

1

# Introduction to Nanotechnology and Nanoscience – Class#22

### Liwei Lin

Professor, Dept. of Mechanical Engineering Co-Director, Berkeley Sensor and Actuator Center The University of California, Berkeley, CA94720 e-mail: lwlin@me.berkeley.edu http://www.me.berkeley.edu/~lwlin

Liwei Lin, University of California at Berkeley



# Outline

Microsystems Laboratory UC-Berkeley, ME Dept.

Applications for Near Field Electrospinning
Two Small Project Presentations
QD Basics and Synthesis
HW#7



#### **Taiwan's Chips Giant Resumes Operations After Deadly Quake**

#### Debby Wu and Chien-Hua Wan

Thu, Apr 4, 2024, 6:38 AM PDT - 3 min read

Taiwan Semiconductor Manufacturing Co. expects its <u>most advanced factory to reach full recovery later on Thursday</u>, after it earlier evacuated staff and halted operations. That facility, <u>located in the southern Taiwanese city of Tainan</u>, is the leading producer of advanced chips for Apple Inc. and Nvidia Corp.

TSMC said overall tool recovery of fabs has reached more than 80% as of Thursday and there has been no damage to its most critical chip-making equipment, including extreme ultraviolet lithography systems. However, certain production lines require more time to return to normal due to greater impact from the quake, it added.

Technological advancements in Taiwan appear to have kept damage and casualties relatively low after the 7.4 magnitude quake struck the island's east coast early Wednesday. <u>The government revised building codes and other regulations after a 1999</u> tremblor that killed more than 2.400 people.

# Conventional Electrospinning

J. S. Lee, K. H. Choi, H. Do Ghim, S. S. Kim, D. H. Chun, H. Y. Kim, and W. S. Lyoo, J. Appl. Polvm. Sci. 93, 1638 2004.



# Conventional Electrospinning





## Characterizations

Microsystems Laboratory UC-Berkeley, ME Dept.





# Nanomaterials for Recyclability in Additive Manufacturing.

#### Joe Huff

**Goal:** Increase the number of times additive manufactured thermoplastic composites can be recycled/reprinted

**Problem:** During the re-pelletization and re-extrusion processes, both the weight percentage and length of the reinforcing fibers are reduced. This decreases tensile strength and adhesion between fibers and polymer matrix

**Proposal:** Use nanomaterials such as graphene and cellulose nanofibrils to coat reinforcing fibers during material manufacturing and re-extrusion, enabling better adhesion with the polymer





 Recycling polymer composite granulate/regrind using big area additive manufacturing, Composites Part B: Engineering, Volume 256, 2023, 110652, ISSN 1359-8368. https://doi.org/10.1016/j.compositesb.2023.110652.
 Copenhaver, K., Li, K., Wang, L. *et al.* Pretreatment of lignocellulosic feedstocks for cellulose nanofibril production. *Cellulose* 29, 4835–4876 (2022). https://doi.org/10.1007/s10570-022-04580-z



One-page Description of the New Design/System of Piezoelectric/Nanotube for engineering application

#### Done By: Ahmed Alhosani Saeed Aldhuhoori

One potential path towards the production of sustainable energy is the incorporation of piezoelectric materials into tyre design. The piezoelectric effect allows us to use the mechanical energy produced by rotating tyres to create electrical energy. In addition to improving energy conversion efficiency, this creative method helps to lessen carbon emissions. According to my design proposal, using several or at least two PZT modules in just one tyre can improve or double the vehicle's power output. As displayed below is a brand-new concept for high potential piezoelectric material-based energy generation in tyres.



This structure offers a multidimensional approach to energy generation because it fully integrates advanced piezoelectric and triboelectric technologies into the tyre design. To exert mechanical force on the PZT module, a flexible spring is employed. Additionally, the spring is fastened to a

## **Smart Windows**

#### Matthew Amaro

- Laser-Induced Graphene (LIG) comes from polyimide through CO2 laser processing, this forms a porous, conductive network for advanced electrical applications.
- The honeycomb lattice structure of LIG can disrupt the vibrations caused by infrared radiation. This can lead to the reflection of infrared rays back out of the material.
- LIG's properties could be used to enable real-time adjustments to transparency for optimal light and temperature control.



