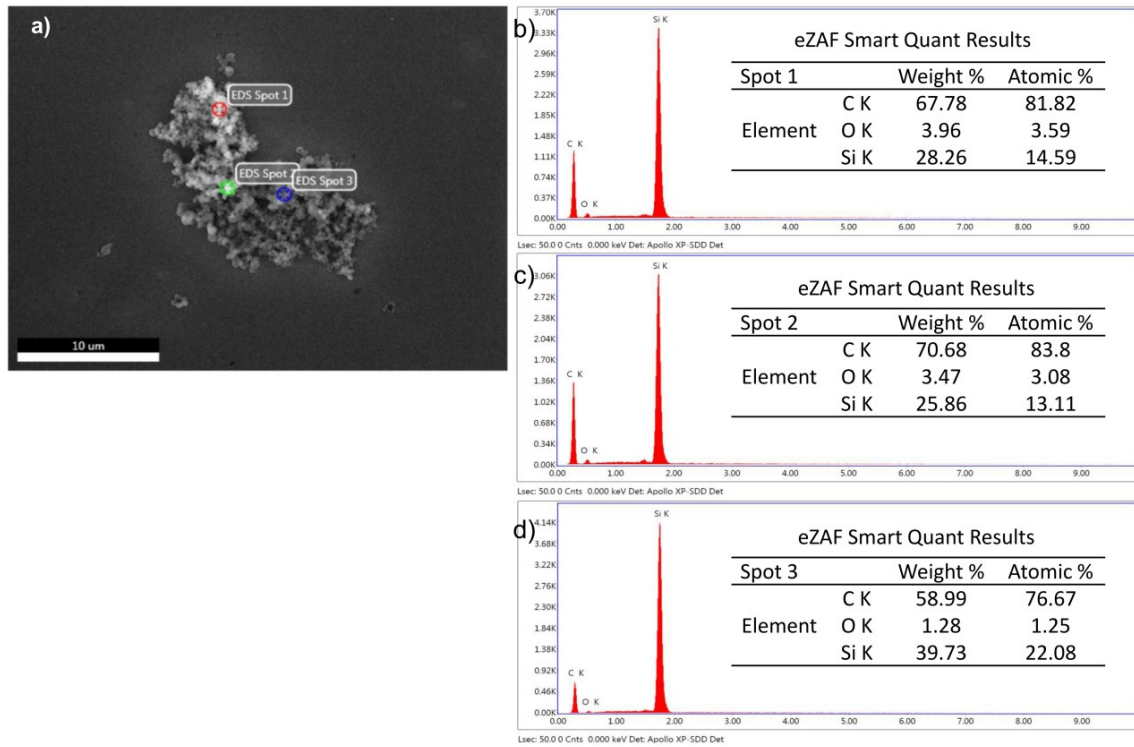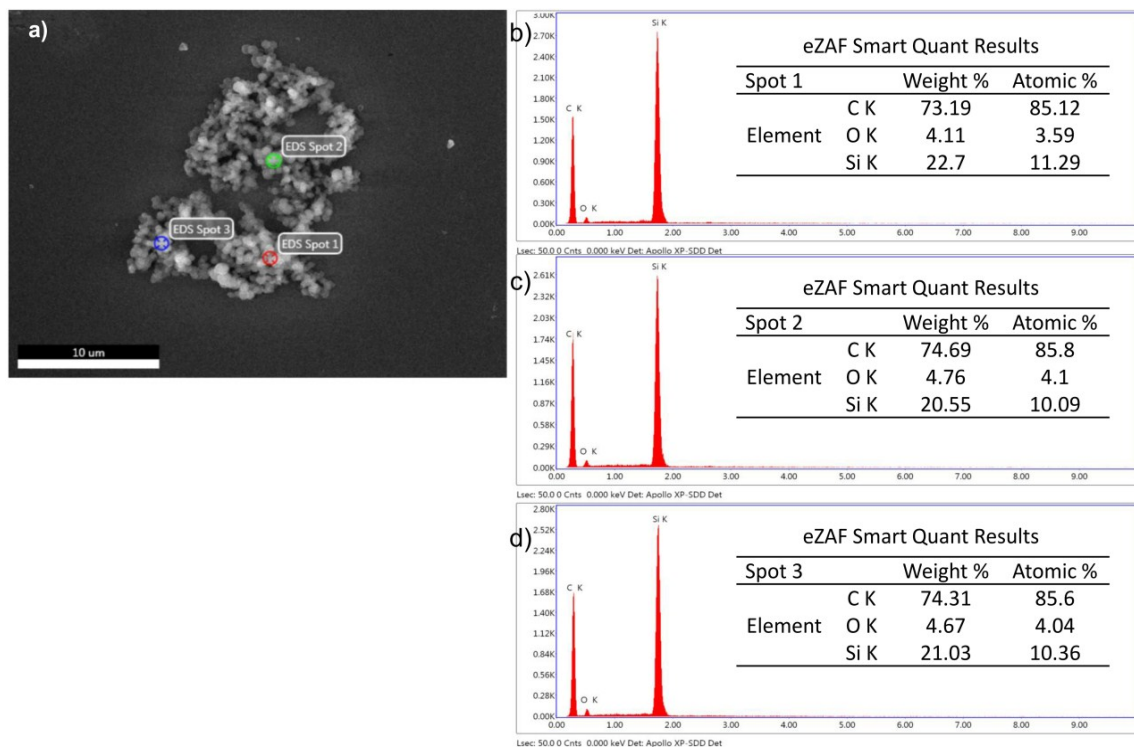

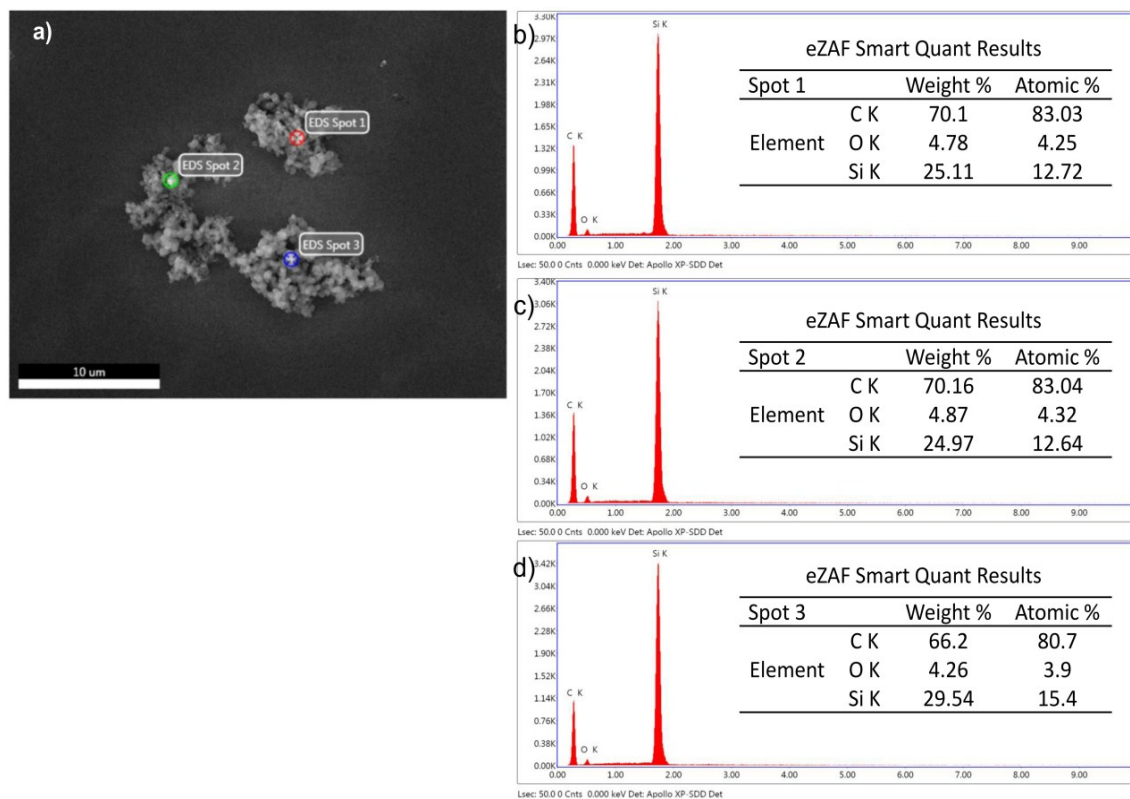**Figure S1.** FT-IR spectra of YPB-x (x=1.5, 3, 6, 15 and 40), YBN and YPQ.

Figure S2. a) SEM image of YBN, b-d) EDX spectra and element contents of YBN.

Spot 1		Weight %	Atomic %
	C K	67.78	81.82
Element	O K	3.96	3.59
	Si K	28.26	14.59

eZAF Smart Quant Results

Spot 2		Weight %	Atomic %
	C K	70.68	83.8
Element	O K	3.47	3.08
	Si K	25.86	13.11

eZAF Smart Quant Results

Spot 3		Weight %	Atomic %
	C K	58.99	76.67
Element	O K	1.28	1.25
	Si K	39.73	22.08

Figure S3. a) SEM image of YPB-40, b-d) EDX spectra and element contents of YPB-40.

