

## Electronic supplementary information

### 1.1. Synthesis and carbonization of bimetallic MOF-74s

Typically, H<sub>4</sub>DHTP (1.5 g, 7.8 mmol) and metal-salts (22.8 mmol) was dissolved in 340 mL of a solvent mixture of DMF:EtOH:H<sub>2</sub>O = 15:1:1 (based on volume) in a Teflon-lined autoclave (500 ml). The metal salts (Zn/Ni/Mn(II) nitrate hexahydrate) comprised any of the combination of 100Zn, 75Zn25Ni/Mn, 50Zn50Ni/Mn and 100Ni/Mn. The Teflon liner containing the slurry was sealed in a stainless steel bomb-reactor and heated at 110 °C for 24 h. After finishing the reaction, the reactors were cooled to room temperature and the product was separated by filtration. The obtained precipitate was adequately washed with DMF and ethanol, and dried in an oven at 100 °C for overnight.

The as-obtained MOF-74s crystals were then carbonized using a tubular furnace (GSL-1500X-50-UL) under N<sub>2</sub>-flow. An aluminum boat containing 1 g of ground MOF-74 crystals was placed in the middle of the tube furnace and the temperature was raised to 1000 °C with a heating rate of 2 °C/min and hold for 6 h at 1000 °C. The carbonized materials were collected after the furnace was cooled to room temperature.

### 1.2. Preparation of MnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and MnO/AC

MnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and MnO/AC were prepared by using impregnation method. An aqueous solution of manganese(II) salts, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and (CH<sub>3</sub>COO)<sub>2</sub>Mn·4H<sub>2</sub>O, were impregnated to the dried γ-Al<sub>2</sub>O<sub>3</sub> and AC, respectively. The γ-Al<sub>2</sub>O<sub>3</sub> impregnated with Mn(NO<sub>3</sub>)<sub>2</sub> was dried under vacuum at 80 °C and calcined at 350 °C for 2 h under air to give MnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. The MnO/AC was obtained by low pressure evaporation of (CH<sub>3</sub>COO)<sub>2</sub>Mn-loaded AC at 50 °C and further treating at 300 °C for 2 h under N<sub>2</sub>.

## 2. Catalytic tests and regeneration of the catalysts

*Oxidation of BA.* The MDNM(100Zn), MDNM(75Zn25Mn), MDNM(50Zn50Mn), and MDNM(100Mn) together with MnO/AC and MnO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> were used as catalysts for the oxidation of BA. To a three-necked round-bottomed flask, BA (0.5 mmol), H<sub>2</sub>O (2 mL), and activated catalyst (10 mg) were added and the mixture was stirred for 24 h at 110 °C under atmospheric conditions. After finishing the reaction, the products were separated from the catalyst by a syringe-filter (polytetrafluoroethylene, hydrophobic, 0.5 μm), subsequently analyzed with a UV-vis absorption spectra measurement (UV-1800, Shimadzu) (at 248 nm) to estimate the conversion of BA into benzaldehyde.

*Oxidative and adsorptive desulfurization of DBT.* To the DBT solution (10 mL, 1,000 mg/L, in n-octane) in a glass reactor (30 mL) equipped with a condenser, acetonitrile (5 mL), H<sub>2</sub>O<sub>2</sub> (0.114 mL, 30% aqueous solution) and dried catalyst (20 mg) were added. Acetonitrile was used as an extractive solvent, H<sub>2</sub>O<sub>2</sub> acted as oxidant; and MDNM(100Zn), MDNM(75Zn25Mn) and MDNM(100Mn) were applied as the catalysts. Then the reaction mixtures were vigorously stirred at 80 °C for the set times. The liquid portion, after cooled down to room temperature after finishing the reaction, was separated by filtration using a syringe filter. The n-octane (nonpolar) and acetonitrile (polar) phases were separated, and the residual concentration of DBT in the n-octane was analyzed using UV absorbance at 325.6 nm. The oxidized product (dibenzothiophene sulfone) was also confirmed by UV at 277 nm.

The batch adsorption of DBT over the MDNM(100Zn), MDNM(75Zn25Mn) and MDNM(100Mn) was also conducted to compare the ODS and ADS efficiencies in removing DBT from the model fuel. The adsorption tests were carried out similar to oxidative desulfurization with MDNM(100Zn), MDNM(75Zn25Mn) and MDNM(100Mn). Dried MDNMs (20 mg each) were added to the DBT solution (10 mL, 1,000 mg/L); however, H<sub>2</sub>O<sub>2</sub> was not added. The mixture, maintained at 80 °C, was shaken for the set times. The liquid

portion was collected by filtration and residual DBT in n-octane was analyzed using UV absorbance.

*Reduction of 4-NP.* The MDNM(100Zn), MDNM(75Zn25Ni), MDNM(50Zn50Ni), and MDNM(100Ni) were applied as catalysts in the reduction of 4-NP in water. For the catalytic reduction of 4-NP, the aqueous solution of 4-NP (20 mL, 1,000 mg/L) was mixed with the freshly prepared NaBH<sub>4</sub> aqueous solution (0.5 M, 1.0 mL). Then the catalyst (0.01 g) was added to the reaction mixture, and the reaction was monitored by UV absorbance at 400 nm.

*Recycling of catalysts.*

The recyclability of the catalysts such as MDNM(75Zn25Ni) and MDNM(75Zn25Mn) was examined for the reduction of 4-NP and aerobic oxidation of BA, respectively, at the very same reaction conditions as described above after adequate regeneration. The catalyst MDNM(75Zn25Ni) was separated magnetically and MDNM(75Zn25Mn) was recovered by filtration from the reaction mixture after each catalytic reaction. The separated MDNM(75Zn25Ni) and MDNM(75Zn25Mn) were washed thoroughly with water, and ethanol, respectively, and then dried under vacuum at 100 °C for overnight.

