Electronic Supplementary Material (ESI) for Green Chemistry.

Synthesis of ZIF-Derived Hollow Yolk-Shell Co@CN Catalyst for the Oxidative Esterification of 5-Hydroxymethylfurfural

Kang-kang Sun[a], *Shu-jie Chen*[b], *Ze-lin Li*[a], *Guo-Ping Lu*[a]* and *Chun Cai*[a]*

[a] Chemical Engineering College, Nanjing University of Science & Technology,

Xiaolingwei 200, Nanjing 210094, P. R. China.

[b] School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou

510006, P. R. China.

1 Experimental

1.1. Materials

All chemicals such as 2-Methylimidazole (2-MeIm), $Co(NO_3)_2\cdot6H_2O$, $Zn(NO_3)_2\cdot6H_2O$, tetraethyl orthosilicate (TEOS) and 5-Hydroxymethylfurfural (HMF) were purchased from commercial suppliers and used directly without further purification.

1.2. Synthetic procedures

1.2.1. Synthesis of ZIF-67@SiO_2@ZIF-8

ZIF-67@SiO_2@ZIF-8 was synthesized with the following steps. Typically, 0.45 g of $Co(NO_3)_2\cdot6H_2O$ and 0.5 mL of TEOS were dissolved in 3 mL of DI water. Meanwhile, 5.5 g of 2-MeIm was dissolved in 35 mL of DI water by sonication for 0.5 h. The obtained 2-MeIm solution was added to the above salt solution gradually and stirred for

6 h at room temperature. The ZIF-67@SiO_2 was obtained by centrifugation and washed with methanol for several times. After that, the obtained sample and 5.9 g of $Zn(NO_3)_2·6H_2O$ were dissolved in 100 mL of methanol. Then 6.1 g of 2-MeIm dissolved in 100 mL methanol was added to the above solution with stirring for 24 h at room temperature. The obtained sample was centrifuged and washed with methanol. The final product was dried under vacuum at 150 ℃ for 12 h.

1.2.2. Synthesis of Co@CN.

The pyrolysis of ZIF-67@SiO_2@ZIF-8 was carried out in a tubular furnace under a nitrogen atmosphere. The sample was heated from room temperature to 900 °C at a heating rate of 5 °C/min and kept at this temperature for 3 h. After cooling to room temperature, the obtained black powder was added into NaOH solution (0.5 M) and stirred under the protection of argon atmosphere for 48 h to remove the SiO_2 shell. The resulting Co@CN was isolated by centrifugation and washing with deionized water and methanol, and dried under vacuum overnight at 80 ºC.

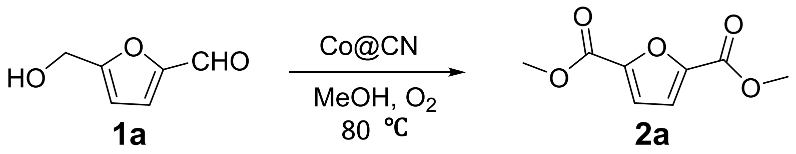
1.3. Characterization

GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. XRD analysis was performed on Shimadzu X-ray diffractometer (XRD-6000) with Cu Kα irradiation. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120 kv. High Resolution Transmission electron microscopy was performed on Philips-FEI Tecnai G2 F20 operating at 300kv. Scanning electron microscopy (SEM) images were performed using a Hitachi S-4800 apparatus on a sample powder previously dried and sputter-coated with a thin layer of gold. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250Xi spectrometer, using an Al Kα X-ray source (1350 eV of photons) and calibrated by setting the C 1s peak to 284.80 eV. Inductively coupled plasma mass spectrometry (ICP-MS) was analyzed on Optima 7300 DV. BET surface area and pore size measurements were performed with N_2 adsorption/desorption isotherms at 77 K on a Micromeritics ASAP 2020 instrument. Before measurements, the samples were degassed at 150 °C for 12 h.

