A graphene-carbon nanotube hybrid for high performance proton exchange membrane fuel cells (PEMFC)

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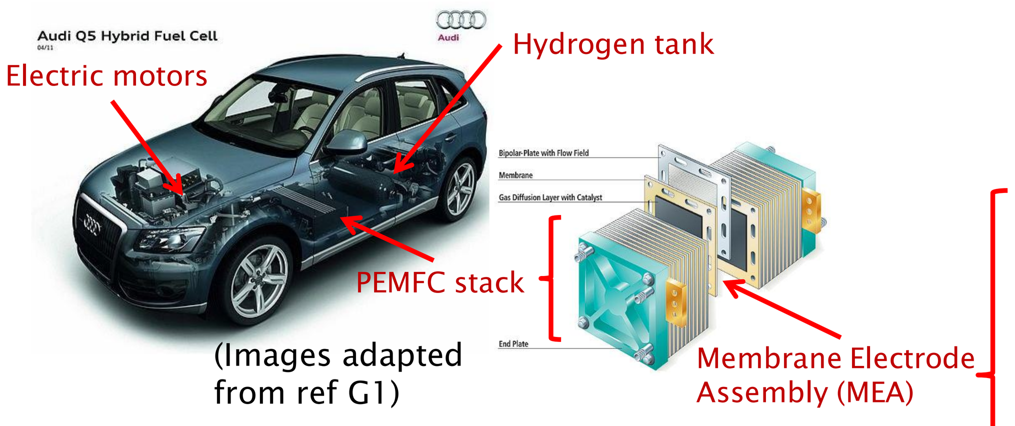
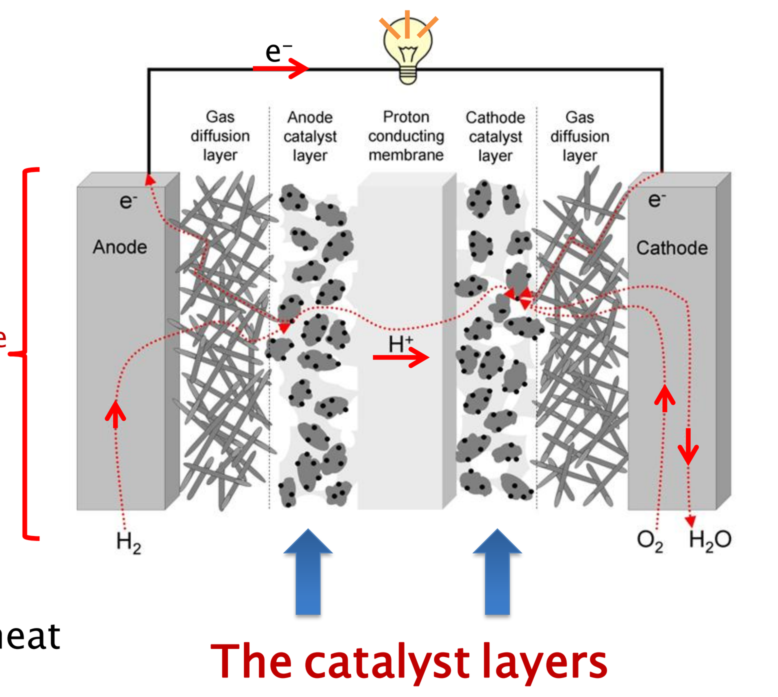
1. Introduction and objective





Proton Exchange Membrane Fuel Cell (PEMFC) is a suitable renewable energy technology for transportation [1,2]

- Combustion engine: $C_xH_y + O_2 \rightarrow CO_2 + H_2O$ + heat
- PEMFC: $H_2 + O_2 \rightarrow H_2O$ +heat + electricity

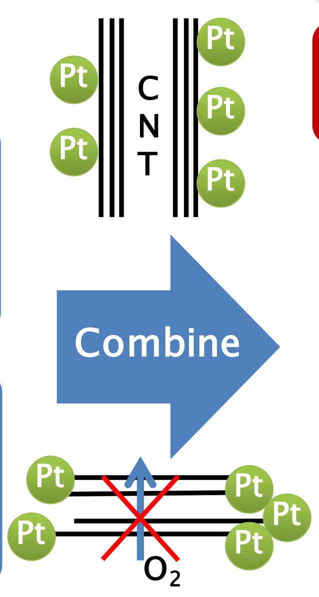
Challenges of the catalyst layer
- Low Pt utilisation due to the too small pore size of the carbon black support
- Carbon corrosion in the carbon black due to the low crystalinity