**Table S1** Explanation on the MOF-74s and the obtained MDNMs, via pyrolysis of the MOF-74s.

Precursor MOFs	Composition (at%) of constituent metals in the precursors for MOF-74s	Carbonized products, MDNMs
MOF-74(100Zn)	100%Zn	MDNM(100Zn)
MOF-74(75Zn25Ni)	75%Zn, 25% Ni	MDNM(75Zn25Ni)
MOF-74(50Zn50Ni)	50%Zn, 50% Ni	MDNM(50Zn50Ni)
MOF-74(100Ni)	100% Ni	MDNM(100Ni)
MOF-74(75Zn25Mn)	75%Zn, 25% Mn	MDNM(75Zn25Mn),
MOF-74(50Zn50Mn)	50%Zn, 50% Mn	MDNM(50Zn50Mn)
MOF-74(100Mn)	100%Mn	MDNM(100Mn)

**Table S2** Unit cell parameters of MOF-74s.

Materials	a= b	c	Cell volume
MOF-74 (calculated)	31.86	12.85	11295.33
MOF-74(100Zn)	31.65	12.81	11118.55
MOF-74(75Zn25Mn)	31.35	12.74	10843.38
MOF-74(50Zn50Mn)	31.22	12.69	10710.17
MOF-74(100Mn)	31.23	12.65	10685.47
MOF-74(75Zn25Ni)	31.39	12.71	10850.92
MOF-74(50Zn50Ni)	31.34	12.73	10829.80
MOF-74(100Ni)	31.27	12.72	10772.55

**Table S3** Chemical compositions of MOF-74s and MDNMs

Materials	Ni (wt%)	Mn (wt%)	Zn (wt%)
MOF-74(75Zn25Ni)	8.3	–	19.8
MDNM(100Ni)	92.1	–	–
MDNM(50Zn50Ni)	77.8	–	0.18
MDNM(75Zn25Ni)	43.9	–	0.19
MOF-74(75Zn25Mn)	–	8.54	17.3
MDNM(100Mn)	–	40.0	–
MDNM(50Zn50Mn)	–	26.0	0.01
MDNM(75Zn25Mn)	–	19.8	0.41
MnO/AC	–	29.3	–
MnO <sub>2</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	–	19.1	–

**Table S4** Estimated d-spacing from corresponding HR-TEM and SAED analyses. Calculated d-spacings based on crystal structures of Ni and MnO are also shown.

Materials	hkl	d-spacing (nm)		
		calculated	HR-TEM	SAED pattern
MDNM(75Zn25Ni)	111*	0.205	0.205	0.203
	200*	0.176	0.179	0.173
MDNM(75Zn25Mn)	111**	0.256	0.253	0.253
	200**	0.222	0.219	0.221

\*hkl of FCC Ni, \*\*hkl of cubic MnO

**Table S5** Pseudo-first-order rate constants and correlation coefficients of the oxidation and adsorption of DBT over MDNM(100Zn), MDNM(75Zn25Mn) and MDNM(100Mn) and at 70 °C.

Materials	Rate constant $k$ ( $\text{min}^{-1}$ )	$R^2$	Remark
MDNM(100Mn)	$1.4 \times 10^{-2}$	0.995	Calculated based on both oxidation and adsorption
MDNM(75Zn25Mn)	$6.4 \times 10^{-2}$	0.991	Calculated based on both oxidation and adsorption
MDNM(100Zn)	$7.7 \times 10^{-3}$	0.994	Calculated based on both oxidation and adsorption
MDNM(100Mn)	$1.2 \times 10^{-2}$	0.993	Calculated based on oxidation only
MDNM(75Zn25Mn)	$5.8 \times 10^{-2}$	0.978	Calculated based on oxidation only
MDNM(100Zn)	$7.7 \times 10^{-4}$	0.992	Calculated based on oxidation only



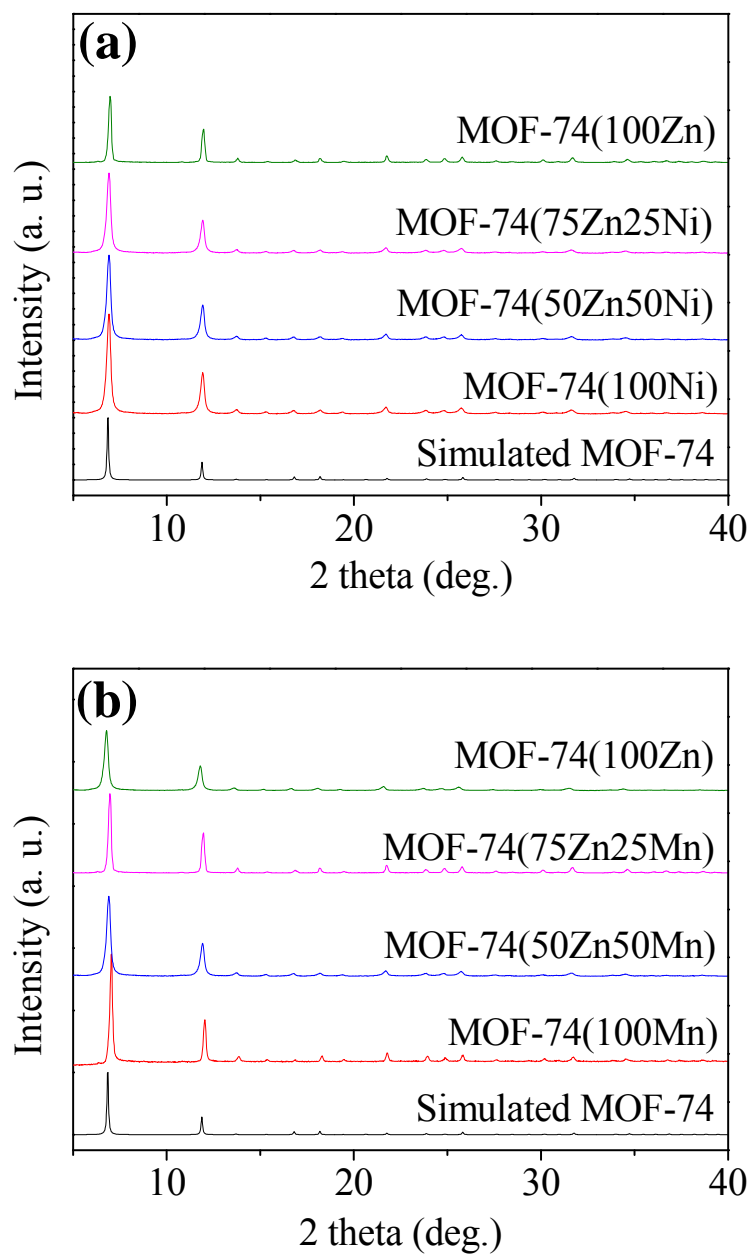
**Table S6** Comparison of the rate constant for the reduction of 4-NP over the reported catalysts and the MDNM(75Zn25Ni).

