

**Supporting information**

**Identifying active sites of CoNC/CNT from pyrolysis of  
molecularly defined complexes for oxidative esterification  
and hydrogenation reactions**

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**EELS analysis:** The Co-L<sub>2,3</sub> intensity ratio was determined by the method described by Pearson et al. <sup>1</sup>A 50eV width window was selected beginning at 50 eV past the onset of the L<sub>3</sub> white line. The linear fit curve of the loss intensity in this energy interval was extrapolated toward smaller energy losses. This line was then modified into a double step with the same slope with onsets occurring at the white-line maxima. The ratio of the step heights was chosen as 2:1 in accordance with the multiplicity of the initial states (four 2p<sub>3/2</sub> electrons and two 2p<sub>1/2</sub> electrons).

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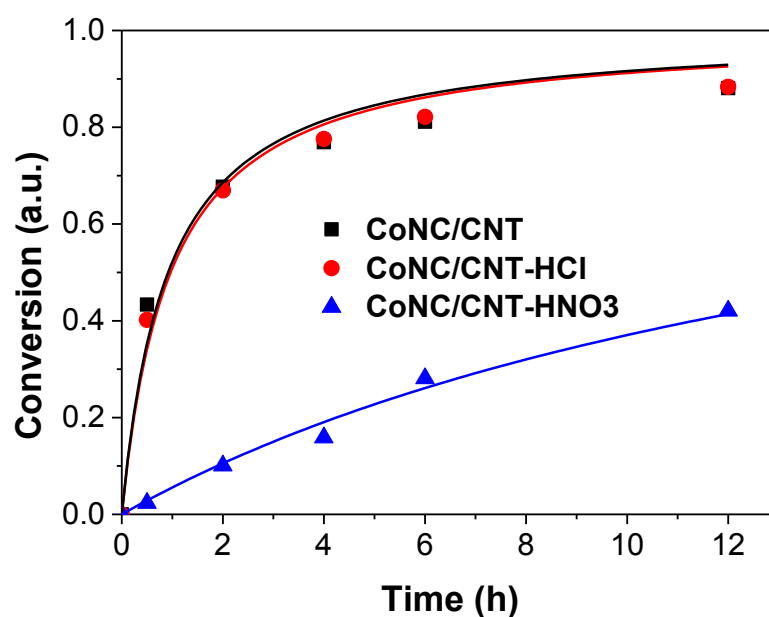
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**Table S1.** Catalytic performances of FeNC/CNT and CoNC/CNT catalysts in the oxidative esterification of BA (Scheme 1)<sup>a</sup>

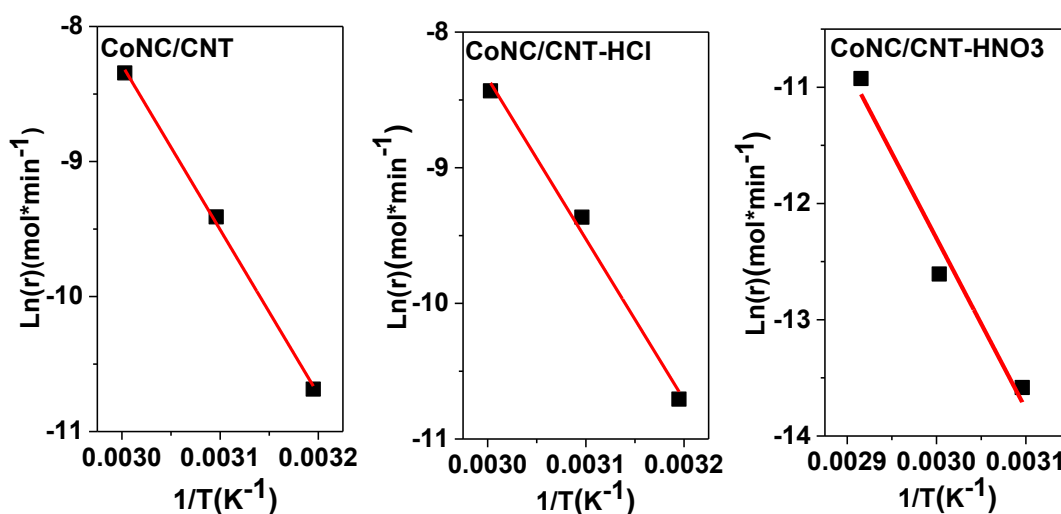
Entry	Catalysts	Composition	$S_{\text{BET}}$	Conv.	Selectivity (%)	
					BDH	MB
		Co/Fe/N (w%)	( $\text{m}^2/\text{g}$ )	(%)		
1	FeNC/CNT	-/1.54/0.33	131.4	24.5	82.9	17.1
2	CoNC/CNT	1.81-/1.42	155.9	88.1	8.4	91.6