Desirable catalyst support [3]
- Highly graphitic, high electrical conductivity
- High surface area and porous, preferably 20-40 nm pore sizes
- Exposure of graphitic edges

Graphitic nanomaterials

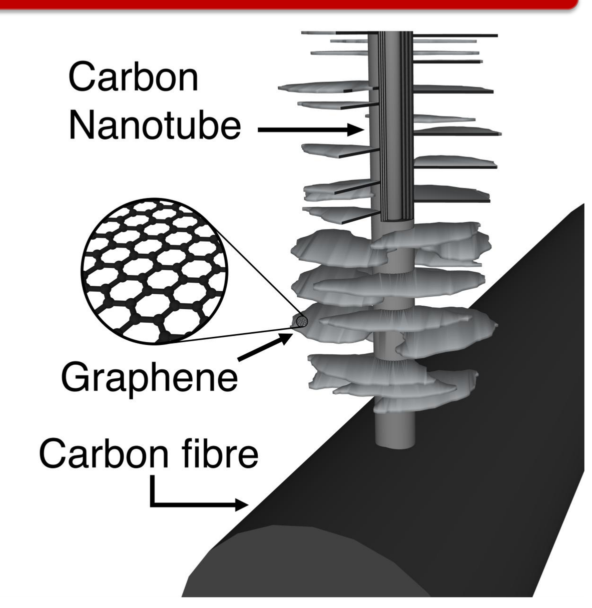
Carbon nanotubes: Porous but expose basal graphitic plane

Graphene: Active edge planes but restacks due to the 2D morphology

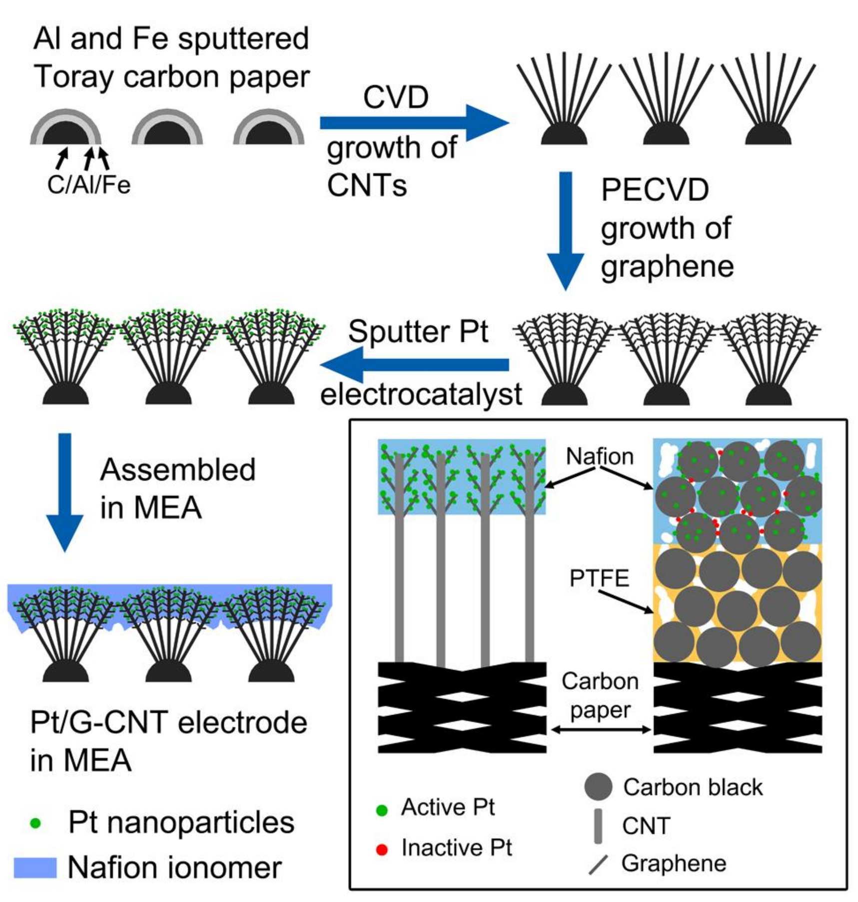


Proposed carbon support nanostructure [4]

