



Materials and Structural Design for Advanced Energy Storage Devices

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Introduction and Motivation

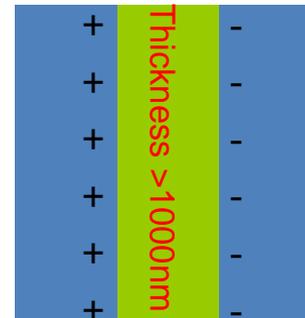
Portable electronics



Electrical vehicle 20-30% CO₂ emission



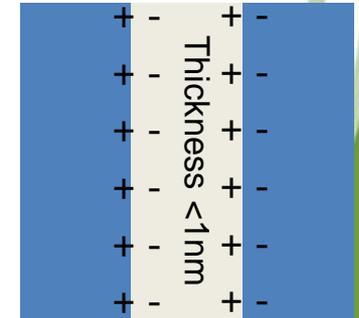
Capacitor



$$E = \frac{1}{2} CV^2$$

$$C \propto 1/\text{thickness}$$

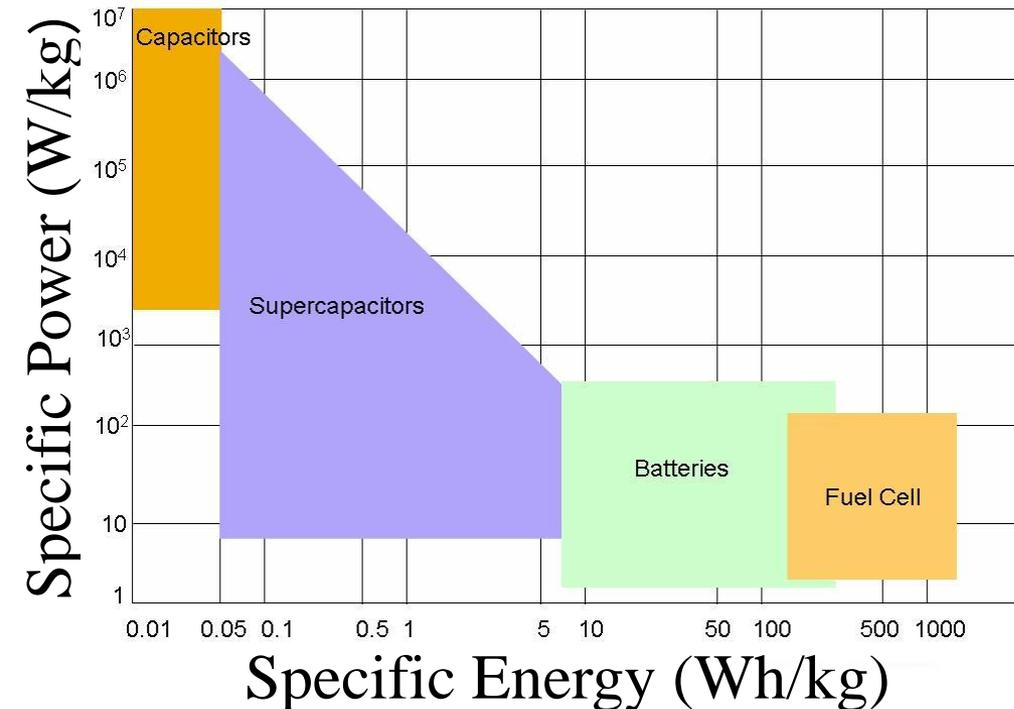
Supercapacitor



Electrolyte solution

Important Parameters:

1. Energy and Power density
2. Cycle life and safety
3. Cost



Supercapacitors

Electric Double-Layer
Capacitors

+

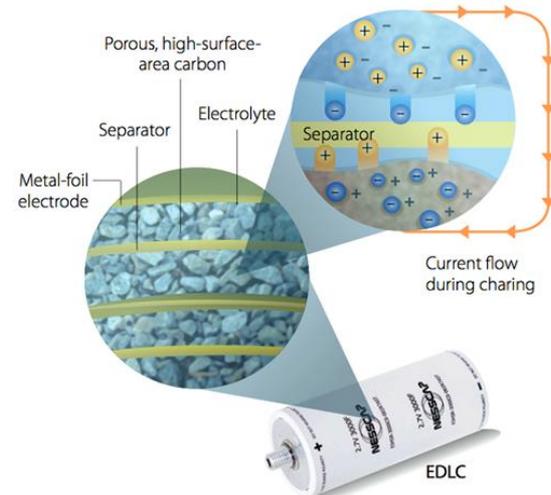
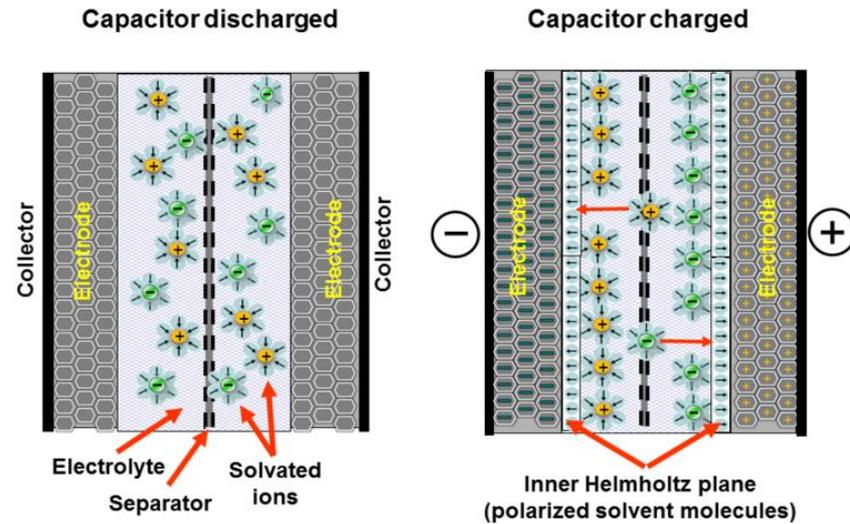
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Pseudocapacitors

Hybrid Capacitors

Electric Double Layer Capacitor

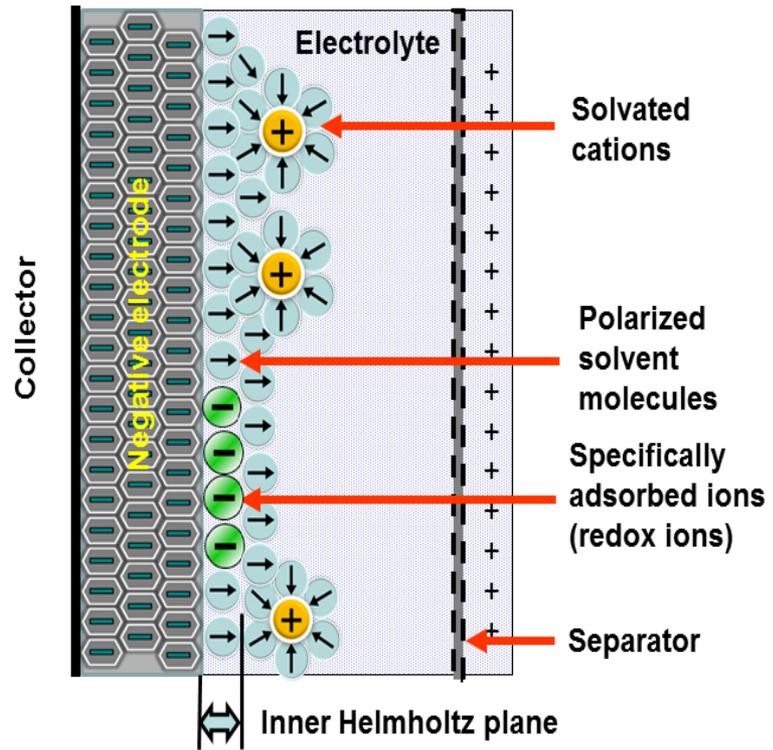
- EDL formed with electrode and electrolyte with solvent molecules between as dielectric.
- Store energy by adsorbing electrolyte ions onto the surface of the electrode
- Fast acting. Low energy potential, charge confined to surface



Pseudocapacitor

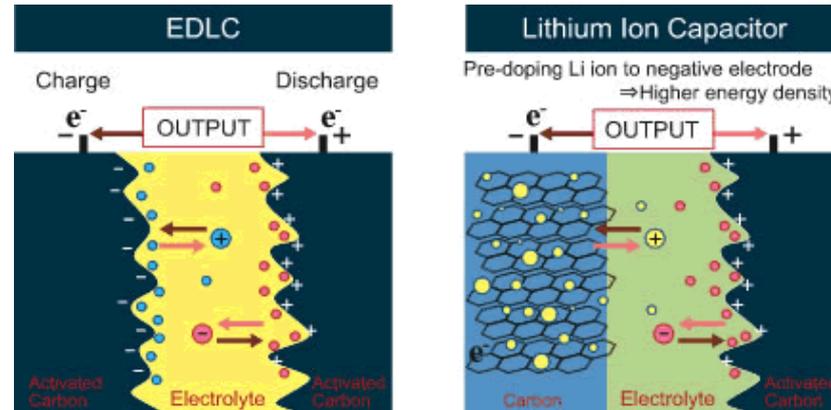
- Rely on redox reactions that take place at the electrode
- Electrode materials typically made up of transition metals, conducting polymers, or compound with O and N functional groups
- Higher Energy density but lower cycling life

