Approaches for the modification of macroscopic carbon nanotube assemblies with atmospheric-pressure plasma

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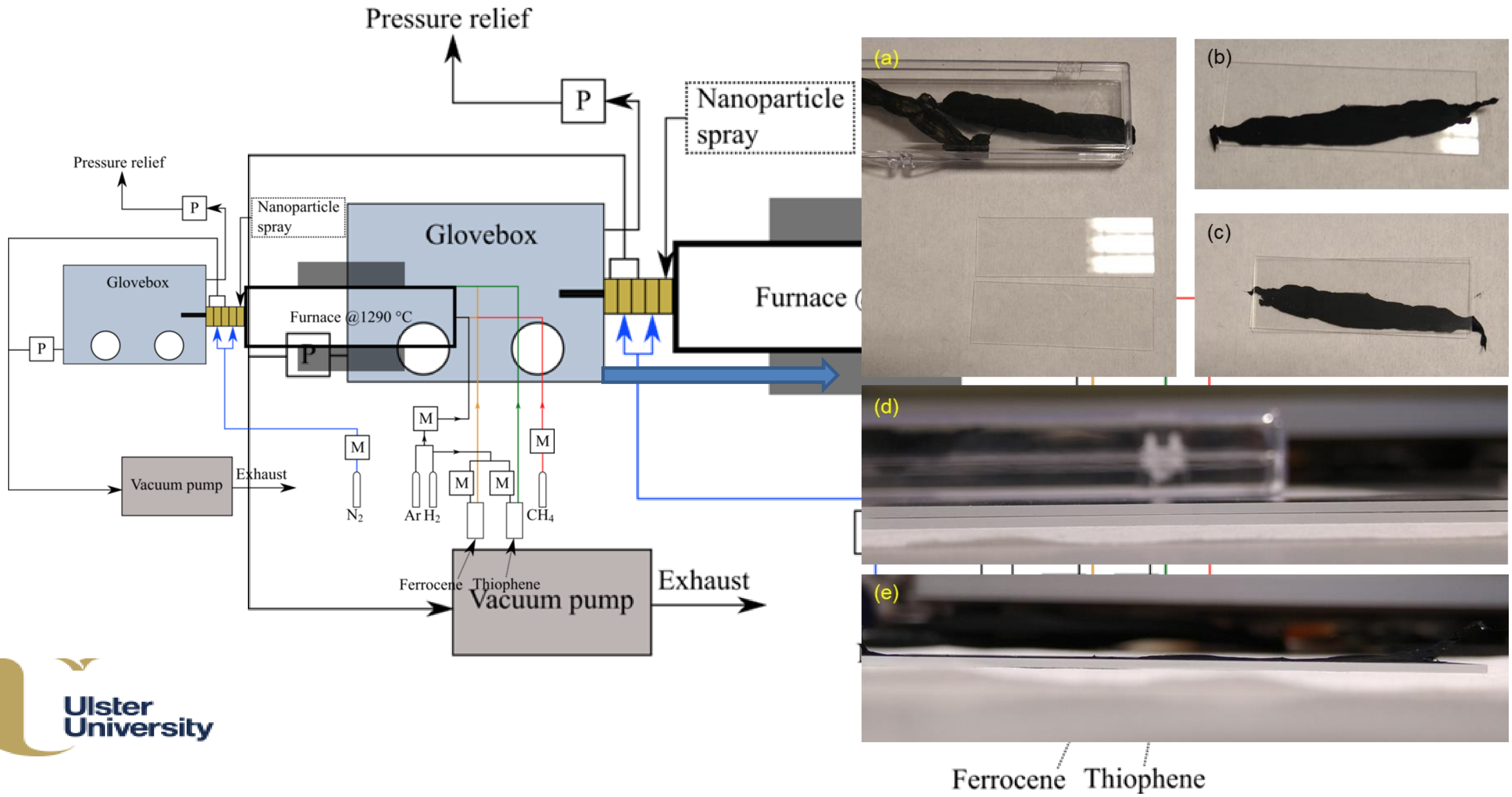
Overview

Two-part talk

- We use a floating-catalyst chemical vapour deposition system to make macroscopic carbon nanotubes.
- We then have two ways to modify them:
    - Two-step by modifying the CNT post treatment, i.e. functionalisation.
    - In-line/single-step by adding a plasma system to the reactor, i.e. nanocomposite material.
- This talk will address efforts on both of these topics.

The macroscopic carbon nanotube assembly systems



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Functionalising macroscopic CNTs with a hybrid plasma-liquid system

Modification and enhancement of CNTs can lead to advances in technology

Importance

Carbon nanomaterials have an array of properties which are attractive to many different applications.

Bolstering specific properties can lead to advances in technology.

Often surface chemistry can limit the usage of carbon nanomaterials due to reduced interaction with a surface, poor solubility etc.

What we know

Modification of the surface chemistry by means of modified surface groups can improve dispersions in different typical solvents or resins*.

Substitution of carbons in the chain can modify the properties of the materials, such as pyridine or pyrrole groups to enhance capacitive behaviours** or the inclusion of graphitic nitrogen to provide superior electron transport***.

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J. Mater. Sci.* **2013, *48* (3), 1005–1013. https://doi.org/10.1007/s10853-012-6830-3.

***Adv. Funct. Mater.* **2009**, *19* (3), 438–447. https://doi.org/10.1002/adfm.200801236.

****J. Solid State Electrochem.* **2011**, *15* (1), 175–182. https://doi.org/10.1007/s10008-010-1087-8.

How do we achieve doping in greater quantities than traditional chemical routes? - PiNE

What we know

Typical functionalisation synthesis routes

- Strong oxidants such as sulfuric or nitric acids.*
- Low-pressure plasma.**
- Growth with nitrogen source added.***

Pros

- Select of ideal carbon nanomaterials.
- Purification of contaminants.

Cons

- Long production time with any further cleaning or purification step exacerbating this further.
- Handling of harsh or hazardous chemicals.
- Cleaning stage may degrade the material.
- Throughput limitation of the vacuum filtration steps.
- Limited integration of functional groups (oxidants or grown with nitrogen source).

Experiment

Here we use a plasma-induced non-equilibrium electrochemistry system to dope macroscopic assemblies of CNTs with nitrogen and/or oxygen groups.

Hypothesis

Novel, plasma-exclusive chemical routes could lead to enhanced dopant content.

*_Sol. Energy Mater. Sol. Cells_ **2016**, _157_, 652–659. https://doi.org/10.1016/j.solmat.2016.07.032.
**J. Mater. Sci. 48 (2013) 7620–7628. https://doi.org/10.1007/s10853-013-7579-z.
***J. Phys. Chem. Solids. 104 (2017) 52–55. https://doi.org/10.1016/j.jpcs.2016.12.023.