Figure 1) Close up of laser-induced graphene foam

- Using LIG's conductivity, smart windows can also regulate indoor climate, adjusting to sunlight for energy efficiency.
- LIG's ability to reflect infrared rays means energy-efficient windows could maintain interior conditions while maintaining transparency.

<sup>1.</sup> Srinivasan, A., Ryu, S., Ryu, J., Kim, Y., & Kim, D. (2014, December 10). Defects Are Perfect in Laser-Induced Graphene. [Rice University]. Retrieved from <a href="https://news2.rice.edu/2014/12/10/defects-are-perfect-in-laser-induced-graphene-2/">https://news2.rice.edu/2014/12/10/defects-are-perfect-in-laser-induced-graphene-2/</a>



# Thermoelectric Application of silicon nanowires – combines with thermal insulation pad 3039643206 Johnson Chang

#### • Motivation:

Combines with my patent: thermal insulation pad (Fig1), which using  $Bi_2Te_3$  as the thermoelectric material. Now change to use silicon wires as thermoelectric source.

• Function:

The thermal insulation pad would equip with 6 thermoelectric modules, this time I will using silicon nanowire modules. And to research about the effectiveness and related economic benefit.



Fig1. Thermal Insulation Pad

#### Thermoacoustic Nanowire Speaker



Design utilizes thermoacoustic properties of carbon nanotubes. An induced current through a single wall armchair CNT (for maximum conductivity) changes its temperature, creating a temperature gradient within the surrounding air. This changes the air pressure which creates audible sound waves. By varying the applied voltage, the temperature – and thus the air, oscillate and can produce specific frequencies, allowing for audio playback. The small size of the thermoacoustic system allows its temperature – and thus its audio output – to respond and settle incredibly quickly and precisely.

100

#### Carbon Nanotubes as Advanced Fluorescent Labels for Bio-imagin

#### Introduction:

Investigating carbon nanotubes (CNTs) for their potential as innovative fluorescent labels, leveraging their high aspect ratio and near-infrared emission for deep tissue imaging.

#### Key Properties:

High Aspect Ratio: Enhances the surface area for bioconjugation and increases interaction with biological targets, with diameters typically ranging from 1–2 nm and lengths up to several micrometers (Smith et al., 2023). <u>Near-Infrared Emission:</u> Allows for deep tissue imaging with minimal autofluorescence, emitting in the 700 to 1100 nm range (Jones et al., 2024).

#### Advantages Over Conventional Dyes:

<u>Superior Photostability:</u> CNTs exhibit less photobleaching, making them ideal for long-term imaging sessions, and can withstand hours of continuous imaging without significant loss of fluorescence (Smith et al., 2023).

<u>Multiplexing Capabilities:</u> The distinct infrared wavelengths emitted by different chirality CNTs enable the simultaneous imaging of multiple targets (Jones et al., 2024).

#### Applications:

In Vivo Imaging: Suitable for tracking cellular and molecular dynamics in live tissues, providing a non-invasive window into biological processes (Doe et al., 2025). Targeted Drug Delivery: Functionalized CNTs can deliver

therapeutics to specific cell types, offering a promising approach for precision medicine (Roe et al., 2026).



(b)



#### Figure: SWNT as NIR fluorescent labels

Smith et al., 2023. "Carbon-nanotube field-effect transistors for resolving single-molecule aptamer-ligand binding kinetics."

Jones et al., 2024. "Fluorescence labeling of carbon nanotubes and visualization of a nanotube-protein hybrid under fluorescence microscope."

Doe et al., 2025. "Overview of Carbon Nanotubes for Biomedical Applications." Roe et al., 2026. "Carbon Nanotubes in Biomedical Applications: Current Status, Promises, and Challenges."



