

Preparation and Characterization of CuO based Core-Shell Heterostructure Nanowires for Photodetector Application

1



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Layout

2

- Introduction
- Core-Shell Heterostructures
- Preparation & Characterization of CuO Based Heterostructure nanowires
- Results & Discussions
- 1) CuO/CdSe core- shell heterostructure nanowires.
- 2) CuO/CdS core- shell heterostructure nanowires
- Conclusions

Introduction

3

- Pure 1D semiconductor nanowires cannot absorb wavelengths below their band gap, limiting their use for wide spectral sensitivity in standard devices.
- alternatively one-dimensional (1D) semiconducting heterostructures are considered as the most promising sensitive photo detection materials due to they not only offer the high photoconductive gain and property benefits as 1D nanostructures but also with the added benefit of multifunctions or new properties arising from the synergistic effects of combining heterojunction materials.
- Furthermore, the formed heterojunction interface can greatly enhance these PDs' detectivity, fast response speed and responsibility.

Types of Semiconducting Heterostructures

Semiconductor heterostructures are typically classified as type-I or type-II, depending on the relative alignment of conduction- and valence-band edges of the materials that are combined at the heterointerface.



In the type-I structures, both the conduction and the valence band edges of one semiconductor (Figure a) are located within the energy gap of the other semiconductor. In this case, an electron-hole (e-h) pair excited near the interface tends to localize in semiconductor, which provides the lowest energy states for both electrons and holes.

In the type-II case structures(Figure b), the lowest energy states for electrons and holes are in different semiconductors; therefore, the energy gradient existing at the interfaces tends to spatially separate electrons and holes on different sides of the heterojunction. The corresponding “spatially indirect” energy gap is determined by the energy separation between the conduction-band edge of one semiconductor and the valence band edge of the other semiconductor.

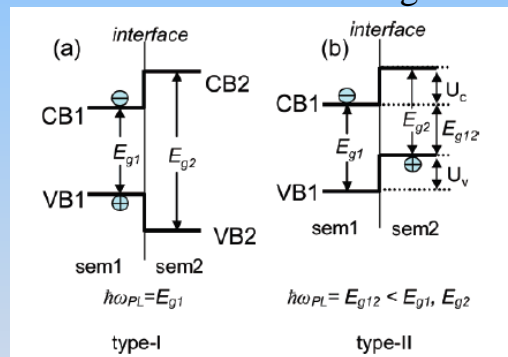
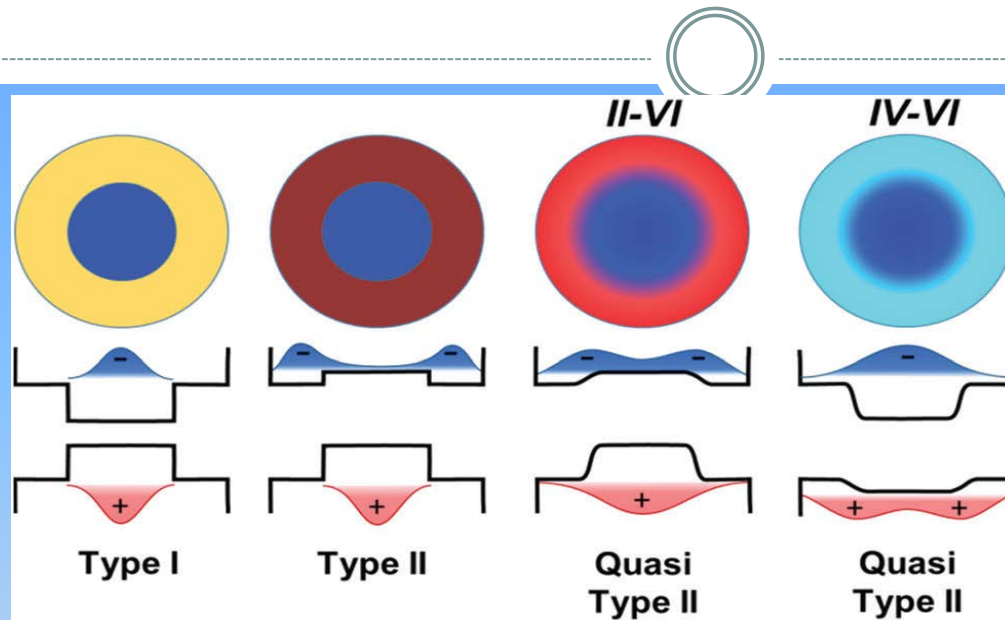


Figure . Type-I (a) and type-II (b) band-edge alignments at the

The semiconducting core-shell hetero structure not only allows efficient use of intrinsic material properties from individual components but also improves the charge carrier collection favored by radial geometry where electrons and holes are spatially confined in different conducting channels of type-II heterostructures, thus decreasing recombination losses.

Particles Wave in Heterostructures



Schematic illustration of the different types of core/shell heterostructures (top row) and their energy band diagrams (bottom row) with possible electron (blue curves) and hole (red curves) wavefunction.