Experimental design

Characterisation of modified properties

Research Questions

1. How has the surface chemistry been modified?
   - X-ray photoelectron spectroscopy
   - Contact angle

2. Is the graphitisation significantly affected by the treatment?
   - Raman spectroscopy

3. How does it affect application?
   1. Tested as direct absorption solar thermal collector nanofluid.

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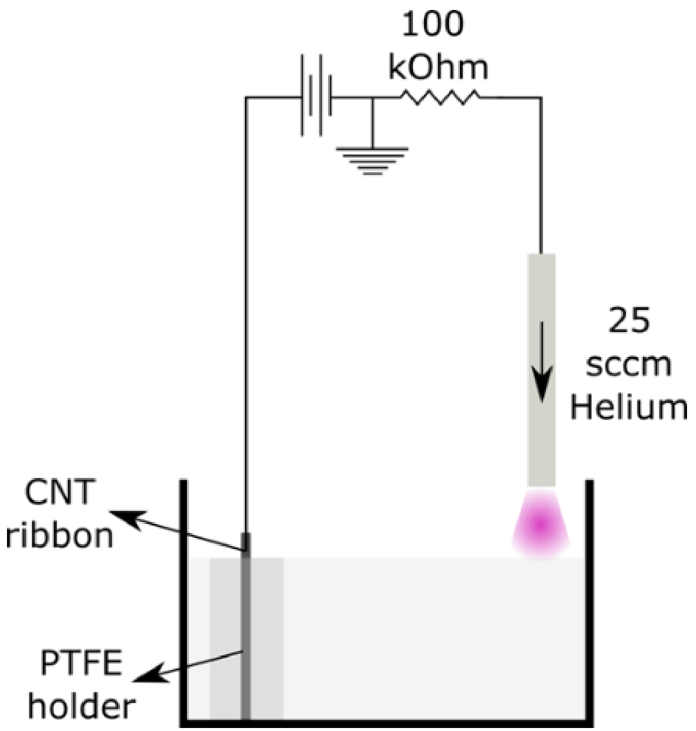
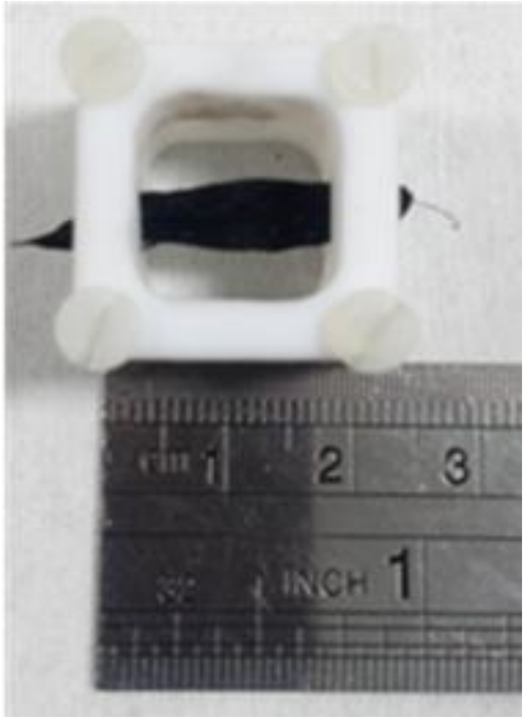
The plasma system

DC-powered, plasma-induced non-equilibrium electrochemistry (PiNE)





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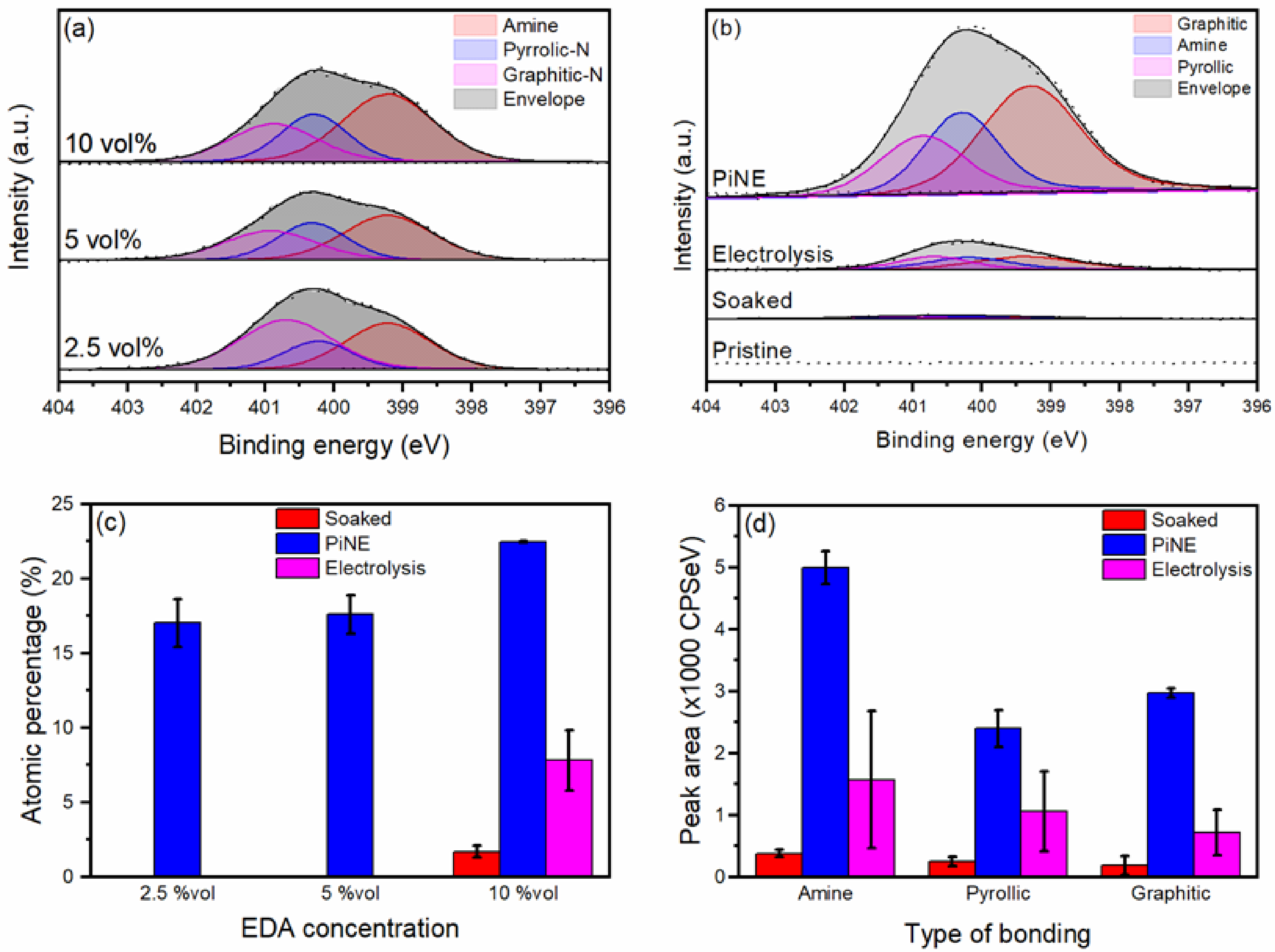
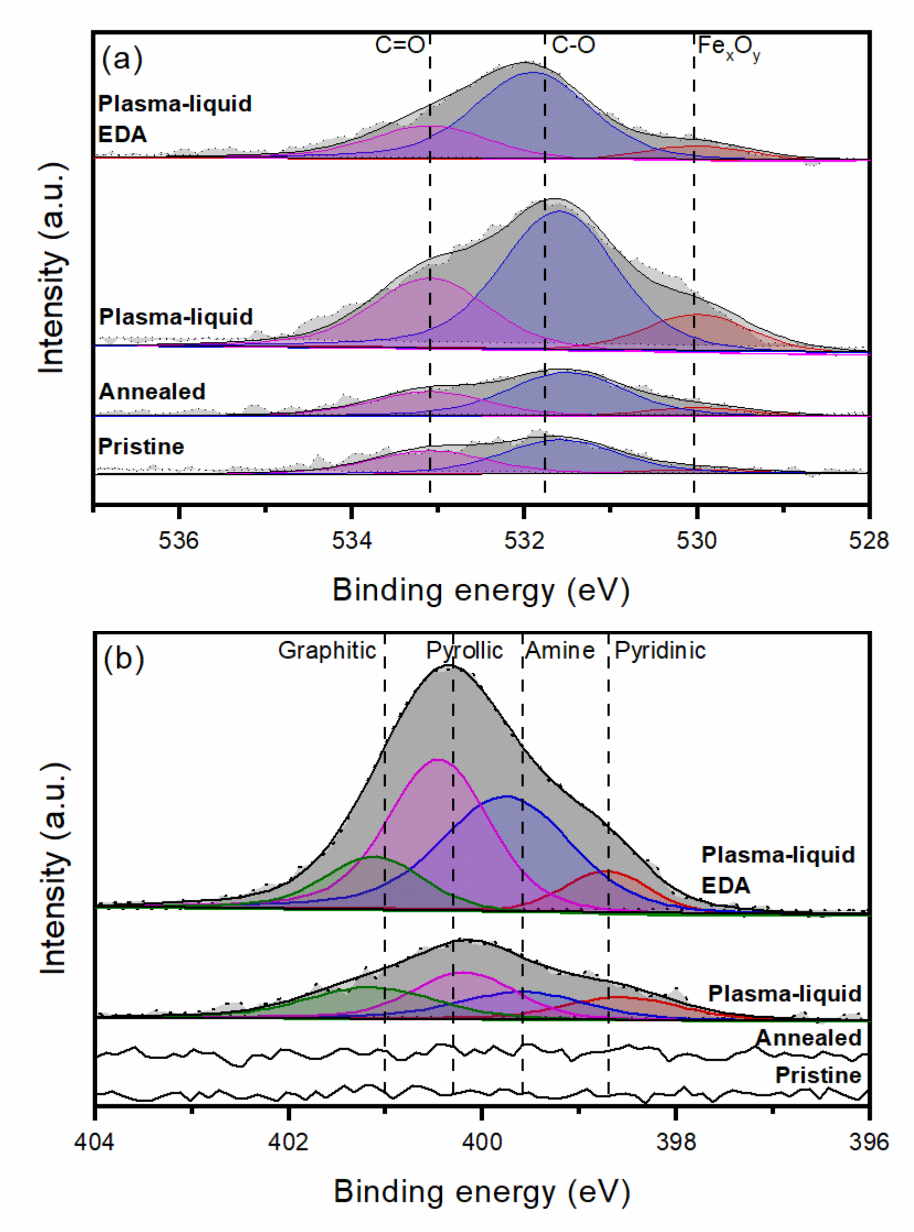
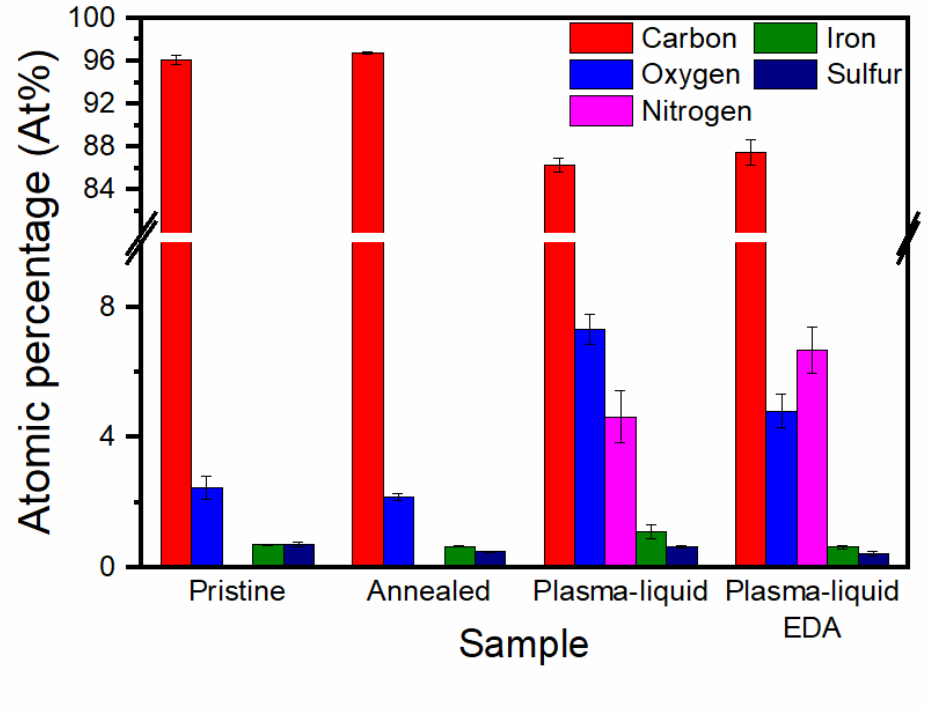
How has the surface chemistry been modified?

