EFFECT OF QUANTUM DOTS ON WORKING PHOTOELECTRODE OF QUANTUM DOTS SENSITIZED SOLAR CELL

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ABSTRACT: *This paper reports the synthesis and Optical analysis of quantum dot-sensitized solar cell's (QDSSC's) Working photoelectrode. Numbers of working photoelectrodes based on ZnO Nanorods, sensitized with Ag_2S quantum dots, are prepared by chemical Method. SEM images reveal that ZnO Nanorods are hexagonal in nature and have diameter of 75 nm. TEM image clearly shows that the average size of Quantum dots is approximately 7 nm which are uniformly deposited on the surface of ZnO Nanorods. UV-Visible spectroscopy is used to analyze the absorption spectra of working photoelectrodes which shows that the maximum amount of solar spectrum is absorbed by the working photoelectrode with 11 SILAR cycles. Electrochemical activity shows that the anodic current increases from 0.20mA to 8.75mA with increasing content of Ag_2s Quantum dots.*

Keywords: Silver Sulphide Quantum dots sensitized photoelectrode, ZnO Nanorods Array, chemical synthesis.

I. INTRODUCTION

Fossil fuels are depleting day by day so alternative renewable energy resources have drawn a great interest of scientists all over the world to find out ways of utilizing the solar light in photovoltaics, which is plentiful, nonpolluting and never-ending source of energy[1]. The energy reaching earth by sunlight in an hour is $4.3x10^{20}$J which is sufficient to fulfill the energy demand of the whole planet for an year which is $4.1x10^{20}$J [2]. Solar cells made with the help of Dye had great optical absorption in visible range (0.4-0.7μm),but little absorption in infrared region of electromagnetic spectrum, for which more than 50% of the solar light (0.3 -2.5μm) cannot be utilized by the dye [3]. Hence a great deal of photon energy is wasted over the difference among lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), because one photon generates one exciton only and rest of the photon energy is wasted as heat. A good alternative of Dye are semiconductor nanocrystals known as quantum dots. Quantum dots have several advantages as tunable energy gaps [4], large absorption coefficients [5], and multiple electron-hole pair production [6]. Quantum dots help the total consumption of energy of a photon by the phenomenon of MEG (multiple exciton generation) through single photon. [7].

ZnO is used in the fabrication of working photoelectrode for quantum dots sensitized solar cells due to its suitable bandgap (3.37eV) [8] and high electron mobility almost [205–300 $cm^2/(V\ s)$] for bulk ZnO [9] . Besides, ZnO has high crystallinity and can be easily modified to various nanostructured morphologies. It is inexpensive, available in nature abundantly and simply prepared due to its ease of crystallization and anisotropic growth. It is hexagonal Wurtzite. The internal electrical field of ZnO is in the direction of the c-axis that helps the flow of charge, resists the recombination of the electrons with holes [10] and supports higher electron mobility [11]. It has superior optical properties, physical properties and crystal quality of seed layer [12] when used as working photoelectrodes in quantum dot (QD) - sensitized solar cells.

ZnO having a large bandgap, cannot absorb adequate visible light alone [13]. For this reason, sensitizers with a broadband photoresponse in the IR region are needed [14]. Quantum dots show good absorption in the IR region of the solar spectrum.

Ag_2S is a quantum dot sensitizer, associated with I-VI compound semiconductor materials. It has monoclinic crystal structure and optimal energy band of 1.13 eV [16], and is an appropriate solar light absorber [17]. Quantum dots are deposited on ZnO Nanorods using chemical method, which is cost-effective and is industrially utilized to large area deposition, also using this method we can control the composition and thickness according to our desire.

Photoelectrodes with TiO_2 nanotube arrays, sensitized with Ag_2S Quantum dots are fabricated by Yi Xie et al. using photodeposition technique [14]. In present work Chemical synthesis is used for Ag_2S Quantum dots-sensitized photoanode which is cost effective method. The ZnO Nanorods are sensitized by Ag_2S QDs instead of TiO_2, as electron mobility and rate of transoportation of the electron in the ZnO structure is 10-100 times better than TiO_2[18] .This research work results in better absorption of Electromagnetic spectra due to Quantum dots sensitized ZnO Nanorods, hence better efficiency of QDSSCs is expected.

Schematic Diagram of multiple layer working photoelectrode for Quantum dots sensitized solar cell is shown in Fig 1.

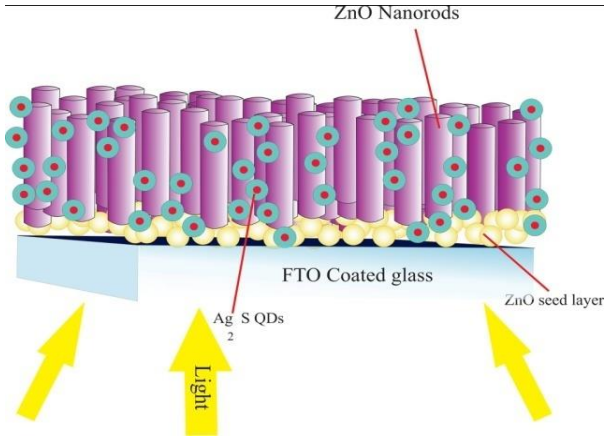

Fig. 1: Schematic diagram of Quantum dots sensitized Working Photoelectrode for Solar Cell

II. MATERIALS AND METHODS

All chemicals are used as received from Sigma Aldrich with no further purification.

