

ZnO-TiO₂ Core-Shell Nanowires for **Dye-Sensitized Solar Cells**

By

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Certificate

This is to certify that **Ms Bojja Jyothsna**, an undergraduate student of the Department of Chemical Engineering, NIT Warangal, has successfully completed her summer internship project titled " **ZnO-TiO₂ Core-Shell Nanowires for Dye- Sensitized Solar Cells** " during the Outreach Programme organized by the Indian Institute of Science, Bangalore, in the Department of Chemical Engineering during May-June 2012 under my supervision.

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List of Contents

	<u>Page Numbers</u>
A. List of Figures	6
B. Abstract	7
1.Introduction	8
2. Literature Review	10
2.1 Working principle and structure of dye-sensitized solar cells	10
2.2 Dye sensitizer	12
2.3. Electrolyte	12
2.4. Conducting substrates	12
2.5. Nanocrystalline semiconductor oxide film electrode	12
2.6. Nanowire	13
2.7 ZnO Nanowires	13
2.8 Fabrication techniques of ZnO nanowire arrays	13
2.9 Deposition of TiO ₂ films	14
3. Experimental Section	15
3.1 Chemicals Used	15
3.2 Growth of ZnO nanowires on silicon substrate	15

3.2.1 Equal concentrations of Zinc nitrate and Hexamine	15
3.2.2 Increasing the molar ratio of Hexamine to Zinc nitrate	15
3.3 Growth on Au-coated silicon substrate	16
3.4 Effect of applying voltage	16
3.5 Preparing TiO ₂ sol by sol-gel process	16
3.6 Deposition of TiO ₂ sol	16
4. Results and discussion	17
4.1 The ZnO nanowire morphology in different growth solutions on Silicon substrate	17
4.2 Effect of applying voltage on growth	20
4.3 TiO ₂ coated ZnO nanowires	21
5. Conclusion : Work ahead	23
6. References	24

A. List of figures

Fig.1 Schematic representation of Dye-Sensitized Solar Cell (A), energy levels representation and the corresponding reactions (B)

Fig. 2 Schematic representation of a nanowire-based dye sensitized solar cell

Fig. 3 SEM images of randomly grown ZnO nanowires grown with 0.05M Zinc nitrate and 0.05M Hexamine precursor solutions at 75°C for 2 hours on silicon substrate

Fig. 4 SEM images showing dense array of ZnO nanowires grown with 14.3 mM Zinc nitrate and 26 mM Hexamine precursor solutions at 75°C for 2 hours on silicon substrate

Fig. 5 SEM images of ZnO nanowire bundles grown with 0.05M Zinc nitrate and 0.05M Hexamine precursor solutions at 75°C for 2 hours on Au-coated silicon substrate

Fig. 6 SEM images of ZnO nanowires grown with 0.05M Zinc nitrate and 0.05M Hexamine precursor solutions at 75°C for 2 hours with applied negative voltage of 2V on Au-coated silicon substrate

Fig. 7 SEM images (A) TiO₂ Sol on silicon substrate (B) Silicon substrates of TiO₂ dip-coated ZnO nanowire arrays for a period of 2mins and annealed at 550 °C for 1 hr

Fig. 8 SEM images of silicon substrates of TiO₂ dip-coated ZnO nanowire arrays for a period of 2mins, dipped in 3% HCl for 3 secs and annealed at 550 °C for 1 hr

Fig. 9 SEM images of silicon substrates of TiO₂ dip-coated ZnO nanowire arrays for a period of 5 mins and annealed at 550 °C for 1 hr

B. Abstract

Dye-sensitized solar cells (DSCs) have significant potential as a low cost alternative to conventional photovoltaic(PV) devices. These DSCs are typically constructed from thin films of TiO_2 or ZnO nanoparticles that are sintered into a mesoporous network with a large internal surface area for the adsorption of light-harvesting dye molecules[1]. The performance of those nanoparticle-based DSCs is greatly limited by their trap-limited diffusion process. Replacing the nanoparticle film with a dense array of ZnO nanowires offer larger surface area than bulk film material, direct electron pathways from the point of injection to the collection electrode, reduced reflection, effective light-scattering centers and improved band gap tuning. Furthermore, nanowires may be synthesized at low temperatures, without sintering, to enable fabrication of inexpensive solar-to-electric conversion systems on flexible substrates. These nanowire arrays when combined with TiO_2 , produce a core-shell structure that reduces the combination rate.

This project is focused on synthesis of ZnO nanowires arrays on silicon substrates and Au-coated silicon substrates by hydrothermal growth process with and without application of voltage under varying concentration of growth solution, following which the arrays are dip coated by thin shells of TiO_2 sol prepared by sol-gel process to obtain ZnO- TiO_2 core shell structure. The morphologies of the ZnO nanowire arrays and TiO_2 coated ZnO nanowire arrays were investigated using Scanning Electron Microscope (SEM).

Finally, detailed results of all attempts along with their implications are reported. The further work that is crucial to the development and application of nanowire-based dye sensitized solar cells is discussed in the concluding section.

1.Introduction

Solar energy conversion is a highly attractive process for clear and renewable power. The supply of energy from the sun to the earth is estimated to be 3×10^{24} J/year, which is 10^4 times more than what mankind consumes currently [1]. In other words, covering only 0.1% of the earth's surface with a conversion efficiency of 10% would be enough to satisfy our current needs [1]. Solar cells convert solar energy into electricity. They have undergone three generations with an evolution from the initial single silicon solar cells [2] to the second generation solar cells based on semiconductor thin films [3,4] and, now, the third generation solar cells represented by dye-sensitized solar cells (DSCs) and organic semiconductor solar cells [5–8]. Compared with the first and second generation solar cells based on conventional semiconductor materials with conversion efficiencies of 20–30%, currently the third generation solar cells still demonstrate efficiencies relatively low [9,10].

