Nanotechnology for Batteries

Afriyanti Sumboja, PhD

Fakultas Teknik Mesin dan Dirgantara

Institut Teknologi Bandung

materials electrochemistry laboratory ITB

Nanotechnology

materials
electrochemistry
laboratory
ITB

Nanotechnology: Small, Different, New

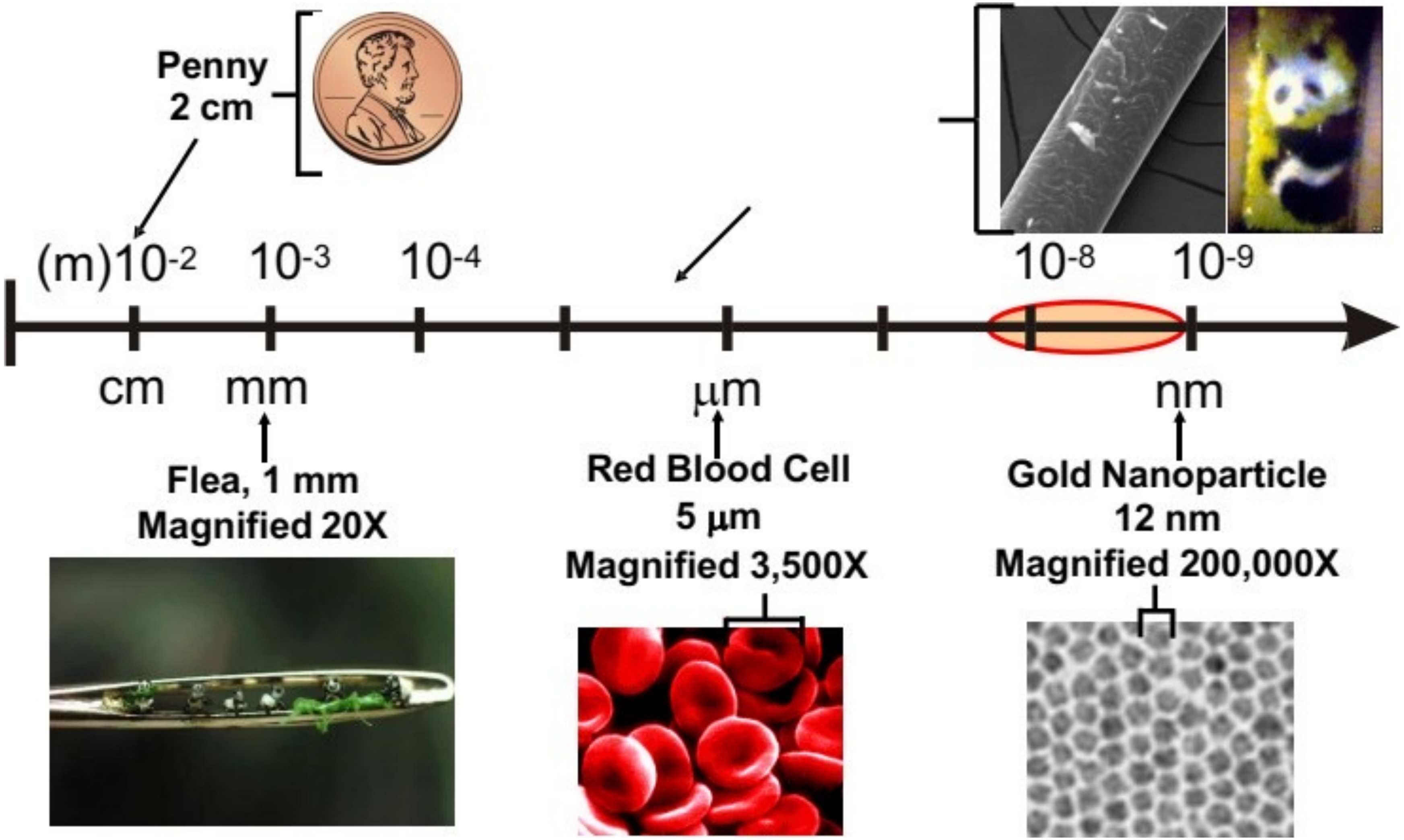
Key Ideas:

- Nanometer is extremely small
- Materials may behave differently at the nanometer scale
- The new behavior can be harnessed for new technologies

- **Nanoscience:** Study of phenomena and manipulation of materials at the atomic, molecular, and macromolecular scales, where properties differ significantly from those at larger scales.

- **Nanotechnology:** Design, characterization, production, and application of structures, devices, and systems by controlling the shape and size at the nanometer scale

How small is nano?



What are the key challenges of nanoscience & nanotechnology?

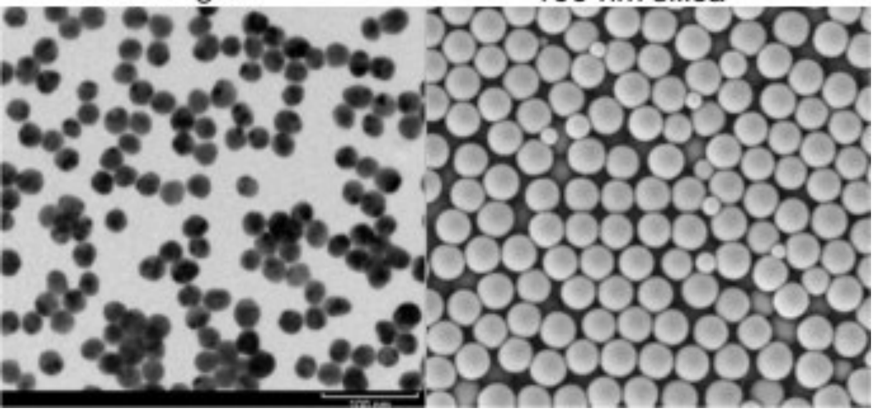
- **Understanding properties**
  - "Nanoland" lies between the macro world and single atoms/molecules
- **Making nanomaterials**
  - Self-assembly, top-down vs. bottom-up
- **Characterizing nanostructures**
  - Imaging and measuring small things
- **Nanosystem integration and performance**
  - How do we assemble nanostructures into systems

What is Nanomaterials?

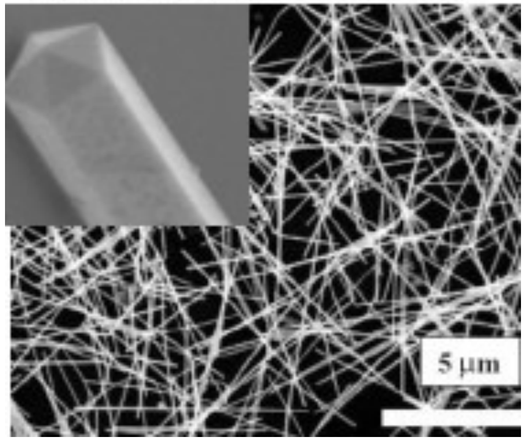
Generic term for materials that have at least one dimension < 100 nm

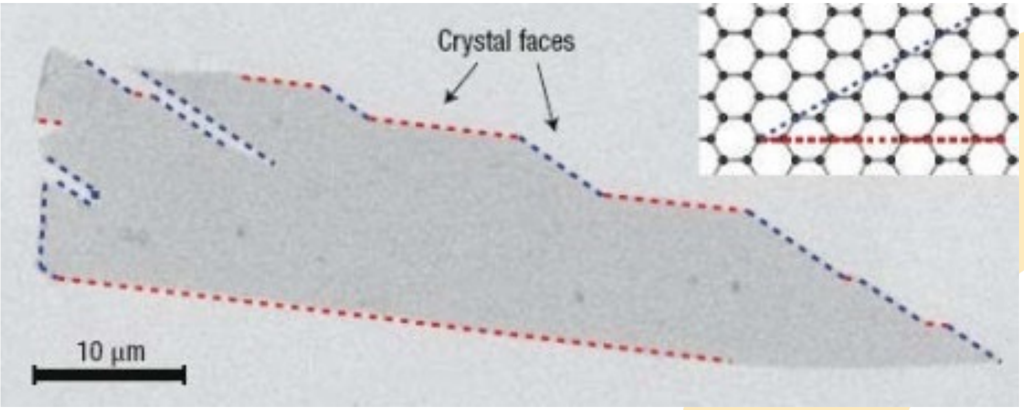
- 2D nanomaterials: 1 dimension < 100 nm (e.g., thin films, nanoplates)
- 1D nanomaterials: 2 dimensions < 100 nm (e.g., nanowires, nanotubes)
- 0D nanomaterials: 3 dimensions < 100 nm (e.g., spherical nanoparticles)

25 nm gold 100 nm silica



Ag (5-fold tip, 70 nm/ 6um)





Defining characteristics of nanomaterials

- Characteristics length of the structures has, at least, one dimension in the 1-100 nm range.
- When this happens, it becomes comparable with the critical length scales of physical phenomena.
- ”Nano” studies are based on the recognition that nanomaterials impart new properties and behavior compared to much larger structures.