<sup>a</sup> Reaction conditions: 0.4 ml BA, 32 ml  $\text{CH}_3\text{OH}$ , 0.1 g  $\text{K}_2\text{CO}_3$ , 0.2 g catalyst, 60 °C, 2 MPa  $\text{O}_2$ , 12 h

For comparison, FeNC/CNT catalyst was synthesized using 90 mg of  $\text{Fe}(\text{OAc})_2$ , 205 mg of 1,10-phenanthroline (Fe : phenanthroline = 1:2 (mol)) and 650 mg of CNTs with the same procedure. As shown in Table S1, the conversion of CoNC/CNT is about 3.5 folds higher than FeNC/CNT.



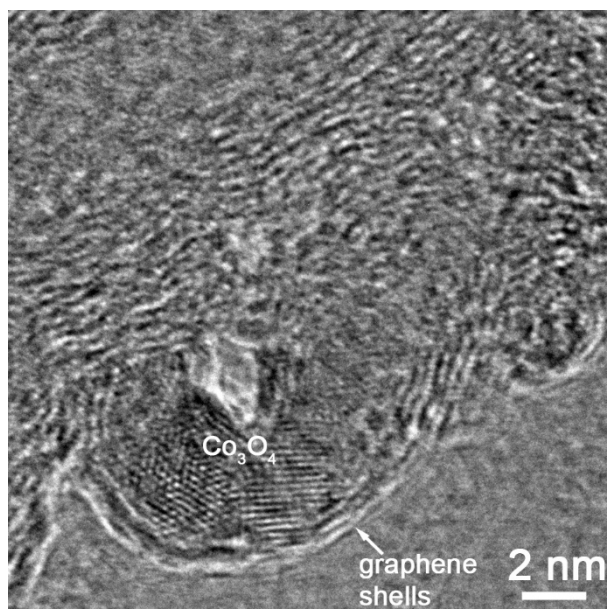
**Fig. S1** Time courses of CoNC/CNT, CoNC/CNT-HCl, CoNC/CNT-HNO<sub>3</sub> in the oxidative esterification of BA. The curves are fitted by the pseudo-second-order kinetics. Reaction conditions: 0.4 ml BA, 32 ml  $\text{CH}_3\text{OH}$ , 0.1 g  $\text{K}_2\text{CO}_3$ , 0.2 g catalyst, 60 °C, 2 MPa  $\text{O}_2$ .



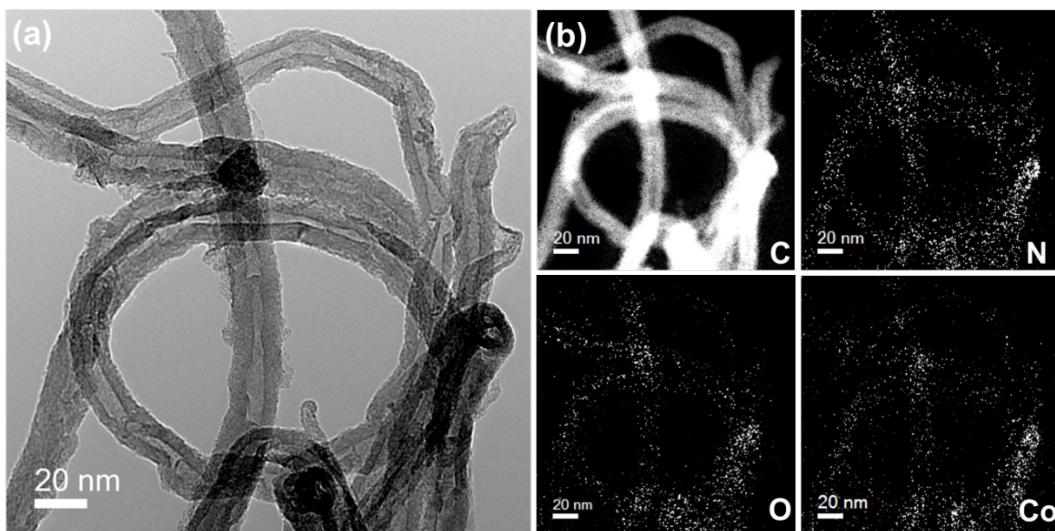
**Fig. S2** Arrhenius plots of the oxidative esterification over CoNC/CNT, CoNC/CNT-HCl and CoNC/CNT-HNO<sub>3</sub>. Different reaction conditions were used for different catalysts to ensure the conversion of BA lower than 10%.