eZAF Smart Quant Results

Spot 1		Weight %	Atomic %
	C K	73.19	85.12
Element	O K	4.11	3.59
	Si K	22.7	11.29

eZAF Smart Quant Results

Spot 2		Weight %	Atomic %
	C K	74.69	85.8
Element	O K	4.76	4.1
	Si K	20.55	10.09

eZAF Smart Quant Results

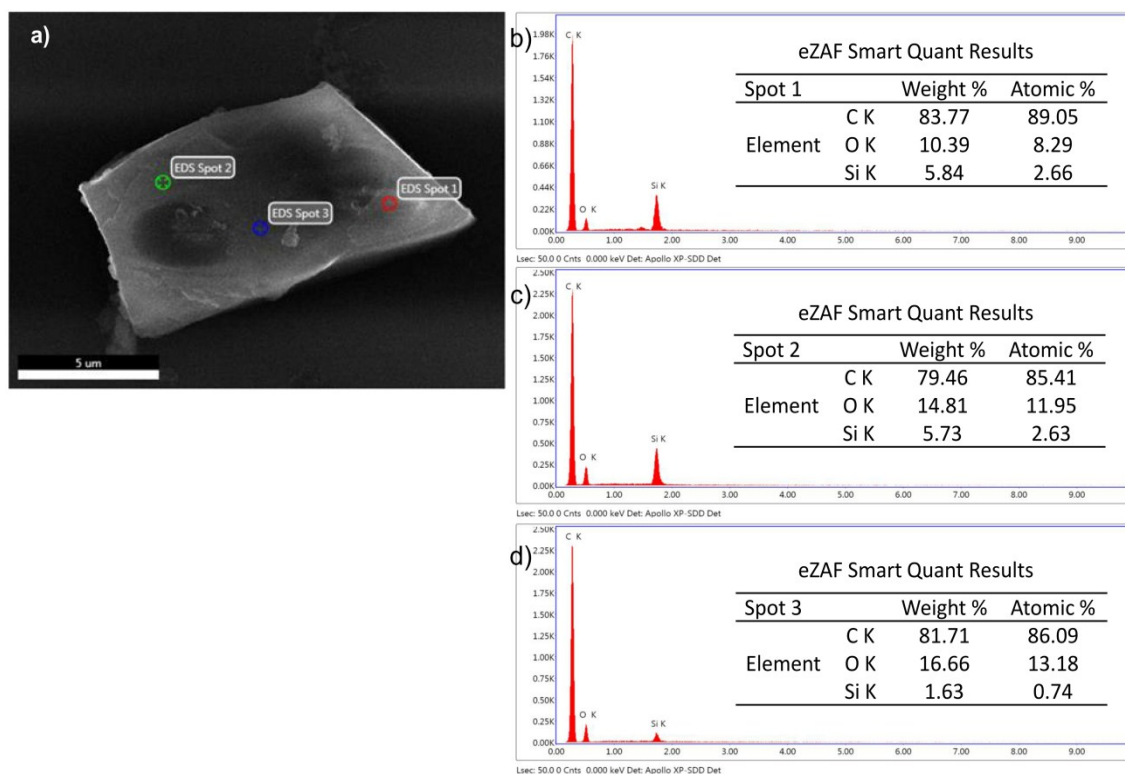| Spot 3		Weight %	Atomic %
	C K	74.31	85.6
Element	O K	4.67	4.04
	Si K	21.03	10.36

Figure S4. a) SEM image of YPB-15, b-d) EDX spectra and element contents of YPB-15.

eZAF Smart Quant Results			
Spot 1		Weight %	Atomic %
	C K	70.1	83.03
Element	O K	4.78	4.25
	Si K	25.11	12.72

eZAF Smart Quant Results			
Spot 2		Weight %	Atomic %
	C K	70.16	83.04
Element	O K	4.87	4.32
	Si K	24.97	12.64

eZAF Smart Quant Results			
Spot 3		Weight %	Atomic %
	C K	66.2	80.7
Element	O K	4.26	3.9
	Si K	29.54	15.4