Batteries

materials
electrochemistry
laboratory
ITB

Batteries

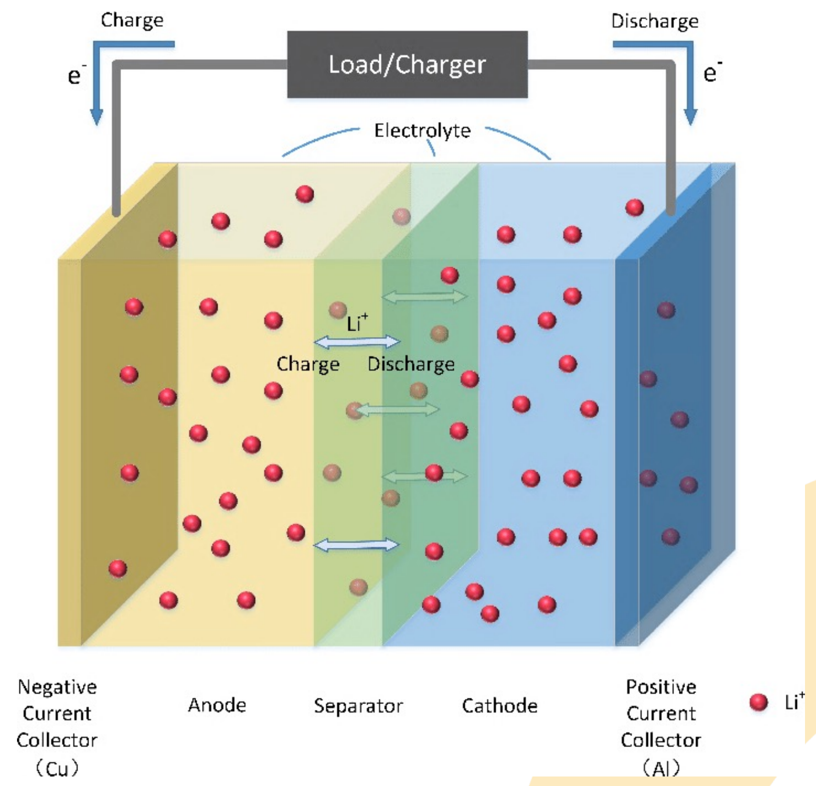
- **Energy storage devices**
  - Fuel and oxidant are stored within the device
- **Energy conversion devices**
  - Fuel and oxidant are stored external to the device

- Battery is a device that allows energy to be stored in a chemical form and to be released as electrical energy when needed
- There are wide range of battery types, sizes, designs, operating temperatures, control mechanisms, and chemistries

Component of a battery

- Consist of two or more voltaic cells that are connected in series to provide a steady dc voltage, which is produced by chemical reaction in the cell

- **Positive electrode/cathode**: electrode to which cations migrate, undergoes reduction during discharge.
- **Negative electrode/anode**: electrode to which anions migrate, underges oxidation during discharge.
- **Electrolyte**: medium for ion transfer, enables ion transfer between the two electrodes
- **Separator**: electrically isolates the positive and negative electrode

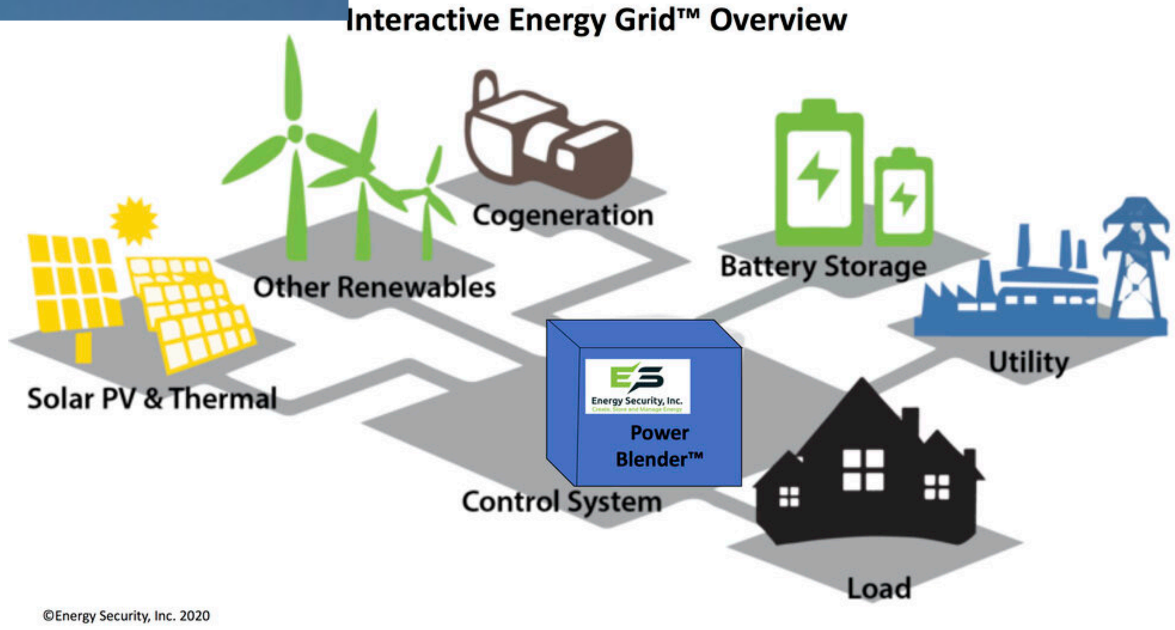


Capacity

- Amount of “charge” that can be stored per unit weight or volume (Ah/kg or mAh/g)
- Capacity is proportional to the size of the battery
- A battery have 200 Ah rating. How long can this battery supply 20 amperes?

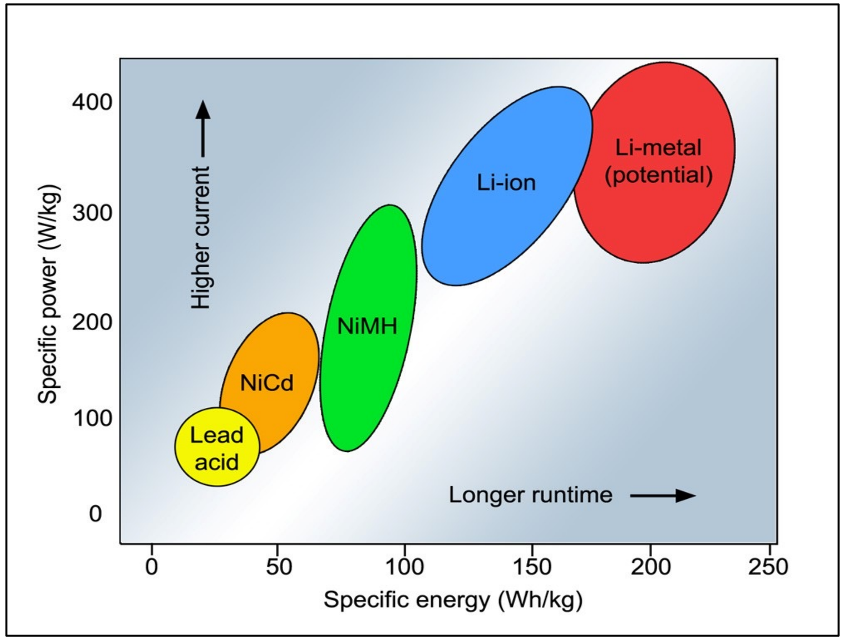
$$Time = \frac{Capacity}{Load\ current} = \frac{200\ Ah}{20\ A} = 10\ hours$$