Compared to individual-component semiconductors, 1D semiconducting heterostructures have the capability of showing not only multifunctionalities but also some unique and markedly improved optical and optoelectronic properties, due to the combination of different functional components. Particularly in the field of photodetector research, studies have indicated that devices constructed from 1D semiconducting heterostructures can exhibit excellent optoelectronic performances that are superior to those of individual constituents

The Ultraviolet Spectra



* Photodetection in the ultraviolet (UV) region has drawn extensive attention owing to its various applications in industry, instrument, and our daily life. UV light is typically divided into four spectral regions: UV-A (for wavelengths between 400 and 320 nm), UV-B (for wavelengths between 320 and 280 nm), UV-C (for wavelengths between 280 and 200 nm), and far UV (for wavelength between 200 and 10 nm, which reaches the X-ray spectral low energy frontier).

* Most of the UV light from the Sun is absorbed by the atmospheric ozone layer. Solar radiation with wavelength longer than 280 nm can penetrate the atmosphere and reach the Earth. For this reason, UV detectors that have high sensitivity to UV-C and far UV radiation compared to radiation with wavelength longer than 280 nm can be called 'solar-blind'. The detection of UV radiation presents a wide range of applications, such as chemical, environmental and biological analysis or monitoring, flame and radiation detection, astronomical studies, and optical communications.

* A high-performance photodetector should satisfy the *5S requirements of high sensitivity, high signal-to-noise ratio, high spectral selectivity, high speed, and high stability.*

Materials For UV Photodetectors



Metal oxide (CuO) one dimensional (1D) heterostructure nanomaterials have been found to be the potential candidates because of their ideal band gaps, low costs fabrication of device, easy synthesis process and natural abundance on earth crust

Among various oxide based core-shell heterostructures, copper oxides (CuO and Cu₂O) which exhibit p-type semiconductors characteristics are being examined broadly due to their ideal band gaps (E_g (CuO) = 1.4 eV, E_g (Cu₂O) = 2 eV) as strong absorption in the solar spectrum region, non-toxic and low costs of fabrication.

Enhancement in performance efficiency has been observed either in core or layer in the CuO based core-shell heterostructure.

Similarly, CdSe, with a direct band gap of 1.7 eV at room temperature is also an important n-type semiconductor.

The band off set of CdSe/CdS and CuO can meet the requirements to construct a high performance photodetector.

Materials and methods



Synthesis of CuO nanowires

In this work, p-type-CuO-core/n-type-CdSe-shell heterostructure nanowires arrays have been synthesized by two steps methods. Though there are various methods, in the first step, adopting a simple and low cost thermal oxidation method, semi-aligned CuO nanowires has been grown on copper substrate

In the first step,copper foils (0.1 mm thickness) have been used for the synthesis of CuO nanowires. These copper foils were cleaned in an aqueous solution of 1.0 M hydrochloric acid.

The Cu foils were then rinsed with deionized water in order to remove residuals oxygen contents and acid on the surface of Cu foils and dried properly. Cu foils are then kept inside a horizontal tubular furnace with both end open in order to provide air to substrate. The oxygen present activates in forming CuO nanowire of Cu foil.

The preparation temperature for the thermal oxidation is 500⁰C for 4 hour with a heating rate 10⁰C per minute whereas the furnace was allowed to cool naturally. A black, fragile product onto the surface of copper foils was recovered.

Synthesis of CuO/CdSe & CuO/CdS Core-Shell Heterostructure Nanowires by Chemical Vapor Deposition (CVD) Technique



In the second step, the synthesis of CuO-CdSe/CdS core-shell heterostructure nanowires has been done by chemical vapor deposition (CVD) technique where the grown CuO nanowires acts like a templet on which CdSe shell crystal structure is grown.

The grown CuO nanowires Cu foils by thermal oxidation have been used as the substrate for formation of CdSe shell layer with CuO core which was placed at the downstream of the furnace (Position B in figure).

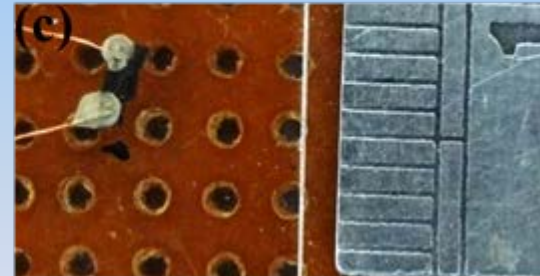
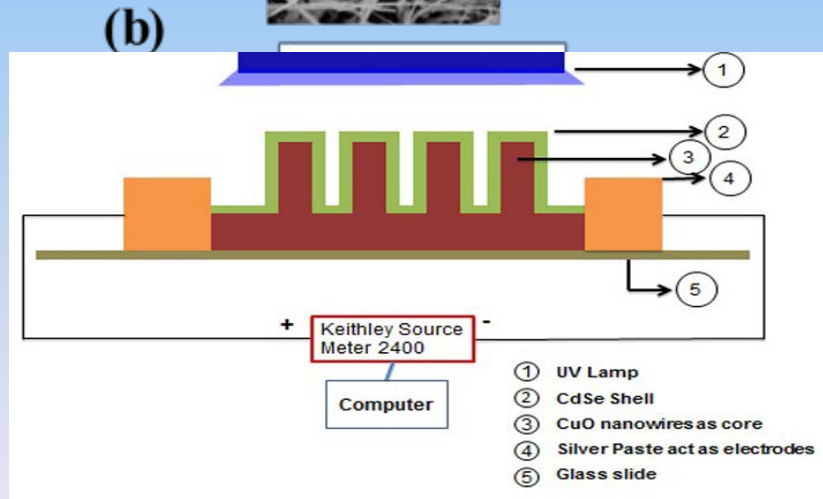
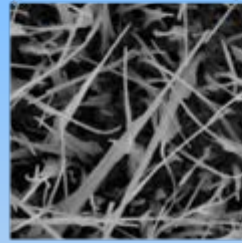
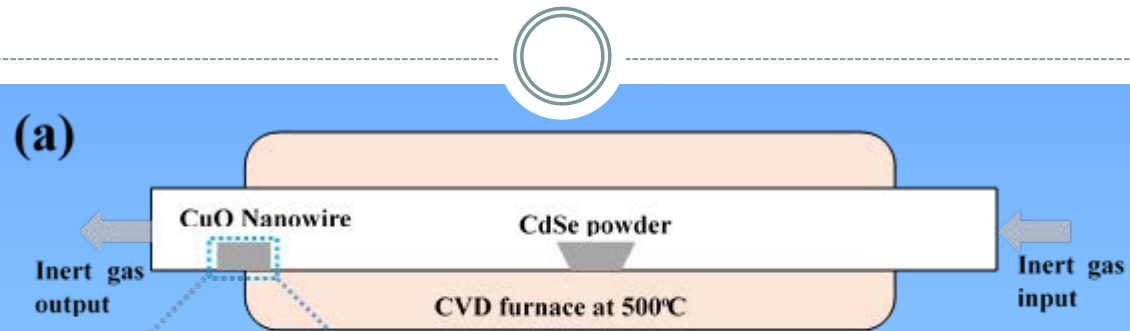
A constant vacuum and the flow of nitrogen were maintained simultaneously during the whole time of experiment.

