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Development of 3D graphene structures and their prospective applications

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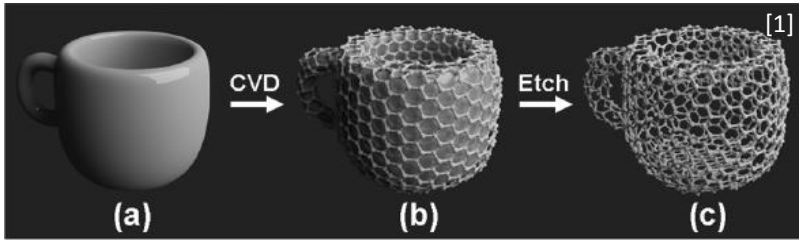
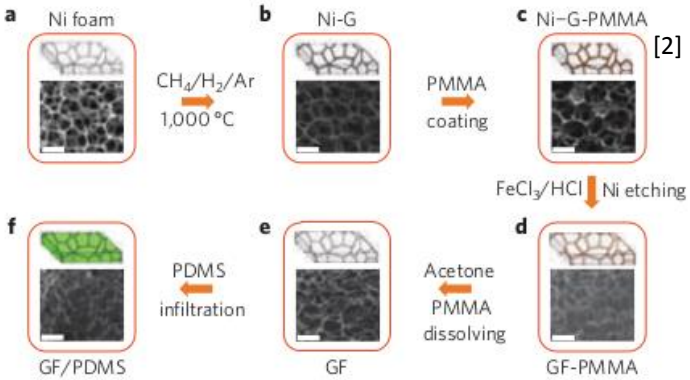
IMM Institute for Microelectronics and Microsystems
Bologna Section



[1]

We can grow graphene in virtually any shape we want!

→ **3D graphene materials**
e.g. graphene foams



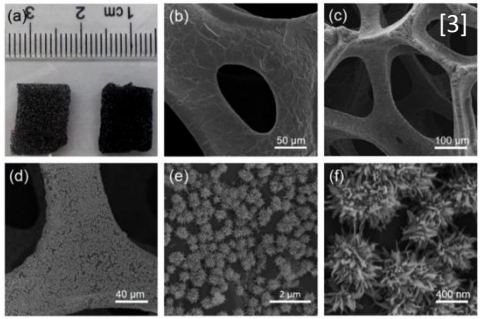
[2]

Applications

- Electrodes in supercapacitors, wearable devices, dye-sensitised solar cells, Li-ion batteries
- Electrochemical catalysts
- Gas sensing
- Adsorbents
- Thermal interface material
- Composites with polymers for flexible, foldable and stretchable conductors

Composites

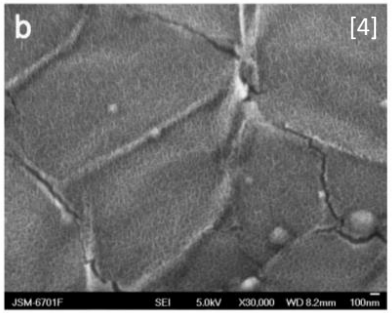
CuO nanoflowers



[3]

Biosensing

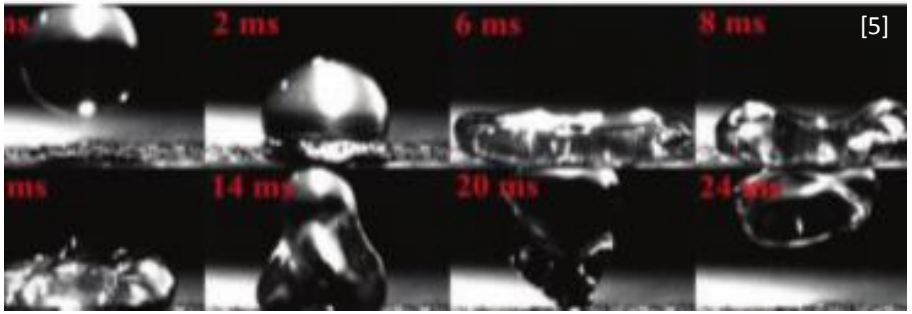
$Ni(OH)_2$



[4]

H_2 fuel cells

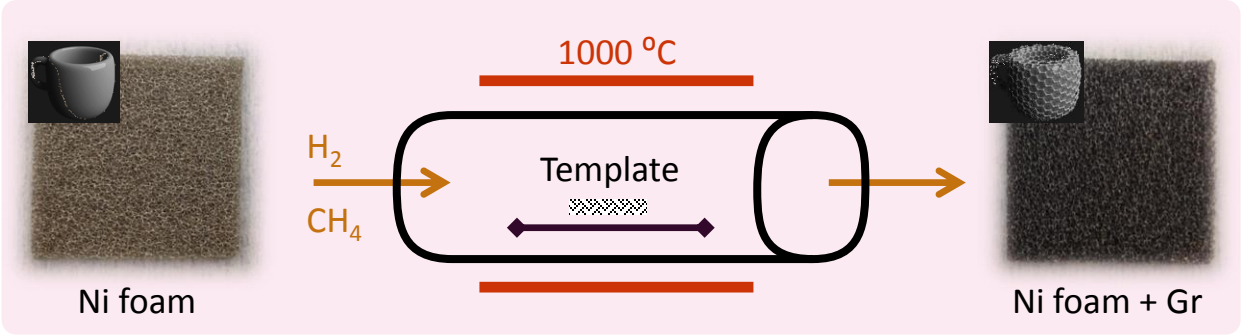
Teflon



[5]

Superhydrophobic coatings

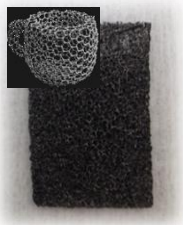
1. J Mater Chem C 2 (2014) 1879-1886
2. Nat Mater 10 (2011) 424-428
3. Biosens Bioelectron 59 (2014) 384-388
4. Int J Hydrogen Energy 39 (2014) 7876-7884
5. Small 9 (2013) 75-80



Metal foam precursors are washed thoroughly by ultrasonication in dilute HCl, DI water and acetone to remove contaminants

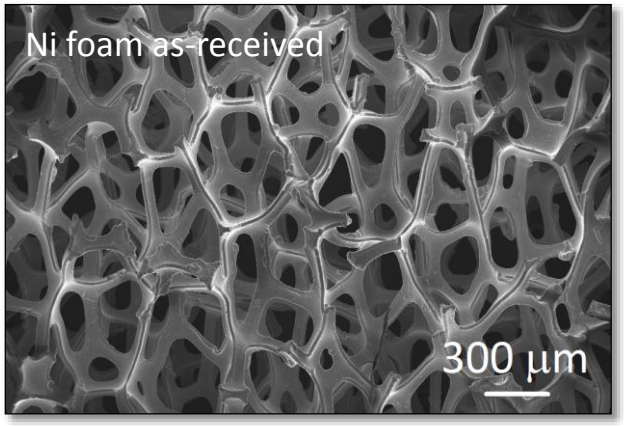
- Templates are annealed at 1000 °C under 50 sccm H_2 for 30 min to remove surface oxides
- Deposition is performed at atmospheric pressure under 500 sccm H_2 and 50 sccm CH_4 for 10 min

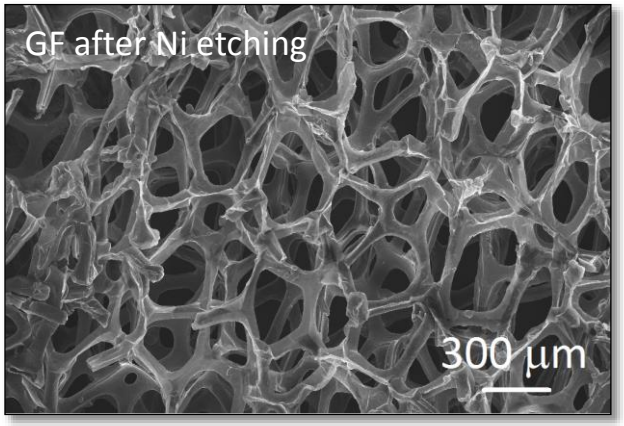
Ni is etched in 4.5% $FeCl_3$ at 80 °C overnight then salt residuals are removed using 10% HCl at 80 °C

