Supplementary Information for:

Carbon nanofiber with selectively decorated Pt both on inner and outer walls as an efficient electrocatalyst for fuel cell applications

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Results:

Figure SI 1: HR-TEM images of (a) pristine (CNF-Pt) and (b) functionalized (FCNF-Pt) nanofiber supported catalyst synthesized using a conventional polyol process.

Figure SI 2: XPS spectra of CNF-Pt where core levels of (a) C1s (b) O1s and (c) Pt 4f are deconvoluted separately the circles represent the experimental data, red line represent the fitting data for overall signal, the black lines are the deconvoluted individual peaks for different species present in the sample.
The XPS analysis of core level spectra of CNF-Pt (Figure SI 2) and FCNF-Pt (Figure SI 3) confirms the formation of Pt-carbon nanofiber hybrid electrocatalyst. The peak position, line shape and peak to peak separation are the standard measure of the Pt oxidation state. For example, the B.E. for Pt 4f doublet (71 eV and 75 eV) is consistent with Pt $^0$ oxidation state in case of both the catalysts [Figure SI 2(c) and SI 3(c)]. Interestingly, this analysis suggests that, a slight shift in the binding energy (BE) of 4f peak occurs due to the catalyst support, where a charge transfer could occur from the electron rich nanofiber support to the Platinum metal.

Figure SI 2(a) shows C1s XP spectrum of CNF-Pt, where the deconvolution of the peak with respect to Gaussian fitting shows two distinct peaks at 284.5 eV and 286.1 eV, respectively. We have taken 284.5 eV peak as the reference peak for sp$^2$ carbon of nanotubes, while peak at 286.1 eV is attributed to the C1s peak for physisorbed C-Pt linkage. In case of FCNF-Pt [Figure SI 3(a)] other than the above mentioned two peaks, two peaks at 288.2 eV and 289.7 eV is also observed. These peaks confirms the presence of other oxygenated functional groups like –OH, -COOH on the nanofiber side walls after functionalization and since the peak positions are assigned on the basis of the C1s peak at 284.5 eV, all these do not affect the other B.E. values.

A comparison of O1s XP spectra of both samples also confirms the functionalization of nanofiber support. Accordingly, Figure SI 2(b) shows two different peaks after a similar fitting procedure; a peak at binding energy 532.4 eV could be due to the presence of small amount of oxygenated species and the peak at 535.5 eV might be due to the adsorbed moisture. However, XP spectra of FCNF-Pt [Figure SI 3(b)] clearly indicate two different functionalities after the functionalization. Accordingly, a peak at 531.2 eV could be assigned to the double bonded oxygenated groups like –COOH. Similarly, a peak at 533.2 eV could be assigned to the single
bonded oxygenated species like –OH species. In addition, a broad and less intense peak at 535 eV is assigned to the adsorbed moisture.

Figure SI 3: XPS spectra of FCNF-Pt where core levels of (a) C1s, (b) O1s and (c) Pt 3d are deconvoluted separately; the circles represent the experimental data, red line represents the fitting data for overall signal, the black lines are the deconvoluted individual peaks for different species present in the sample.