Dye-sensitized solar cell (DSC) is a new type of low-cost photovoltaic cell, which belongs to the group of thin-film solar cells. It was manufactured by Michael Grätzel in 1991 and named Grätzel cells [11]. DSC is a type of photochemical cell that consist of an electrolyte sandwiched between a cathode and transparent anode. This cell is highly realizable because it is made of low-cost materials and does not need elaborate apparatus to manufacture. In massive production, it is obviously less expensive than traditional solid-state cell. It can be engineered into flexible sheets and resists to mechanical stress. In addition, it can be fabricated to flexible sheet with high transparency for variety uses in the community. In DSC, the photoelectrons are provided from the sensitizing dye solution (photosensitive ruthenium-polypyridine dye).

DSC is composed of nanocrystalline semiconductor oxide film electrode, photosensitive dye, electrolytes, counter electrode and transparent conducting substrate. There are several kind of semiconductor oxides such as ZnO, Nb₂O₅, SnO₂ and TiO₂ used to manufacturing DSCs, but nanostructured ZnO has attracted extensive interest because of its wide and direct band gap of 3.37 eV at room temperature which gives ability for high temperature and high power operation and large exciton binding energy (60 meV) which gives stability against thermal dissociation of excitons. Electron mobility in ZnO is very high and it has the wide variety of nanostructures with a wide variety of synthesis routes.

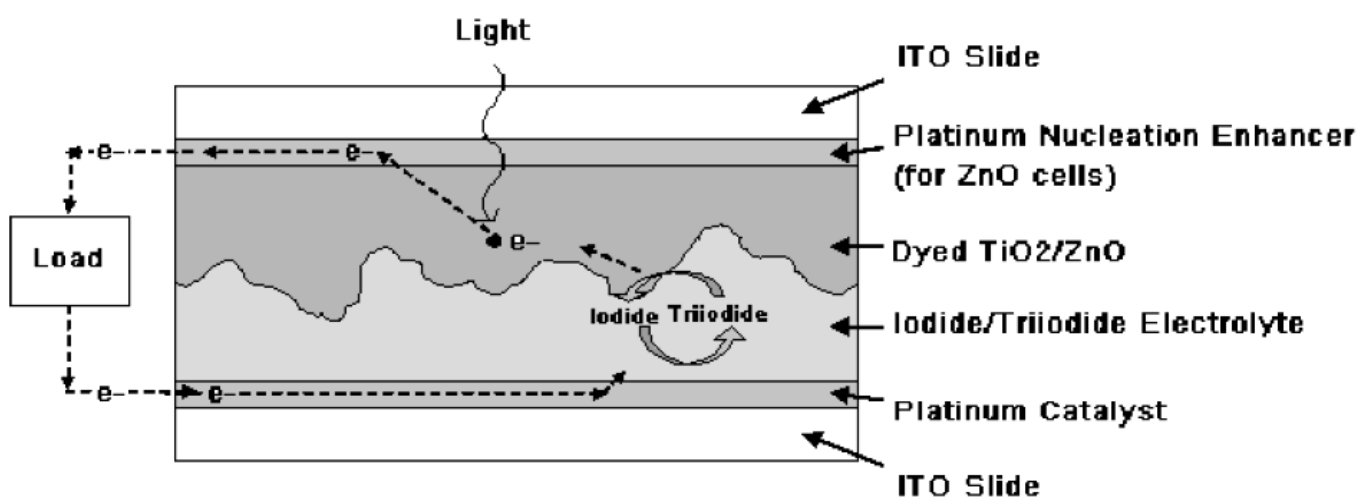
The nanostructured ZnO also has high melting point, excellent chemical stability and non-toxicity. In addition, ZnO is a low cost of material and it can be fabricated in different morphology such as nanowire, nanotube and nanocomb shape. Although DSC is has lower efficiency when compared with traditional semiconductor solar cell, it can still contribute to photovoltaic industry and renewable energy generation. Therefore, it is worth to research and make the improvement in the future. In this project, zinc oxide nanowires were grown on substrates by hydrothermal synthesis, which was the low cost method to fabricate ZnO nanowires layer and the wires obtained are dip-coated with TiO₂ prepared by Sol-gel process. The morphologies of the ZnO nanowire arrays and TiO₂ coated ZnO nanowire arrays were investigated using Scanning Electron Microscope (SEM).

2. Literature Review

2.1. Working principle and structure of dye-sensitized solar cells

The structure of a dye-sensitized solar cell contains two sheets of transparent conductive oxide layer (TCO) coated glass. The working electrode is made by one of the glass plates, which coated with a small dye-sensitized semiconductor particles film. The counter-electrode is made by the other of glass coated with a catalyst. The electrolyte of the cell is sandwiched by two glass plates to form the solar cell [12]. The dye molecules D is used to intake light and the light photons induce dye photo excitation, D^* (Fig.1(1)) and emit an electron to the semiconductor (Fig.1(2)). Afterwards, the injected electron filters through the semiconductor and reach the collector (TCO). Then, the electron goes through the outer circuit to reach the counter-electrode (the other TCO) to perform electrical work (Fig. 1(3)). The electron is then transferred to the electrolyte where it reduces the oxidant species, Ox (Fig. 1(4)); subsequently, the reducing agent formed, Red , reduces the excited dye, D^+ , returning it to the ground state, D (Fig. 1(5)), and completing the circuit [13].

(A)



(B)