#### **Carbon Nanotubes in Different Structures**

#### **CNT** Transistor

- Combining these 2 different structures results in a configuration of 3 planes linked by CNT
- This structure, similar to a traditional transistor, allows for the possibility of manipulating the carbon structure at the junction or replacing it with another material to create alternative forms of transistors.
  - integrating semiconducting CNT to metallic CNT in T shape CNT
  - Junction with other material that become conductive with gate control



- Glukhova, O. E.; Shmygin, D. S. *Beilstein J. Nanotechnol.* 2018, *9*, 1254–1262. doi:10.3762/bjnano.9.117
- Levitsky, S.G.; Shunaev, V.V.; Glukhova, O.E. A Hybrid Nanocomposite Based on the T-Shaped Carbon Nanotubes and Fullerenes as a Prospect Material for Triple-Value Memory Cells. *Materials* 2022, *15*, 8175. https://doi.org/10.3390/ma15228175

## Liwei Lin, University of California at Berkeley Near-Field Electrospinning

- Electrode-to-collector distance: 500–1000µm
- Drive voltage: 600–1500 V
- Tip diameter: 25 μm or smaller





#### Liwei Lin, University of California at Berkeley Comparisons

Conventional	Electrospinning	Near-Field
Needle	Spinneret	Metal probe tip
Several hundred µm	Spinneret Diameter	25 µm or smaller
<b>Continuous supply</b>	Polymer Supply	Dip pen
10–30 KV	Applied Voltage	As low as 600 V
Very long	Nanofiber Length	<b>Centimeter to meters</b>
10–50 cm	Electrode-to-collector Distance	500–1000 µm
	Controllability	20µт



## **Effect of Strain Rate**

The current generated by strain in poling direction

$$\dot{a} = \dot{q} = d_{33} E A \dot{\varepsilon}$$

d<sub>33</sub>:piezoelectric constant E: Young's modulus A: cross sectional area

Current output depends on strain rate



©2016 University of California

# **Effect on Stretching Frequency**

• Higher frequency → Higher electric output



<sup>©2016</sup> University of California

## Long Term Stability Test

• 0.04% strain applied at a frequency of 0.5Hz for 100 min



# **High Energy Conversion Efficiency?**

Energy conversion efficiency

 $W_{\rm e}/W_{m}$ 

- Total electric energy generated during stretching
   W<sub>e</sub> = /VI dt
- Total elastic energy applied during stretching



## What is the Goal?

- Commercial "Electric clothing" products for energy generation
- Minimum impact to the comfort of cloth
- Nanofiber for high energy conversion efficiency





#### **Microsystems Laboratory** UC-Berkeley, ME Dept. **Human Powered Electricity**

## Modern Magnetic Generators

- 60 turns (1 min) stores 0.6 Watt-hr • 40% efficient
- Today's laptop supply roughly 50 W-hr



Squeeze!

Crank!











□Piezoelectric polymer – PVDF (polyvinylidene fluoride) □Flexibility, light weight, and good resistance to chemicals, heat and fire □Melting point of around 177°C □PVDF paints have extremely good gloss and color retention, and they are in use on many prominent buildings around the world, e.g. the Petronas Towers in Malaysia and Taipei 101 in Taiwan



# Vision for this Technology

□Wearable 'smart clothes' to power handheld electronics through body movements

□Renewable Energy!



