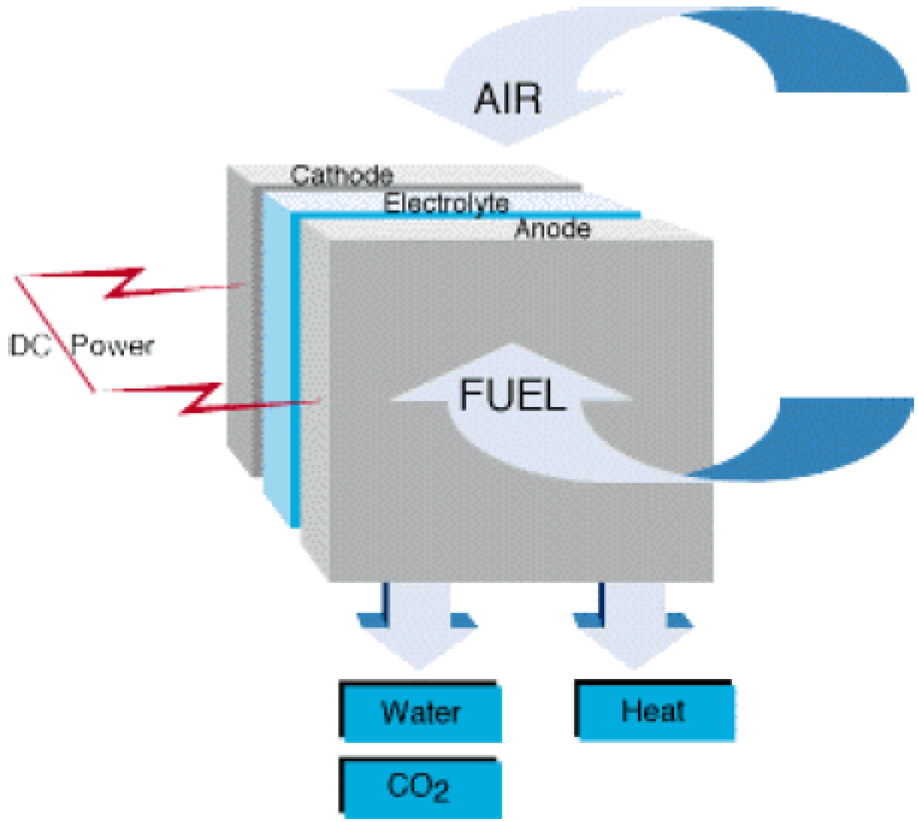
How a fuel cell function

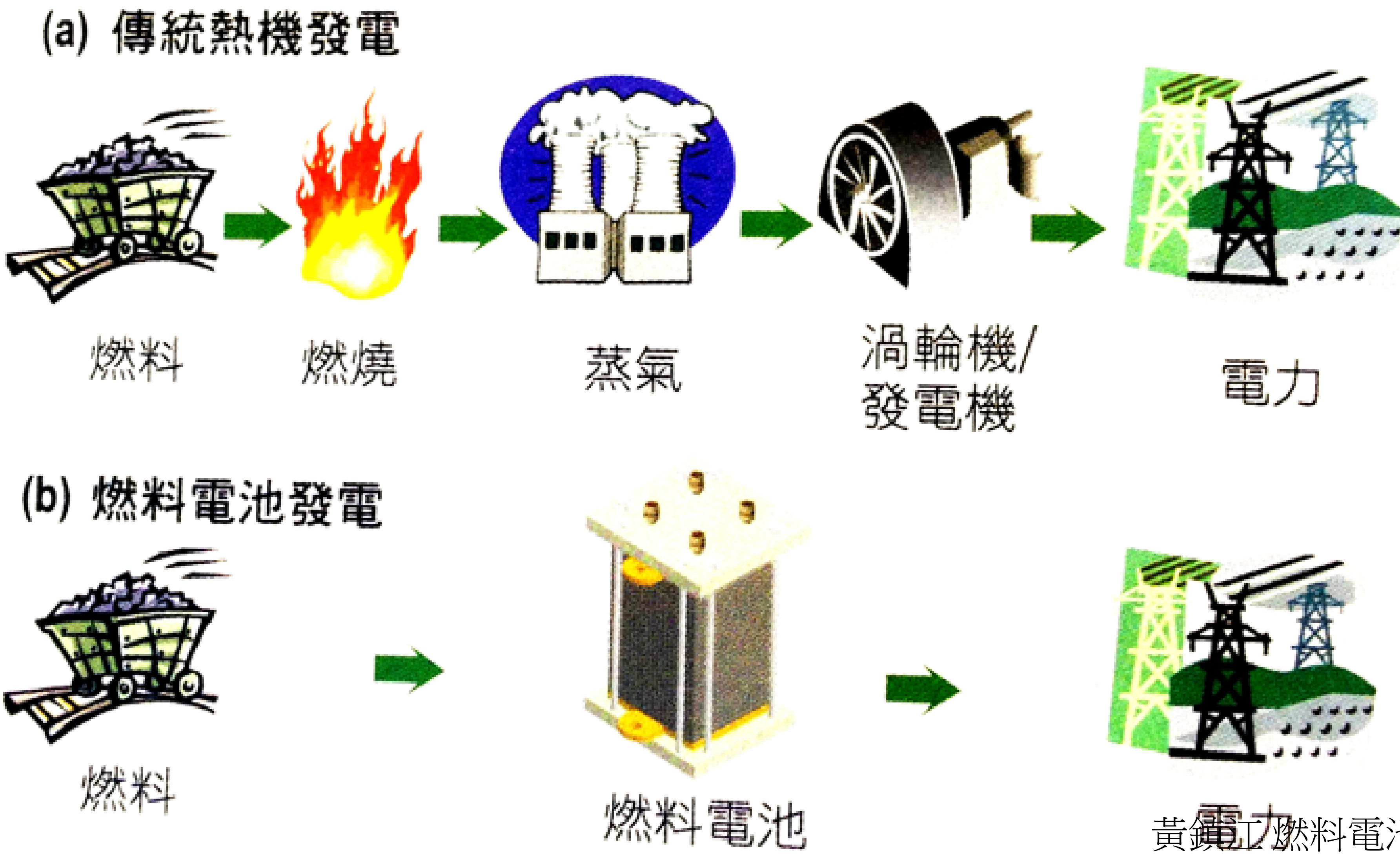
•Unlike battery, fuel cell does not run down or require recharging.

•Fuel cell consists of two electrodes sandwiched around an electrolyte.

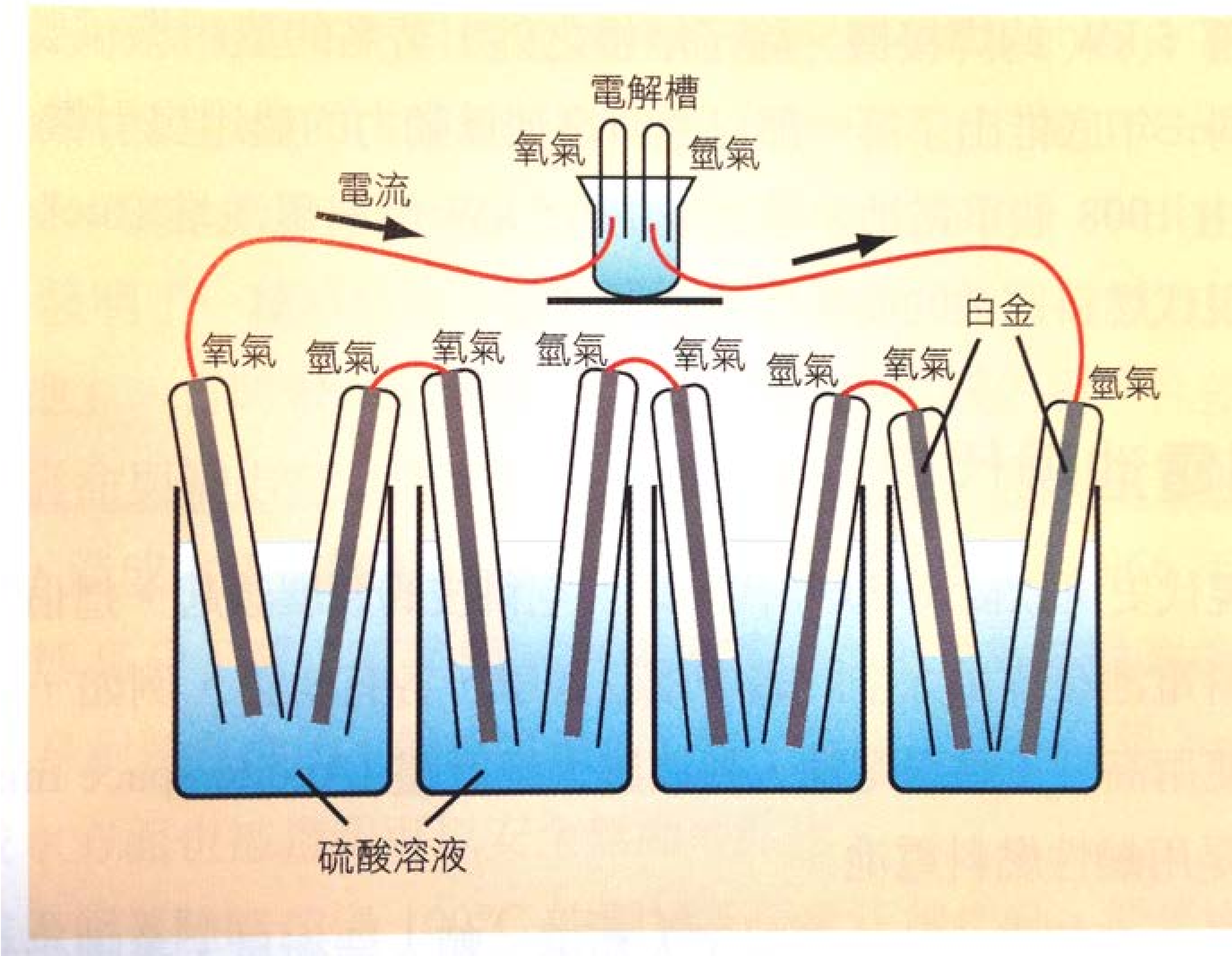
•Encouraged by catalysts, H_2 (fuel) and O_2 (air) occur anodic and cathodic reaction (with electrons create a separate current) then generate electricity, water and heat by chemical reaction.



燃料電池與傳統熱機的火力發電比較

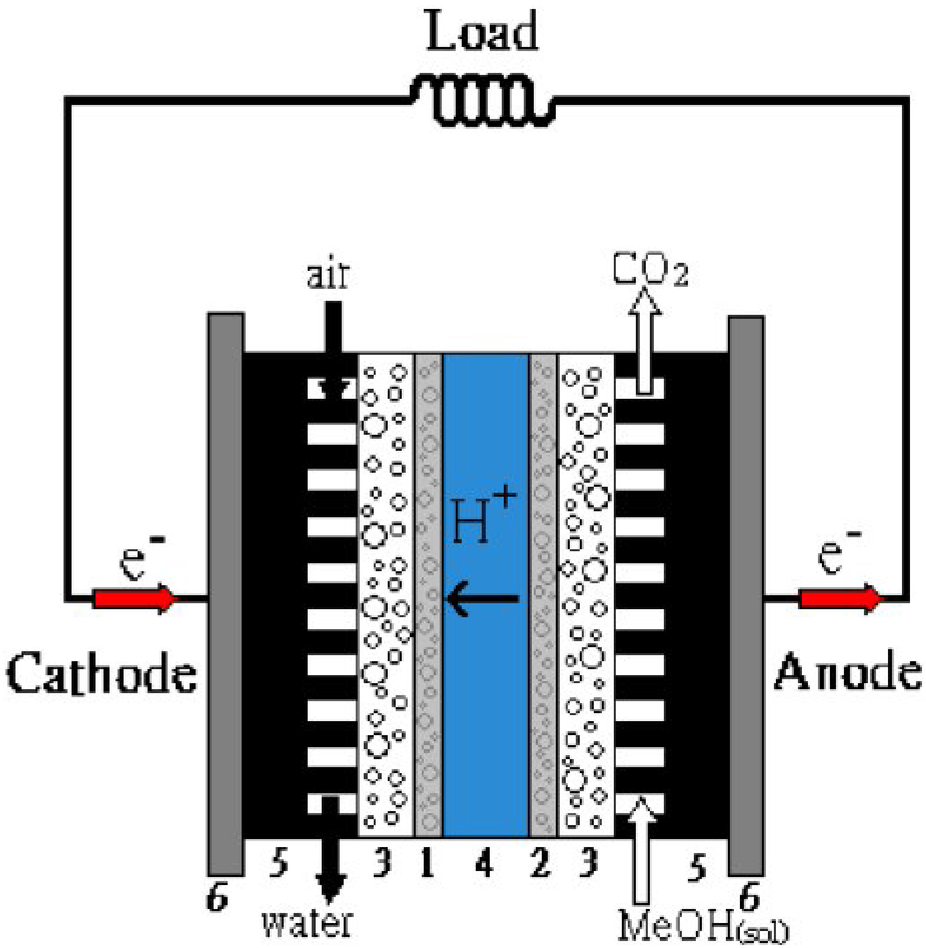


Willam R. Grove 進行的氣體電池實驗



黃鎮江 燃料電池

DMFC, direct methanol fuel cell



Anode

$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Electrolyte

Cathode

$3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

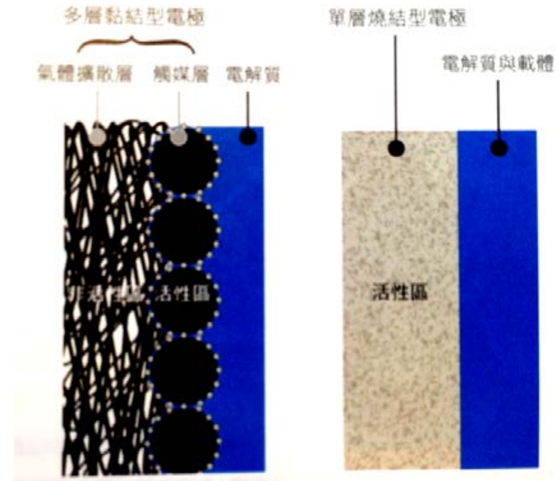
Overall

$CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

觸媒與多孔氣體擴散電極

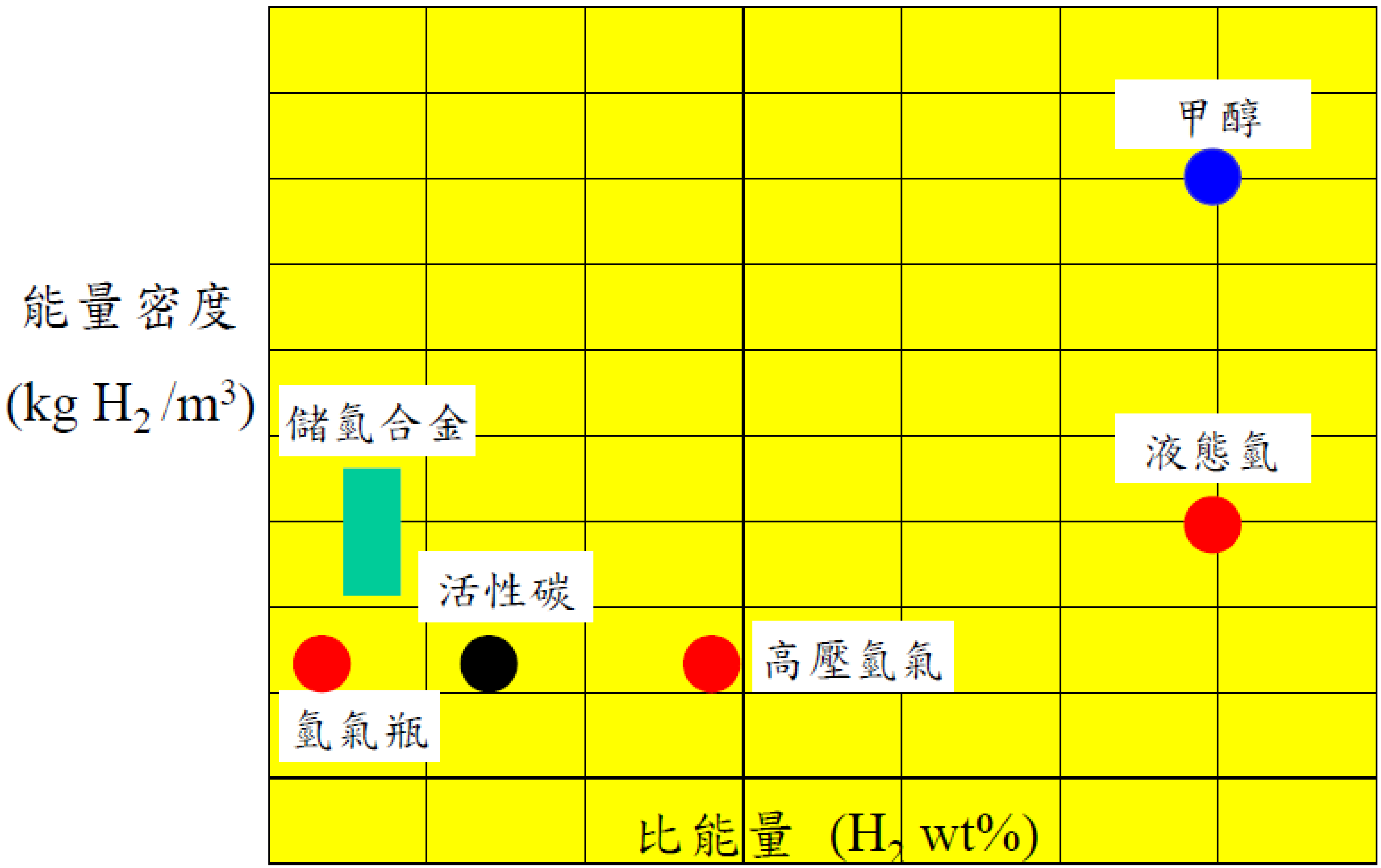
表 1-5　燃料電池使用觸媒電極結構之比較

種類	AFC	PEMFC	PAFC	MCFC	SOFC
陽極觸媒	雷尼鎳、鉑/碳	鉑/碳	鉑/碳、鉑釕/碳	鎳-鉻合金、鎳-鋁合金	鎳/YSZ
陰極觸媒	雷尼鎳、鉑/碳	鉑/碳	鉑/碳	鋰化-氧化鎳	摻鍶錳酸鑭
電極結構	單層雷尼鎳電極或多層黏結型電極	多層黏結型電極	多層黏結型電極	單層燒結型電極	單層燒結型電極



- 主要可分為單層燒結型電極以及多層的黏結型電極
- 單層：將金屬觸媒與電解質之混合粉末以燒結方式製作多孔結構
- 多層：在高分散型觸媒內填加黏結劑 (PTFE)後黏貼至氣體擴散層上。擴散區為非活性區

燃料電池用燃料系統之比較

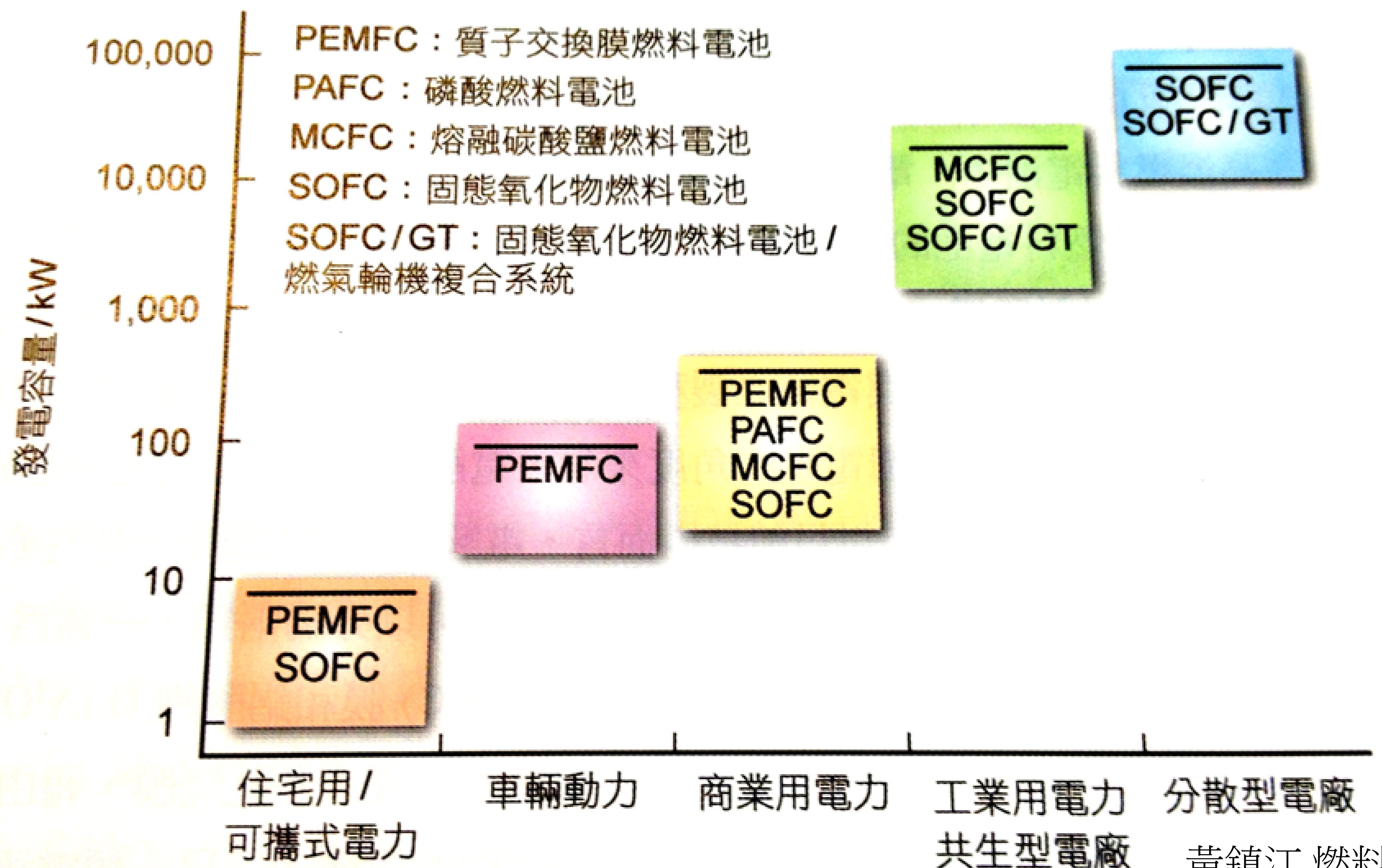


燃料電池的分類

- 依電解液性質可分為五類

1) 鹼性燃料電池 （ alkaline fuel cell,AFC)
2) 磷酸燃料電池 (phosphoric acid fuel cell, PAFC)
3) 質子交換燃料電池 (proton exchange membrance fuel cell, PEMFC)
4) 溶融碳酸鹽燃料電池 (molten carbonate fuel cell, MCFC)
5) 固態氧化物燃料電池 (solid oxide fuel cell, SOFC)

燃料電池發電容量與適用範圍

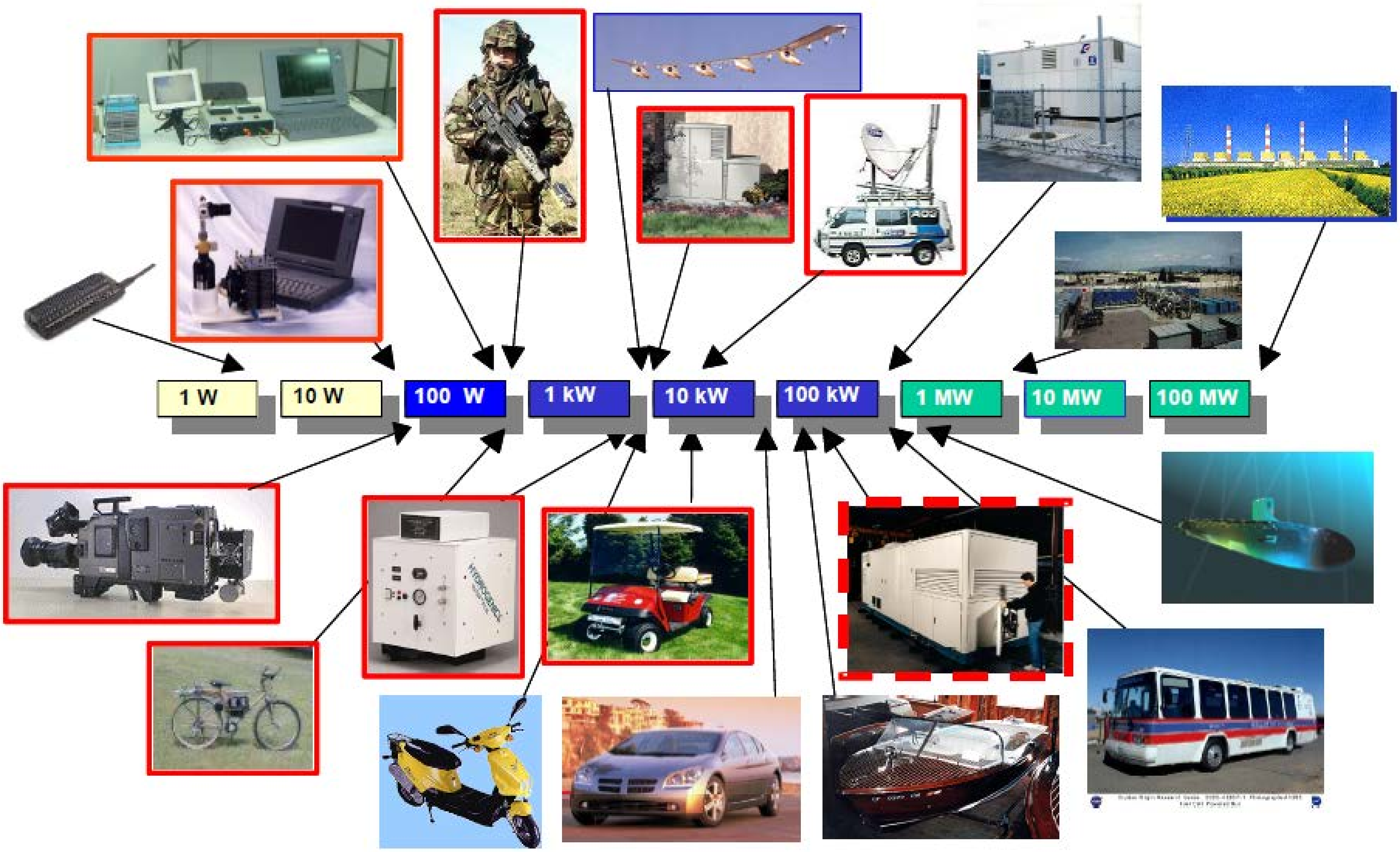


黃鎮江 燃料電池

燃料電池特點

- 效率高：目前工作的燃料電池效率可達40-60%,平均單位質量燃料所產生的電能，僅次於核能
- 噪音低：結構簡單且沒有運轉機件
- 污染低：氫氣為主要燃料。
- 進料廣：只要含有氫原子的物質都可以當作燃料來源，包括天然氣、石油、燃煤、酒精、甲醇。
- 用途多：可提供的電力範圍在1W~1000MW間

Fuel Cell



能源與環境

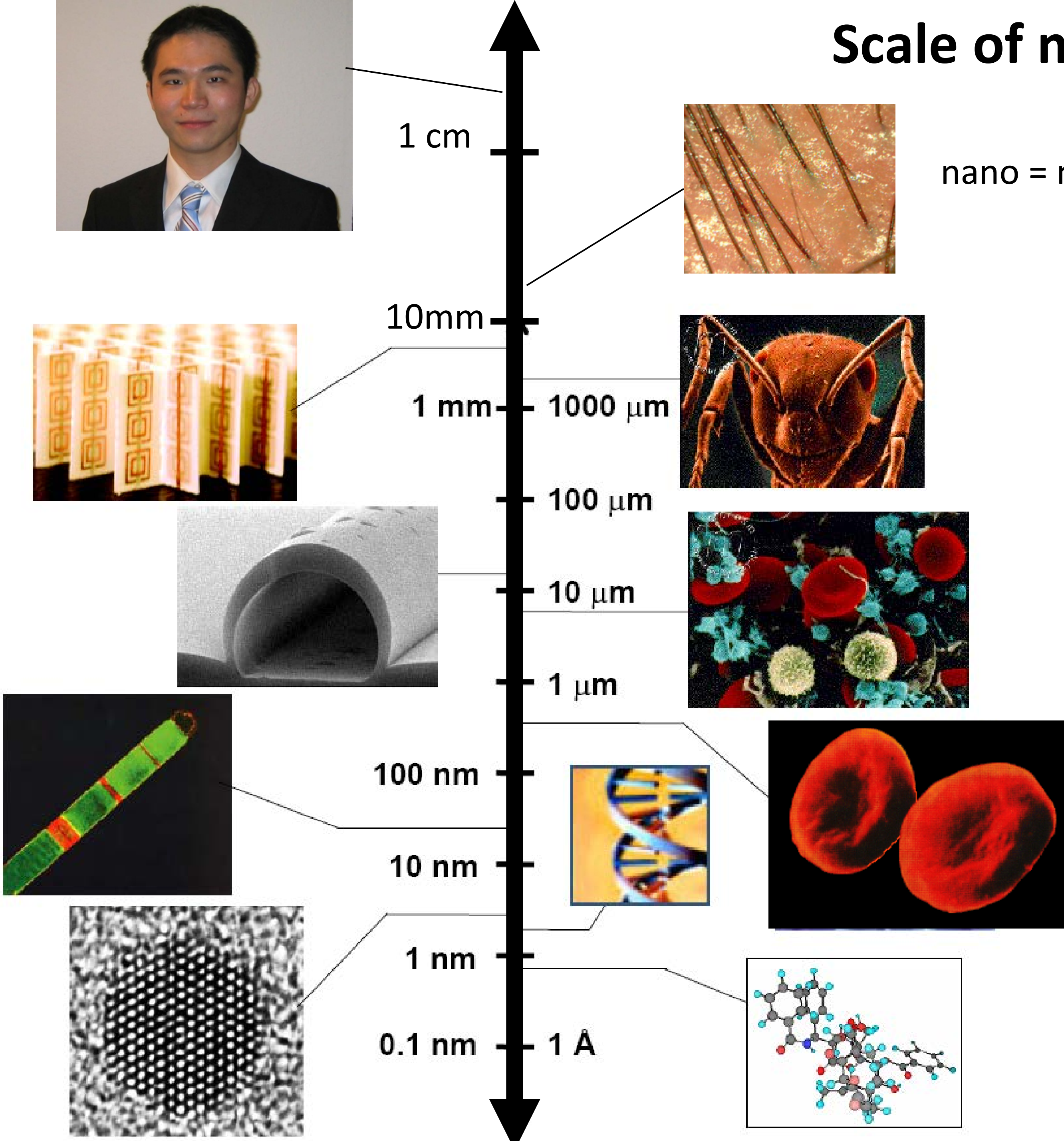
奈米材料於綠能科技的應用

Hsing-Yu Tuan (段興宇)

Assistant Professor in Chemical Engineering,
National Tsing Hua University

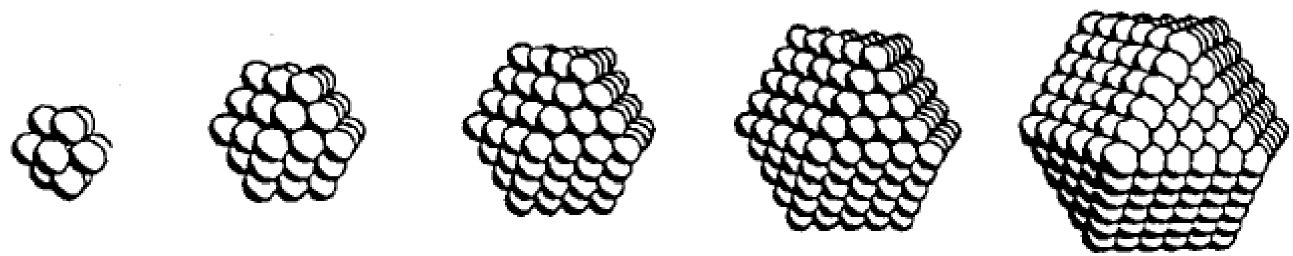
Scale of materials

nano = n = 10^{-9}



Inorganic Nanomaterials: a inorganic kind of polymer

Full-shell "magic number" clusters

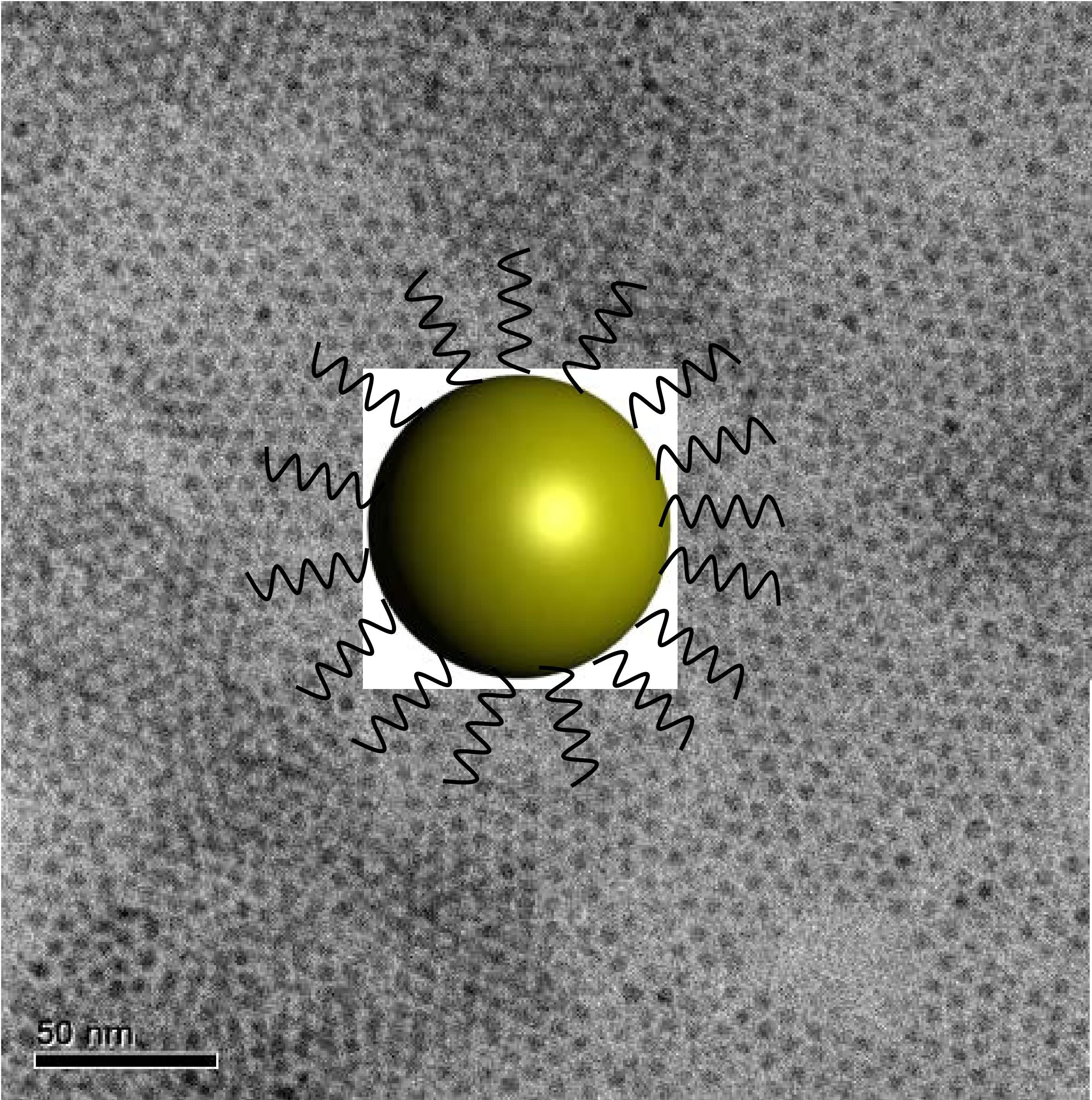


Number of shells	1	2	3	4	5
Number of atoms in cluster	13	55	147	309	561
Percentage of surface atoms	92	76	63	52	45

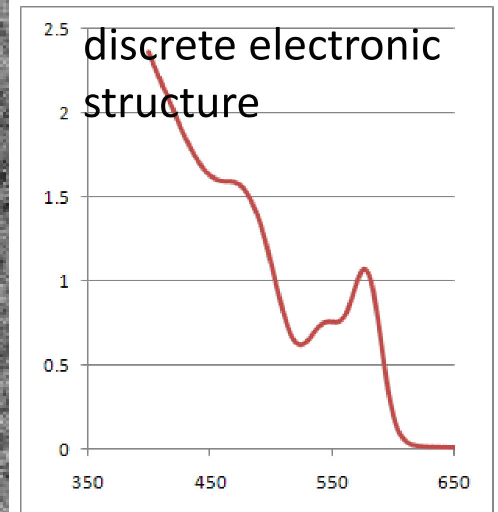
Figure 4. Idealized representation of full-shell metal clusters with "magic numbers" of atoms, which are built upon the densest sphere packing (modified with permission from ref. [49c], copyright 1999 Elsevier).