Figure S5. a) SEM image of YPB-6, b-d) EDX spectra and element contents of YPB-6.
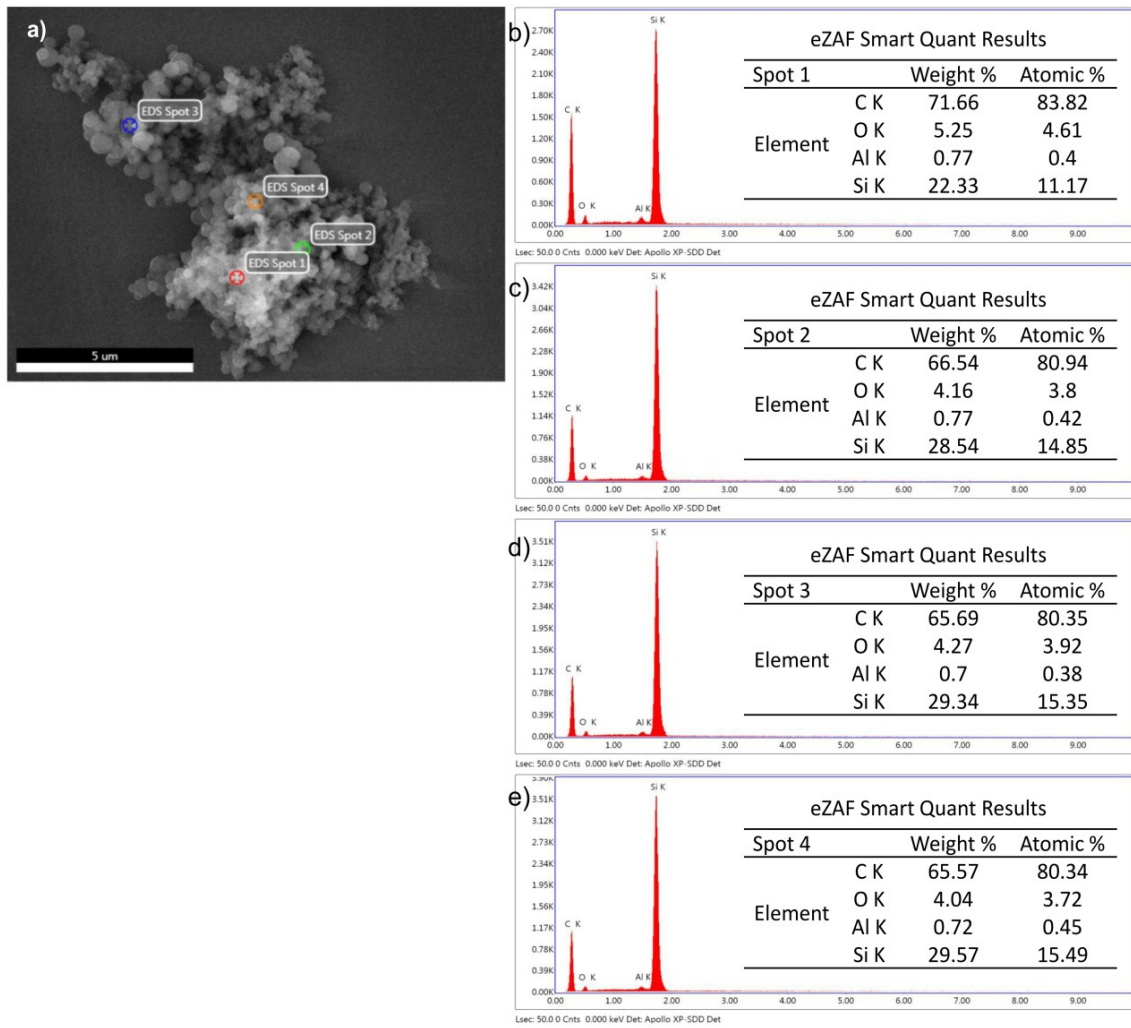
Figure S6. a) SEM image of YPB-3, b-d) EDX spectra and element contents of YPB-3.

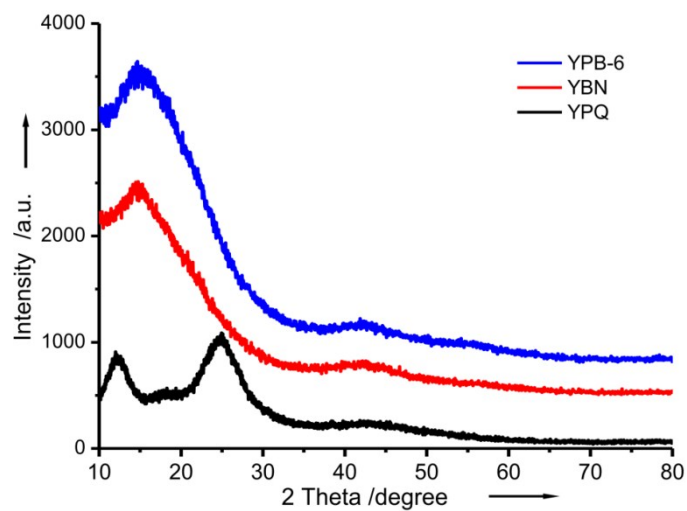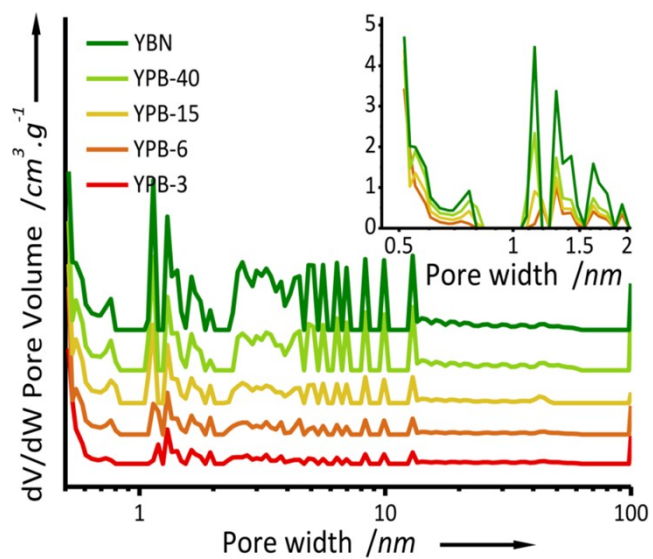**Figure S7.** a) SEM image of YPQ, b-d) EDX spectra and element contents of YPQ.

