

*Supporting Information for*

# **Catalytically-Active Bimetallic Nanoparticles Supported on Porous Carbon Capsules Derived From Metal-Organic Framework Composites**

*Hui Yang<sup>a\*</sup>, Siobhan Bradley<sup>b</sup>, Andrew Chan<sup>c</sup>, Geoffrey I. N. Waterhouse<sup>c</sup>, Thomas Nann<sup>b</sup>, Paul E. Kruger<sup>d\*</sup>, and Shane G. Telfer<sup>a\*</sup>*

<sup>a</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, Institute of Fundamental Sciences, Massey University, Palmerston North 4442, New Zealand.  
*E-mail: s.telfer@massey.ac.nz*

<sup>b</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington 6140, New Zealand.

<sup>c</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical Sciences, The University of Auckland, Auckland 1142, New Zealand.

<sup>d</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Canterbury, Christchurch 8140, New Zealand.

## 1. Chemicals

Zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , AJAX Chemicals, >98%), cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich,  $\geq 98\%$ ), Nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich,  $\geq 98.5\%$ ), potassium hydroxide (KOH, Sigma-Aldrich, 90%), chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich,  $\geq 37.5\%$  Pt basis), platinum on carbon (Pt/C, Sigma-Aldrich, 10wt.% Pt basis) hexadecyltrimethylammonium bromide (CTAB, Sigma-Aldrich,  $\geq 99\%$ ), 2-methylimidazole (Sigma-Aldrich, 99%), tannic acid (TA, Sigma-Aldrich, ACS reagent), resorcinol (Sigma-Aldrich, 97%), formaldehyde (HCHO, BDH Chemicals, 37% in  $\text{H}_2\text{O}$ , contains 10-15% methanol as stabilizer), Methanol (MeOH, Merck, >99.9%), hexane (Merck,  $\geq 98\%$ ), 2-propanol (HiPerSolv, 99.8%), mesitylene (Merck, >98%), 1-chloro-2-nitrobenzene (Sigma-Aldrich,  $\geq 99\%$ ), 2-chloroaniline (Merck,  $\geq 98\%$ ), aniline (BDH Chemicals, >99%), nitrobenzene (BDH Chemicals,  $\geq 99\%$ ), 4-nitrophenol (Sigma-Aldrich,  $\geq 99\%$ ), 4-aminophenol (Sigma-Aldrich,  $\geq 99\%$ ), 4-nitroacetophenone (Sigma-Aldrich, 98%), 4-aminoacetophenone (Sigma-Aldrich, 99%), 4-nitroanisole (Sigma-Aldrich, 97%), 4-anisidine (Sigma-Aldrich,  $\geq 99\%$ ), 4-nitrotoluene (Sigma-Aldrich, 99%) and 4-toluidine (Riedel-de Haen, 99%) were obtained from commercial sources and used without further purification.

## 2. Instrumentation

Powder X-ray diffraction (PXRD) was performed on a Rigaku X-ray diffractometer with Cu  $\text{K}\alpha$  source. Thermogravimetric analyses (TGA) were performed on a TA Instruments Q50 instrument. Measurements were made under an Ar flow with a heating rate of 3  $^\circ\text{C}/\text{min}$ . BET surface areas were determined from  $\text{N}_2$  adsorption/desorption isotherms at 77 K using automatic volumetric adsorption equipment (Quantachrome, Autosorb iQ2) after pretreatment under vacuum at 100  $^\circ\text{C}$  for 5 h. Scanning Electron Microscope (SEM) images and energy dispersive spectra (EDS) were recorded on a FEI Quanta 200 Environmental Scanning Electron Microscope with an EDS module. Transmission Electron Microscope (TEM) images were recorded on FEI Tecnai G<sup>2</sup> Biotwin Transmission Electron Microscope with operating voltage at 100 kV. Scanning Transmission Electron Microscopy (STEM) and High Resolution Transmission Electron Microscope (HRTEM) analysis were carried out with JEOL JEM-2010 Transmission Electron Microscope with operating voltage at 200 kV. Atomic Absorption Spectroscopy (AA) was conducted on a GBC Xplora AAS spectrometer system. Raman spectra were measured from powder samples with a Cobalt Samba single-mode 532 nm diode laser on quartz substrates. X-Ray Photoelectron Spectroscopy (XPS) analyses were performed using Kratos Axis DLD equipment. Fourier transform infrared spectra (FTIR) were recorded on a ThermoElectron Nicolet high-resolution FT-MIR/FT-FarIR. The hydrogenation products were analysed by high performance liquid chromatography (HPLC, Thermo scientific ultimate 3000) and

NMR (Bruker Avance spectrometers, 500 MHz). Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

### **3. Synthetic procedures**

#### **Synthesis of polyhedral ZIF-8 nanocrystals**

ZIF-8 polyhedra were prepared using a reported procedure with a slight modification.<sup>1</sup> In a typical synthesis, 4 g of 2-methylimidazole was dissolved in 60 mL of methanol (MeOH) to form a clear solution. 1.68 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 20 mL MeOH was added into above solution followed by vigorous stirring for 1 h. The mixture was then incubated at room temperature without stirring. After 24 h, the product was isolated as a white powder by centrifugation and washed several times with deionized water and MeOH, and finally dried overnight under vacuum (yield = 1.06 g).

#### **Synthesis of polyhedral bimetallic ZIF-8CoZn (5% Co) nanocrystals**

ZIF-8 CoZn (5% Co) polyhedra were prepared using a reported procedure with a slight modification.<sup>2</sup> In a typical synthesis, 4 g of 2-methylimidazole was dissolved in 60 mL of MeOH to form a clear solution. 1.6 g of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.08 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 20 mL MeOH was added into above solution with vigorous stirring for 1 h. The mixture was then incubated at room temperature without stirring. After 24 h, the product was isolated as a light purple powder by centrifugation and washed several times with deionized water and MeOH, and finally dried overnight under vacuum (yield = 1.02 g).

#### **Synthesis of polyhedral ZIF-67 nanocrystals**

ZIF-67 polyhedra were prepared using a reported procedure with a slight modification.<sup>3</sup> In a typical synthesis, 0.87 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1 g of 2-methylimidazole were dissolved separately in 30 mL of methanol solution. After mixing the above two solutions at room temperature for 24 h, the resulting purple powder was collected by centrifugation, washed with methanol several times and finally dried under vacuum (yield = 0.62 g).

#### **Synthesis of 2.8 nm PVP-stabilized Pt nanoparticles**

2.8 nm PVP-stabilized Pt nanoparticles (PtNPs) were synthesized using a reported procedure with a slight modification.<sup>4</sup> A mixture of PVP (533 mg,  $M_w = 40,000$ ), MeOH (180 mL), and aqueous solution of  $\text{H}_2\text{PtCl}_6$  (6.0 mM, 20 mL) were placed in a flask (500 mL) and refluxed for 3 hours under air. Finally, methanol was removed under reduced pressure. The resulting aqueous dispersion of Pt nanoparticles was stored for further use.

### Synthesis of the ZIF/Pt composites

0.2 g of ZIF-8 polyhedra were dispersed in 80 mL of MeOH by sonication for 30 min and stirred at room temperature for 1 h. Subsequently, a 1.2 mL aliquot of the above solution of PtNPs was added with vigorous stirring for 4 h. The mixture was then incubated at room temperature without stirring. After 24 h, the product was isolated as a light grey powder by centrifugation and washed several times with deionized water and MeOH, and finally dried overnight under vacuum. ZIF-8CoZn/Pt and ZIF-67/Pt composites were synthesized using a similar synthetic route, only changing the polyhedra ZIF-8 to ZIF-8CoZn or ZIF-67 polyhedra.

### Synthesis of K-TA

In a typical synthesis, a freshly prepared tannic acid (24 mM, 10 mL) solution was adjusted to pH=8 by aqueous KOH solution (6 M). After stirring for 5 min, the product was collected by centrifugation, washed several times with de-ionized water and MeOH, and dried overnight under vacuum.

### Synthesis of hollow RF

ZIF-8@RF was (10 mg) dispersed in DI water (10 mL) then 0.05 mL HCl (5%) was dropped in. After several minutes, the product was obtained.

### Synthesis of 4-nitrobenzyl alcohol and 1-(4-nitrophenyl)ethanol

4-Nitrobenzyl alcohol was synthesized using a reported procedure<sup>5</sup> with a slight modification. 4-Nitrobenzaldehyde (5.00 g) was diluted in absolute ethanol (30 mL), then a suspension of NaBH<sub>4</sub> (1 g) in 10 mL of absolute ethanol was added. The reaction mixture was allowed to stir for 1 h at 0 °C. Then the reaction mixture was quenched with aq. NaOH (2M) and stirred until the solution was homogeneous. Water was added and the ethanol was removed under reduced pressure. The aqueous mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x) and the combined organic extracts were washed with NaHCO<sub>3</sub> (saturated solution), then water. The solution was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuum (yield= 4.9 g). <sup>1</sup>H NMR: (500 MHz, DMSO): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 5.52 (s, 1H), 4.64 (d, *J* = 3.8 Hz, 2H) ppm.

1-(4-Nitrophenyl)ethanol was synthesized using a similar synthetic route, only changing the 4-nitrobenzaldehyde to 4-nitroacetophenone. <sup>1</sup>H NMR: (500 MHz, CDCl<sub>3</sub>): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 5.02 (q, *J* = 6.5 Hz, 1H), 2.02 (s, 1H), 1.52 (d, *J* = 6.5 Hz, 3H) ppm.



### Synthesis of 4-aminobenzyl alcohol and 1-(4-aminophenyl)ethanol

In a typical synthesis, 2 g of 4-nitrobenzyl alcohol and 0.2 g of Pt/C (10% Pt) were dissolved in 20 mL of MeOH in a glass reactor, then the glass reactor was evacuated and charged with 50 psi H<sub>2</sub>, then stirred at room temperature for 24 h. The product was filtered and concentrated *in vacuo* (yield= 1.5 g). <sup>1</sup>H NMR: (500 MHz, DMSO):  $\delta$  6.95 (d, *J* = 8.3 Hz, 2H), 6.50 (d, *J* = 8.3 Hz, 2H), 4.91 (s, 2H), 4.76 (t, *J* = 5.4 Hz, 1H), 4.28 (d, *J* = 4.8 Hz, 2H) ppm.

1-(4-aminophenyl)ethanol was synthesized using a similar synthetic route, only changing the 4-nitrobenzyl alcohol to 1-(4-nitrophenyl)ethanol. <sup>1</sup>H NMR: (500 MHz, DMSO):  $\delta$  6.97 (d, *J* = 8.3 Hz, 2H), 6.49 (d, *J* = 8.3 Hz, 2H), 4.86 (s, 2H), 4.76 (d, *J* = 4.1 Hz, 1H), 4.57–4.49 (m, 1H), 1.25 (d, *J* = 6.4 Hz, 3H) ppm.

### Atomic Absorption Spectroscopy (AA) measurements

The weight percentage (wt%) of Pt, Co and Ni in the NHPC-supported nanoparticle composites was determined by atomic absorption spectroscopy (AA). To prepare samples, 80 mg of M@NHPC was dissolved in aqua regia (10 mL) at 80 °C for 24 h in a high pressure reaction vessel. After cooling, the solution was filtered through a 0.2  $\mu$ m syringe filter to remove carbon particulates then diluted by 2 M HNO<sub>3</sub> (10 mL) for measurements.

**Table S1.** Summary of the surface areas and pore volume (0.95 bar) calculated using the BET and Horvath–Kawazoe equation methods from N<sub>2</sub> adsorption isotherms at 77 K for the ZIF-8-based composite materials.

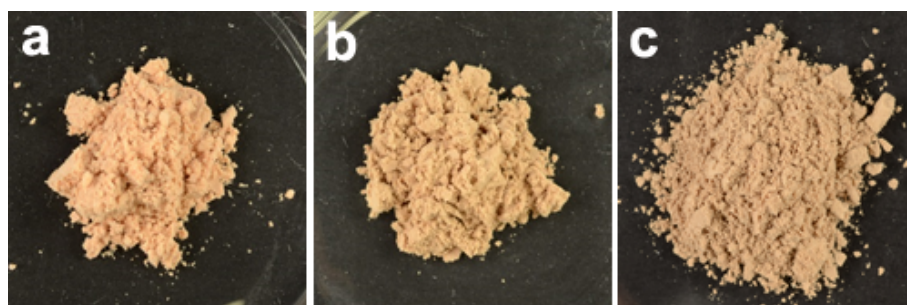
Sample	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )
ZIF-8	1710	0.70
ZIF-8@K-TA	1060	0.56
ZIF-8@Co-TA	850	0.46
ZIF-8@Ni-TA	880	0.51
ZIF-8/Pt@K-TA	610	0.35
ZIF-8/Pt@Co-TA	490	0.28
ZIF-8/Pt@Ni-TA	430	0.24
ZIF-8@RF	1240	0.65
ZIF-8/Pt@RF	650	0.57

## 4. Materials characterization

### 4.1 Photographs

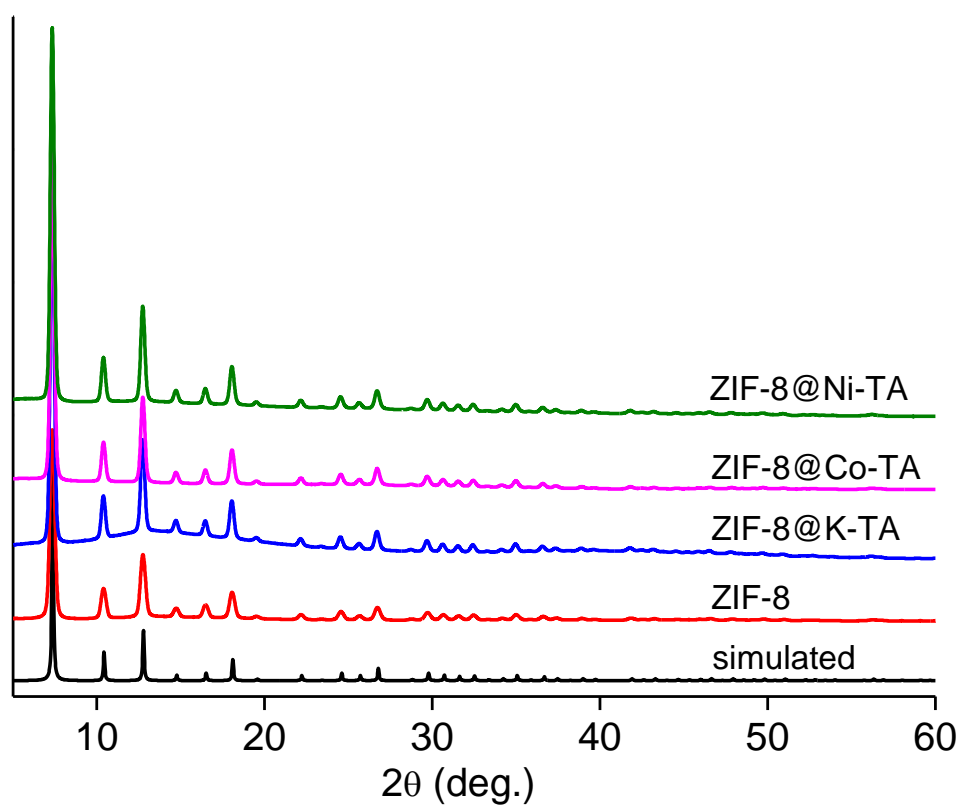


**Figure S1.** Photographs of (a) ZIF-8; (b) ZIF-8@K-TA; (c) ZIF-8@Co-TA; (d) ZIF-8@Ni-TA; (e) ZIF-8/Pt; (f) ZIF-8/Pt@K-TA; (g) ZIF-8/Pt@Co-TA; (h) ZIF-8/Pt@Ni-TA.

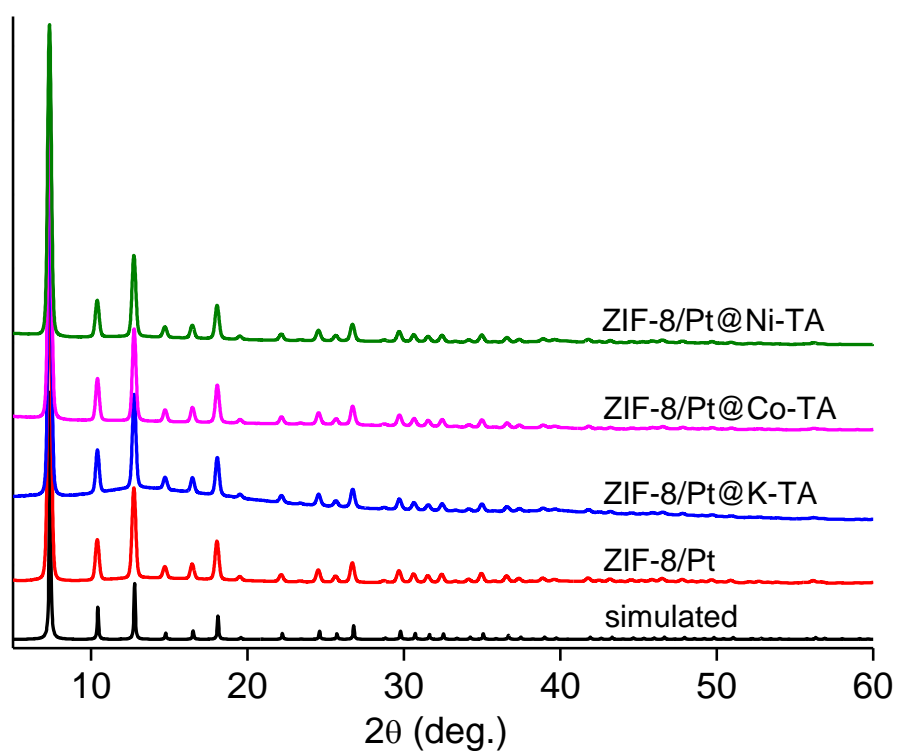


**Figure S2.** Photographs of (a) ZIF-8@RF; (b) ZIF-8/Pt@RF; (c) ZIF-8/Pt@CoRF\_a.

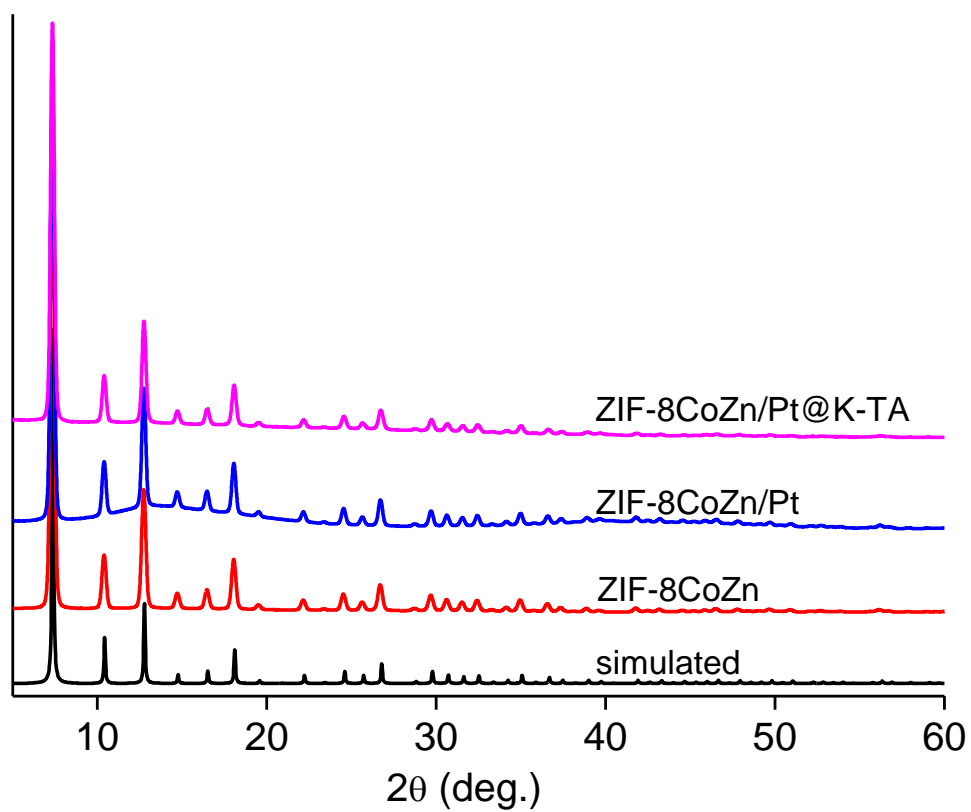
## 4.2 Powder X-ray Diffraction (PXRD)



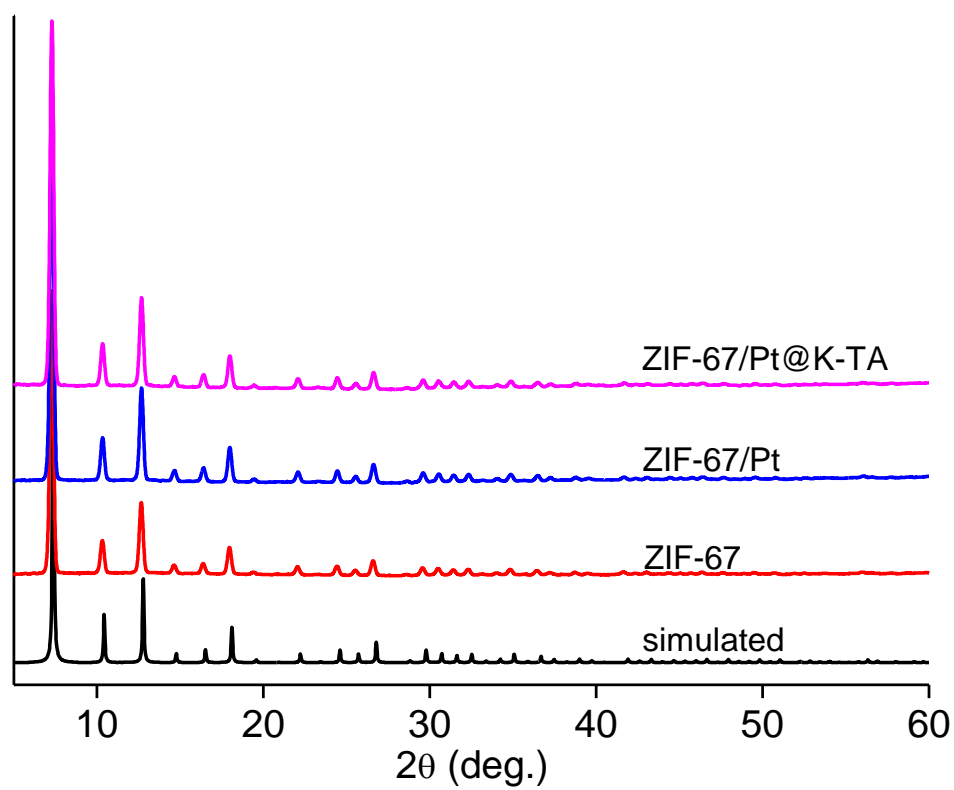
**Figure S3.** PXRD patterns of as synthesized materials.