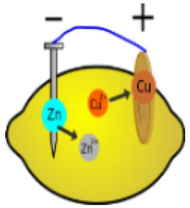
Next generation of batteries



Power vs. Energy Density

Power

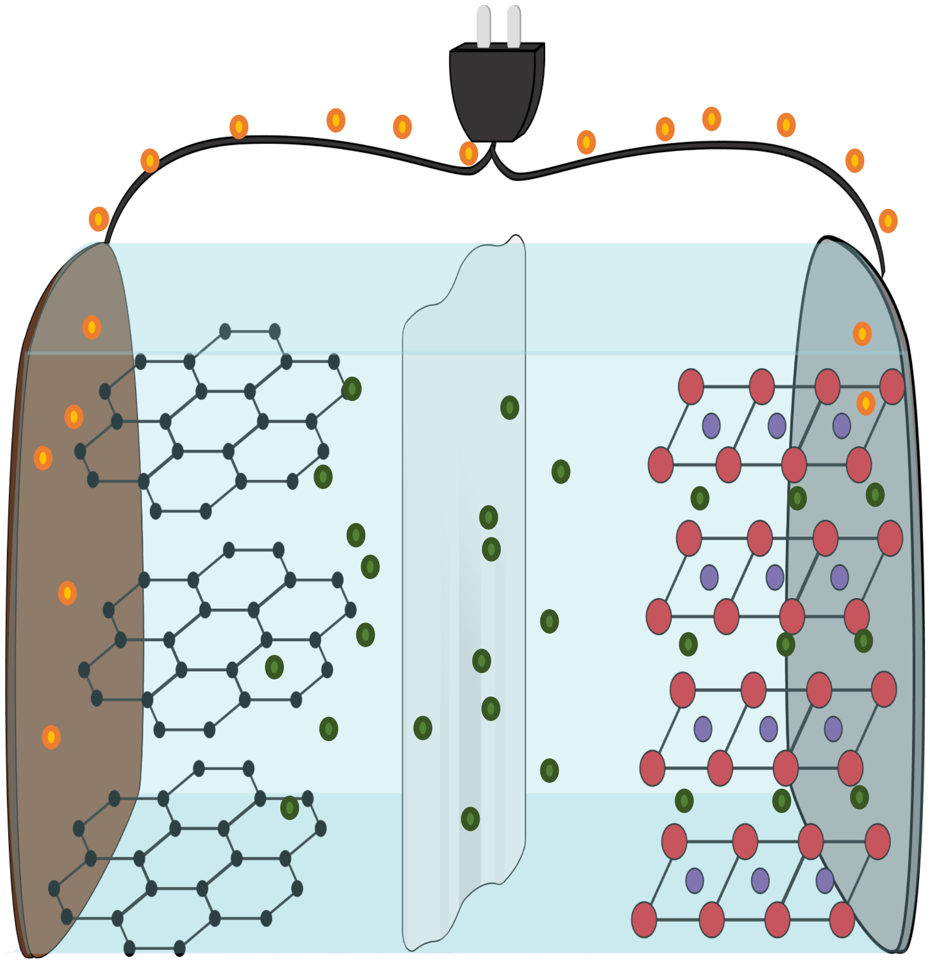




Energy

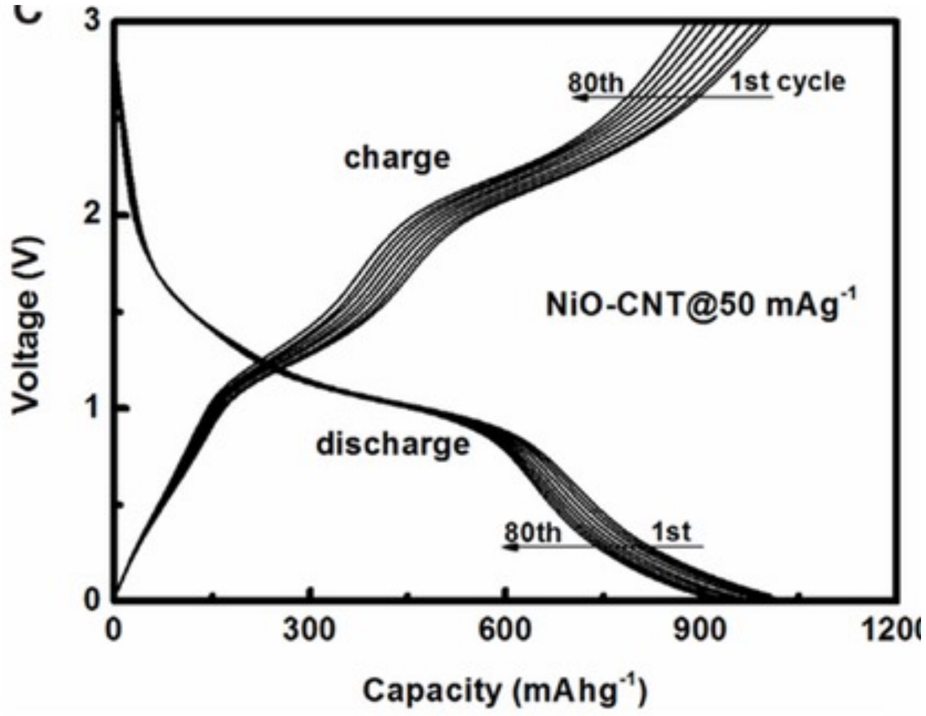
Specific energy: Capacity a battery can hold (Wh/kg)
Specific power: Ability to deliver power (W/kg)

Li-ion batteries



- Make use of reversible reaction of Li ions with the electrode
- **Positive electrode**: Lithiated form of a transition metal oxide ($LiCoO_2$, $LiMn_2O_4$)
- **Negative electrode**: graphite
- Both materials are layered materials, through which lithium can move easily.
- **Electrolyte**: solid lithium-salt electrolytes ($LiPF_6$)

Energy density: Why doesn't my battery last all day



- **Energy**: area under the discharge curve
- How can we increase energy density of a battery?
  - Increase capacity (x-axis)
  - Increase voltage (y-axis)

Cathode

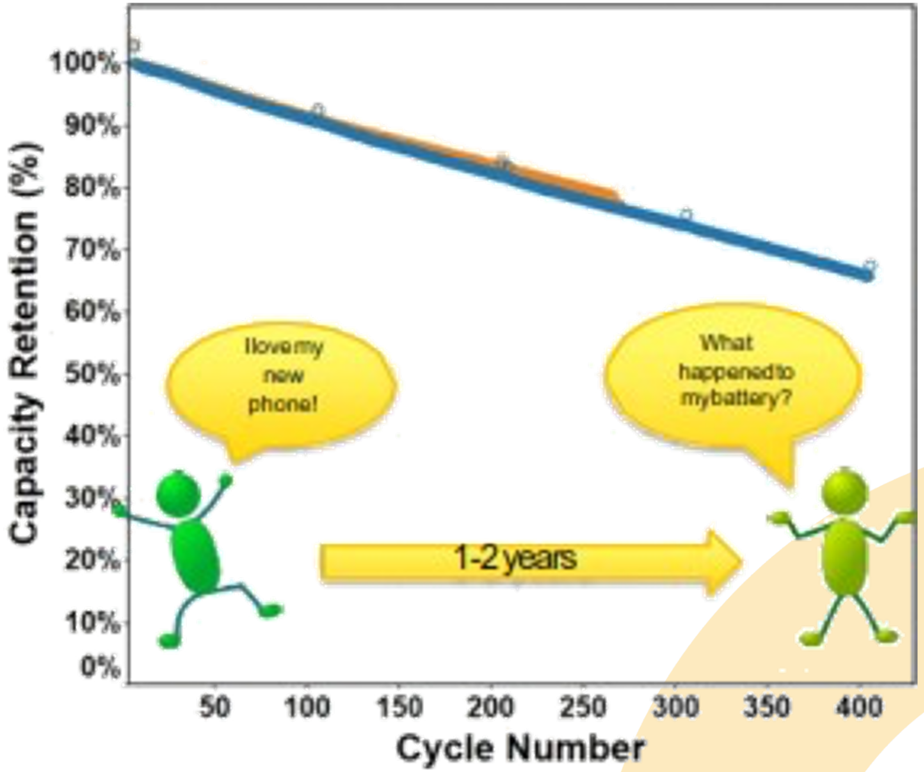
- More Li^{+} per unit volume
- Higher voltage
- Increase density of materials
- Pack more cathode to battery volume