Pseudocapacitance with specifically adsorbed ions

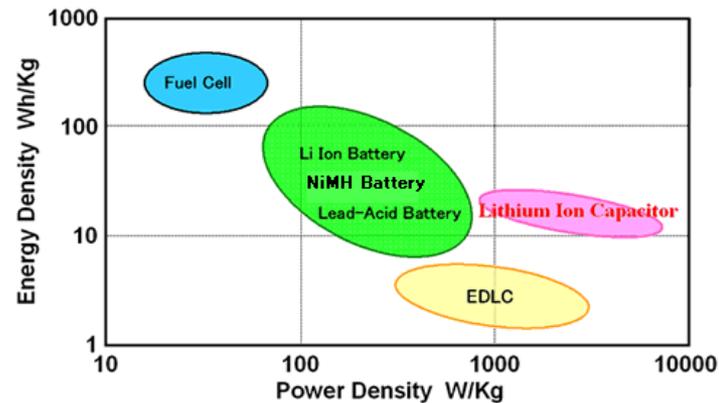


Hybrid capacitor

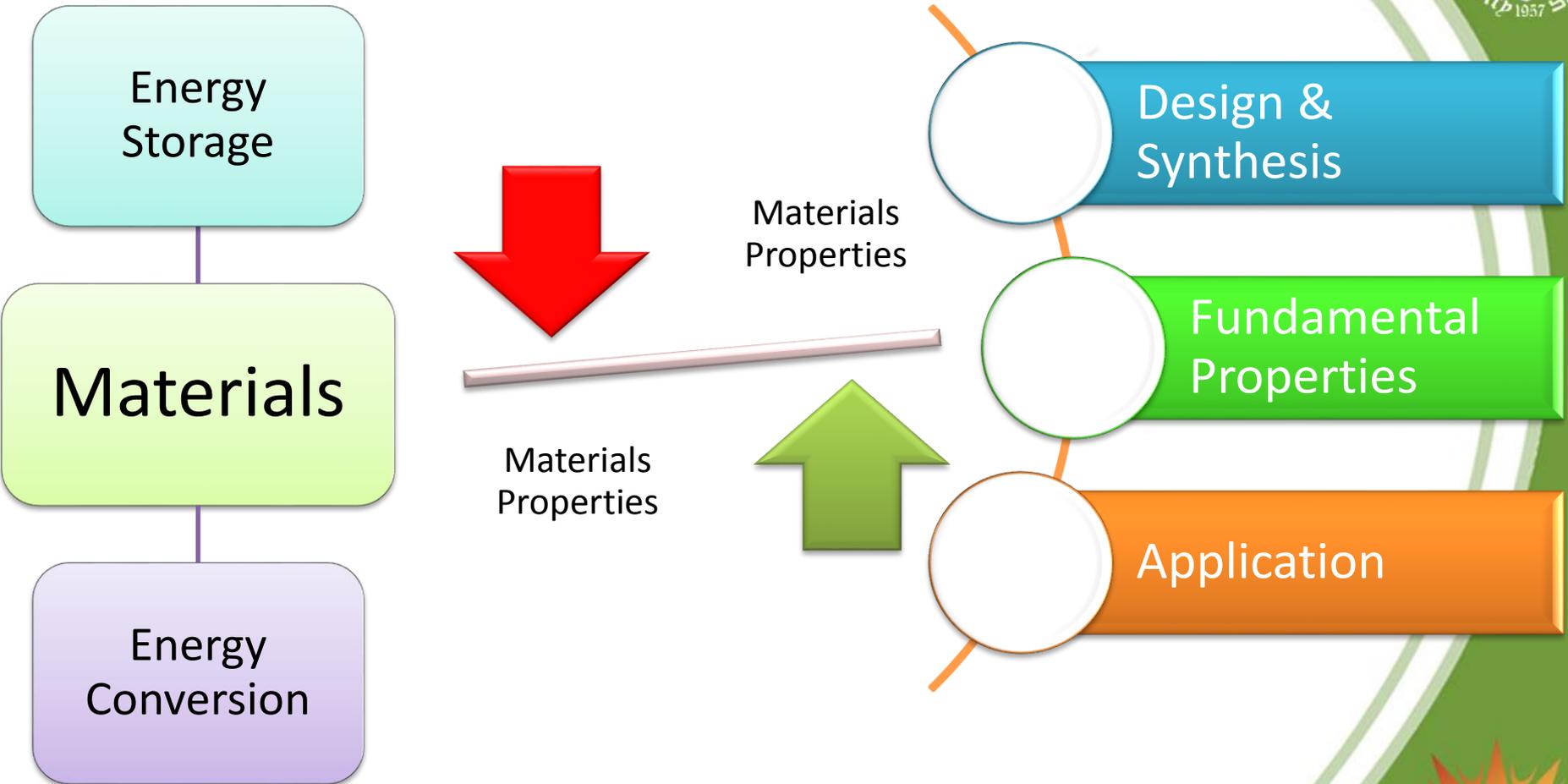
- A combination of EDLC and pseudocapacitors. Optimizes power density of EDLC with energy density of pseudocapacitor



- One common example is the Li ion capacitor which is a current leader in the field



Design Considerations



A balance between different materials properties is highly desirable for ultra efficient devices for energy storage and conversion devices

Materials Challenges



Reactions occur at the electrode surfaces

- ✓ We want to get as high a surface area as possible
 - Need to have ions and electrons together for reactions to occur
 - However
 - e.g. Nanomaterials behave differently than bulk materials
 - Energy of the reactions also depend on the surface properties
- ✓ Electrons must still be able to get outside the cell
 1. Electron resistance cannot be too high
 2. Separator must be robust and allow rapid transfer of ions
 3. Fundamental materials properties need to be understood

Basic materials properties

1. Transport in porous materials
2. Interfacial properties

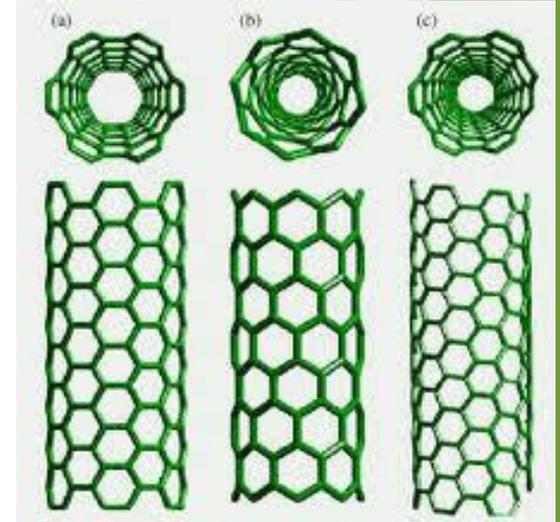
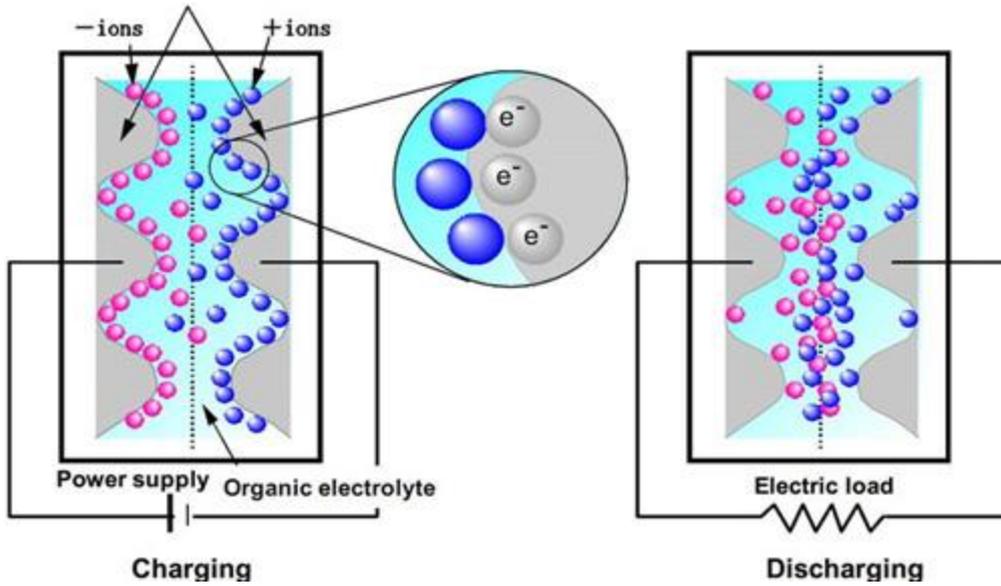




