Design, Fabrication, Characterization, and Application of Semiconductor Nanocomposites

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I. A perfect integration of zero and one dimensional nanomaterials for photodetectors with ultrahigh gain and wide spectral response.

II. Photon down conversion and light trapping in hybrid ZnS nanopartcles/Si Nanotips solar cells.

III. Light fountain composed of photonic crystals and semiconductor nanowires.

IV. Liquid crystals and CdSe nanotubes nanocomposites for smart emission devices.

V. Liquid crystal devices with built-in solar cells.

VI. An Advanced Alternative for Electrically Tunable Light Emitters: Graphene/SiO_2/p-GaN Diodes.

I.A perfect integration of zero and one dimensional nanomaterials for photodetectors with ultrahigh gain and wide spectral response.

1.Motivation

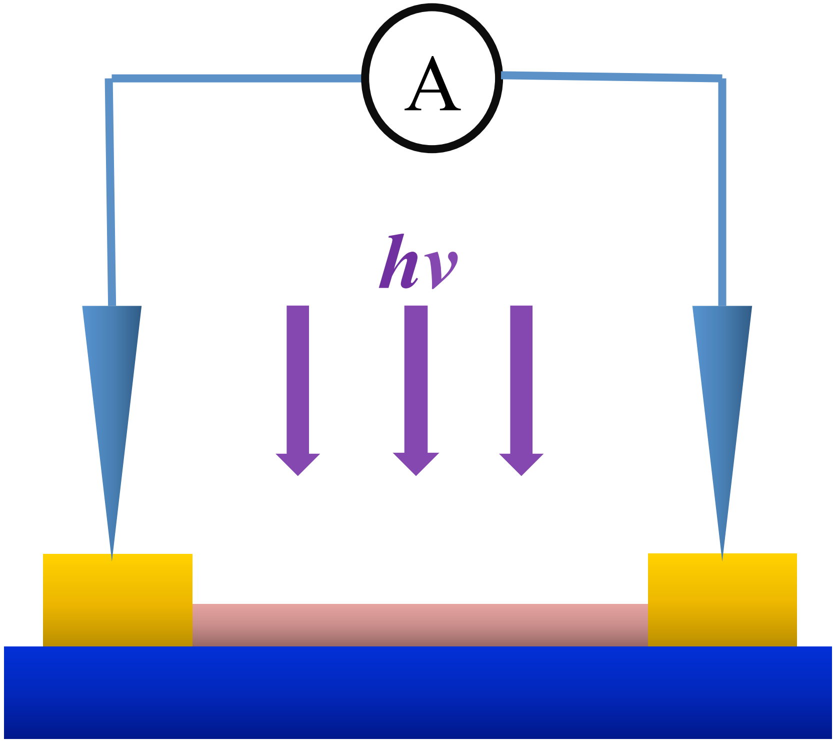
Nanowire: good conductor, good field emitter, good sensor, anisotropic properties…etc.
Quantum dot: large absorption coefficient, tunable band gap, good light emitter, photonic crystals…etc.

What kind of novel properties can we discover by the integration of QDs and NW?

A perfect nano-photodetector!

To obtain single nanowire photodetector with ultrahigh and wide spectral response.

PHOTOCONDUCTIVITY



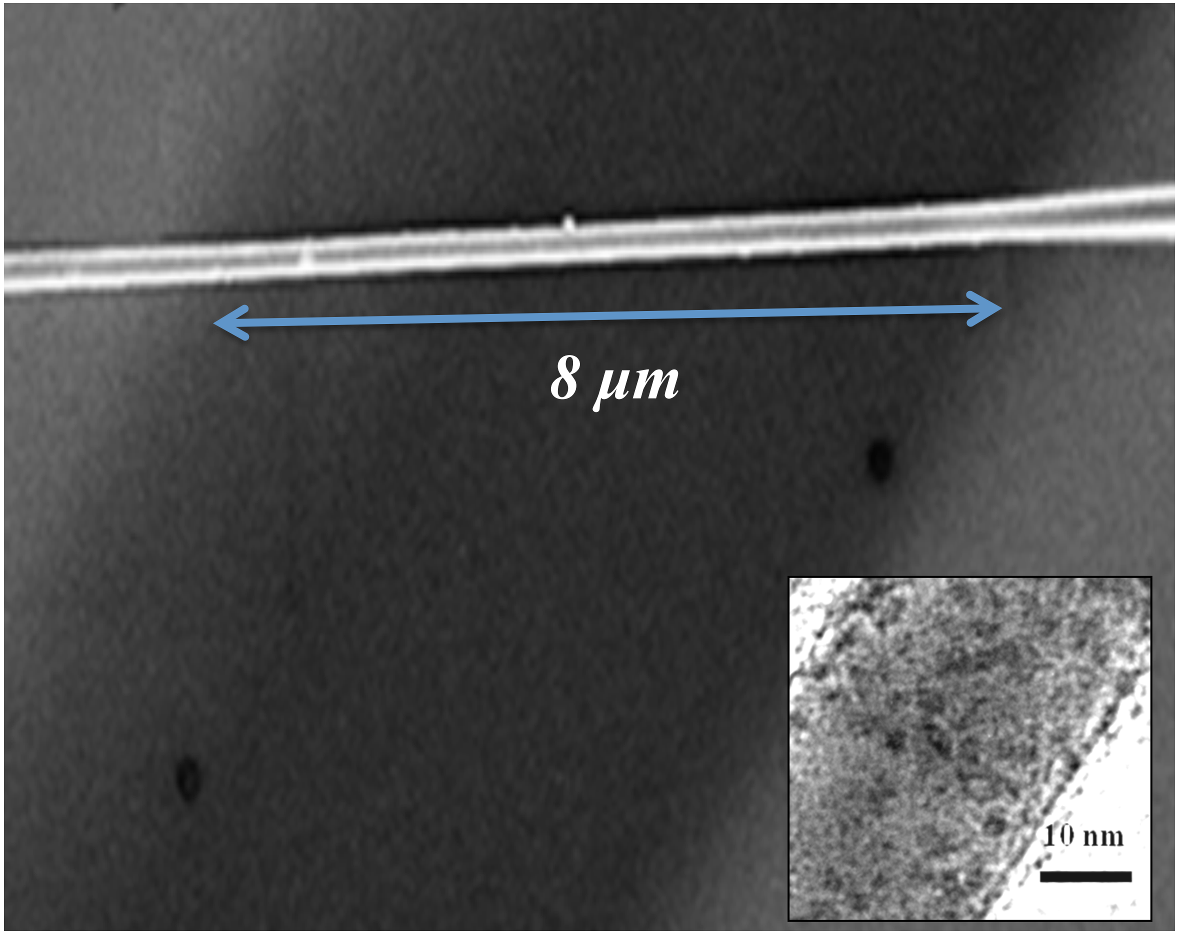
As the incident light with photon energy is larger than the energy gap of the semiconductor, electron-hole pairs are produced by the absorbed photons, result in the increment of conductivity.

2.Sample design and underlying principle

i) Sample design

The integration of zero (semiconductor quantum dots) and one dimensional (nanowire) nanomaterials.

QD-NW COMPOSITE DEVICE

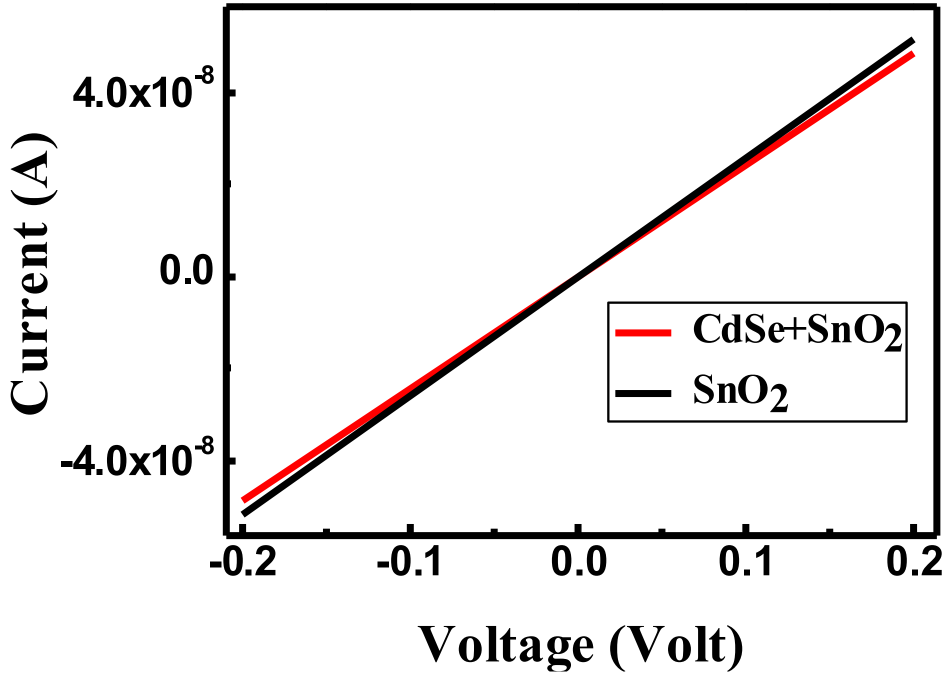


ii) Underlying principle

a) quantum dots have a high absorption coefficient.
b) Nanowire provides an excellent conduction path.
c) A suitable selection of energy band alignment (type II) between QD and NW enables to cause the spatial separation of photogenerated electron and hole.
d) The coupling strength between QD and NW is enhanced by the inherent nature of the large surface to volume ratio of nanomaterials.
e) QDs and NW have different spectral response.

3. Results and discussion

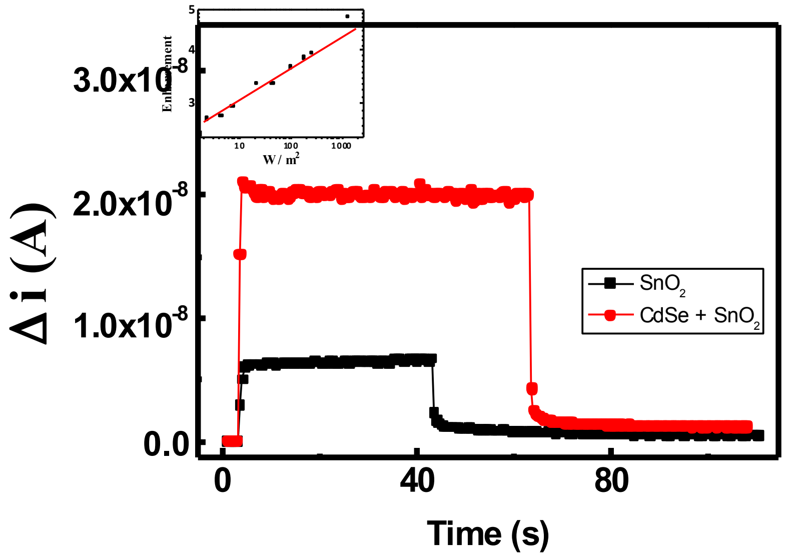
DARK CURRENT MEASUREMENT



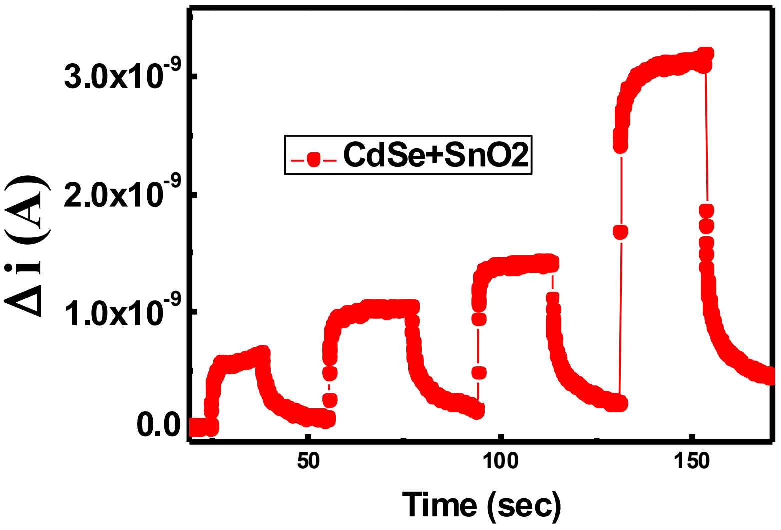
I-*V* characteristics of the pristine SnO_2 NW and the CdSe quantum dots decorated NW

It shows that after the decoration of CdSe QDs, it slightly alters the conduction of SnO_2 NW.

PHOTOCURRENT MEASUREMENT



Photoresponse of the two samples with a bias of 0.1 V and under the illumination of a He-Cd laser (325nm) with an excitation intensity of 100 W/m^2. (Inset: The relation between the illumination power and the photocurrent enhancement.)



Photoresponse of CdSe QDs decorated SnO$_2$ NWs under the illumination of green laser (532nm) with different excitation intensity of 2.5, 6, 9.5, 376 W/m^2, respectively.

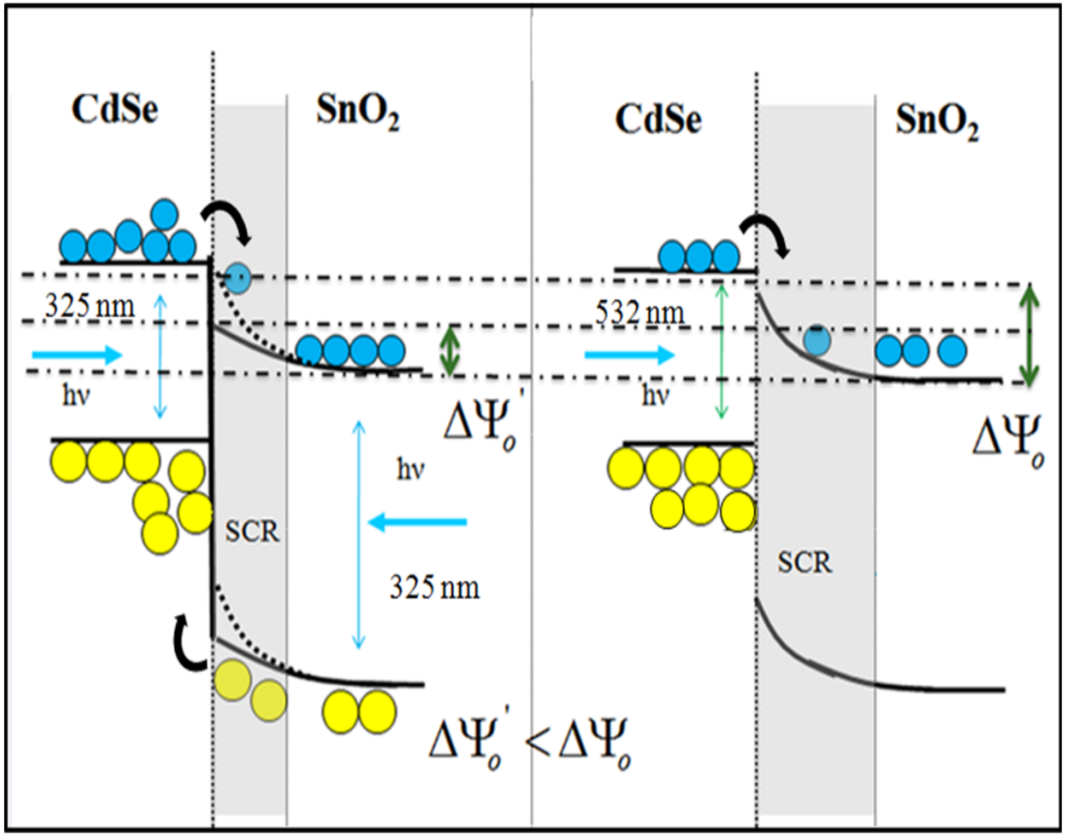
New findings:

After the decoration of CdSe QDs:

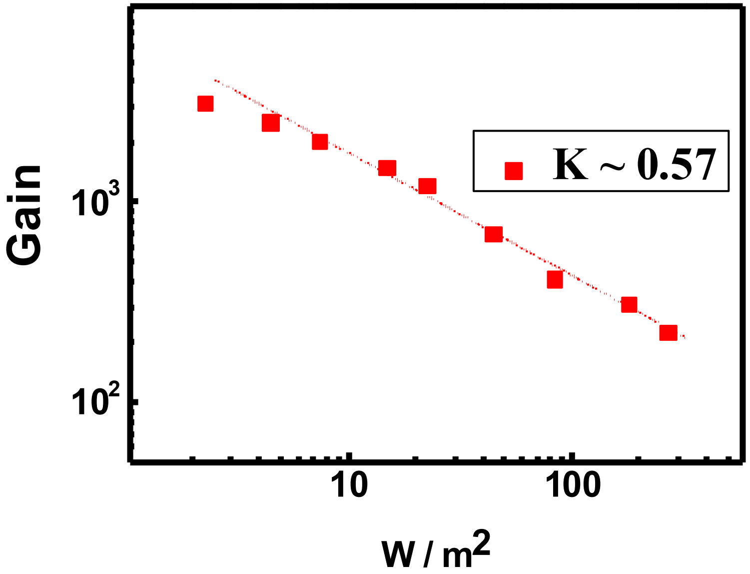
i) The photoresponse is greatly enhanced.

ii)The spectral response can be extended to the visible region (the band gap of QDs).

MECHANISM



325 nm **532 nm**



Photoresponse gain contributed by CdSe QDs as a function of illumination intensity at excitation wavelength of 325 nm.

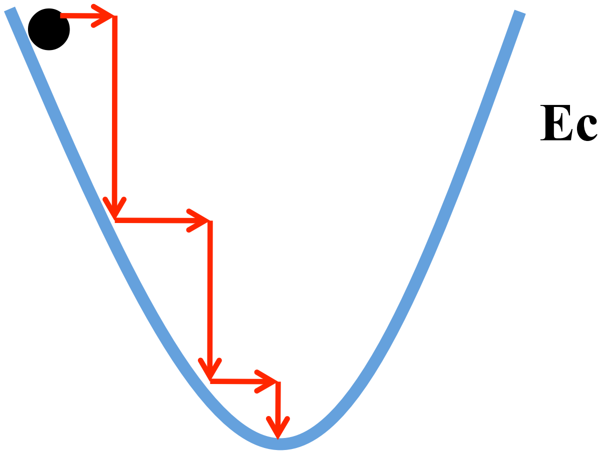
CONCLUSION

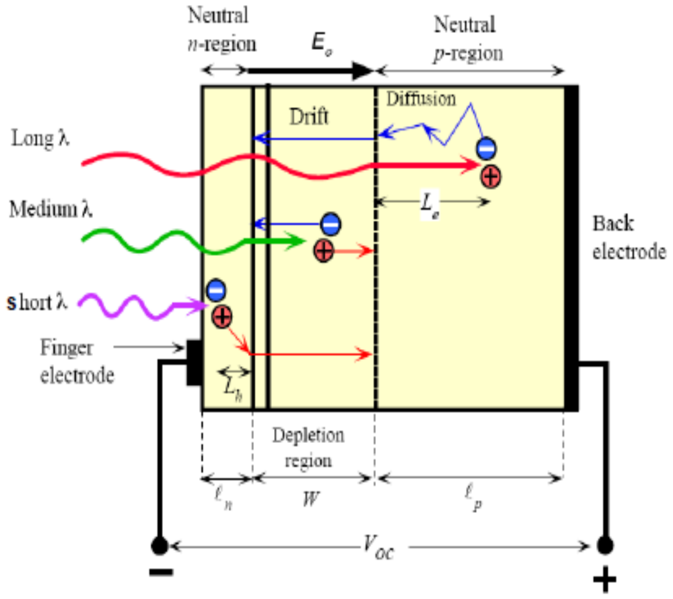
- In summary, CdSe QDs decoration has been utilized to enhance the photoresponse in SnO_2 NWs drastically, even if the photon energy is not large enough to induce electron-hole pairs in NWs.
- The photoresponse spectrum can be extended to include different wavelengths by decorating suitable QDs.