1.4. Catalytic Reactions

Typically, a calculated mount of Co@CN (20 mg) in methanol (1 mL) was placed in a 25 mL sealed tube, and HMF (0.2 mmol) was added to the mixture under atmospheric oxygen with a magnetic to initiate the reaction at 80 °C for 12 h. After the reaction was completed, the liquid phase were analyzed by GC/MS. The yield of the product was determined by GC with nitrobenzene as an internal standard. The recyclability of the Co@CN was investigated under the same reaction conditions (0.2 mmol HMF in 1 mL of methanol, magnetically stirring, atmospheric oxygen, 80 °C, 12 h, catalysts 20 mg) by using the recovered catalysts. After each cycle, the catalyst was isolated from the solution by centrifugation, washed three times with methanol, and dried under vacuum to remove the residual solvent and then reused for another reaction cycle.

2. E Factor studies



Typically, a calculated amount of Co@CN (3.8 mol% of Co) in methanol (1 mL) was placed in a 25 mL sealed tube, and HMF (2 mmol, 252 mg) was added to the mixture under atmospheric oxygen with a magnetic to initiate the reaction at 80 °C for 24 h. After the reaction was completed, the solvent was removed under reduced pressure, and the crude product was purified by recrystallization with methanol to afford the pure product **2a** (309.1 mg, 84% yield). The catalyst was isolated from the solution by centrifugation, washed three times with methanol (2 mL*3), and dried under vacuum to remove the residual solvent and then reused for another reaction cycle.

$$\begin{aligned}\begin{matrix}\text{E factor}\\\text{without recycling}\\\text{solvent}\end{matrix} &= \frac{\text{total organic solvent wastes (kg)}}{\text{product (kg)}}\\ &= \frac{\text{methanol (solvent)}}{\text{isolated pure product}}\\ &= \frac{791.8*7\text{ mg}}{309.1\text{ mg}}\\ &= 17.9\end{aligned}$$

$$\begin{aligned}\begin{matrix}\text{E factor}\\\text{recycling}\\\text{solvent}\end{matrix} &= \frac{\text{total organic solvent wastes (kg)}}{\text{product (kg)}}\\ &= \frac{\text{methanol (solvent)}}{\text{isolated pure product}}\\ &= \frac{791.8*7*14\%\text{ mg}}{309.1\text{ mg}}\\ &= 2.5\end{aligned}$$

3. XRD patterns

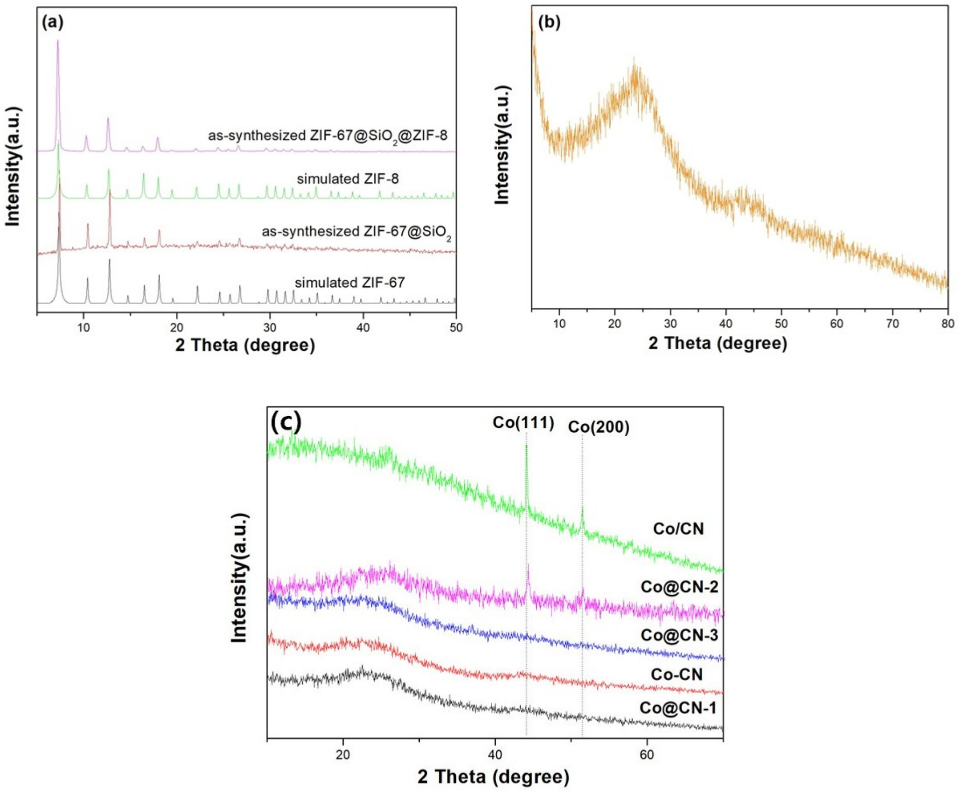
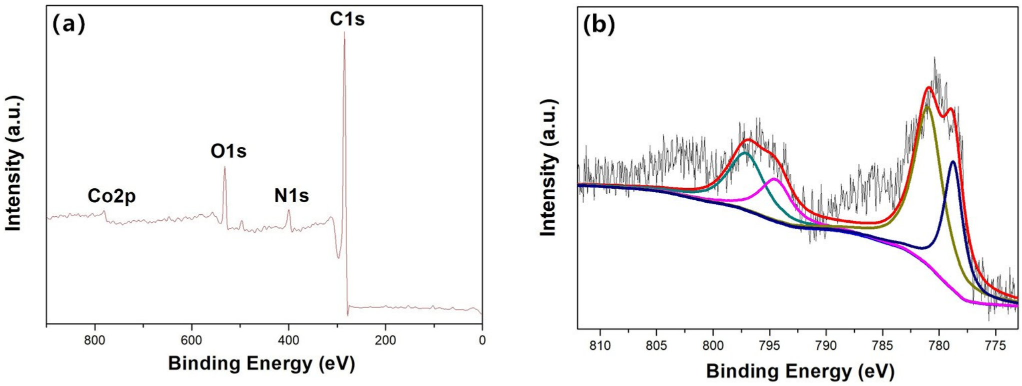