Ethylenediamine content effect

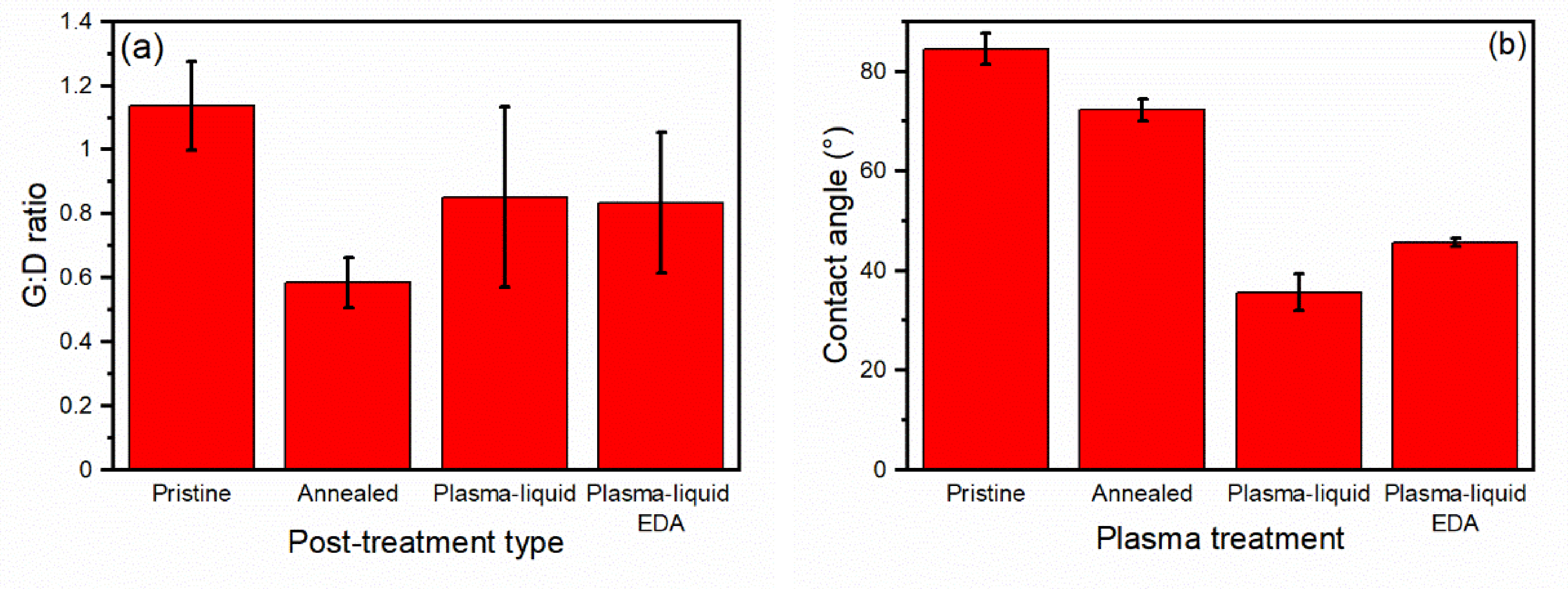


How has the surface chemistry been modified?

