Electronic Supplementary Material (ESI) for Green Chemistry.

Enhanced catalytic activity of cobalt nanoparticles encapsulated with *N*-doped porous carbon shell derived from hollow ZIF-8 for efficient synthesis of nitriles from primary alcohols in water

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1 Experimental

1.1. Materials

All chemicals such as 2-Methylimidazole (2-MeIm), $Co(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, benzyl alcohol and aqueous ammonia (25-28%) were purchased from commercial suppliers and used directly without further purification.

1.2. Synthetic procedures

1.2.1. Synthesis of ZIF-67

ZIF-67 was synthesized with the following steps. Typically, 1.43 g $Co(NO_3)_2 \cdot 6H_2O$ was dissolved in 100 mL methanol. Meanwhile, 3.24 g 2-MeIm was dissolved in 100 mL methanol by sonication for 10 min. The obtained 2-MeIm solution was added to the above salt solution under vigorous stirring at room temperature for 24 h. The obtained sample was centrifuged and washed with methanol. The final product was dried under vacuum at 60℃ for 12 h.

1.2.2. Synthesis of ZIF-8

In a typical procedure, 3.5 g $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved into 100 mL methanol, and then mixed with 80 mL methanol containing 2-MeIm (0.6 M) quickly. The solution was kept at 35℃ for 12 h with stirring. The ZIF-8 was collected by centrifugation, washed several times with methanol, and vacuum-dried overnight at 80℃.

1.2.3. Synthesis of ZIF-67@ZIF-8

ZIF-67@ZIF-8 was synthesized with the following steps. Typically, 0.3 g ZIF-67 and 3.5 g $Zn(NO_3)_2·6H_2O$ were added to 100 mL methanol under ultrasonic. 80 mL methanol solutions of 2-MeIm (0.6 M) were then added into the mixture gradually and stirred for 12 h at 35℃. Finally, the ZIF-67@ZIF-8 was separated, washed (methanol) and dried at 80℃ under vacuum.

1.2.4. Synthesis of Co@NC, Co/NC and NC (ZIF-8).

The pyrolysis of ZIF-67@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 2 h. The resulting catalyst was denoted as Co@NC. The Co/NC and NC (ZIF-8) were prepared by a similar method using ZIF-67 and ZIF-8 instead of ZIF-67@ZIF-8 respectively.

1.2.5. Synthesis of Co/AC and Co/ZrO_2.

Co/AC and Co/ZrO_2 were prepared by the typical impregnation method as follows: 1.0 g support (Co/AC and Co/ZrO_2) was dispersed into 30 mL aqueous solution of metal precursors ($Co(NO_3)_2·6H_2O$) under ultrasonic. Lysine aqueous solution (0.53 M) was then added into the mixture with vigorous stirring for 30 min. To this suspension, $NaBH_4$ aqueous solution (0.05 M) was added dropwise, the mixture was further stirred for 60 min and then aged for 24 h. Finally, the solid was separated, washed (water and ethanol) and dried at room temperature under vacuum.

1.3. Characterization

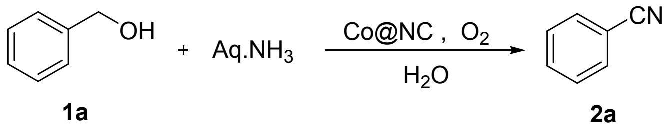
GC-MS was performed on an ISQ Trace 1300 in the electron ionization (EI) mode. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 μm × 0.25 μm, carrier gas: H_2, FID detection. XRD analysis was performed on Shimadzu X-ray diffractometer (XRD-6000) with Cu Kα irradiation. Transmission electron microscopy (TEM) images were taken using a PHILIPS Tecnai 12 microscope operating at 120 kv. The static water contact angles were measured at room temperature using an Optical Contact Angle & Interface Tension Meter SL200KS (KINO, USA) equipped with CASTV2.28 software. Once a drop of water was deposited on tested surfaces and the contact angle determined from pictures were immediately captured. CO_2-TPD data were obtained on a Micromeritics AutoChem II

2920 instrument. 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 amount of Co@NC (4 mol% of Co) and aq. NH_3 in H_2O (1 mL) were placed in a 25 mL sealed tube, and primary alcohol (0.2 mmol) was added to the mixture under atmospheric oxygen with a magnetic to initiate the reaction at 50°C for 12 h. After reaction, the mixture was extracted with ethyl acetate and the product were analyzed by GC/MS (ISQ Trace 1300). The yield of the product was determined by GC (Agilent 7890A) with nitrobenzene as an internal standard. Next, the solution after extracted, containing Co@NC, was submitted to another reaction cycle under the same conditions.