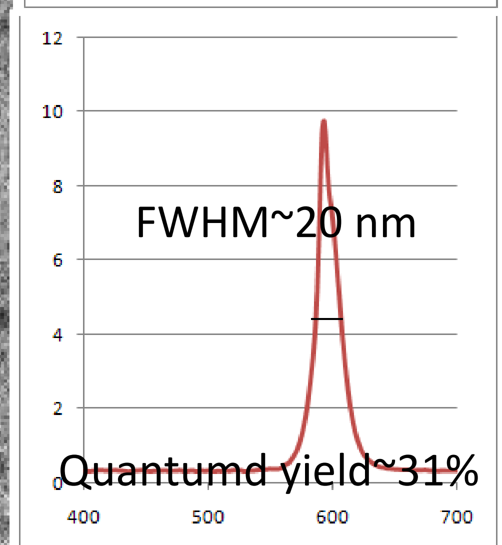
-For example,….Au13, Au20, Pt38, Au55, Rh55, Pt309, Pd561, Pd1415, Pd2057…
-n could be over million

CdSe nanocrystals

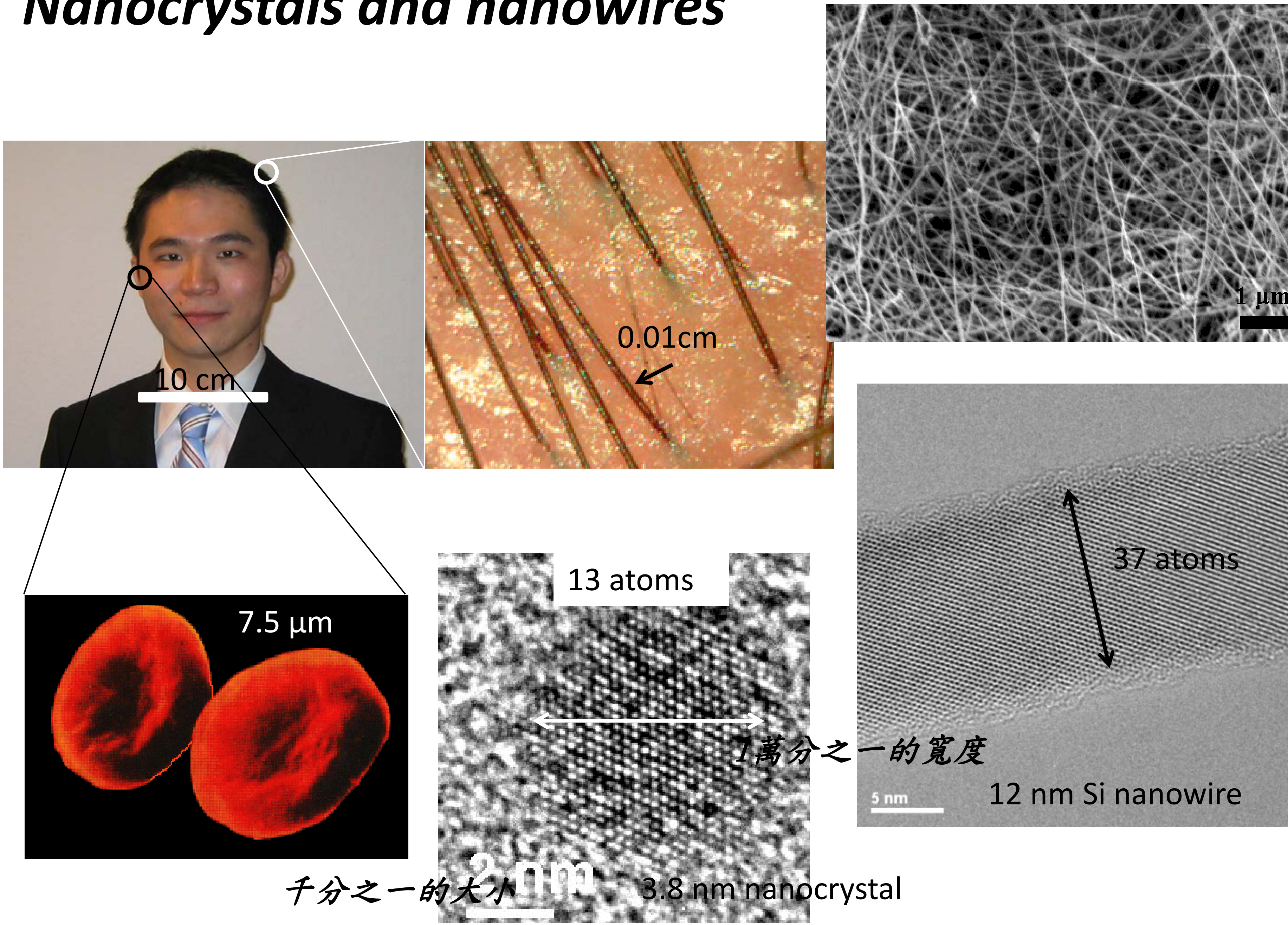


Average:4.69nm
Size variation less
Than 20%

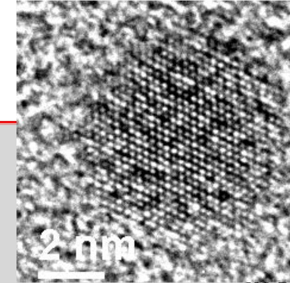




Nanocrystals and nanowires



Periodic Table of the Elements



	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 Sg	107 Ns	108 Hs	109 Mt	110 110	111 111	112 112	113 113					

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Nanomaterials for Energy: Niche

Size and shape-dependent properties

Cost effective Large-Scale Production

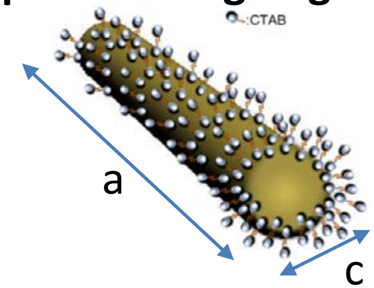
Nano-scale structure/composition engineering via facile synthetic routes

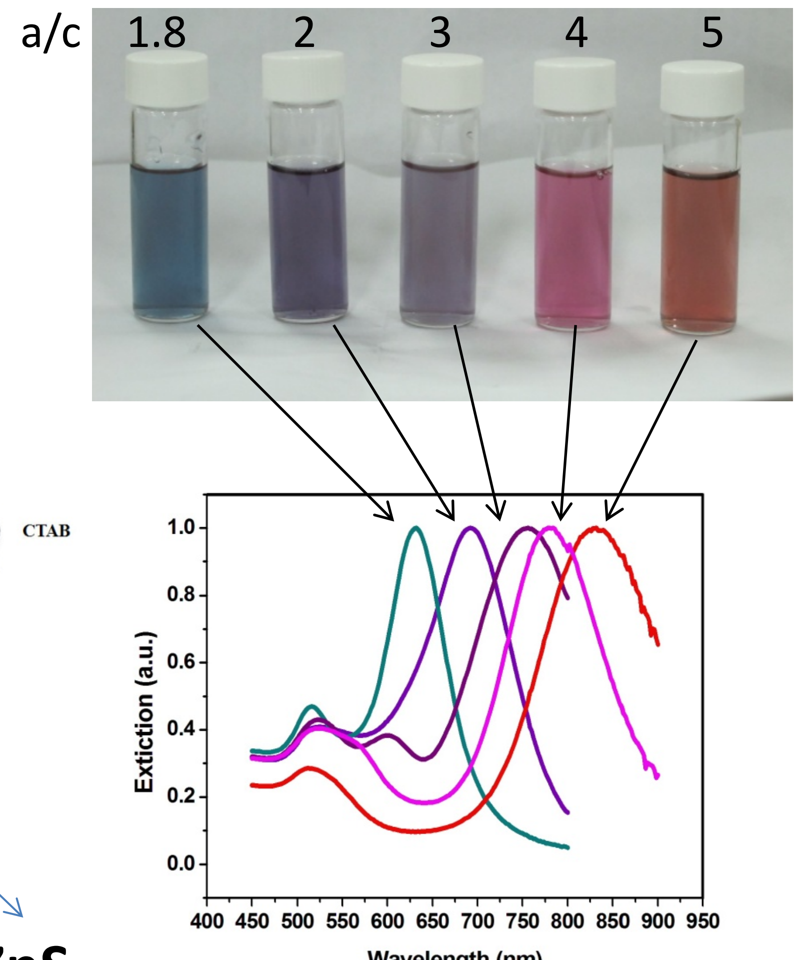
Fast and Continuous processing for device fabrication

Size and shape-dependent properties

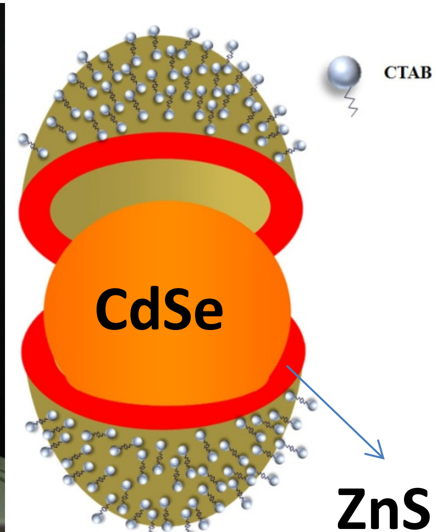
Size Dependent optical properties f CdSe quantum dots

Plasmon absorption tuning of gold nanorods

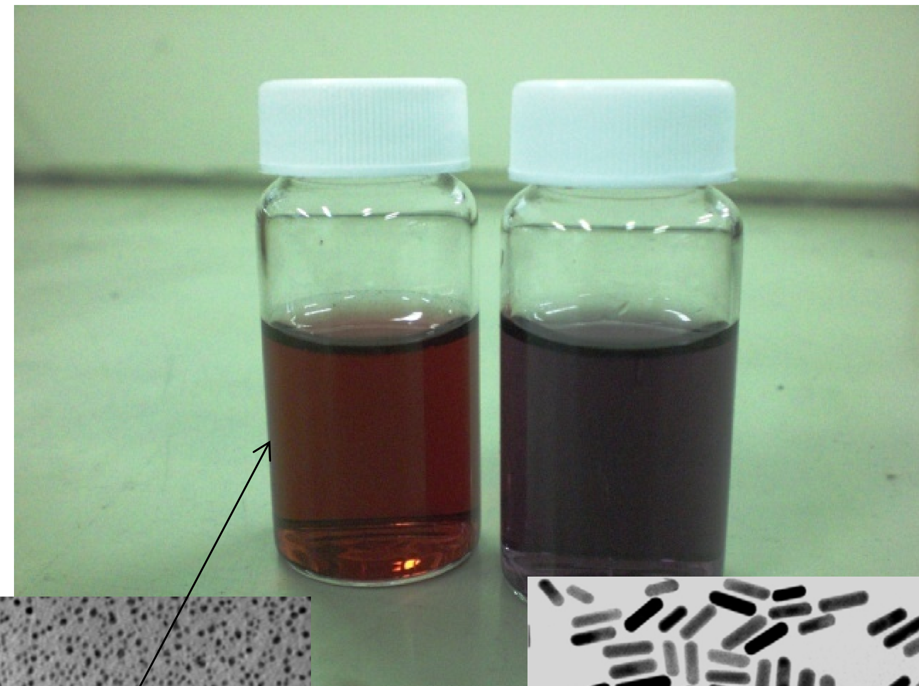


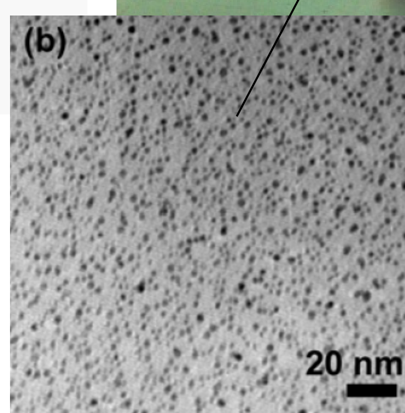


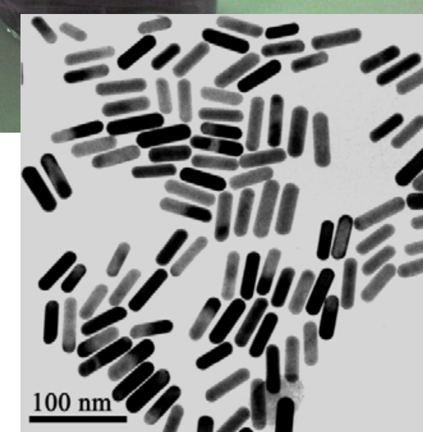
Bright water-soluble CdSe/ZnS/CTAB quantum dots



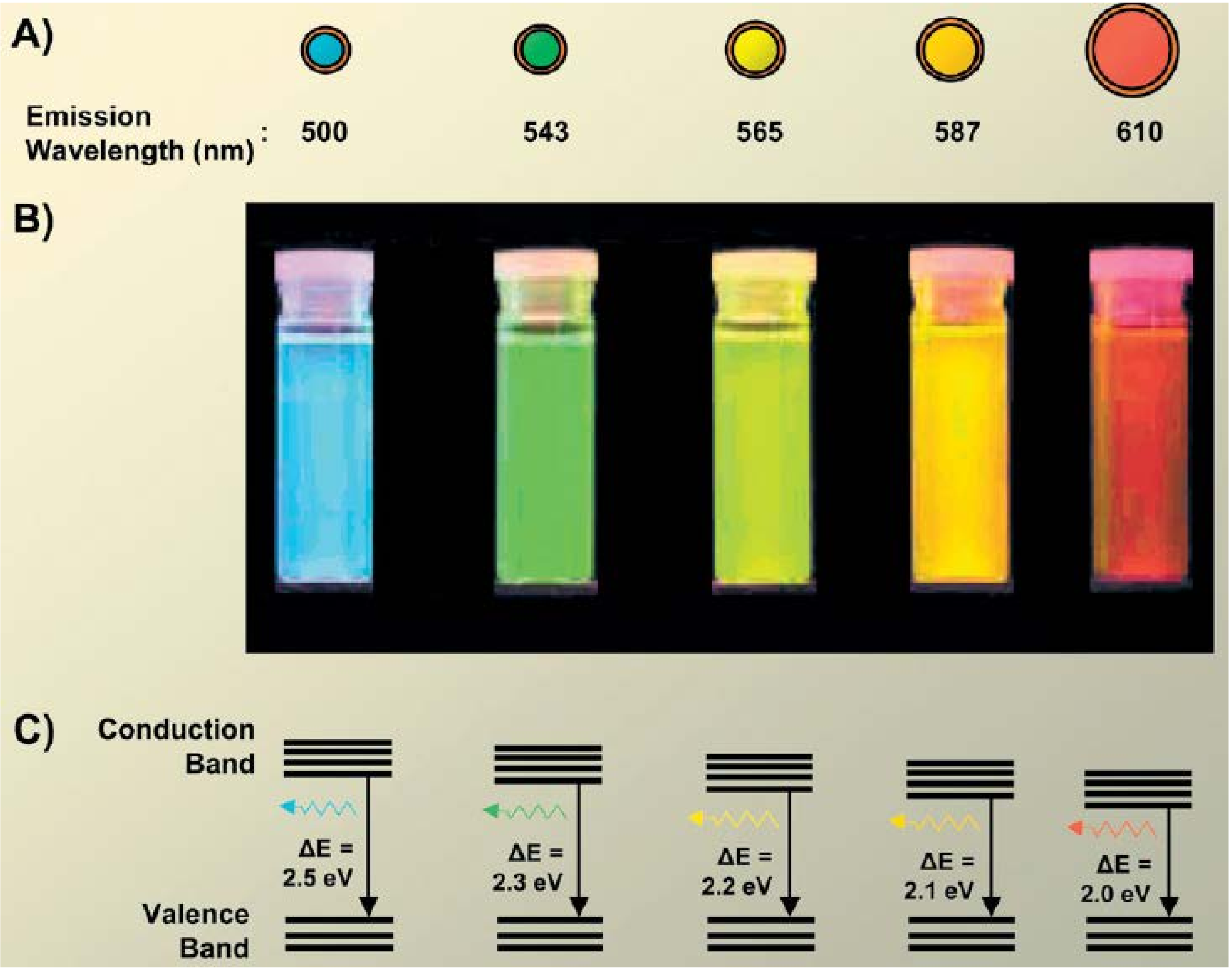
Color comparison between bulk gold and nanogold



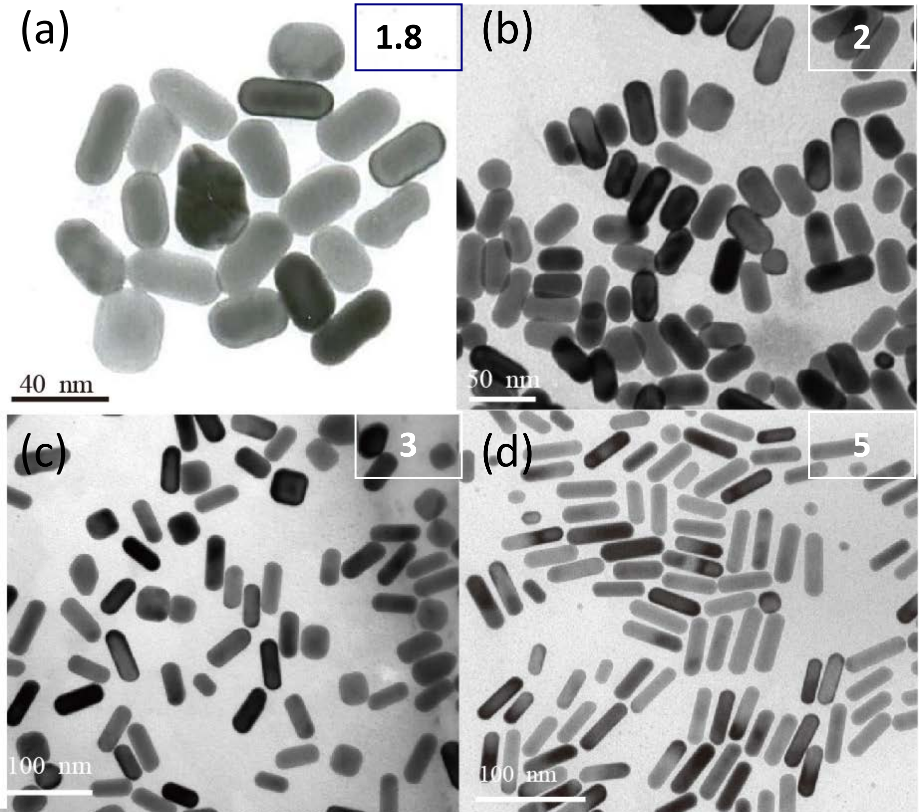


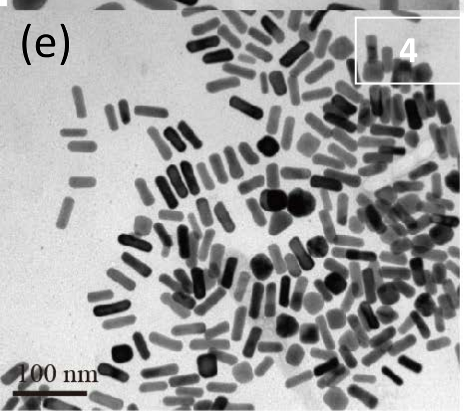


Optical properties of CdSe Qdots



Characteristic of nanomaterials: plasmonic effect

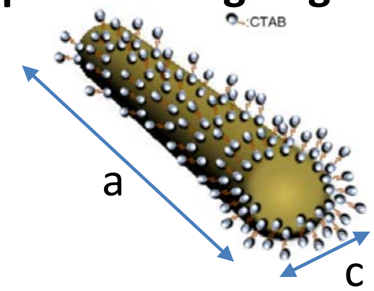


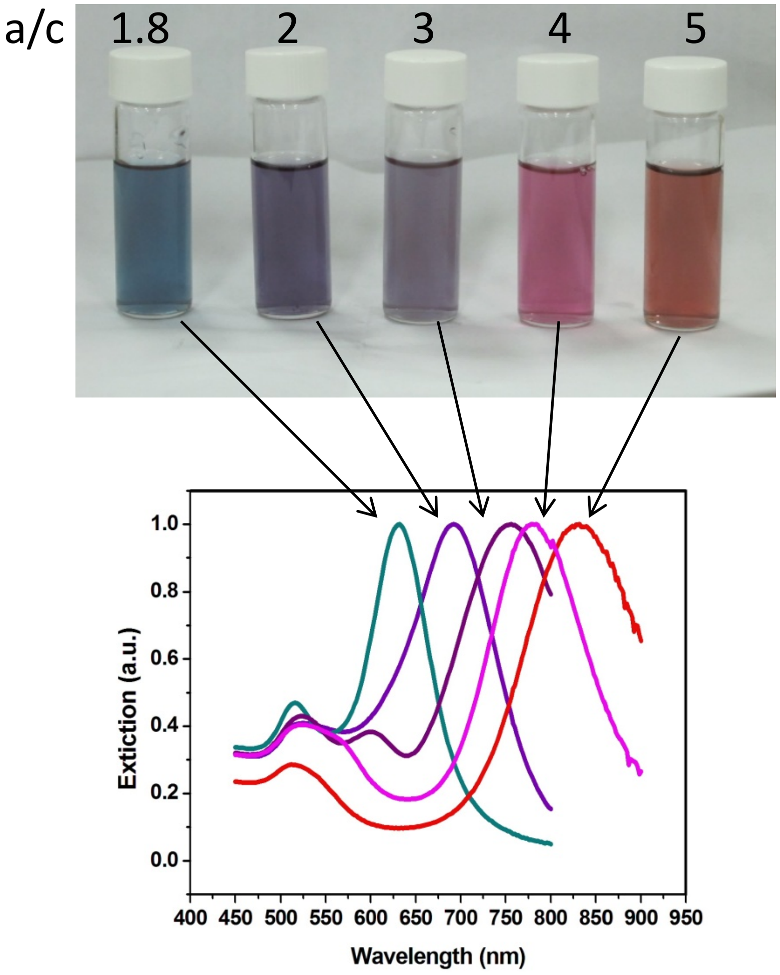


CTAB-GNRs with different aspect ratio from (a)~(e)

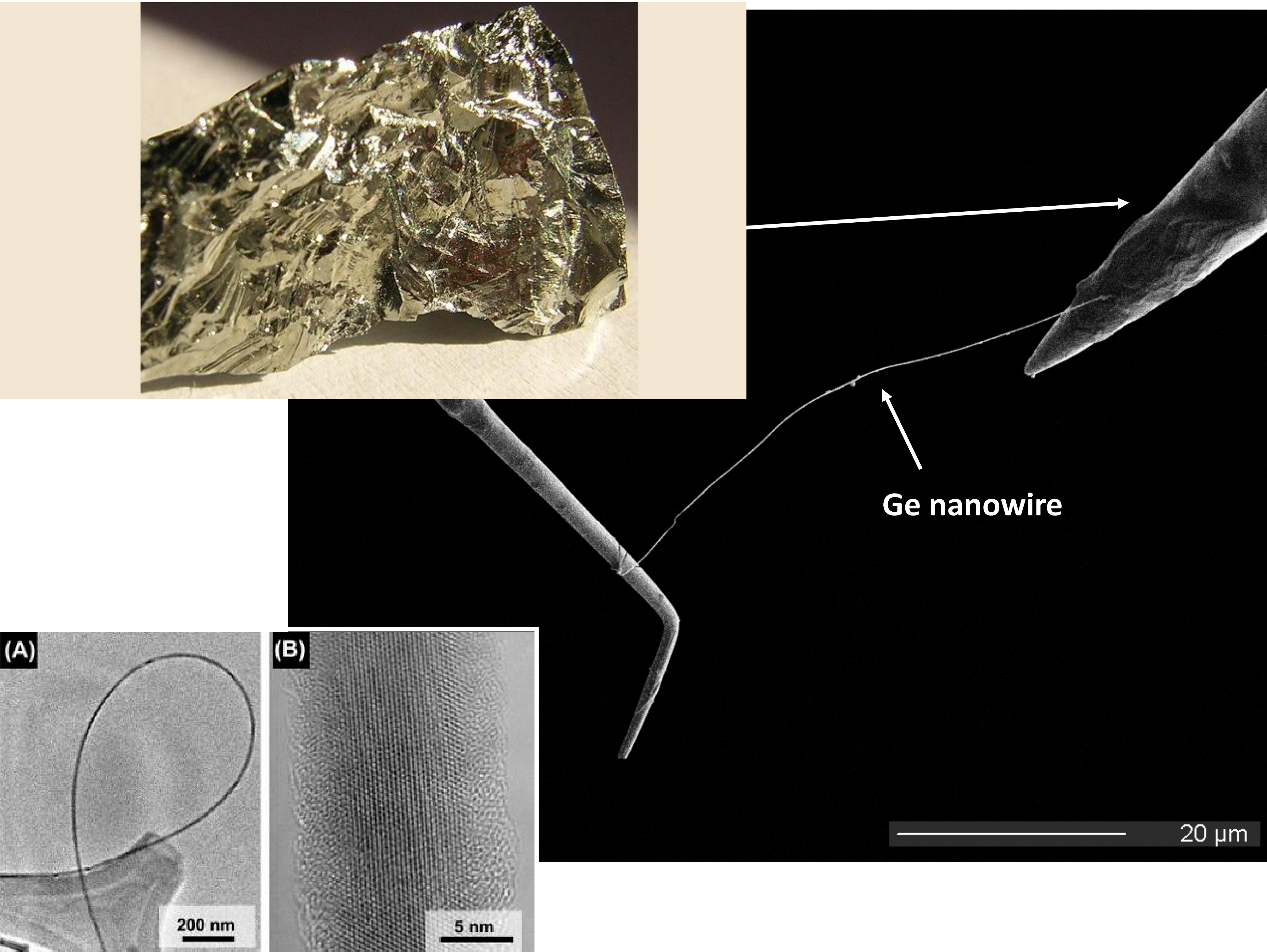
->(1.8~5)

Plasmon absorption tuning of gold nanorods





Characteristic of nanomaterials: flexible mechanics



Various carbon nanomaterials

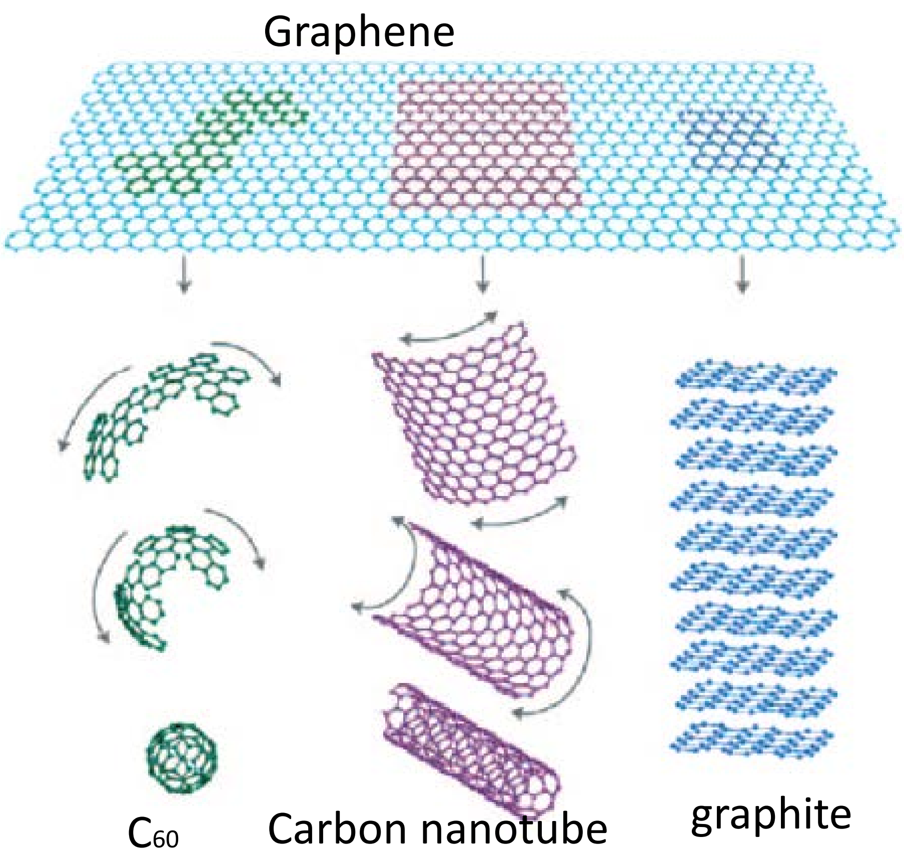
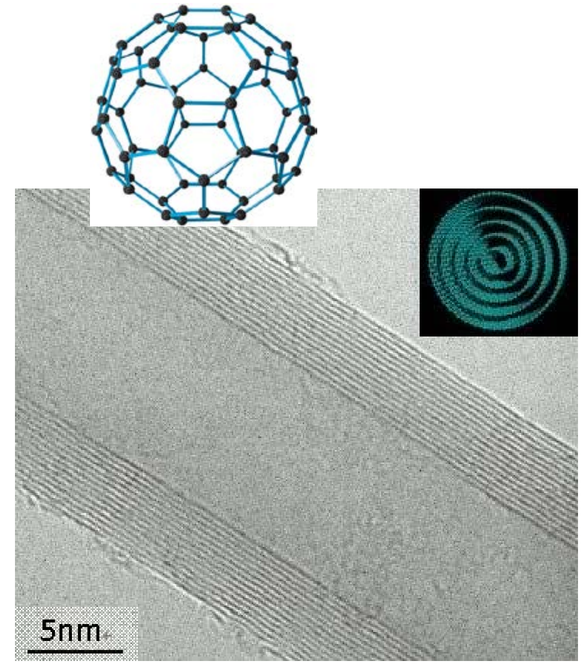
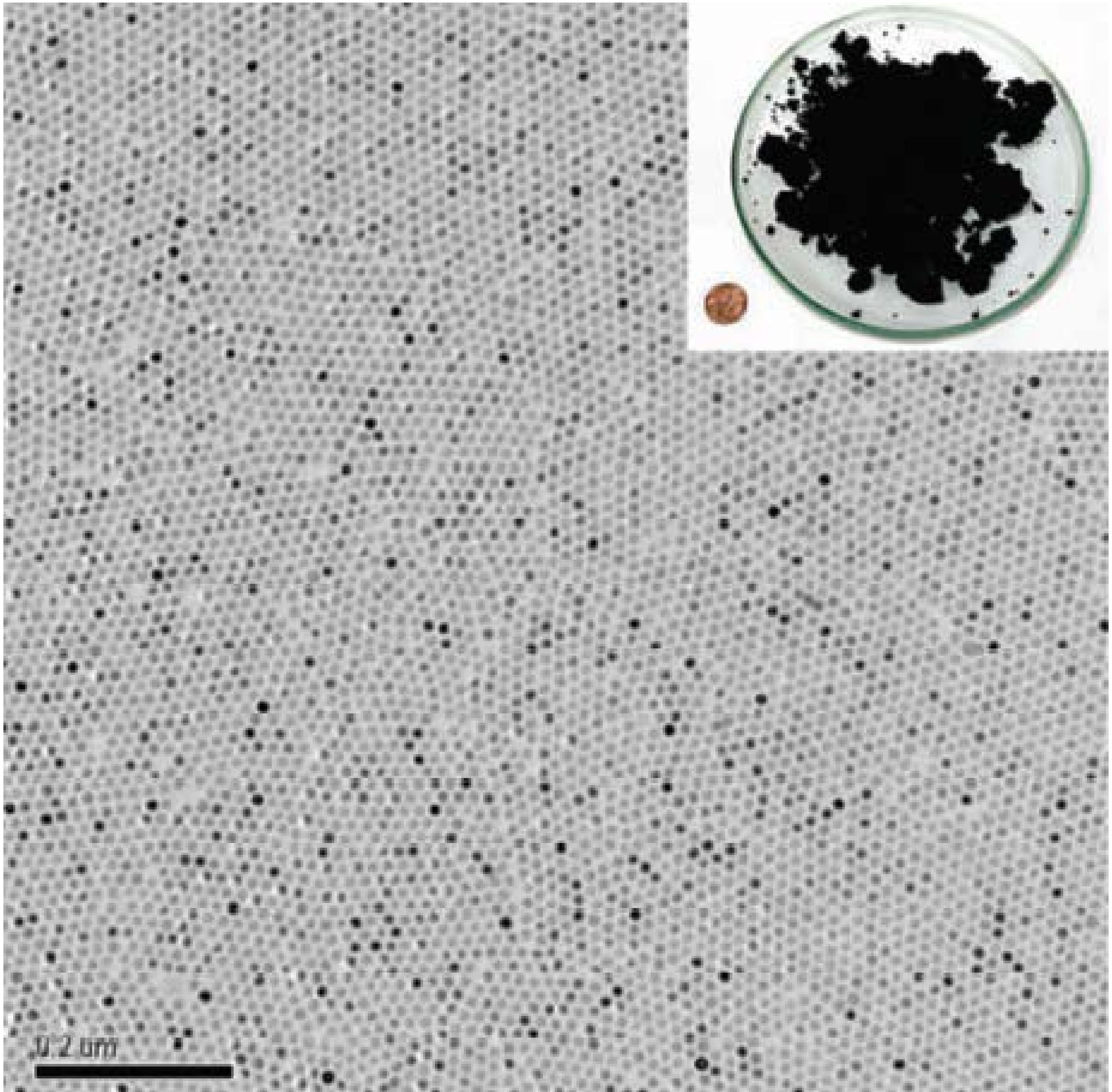


Figure 1. Graphene: the parent of all graphitic forms. (From Ref. [1a].)



Cost effective Large-Scale Production

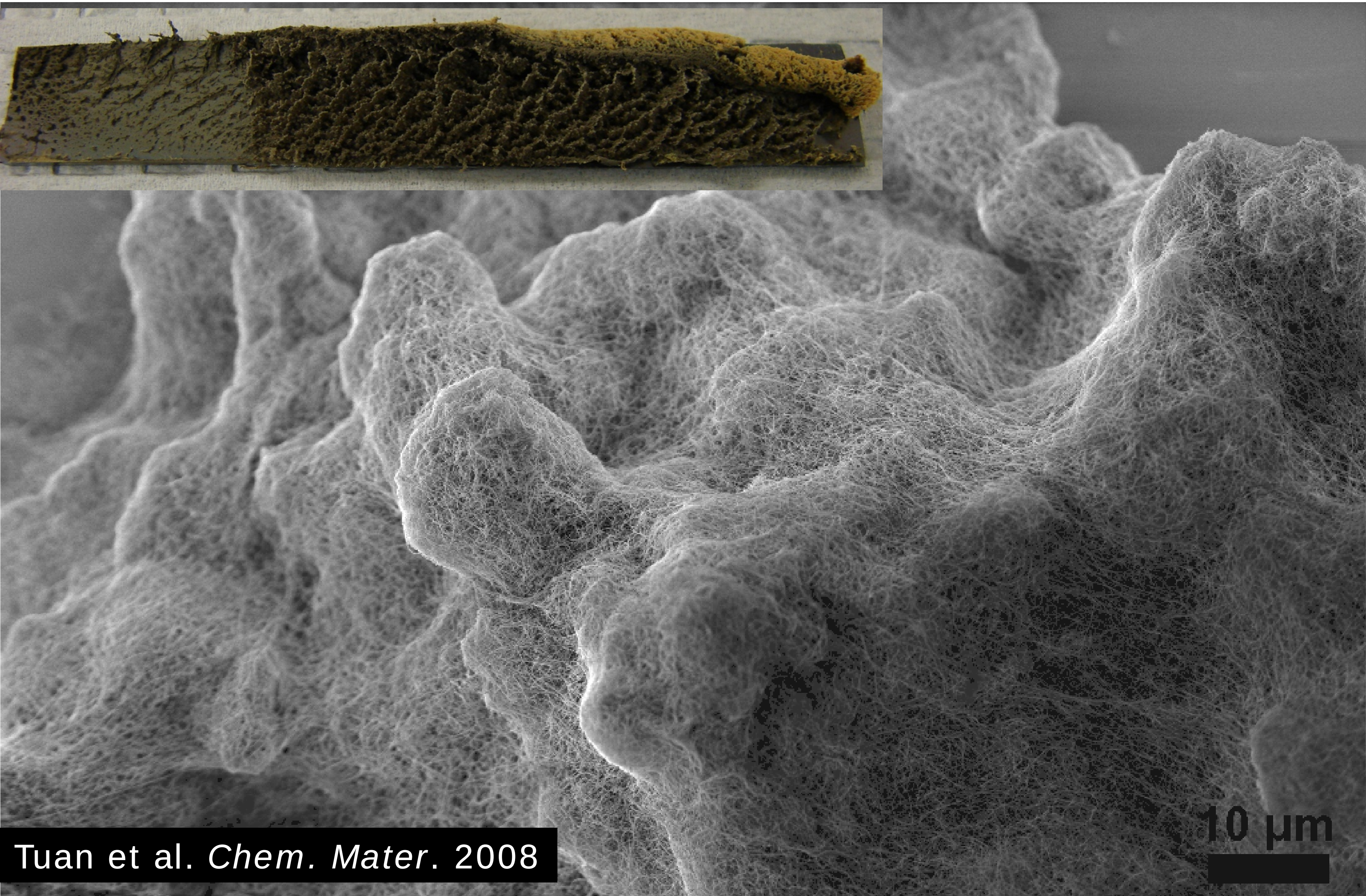
Gram-scale Fe3O4 nanocrystal production



You need larger glassware

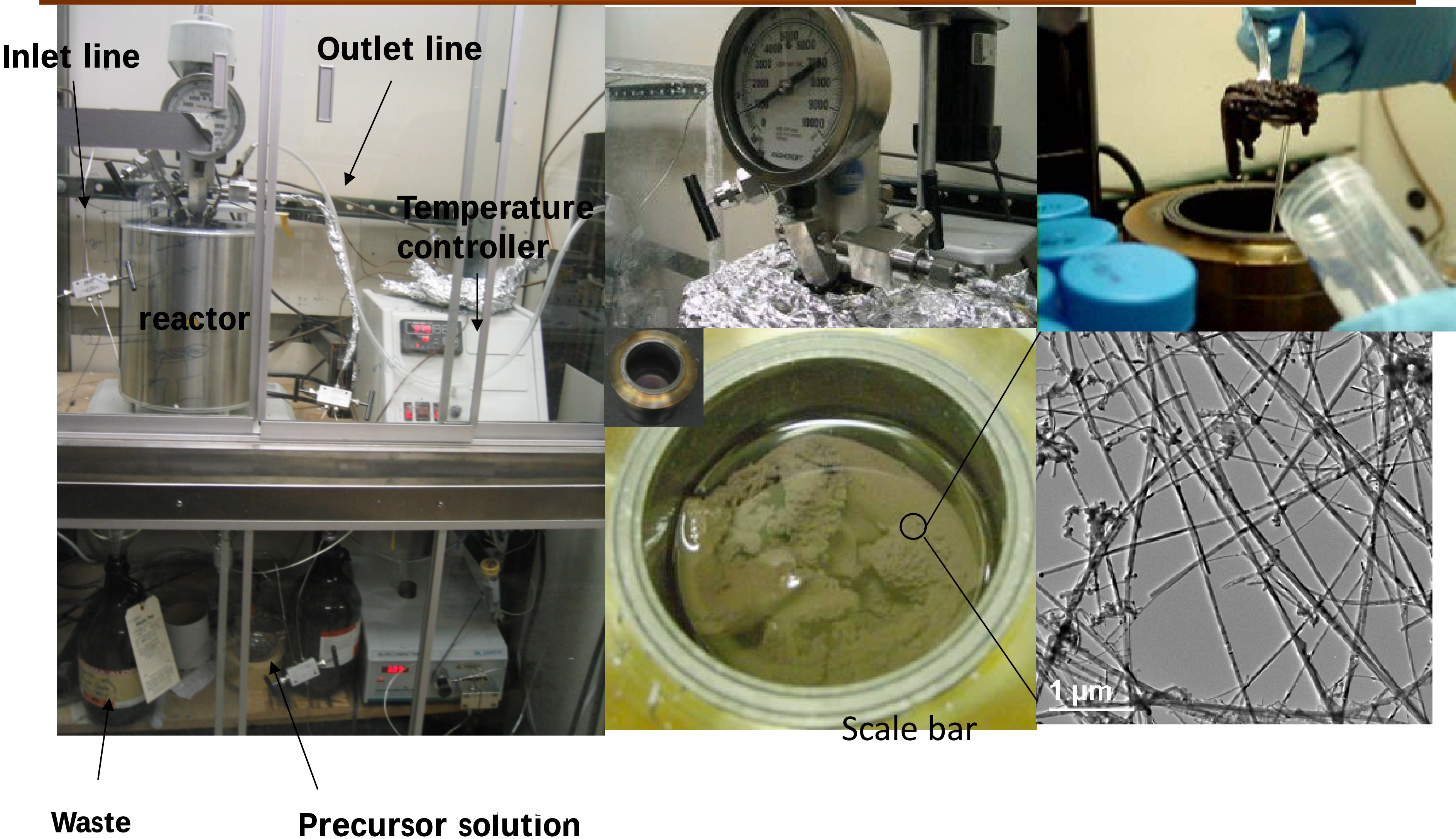
Hyeon et al., *Nat. Mater.*, 2004

Chemical Engineering: Scale-Up synthesis of Silicon Nanowires



Tuan et al. *Chem. Mater*. 2008

Chemical Engineering: Scale-Up synthesis of Silicon Nanowires



250 ml Parr reactor operation

~1 gram germanium nanowires
~high quality, pure nanowires

Large-scale Synthesis of Nanomaterials

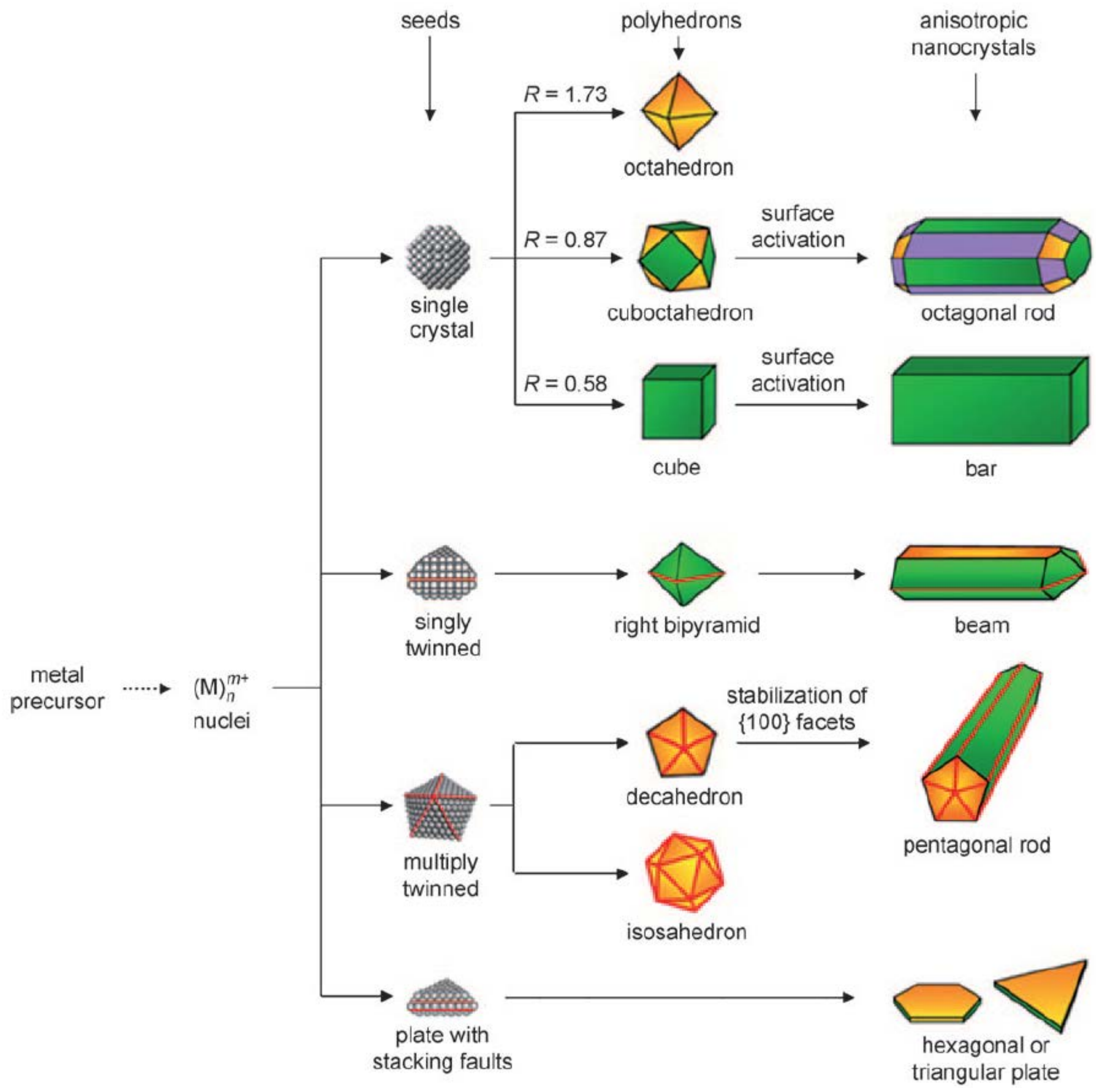
-Kg/day production!