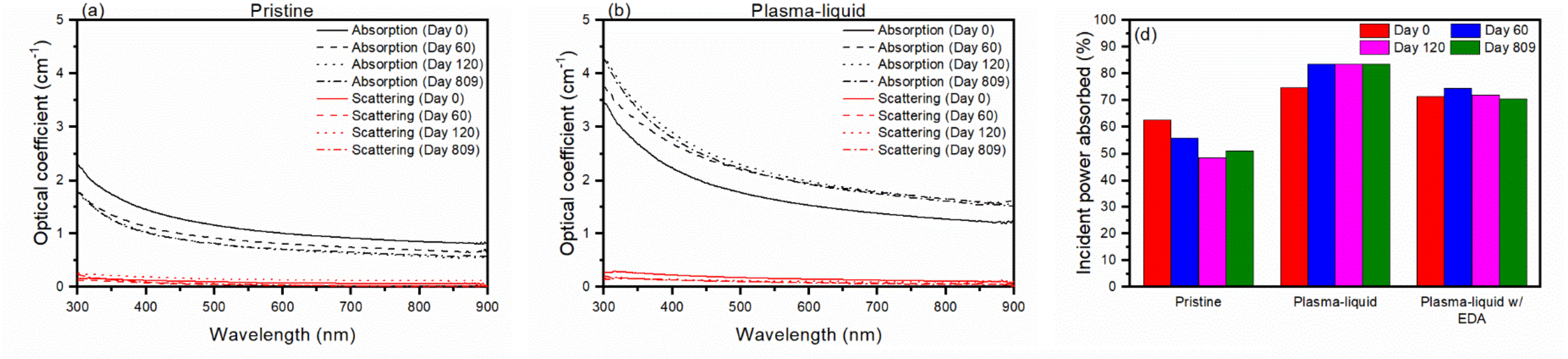


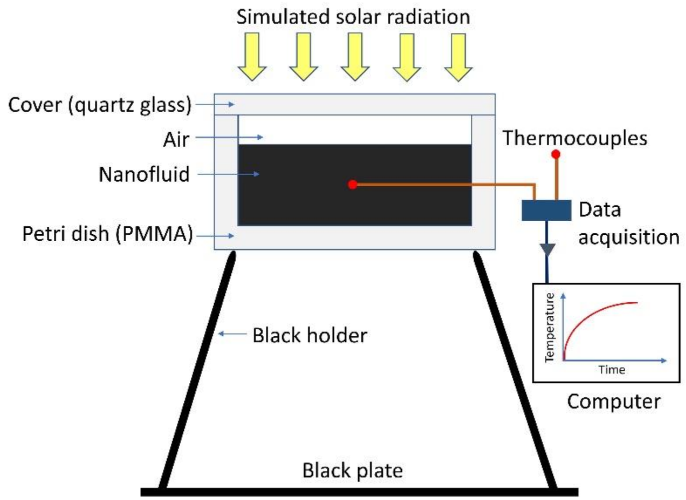


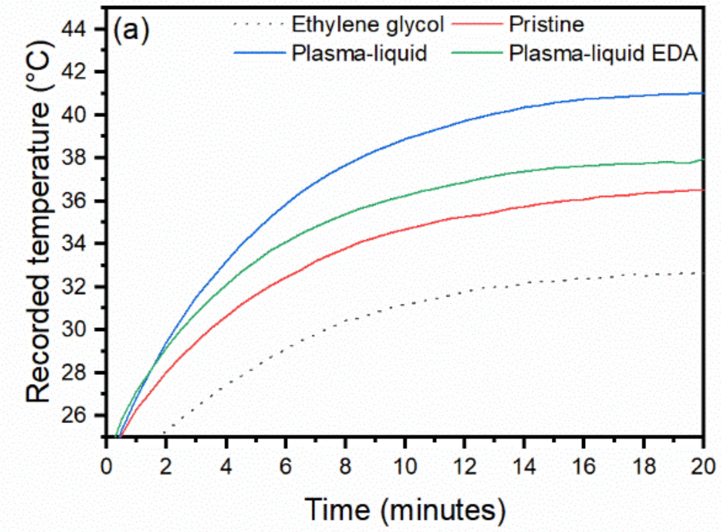
Is the graphitisation significantly affected by the treatment?



Potential application as solar thermal absorption fluid







Conclusions

PiNE can modify the surface chemistry of the CNTs rapidly

1. Successfully doped the CNT structures with nitrogen and oxygen groups.
2. Demonstrated the modification of the contact angle.
3. Enhanced surfactant-free stability as a nanofluid

Currently assessing the modified CNTs as potential electrodes for fuel cells (OER/ORR/HER).

Toward a single-step process to produce Zn-CNT hybrid materials

Carbon and zinc have relative abundance and low cost-to-performance ratios

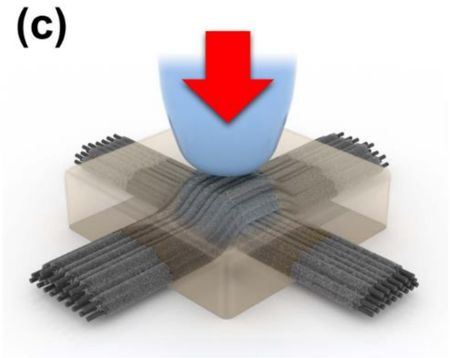
Importance

New devices and applications are increasingly requiring tailored material properties, necessitating the development novel nanocomposites.

In addition to the material-specific properties there are two other key requirements to the success of new technologies, low-cost to performance ratio and a relative abundance of the materials.

What we know

Two materials which can satisfy these requirements are zinc and carbon, with their derivative forms such as oxides or sulphides as well as micro- or nano-geometries widening the research impact to a myriad of applications.



Embeddable stress[1] and strain[2,3] sensors

(1) Calestani, D. *Nanotechnology* **2018**, *29* (33).

(2) Mai, W. *Chem. Phys. Lett.* **2012**, *538*, 99–101.

(3) Hassan, G. *Compos. Part A Appl. Sci. Manuf.* **2018**, *107* (November 2017), 519–528.

Applications of Carbon-Zn hybrid materials

Supercapacitors[6,7]

(6) Guo, Y. *RSC Adv.* **2016**, *6* (23), 19394–19403.

(7) Sankapal, B. R. *Electrochim. Acta* **2016**, *192*, 377–384.

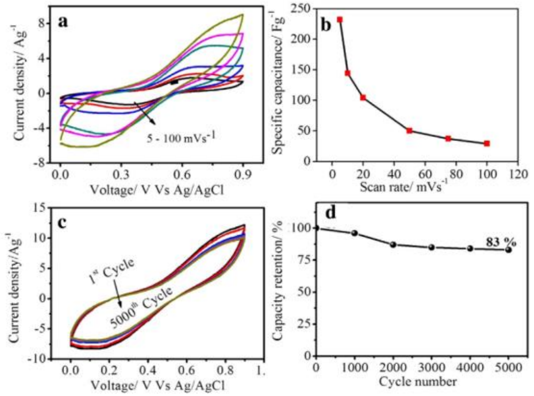
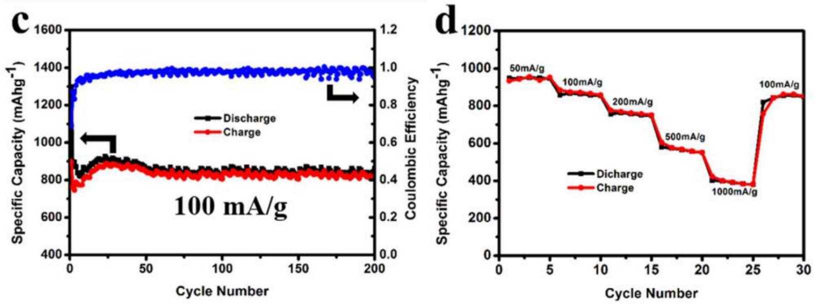


Fig. 6. a) CV curves of ZCN thin films at different scan rates in 0.5 M H_2SO_4, b) The variation of specific capacitance with different scan rate, c) Cyclic stability of ZCN thin film at 200 mV.s^{-1} scan rate, d) Plot of capacity retention of ZCN thin films electrode with number of cycles.



Electrochemical sensors[4,5]

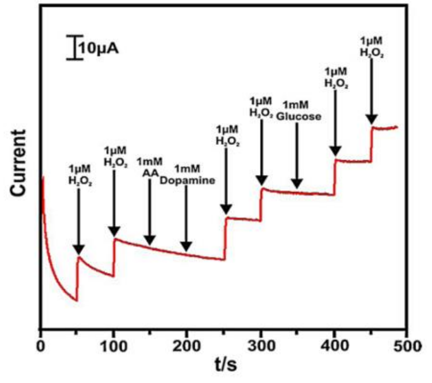


Fig. 6. Amperometric *i–t* response at RGO/ZnO modified rotating disc GCE for the successive additions of 1 μM H_2O_2, 1 mM AA, 1 mM DA, and 1 mM glucose solutions into the continuously stirred N_2 saturated 0.05 M PBS (pH 7). Applied potential: −0.38 V; rotation rate: 1200 rpm.

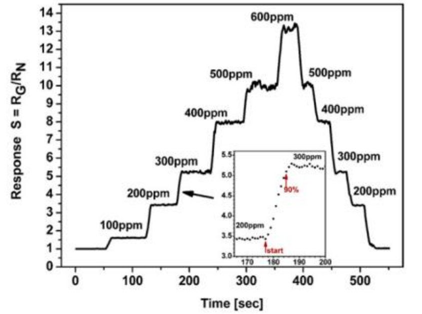


Fig. 5. Response transient of the ZnO-C sensor under exposure to different O_2 concentrations (100–600 ppm of O_2 in pure nitrogen) at 280 °C. The inset underlines the fast response time.

(4) Palanisamy, S. *Sensors Actuators, B Chem.* **2012**, *166–167*, 372–377.

(5) Tonezzer, M. *B Chem.* **2010**, *150* (2), 517–522.

Flexible lithium-ion battery anodes[8–12]

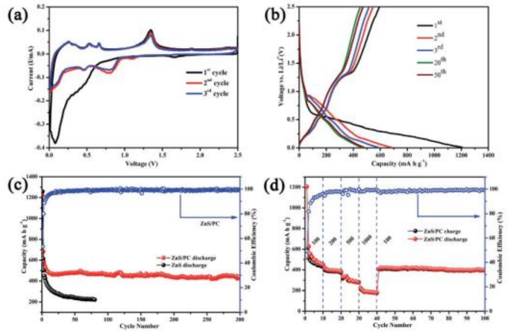


Fig. 4 (a) Cyclic voltammograms of the ZnS/PC, (b) charge–discharge curves of the ZnS/PC, (c) cycling property of the ZnS/PC and pure ZnS at 100 mA g^{-1} and (d) the capability of the ZnS/PC at various current densities.