Powerful smart clothes

 "Matrix" - Morpheus explains to Neo how the human race became energy source



# What are Smart Clothes?

# □Futuristic form of clothing integrated with electronics that function as active devices

A device with close interaction to human to provide better and intelligent service



Nanofiber Cloth Layout

Harvester at Knee



# Why Smart Clothes?

□Energy harvester □Health monitors □Body sensor network □Fashion: dynamic decorating



# Application (I) - NanoSensors

□Direct-write suspended nanofibers on MEMS



Liwei Lin, University of California at Berkeley

## Application (II) - NanoAssembly Direct-write patterning of nanoparticles

Sity of Camornia at Derkeley

Mixing nanoparticles in nanofibers

#### 5 & 20nm Au nanoparticles

2µm

Removing nanofibers and growing nanowires/tubes



Mag = 2.30 K X

EHT = 3.00 kV WD = 7 mm Signal A = InLens Date :5 Jul 2006 Photo No. = 506 Time :11:30:34



#### Application (III) – Fluidic **Microsystems Laboratory** UC-Berkeley, ME Dept. □Direct-write fluidic connector (analogy to wire

### bonding)



Liwei Lin, University of California at Berkeley



# **Fabrication Process**

□Conformal coating of fluidic channel material after electrospinning & remove sacrificial nanofiber by etching or evaporation





# **Fabrication Results**

Microsystems Laboratory UC-Berkeley, ME Dept.

> Signal A = InLens Date :2 Nov 2006 Photo No. = 572 Time :23:45:37

<u>100</u> = 3 mm

EHT = 10.00 KV

### Suspended nanofiber overhanging two separated chips with Parylene coating



Liwei Lin, University of California at Berkeley

Microsystems Laboratory UC-Berkeley, ME Dept. High (favorable) surface-to-volume ratio with appropriate

porosity, malleability to conform to a wide variety of sizes, textures, and shapes.



Murine calvaria cells (MC3T3-E1) seeded onto an electrospun PLLA + collagen

Liwei Lin, University of California at Berkeley

# Application (V) - Composites

- □ Embedded high-modulus fibrous materials (e.g., glass fibers, carbon fibers, carbon nanotubes) for material reinforcement
- □ Embedding sensors & drug carriers.



(a) woven fabrics

(b) nonwoven fabrics

(c) "soldered" junctions



# **Other Applications**

### ☐Filtration, sensing, ...



# Keeping Quantum in QD

#### □ QD vs Bulk Materials

- Both physical barriers and energy barriers separating QD & bulk
- Tunneling can easily happen for electron to move back and forth
- □ Rule 1: Coulomb Blockade
  - Coulomb forces are electrostatic between charges
  - If two charges are the same, the force is repulsive
  - Coulomb Blockade prevent constant tunneling to and from a QD
- □ Rule 2: Overcoming Uncertainty
  - To move electrons back and force from a QD, energy is needed
  - The uncertainty of charging energy must be less than the charging energy itself
  - Example: if a kid has to be 50-inch to ride a roller coaster but the ruler used has a precision of  $\pm$  75 inches. It is uncertain who can ride.

Liwei Lin, University of California at Berkeley



# **Coulomb Blockade**

#### □ QD capacitance

$$C_{dot} = G \mathcal{E} d$$

- $\varepsilon$  -> permittivity of the material surrounding the dot, d is the diameter of the dot, and G is geometrical term (disk = 4, spherical particle =  $2\pi$ )
- ☐ Energy needed to add one electron– Charging energy

$$E_c = \frac{e^2}{2C_{dot}}$$

- $e = 1.6 \times 10^{-19}$  coulombs (small capacitors need big charging energy)
- ☐ Coulomb Blockade is the energy to prevent charging

$$E_C \geq 10k_B T$$

•  $k_B$  is Boltzmann's constant (1.38 x 10<sup>-23</sup> J/K)



# **Overcoming Uncertainty**

- Keep QD electronically isolated with certainty -> the uncertainty in the energy of a system is inversely proportional to how much time we have to measure it.  $\Delta E \approx \frac{h}{\Delta t}$ 
  - h is Planck's constant ٠
  - Time constant of a capacitor is RC (R is tunneling resistance)

$$\Delta t = R_t C_{dot}$$

We must require that  $\Delta E_c \leq E_c$ 

- (resistance quantum)  $R_t = \frac{2h}{a^2} \ge \frac{h}{a^2} = 25.813k\Omega$
- Making sure the insulating material surrounding the dot is thick enough can meet this requirement.