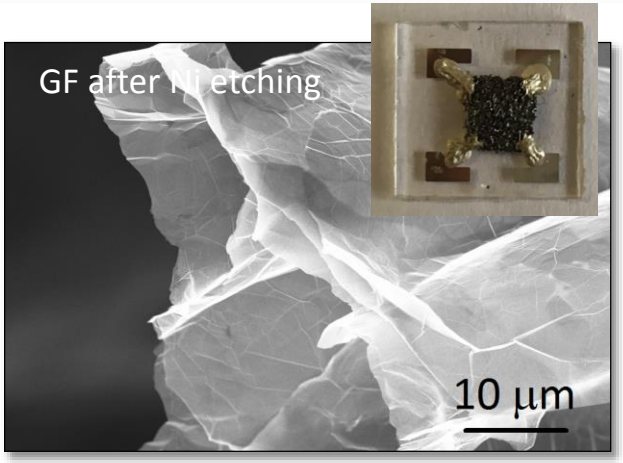


Graphene foam

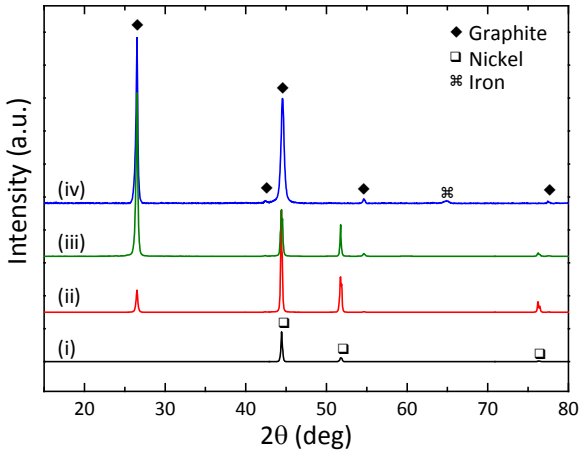
σ ~ 10 S/cm



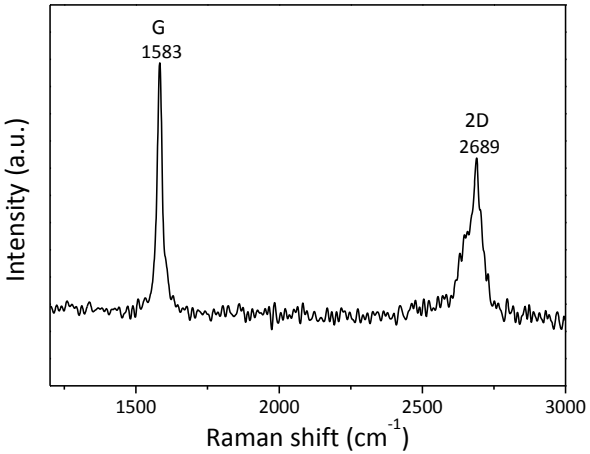




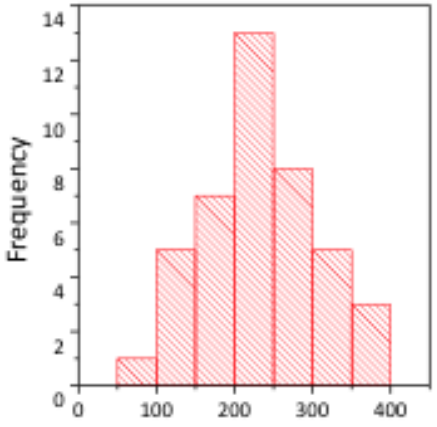
GF retains the structure of the Ni foam after it has been etched away, even without polymer support. Pore size ~100-400 µm. Hollow interior with graphene wall thickness 10-20 nm.



Hot $FeCl_3$ is very effective at removing Ni but traces of Fe remain



Multilayer graphene with minimal defects

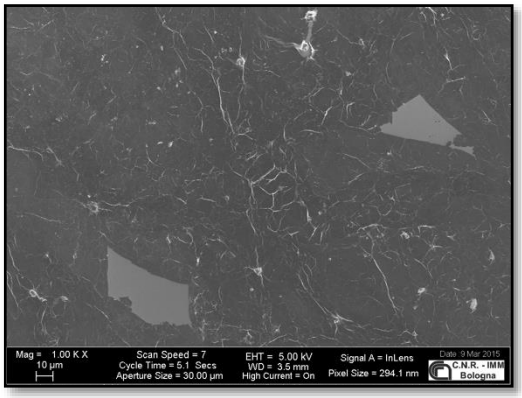


Pore size ~100-400 µm

500 sccm H_2 + 100 sccm CH_4

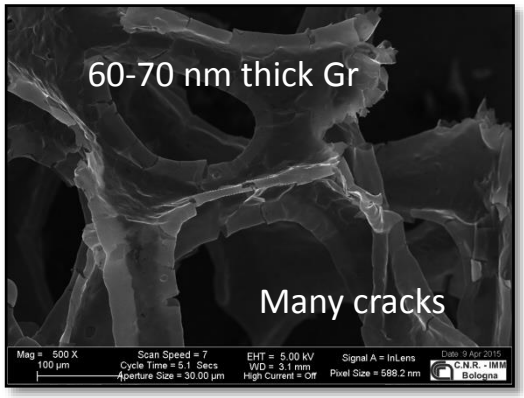
Could not be collected after PMMA removal

200 sccm H_2 + 100 sccm CH_4



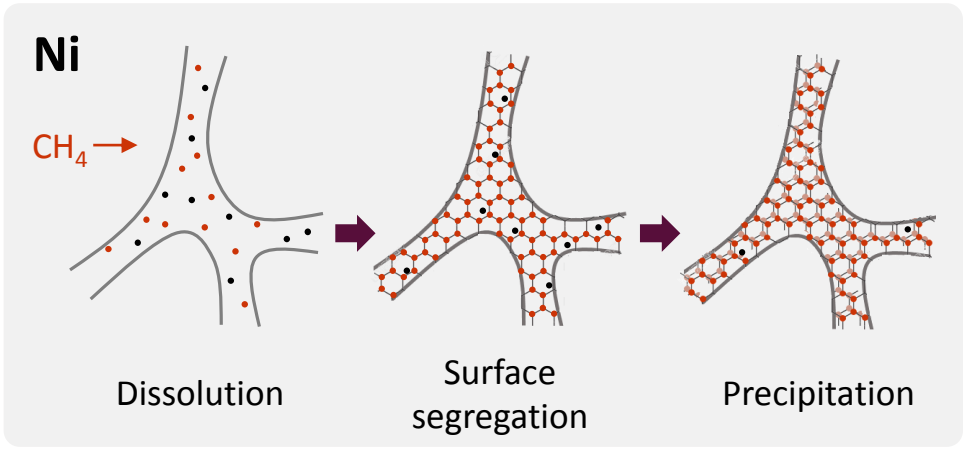
Collapsed into a film

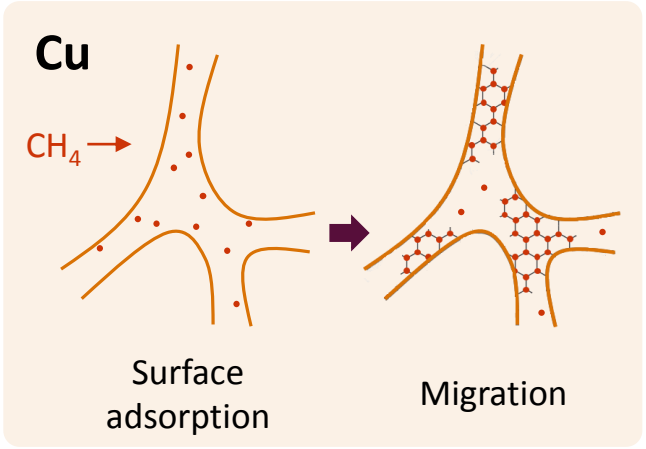
100 sccm H_2 + 100 sccm CH_4



Free-standing but broken graphene foam

The different appearance using Cu is most likely a result of the surface adsorption growth mechanism of graphene on Cu compared to dissolution-segregation-precipitation on Ni [6]

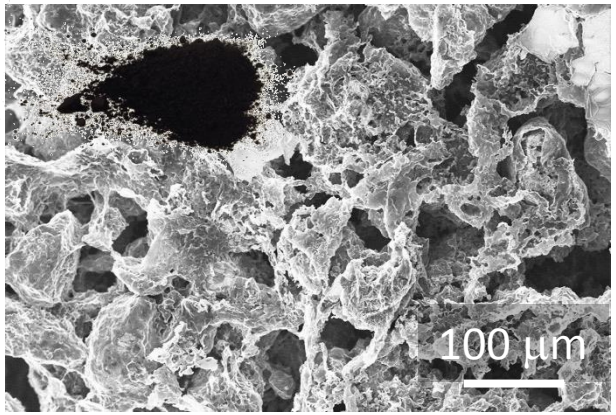


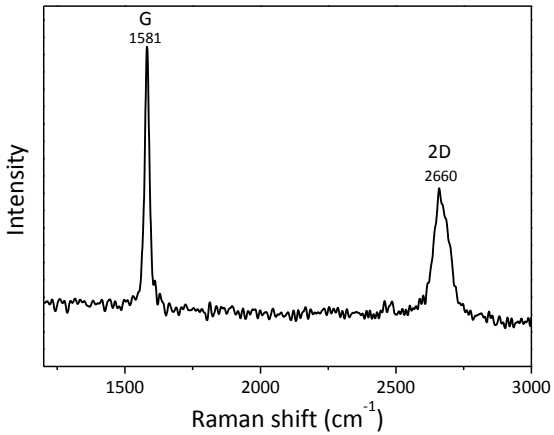


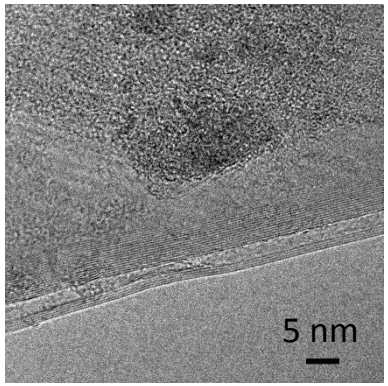
6. Nano Lett. 9 (2009) 4268-4272

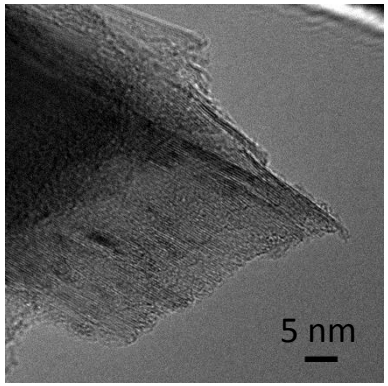
A smaller pore size could result in GF with better structural integrity as well as a greater volumetric energy density

