

Supplementary online materials

Individual Fe-Co Alloy Nanoparticles on Carbon Nanotubes: Structural and Catalytic Properties

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Experimental details

Commercial CNTs (Applied Sciences Inc, HHT) was used as the support after refluxing in concentrated HNO_3 at 140°C for 2 h to functionalize the surface by oxygen-containing functional groups. The dried samples were washed by deionized water and then calcined at 450°C for 2 h in a helium flow. Elemental analysis revealed that the content of residual active metals in purified CNTs is negligible.

Briefly, the synthesis was performed typically as follows. 3mL solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dropped on 500 mg CNTs powder under the continuous stirring. The obtained sample was partially dried at room temperature inside a fume cupboard. 1 mL solvent (10% ethanol-water) was dropped in the same way and then treated the paste by ultrasonic treatment (20 s). Finally, the sample was then dried at room temperature overnight in the fume until the moist almost disappeared, calcined at 350°C for 2 h, and reduced by H_2 at 400°C for 2 h. Each sample was labeled by the Co/Fe atomic ratio according to the set value, *i.e.* Co_2Fe (Co/Fe=2.0), CoFe (Co/Fe=1.0), and CoFe_5 (Co/Fe=0.2). To prepare the CoFe_5 -out-CNTs sample, 7.5mL benzene was used to pre-fill the inner channel of CNTs. After the surface moist was almost disappeared, we did the same procedures for preparation of CoFe_5 -in-CNTs sample as described above.

For catalytic evaluation, 50 mg of sample (powder, < 50 μm) was loaded in a quartz tube fixed bed reactor. Pure gaseous NH_3 (30mL/min) was passed through the catalyst bed and the temperature was increased to 600 $^\circ\text{C}$ with a heating rate of 10 $^\circ\text{C}/\text{min}$. The effluent gas was analyzed by an on-line gas chromatograph (3000A MicroGC, Agilent), equipped with two lines, a PLOTU pre-column / Molsieve column combination with Ar as carrier gas for N_2 , H_2 and CH_4 , and a PLOTU column with He as carrier gas for NH_3 and CH_4 . Both lines were equipped with TCD detectors.

The microstructure of both CNTs and metal particles were examined *ex-situ* in a Philips CM200 FEG transmission electron microscope (TEM) equipped with electron energy loss spectroscopy (EELS) and Energy Dispersive X-ray (EDX) detectors. X-ray diffraction measurements were conducted over a Philips PW3710 X'PERT diffractometer with $\text{Cu K}\alpha$ radiation. Surface analyses were performed on a modified PHOIBOS HSA3500 MCD system equipped with facilities for X-ray photon spectroscopy (XPS, $\text{Mg K}\alpha$ 1253.6 eV) tests. Bulk and surface chemical compositions were determined by EDX in TEM and XPS techniques.

Figure S1. Elemental composition of nanoparticles inside the used 5%CoFe/CNTs. (Left) dark-field STEM image; (right) line scan EDX spectra of typical nanoparticles.

