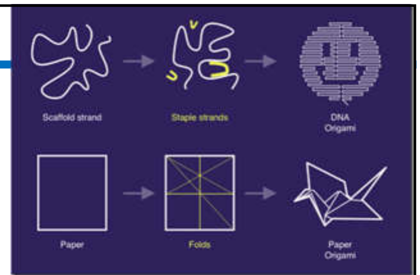
Copying Biology…

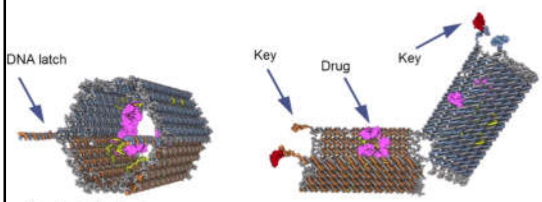


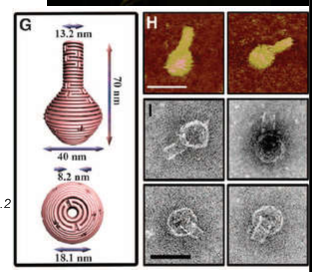
I. example: DNA origami

Nanoscale folding of DNA to create non-arbitrary two- and three-dimensional shapes at the nanoscale. Based on well established knowledge of DNA structures and possibility to set arbitrary base sequences, which then determines interactions and final shape. There are multiple smaller "staple" strands, which bind the longer in various place. First staples are designed by a program, then DNA is mixed, heated and cooled. During cooling, the various staples pull the long strand into the desired shape.

True **bottom-up self-assembly method**, which is considered promising alternatives that offer cheap, parallel synthesis of nanostructures under relatively mild conditions.
Possible to do 3D structures, used e.g for drug delivery.

(Up) Principle of DNA origami, (Right) Realization of 2D and also 3D structures (Bottom) Smart DNA nanobot for drug delivery, which opens and closes. The aim is to attack cancer cells. Size:35nm in width.



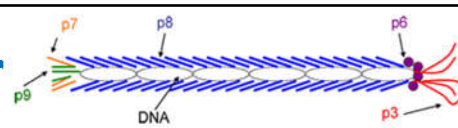


See D. Natelson Section 11.2.2

Source: Wikipedia

https://ninithi.com/2015/08/20/smart-dna-nanobots-mount-a-deadly-attack-on-cancer-cells-first-human-trial-this-year/

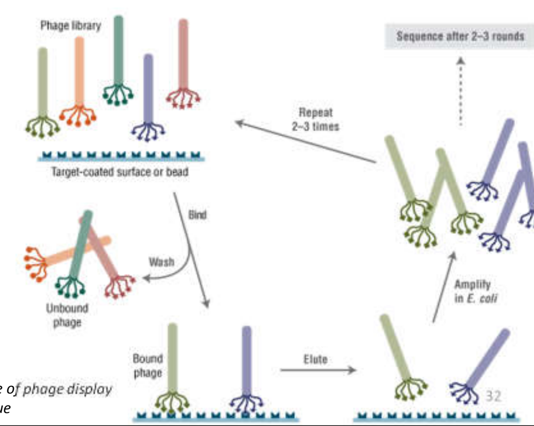
Copying Biology…



II. example: Virus enabled synthesis and assembly

Idea: Biological systems use proteins to manipulate inorganic materials like patterning bones, seashells. Try to program it do for us. **Phage display technique:**
Bachteriphages viruses pray upon bacteria
Special one called M13. Diameter 9nm Length 900nm. It contains a single DNA with 6407 bases, which encodes proteins that constitutes the phage's protein coat. It attracts E. coli bacteria, which reproduces them. Protein p3 is essential for binding to E. coli.
It is know which DNA segment codes the proteins in the coating. Try to modify them to have affinities to desired materials.

Procedure - bio amplification with spirit of evolution:
- Started with M13 with broad varying composites of P3 (or recently also P8) . - Expose test surface with desired material, - Wash away phages do not bind strongly, - Bound phages eluted separately and introduced to *E. coli* for reproduction for amplification,
- Repeat the process and DNA sequence the outcome. → try to understand binding mechanisms or motifs.