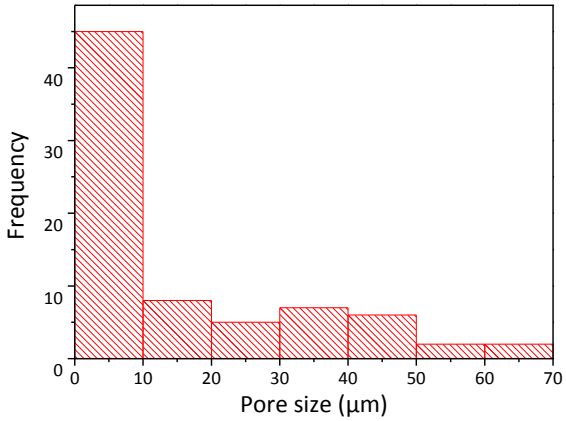
GF were synthesised on a template of Ni nanoparticles, sintered into a 3D network





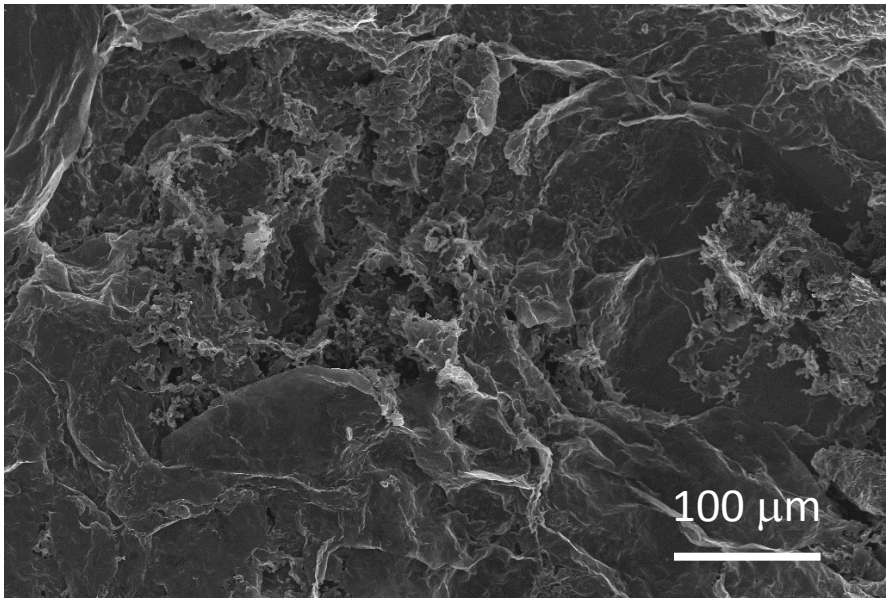




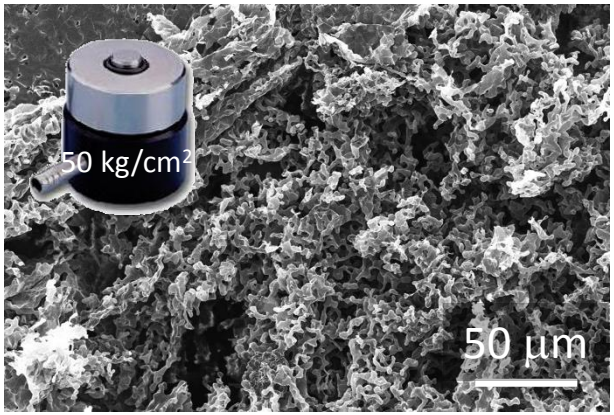


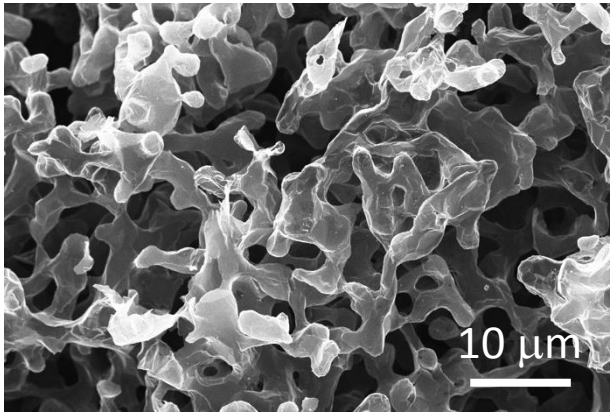
Resulting GF had few layer and multilayer areas, few defects and much smaller pores BUT the pore size distribution was not well controlled

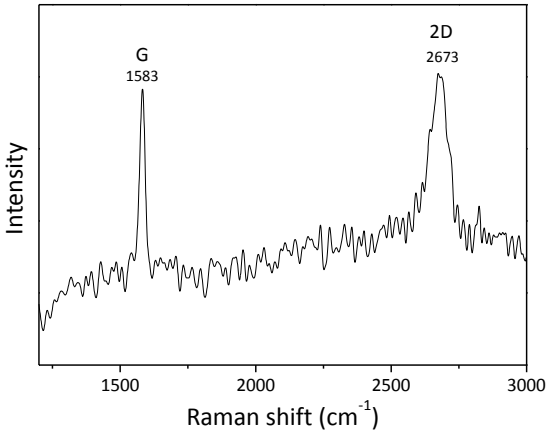
To try to control the pore size distribution, nanoparticles were first pressed into pellets but the minimum pressure reachable using a hydraulic press was too high to form porous materials

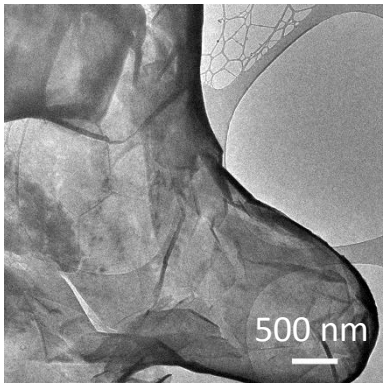


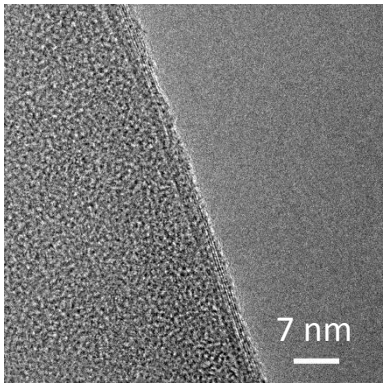
Optimised GF were grown on a template of a mixture of Ni and NiO nanoparticles, hand-pressed into a pellet with ~50 kg/cm^2 pressure

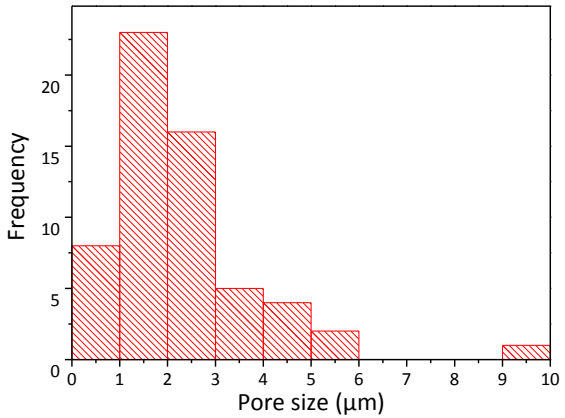




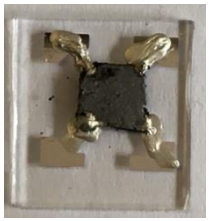






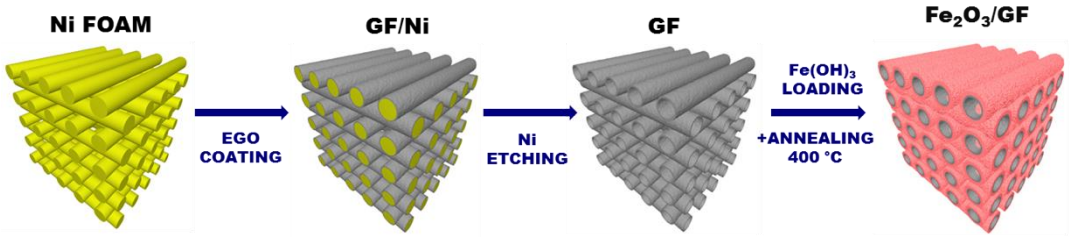


σ ~ 25 S/cm



As before, the resulting GF had few layer and multilayer areas, and few defects but also a well-controlled pore-size distribution in the range of <1-5 µm

Previous work in our groups:



CARBON 84 (2015) 254–262
Available at www.sciencedirect.com
ScienceDirect
journal homepage: www.elsevier.com/locate/carbon

Electrochemically exfoliated graphene oxide/iron oxide composite foams for lithium storage, produced by simultaneous graphene reduction and $Fe(OH)_3$ condensation

Zhen Yuan Xia [a], Di Wei [b], Elzbieta Anitowska [a], Vittorio Bellani [c], Luca Ortolani [d], Vittorio Morandi [d], Massimo Gazzano [a], Alberto Zanelli [a], Stefano Borini [b], Vincenzo Palermo [a,]*