II. Photon down conversion and light trapping in hybrid ZnS nanoparticles/Si Nanotips solar cells

Motivation

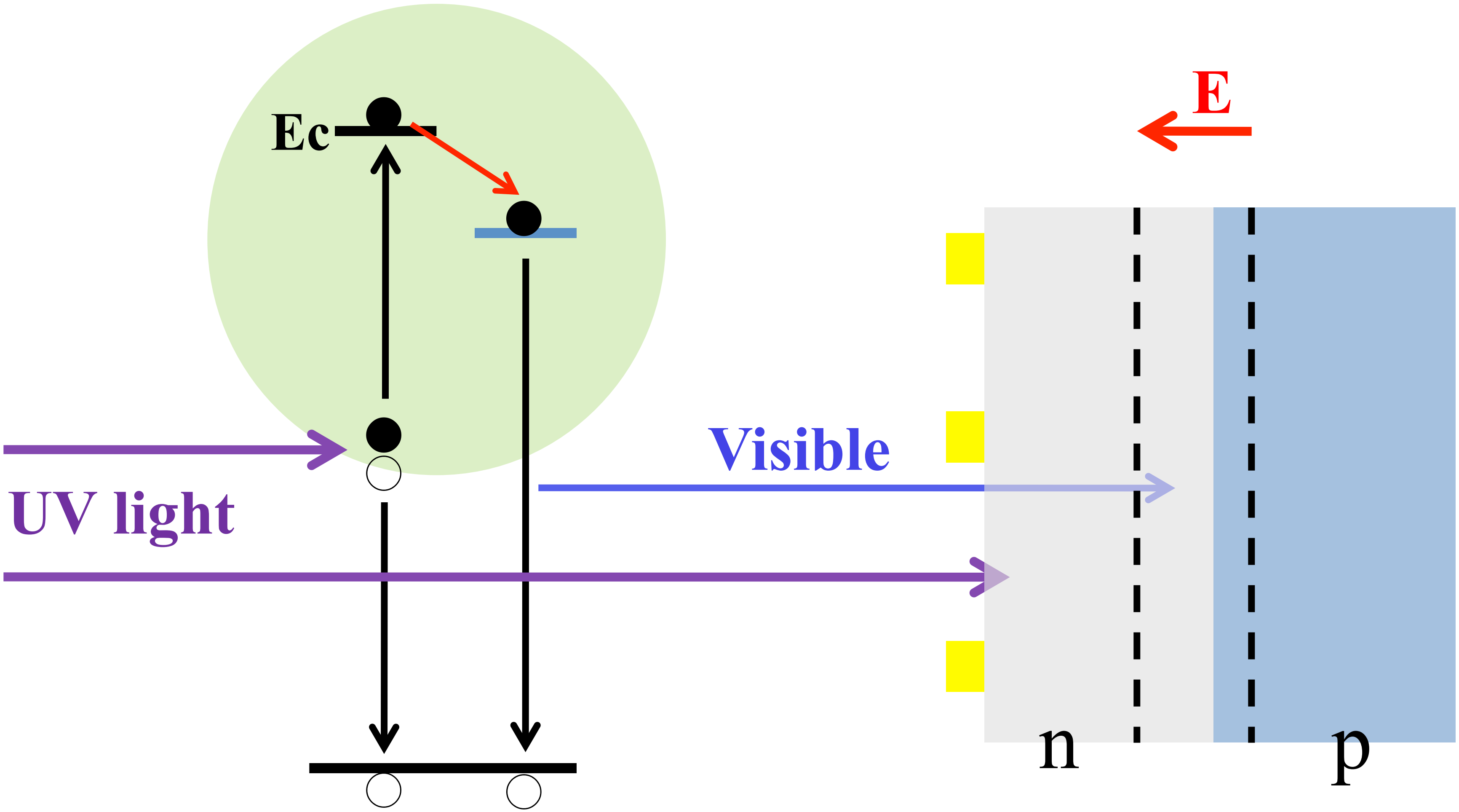
The major part of the energy losses (~52%) is related to the spectral mismatch, known as thermal losses or quantum losses. A large part of high energy photons is lost as heat through phonon scattering, resulting in the limitation of power conversion efficiency of silicon solar cells.





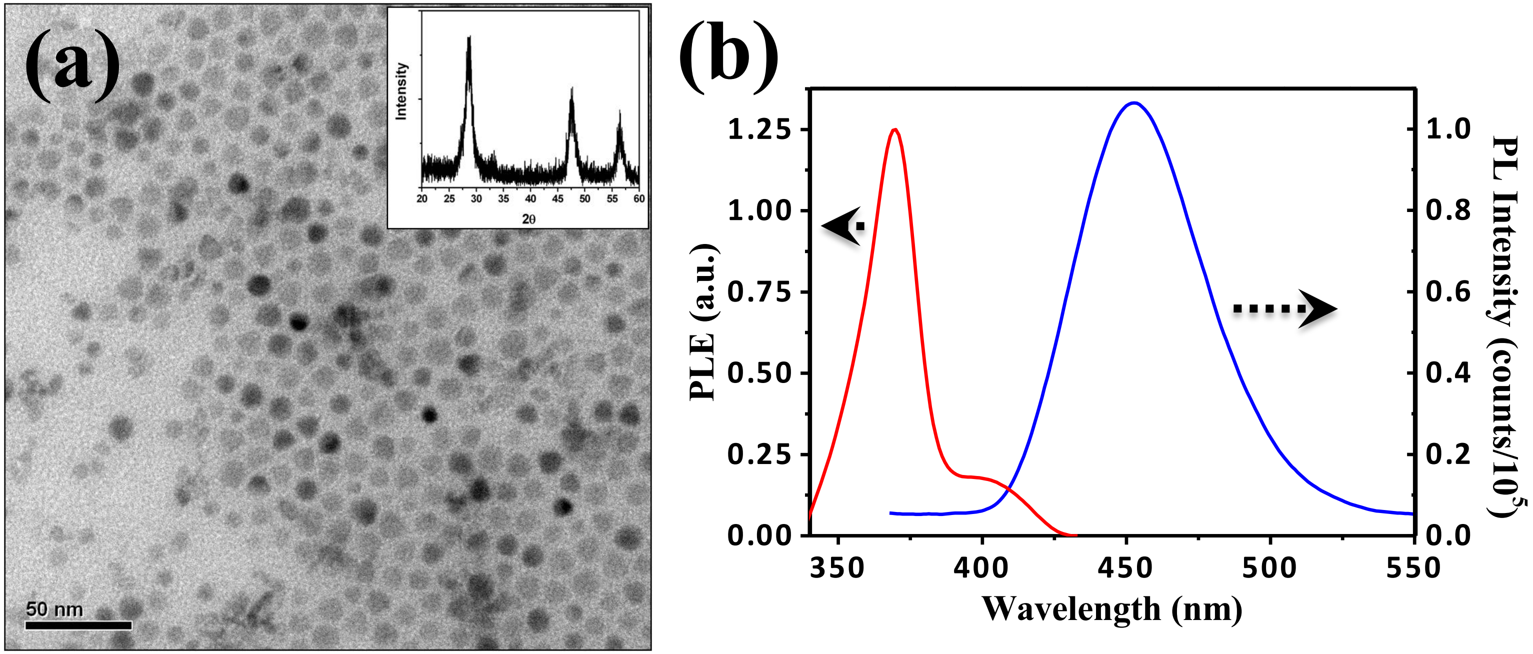
Key ：Frequency Downconversion

Frequency Downconversion

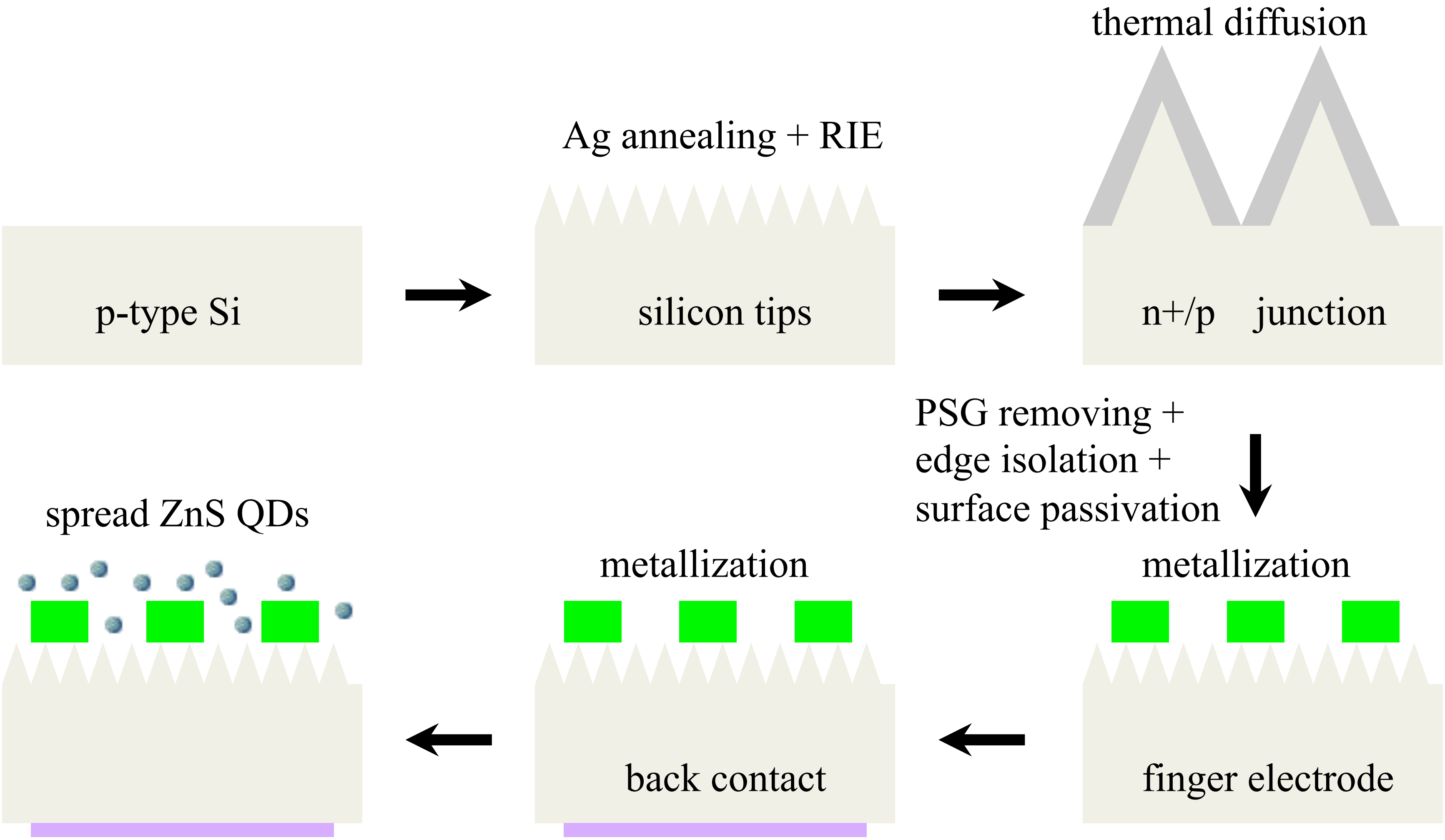


ZnS QDs

- Amongst all Ⅱ-Ⅵ semiconductor NPs, ZnS is a promising candidate for PV applications because of its nontoxicity, low cost, high refraction index and abundance in earth.
- ZnS is a wide band gap material.



Device fabrication



p-type Si

Ag annealing + RIE

silicon tips

thermal diffusion

n+/p junction

PSG removing +
edge isolation +
surface passivation

metallization

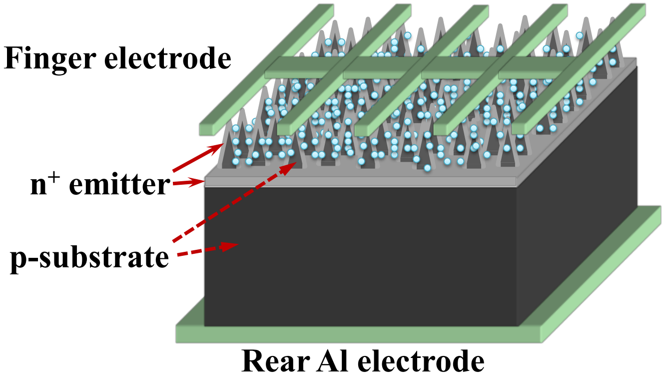
finger electrode

metallization

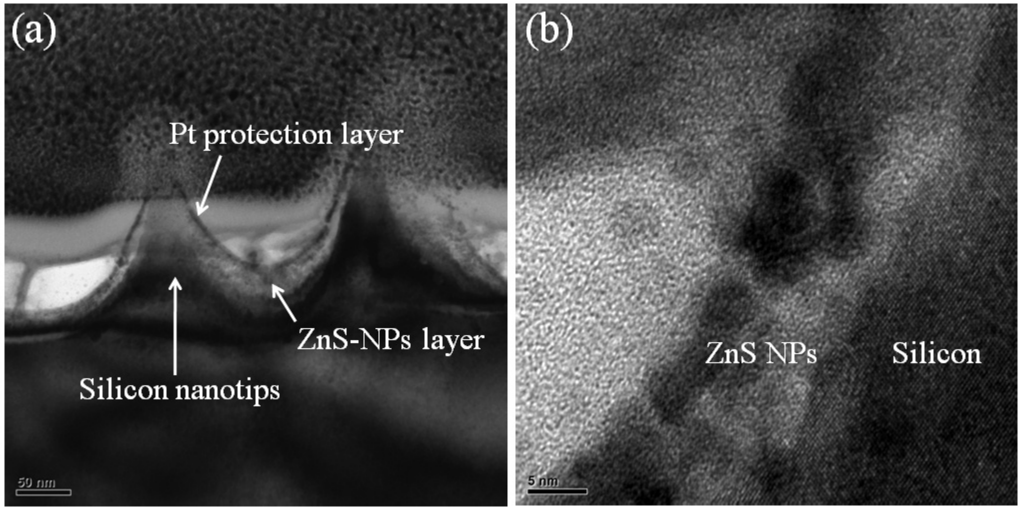
back contact

spread ZnS QDs

Device Structure

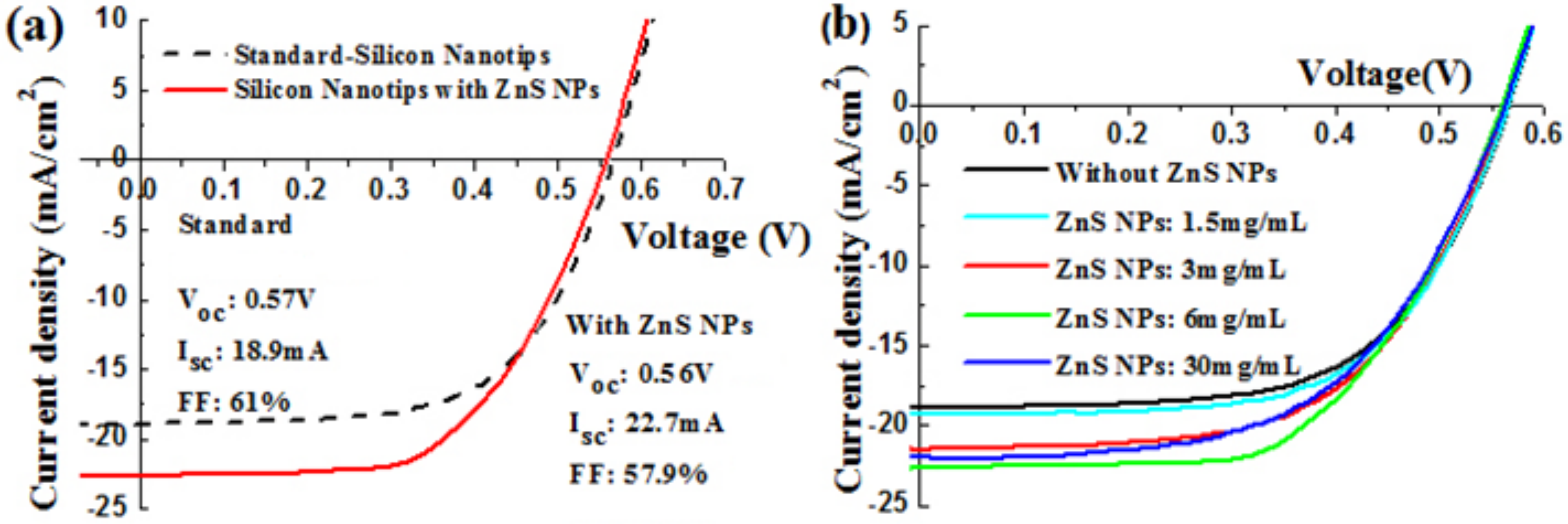


The thickness of the ZnS layer is about 30 nm ~ 50 nm (for the concentration of 6 mg/mL), depending on the position of silicon nanotips.

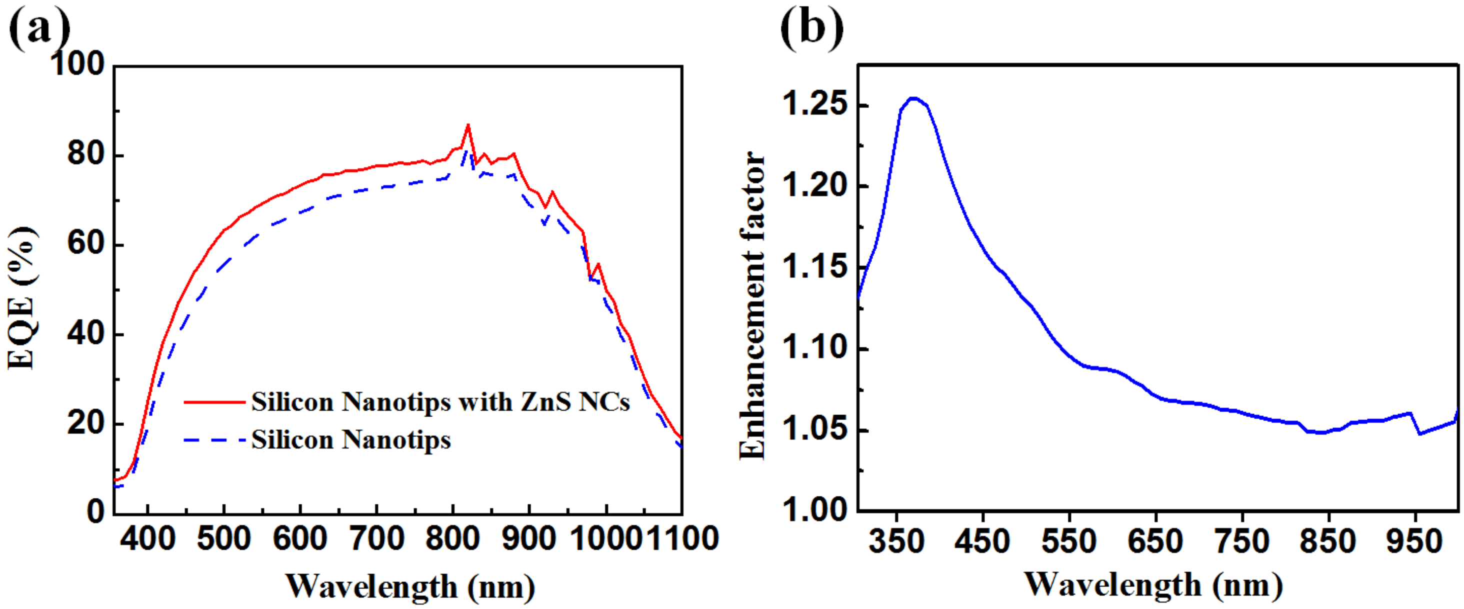


I-V characteristics under AM1.5 illumination

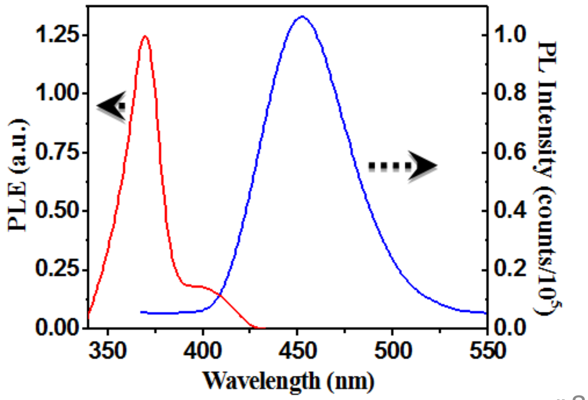
The comparison highlights the fact that 6 mg/mL ZnS NPs are effective in increasing the short-circuit current density from 18.9 to 22.7 mA/cm^2 and Voc remains the same.



