

## **ELECTRONIC SUPPORTING INFORMATION**

### **Synthesis of Pd-coated FeCo@Fe/C core-shell nanoparticles: A microwave-induced ‘top-down’ nanostructuring and decoration**

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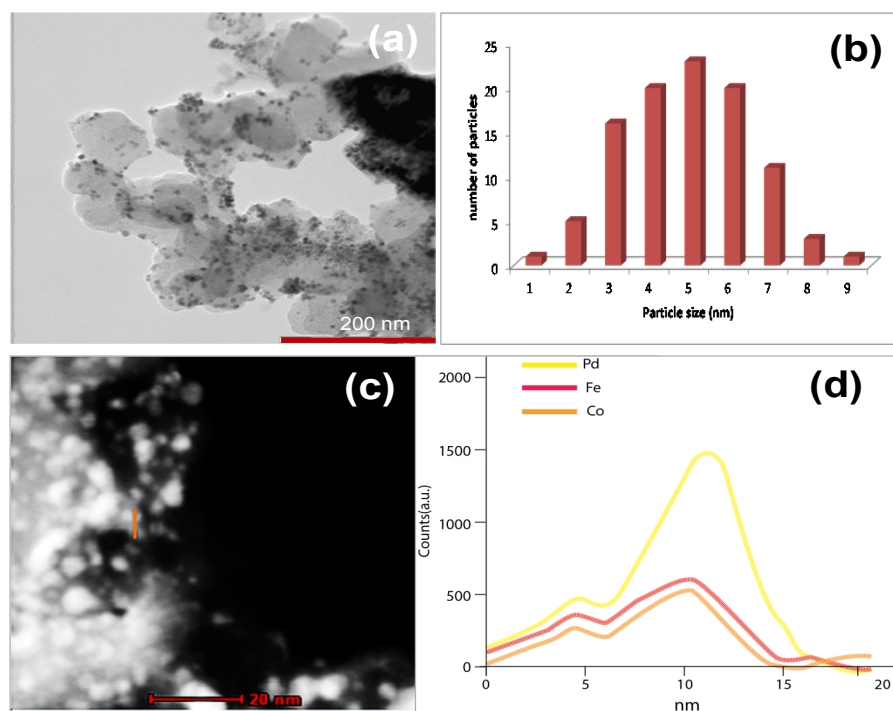
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## EXPERIMENTAL