Graphene-Carbon Nanotube hybrid
- Directly grow graphene onto CNT structure
- Expose numerous edge planes
- Remain porous



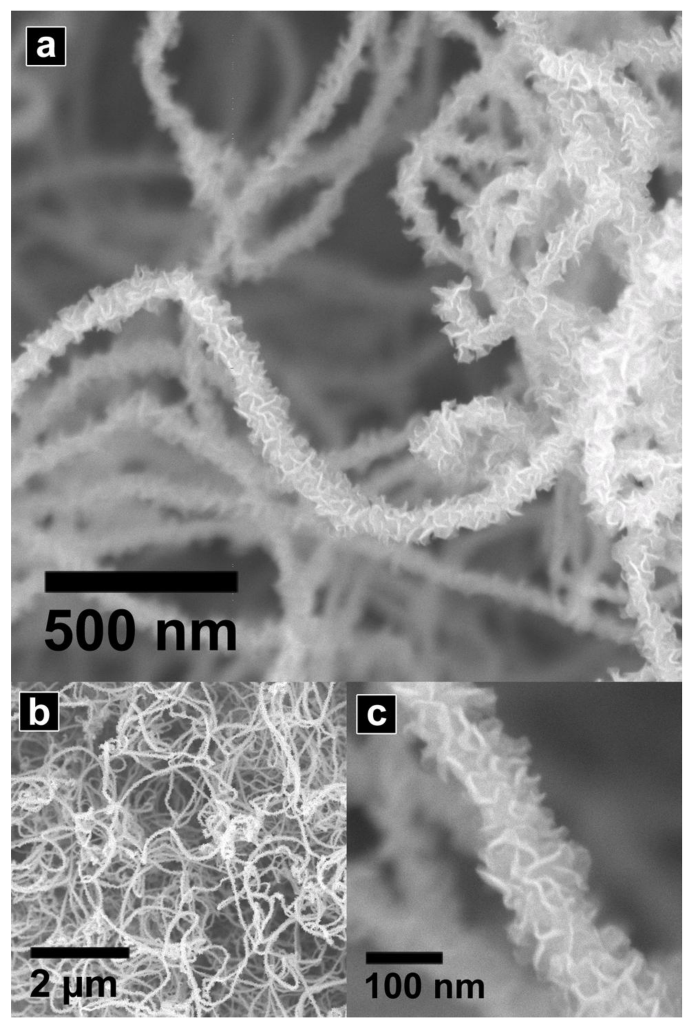
2. Method



1. Direct growth of carbon nanotubes (CNT) on Toray carbon paper using the thermal chemical vapour deposition (CVD) method
2. Direct growth of graphene onto the CNT scaffold, forming **the graphene-carbon nanotube hybrid (G-CNT)**, using the radio frequency plasma enhanced chemical vapour deposition (PECVD) method
3. Deposition of platinum on the G-CNT hybrid at an ultra-low loading of 0.04 mgPt/cm², using the magnetron sputtering method
4. Assembling into the membrane electrode assembly (MEA) of the PEMFC

Scheme 1. Schematic illustration of the Pt/G-CNT cathode fabrication process and (inset) the structural comparison of the Pt/G-CNT cathode (left) and the conventional carbon black-based cathode (right).

3. Results and Discussions [4]



Morphological characterisation of the G-CNT hybrid with SEM
- Unique nanostructure with the graphene grown densely along the CNT scaffold
- Overall diameter of approximately 100 nm
- Expose a high density of active graphene edges while retaining the porous structure of CNT
- When used as the Pt catalyst support in PEMFC, a high density of anchor points for Pt nano-particles attachment is provided
- Direct electrical conducting pathways from the Pt catalyst nanoparticles to the carbon paper are offered

Figure 1. SEM micrographs of the G-CNT hybrid at (a) medium magnification, (b) lower magnification and (c) higher magnification.