Materials for Supercapacitors



Double Layer Capacitors



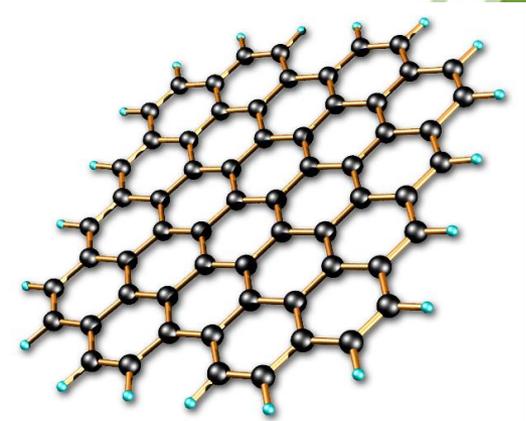
CNT_s



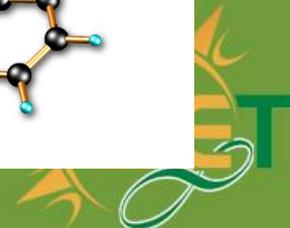
Carbon Aerogel



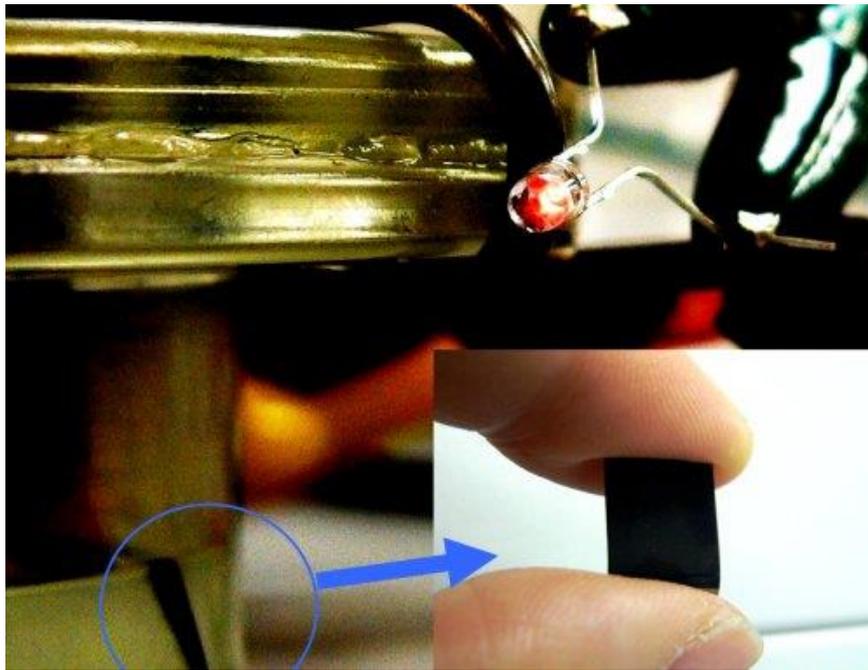
Activated Carbon



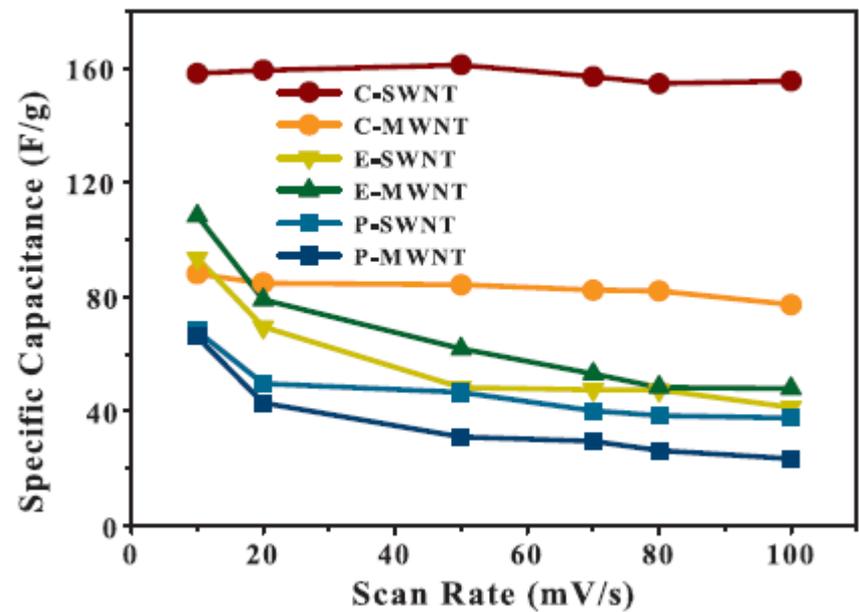
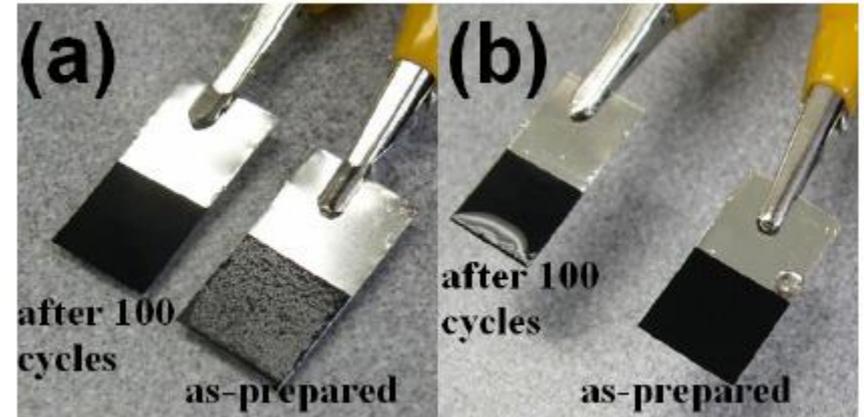
Graphene



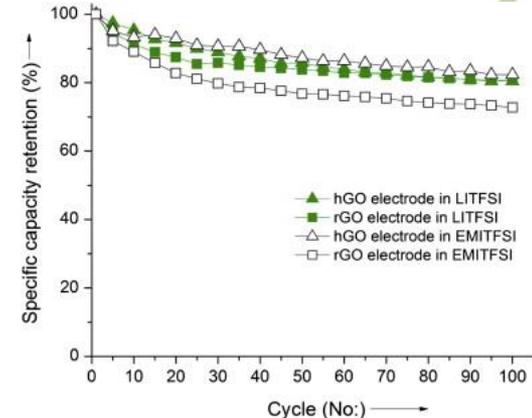
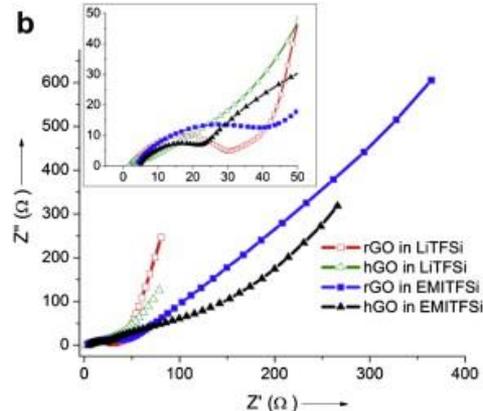
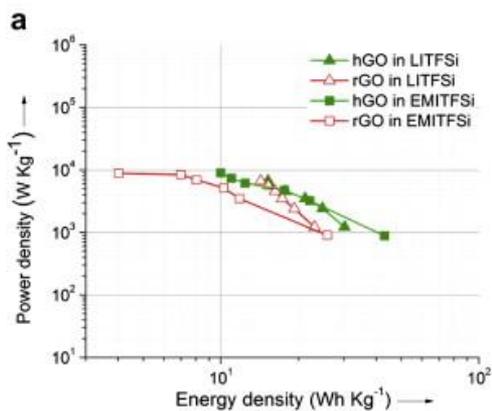
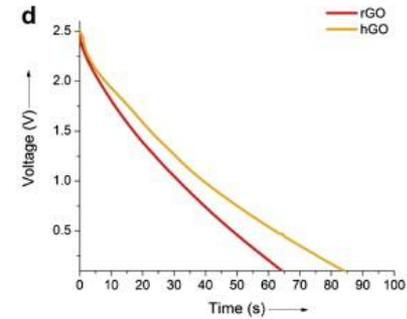
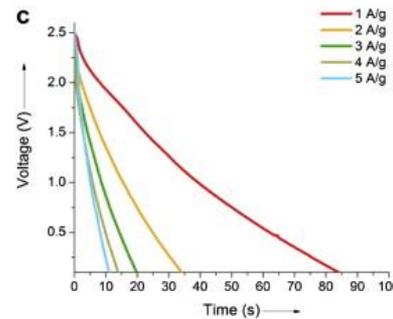
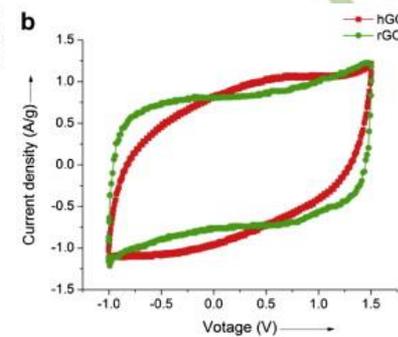
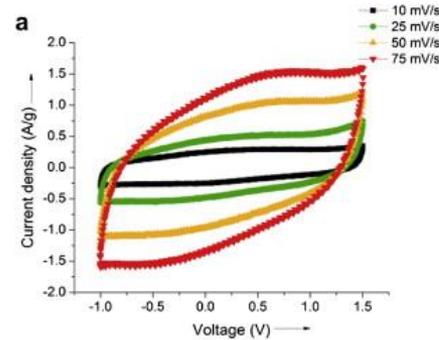
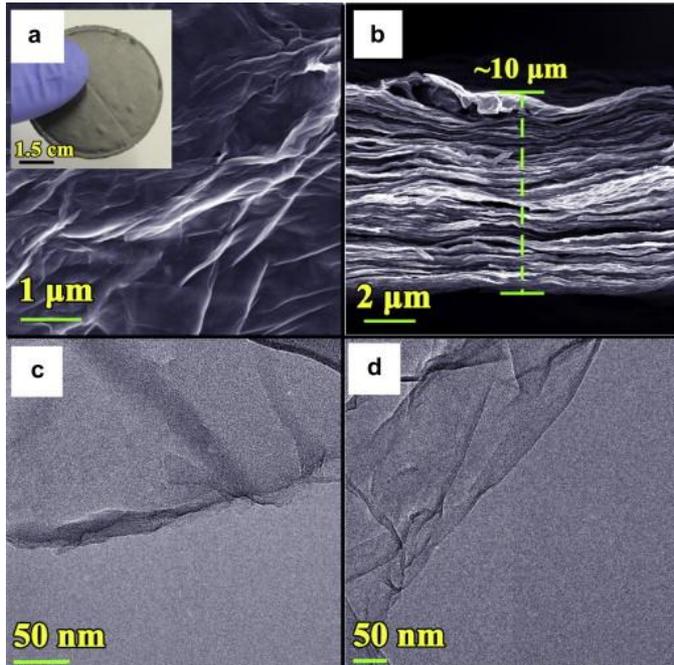
CNTS



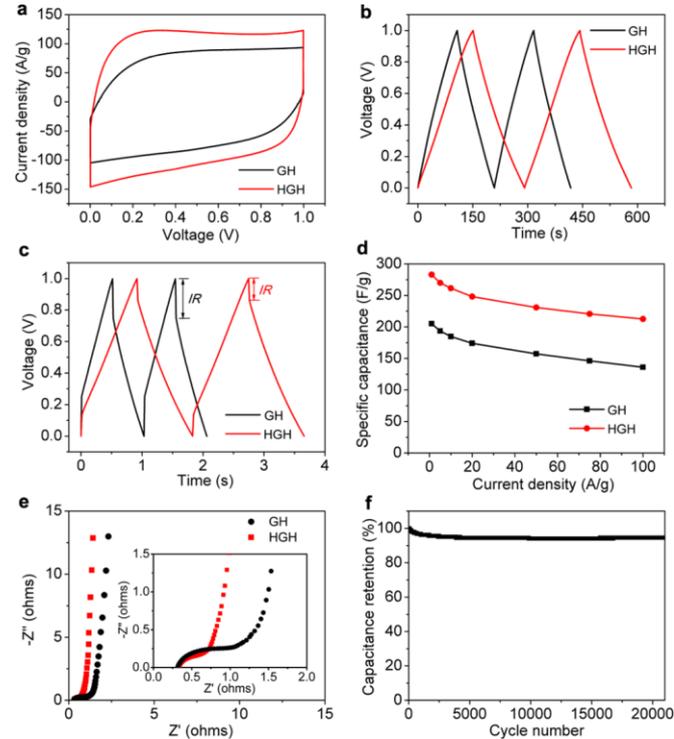
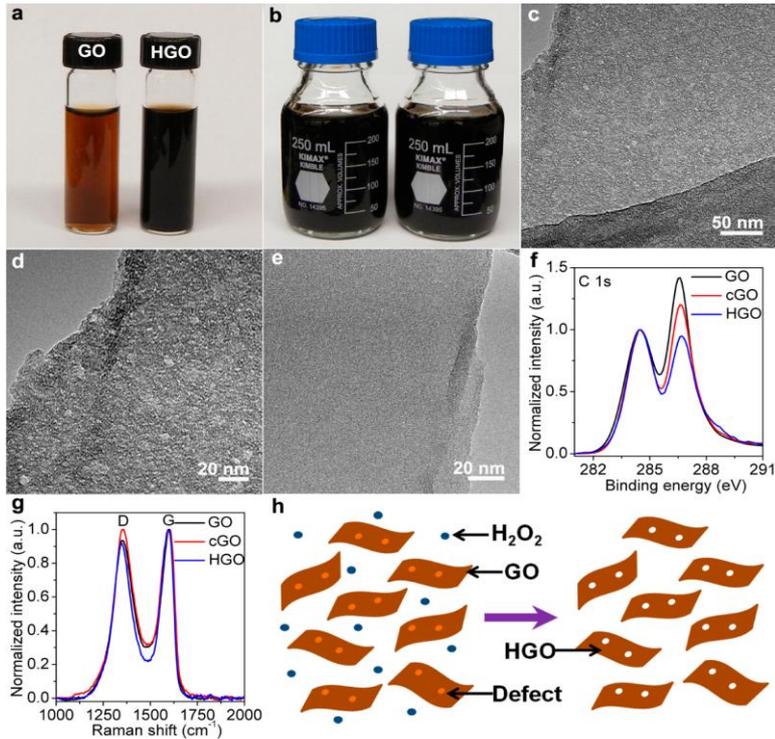
C – carboxylic
E – Ester
P - Purified