Catalysts	Reaction conditions			$k$ (s <sup>-1</sup> )	Relative k-values <sup>c</sup>	Ref.
	NaBH <sub>4</sub> /4-NP (mol/mol)	4-NP conc. (M) <sup>a</sup>	Catalyst/4-NP (mg/mg) <sup>b</sup>			
MDNM(75Zn25Ni)	3.5×10 <sup>0</sup>	3.0×10 <sup>-3</sup>	5.0×10 <sup>-1</sup>	4.2×10 <sup>-3</sup>	13.1	This work
Ni/RGO	1.0×10 <sup>3</sup>	2.0×10 <sup>-4</sup>	3.6×10 <sup>1</sup>	1.8×10 <sup>-3</sup>	5.62	[1]
Ni/RGO	3.0×10 <sup>2</sup>	4.2×10 <sup>-1</sup>	4.7×10 <sup>0*</sup>	2.5×10 <sup>-4</sup>	0.78	[2]
Ni/RGO	1.3×10 <sup>3</sup>	3.9×10 <sup>-4</sup>	1.1×10 <sup>2</sup>	1.2×10 <sup>-3</sup>	3.75	[3]
Ni NPs	2.0×10 <sup>2</sup>	9.0×10 <sup>-4</sup>	7.2×10 <sup>1*</sup>	2.7×10 <sup>-3</sup>	8.43	[4]
RANEY <sup>®</sup> Ni	2.0×10 <sup>2</sup>	9.0×10 <sup>-3</sup>	7.2×10 <sup>1*</sup>	3.2×10 <sup>-4</sup>	1	[4]

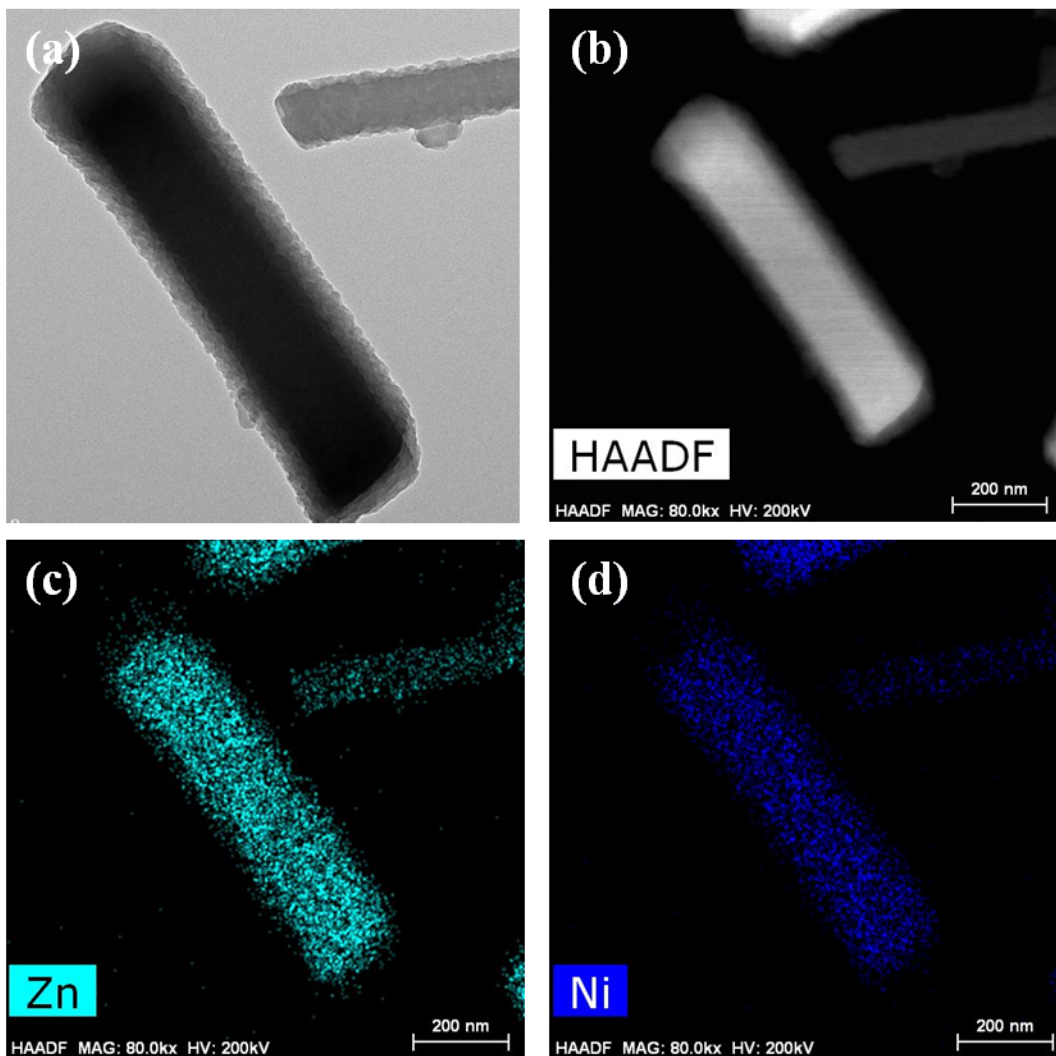
<sup>a</sup>Molar concentration of 4-NP in water.

<sup>b</sup>The amount of catalyst is based on total weight of catalyst (rather than pure Ni); however, the weights when showed with“\*” symbol are based on pure Ni.