-Chemists investigate new chemistry

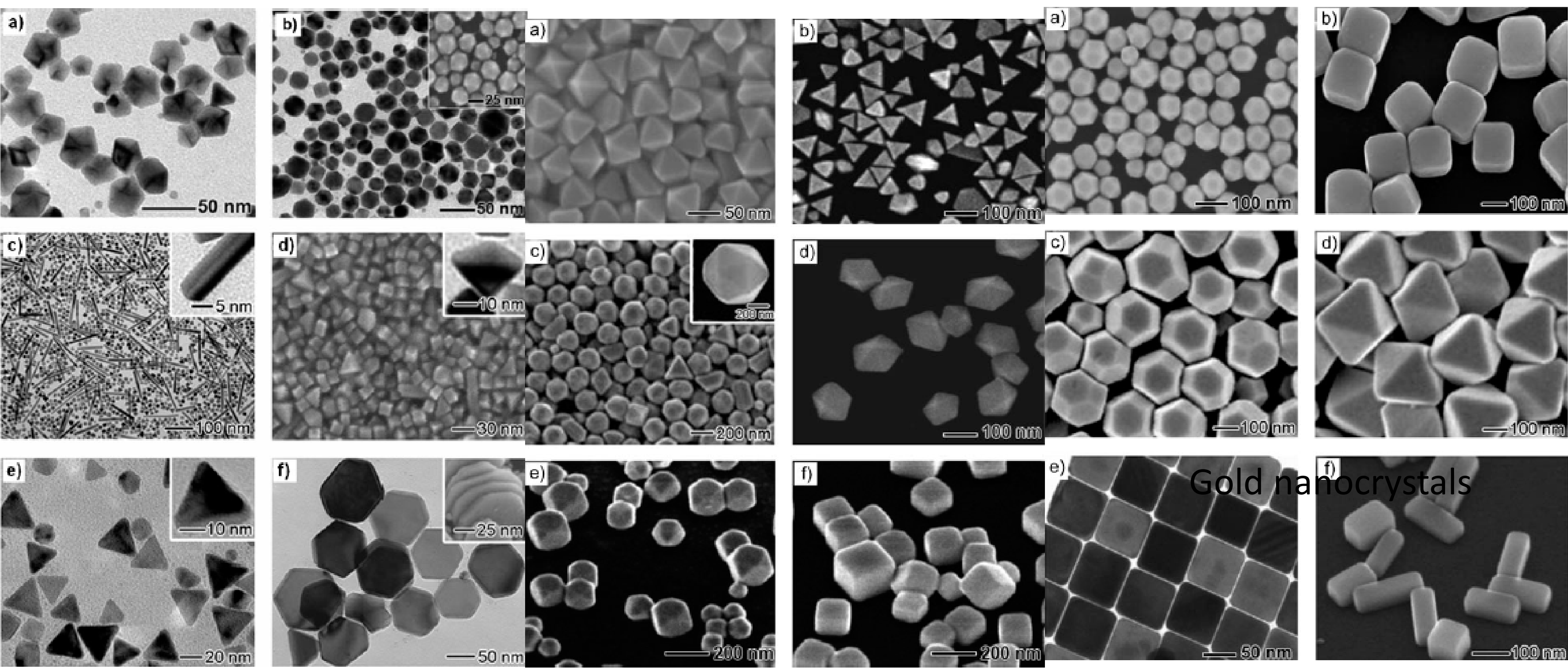
-Chemical Engineers develop the large-scale process ---←$$$$$$$$

Nano-scale structure/composition engineering via facile synthetic routes

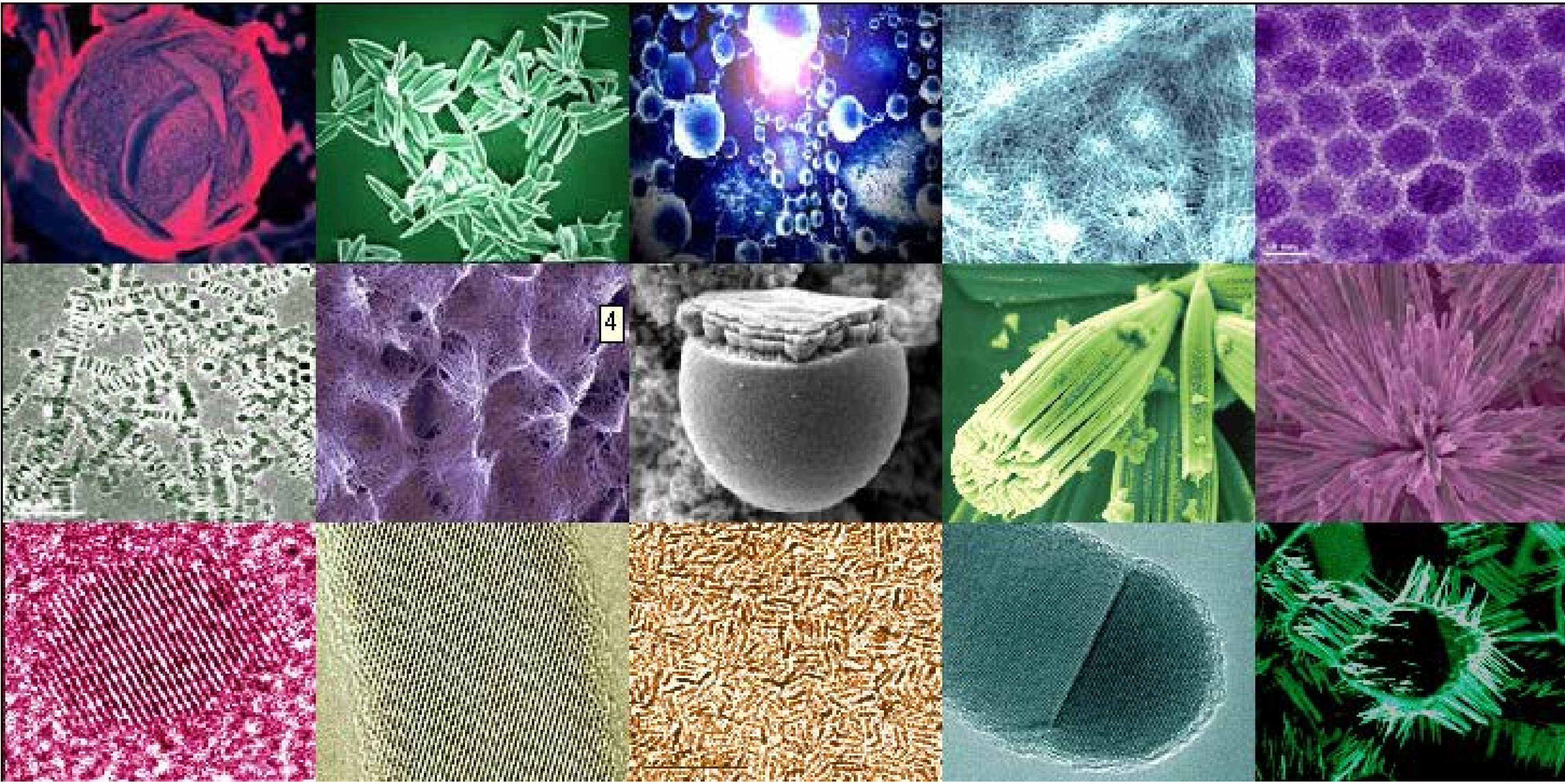
Artificial design of nanostructures



Morphology control of nanostructures

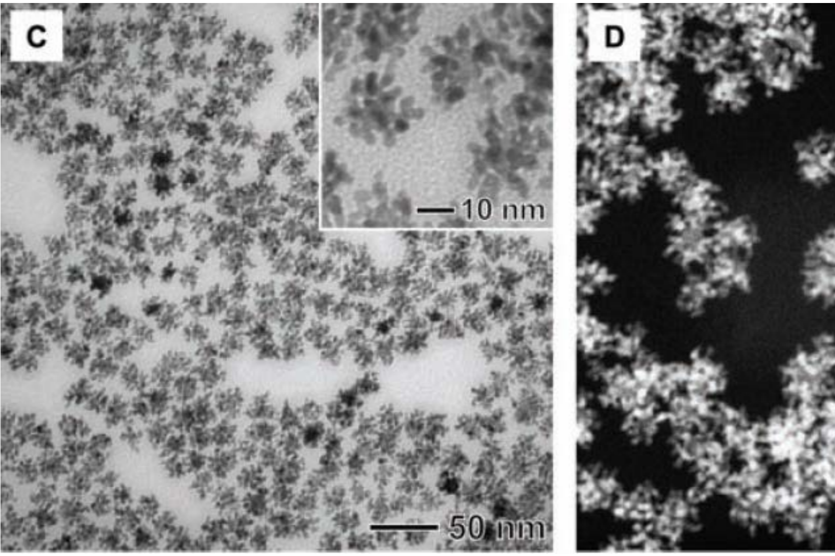


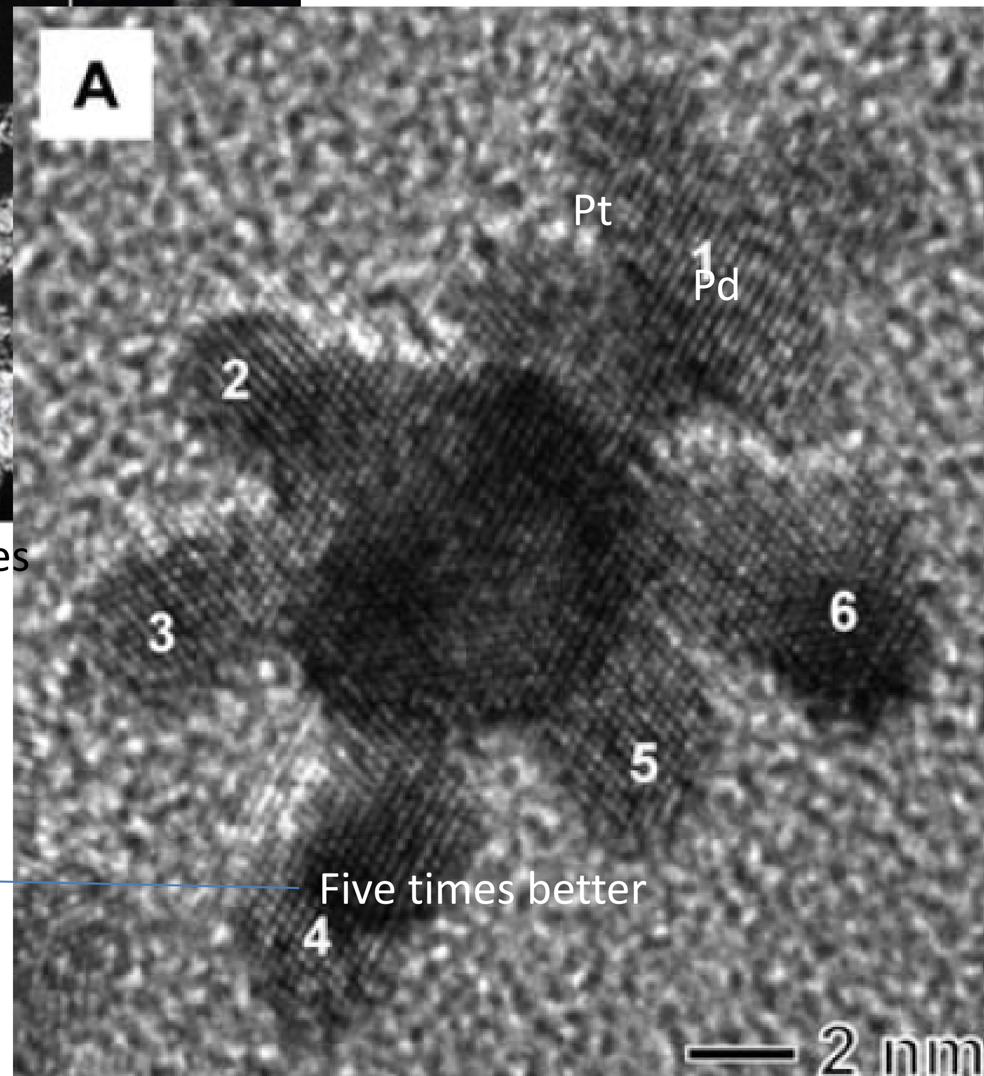
Size, shape, and structure control of various nanomaterials



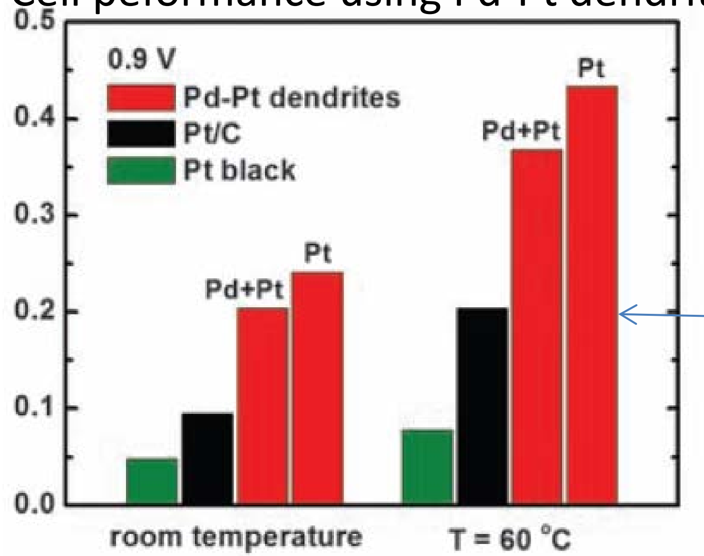
Interested materials: Au、Ag、Cu、Fe、Si、Ge、ZnO、TiO2、CIGS、NaYF4:Er+2

Ultrahigh surface area of nanocrystals

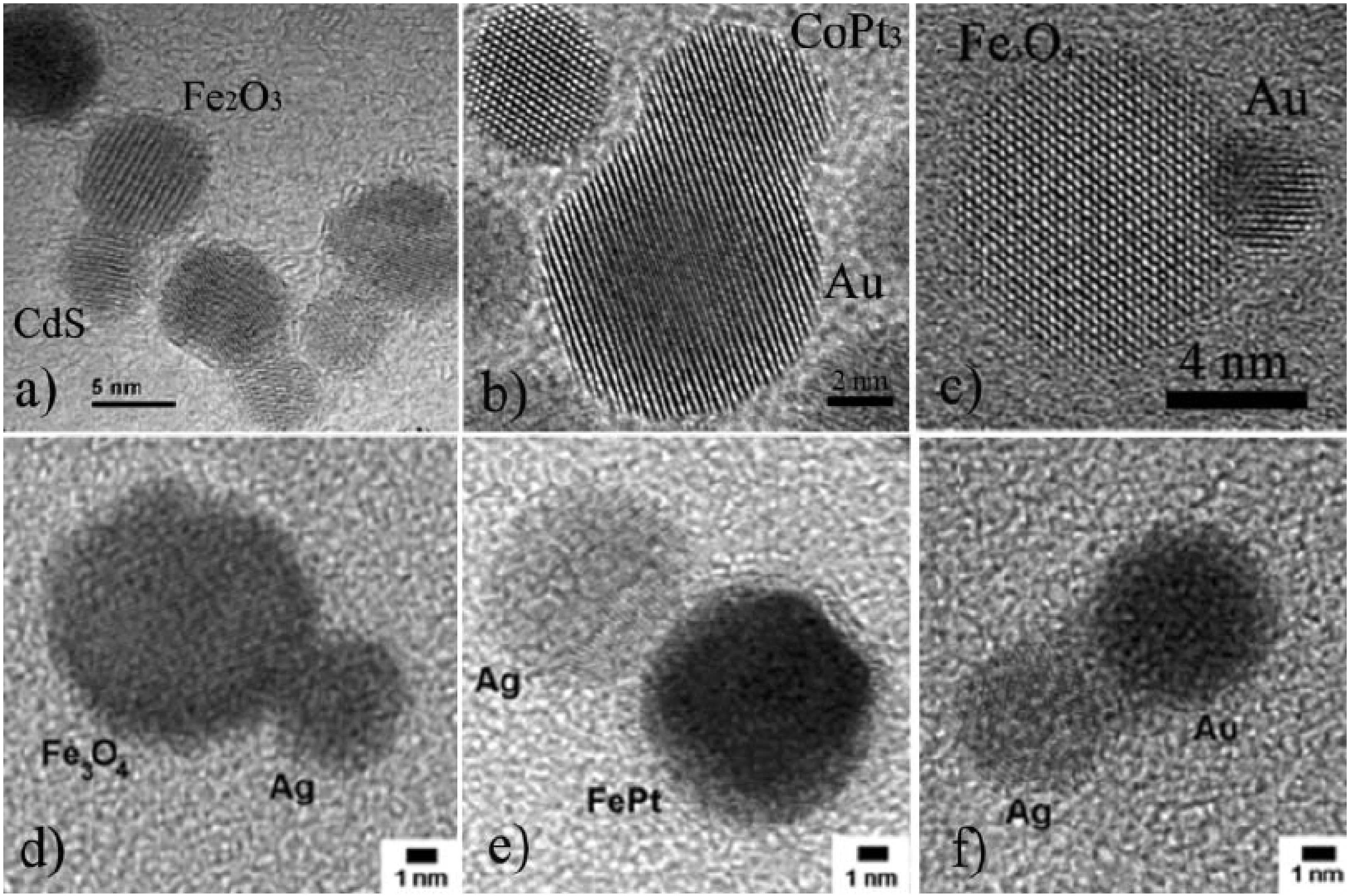




Fuel Cell peformance using Pd-Pt dendrites

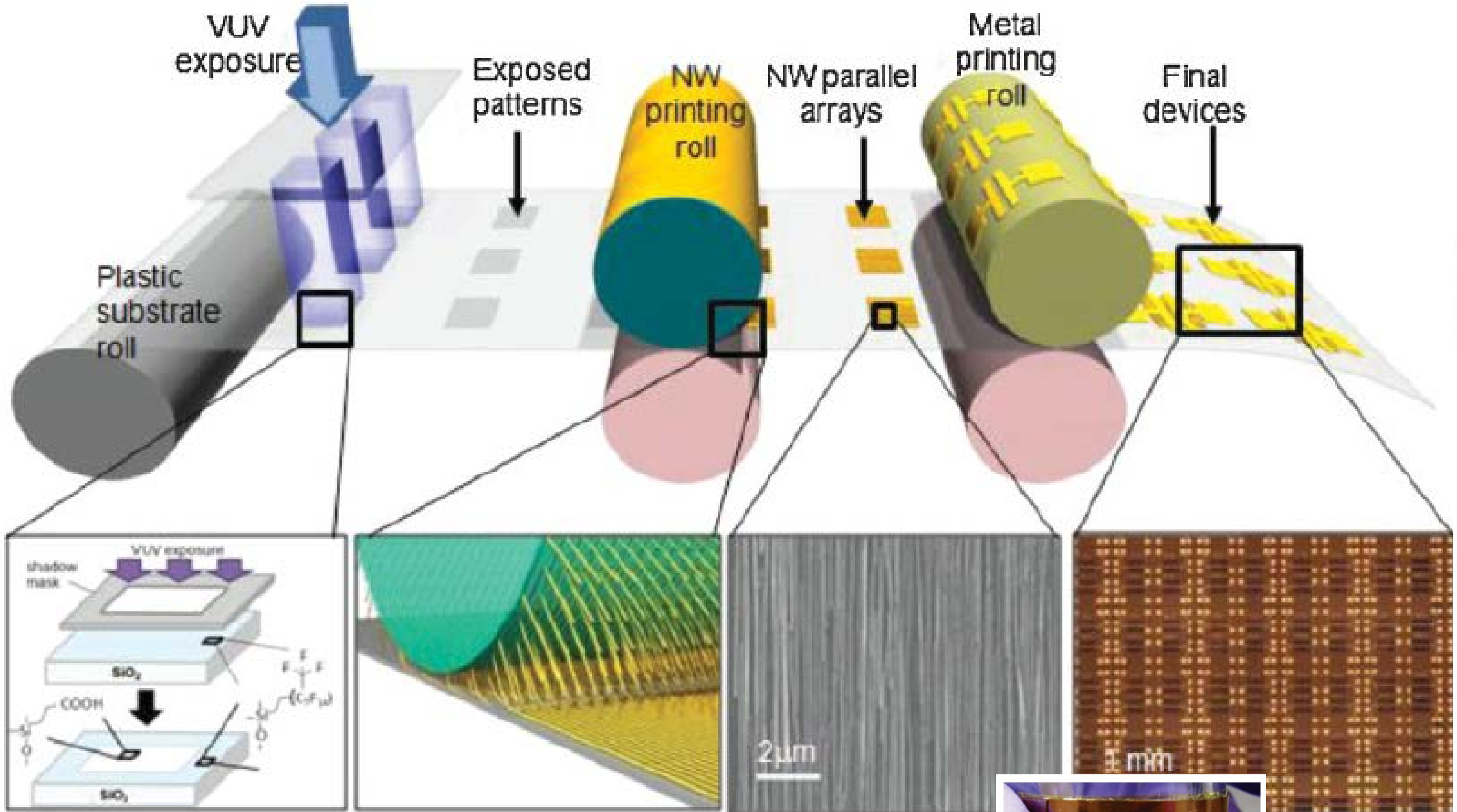


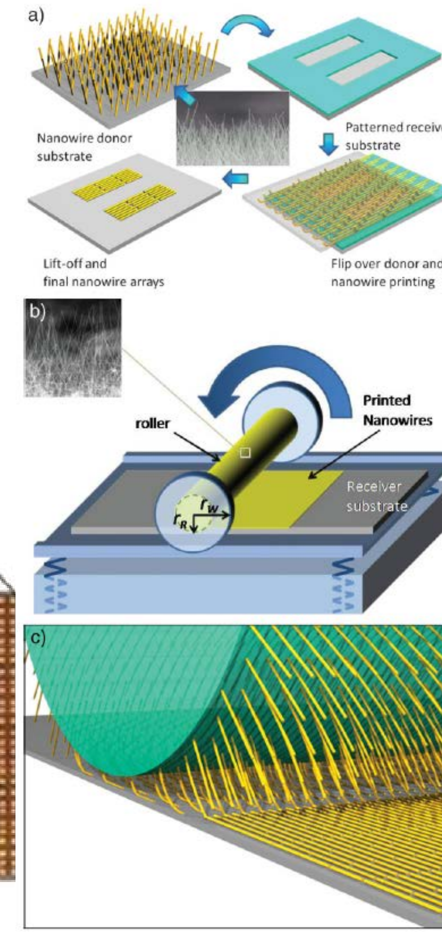
Heterodimers and oligomers of nanocrystals

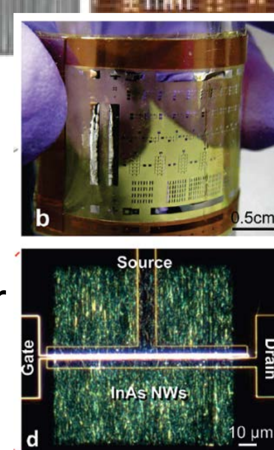


Fast and Continuous processing for device fabrication

Cost-effective processing: Roll-to-Roll and nonvacuum







High-performance silicon nanowire transistor as a ultrasensitive biosensor

Javey et al., *Adv Mater.* 2009

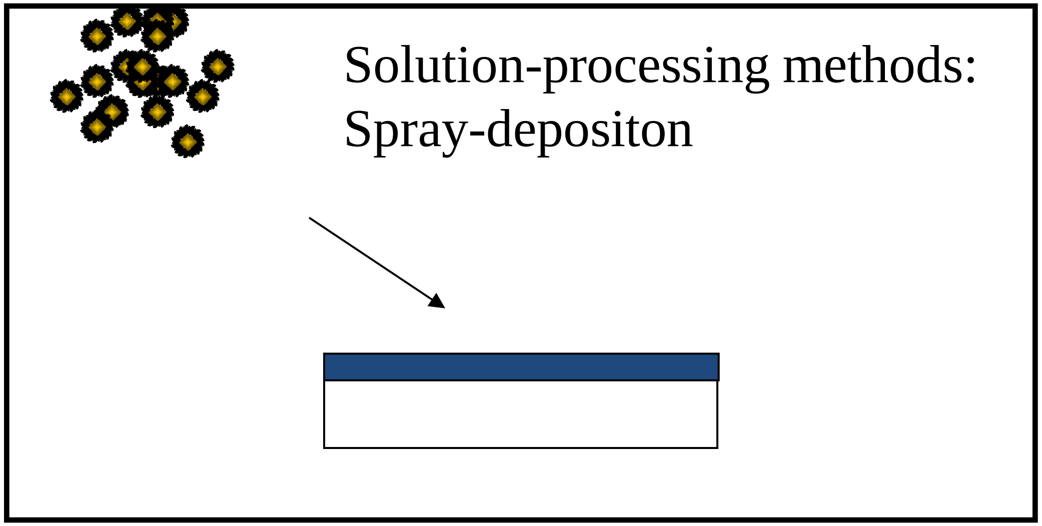
Tuan et al., *Angew Chemie*. 2005

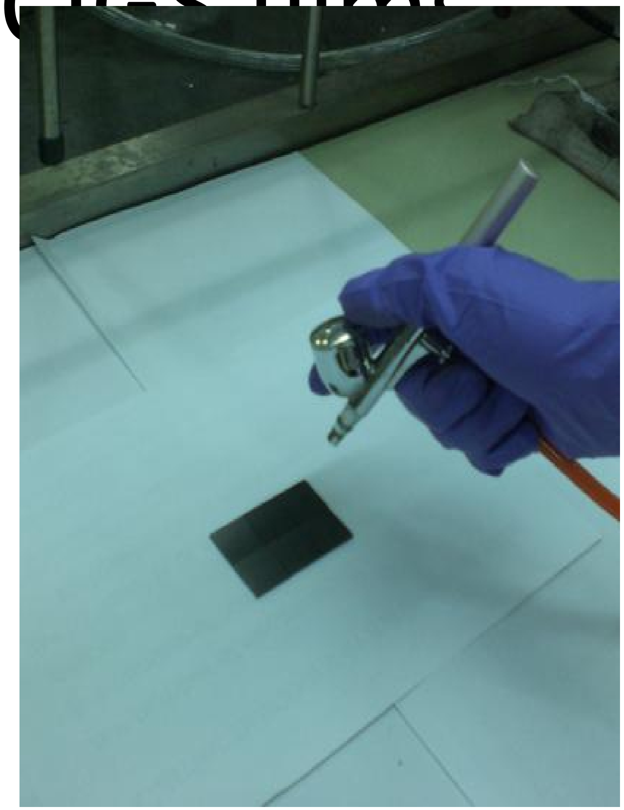
Whang et al., *Nano Lett*. 2003

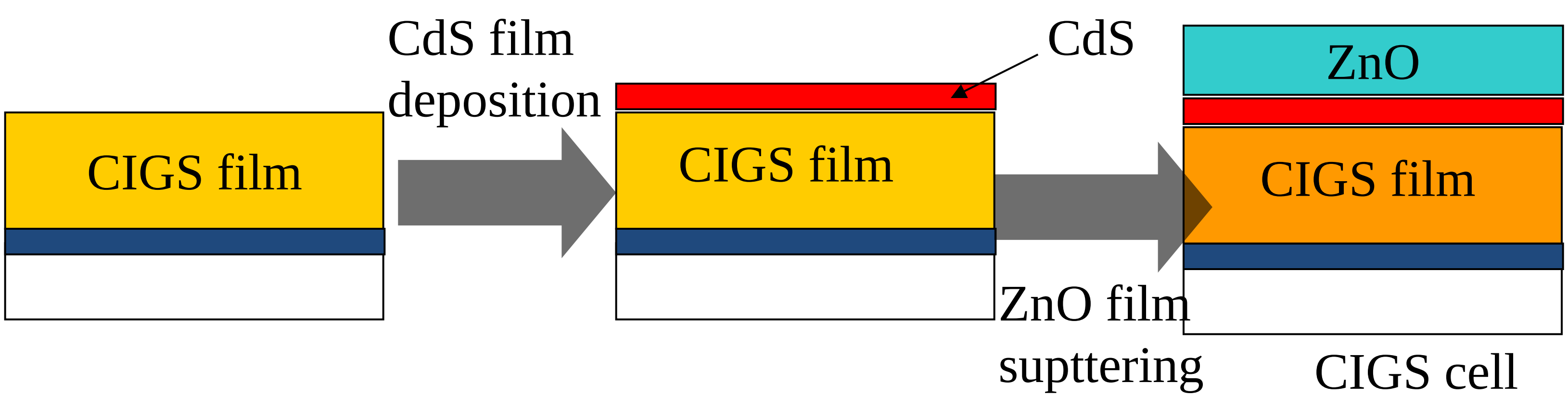
Whang et al., *Nano lett*. 2003

Andrew B et al., *App. Phys. Lett*.,2005

Spray deposition of CIGS films

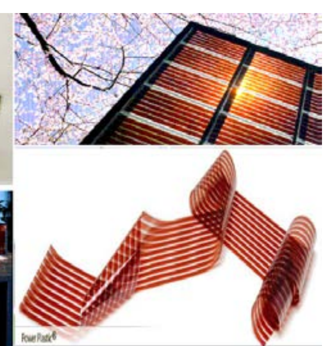


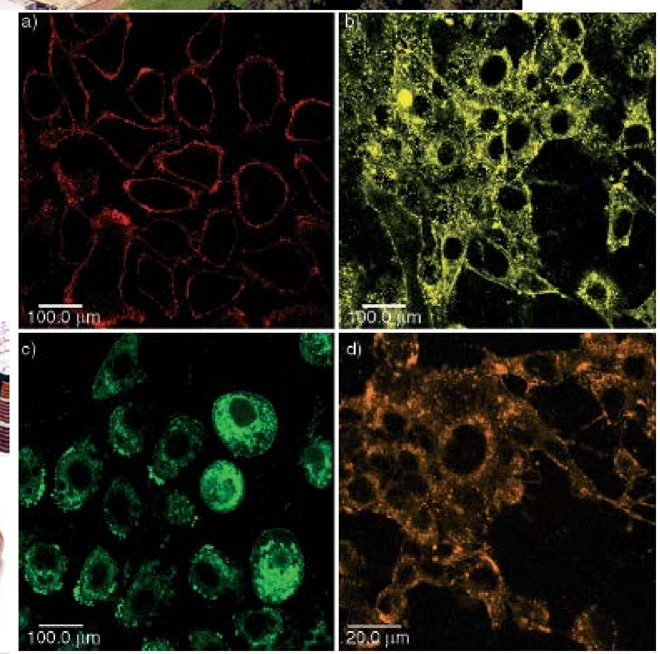




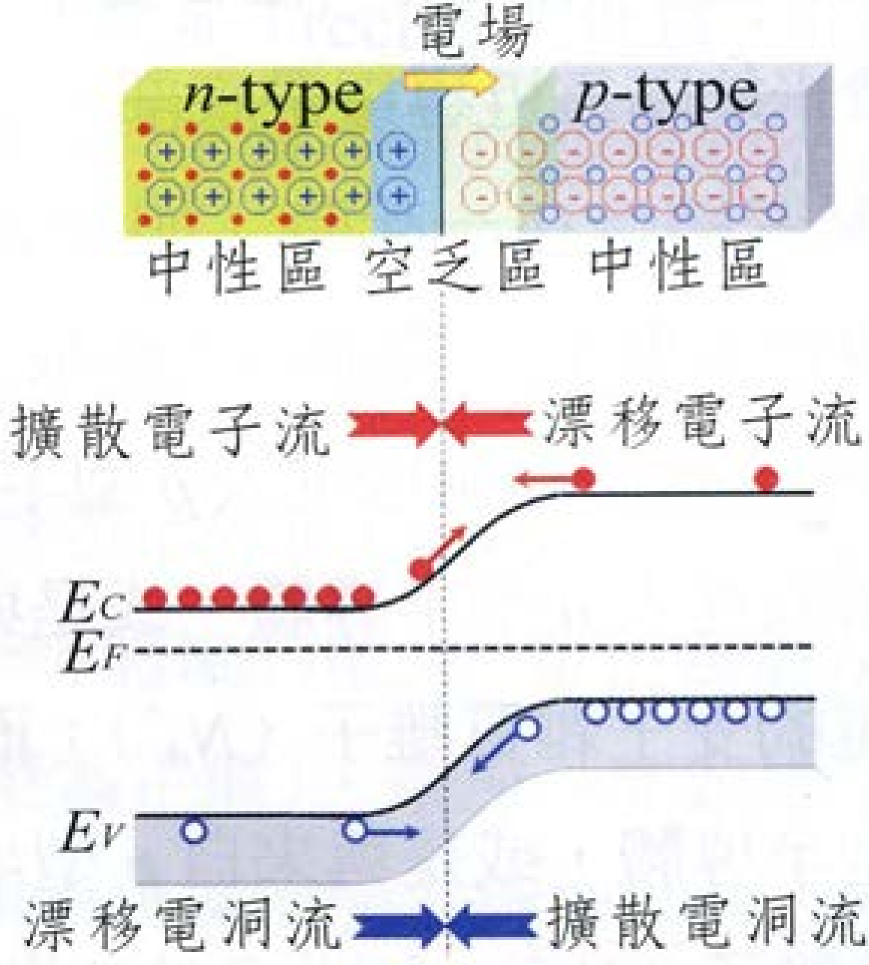
Nanomaterial Applications

Bio+Energy+Environment, almost everything can be involved



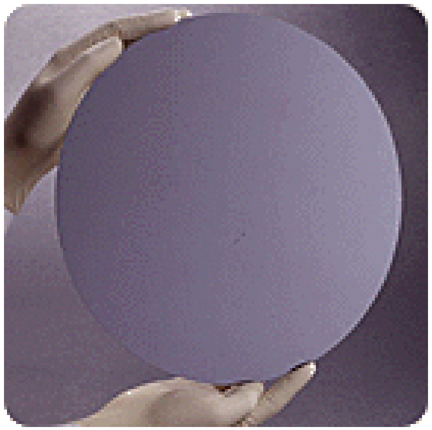


P-N junction : Frame structure for optoelectronic applications



(c)

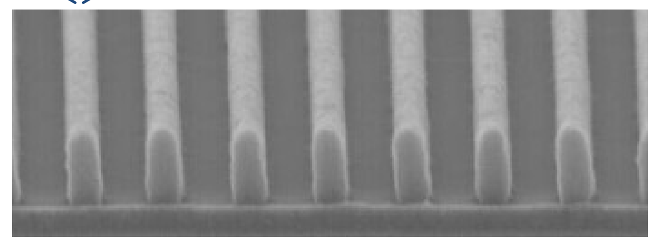
Traditional Si-based semiconductor process



photolithography

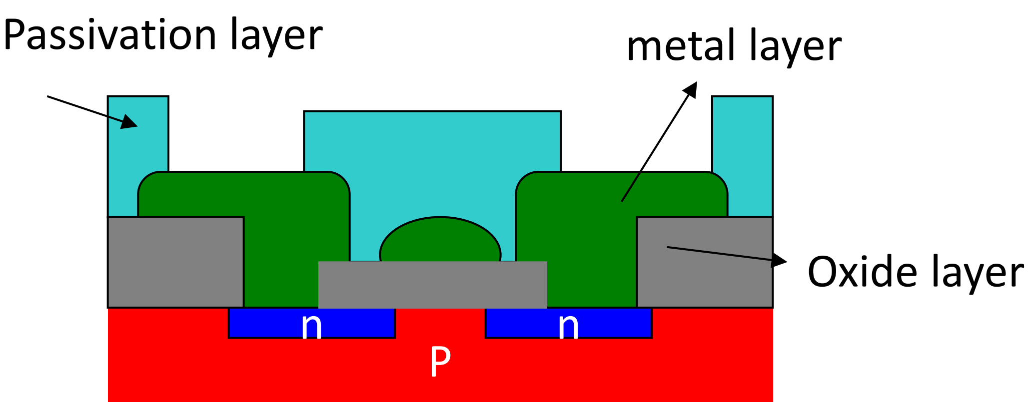
"*Top down*" **photolithography method**

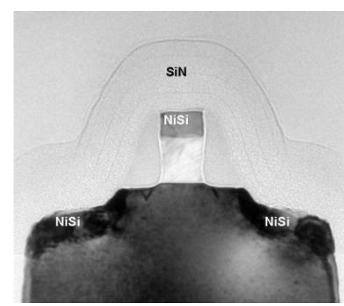
80nm



Pattering,
layering,
, heat treatment
, doping

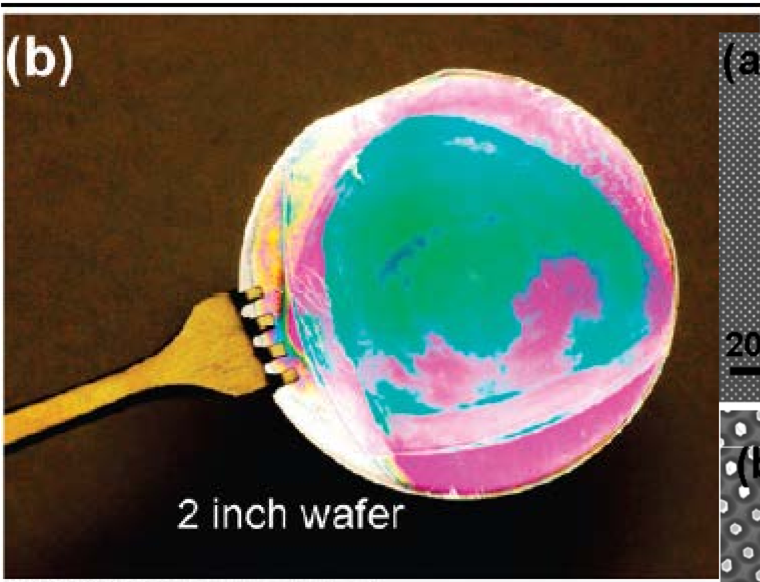
Toward smaller size?
- the resolution limit of photolithography
- the extremely high cost of equipment

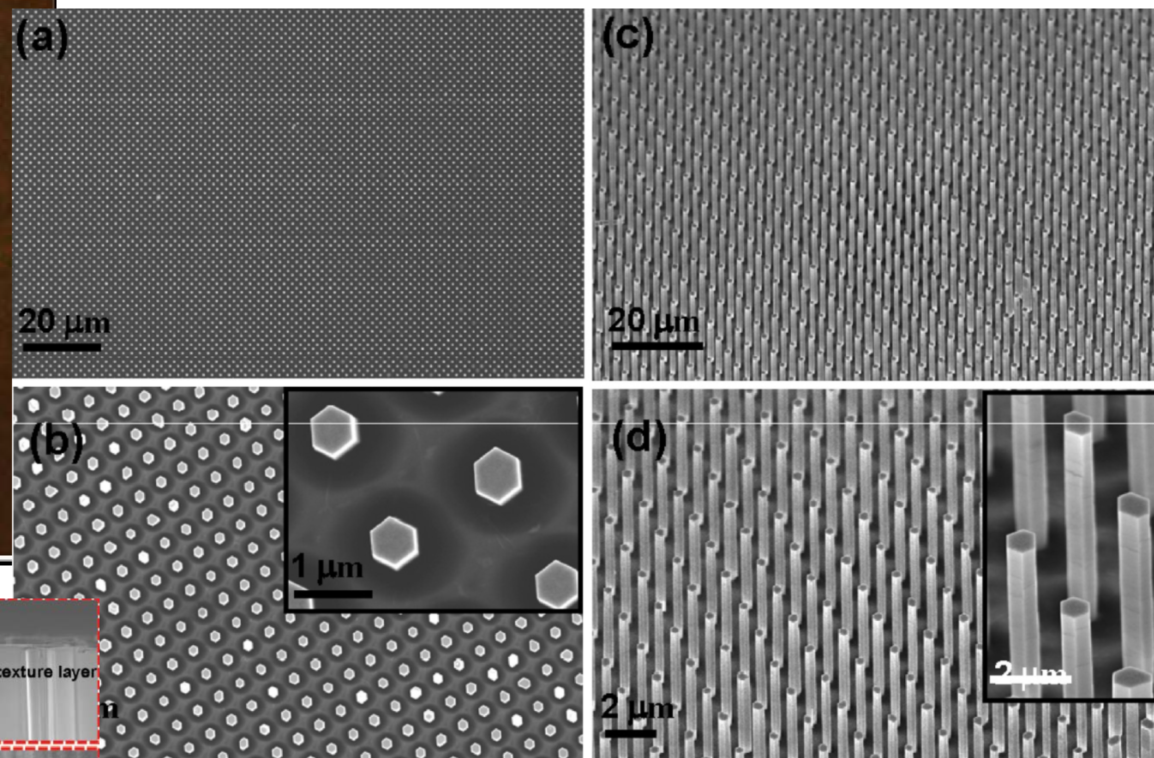


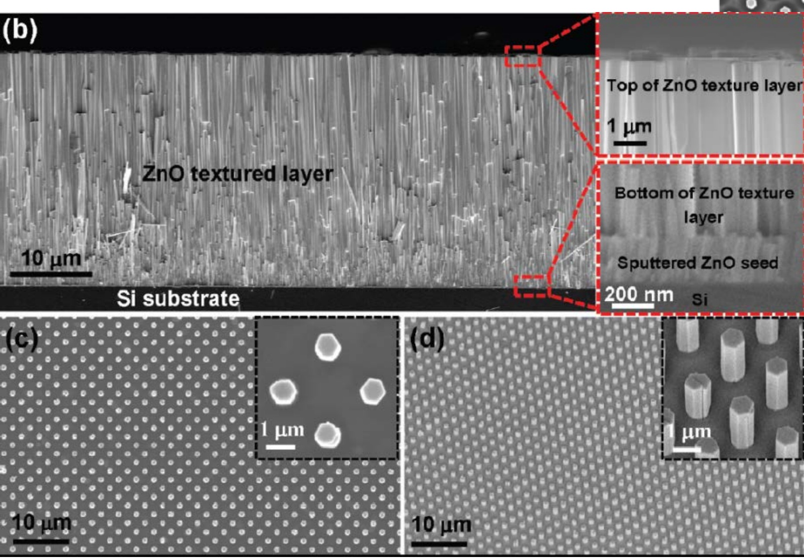


<u>Intel's</u> 65nm **<u>nMOS transistor</u>**

Make Devices on Si wafer







-Vertical ZnO nanowires nanowires can be grown throughout the whole wafer

Nano Letters 2010

Make devices on plastic

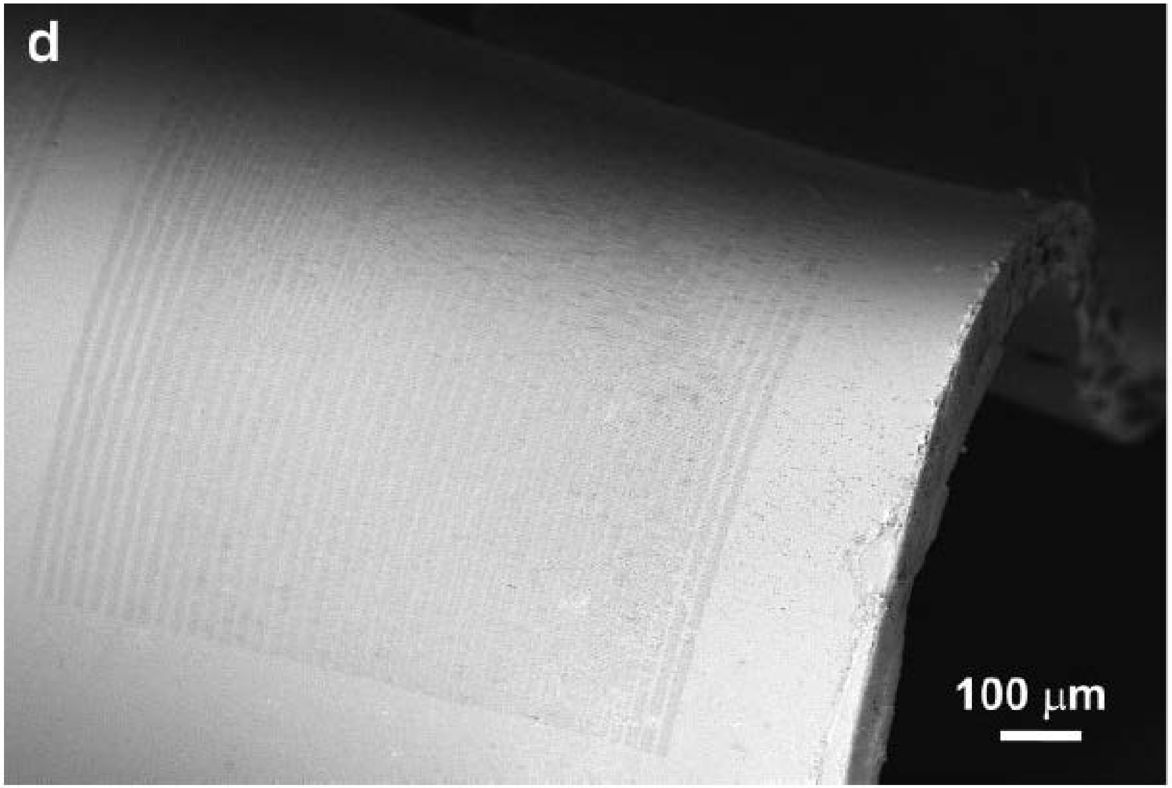
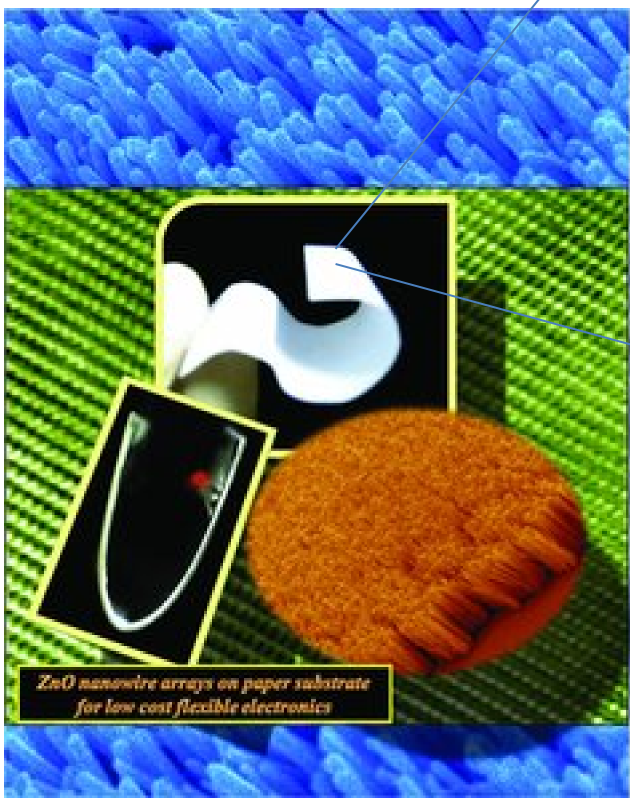
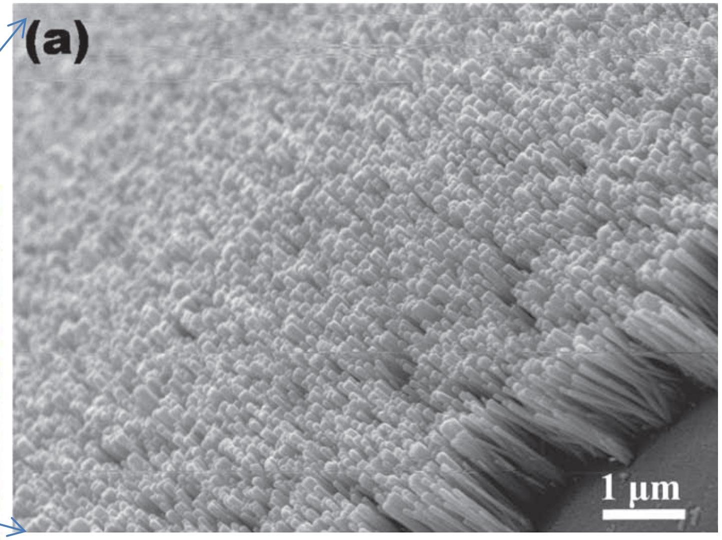


Figure 7. SEM images of the two-segment NW arrays a) on a ZnO substrate and b) after transferring on a flexible substrate. c) Bright-field optical image of the NW arrays on the flexible substrate. d) Low-magnification SEM image of the two-segment NW arrays on a flexible substrate. e) Current–voltage (*I*–*V*) curves of the as-transferred NW arrays in dark environment, under room light, and under UV illumination.