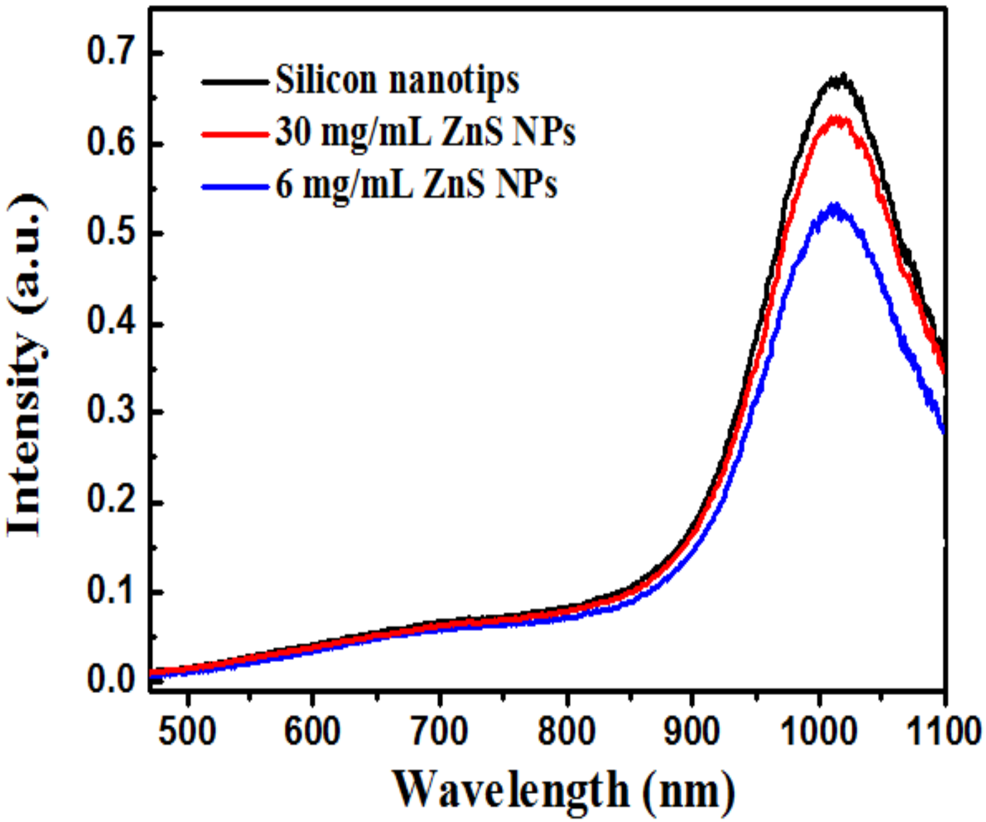
External Quantum efficiency



For the spectral response above 425 nm, since there is no PLE signal from ZnS NPs, frequency down conversion can not entirely account for the enhancement of EQE.



Reflectance



Complementary Experiments

- We have attempted PbS and CdSe QDs, but the results are not as good as that of ZnS QDs on silicon tips solar cells.
- PbS QDs are intrinsic p-type materials, and thus form an opposite direction of p-n junction to the original one.
- CdSe QDs on top of the cell absorb and diminish the numbers of visible photons and thus the enhancement is less than ZnS QDs even though they have a good quantum yield.

Conclusion

We have shown that the hybrid system can significantly enhance power conversion efficiency under AM1.5 illumination. The underlying mechanism of the enhancement can be attributed to frequency down conversion as well as light trapping. We believe that this approach may find promising applications in silicon-based solar cells and open a new possible scheme to explore semiconductor NPs for energy devices.

III. Light fountain composed of photonic crystals and semiconductor nanowires

1. Motivation

Semiconductor nanowires possess many unique properties attracting scientific as well as industrial interests.

Photonic crystals own the formation of photonic band gap leading to various applications, including waveguides, emitters, filters, reflectors,…,etc.

What kinds of properties can be created, if both photonic crystals and semiconductor nanowires are combined together?

2. Material

Photonic crystals: $Tb(OH)_3/SiO_2$ core/shell nanoparticles Tb atom provides stable, strong, and narrow multiple emissions covering from UV to visible range.

SiO_2 shell is very useful in manipulating inter-particle interaction and in biological targeting application.

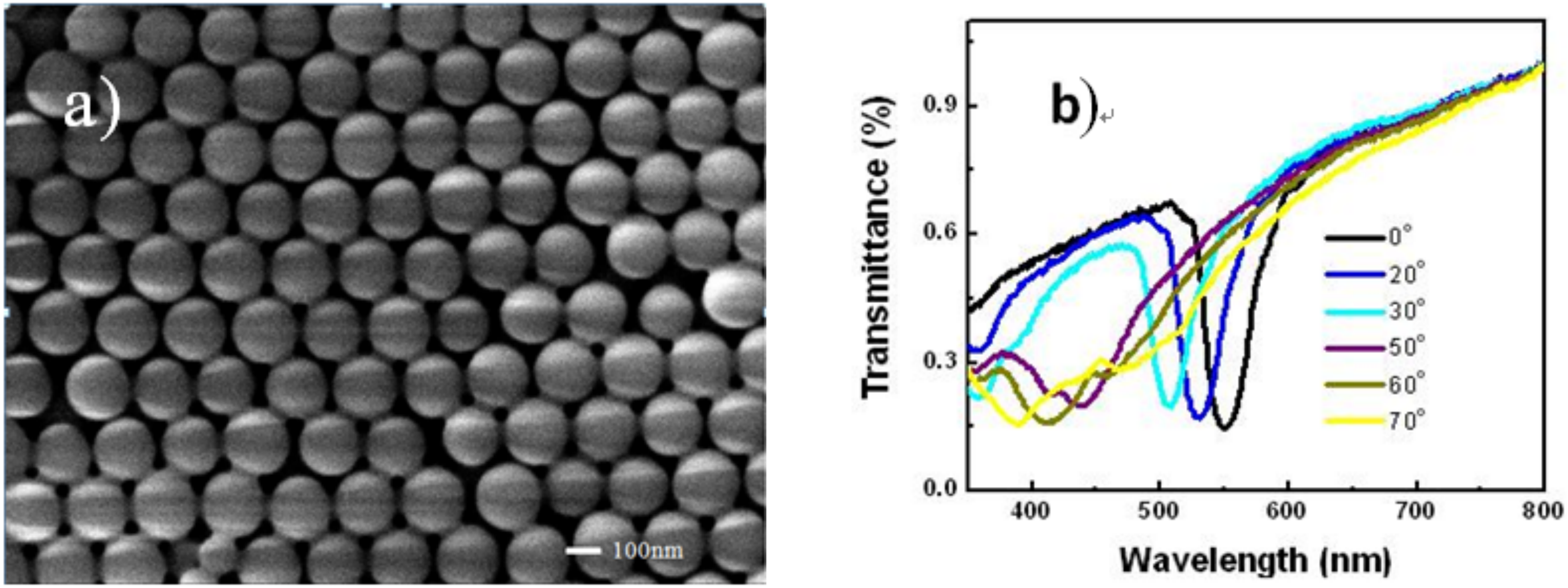


Figure (a) Scanning electron microscope (SEM) image of fcc close-packed lattice structure of $Tb(OH)_3/SiO_2$ core/shell nanospheres (d = 250 nm) (b) Transmittance spectrum of $Tb(OH)_3/SiO_2$ photonic crystals, which clearly displays the formation of stop band.

Semiconductor nanowires: SnO_2 nanowires

a wide band gap semiconductor (3.6 eV), good emitter, sensor, and waveguide…

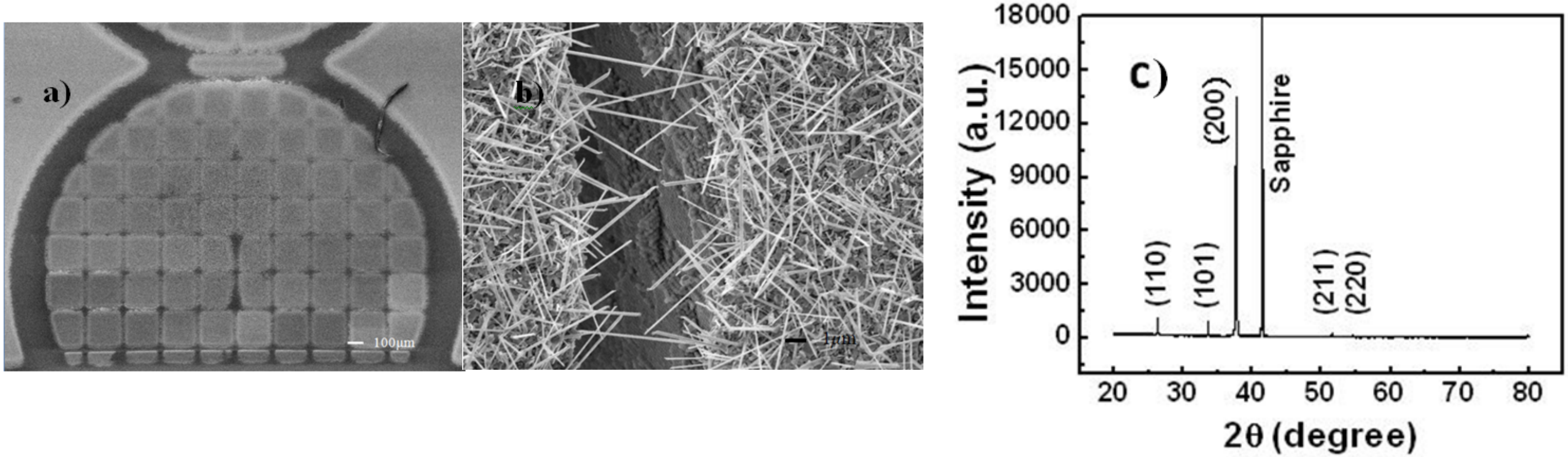


Figure 2. (a) Scanning electron microscope (SEM) image of SnO_2 nanowires on $Tb(OH)_3$/SiO_2 photonic crystals with a metal grid as the mask. (b) Enlarged SEM image of Fig. 2(a). (c) X-Ray diffraction (XRD) pattern of SnO_2 nanowires.

3. New finding

The nanocomposite consisting of photonic crystals and semiconductor nanowires acts like a light fountain.

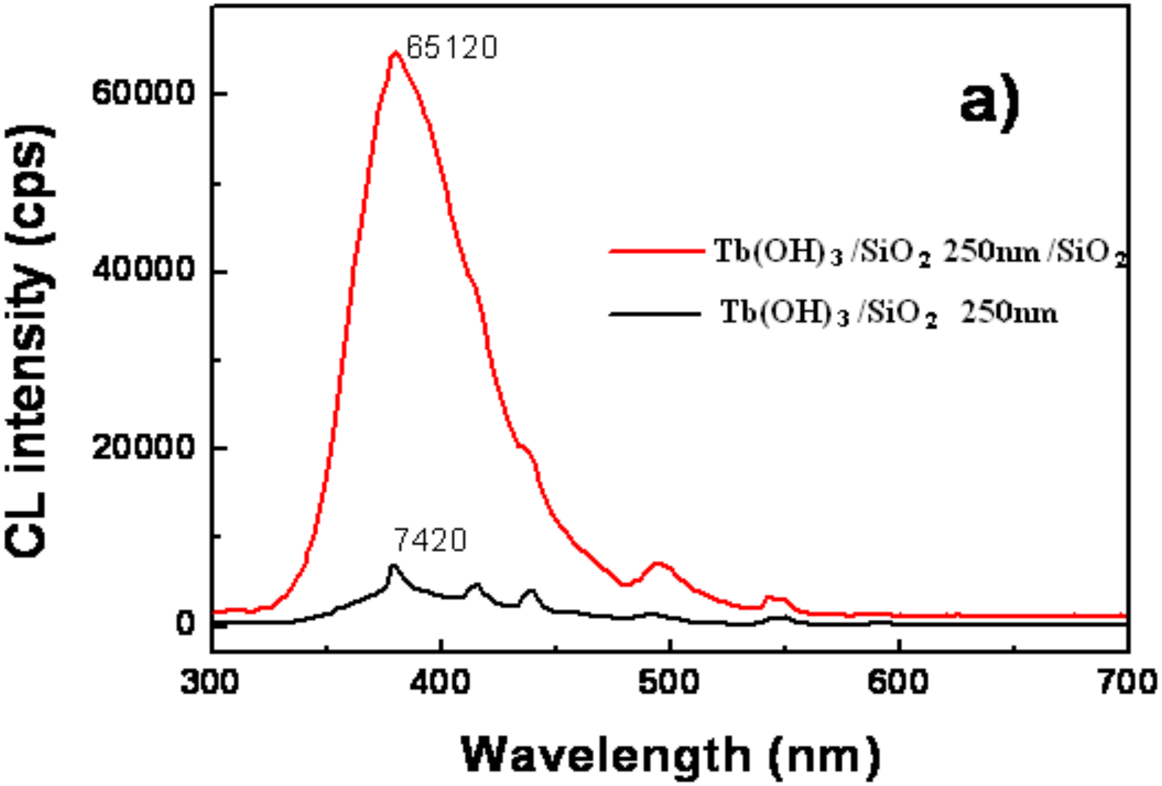
The periodic structure of SiO_2 nanoparticles confines the emission of Tb atoms inside photonic crystals.

SnO_2 nanowires serve as waveguides to extract light out of photonic crystals.


Sherwin Photography

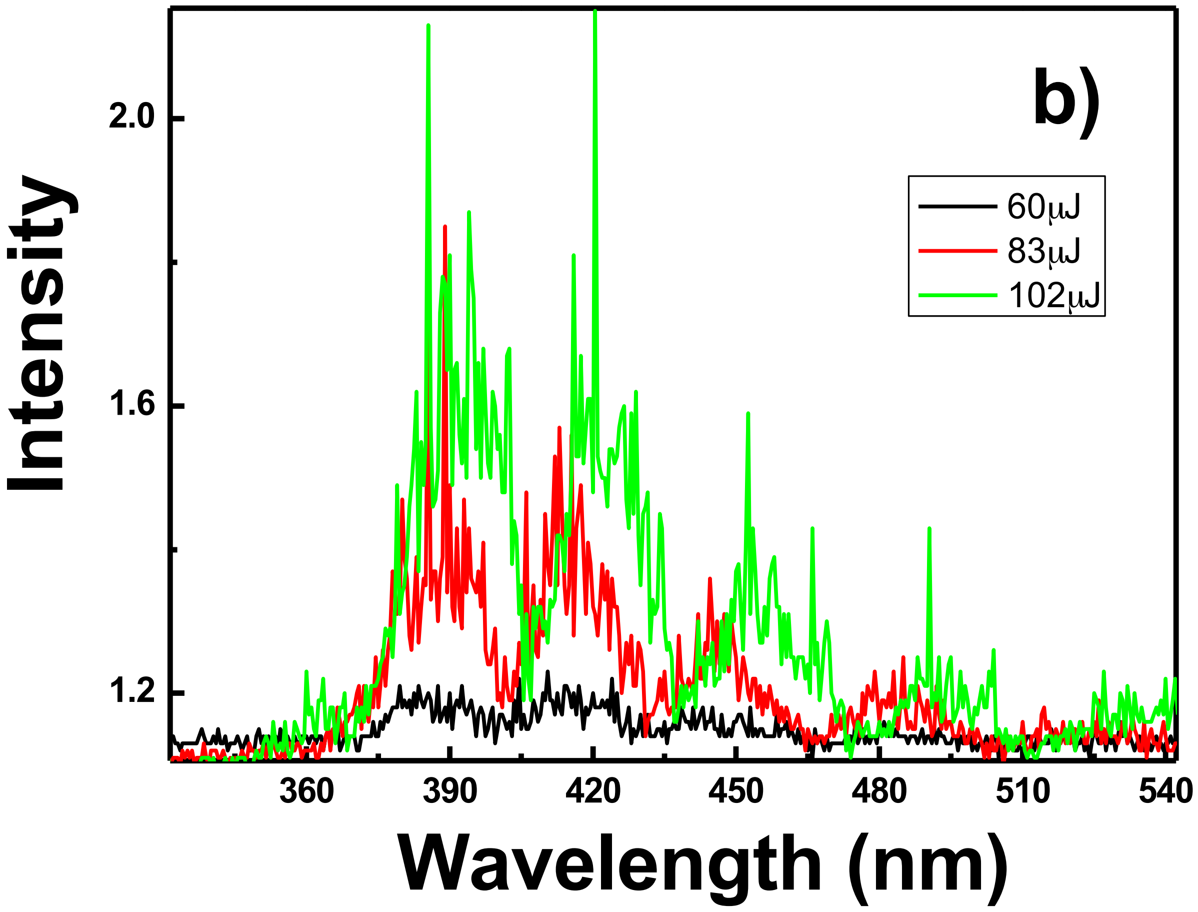

LG STORES
Jetway SLG15
Jecci Five SLG51
Fisher-Price SLG K3
Garfield
Pretty Valley SLG17
potato &
ADDEN

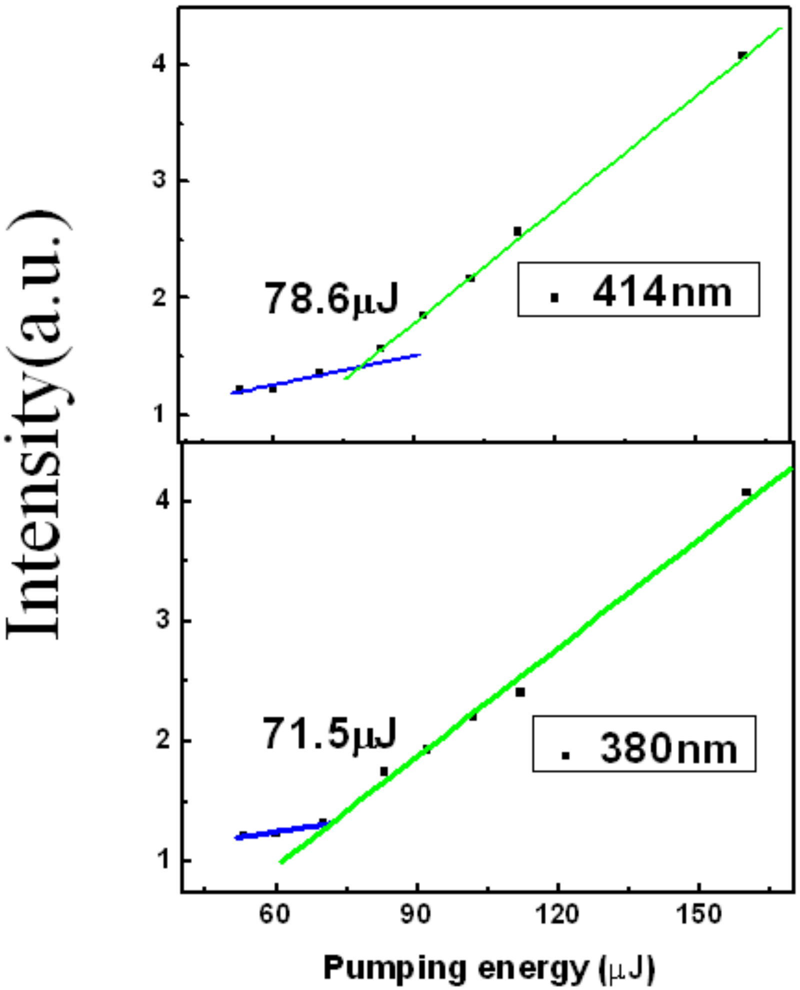
4. Results and discussion

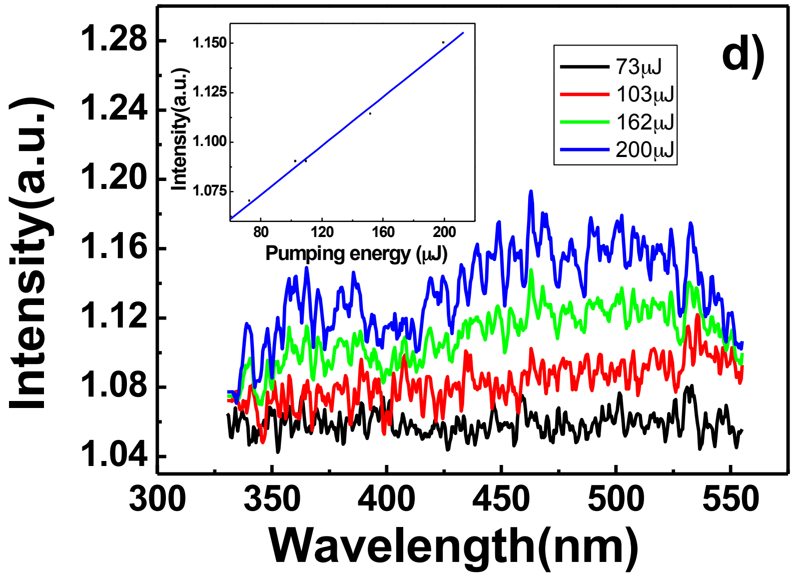


Without SnO_2 nanowires, the emission intensity is very small.