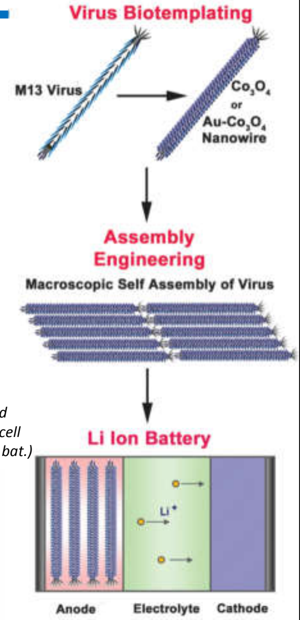


Principle of phage display technique

See D. Natelson Section 11.2.3 also Wikipedia

Copying Biology…

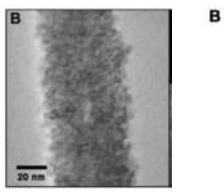
Principle of virus templated production of battery electrodes



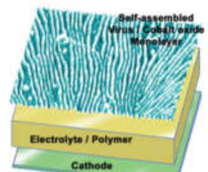
E.g.1: **Develop a library of peptides that bind selectively to semiconductors.** Start with 10^9 combinations of P3 . Genomes of best binders were analyzed to get trends. E.g. groups were found which selectively bind to GaAs(100) and not to Si.

E.g.2: **virus templated synthesis for electrodes of Li ion battery.**
Cobalt oxide has shown excellent electrochemical cycling properties and thus promising as an electrode for advanced lithium batteries. Try to use viruses and bio assembly to produce electrodes.
- Develop P8 with binding affinity for Co_3O_4 and Co_3O_4 -Au nanoparticles. → Cover M13 with Co_3O_4 and Co_3O_4 -Au .
- Two dimensional assembly of viruses on polyelectrolyte multilayers by liquid crystalline ordering → It works as a promising electrode with high surface area.

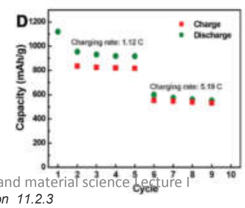
(Left) High resolution TEM image of a Co3O4 viral nanowire



(Down) AFM image of the naowire array on polimer electrolites



(Down) Capacity for the assembled monolayer of Co_3O_4 nanowires/Li cell (theoretical limit is 3800 for Li ion bat.)



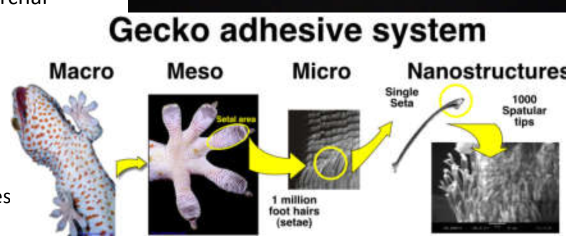
K.T. Nam et al. Science 312, 885 (2006)

See D. Natelson Section 11.2.3

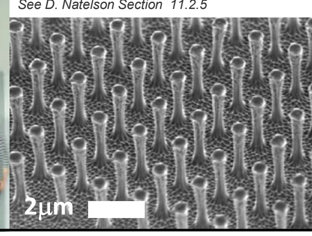
Copying Biology…

Gecko tape – Nanofabrication to mimic bio
Gecko's feet are coated with hearlike structures (Seta scale ~μm) and all ended with nanoscale projections called spatulae.
Results in a remarkable adhesive property due to van der Waals and large contact area of this hierarchal structure. I.e. adhesion ~ $10 Ncm^{-2}$

Try to immitate with nanostructure. E.g. by using polimer nanorods (see image) or CNTs. Very strong reversible adhesion can be achieved.
See products e.g. nanoGripTech.com: Dry adhesives



See D. Natelson Section 11.2.5



(Top) Biological example, the micro and nanostructure of Gecko's feet.
(Left) Millions of synthetic setae from polimer nanorods and resulting adhesion experiment (Bottom) products from nanoGripTech

Chemistry at the nanoscale

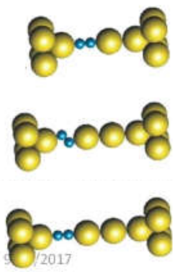
E.g. Nano-catalyst

- Role of Catalysts: - reduce the temperature of a transformation, -reduce reagent-based waste and - enhance the selectivity of a reaction → green chemistry

Catalysts play essential role in production of medicines, fine chemicals, polymers, lubricants …

- Nano size: a) High surface to volume ration b) also different electronic and structural structure an nanoscale→ new chemical properies could show up.