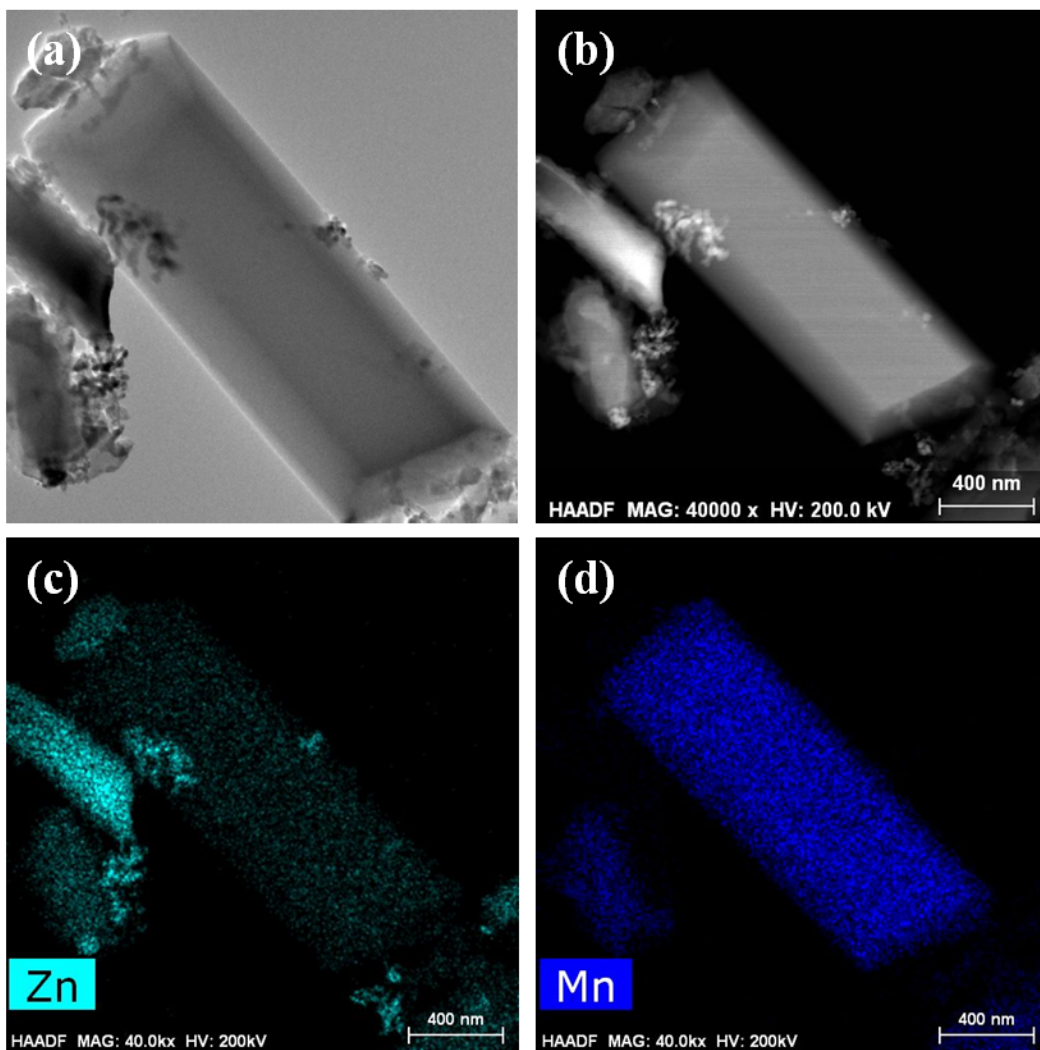
<sup>c</sup>The relative  $k$  values were calculated in comparison with the  $k$ -value of RANEY<sup>®</sup>Ni (as unity).



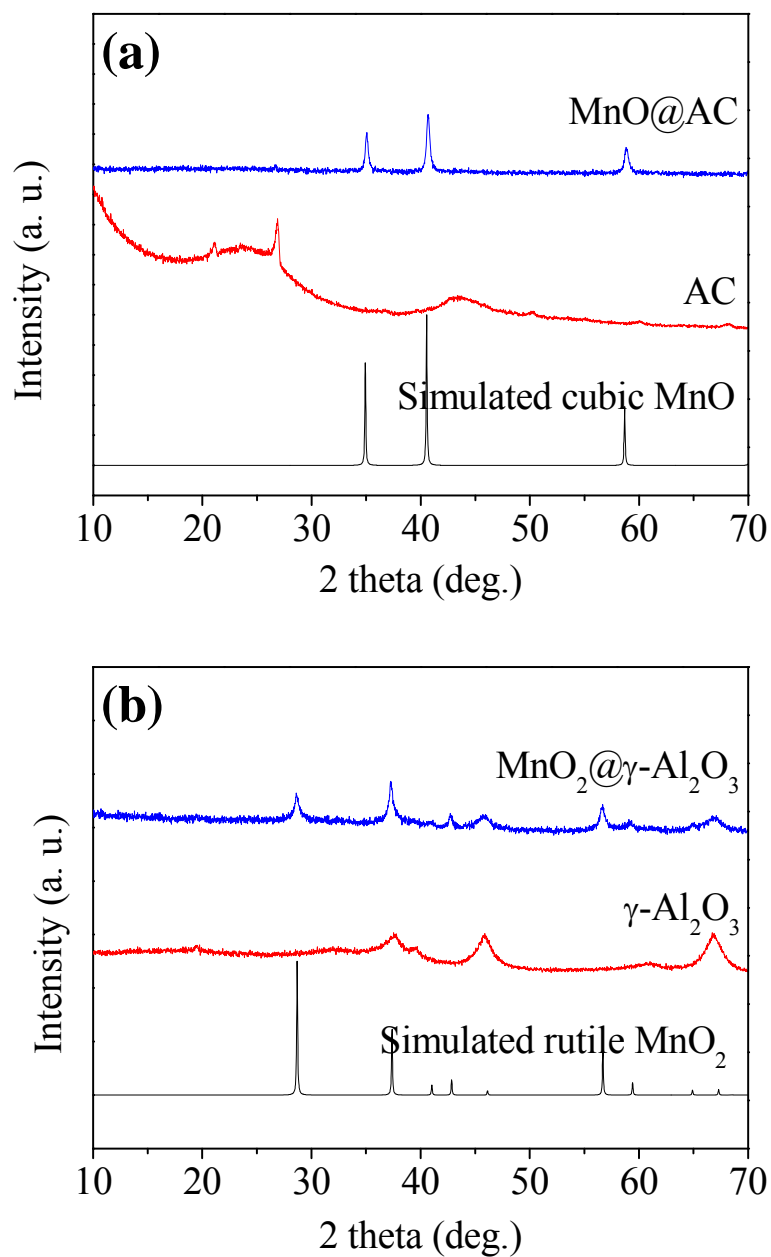
**Fig. S1** XRD patterns of the (a) MOF-74(100Ni), MOF-74(50Zn50Ni), MOF-74(75Zn25Ni), and MOF-74(100Zn) and (b) MOF-74(100Mn), MOF-74(50Zn50Mn), MOF-74(75Zn25Mn), and MOF-74(100Zn). Simulated XRD patterns of the MOF-74 was also shown on figure a and b, for comparison.