Fig. S1. XRD patterns of (a) simulated ZIF-67, as-synthesized ZIF-67@SiO$_2$, simulated ZIF-8, and as-synthesized ZIF-67@SiO2@ZIF-8; (b) Co@CN; (c) Co/CN, Co@CN-2, Co@CN-3, Co-CN and Co@CN-1; Co@CN-3 is the catalyst after being recycled for 5 times.

4. XPS spectra



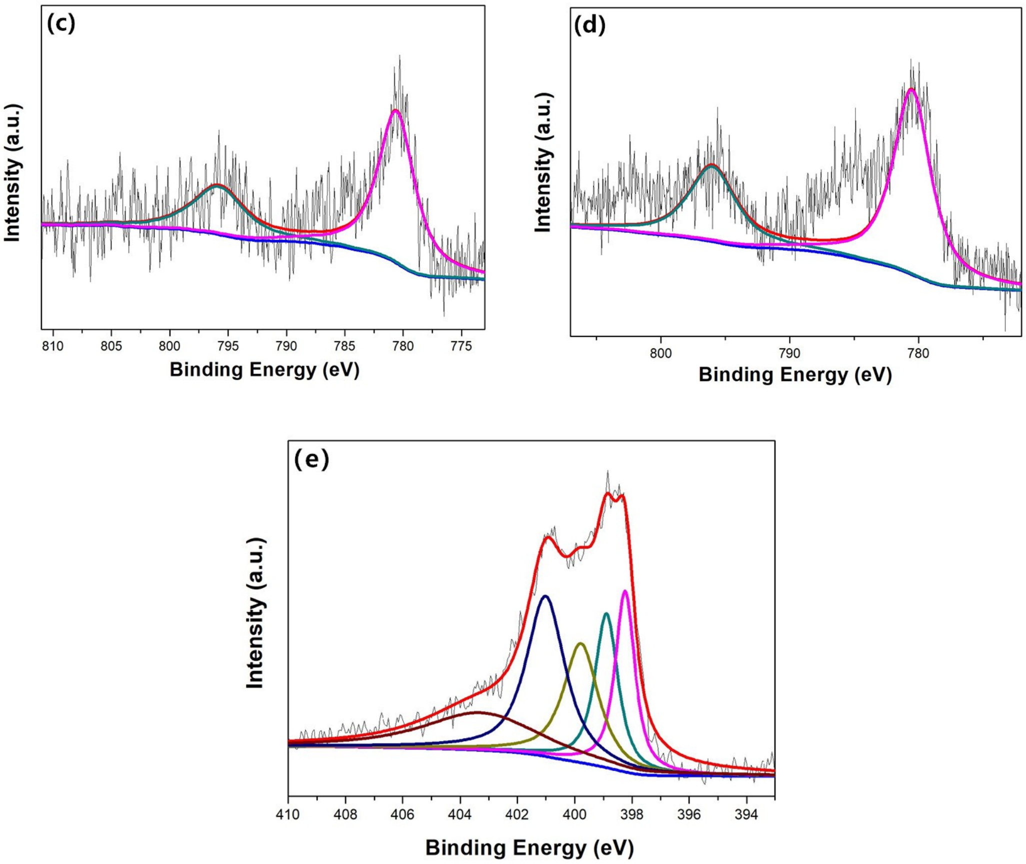


Figure S2. (a) XPS survey spectrum of the sample Co@CN; The Co 2p spectra of (b) Co/CN, (c) Co-CN, and (d) Co@CN-3. And the N 1s spectra of Co-CN (e).

