

## **Electronic Supporting Information**

# **Electro-oxidation of ethylene glycol and glycerol at palladium-decorated FeCo@Fe core-shell nanocatalysts for alkaline direct alcohol fuel cells: Functionalized MWCNT supports and impact on product selectivity**

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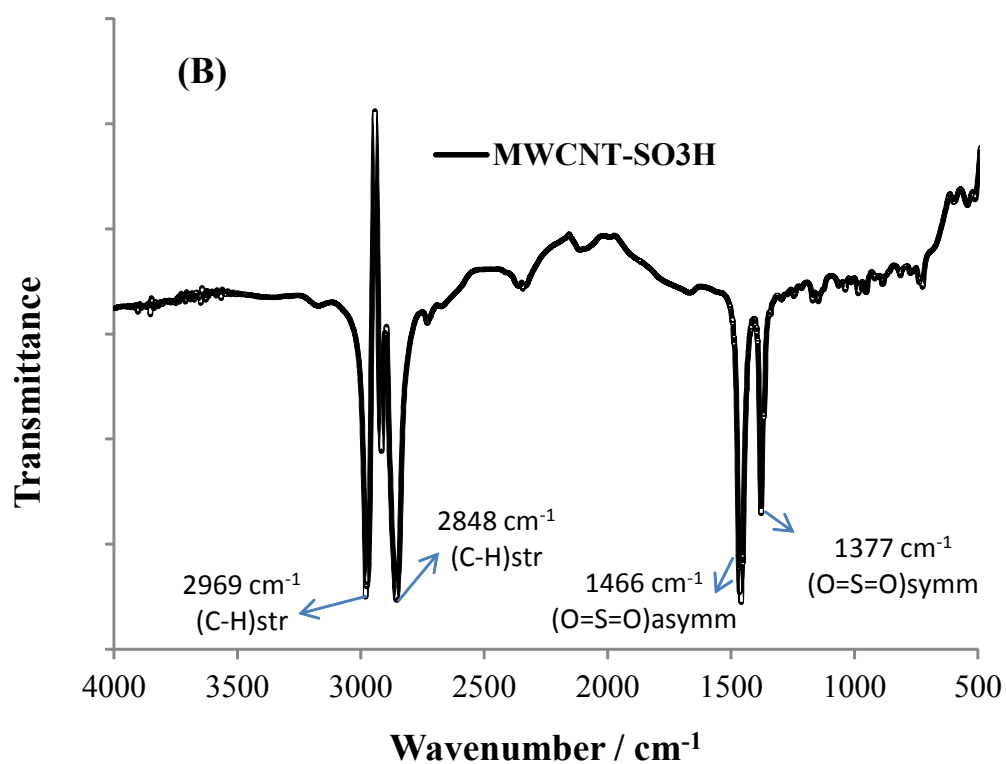
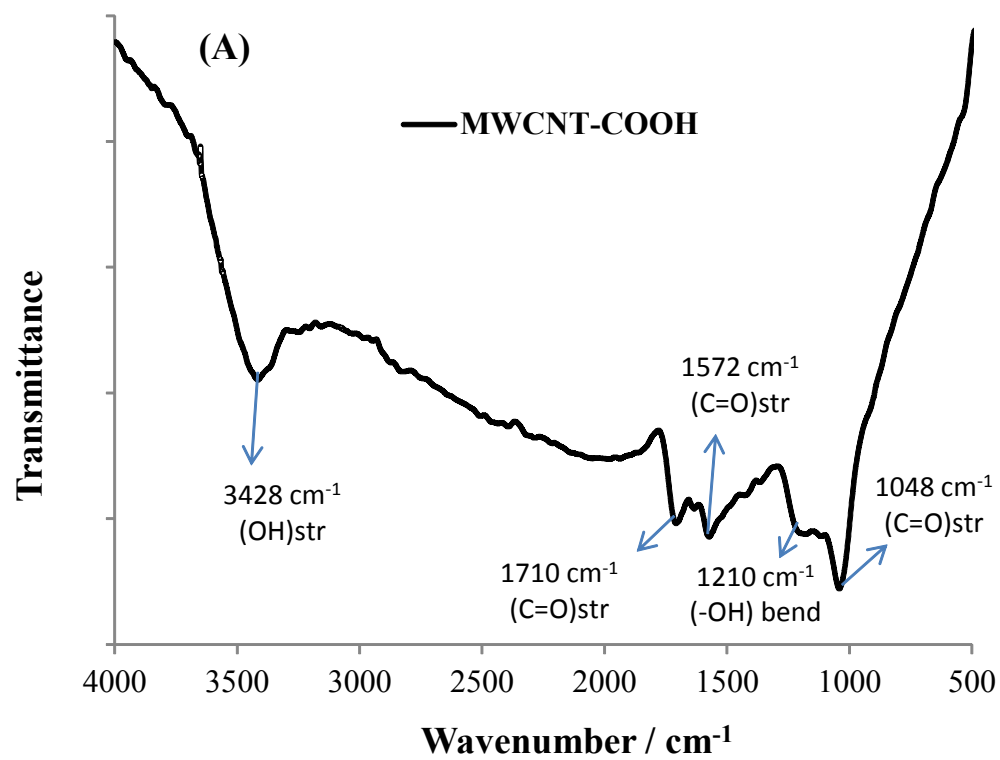
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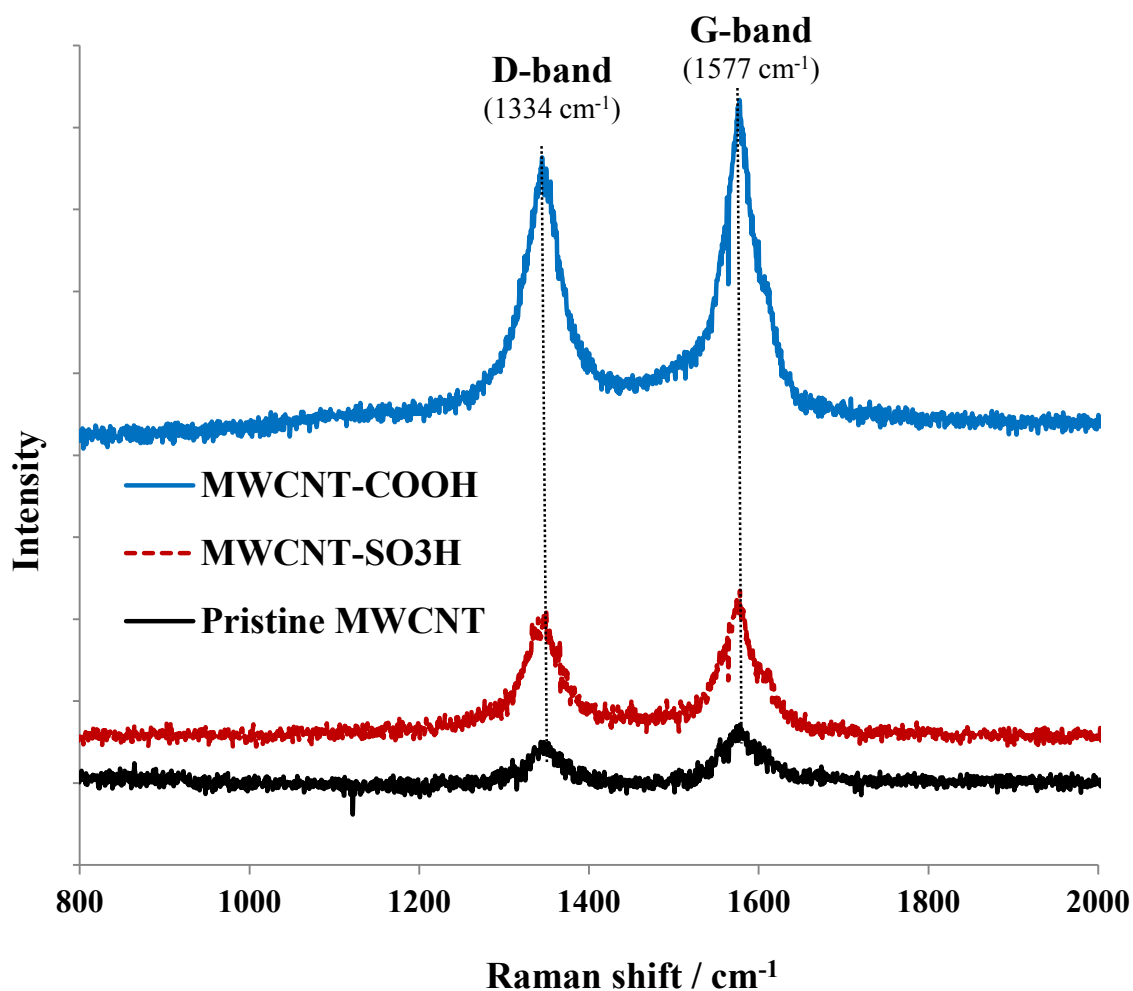
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The main objective of the study is to use literature-established techniques to functionalise MWCNTs with  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$  and subsequently use them as support for the Pd-based core-shell catalysts. FTIR and Raman were used to confirm the successful functionalization of the MWCNTs with  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$  functional groups. The concentrations of the  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$  were not determined, but it is known that for MWCNTs, the concentric arrangement of the graphene layers does not allow for the attainment of the surface atomic oxygen percentages higher than 7–8%.<sup>1</sup>