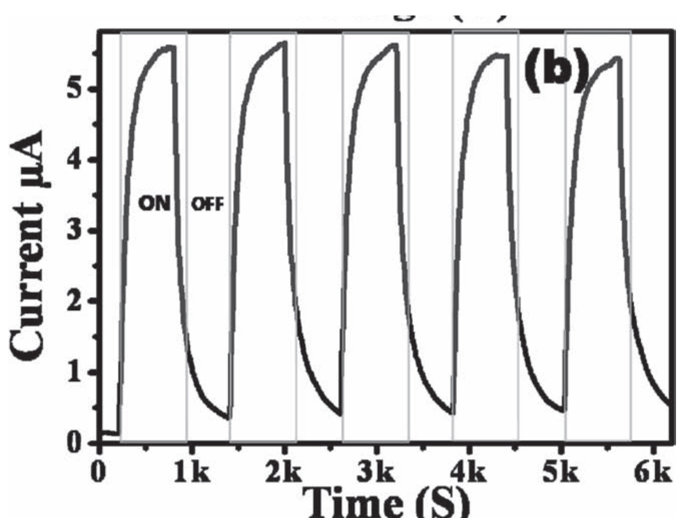
AFM, 2010

Make optoelectronic devices on paper





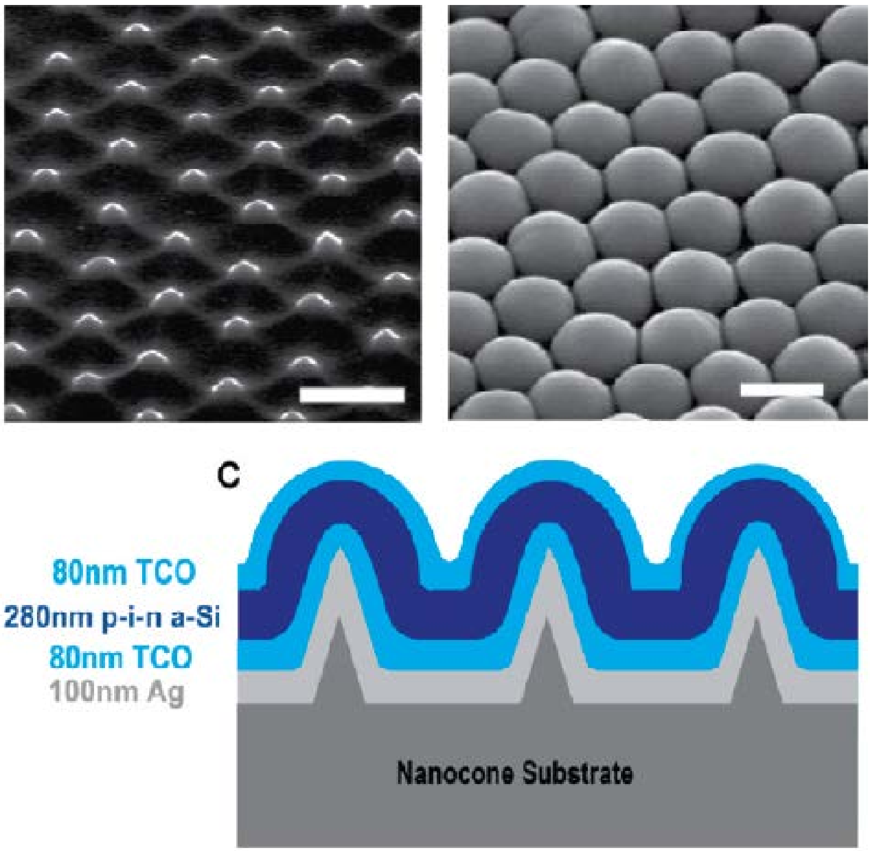
A ZnO/Paper UV sensor



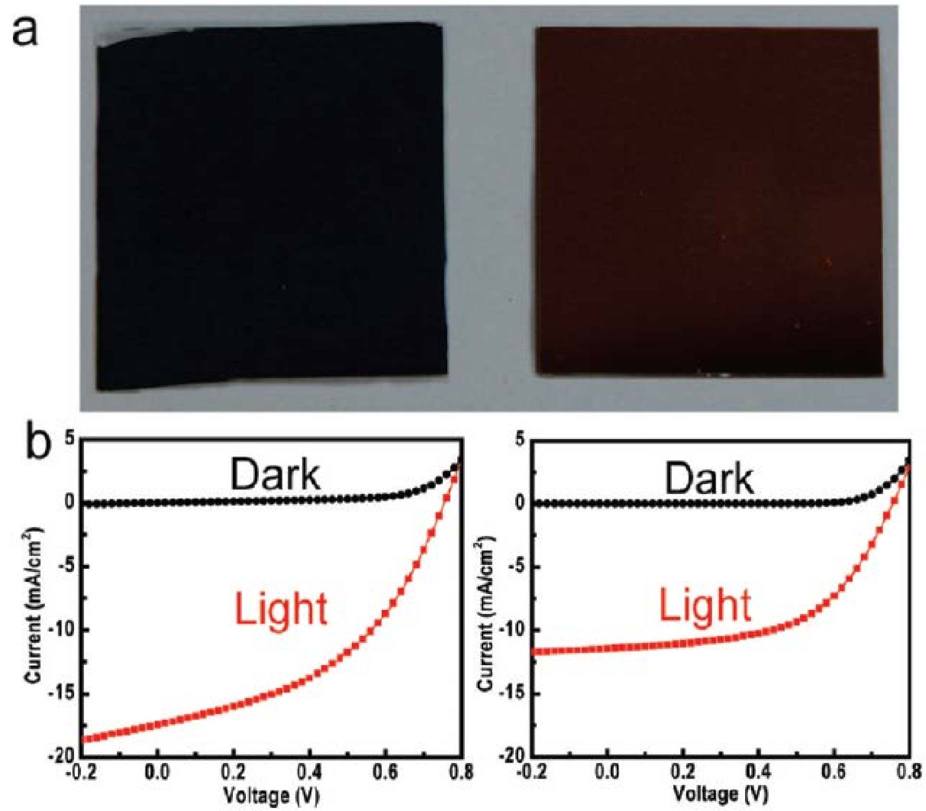
Adv Mater. 2010

Nanodome solar cells

Dome-shaped surface can trap light efficiently

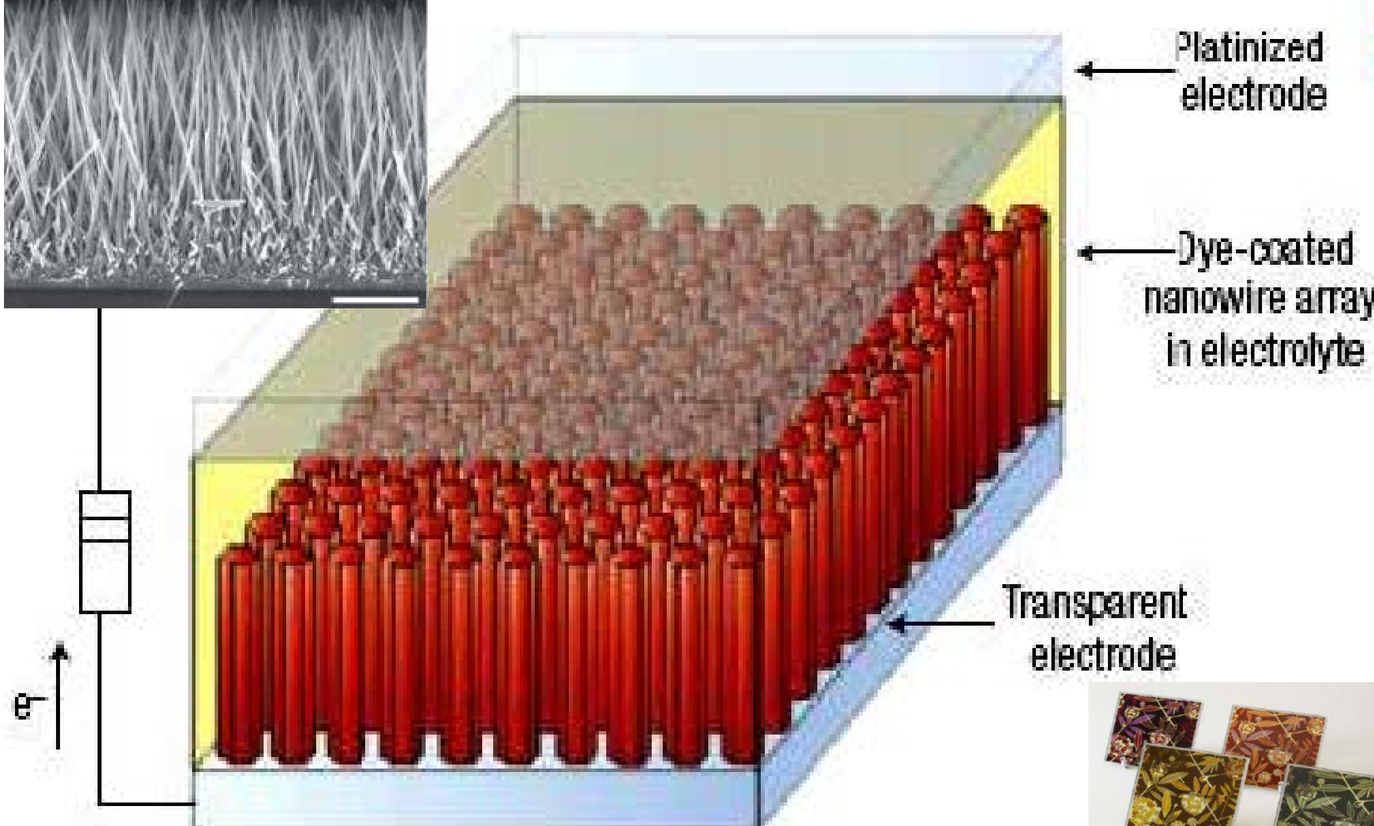


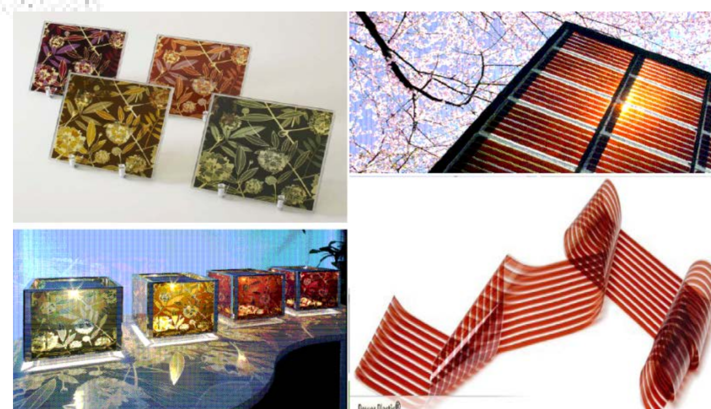
Much better light harvest!



Dry-sensitized nanowire solar cell

Use ZnO nanowires
as a new photoelectrode

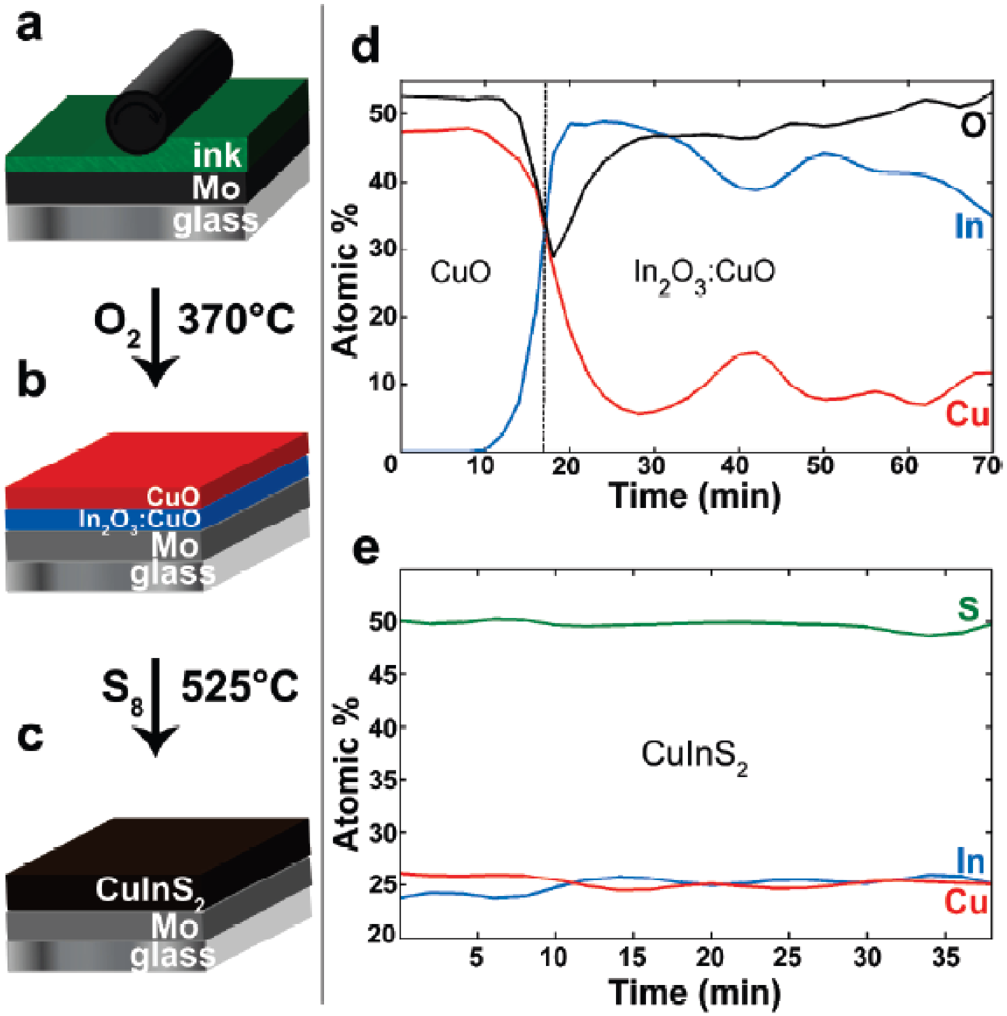


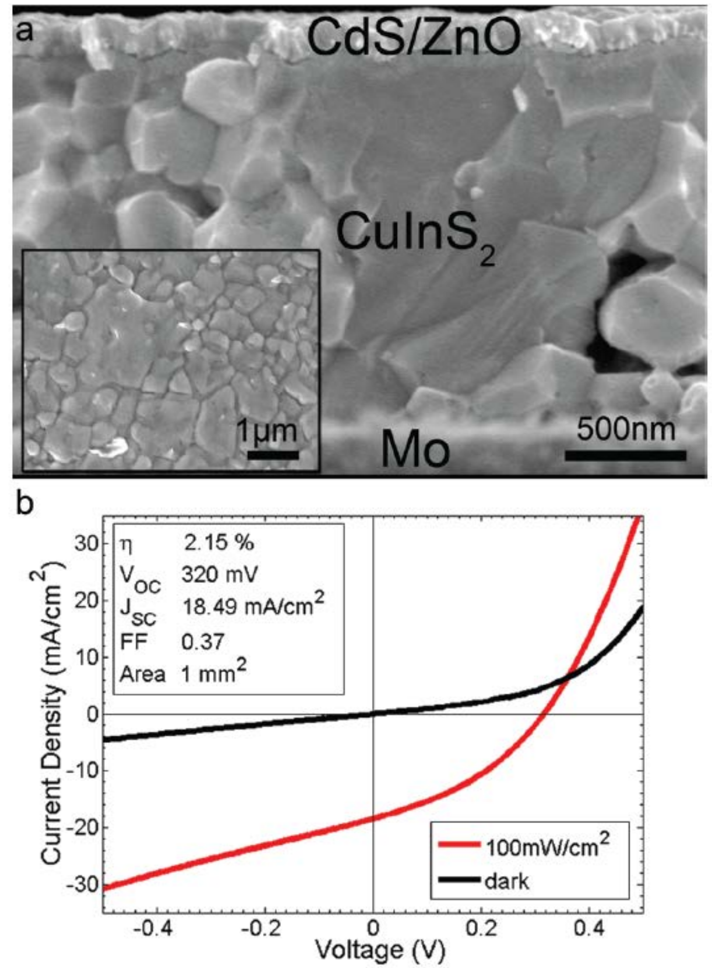


η=1.2-1.5%

Yang et al., *Nature Materials*, 2005

CuInS2 Solar Cells by Air-Stable Rolling

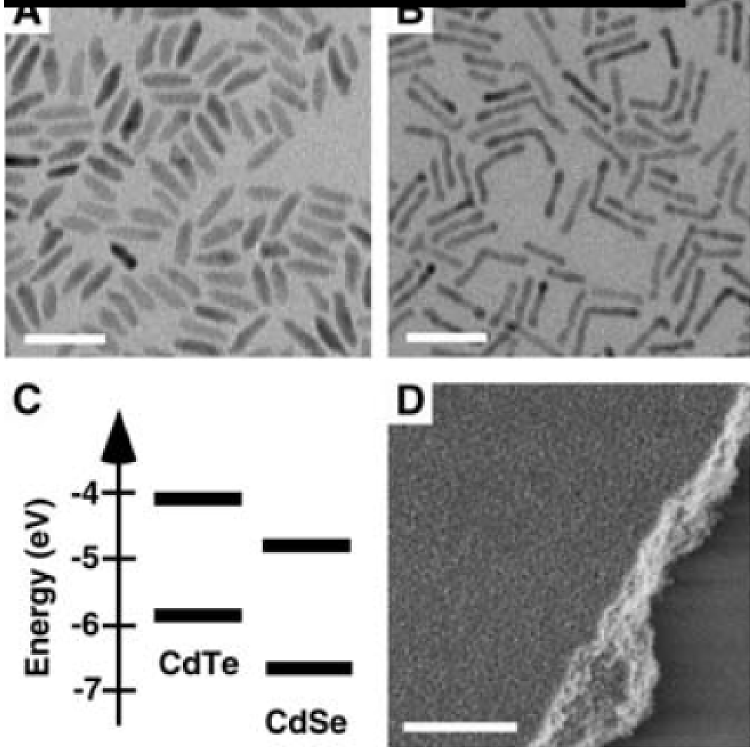


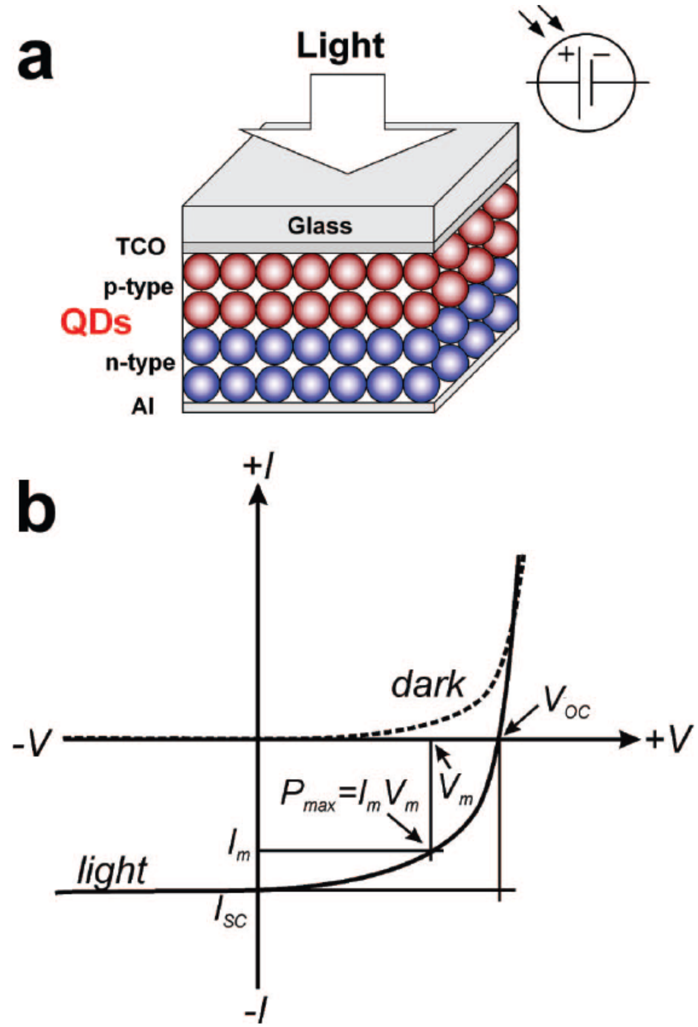


JACS 2010

Nanomaterial-based solar cell

CdTe/CdSe nanorod solar cell



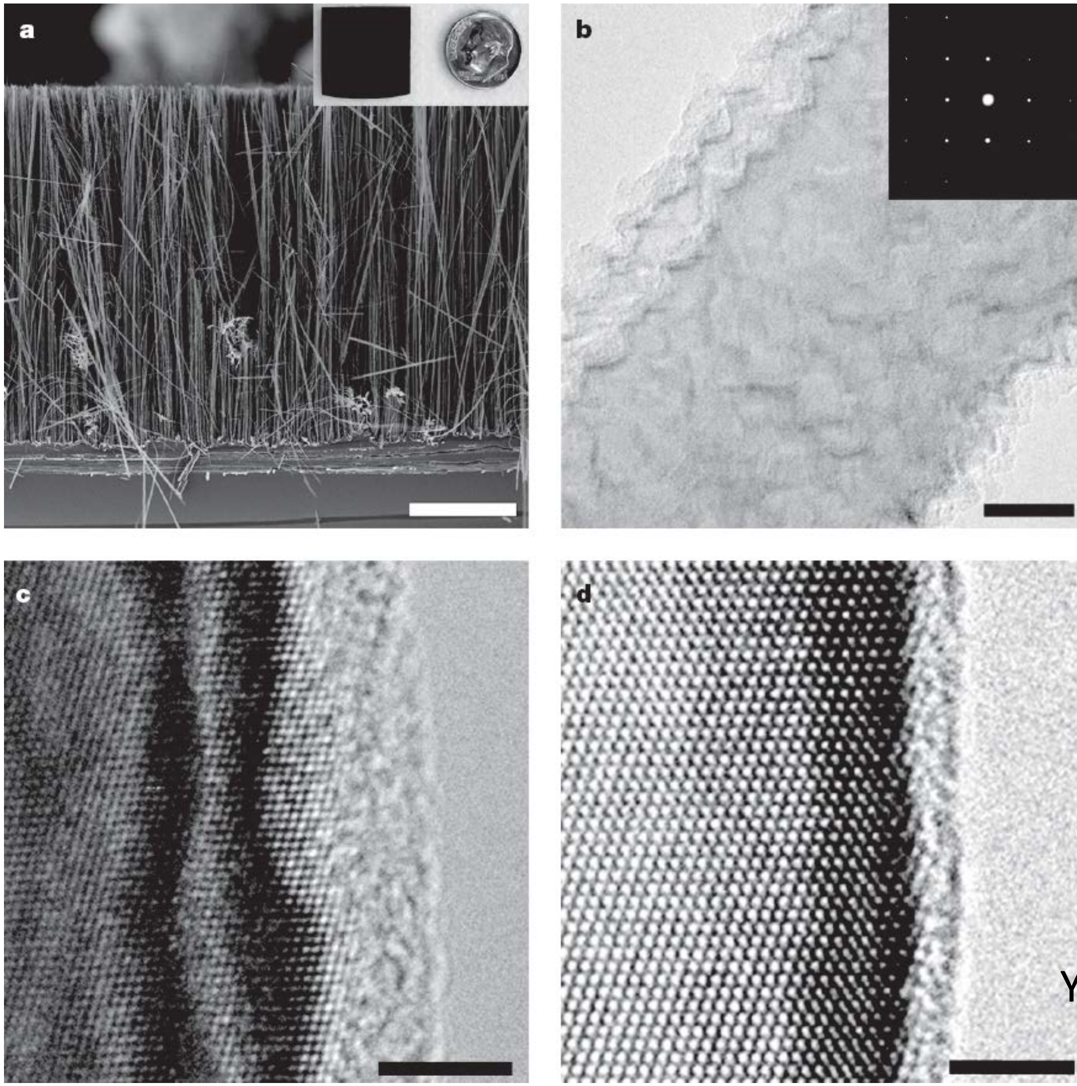


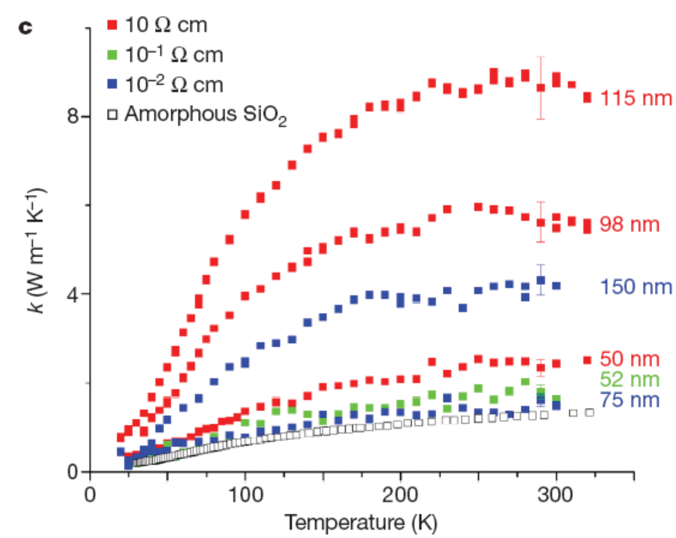
Alivisatos et al., Science, 2005

η=2.9%

Si nanowire-based thermoelectrics

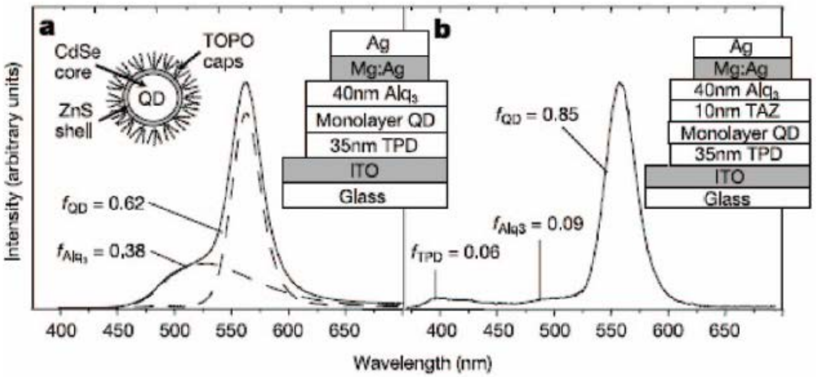
Transfer heat to energy



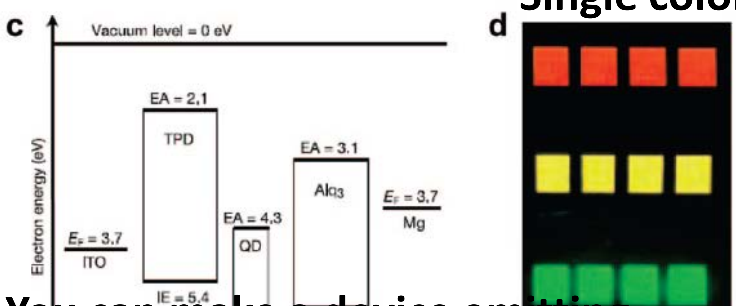


Yang et al., Nature, 2007

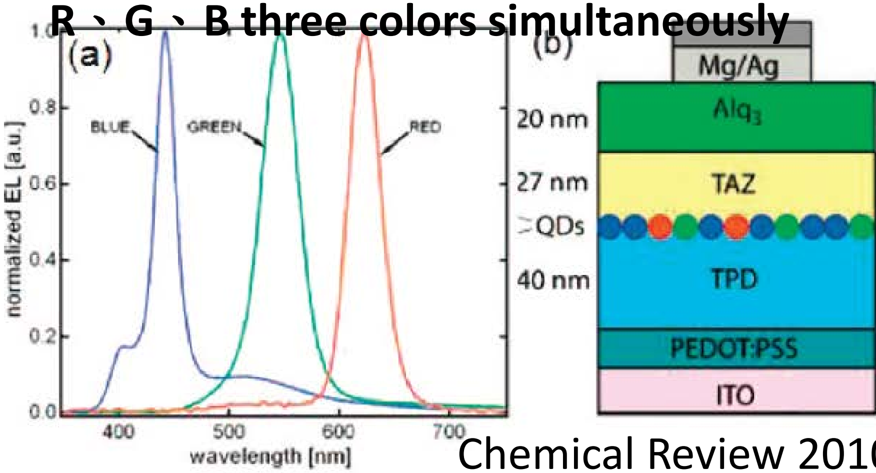
CdSe/ZnS nanocrystal LED

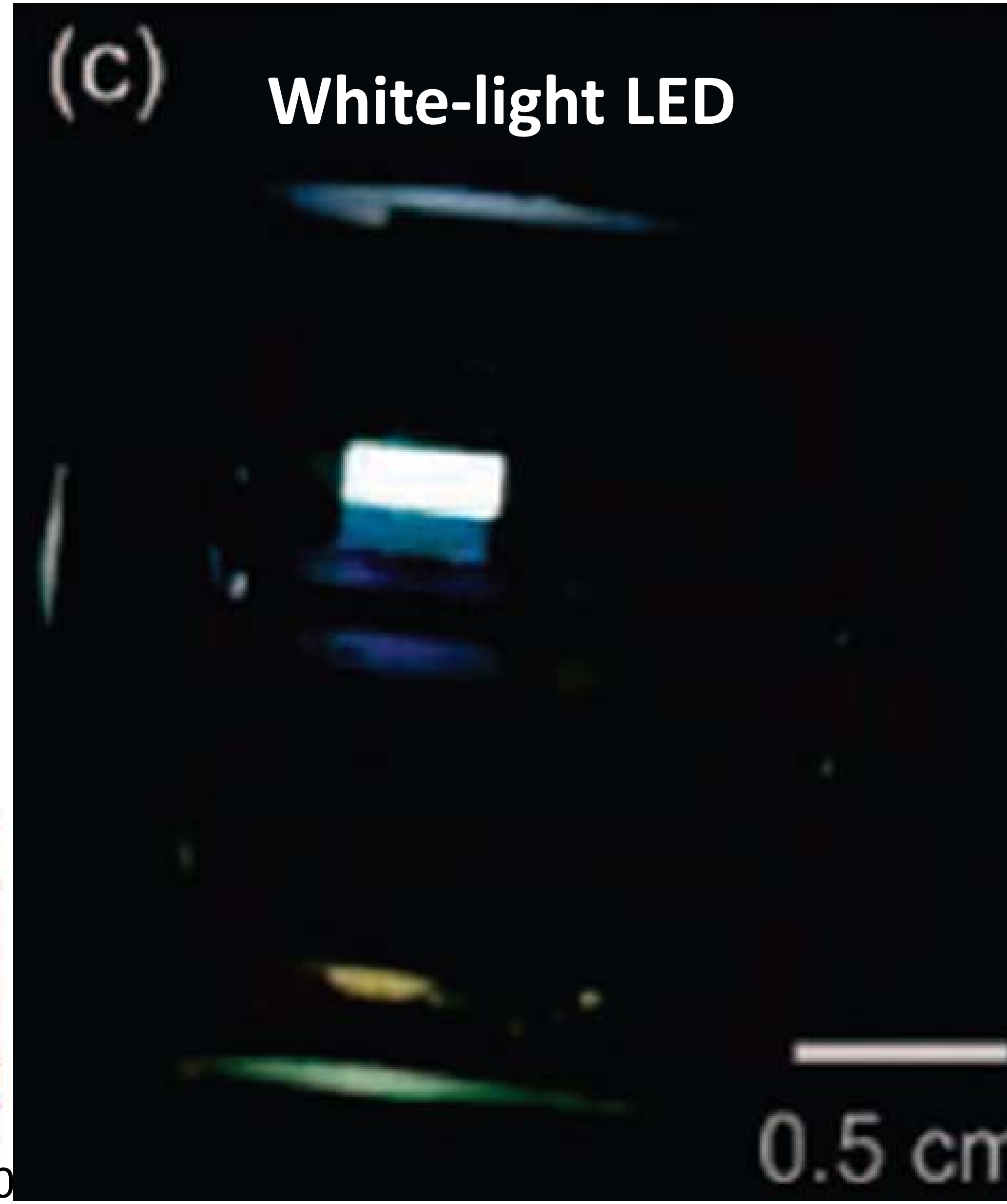


Single color



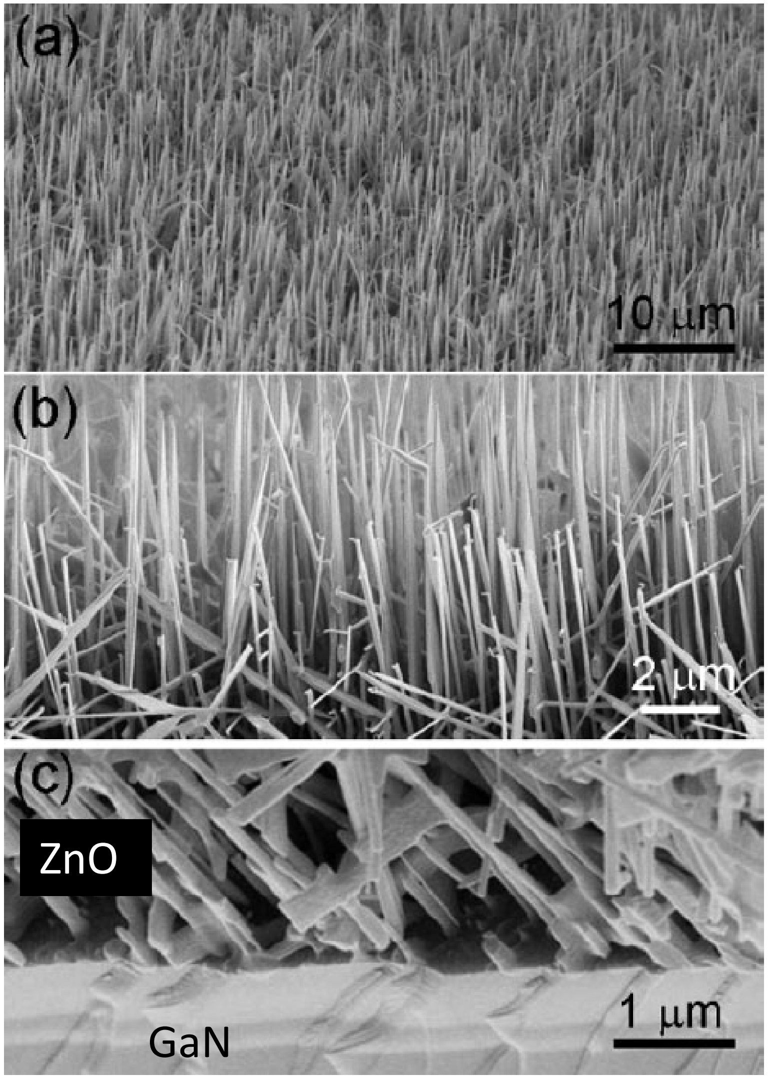
You can make a device emitting R、G、B three colors simultaneously

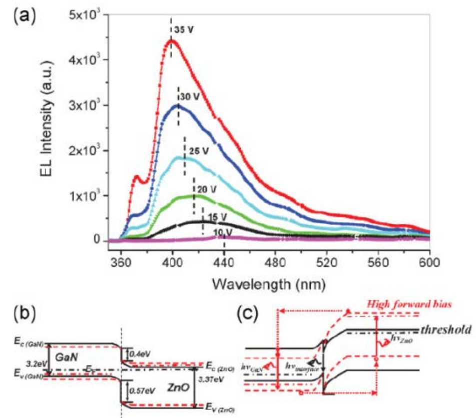


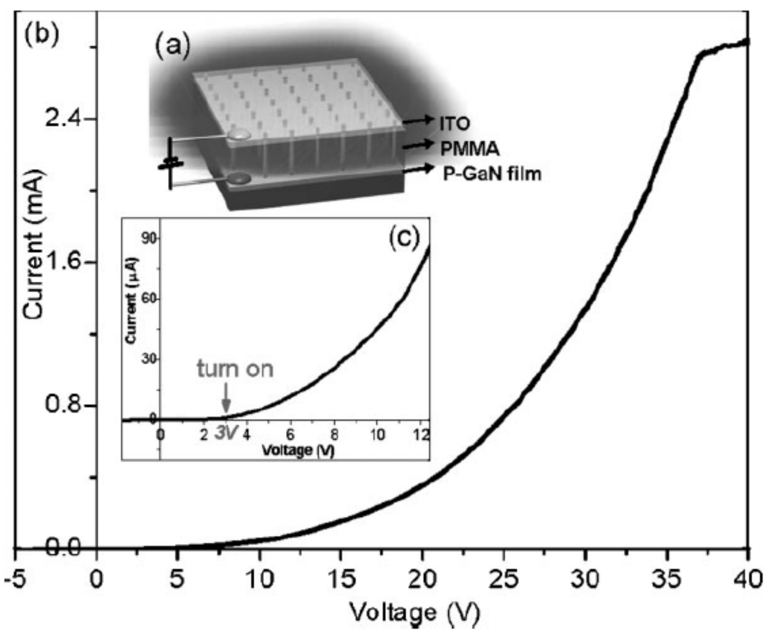


Chemical Review 2010

ZnO nanowire /GaN substrate LED

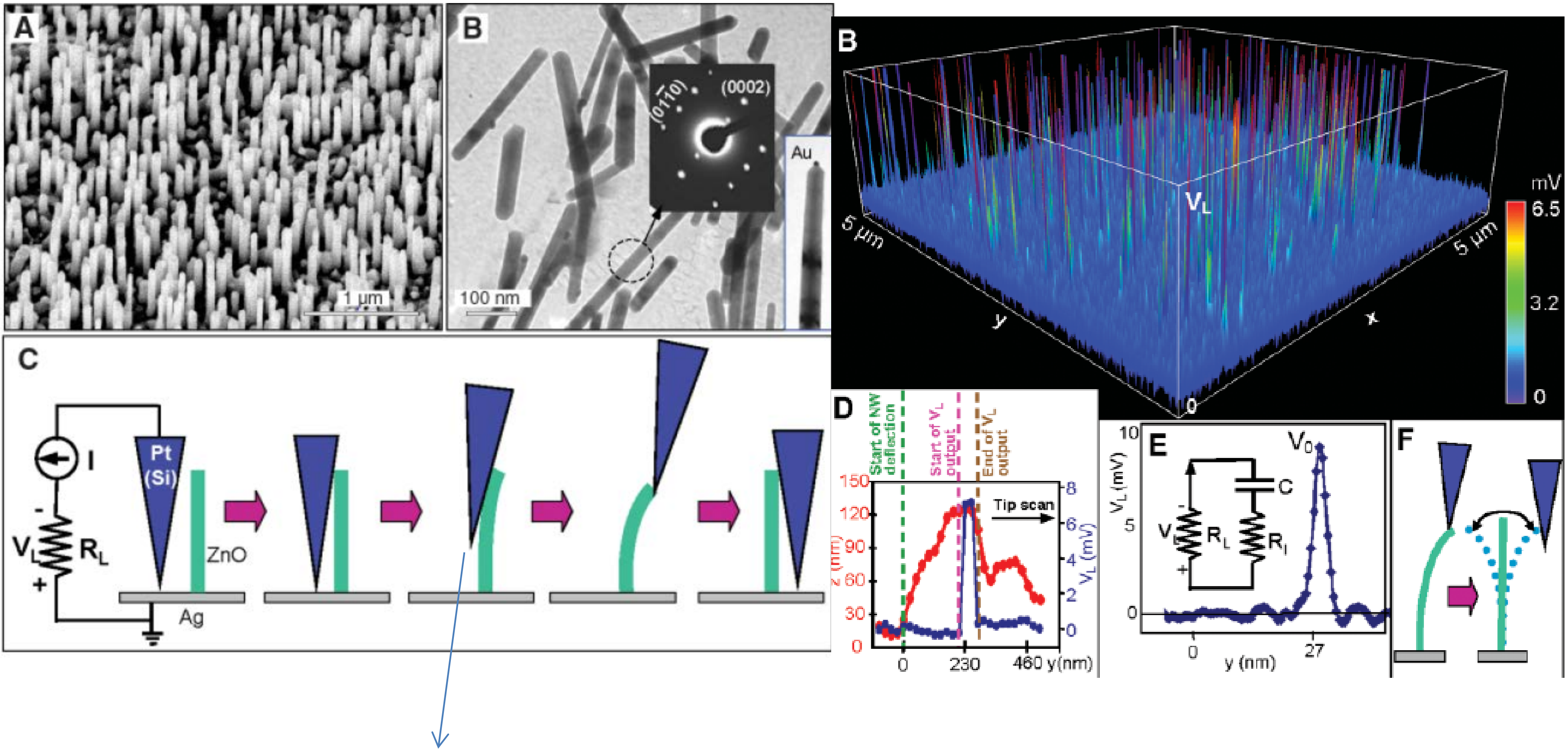






Zhang et al., Adv Mater., 2009

Piezoelectric nanogenerator

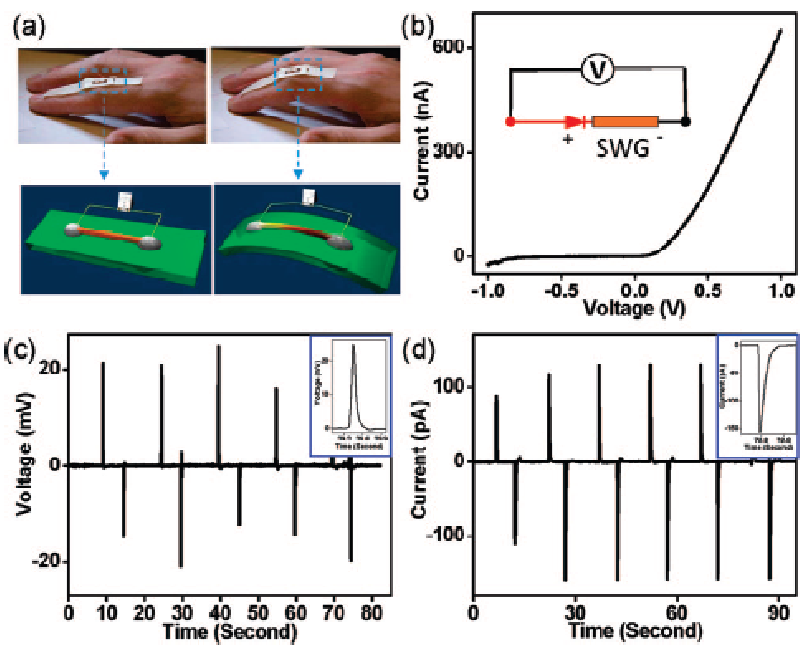


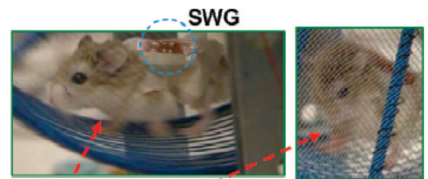
Transfer mechanical energy to electric energy