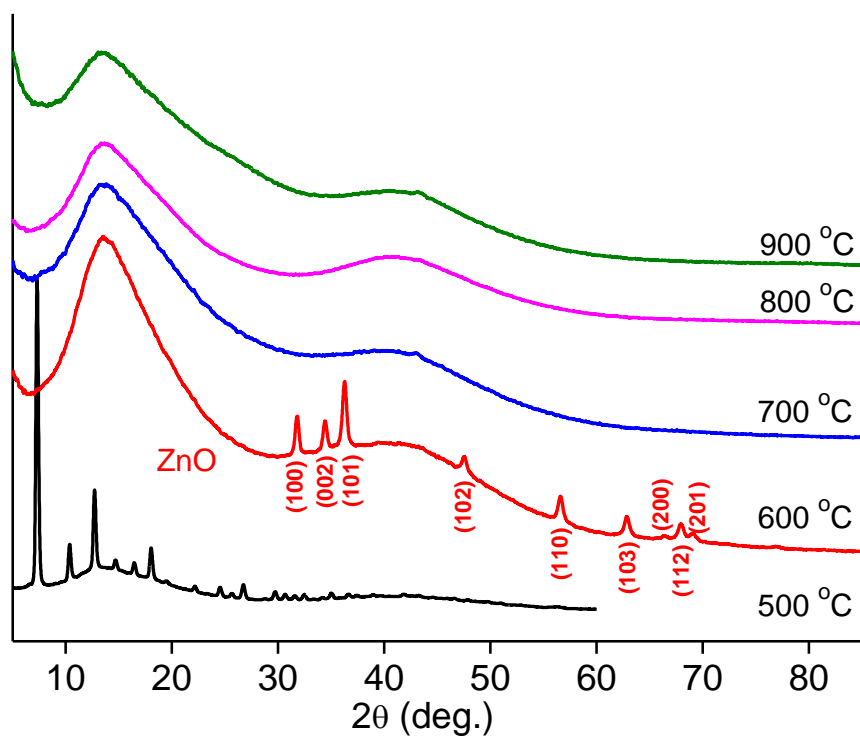
**Figure S4.** PXRD patterns of as synthesized materials.



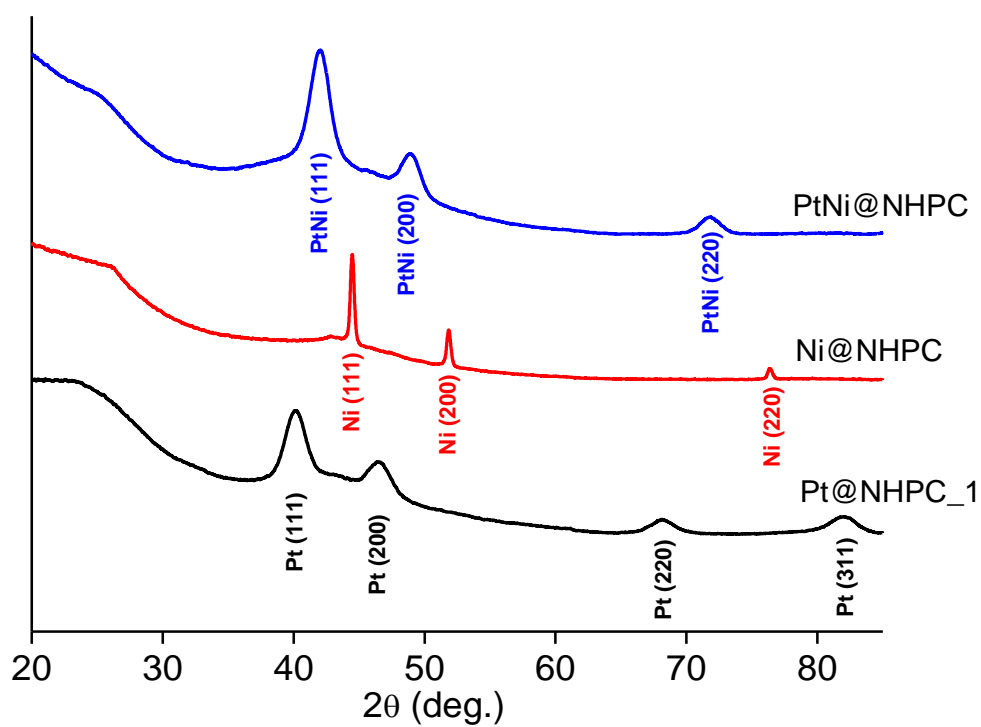
**Figure S5.** PXRD patterns of as synthesized materials. The simulated pattern refers to that calculated from the SCXRD structure of ZIF-8.



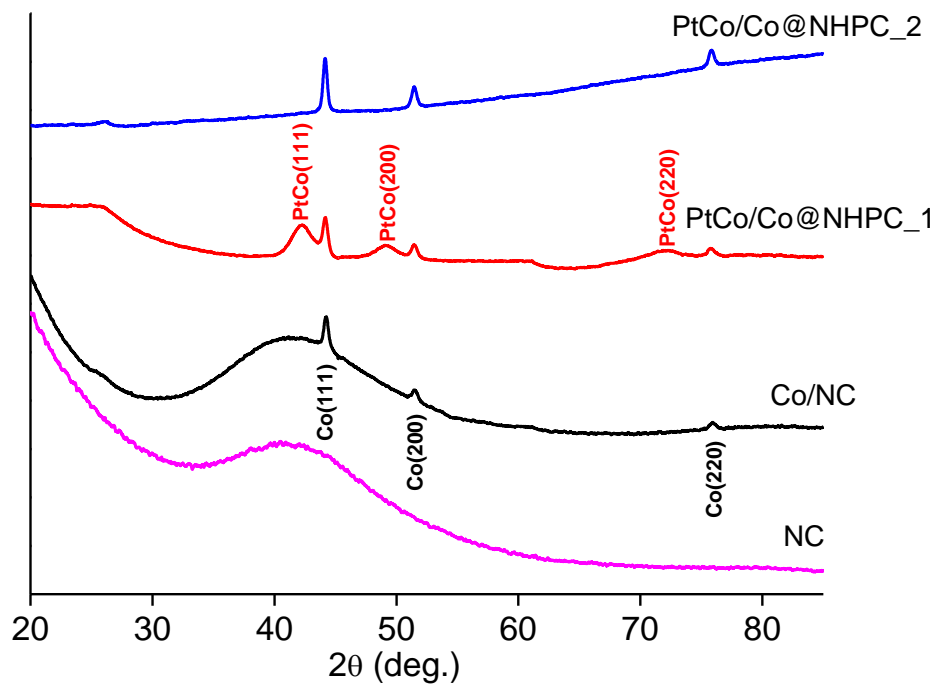
**Figure S6.** PXRD patterns of as synthesized materials.



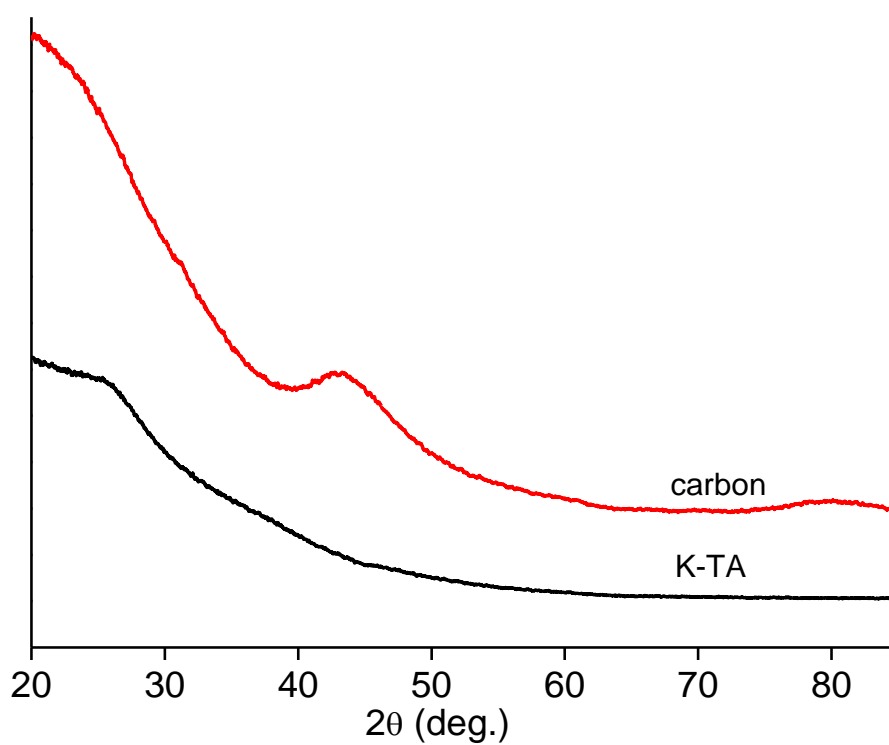
**Figure S7.** PXRD patterns of ZIF-8@K-TA calcined at different temperatures.



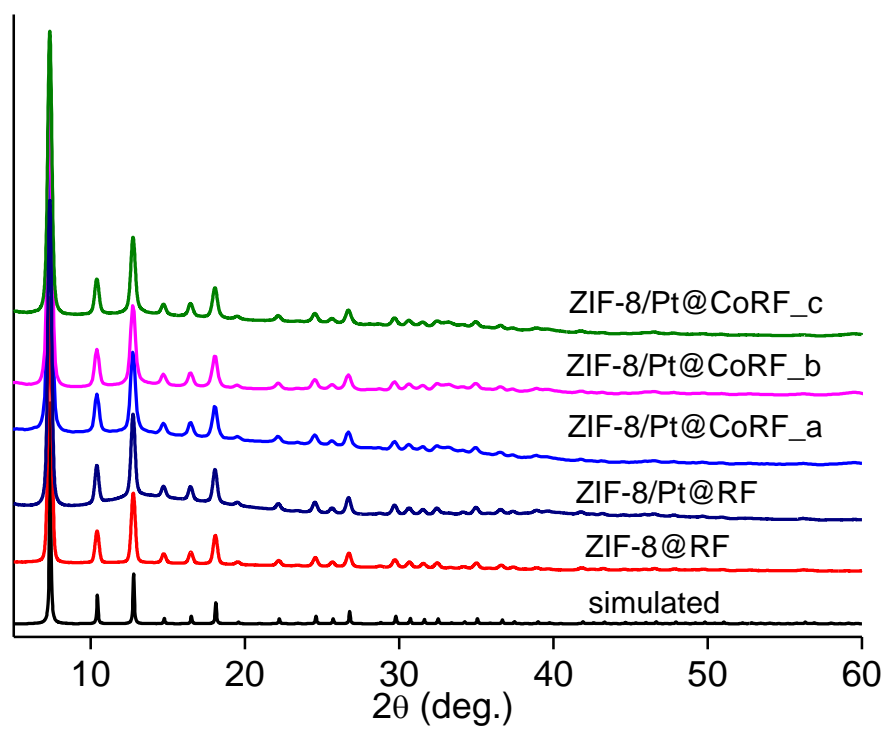
**Figure S8.** PXRD patterns of as synthesized materials.



**Figure S9.** PXRD patterns of as synthesized materials.



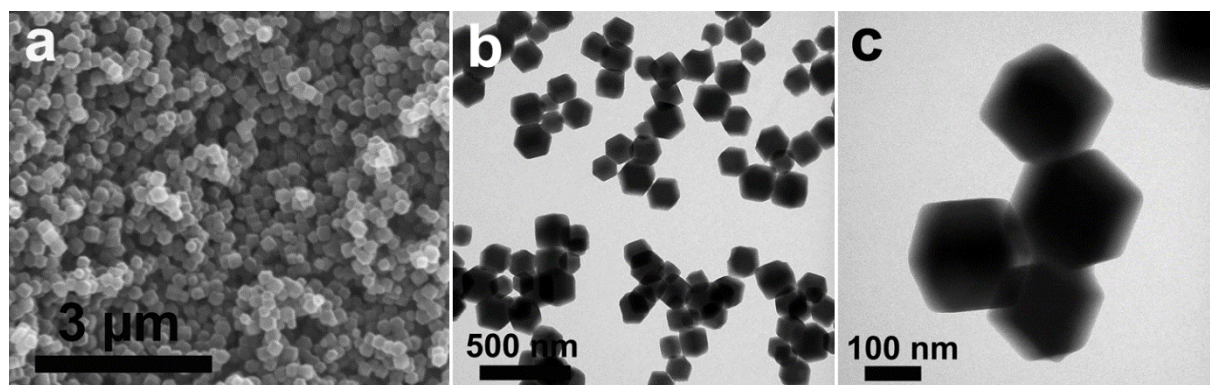
**Figure S10.** PXRD patterns of as synthesized potassium-tannic acid (K-TA) and potassium-tannic acid derived carbon.



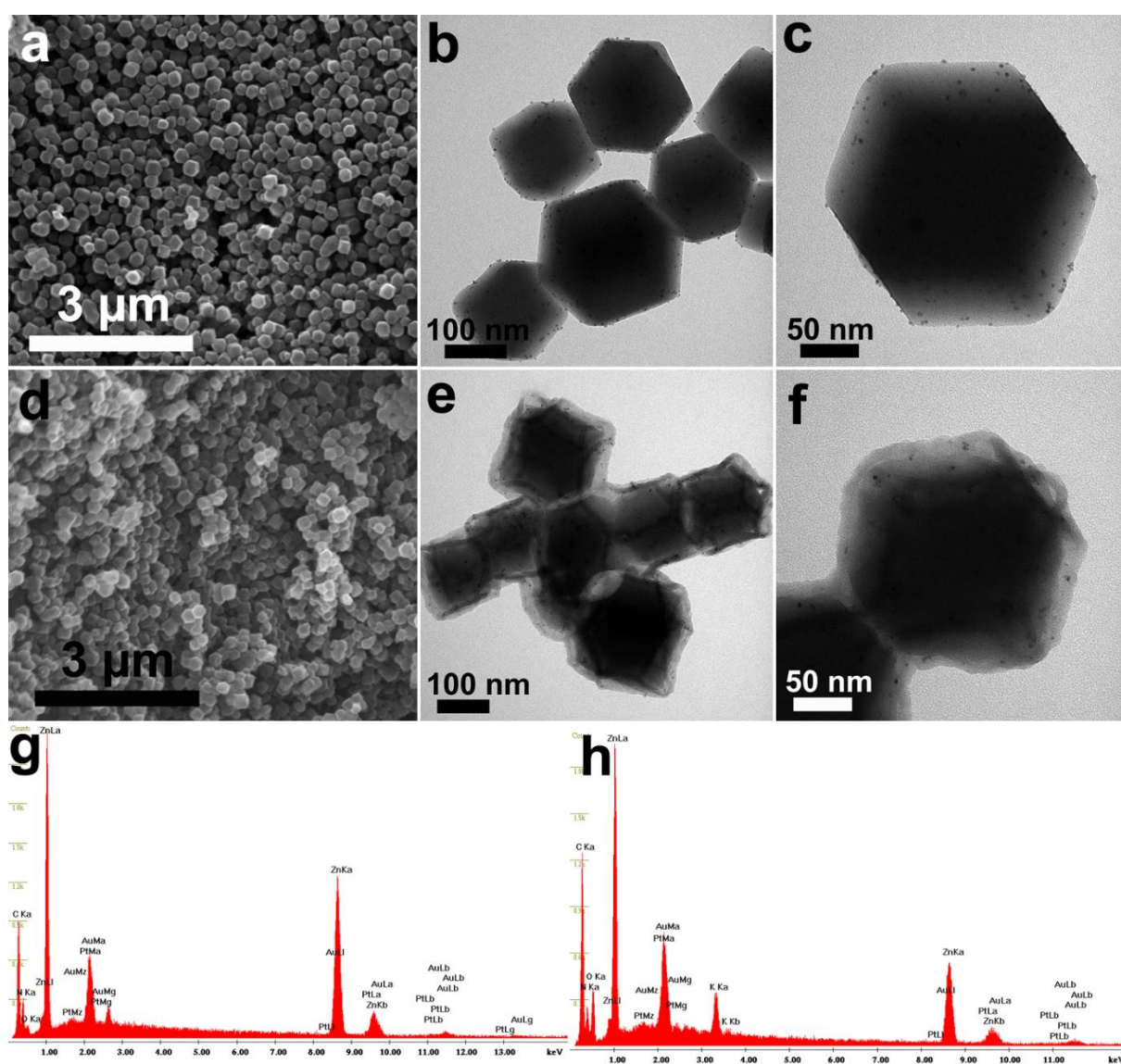
**Figure S11.** PXRD patterns of as synthesized materials.



#### 4.3 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

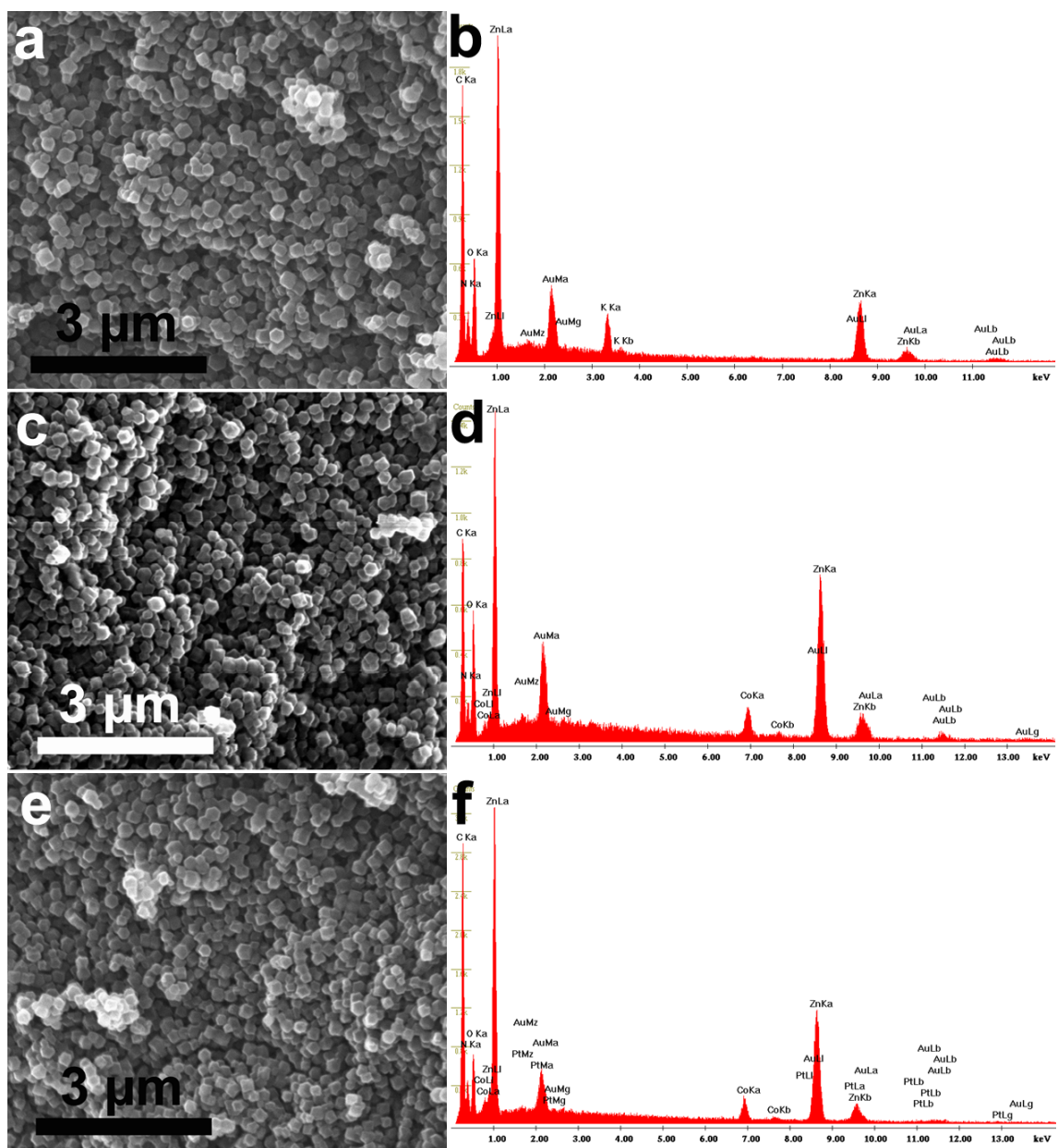


**Figure S12.** SEM image (a) and TEM images (b, c) of polyhedral ZIF-8 nanocrystals.

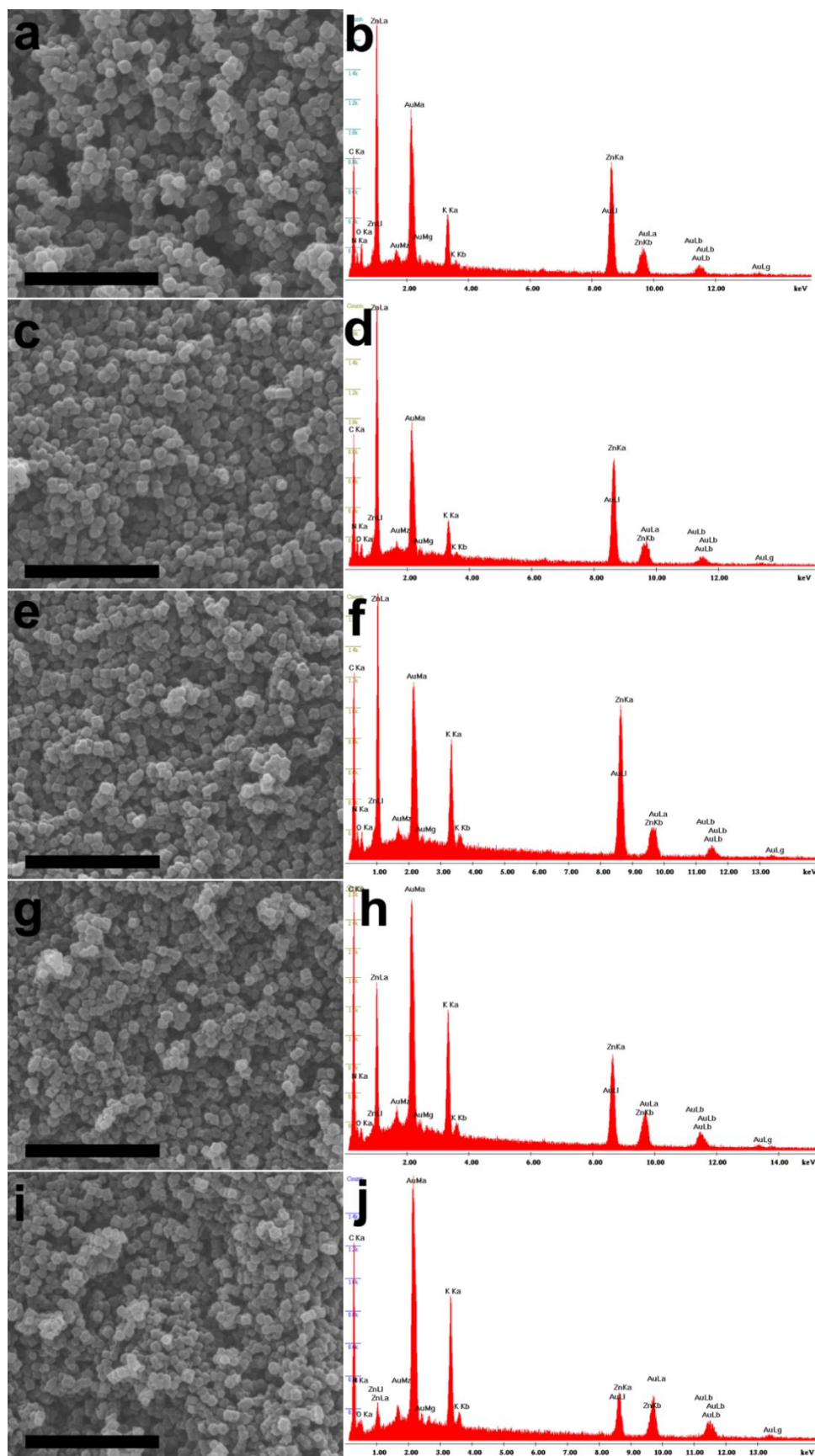


**Figure S13.** SEM, TEM images and EDS spectra of polyhedral ZIF-8/Pt (a, b, c, g) and ZIF-8/Pt@K-TA nanocrystals (d, e, f, h).