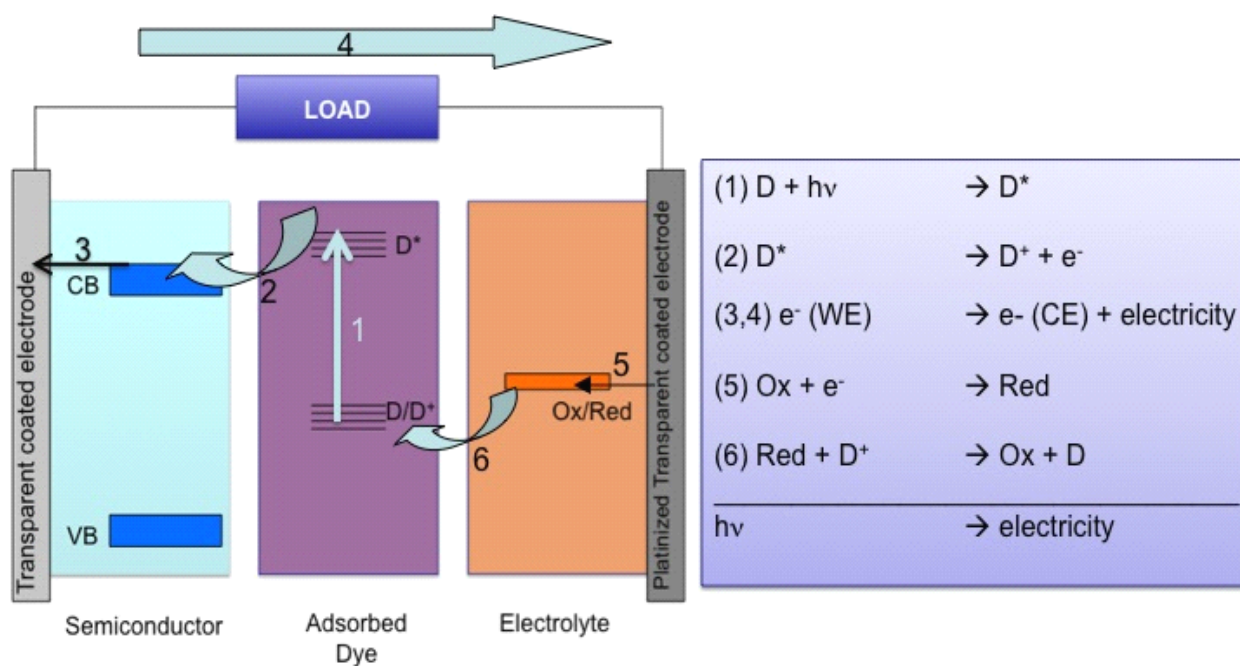


Fig. 1 Schematic representation of Dye-Sensitized Solar Cell (A), energy levels representation and the corresponding reactions (B) [12].

2.2. Dye sensitizer

The dye is the photoreceptor, which sensitizes the semiconductor. The dye should include a broad absorption spectrum, adequate ground and excited energy states, long, no toxicity and good absorption to the semiconductor's surface, etc. [12].

2.3. Electrolyte

The electrolyte is the inner charge carrier for a dye-sensitized solar cell. Tri-iodide/iodide (I_3^-/I^-) redox couple is the traditional standard electrolyte used in dye-sensitized solar cell.

The I_3^-/I^- redox couple can work well due to kinetics. The photo oxidized dye injects an electron into the conduction band of the semiconductor much faster than electron recombination with I_3^- . In addition, the oxidized dye preferably reacts with I^- then recombines with the injected electron [14]. Finally, the two electron process of I^- regeneration from I_3^- occurs swiftly enough at the catalyst-coated CE to be productive. These combined processes lead to coherent I_3^- diffusion towards the counter-electrode and I^- diffusion in the opposite direction towards the TiO_2 electrode [14].

2.4. Conducting substrates

The substrates of DSCs are usually made by transparent conducting oxide coated glass. Good TCO should have high electrical to collect all the generated photocurrent efficiently, and high transparency. The most commonly used is fluorine doped tin dioxide ($SnO_2:F$ or FTO), because FTO's thermal steadiness and low [15]. Indium tin oxide ($In_2O_3:Sn$ or ITO) is also extensively used because it has higher specific conductivity.

2.5. Nanocrystalline semiconductor oxide film electrode

There are several metal oxides used as the semiconductor oxide film electrode in DSCs, such as TiO_2 , ZnO , SnO_2 and Nb_2O_5 . Among these metal oxides, TiO_2 is preferred semiconductor in DSCs, because TiO_2 has a wide band gap energy (3.2 eV, and absorbs light only below 388 nm) making it invisible to most of the solar spectrum, which can lower the recombination rate of photo injected electrons. Also, TiO_2 has high thermal stability, good chemical inertness, no-toxicity and it is relatively cheap [16].

A standard semiconductor layer contains nanostructure mesoscopic morphology to provide large specific surface area for dye absorption. TiO_2 films can be deposited by screen-printing [17]. The TiO_2 film

morphology can influence the electron recombination rate, which can affect the DSCs performance. In addition, the thickness of the TiO_2 films is a key factor to influence the conversion efficiency of DSCs [18].

2.6. Nanowire

Recent research field in morphology is using nanostructures such as nanotubes and nanowires to replace the semiconducting layer in DSC electrodes. Dense nanowires morphology can provide high surface area for dye adsorption and direct conduction paths for the electrons from the point of injection to the collection electrode. In addition, the aspect ratio of nanowire arrays and the length of the nanowires are also studied to increase the length of with small diameter. By increasing the length and aspect ratio of ZnO nanowires, the solar cell conversion efficiency and the short circuit current can be promoted [19].

2.7 ZnO Nanowires

ZnO is a wide-band-gap semiconductor that possesses an energy-band structure and physical properties similar to those of TiO_2 , but has higher electronic mobility that would be favorable for electron transport than TiO_2 ^{20,21}, with reduced recombination loss when used in DSCs. Although the conversion efficiencies of 0.4–5.8% obtained for ZnO are much lower than that of 11% for TiO_2 [22], ZnO is still thought of as a distinguished alternative to TiO_2 due to its ease of crystallization and anisotropic growth. ZnO grows hydrothermally as single nanowire unlike TiO_2 , which is most easily deposited as a layer of sintered nanocrystals. ZnO has the richest variety of nanostructures with a wide variety of synthesis routes.

2.8 Fabrication techniques of ZnO nanowire arrays

Several approaches, including vapor–liquid–solid (VLS) growth [23], chemical vapor deposition (CVD) [24,25], electrochemical deposition (ED) [26] and hydrothermal approaches [27–30], have been developed for fabricating well-aligned 1D ZnO nanostructures. Compared to VLS, CVD and ED methods which require sophisticated equipments and harsh conditions, the hydrothermal route is an avenue for easy and cost-effective fabrication of large scale ordered ZnO nanowire arrays.