Example1: Chemistry of gold. Au in bulk form know as chemically inert, but it has remarkable catalitic properties at nanoscale due to the the strongly modified electronic structure of gold nanoclusters /nanostructures as their size and/or dimensionality are reduced.

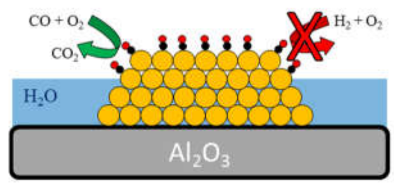


(Left) Interaction of gold and H2 molecule Au atoms with low cooridnation can bind so strongly to H2 that it can even pull a gold atomic chain. (Right) Set up for selective catalytic reaction for $CO+O_2$ → CO_2, which blocks O_2+H_2→ HO_2 using Au nanparticles (yellow) and water.

Example2:

H2 is important industrial product. However CO is also produced in such processes, which is highly undesired for e.g. ammonia production or in fuel cells. → Find a cheap way to remove CO down to 50pmm range. Way out: generate $CO+O_2$ → CO_2 reaction.

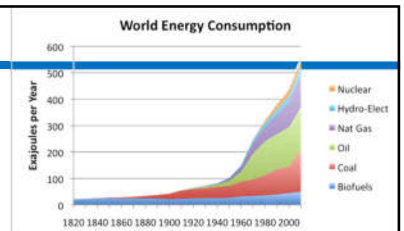
Au nanoparticles can catalyze $CO+O_2$ → CO_2 reaction while O_2+H_2→ HO_2 is efficiently blocked by using proper water pressure and flow velocity of the gas. (HO groups on Au surface helps.)



Read more at:
Johnny Saavedra et al., Nature Chemistry (2016). DOI: 10.1038/nchem.2494
http://phys.org/news/2016-05-tuning-gold-nanoparticle-catalyzed-carbon.html

Csonka et al. PRB 73, 075405 (2006)
www.researchgate.net/publication/284727255_Catalysis_A_brief_review_on_Nano-Catalyst

Potential future impact of Nano



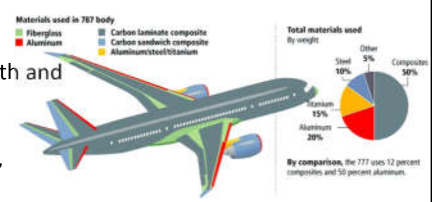
E.g. Energy sector

Sustainability of our need? – Strongly increasing consumption, - Oil, coal, gas are dominating …
How Nano does and will help?

Efficiency Reduce sharply the energy consumption:

- Light, strong, multifunctional materials

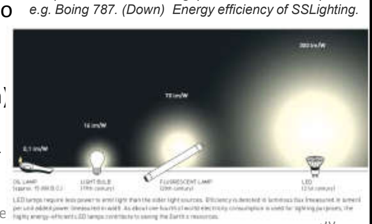
Reducing mass while maintaining necessary structural strength and performance. E.g. carbon fiber composites demonstrate the potential (presently micro)
or multifunctional systems incorporating nanomaterials (e.g., windows that incorporate solar cells).



(Upup) World energy consuption vs. Time. (Up) Carbon composites as dominating parts of modern airplanes e.g. Boing 787. (Down) Energy efficiency of SSLighting.