Science 2006

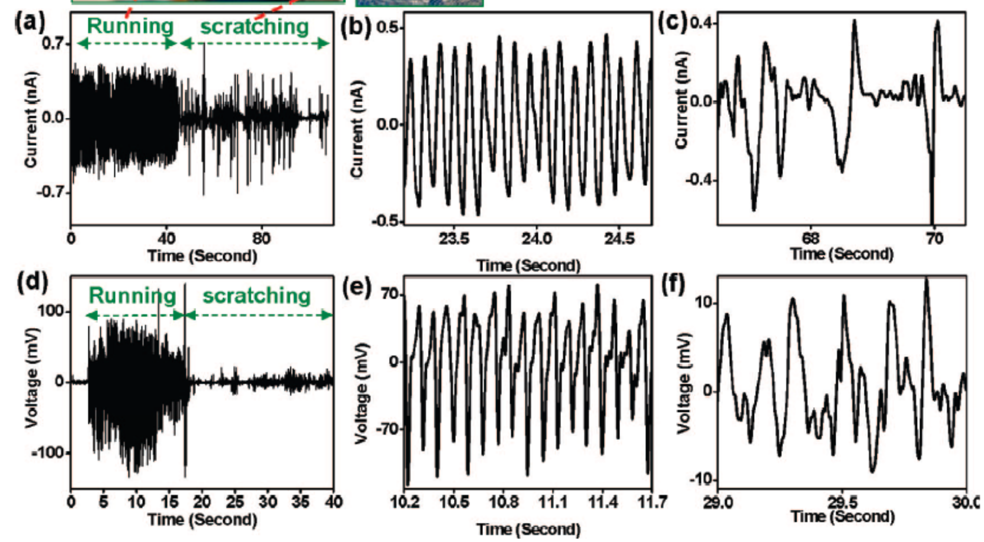
Muscle-Movement-Driven nanogenerator

Finger movement-drive



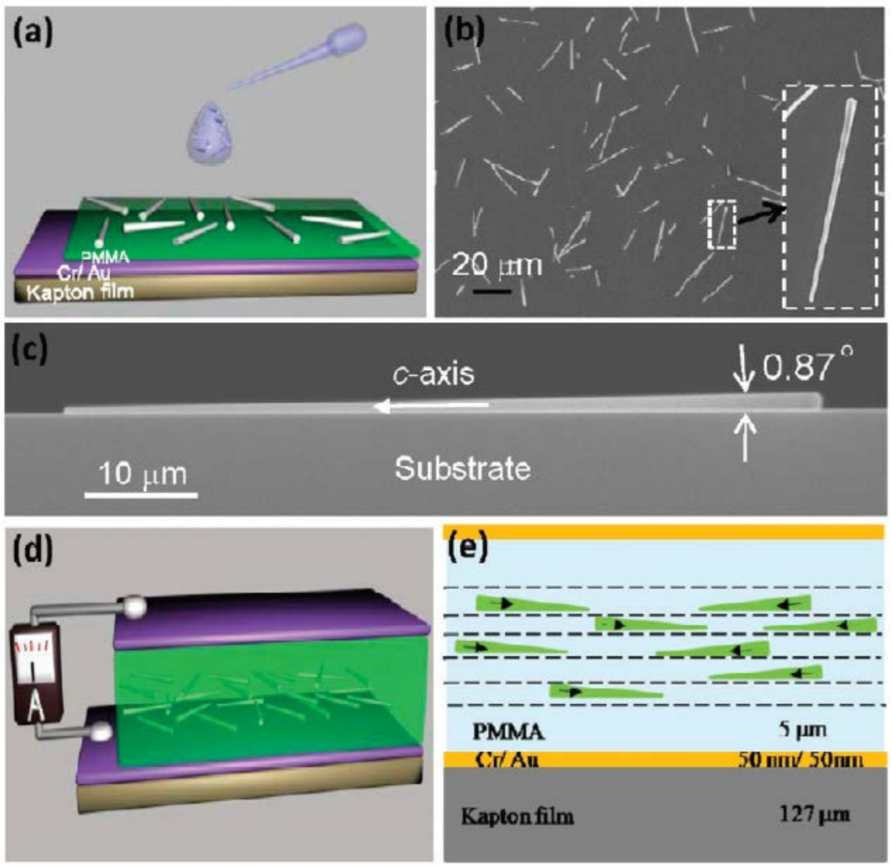


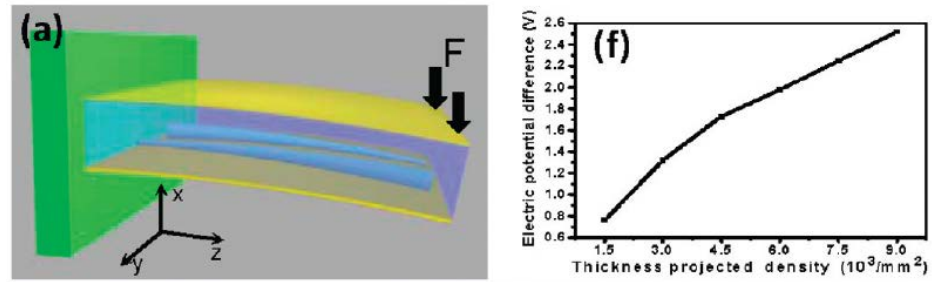
Mouse movement-drive

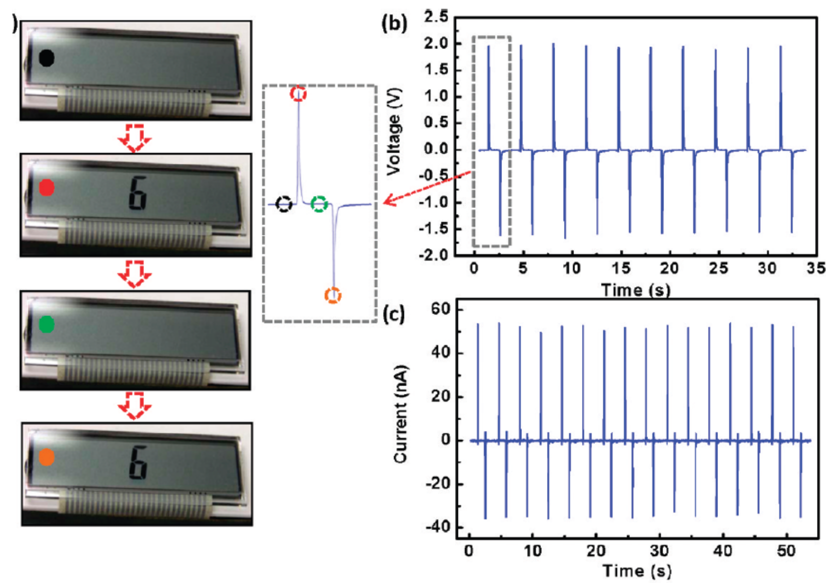


Nano Letters 2010

Nanogenerator for driving LCD display

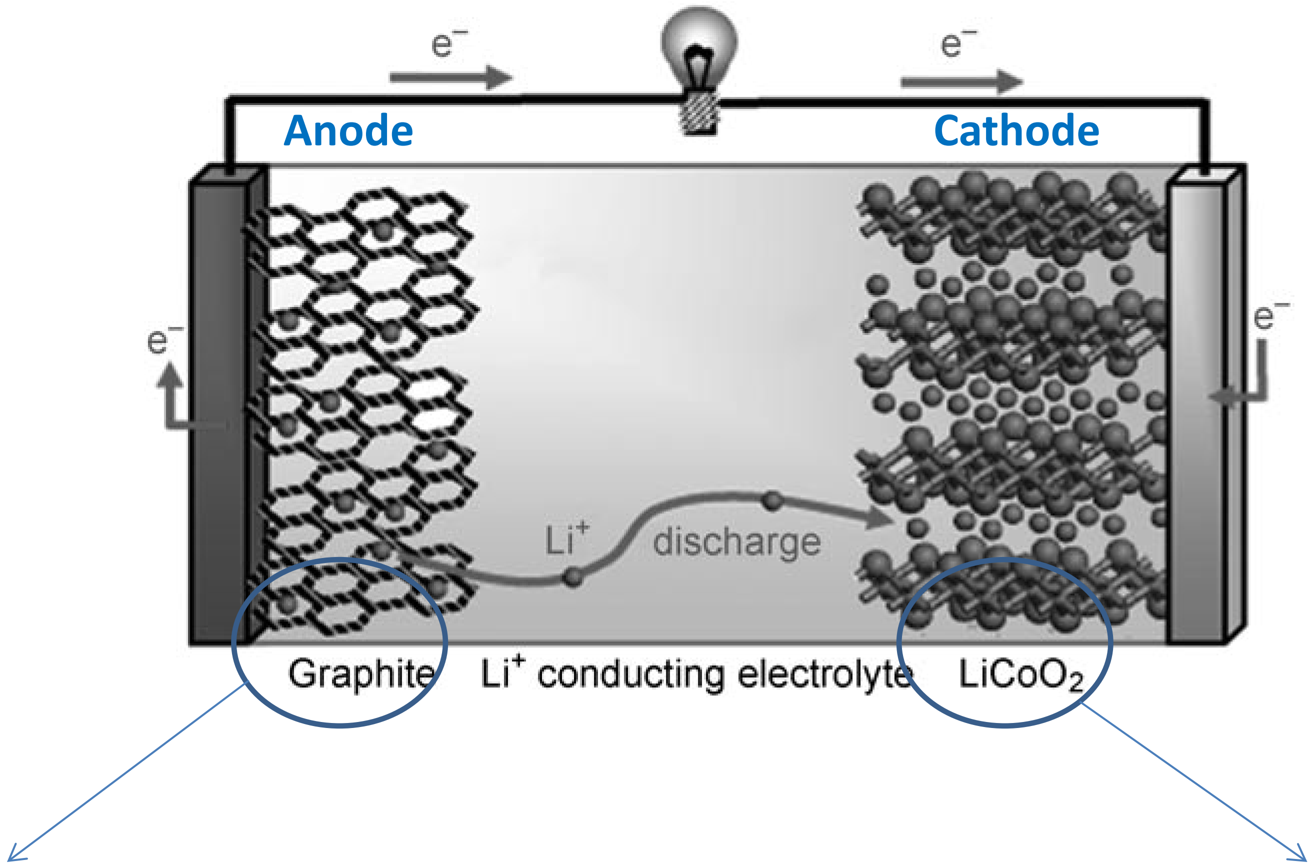






Nano letters 2010

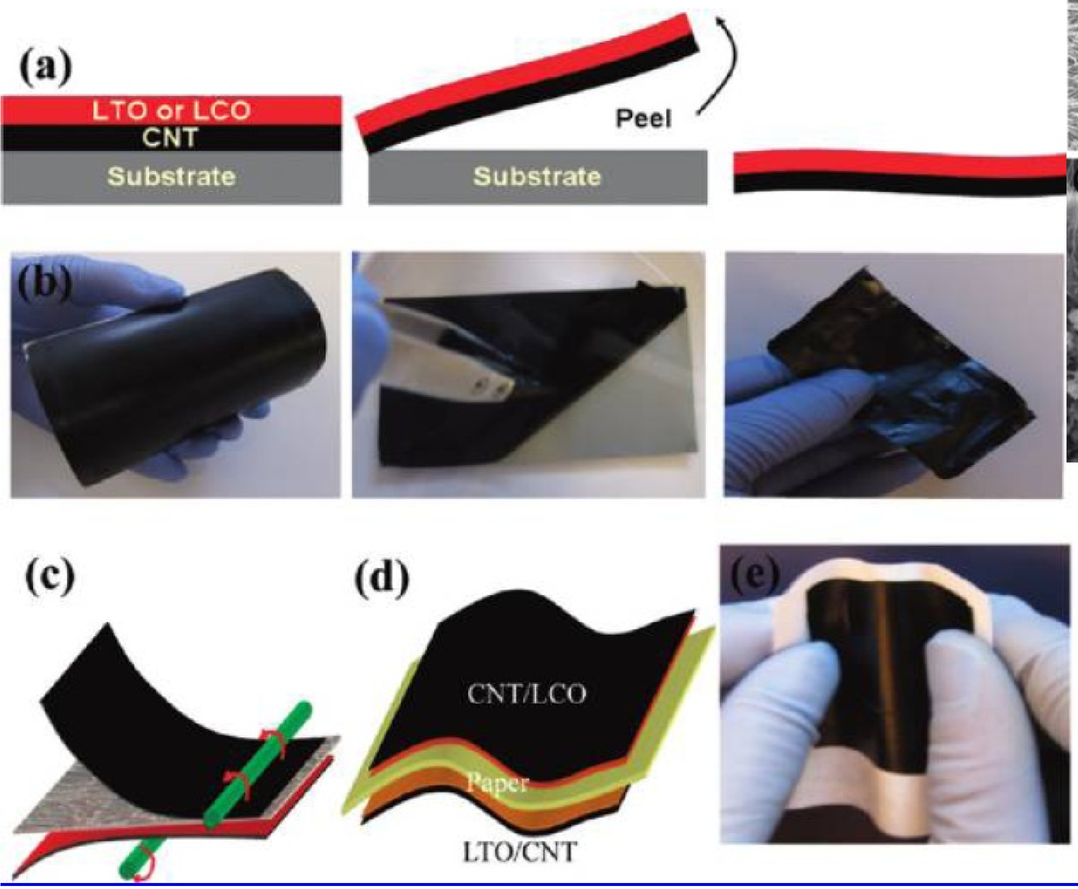
New Electrodes for Lithium batteries

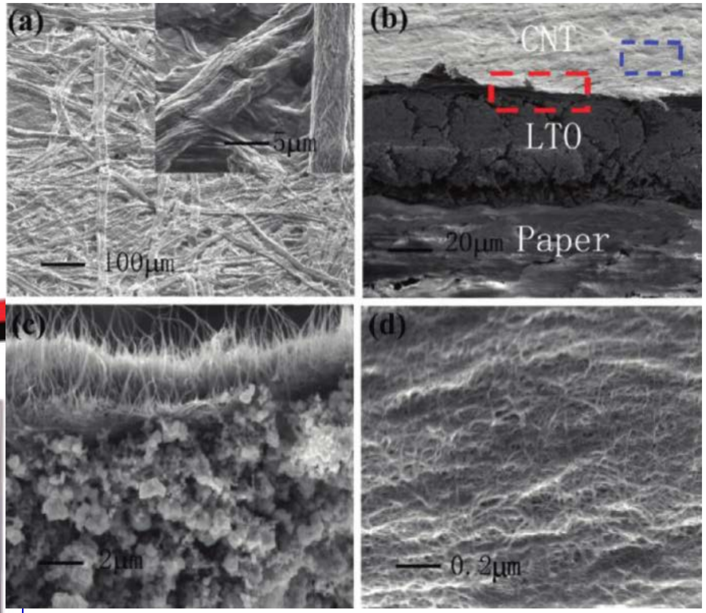


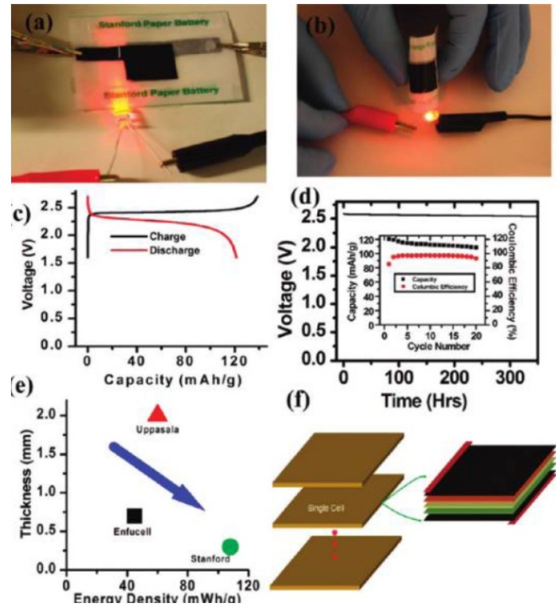
-Only ~ 375 Ahg-1
-Replaced by new material:
- Si (~4400、Ge~1600、SnO2~782 Ahg-1

-New structure (mesoporous、branched)
-New material (Li2S : 1166 Ahg-1)

Lithium ion Paper batteries



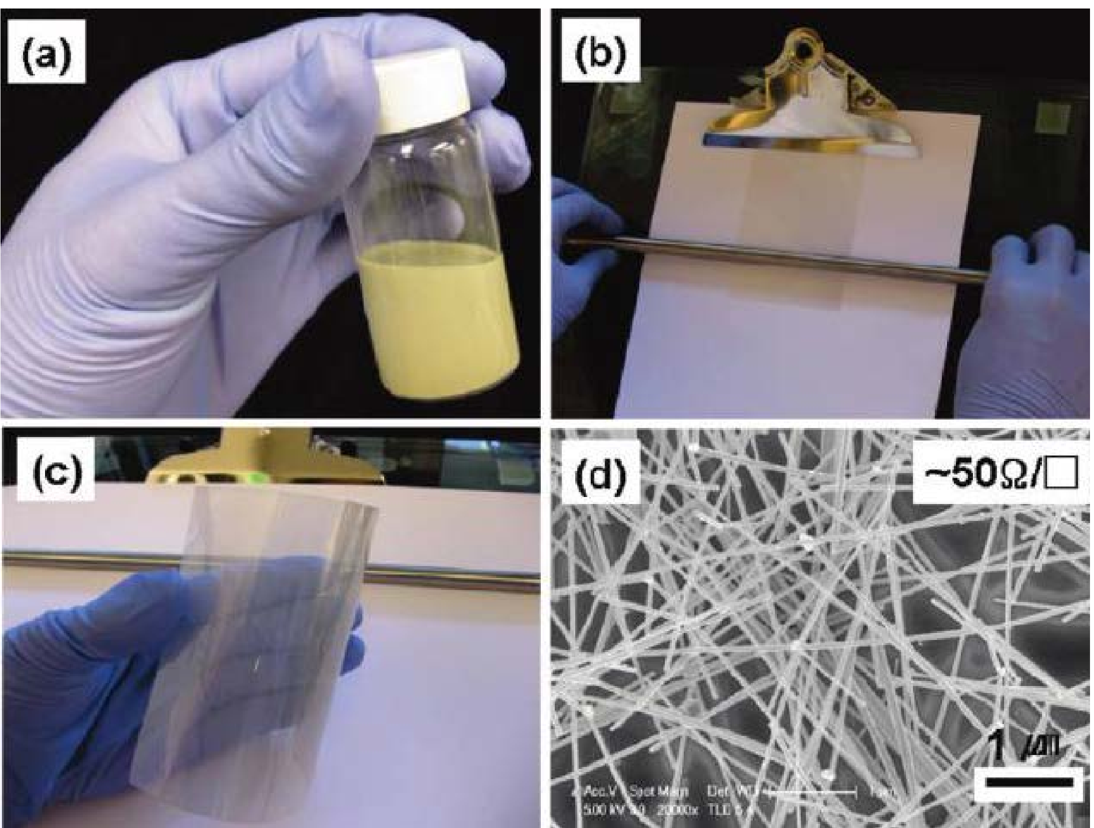


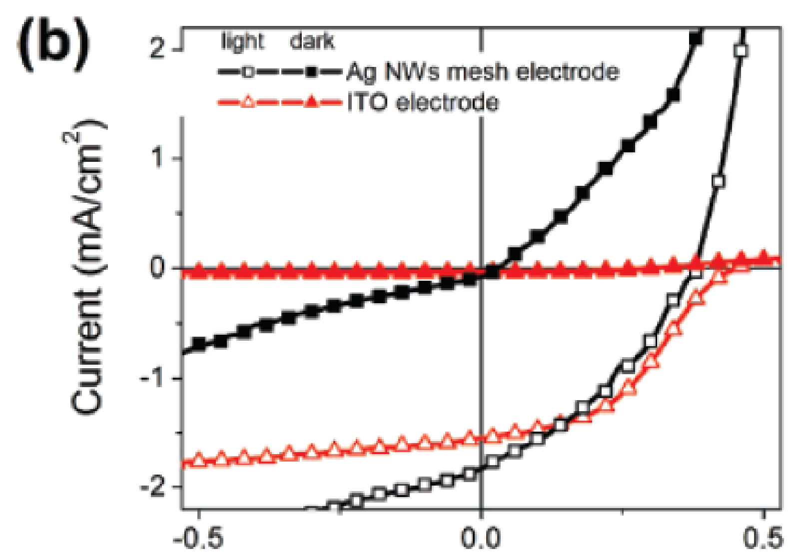


ACS Nano 2010

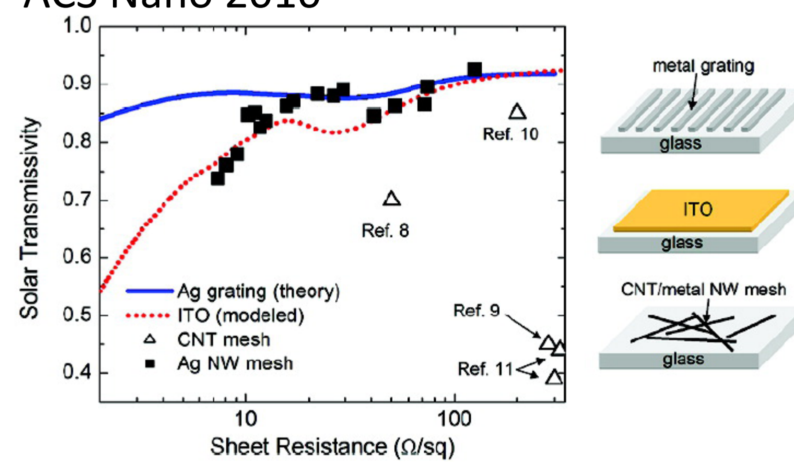
Silver nanowire transparent conducting glass or plastic (replace ITO)

Coating Silver nanowires on a substrate to make
It conductive

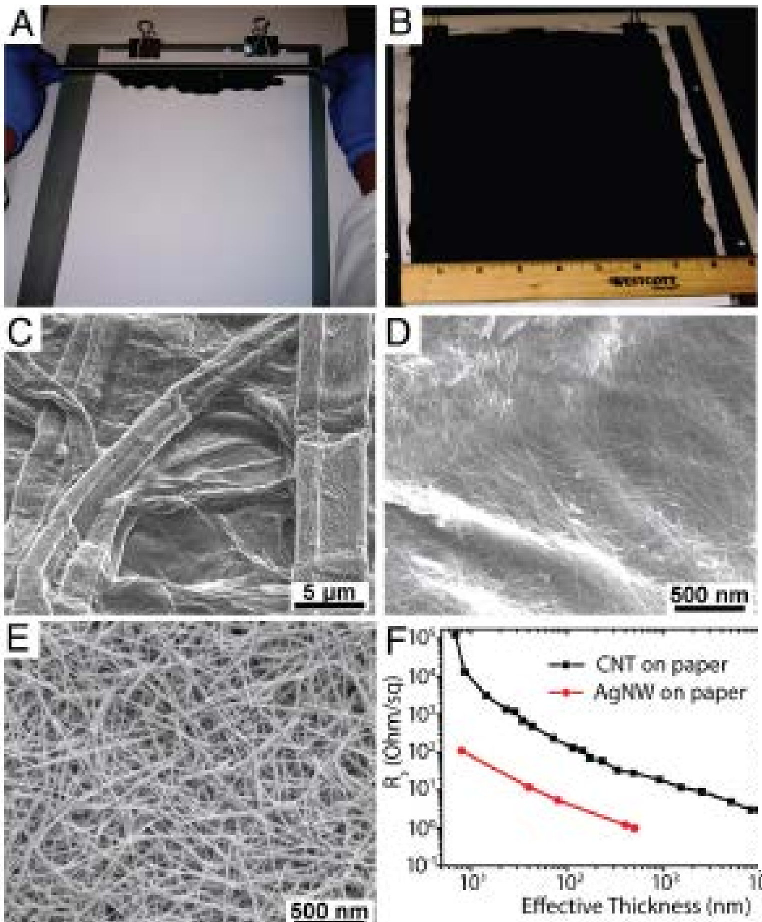


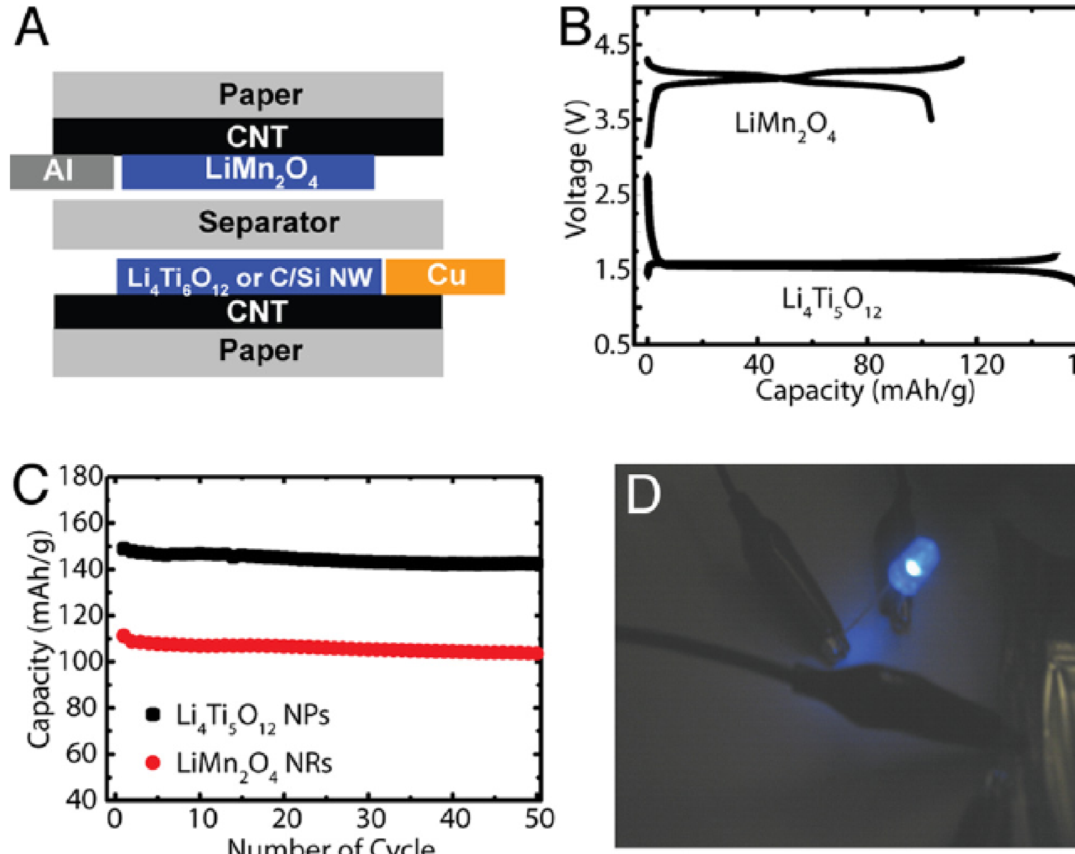


Nano letters 2008
ACS Nano 2010



Nanotubes + ink + paper = conducting paper





Highly conductive paper for energy-storage devices

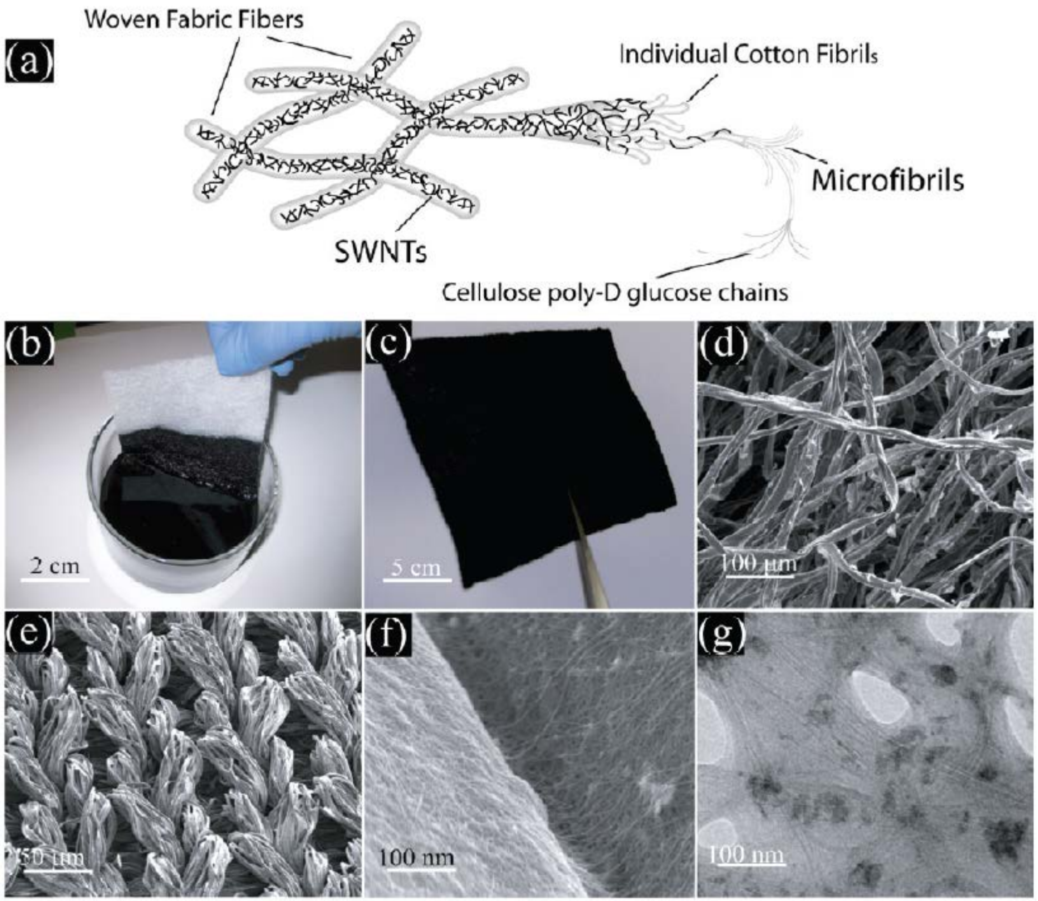
Liangbing Hu[a,1], Jang Wook Choi[a,1], Yuan Yang[a,1], Sangmoo Jeong[b], Fabio La Mantia[a], Li-Feng Cui[a], and Yi Cui[a,2]

Departments of [a]Materials Science and Engineering and [b]Electrical Engineering, Stanford University, Stanford, CA 94305

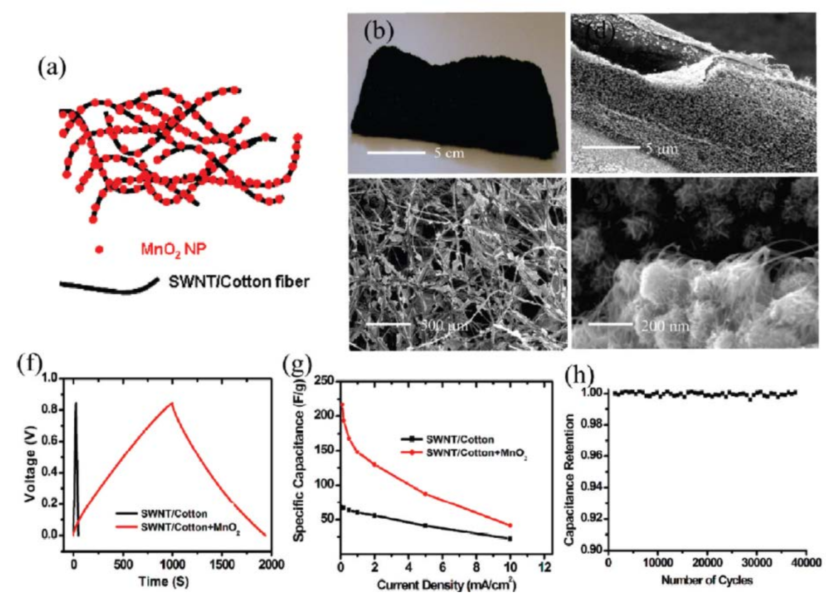
Edited by Charles M. Lieber, Harvard University, Cambridge, MA, and approved October 21, 2009 (received for review August 6, 2009)

PNAS 2010

Stretchable, Porous, and Conductive Energy Textile

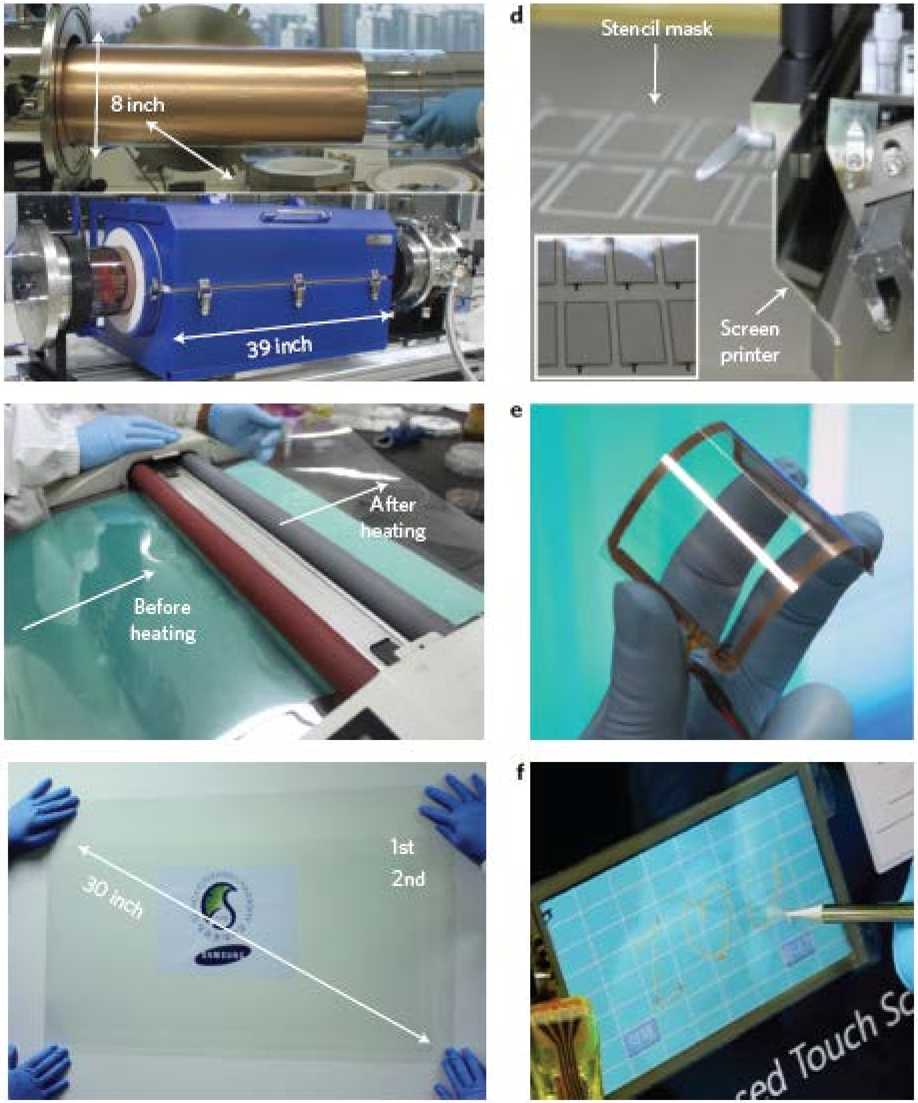


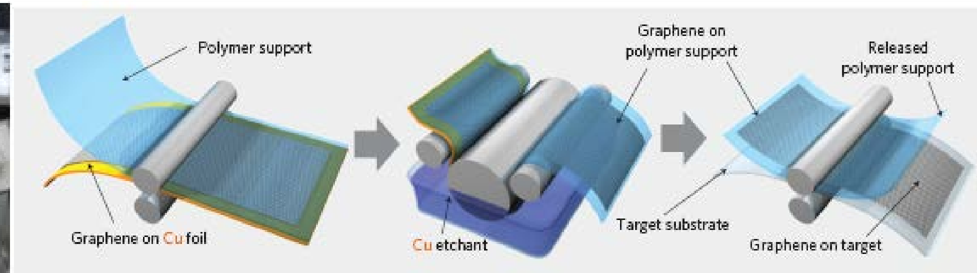
Textile capacitor

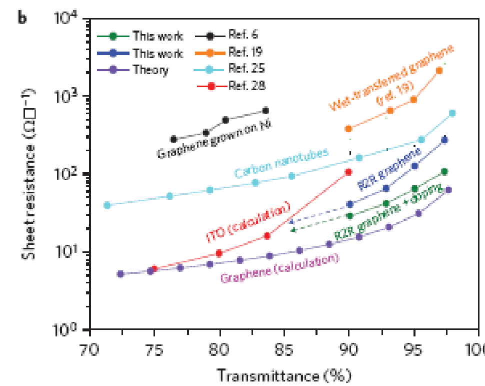


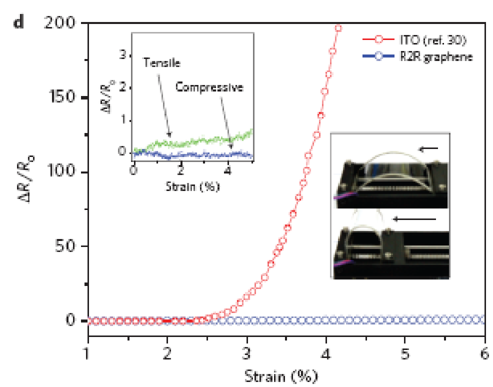
Nano Letters 2010

Roll-to-Roll production of 30-inch graphene films for transparent electrodes









Resistance
Not affected
under
strain

Nanostructures as high-performance anodes for Lithium-ion battery

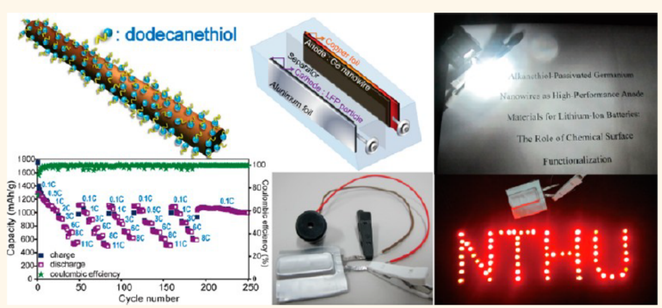
Alkanethiol-Passivated Ge Nanowires as High-Performance Anode Materials for Lithium-Ion Batteries: The Role of Chemical Surface Functionalization

Fang-Wei Yuan, Hong-Jie Yang, and Hsing-Yu Tuan*

Department of Chemical Engineering, National Tsing Hua University, 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30013, ROC

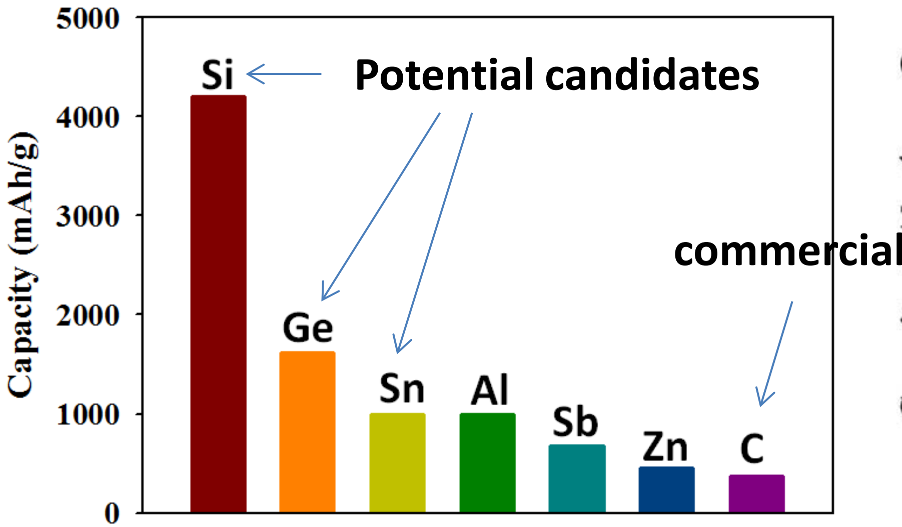
段興宇
清大化工系

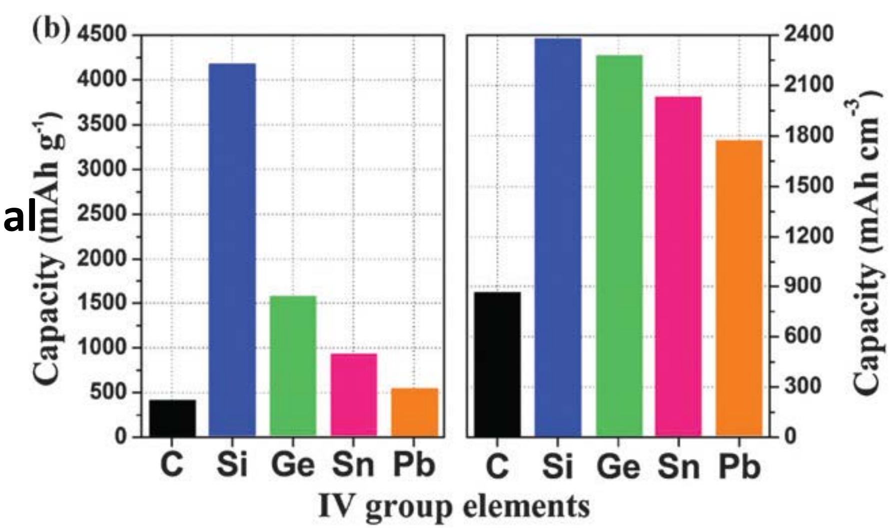
ABSTRACT We demonstrate that dodecanethiol monolayer passivation can significantly enhance the anode performance of germanium (Ge) nanowires in lithium-ion batteries. The dodecanethiol-passivated Ge nanowires exhibit an excellent electrochemical performance with a reversible specific capacity of 1130 mAh/g at 0.1 C rate after 100 cycles. The functionalized Ge nanowires show high-rate capability having charge and discharge capacities of ~555 mAh/g at high rates of 11 C. The functionalized Ge nanowires also

