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Module-6 : Semiconductor Nanomaterials



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CONTENT

- Flexible solar cells (159)
- Flexible Energy Storage Devices (227)
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TEXT BOOK: Yugang Sun, John A Rogers and Willium Andrew- Semiconductor Nanomaterials for Flexible Technologies. From Photovoltaics and Electronics to Sensors and Energy Storage/Harvesting Devices (2010, 1st Edition, Elsevier)

Flexible solar cells (159):

- The development of flexible solar cells is to reduce the weight and cost, to improve shock resistance and to facilitate transportation, storage and installation, compared to conventional systems.
- Although many studies report flexible devices using thin films of organics, amorphous and polycrystalline Si and other inorganic semiconductors.
- Systems made with one-dimensional (1D) nano/microstructures of inorganic semiconductors with high crystallinity (even monocrystallinity) provide significant enhancement in energy conversion efficiency.

Basic Operating Principles of Solar Cells

- The most important component of a solar cell (or photovoltaic device) is a semiconductor that can strongly absorb photons to excite electrons in the valence band to the conduction band, thereby leaving holes (i.e. positive charges) behind.
- The separated electrons and holes must diffuse in different directions to avoid electron–hole recombination.
- The charge separation is usually driven by a potential difference induced by band bending at an interface in the semiconductor.
- Depending on the characteristics of interface, photovoltaic devices are classified into two major categories:
 1. p–n junction cells and
 2. photoelectrochemical (PEC) cells.

p–n junction cells

- Since the birth of the first practical solar cell, which was **based on a p–n junction formed in Si**, extensive efforts have been devoted to exploring p–n junctions with new materials and integrating multiple **p–n junctions to increase the photon-to-electricity conversion efficiency of the resulting cells**.
- Figure 6.1 presents the configuration of a p–n junction solar cell and the mechanism for **charge separation and migration under illumination**.
- **Atypical cell consists** of a layer of **p-type semiconductor material (i.e. p-type base)** intimately **overlaid with a layer of n-type semiconductor (i.e. n-type emitter)**, leading to the formation of a p–n junction (Figure 6.1a).
- **Formation of the junction causes band bending of both n- and p-semiconductor at the interface**, i.e. **the conduction and valence bands bend downward in the p-type side and upward in the n-type side**, **owing to matching of Fermi levels (E_f) of both sides** (Figure 6.1b).

- A back contact and front finger contact serve as both charge collectors and electrical connection to external load.
- The use of arrayed finger contacts in the front (i.e. the side of n-type emitter) of the cell minimizes the absorption of sunlight by the contacts.
- When a photon reaches the surface of the n-type emitter, there are several possibilities:
 - (1) the photon passes through both n- and p-type semiconductor layers, usually when its energy is lower than the bandgap (E_g) of the material;
 - (2) the photon is absorbed by the semiconductor, when its energy is higher than the bandgap of the semiconductor; and
 - (3) the photon reflects from the semiconductor surface.
- An antireflection coating layer can minimize the probability of this third outcome.

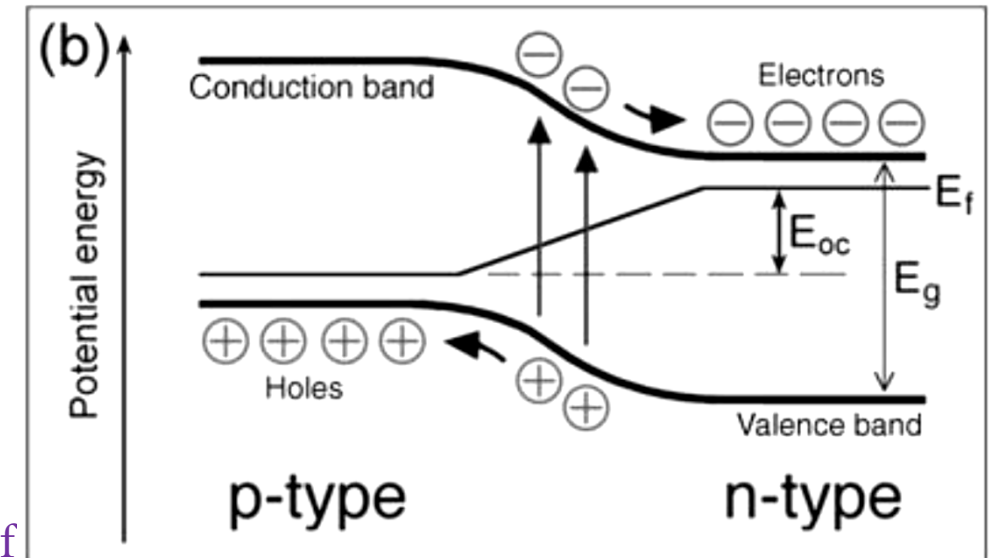
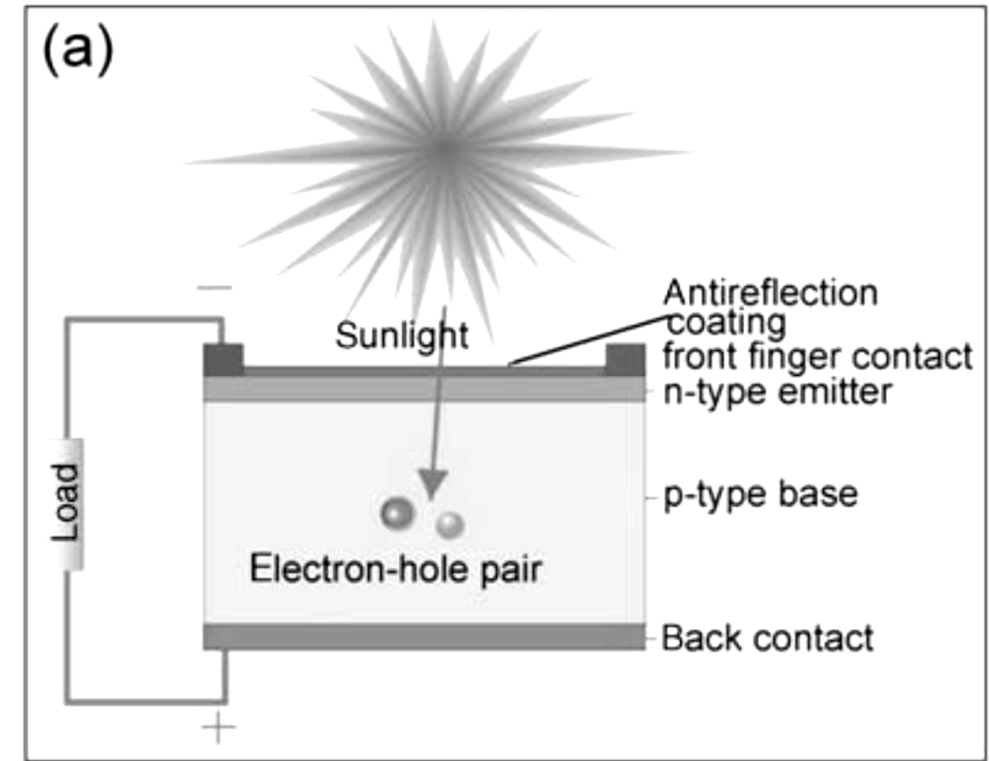
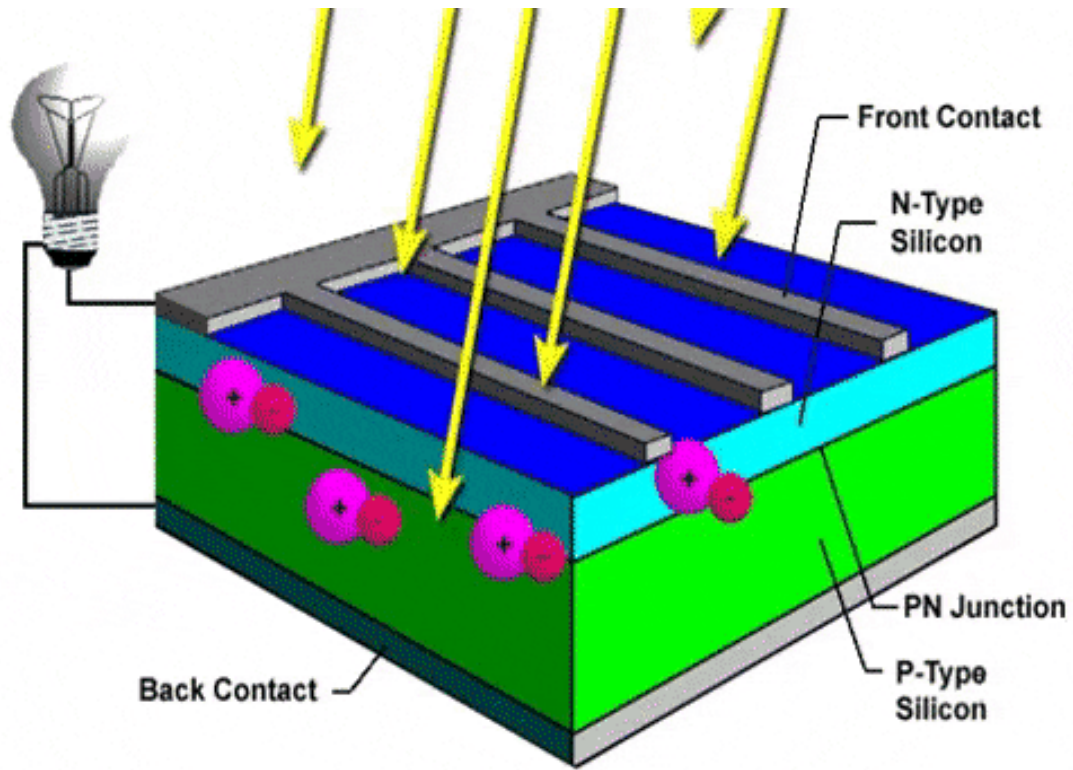