Reaction conditions for CoNC/CNT and CoNC/CNT-HCl: 8 ml BA, 24 ml CH<sub>3</sub>OH, 0.1 g K<sub>2</sub>CO<sub>3</sub>, 0.05 g catalyst, 2 MPa O<sub>2</sub>.

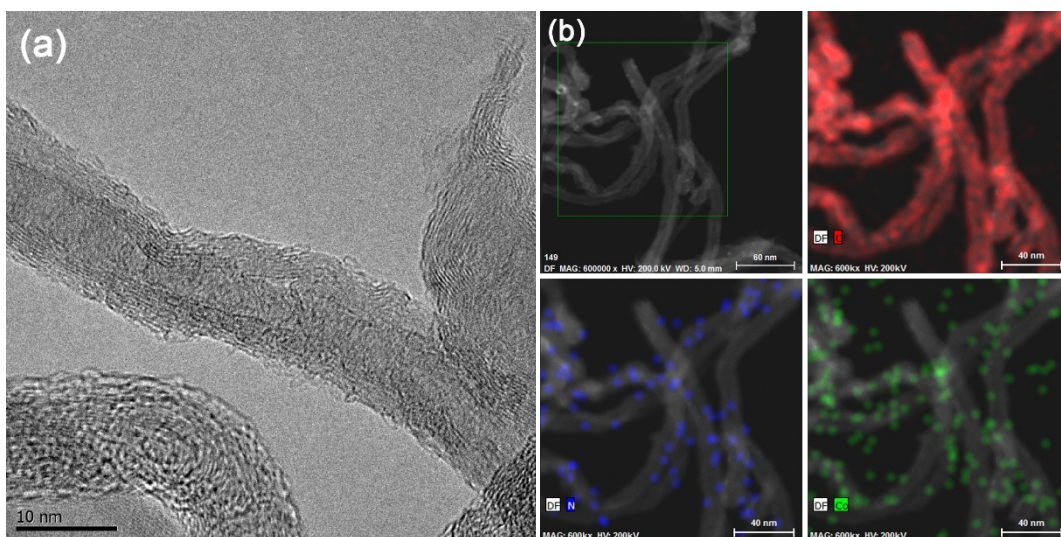
Reaction conditions for CoNC/CNT-HNO<sub>3</sub>: 0.4 ml BA, 32 ml CH<sub>3</sub>OH, 0.1 g K<sub>2</sub>CO<sub>3</sub>, 0.2 g catalyst, 2 MPa O<sub>2</sub>.



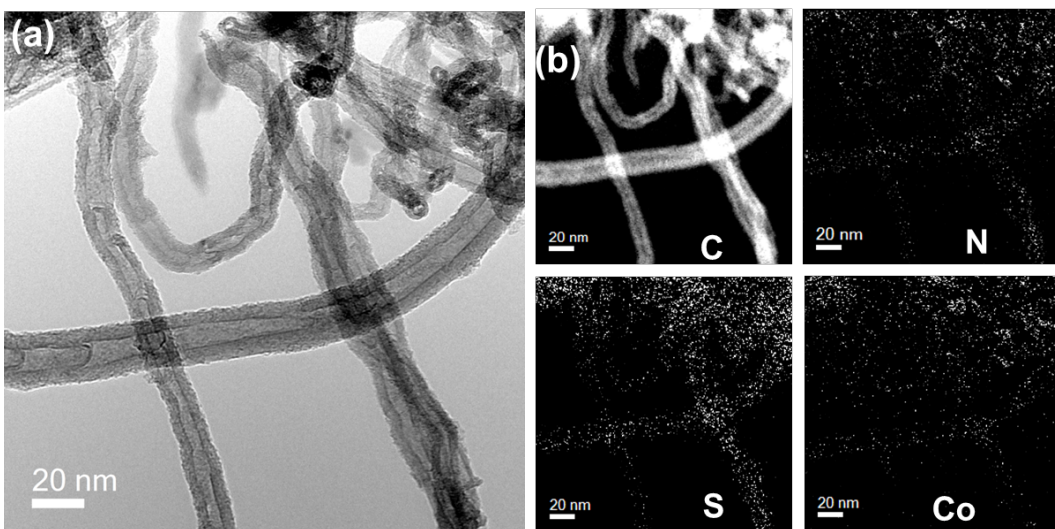
**Fig. S3** HRTEM image of a Co<sub>3</sub>O<sub>4</sub>@graphene core-shell structure on CoNC/CNT-HCl. This structure is only occasionally observed.