(8) Zhang, Y. *Mater. Lett.* **2016**, *184*, 235–238.

(9) Zhang, W. *J. Alloys Compd.* **2020**, *816*, 152633.

(10) Zhang, H. *ACS Appl. Mater. Interfaces* **2017**, *9* (43), 37813–37822.

(11) Köse, H. *J. Power Sources* **2015**, *295*, 235–245.

(12) Fu, Y. *RSC Adv.* **2015**, *5* (106), 86941–86944.

Flexible hybrid nanomaterials have strong promise but how do we make small things big?

What we know

Typical nanocomposite synthesis routes

- Solvothermal
- Wet chemistry
- Sol-gel
- Microwave-based plasma

Pros

- Select of ideal carbon nanomaterials.
- Purification of contaminants.
- Generation of beneficial functional groups.

Cons

- Long production time with any further cleaning or purification step exacerbating this further.
- Cleaning stage may degrade the material.
- Throughput limitation of the vacuum filtration steps.
- Protracted reaction times up to 37.5 hours excluding an overnight drying procedure.*
- Handling of hazardous chemicals.

Experiment

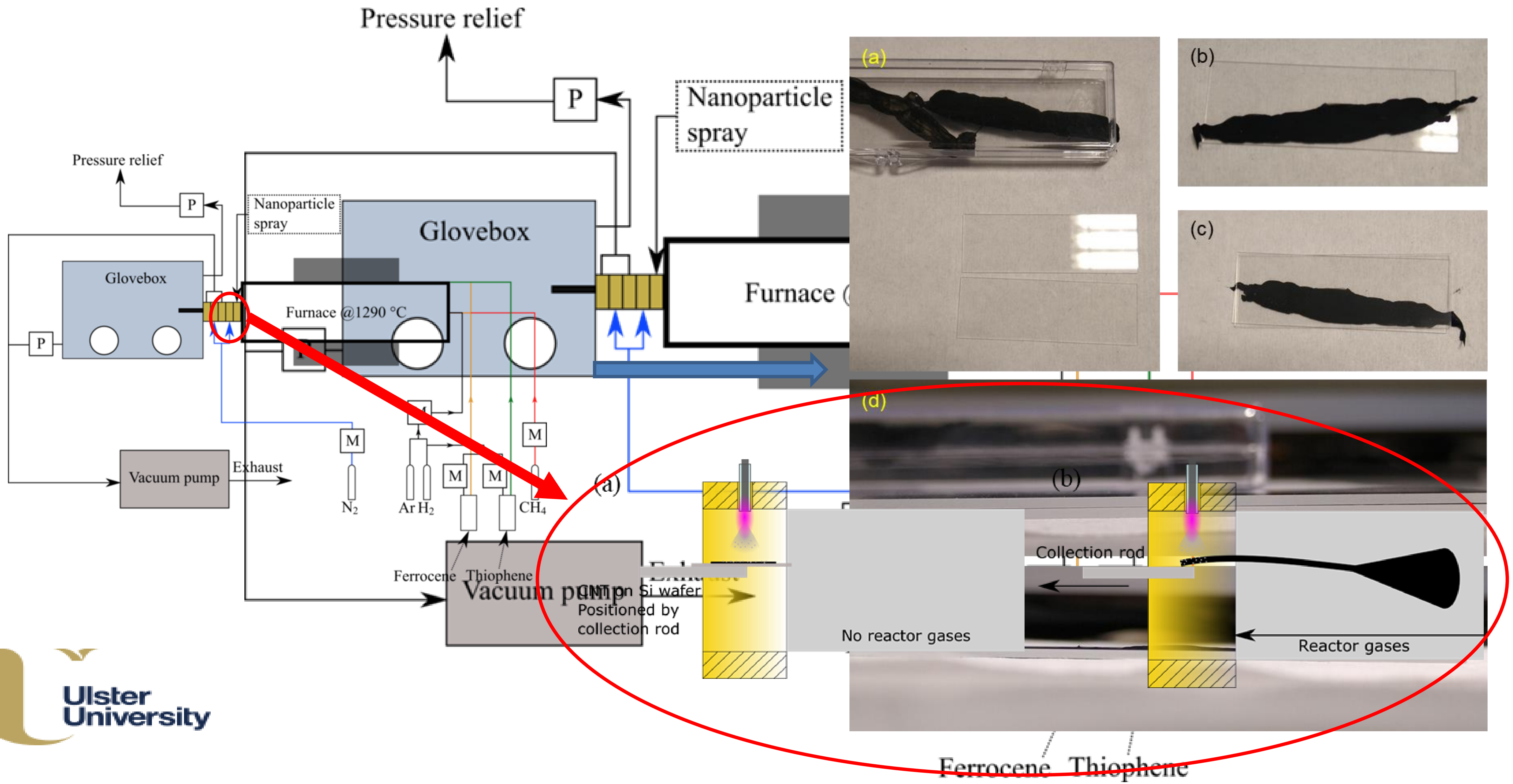
Here we treat implement an atmospheric-pressure microplasma system into our FC-CVD furnace to produce a Zn-CNT composite material in a single step.

Hypothesis

Depositing Zinc as the CNT aerogel condenses will allow for superiority through-thickness penetration of the Zinc-based materials.

* Ramli, N. I. T. *Electrochim. Acta* **2017**, *228*, 259–267.

The macroscopic carbon nanotube assembly systems



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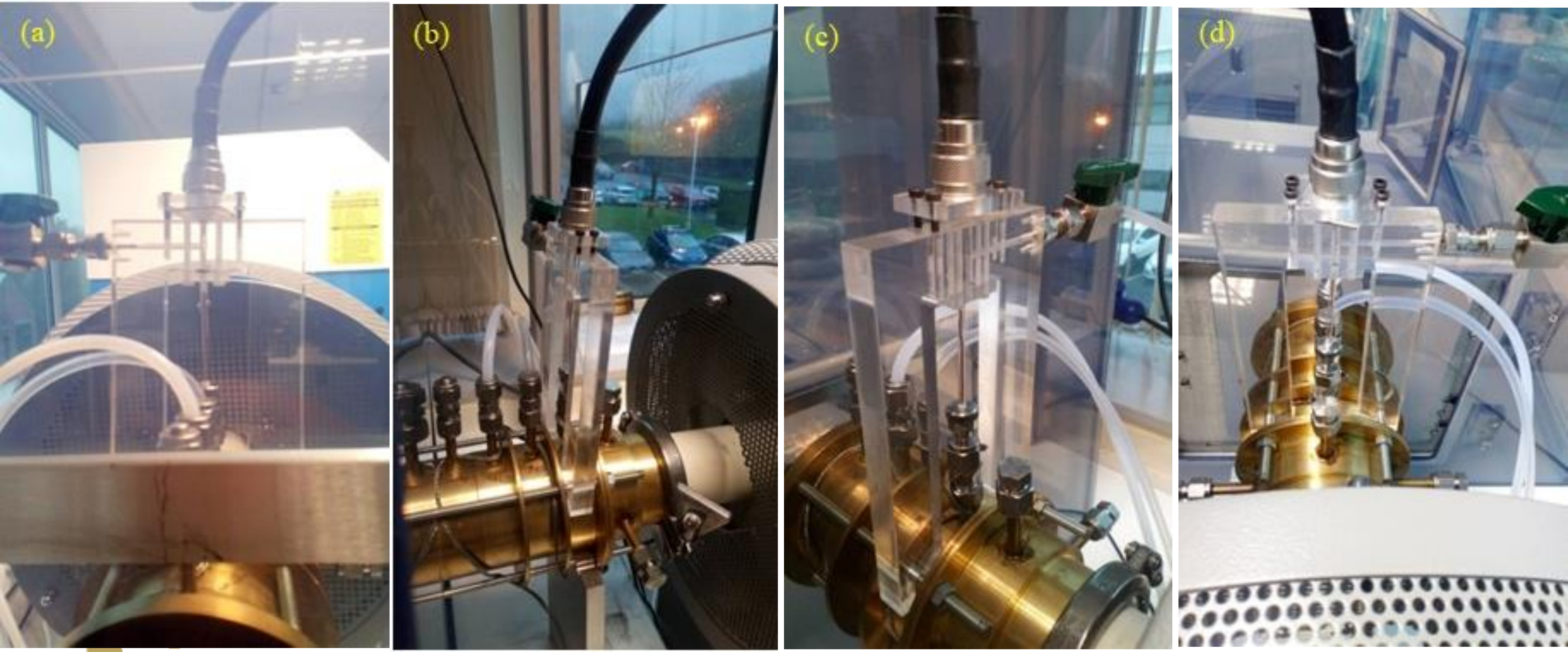
Plasma generated from and consuming a sacrificial metal wire



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Capillary: 2 mm I.D. 3 mm O.D.
Gas: Helium 1 slm
RF Power: 45-60W
Matching network: Custom, 2 variable capacitors and fixed inductor.