Figure S1 compares the FTIR spectra of MWCNT-COOH (Fig. S1A) and MWCNT-SO<sub>3</sub>H (Fig. S1B). The MWCNT-COOH showed intense band at 3428 cm<sup>-1</sup> due to the stretching vibrational modes of the O-H group, very weak bands at ~2888 and ~2333 cm<sup>-1</sup> due to symmetric and asymmetric C-H of aryl groups. The bands at 1719 and 1587 cm<sup>-1</sup> are due to the C=O stretching vibrations from carboxylic and carbonyl groups. The strong band at 1225 cm<sup>-1</sup> is O-H bending deformation in  $-\text{COOH}$ . The peak at 1056 cm<sup>-1</sup> is assigned to C-O stretching vibrations of epoxides, or cyclic ethers. Interestingly, upon sulphonation of the MWCNT-COOH, the intense bands due to the OH (3428 cm<sup>-1</sup>) and C=O (1719 and 1587 cm<sup>-1</sup>) groups disappear leading to two strong bands at 1467 and 1380 cm<sup>-1</sup> which are the characteristic absorption bands of organic sulfonate groups; the O=S=O asymmetric and O=S=O symmetric stretching motions respectively. The intense bands at 2980 and 2862 cm<sup>-1</sup> are attributed to C-H stretching motions of aromatic and unsaturated alkyl groups. The group of bands at 995, 888, 766 cm<sup>-1</sup> are assigned to the C-O stretching vibrations of substituted pyridines or aromatic rings.