Spot 1		Weight %	Atomic %
	C K	83.77	89.05
Element	O K	10.39	8.29
	Si K	5.84	2.66

Spot 2		Weight %	Atomic %
	C K	79.46	85.41
Element	O K	14.81	11.95
	Si K	5.73	2.63

Spot 3		Weight %	Atomic %
	C K	81.71	86.09
Element	O K	16.66	13.18
	Si K	1.63	0.74

Figure S8. XRD patterns of YPB-6, YBN and YPQ.

Figure S9. Pore size distribution of YPB-x and YBN (the inset shows the pore size distribution from 0 to 2 nm).
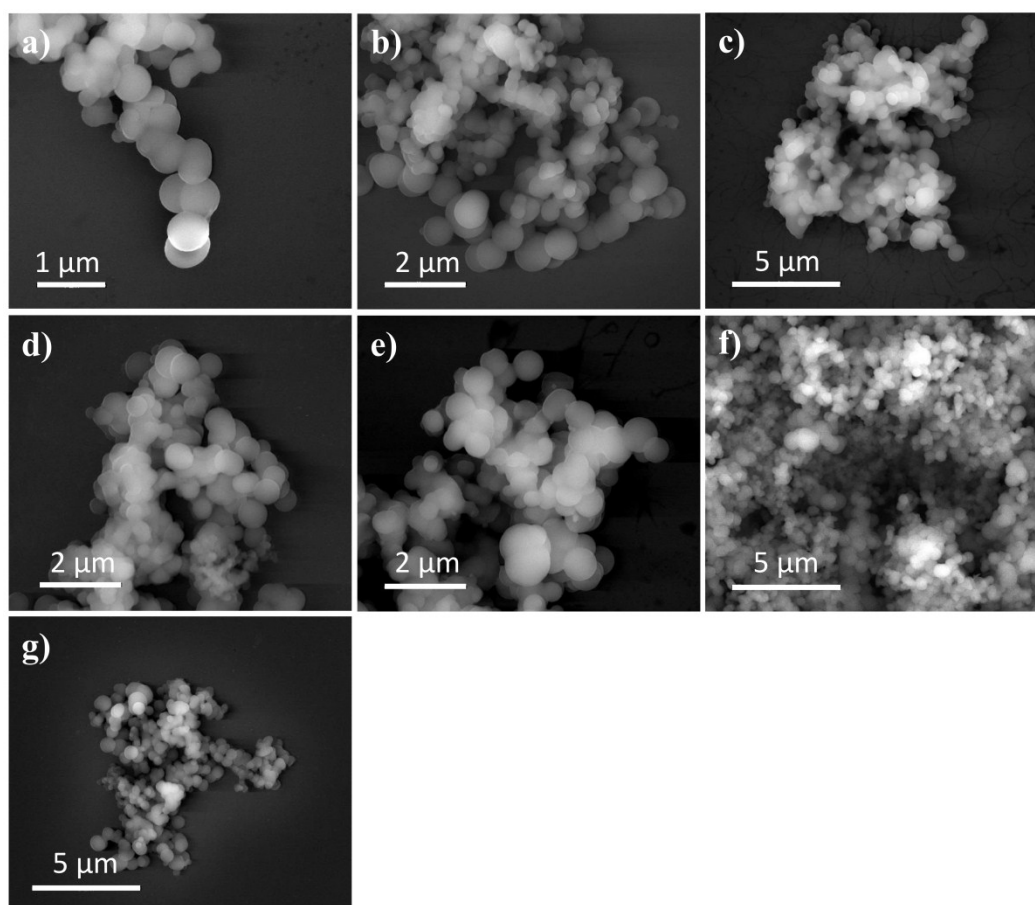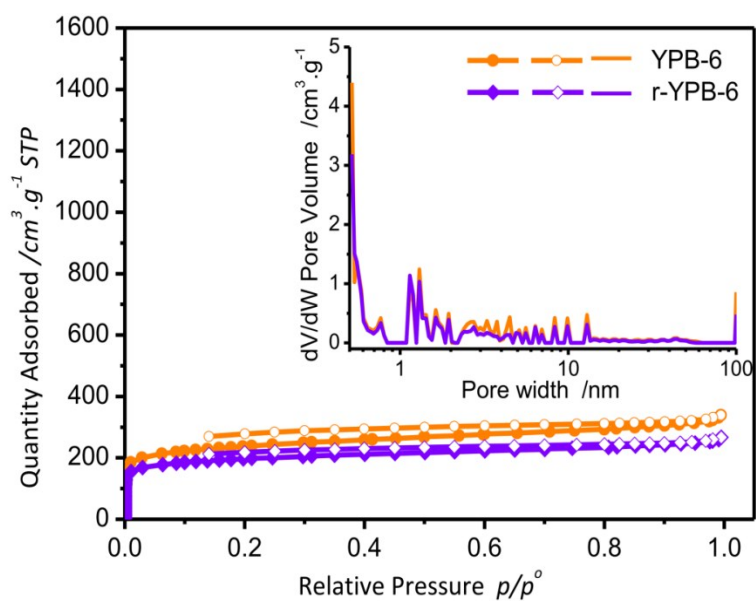