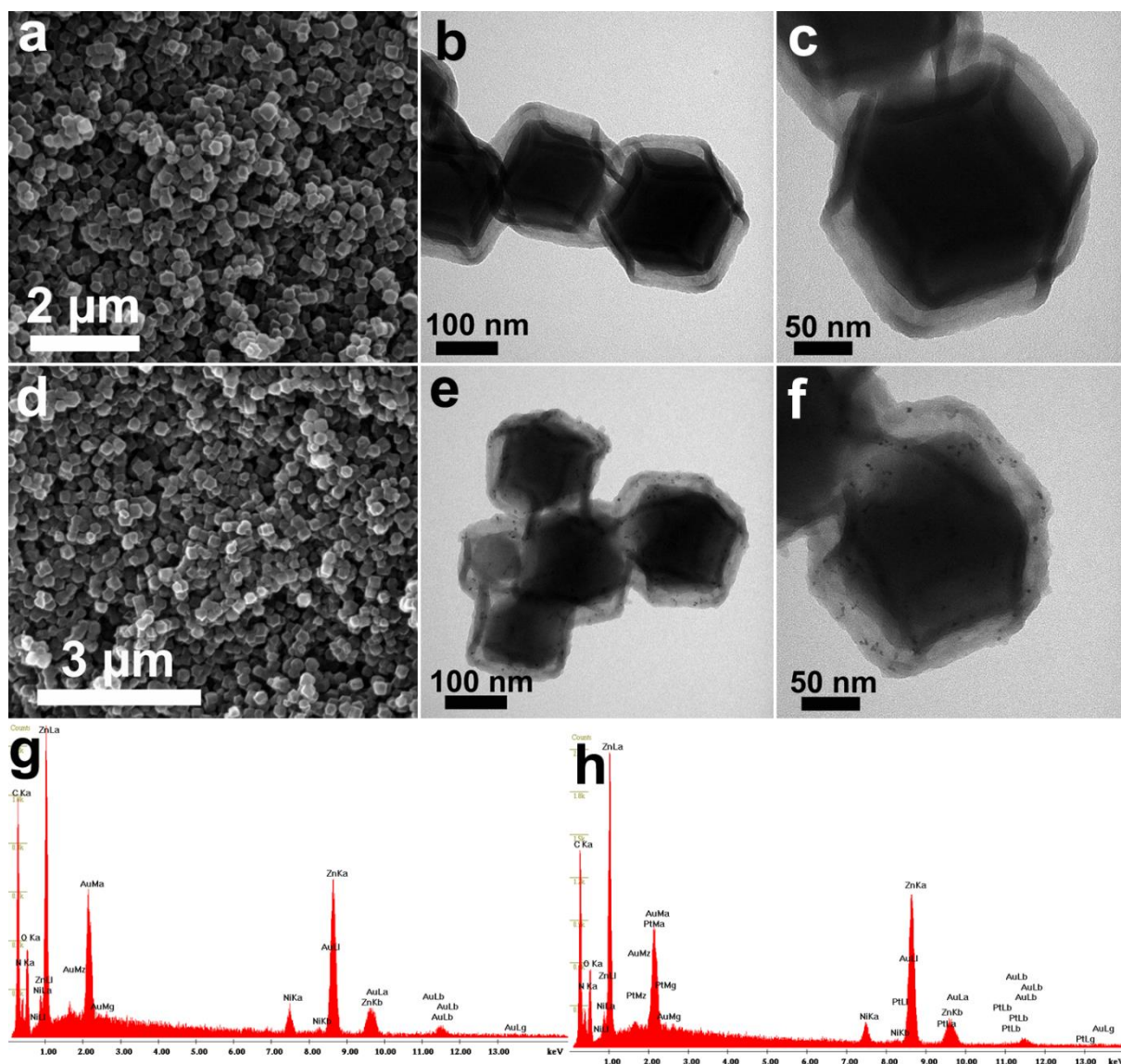




**Figure S14.** SEM images and EDS spectra of ZIF-8@K-TA (a, b), ZIF-8@Co-TA (c, d) and ZIF-8/Pt@Co-TA (e, f).

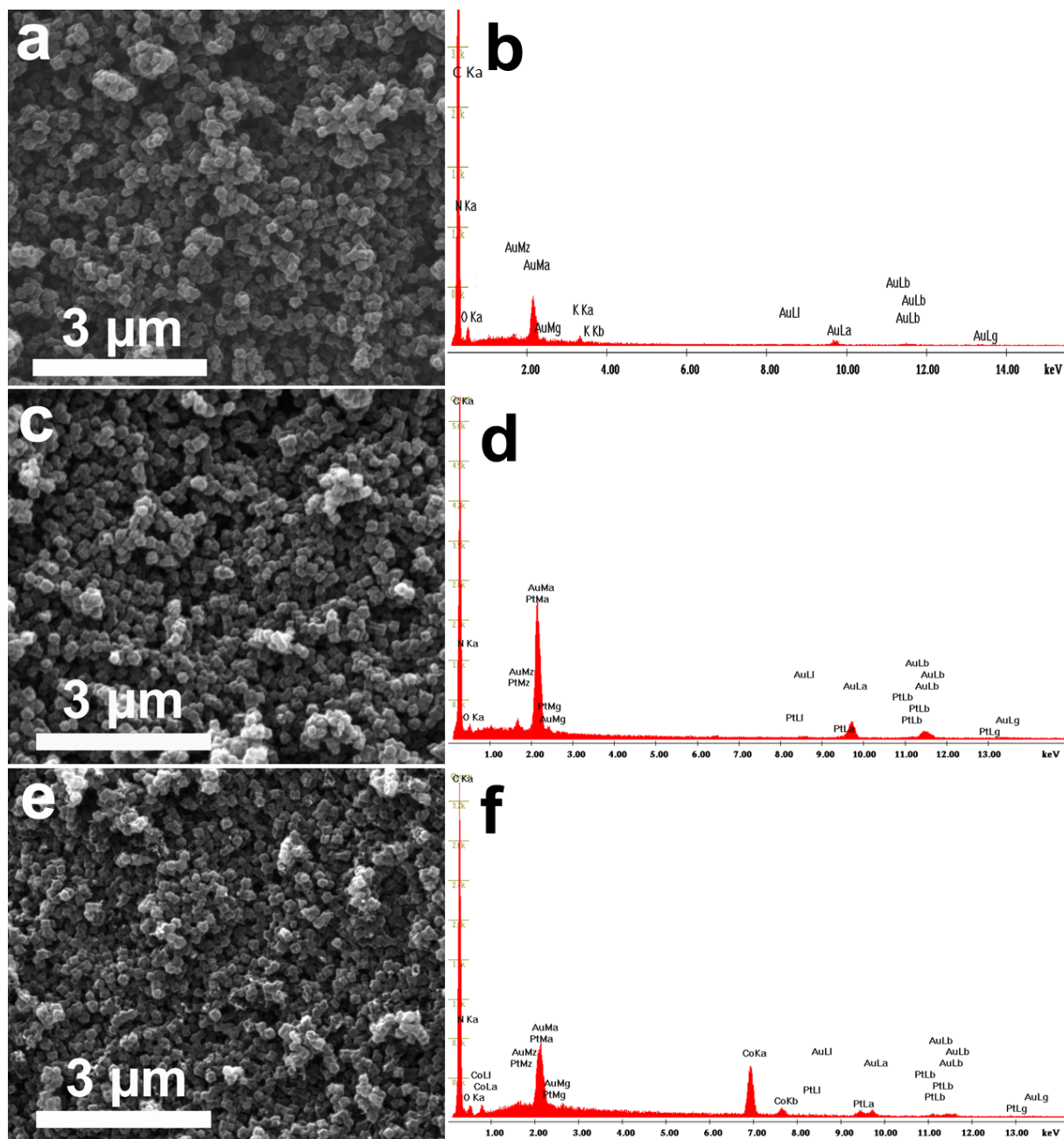


**Figure S15.** SEM images and EDS spectra of ZIF-8@K-TA calcined at 500 °C (a, b); 600 °C (c, d); 700 °C (e, f); 800 °C (g, h) and 900 °C (i, j). Traces of zinc are apparent in j since the sample was not held for three hours at 900 °C as per our standard synthesis method.

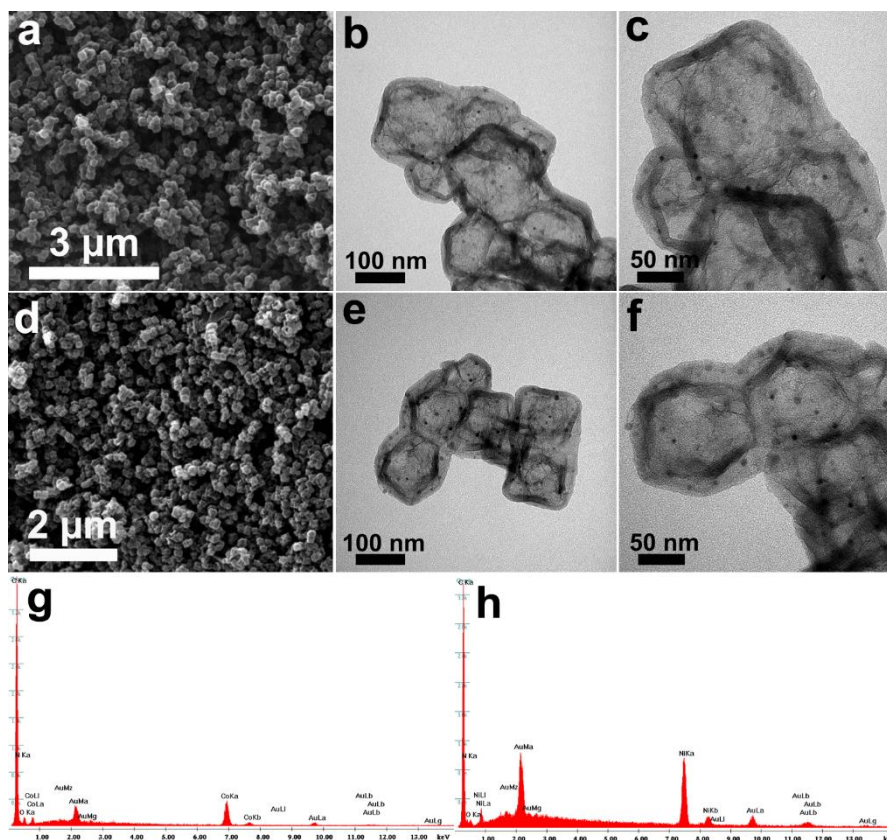


**Figure S16.** SEM, TEM images and EDS spectra of ZIF-8@Ni-TA (a, b, c, g) and ZIF-8/Pt@Ni-TA (d, e, f, h).

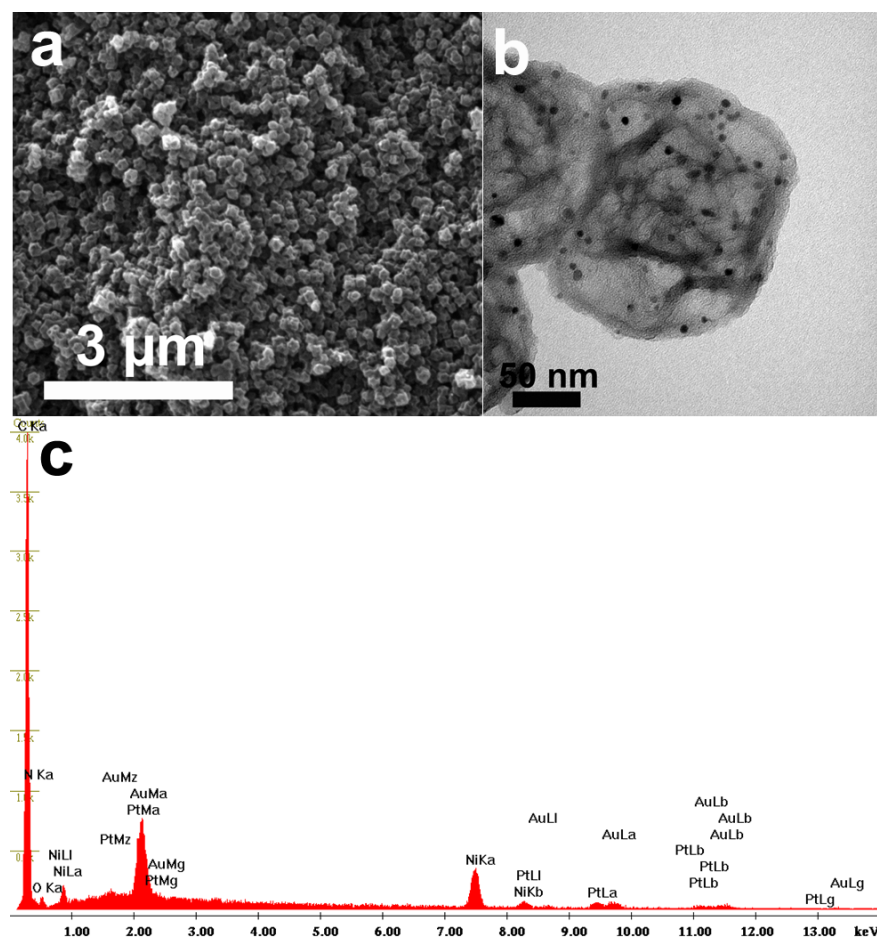




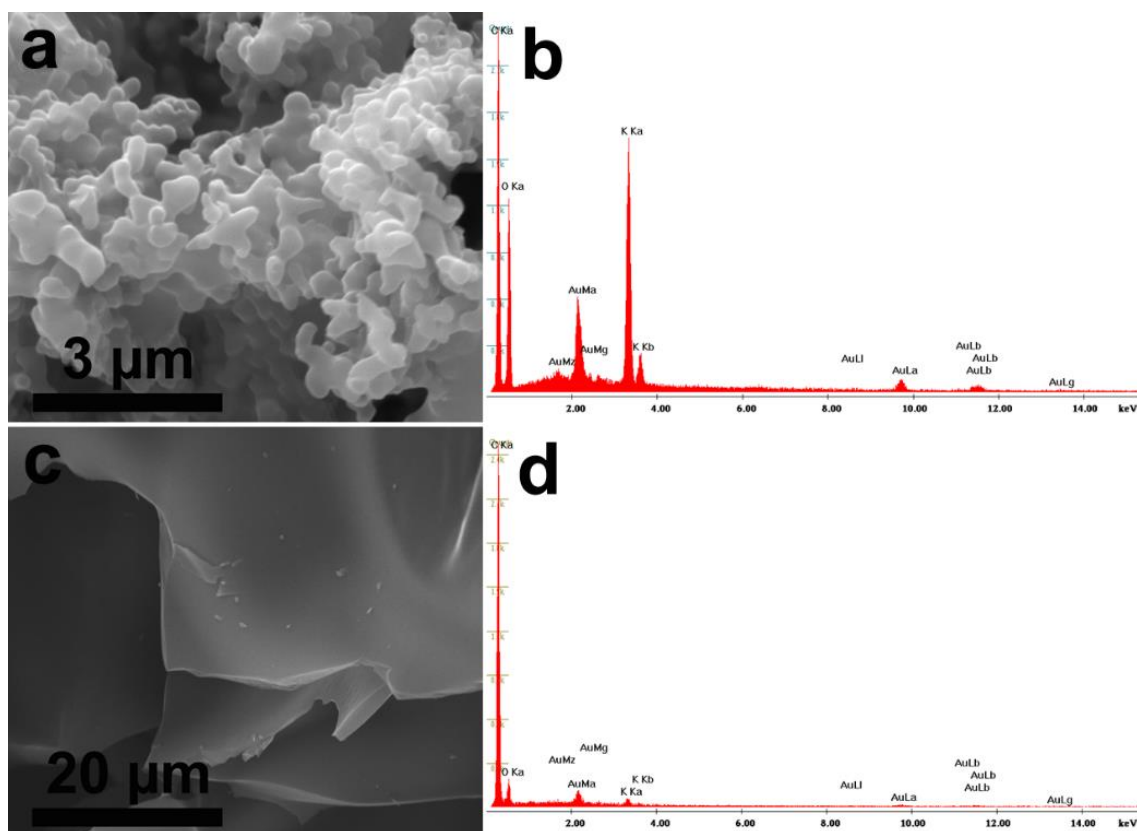
**Figure S17.** SEM images and EDS spectra of NHPC<sub>1</sub> (a, b), Pt@NHPC<sub>1</sub> (c, d) and PtCo@NHPC<sub>1</sub> (e, f).



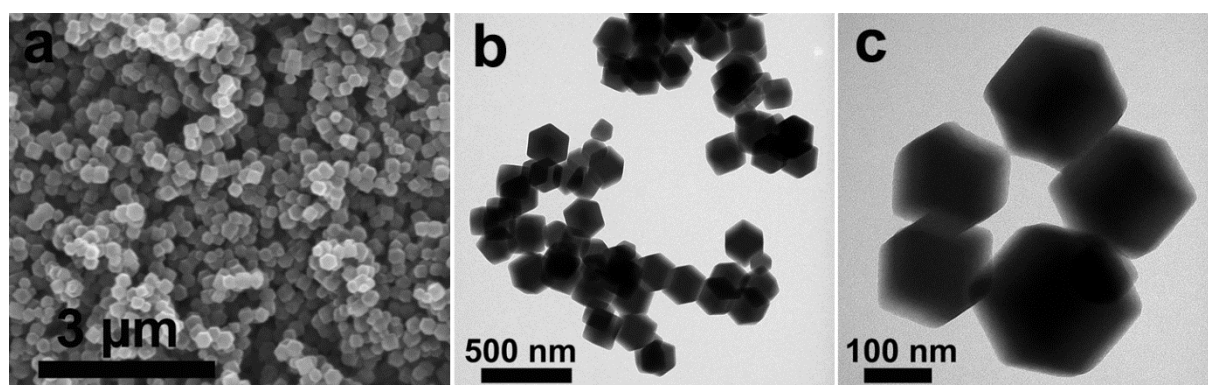
**Figure S18.** SEM, TEM images and EDS spectra of Co@NHPC<sub>1</sub> (a, b, c, g) and Ni@NHPC<sub>1</sub> (d, e, f, h).



**Figure S19.** SEM, TEM images and EDS spectra of PtNi@NHPC<sub>1</sub>.

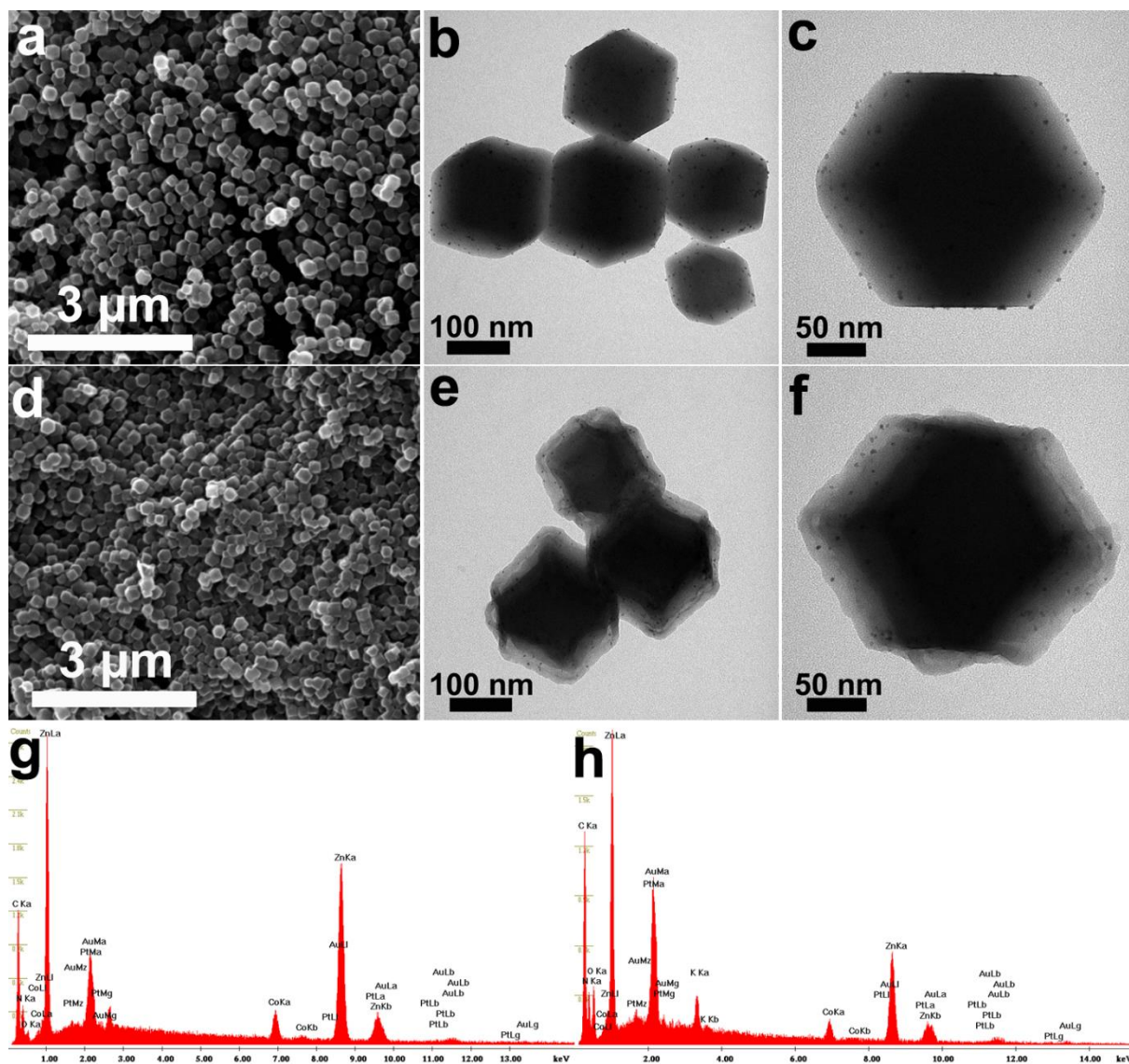


**Figure S20.** SEM images and EDS spectra of potassium-tannic acid (a, b) and potassium-tannic acid derived carbon (c, d).