2. E Factor studies



Typically, a calculated amount of Co@NC (4 mol% of Co), aq. NH_3 and H_2O (1 mL) were placed in a 25 mL sealed tube, and primary alcohol (2 mmol) was added to the mixture under atmospheric oxygen with a magnetic to initiate the reaction at 50°C for 24 h. After the reaction was completed, the product was exacted with ethyl acetate (3×0.3 mL). The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel to afford the pure product **2a** (167 mg, 81% yield).

$$\begin{aligned}\text{E factor} &= \frac{\text{total organic solvent wastes (kg)}}{\text{product (kg)}}\\ &= \frac{\text{ethyl acetate (extraction)}}{\text{isolated pure product}}\\ &= \frac{3 \times 270.6\ \text{mg}}{167\ \text{mg}}\\ &= 4.9\end{aligned}$$

3. SEM images

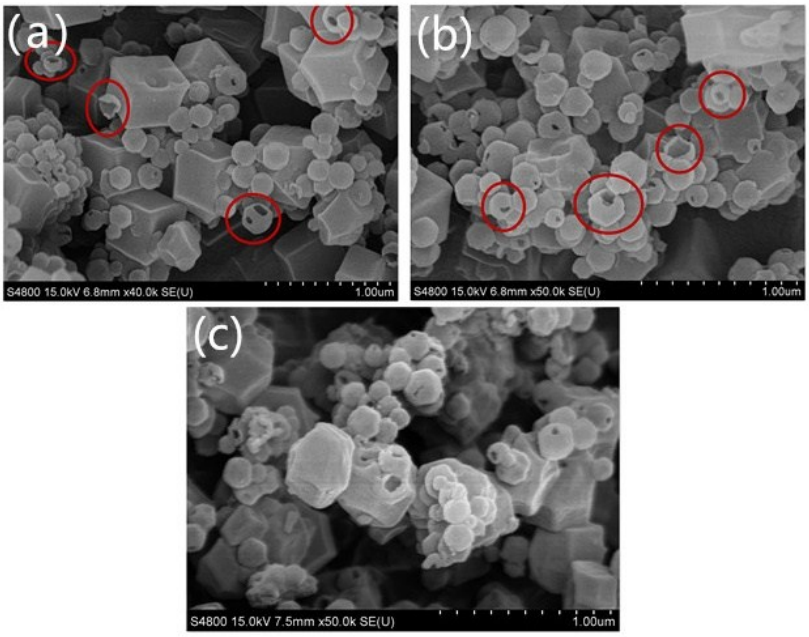


Fig. S1. SEM images of (a, b) ZIF-67@ZIF-8 and (c) Co@NC.