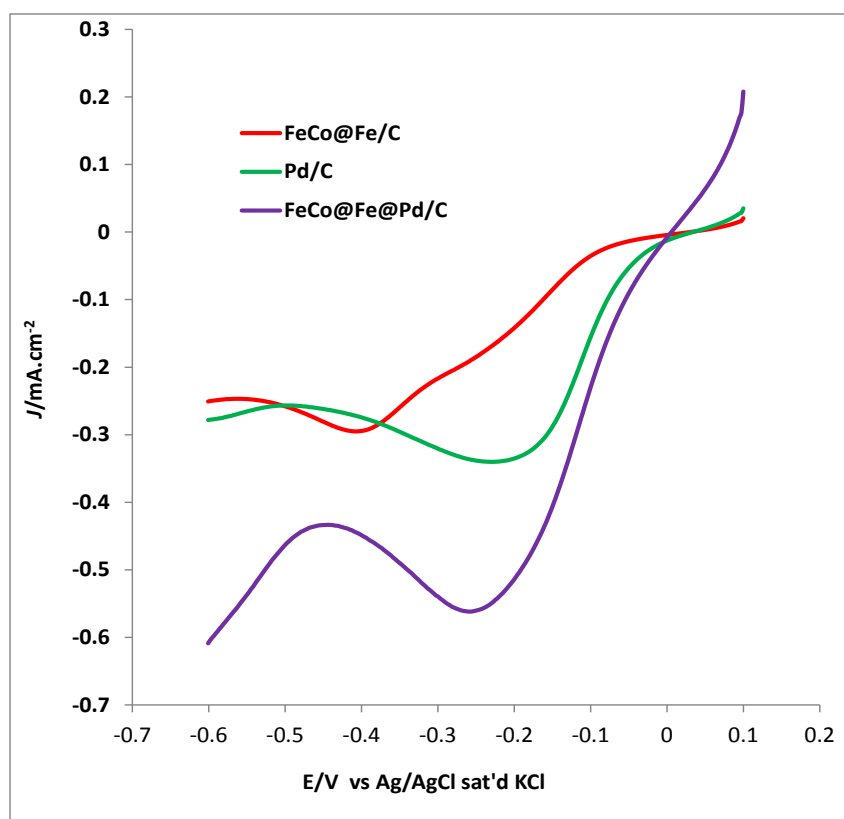
**Synthesis:** The FeCo@Fe/C was obtained by reduction of the salts of the component elements through hydrogenation. Briefly, a mixture of 0.5302 g of FeCl<sub>2</sub>·4H<sub>2</sub>O (3 mmol) and 0.3650 g of CoCl<sub>2</sub>·6H<sub>2</sub>O (1.5 mmol) were dissolved in 20 mL of deionised water. 0.15 g of Vulcan XC-72 carbon was dispersed in the solution. The mixture was heated under magnetic stirring at 60 °C, and the resulting paste was ground slightly in agate mortar and was heated in a tube furnace at 300 °C under flowing H<sub>2</sub>/Ar for 2h. It was further annealed at 500 °C for 2h for complete reduction. The fine powder was cooled to room temperature under Ar gas. The FeCo@Fe@Pd/C nanoparticles were prepared by a solvothermal microwave reaction. A 0.20g (1 mmol) of the as-prepared carbon supported FeCo@Fe was added to 0.35 g (3 mmol) of PdCl<sub>2</sub> salt in a 1:3 nominal Fe: Pd mole ratios. 40 ml of ethylene glycol was added to the mixture under constant stirring, followed by an addition of 0.15 g polyvinyl pyrrolidone (PVP) which served as the stabilizer. The suspension was then transferred to a quartz vessel in an Anton Paar microwave reactor (Anton Parr Synthos 3000) equipped with a wireless pressure and temperature sensor. The reactor was operated at a power of 500 W, the sample temperature was ramped and kept to ~198 °C for 15 minutes while the pressure was raised to 80 bar. The resulting precipitate was repeatedly washed with acetone and deionised water to remove traces of ethylene glycol and other impurities. The carbon supported core-shell nanomaterial was dried at 100 °C. Pd nanoparticles of same mass loading (3 mmol) as the core-shell were also synthesized using the same procedure.

**Characterization:** The nanoparticles were prepared for X-ray diffraction (XRD) analysis using a back loading preparation method. They were analysed on a PANalytical X'Pert powder diffractometer with Co K $\alpha$  radiation. The phases were identified using X'Pert Highscore plus software. Transmission electron microscopy (TEM) images were taken on a JEOL JEM 2000EX microscope at an accelerating voltage of 200kV. High resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were obtained on a Tecnai F-20 instrument equipped with Gatan high-angle annular dark field detector (HAADF) field emission high-resolution scanning transmission electron microscope (STEM) operated at an accelerating voltage of 200kV, Gun extraction voltage was 4500V. Energy dispersive spectroscopy (EDS) line scan was also performed using this instrument in the STEM mode. Specimens for all of the TEM analyses prepared by were by dispersing the nanoparticles in methanol, sonicating for 1 min in order to ensure adequate dispersion of the nanostructures, evaporating one drop of the solution onto 300 mesh Cu grid, coated with a lacey carbon film. Scanning electron microscopy (SEM) images were obtained utilizing a field emission scanning electron microscope (FESEM Zeiss-Leo DSM982).