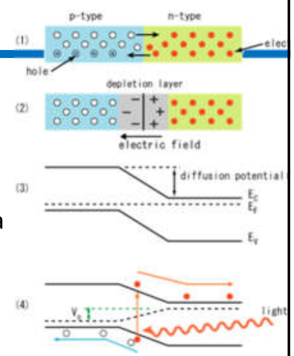
- Reduce loss during electrical transmission Use of nanomaterials to enable *local* generation and storage of electrical energy

- **Solid state lighting** (Lighting is 20% of overall energy consumption) Normal bulb: 15 lumens/W, LED ~300lumens/W. Nanostructuring the LED semiconductor materials as a photonic band gap system → possibility to further improve

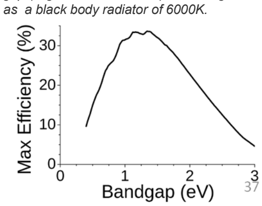


Nattelson Section 12.1.

Potential applications of Nanotechnology



(Up) Operation principle of pn-junction solar cell. (1-2) At the interface of a p and n dopped semiconductor depletion layer forms with electric field (3) in this region. This could separate electron and holes generated by photon absorption. (Down) Theoretical limit of efficiency of solar cells using pn jucntions created from a semiconducor with fixed band gap (E.g. for silicon 1.1eV.) assuming the Sun as a black body radiator of 6000K.



Power generation by solar cells:

Flux of energy from the Sun in the form of light 340W/m2 (direct sunlight). Energy demand of word: 24TW= 24 10^{12}W (continuous). E.g. with 10% conversion efficiency 7x10^{10} m2. This is ~ 75% of area of HU.

Most widely used silicon solar cells. PN junctions where built in E field separates electrons and holes.

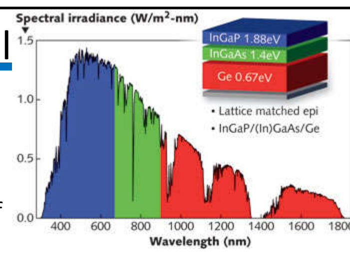
Schockley–Queisser limit on efficiency in *pn* junction cells: max. 34% (Taking into account blackbody radiation, thermalization of extra energy, and the spectrum of sunlight, (band gap 1.34eV), 1 photon → 1 e-h pair)

Goals: go beyond this limit or decrease fab price etc

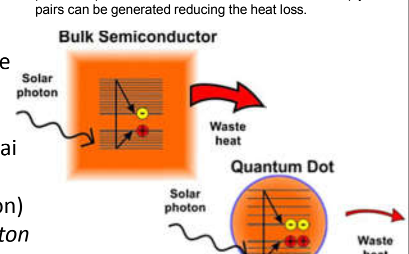
(RIght) World biggest solar plant (2013) Mojave Desert of California, US. It has an installed capacity of 354MW and generates 662GWh of power annually. Area: 6.5 km^2. → 10000 such plants are rquired.

Nattelson Section 12.1. also Wikipedia

Potential applications of Nanotechnol



(Up) The spectrum of the Sun light with colored segments which is absorbed by different layers of a multilayered semicopnductor cell. (Down) Principle of multiexciton generation in nanocrystal quantum dots. In bulk semicondcutors $\hbar\omega$-E_g converts to heat after generating e/h pairs. In quantum dots without k conservation multiply e/h pairs can be generated reducing the heat loss.



C. Smith et. al. Nanomaterials ***2014****, 4(1), 19;*
A. Polman et al. Nat. Mat., 11, 174 (2012).

Power generation by solar cells:

Goals: go beyond SO limit or decrease fab price etc

Various strategies with ingredients from nanotechnology

- **Multijunction cells:** For Si pn-junctions the efficiency limit is 32% →try other III-V semiconductors and even a multilayer of them. First blue, later green then red absorption layers. Get them down to nano thicknesses. Efficiency: 43% (2015). Theoretical limit with infinite number of layers is 86.8% Expected efficiency: 50-70%
- **Hybrid organic/inorganic solar photovoltaics:** Chemically synthesized semiconductor nanocrystals with organic semiconducting polymers. Optical absorption can be tuned by quantum confinement.
  Nanocrystals for ***multiexciton generation and carrier multiplication****:* When $\hbar\omega > E_g$ photon generates a hot e-h pai then with inelastic processes $\hbar\omega$-E_g converts to heat. In nanoparticles (no translation invariance → no k conservation) collisional excitation or Auger scattering take place → *Photon with 3E_g* energy can generate 3 e-h pairs! Using narrow gap Semiconductor 1 photon→ >2 particles. → Go above Schockley-O. limit.