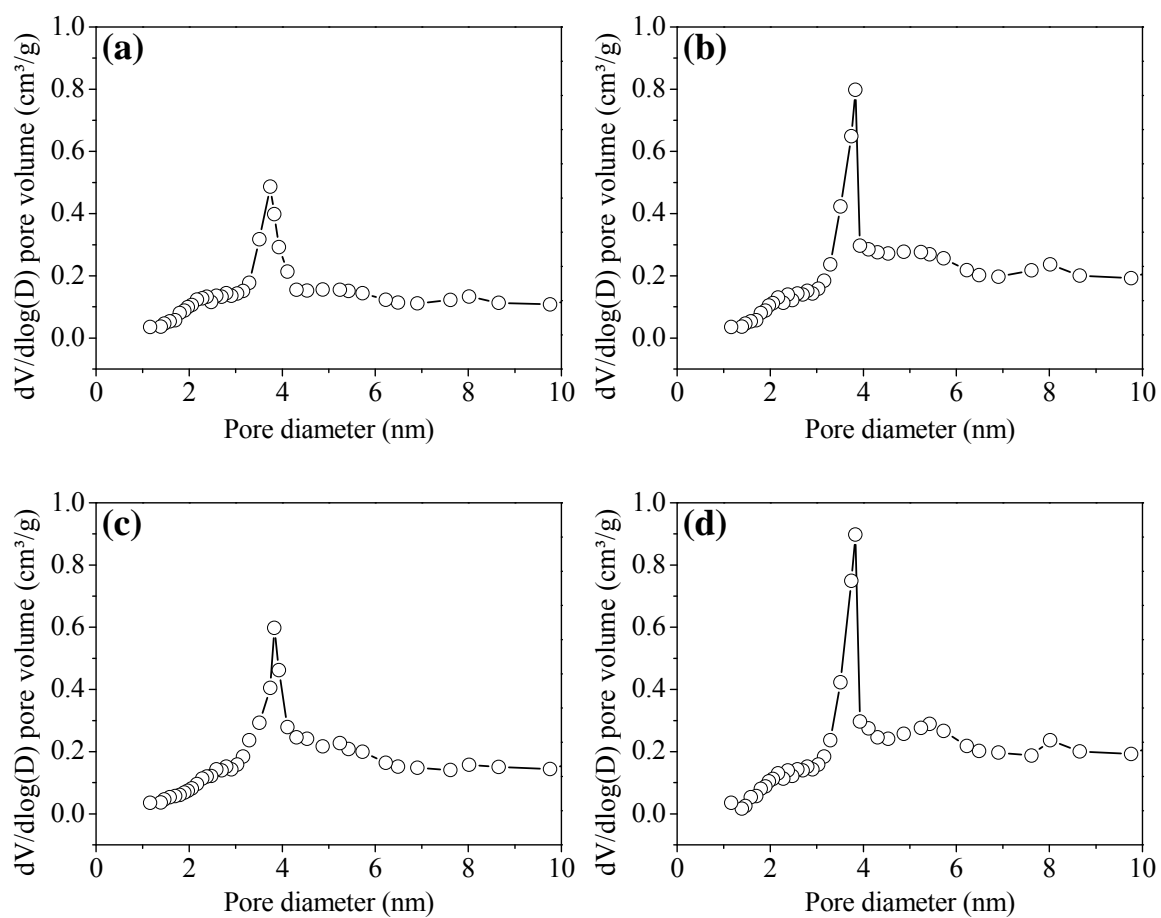
**Fig. S2** (a) FE-TEM image, (b) HADIF image, (c) mapping of Zn and (d) mapping of Ni for the MOF-74(75Zn25Ni).



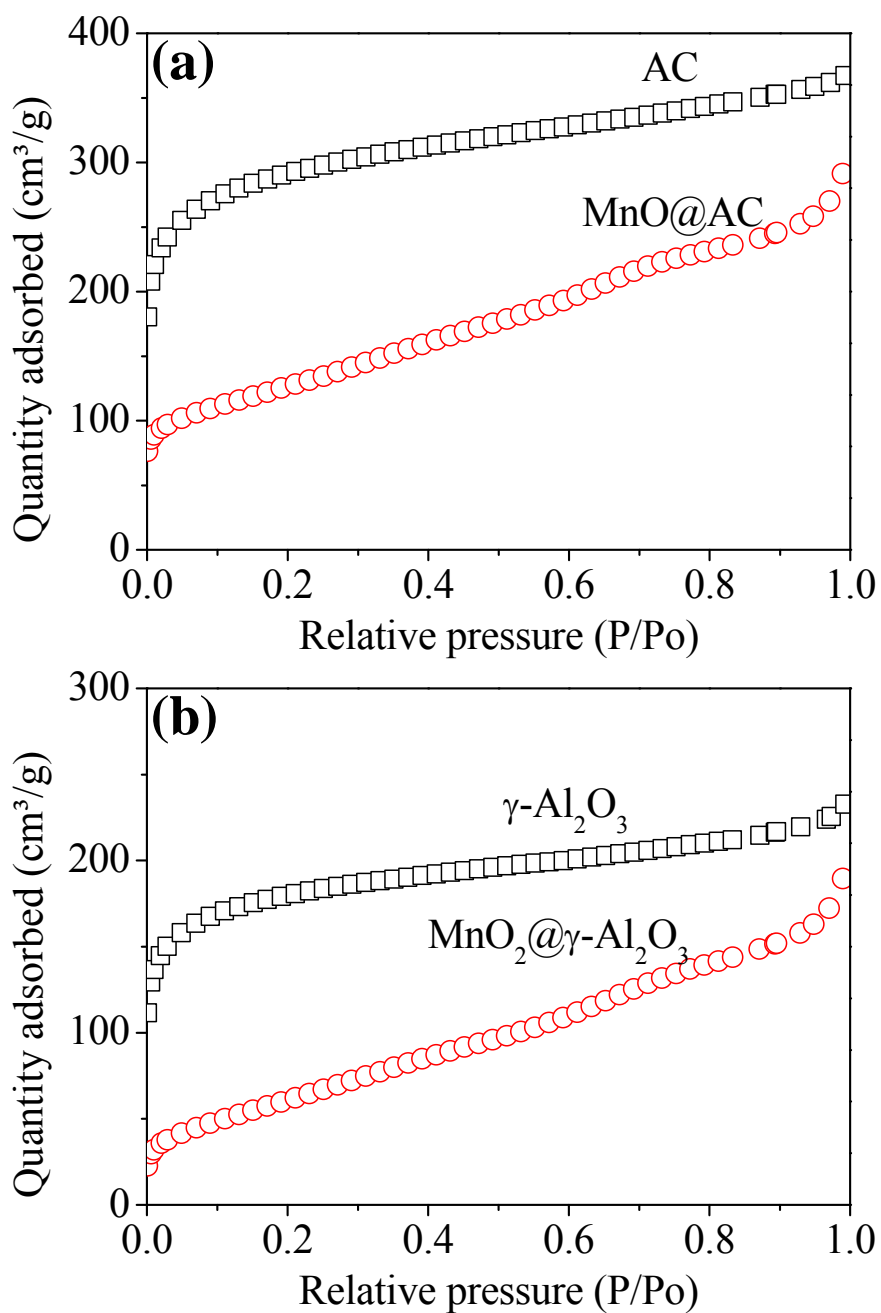
**Fig. S3** (a) FE-TEM image, (b) HADIF image, (c) mapping of Zn and (d) mapping of Mn for the MOF-74(75Zn25Mn).