At first, a rotary van pump is used to maintain vacuum of the order of 0.1mbar inside the chamber. Then the flow of nitrogen gas has been used as the carrier gas, purging from one end in order to carry the CdSe/CdS vapors.

Then the power supply is put on after setting the reaction temperature 400°C with dwelling time 30 minutes at a heating rate of 10°C/minute.

Thereafter the power supply to the CVD is switched off and allowed the furnace to cool down to room temperature automatically. The product material CuO-CdSe/CdS is recovered for various characterizations.

Materials and methods



Characterizations

11

- SEM characterization for morphology.
- Structure by X-ray diffraction
- UV-Vis spectra:
- Raman spectra
- Current–voltage by four probe contact method using a Keithley 2400 source meter under light.
- Photodetection measurement

1. Results and Discussions(CuO/CdSe)

SEM Micrograph of CuO & Schematic of Growth Process

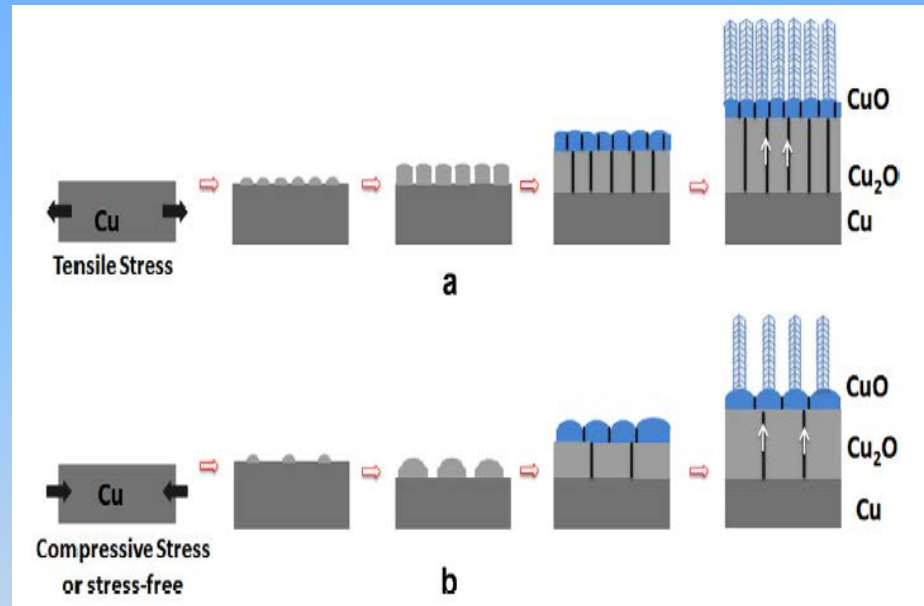
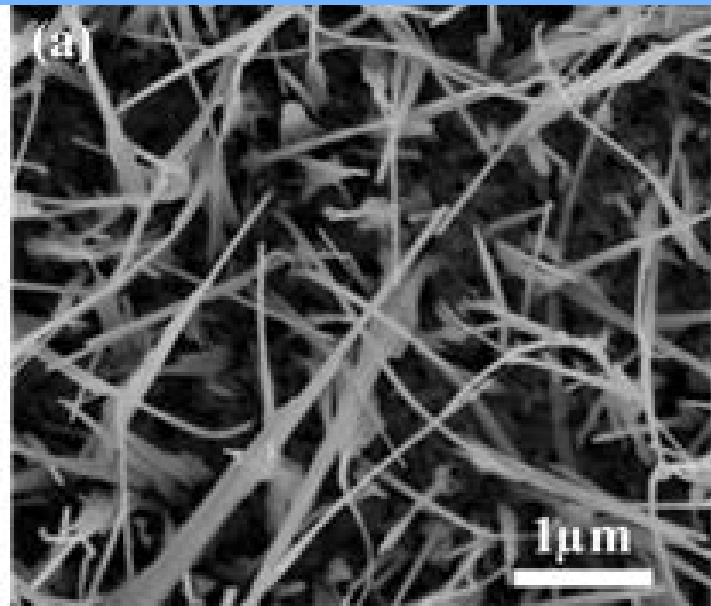


Figure. Semi-Aligned Grown CuO

The results suggest that CuO nanowires are formed as a result of the competition between grain boundary and lattice diffusion of Cu atoms across a Cu₂O layer[1].