Figure: (a) Schematic illustration of the operating principles of a p-n junction solar cell for converting photon energy to electricity. (b) Energy levels and charge flow at the p-n junction.

- Photogenerated electrons concentrated in the conduction band and the corresponding holes in the valence band tend to move across the interface of the p–n junction of a solar cell, owing to the action of the electrical field associated with band bending.
- The diffusion of electrons and holes to different directions, i.e. to the n-type and p-type side, respectively, leads shifts of the Fermi levels of both n- and p-type regions (i.e. upward for n-type and downward for p-type).
- These shifts result in a built-in potential, which equals the open circuit voltage (V_{oc}) if the cell is ideally equivalent to a current source in parallel with a diode (Figure 6.1b).
- This potential drives all the mobile charge carriers out of the region adjacent to the junction, which is called the depletion region (or space charge region), under constant light illumination.
- When ohmic metal–semiconductor contacts are made to both the n-type and p-type sides of the cells and electrodes connect to an external load, electrons created on the n-type side and those that migrate from the p-type side power the load (Figure 6.1a).

- The electrons continue to move in the wire until they reach the p-type semiconductor, where they recombine with holes created on the p-type side and those that migrate from the n-type side.
- The performance of a photovoltaic cell is usually characterized by the energy conversion efficiency (η), which corresponds to the percentage of optical energy that is converted to electrical energy when the cell is connected to an electrical circuit.

$$\eta = \frac{P_m}{E \times A_c}$$

This parameter is determined by the ratio of the maximum power point (P_m , in W) divided by the product of the input light irradiance (E , in W/m^2) under standard test conditions (STC) and the surface area of the cell (A_c in m^2):

For solar cells, STC specifies a temperature of 25C and an irradiance of 1000 W/m² with an air mass 1.5 (AM 1.5) spectrum, which corresponds to the irradiance and spectrum of sunlight incident on a clear day on a surface at 37 degrees with respect to the sunlight and the sun at an angle of 41.81 degrees above the horizon.

P_m is determined by the product of current (I) and voltage (V) at the maximum power point. The overall behavior of a solar cell is also often characterized with a fill factor (FF) that corresponds to the ratio of P_m divided by V_{oc} and the short circuit current (I_{sc}):

$$FF = \frac{P_m}{V_{oc} \times I_{sc}} = \frac{\eta \times A_c \times E}{V_{oc} \times I_{sc}}$$

- **Conventional** p–n junction solar cells are usually manufactured with thick, rigid supports consisting of semiconductor wafers surrounded by glass and metal packaging materials.
- For example, monocrystalline Si solar cells and polycrystalline Si solar cells consist of **thick p-type base Si wafers and glass substrates to support the p–n junctions**, respectively.
- The **rigidity associated with these designs restricts application possibilities, and increases the cost and difficulty of transport and installation.**
- **Exploiting thin plastic sheets as supports can change this scenario**, thereby enabling the possibility of **mechanically flexible solar cells**. In such a scenario, the p–n junctions (i.e. the critical components of the solar cells), of course, must also be flexible. As discussed in Chapter 10, elementary bending mechanics dictates that even **monocrystalline inorganic semiconductors become flexible when their thicknesses are sufficiently small**, e.g. on the scale from tens of nanometers to tens of micrometers.
- In this chapter, flexible solar cells made of transfer-printed microribbons on plastic substrates are discussed, and several examples of modules produced in this manner are presented (see Flexible p–n junction solar cells, below).

- Defined: A material or device that converts photons of light energy to electrical voltage and current.
- A photon with short enough wavelength can cause an electron in a PV material (semiconductor, such as Si) to break free of the atom that holds it.
- If a nearby electric field is provided, electrons can be swept toward a metallic contact, where they can become part of an electric current.

- When electron freed, other electrons in lattice may fill the hole, thus moving the location of net positive charge.
- Band-gap energy E_{bg} (J) = $hn = hc/\lambda_{bg}$
- $h=6.626 \times 10^{-34}$ J-s; c =speed of light 3×10^8 m/s; n =frequency, Hz; λ_{bg} =band-gap wavelength, m
- $\rightarrow \lambda_{bg}=hc/E_{bg}=1.11$ mm when $E_{bg}=1.12$ eV
- As such, silicon solar cells produce electricity only for solar wavelengths less than 1.11 mm.