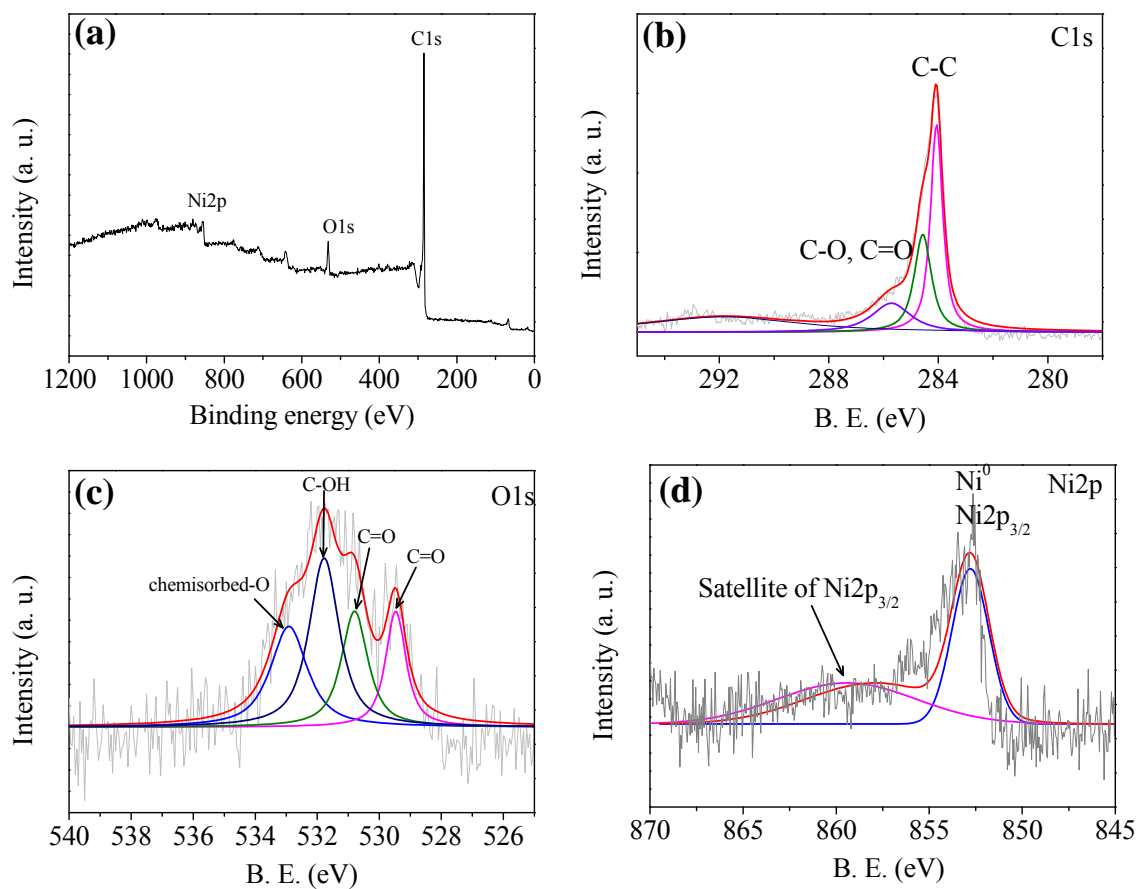
**Fig. S4** XRD patterns of the (a) AC and MnO@AC, and (b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>@ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Simulated XRD patterns of cubic MnO (manganosite) and rutile MnO<sub>2</sub> were also shown on figure a and b, respectively, for comparison.



**Fig. S5** Pore size distribution (PSD) curves of (a) MDNM(50Zn50Ni), (b) MDNM(75Zn25Ni), (c) MDNM(50Zn50Ni) and (d) MDNM(75Zn25Mn). The PSD curves were obtained from the desorption branches of the  $\text{N}_2$ -isotherms.