[1]Gon, A. M. B.; Campos, L. C.; Ferlauto, A. S.; Lacerda, R. G. On the growth and electrical characterization of CuO nanowires by thermal oxidation. *J. Appl. Phys.* **2009**, *106*, 34303-34307.

SEM Micrograph & XRD

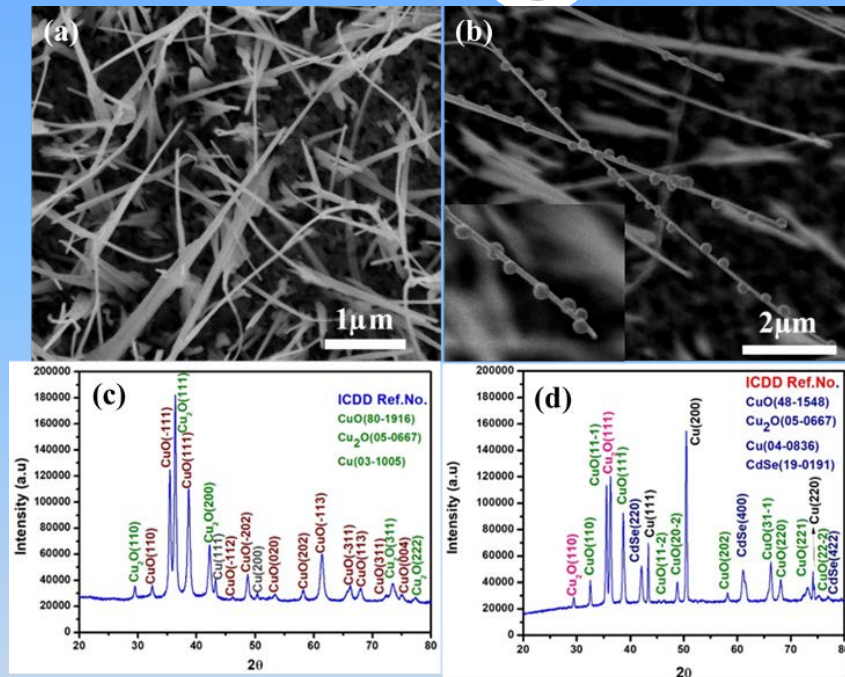


Figure SEM image of (a) CuO NWs grown by thermal oxidation, (b) CuO/CdSe NWs grown by CVD. Inset is the high magnified image of CuO/CdSe NWs. XRD of (c) CuO NWs, (d) CuO/CdSe NWs.