Graphene Nanosheet for EDLC



Solution Processable Holey Graphene Oxide



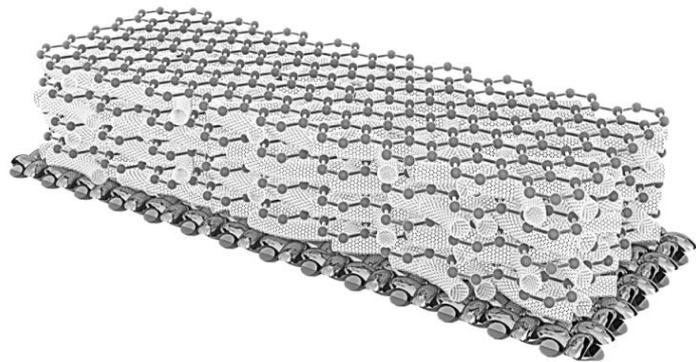
Graphene Sandwich between MWCNTs layers for Energy Storage Devices



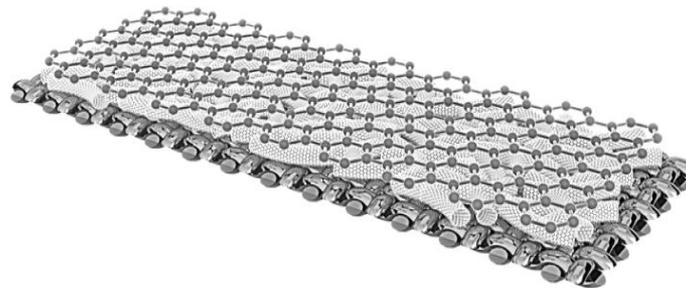
(a) Fibrous carbon cloth substrate



(b) Deposition of MWCNTs layer

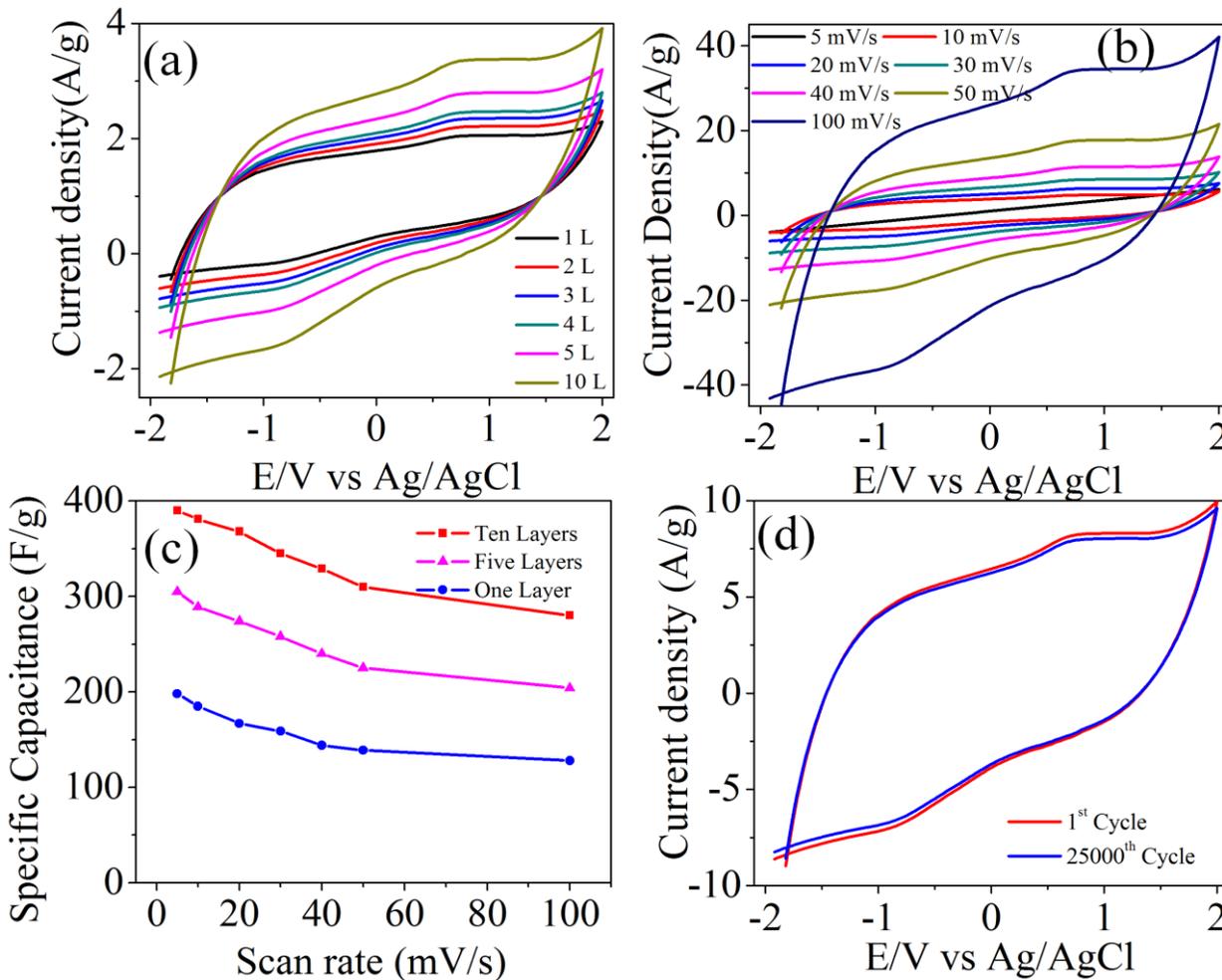


(d) Repeat steps (b) and (c) to obtain the desired number of layers



(c) Transfer of graphene on the layer of MWCNTs

Graphene Sandwich between MWCNTs layers for Energy Storage Devices



Pseudocapacitors

Store energy using fast surface redox reactions

Metal oxides:

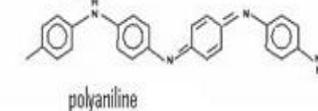
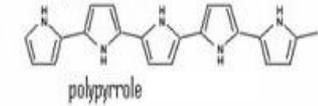
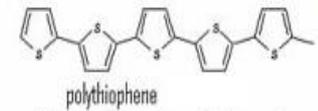
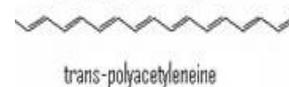
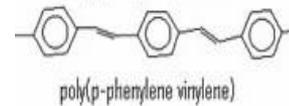
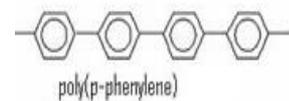
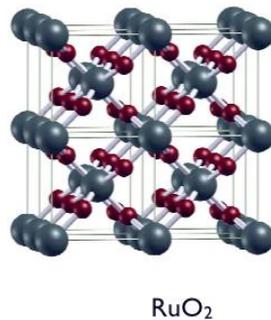
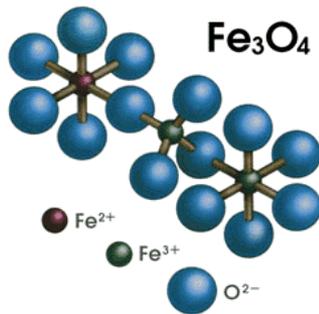
Capacity 1300 F/g (RuO_2)

Nominal voltage 1.2 V

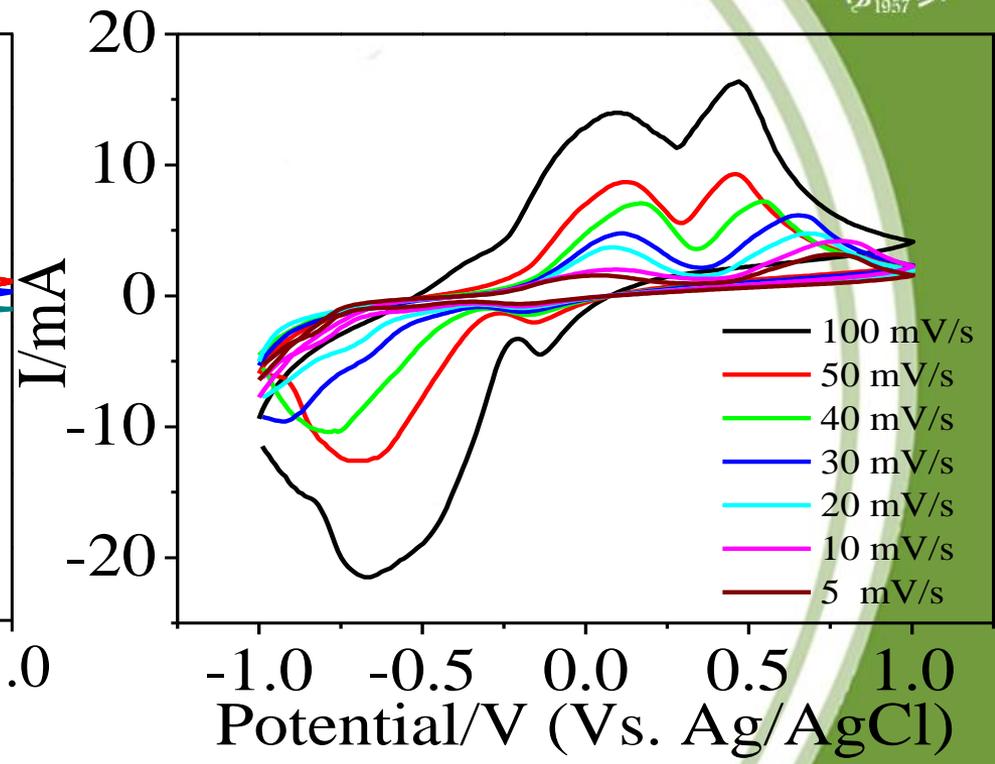
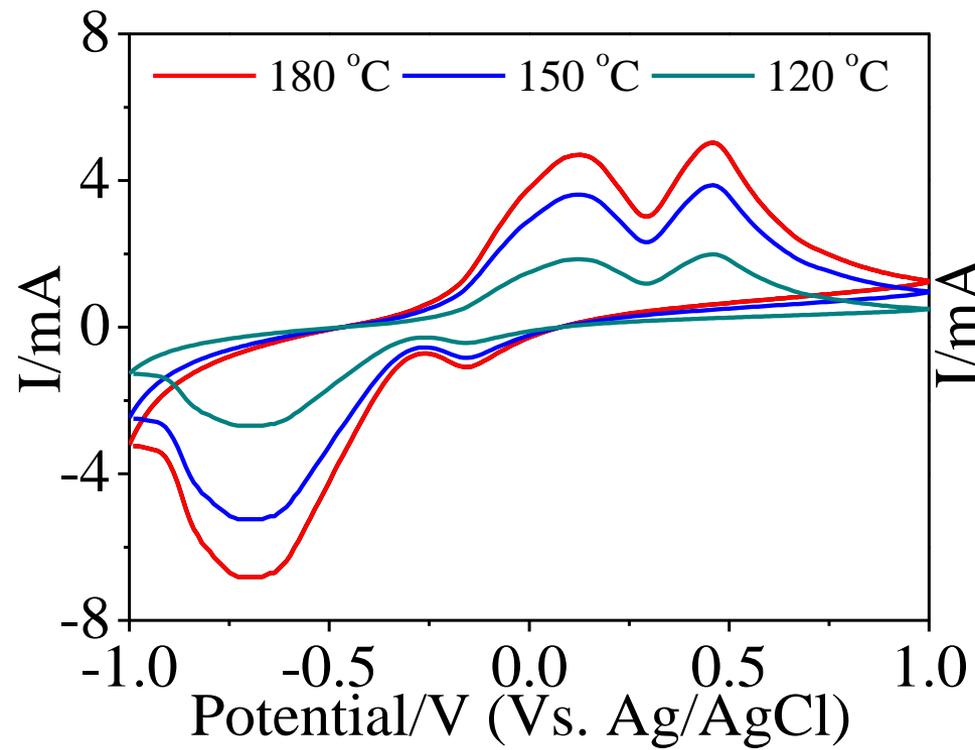
Conducting polymers:

Capacity 30 – 40 mAh/g

Nominal voltage 1.0 V



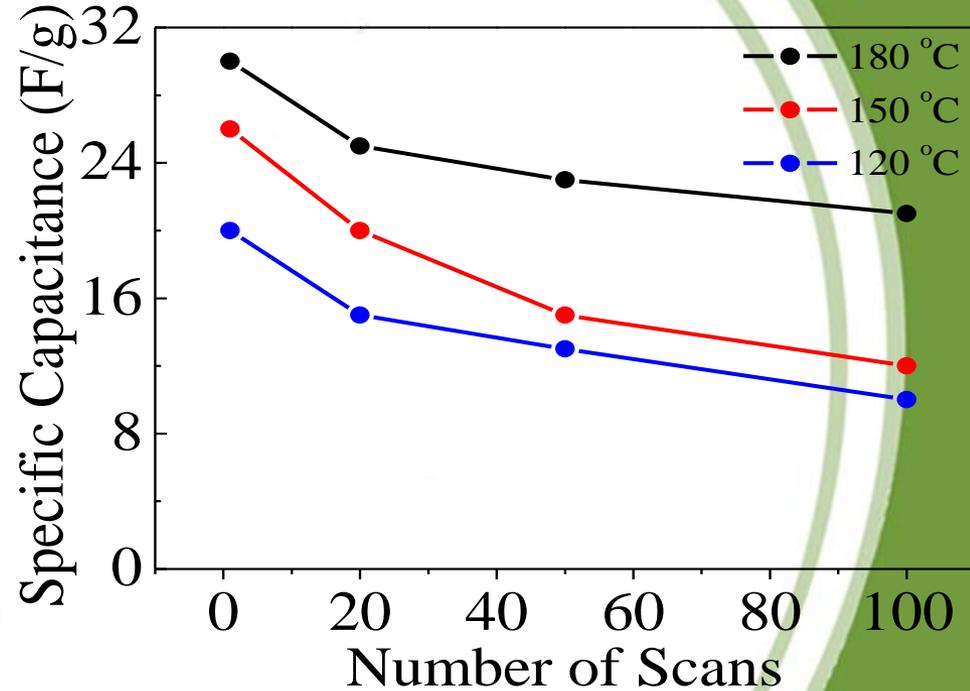
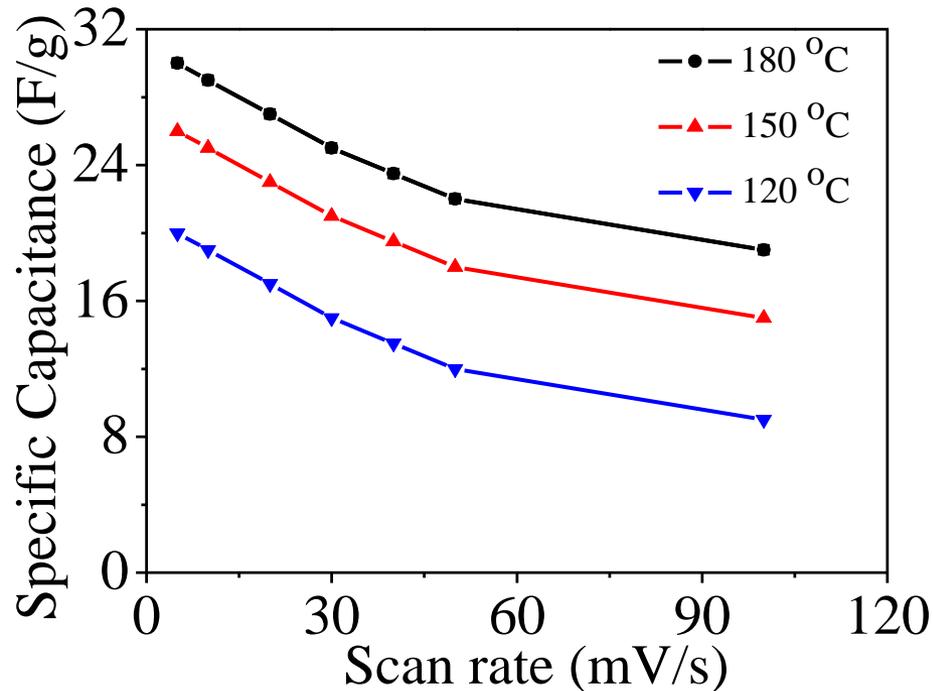
MoO₃ Nanorods for Energy Storage Applications



- Maximum current was obtained from the samples synthesized at 180 °C which was due to the increase of crystallinity and morphology.



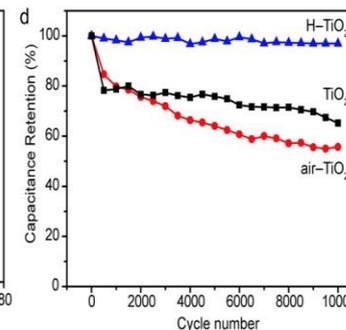
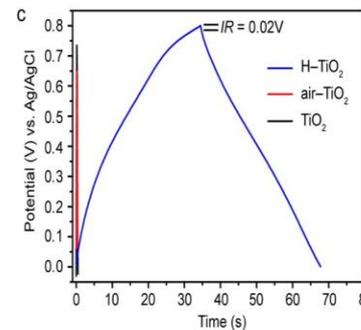
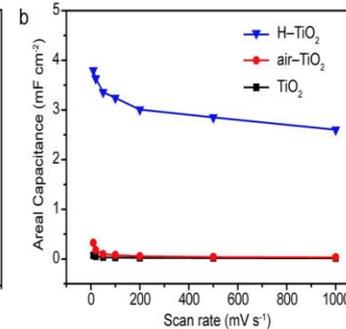
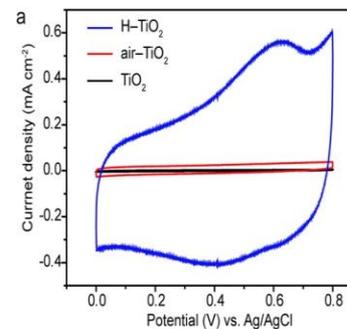
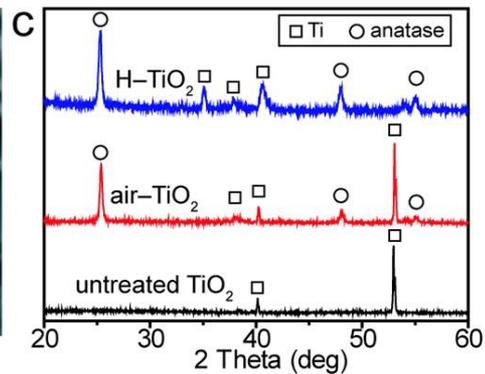
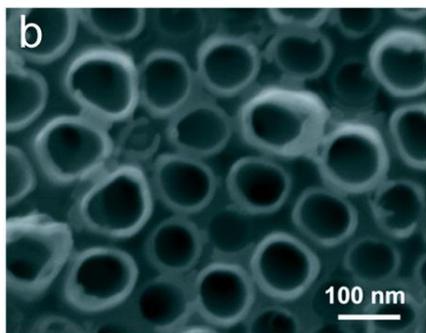
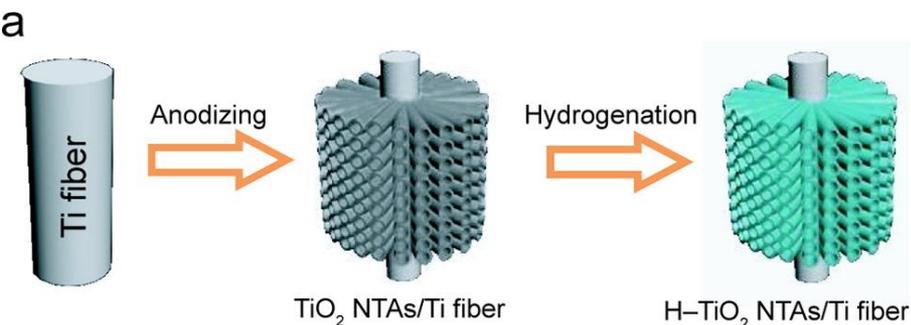
MoO₃ Nanorods for Energy Storage Applications



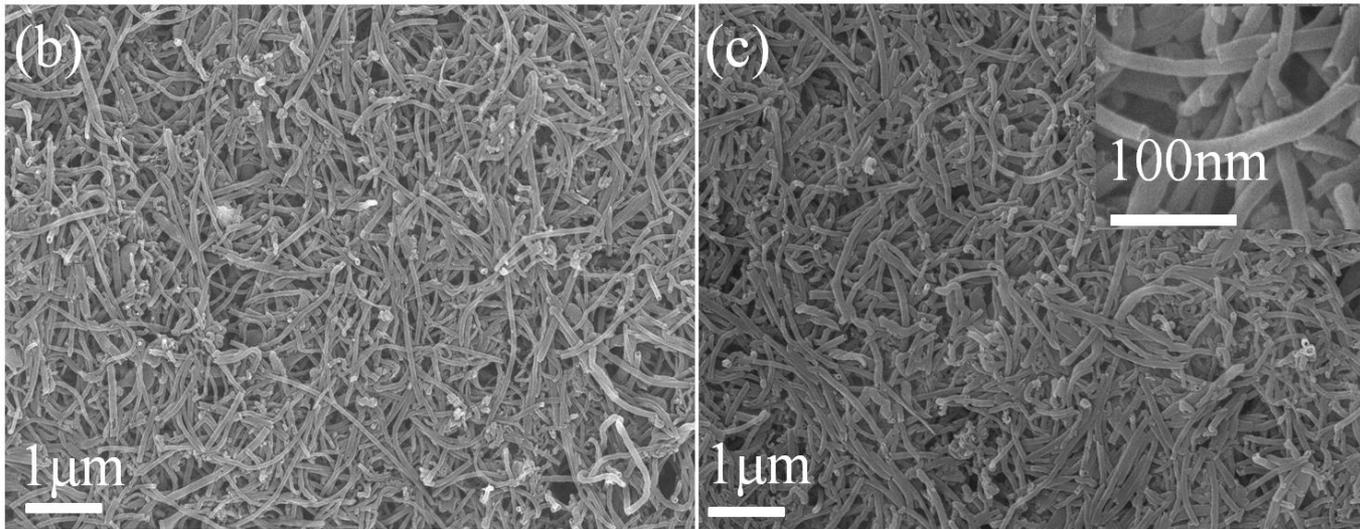
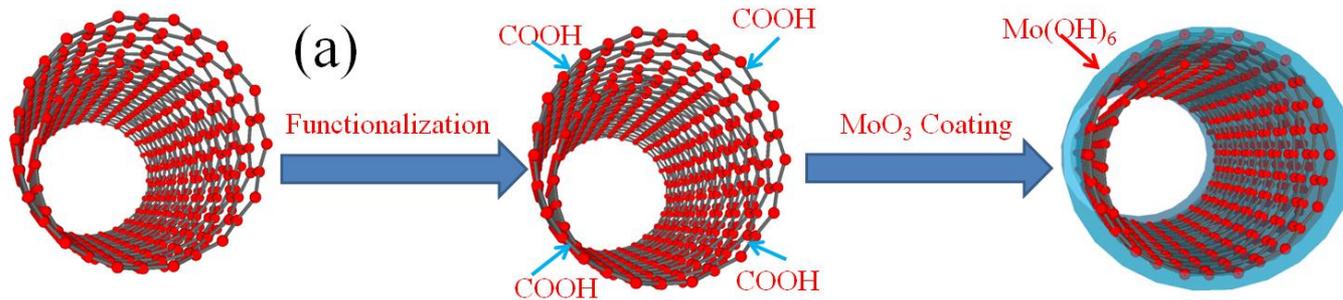
- The increase in ionic resistivity at higher scan rate leads to a drop in the capacitance of the nanorods.
- The specific capacitance of as synthesized nanorods at 180 °C was found to be higher than that of nanorods synthesized at 120 °C, and comparable to that of the 150 °C (at a scan rate of 5 mV/s).