Can deposit some materials onto the surface

- Material successful deposited.
- Some limitations as to coverage.

Experimental design

Characterisation of modified properties

Research Questions

1. How has the material combined?
   - Scanning electron microscopy
   - Transmission electron microscopy

2. Is the graphitisation significantly affected by the treatment?
   - Raman spectroscopy

3. What chemical state is the Zinc in (and how far does the Zinc material penetrate)?
   - X-ray photoelectron spectroscopy (depth profiling)

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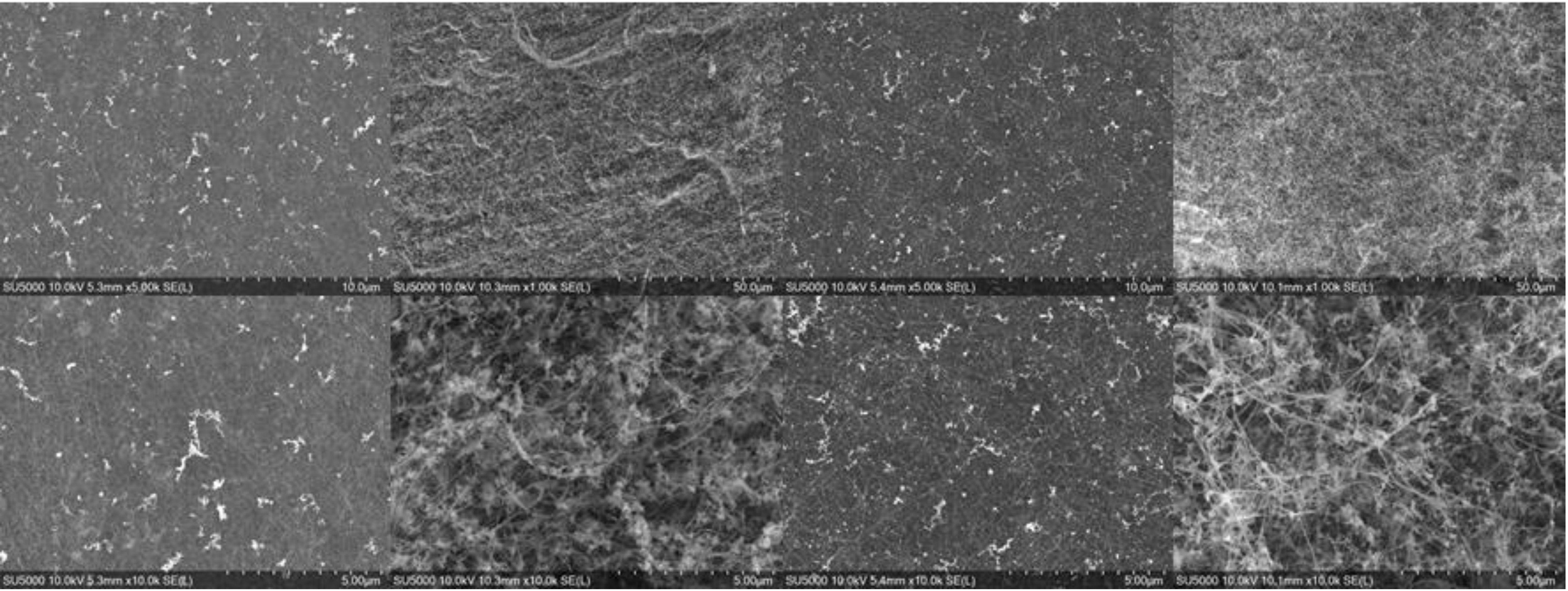
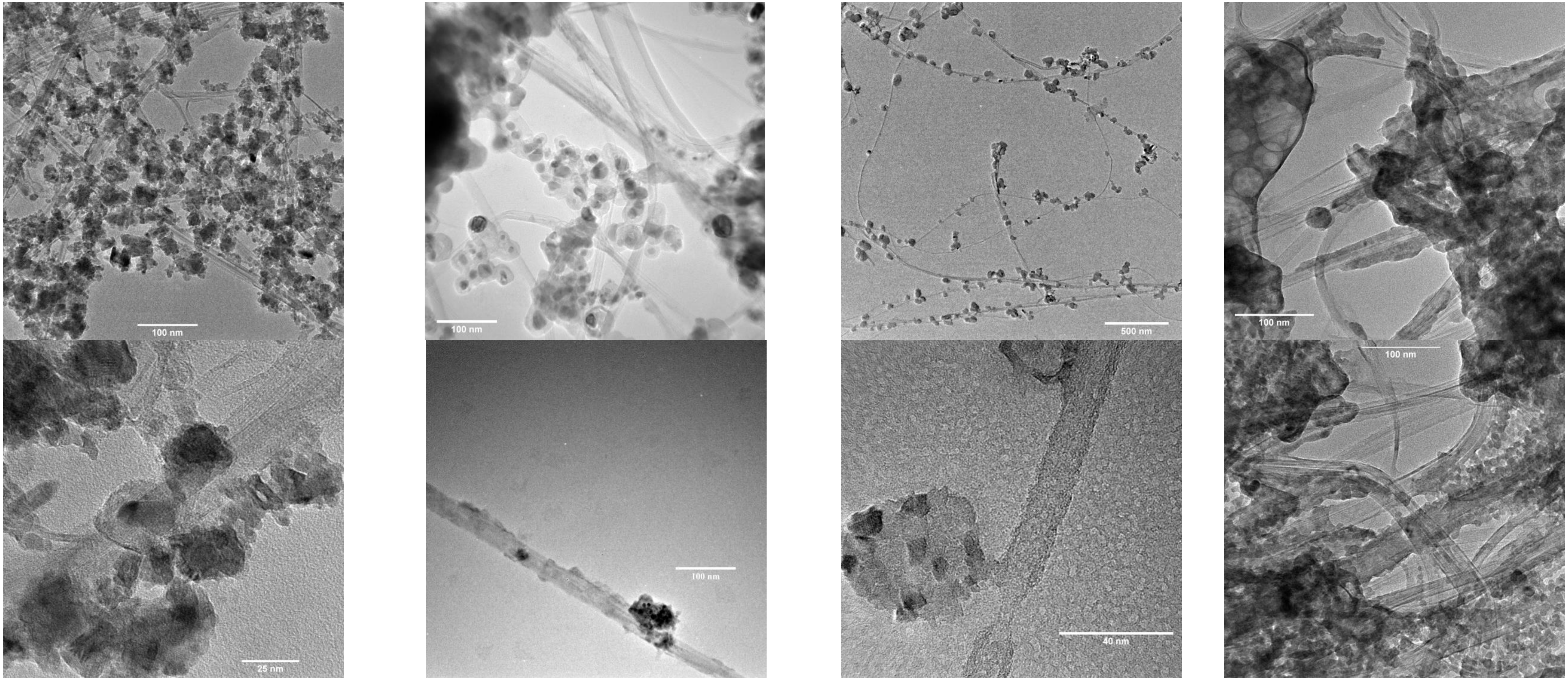
Treating the CNTs in-line allows for superior coverage at both 45 W and 60W