Only wavelengths less than 1.11 μm result in electricity production from pure Si cells

Other band gaps (eV) **and** band-gap wavelengths (μm):

Si	1.12	1.11	
a-Si	1.7	0.73	Amorphous silicon
CdTe	1.49	0.83	Cadmium telluride
CuInSe ₂	1.04	1.19	Copper indium selenide
CuGaSe ₂	1.67	0.74	Copper Gallium selenide
GaAs	1.43	0.87	Gallium Arsenide

Shorter band-gap wavelength $\rightarrow$ higher band-gap energy

Of total solar spectrum, PV converts energy below max wavelength, and for each wavelength only up to max band-gap energy (E_{bg}). Thus, for Si,

- 30.2% of solar spectrum unavailable below $\lambda_{bg}=1.11 \text{ } \mu\text{m}$ because $h\nu < E_{bg}$
 - 20.2% unavailable above $\lambda_{bg}= 1.11 \text{ } \mu\text{m}$
 - $\rightarrow 49.6\%$ available
 - Another 7% loss due high temperatures (Stefan Boltzmann losses $\propto T^4$)
 - Another 10% loss due to recombination of electrons
- $\rightarrow 33.7\%$ max efficiency for single-junction PV cell=Shockley-Queisser limit

Types of PV Cells

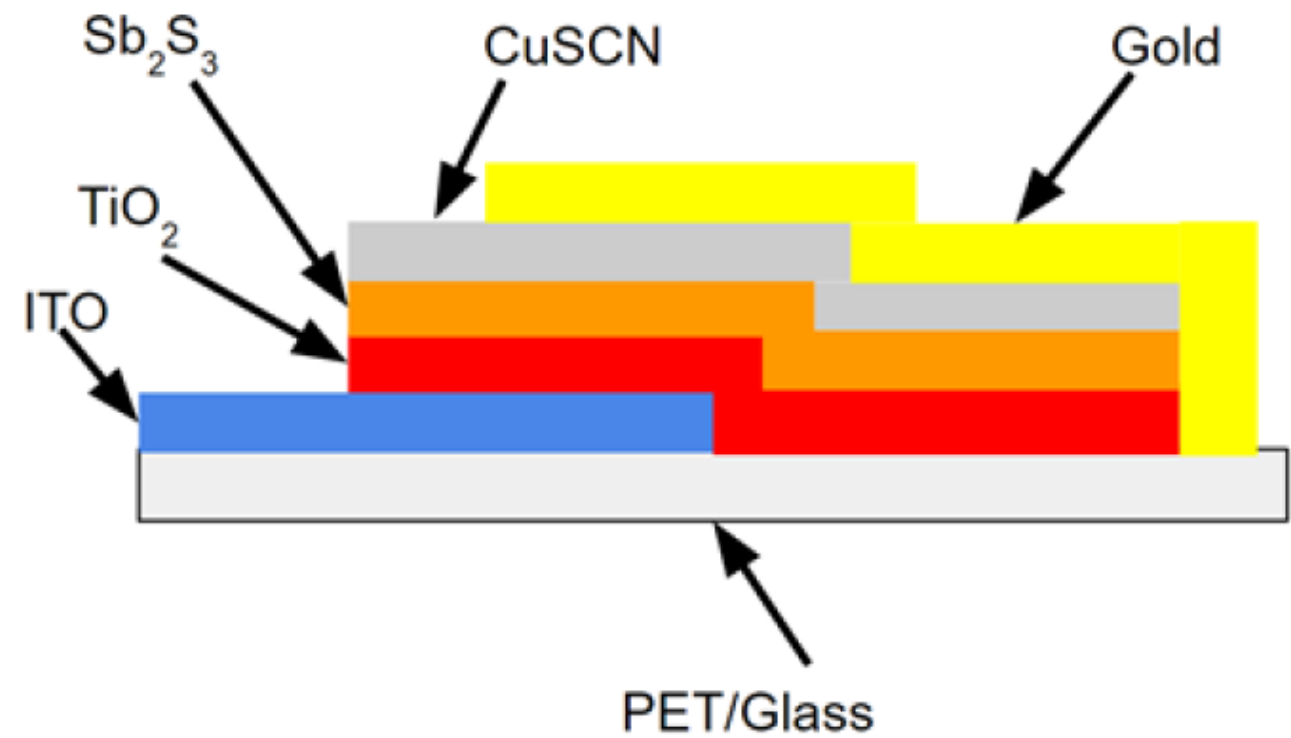
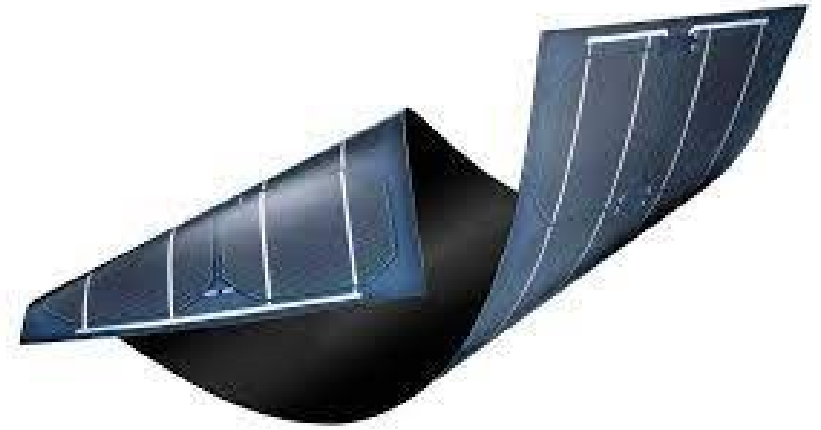
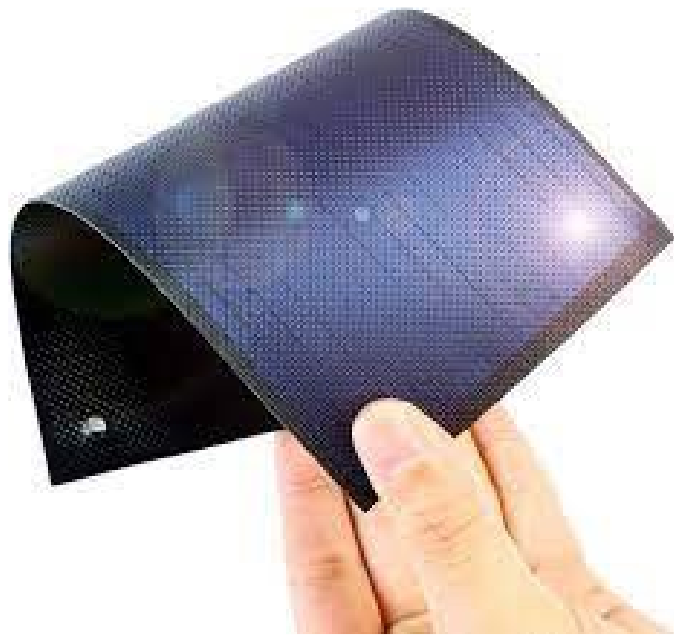
- Si 2nd most abundant element = 20% of Earth's crust.
- Si from high quality Silica or quartz (SiO_2) from mines or sand.
- Single crystal Si (sc-Si) – uniform structure
- Polycrystalline Si (poly-Si) rock like chunks of a multifaceted metal – less expensive and less efficient than sc-Si
- Amorphous Si (a-Si) made by vapor deposition of silane & hydrogen gas – used in thin-film PV cells.