TEM Micrographs of CuO/CdSe Core Shell

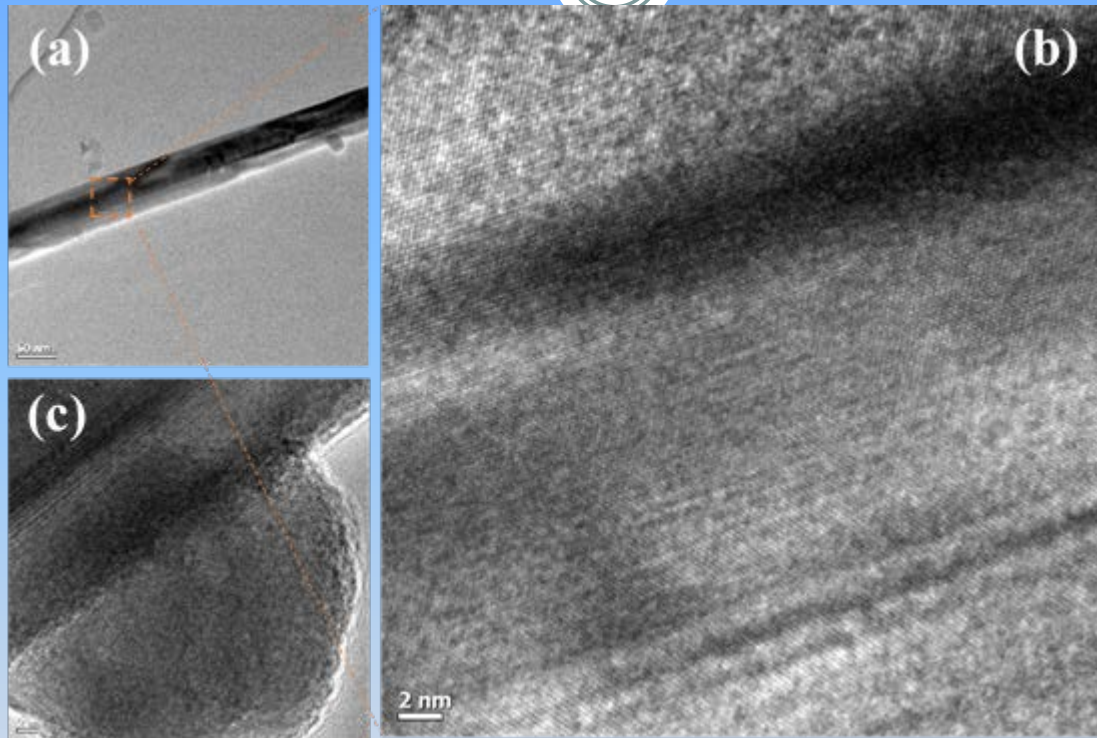


Figure (a) TEM image of CuO/CdSe NWs. (b) HRTEM of CuO/CdSe NWs which is taken at the selected area in orange color. (c) HRTEM Image of the bead structure of CdSe that is attached in NWs.

Raman & UV-Vis Spectra(CuO/CdSe)

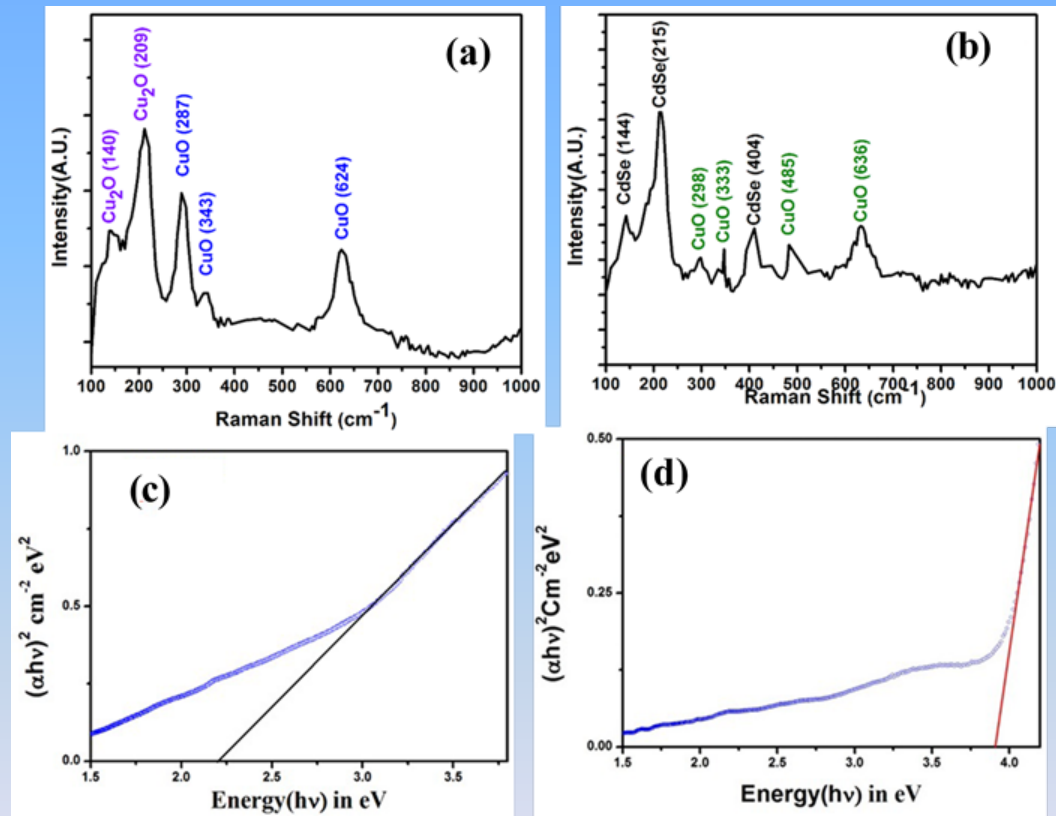


Figure. Raman spectra of (a) CuO NWs, (b) CuO/CdSe NWs. UV-Vis Spectra of (c) CuO NWs, (d) CuO/CdSe NWs.