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e S10. SEM images of YPB-15 dispersed in different solvents: a) petroleum ether, b) methylbenzene, c) chloroform, d) DMF, e) chloroform and methanol (3:1), f) tetrahydrofuran, g) ethanol.
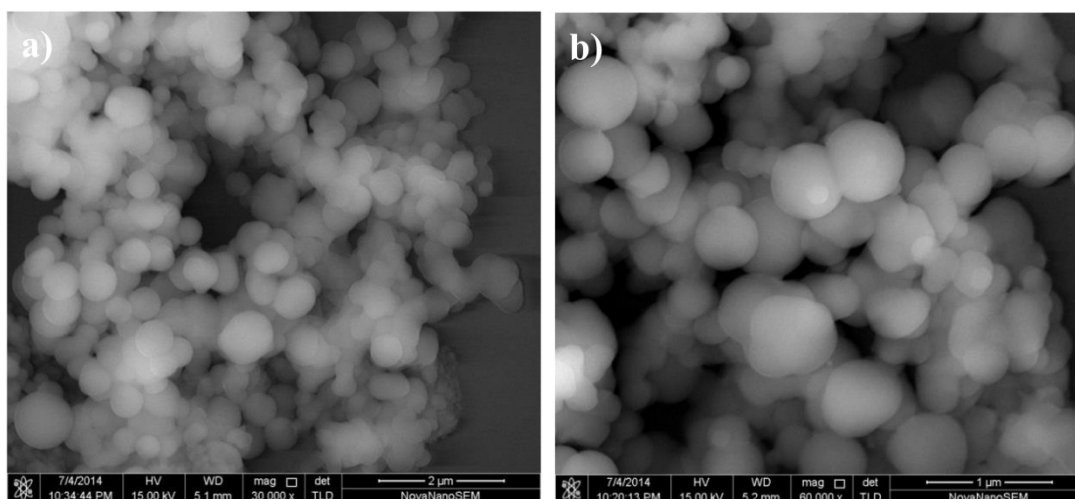
Figure S11. SEM images of a) YPB-15 and b) YPB-6 after the catalytic nitrobenzene reduction reactions, respectively.