45W Off-line | 45W In-line | 60W Off-line | 60W In-line

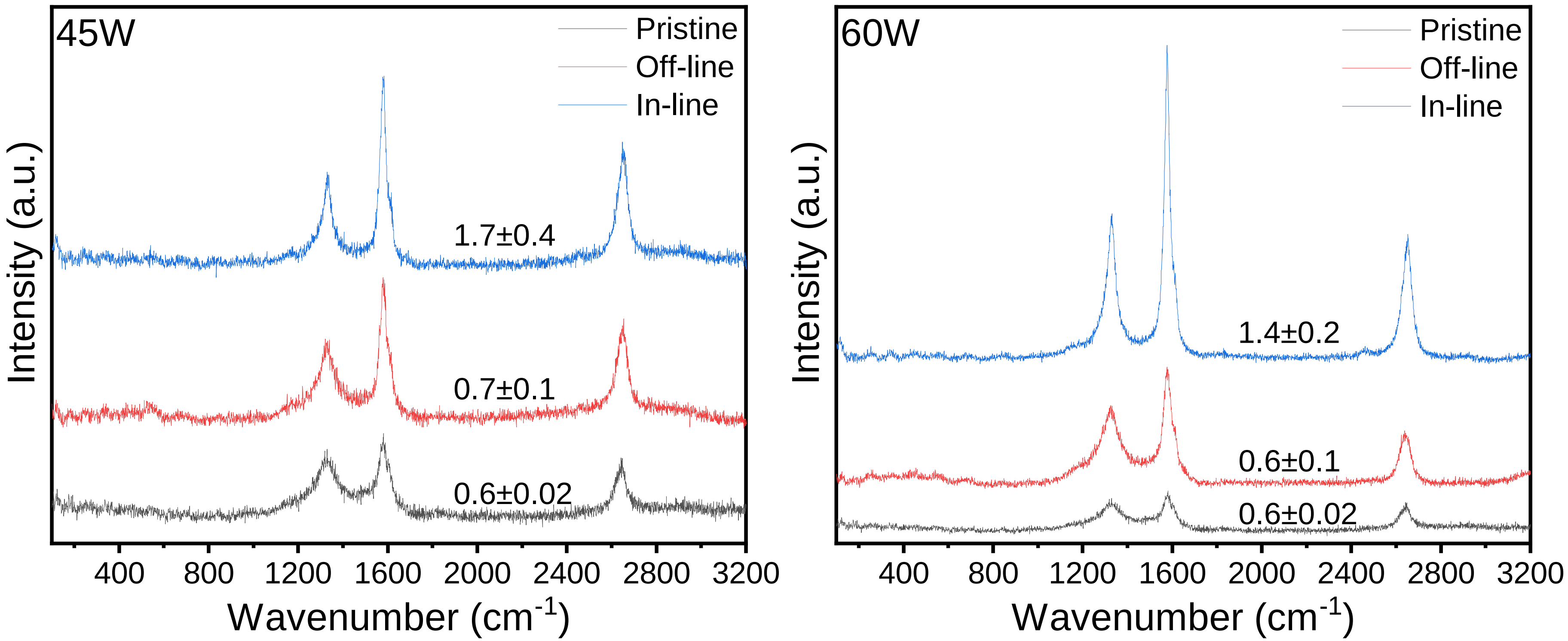


CNTs are covered individually and not as a two distinct phase film

45W Off-line | 45W In-line | 60W Off-line | 60W In-line



Bonus effect: The CNTs are purified by the plasma In-line



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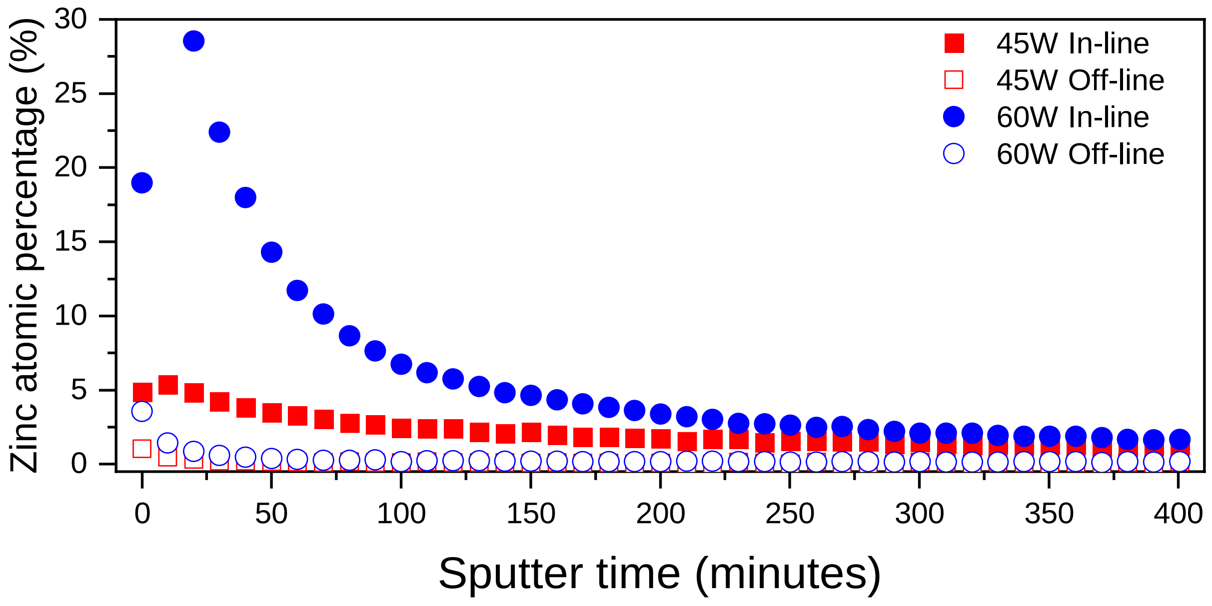
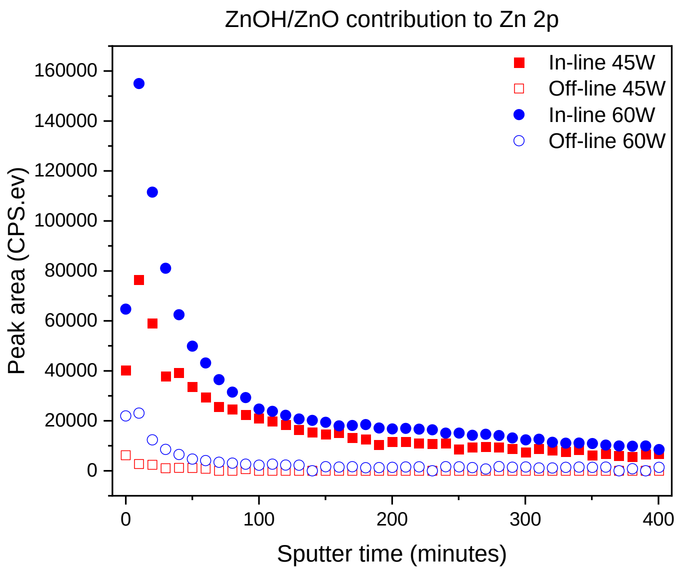
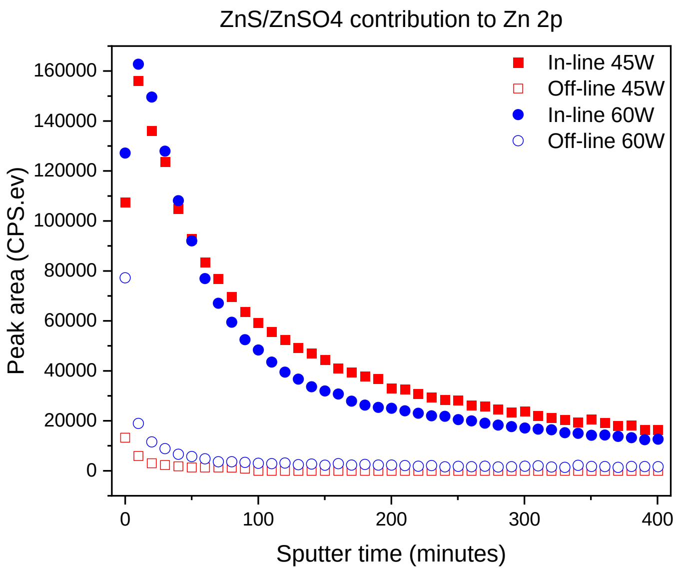
XPS: Zinc content increases and penetrates further in-line

- In-line > Off-line for at%
- In-line > Off-line for depth
- In-line produces more $ZnS/ZnSO_4$