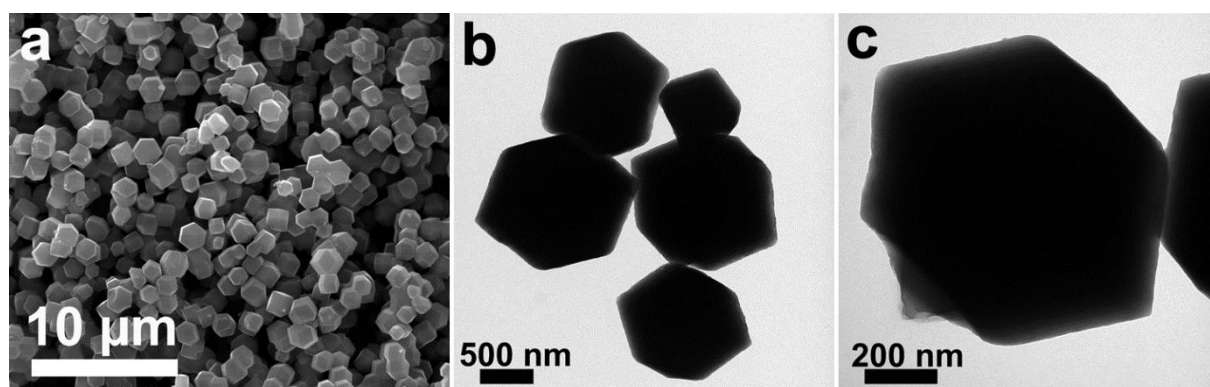


**Figure S21.** SEM image (a) and TEM images (b, c) of polyhedral ZIF-8CoZn nanocrystals.

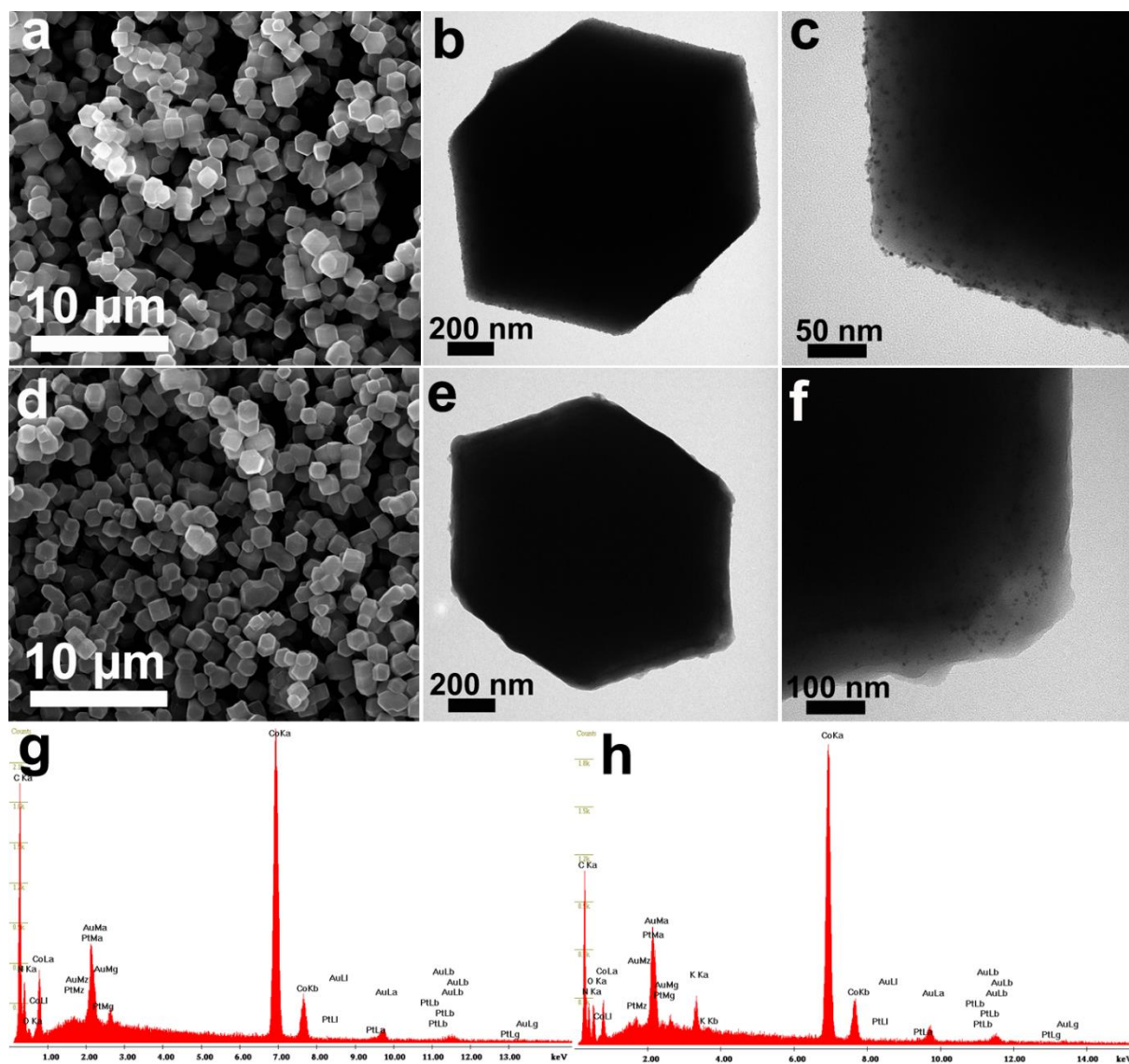




**Figure S22.** SEM, TEM images and EDS spectra of polyhedral ZIF-8CoZn/Pt (a, b, c, g) and ZIF-8CoZn/Pt@K-TA nanocrystals (d, e, f, h).

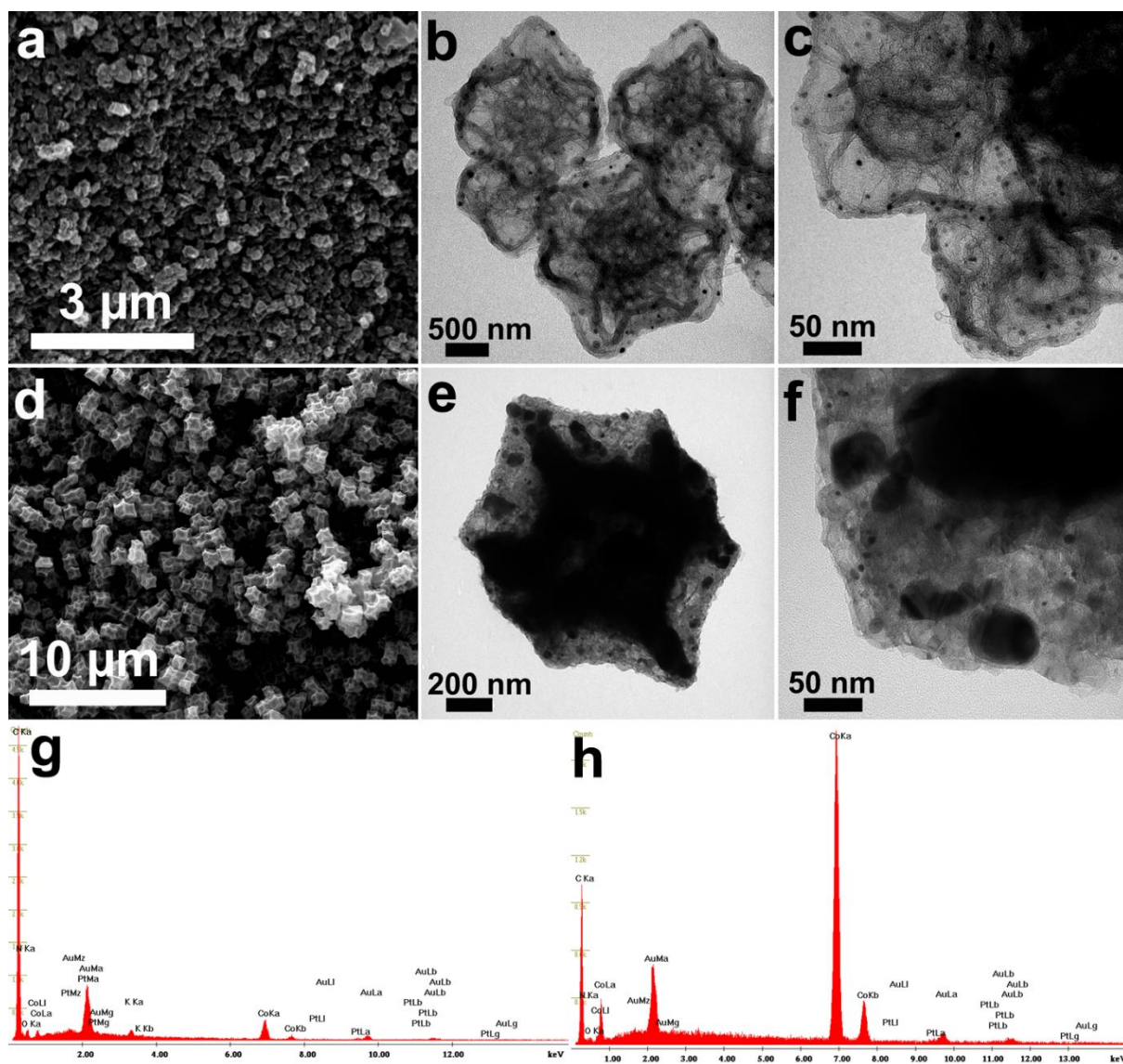


**Figure S23.** SEM image (a) and TEM images (b, c) of polyhedral ZIF-67 nanocrystals.



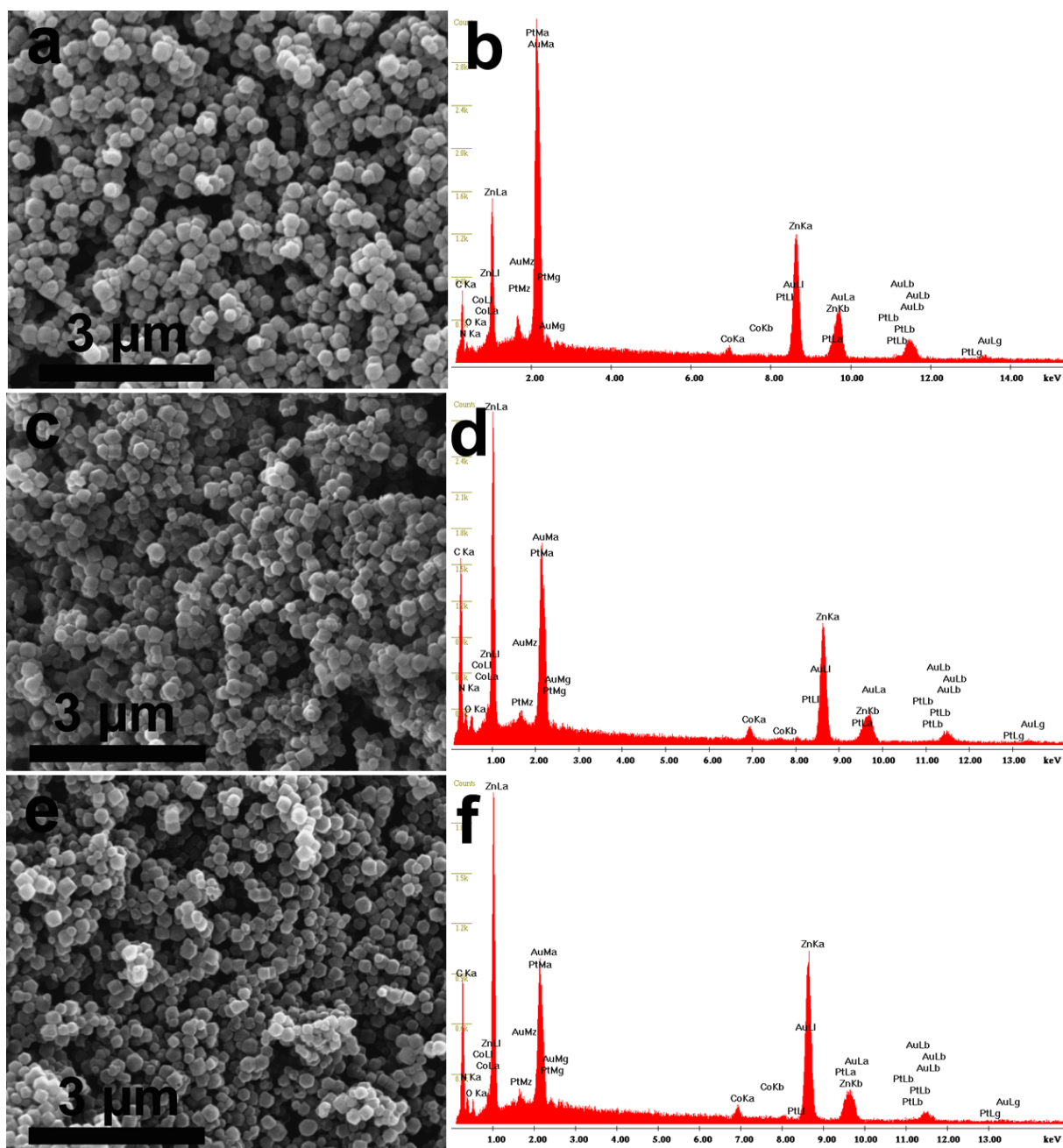
**Figure S24.** SEM, TEM images and EDS spectra of ZIF-67/Pt (a, b, c, g) and ZIF-67/Pt@K-TA nanocrystals (d, e, f, h).



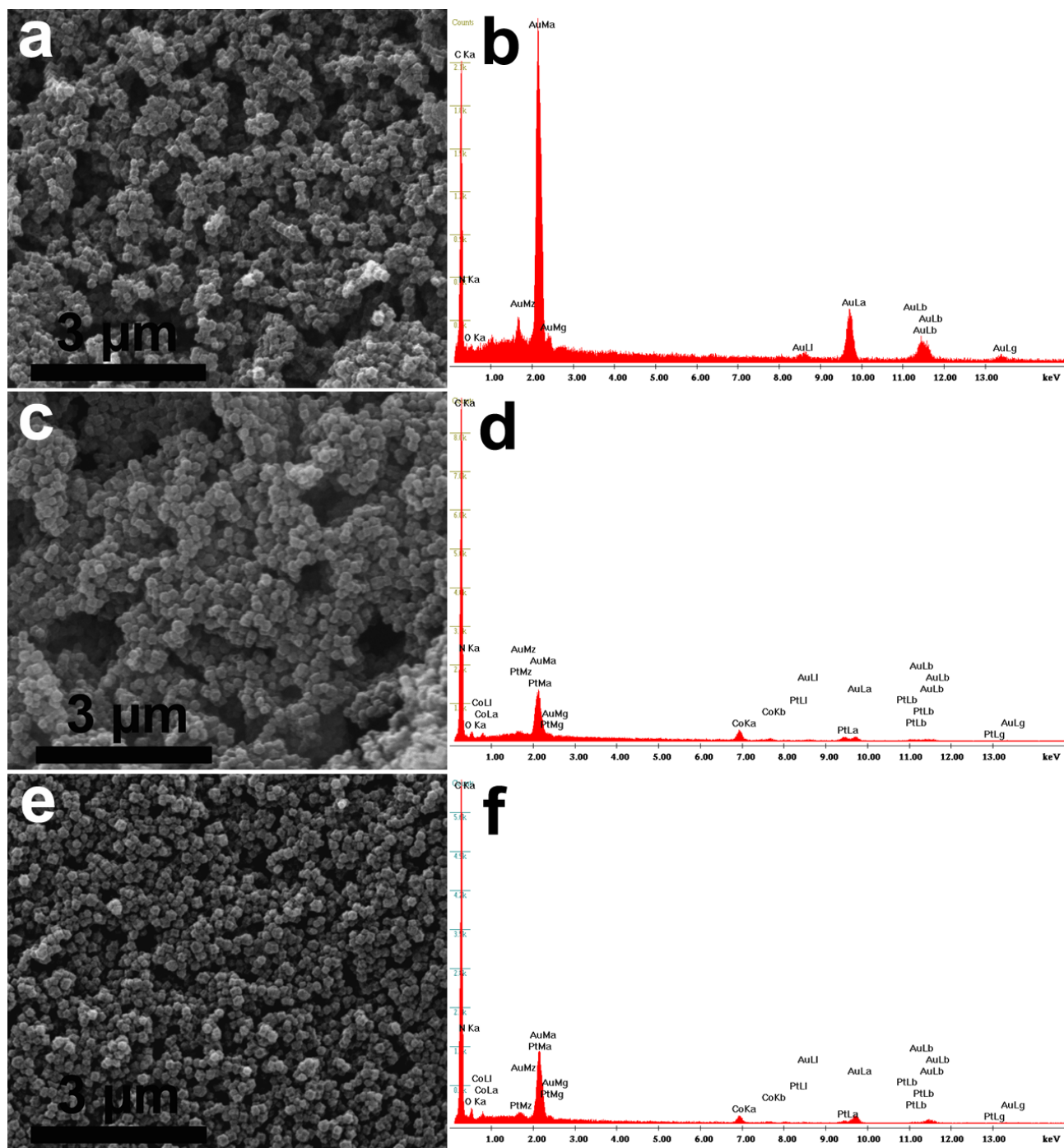


**Figure S25.** SEM, TEM images and EDS spectra of PtCo/Co@NHPC<sub>1</sub> (a, b, c, g) and PtCo/Co@NHPC<sub>2</sub> (d, e, f, h).