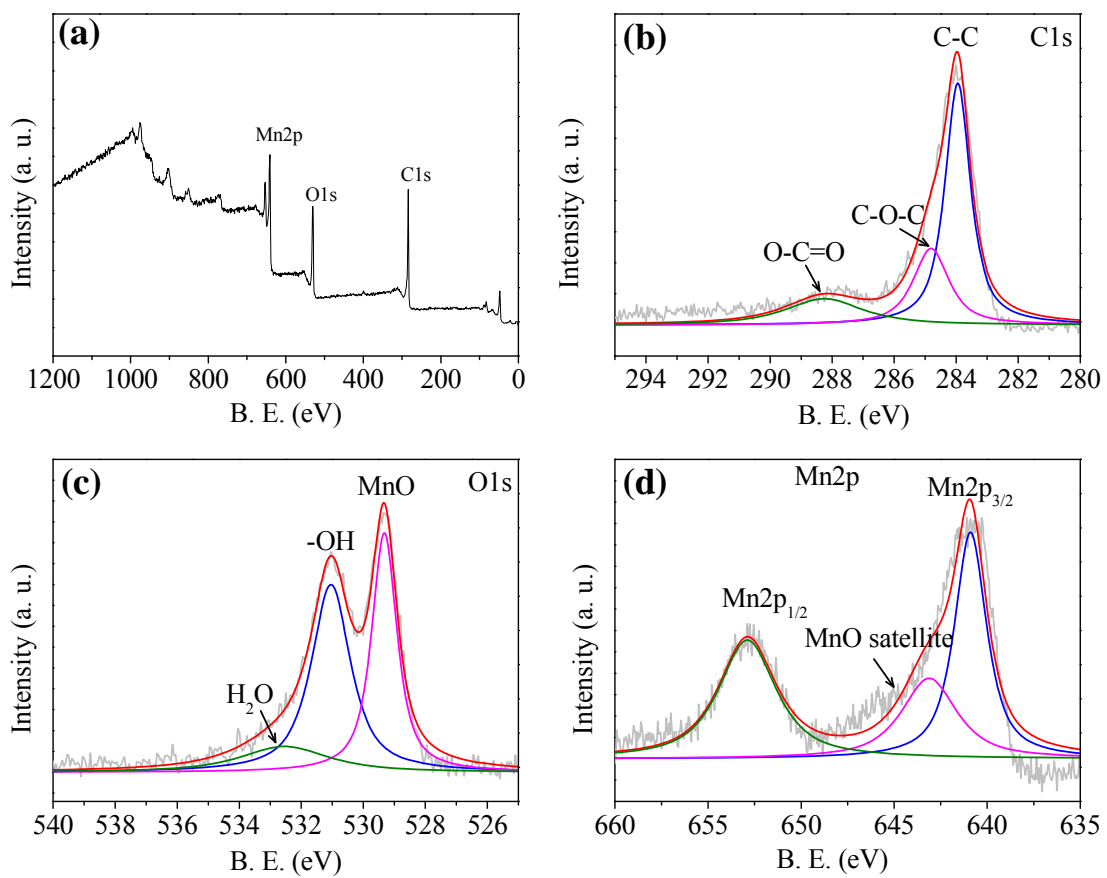


**Fig. S6** N<sub>2</sub> adsorption-desorption isotherms of the (a) AC and MnO@AC, and (b)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>@ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

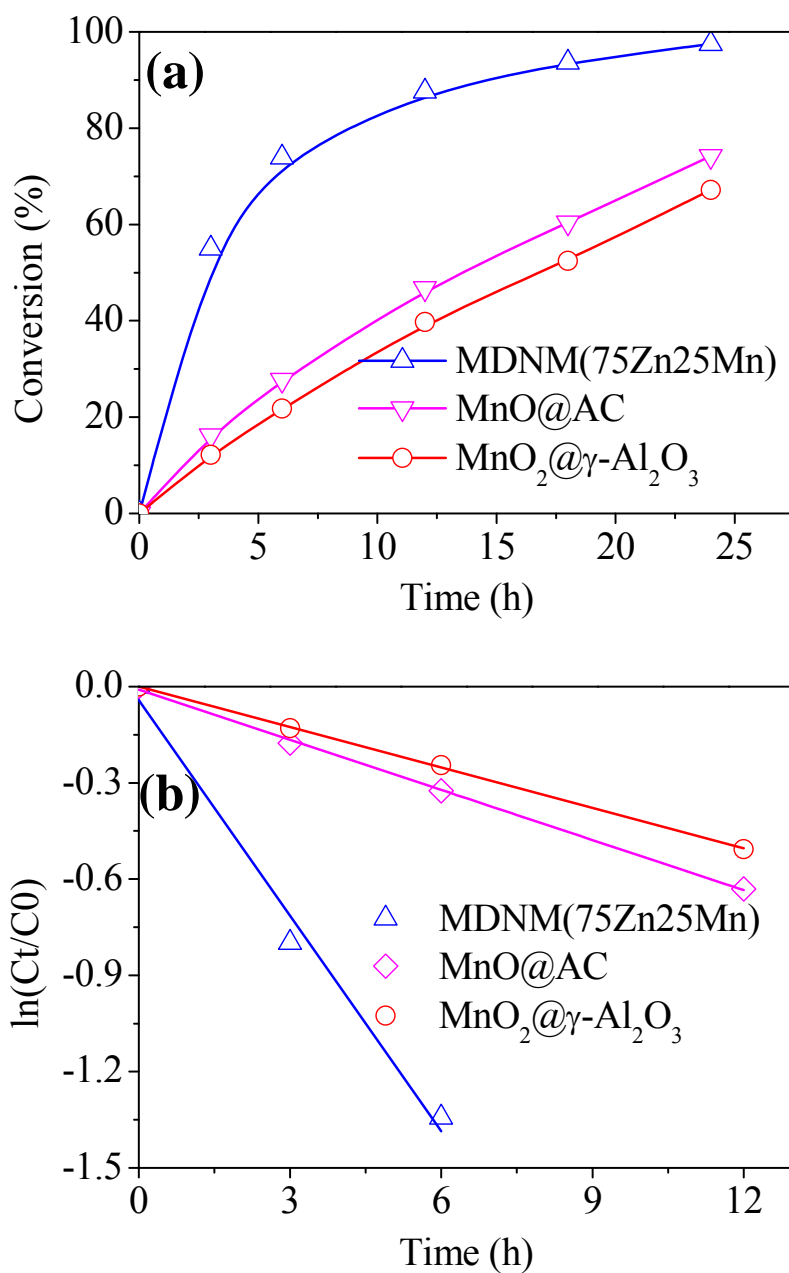


**Fig. S7** (a) XPS survey spectrum, and high resolution (b) C<sub>1s</sub>, (c) O<sub>1s</sub> and (d) Ni<sub>2p</sub> spectra of MDNM(75Zn25Ni).