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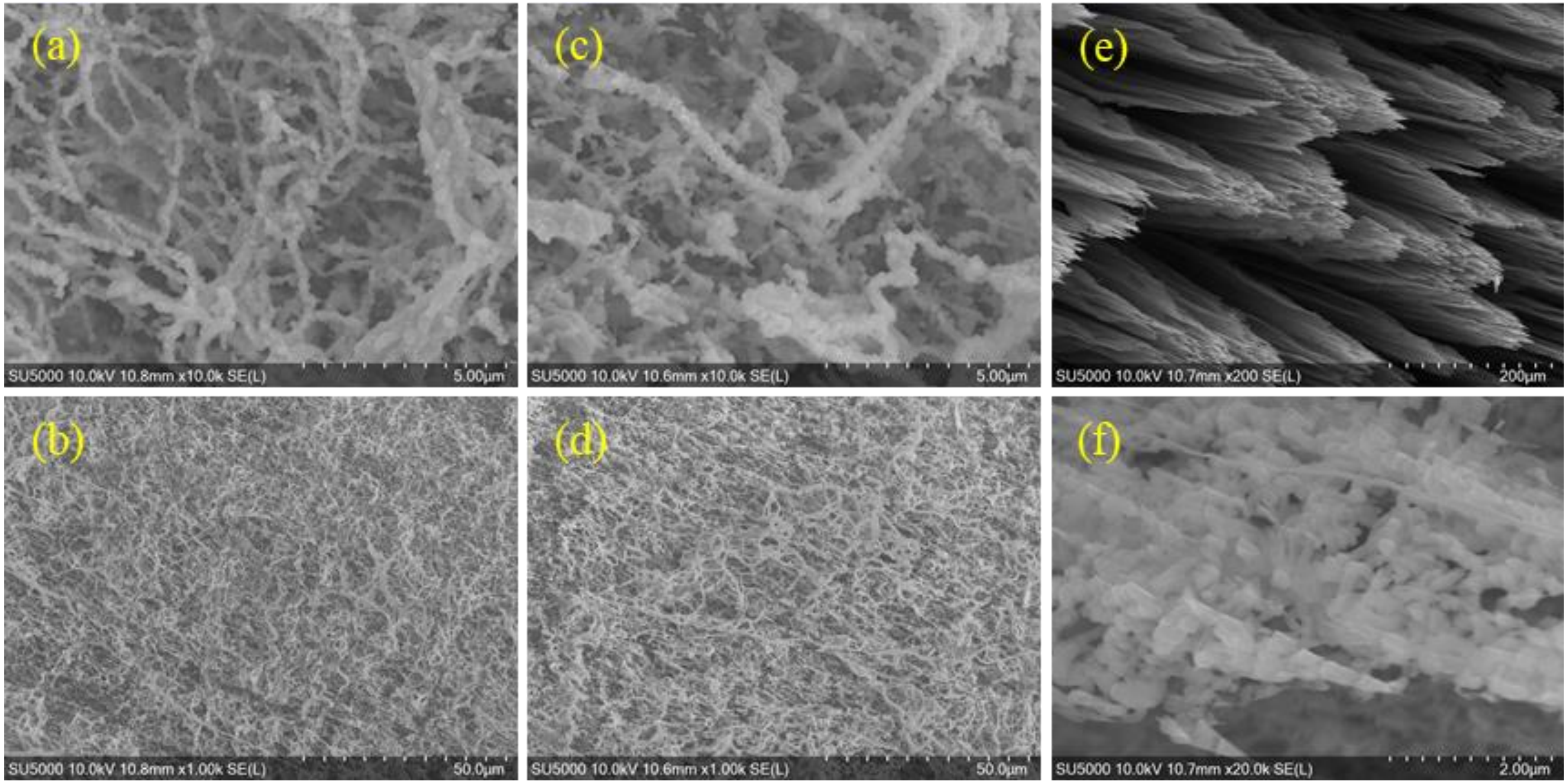
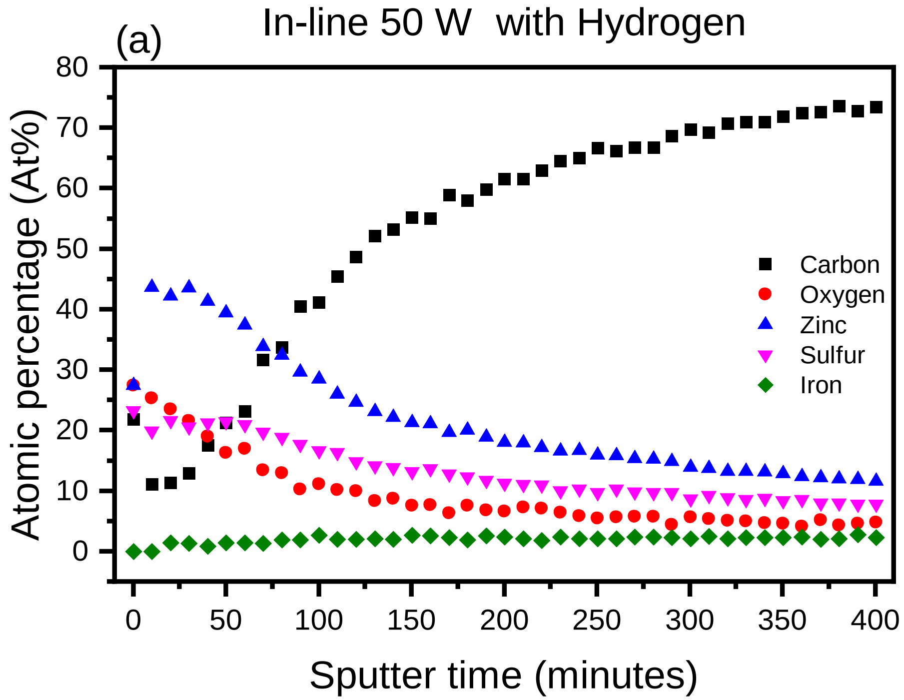
Improving the deposition rate

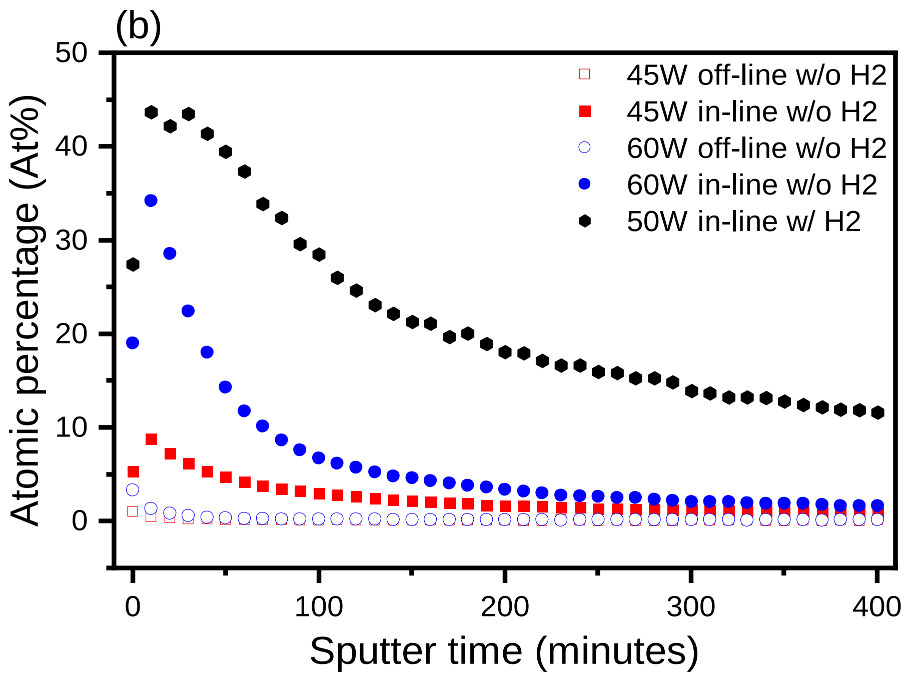
Simple, add hydrogen to the plasma gas feed




1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
INCH 1 2 3 64 4 16 5 6

Hydrogen allows not only more, but deeper Zinc penetration into the matrix.





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Conclusions

To our knowledge the first demonstration of in-line, single-step macroscopic CNT hybrid materials.

1. Successfully deposited material and demonstrate the single-step formation of a CNT-Zn composite material.
2. Processing in-line and off-line yields a different Zn-based material.
3. Superior individual CNT coatings by depositing in-line.
4. Addition of hydrogen to the plasma drops the power required to produce particles and increases deposition rate.

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