Power dependence







Lasing behavior can be easily achieved based on light fountain.

5. Summary

① A new nanocomposite consisting of photonic crystals and semiconductor nanowires have been designed.

② This new nanocomposite can act like a light fountain.

③ Light fountain can easily achieve lasing action.

IV. Liquid crystals and CdSe nanotubes nanocomposites for smart emission devices

1. Motivation

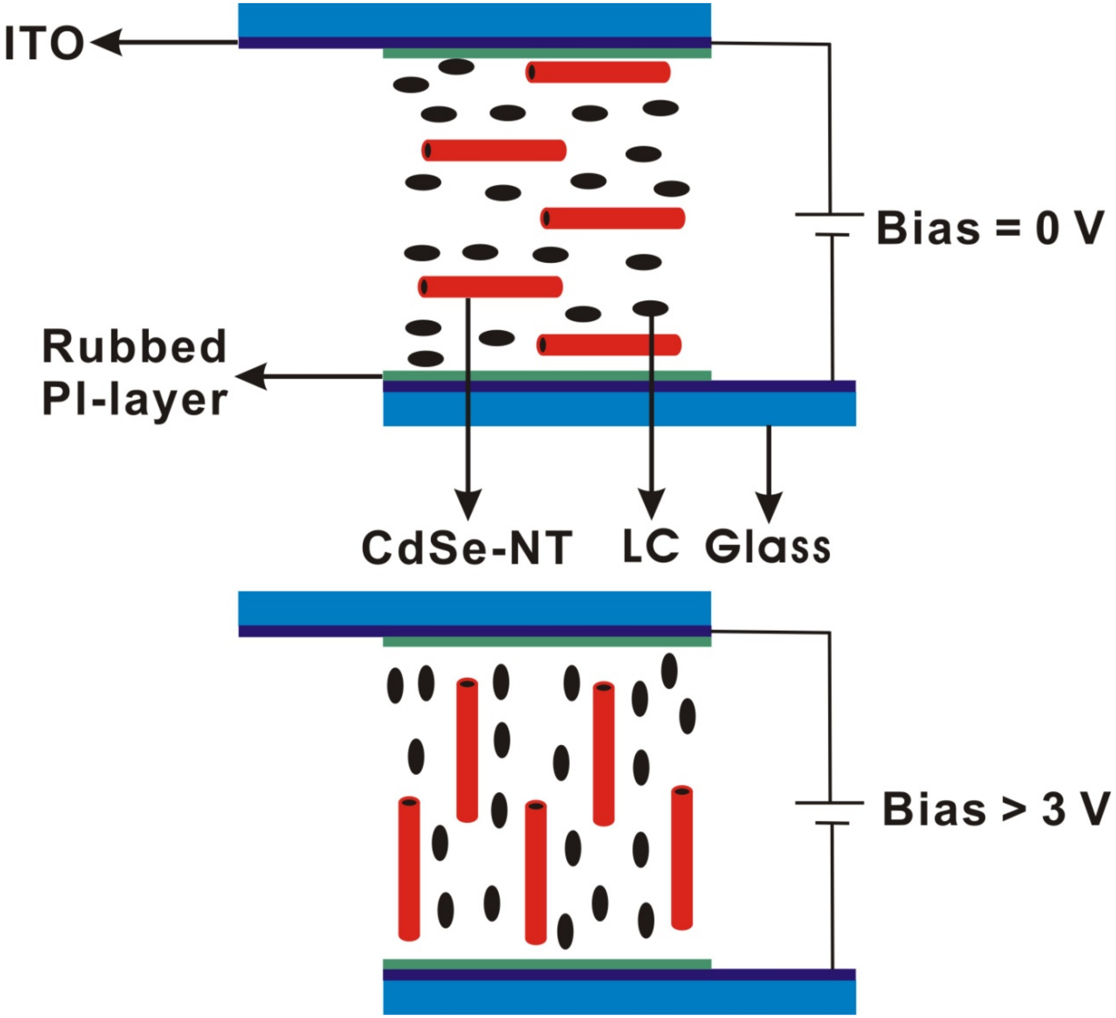
It has been shown that one-dimensional semiconductor nanostructures have many unique properties, including thermal, electrical, optical, chemical, and mechanical properties.
The next step is to integrate them with existing technologies to realize their potential applications.

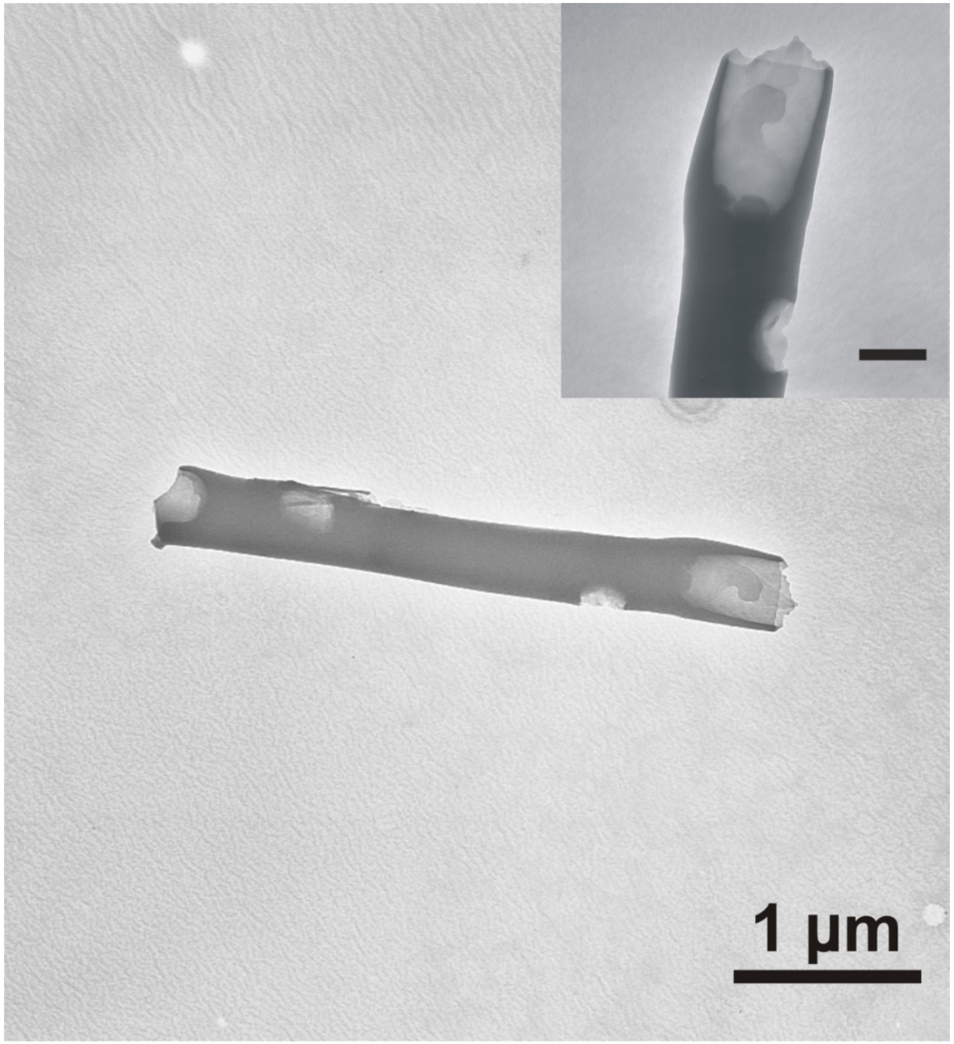
2. Basic principle

Due to the high surface to volume ratio of one dimensional nanostructures, it enhances the interaction between nanowires and its environment.

Therefore, if we intentionally incorporate nanowires in a LC device, it is possible to manipulate the properties of one-dimensional semiconductors through the interaction between LC and nanowires.

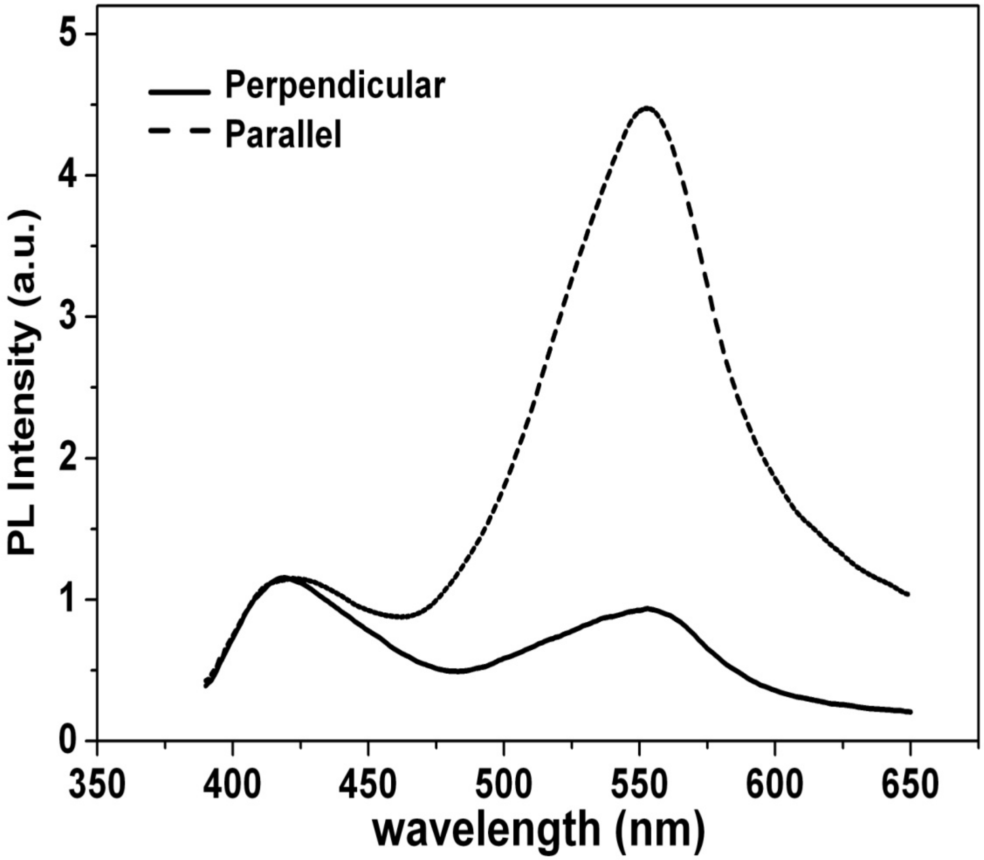
3. Sample structure



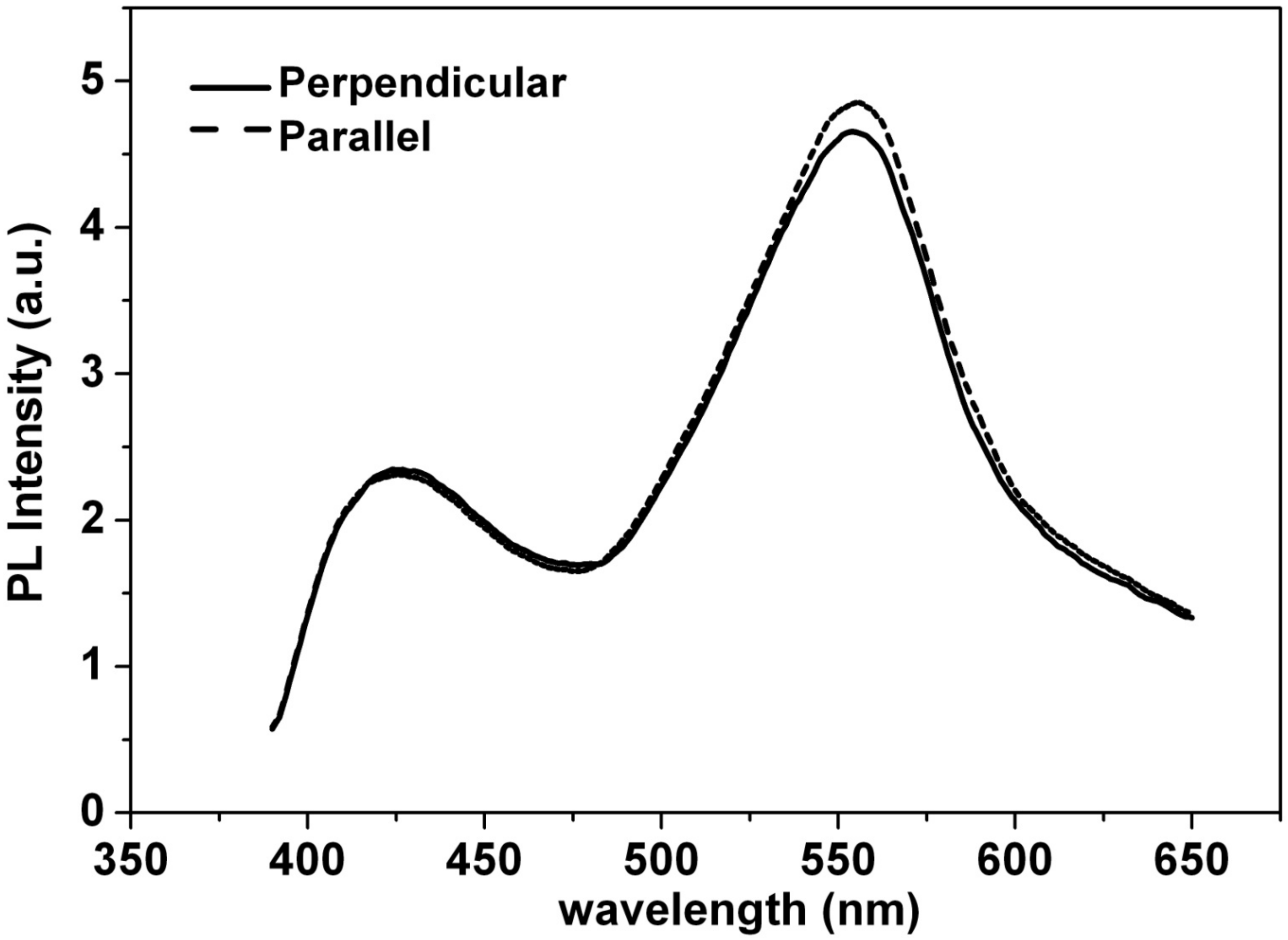


SEM image of CdSe nanotube.

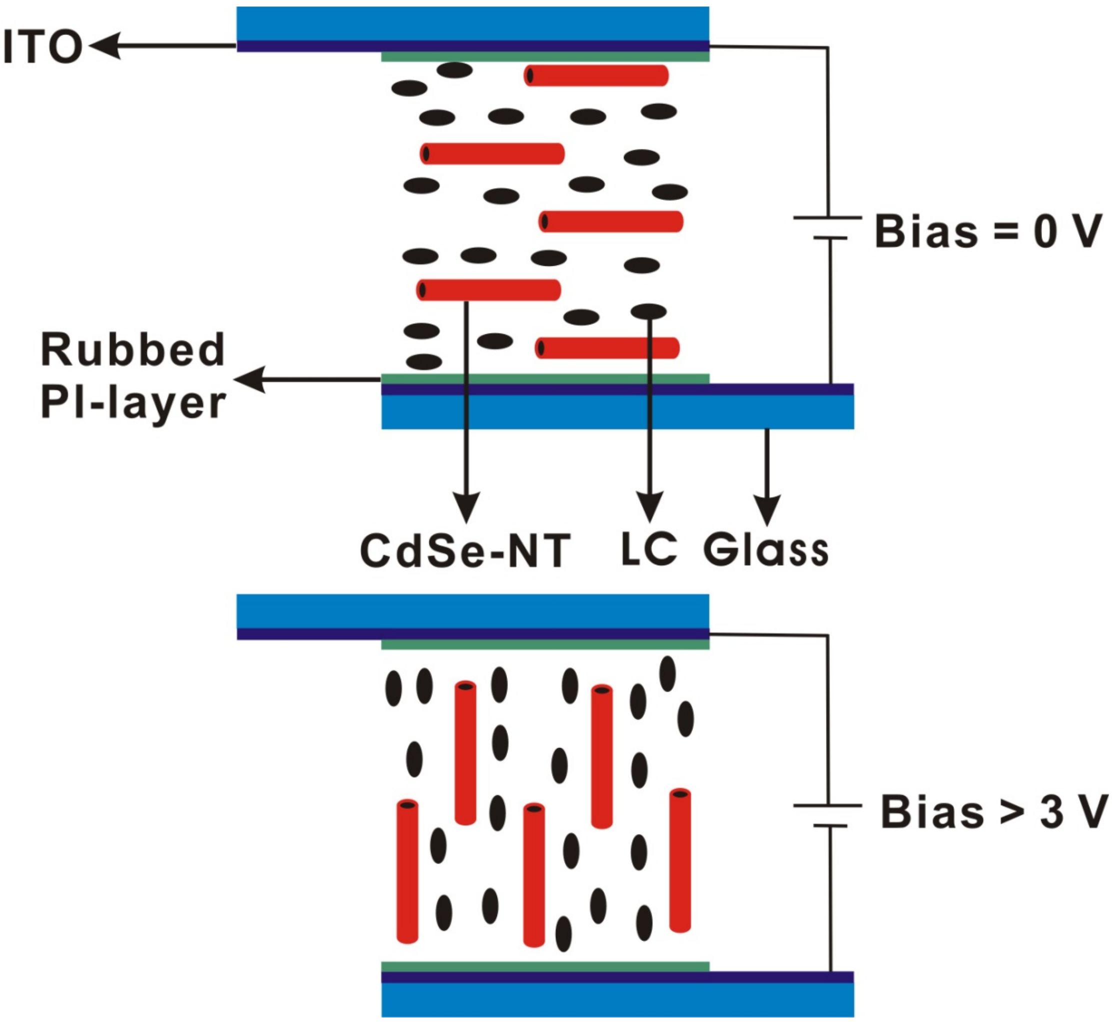
4. Experimental results



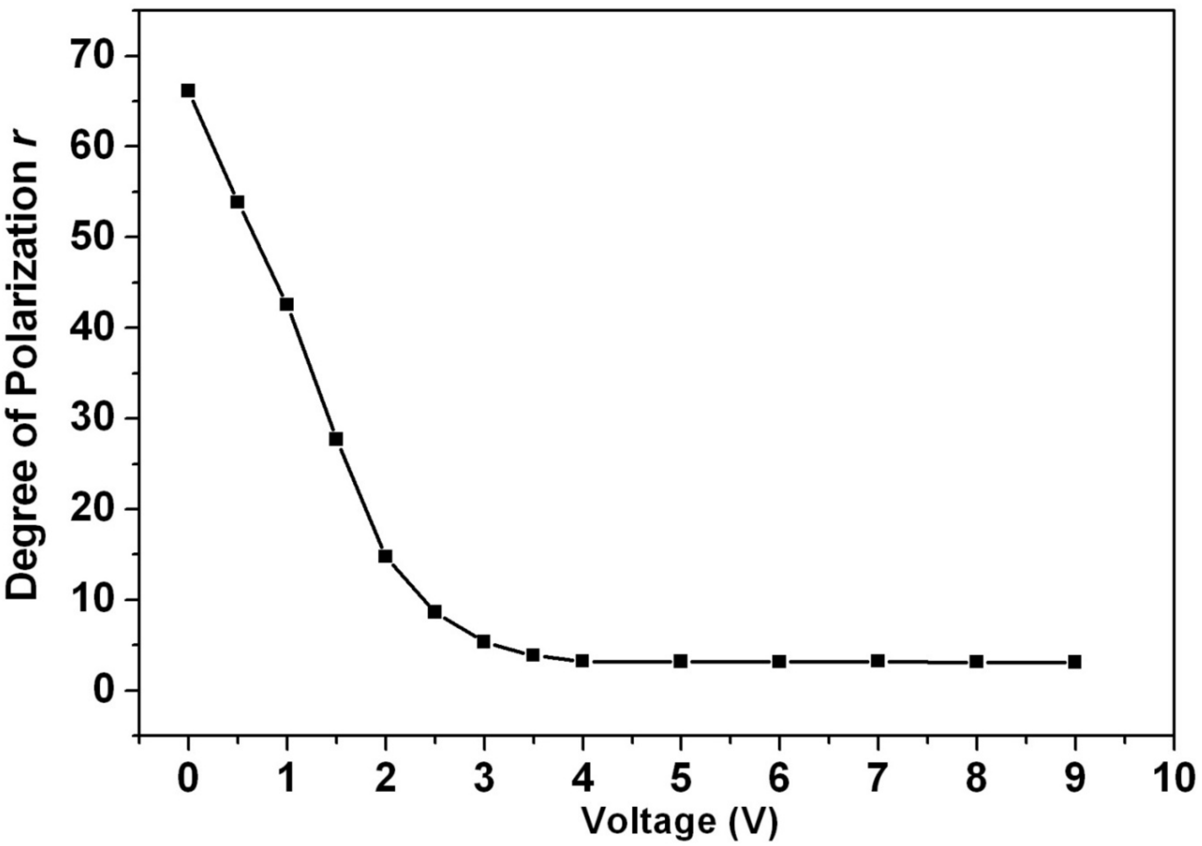
It shows that with the assistance of liquid crystal molecules, the CdSe nanotubes are well aligned along the rubbed PI direction. We therefore provide a convenient way to obtain well aligned nanotubes.