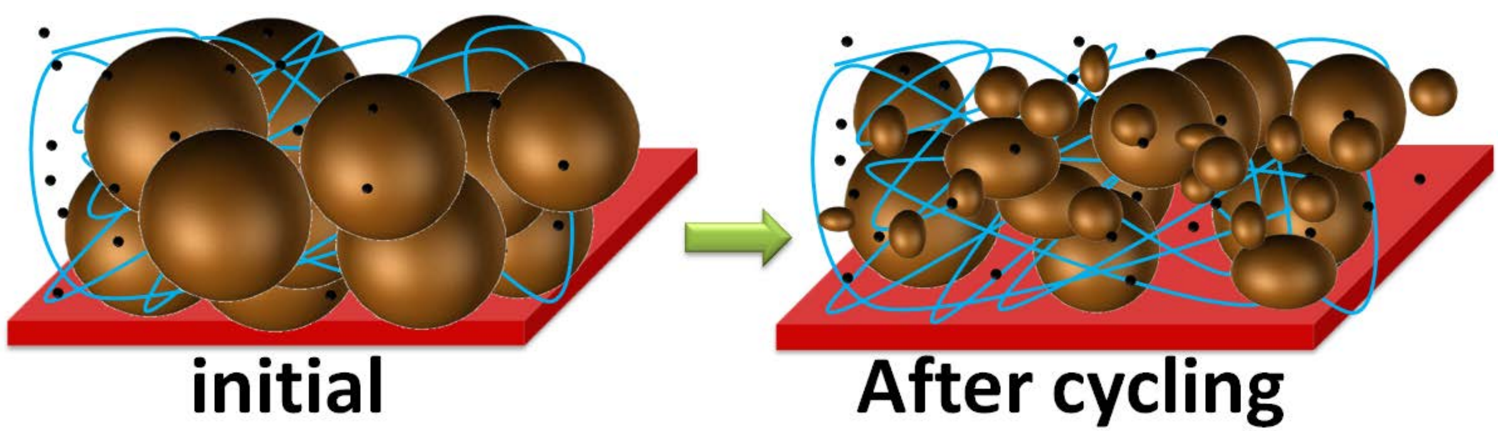


Tuan et al. ACS Nano, in press

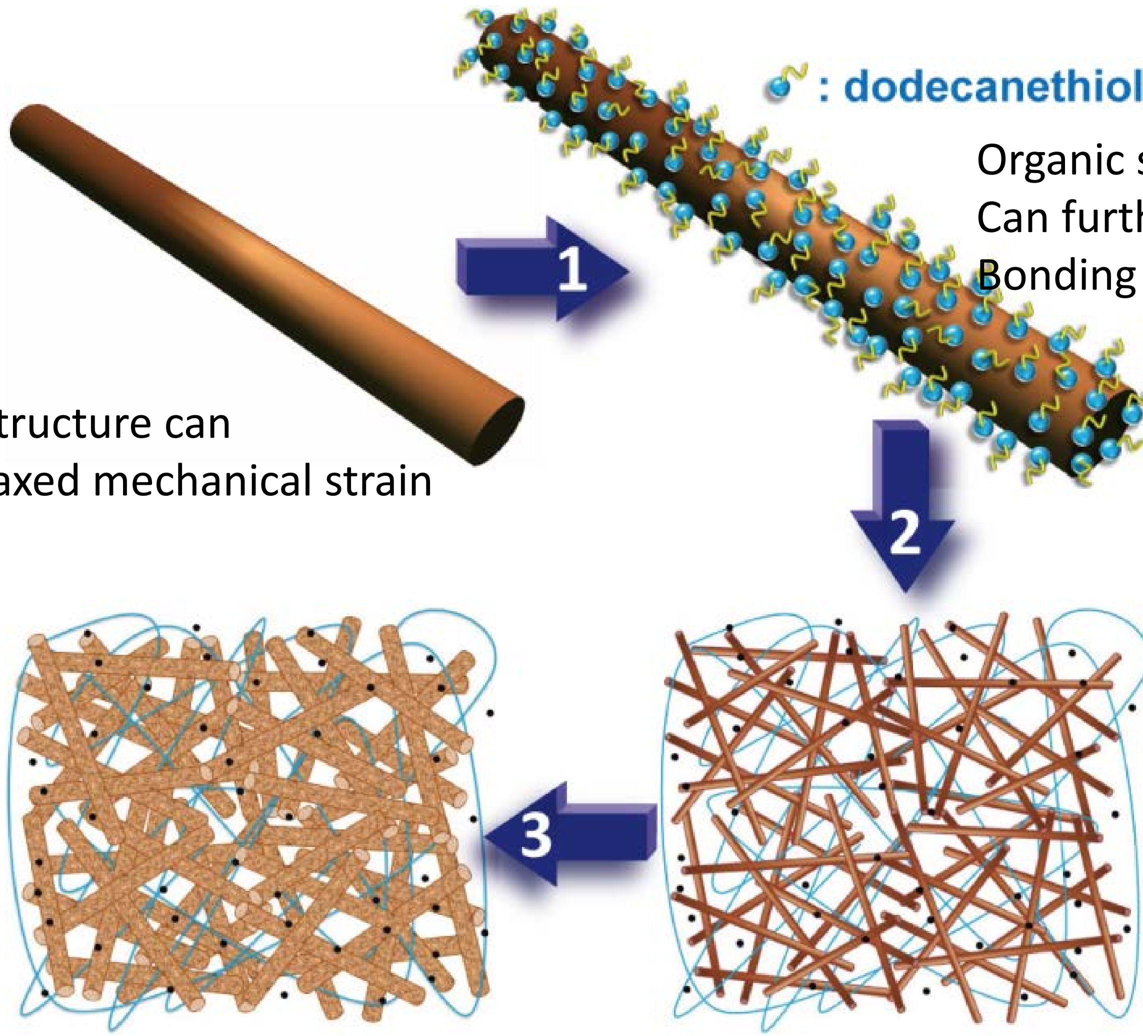
Alloying material for Lithium-ion anode







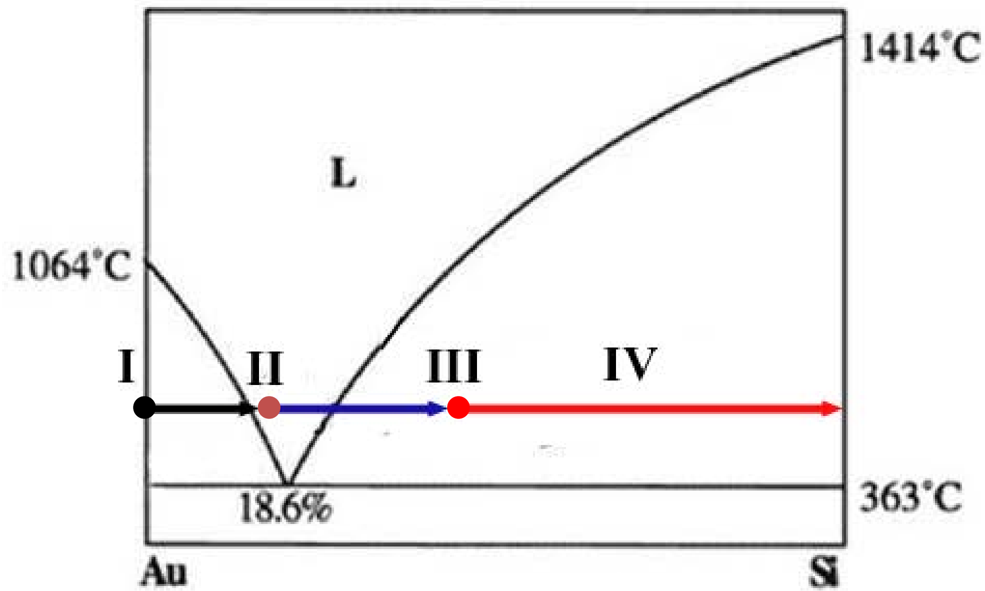
Using Ge nanowires as anode

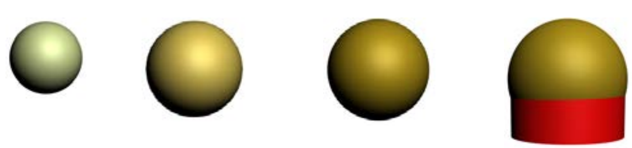


Organic surfactant
Can further make strong C-F
Bonding With PVDF

Nanowire structure can
tolerate relaxed mechanical strain

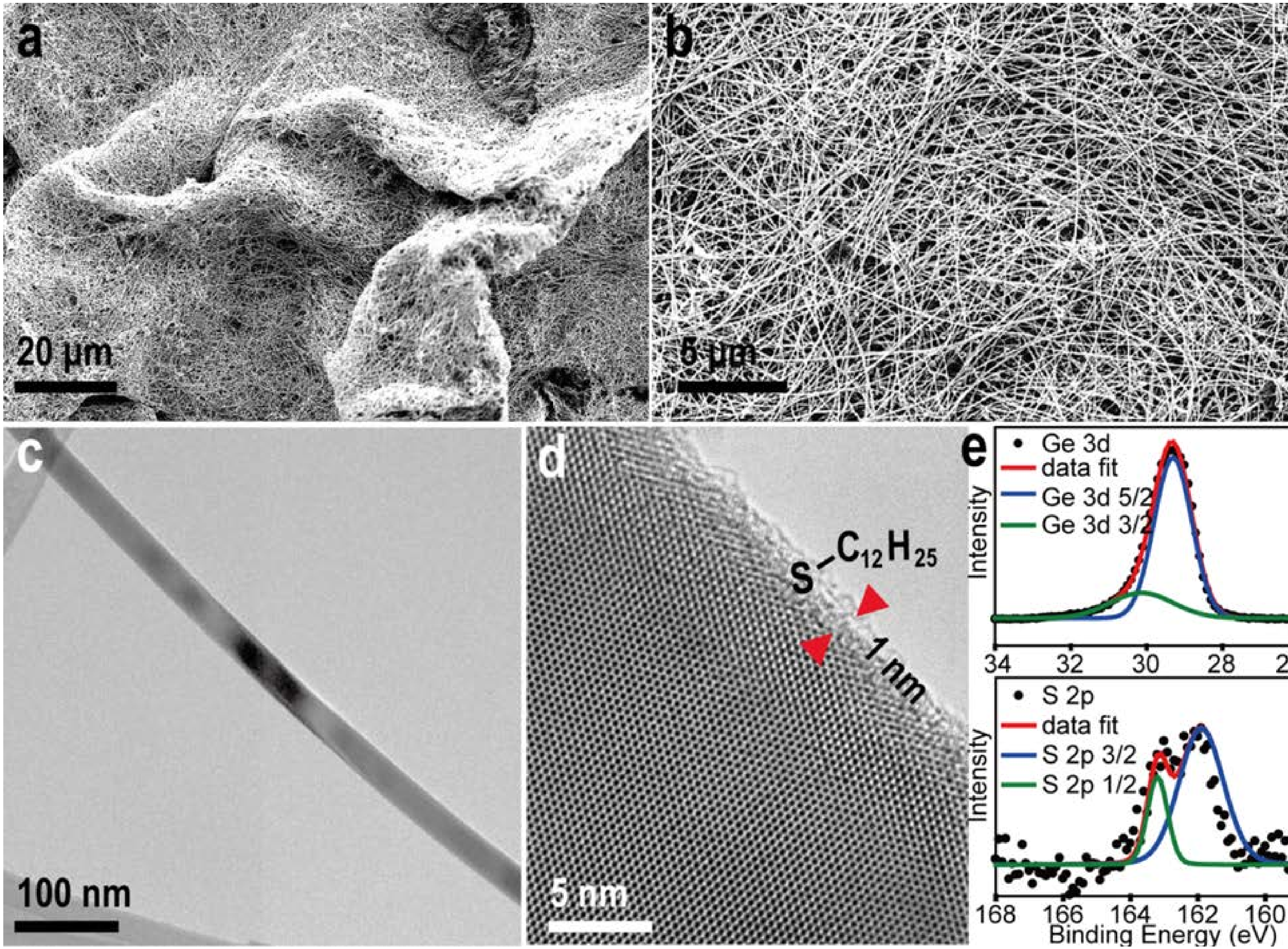
Growth of nanowires: metal seeded vapor-liquid-solid approach



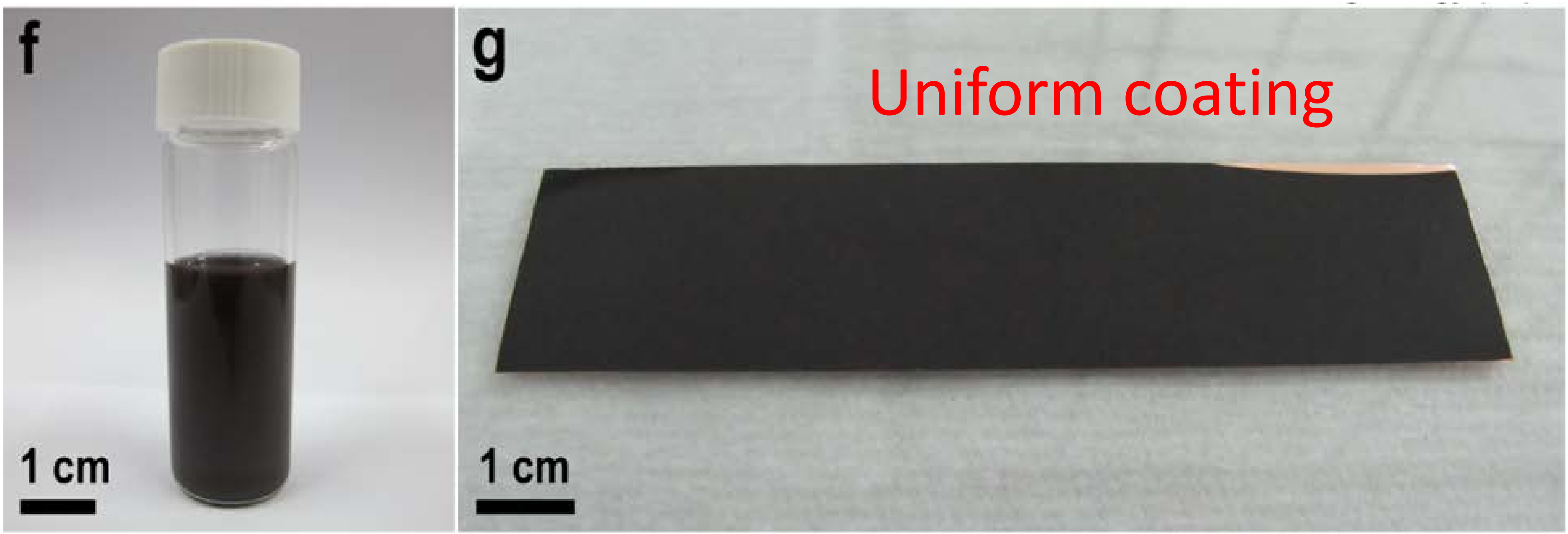


-metal nanoparticle-seeded Si and Ge nanowire synthesis
-most widely used metal is Au
-metal nanoparticles can control Si nanowire size

Germanium nanowire



Germanium Inks and coin cell fabrication

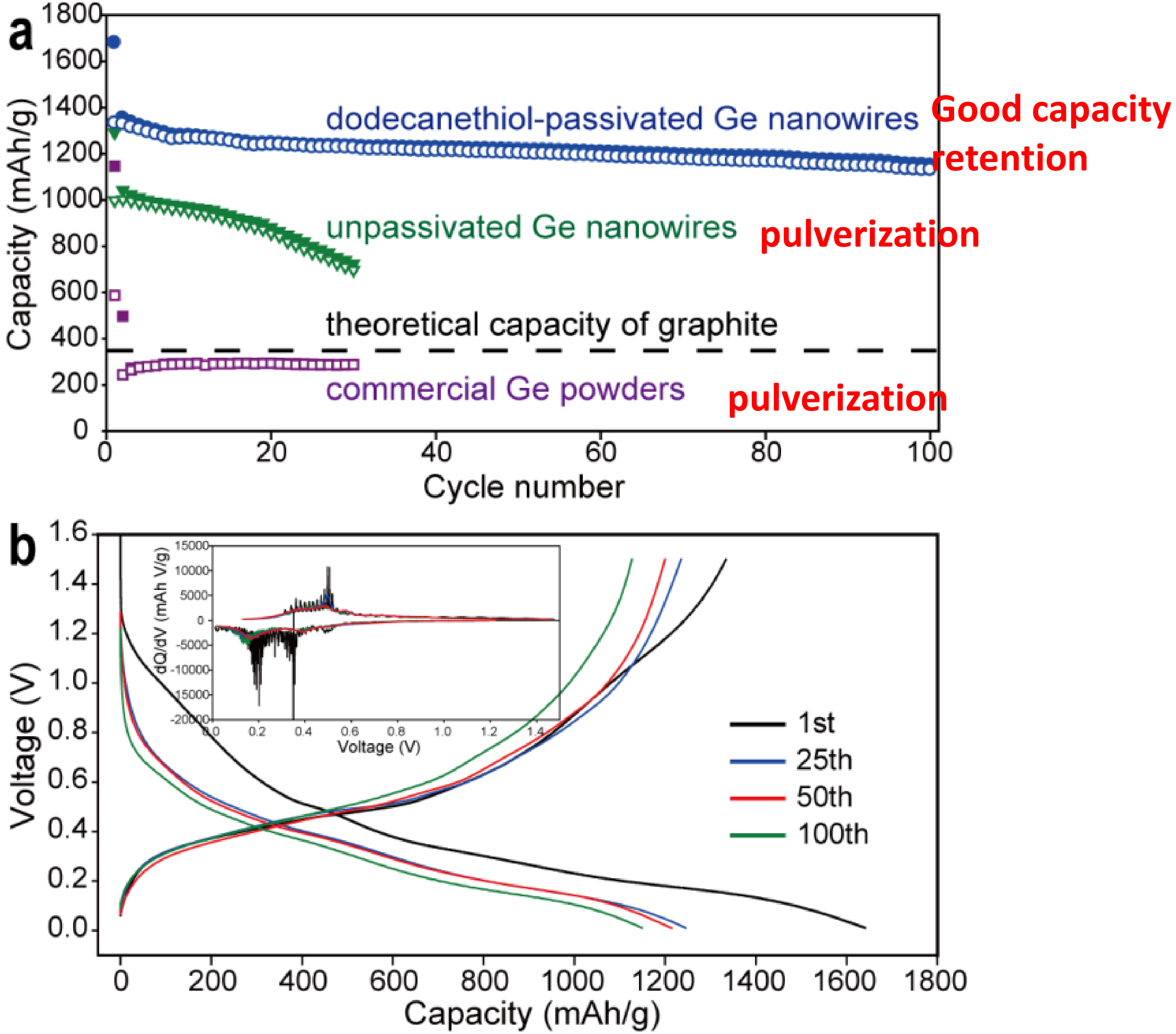


Uniform coating

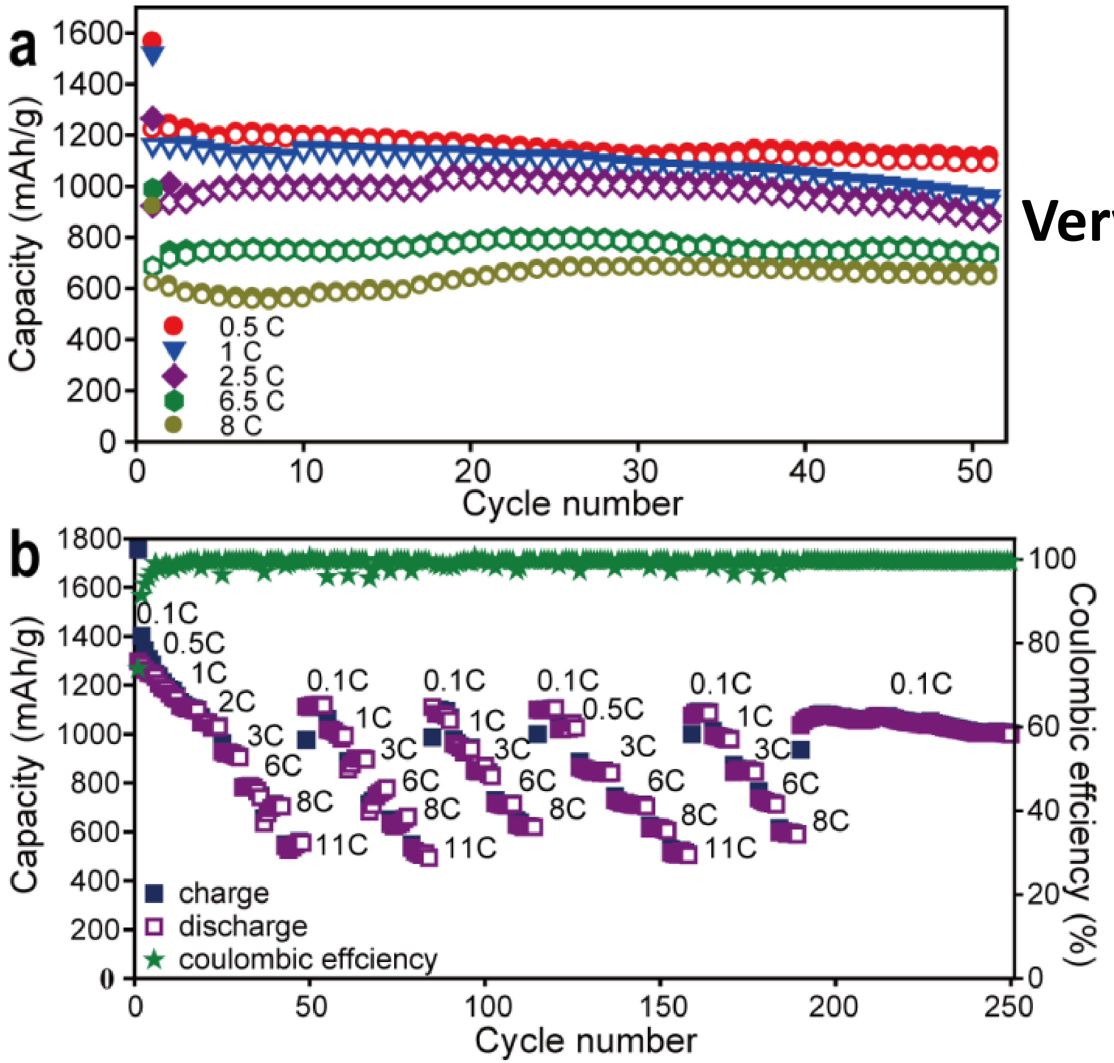
Stable suspension

Coin cell

Performance of Ge nanowire anode



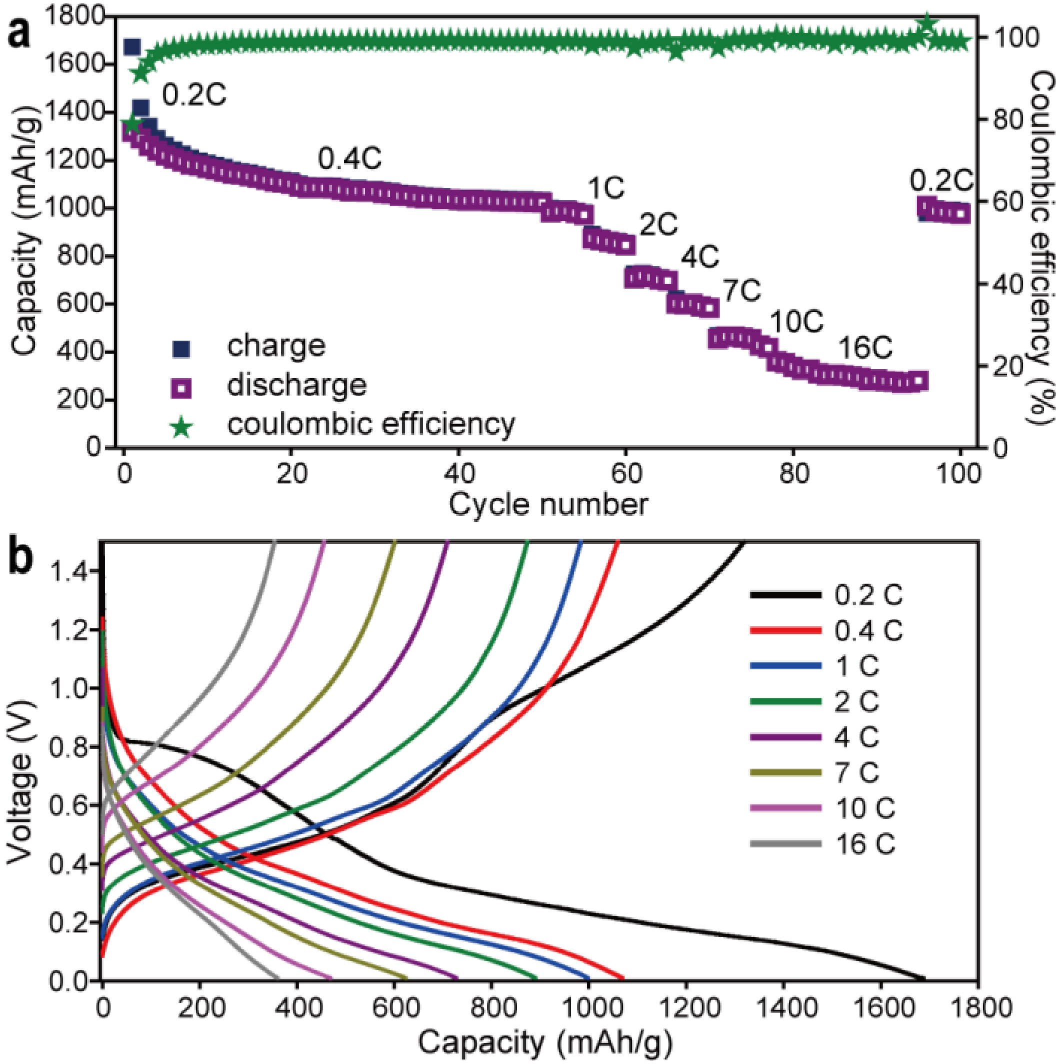
High-rate capability of Ge nanowire anode



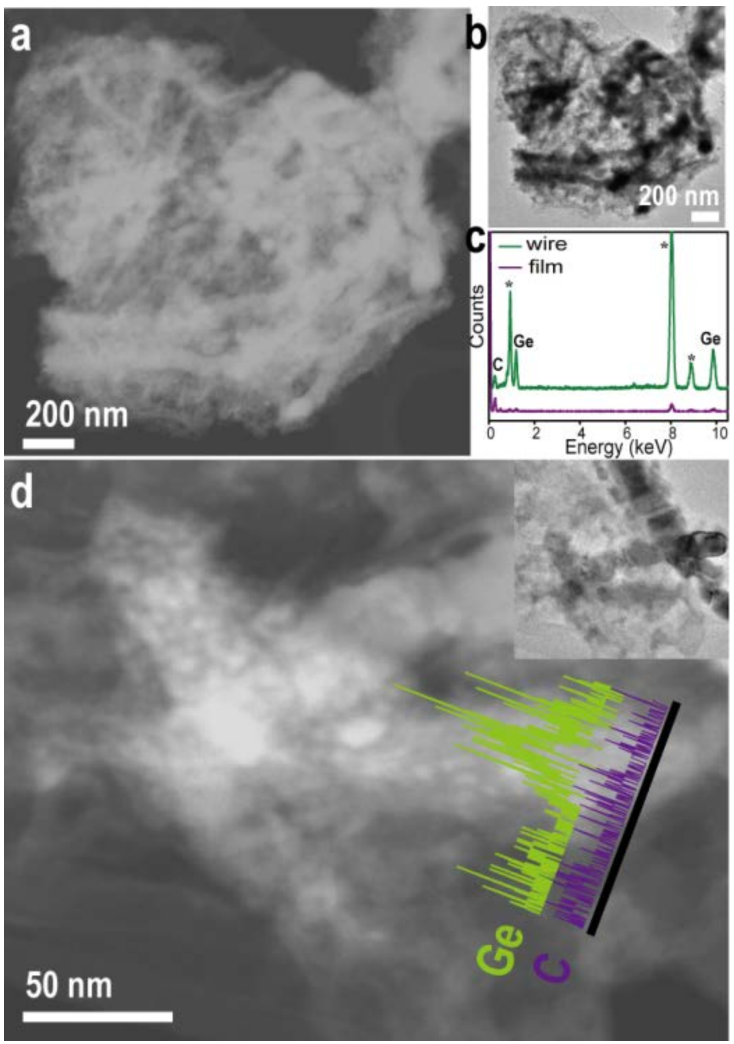
Very good high rate capability

Five repeated cycles

High temperature performance (55 °C) of Ge nanoiwre anode

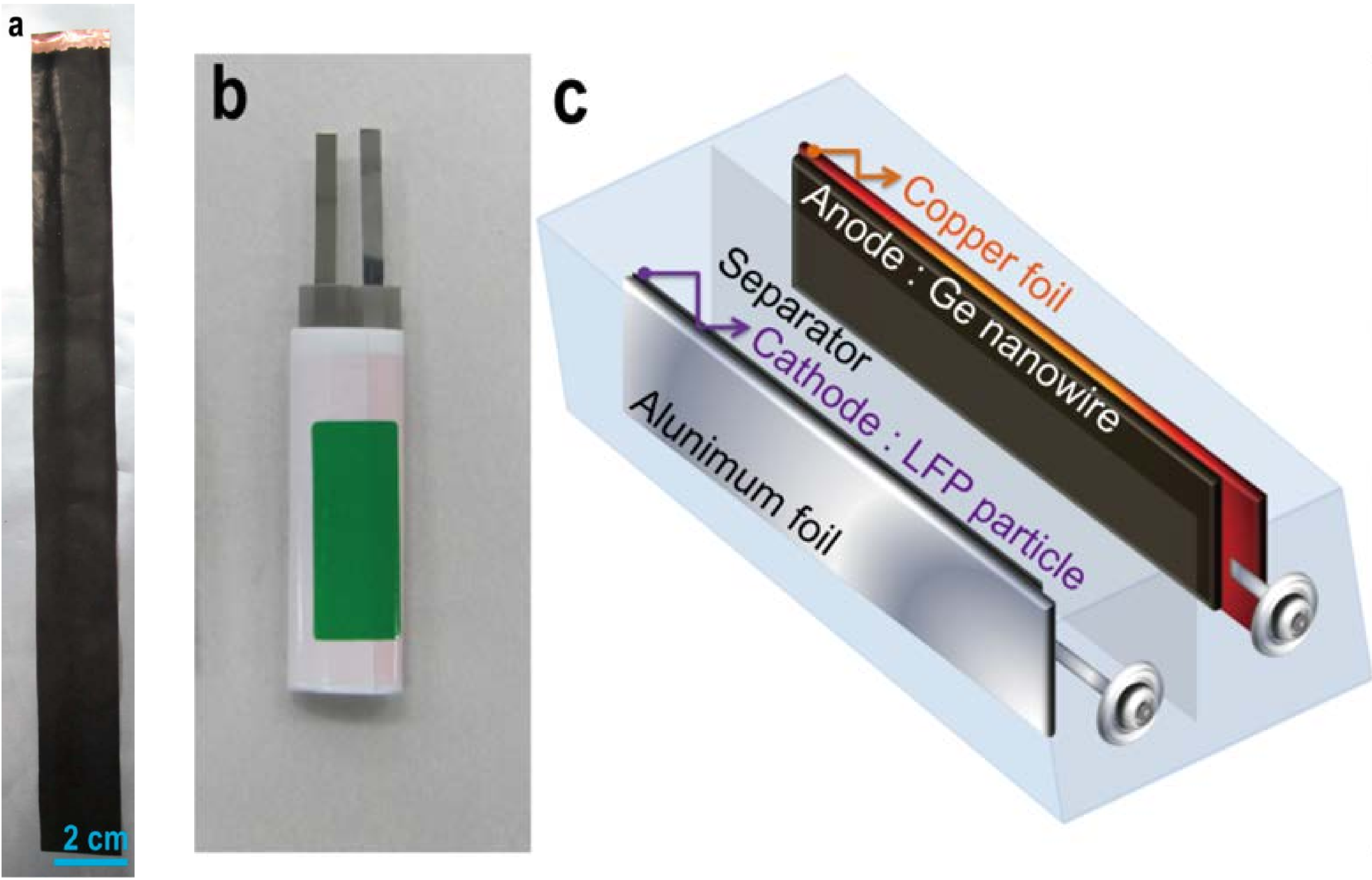


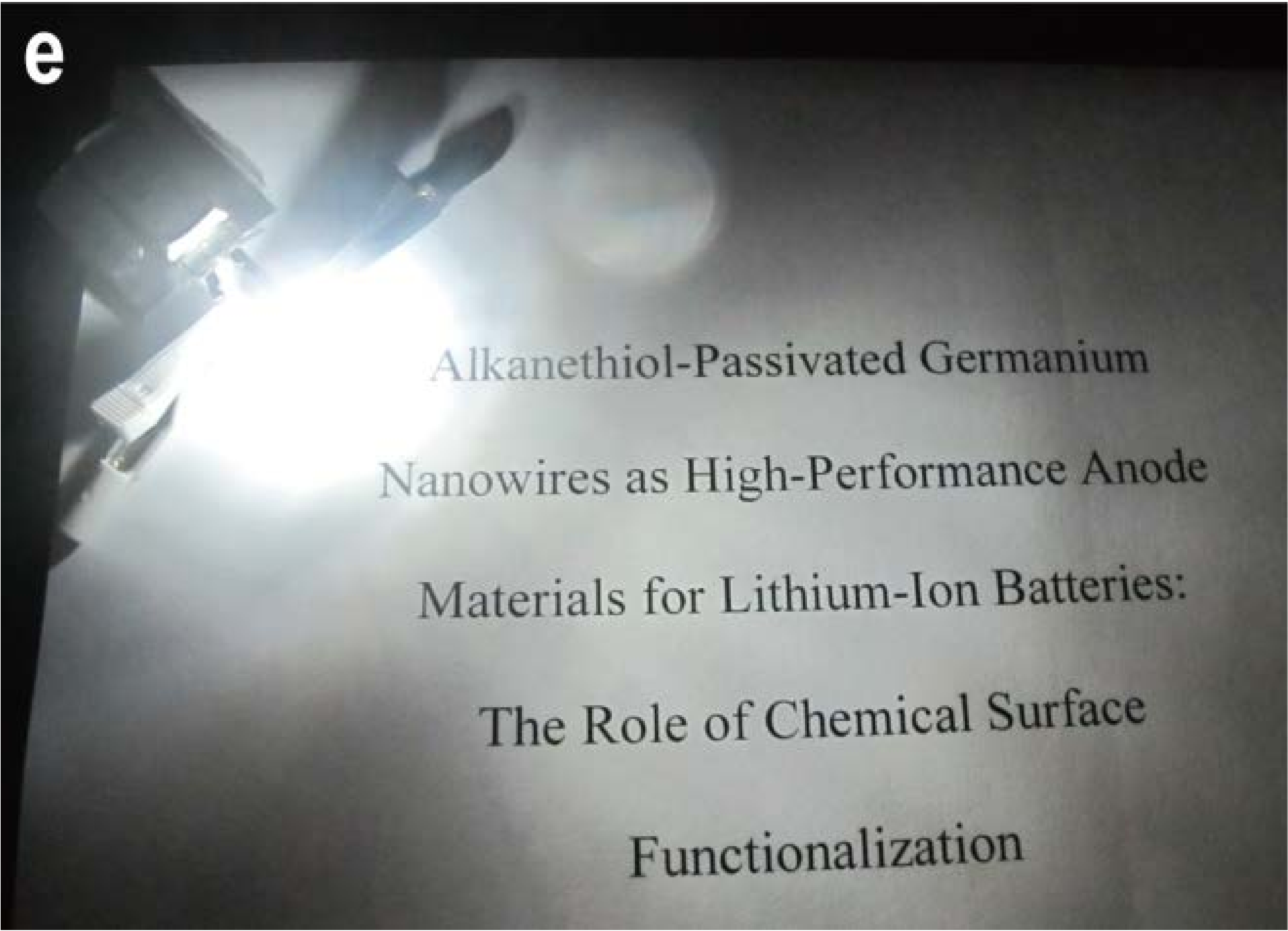
Robust nanowire/PVDF structure

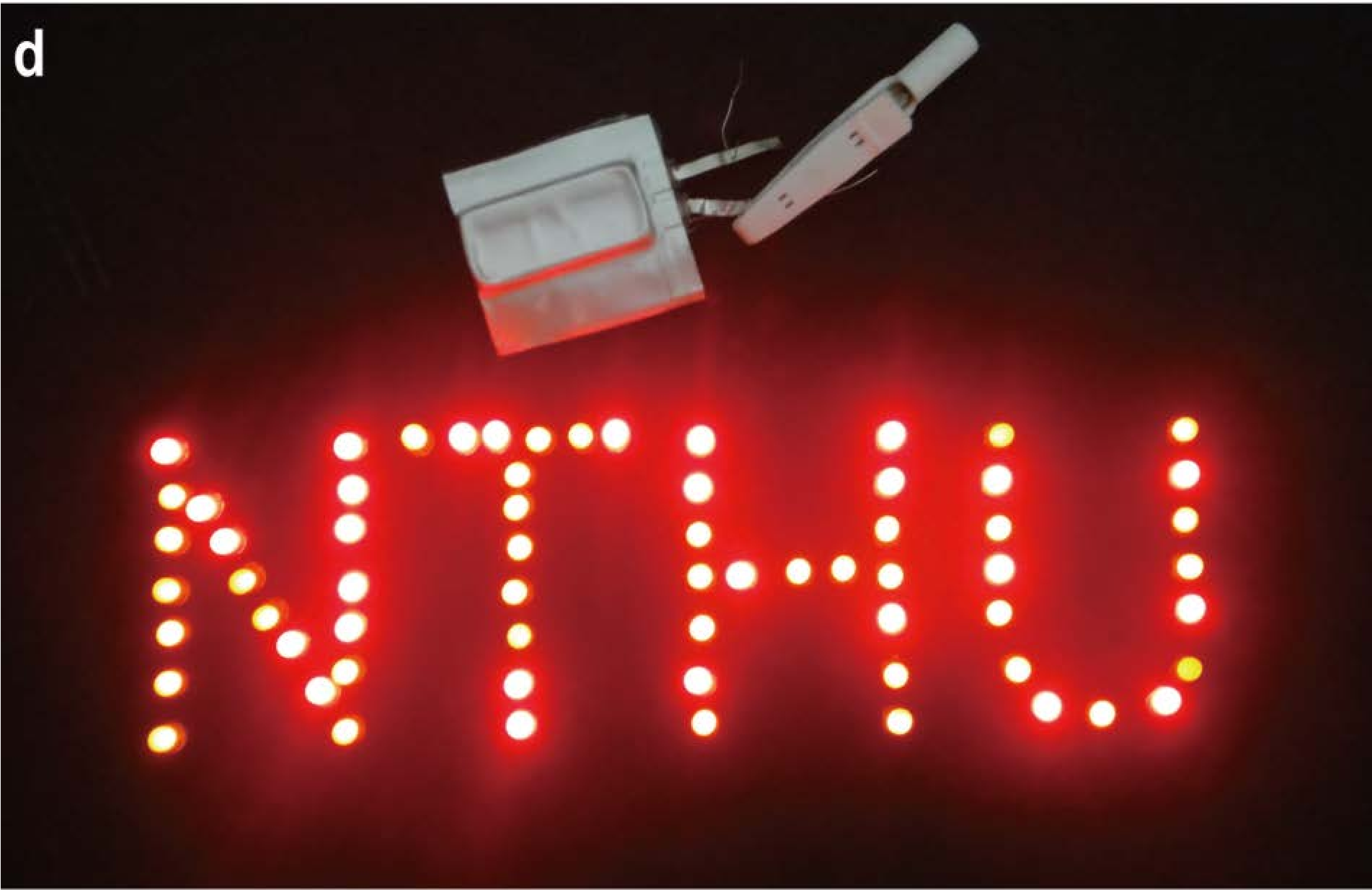


After many cycles of
lithium insertion and extration,
the structure is still very robust

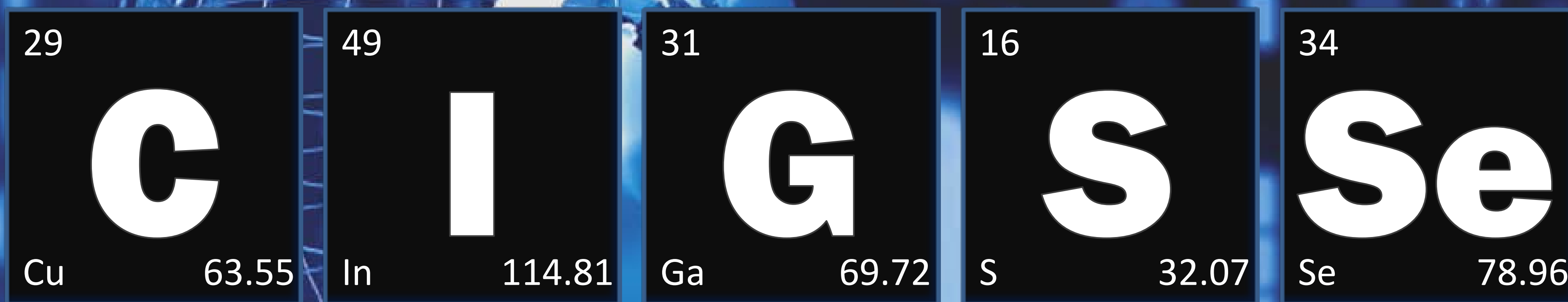
A large-area assembled full cells




e
Alkanethiol-Passivated Germanium
Nanowires as High-Performance Anode
Materials for Lithium-Ion Batteries:
The Role of Chemical Surface
Functionalization


d
NTHU

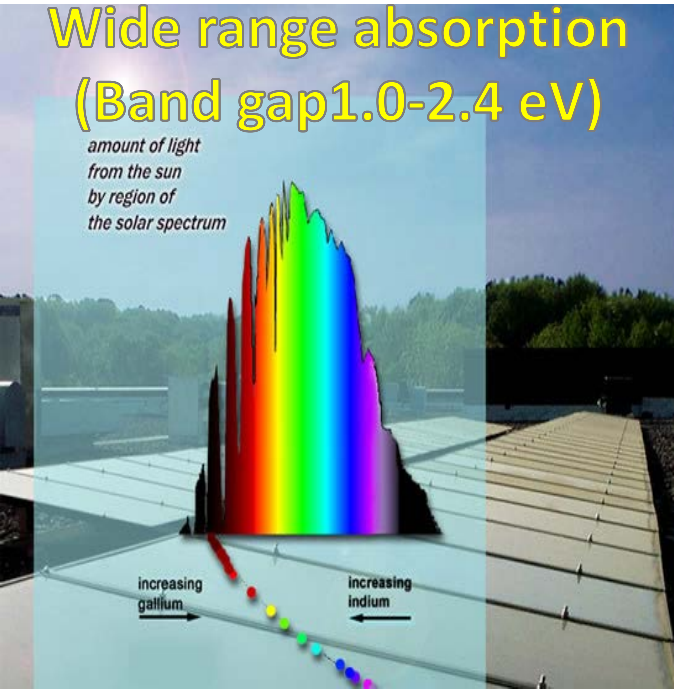
Synthesis of $CuIn_{1-x}Ga_x(S_ySe_{1-y})_2$ (CuInGaSSe) Nanocrystal inks for low-cost photovoltaic devices



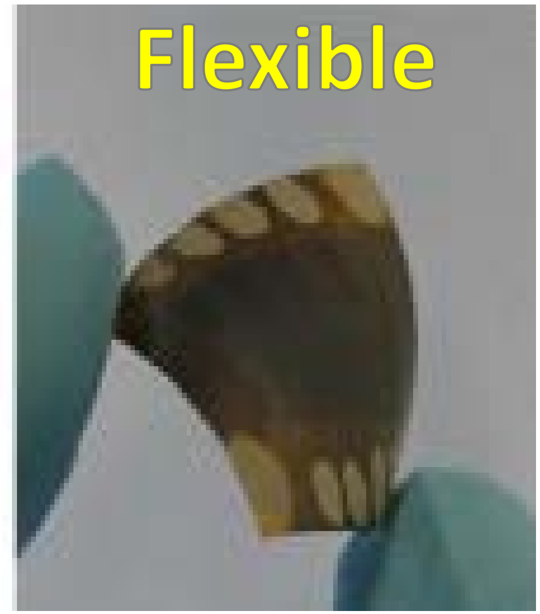
Tuan et al.