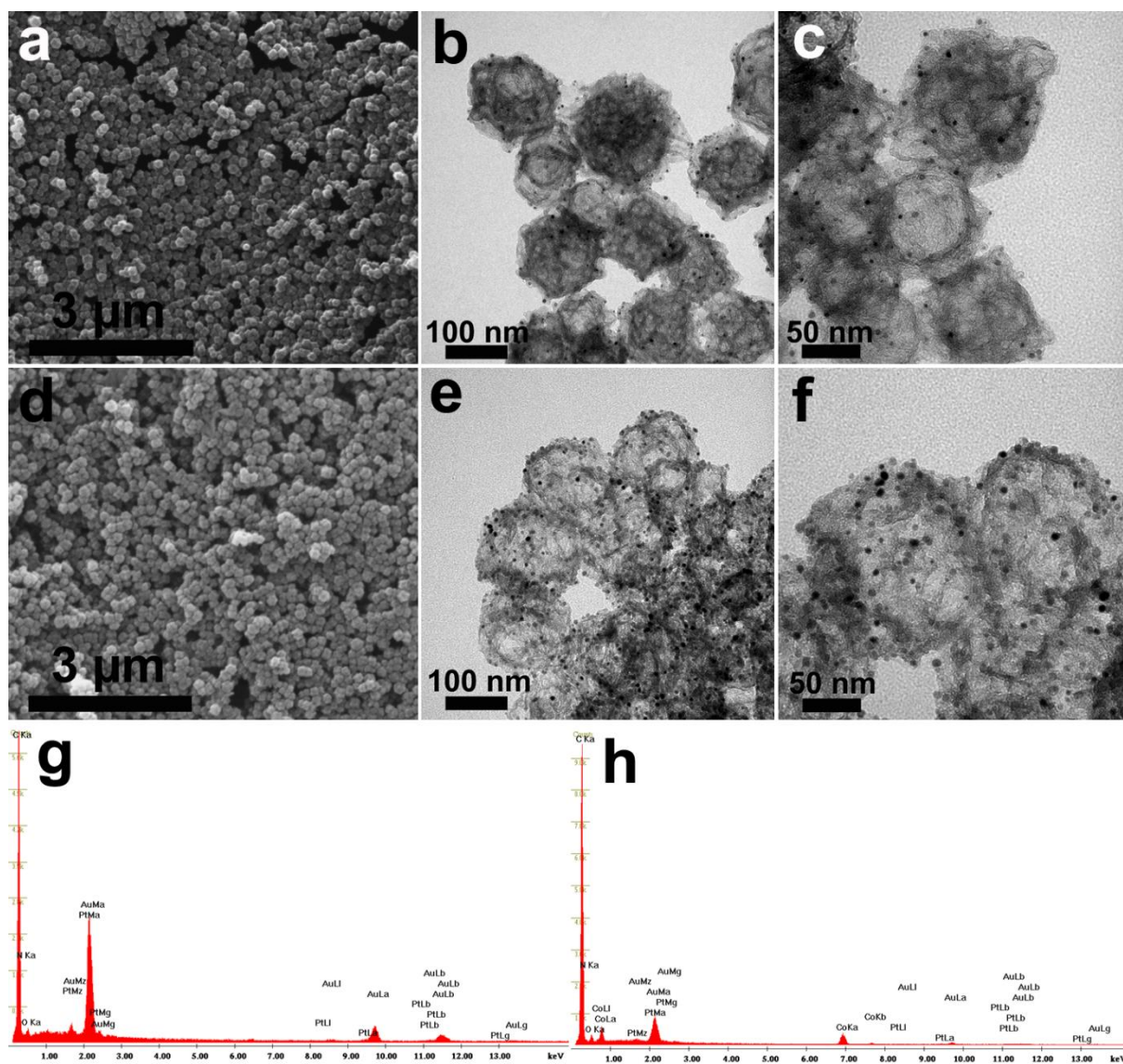




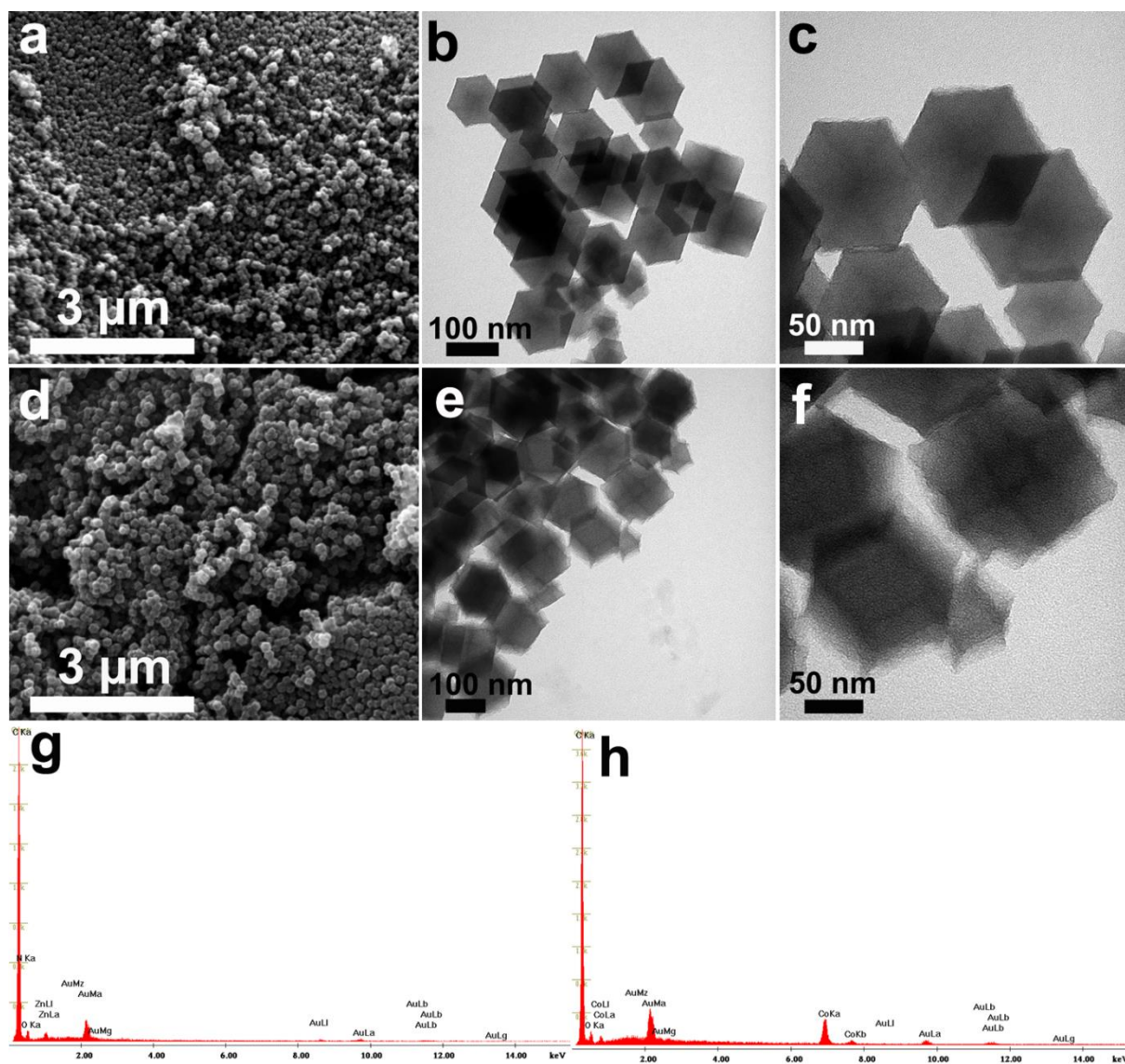




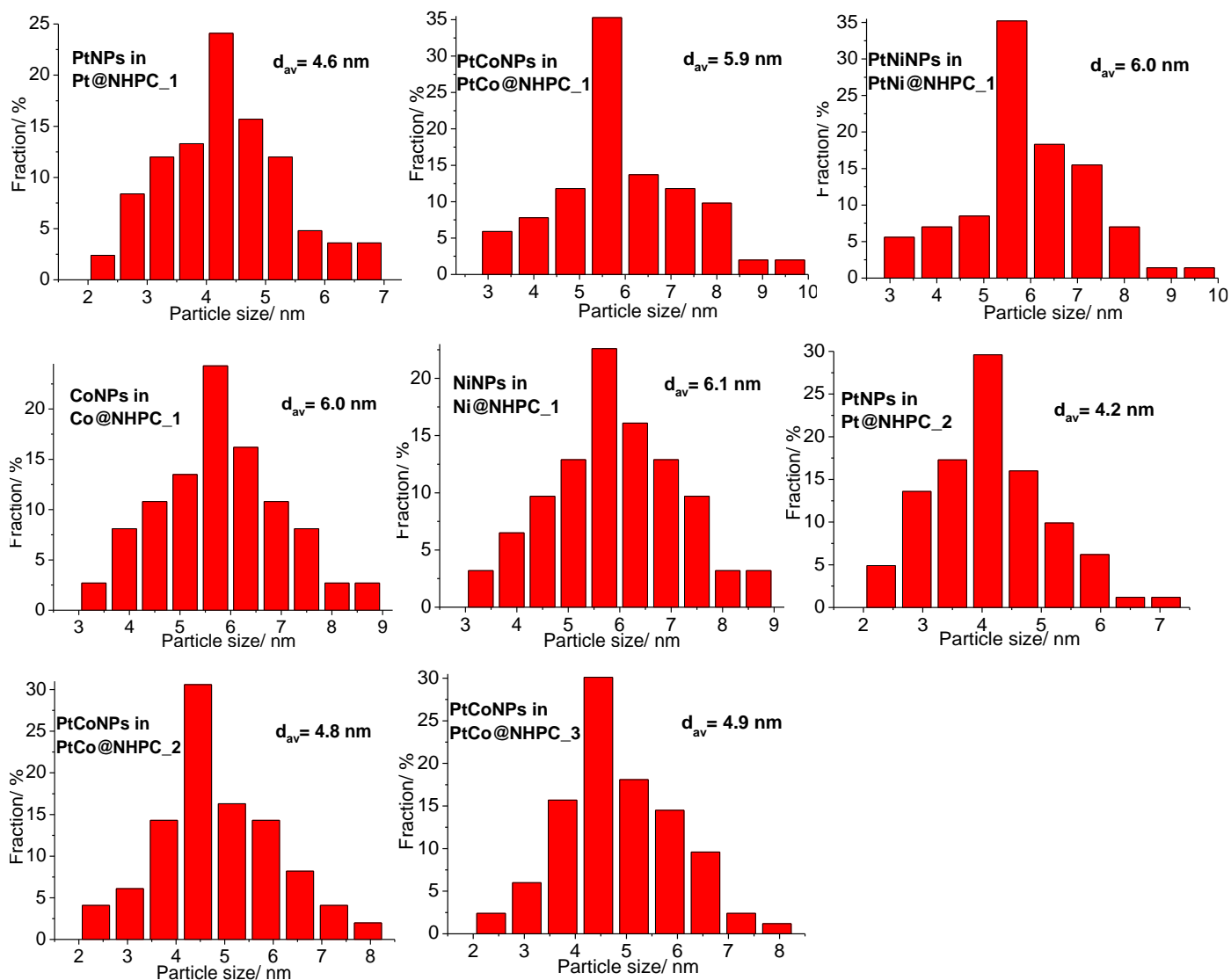
**Figure S29.** SEM images and EDS spectra of NHPC\_2 (a, b), PtCo@NHPC\_2 (c, d) and PtCo@NHPC\_3 (e, f).



**Figure S30.** SEM, TEM images and EDS spectra of Pt@NHPC<sub>2</sub> (a, b, c, g) and PtCo/Co@NHPC<sub>3</sub> (d, e, f, h).

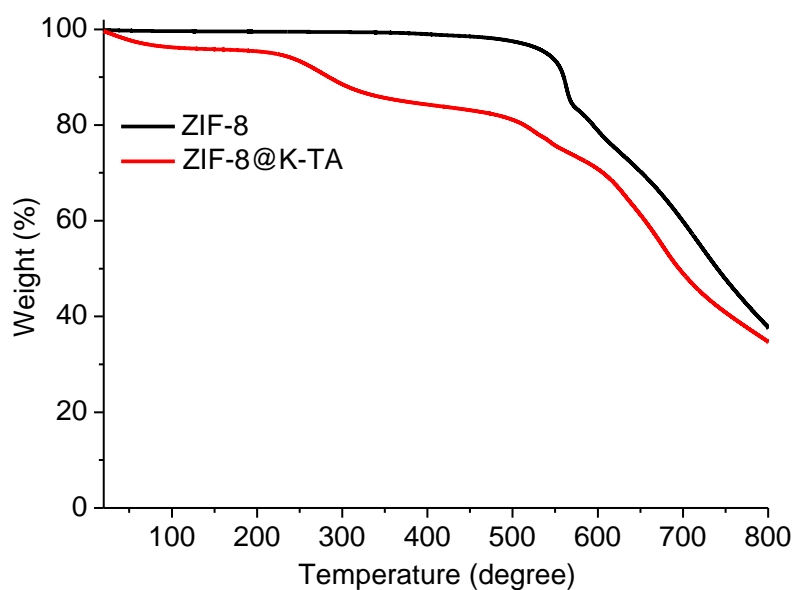


**Figure S31.** SEM, TEM images and EDS spectra of NC (a, b, c, g) and Co/NC (d, e, f, h).



**Figure S32.** Histograms of nanoparticle and average particle sizes for materials.

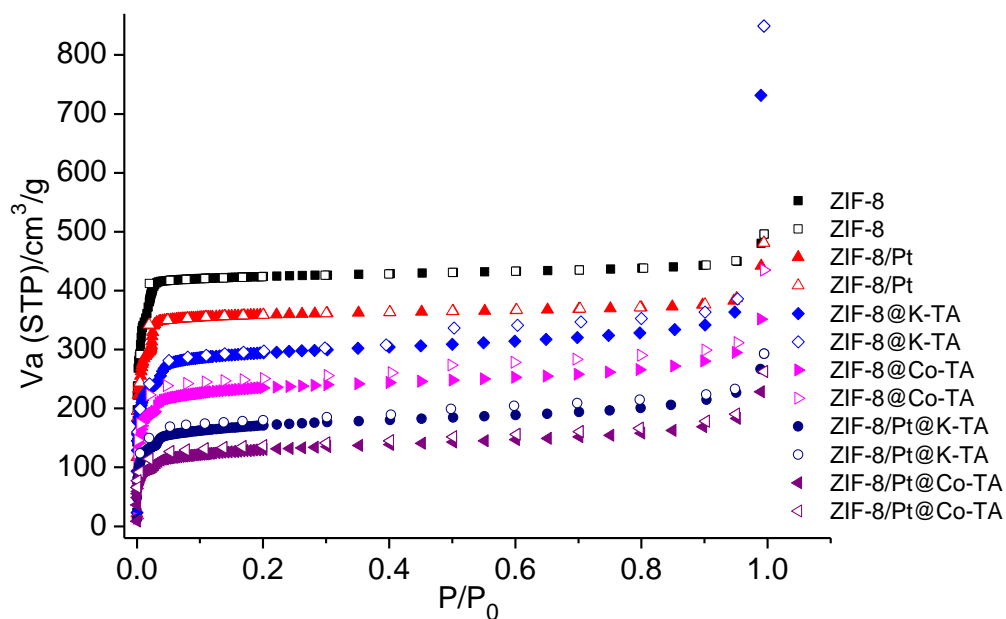
#### 4.4 Thermal gravimetric analysis (TGA)



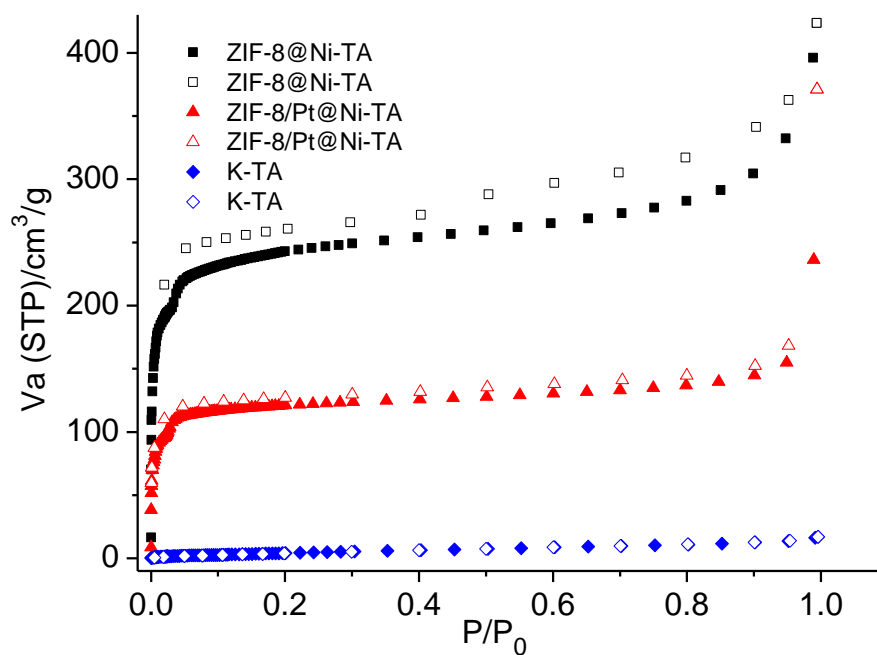
**Figure S33.** Thermogravimetric analysis of ZIF-8 and ZIF-8@K-TA.



#### 4.5 Nitrogen sorption measurements, pore size analysis and surface area calculations:

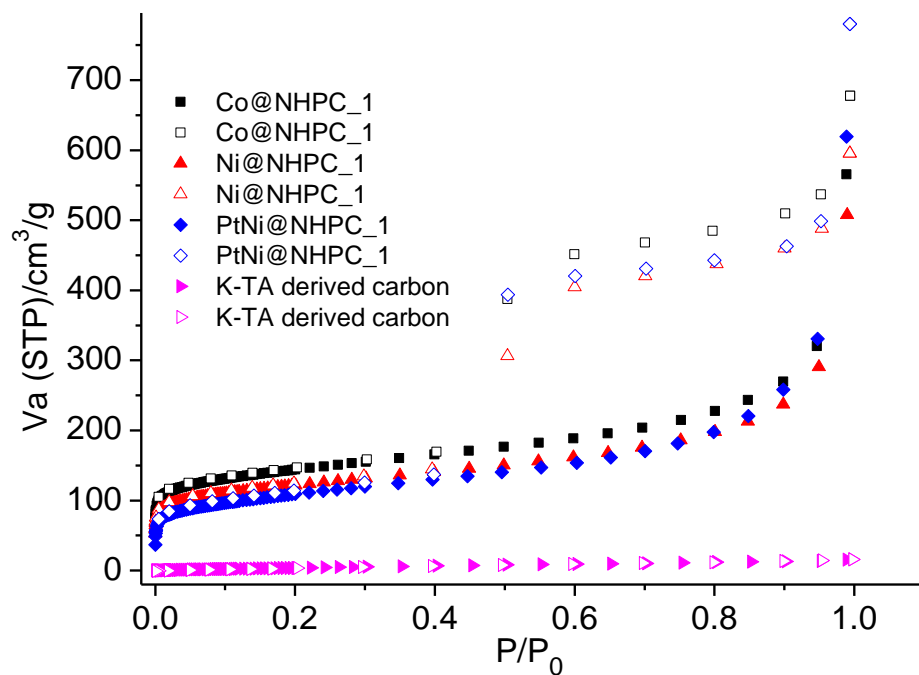


**Figure S34.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.

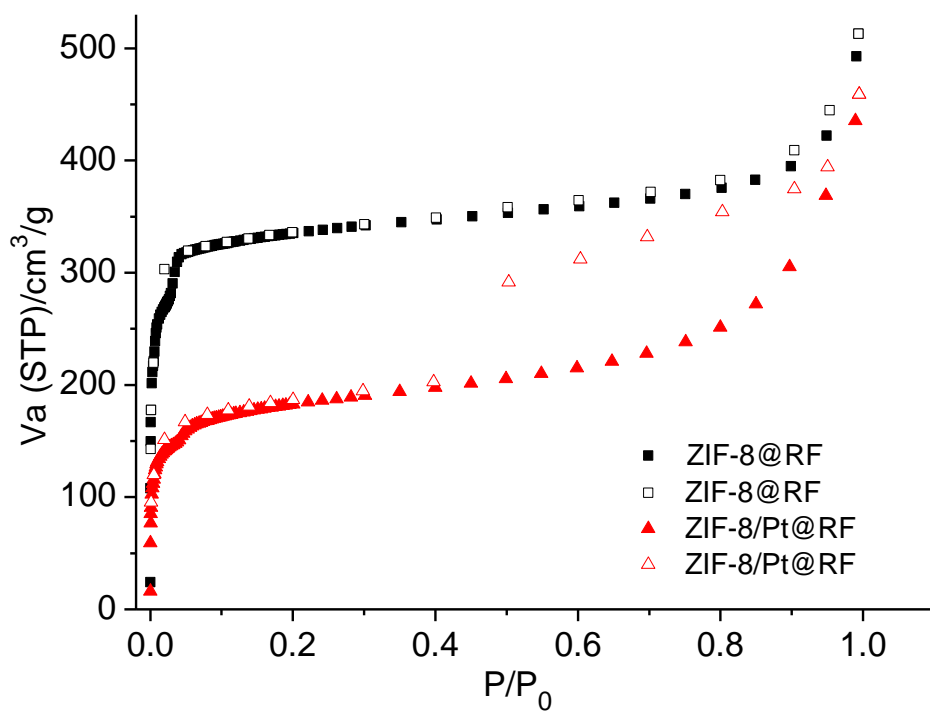


**Figure S35.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.

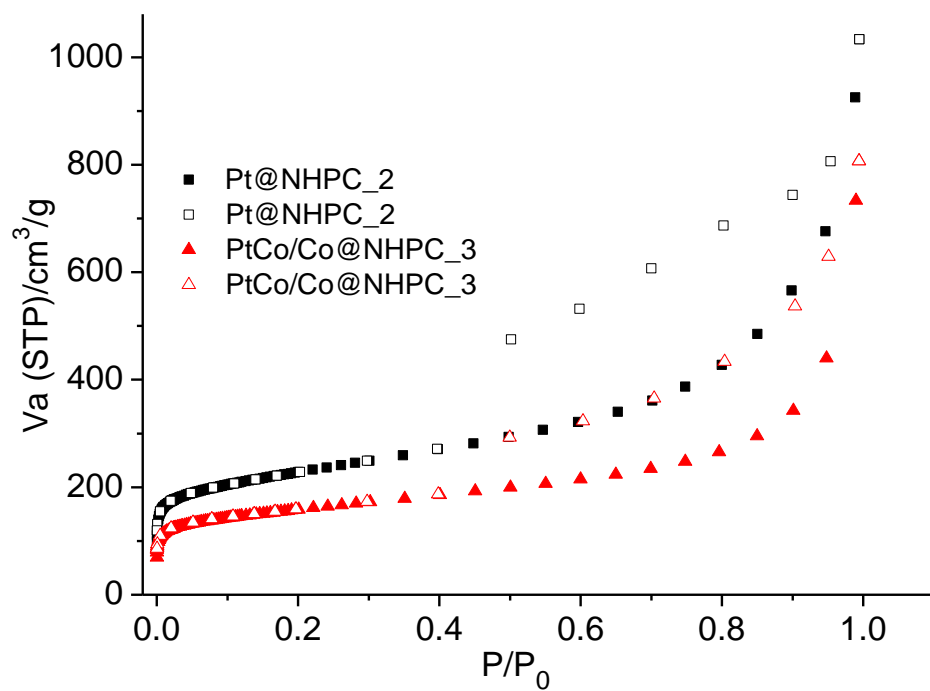




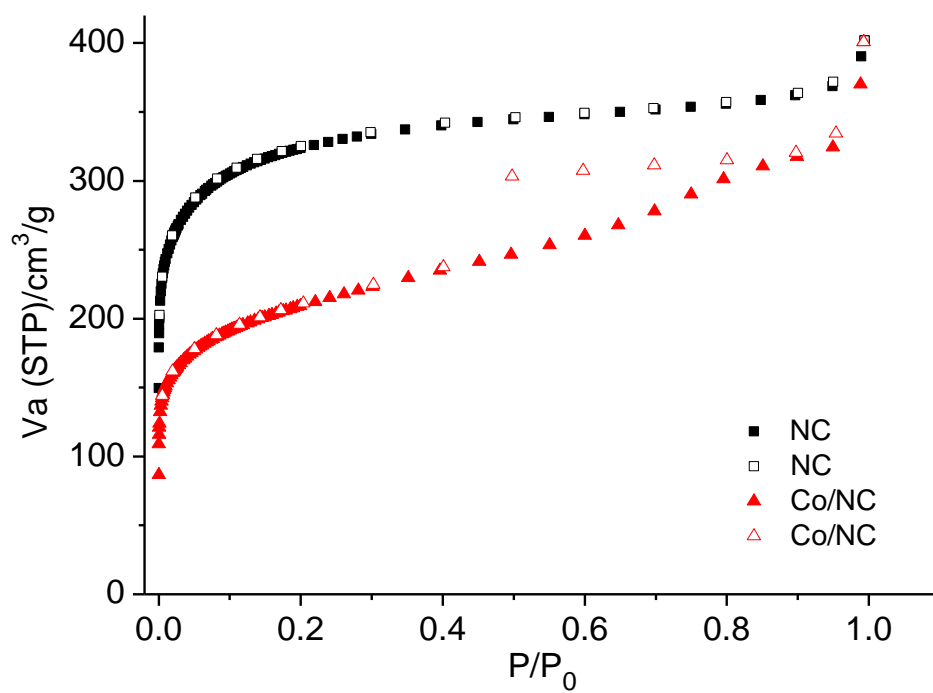
**Figure S36.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.



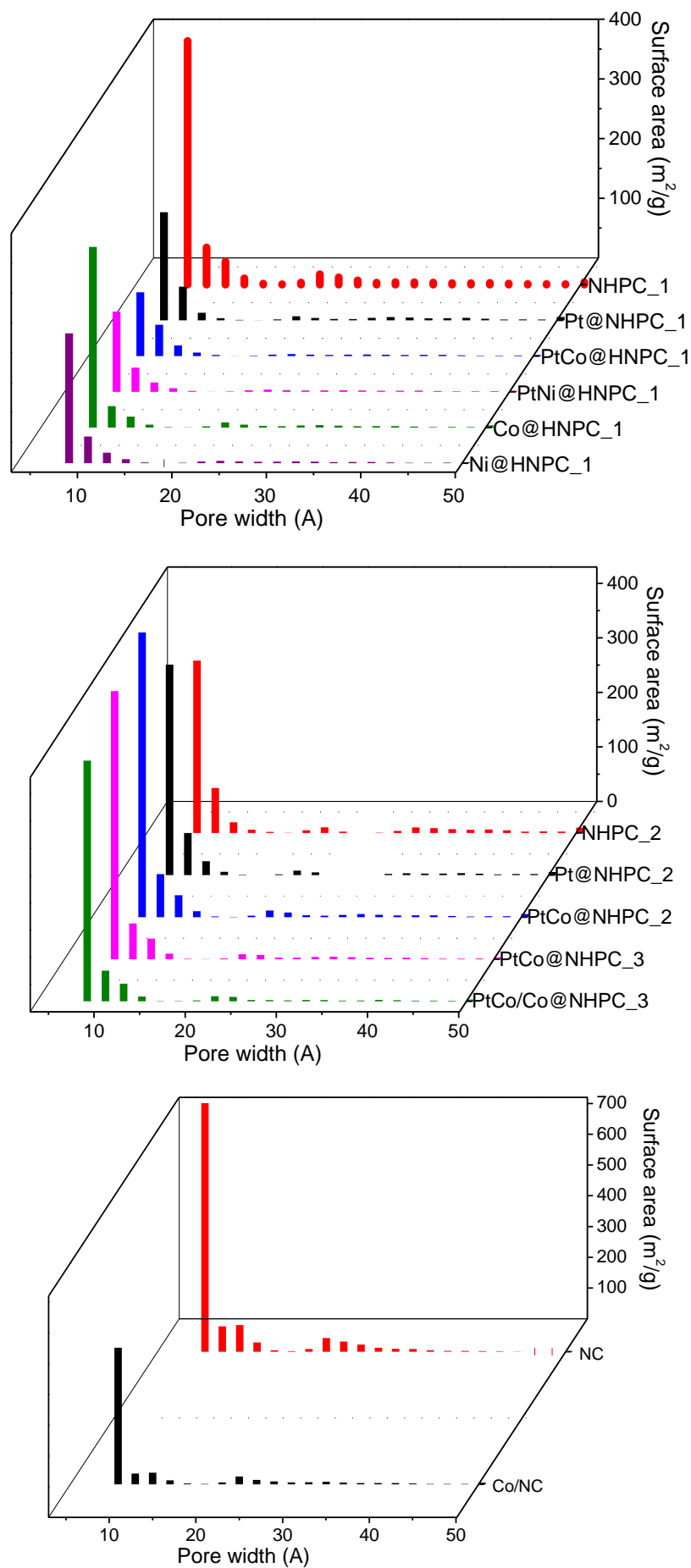
**Figure S37.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.