After applying an external bias above 3 V, the optical anisotropy almost disappears.



The above result arises from the reorientation of CdSe nanotubes driven by LC molecules.



Degree of polarization as a function of external bias.

The saturation above 3V is consistent with the voltage required to switch LC molecule from lateral to perpendicular orientation.

The magnitude of the measured optical anisotropy can be understood in terms of the dielectric contrast between the nanotube and LC. When the polarization is perpendicular to the cylinder, the electric field is attenuated by a factor of

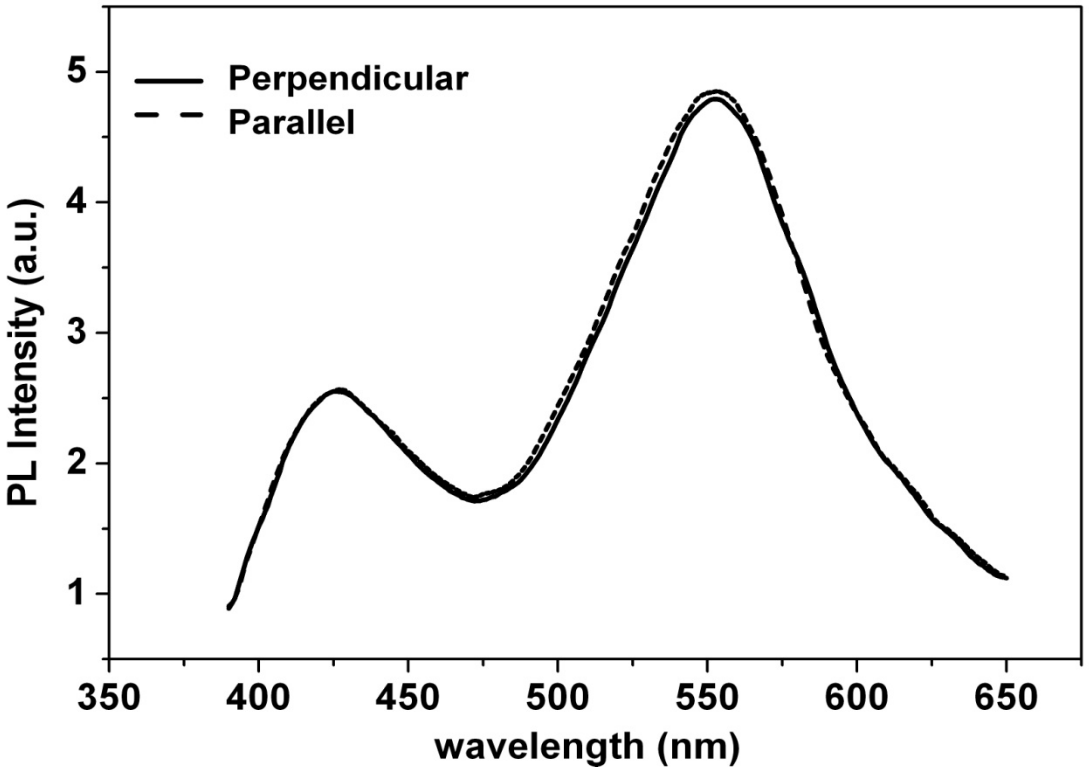
$$\boldsymbol{\sigma=2\epsilon_{LC}/(\ \epsilon_{LC}+\epsilon_{CdSe}),}$$

and the anisotropic ratio

$$\boldsymbol{r=(1-\sigma^2)/(1+\sigma^2)\quad r=0.72},$$

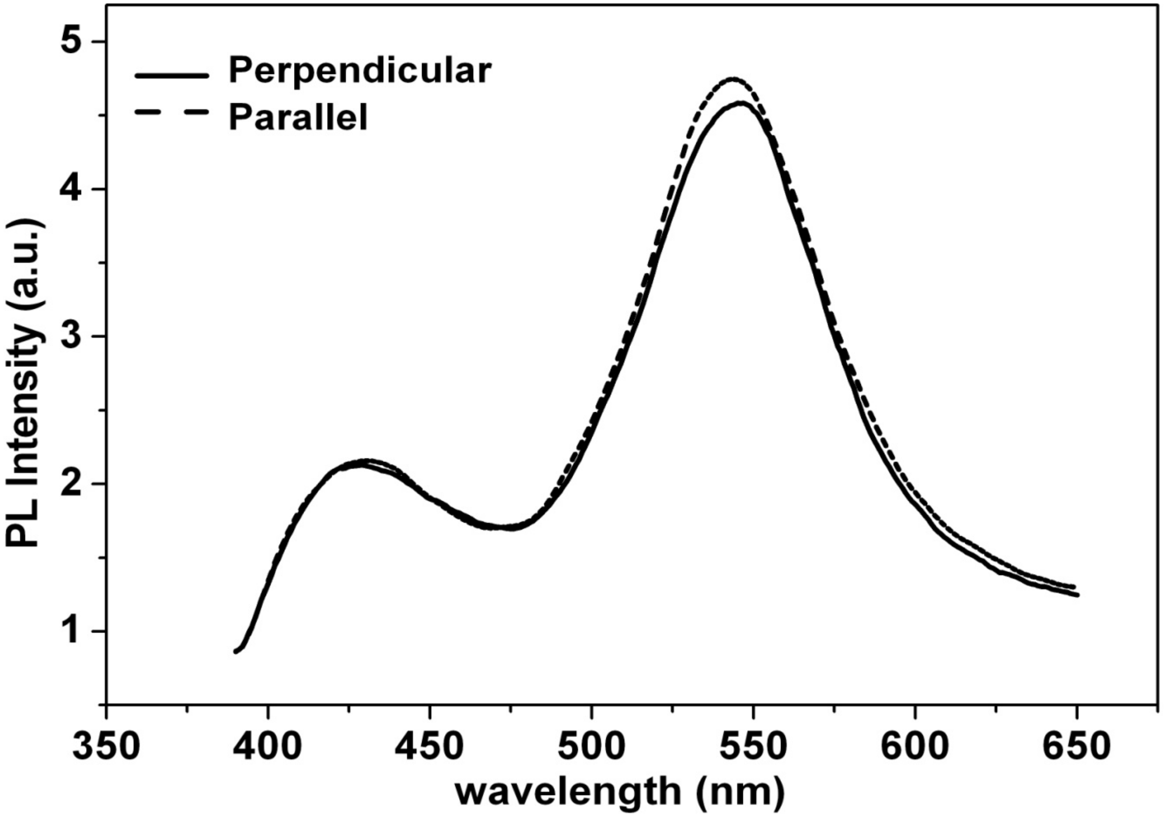
which is in good agreement with the experimental value of 0.68.

To demonstrate that the observed polarized emission is due to well aligned CdSe nanotubes, a device consisting of DI water and CdSe nanotubes has been fabricated.



The result shows that without LCs, CdSe nanotubes are randomly distributed.

A LC device consisting of LCs and CdSe nanoparticles has also been fabricated.



This result shows that without the intrinsic anisotropy of CdSe nanotubes, the optical polarization can not be detected.

5. Conclusion

① An alternative way of obtaining well aligned nanowires has been provided.

② Most importantly, it is possible to manipulate emission anisotropy electrically based on the device consisting of LCs and semiconductor nanotubes.

③ Electrically driven emission polarization of LCs-NTs composite devices can open up new applications for one-dimensional nanostructures in many smart devices utilizing well mature LCD technologies.

This work has been selected as Research News in Photonics Spectra Magazine.

V. Liquid crystal devices with built-in solar cells

1. Motivation

The existing technology of LCD is using electric field to drive liquid crystals.

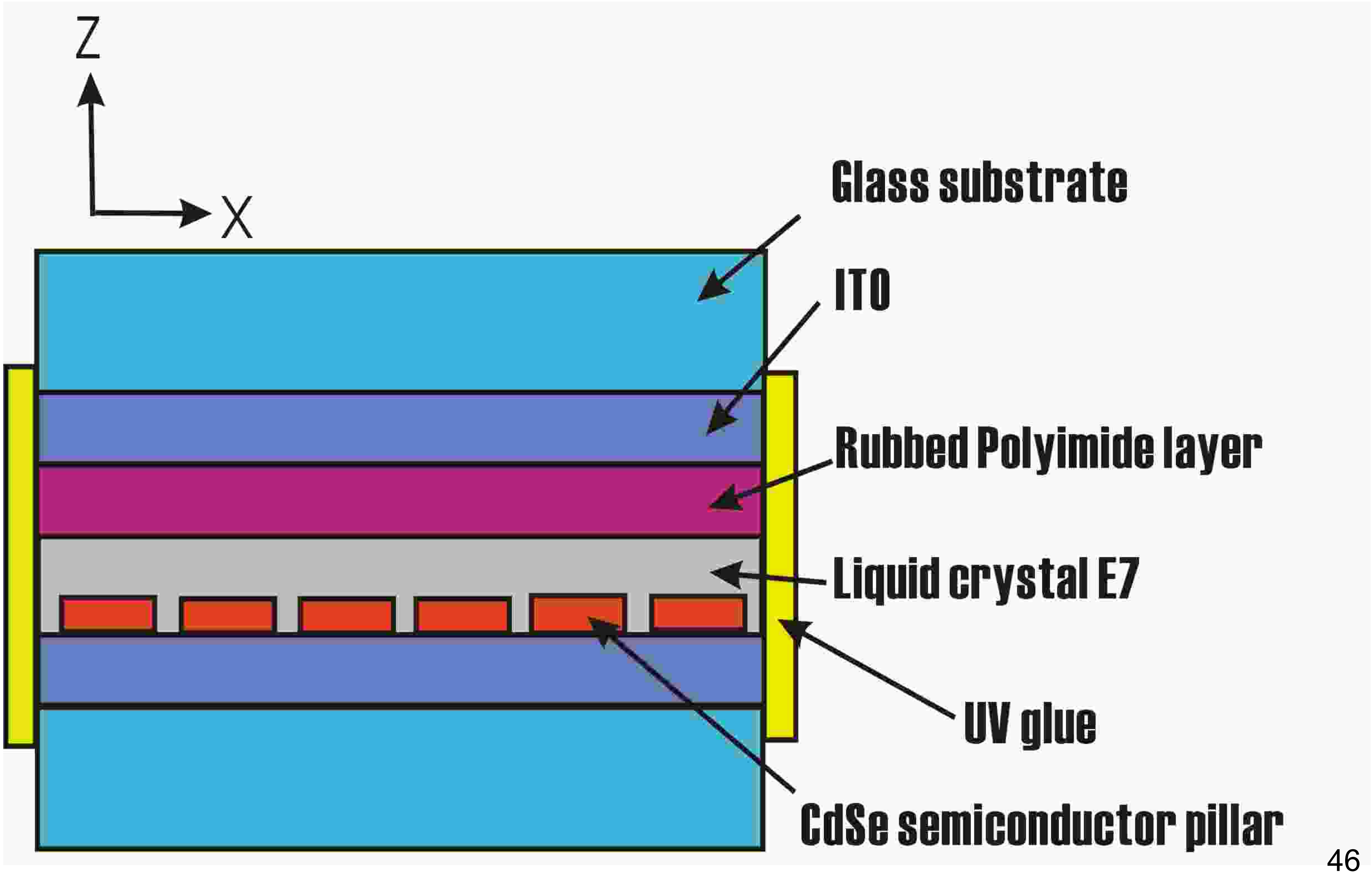
Can we drive LC by a light beam without an external bias?

2. Basic principle

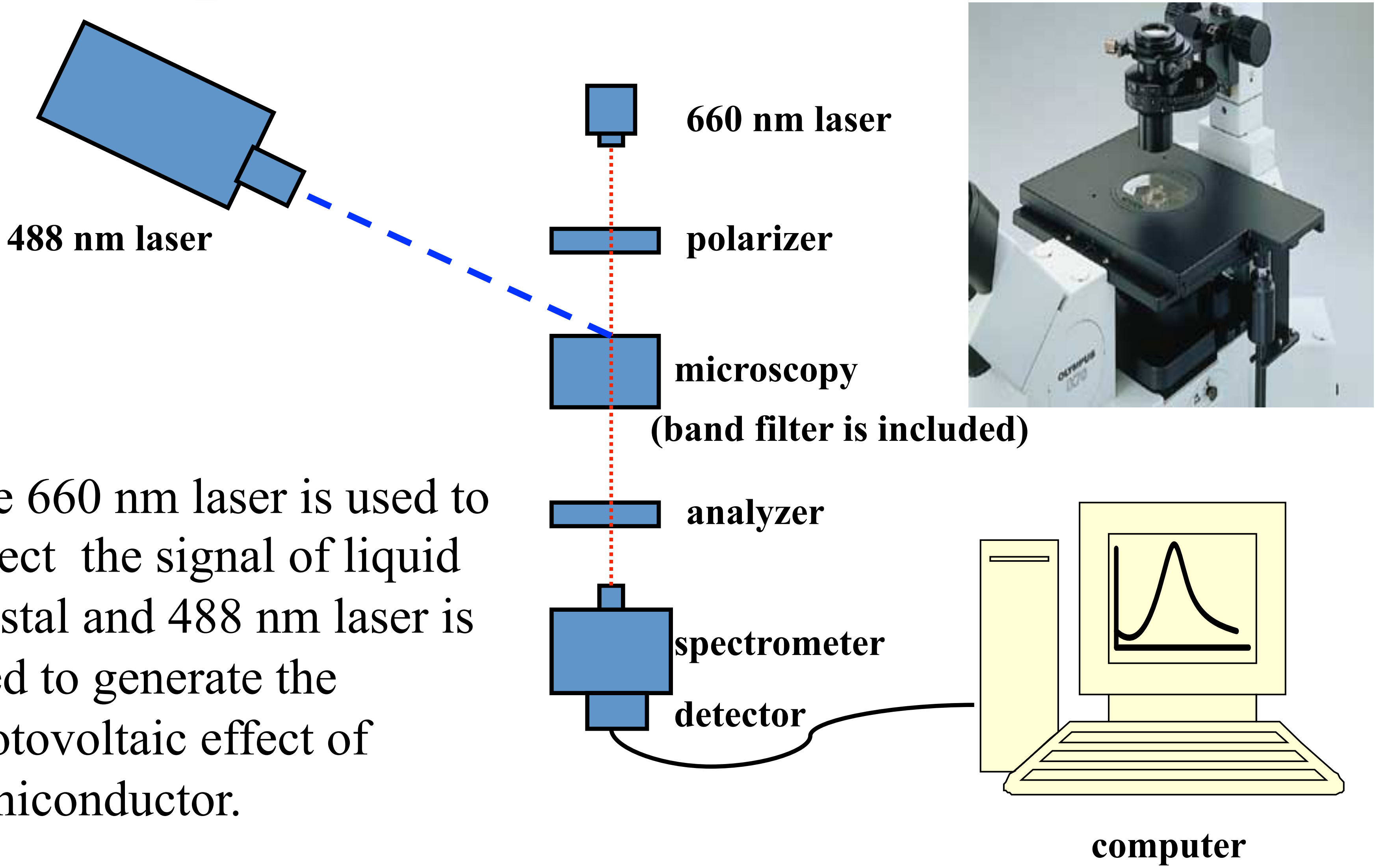
It is well known that a semiconductor Schottky diode can generate photo-voltage under light illumination.

If we can build such solar cells in LC devices, it has a good chance to drive LC optically.

3. Sample structure



Experiment – instrument setup



488 nm laser

660 nm laser

polarizer

microscopy

(band filter is included)