Types of PV Cells

- First generation: 200 mm thick
 - (sc-Si or poly-Si)
- Second generation: thin film (1-10 mm thick)
 - (GaAs, CdTe, CIGS, or a-Si)
- Third generation: Multijunction tandem cells
 - Single thin film with multiple materials or stack of different thin films
 - One film: 33.7% max efficiency; two: 47%; three: 53%

PV Modules and Arrays

- One PV cell = ~ 0.5 V
- Module = 72, 96, or 128 pre-wired cells in a series in a package
- Array = modules wired in series to increase v or in parallel to increase i .
- For array, must optimize modules in series or parallel for $\max.(p) = vi$



Construction

- In this structure, the study will center around the effects that cell layers have on flexibility and efficiency, by modifying the ZnO layer and changing what is used as the n-type semiconductor: namely; Antimony Sulfide, or Sb₂S₃.
- The ZnO layer will be constructed of nanowires, and we will investigate the effect of changing the wire concentration, shape, length, and thickness. Both the inorganic n-type semiconductor, Sb₂S₃, as well as the p-type semiconductor, CuCSN, will be altered by tuning the morphology, ratio of the p and n-type layers, and thickness.
- Fatigue and bending tests will be applied to each cell, to observe the effect of modifications to the structures flexibility.
- Traditional efficiency tests will also be applied before and after bending, but not during due to difficulties calculating area and applying bending during testing.
- Lastly given appropriate time and sufficient testing of the individual cells, mechanical design ideas will be applied to the structure of the solar panel to investigate covering larger areas while still maintaining flexibility and good efficiency.

PROS



CONS

Easy to install – can be easily mounted using magnets or adhesives and are often completed as DIY projects

More prone to damage because of their organic solar cells

Portable and lightweight – can be used on roofs that aren't structurally ideal for a regular system

Have a much shorter lifespan

Flexible for uneven surfaces or curved surfaces – they can work for many different solar projects

Lower efficiency – you'll need many more panels (and more space) to produce the same amount of electricity as traditional solar panels

Less expensive – they typically take less time and labor to install

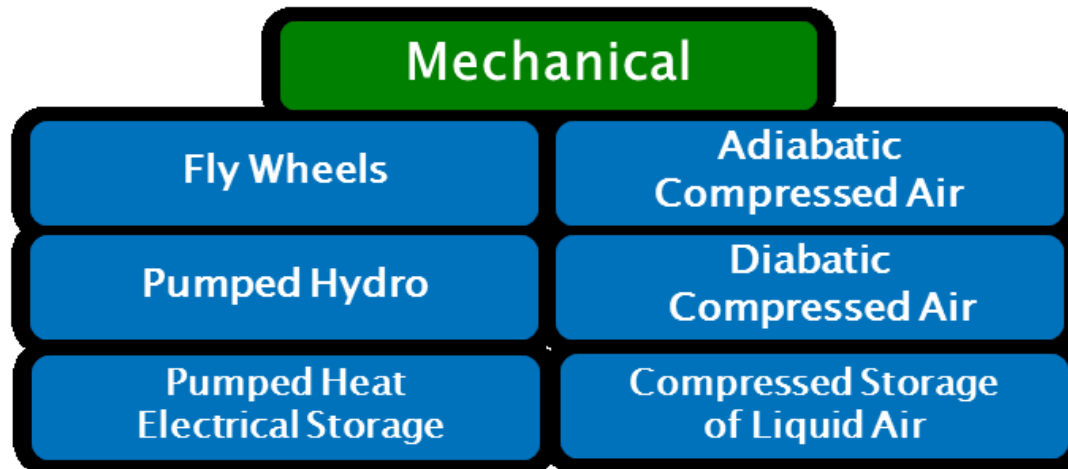
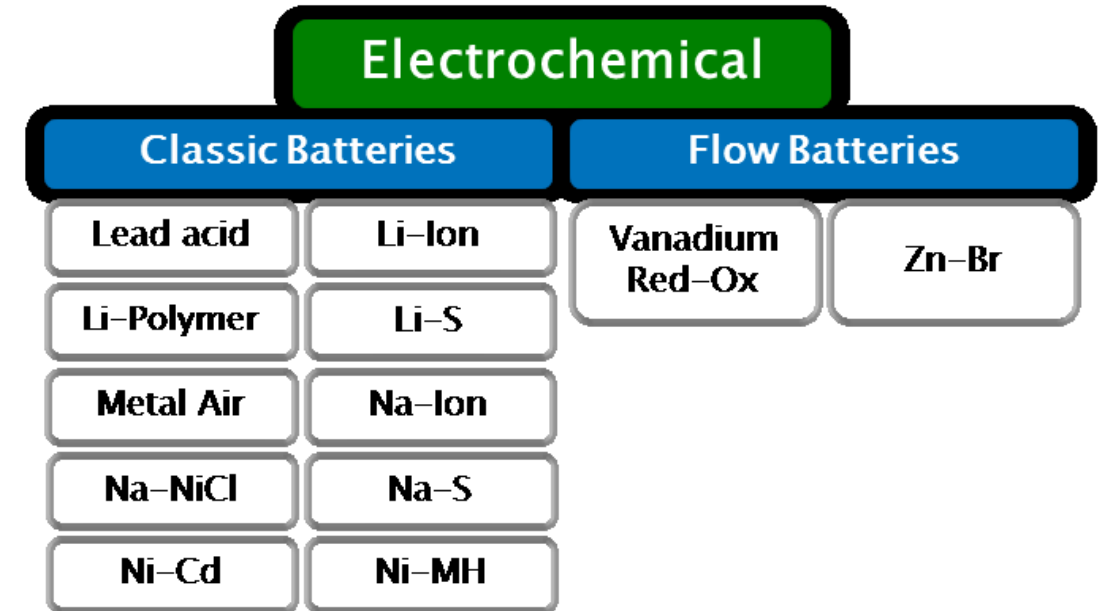
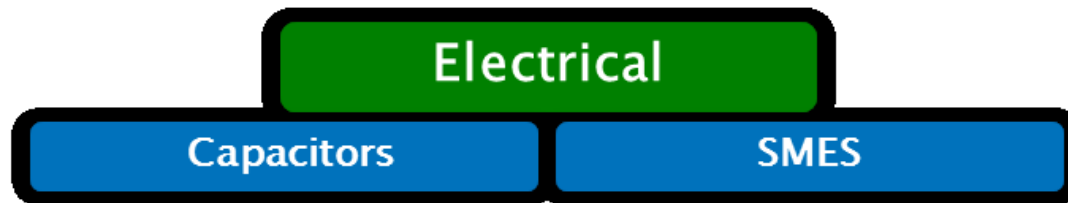
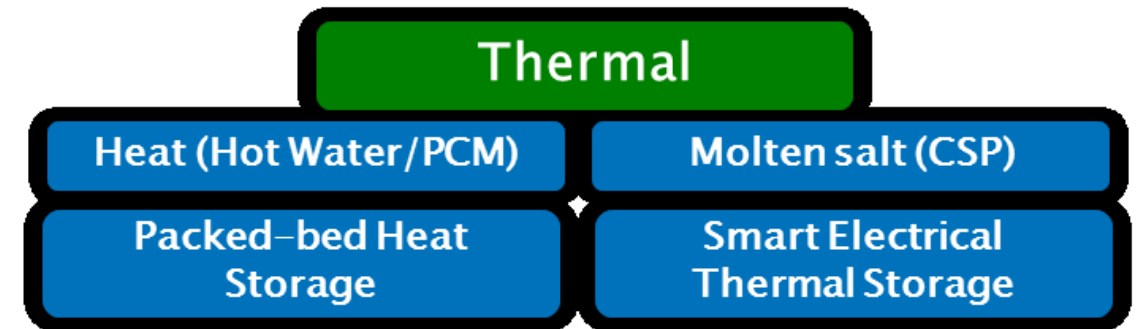
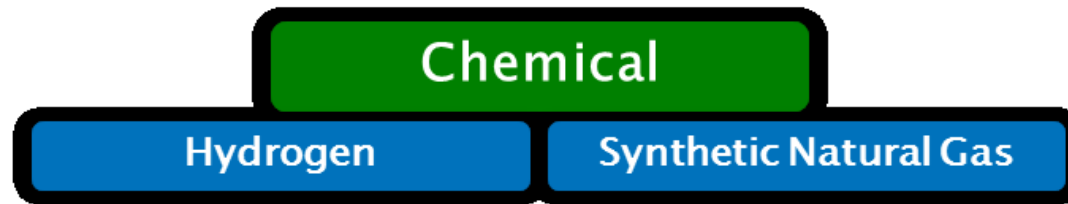
Have a shorter or no warranty, meaning your investment isn't as protected