Nattelson Section 12.1. also Wikipedia

Potential applications of Nanotechnology

Power generation by solar cells:

- Dye-sensitized or Grätzel solar cells (DSSC):

Efficiency: 10-12% Hope to get cheap manufacturing.

Steps of photon to current conversion:

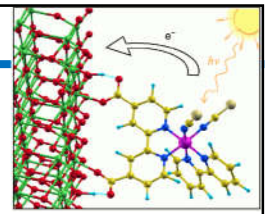
- photon is absorbed by Ru complex photosensitizers on TiO_2 (or ZnO) nanoparticle surface
- photosensitizers are excited and e is injected to TiO2 conduction band
- Electron diffuses to TCO contact via TiO2 nanoparticles
- Oxidized photosensitizer from I^- ion,which is oxidized to , I_3^-
- I_3^- diffuses toward the counter Pt electrode and then it is reduced to I^- ions

Nanoparticles with *large surface area* to contain large amount of dyes.

Pro/contras:

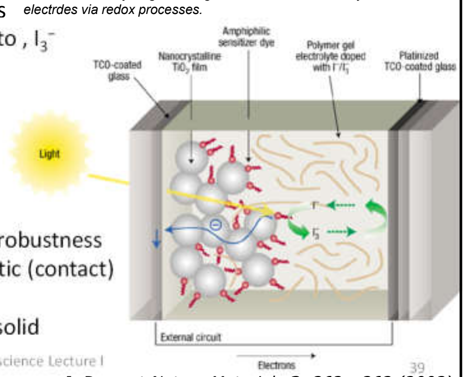
+ Inexpensive compared to the silicon solar cells,
+ no recombination due to e/h separation, + mechanical robustness
- costly Ru (dye), Pt (catalyst) and conducting glass or plastic (contact) are needed → Replace Pt by CoSx (2010), graphene …

Electrolyte has T instablities (freeze , thermal expand) → solid electrolites since 2012



(Up) Molecular dye anchored to TiO nanoparticle. The Ru^{2+}-bipyridine complex can be excited by visible photon to a state where it inject an e to TiO2 nanoparticle http://www.ifm.liu.se/compchem/research/solarcells/

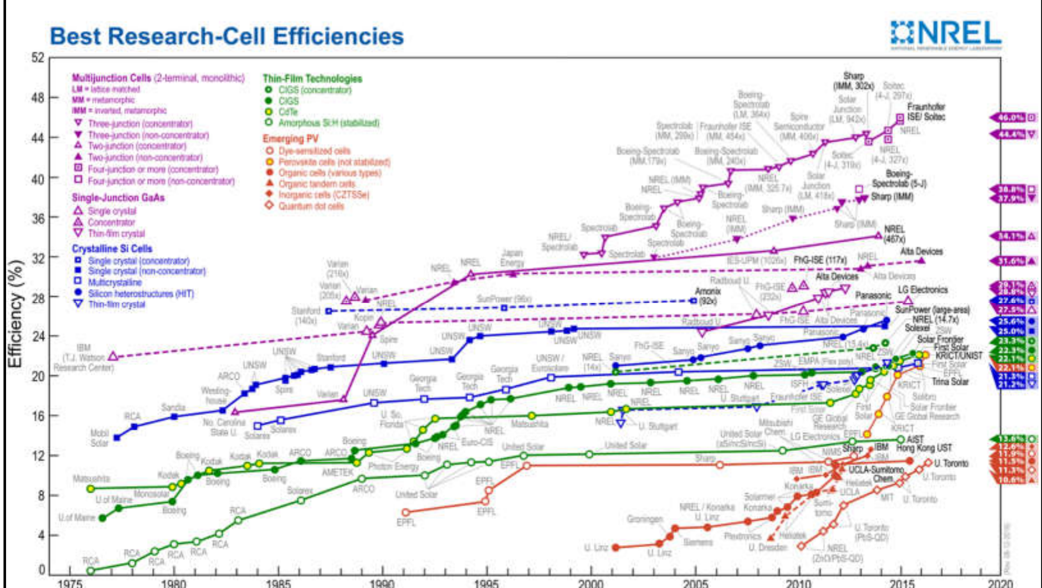
(Down) Structure of the DSSC: transparent conducting electrode TCO with nanocrystalline TiO2 film coated with dye molecules. It interacts with an electrolyte generating e transfer between dye and conter electrdes via redox processes.