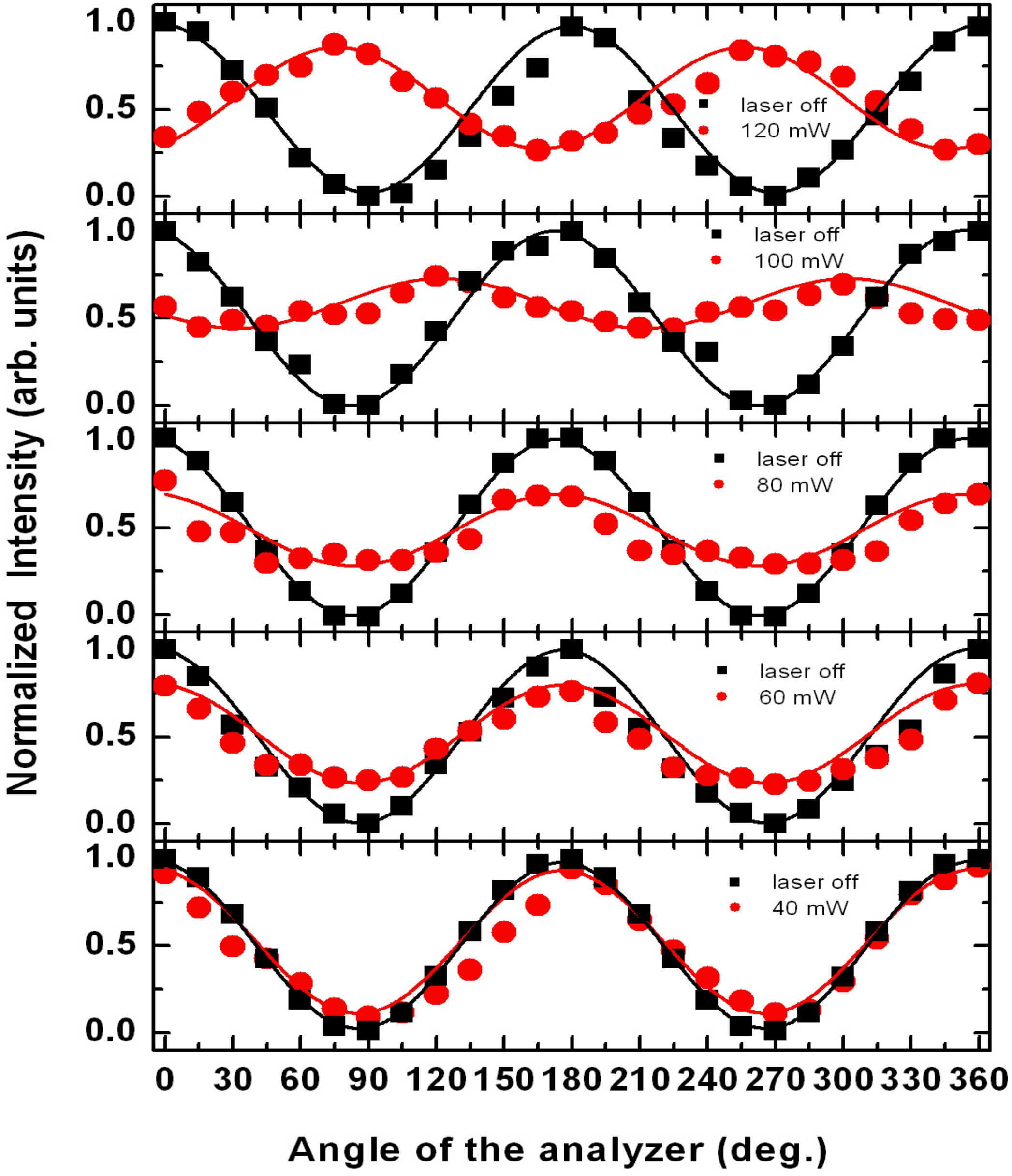
analyzer

spectrometer

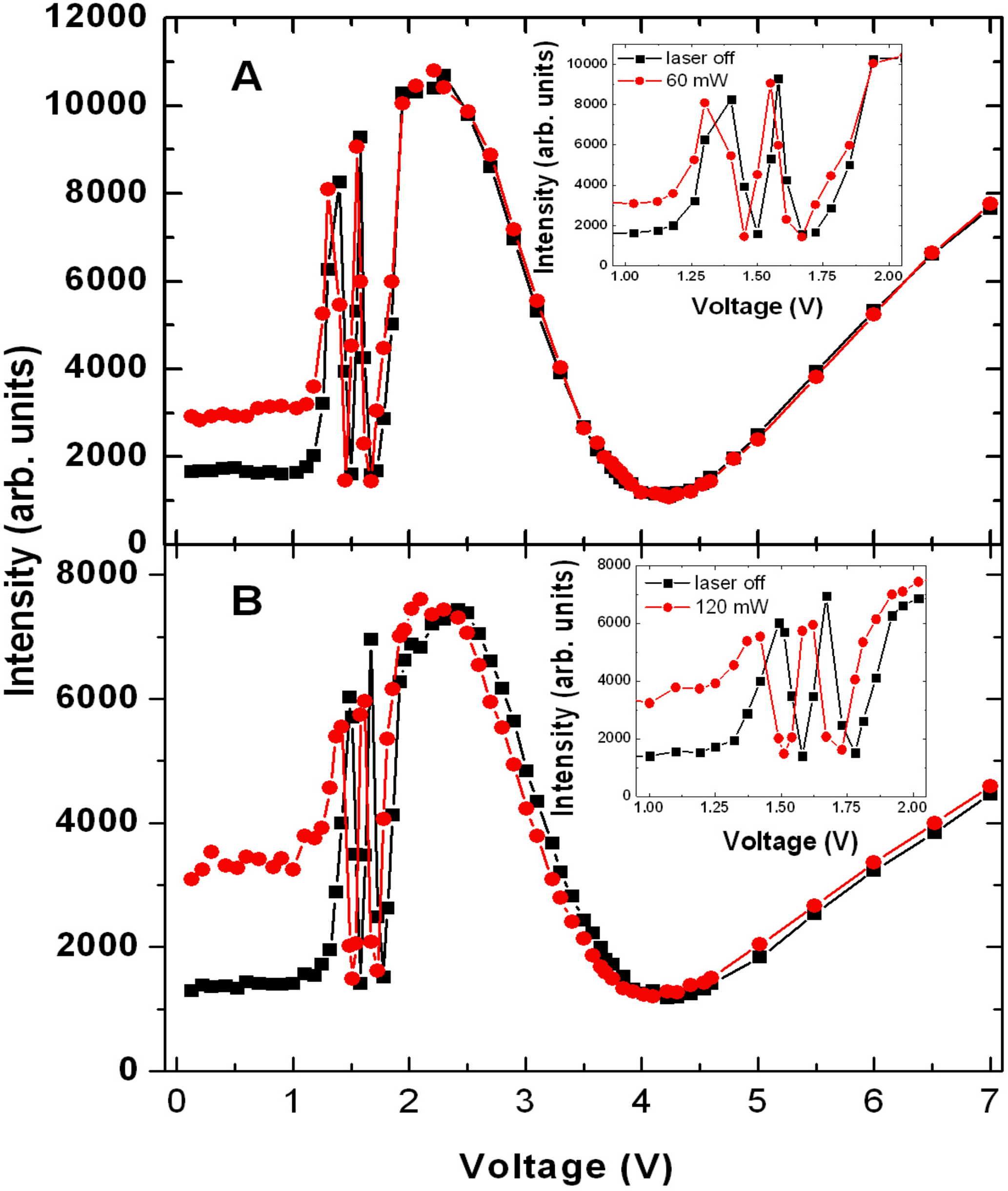
detector

computer

The 660 nm laser is used to detect the signal of liquid crystal and 488 nm laser is used to generate the photovoltaic effect of semiconductor.



1.0
0.5
0.0
laser off
120 mW
laser off
100 mW
laser off
80 mW
laser off
60 mW
laser off
40 mW
Normalized Intensity (arb. units)
0
30
60
90
120
150
180
210
240
270
300
330
360
Angle of the analyzer (deg.)


A
B
laser off
60 mW
laser off
120 mW
Intensity (arb. units)
Voltage (V)
0
2000
4000
6000
8000
10000
12000
0
1
2
3
4
5
6
7
1.00
1.25
1.50
1.75
2.00

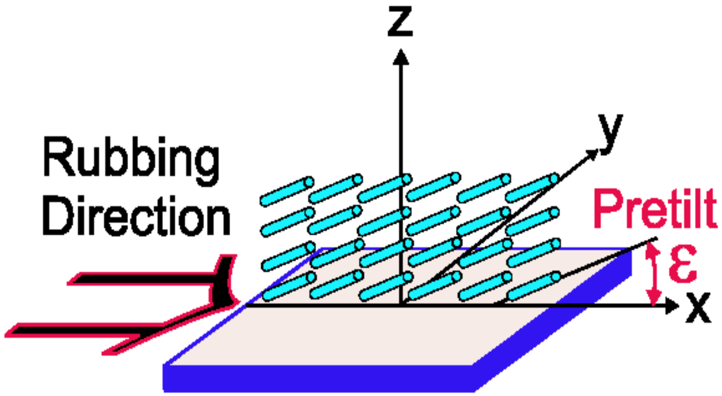
According to the electrical measurement, the driving mode of LC in our system is referred to as the *electrically controlled birefringence mode* (ECB-LCD). Then we can calculate the variations of pretilt angle in LC from the optical measurement using the following equations:

$$\mathrm{T} = \frac{1}{2}\sin^2\frac{\Gamma}{2}$$

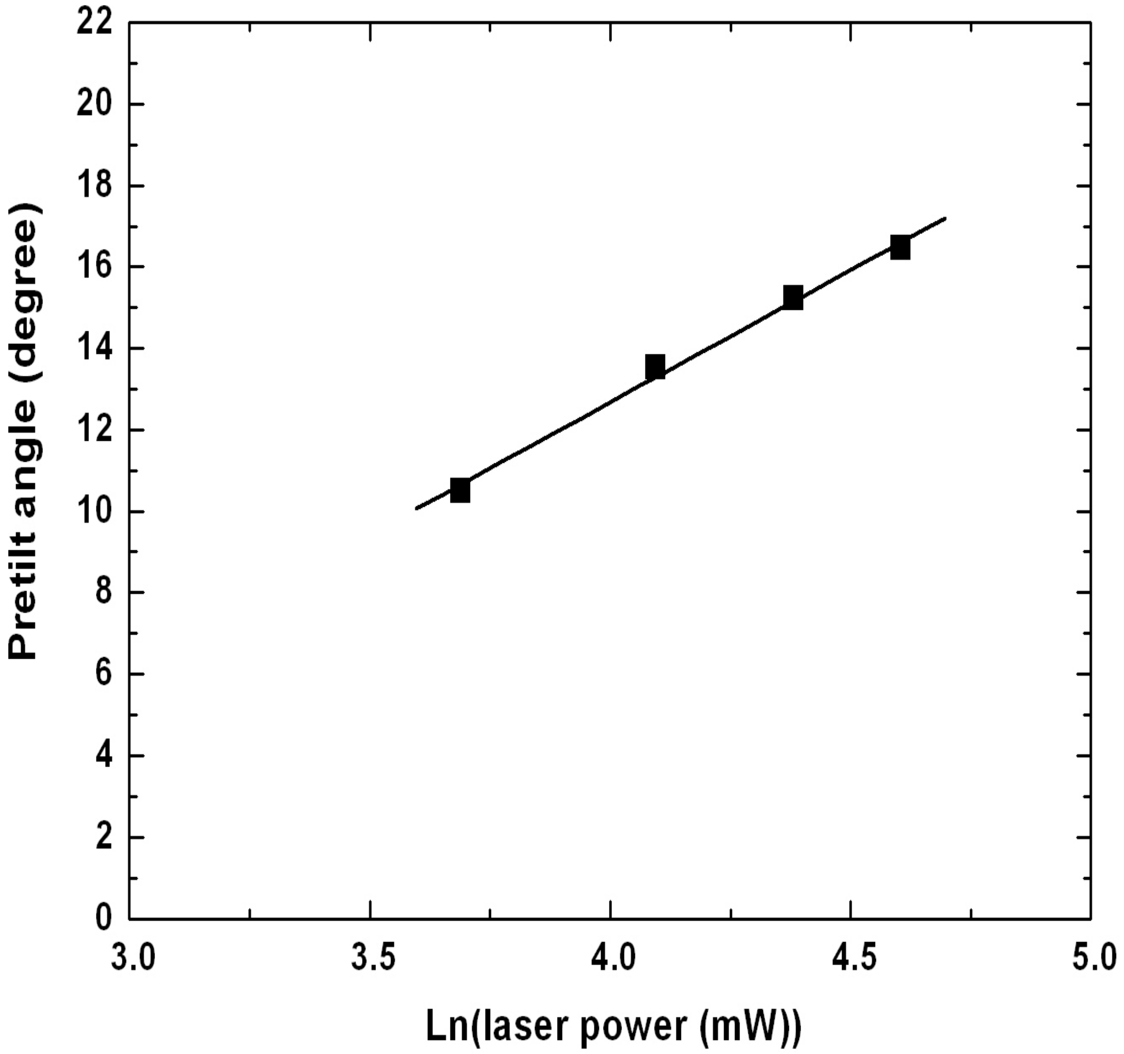
(crossed polarizers)

$$\Gamma = \frac{2\pi}{\lambda}\int\left[n_e(\theta) - n_o\right]dz$$

$$\frac{1}{n_e^2(\theta)} = \frac{\sin^2\theta}{n_o^2} + \frac{\cos^2\theta}{n_e^2}$$



where T is the transmission , Γ is the phase retardation , n_e and n_o are the principal refractive indices of the LC, θ is the pretilt angle.



It is consistent with the prediction of photovoltaic effect.

4. Conclusion

We therefore have successfully demonstrated that LC devices can be derived optically.

It opens a new avenue for the LC devices. It also serves as a new pathway for the interplay between semiconductors and LCs research.

V. An Advanced Alternative for Electrically Tunable Light Emitters: Graphene/SiO$_2$/p-GaN Diodes

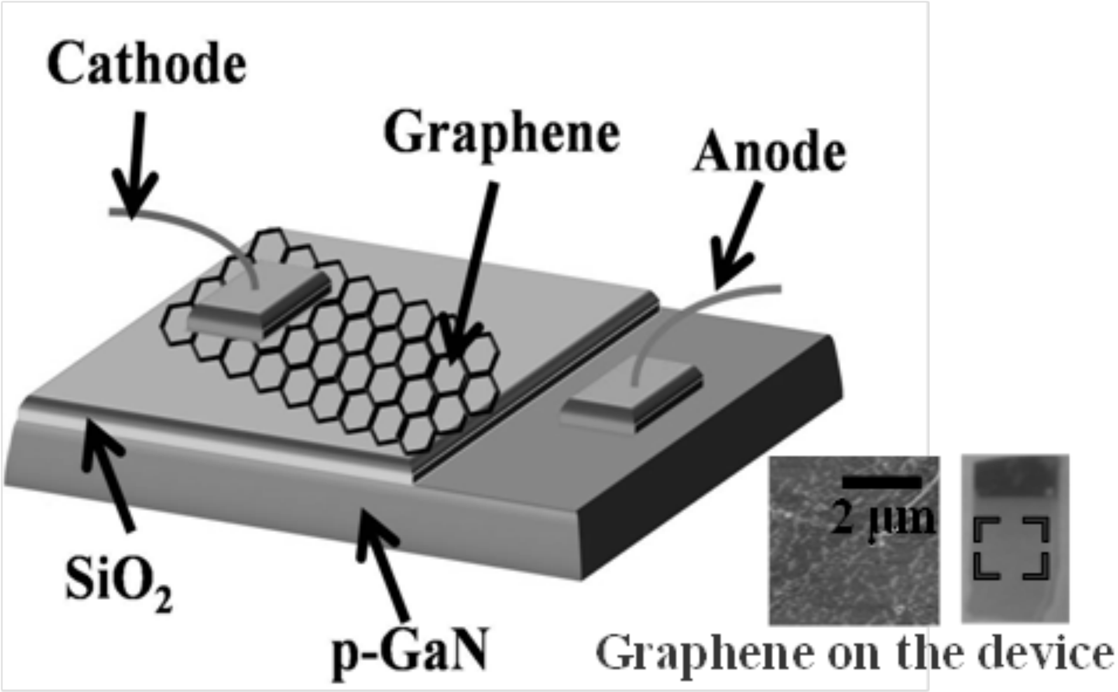
1.Motivation

Graphene is a single layer of carbon with exceptional properties, such as high electron and hole mobility, high transparency, and high robustness.

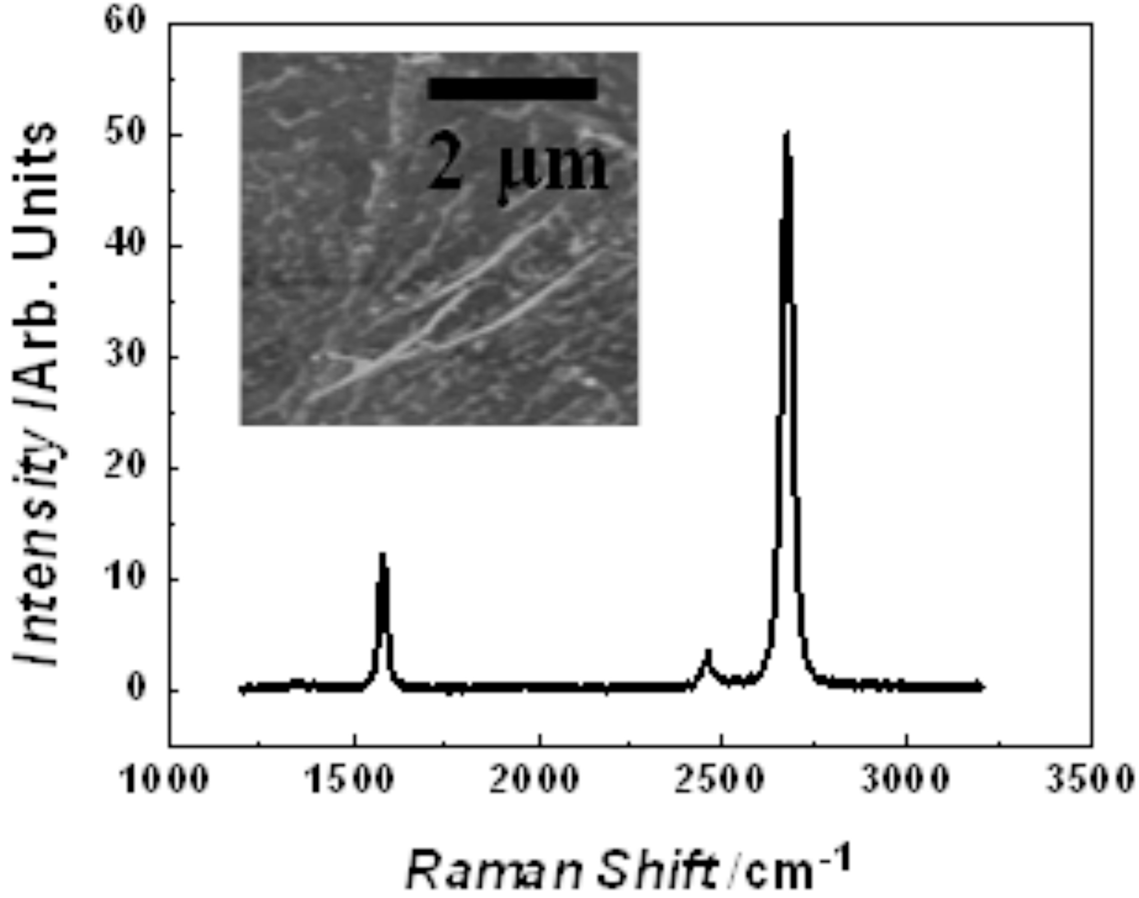
Combining with current semiconductor technology, one should be able to create novel devices.

An alternative for electrically tunable light emitters.

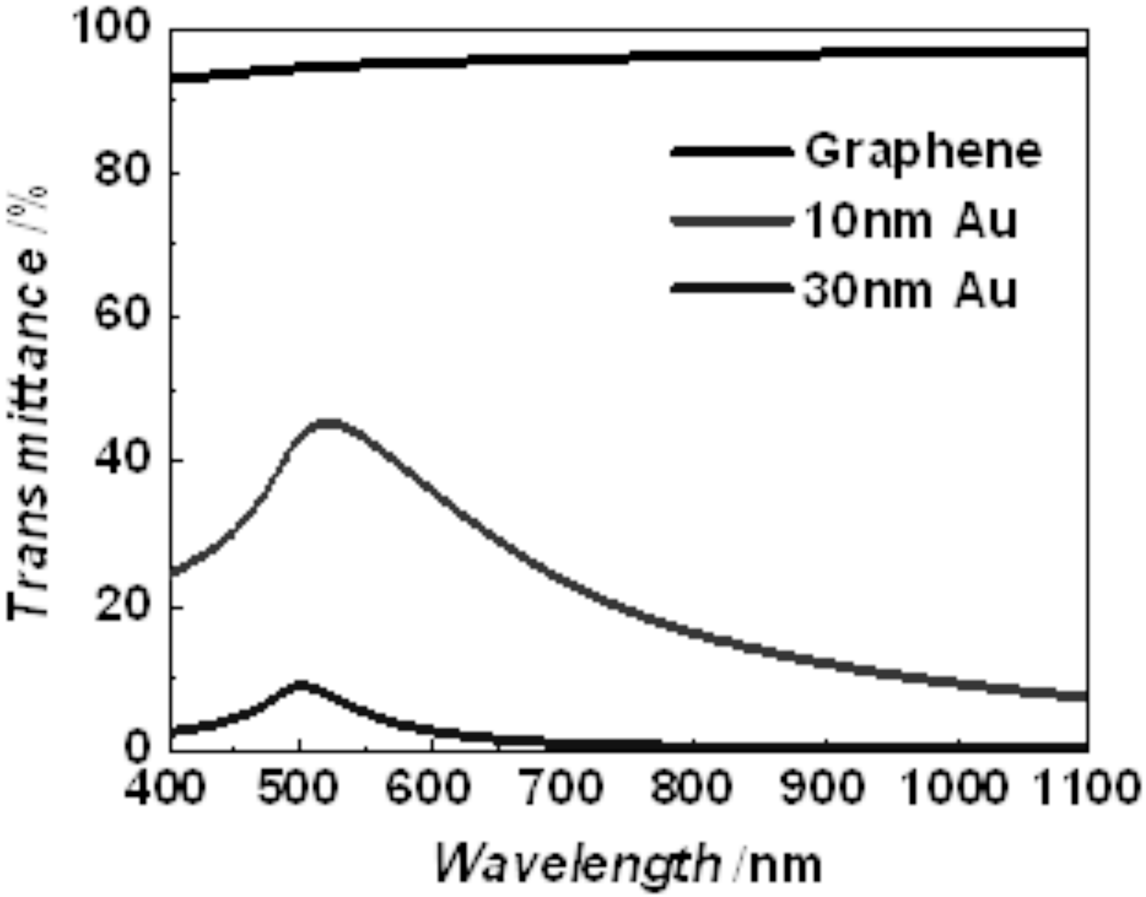
2.Sample design



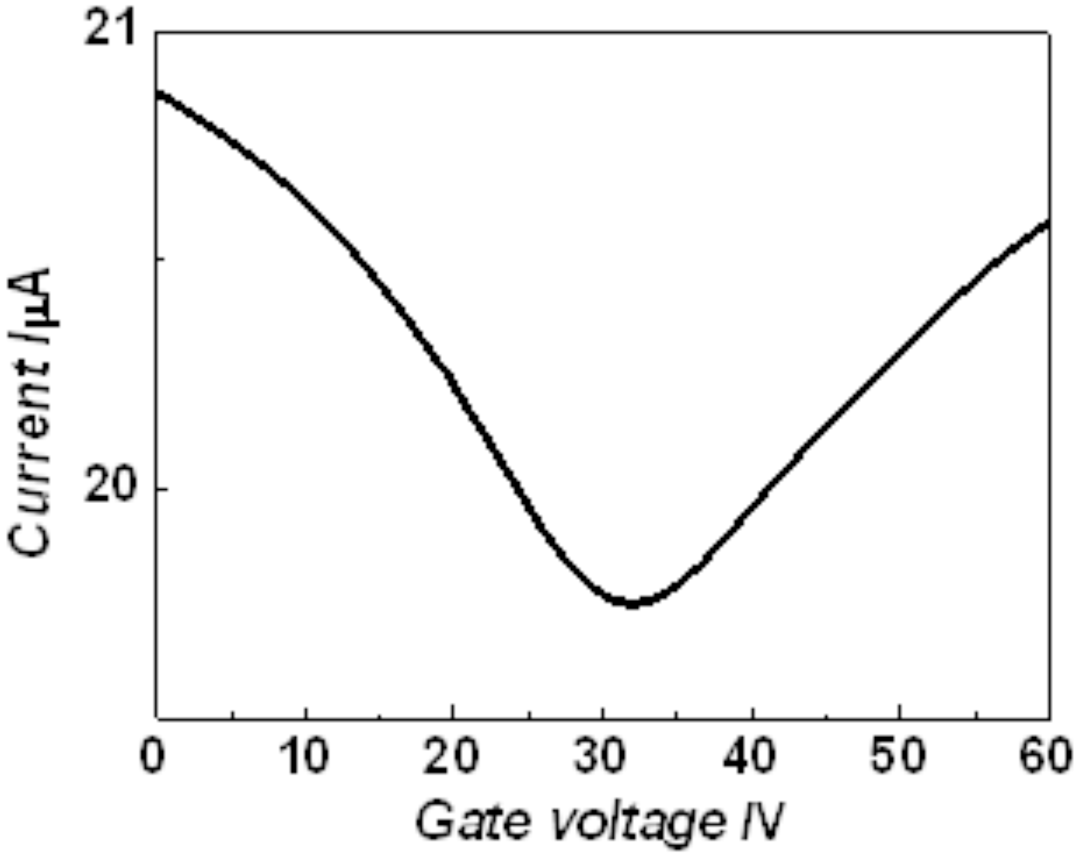
Schematics of graphene/SiO_2/p-GaN MIS-LED (inset) AFM image of the graphene electrode and photograph of the device.