Figure S12. Nitrogen adsorption/desorption isotherms of YPB-6 and r-YPB-6 (the inset shows the pore distribution of YPB-6 and r-YPB-6).
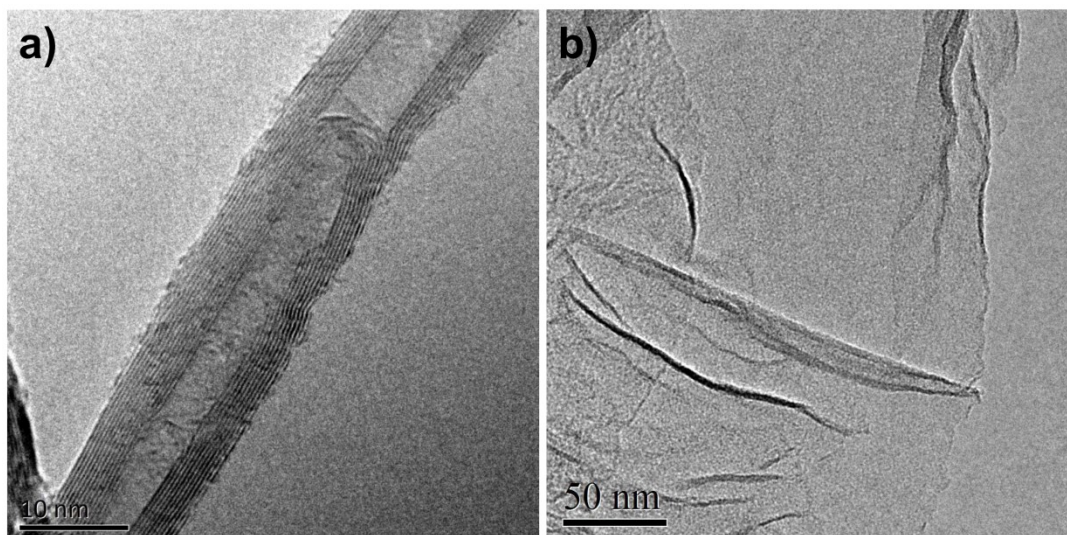
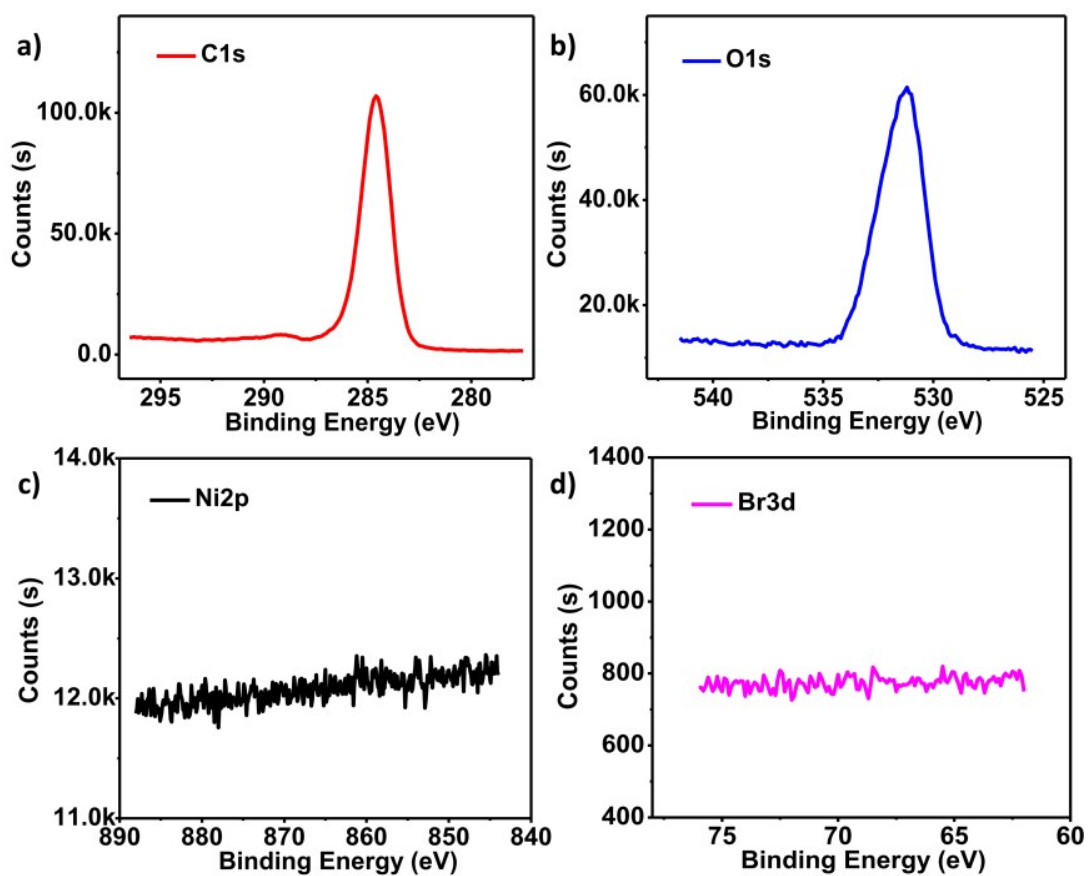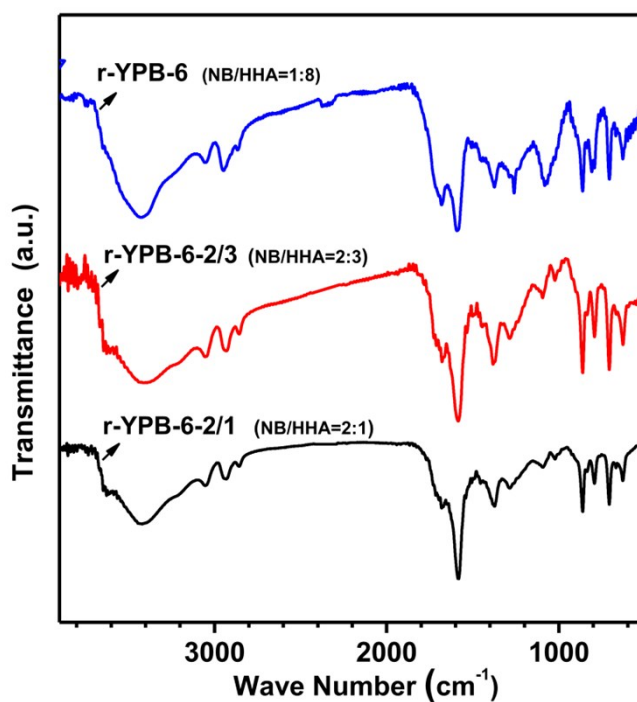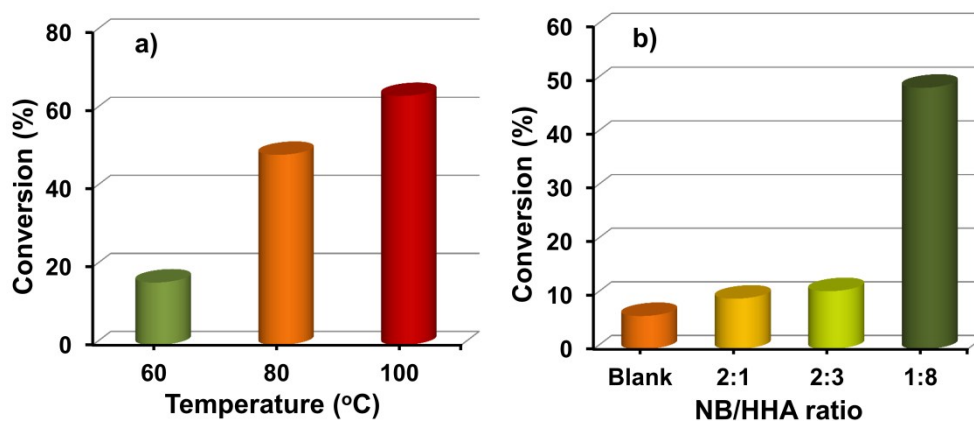**Figure S13.** TEM images of a) oCNT and b) graphene.