- ***Energy & Environmental Science***, 2011, 4, 4929-4932
- ***The Journal of Physical Chemistry C***, 2011, 115(5), 1592-1599
- ***Langmuir***, 2012, **accepted**

CIGS solar cell characteristics



Berkely lab news center website

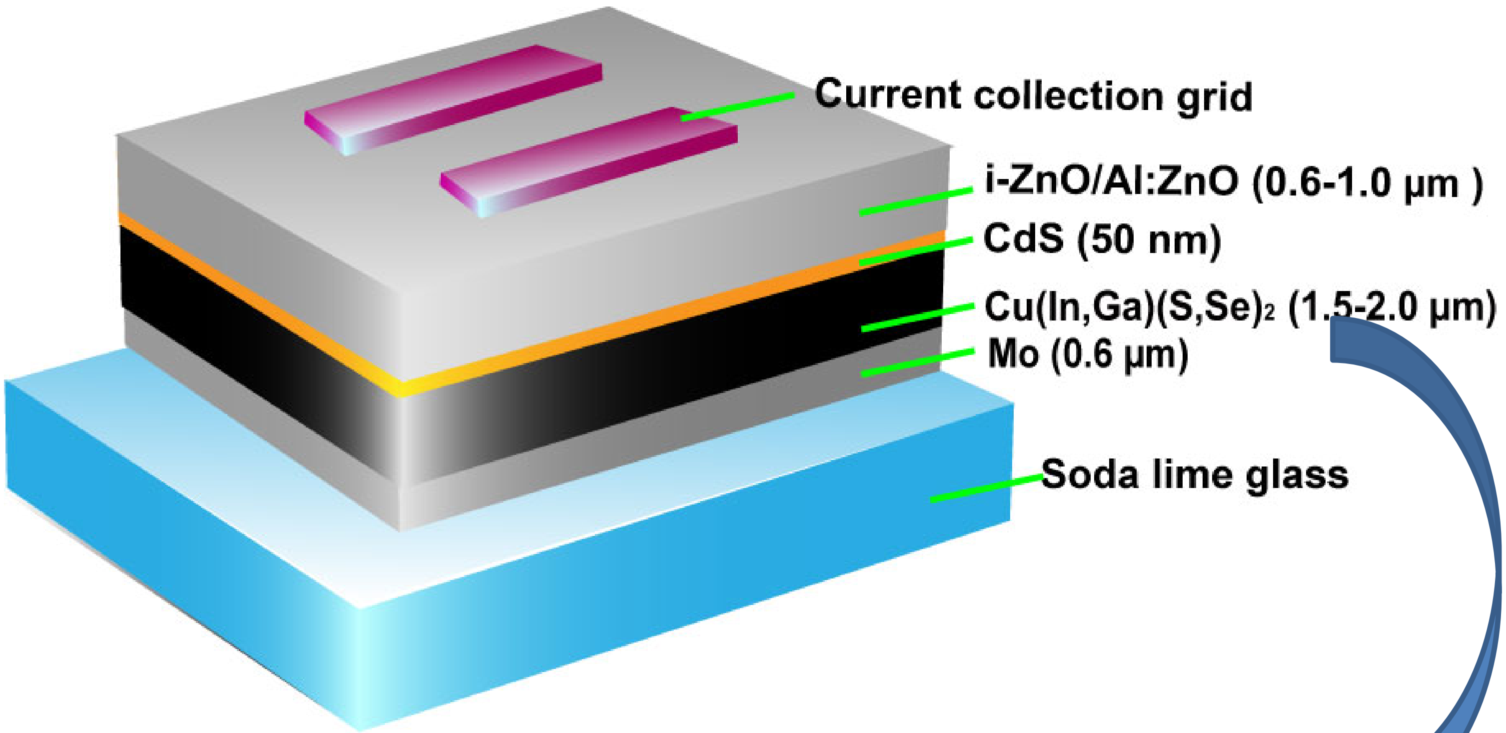


Journal of Solid State Chemistry
189 (2012) 2-12

Cu(In,Ga)(S,Se)$_2$ (CIGS) device structure

Total device thickness less than 5 μm (Crystalline Si module~200 μm)

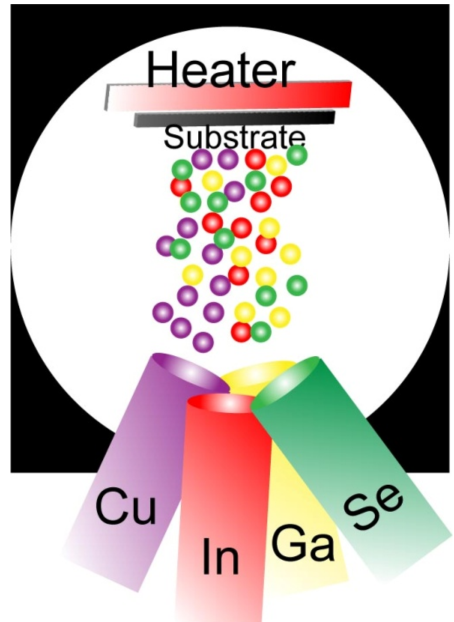
Schematic picture



The CIGSSe absorber layer can be made via a **vacuum** or a **nonvacuum** route.

Vacuum-based CIGS film deposition

Could make the Highest efficiency cell in the lab ~20%, but



TIME-CONSUMING

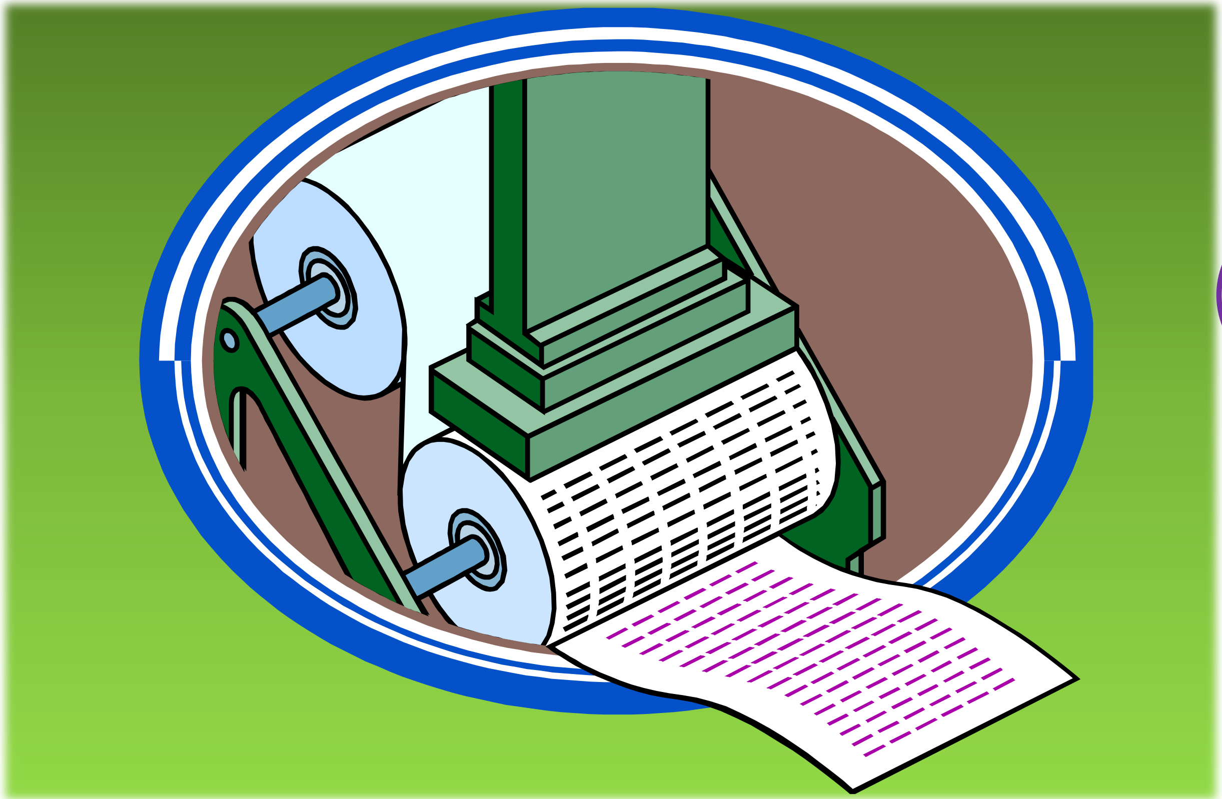
LOW THROUGHPUT

EXPENSIVE

DIFFICULT TO CONTROL STOICHIOMETRY OVER LARGE AREAS

POOR MATERIALS UTILIZATION (30-50%)

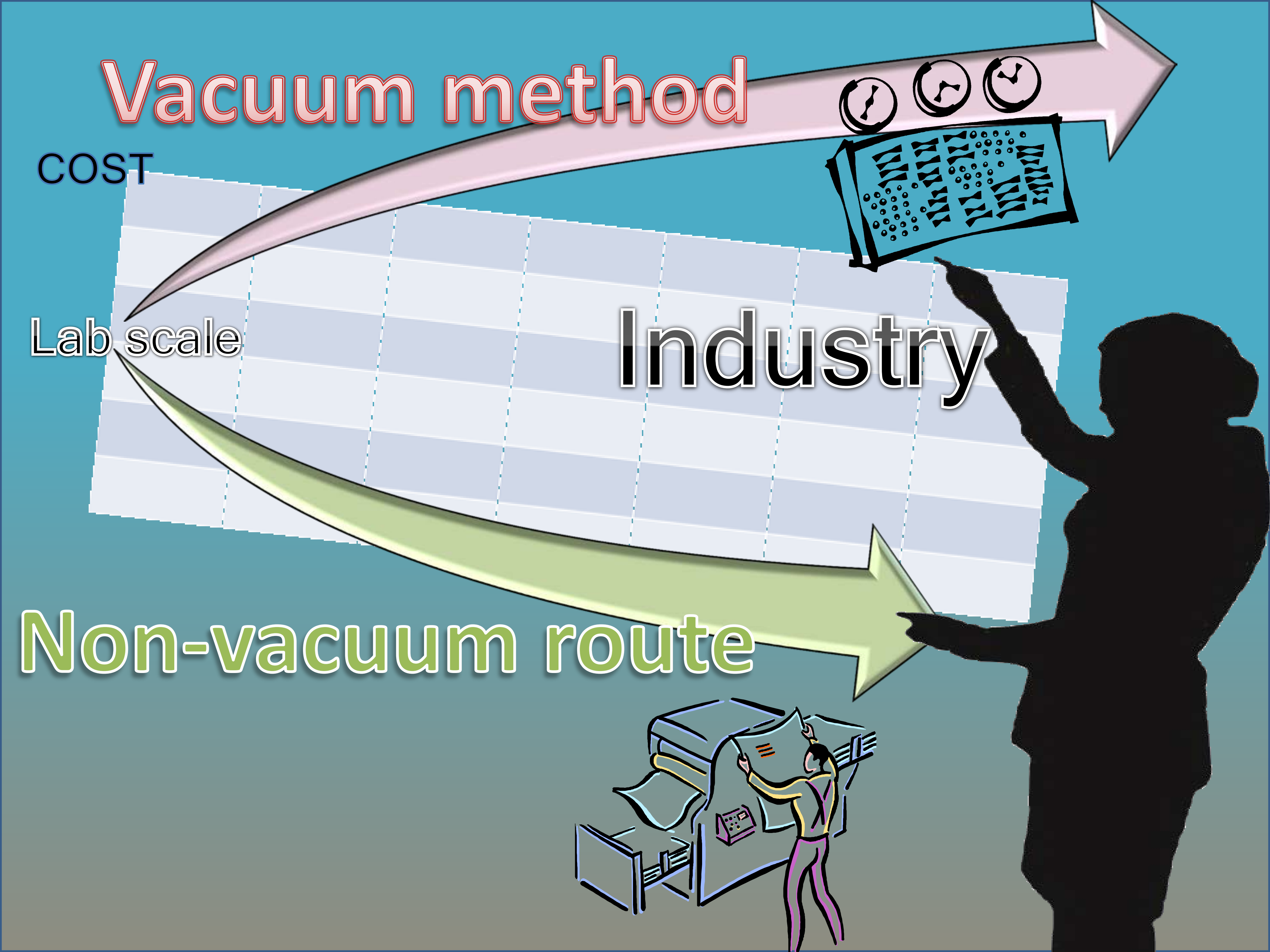
Non-Vacuum Processing for CIGS thin film deposition

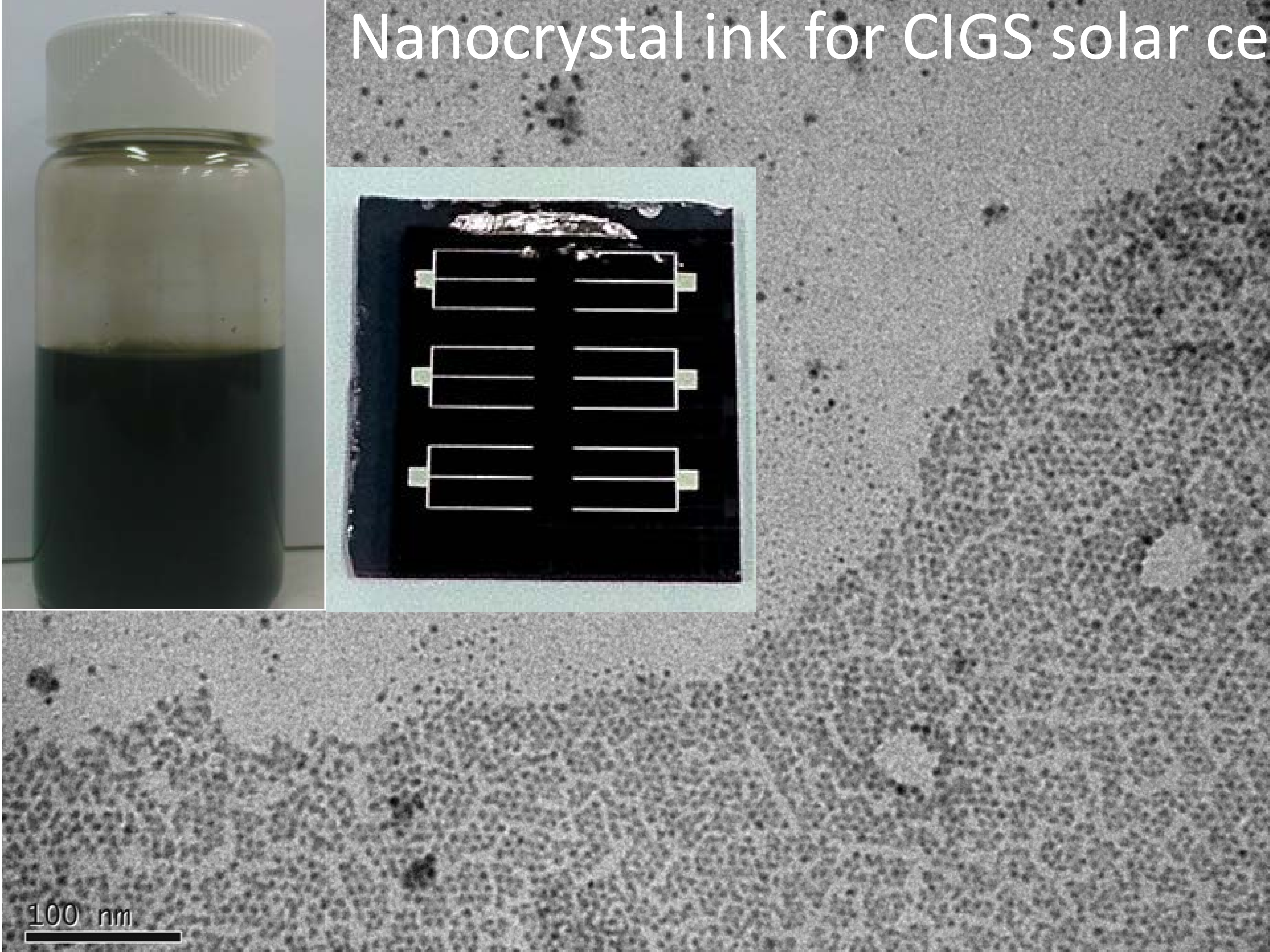


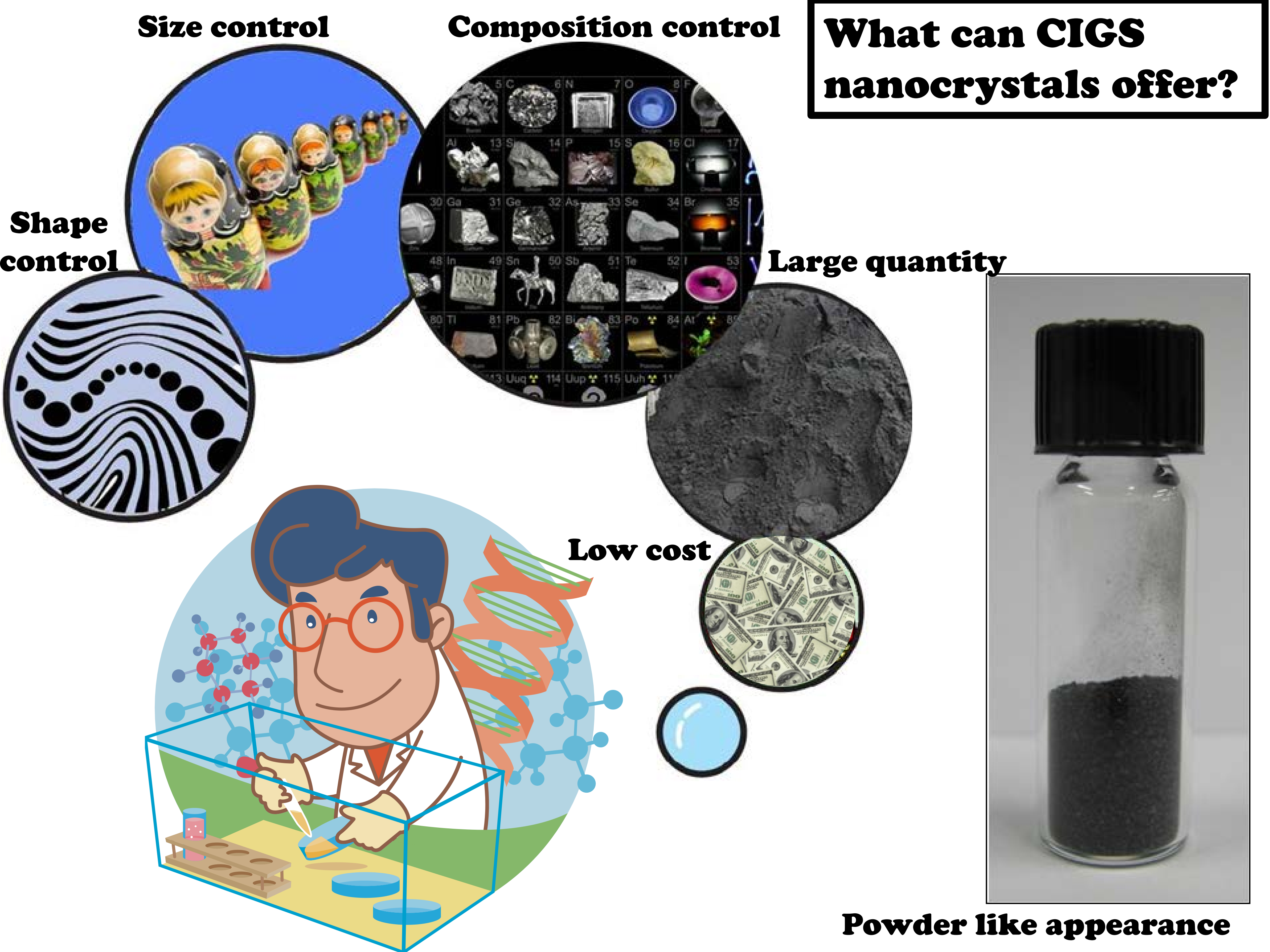
ROLL-TO-ROLL PROCESSING

COST EFFECTIVE

STOICHIOMETRY CONTROLLABLE OVER LARGE AREA


Vacuum method
COST
Lab scale
Industry
Non-vacuum route


Nanocrystal ink for CIGS solar ce
100 nm


What can CIGS nanocrystals offer?
Size control
Composition control
Shape control
Large quantity
Low cost
Powder like appearance

Outline

2008.10
CIGS project begin

2008.10
Ternary nanocrystal phase & size control

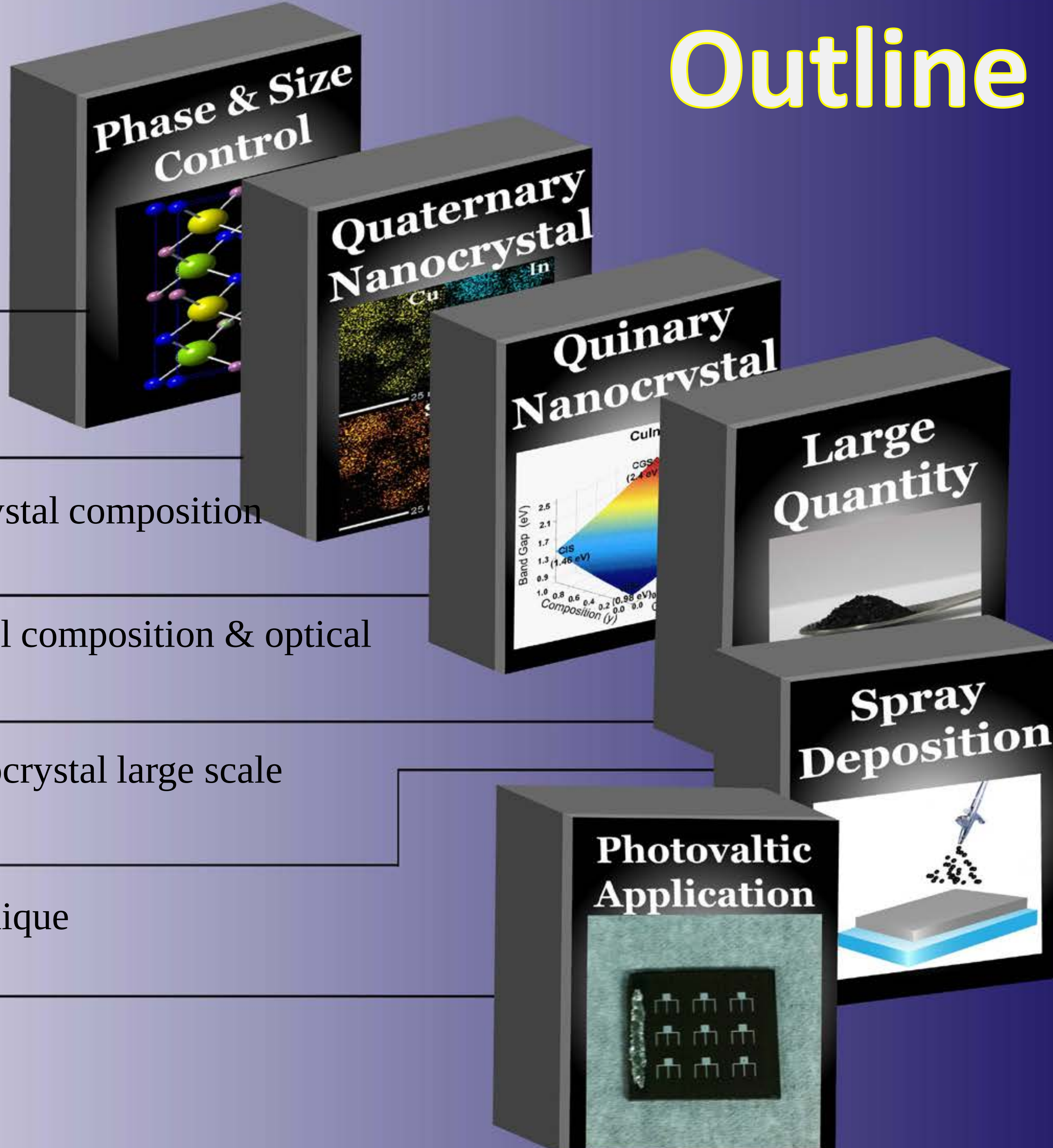
2010.02
Tuning quaternary nanocrystal composition & optical properties

2010.09
Tuning quinary nanocrystal composition & optical properties

2011.06
$CuIn_{1-x}Ga_x(S_ySe_{1-y})_2$ Nanocrystal large scale production over 1 g yield.

2011.06
Developing spraying technique

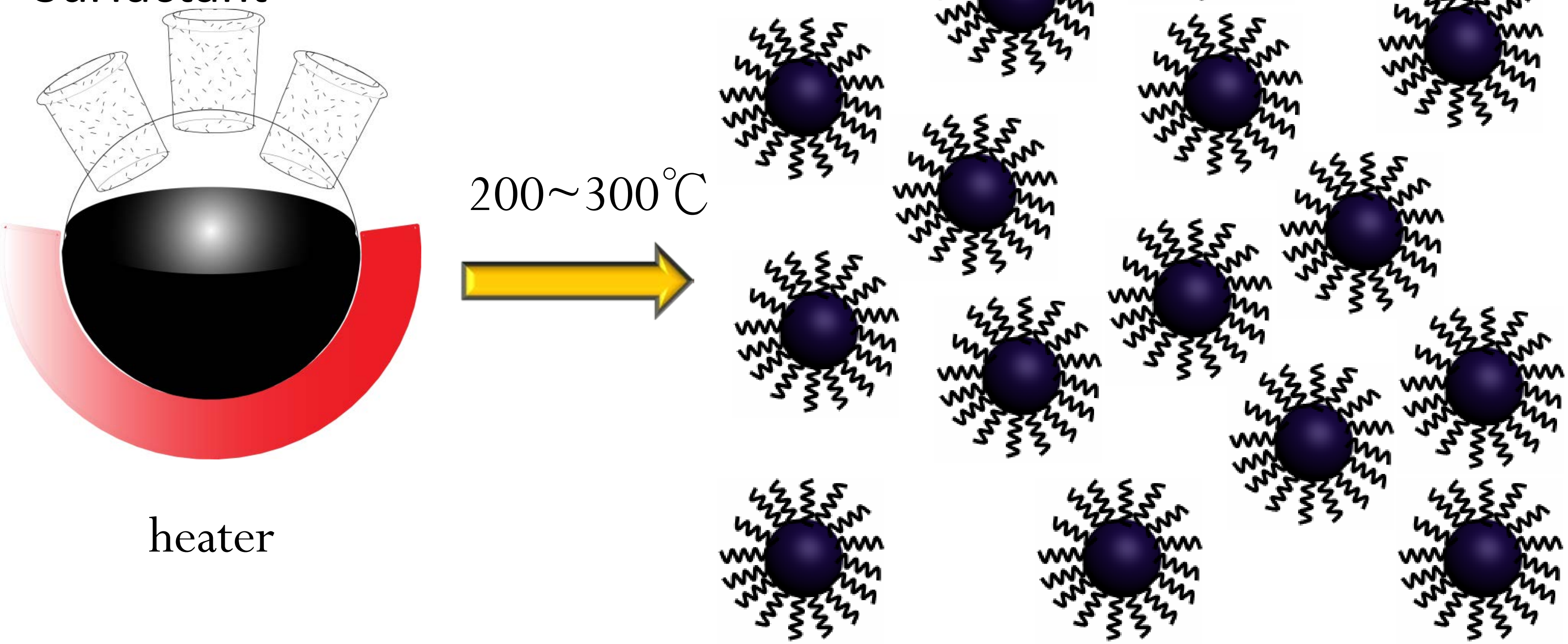
2011.10
Solar cell devices made



Facile Batch reaction Synthesis

Hot Solvent Method

-Cu, In, Ga, S, Se precursors
-Solvent
-Surfactant

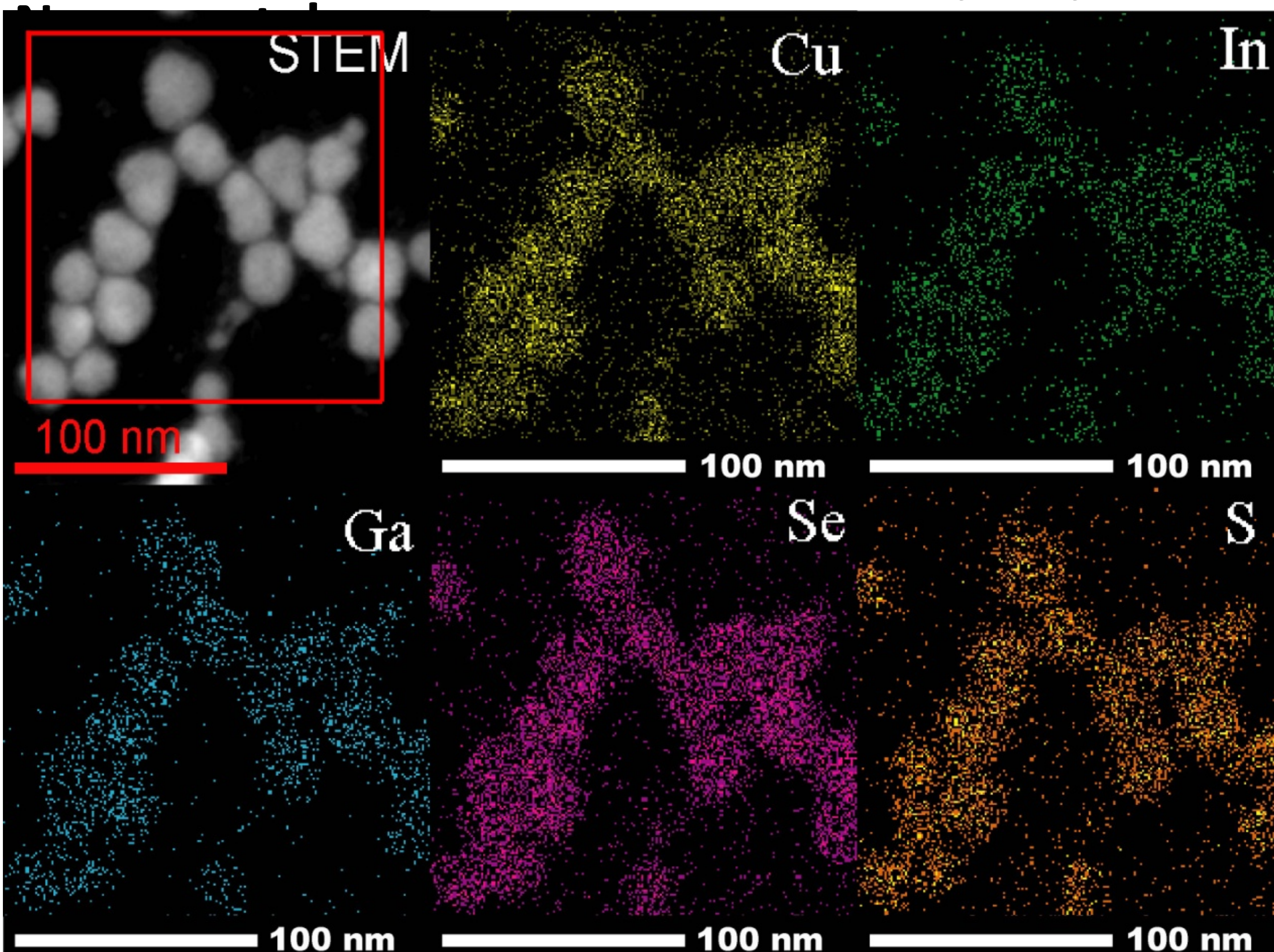


$CuIn(S_{1-x}Se_x)_2$

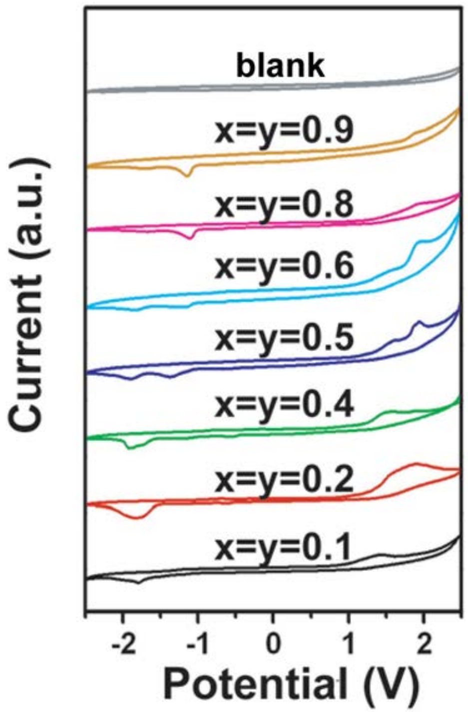
$CuIn_xGa_{1-x}Se_2$

$Cu(In_{1-x}Ga_x)(S_ySe_{1-y})_2$

Composition Tuning of $Cu(In_{1-x}Ga_x)(S_ySe_{1-y})_2$

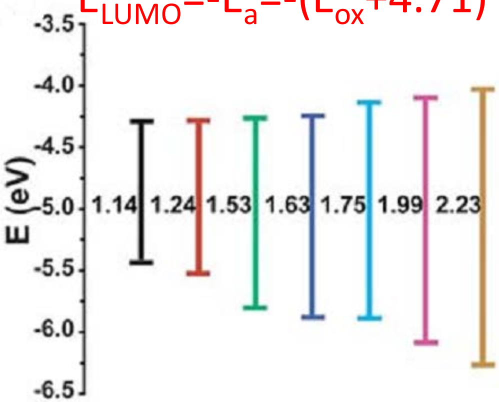


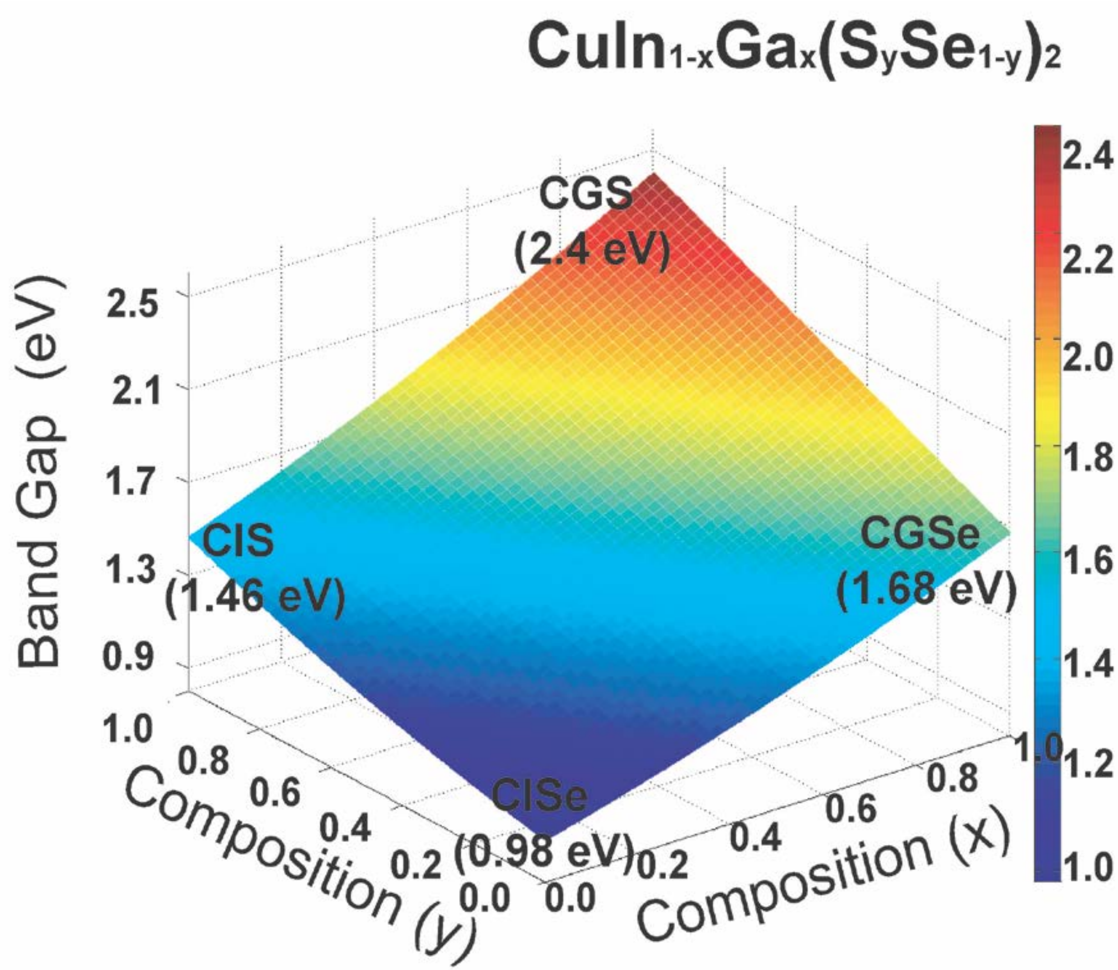
Cyclic voltammograms of $Cu(In_{1-x}Ga_x)(S_ySe_{1-y})_2$ nanocrystals