Photocurrent

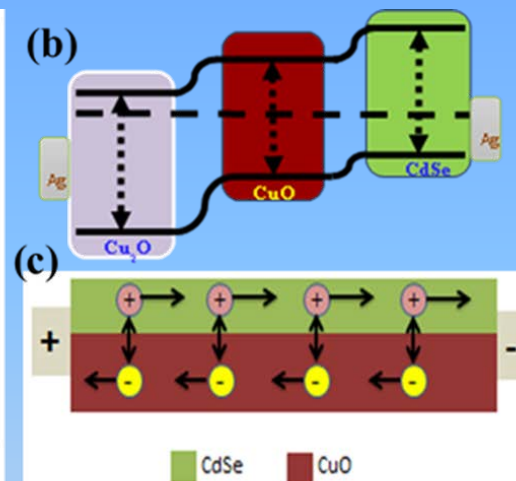
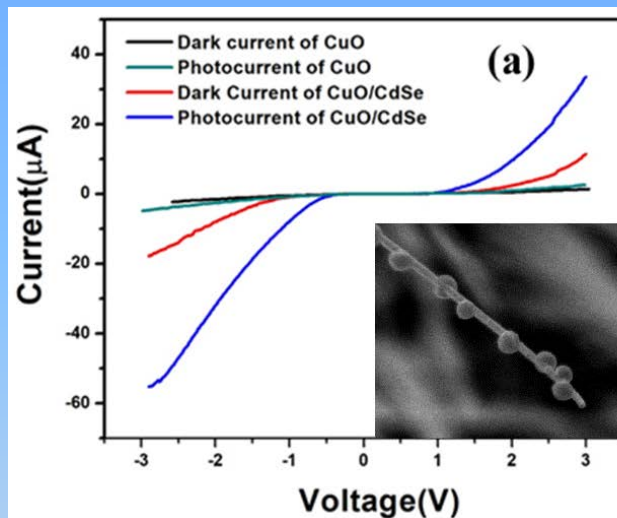
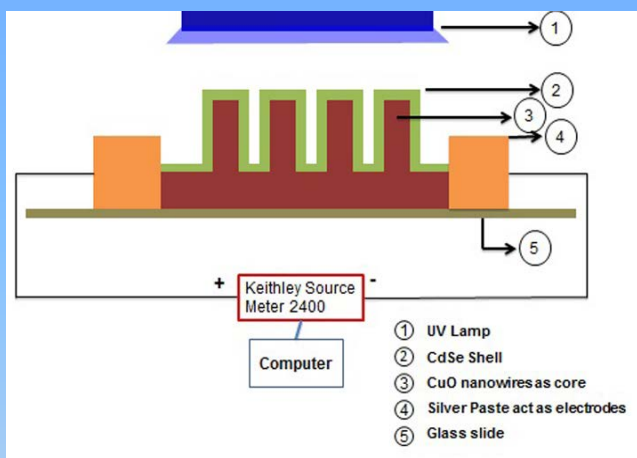


Figure 5. (a) Dark (Black) and Photocurrent (Green) of CuO NWs. Dark (Red) and Photocurrent (Blue) of CuO/CdSe NWs. (b) Type-II band alignment of CdSe, CuO and Cu₂O. (c) Electron hole pair separation and charge transfer in CuO/CdSe NWs.

Responsivity & External quantum efficiency



The fabricated CuO/CdSe core-shell heterostructure NWs as photodetector device showed responsivity 0.63A/W with external quantum efficiency approximately 3.14×10^2 % under illumination of wavelength 254 nm. The strong response of CuO/CdSe NWs photodetector is explained by the Type-II band alignment which cause the separation of photo generated electron–hole pairs and their charge transfer at the junction.

$$R_{\lambda} = \frac{I_{light} - I_{dark}}{P_{ill}} \quad P_{in} = I_{in} \cdot A$$

I_{light} and I_{dark} is the current under illumination of light and in dark, respectively. I_{ill} is the illumination intensity (1.32mW/cm^2) and A is the active area (0.04cm^2).

Moreover, the responsivity is related to The external quantum efficiency was calculated from the equation given below.

$$\eta_{ext} = \frac{R_{\lambda} hc}{\lambda q \Gamma_G}$$

Where η_{ext} is the external quantum efficiency (EQE), q is the electronic charge, h is Planck's constant, ν is the frequency of the light, Γ_G is the internal gain(internal gain has been taken 1).

2.Results & Discussions(CuO/CdS)

SEM Micrographs and XRD

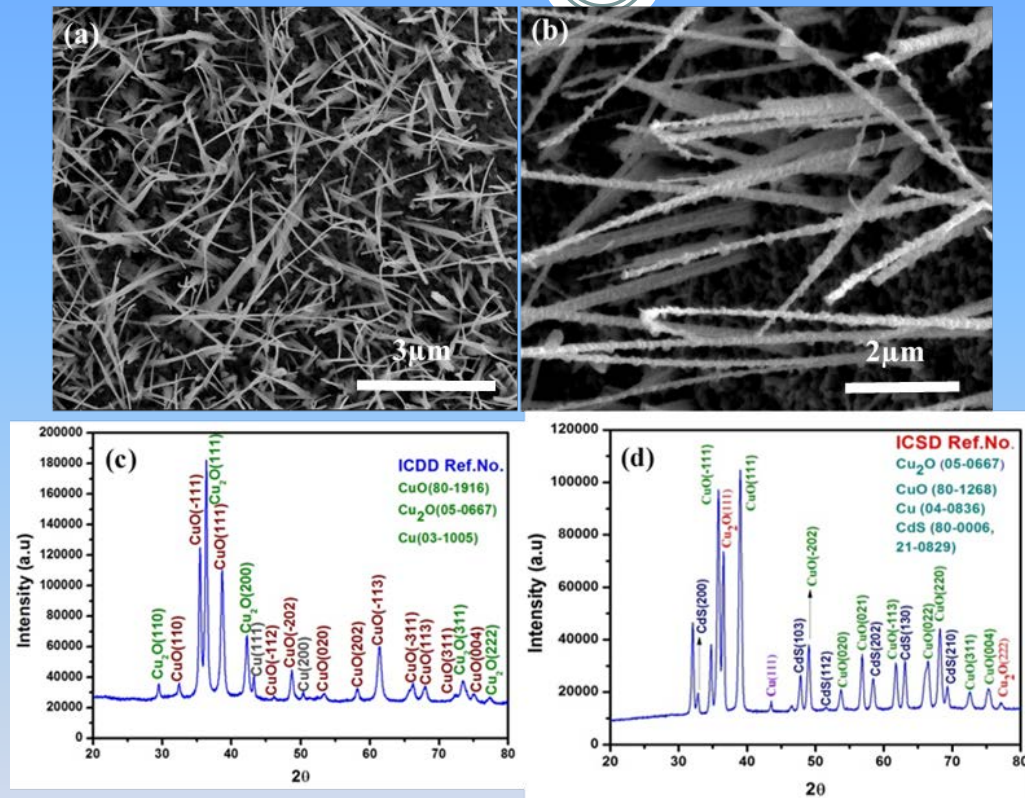


Figure 2. FESEM image of (a) CuO nanowires, (b) CuO/CdS core-shell nanowires. X-ray diffraction of (c) CuO nanowires, (d) CuO/CdS core-shell nanowires.