Applications

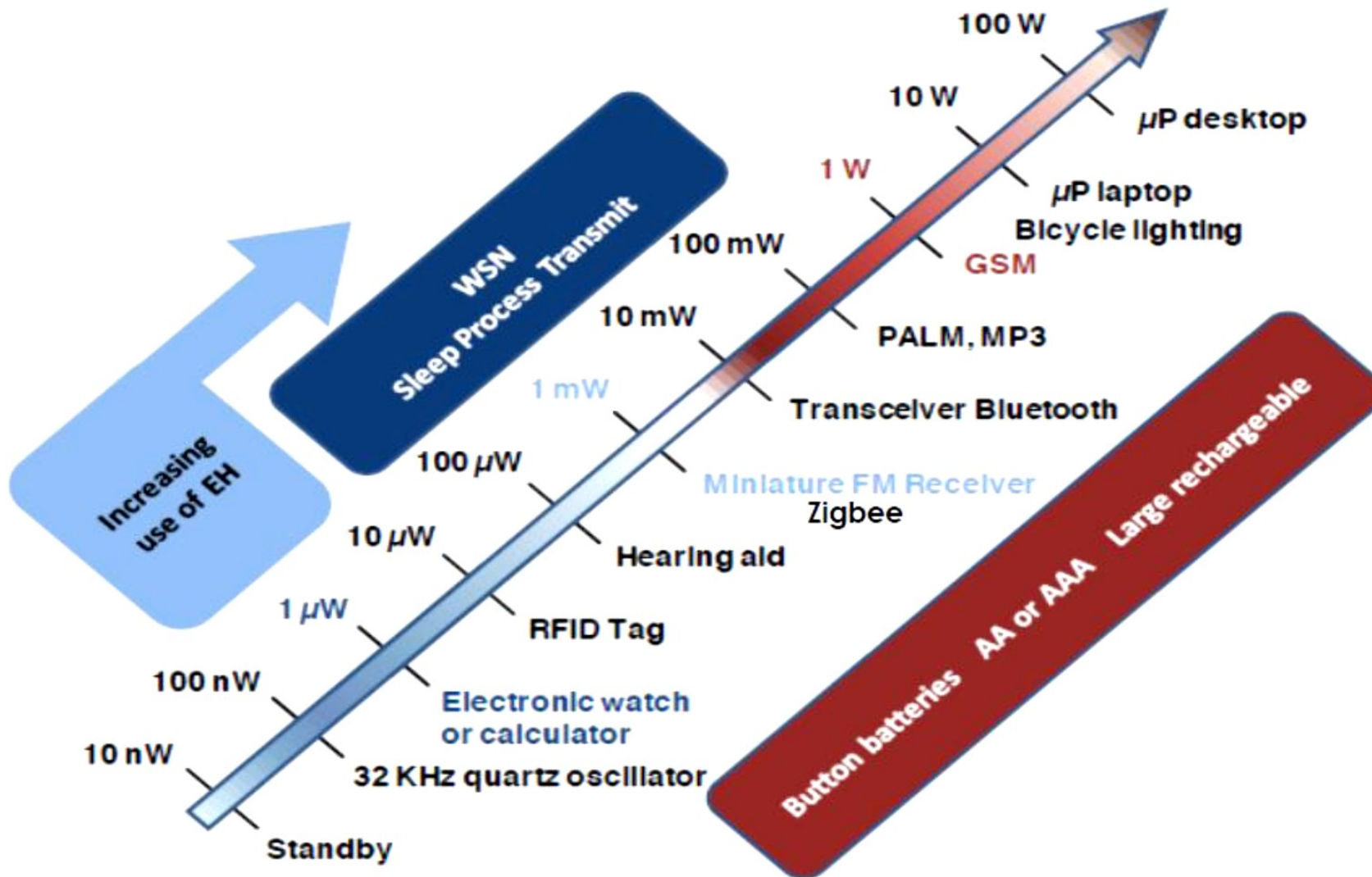
- They can be used as wall paper and window shades for producing electricity from room lighting.
- They can also be manufactured on clothing, which can in turn be used to charge portable electronic devices like mobile phones and media players.
- Flexible solar modules can be used on curved roofs, or roofs where it does not make sense to install a rack mounting system.

Flexible Energy Storage Devices (227)

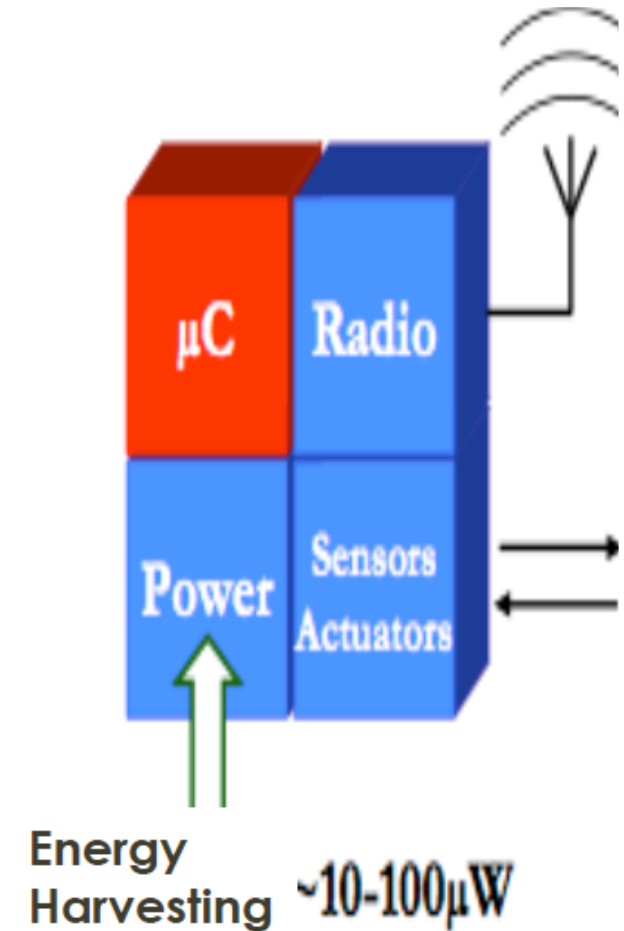
- Energy storage systems are critical components, especially when the harvested renewable energy is to be stored in remote locations. Types of energy storage system include batteries, supercapacitors and hydrogen storage.
- In all of the energy storage devices, the materials and technology play a key role. Nanotechnology provides crucial tools to drastically improve the efficiency of energy storage devices based on exploiting the material properties at the nanoscale (e.g. nanoparticles, nanowires and nanotubes).
- Nanomaterials have been investigated for the past two decades and the whole scenario was given a boost with the discovery of carbon nanotubes (CNTs).
- They play an enormous part in hydrogen storage (nano-magnesium or nano-magnesium alanate with nano-titanium as catalyst), supercapacitors (CNTs) and rechargeable batteries (e.g. using nanostructured anodes like silicon nanowires in lithium-ion batteries).