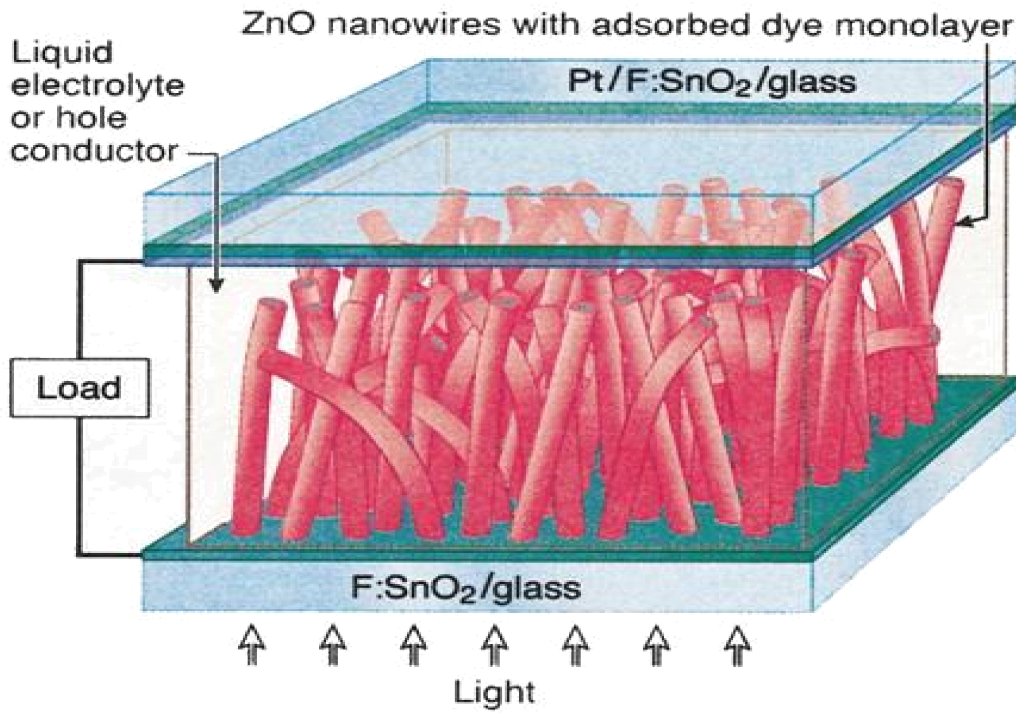


Fig. 2 Schematic representation of a nanowire-based dye sensitized solar cell [26].

2.9 Deposition of TiO₂ films

The deposition of TiO₂ films has been achieved earlier by various researchers by a wide range of methodologies, which include ion beam sputtering, activated reactive evaporation, chemical vapor deposition, sol-gel process etc. The advantages offered by sol-gel process over other conventional film deposition techniques include low process cost, simplicity, easy coating of large surfaces, and plausible porosity in films along with possibility of low temperature processing. Sol-gel derived TiO₂ films are deposited using dip-coating technique and annealed 550 °C temperature from a precursor sol based on titanium isopropoxide and diethanolamine (stabilizing agent) in ethanol. Introduction of ethanol prior to diethanolamine induces immediate precipitation due to highly reactive alkoxide (Titanium Isopropoxide in the present study), therefore diethanolamine, which has been added as a stabilizing agent for hydrolysis.

3.Experimental section

3.1 Chemicals used

1. Zinc Nitrate LR ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) from S d FINE-CHEM LIMITED
2. Hexamine or Hexamethylenetetramine HMT ($(\text{CH}_2)_6\text{N}_4$) from Qualigens Fine Chemicals
3. Ethanol Absolute 99.9% from Commercial Alcohols
4. Titanium tetra IsoPropoxide from Spectrochem Pvt Limited
5. Diethanol Amine from S d FINE-CHEM LIMITED

3.2 Growth of ZnO nanowires on silicon substrate

3.2.1 Equal concentrations of Zinc nitrate and Hexamine

In order to grow the ZnO nanowires, the precursor solutions were prepared by mixing $\text{Zn}(\text{NO}_3)_2$ (0.05 M) with hexamine ($(\text{CH}_2)_6\text{N}_4$), 0.05 M) [31] . Total 80mL solution with ratio 1:1 of zinc nitrate hydrate and HMT were mixed in a glass bottle. Silicon substrate was fixed on slide by adhesive tape and then put into the bottle vertically with the polished side facing towards the glass bottle. The hydrothermal growth was carried out at 75°C with magnetic stirring for 2 hours. The morphology and size distribution of the nanowires were characterized using Scanning Electron Microscopy(SEM).

3.2.2 Increasing the molar ratio of Hexamine to Zinc nitrate

The precursor solutions were prepared by mixing $\text{Zn}(\text{NO}_3)_2$ (14.3 mM) with hexamine ($(\text{CH}_2)_6\text{N}_4$), 26 mM) [32]. Total 80mL solution with ratio 1:1 of zinc nitrate hydrate and HMT were mixed in a glass bottle. Silicon substrate was fixed on slide by adhesive tape and then put into the bottle vertically with the polished side facing towards the glass bottle. The hydrothermal growth was carried out at 75°C with magnetic stirring for 2 hours. The morphology and size distribution of the nanowires were characterized using Scanning Electron Microscopy(SEM).

3.3 Growth on Au-coated silicon substrate

The same experimental procedure narrated in 3.2.1 was followed and instead of silicon substrate, Au-coated silicon substrate is used. The morphology and size distribution of the nanowires were characterized using Scanning Electron Microscopy(SEM).

3.4 Effect of applying voltage

The same experimental procedure narrated in 3.3 was followed with an applied negative voltage of 2V to the Au-coated silicon substrate. The morphology and size distribution of the nanowires were characterized using Scanning Electron Microscopy(SEM).

3.5 Preparing TiO_2 sol by sol-gel process ^[33,34]

Titanium isopropoxide (TIP), diethanolamine and ethanol have been used as the starting materials. The relative volume ratio of each chemical in the sol is $\text{TIP}:\text{DEAH}_2:\text{C}_2\text{H}_5\text{OH}= 3:1:20$. The experimental technique used involves 2 ml of diethanolamine initially being stirred with 10 ml of ethanol followed by addition of 6 ml of TIP. After magnetically stirring the solution for 30 mins, another 30 ml of ethanol has been added and the stirring was continued for 2 hours at room temperature. The obtained solution was hydrolyzed by the addition of a mixture of 0.45 ml deionized water and the stirring was continued for 1 more hour which gives TiO_2 sol.