TEM Micrographs and Raman

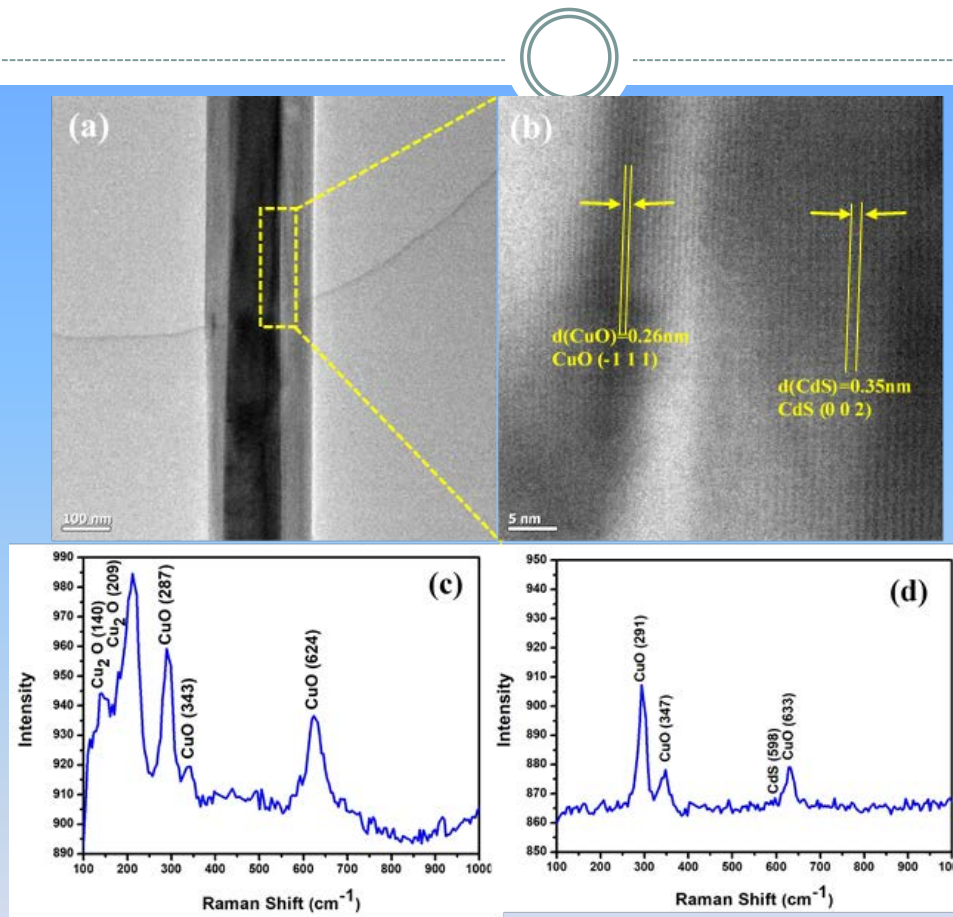


Figure TEM image of CuO nanowire, (b) HRTEM image of CuO/CdS core/shell nanowires, Raman spectra of (a)CuO nanowire, (d) CuO/CdS core/shell nanowires.