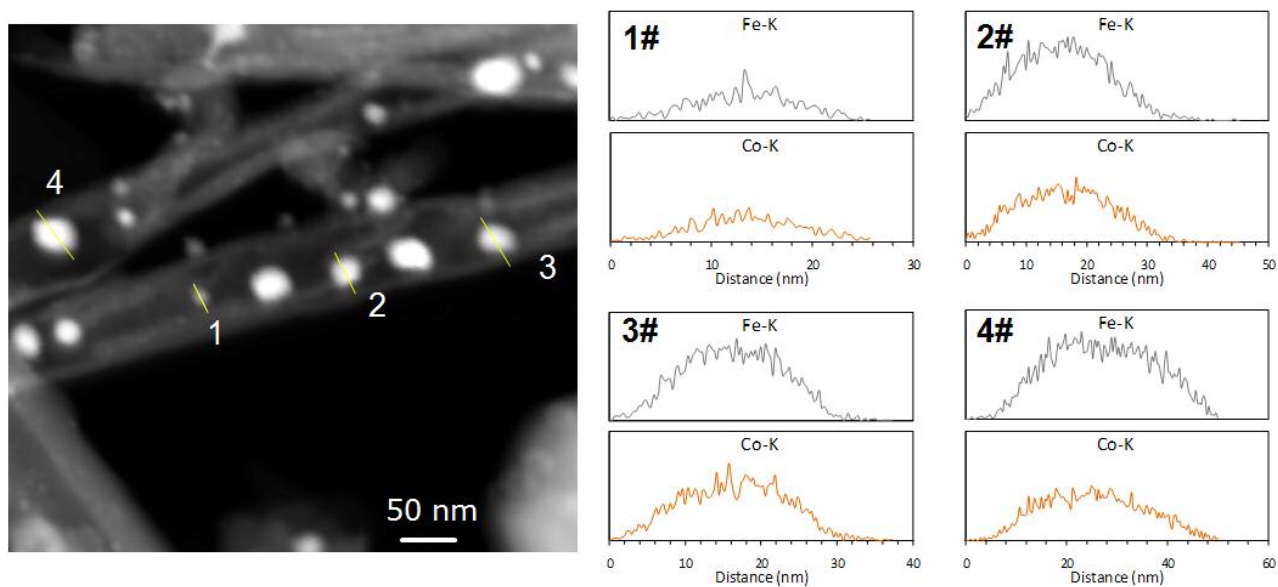


Figure S2. Microscopic characterizations of the catalysts after reaction. (a) Elemental mappings of Fe and Co in the used catalysts; (b) HRTEM images of 5%Co₂Fe/CNTs; (c) HRTEM images of 5%CoFe/CNTs; and, (d) HRTEM images of 5%CoFe₅/CNTs.