Anode

- More Li^{+} per unit volume
- Lower voltage
- Increase density of materials
- Use less battery volume for the anode

Why battery performance of my old phone keep decreasing?

- Loss of lithium due to reaction of electrolyte with active material
- Continuous formation of SEI results in gradual loss of lithium to move back and forth
- Impedance rise in the cell due to SEI formation or other problem
- A new phone most certainly has a better battery
  - Higher capacity, higher voltage
- But WHAT ELSE does it has
  - Bigger display, brighter display
  - More processors, we use it differently….



Nanotechnologies and Batteries

materials
electrochemistry
laboratory
ITB

High Energy Density Batteries

REVOLUTION IN TRANSPORTATION and RENEWABLE

~10 Wh

~70 Wh

~85,000 Wh

World ~10 TWh

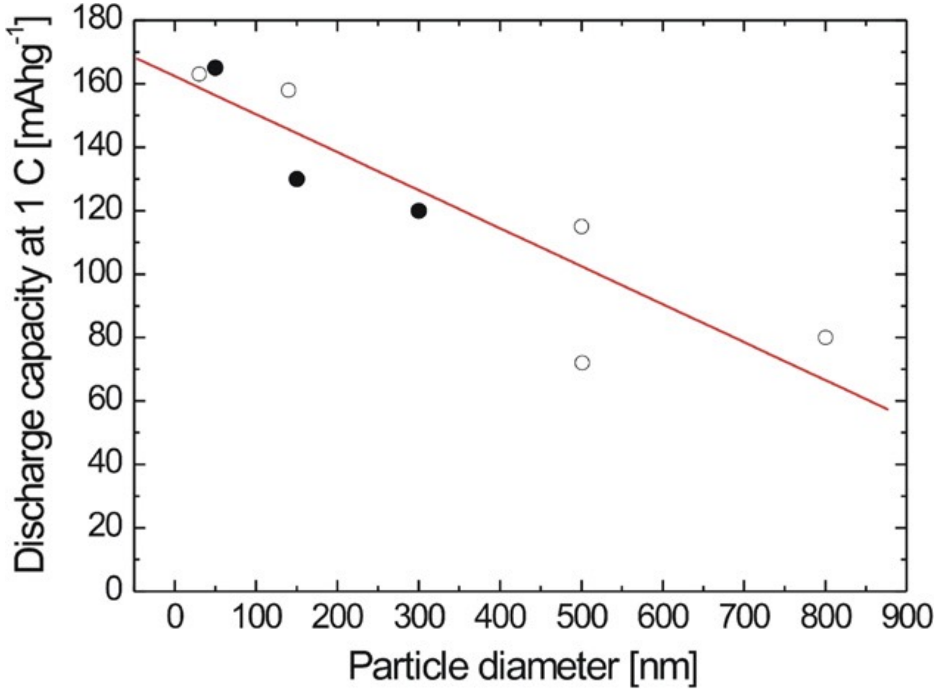
High energy density (weight/volume):
- Range increase
- Lower cost

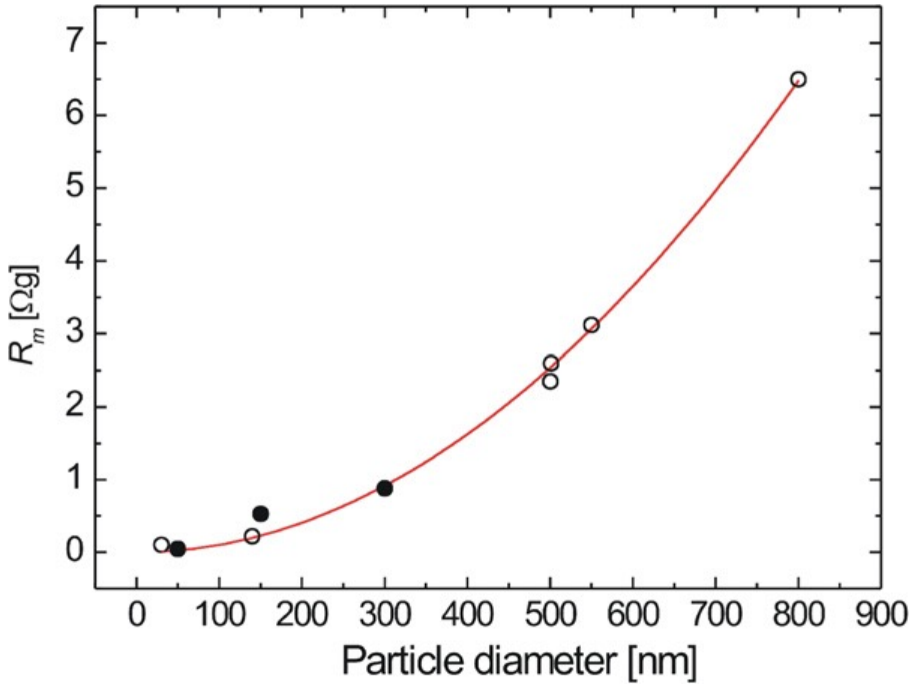
Conventional batteries have low energy densities, so they either have a short lifespan or require frequent charging.
Nanocrystalline-based batteries have more energy and require less charging.

Achieving better battery performance with nanotechnology

- **Kinetics**: Small dimensions provide a short path for charge transport.
- **Large surface area** per unit mass provides more area for direct adsorption of electrolyte ions, creating more active region per unit mass.
- **Thermodynamics**: Changes in the potential of certain materials when synthesized at the nanoscale or become nano-sized during battery cycling.
- **New mechanism for lithium-ion storage**: excess lithium-ion storage at the interface of boundary regions takes place by a “capacitive-like” charge separation.
- **Enhanced mechanical properties**: accommodate large volume changes of the electrode material, due to faster stress relaxation times, retaining battery high capacity and cycle life.