5. ^{1}H and ^{13}C NMR spectra of FDMC

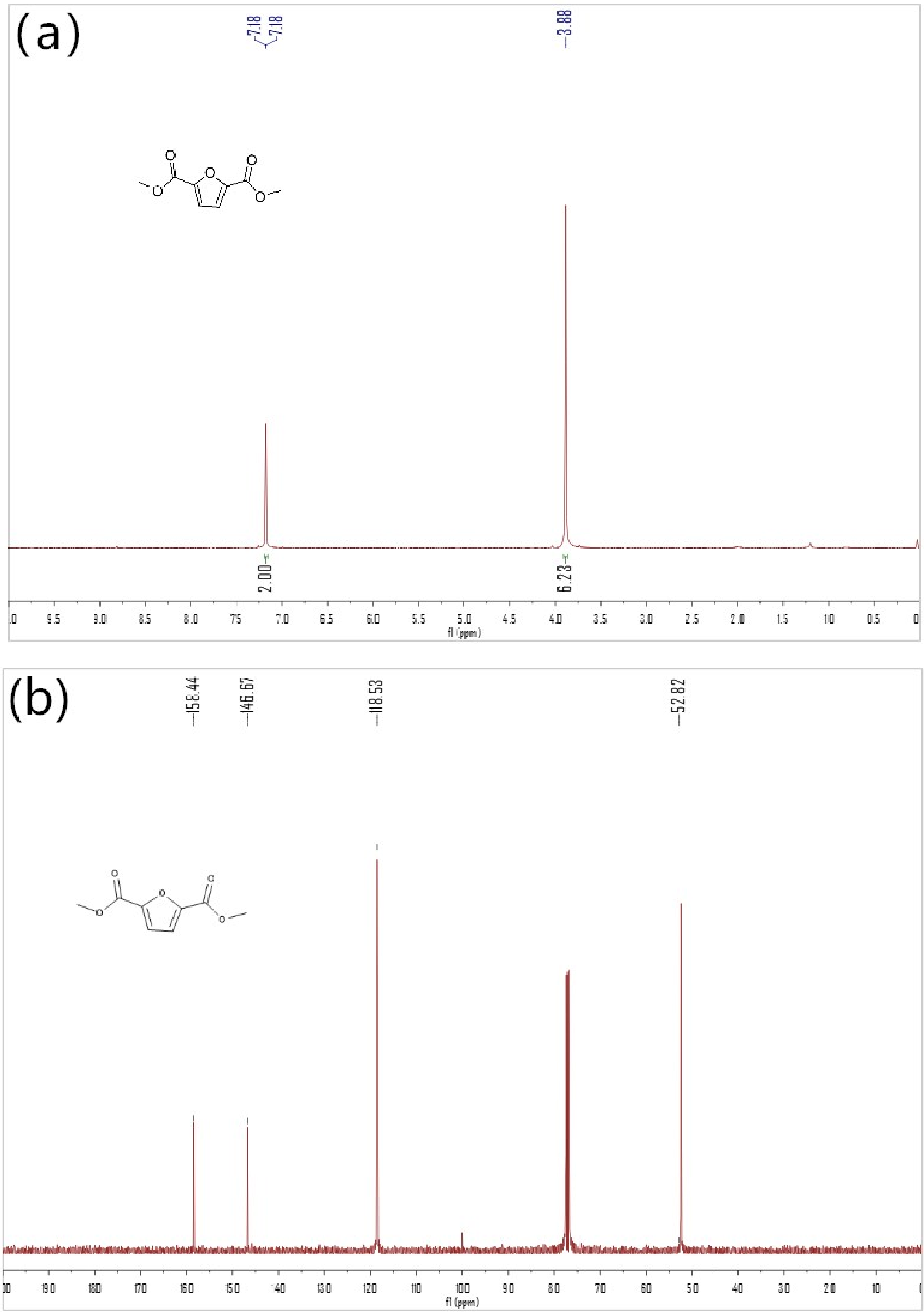


Fig. S3. ^{1}H NMR and ^{13}C NMR spectra of FDMC

6. HRTEM images of Co@CN

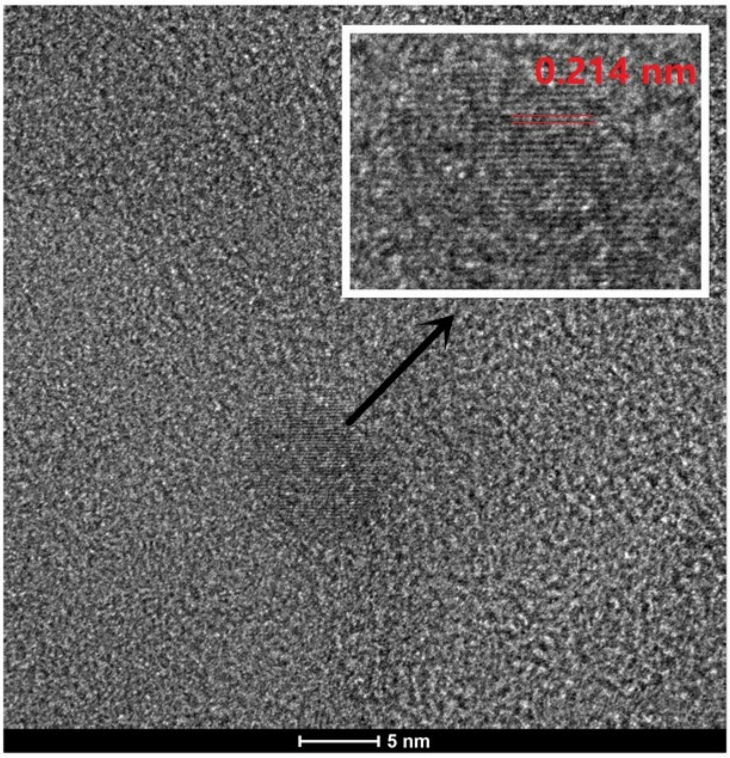


Fig. S4. HRTEM images of Co@CN

7. ICP-MS results of the as prepared Co@CN catalyst

Table S1. ICP-MS analysis of the as prepared Co in Co@CN

Materials	**Element**	**Metal Content (mg/kg)**	**Element**	**Metal Content (mg/kg)**