3.6 Deposition of TiO_2 sol ^[33]

The TiO_2 sol obtained in 3.5 was dip coated on ZnO nanowire templates by dipping one template for 2 mins in the sol and the other was dipped for 5 mins. The deposited films were dried at 100°C for 10 min, and annealed at 550°C for 1 h to obtain ZnO/ TiO_2 core-shell nanowire arrays. The ZnO/ TiO_2 core-shell nanowire arrays were immersed 3% (vol) diluted hydrochloric acid aqueous solution at room temperature for 3–4 s, for removal of ZnO nanowire template[32]. The samples were characterized using scanning electron microscopy (SEM).

4.Results and Discussion

4.1 The ZnO nanowire morphology in different growth solutions on silicon substrate

In Fig. 3, when 0.05M Zinc nitrate and 0.05M Hexamine were used in the growth solution, very less denser ZnO nanowires were deposited randomly resulted on the silicon substrate.

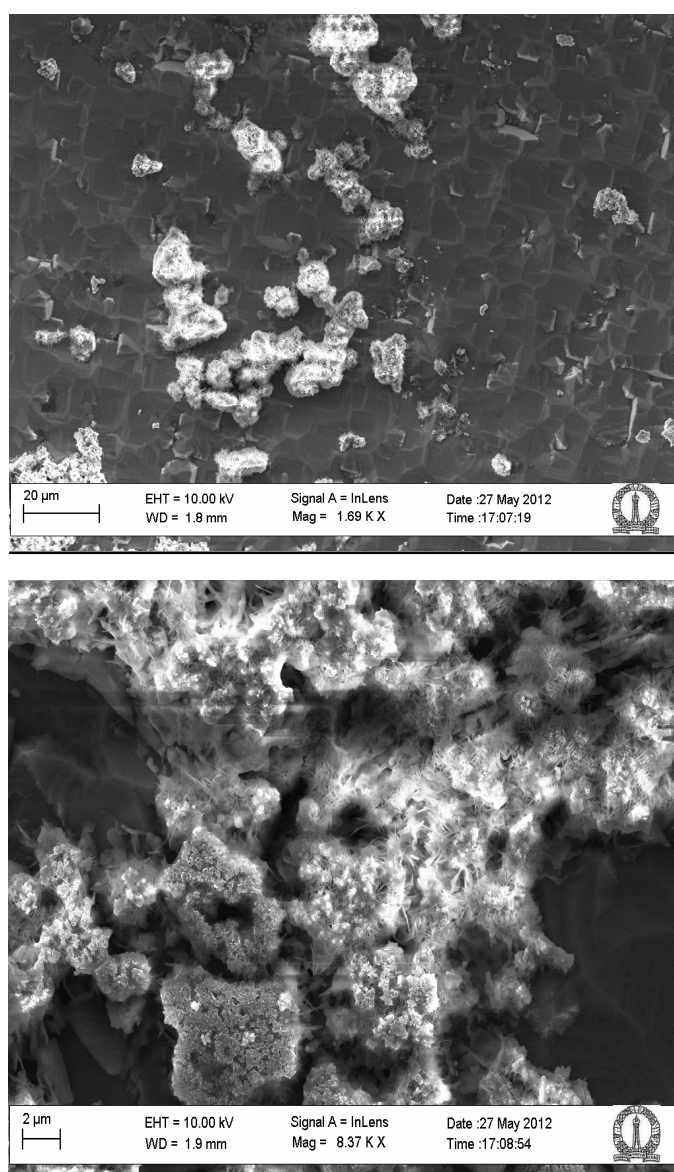


Fig. 3 SEM images of randomly grown ZnO nanowires with 0.05M Zinc nitrate and 0.05M Hexamine precursor solutions at 75°C for 2 hours on silicon substrate.

In Fig. 4, when 14.3 mM Zinc nitrate and 26 mM Hexamine were used in the growth solution, dense arrays of ZnO nanowires with hexagonal surface and a typical diameter of 2 μm are obtained. A relatively low concentration of precursor used here resulted in dense nanowire array indicating that relatively low Zn^{+2} concentration favours the growth of nanowires with smaller diameter. When the nanowires are close-packed, individual nanowires trend to grow vertically to the plane due to guiding effect of neighbour nanowires. The nanowires could not achieve close-packed structure and could not grow perpendicularly to the silicon substrate. Hence, the nanowires were randomly oriented.