**Figure S1:** Comparative IR spectra of (A) MWCNT-COOH and (B) MWCNT-SO<sub>3</sub>H.

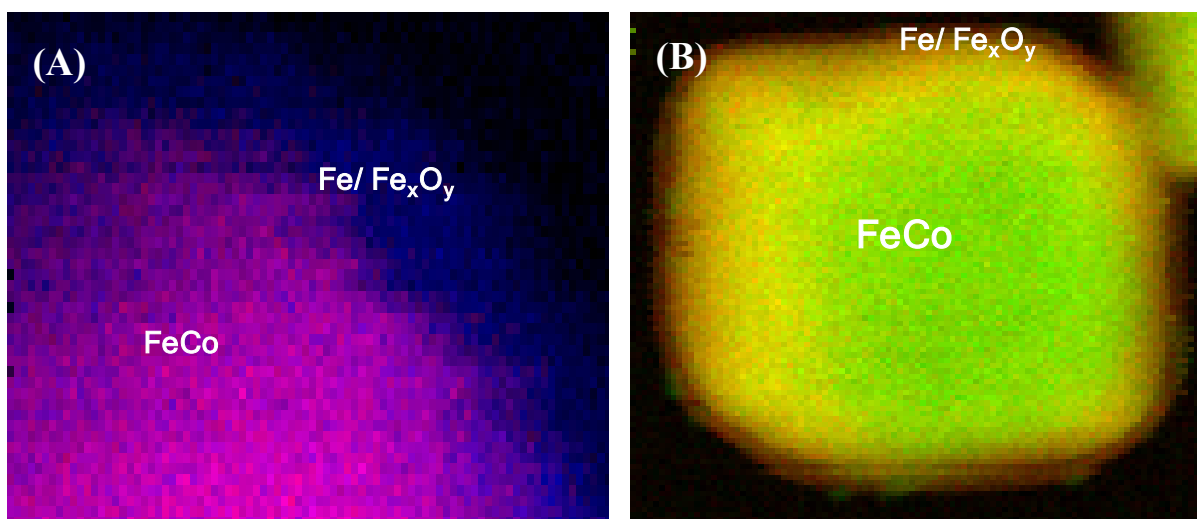


**Figure S2:** Raman spectra of Pristine MWCNT, carboxylate functionalised MWCNT (MWCNT-COOH) and sulfonate-functionalised MWCNTs (MWCNT-SO<sub>3</sub>H).

Figure S2 shows the Raman spectra of pristine MWCNT, MWCNT-COOH and MWCNT-SO<sub>3</sub>H. The D-band reflects the disorder in the MWCNT (sp<sup>3</sup> C), thus increase in the intensity of the D-band is an indication of the rise in the defect density (amount of defects) in the MWCNTs or a decrease in the structural order of the carbon nanotubes bundles. These defects arise from the added functional groups, missing carbon atoms in the walls of the carbon nanotubes or the inhomogeneous decoration of the tube wall by functional groups.