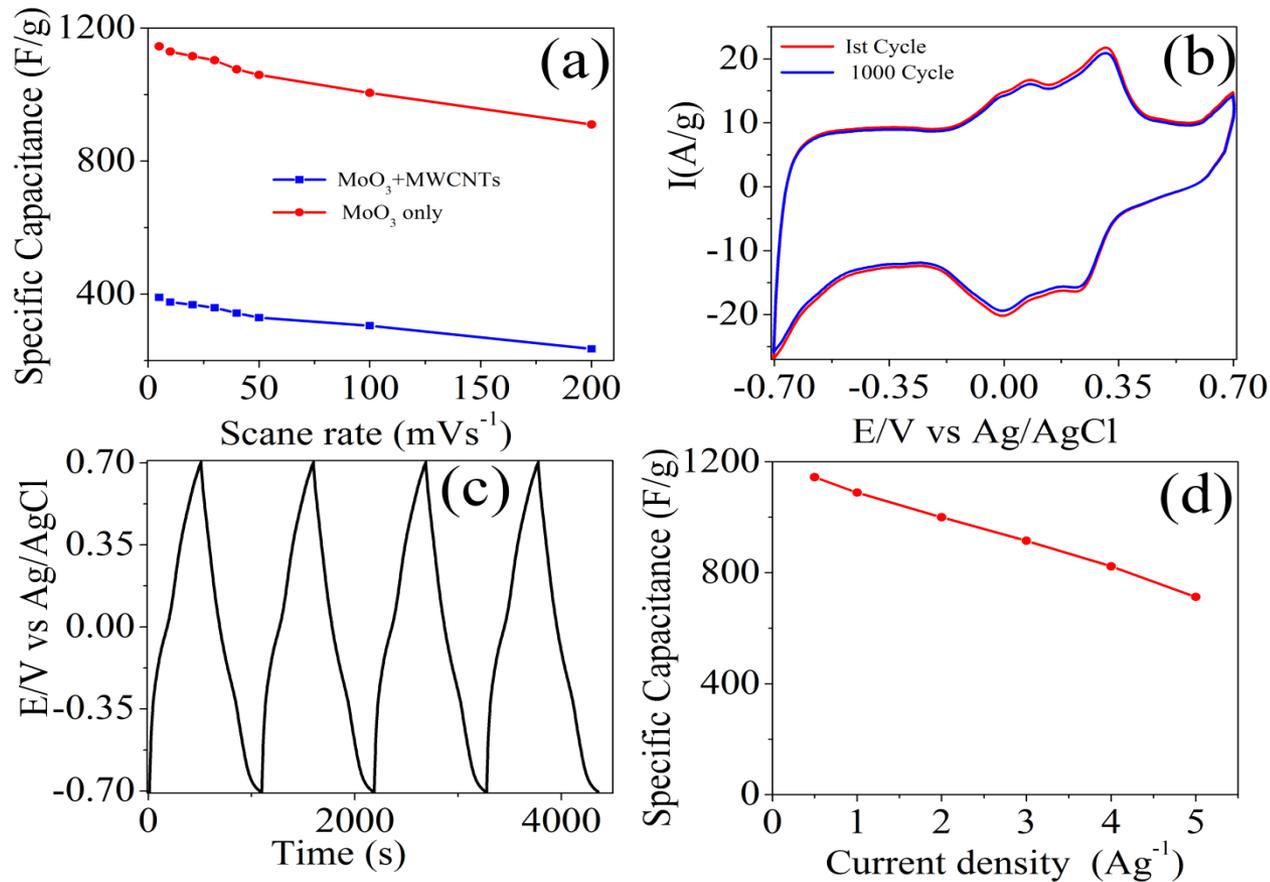
Hydrogenated TiO_2 as Supercapacitors



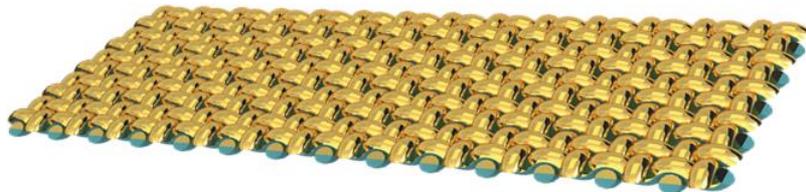
Ultra-thin Solution-based coating of Molybdenum Oxide on Multiwall Carbon Nanotubes



Ultra-thin Solution-based coating of Molybdenum Oxide on Multiwall Carbon Nanotubes



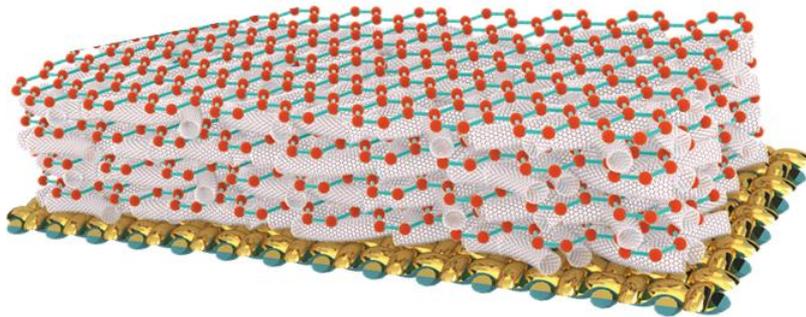
Ultrathin Metal Oxide Sandwich between Graphene layers for Energy Storage Devices



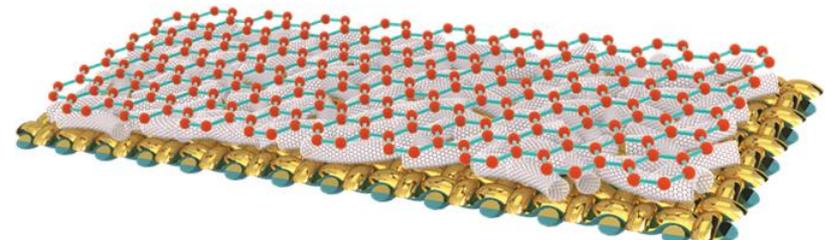
Ni/Cu/Ni/Au Coated Textile Fiber Substrate



Deposition of metal oxide coated MWCNTs layer



Repeat the steps to obtain the desired number of layers

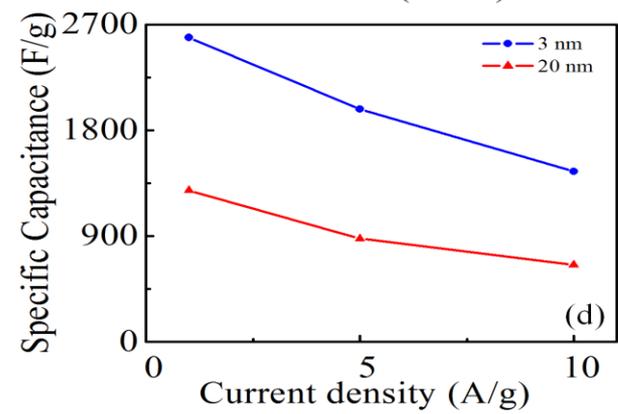
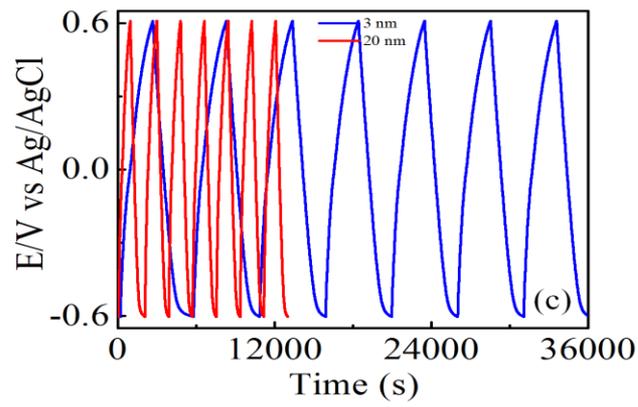
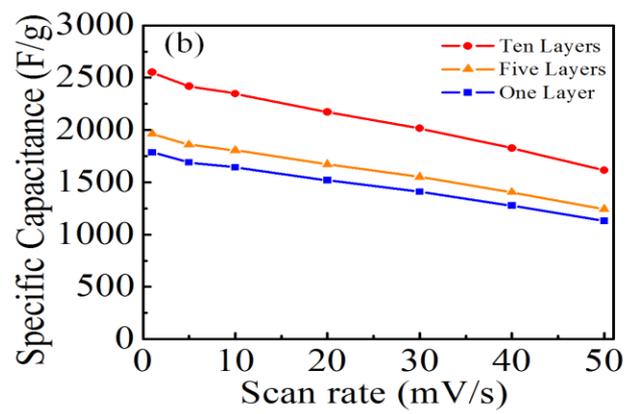
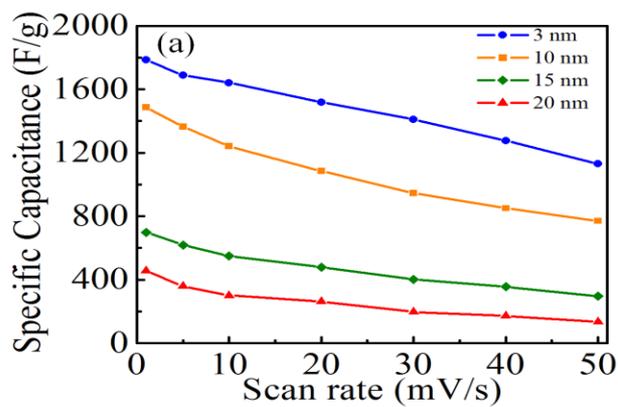


Transfer of Graphene on the Layer of metal oxide coated MWCNTs

Imran Shakir, *et.al* Nanoscale 6 (8), 4125-4130

Imran Shakir, *Electrochimica Acta* 129, 396-400

Ultrathin Metal Oxide Sandwich between Graphene layers for Energy Storage Devices



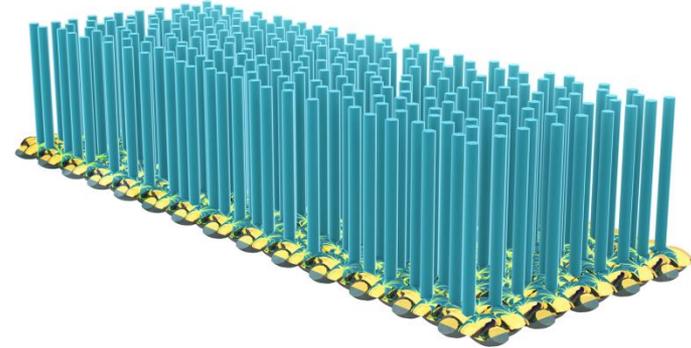
● The specific capacitance of metal oxide with thickness of 3 nm sandwich between graphene was found to be higher than that of higher thickness (2590F/g).