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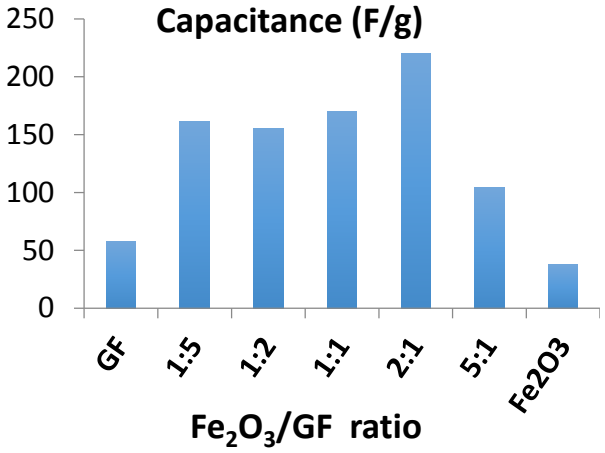
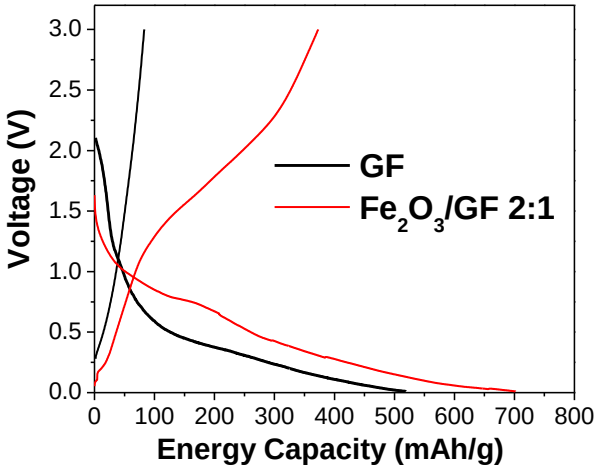
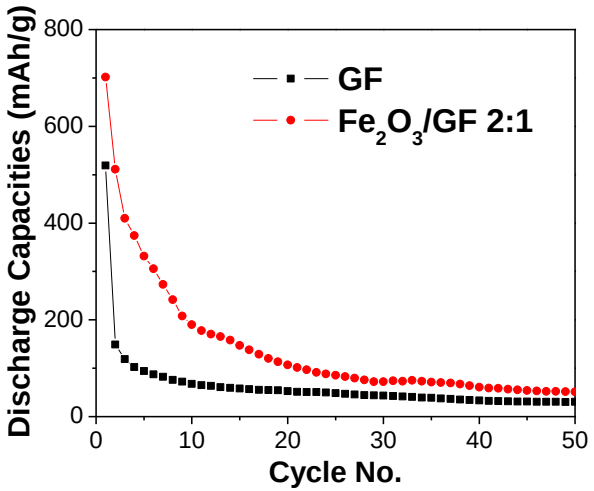
Combining GF with Fe_2O_3 leads to significantly improved specific capacity. A free-standing GF/Fe_2O_3 composite could be used as an electrode in Li-storage materials without the need for a Cu or Ni current collector or polymer binder.





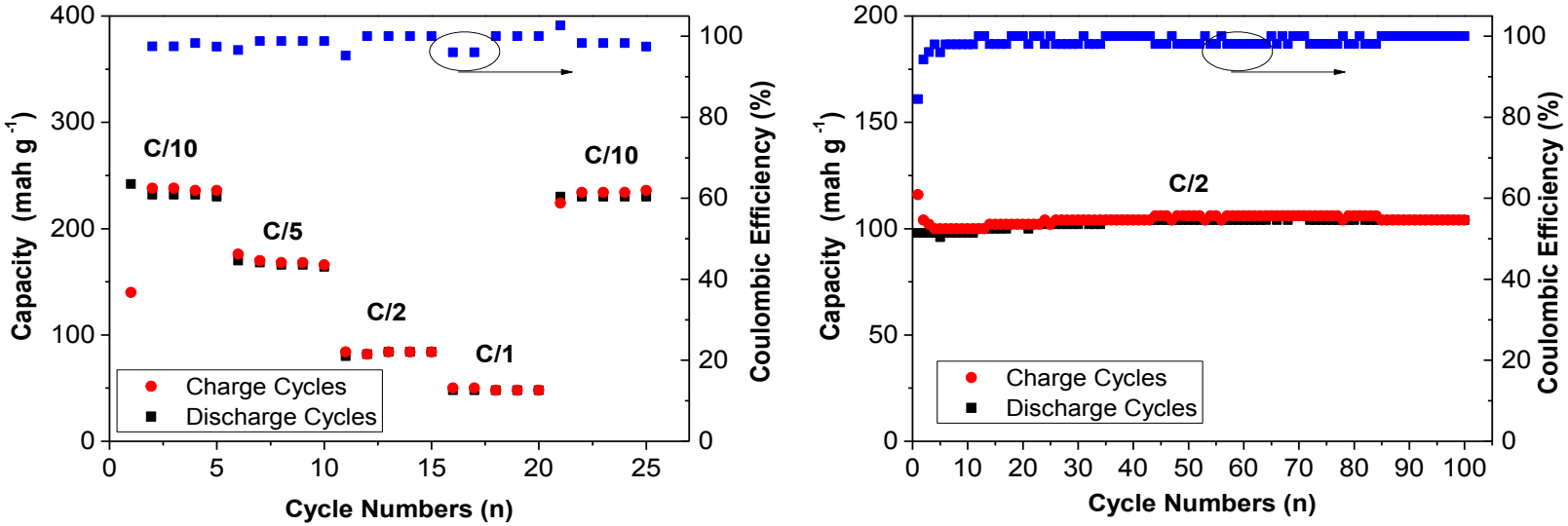


The cycling capability of the GF was poor, perhaps due to the discontinuous nature of the EGO. Could CVD GF provide a better result?

6. Carbon 84 (2015) 254-262

A first test of the electrochemical properties was performed on GF with Ni still inside:

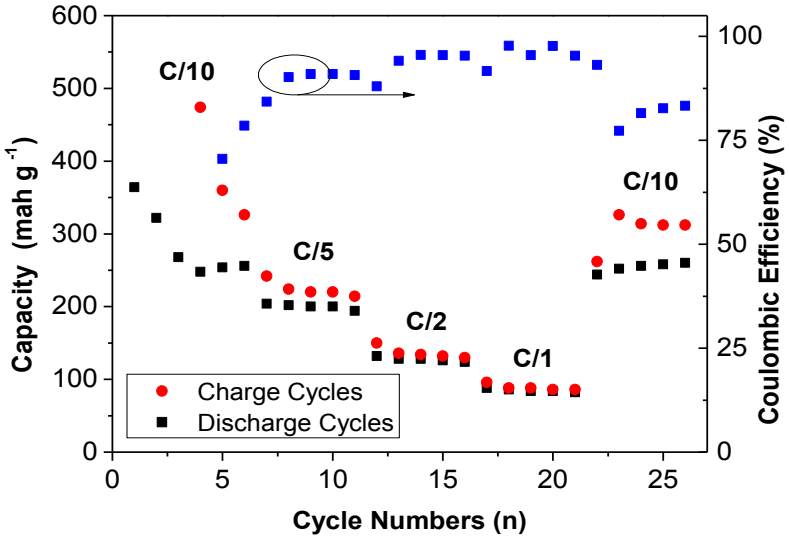
CVD-G on Ni Foam

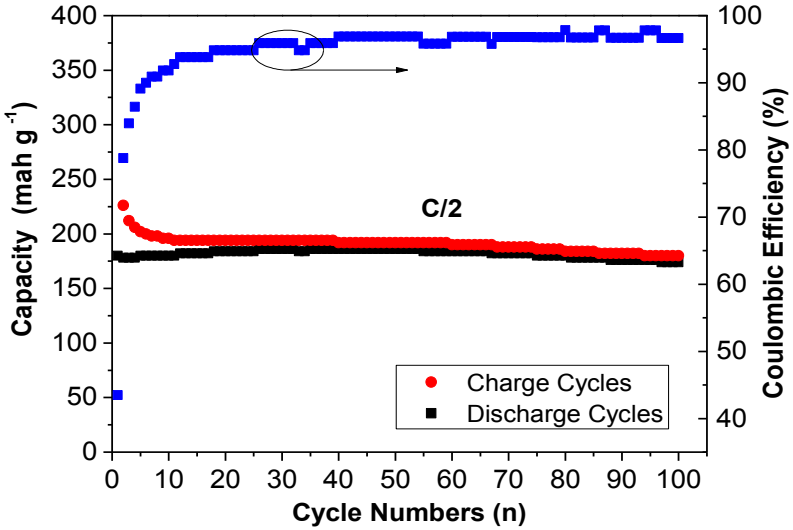


Conditions: 3-electrode configuration, with working electrode CVD graphene on Ni foam (ø 9 mm) and lithium foil as counter/reference electrode. Electrolyte 1 M $LiPF_6$ (LP30, BASF) in a 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)

Given these promising results, measurements were also performed on free-standing GF:

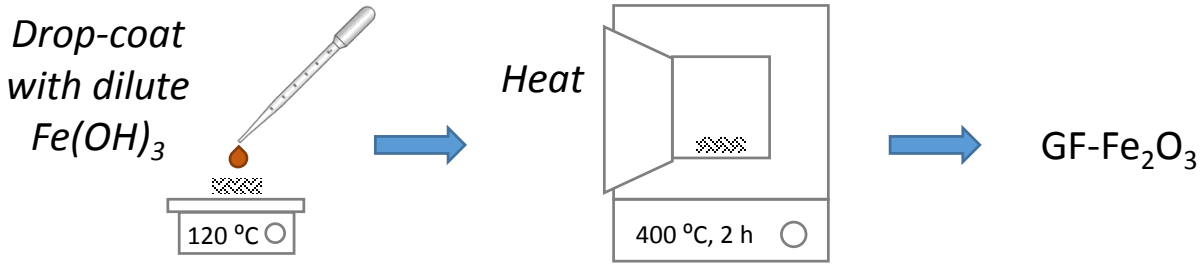
Free-standing CVD-G

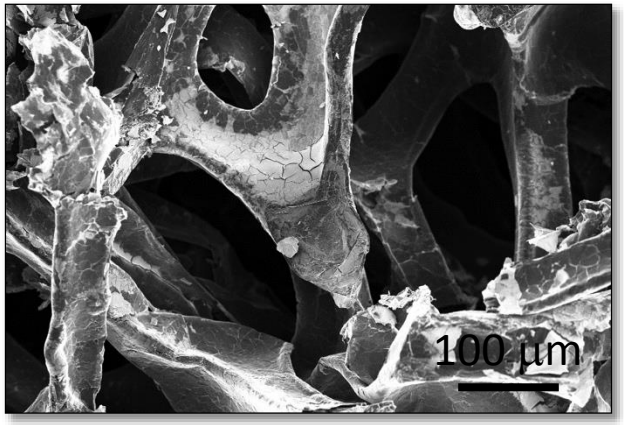


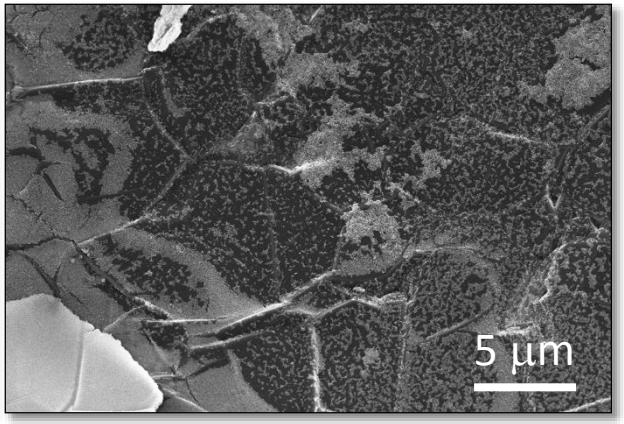


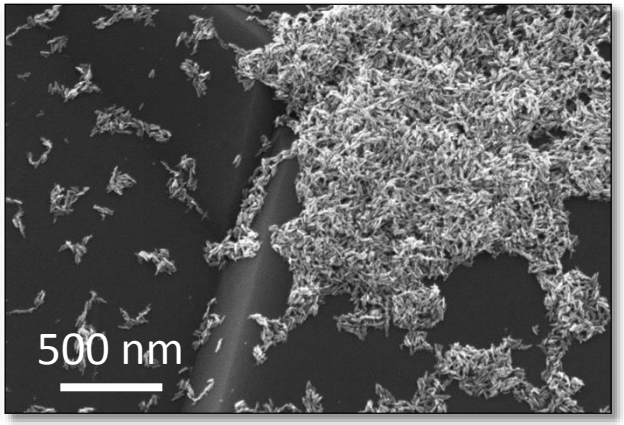
The GF showed excellent performance over 100 cycles. However, they were very fragile so a lot of care needed to be taken when assembling the cells!

CVD GF were functionalised by a chemical procedure similar to that used for the EGO GF





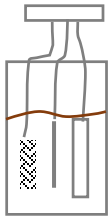


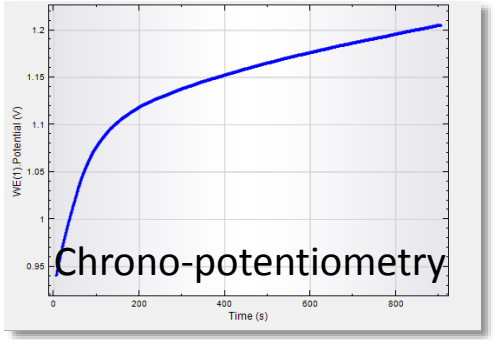


Due to the hydrophobicity of CVD graphene, the coating was sparse and uneven

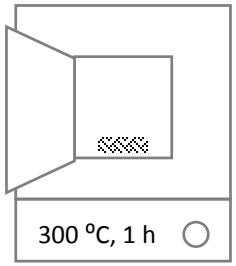
To create a more even coating, the deposition was instead performed electrochemically

Electrochemical deposition of FeO(OH)



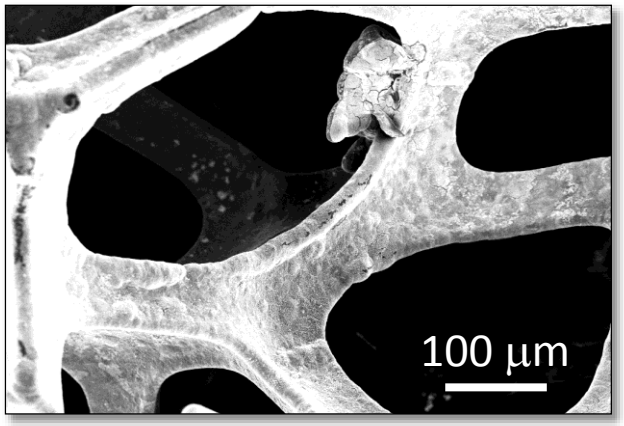


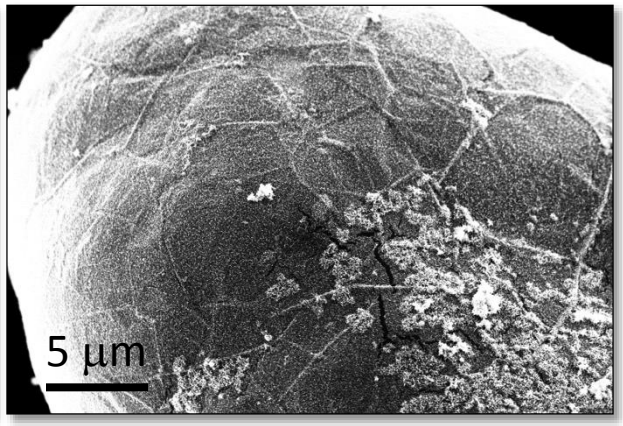
Heat

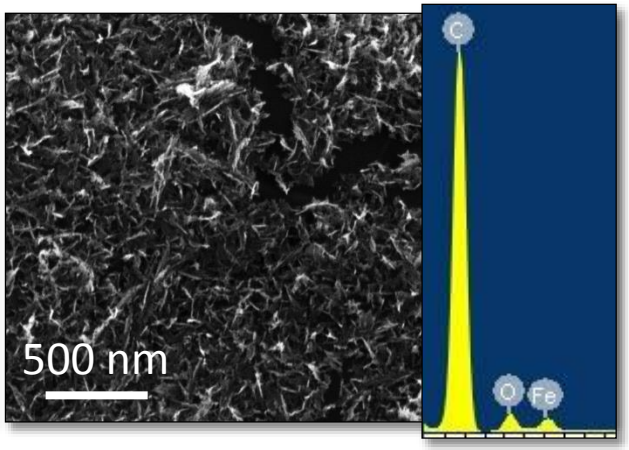


$GF\text{-}Fe_2O_3$

Porous Iron Oxide was deposited at an anodic current density of 0.125 mA cm^{-2} in an aqueous solution of 0.2 M CH_3COONa, 0.1 M Na_2SO_4 and 0.1 M $Fe(NH_4)_2(SO_4)_2.6H_2O$ at room temperature for 15 minutes, and further annealing at 300 °C for 1 hour [7]





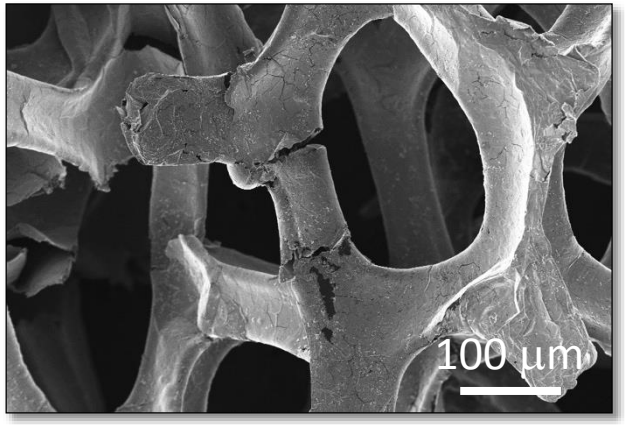


In this way, the outer branches of GF were evenly decorated with a layer of flower-like Fe_2O_3 nanocrystals. However, the inner branches were not completely covered

7. J. Electrochem. Soc. 156 (2009) A737-A743

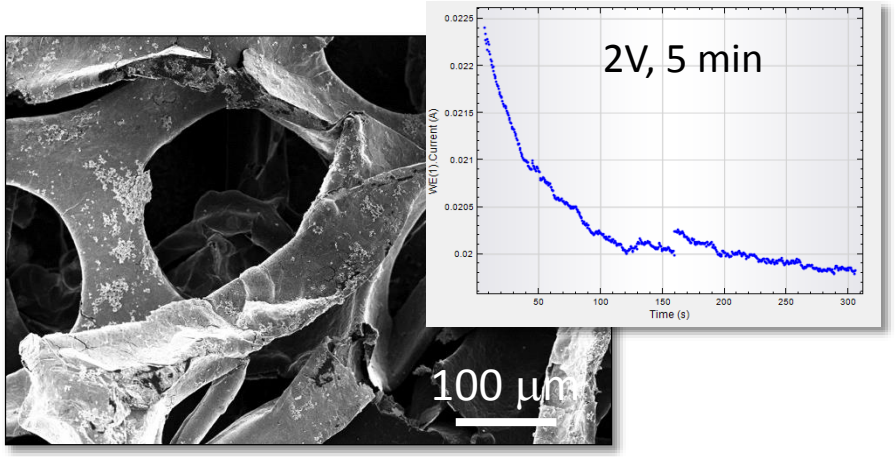
A series of treatments were attempted to improve coverage of the inner branches of GF