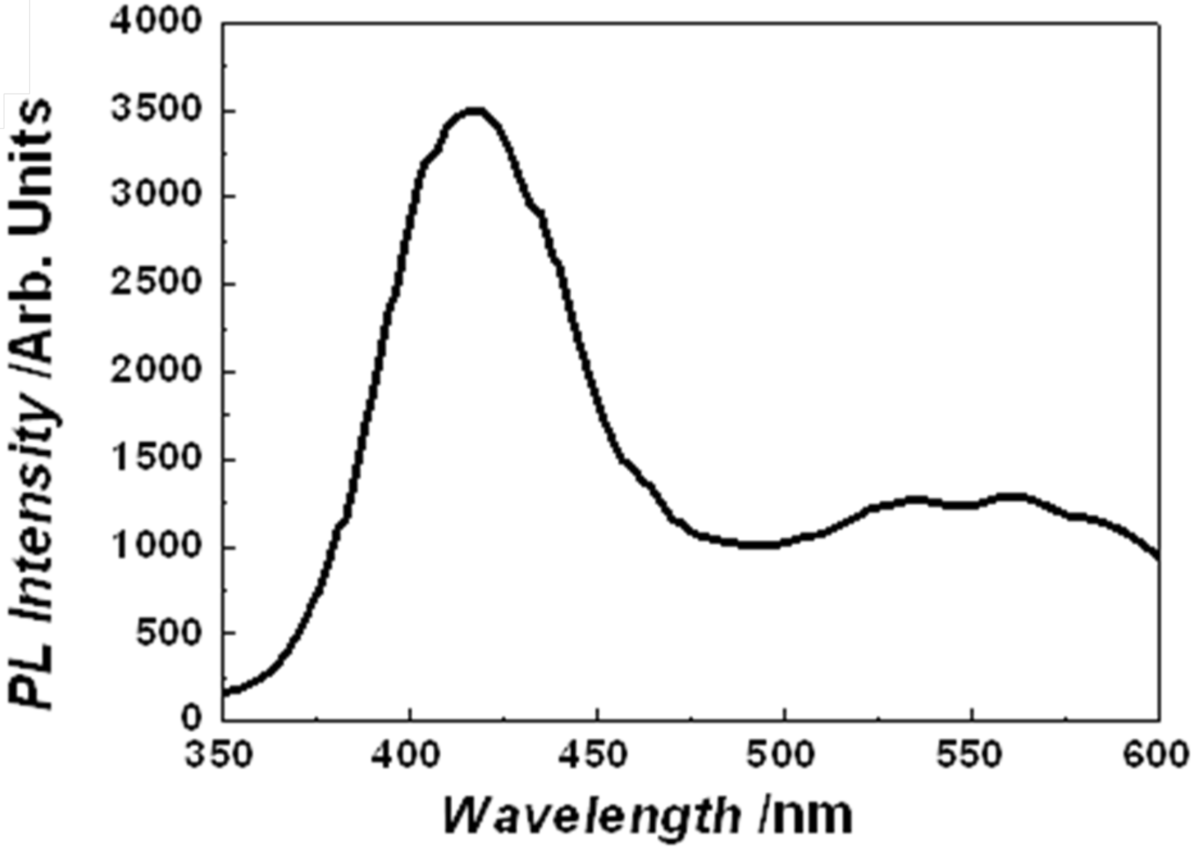
The 2D peak at ~2690cm^{-1} and a small G/2D ratio show typical characteristics of single layer graphene with good quality.



The transmittance spectra show high transparency of graphene compared with Au thin films.

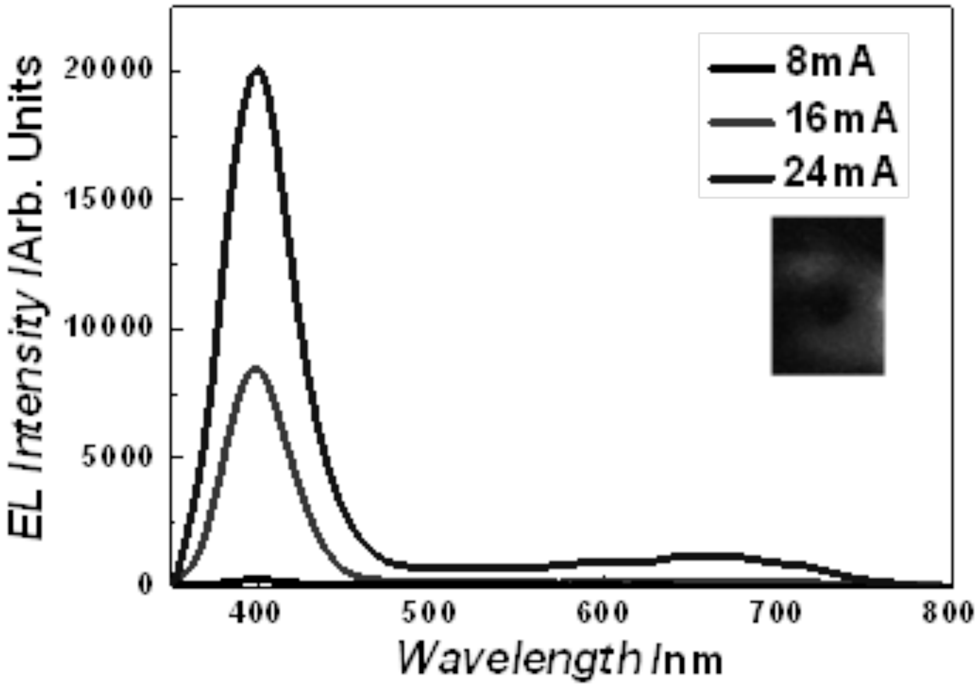


The characteristics of I_{ds} vs. Vg of the graphene FET exhibits a Dirac point at around 30V, corresponding to a p-type doping. The calculated field-effect mobility is about 1100cm^{2}v^{-1}s$^{-1.}$

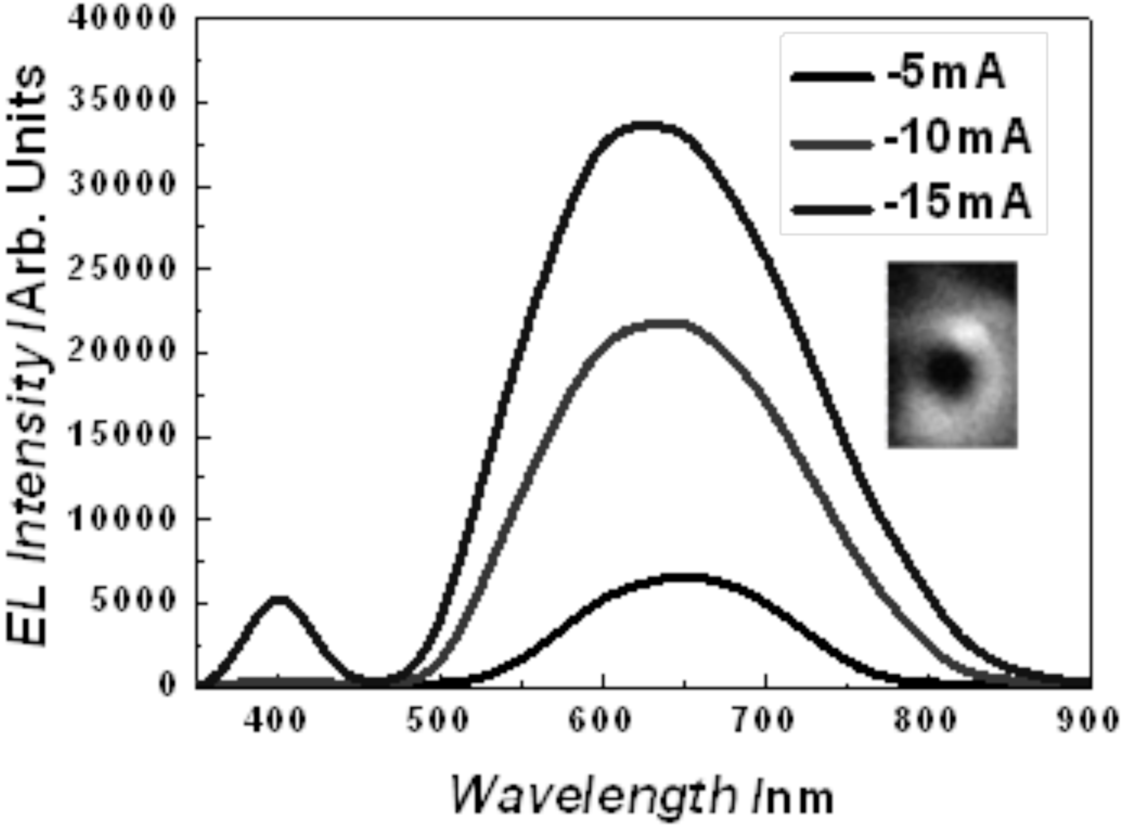


Photoluminescence spectrum of p-GaN at room temperature.

3.Results and discussion



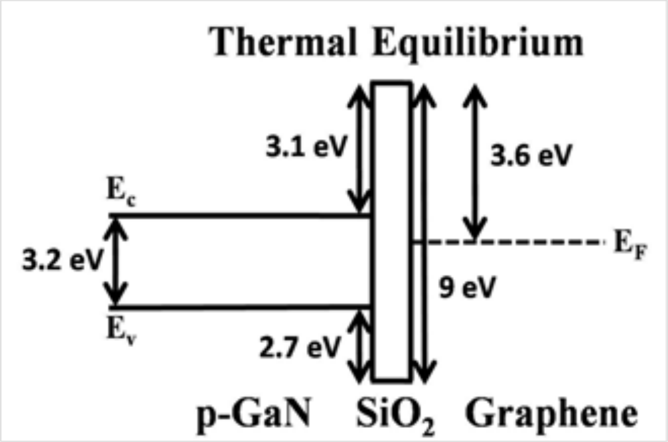
Electroluminescence spectra of graphene/SiO_2/p-GaN MIS-LED under forward bias at different injection currents at room temperature.



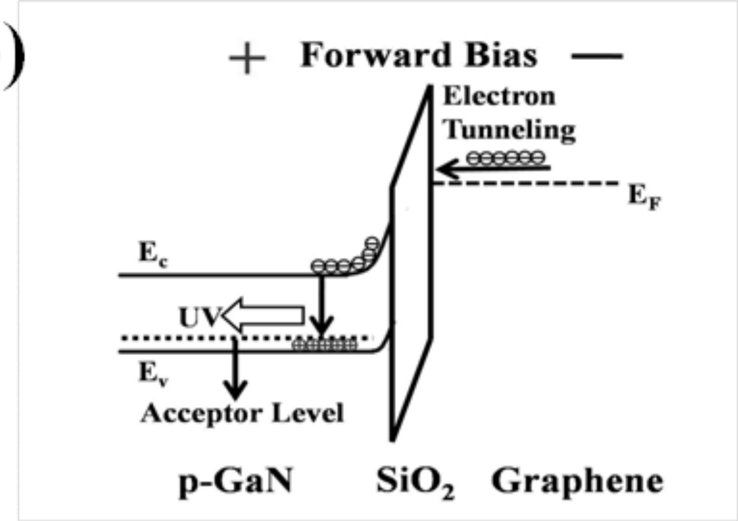
Electroluminescence spectra of graphene/SiO_2/p-GaN MIS-LEDs under reverse bias at different injection currents at room temperature.

Energy band diagram of graphene/SiO_2/p-GaN MIS-LED

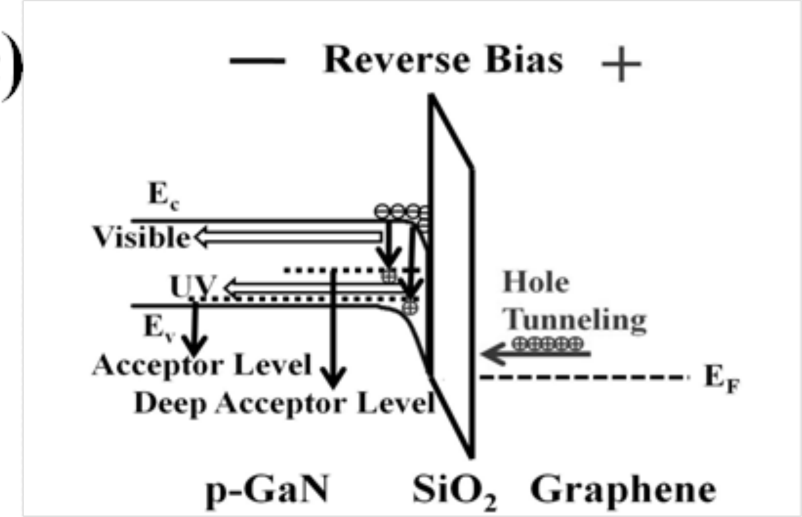
(a)



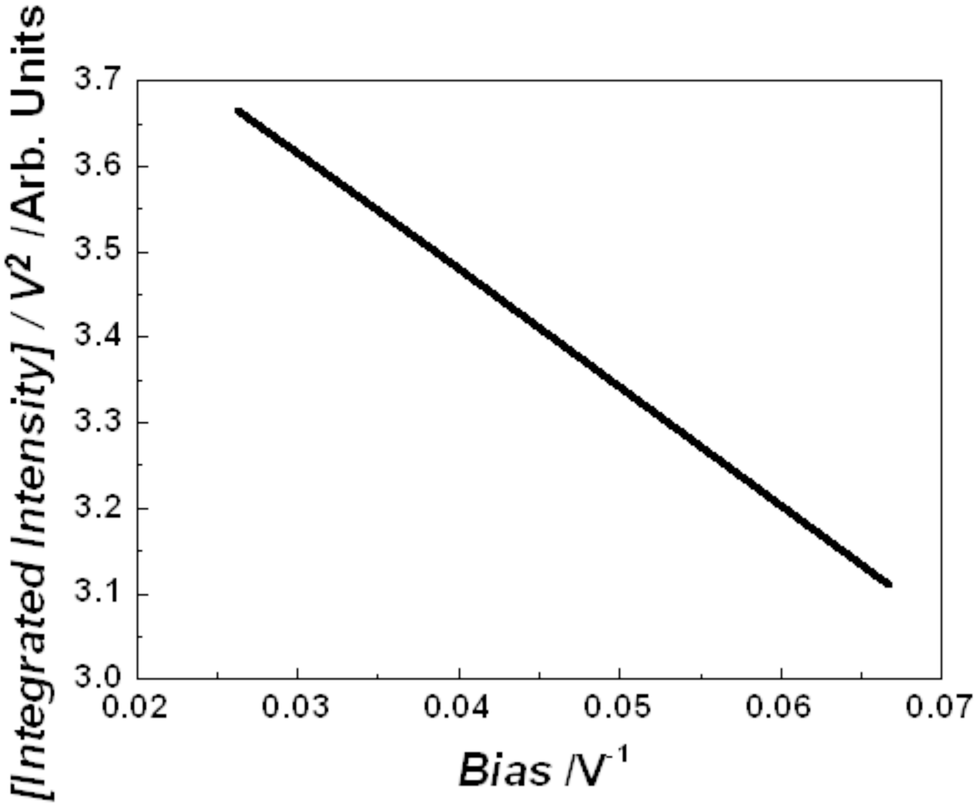
(b)



(c)

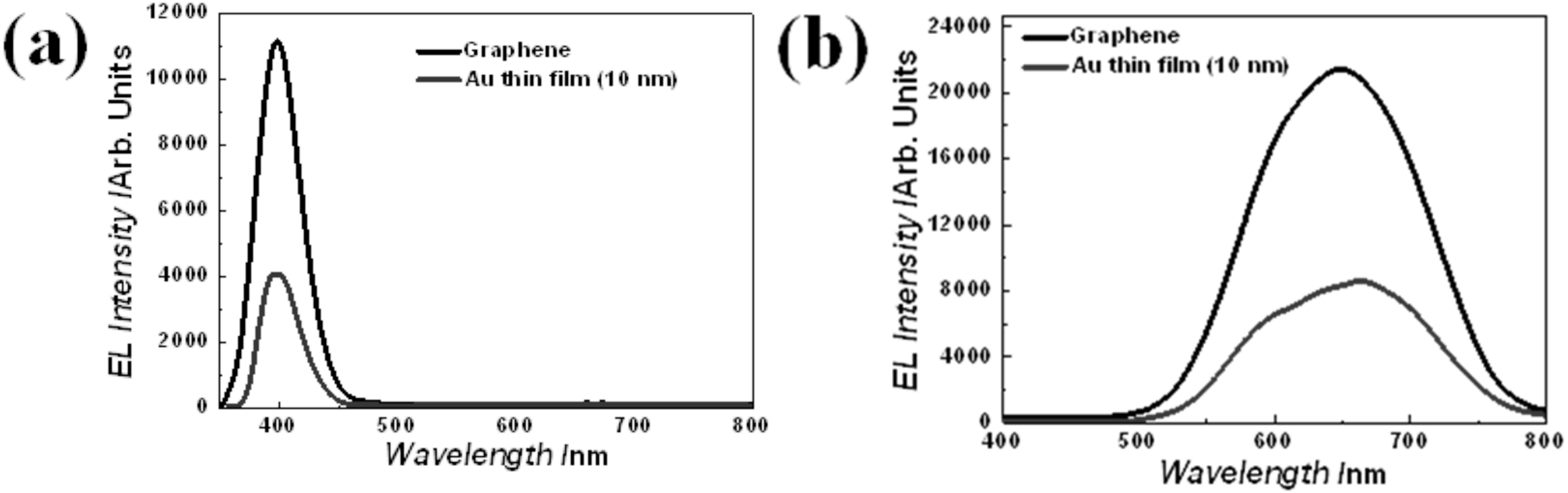


The integrated intensity I vs applied bias V can be explained well by the tunneling model



I/V^2 is a linear function of V^{-1}.