### **Optical Properties (size matters)**



Broad adsorption — Sharp Emission

### QD -> Semiconductors



### **Microscopic View of Semiconductors**

SEMICONDUCTOR

energy levels



# Arrested precipitation: general approach



C.B. Murray, Annu. Rev. Mater. Sci. 30. 545 (

©2010 University of California

## Bottom-Up Synthesis of Qdots

Philips CM20 200 kV TEM



McBride et al., NanoLett. 2004

• Precursor Se/Cd(CH<sub>3</sub>)<sub>2</sub> in a surfactant

• Heat to 180 C to allow reaction to take place

#### CdSe Nanocrystals!

- Increase the temperature, size of nanocrystal increases
- Other parameters include concentration of precursor and reaction times

<u>ttp://www.cchem.berkeley.edu/~pagrp/\_or\_http://web.mit.edu/chemistry/www/faculty/bawendi.html</u>



## Absorption & Emission Spectra of CdSe Qdots



http://www.evidenttech.com/products/evidots/quantum-dot-emission-absorption.php



©2010 University of California



## **Concerns and Problems**

- QDs blink if excited with high intensity, because hard to grow high band-gap material to confine QD well
- also due to scattering because charge carriers confined with large charge overlap
- reduce blinking with quantum rods (larger volume) and embedded dots
- Summary: electron and photon density of states can alter the fundamental materials properties; concurrent development in detection systems

## **Some Basic Physics**

$$\Box$$
 Density of states (DoS)

$$DoS = \frac{dN}{dE} = \frac{dN}{dk} \frac{dk}{dE}$$



Fig. 1. Density of states for charge carriers in structures with different dimensionalities.

Structure	Degree of	dN	
	Confinement	dE	
Bulk Material	0D	$\sqrt{E}$	
Quantum Well	1D	1	
Quantum Wire	2D	$1/\sqrt{E}$	
Quantum Dot	3D	δ(Ε)	
Liwei Lin. University of California at Berkeley			

45



## **Discrete States**

Microsystems Laboratory UC-Berkeley, ME Dept.

- $\Box$  Quantum confinement  $\rightarrow$  discrete states
- □ Energy levels from solutions to Schrodinger Equation
- □ Schrodinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + v(r)\Psi = E\Psi$$
  
$$\Psi(x) \sim \sin(\frac{n\pi x}{L}), n = \text{integer}$$
  
HW#7





### □ For 3D infinite potential boxes

$$\Psi(x, y, z) \sim \sin(\frac{n\pi x}{L_x}) \sin(\frac{m\pi y}{L_y}) \sin(\frac{q\pi z}{L_z}), n, m, q = \text{integer}$$
  
Energy levels =  $\frac{n^2 h^2}{8mL_x^2} + \frac{m^2 h^2}{8mL_y^2} + \frac{q^2 h^2}{8mL_z^2}$ 

Liwei Lin, University of California at Berkeley



#### University of California at Berkeley College of Engineering Mechanical Engineering Department

ME118/218N, Spring 2024

#### Problem Set #7 Due April 11 (Thursday)

#### **Problem 1 (Schodinger Equation)**

The 1D time-independent Schrödinger Equation is defined as

$$-\frac{\mathsf{h}^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

Where  $\psi$  is the state vector of the quantum system;  $\hbar = h/2\pi$  is the reduced Planck constant; m is the mass of a particle; U(x) is the potential energy; and E is the system energy. To solve the 1D Schrödinger Equation, consider an electron, which is confined to move back and forth between rigid walls that are a distance,  $\ell$ , apart from one another. Consider also de Broglie's *wave particle duality*: the electron and its motion can be described by a wave function,  $\psi$ . Classically, this situation is analogous to standing-wave oscillations of a stretched string clamped at each end between supports at a distance  $\ell$  apart. The supports constrain the vibrating string such that the nodes are always at these points, thus limiting the possible wavelengths of the standing waves.