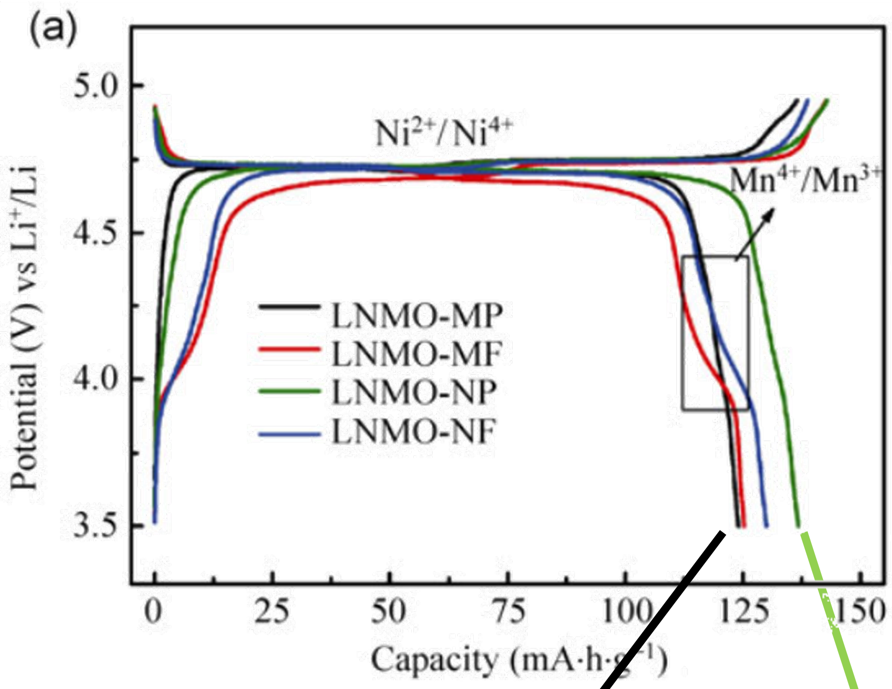
Example: particle size effect on LFP Cathode

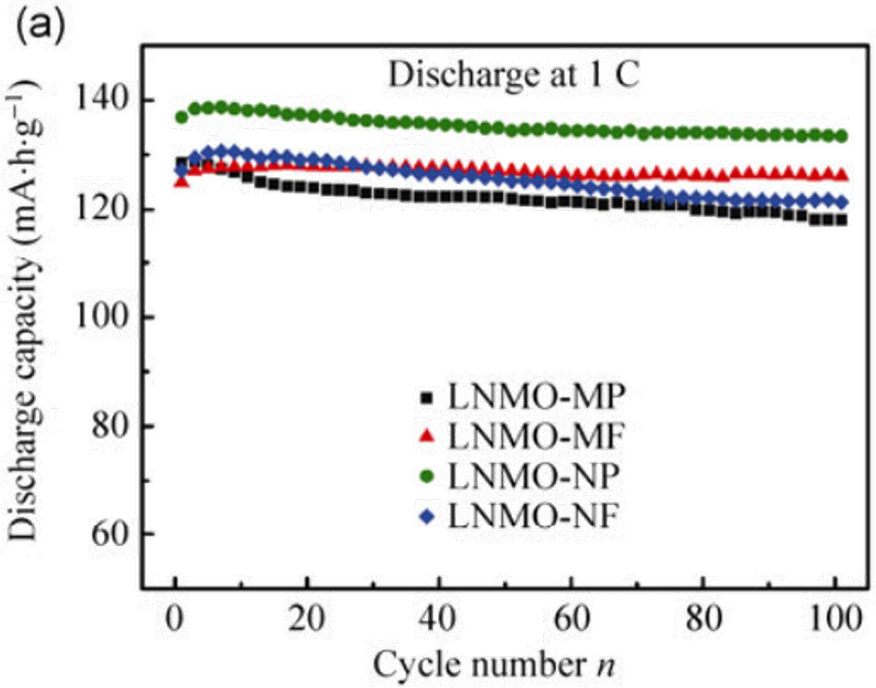


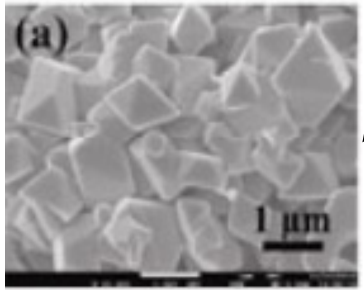


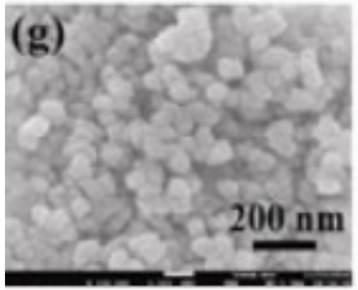
Electrochemistry Communications 2007, 9, 2778

Example: Size effect on LNMO cathode









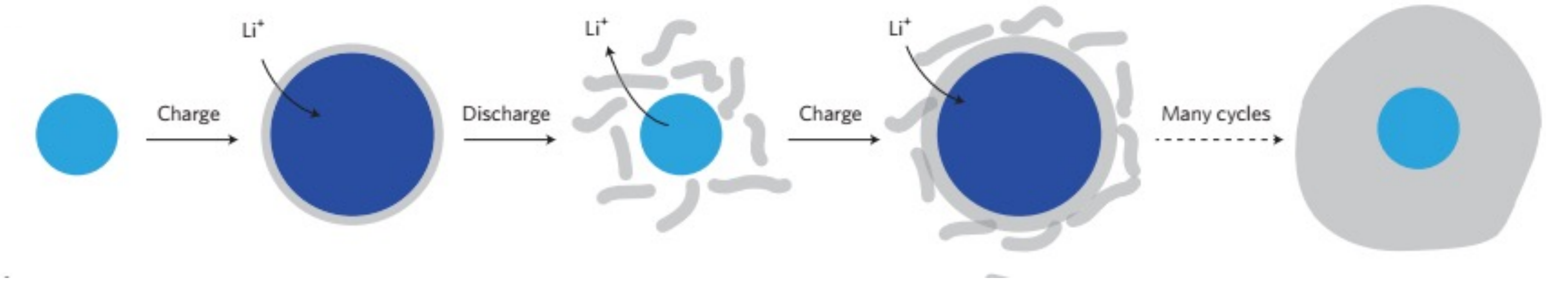
Nanosize LNMO (LNMO-NP) achieve high energy capacity (136 mAh g^{-1}) and better retention (95.7%). Due to short Li^+ diffusion distance and minimal Mn^{3+} dissolution and volume expansion compared to the bulk material.

Example: Nanostructuring of silicon anode

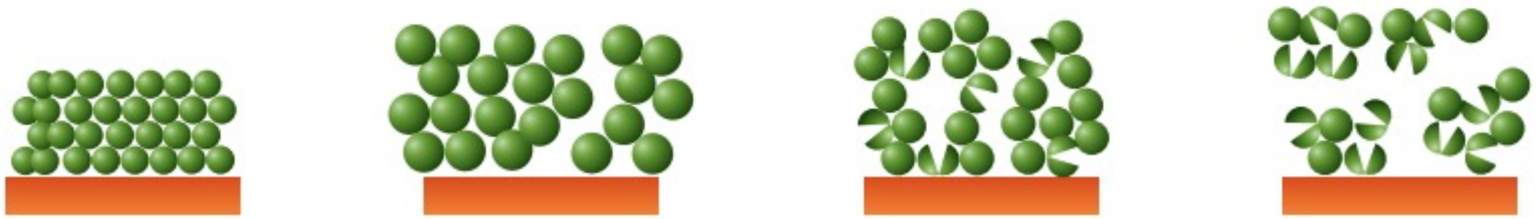
Anode materials	C (graphite)	Li metal	Si
Lithiated phase	LiC_6	Li	$Li_{4.4}Si$
Theoretical specific capacity ($mAh.g^{-1}$)	372	3862	4200
Volume change (%)	12	100	320
Potential vs. Li (V)	0.05	0	0.4
Pros	Stable	High capacity	Highest capacity
Cons	Low capacity	Not safe, dendritic lithium	Large volume change, SEI and particle pulverization