Removal of Fe_2O_3 and re-deposition



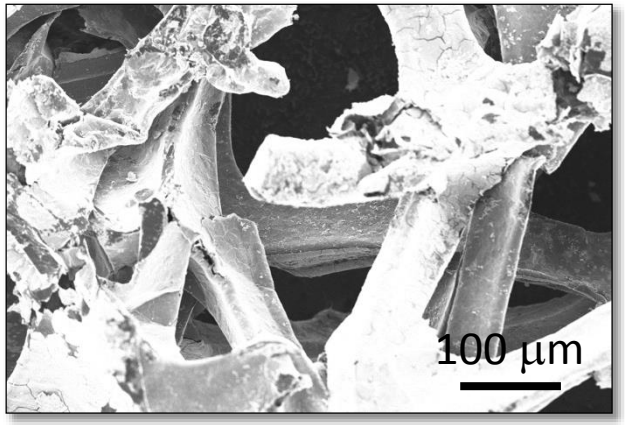
Very effective but wasteful and not easily reproducible

EC oxidation pre-treatment (chrono amperometry)



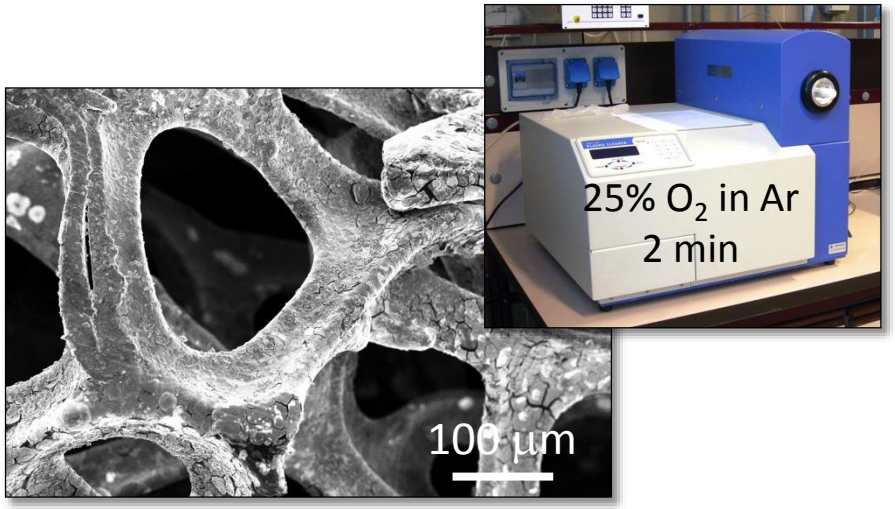
Ineffective

Ethanol pre-treatment



Effective as EtOH wets hydrophobic GF

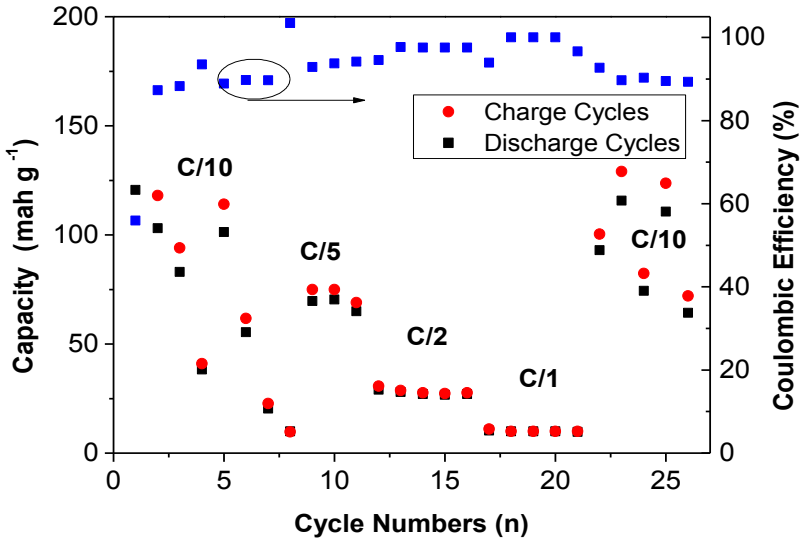
Plasma pre-treatment

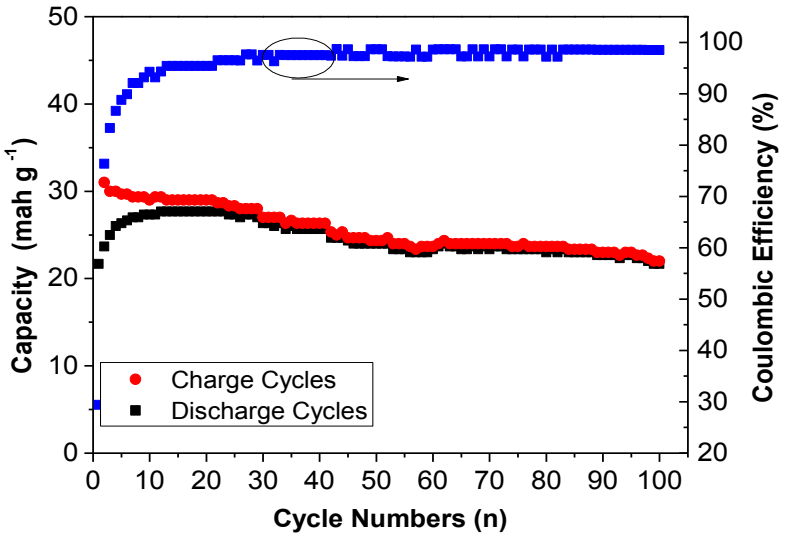


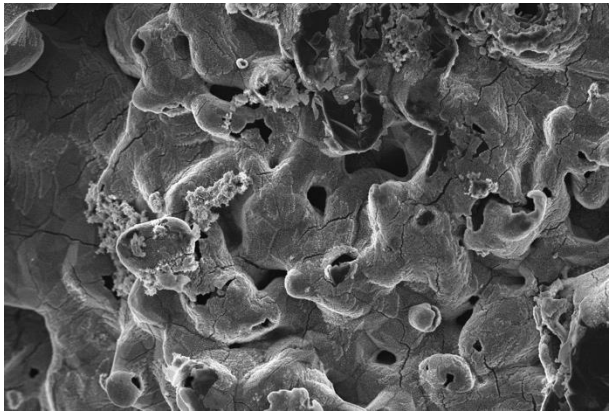
Effective oxidation of all surfaces

Electrochemical performance to be confirmed!

Reduced pore-size GF are less fragile than those with very large empty pores. Preliminary measurements showed good potential but some deterioration, probably due to contaminants

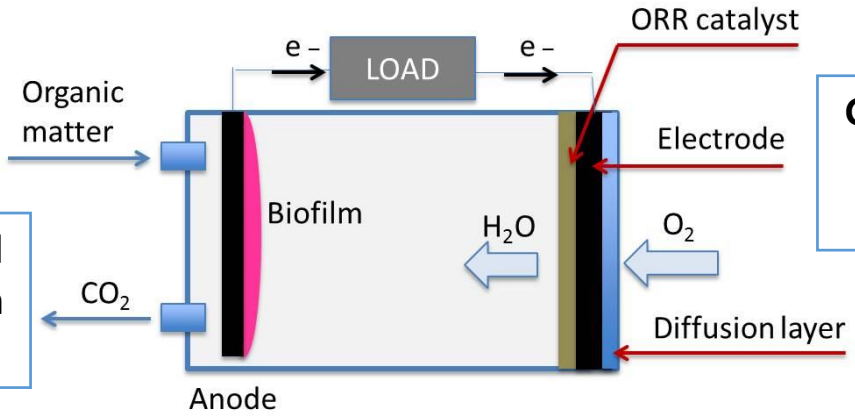






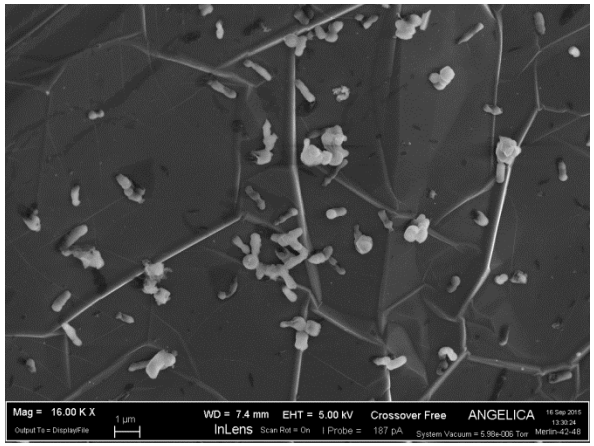
These GF were functionalised with Fe_2O_3 nanocrystals as before. They were evenly decorated with nanocrystals, even without pre-treatment. Electrochemical measurements are to be performed