4. XPS survey spectrum of the sample Co@NC.

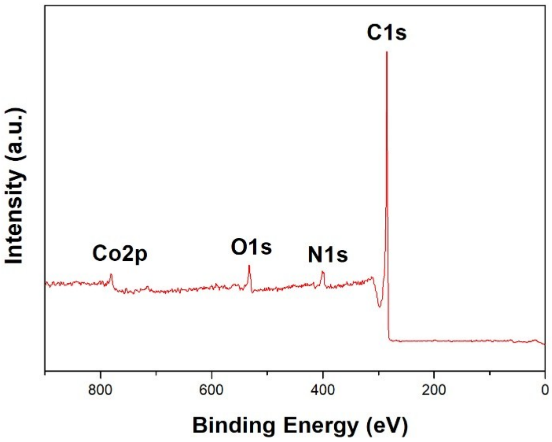


Figure S2. XPS survey spectrum of the sample Co@NC

5. Raman spectra of Co@NC.

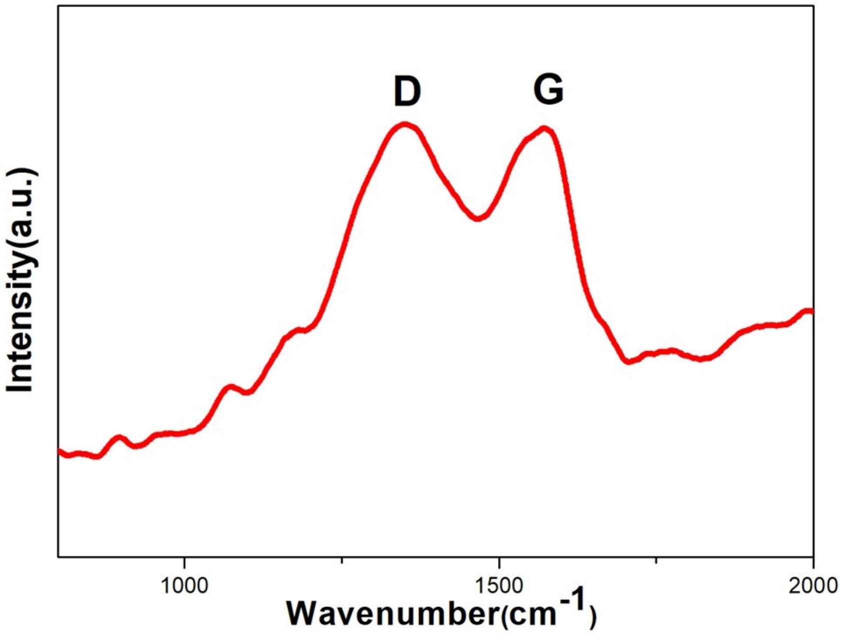


Fig. S3. Raman spectra of Co@NC

6. Hydrophilic nature of Co@NC.

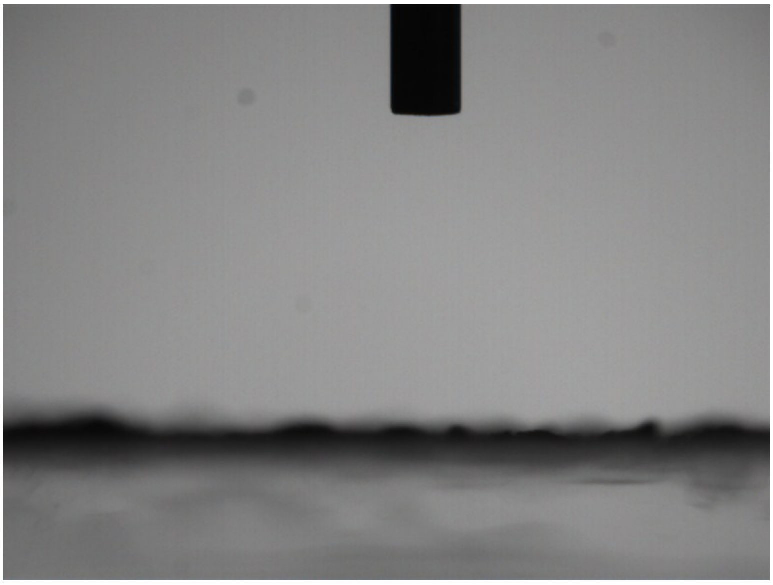


Fig. S4. The air–water contact angles of Co@NC

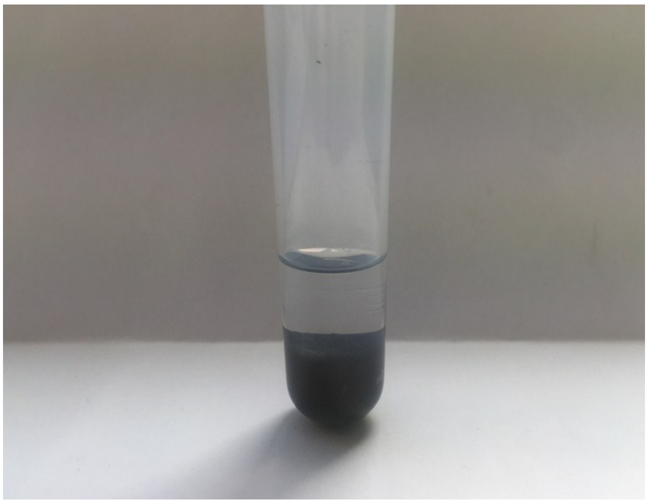


Fig. S5. The dispersion of Co@NC in a biphasic solution (ethyl acetate and water).

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

Table S1. ICP-MS analysis of the as prepared Co and Zn in Co@NC.

Materials	**Element**	**Metal Content (mg/kg)**	**Element**	**Metal Content (mg/kg)**
Co@NC	Co	34416	Zn	556
Co@NC[a]	Co	34226	Zn	544

[a] Co@NC is the catalyst after six cycles.

8. Pore structure of the Co@NC

Table S2. Pore structure of the Co@NC

Samples	**BET surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Mean pore size (nm)**
Co@NC	1042	1.25	5.22