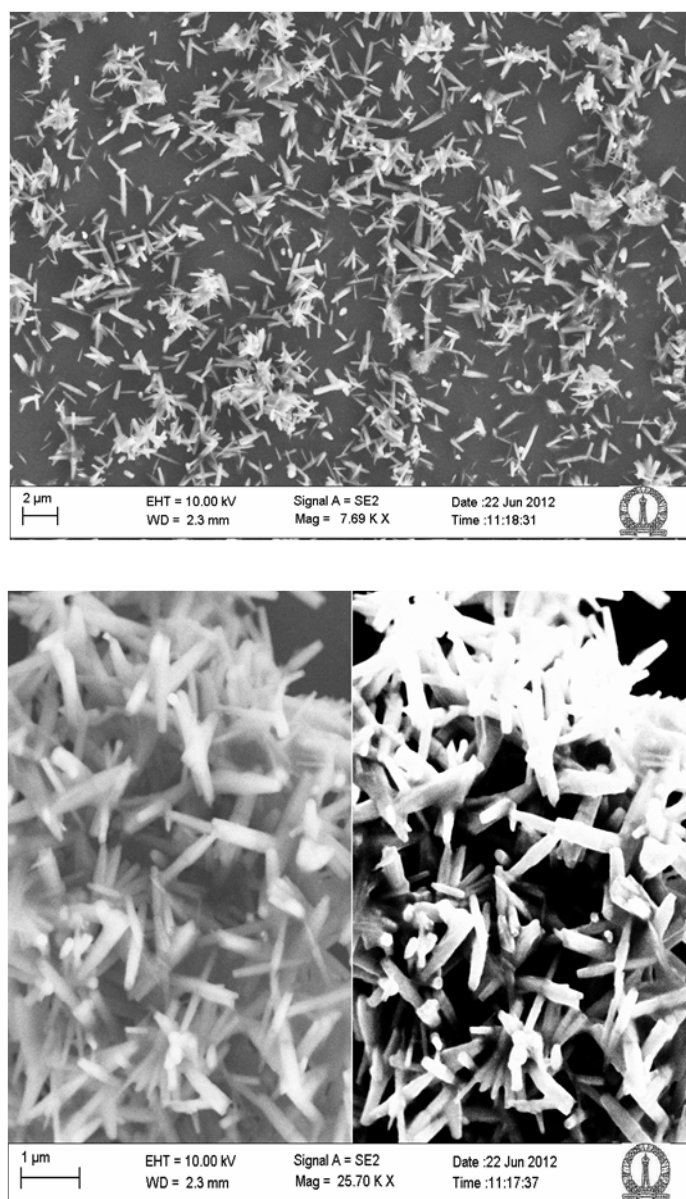


Fig. 4 SEM images showing dense array of ZnO nanowires grown with 14.3 mM Zinc nitrate and 26 mM Hexamine precursor solutions at 75°C for 2 hours on silicon substrate.

In Fig. 5, when 0.05M Zinc nitrate and 0.05M Hexamine were used in the growth solution, bundles of ZnO nanowires were observed in some places on the Au-coated silicon substrate. Growth was non uniform and alignment of wires was random.

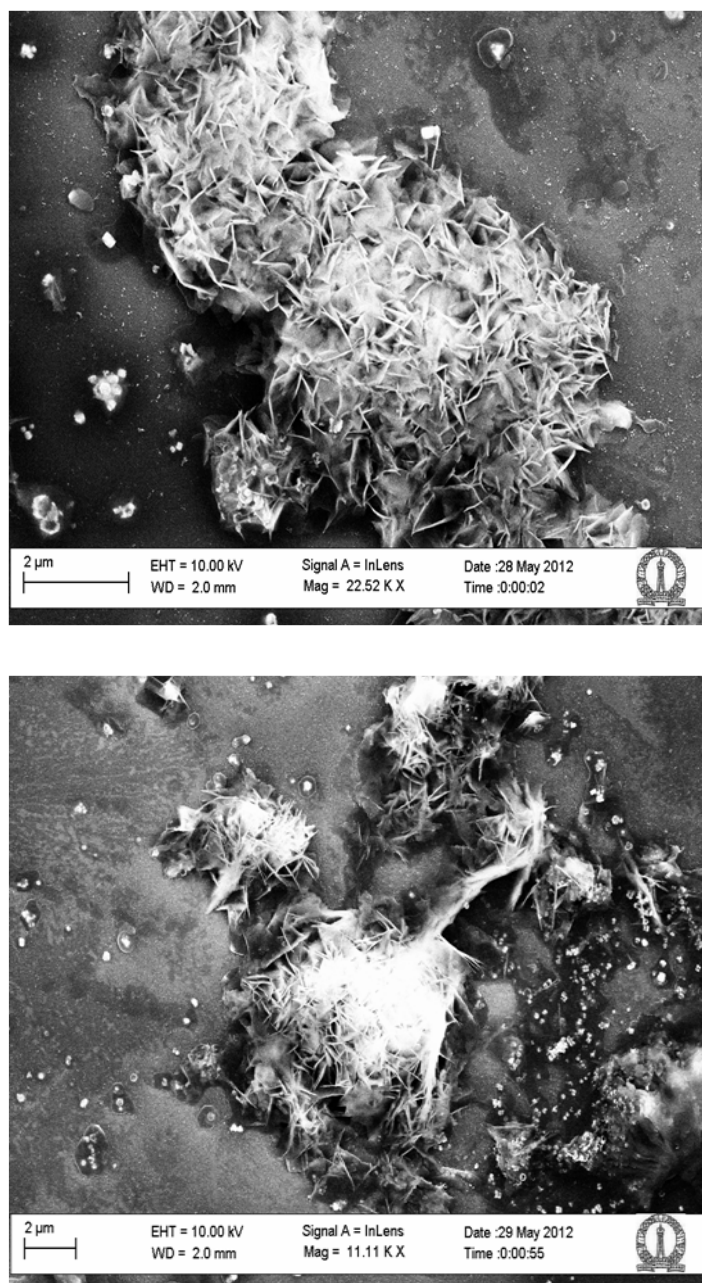


Fig. 5 SEM images of ZnO nanowire bundles grown with 0.05M Zinc nitrate and 0.05M Hexamine precursor solutions at 75°C for 2 hours on Au-coated silicon substrate.

4.2 Effect of applying voltage on growth

In Fig. 6, when a negative voltage of 2V is applied to Au-coated silicon substrate hexagonal nanowires of typical diameter of 200nm were obtained. Application of negative voltage dramatically increased the nucleation density and dense arrays of nanowires were obtained.