Example: Nanostructuring of silicon anode

SEI pulverization

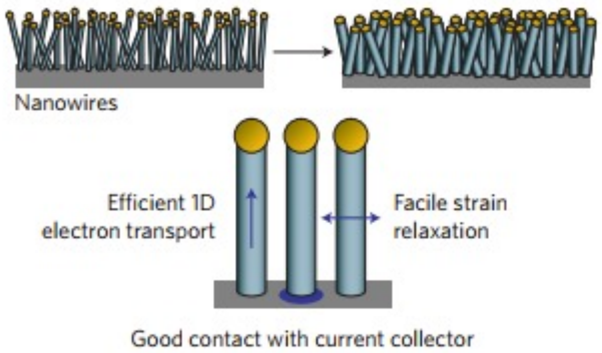


Electrode Failure: Particle cracking

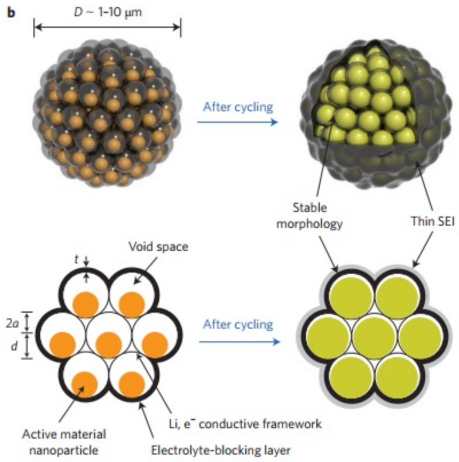


Example: Nanostructuring of silicon anode

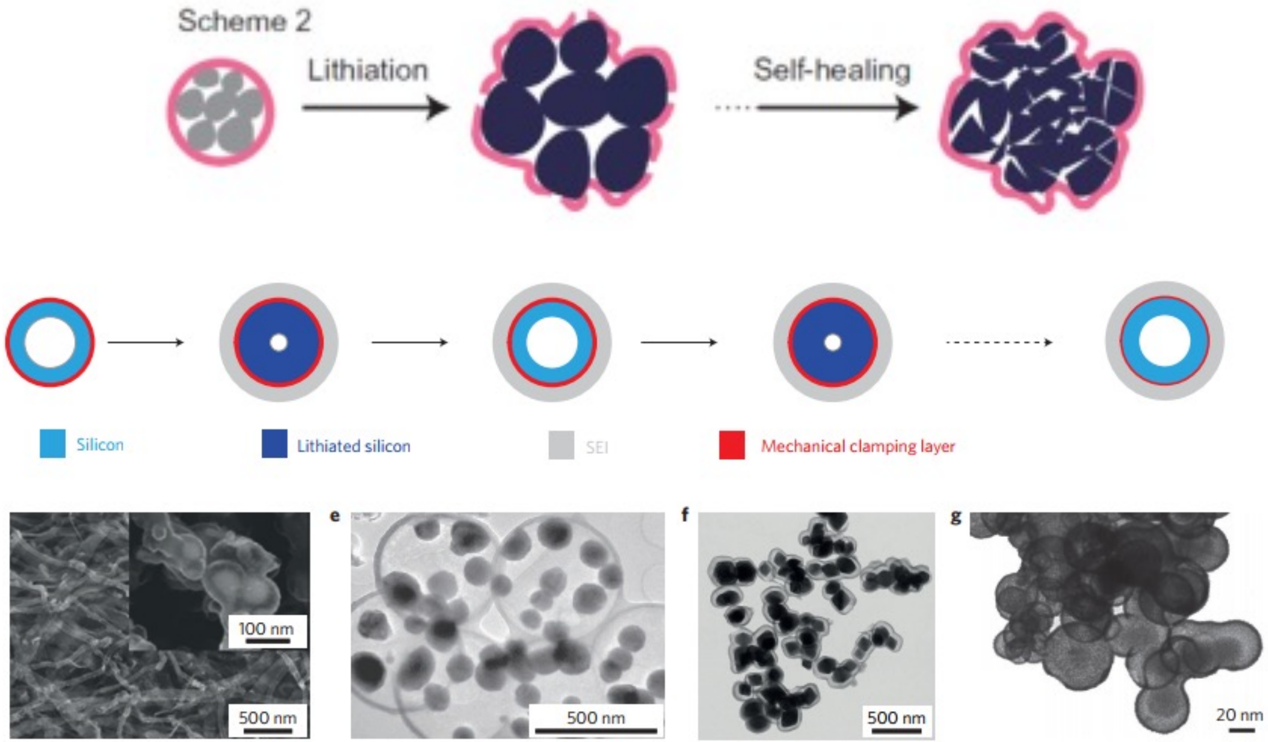
Nanowires



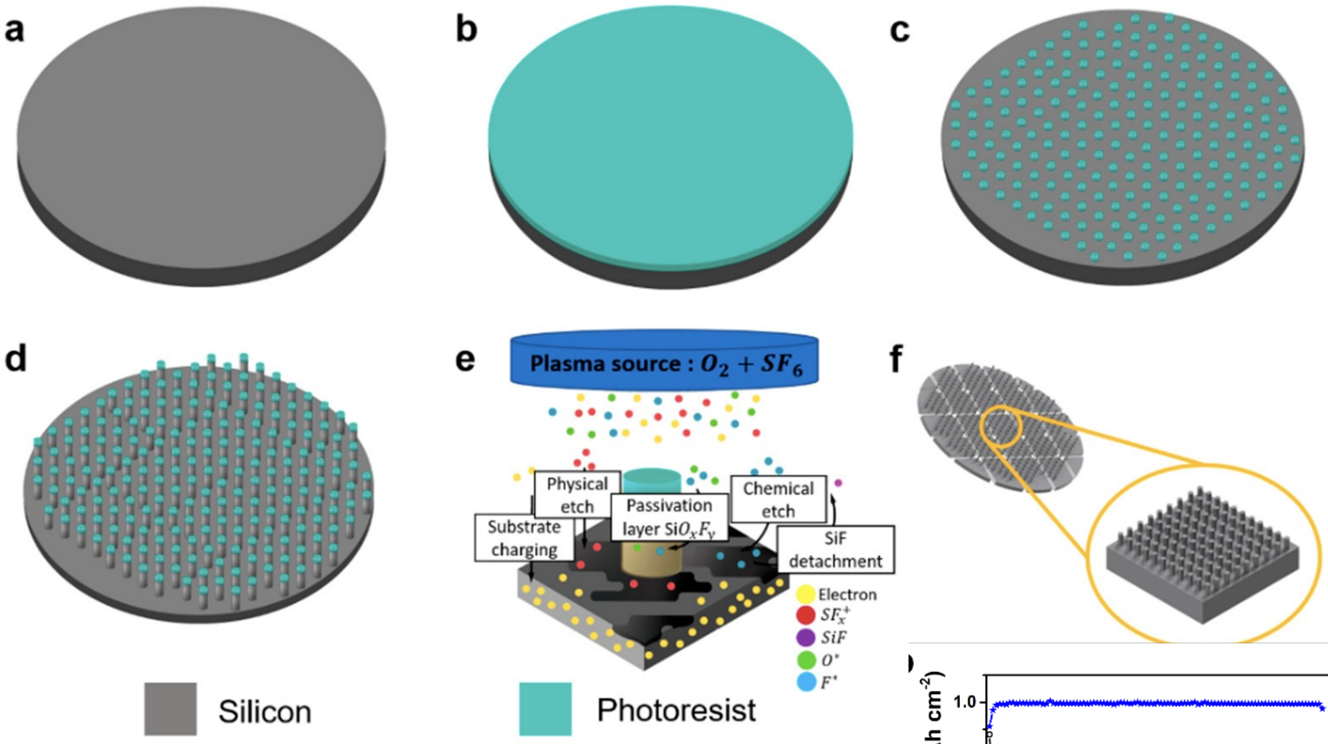
Nanocomposite

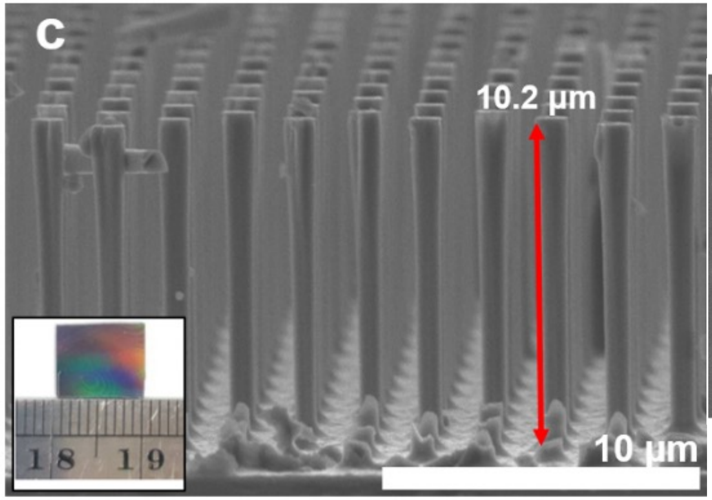


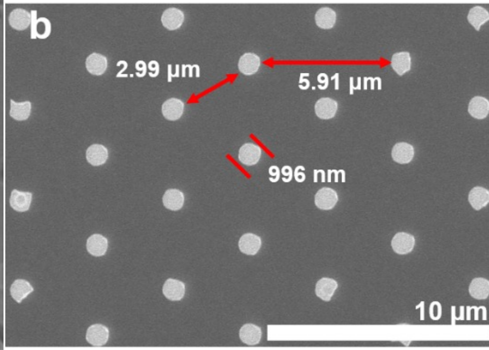