POWER CONSUMPTION FOR VARIOUS APPLICATIONS



Autonomous Wireless Sensors Network



- In recent years, there has been a **growing demand for flexible electronics**, e.g. **printed electronics and flexible displays**, and **flexible energy storage devices**. In particular, the flexible energy storage device is a **nascent technology**.
- Flexible energy storage devices have **numerous applications**, such as **active radiofrequency identification tags**, **integrated circuit smart cards** and **portable electronics**.
- The **flexibility** gives an added **advantage** as they can be **embedded in tiny** and **flexible electronic devices**. For these flexible energy storage devices to be **used on a daily basis**, they need to exhibit **excellent cyclability**, and **high power and energy densities**.
- The **main elements needed in a flexible energy storage device** are **flexible electrodes and separators**.

- Li-ions from the cathode (LiCoO_2) intercalate into the crystal structure of the anode (carbon/graphite) during charging, and the ions reverse direction, leaving the anode and re-entering the cathode structure, during discharging.
- The movement of ions in the anode and cathode hosts should not change or damage the host crystal structure. If it does, this leads to a shorter cycle and life of the battery.
- This shows that the physical, structural and electrochemical properties of cathode and anode materials are critical to the battery's performance. Hence, nanomaterials play a crucial role in these electrode materials.
- Nanomaterials such as nanotubes are excellent electrode materials owing to their unique accommodation of the Li-ion insertion/removal, lack of reactivity with the materials, higher electrode/electrolyte contact area (leading to higher charge/discharge rates) and higher electronic conduction.

- CNTs exhibit exceptional electrical conductivity, and are ultralight, low density and highly elastic. CNTs exhibit extreme structural flexibility when subjected to large strains and angles without structural failure.
- CNTs exhibit supercompressibility when the CNTs are compressed to 15% strain; the CNTs will recover to nearly their original length after every cycle in a strong cushioning effect.

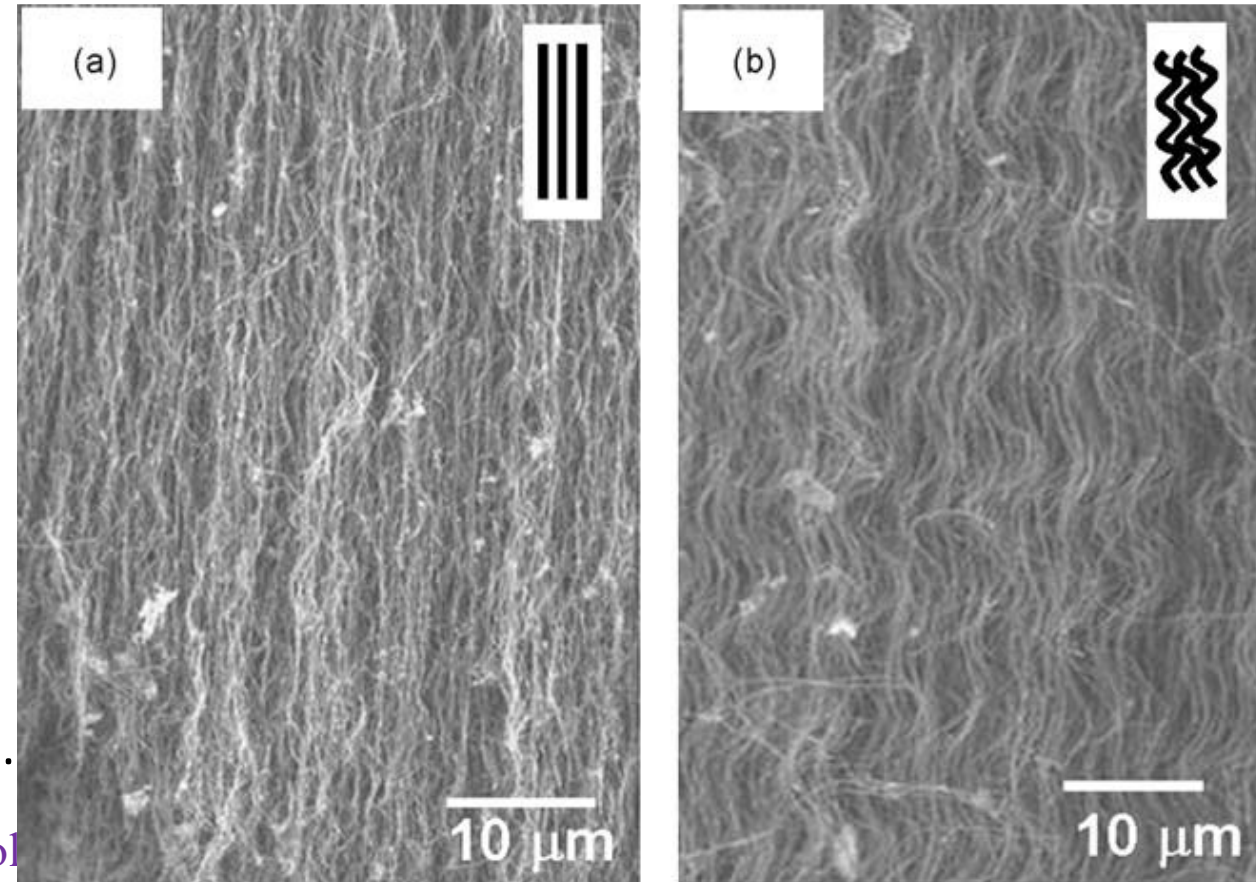


Figure: SEM image of carbon nanotube (CNT) block grown by thermal chemical vapor deposition.
(a) Before compression; (b) after mechanical compression.

- Figure 8.1(a) shows a CNT block (length of CNT 3 mm) before compression and Figure 8.1(b) shows the CNT block after undergoing 100 K cycles of mechanical compression. When the aligned CNTs are repeatedly stressed for a few hundred cycles, the CNTs can recover to nearly their original length.

Nanocomposites

- Integrated CNT–polymer composite is one of the best integrated structures for mechanically flexible energy storage devices. These nanocomposites enable various functional devices in a wide range of innovative products such as smart cards, displays and implantable medical devices.
- In recent years, supercapacitors and batteries have been demonstrated based on CNT–polymer composites.