Figure S14. XPS spectra of YPB-6: a) C1s; b) O1s; c) Ni2p and d) Br3d.

Figure S15. FT-IR spectra of recovered YPB-6 after catalysing NB reduction with different NB/HHA ratio (80 °C, 6h): r-YPB-6: the molar ratio of NB and HHA was 1:8; r-YPB-6-2/3: the molar ratio of NB and HHA was 2:3; r-YPB-6-2/1: the molar ratio of NB and HHA was 2:1.

Figure S16. a) The influence of reaction temperature on the catalyst activity (NB conversion); b) The effect of NB/HHA ratio (2:1, 2:3 and 1:8) on the catalyst activity (NB conversion), (Blank means the reaction with NB/HHA ratio at 1:8 in the absence of catalyst).
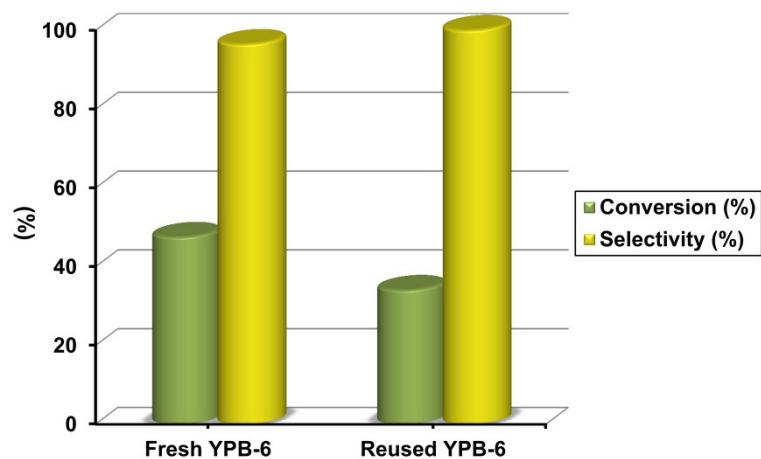
Figure S17. Reuse performance of YPB-6.

Table S1. Element analysis and EDS results of YPB catalysts and YPQ.

Catalyst	EA[a]				EDS[b]	
	C (wt.%)	O (wt.%)	H(wt.%)	N(wt.%)	C (wt.%)	O (wt.%)
YBN	91.04	1.66	5.07	1.07	99.57	0.43
YPB-40	90.09	2.62	4.97	0.93	96.76	3.24
YPB-15	88.66	3.89	4.88	0.86	94.56	5.44
YPB-6	87.32	6.31	4.72	0.82	93.87	6.13
YPB-3	84.67	9.54	4.47	0.50	93.17	6.83
YPQ	76.36	18.27	3.73	0.12	80.42	19.58

[a] Weight content from CHN/O elemental analysis. [b] Surface element contents of polymers from EDS (average values of more than 30 spots for every samples).