Nanocoating

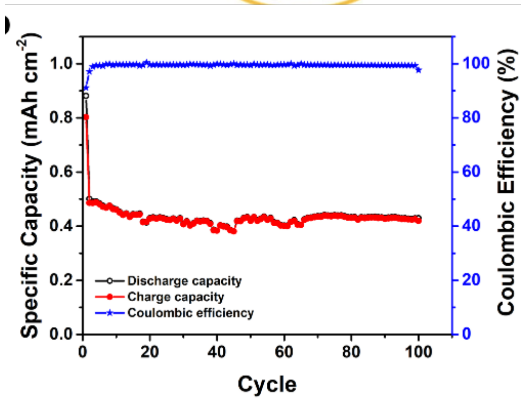


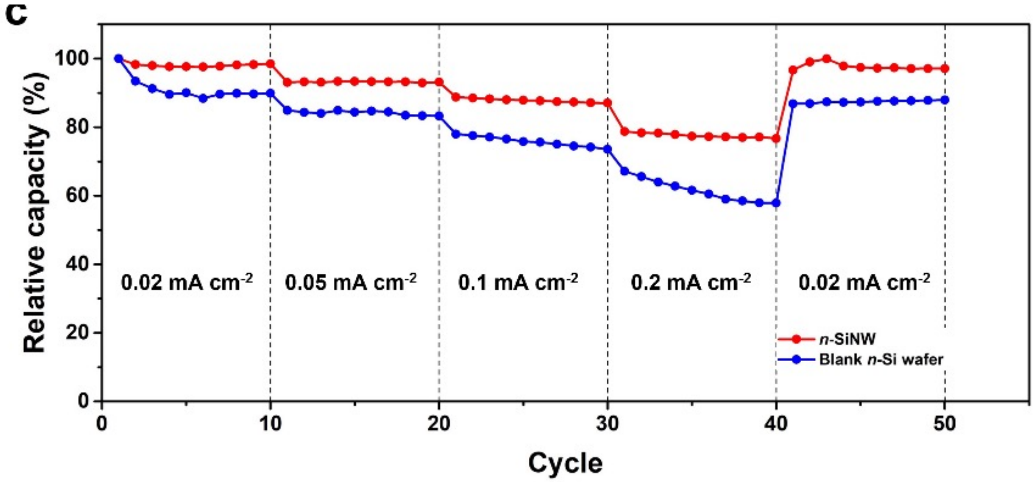
Example: Nanostructuring of silicon anode







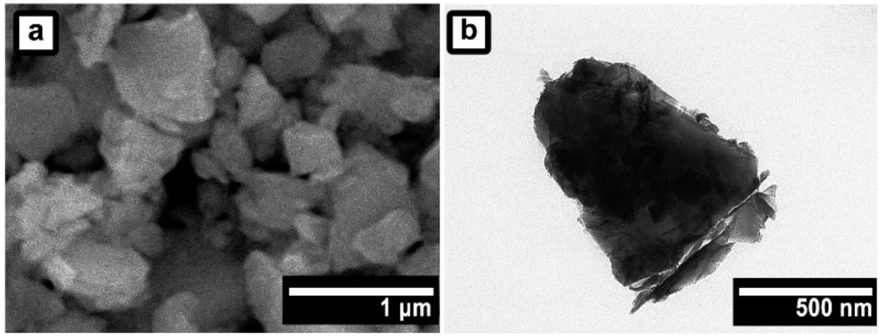




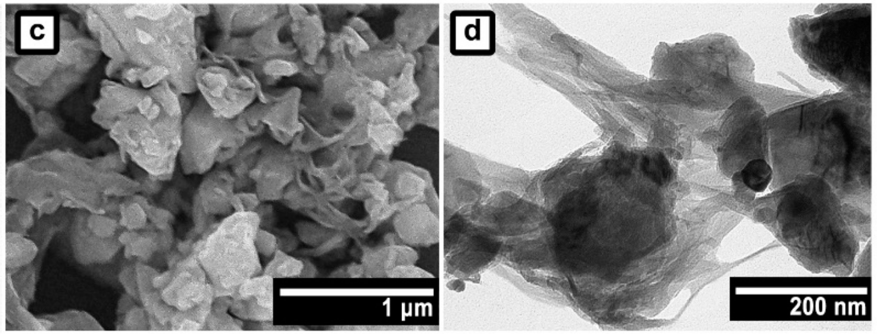
A.P. Nugroho, N.H. Hawari, B. Prakoso, A.D. Refino, N. Yulianto, F. Iskandar, E. Kartini, E. Peiner, H.S. Wasisto, A. Sumboja, *Nanomaterials* 2021, 11, 3137.

