SYNTHESIS, BAND GAP ENGINEERING AND PHOTOVOLTAIC APPLICATIONS OF MULTINARY SEMICONDUCTOR NANOWIRE/NANOCABLE ARRAYS

XU JUN

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XU Jun
許俊

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Abstract

Band gap engineering provides semiconductors with tunable and controllable properties for their applications in optoelectronic and photovoltaic devices. The present work systematically investigates controllable synthesis of one dimensional (1D) multinary nanostructures through simple chemical methods, their band gap engineering *via* composition variation and their photovoltaic performances. New materials and device structures are explored to achieve efficient photovoltaic performance. Physical processes involved in the nanoscaled synthesis, including phase transformation, ions exchange, Kirkendall effect, and Ostwald ripening, and their implication to morphologies and properties of the nanomaterials have been studied.

Bundles of homogeneously alloyed $Cu_{2-x}(S_ySe_{1-y})$ nanowires with lengths of several hundreds of micrometers and diameters of 200−500 nm have been controllably prepared over the whole composition range of y ($0 \leq y \leq 1$) *via* a simple water-evaporation method. The nanowire bundles have similar copper contents ($0.37 \leq x \leq 0.44$), morphologies, and the same face centered cubic (fcc) crystal structure and growth orientation of [110] over the entire composition range of y. This is the first report on fcc ternary $Cu_{2-x}(S_ySe_{1-y})$ phase. The lattice parameter of the fcc $Cu_{2-x}(S_ySe_{1-y})$ compounds changes linearly with the S content, which is consistent with that described by the Vegard's Law. Both the direct and the indirect band gaps of the nanowire bundles are found to have quadratic relationships with the S content. (Publication: *Adv. Funct. Mater.* **2010**, *20*, 4190–4195)

Using the fcc $Cu_{2-x}Se$ nanowire bundles as sacrificial template, bundles of hexagonal CuSe and tetragonal $CuInSe_2$ nanowires as well as bundles of $CuInSe_2/CuInS_2$ core/shell nanocables are prepared by simple chemical approaches and demonstrated as a novel means for synthesis of I-III-VI chalcopyrite photovoltaic

materials. Mechanisms for the chemical conversions and phase transformations are investigated in detail. Formation of $CuInSe_2/CuInS_2$ core/shell nanocables with increasing shell thickness shifts x-ray diffraction (XRD) peaks of the $CuInSe_2$ cores to higher 2θ degrees, and also enhances the optical absorption properties over the visible-near infrared region, which is obviously beneficial for their photovoltaic applications. (Publication: *ACS Nano* **2010**, *4*, 1845–1850)

Highly-ordered arrays of Cu-rich and Cu-deficient $CuInSe_2$ nanotubes as well as $ZnO/CuInSe_2$ core/shell nanocables have been synthesized on transparent glass substrates *via* a simple ions-exchange route using ZnO nanorod arrays as sacrificial templates. Chemical conversions and phase transformations from hexagonal ZnO to cubic ZnSe, hexagonal CuSe and tetragonal $CuInSe_2$ are demonstrated. Large differences in their solubility product constants (K_{sp}) are crucial for direct ions-exchange in the conversions. The absorption coefficient of the $CuInSe_2$ nanotubes in visible region is on the order of 10^4 cm^{-1}. Arrays of ZnO based nanocables can serve as promising photoelectrodes for photoelectrochemical (PEC) solar cells. Power conversion efficiency of the $ZnO/Cu_{1.57\pm0.10}In_{0.68\pm0.10}Se_2$ cell is about double that of the ZnO/CuSe cell. (Publication: *ACS Nano* **2010**, *4*, 6064–6070)

Arrays of $ZnO/Zn_xCd_{1-x}Se$ ($0 \leq x \leq 1$) core/shell nanocables with composition-tunable shells have been synthesized *via* a simple ions-exchange route using ZnO nanowires as sacrificial templates. Through the effects of stoichiometry, and the type-II heterojunction, optical absorptions of the nanocable arrays can be controllably tuned to cover almost the entire visible spectrum. The lattice parameter and the band gap of the ternary $Zn_xCd_{1-x}Se$ shells show respectively linear and quadratic relationships with the Zn content (x). While the 1D ZnO/TiO_2 nanoarray based quantum dot sensitized solar cells (QDSSCs) have a typical efficiency below 4%, these $ZnO/Zn_xCd_{1-x}Se$ nanocables arrays are demonstrated to be promising photoelectrodes for PEC solar cells, giving a

maximum power conversion efficiency up to 4.74% and external quantum efficiencies (EQE) as high as 82%. (Publication: *Nano Lett.* **2011**, *11*, 4138–4143)

A novel architecture with dual hollow structures has been demonstrated by synthesis of highly-ordered array of Cu_2O nanotubes constructed from hollow nanospheres with diameters of 165−185 nm and shell thicknesses of 20−40 nm. Formation mechanisms are carefully investigated, revealing that formation of Cu_2O nanotubes is the results of the “Kirkendall effect”; while evolution of the Cu_2O hollow nanospheres in the walls is resulted from the “Ostwald ripening” process. Furthermore, the Kirkendall effect involved in the nanoscaled synthesis has been directly proved by introducing a $Cu_{2-x}Se$ interlayer with thickness about 5−10 nm into the hierarchical Cu_2O nanotubes, resulting in formation of arrays of $Cu_2O/Cu_{2-x}Se$ heterogeneous nanotubes, in which Cu_2O hollow semi-nanospheres are covered on both the inner and the outer surfaces of $Cu_{2-x}Se$ shells. From the microstructures, the diffusion rate of copper ions through the $Cu_{2-x}Se$ shells is estimated to be double that of ascorbic acid molecules. (Publication: *Cryst. Growth Des.* **2009**, *9*, 4524–4528)

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List of Symbols and Abbreviations

1D	One Dimensional
CIS	Copper-Indium- Selenide, $CuInSe_2$
CIGS	Copper-Indium-Gallium-Selenide, $Cu(In_xGa_{1-x})Se_2$
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
EELS	Electron Energy Loss Spectroscopy
SAED	Selected Area Electron Diffraction
EDS	Energy Dispersive X-Ray Spectroscopy
FFT	Fast Fourier Transform
UV	Ultraviolet (light in the range of 200–400 nm)
Vis	Visible (light in the range of 400–700 nm)
K	Formation Constant
K_{sp}	Solubility Product Constant
TEG	Triethylene Glycol
PV	Photovoltaic
PEC	Photoelectrochemical
QDSSCs	Quantum Dot Sensitized Solar Cells
J-V	Current Density-Voltage
J_{SC}	Short-Circuit Current Density
V_{OC}	Open-Circuit Voltage
FF	Fill Factor
η	Power Conversion Efficiency
EQE	External Quantum Efficiency

IPCE	Incident Photon to Charge Carrier Efficiency
AM1.5G	Air Mass 1.5 Global
E_g	Band Gap Energy
E_f	Fermi Level Energy
VB	Valence Band
CB	Conduction Band
a	Absorption Coefficient
h	Planck's Constant
λ	Wavelength of Light
q	Charge on Electron