- One interesting form of thin flexible energy storage device is to build a variety of storage systems based on the basic building block, i.e. an integrated nanocomposite sheet consisting of electrode, spacer and electrolyte.
- A nanocomposite which consists of cellulose, room temperature ionic liquid (RTIL) and CNTs fits the characteristics of a spacer, electrolyte and electrode. These provide inherent flexibility as well as porosity to the system.
- **Cellulose**, the main constituent of paper and an inexpensive insulating separator structure with excellent biocompatibility, can be made with adjustable porosity.
- The major challenge in fabricating CNT-integrated cellulose composites is that cellulose is insoluble in most of the common solvents. This issue is solved here by using an RTIL, 1-butyl, 3-methylimidazolium chloride ([bmIm][Cl]), which dissolves up to 25% (w/w) of unmodified cellulose by using microwave irradiation.
- The ionic nature of RTIL permits it to be used as an electrolyte in supercapacitors, allowing the assembly of all three components via a simple scalable process.

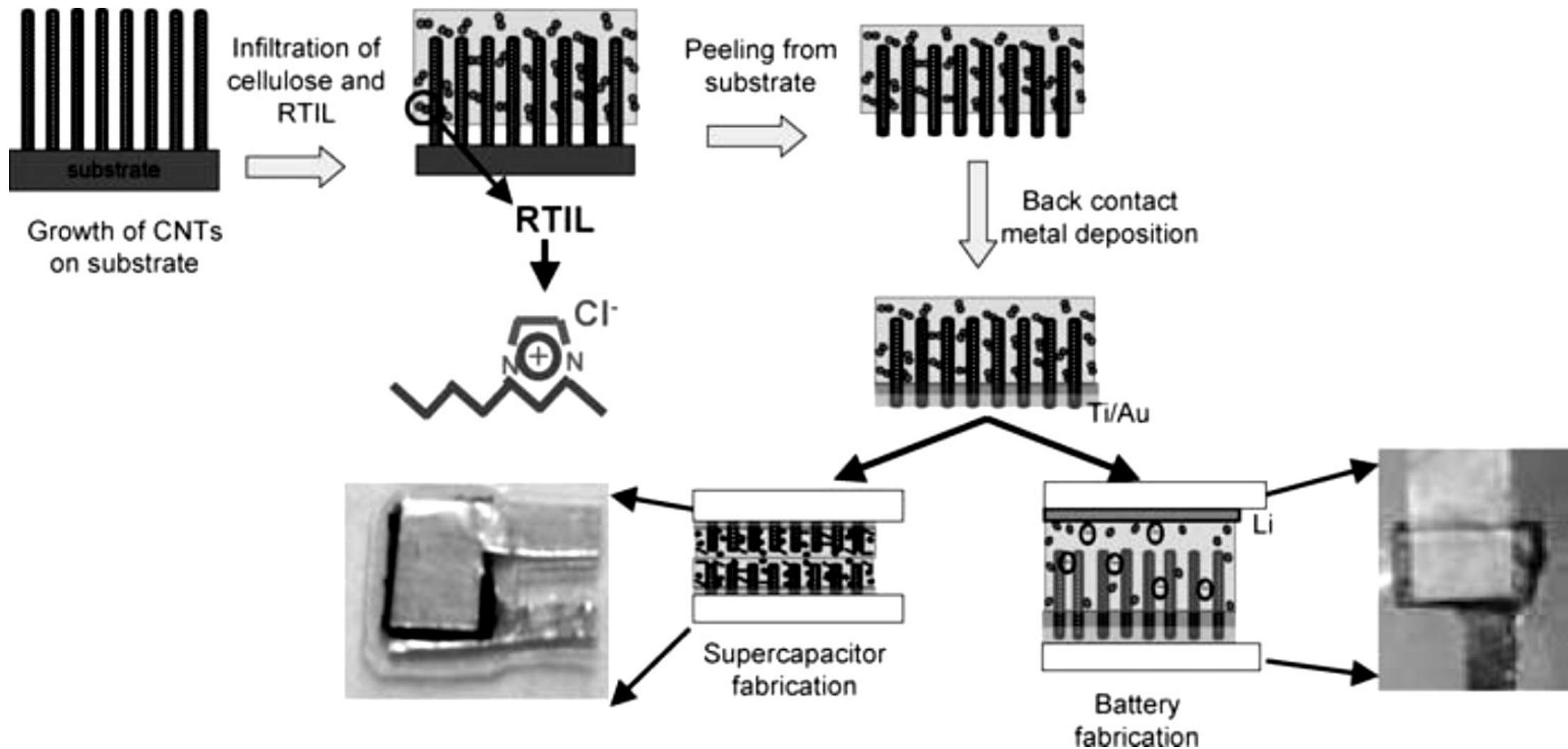


Figure: Flow diagram to fabricate flexible energy storage devices. The fabricated nanocomposite is the basic building block for the energy storage devices. CNTs: carbon nanotubes; RTIL: room-temperature ionic liquid.