Example: Nanostructuring of silicon anode

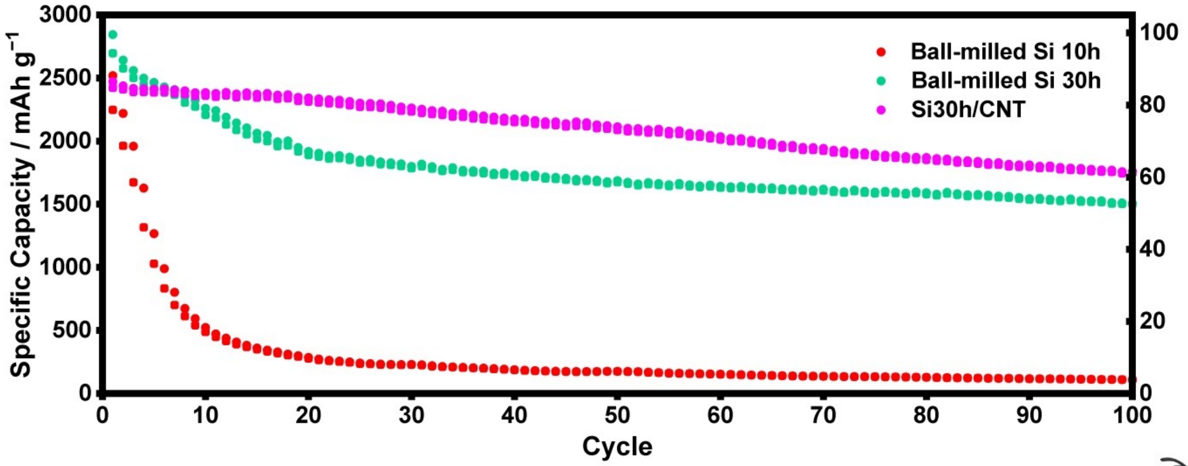
Silicon nanopowder

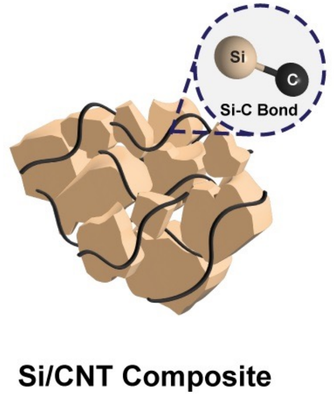


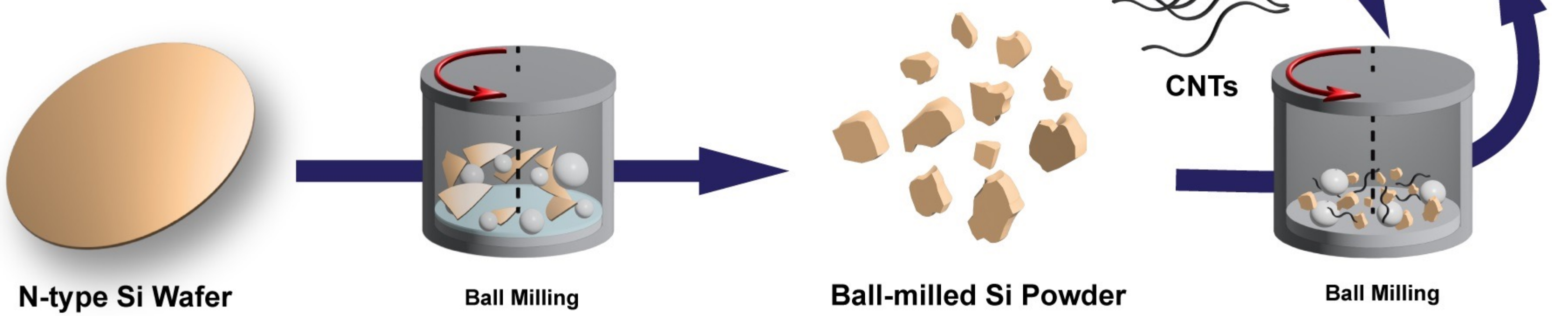
Silicon/Carbon nanotube



Electrochemical performance

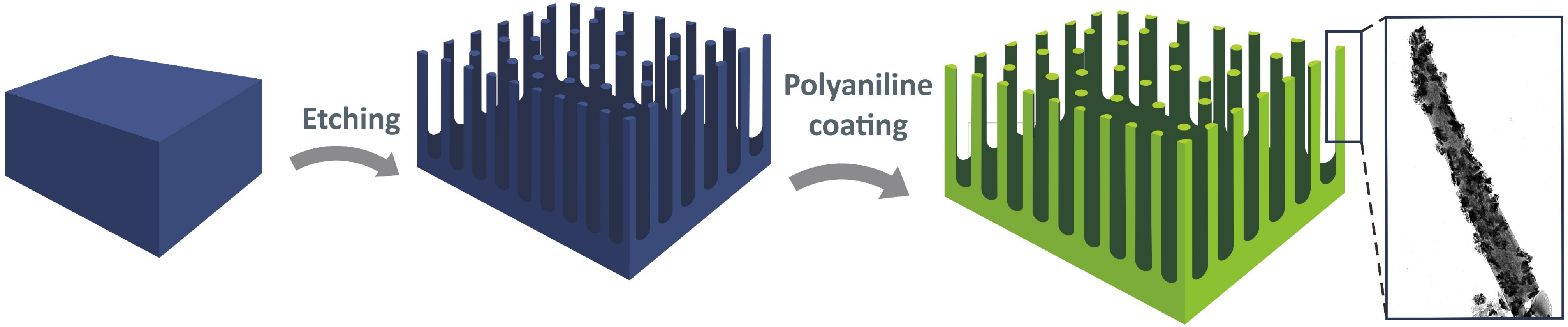


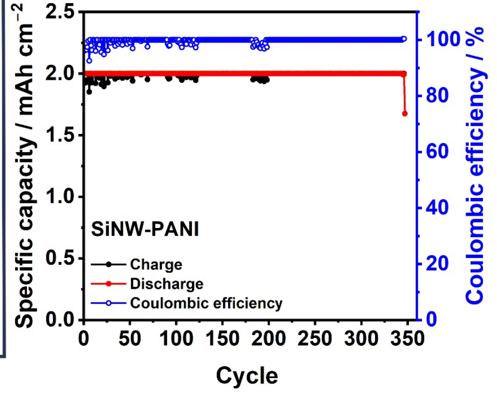




P.Y.E. Koraag, A.M. Firdaus, N.H. Hawari, A.D. Refino, F. Iskandar, E. Peiner, H.S. Wasisto, A. Sumboja, *Batteries* 2022, 8, 165.

Example: Nanostructuring of silicon anode

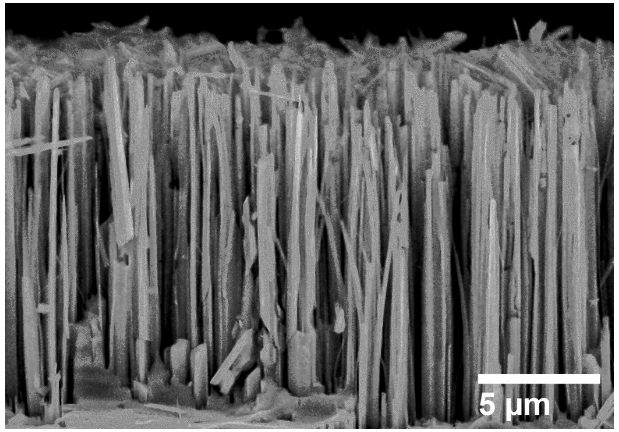


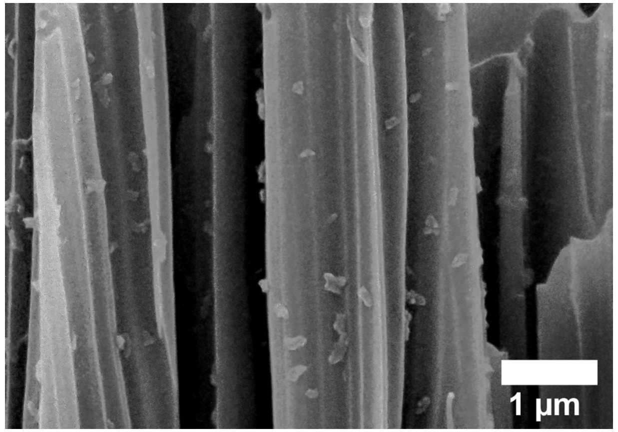


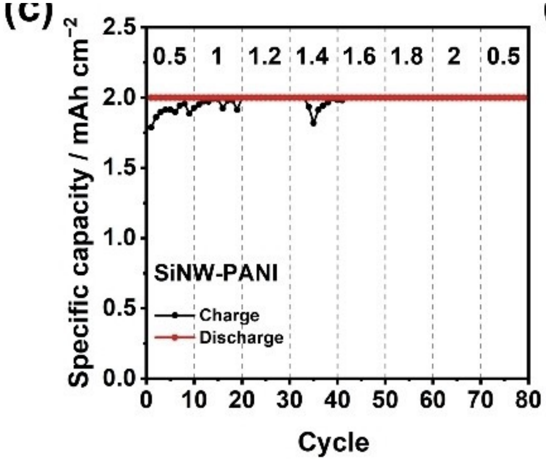
p-type Si wafer

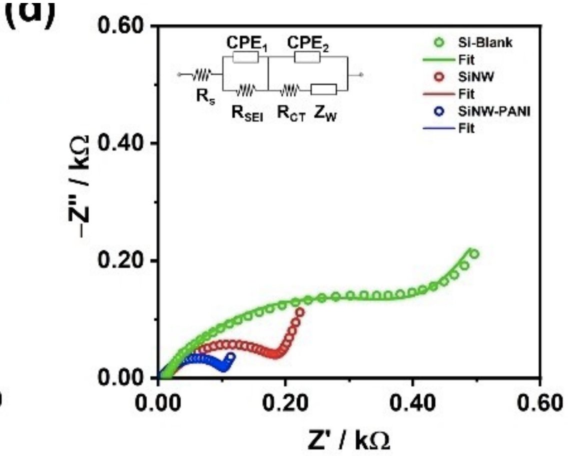
Si nanowire

Si-polyaniline nanowire anode









C. Eldona, N.H. Hawari, F.H. Hamid, W. Dempwolf, F. Iskandar, E. Peiner, H.S. Wasisto, A. Sumboja, *Chemistry–An Asian Journal* 2022.