Microstructural characterisation of the G-CNT hybrid with TEM
- Semi-transparent appearance suggests an ultra-thin morphology of the graphene sheets
- HRTEM image confirms the layered structure of the graphene sheets, comprising of a few graphitic layers

Raman spectroscopy confirms the graphitic nature of the G-CNT hybrid with strong graphitic signature peaks D, G, 2D, etc

X-ray Photoelectron Spectroscopy (XPS) confirms the high purity of the G-CNT hybrid. The G-CNT hybrid is confirmed as a carbon-based material.

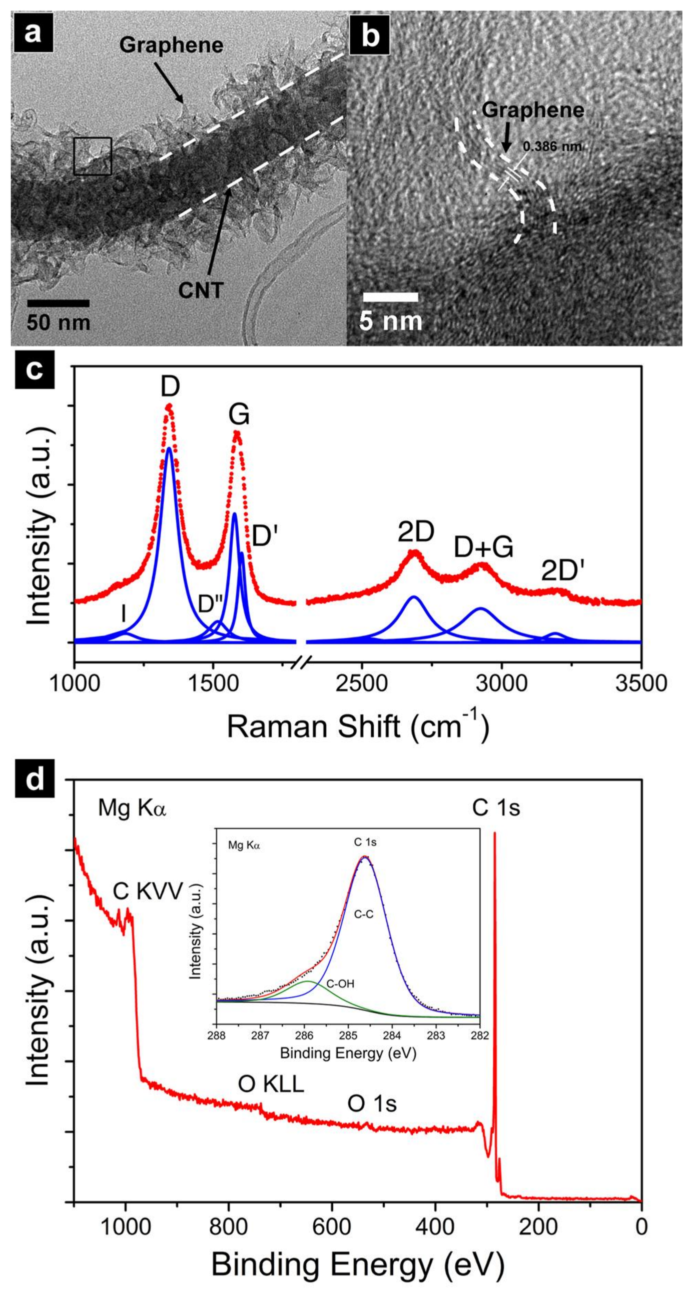
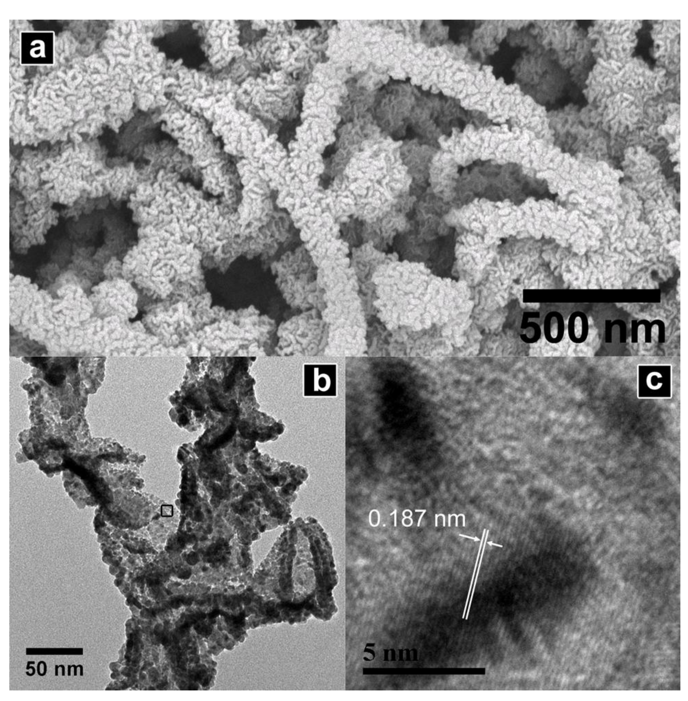