UV-Vis Spectra

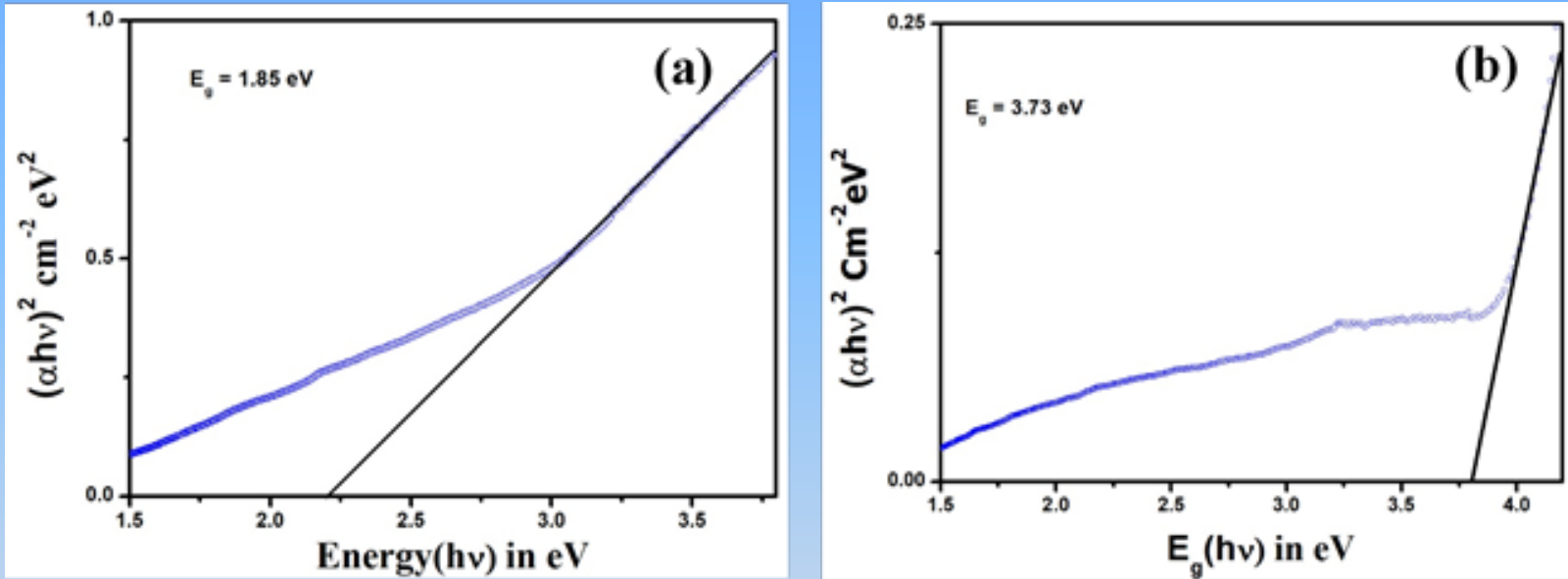
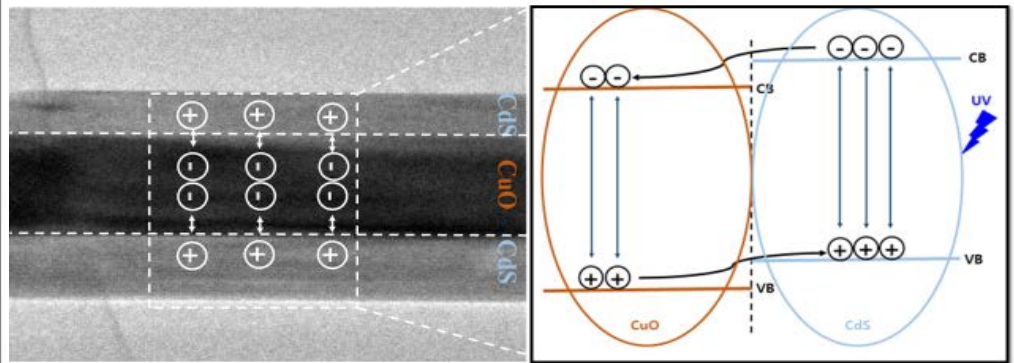
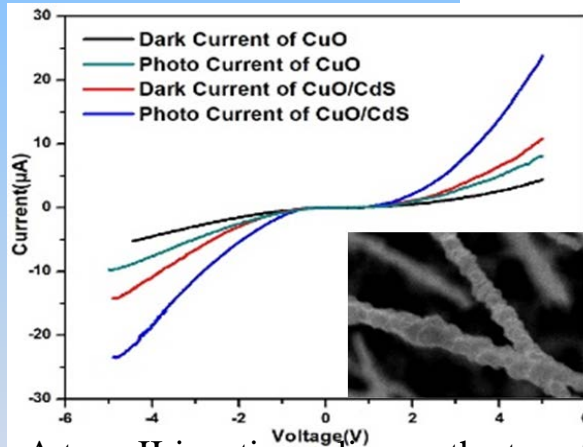
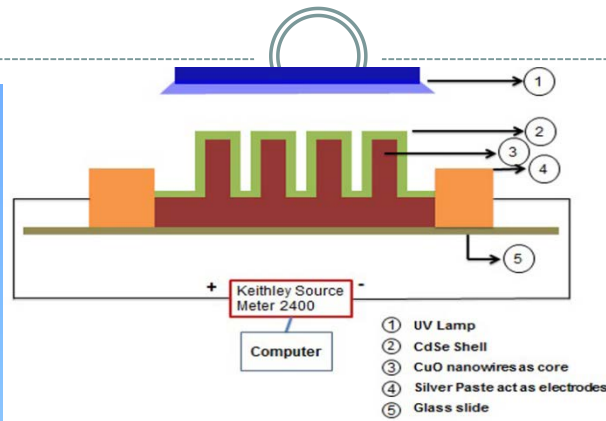


Figure UV-VIS spectra of (a) CuO nanowires, (b) CuO/CdS core/shell nanowires

Photocurrent Measurement



A type II junction relies on the transfer of photo excited electrons and holes from B to A due to more negative CB position of B. Holes can travel in the opposite direction from the more positive VB of A, leading to all-round efficient charge separation and enhanced photoconductivity.

The presence Cu_2O (a p-type Mott insulator) at the root of CuO does not affect electron transfer from p-type CuO to n-type CdS NWs on excitation with light.

Conclusion



- Synthesized CuO nanowires, CuO/CdSe and CuO/CdS heterostructures nanowires.
- Characterized materials show confirmed structural properties.
- Photocurrent reveals that the prepared core-shell heterostructure nanowires could be used efficiently for photodetection.



Thank you