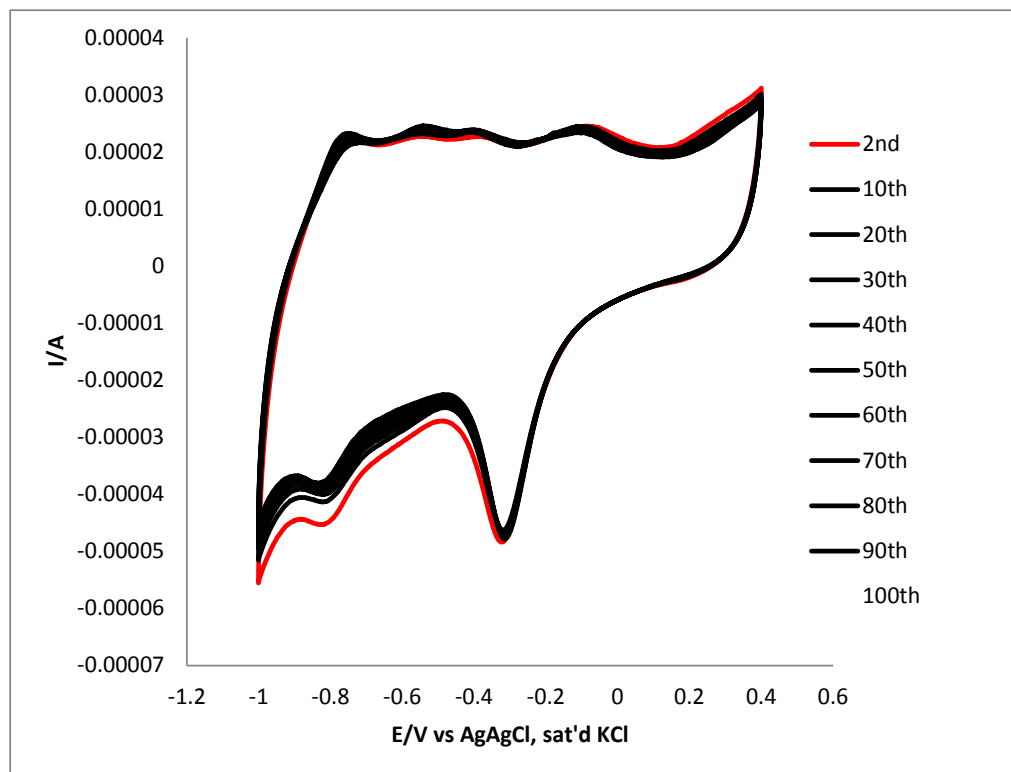
**Electrochemistry:** All electrochemical experiments were carried out using an Autolab Potentiostat PGSTAT 100 (Eco Chemie, Utrecht, The Netherlands) driven by version 4.9 of GPES softwares. A glassy carbon working electrode (GCE) was used for cyclic and linear voltammetry (CV and LSV) testing. A rotating disk electrode (RDE) (Autolab Netherlands, active areas 5mm) was used to test the ORR activity. A Pt rod and Ag|AgCl (saturated 3 M KCl) were used as a counter and reference electrode, respectively. 1.0mg of the nanoparticle was dispersed in 1.0ml of ethanol, and 100 $\mu$ L of 5% Nafion added. The mixture was ultrasonicated for 3 min to make a uniform ink. The working electrode was prepared by dropping 10  $\mu$ L of the catalyst ink on the GCE and allowing it to dry in an oven at 60°C. The CV and LSV tests were performed in high purity nitrogen-saturated 0.1M KOH. For the ORR activity test, linear scans were conducted using the same voltage from 1600 rpm in 0.1 M KOH bubbled with high purity O<sub>2</sub>.



**Figure SI 1:** (a) HRTEM and (b) particle size distribution of FeCo@Fe@Pd/C; (c) and (d) HAADF-STEM image and cross-sectional compositional line profiles of two particles of FeCo@Fe@Pd core-shell-shell.



**Figure SI 2:** Comparative linear sweep voltammograms obtained in 0.1 M KOH saturated with oxygen using GCE modified with Pd/C, FeCo@Fe/C, and FeCo@Fe@Pd/C. Scan rate =  $25 \text{ mVs}^{-1}$ .



**Figure SI 3:** Continuous cyclic voltammograms (100 cycles) obtained in 0.1 M KOH using GCE modified with FeCo@Fe@Pd/C.