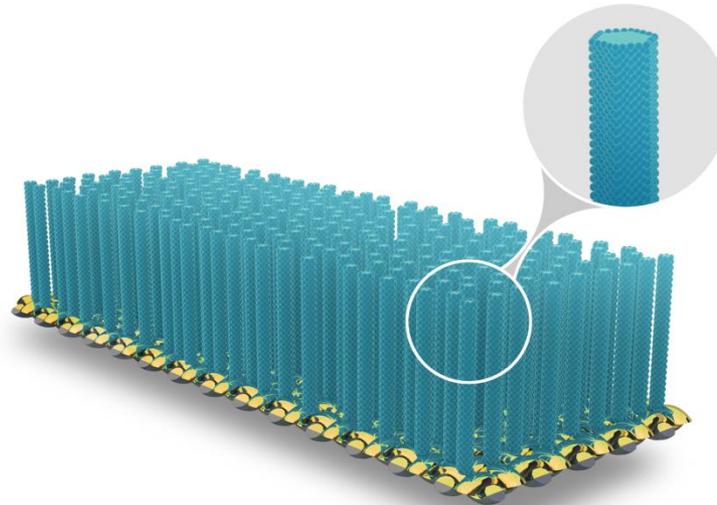
Ni(OH)₂-coated ZnO Nanowire-based Energy Storage Devices



Step 1: Preparation of Ni/Cu/Ni/Gold textile fiber

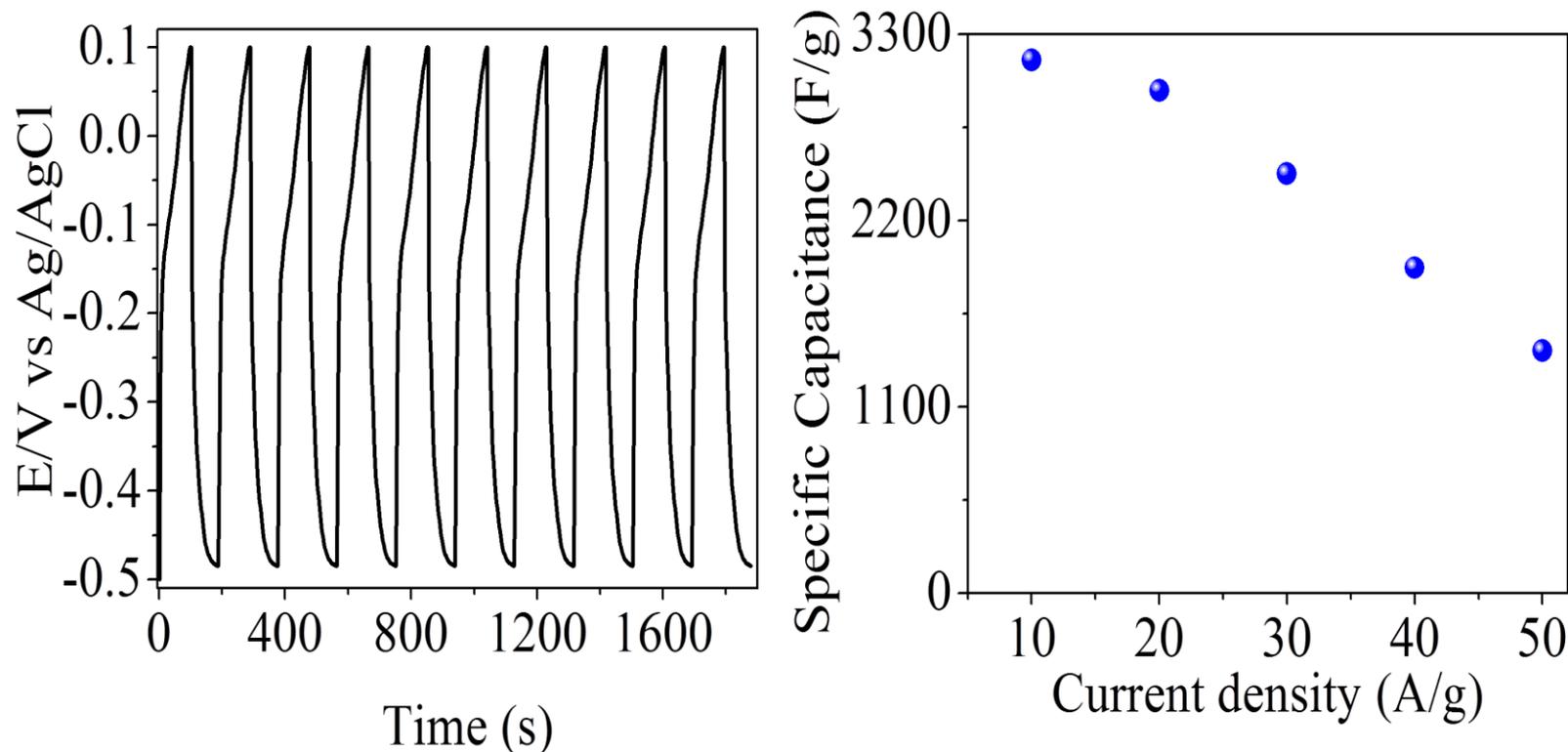


Step 2: Hydrothermal growth of ZnO nanowires



Step 3: Synthesis of Ni(OH)₂-coated ZnO nanowires

Ni(OH)₂-coated ZnO Nanowire-based Energy Storage Devices



- The Ni(OH)₂ coated ZnO nanowires electrodes show a nonlinear charge–discharge curve, which indicates electrode have pseudocapacitive behavior with a specific capacitance of 3200 F/g.



Materials for lithium Ion Battery



Design Considerations



1. Volumetric and/or gravimetric energy density
2. Cycle life
3. Safe operation
4. Energy losses in course of charge/discharge cycle
5. Power performance, needed for some applications
6. Environmentally friendly and inexpensive.



Materials Requirements

- Large reversible capacity reversible capacity
- Small irreversible capacity
- Desirable charge profile charge profile
- Desirable kinetics (rate capability)
- Long cycle and calendar life
- Ease of processing
- Safety
- Compatibility with electrolyte and binder systems
- Low cost



Major Types of Materials



- Layered oxides with the $\alpha\text{-NaFeO}_2$ -type structure
- Oxides with a spinel structure
- Poly-anion oxides with the olivine and olivine-related structures



Anode Materials



1. Current Materials

1. Carbonaceous
 1. Graphite
 2. Hard Carbon
 3. Soft Carbon
2. Titanium Oxide

2. Future Materials

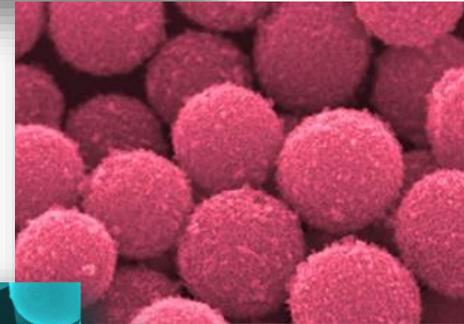
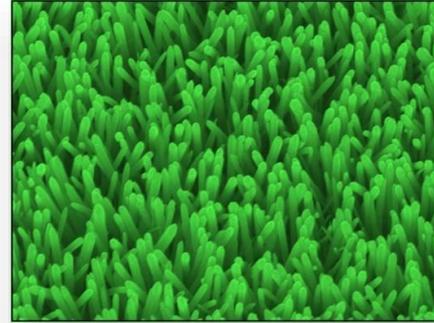
1. Silicon
2. Nanomaterials
3. Other



Structure and Designing Options

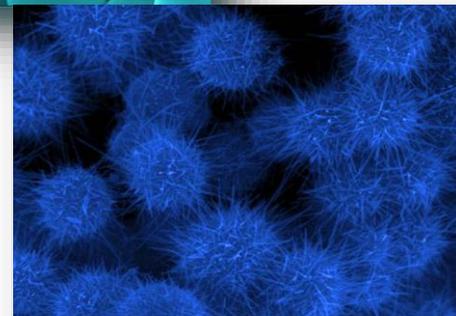
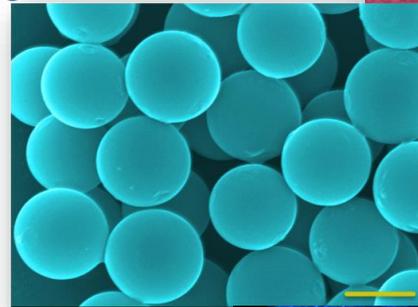
Some limitations such as:

1. Low electronic conductivity
2. Low ionic conductivity
3. Charge recombination
4. Wide band gap



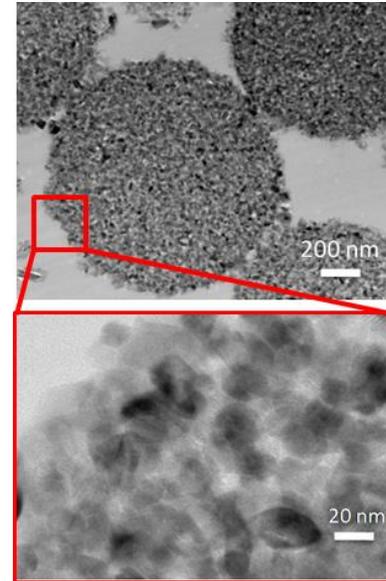
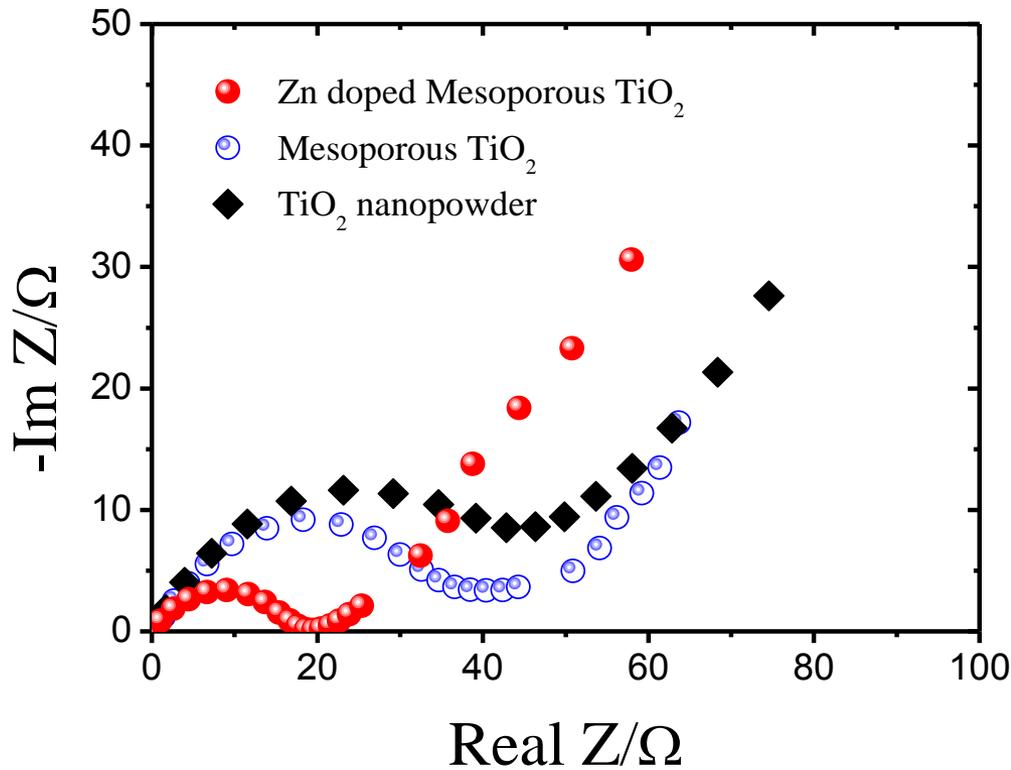
These limitations can be overcome by:

1. Tuning shape and size
2. Composite structures
3. Doping



Impedance Analysis

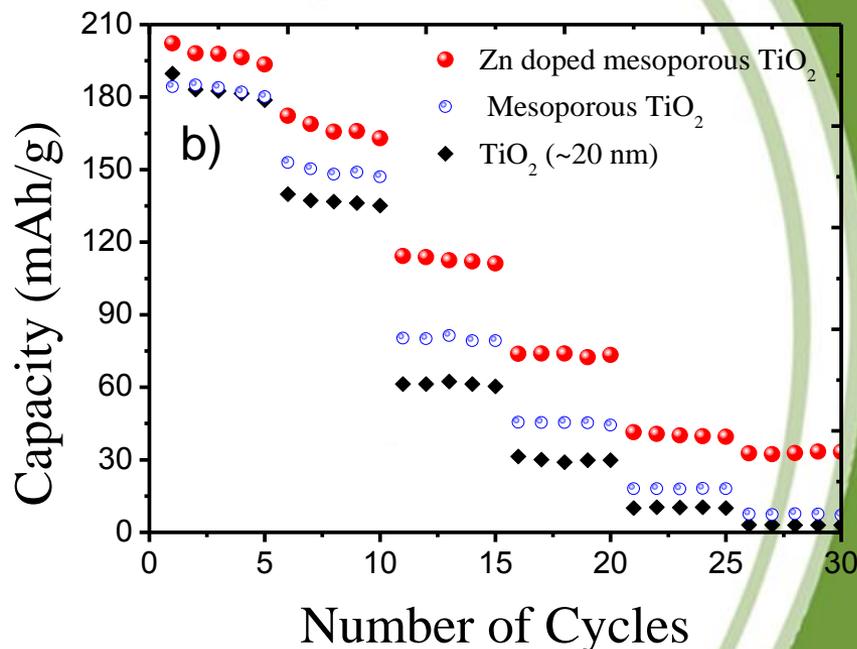
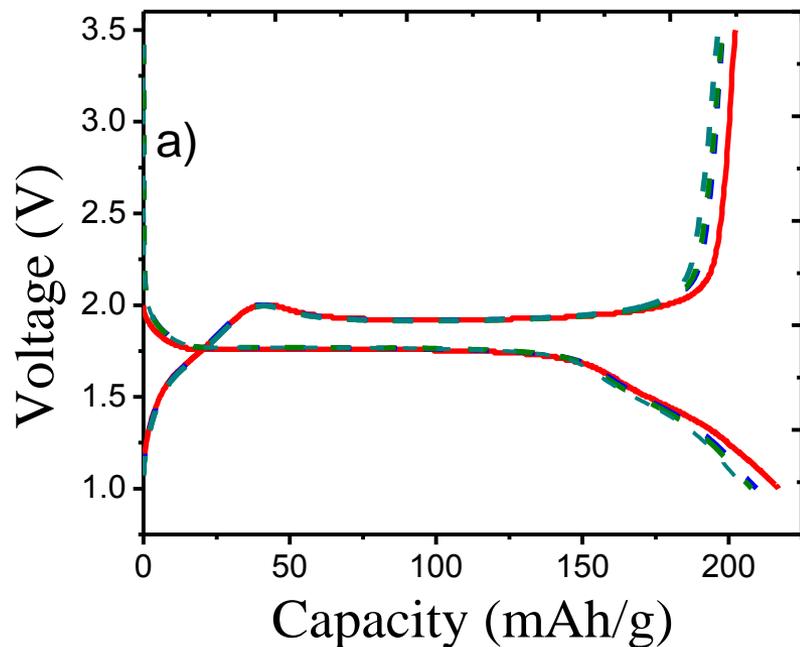
Zn Doped Mesoporous TiO₂ Microspheres



Nyquist plots for Zn doped mesoporous TiO₂ microspheres and 20 nm anatase TiO₂ nanopowder

Charge-Discharge Results

Zn Doped Mesoporous TiO₂ Microspheres

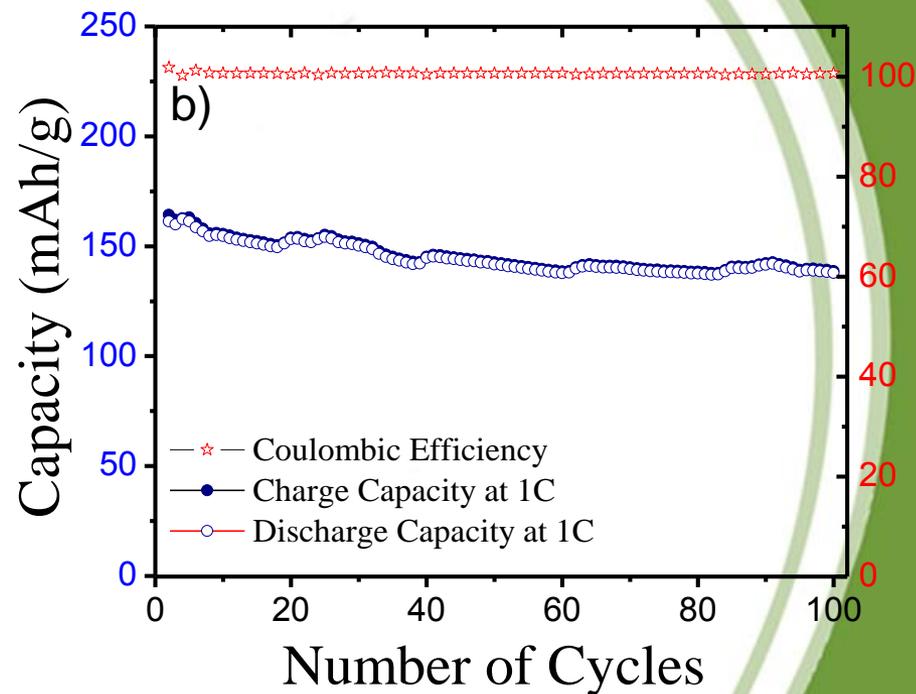
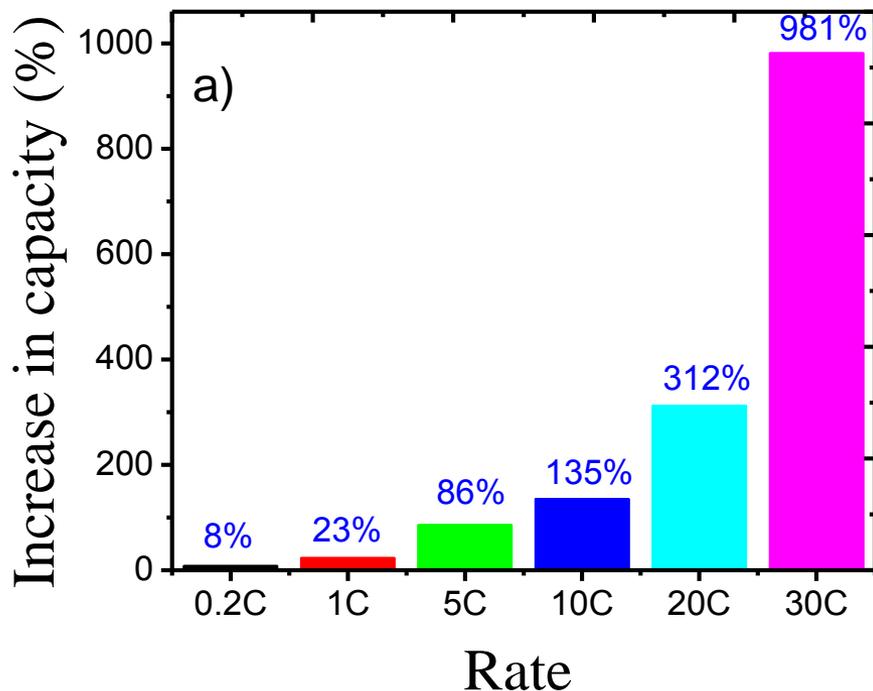


(a) Charge-discharge profiles for Zn doped mesoporous TiO₂ at C/5 charge-discharge rates. (b) Discharge capacity of Zn doped mesoporous TiO₂ and 20 nm anatase TiO₂ nanoparticles at different discharge rates



Charge-Discharge Results

Zn Doped Mesoporous TiO₂ Microspheres



(a) Percentage increase in discharge capacity of Zn doped mesoporous TiO₂ and 20 nm anatase TiO₂ nanoparticles at different discharge rates. (b) Cycling performance and Coulombic efficiency of Zn doped mesoporous TiO₂ up to 100 cycles at 1C charge/discharge rates.





Thank you for your attention!