Nattelson Section 12.1. also Wikipedia

J. Durrant Nature Materials **2**, *362 - 363 (2003)*

Potential applications of Nanotechnology



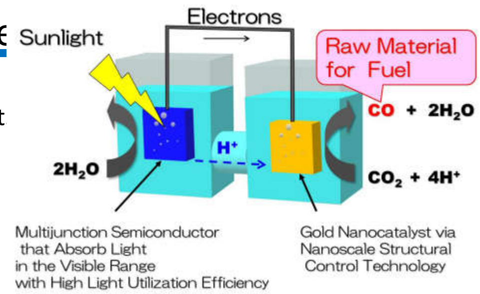
https://en.wikipedia.org/wiki/Multi-junction_solar_cell#/media/File:Best_Research-Cell_Efficiencies.png

Potential applications of Nanote

- Artificial photosynthesis:

Idea: sunlight drives chemical reactions to store it energy in chemical form.
E.g. Convert $2H_2O$ into $2\ H_2 + O_2$
Or covert $CO_2 \rightarrow CO$
CO is a source for production of methanol, which can be used as a substitute for gasoline and for manufacture others (adhesives, medicines and PET …)
Clear advatage volume energy density.
E.g. lithium-ion battery: ~2 MJ/L, gasoline: 36 MJ/L.

Operation principle: Photon absorbed in engineered e.g. nanostructure → e/h pairs. → spetially separated e.g. by band bending → e ends up at the surface where chemical species can be reduced
Role of nanostructures: high specific surface area, special surface sites for engineering



(Up) Highest Efficiency Artificial Photosynthesis Technology by Toshiba (2014) Efficiency: 1.5%
https://www.toshiba.co.jp/rdc/rd/detail_e/e1412_01.html
http://phys.org/news/2015-09-molecular-catalyst-artificial-photosynthesis-carbon.html

Nattelson Section 12.1. also Wikipedia

Potential applications of Nanotechnology

Storing energy

Nanostructured materials important in energy storing systems:
Batteries and supercapacitors

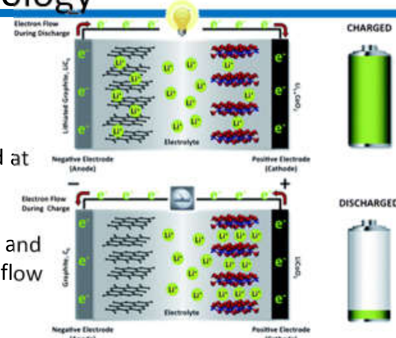
- **Batteries**

Energy is stored electrochemically through reactions performed at the two electrodes mediated by an electrolyte.
E.g. lithium ion batteries
Discharging process: Li^+ ions are deintercalated from the anode and transported to the cathode, where they are reduced. Electrons flow from the anode through the load to the cathode.
Charging process: positive voltage is applied to the cathode → current in the opposite direction
Structure: Li ion permeable separator between anode and cathode, graphitic carbon anode, $LiCoO_2$ cathode.
Important parameters:

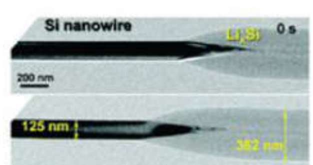
- mass-specific capacity: e.g. graphite electrode 370 mAh/g
- Speed of charging/discharging - Many cycles without degradation

Ideas from nanotechnology:
- Silicon as anode: theoretical capacity 4000mAh/g. $Li_{4.4}Si$ alloy is a stable structure. But large lithium filling → 300% volume change. Bulk Si can not sustain, but nanostructered could!