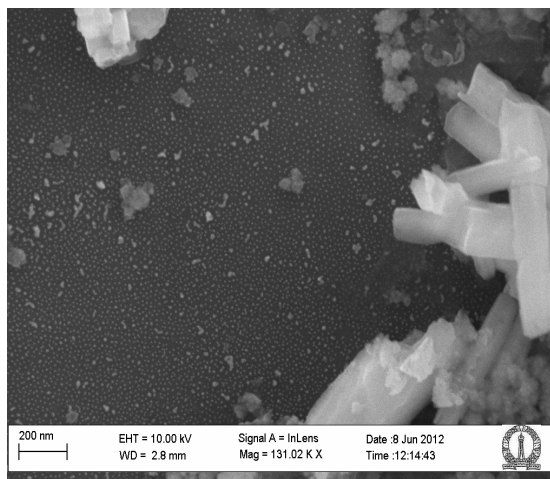
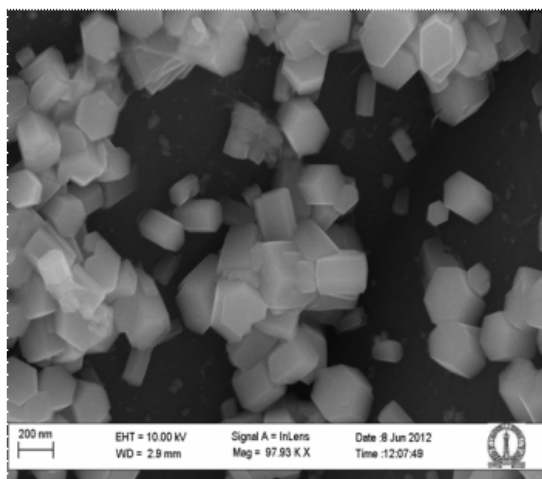
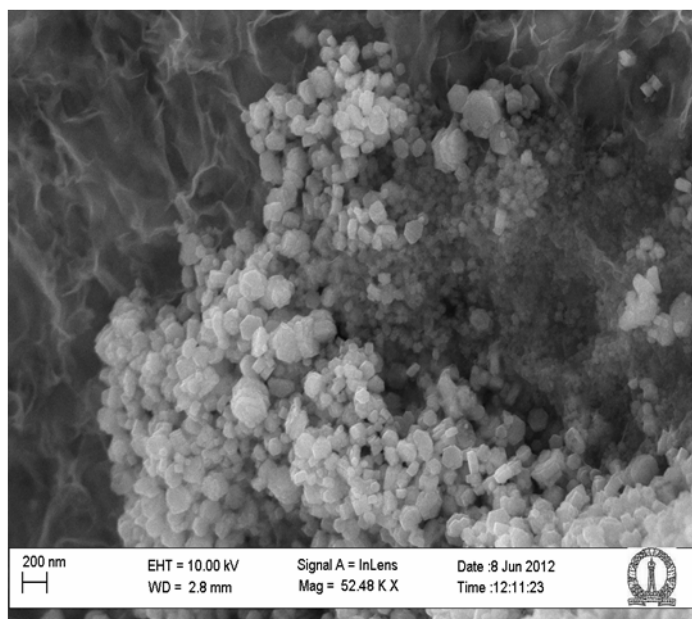
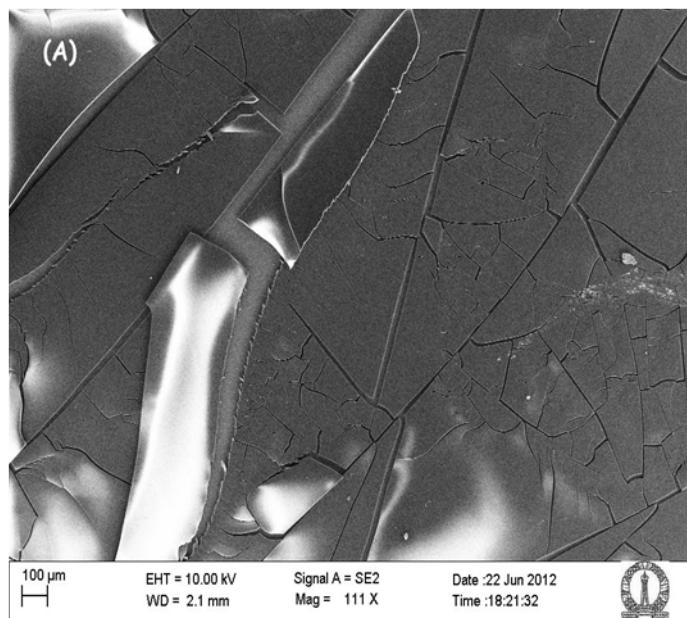


Fig. 6 SEM images of ZnO nanowires grown with 0.05M Zinc nitrate and 0.05M Hexamine precursor solutions at 75°C for 2 hours with applied negative voltage of 2V on Au-coated silicon substrate.

4.3 TiO₂ coated ZnO nanowires

SEM images of TiO₂ sol and TiO₂ coated ZnO nanowire arrays are shown below. Complete evidence of this fact, however, only can be obtained only by XRD analysis



(B)

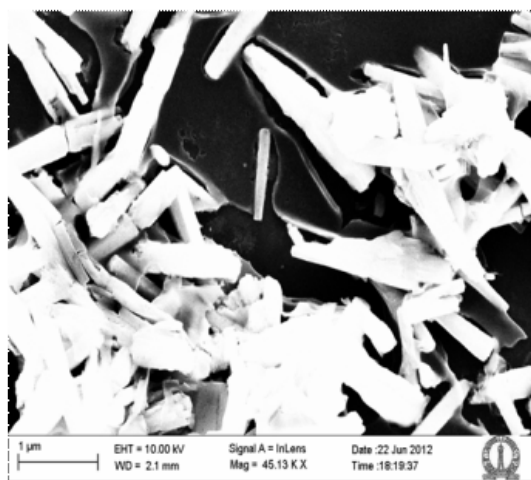
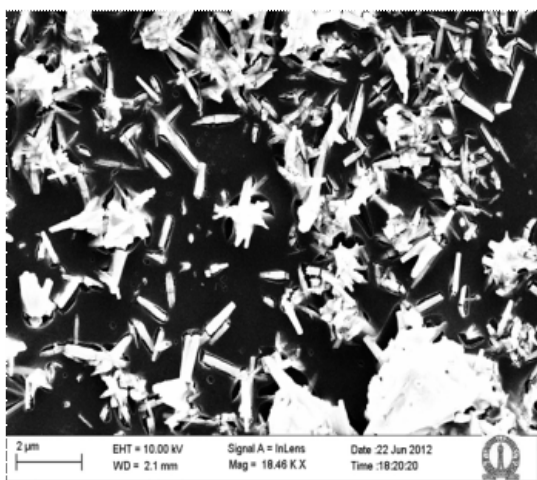


Fig. 7 SEM images (A) TiO₂ sol on silicon substrate (B) silicon substrates of TiO₂ dip-coated ZnO nanowire arrays for a period of 2mins and annealed at 550 °C for 1 hr

The SEM images are shown below are of substrates dip-coated with TiO_2 sol are washed with 3% HCl to remove ZnO nanowire templates.