Co@CN	Co	22213	Zn	428
Co@CN[a]	Co	22116	Zn	432

[a] Co@CN is the catalyst after five cycles.

8. Pore structure of the Co@CN

Table S2. Pore structure of the Co@CN

Samples	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Mean pore size (nm)**
Co@CN	857	1.5	7.2

Co@CN[a]	801	1.0	5.0

[a] Co@CN was not treated with NaOH.

9. Raman spectra

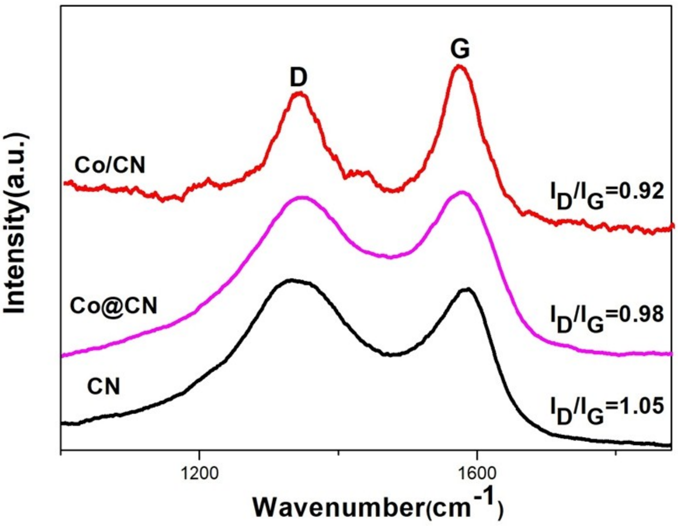


Fig. S5. Raman spectra of Co/CN, Co@CN and CN (ZIF-8).