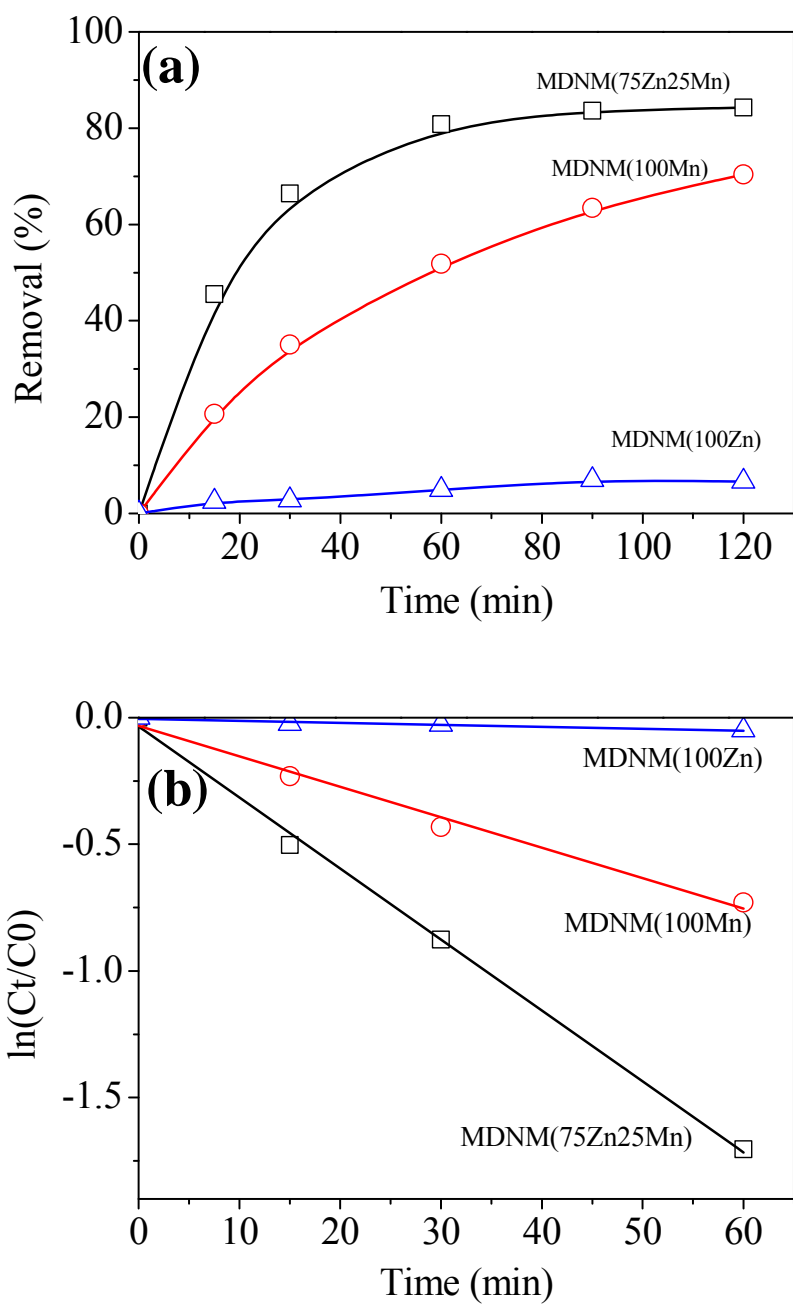




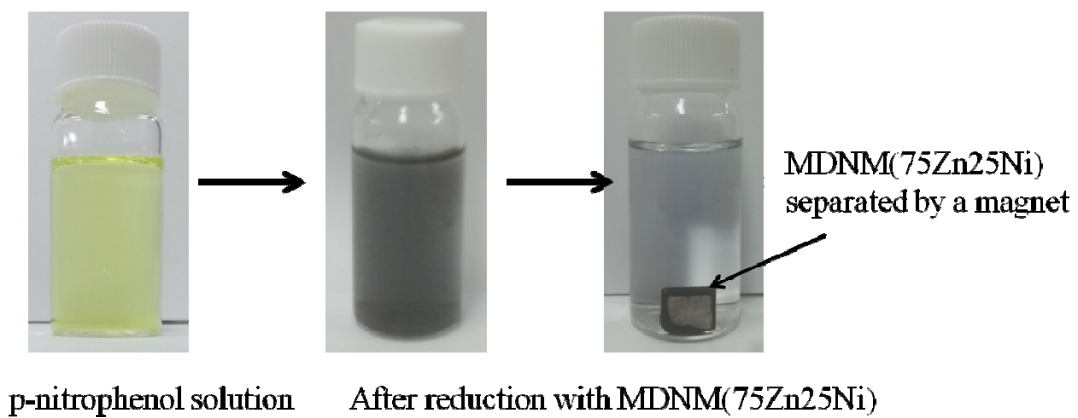
**Fig. S8** (a) XPS survey spectrum, and high resolution (b) C<sub>1s</sub>, (c) O<sub>1s</sub> and (d) Mn<sub>2p</sub> spectra of MDNM(75Zn25Mn).



**Fig. S9** (a) Effect of time on conversion of benzyl alcohol over MDNM(75Zn25Mn), AC, MnO@AC and MnO<sub>2</sub>@ γ-Al<sub>2</sub>O<sub>3</sub> at 110 °C. (b) Plots of the pseudo-first-order kinetics for the benzyl alcohol oxidation.



**Fig. S10** (a) Effect of time on removal of DBT based on only oxidation (contribution of adsorption in removal was eliminated) with MDNM(100Zn), MDNM(100Mn) and MDNM(75Zn25Mn) catalysts at 80 °C. (b) plots of pseudo-first-order kinetics based on the data in figure (a).



**Fig. S11** Pictograms to show the reduction of 4-NP over MDNM(75Zn25Ni) in water from the change of solution color; and the magnetic separation of the used catalyst.

## References

1. Y. Tian, Y. Liu, F. Pang, F. Wang and X. Zhang, *Colloids Surf., A*, 2015, **464** 96-103.
2. Z. Ji, X. Shen, G. Zhu, H. Zhou and A. Yuan, *J. Mater. Chem.*, 2012, **22**, 3471-3477.
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