How Lithium-Ion Batteries Work

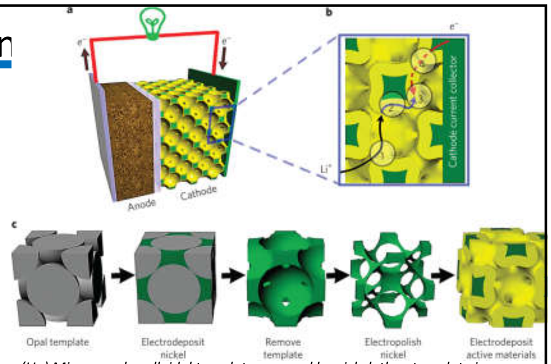


(Up) Structure and operation principle of Li ion batteries. Ion and electron flow are shown fduring discharging and charging process.
(Down) TEM image of Si nanowire as Li is intercallates and increase the volume. Large surface of Si nanowire allows the relaxation of the huge strain



Wikipedia *Nattelson Section 12.1.2*

Potential applications of Nan



(Up) Micron scale colloidal template, covered by nickel, then template is removed. Electrodepsition of active electrode layer results an ultra high surface electrode where charging tkaes place fast.
H. Zang et. al. Nature Nanotechnology 6, 277–281 (2011)

E.g. lithium ion batteries

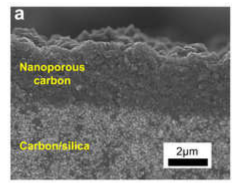
- Max. speed of charging/discarging important. High surface area electrodes → high speed operation would require high speed

E.g. inverse opal structures with open framework can be created by nanotech and coated with active electrode material. → Battery which can charge in seconds!
It out-power supercapacitors while retaining comparable energy density of batteries.

E.g. supercapacitors

Energy stored electrostatically through the arrangement of charge on two non-reacting electrodes and the polarization of a dielectric medium.
Used: cars to store breaking energy, trams, memory back-ups in electronics.
Important:
- Very high surface area of electrodes: ~m^2/g → nanostructured electrode materials
- Be fast: RC is small → good conducting material

Pro/contras
+ Rate is not limited by reaction kinetics + Lifetime is longer.
- Energy density is low: ~50kJ/l



(Down) Carbide derived carbon (CDC) electrodes which consist nm scale pores → Due to pores 75% more energy storage capacity using as electrode in supercapacitor.

Wikipedia *Nattelson Section 12.1.2* *C. Shen et. Al. Scientific Reports* **3**, Article number: 2294 (2013)

Potential applications of Nanotechnology

Environmental protection – with nanoparticles

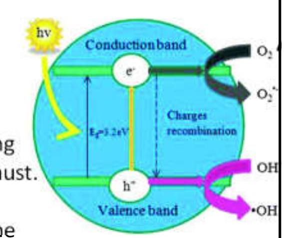
- **Automobile exhaust systems**: metal nanoparticle catalyst are widely used.

E.g. filter system of a Diesel engine

- Diesel oxidation catalysts (DOC): Role is to convert CO to CO_2 and remaining hydrocarbons to CO_2 and H_2O. (90% efficiency). → reduce such pollutants
  AlOx, palladium, platinum nanostructures are widely used
- Diesel particle filters (DPF): high levels of particulate matter (soot) consisting mainly carbon . One strategy to burn the soot. or e.g. nanoparticle platinum is also tried to convert
- **NOx filtering**: First step NOx absorber (e.g. zeolit trap). Second step: Selective catalytic reduction (SCR) Convert NOx to N_2 and H_2O. Adding gaseous reductant (called DEF) e.g. carbamide, ammonia to the exhaust. Diesel cars emit x10 more then gasoline cars → they convert to fine particles, serious health concerns! And also help in creation of ozone (45% from transportation)

- **Photocatalytic decomposition of hydrocarbon pollutants**

E.g. titania (TiO2) particles in water solution. Photons induce redoc process at the particle surface, generate reactive oxigane e.g. ozone, and also OH group. → oxidize organic contaminants. Used in urban air treatment (e.g. kill viruses, bacterias) or wastewater.



(Up) Automobile exhaust systems contain various catalists where metal nanoparticles are used. (Down) Principle of Photocatalitic decomposition with TiO2 nanoparticles Light generates e and h pairs in the particle. They induce reactions at the surface, like generation of reactive oxigen ions or OH groups.

Wikipedia *Nattelson Section 12.1.2*