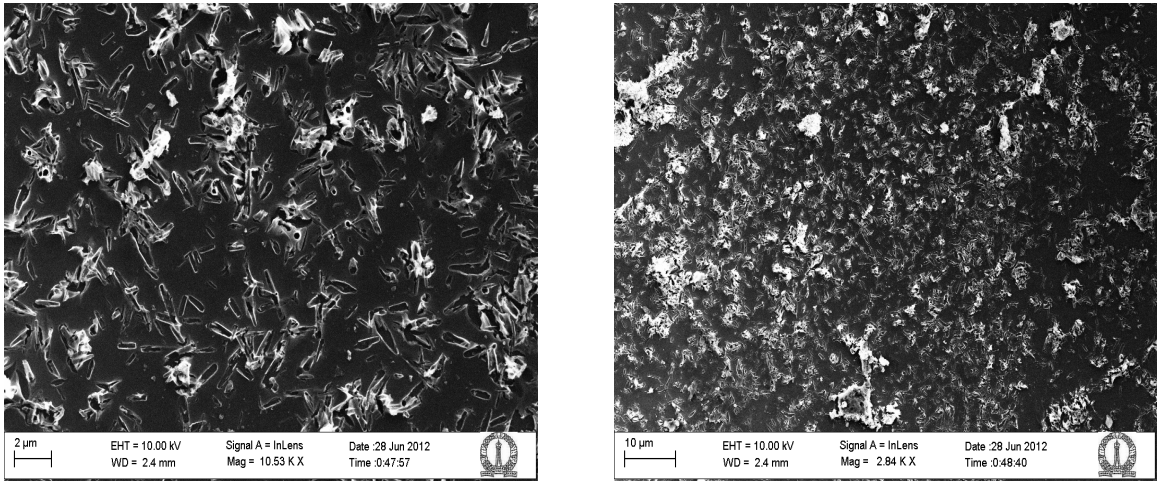


Fig. 8 SEM images of silicon substrates of TiO_2 dip-coated ZnO nanowire arrays for a period of 2mins, dipped in 3% HCl for 3 secs and annealed at 550 °C for 1 hr

The diameter of ZnO nanowires has increased greatly when dipped in TiO_2 solution for 5 mins.

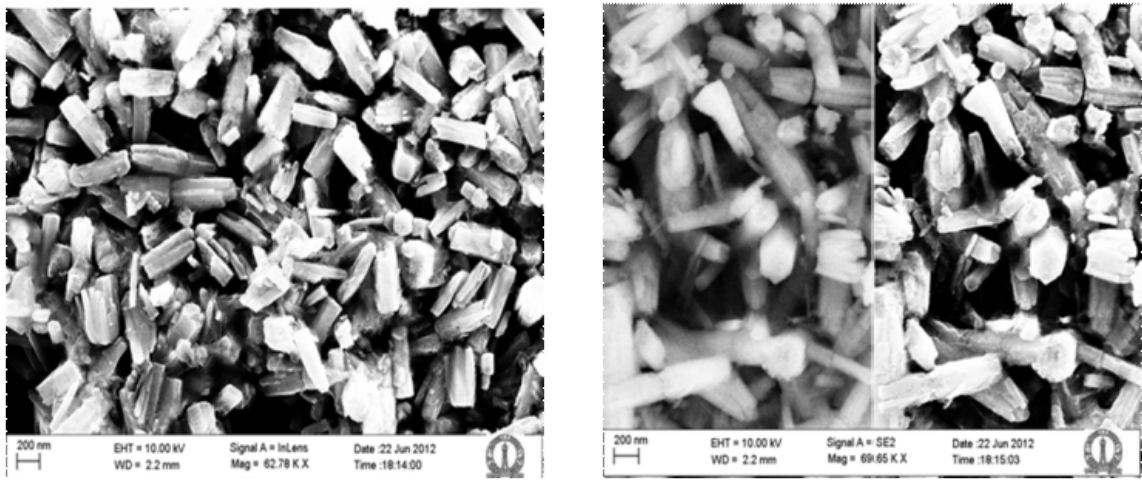


Fig. 9 SEM images of silicon substrates of TiO_2 dip-coated ZnO nanowire arrays for a period of 5 mins and annealed at 550 °C for 1 hr

5.Conclusions : Work ahead

This work provides a brief overview of synthesis of ZnO nanowires arrays on silicon substrates and Au-coated silicon substrates by hydrothermal growth process with and without application of voltage under varying concentration of growth solution. The morphologies of the ZnO nanowire arrays were investigated under Scanning Electron Microscope (SEM) and the images obtained were reported and discussed. ZnO nanowire arrays obtained were dip coated by thin shells of TiO_2 sol prepared by sol-gel process to obtain ZnO- TiO_2 core shell structure. The morphologies of TiO_2 coated ZnO nanowire arrays were also investigated under Scanning Electron Microscope (SEM), images were reported and XRD analysis is to be done for quantitative analysis.

Even though the hydrothermal approaches are simple, economic and suitable for large scale production, the quality of the arrayed ZnO nanowires fabricated using these methods are not as good as that of nanowires prepared via vapor-liquid-solid, chemical vapor deposition, electrochemical deposition methods. While conducting experiments with 2V voltage it is observed that sometimes Au-nanoparticles were getting flaked off the substrate.

Despite the tremendous promise offered by nanowire solar cells, some daunting challenges must be addressed before the benefits can be realized commercially. These challenges include surface and interface recombination, surface roughness, mechanical and chemical stability, nanowire array uniformity, and synthetic scalability. Great progress has been made in most of these areas, but much more work is needed, especially that related to understanding surfaces and interfaces. Even if nanowire devices can realize efficiencies comparable to those of planar devices at much lower costs, practical issues that have not yet been seriously explored such as rapid scaling, integration into modules, and device packaging must be addressed.

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