10. GC-MS spectrum

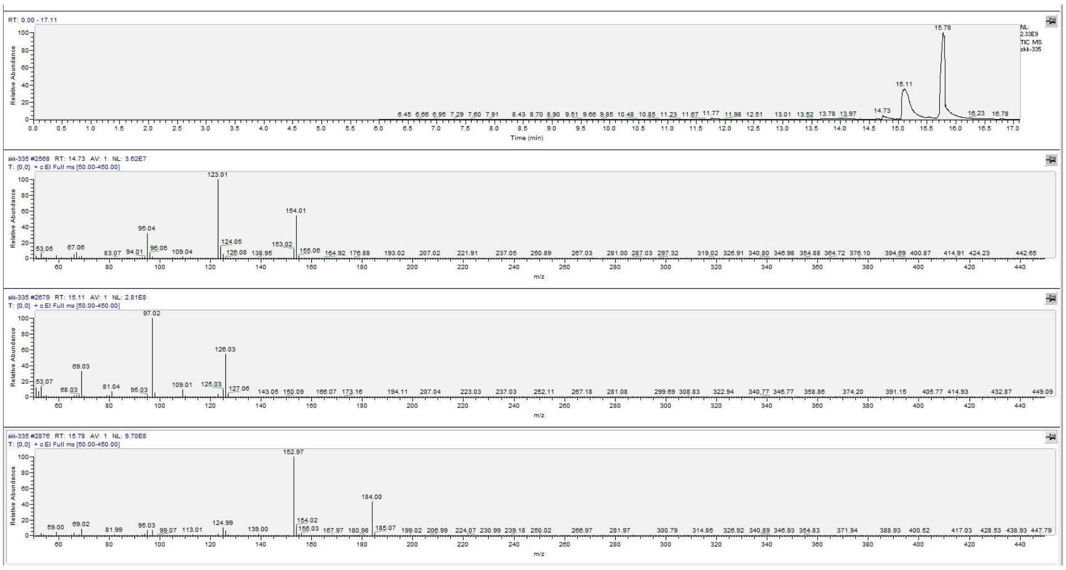


Fig. S6. GC-MS spectrum of oxidative esterification of 5-Hydroxymethylfurfural over Co@CN. Reaction conditions: HMF (0.2 mmol), catalyst (3.8 mol% Co), MeOH (1 mL), 0.1 MPa O_2, 80 °C, 8 h. (14.73: MFF; 15.11: HMF; 15.78: FDMC).

11. TEM and SEM images of Co@CN-3.

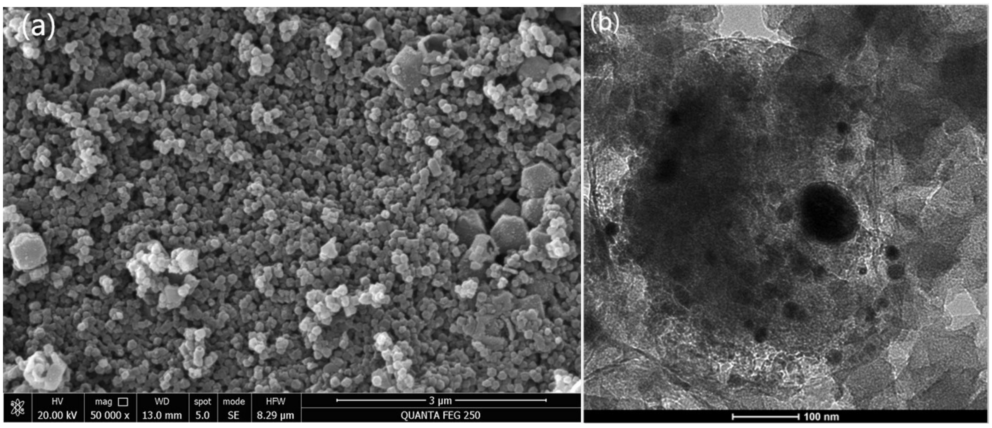


Fig. S7. SEM image (a) and TEM image (b) of Co@CN-3.