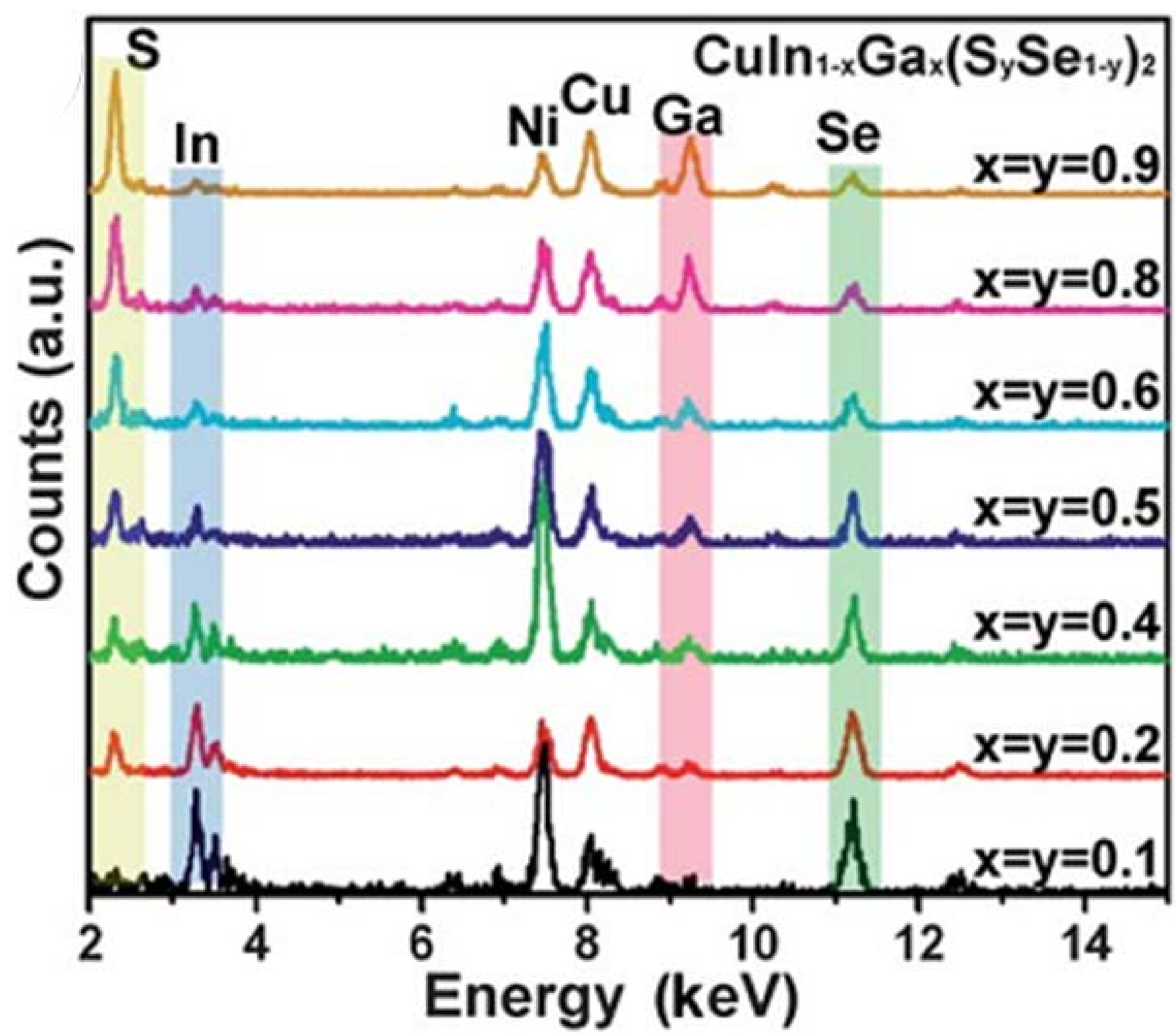
$E_{HOMO}=-I_p=-(E_{ox}+4.71)$ eV

$E_{LUMO}=-E_a=-(E_{ox}+4.71)$ eV

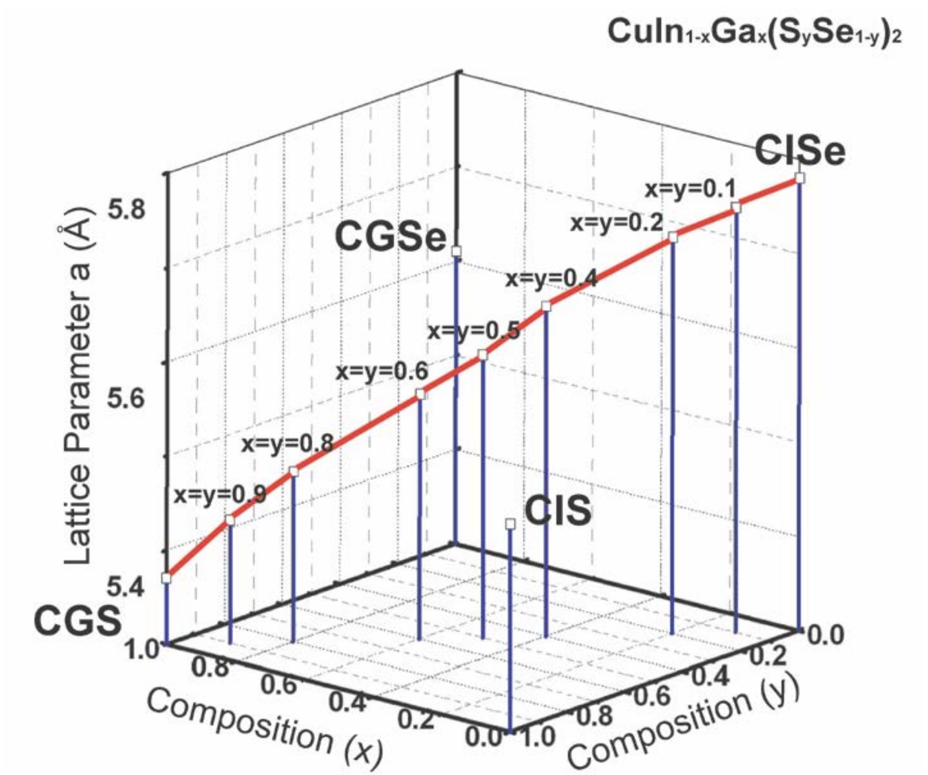


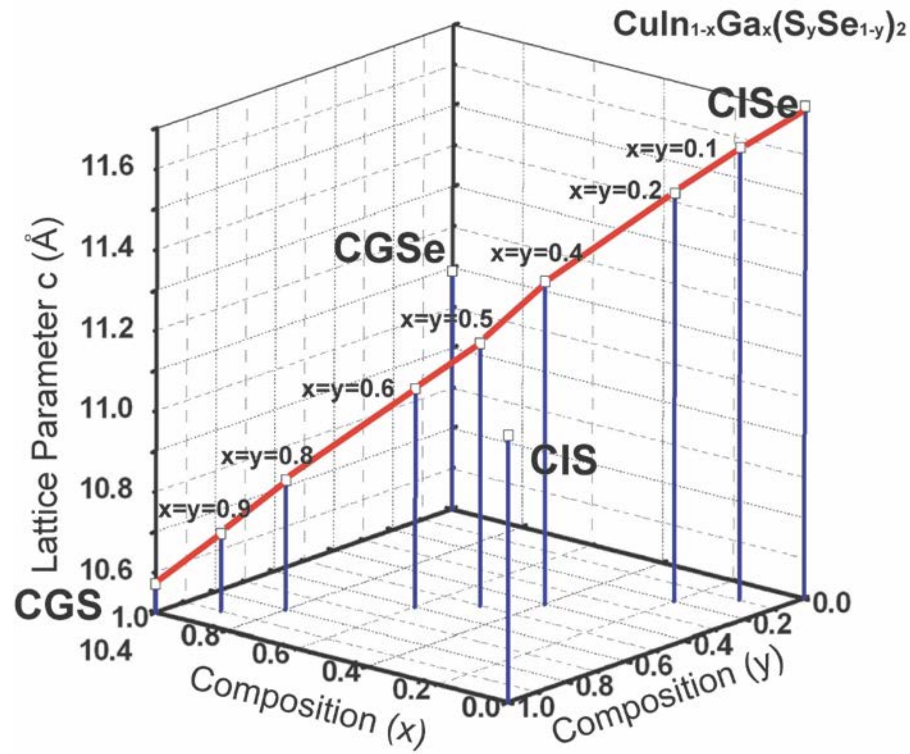


$Cu(In_{1-x}Ga_x)(S_ySe_{1-y})_2$ nanocrystal EDS analysis



$Cu(In_{1-x}Ga_x)(S_ySe_{1-y})_2$ lattice parameter
(derived from XRD)

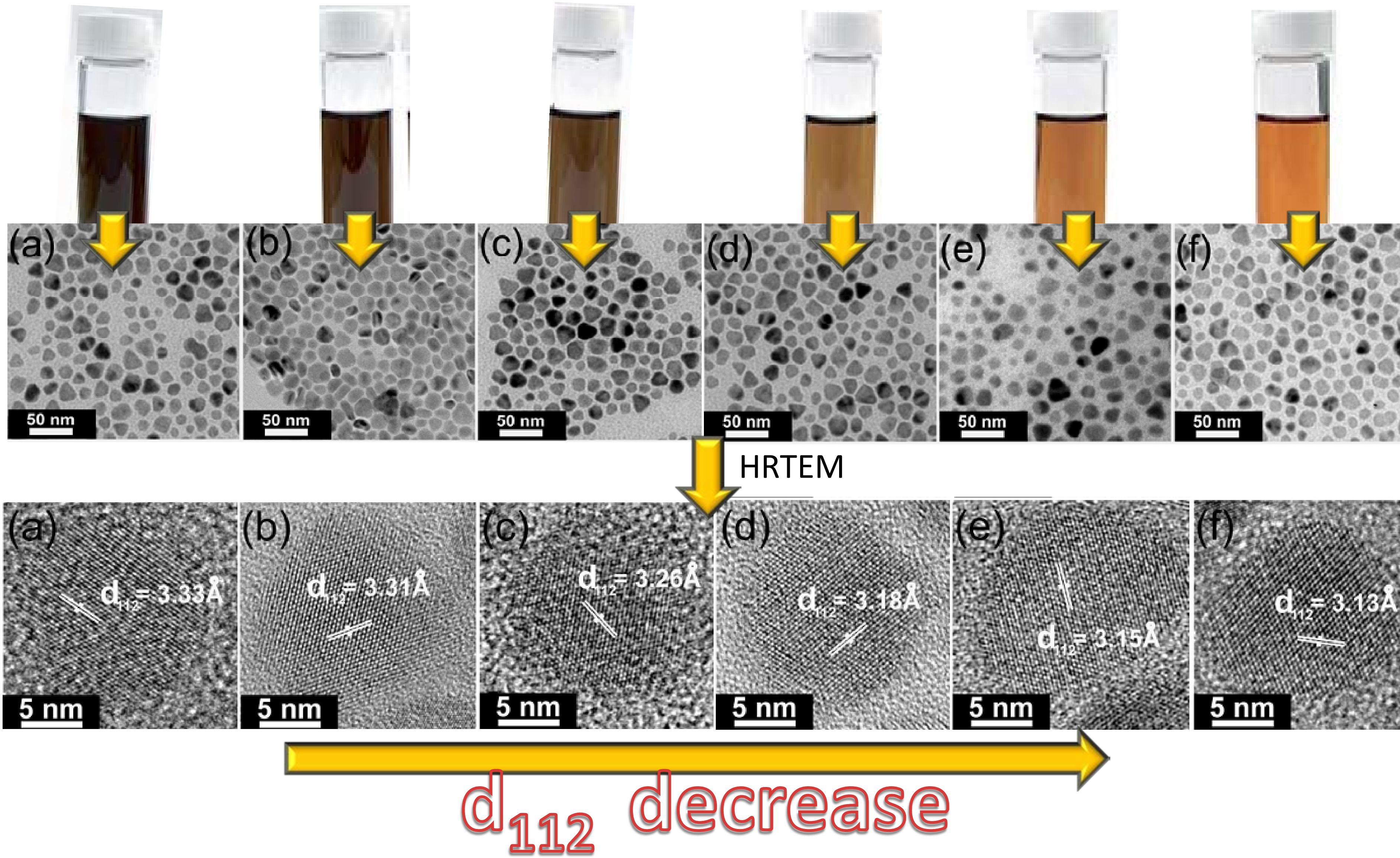


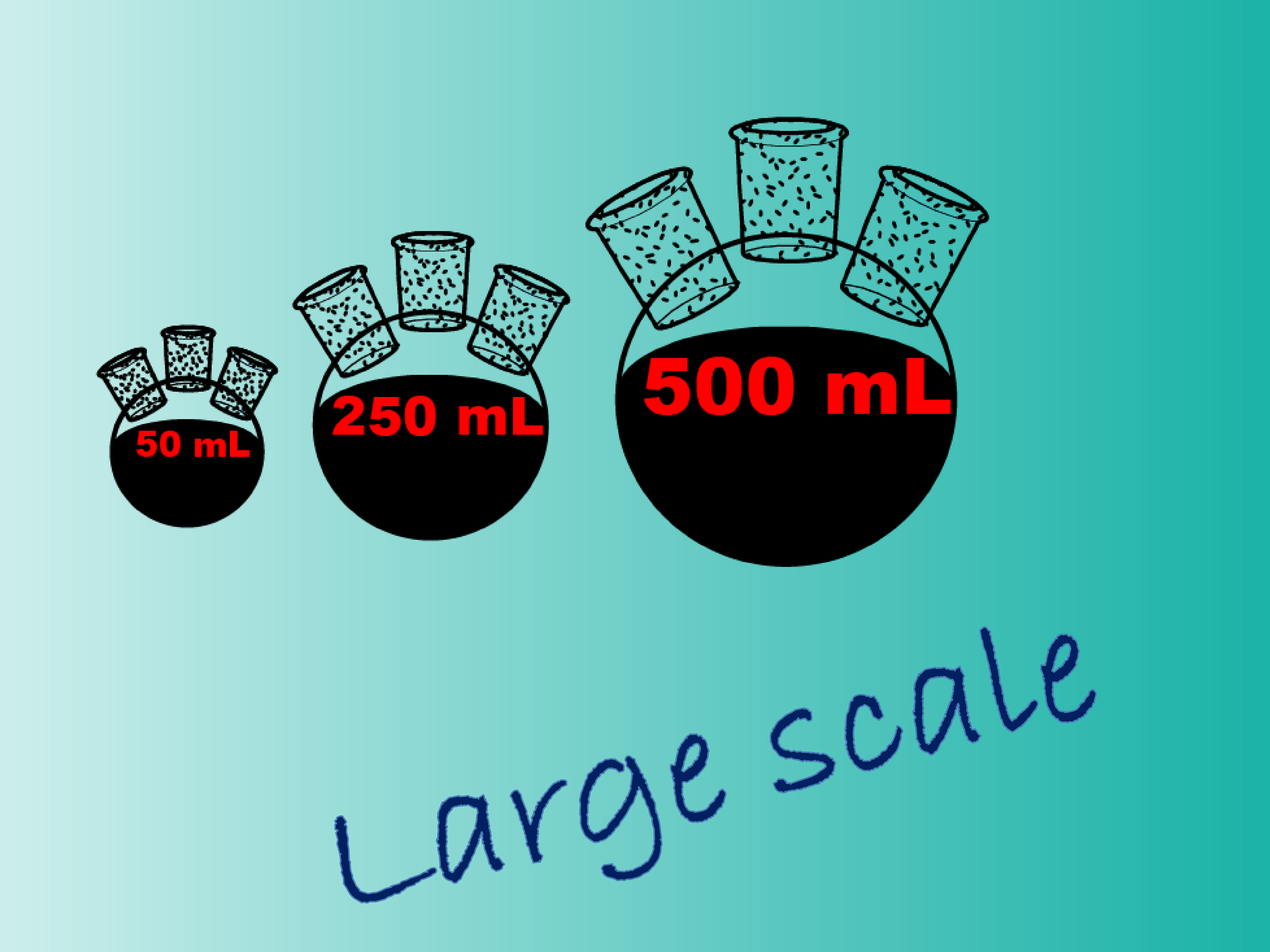


Agree with Vegard's law (red lines)

$CuIn_{1-x}Ga_x(S_ySe_{1-y})_2$ size and shape

x=y=0.1	x=y=0.2	x=y=0.4	x=y=0.6	x=y=0.8	x=y=0.9
Eg=1.08 eV	Eg=1.17 eV	Eg=1.42 eV	Eg=1.71 eV	Eg=2.01 eV	Eg=2.20 eV



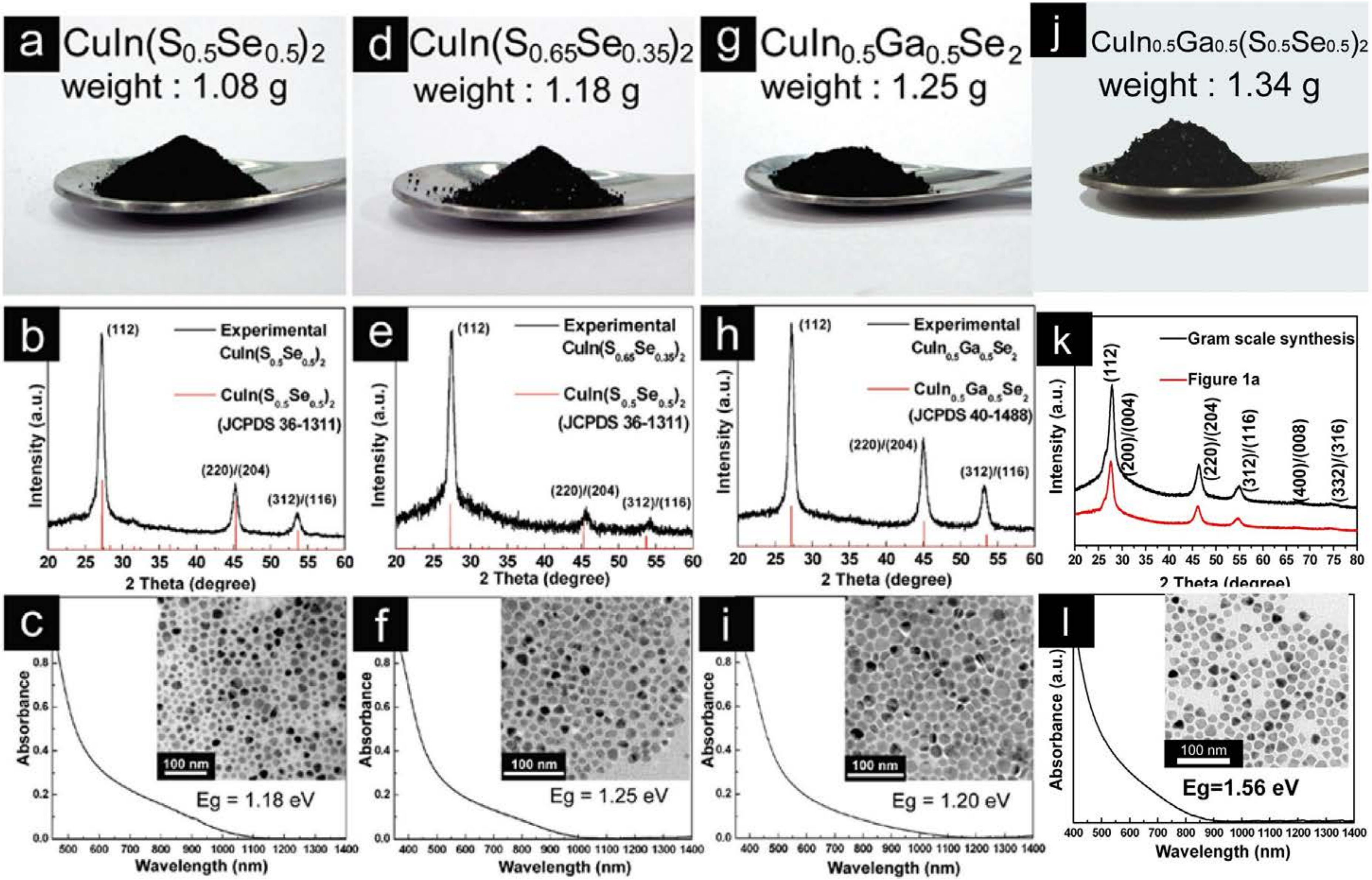

50 mL
250 mL
500 mL
Large scale

Scale-up synthesis of CIGS nanocrystals

Yield > 70 %

Gram-scale production

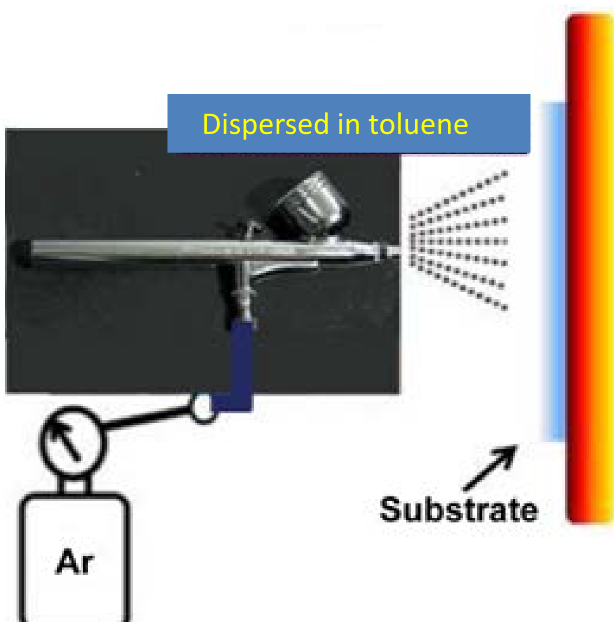
Large scale synthesis + composition tuning

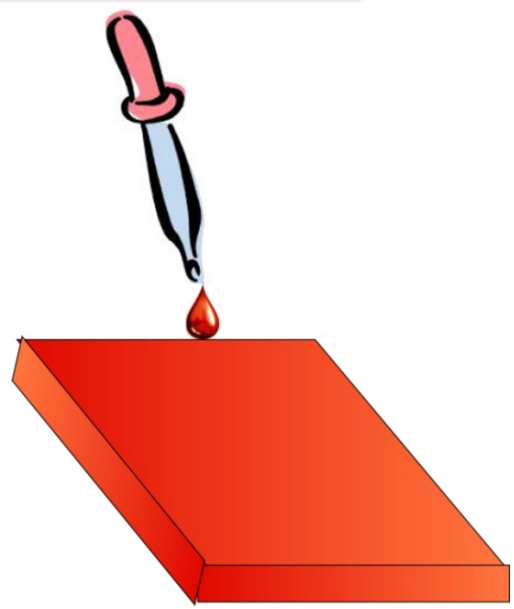


Methods to prepare a absorber film with uniform thickness for photovoltaic device fabrication

Nanocrystal inks

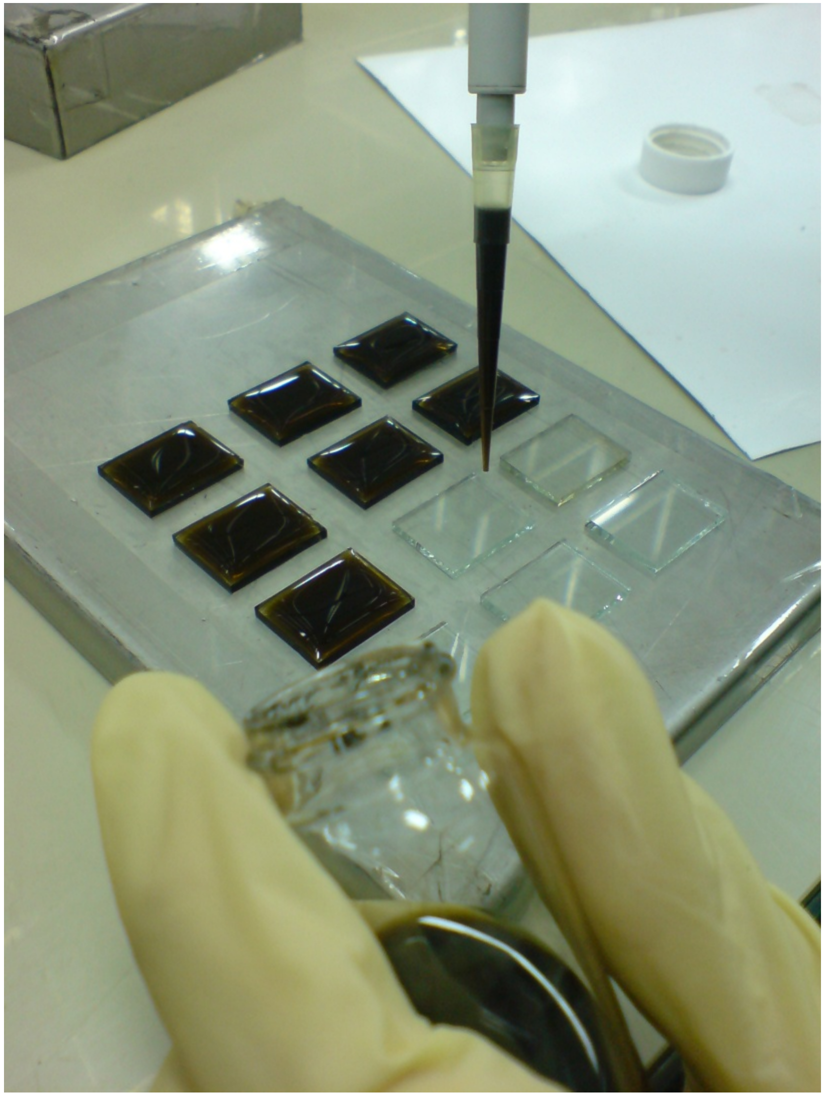
- Spray coating
- Drop casting





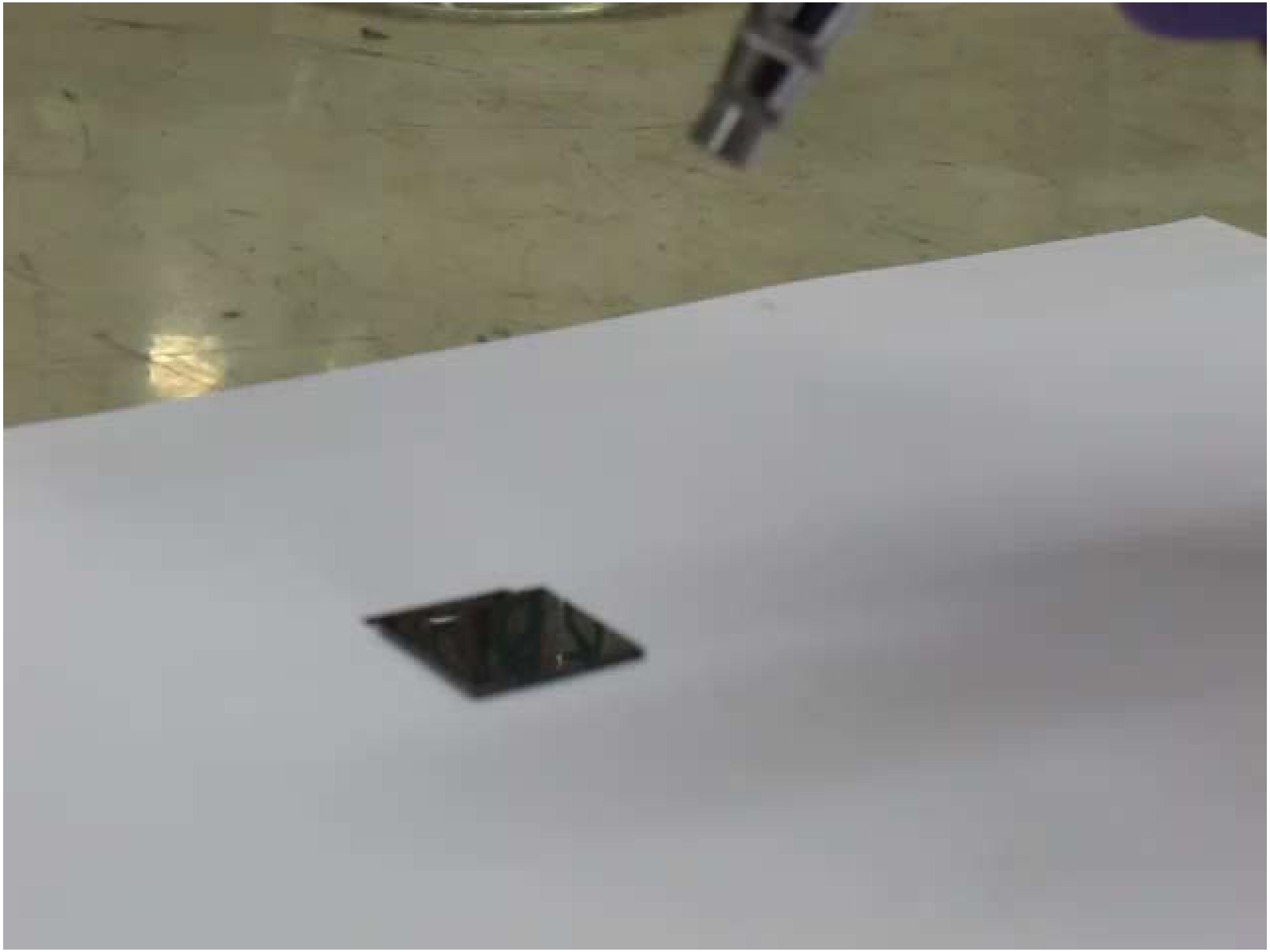
Photos of CIS_2, $CISe_2$, CIGS nanocrystals made in our lab

Drop-casting of $CISe_2$ Nanocrystal

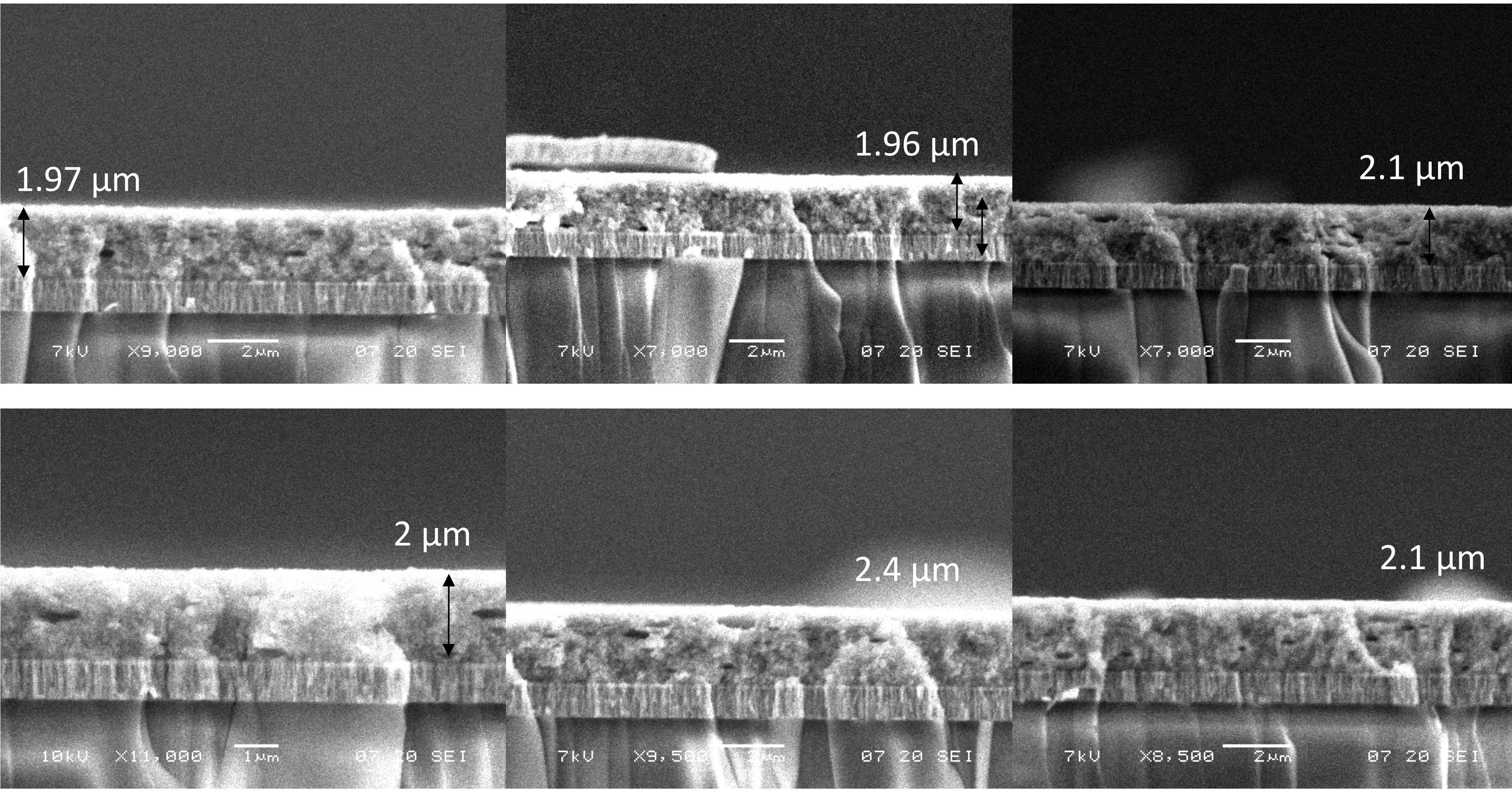


Glass : 20mm×15mm

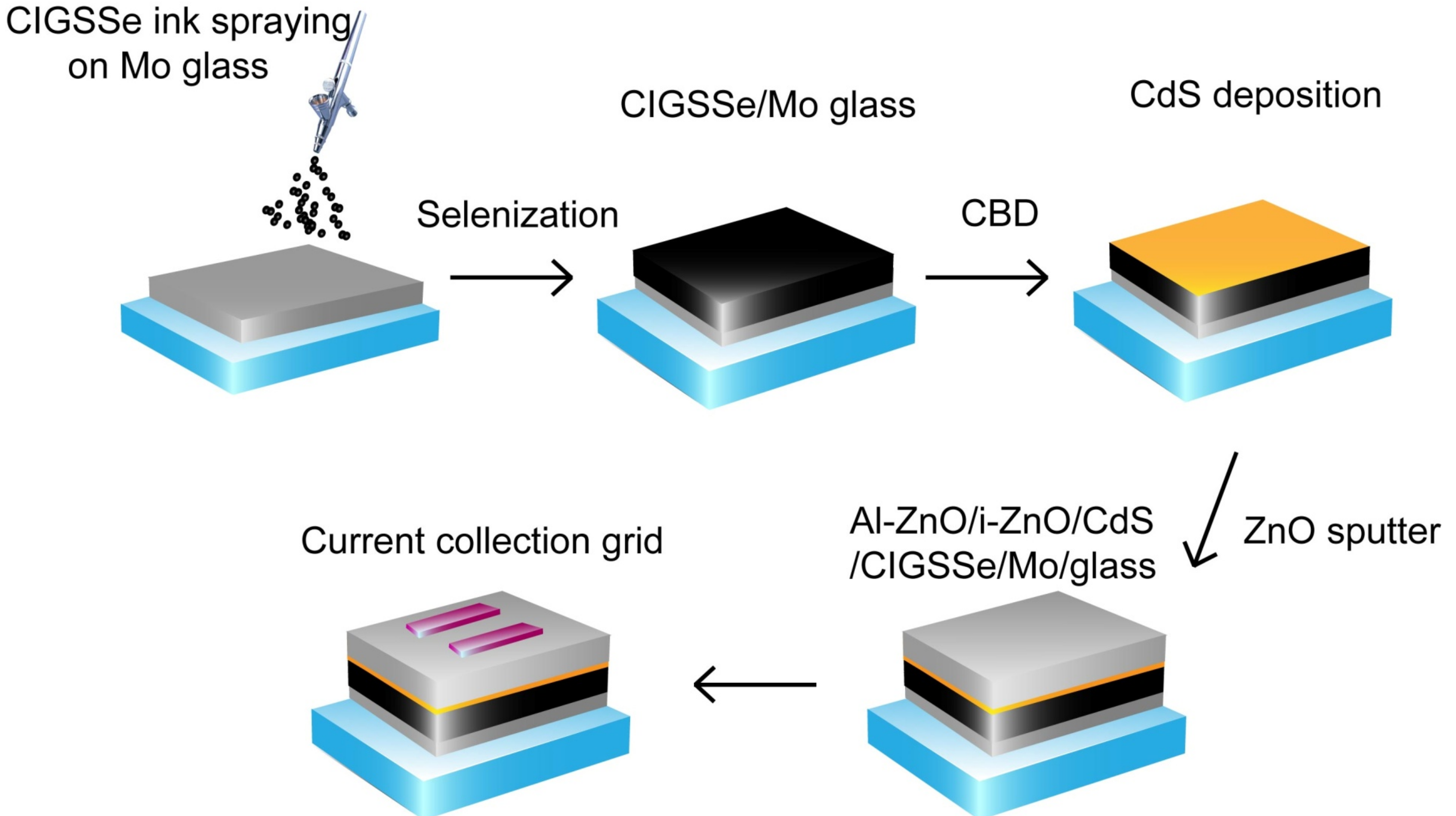
Spray-depositing Nanocrystals on Mo-coated Soda Glass



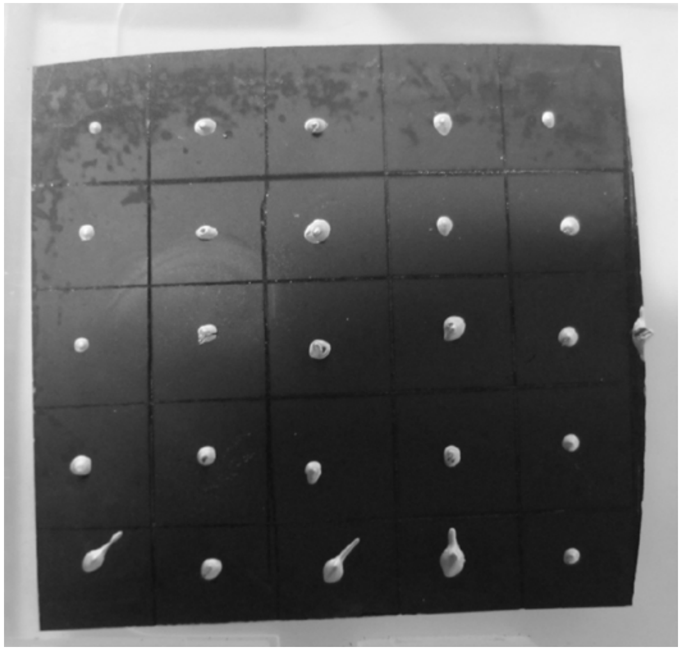
Spray-deposited Film results

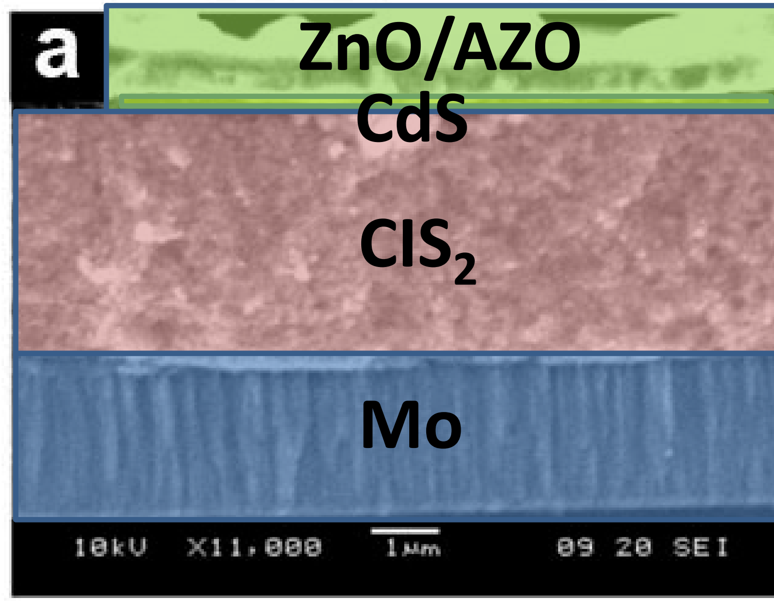


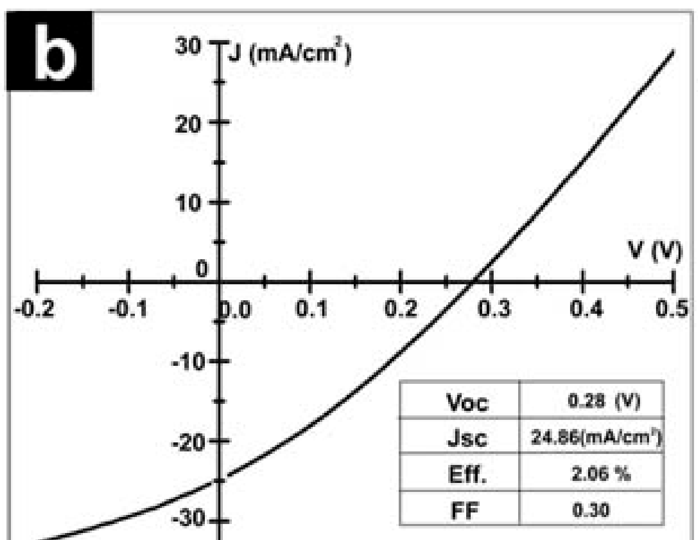
Procedure of CIGS photovoltaic device fabrication

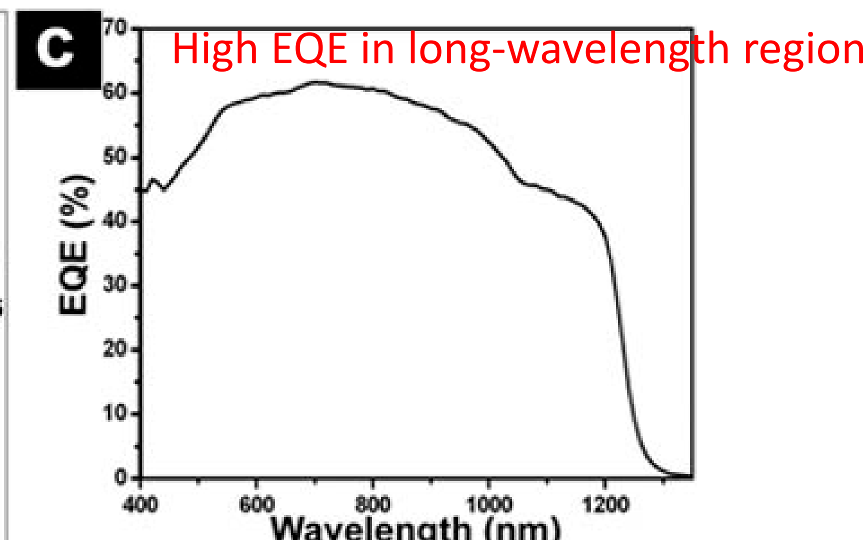


Electrical characteristics of Devices









Energy & Environmental Science

Cite this: *Energy Environ. Sci.*, 2011, **4**, 4929

www.rsc.org/ees

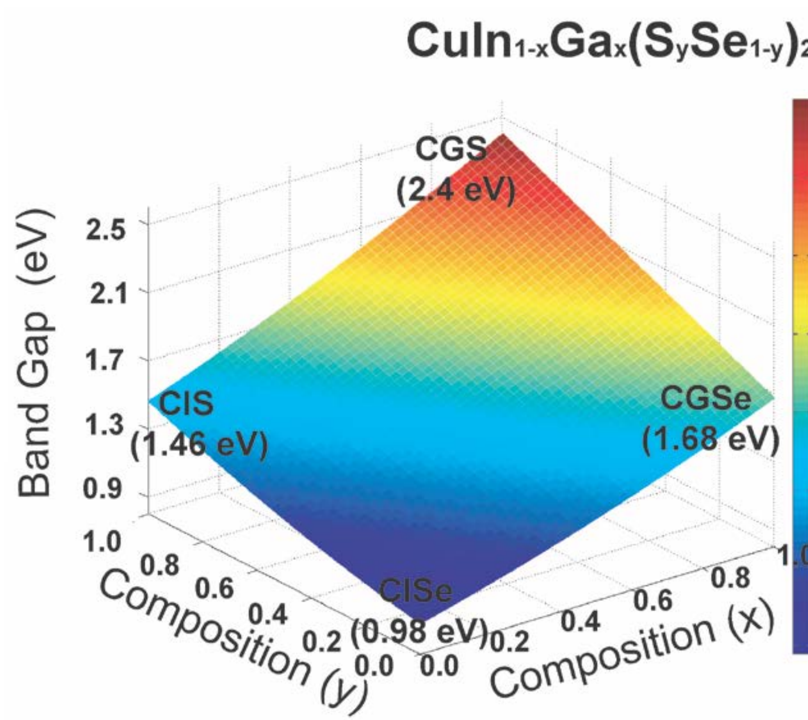
COMMUNICATION

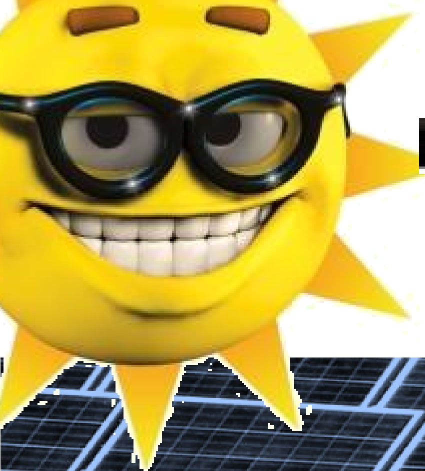
Facile colloidal synthesis of quinary $CuIn_{1-x}Ga_x(S_ySe_{1-y})_2$ (CIGSSe) nanocrystal inks with tunable band gaps for use in low-cost photovoltaics†

Shu-Hao Chang,[a] Ming-Yi Chiang,[a] Chien-Chih Chiang,[b] Fang-Wei Yuan,[a] Chia-Yu Chen,[a] Bo-Cheng Chiu,[a] Tzu-Lun Kao,[a] Chi-Huang Lai[c] and Hsing-Yu Tuan*[a]

Received 11th August 2011, Accepted 26th September 2011
DOI: 10.1039/c1ee02341a

We report, for the first time, colloidal synthesis of quinary $CuIn_{1-x}Ga_x(S_ySe_{1-y})_2$ (CIGSSe) nanocrystals across the entire composition range $(x,y) = 0$ to 1 with band gaps tunable in the range of 0.98 to 2.40 eV by facile chemical synthesis. As a proof-of-concept, thin-film solar cells made by using the CIGSSe nanocrystal inks as an absorber layer precursor exhibited an efficiency over 1% under AM 1.5 illumination.





CIGSSe nanoinks

Composition control

Phase Control

Shape Control

Size control

Phase transfer

Large quantity

Low cost Solar cell appication