Comparison of EL spectra between graphene/SiO_2/p-GaN and Au/SiO_2/p-GaN



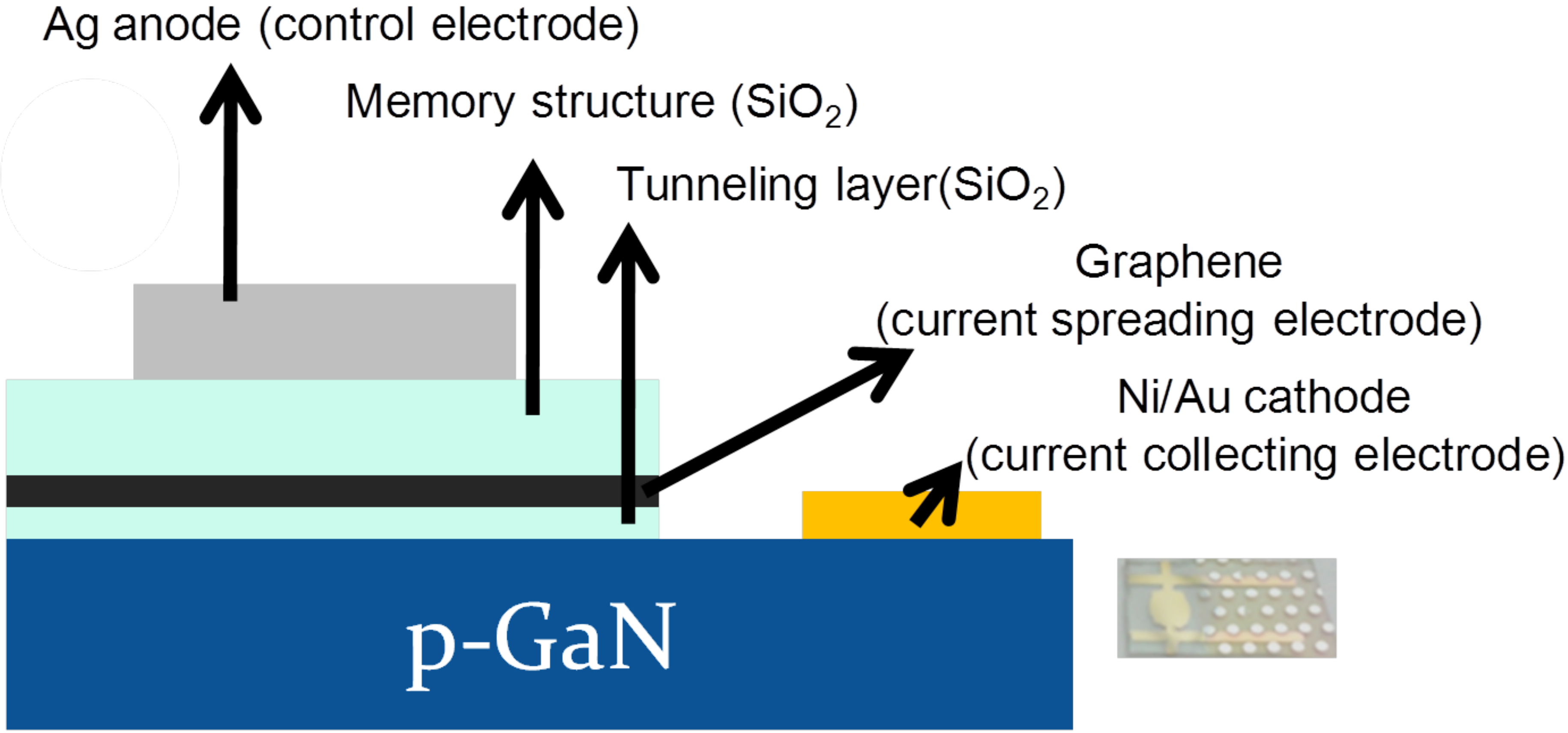
4.Conclusion

- A new MIS-LED with tunable emission spectra under forward and reverse biases has been developed.
- The new device is made possible by taking advantage of high transparency and conductivity of graphene.
- The underlying principle of the MIS-LED arises from the tunneling of electrons and holes, which is different from the standard p-n junction.

5. Light emission memories for electrical and optical communication

Integration of different devices to create new functionalities.

An easy way to integrate memory and light emitting diode to generate a new device called light emitting memory.



Ag anode (control electrode)

Memory structure (SiO_2)

Tunneling layer(SiO_2)

Graphene
(current spreading electrode)

Ni/Au cathode
(current collecting electrode)

p-GaN

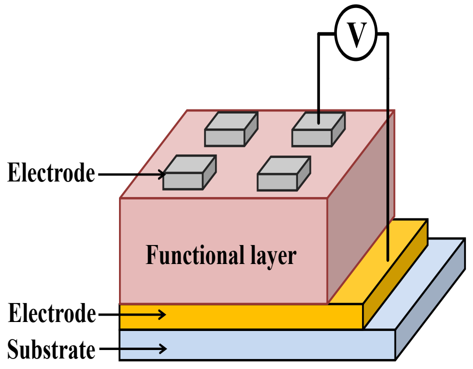
Schematics of light-emitting memory (LEM).

➢ Emerging resistive-type memory devices:

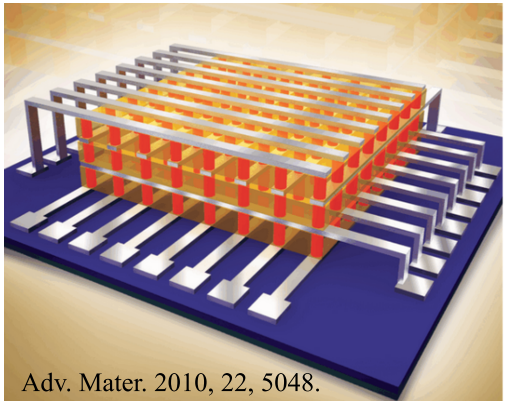
- Advantages of resistive-type memory:

1. Simple structure
2. Facile fabrication
3. Low operation voltage
4. Low cost
5. Roll-to-roll printing
6. Scaling down and 3D stackability
7. High speed for writing, erasing and reading

- Emerging resistive switching memory

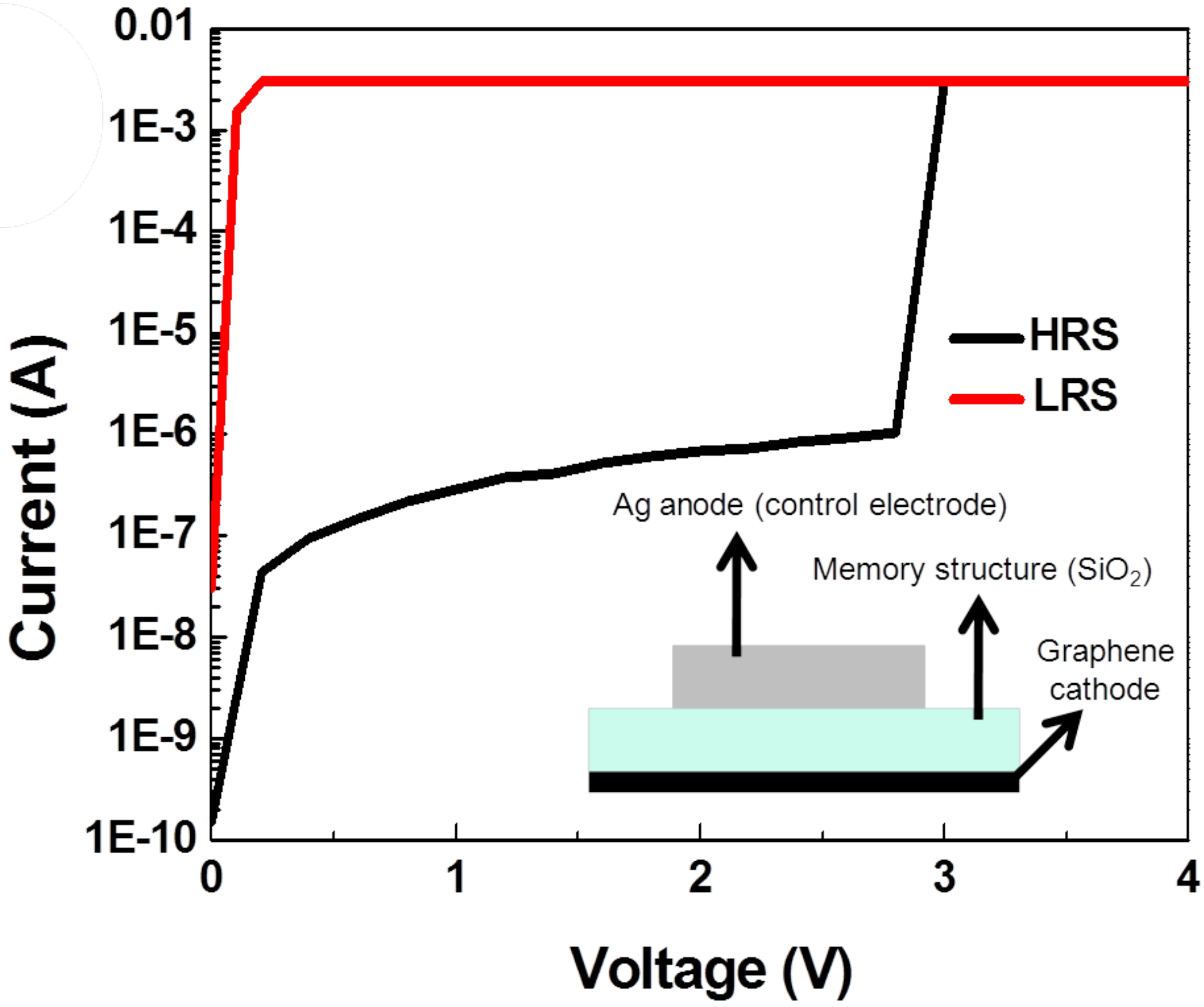


- Resistive switching memories by 3D cross-bar structure

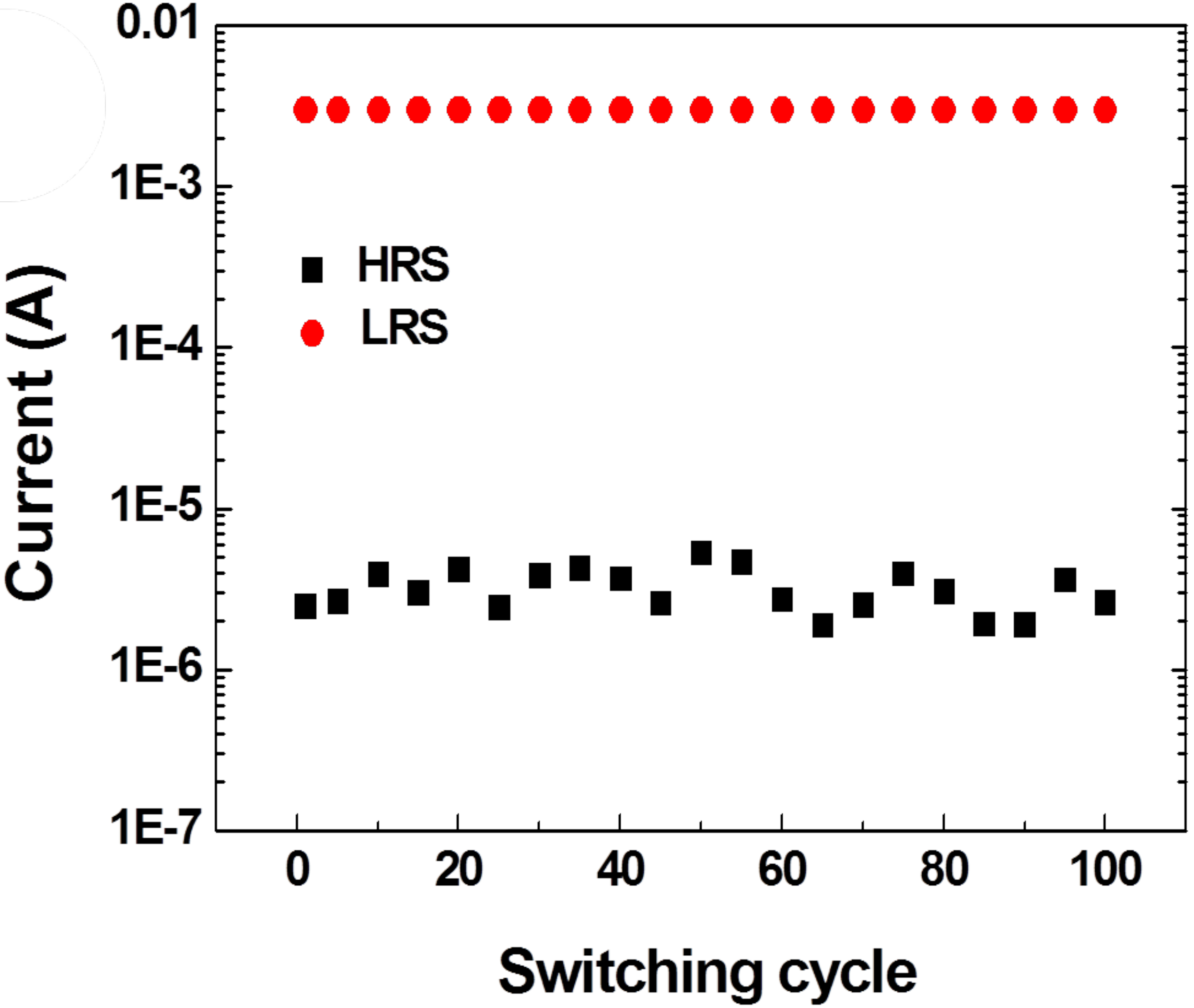


Adv. Mater. 2010, 22, 5048.

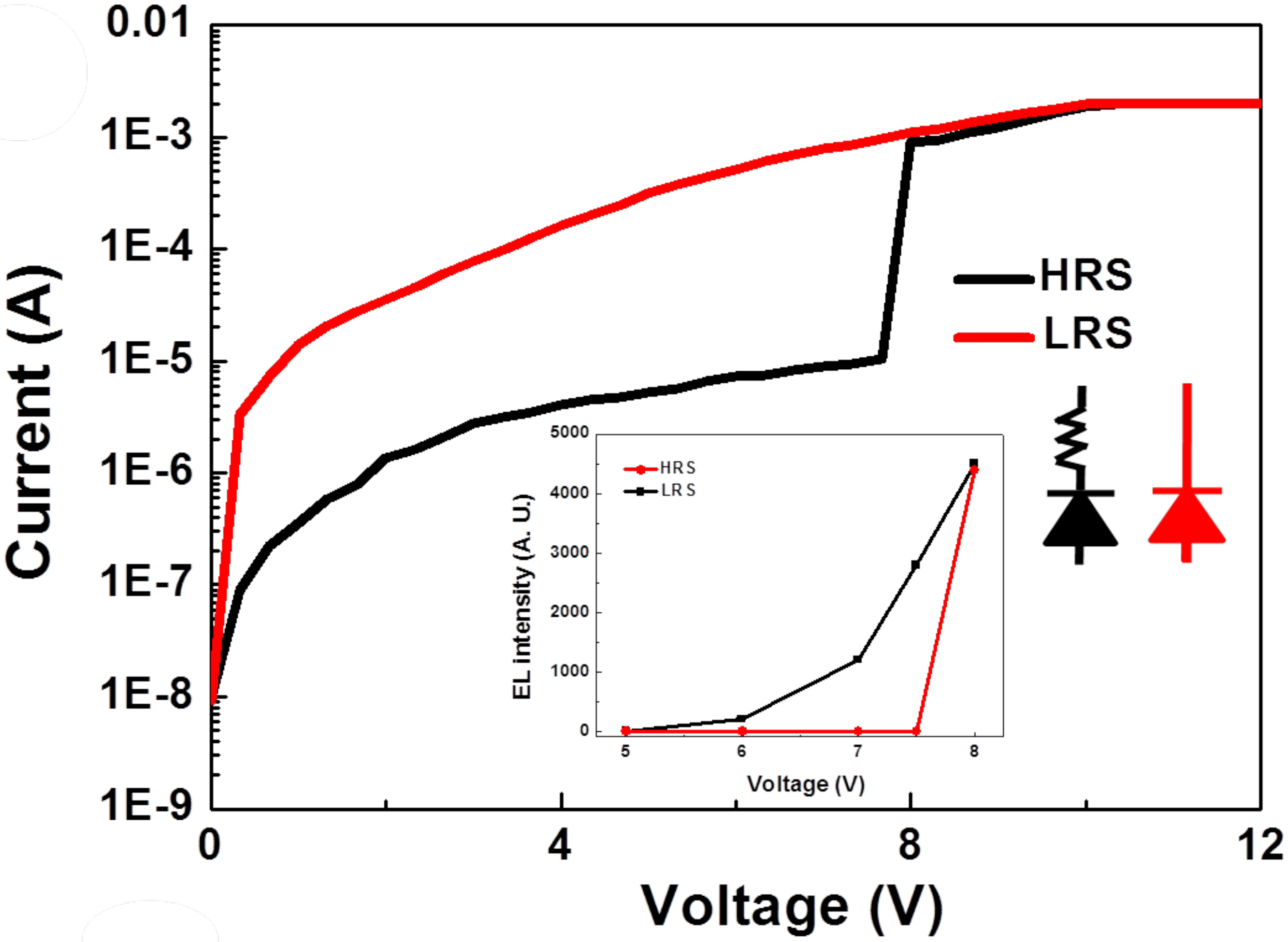
Adv. Mater. 2013, DOI: 10.1002/adma.201301361.



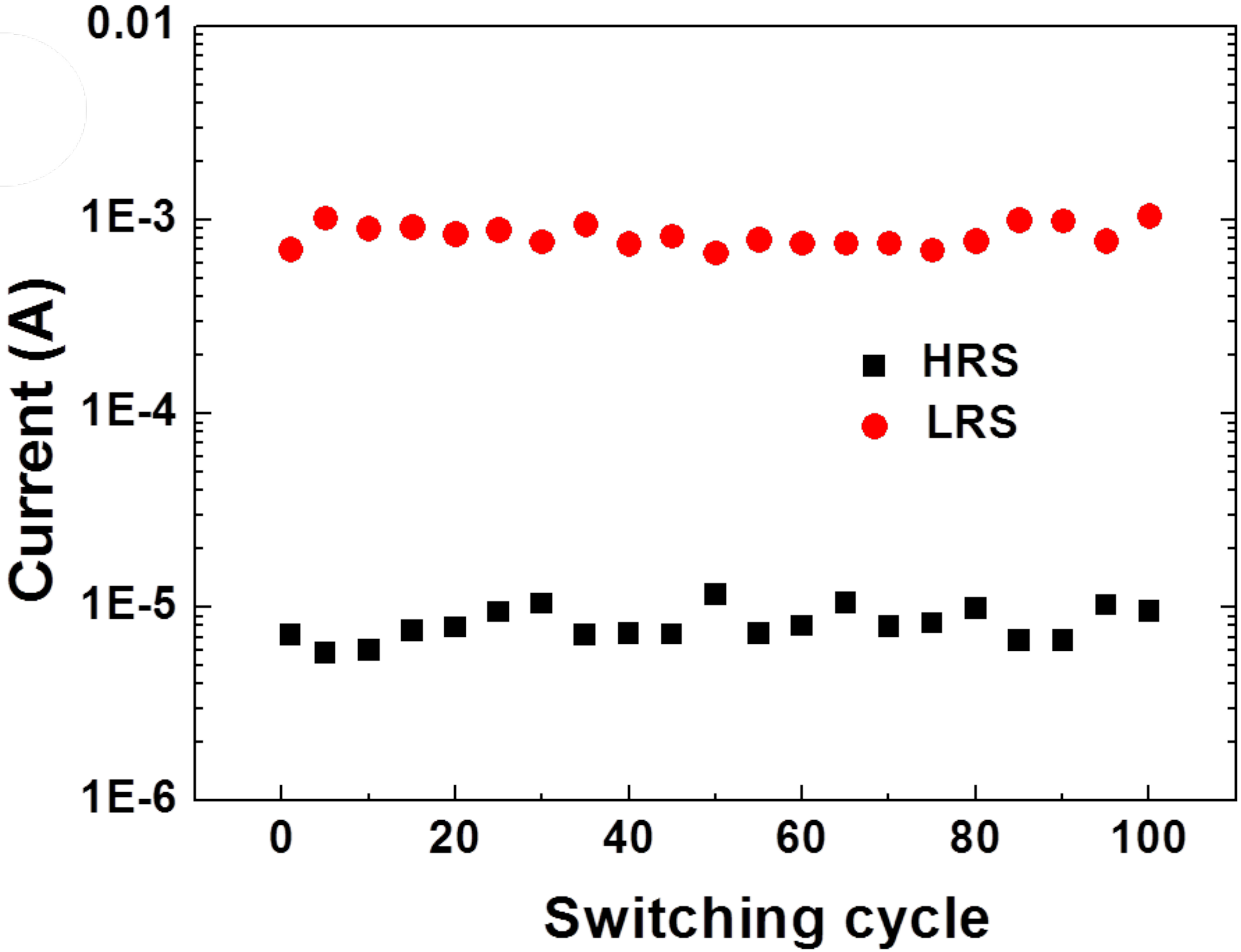
I-V characteristics of Ag/SiO$_2$/graphene memory cell. The inset shows the schematics of Ag/SiO$_2$/graphene memory cell.



Switching behavior of Ag/SiO$_2$/graphene memory cell over 100 cycles. The device is very stable.



I-V characteristics of light-emitting memory (LEM). The inset shows electroluminescence (EL) intensity of LEM as a function of voltage at high resistance state (HRS) and low resistance state (LRS). It has a unique feature of dual functionalities for electrical and optical detections.



Switching behavior of LEM over 100 cycles. The device is very stable.

- The simplest structure of light emitting memories.
- Easy fabrication and high feasibility for practical application.
- Enable for both electrical and optical communication, which is very different from the conventional electrically readable memory devices.