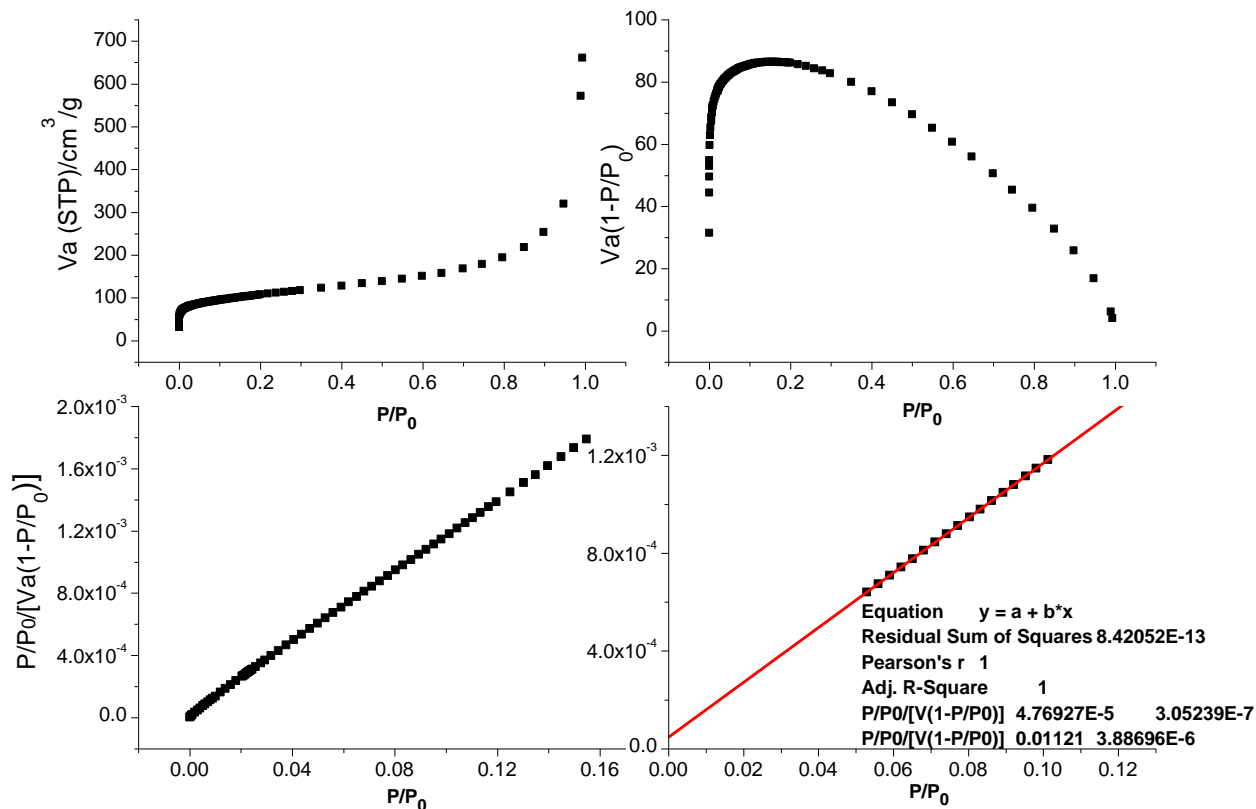
**Figure S38.**  $N_2$  adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.



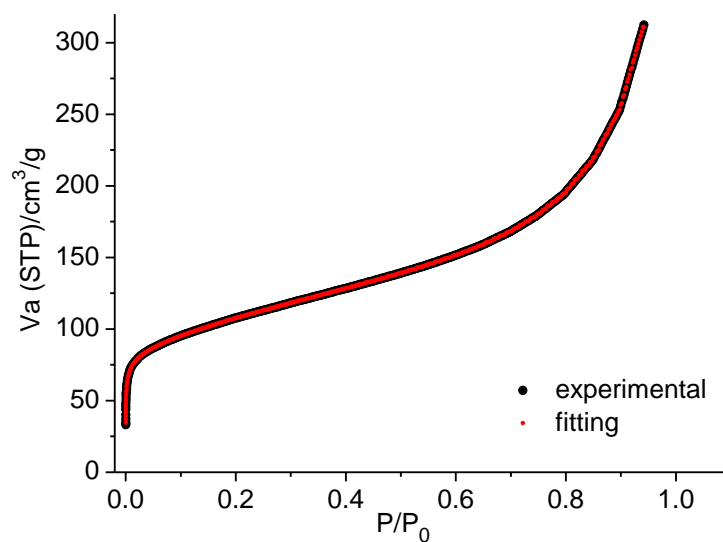
**Figure S39.**  $N_2$  adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.



**Figure S40.** Pore size distribution plots calculated using a DFT method from N<sub>2</sub> isotherms measured at 77 K.



**Figure S41.** Top left: N<sub>2</sub> adsorption isotherm for PtCo@NHPC<sub>1</sub> at 77 K. Top right: Consistency plot for the N<sub>2</sub> isotherm in PtCo@NHPC<sub>1</sub>. Bottom left: Plot  $P/P_0/[v(1-P/P_0)]$  against  $P/P_0$  for the N<sub>2</sub> isotherm of PtCo@NHPC<sub>1</sub>. Bottom right: BET equation plot for PtCo@NHPC<sub>1</sub>.



**Figure S42.** N<sub>2</sub> adsorption isotherm for PtCo@NHPC<sub>1</sub> at 77 K (black). Fitting comparison by QSDFT model (red).

## 4.6 Raman spectra

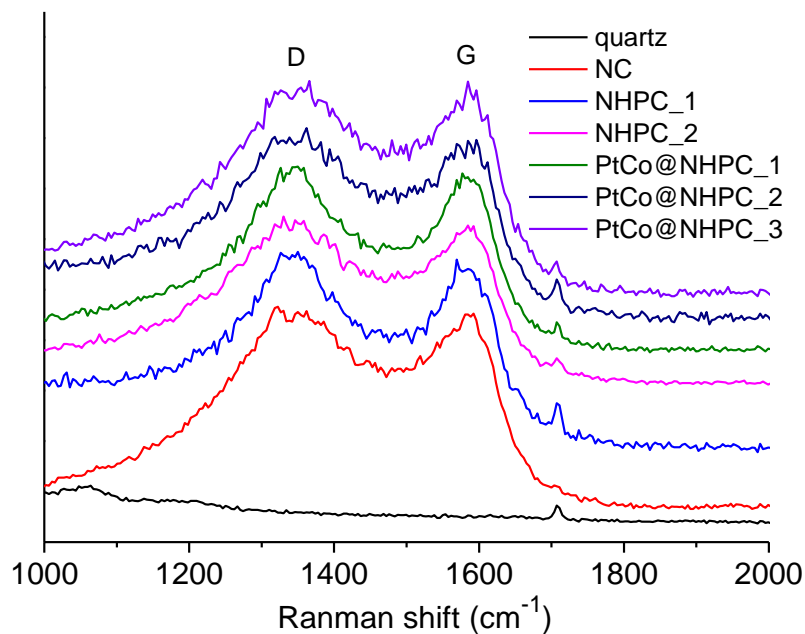


Figure S43. Raman spectra of materials.

## 4.7 X-ray photoemission spectroscopy (XPS)

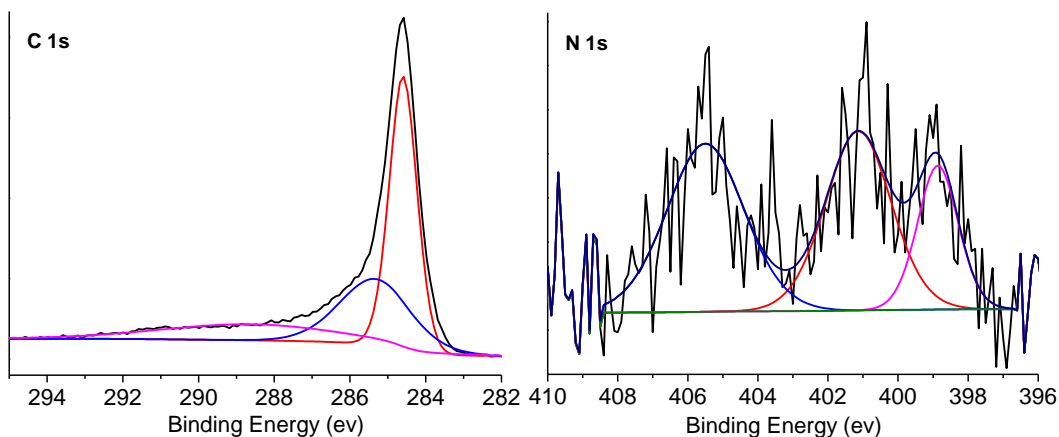


Figure S44. XPS spectra of NHPC\_1.

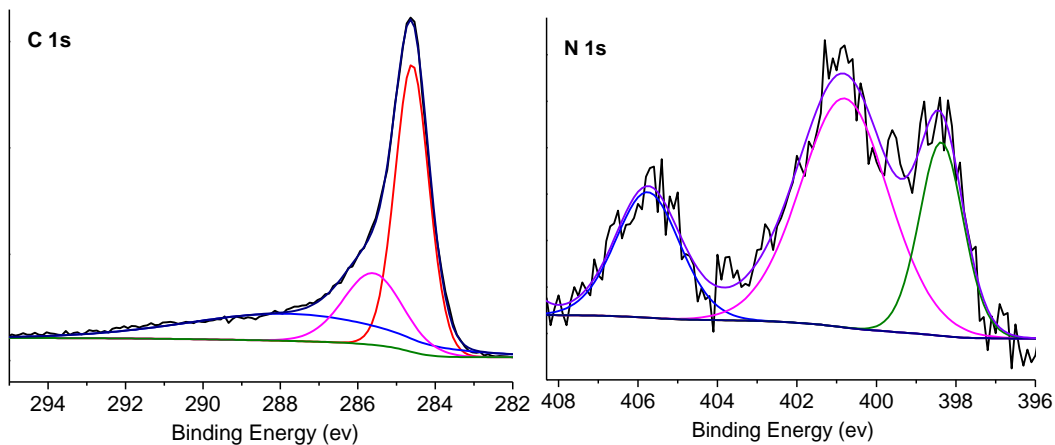
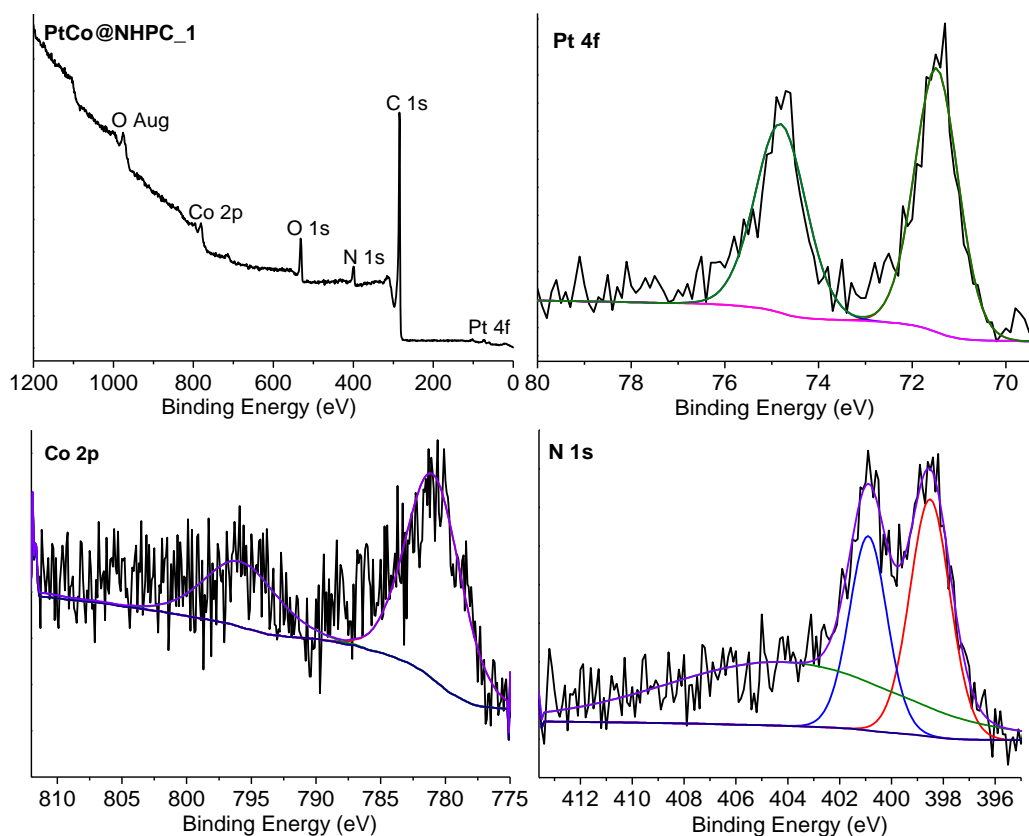
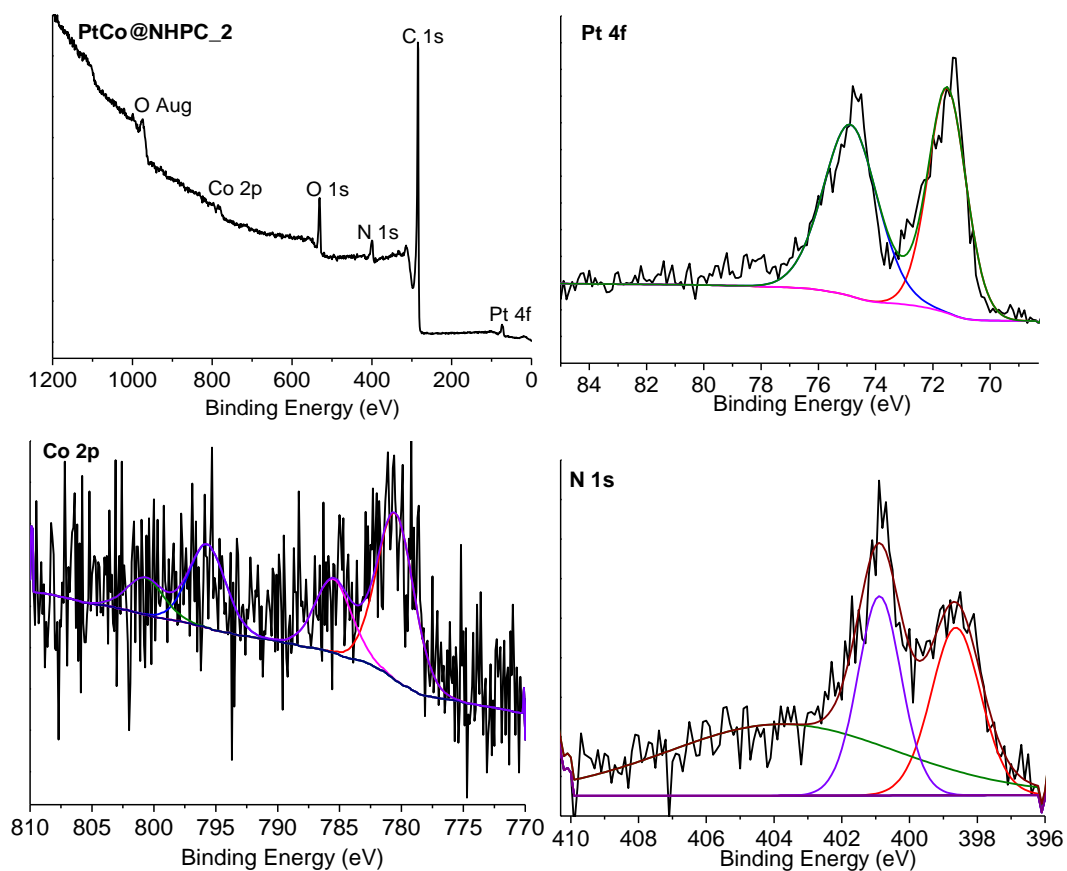


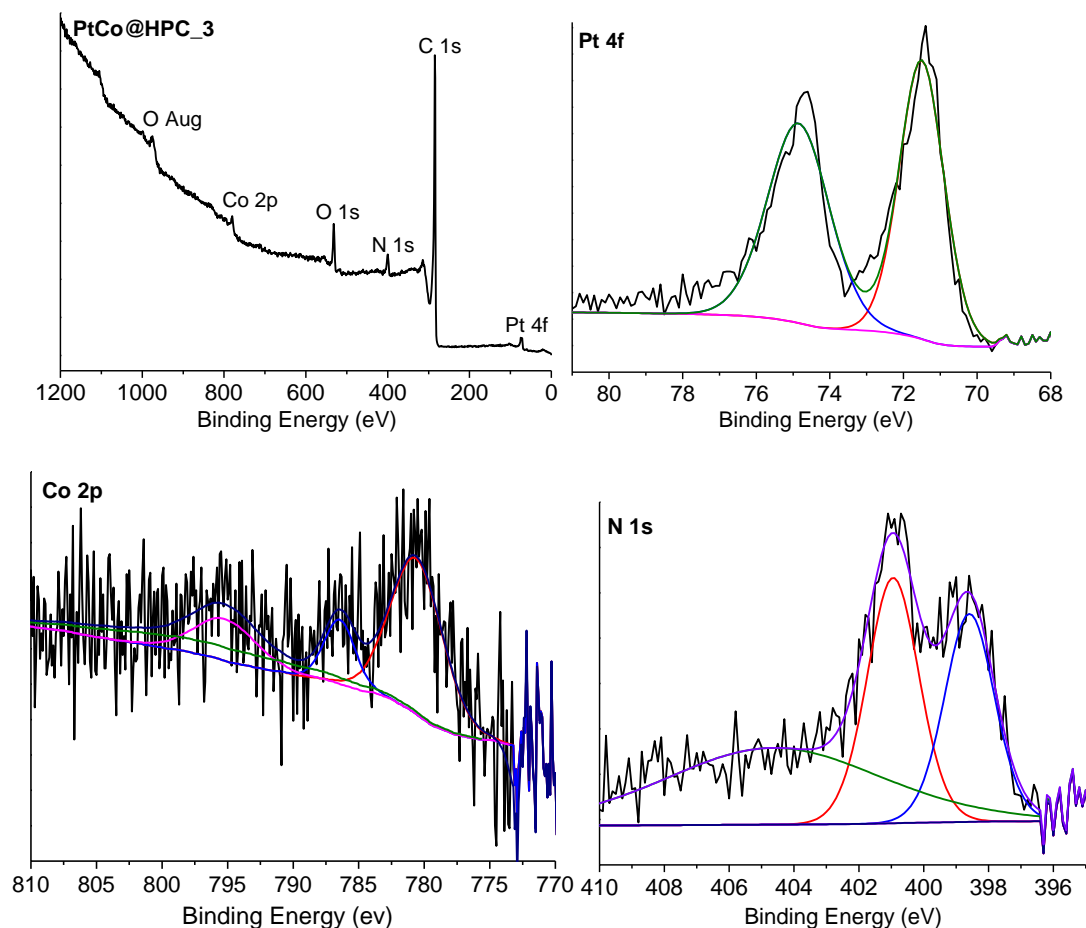
Figure S45. XPS spectra of NHPC\_2.



**Figure S46.** XPS spectra of PtCo@NHPC\_1.

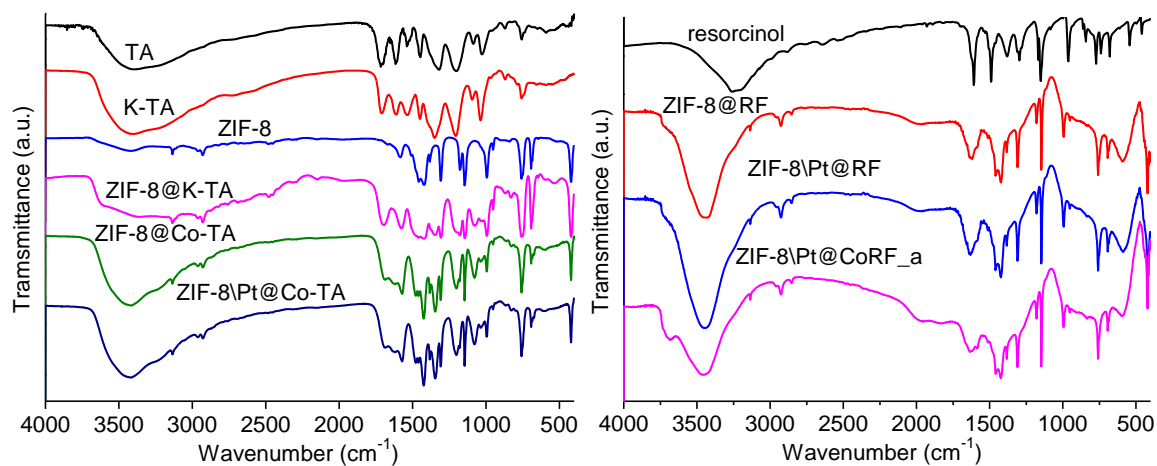


**Figure S47.** XPS spectra of PtCo@NHPC\_2.



**Figure S48.** XPS spectra of PtCo@NHPC<sub>3</sub>.

#### 4.8 Fourier Transform Infrared Spectrophotometry (FT-IR)



**Figure S49.** FTIR spectra of materials.

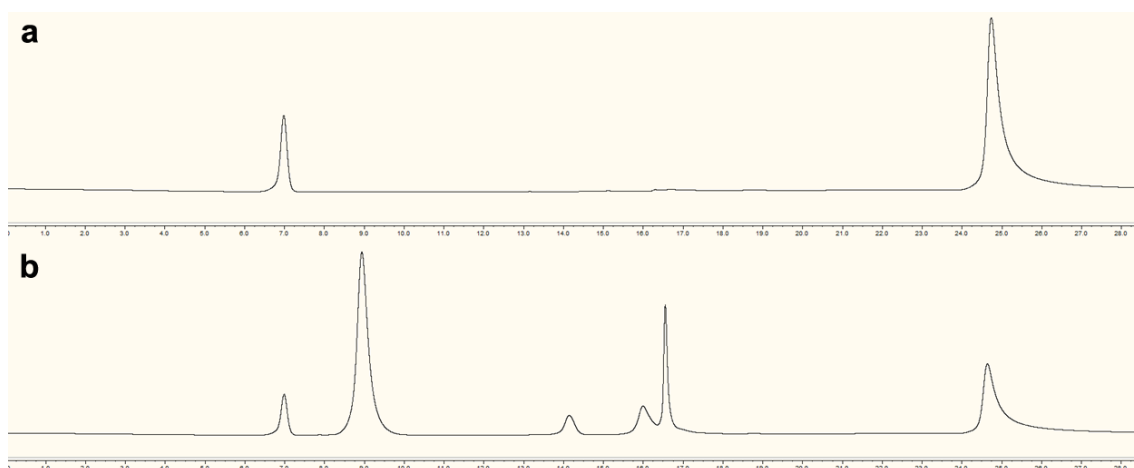
#### 4.9 Hydrogenation of nitroarenes

In a typical experiment, 0.5 mmol of nitroarenes, 5 mL of methanol and 20 mg of catalyst were added into an autoclave reactor (50 mL), which was sealed and purged with H<sub>2</sub> several times. The vessel was the heated at 50 °C

with 6.8 bar H<sub>2</sub> under stirring (400 RPM). Mesitylene was used as internal standard. HPLC analysis used an Econosil silica 100 column.