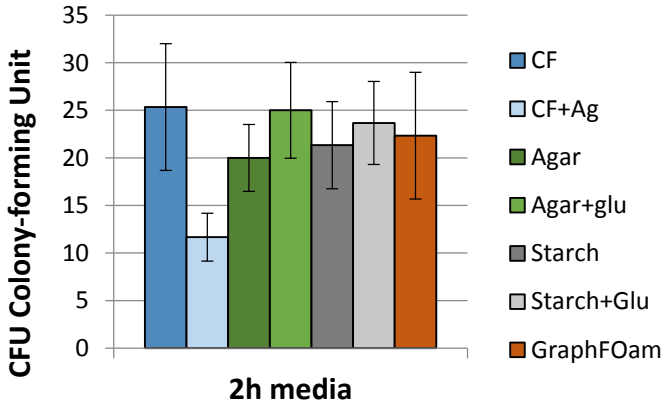
Microbial fuel cells have the ability to convert wastewater and other organic matter into electricity using the natural processes of microorganisms



GF@anode: electrode and support for biofilm growth and proliferation

GF@cathode: electrode and manager of oxidation-reduction reaction (ORR)

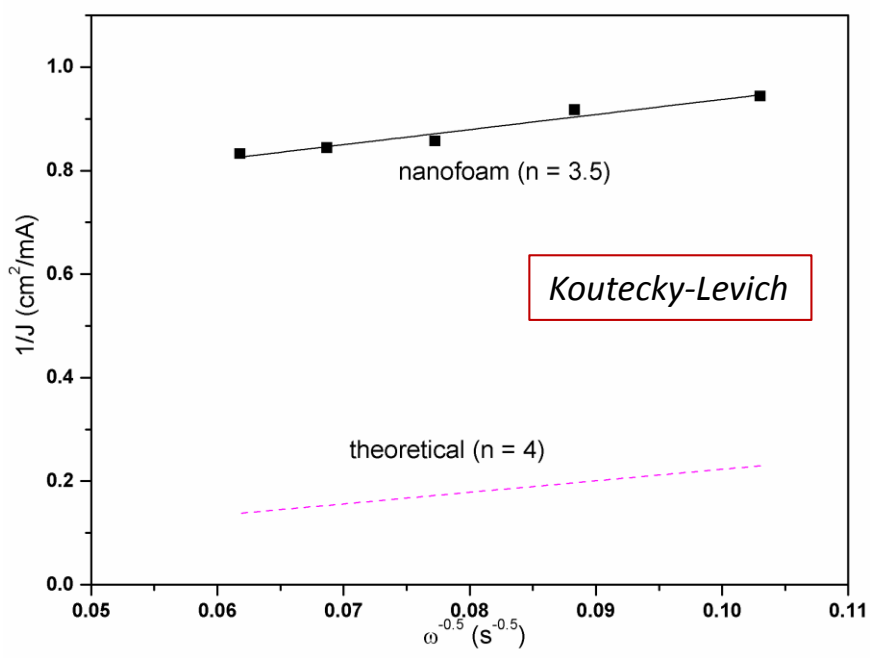


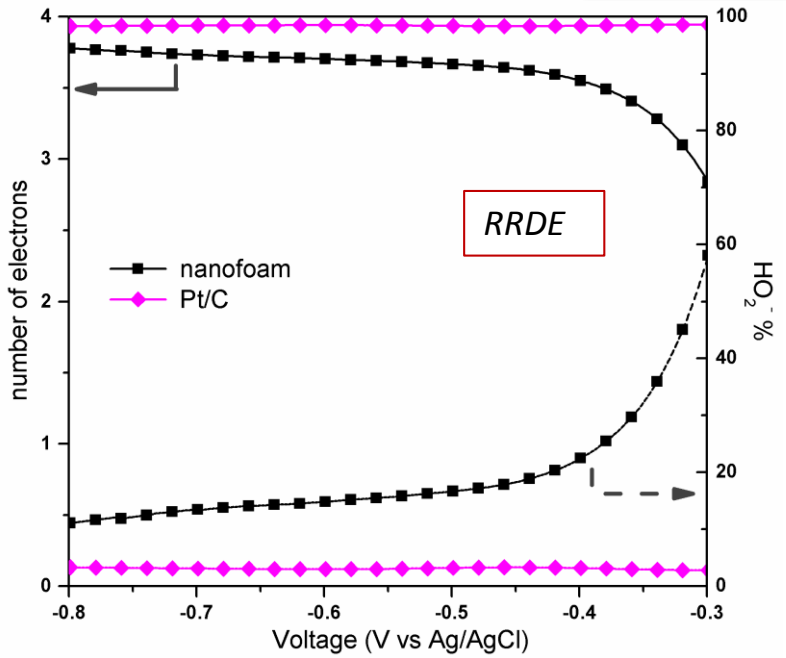


Cytotoxicity tests OK!

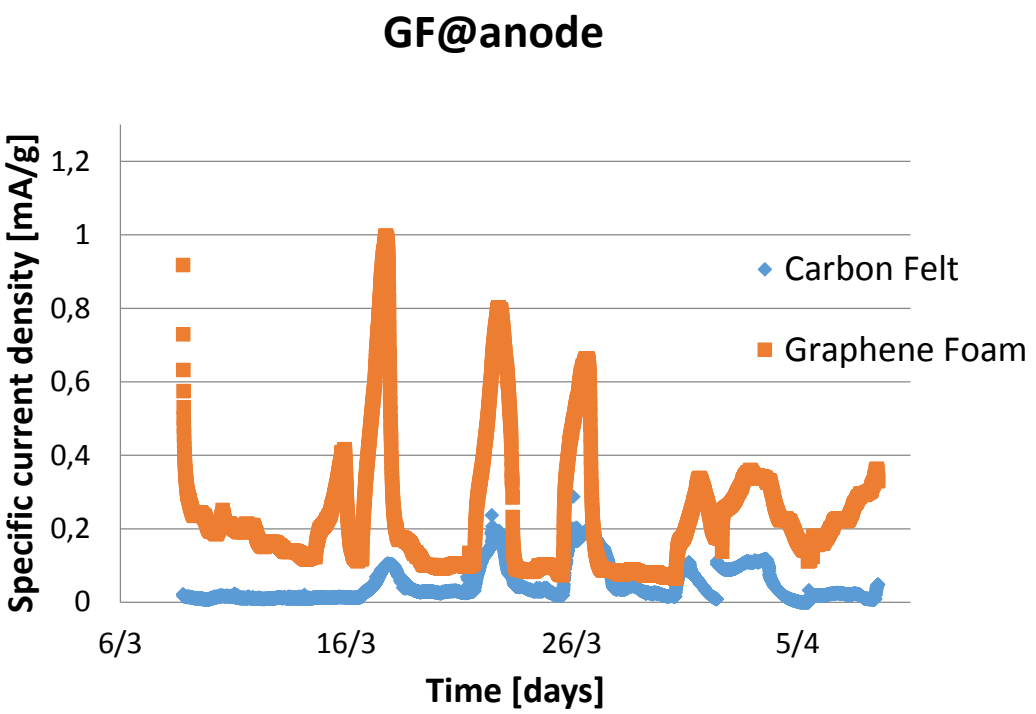
GF@cathode

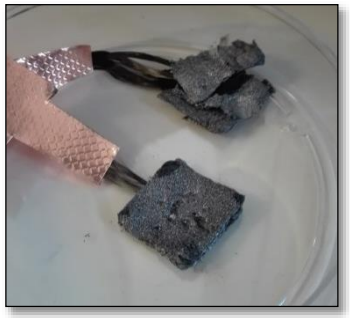
ORR $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$





GF is used as a charge collector and a catalyst for the ORR. Even without modification it performs much better than expected for a simple graphene film – probably residual Fe nanoparticles from the etching procedure provide additional catalytic activity.





GF is used as a substrate for the biofilm, showing significant improvement over standard carbon felt. However, the improvement should be much greater for this class of materials – once again the fragility of the GF leads to deterioration in the result over time.

- High quality GF were simply produced by CVD and the template etching process optimised
- GF with reduced and controlled pore size (1-10 μm) were produced using Ni/NiO nanoparticle templates. These have the potential to overcome problems of fragility while simultaneously introducing new possibilities for applications
- GF of both kinds show good potential for use as battery electrodes. Compared to previous tests, there was little or no deterioration of the capacity over 100 cycles
- CVD GF are very hydrophobic, making them difficult to functionalise by chemical means but after suitable pre-treatments (e.g. ethanol or plasma), CVD GF were successfully functionalised with flower-like Fe_2O_3 nanocrystals using electrochemical methods. Electrochemical measurements are in progress
- GF showed great potential for use as both anode and cathode materials for microbial fuel cells, but problems of fragility need to be overcome

Thank you for your attention

Come and visit booth 26….