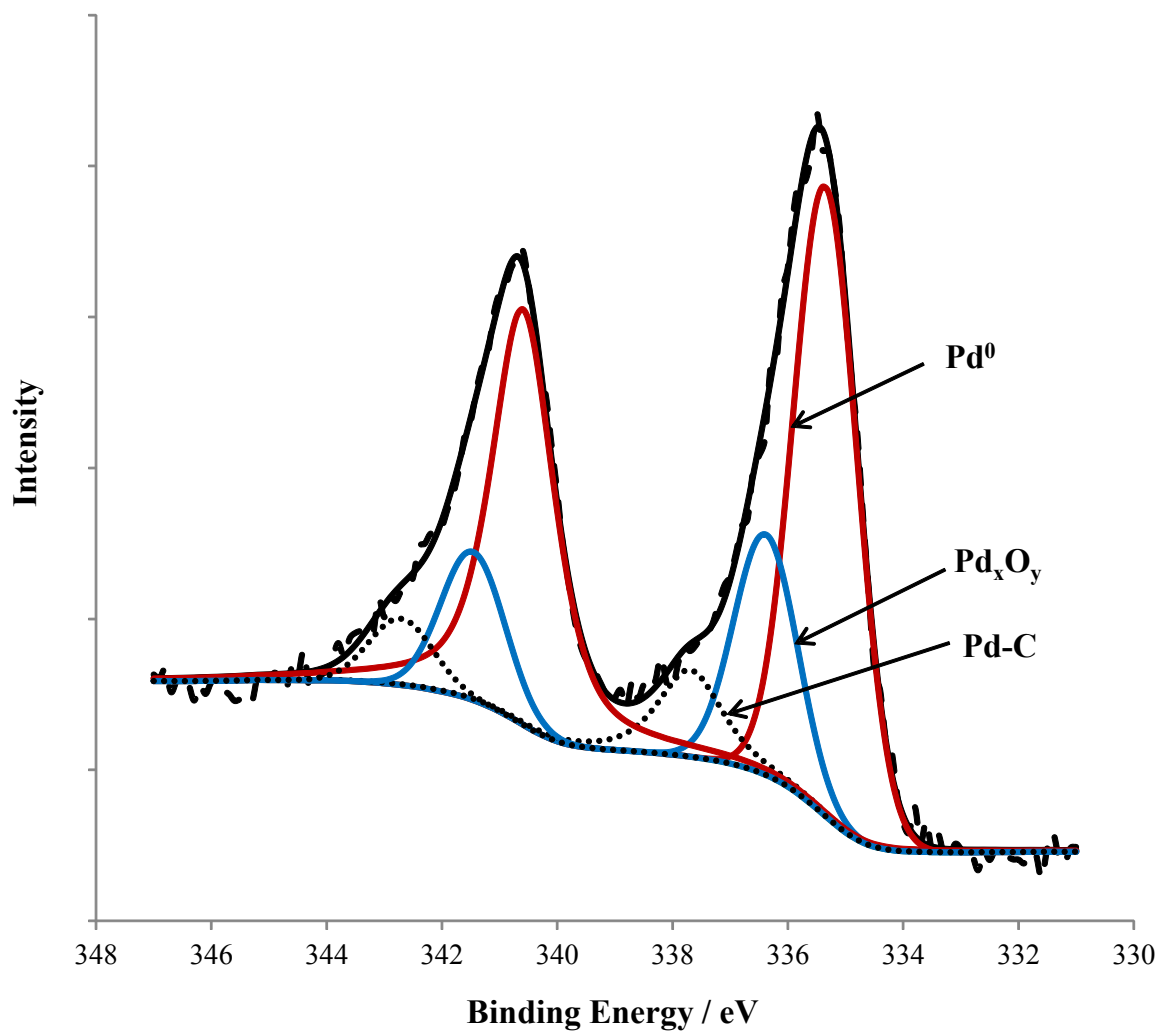
From the Raman spectra, the D-bands appear at *ca.* 1344  $\text{cm}^{-1}$ , while the graphite structure of the MWCNTs, G-band ( $\text{sp}^2$  C) appears at *ca.* 1577  $\text{cm}^{-1}$ . There is no noticeable change in positions of these G-bands for the pristine and functionalised MWCNTs, which means the electronic characteristics remain essentially intact after acid-functionalisation. The degree of functionalization or defects on the MWCNT walls is indicated by the intensity ratios of the D- and G-bands ( $I_D/I_G$ ). The  $I_D/I_G$  values for the MWCNT-COOH, MWCNT-SO<sub>3</sub>H and pristine MWCNTs are  $0.90\pm 0.14$ ,  $0.88\pm 0.12$  and  $0.72\pm 0.10$ , respectively, indicating that the degree of functionalization of MWCNT-COOH and MWCNT-SO<sub>3</sub>H is essentially the same.

As part of the HRTEM, electron energy loss spectroscopy (EELS) was used to visualise the core-shell nature of the core alloy. There was a co-existence of pure iron and iron oxides; nonetheless there were clear contrasts between the inner FeCo alloy and the segregated Fe/Fe<sub>x</sub>O<sub>y</sub> shell around the edges of the core-shell, irrespective of the type of MWCNTs used as support.