#### 4.9.1 Hydrogenation of 4-nitrophenol

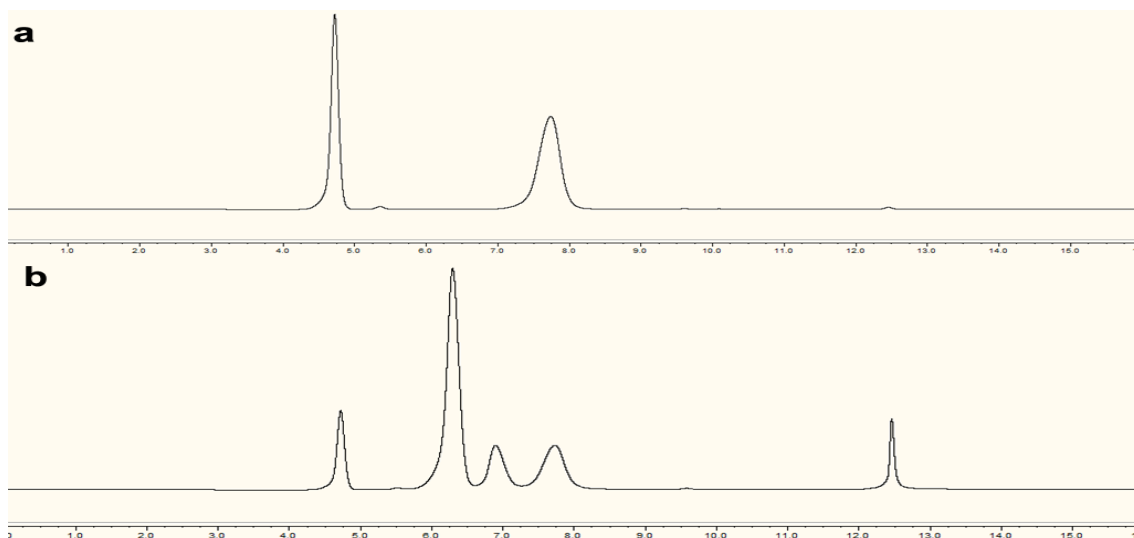
Column temperature was set at 298 K and flowrate at 0.5 mL·min<sup>-1</sup>. UV/vis:  $\lambda$ =251 nm. Gradient used: 0 min., 100% hexane; 0-20 min mark transition and hold from 20-23 min with 50% hexane, 50% 2-propanol; 23-26 min mark transition with 100% hexane; hold from 26-29 min with 100% hexane. The retention time of mesitylene, nitrobenzene, phenol, nitrophenol, aniline and aminophenol are 7.0, 8.9, 14.1, 15.9, 16.6, and 24.6 min, respectively.



**Figure S50.** HPLC chromatograms of the product generated by hydrogenation of 4-nitrophenol by PtCo@NHPC<sub>1</sub> (a); mixture of mesitylene, nitrobenzene, phenol, nitrophenol, aniline and aminophenol (b).

#### 4.9.2 The hydrogenation of 1-chloro-2-nitrobenzene

Column temperature was set at 298 K and flowrate at 0.75 mL·min<sup>-1</sup>. UV/vis:  $\lambda$ =266 nm. Gradient used: 0 min., 100% hexane; 0-15 min mark transition and hold from 15-18 min with 70% hexane, 30% 2-propanol; 18-21 min mark transition with 100% hexane; hold from 21-24 min with 100% hexane. The retention time of mesitylene, nitrobenzene, 1-chloro-2-nitrobenzene, 2-chloroaniline and aniline are 4.7, 6.3, 6.9, 7.7 and 12.5 min, respectively.

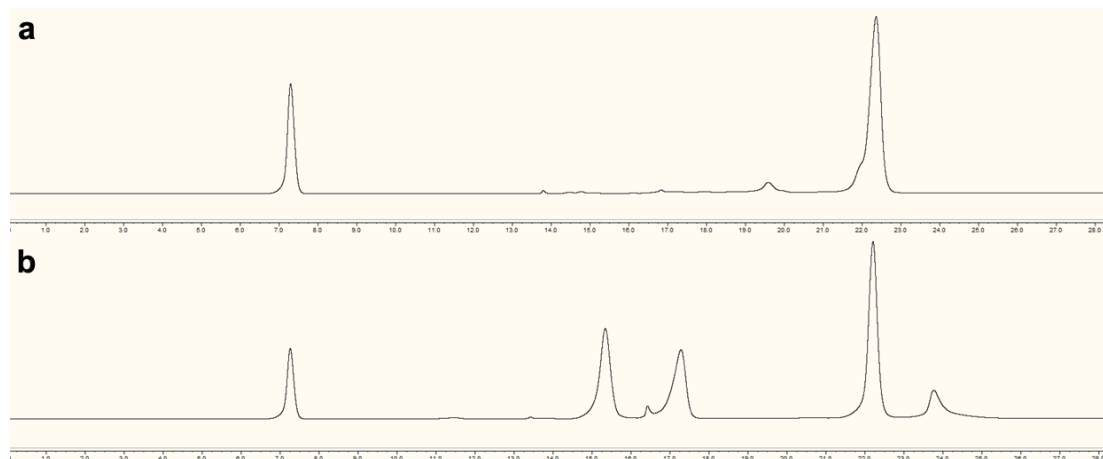




**Figure S51.** HPLC chromatograms of the product generated by hydrogenation of 1-chloro-2-nitrobenzene by PtCo@NHPC\_1 (a); mixture of mesitylene, nitrobenzene, 1-chloro-2-nitrobenzene, 2-chloroaniline and aniline (b).

#### 4.9.3 Hydrogenation of 4-nitroacetophenone

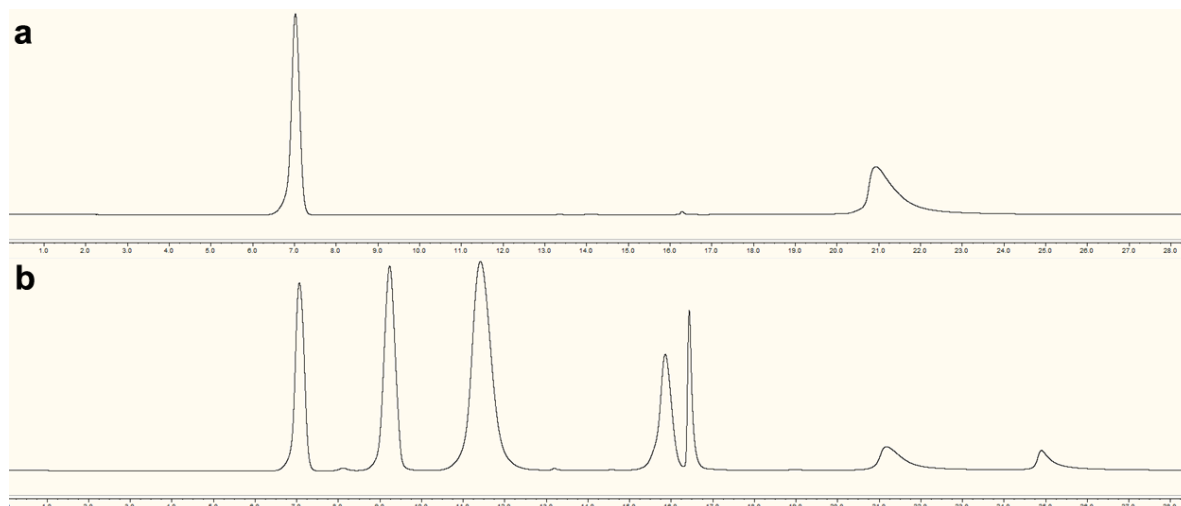
Column temperature was set at 298 K and flowrate at 0.5 mL·min<sup>-1</sup>. UV/vis:  $\lambda=266$  nm. Gradient used: 0 min., 100% hexane; 0-20 min mark transition and hold from 20-23 min with 50% hexane, 50% 2-propanol; 23-26 min mark transition with 100% hexane; hold from 26-29 min with 100% hexane. The retention time of mesitylene, 4-nitroacetophenone, 1-(4-nitrophenyl)ethanol, 4-aminoacetophenone and 1-(4-aminophenyl)ethanol are 7.2, 15.3, 17.3, 22.2 and 23.7 min, respectively.



**Figure S52.** HPLC chromatograms of the product generated by hydrogenation of 4-nitroacetophenone by PtCo@NHPC\_1 (a); mixture of mesitylene, 4-nitroacetophenone, 1-(4-nitrophenyl)ethanol, 4-aminoacetophenone and 1-(4-aminophenyl)ethanol (b).

#### 4.9.4 Hydrogenation of 4-nitroanisole

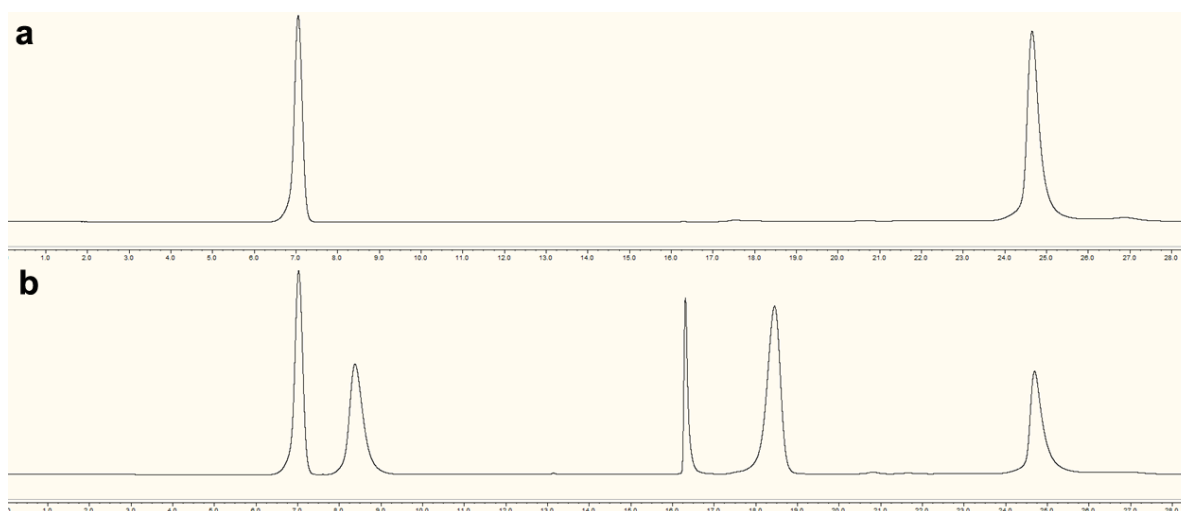
Column temperature was set at 298K and flowrate at 0.5 mL·min<sup>-1</sup>. UV/vis:  $\lambda=266$  nm. Gradient used: 0 min., 100% hexane; 0-20 min mark transition and hold from 20-23 min with 50% hexane, 50% 2-propanol; 23-26 min mark transition with 100% hexane; hold from 26-29 min with 100% hexane. The retention time of mesitylene, nitrobenzene, nitroanisole, 4-nitrophenol, aniline, anisidine and 4-aminophenol are 7.1, 9.2, 11.4, 15.9, 16.4, 21.2 and 24.9 min, respectively.



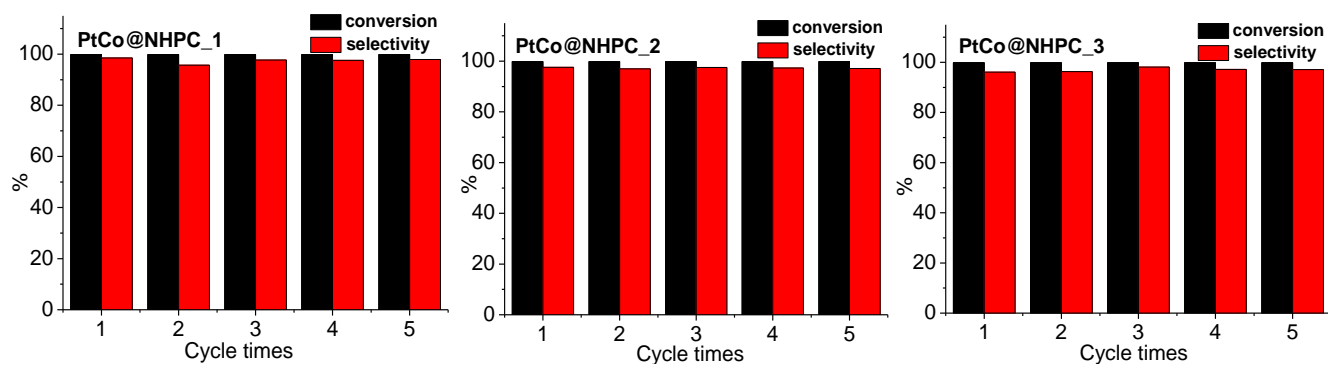
**Figure S53.** HPLC chromatograms of the product generated by hydrogenation of 4-nitroanisole by PtCo@NHPC<sub>1</sub>: (a) after hydrogen by PtCo@NHPC<sub>1</sub>; mixture of mesitylene, nitrobenzene, nitroanisole, 4-nitrophenol, aniline, anisidine and 4-aminophenol (b).

#### 4.9.5 Hydrogenation of 4-nitrobenzyl alcohol

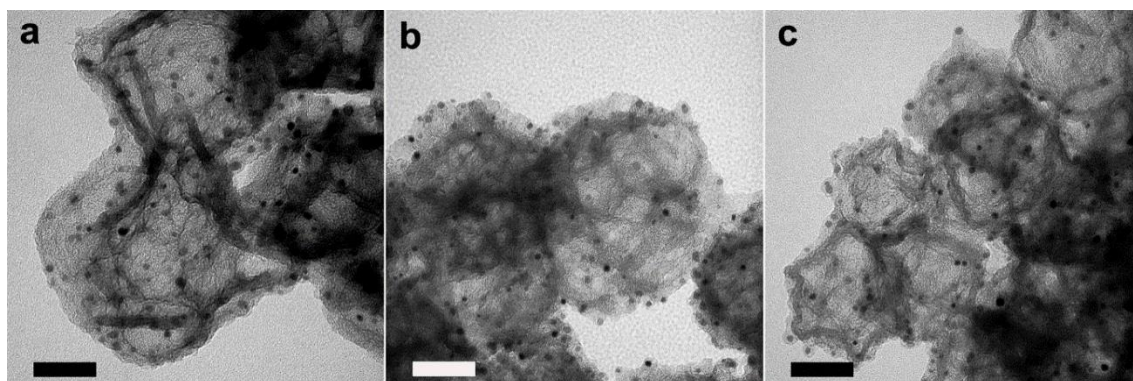
Column temperature was set at 298K and flowrate at 0.5 mL·min<sup>-1</sup>. UV/vis:  $\lambda=266$  nm. Gradient used: 0 min., 100% hexane; 0-20 min mark transition and hold from 20-23 min with 50% hexane, 50% 2-propanol; 23-26 min mark transition with 100% hexane; hold from 26-29 min with 100% hexane. The retention time of mesitylene, 4-nitrotoluene, 4-toluidin, 4-nitrobenzyl alcohol and 4-aminobenzyl alcohol are 7.1, 8.4, 16.3, 18.5 and 24.7 min, respectively.



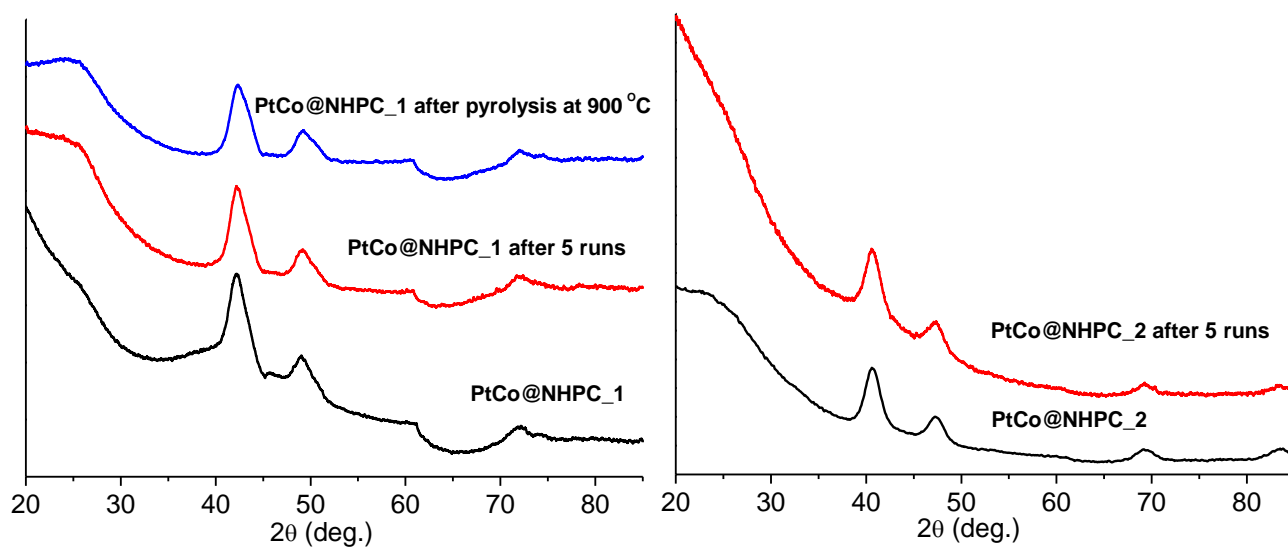
**Figure S54.** H HPLC chromatograms of the product generated by hydrogenation of 4-nitrobenzyl alcohol by PtCo@NHPC<sub>1</sub> (a); mixture of mesitylene, 4-nitrotoluene, 4-toluidine, 4-nitrobenzyl alcohol and 4-aminobenzyl alcohol (b).

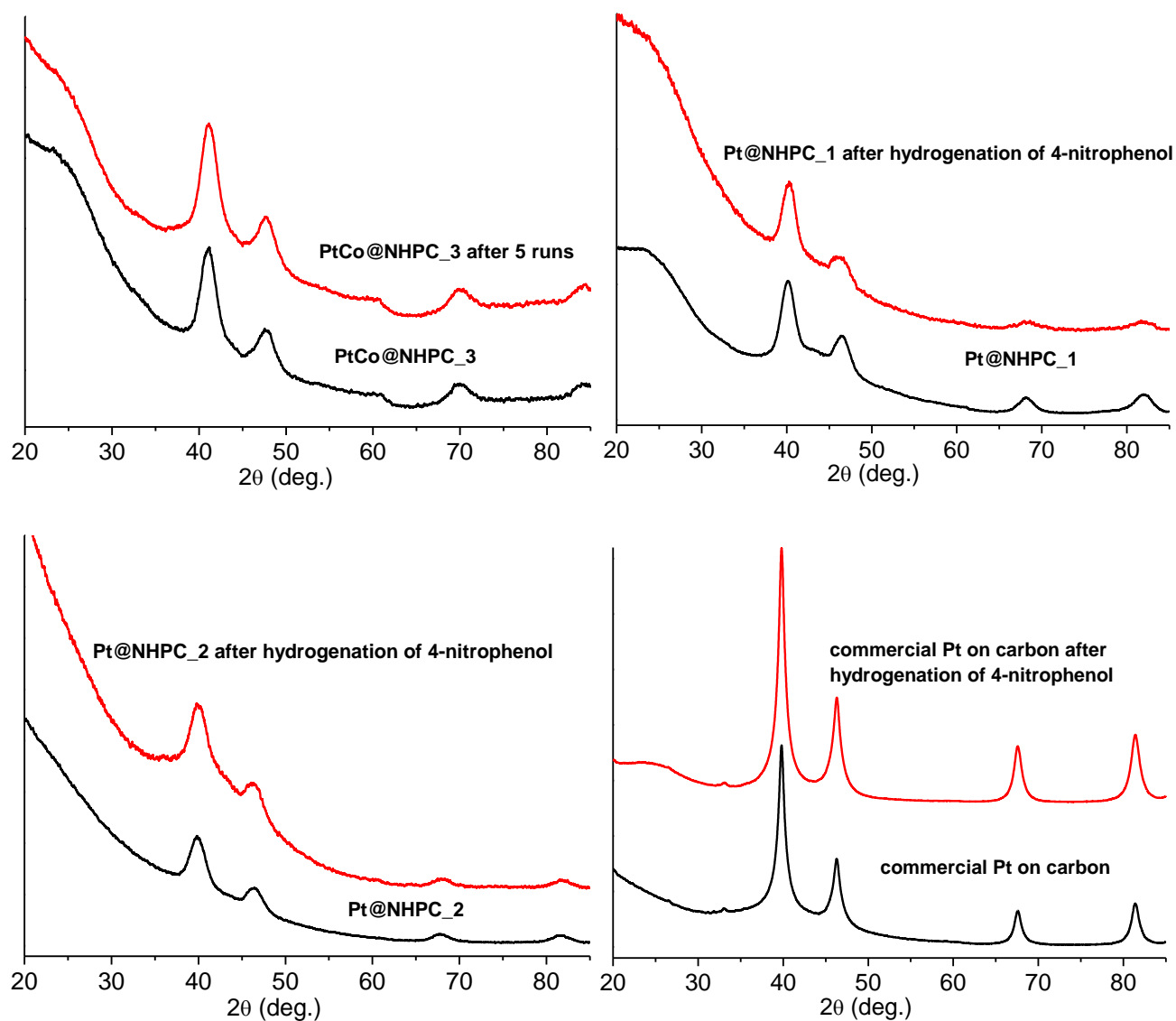


**Figure S55.** Recyclability test of the PtCo@NHPC catalysts.



**Figure S56.** TEM images of PtCo@NHPC\_1 (a), PtCo@NHPC\_2 (b) and PtCo@NHPC\_3 (c) after 5 times hydrogenation of 4-nitrophenol. The scale bar represent 50 nm.