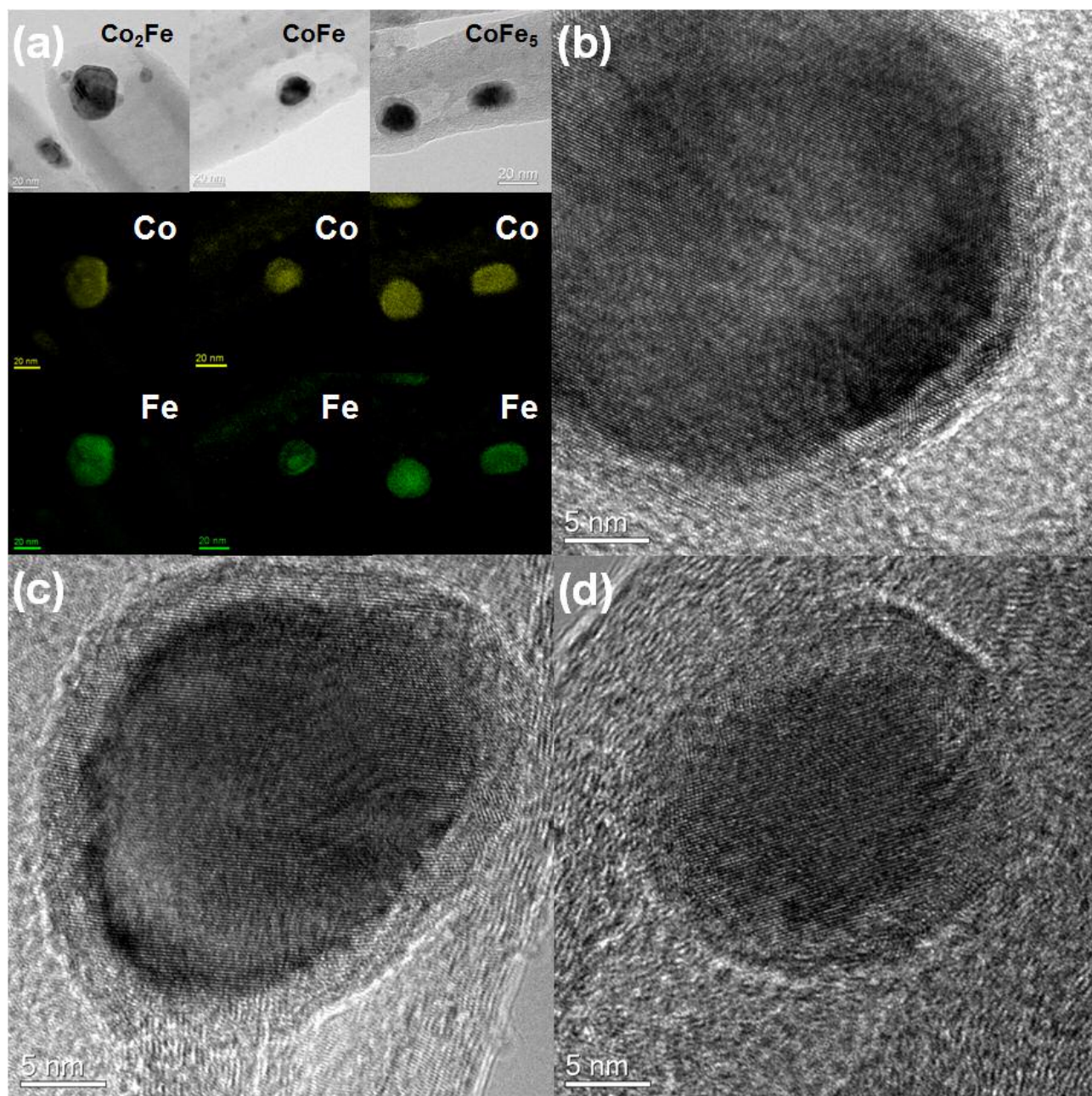


Figure S3. TEM images CoFe₅-in-CNTs and CoFe₅-out-CNTs samples. (a-c) Tilting the sample holder of CoFe₅-in-CNTs with the angles of $\pm 25^\circ$. Sticks: particles inside; circles: particles outside. (d-f) Typical images of the CoFe₅-out-CNTs sample in tilting experiments. Yellow: particles outside; red: particles inside.

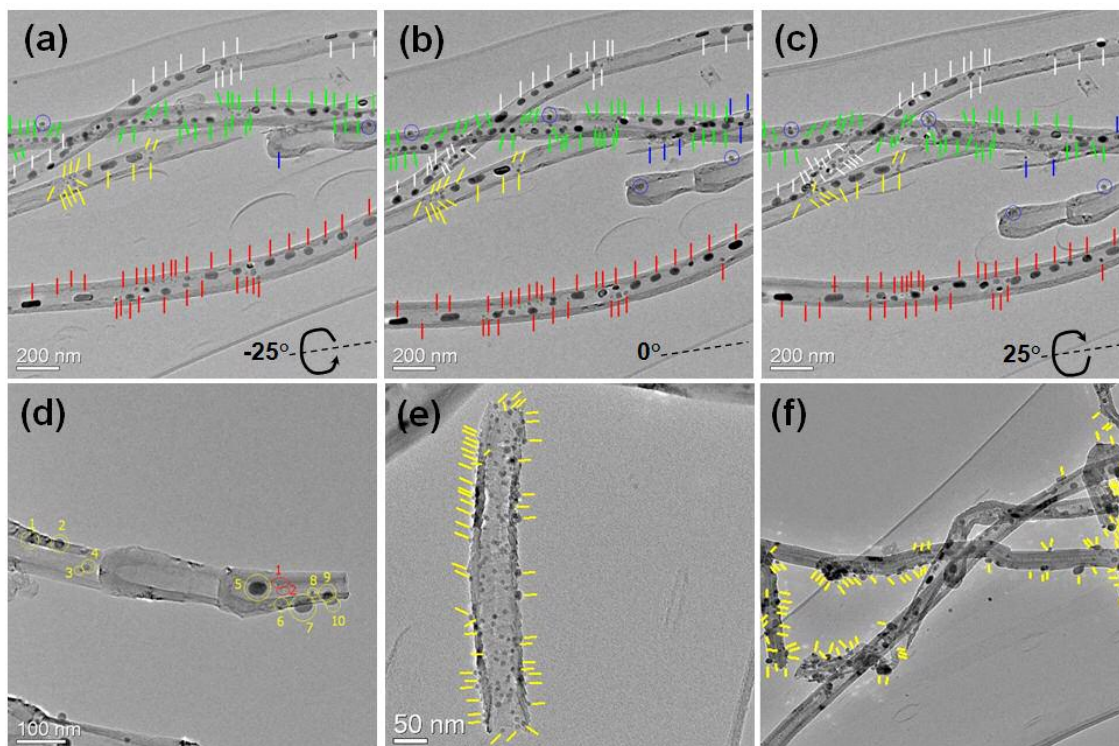


Figure S4. TEM images of the CoFe₅-out-CNTs sample after reaction in Fig. 5b: (a) overview; and, (b) high-resolution image of one aggregated particle.

