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Synthesis and Applications of Heteronanostructured ZnO Nanowires Array

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***Abstract*—**ZnO heteronanostructured nanowires arrays have been fabricated by low temperature solution method. Various heterostructures were synthesized including CdS/ZnO, CdSe/CdS/ZnO nanowires and Co3O4/ZnO, ZnO/SiC nanowires. These multifunctional heterostructure nanowires showed important applications in photocatalysts, sensors, wettability control and solar energy conversion.

***Keywords*—** ZnO nanowires, Heterostructure nanowires, solar energy conversion, photocatalsis.

I. Introduction

The assembly of one dimensional (1D) nanostructures is attracting much attention these days in the fabrication of various nanodevices including nanoelectronic, nanophotonic, sensor, photocatalytic, and energy devices. In particular, wide-bandgap metal-oxide nanowires and heteronanostructures are very useful for the realization of multifunctional nanodevices due to their unique material properties.

In this work, we present synthesis of various heterostructured ZnO nanowires arrays using low temperature solution reactions. Also we have studied the applications of synthesized nanowires in various areas including wettability control, photocatalysts, and solar energy conversion.

II. Experimental

A. Synthesis of ZnO NWs

An ammonia solution reaction was used to synthesize ZnO NWs in wafer-scale. The growth temperature was as low as 60 degree Celcius. Zincnitrate and thiourea was used as source materials to grow ZnO NWs in ammonia water solution. The grown nanowires showed vertically aligned single crystalline ZnO nanowires arrays.

B. Synthesis of heterostructured ZnO NWs arrays

A various heterostructured ZnO nanowires such as CdS/ZnO, CdSe/ZnO, CdSe/CdS/ZnO nanowires were synthesized using two step, low temperature solution reaction. For example CdS coating layer was uniformly deposited on ZnO NWs using SILAR(successive ion layer adsorption reaction) methods, This SILAR method is layer by layer growth of CdS through self-limiting adsorption of Cd and S ions.

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The CdS layer thickness could be controlled by changing the cycle numbers of the SILAR process. This method is very similar with ALD (atomic layer deposition) in semiconductor processing.On the other hand, CdSe nanoparticles were uniformly deposited on ZnO NWs using CBD (chemical bath deposition) method. The nanoparticle size was controlled by reaction parameters such as reaction temperature and concentrations. Typically the reaction temperature was as low as 60 degree Celcius.

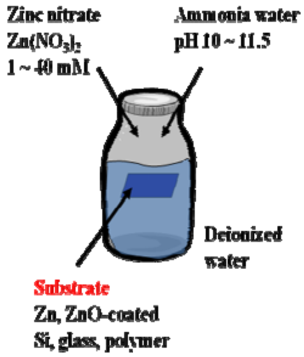


Fig. 1 Experimental setup for ZnO nanowire growth using low temperature ammonia water solution reaction

TABLE I
EXPERIMENTAL REACTION CONDITIONS FOR ZNO NWS GROWTH

Parameters	Conditions
Growth temperature	60 ~ 90 °C
Growth time	6 hr
Zinc salt concentration	1 ~ 40 mM
pH	10 ~ 11.5

C. Characterization

The synthesized nanowires were characterized using SEM (scanning tunneling microscopy) for their morphologies. The crystallinity of NWs was studied using XRD (x-ray diffraction) and the atomic structure was investigated using TEM (transmission electron microscopy).

The wettability of the NW surface was tested through water droplet contact angle (CAs) measurements. To convert the surface energy of NWs surface, SAM (self assembled monolayer) of hydrocarbons was coated on NWs surface. Various SAM molecules such as stearic acid or OTS has been applied.

QDSSC (quantum dot sensitized solar cell) was fabricated using NWs as photoanodes and quantum dots as light sensitizers and noble metals as counter electrodes. A simple two electrode system was fabricated for cell tests. As electrolyte material Na2S and S solution in methanol/diionized water solution.

The cell performance was measured using current density-voltage (I-V) measurements and IPCE (incident photon conversion efficiency).

The optical properties of photoanodes were evaluated using UV-vis absorption spectra.

III. Results and Discussion

In this paper we report a low temperature facile solution reaction method for the fabrication of ZnO nanowires array. Our method realizes a wafer scale vertically aligned nanowires growth with single crystallinity. Also we present various heterostructures of ZnO nanowires such as Co3O4/ZnO, CdS/ZnO and CdSe/CdS/ZnO nanowires. Simple two-step solution methods were used to synthesize these ZnO nanowire heterostructures.