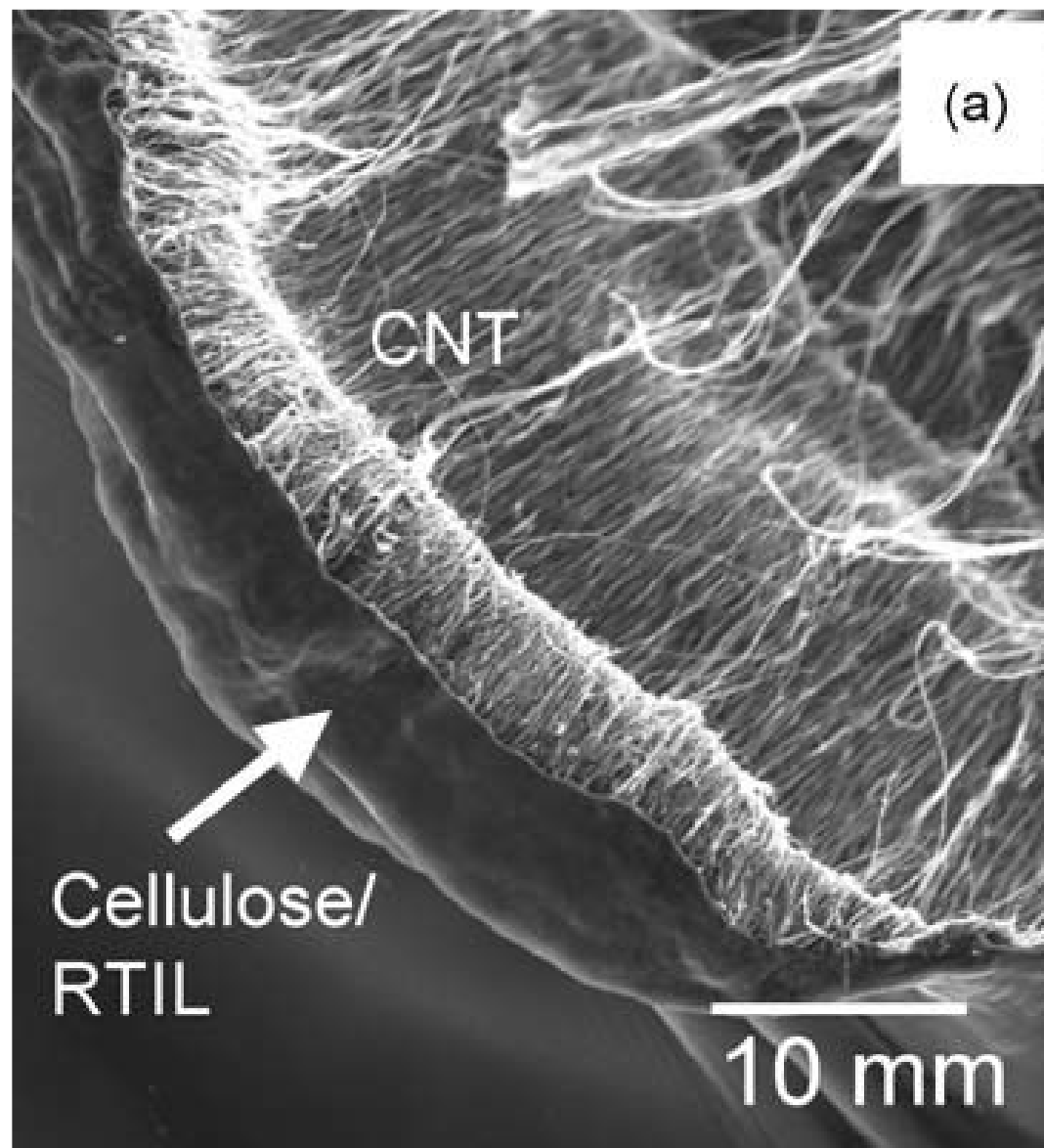


Figure : (a) SEM image of the nanocomposite sheet. CNT: carbon nanotube; RTIL: room-temperature ionic liquid. (b) Photograph showing the nanocomposite sheet and a curled nanocomposite sheet, indicating flexibility.

Flexible Chemical Sensors

- A **sensor** is a device that measures a physical quantity and converts it into a signal which can be read by an observer or by an instrument.
- There are many different types of sensors; based on their detection targets as well as detection mechanisms they can be categorized as mechanical, electromagnetic, thermal, optical, acoustic, radiation and chemical sensors, etc.
- The trend is moving toward sensors with better sensitivity and selectivity and faster response time, which are easier to build, more portable, remotely capable and ideally less expensive.
- More advanced sensor design also tends to be multifunctional, i.e. in addition to its main sensing function, it keeps track of many environmental factors such as temperature, humidity, time, location and event history.

- Better, faster and more compact integrated electronics, as well as rapid developments in nanoscience and engineering, are bringing these goals closer to reality. Many new materials as well as known materials that can be made on the nanoscale, such as carbon nanotubes (CNTs), graphene, various semiconductive nanowires and nanotubes, are now becoming available for building novel sensors..
- For any field application, small form factor, light weight and portability, with uncompromised sensitivity and selectivity, are essential.
- In general, for green and better technology, current research is investigating compactness, portability, reduced energy consumption, higher efficiency, etc.
- To build up such capabilities, miniaturization with integrated and compact design, utilization of nanoscale materials, sensing and electronic components that allow mechanical bendability, etc., are all at various stages of development.

MATERIALS FOR FLEXIBLE CHEMICAL SENSORS

Carbon nanotubes

- The intrinsic electronic properties of single-walled carbon nanotubes (SWNTs) are such that they may be metallic or semiconductive depending on their diameter and the graphitic ring arrangement around the tube wall. Furthermore, CNTs show exceptionally good thermal and mechanical properties. It is expected that CNTs could solve the thermal dissipation problem of nanodevices due to their high thermal conductivity.
- CNTs can transport a significant amount of electric current without the doping problem encountered in silicon (Si)-based field-effect transistors (FETs) because of their graphitic nature and because the covalent bonds among carbon atoms are much stronger.
- CNTs are among the most promising materials anticipated to impact future nanotechnology owing to their unique structural and electronic properties, which have generated great interest for application in a broad range of potential nanodevices.

- Around 2000, individual SWNTs were recognized as being extremely sensitive chemical sensors toward NO₂, NH₃ and O₂ (Table 9.1).

Table 9.1 Recent chemical sensors with measurement type and detection limit

Target analyte	Sensing material	Measurement	Detection limit				
Moisture, H ₂ O	Poly(cellulose-acetate-butyrate)	Capacitance	0–100% RH	NO ₂	PANI/PSSA	Chemiresistor	<20 ppm
	PANI	Chemiresistor	25 ppm		PANI/In ₂ O ₃	SAW	510 ppb
	PPy/TiO ₂ /electrolyte	Impedance	30–90% RH		PANI/PS single nanofiber	Optical	100 ppb
	PAM single fiber	Optical	35–88% RH		PEI/SWNTs	CFET	100 ppt
H ₂	Pd/SWNTs	Chemiresistor	30 ppm–2%	NH ₃	PSSMA/PAH/MWNTs	Chemiresistor	1 ppm
	Pd/SWNT	Chemiresistor	100 ppm		SWNTs	CFET	44 ppb
	Pd thin film/surfactant	Chemiresistor	25 ppm		SWNTs	CFET	2 ppm
	TiO ₂ nanotubes	Chemiresistor	1000 ppm		Graphene	Chemiresistor	5 ppm
O ₂	SWNTs film	Chemiresistor	20%		In ₂ O ₃ nanowires (RT)	CFET	5 ppb
CO ₂	Trapped in seawater under pressure	Raman	18 mmol/kg		SnO ₂ nanowires (100°C)	Chemiresistor	300 ppb
	CNTs/MEMS	Resonant transduction	0–15 vol%		SnO ₂ nanobelts (RT)	UV irradiation	3 ppm
CO	PANI/FeCl ₃ -AlCl ₃	Chemiresistor	10 ppm		PANI/SWNT	Chemiresistor	50 ppb
	PANI/In ₂ O ₃	SAW	<60 ppm		PANI nanofibers ~100 nm	Chemiresistor	100 ppm
	SWNTs-COOH	CFET	1 ppm		BTB doped/PMMA fiber	Optical	3 ppm
	SnO _{1.8} :Ag 5% (400°C)	Chemiresistor	100 ppm		Nafion/SWNTs	CFET	100 ppm
	SnO ₂ nanowires (150°C)	Chemiresistor	10 ppm		SWNTs	CFET	0.1%
	Single SnO ₂ nanowire (260°C)	Chemiresistor	5 ppm		SWNTs + PABS	Chemiresistor	5 ppm
NO	SWNTs/PEI	CFET	5 ppb		Graphene	Chemiresistor	5 ppm
					Graphene	CFET	100 ppm
					PANI/reduced graphene oxide	Chemiresistor	100 ppm
					In ₂ O ₃ nanowires (RT)	CFET	200 ppm

TYPES OF FLEXIBLE CHEMICAL SENSORS

- 1. Chemiresistive sensors**
- 2. Chemical field-effect transistors**
- 3. Chemocapacitance sensors**
- 4. Optical sensors**

INTEGRATION

- 1. Assembly and alignment: nanowires and carbon nanotubes**
- 2. Integrated package**



Thank You!

A graphic featuring the words "Thank You!" in a black, elegant cursive script. The text is centered and underlined with a thick, golden-brown swoosh. Five golden-brown stars are scattered around the text: two above and three below the swoosh.