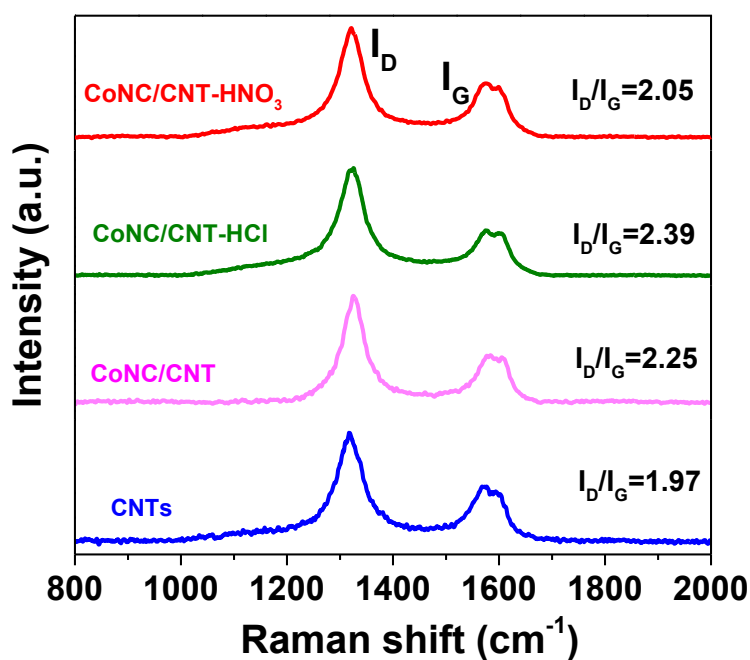
**Fig. S4** (a) TEM and (b) corresponding EFTEM images of CoNC/CNT-HCl.



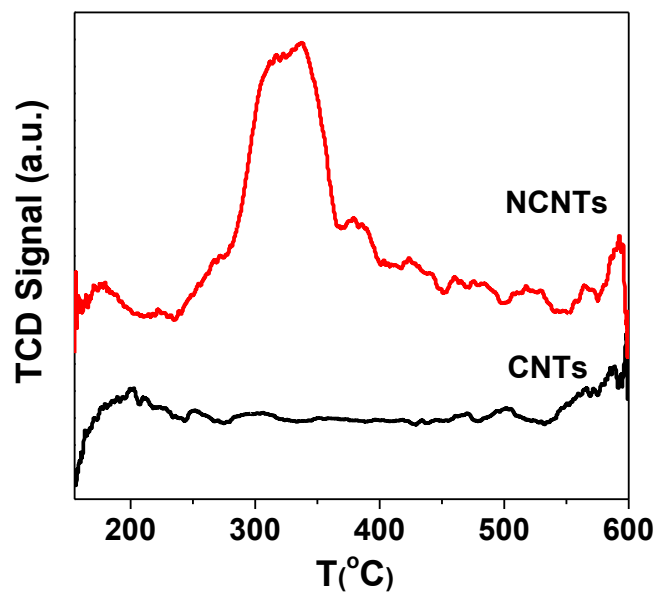
**Fig. S5** (a) HRTEM image and (b) STEM-EDS mapping images of CoNC/CNT-HCl



**Fig. S6** (a) TEM and (b) corresponding EFTEM images of CoNC/CNT-HCl after the adsorption of KSCN.



**Fig. S7** Raman spectra of CoNC/CNT, CoNC/CNT-HCl, CoNC/CNT-HNO<sub>3</sub> and CNTs. The I<sub>D</sub>/I<sub>G</sub> ratios of CoNC/CNT and CoNC/CNT-HCl are obviously higher than that of pristine CNTs, because of the formation of N-doped graphene during the pyrolysis. The I<sub>D</sub>/I<sub>G</sub> ratio of CoNC/CNT-HNO<sub>3</sub> is close to that of CNTs, indicating the destruction of the graphenes under oxidative HNO<sub>3</sub>.



**Fig. S8** H<sub>2</sub>S-TPD profiles of CNTs and N-doped CNTs.

#### References

1. D. H. Pearson, C. C. Ahn and B. Fultz, *Physical Review B*, 1993, **47**, 8471-8478.