**Figure S57.** PXRD patterns of materials.

#### 4.9.6 Turnover frequency (TOF) calculations

Turnover frequencies (TOF) were measured by using 2 mg of catalyst without otherwise altering the catalysis reaction conditions described above. This slowed the progress of the reaction to so that only ~25% of the nitroarenes was consumed over 40 mins. In a typical experiment, 0.5 mmol of 4-nitrophenol, 5 mL of methanol and 2 mg of catalyst were added into a autoclave reactor (50 mL), which was sealed and purged with H<sub>2</sub> several times then heated for 40 min at 50 °C under 6.8 bar H<sub>2</sub> with stirring at 400 RPM. Mesitylene was used as internal standard. The TOFs of these three catalysts were calculated based on their total Pt content.

$$\text{TOF} = n_{\text{oC}} / t_{\text{n}_{\text{cat}}}$$

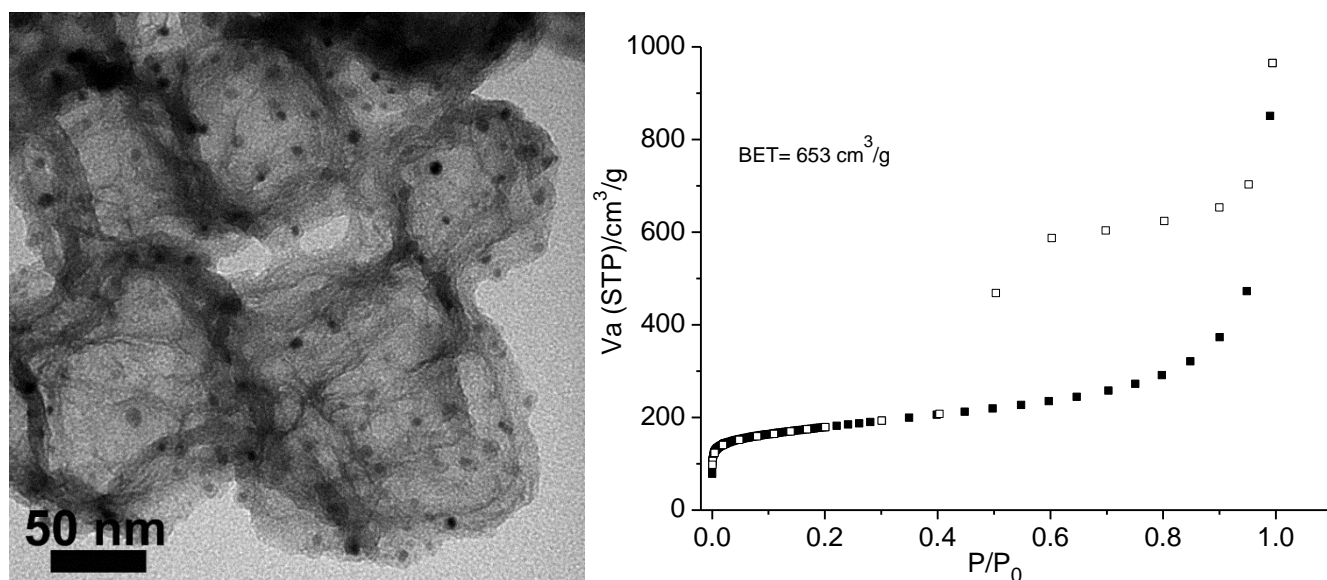
Where  $n_o$  is the initial number of moles of substrate,  $C$  is the percentage conversion of the substrate at a reaction time of  $t$  (h), and  $n_{cat}$  is number of moles of Pt in the catalyst.

**Table S2.** TOFs calculated for PtCo@NHPC catalysts.

catalyst	Co (wt%)	Pt (wt%)	TOF ( $\text{mol}_{\text{converted}} \text{h}^{-1} \text{mol}_{\text{Pt}}^{-1}$ )
PtCo@NHPC_1	3.74	1.72	872
PtCo@NHPC_2	1.4	1.56	1136
PtCo@NHPC_3	2.11	1.63	931

#### 4.9.7 Thermal stability of PtCo@NHPC\_1

PtCo@NHPC\_1 was transferred into a ceramic crucible and placed into a temperature-programmable furnace under a dry argon flow and heated from room temperature to 900 °C over a period of 300 min. After reaching the target temperature, the sample was calcined for a further 3 h at 900 °C then cooled to room temperature.

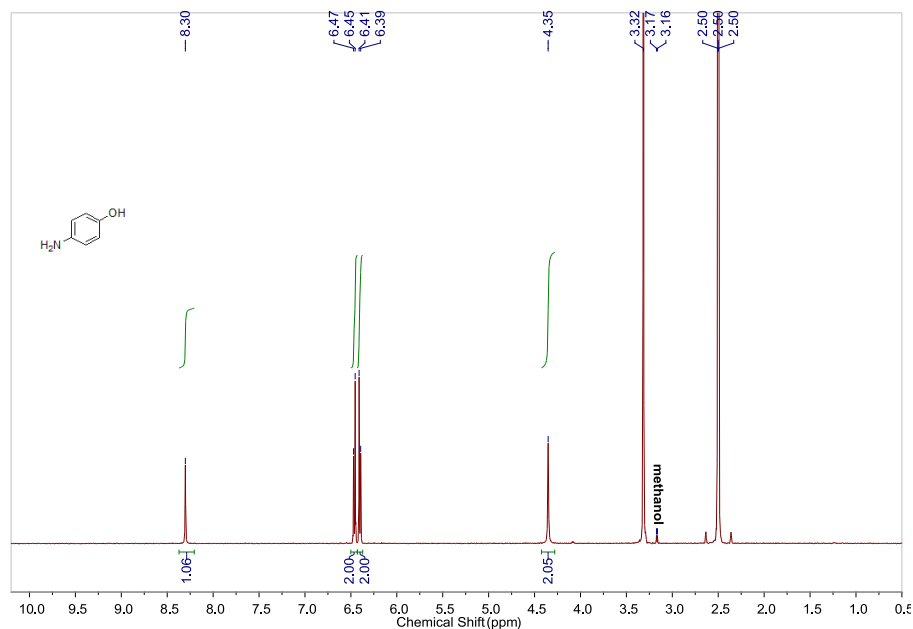


**Figure S58.** TEM image and N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms of PtCo@NHPC\_1 after calcination at 900 °C for 3 h.

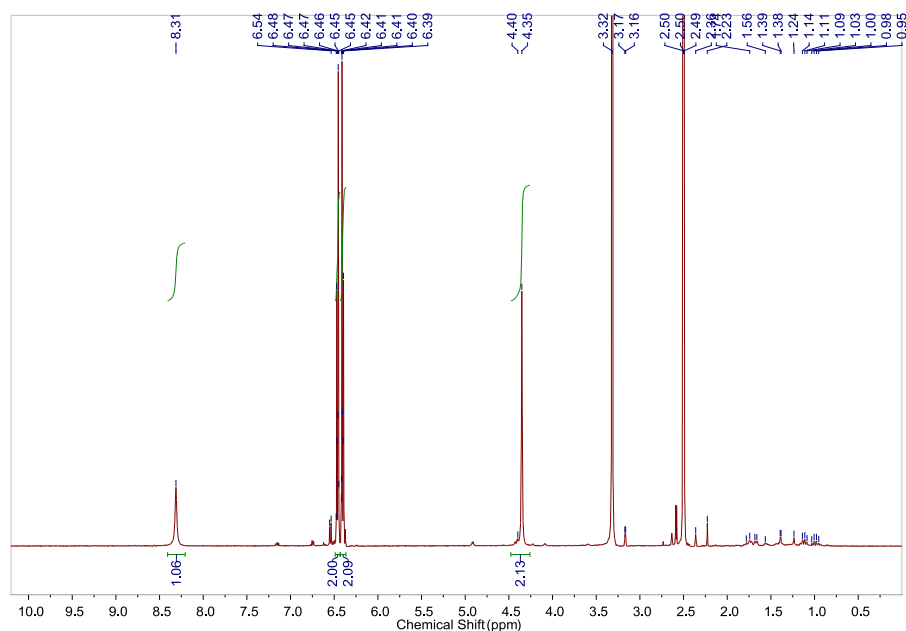


#### 4.9.8 Large-scale hydrogenation of nitroarenes by PtCo@NHPC\_1 and commercial Pt/C

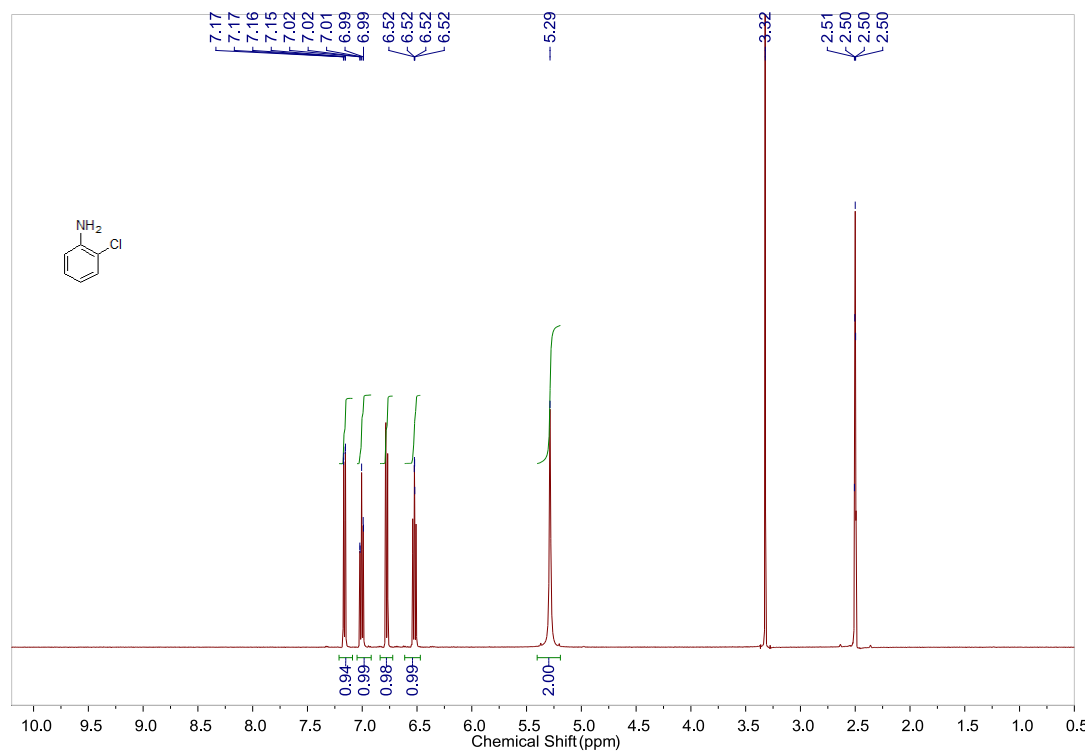
In a typical experiment, 5 mmol of nitroarenes, 5 mL of methanol and 50 mg of catalyst were added into an autoclave reactor (50 mL), which was sealed, purged with H<sub>2</sub> several times, then heated to 80 °C under 6.8 bar H<sub>2</sub> for 3 h with stirring at 400 RPM. Volatiles were removed *in vacuo* then the products analysed by <sup>1</sup>H NMR spectroscopy without further purification.



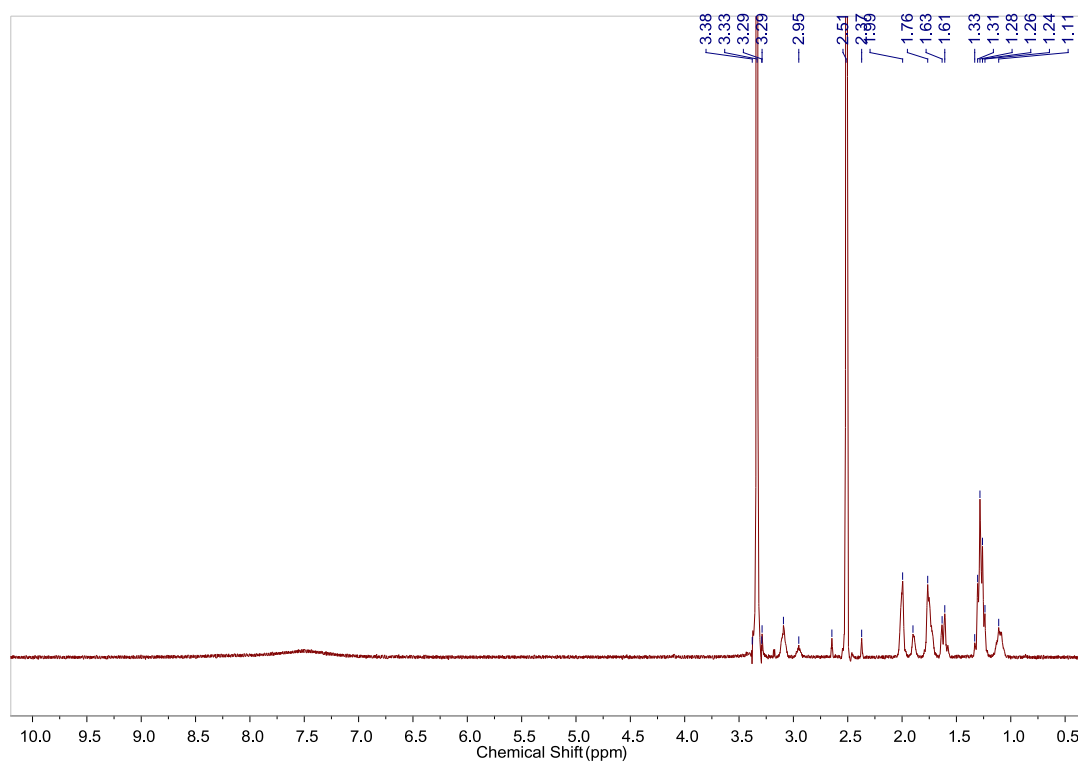
**Figure S59.** <sup>1</sup>H NMR spectrum of 4-aminophenol generated by hydrogenation of 4-nitrophenol on a 5 mmol scale by PtCo@NHPC\_1.



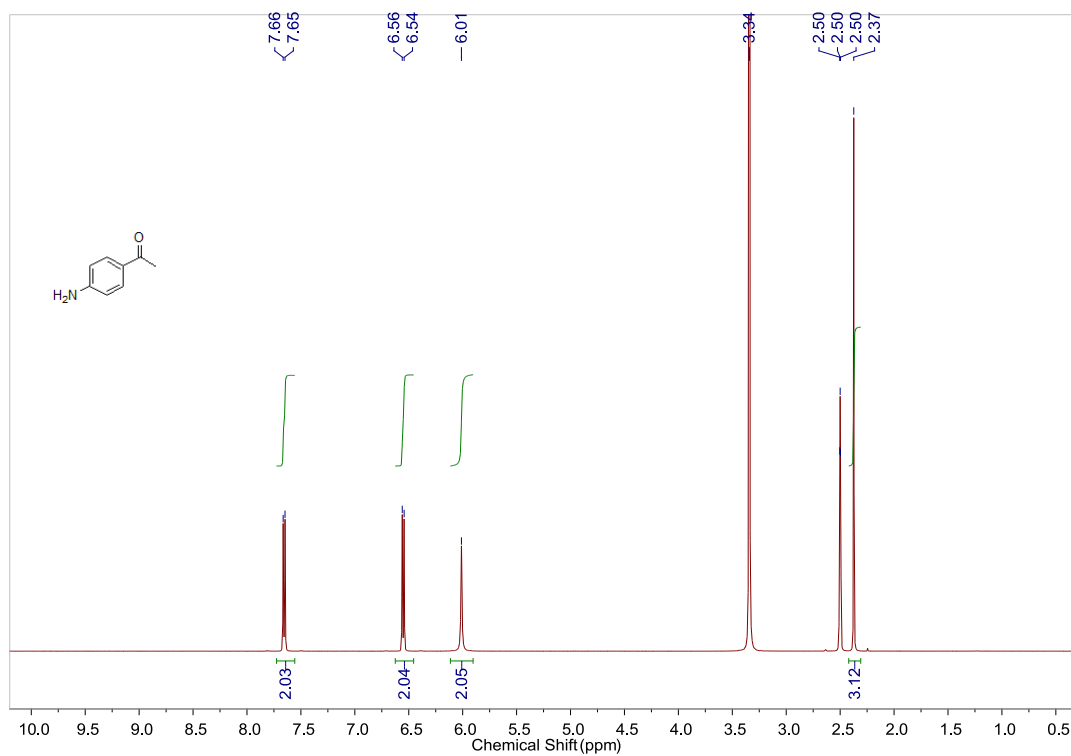
**Figure S60.** <sup>1</sup>H NMR spectrum of the products generated by hydrogenation of 4-nitrophenol on a 5 mmol scale by commercial Pt/C.



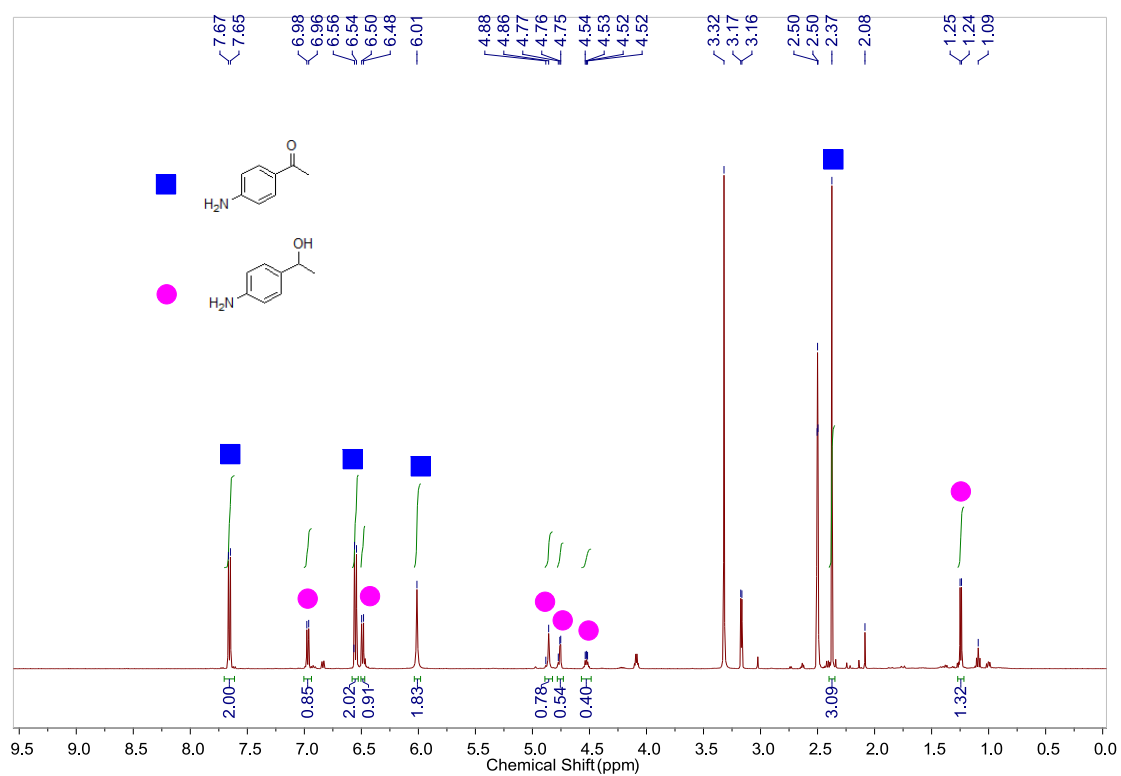
**Figure S61.**  $^1\text{H}$  NMR spectrum of the 2-chloroaniline generated by hydrogenation of 1-chloro-2-nitrobenzene on a 5 mmol scale by PtCo@NHPC\_1.



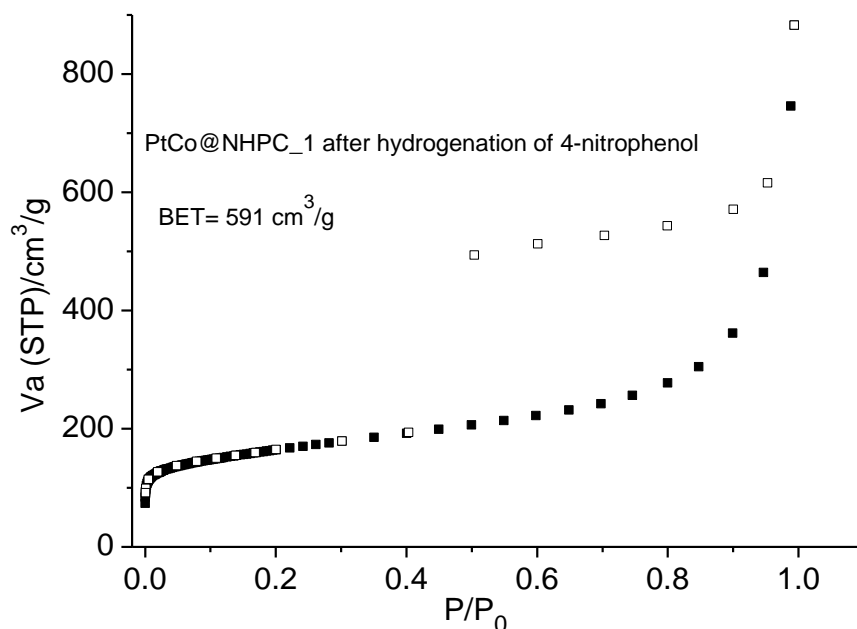
**Figure S62.**  $^1\text{H}$  NMR spectrum of the product generated by hydrogenation of 1-chloro-2-nitrobenzene on a 5 mmol scale by commercial Pt/C.



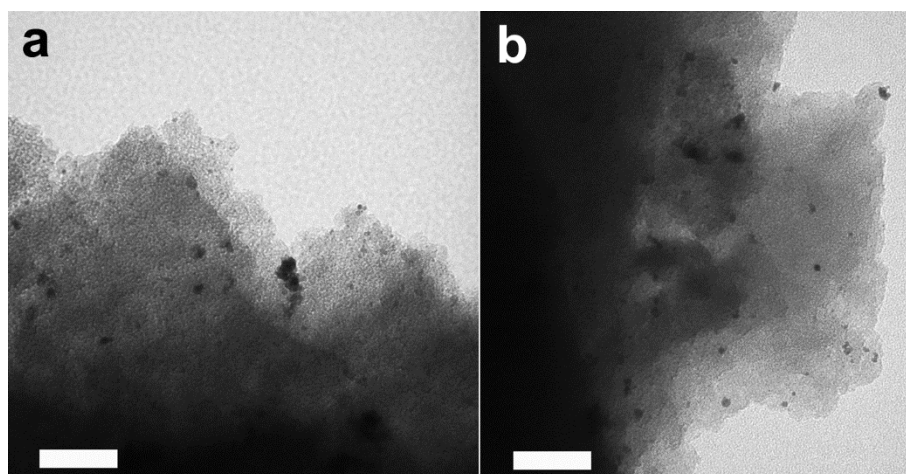
**Figure S63.**  $^1\text{H}$  NMR spectrum of the 4-aminoacetophenone generated by hydrogenation of 4-nitroacetophenone on a 5 mmol scale by PtCo@NHPC<sub>1</sub>.



**Figure S64.**  $^1\text{H}$  NMR spectrum of the product generated by hydrogenation of 4-nitroacetophenone on a 5 mmol scale by commercial Pt/C.



**Figure S65.** N<sub>2</sub> adsorption (filled symbols) and desorption (open symbols) isotherms measured at 77 K.



**Figure S66.** TEM images of commercial Pt/C before (a) and after (b) hydrogenation of 4-nitrophenol. The scale bars represent 50 nm.

## 5. References

- (1) Venna, S. R.; Jasinski, J. B.; Carreon, M. A. *J. Am. Chem. Soc.* **2010**, *132*, 18030.
- (2) Wu, R.; Qian, X.; Zhou, K.; Wei, J.; Lou, J.; Ajayan, P. M. *ACS Nano* **2014**, *8*, 6297.
- (3) Wu, R.; Wang, D. P.; Rui, X.; Liu, B.; Zhou, K.; Law, A. W.; Yan, Q.; Wei, J.; Chen, Z. *Adv. Mater.* **2015**, *27*, 3038.
- (4) Teranishi, T.; Hosoe, M.; Tanaka, T.; Miyake, M. *J. Phys. Chem. B* **1999**, *103*, 3818.
- (5) Desroches, J.; Champagne, P. A.; Benhassine, Y.; Paquin, J.-F. *Org. Biomol. Chem.* **2015**, *13*, 2243.