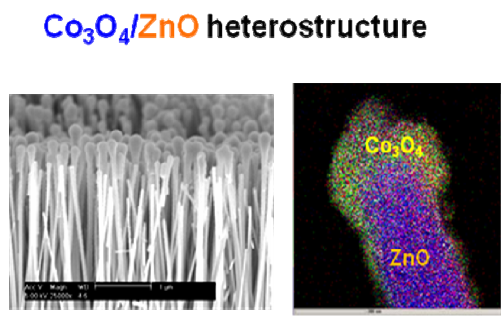


Fig. 2 Co3O4/ZnO heterostructured nanowires [ref. 5]

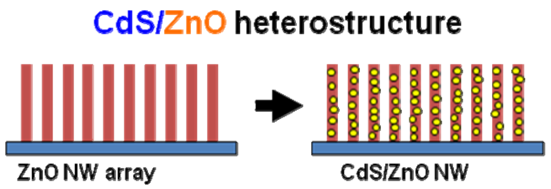


Fig. 3 CdS/ZnO heterostructured nanowires [ref. 1]

The applications of these heteronanostructured ZnO nanowires were studied in various applications including nanosensor, photocatalyst, wettability control of surface, and solar energy conversion device (solar cell). UV sensor was fabricated using a simple deposition of metal electrode on ZnO nanowires, which show a high sensitivity and fast response time. Also chemical modification of nanowires exhibited conversion of surface wettability from hydrophilicity to super-hydrophobicity through chemical modification of NWs. A photocatalytic propertie of the heteronanostructures was investigated using UV/visible light decomposition of organic dyes and the results were compared with bare ZnO nanowire sample.

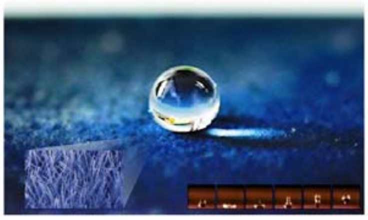
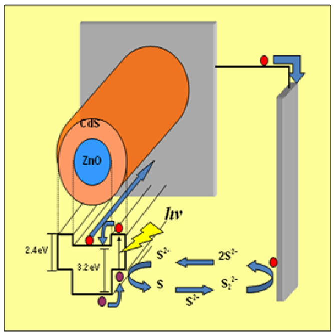
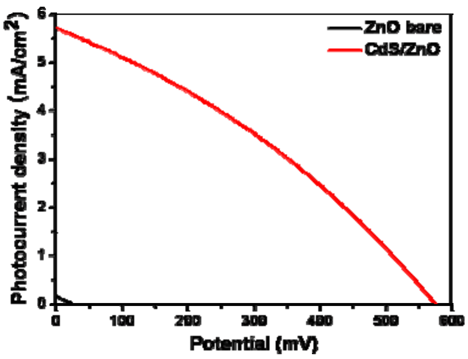


Fig. 4 Superhydrophobic surface fabricated by ZnO NWs with chemical modification [ref. 6]

Solar energy conversion devices were also fabricated using ZnO nanowire heterostructures as photoanodes and our results showed high solar energy conversion efficiency for quantum dot sensitized solar cell (QDSSC) using ZnO heteronanowires.



(a)



(b)

Fig. 4. (a) A schematic diagram of QDSSC using CdS/ZnO NWs as photoanode, (b) I-V results from QDSSC. [ref. 7]

IV. Conclusion

In this paper we present a facile solution based synthetic route for the fabrication of ZnO nanowire arrays and various heterostructures of ZnO nanowires such as CdS/ZnO, Co_3O_4/ZnO and SiC/ZnO nanowires. Simple two-step solution methods were applied to synthesize these ZnO nanowire heterostructures. Synthesized heteronanostructures were characterized using SEM, TEM, XRD and XPS. Basic growth mechanism was investigated for heteronanostructures.

Also, the applications of these novel heteronanostructures were studied. Photocatalytic properties of the heteronanostructures were studied using UV/visible light decomposition of organic dyes and the results were compared with bare ZnO nanowire sample. Heteronanostructures have showed much enhanced photocatalytic efficiencies and the mechanism will be discussed. Also, solar energy conversion devices were fabricated using ZnO nanowire heterostructures as photoanodes and discussion regarding this nanodevice will be presented.

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