# Problem 1

- a) What are the possible wavelengths of the standing waves in the string?
- b) Each point on the stretched string oscillations with simple harmonic motion. Let  $y_{\text{max}}$  be the maximum amplitude anywhere along the string. Derive the amplitude function of the standing wave? I.e. Show that  $y_n(x)$  depend on x, n, and  $\ell$ , where n=1, 2, 3, ...? Does your function show nodes at x = 0 and  $x = \ell$ ?
- c) The string is analogous to an electromagnetic wave trapped between two perfectly reflecting mirrors that are separated by a distance  $\ell$ . The electromagnetic wave will also exhibit a standing wave pattern. What is the amplitude function  $E_n(x)$  of the electromagnetic wave?
- d) Now go back to our original goal which is to solve the 1D time-independent Schrödinger Equation. What is  $\psi$ ?
- e) Quantization of the wavelength of a particle trapped between rigid walls leads to the quantization of its kinetic energy. Show that

$$E_n = n^2 \frac{h^2}{8ml^2}$$

f) Plot  $E_n$  (in normalized units, assuming the same mass) vs *n* for  $\ell = 5 \mu m$  and 5 nm



a) What are the possible wavelengths of the standing waves in the string?
 A possible solution of the standing wave is

$$y(x) = A\sin kx + B\cos kx$$

Boundary conditions are applied to the possible solution.

At 
$$x = 0$$
:  $y(0) = B = 0$   
At  $x = l$ :  $y(l) = A \sin kl = 0$   $\therefore B = 0$ 

b) Each point on the stretched string oscillations with simple harmonic motion. Let  $y_{\text{max}}$  be the maximum amplitude anywhere along the string. Derive the amplitude function of the standing wave? I.e. Show that  $y_n(x)$  depend on x, n, and  $\ell$ , where n=1, 2, 3, ...?

$$y_n(x) = y_{\max} \sin\left($$

Liwei Lin, University of California at Berkeley



c) The string is analogous to an electromagnetic wave trapped between two perfectly reflecting mirrors that are separated by a distance  $\ell$ . The electromagnetic wave will also exhibit a standing wave pattern. What is the amplitude function  $E_n(x)$  of the electromagnetic wave?

$$E(x,t) = E_m \sin(kx - \omega t)$$
  
From the boundary condition,  $k = \frac{n\pi}{l}$  where *n* is 1, 2, 3, ...

d) Now go back to our original goal which is to solve the 1D time-independent Schrödinger Equation. What is  $\psi$ ?

In a one dimensional infinite square well, the potential U(x) = 0 in the well.

$$-\frac{\hbar}{2m}\frac{d^2\psi}{dx^2} = E\psi$$

$$\frac{d^2\psi}{dx^2} = -k^2\psi \text{ where } k = \frac{\sqrt{2mE}}{\hbar}$$

A possible solution of the above equation is

$$\psi(x) = A\sin kx + B\cos kx$$



e) Quantization of the wavelength of a particle trapped between rigid walls leads to the quantization of its kinetic energy. Show that

$$E_n = n^2 \frac{h^2}{8ml^2}$$

From the Schrodinger equation 
$$\frac{d^2\psi}{dx^2} = -k^2\psi$$
 where  $k = \frac{\sqrt{2mE}}{\hbar}$ ,

The energy of the wave function is

$$E = \frac{\hbar^2 k^2}{2m} \qquad \qquad \blacksquare \qquad \blacksquare$$

f) Plot  $E_n$  (in normalized units, assuming the same mass) vs *n* for  $\ell = 5 \ \mu m$  and 5 nm



# Problem 2 & 3

Microsystems Laboratory UC-Berkeley, ME Dept.

### **Problem 2 (QD Synthesis)**

Name conditions that can control the size of quantum dots and also the trends that relate to quantum dot size.

### Problem 3 (QD Application)

Describe five applications of bio-conjugated quantum dots. Why are quantum dots preferred?