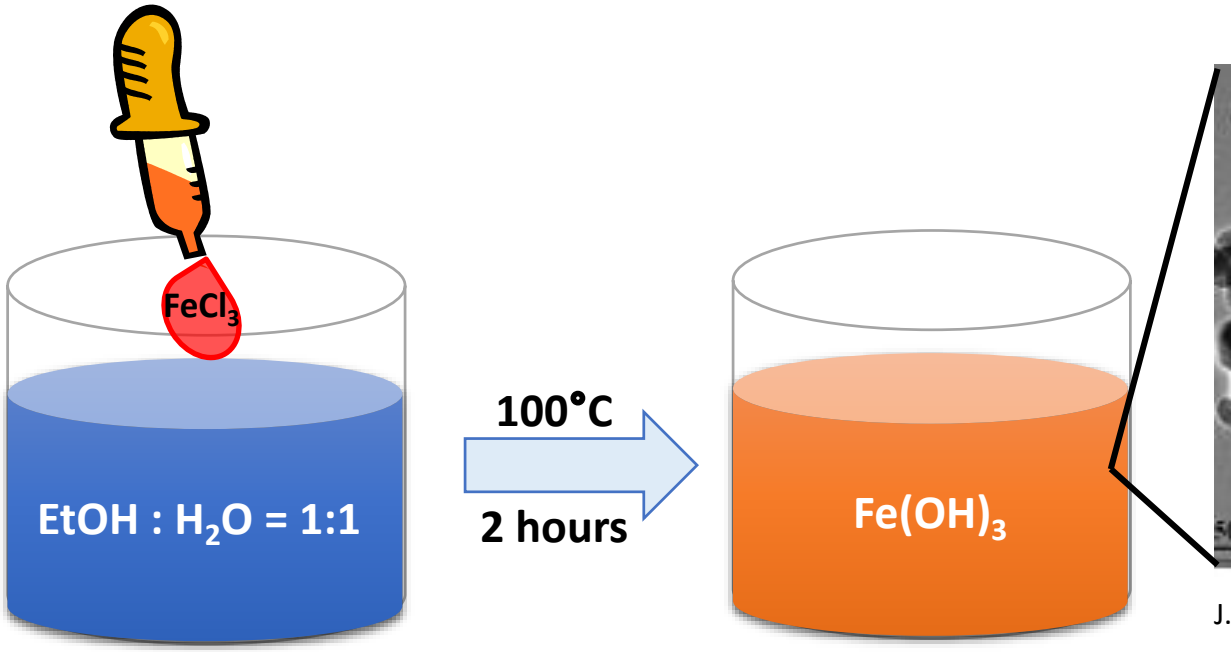
Consiglio Nazionale delle Ricerche

GRAPHENE FACTORY

grafene.cnr.it

GRAPHENE FLAGSHIP

We acknowledge funding by the European Union Seventh Framework Programme under Grant Agreement No. 604391 Graphene Flagship

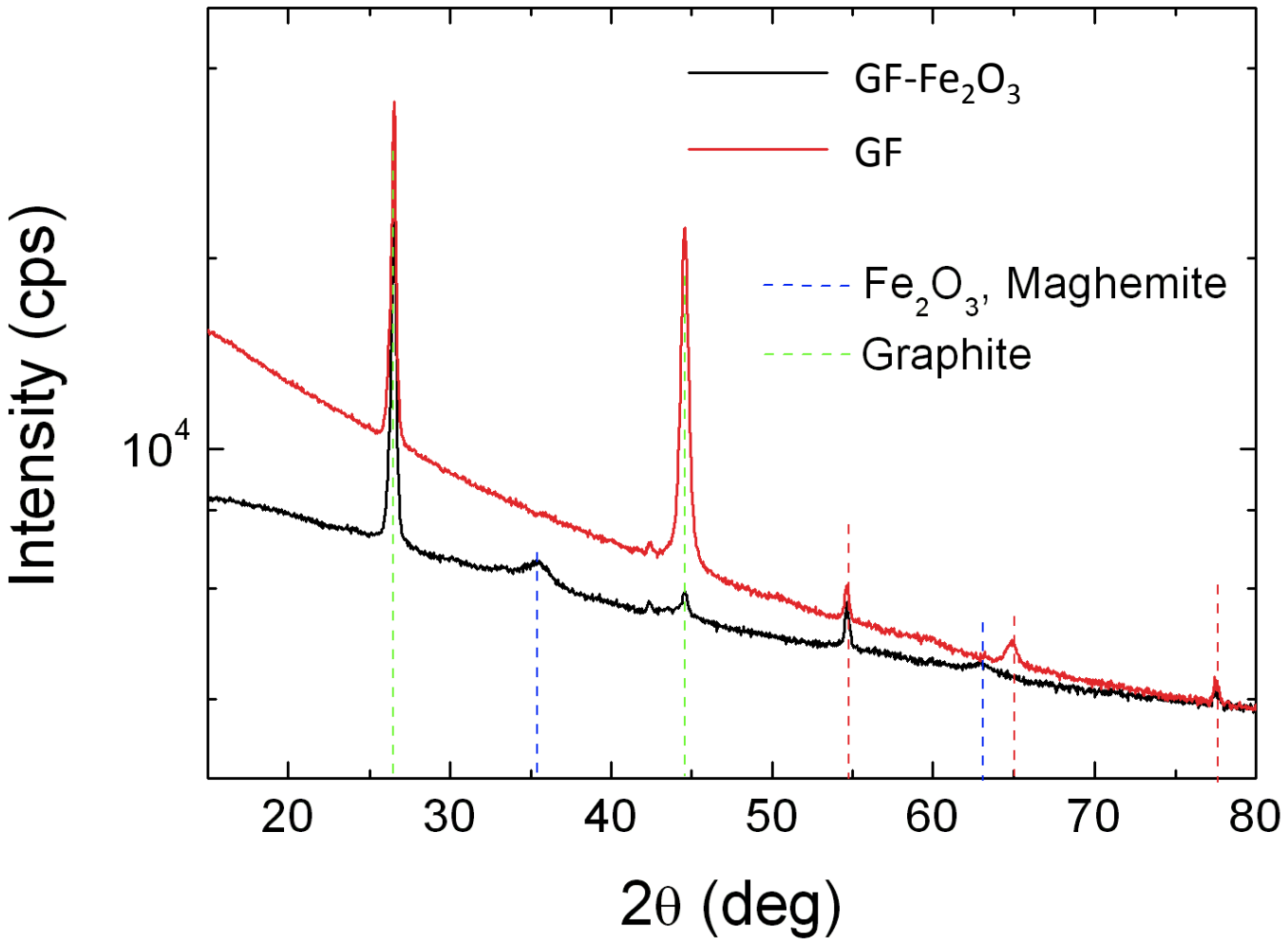


J. Mater. Chem., 2012, 22, 895–902

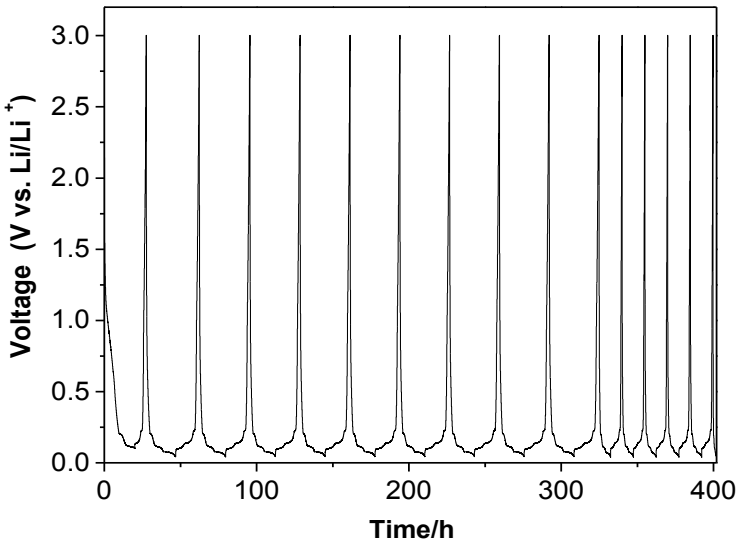
J. Mater. Chem. A, 2013, 1, 7154–7158

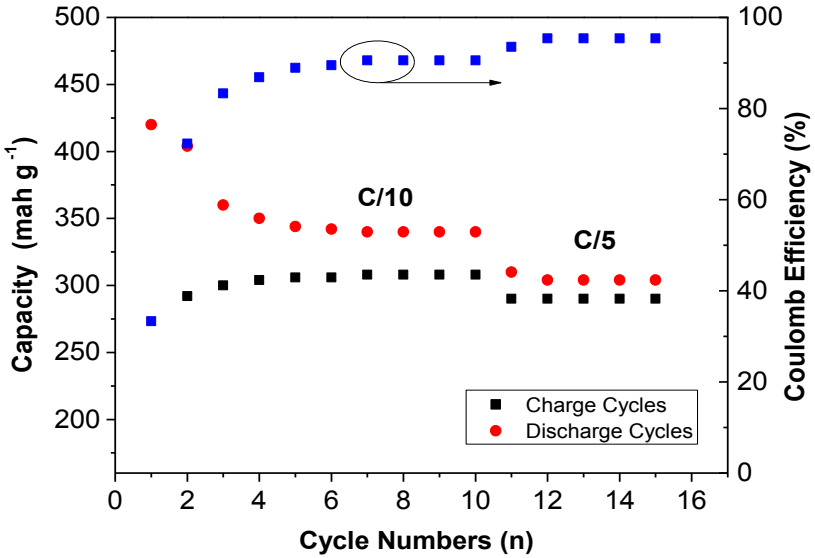
- Facile synthesis of $Fe(OH)_3$ colloidal by hydrolysis of $FeCl_3$
- Avoid hydrothermal routes with high pressure and long time
- $Fe(OH)_3$ could be transformed to α-Fe_2O_3 nano-crystalline by calcination

Xia et al., Carbon **2015**, *84*, 254-262



Crystallites of Fe_2O_3 are estimated to be 5 nm from Scherrer equation





Electrochemical measurements

The working electrodes was CVD graphene on Ni foam (ø 9 mm). The electrodes were measured in an electrolyte-filled jar, using a three-electrode configuration with lithium foil as counter/reference electrode. The electrolyte was 1 M $LiPF_6$ (LP30, BASF) in a 1:1 (w/w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). Cell assembly was performed in Ar atmosphere MBraun Labmaster SP dry box (H_2O and O_2 < 0.1 ppm) and all the electrochemical measurements were carried out by Biologic VSP and PerkineElmer VMP potentiostats/galvanostats.