Figure 2. (a) Bright field TEM micrograph of the hybrid; (b) HR-TEM micrograph of the G-CNT in the region outlined by the black-coloured square in figure (a); (c) Raman spectrum (red curve) with peak fittings (blue curves) of the hybrid; (d) Survey scan XPS spectrum and (inset) high resolution scan of C 1s peaks of the hybrid.



Microstructural characterisation of the Pt/G-CNT hybrid with SEM and TEM
- The resulting material retains the overall structure of the G-CNT hybrid, with the thickening of the leaf-like features due to the deposition of Pt
- Crystalline Pt nanoparticles attach densely on the surface of the G-CNT hybrid, especially along the graphene edges

Figure 3. (a) SEM and (b) TEM micrograph of the Pt/G-CNT hybrid, and (c) HR-TEM micrograph of the hybrid in the region outlined by the black square in figure (b).

Polarisation performance of the Pt/G-CNT-based cathode
- Remarkable improvement over carbon black and CNT supported Pt catalysts throughout the current density range
- ~20% higher power density than the carbon black supported Pt, and a great improvement over the CNT supported Pt
- Reduce the required Pt loading

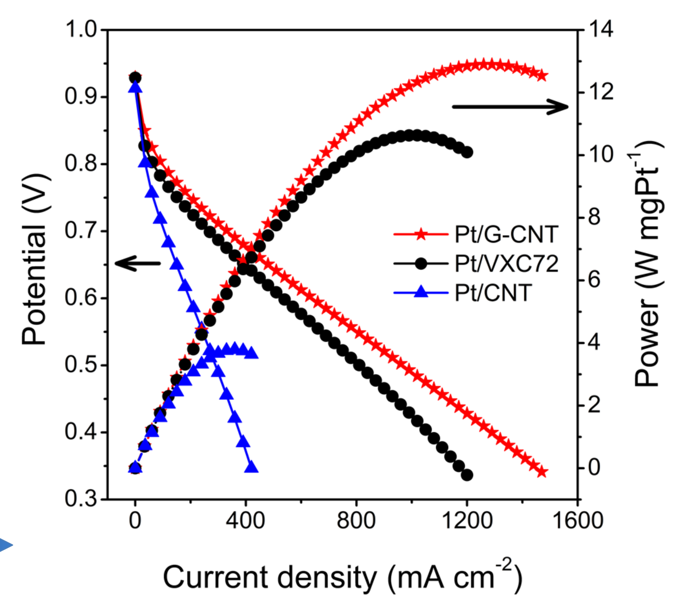


Figure 4. Polarisation measurements of MEAs with Pt/G-CNT, Pt/VXC72 and Pt/CNT cathodes.

4. Conclusions and future work
- The direct growth of the G-CNT hybrid on carbon paper is reported
- The hybrid combines the advantages of an ultra-high density of active graphene edge planes with the porous structure of CNT scaffolds in a single material
- The G-CNT hybrid suggests an effective structure to better utilise the Pt catalyst material and to reduced the required Pt loading in PEMFC

Future work:
- Characterisation of the G-CNT hybrid's 3D structure
- Study the effect of the G-CNT hybrid on the durability of PEMFC

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Graphic sources:
G1. Retrieved on 27/02/2014 from http://www.autoevolution. com (left); http://www.bloggang.com (centre); http://www.pfrang.de (right).