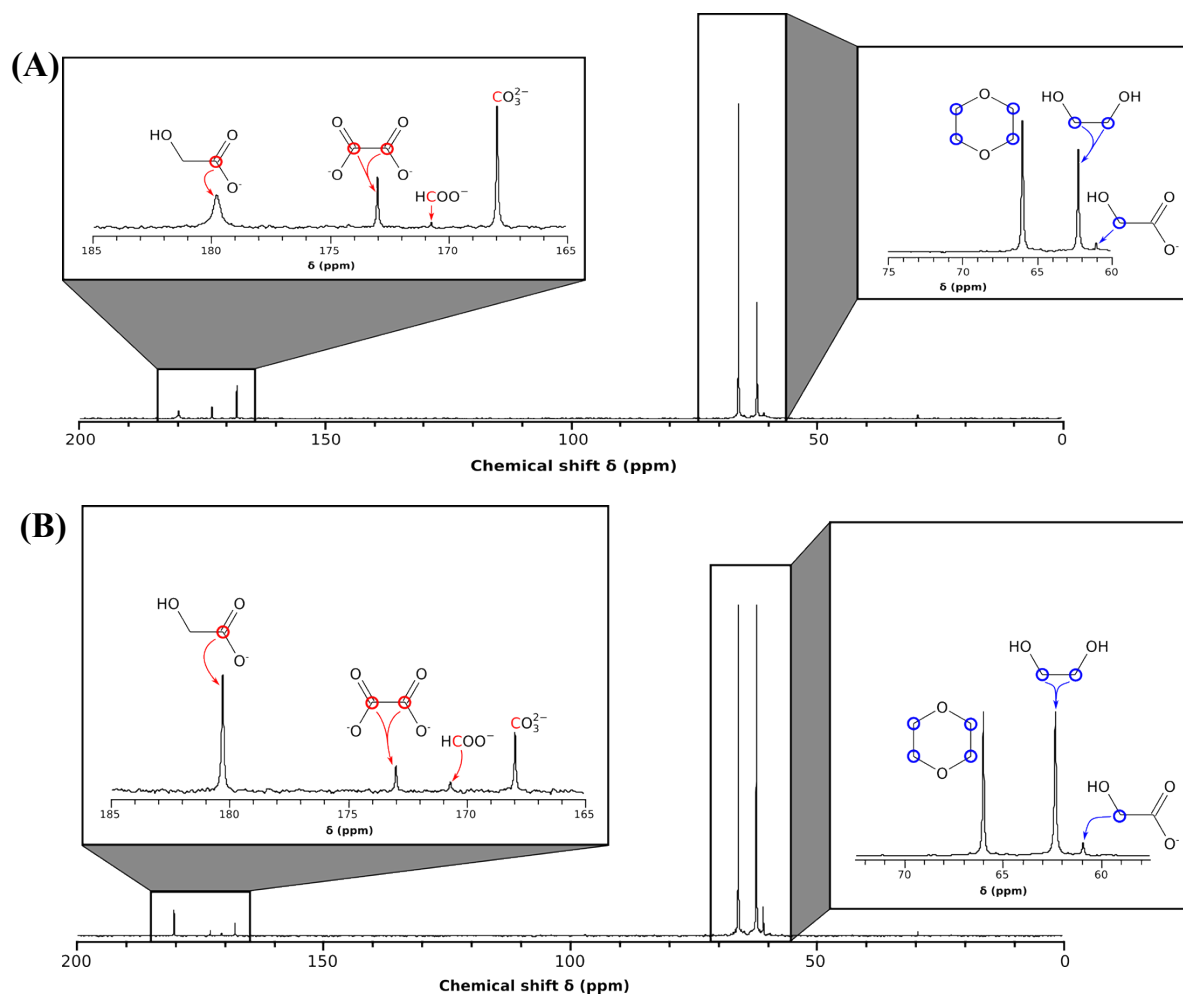


**Figure S3:** Electron energy loss spectral (EELS) images of FeCo@Fe/MWCNT-COOH (A) and FeCo@Fe/MWCNT-SO<sub>3</sub>H (B).

To provide further insights into the existence of the surface oxide layer of Pd on the core-shell, XPS experiments were conducted. The Fe and Co signals were very weak and poorly resolved. The presence of the PdO species is in excellent agreement with other reports that Pd is easily oxidized to PdO in air.<sup>2-4</sup>



**Figure S4:** Typical XPS of FeCo@Fe@Pd/MWCNT-COOH.



**Figure S5:** NMR spectra of the oxidation products of ethylene glycol at FeCo@Fe@Pd/MWCNT-COOH (A) and Pd/MWCNT-COOH (B), Insets are the expanded portions of the main product peaks.

## References

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