A. Pretreatment with $TiCl_4$

First the glass substrate consisting of a layer of Florine doped Tin oxide is cleaned ultrasonically with deionized water, Acetone and Ethanol respectively. Then this cleaned substrate is dipped in the 0.04 M ethanol solution of $TiCl_4$ and is heated at 70°C for 30 minutes. After this, it is sintered at 450°C for 30 minutes, to evaporate the access material from the surface. Allow it to cool to room temperature. By this method a thin film of $TiCl_4$ is produced on the substrate.

B. Deposition of Seed Layer

Single Wafer spin processor unit (Model WS-400BX-8NPP/LITE) is used to deposit a seed layer of ZnO. Pretreated sample with $TiCl_4$ is positioned on the stage of Spin processor and 0.003M $Zn(NO_3)_2.6H_2O$ aqueous solution is poured down drop wise from the window hole at 2000 rpm per 30 sec. A fine film is formed on the substrate. Again, it is sintered for 30 minutes at 450°C in furnace to evaporate the surplus substance from the surface of the substrate, allow it to cool to room temperature. This procedure deposits a fine seed layer on the pretreated FTO coated glass for the synthesis of ZnO Nanorods.

C. Synthesis of ZnO Nanorods

An equimolar (0.035) aqueous solution of $Zn(OAc)_2$ (Zinc acetate dihydrate) and HMTA (Hexamethylenetetramine) are used for the synthesis of ZnO Nanorods using hydrothermal method. Both solutions are placed in an autoclave with samples. The mouth of the autoclave is tightened and it is then heat treated at 85°C for 5 hours. Allow it to cool to room temperature.

D. Formation and Adsorption of Ag_2S Quantum Dots

Ag_2S Quantum dots are produced and adsorbed on ZnO Nanorods using 0.1 M $AgNO_3$ ethanol solution using SILAR (Successive ionic layer adsorption and reaction) method. Samples having ZnO Nanorods are immersed in $AgNO_3$ ethanol solution for 1 minute at room temperature, then these samples are washed with ethanol and immersed in Na_2S methanol solution for 3 minutes. This two step procedure produces one SILAR cycle. Number of SILAR cycles can be varied to deposit Quantum dots on ZnO Nanorods for the fabrication of working photoanodes. If the samples went through n SILAR cycles it is referred to as Ag_2S (n).

III. Characterization Techniques

The structural, surface morphological, and optical and electrochemical characterizations were carried out using SEM: Hitachi (S-4800), TEM: JEOL (JEM2010), XRD: Rigaku, Ultima IV (3KW), UV Vis: Genesys 10S and potentiostat/Galvanostat (Model 263A**).**

IV. RESULTS AND DISCUSSION

Pretreatment is done to grow thin film of TiO_2, to avoid the direct contact of FTO with electrolyte. After it ZnO seed layer is synthesized having particle size of about 200nm. Smaller diameter ZnO Nanorods grow, which are hexagonal in nature and about 75 nm in diameter on the prepared seed layer.

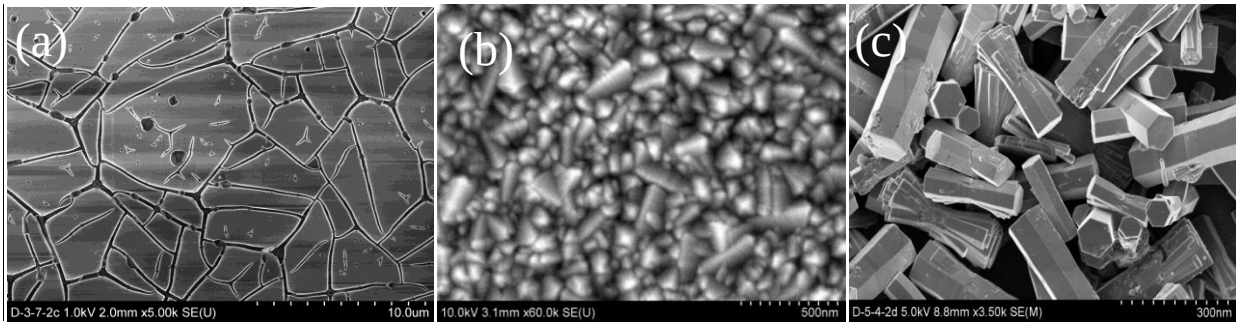

Fig. 2: SEM images of FTO coated glass substrate (a) TiO_2 Film (b) Seed Layer (c) ZnO Nanorods

Uniform deposition of Quantum dots on a working photoelectrode with 5 SILAR cycles is shown in Fig. 3, The Quantum dots are well separated with very little or no aggregation on the surface of ZnO Nanorod. The average diameter of Ag_2S quantum dots is observed to be 7 nm.

The UV–Vis spectra of Photoanodes with different SILAR cycles are shown in Fig. 4. The UV-light with wavelength below 400 nm is mainly absorbed by ZnO Nanorods and shifts towards the visible light region with the adsorption of Ag_2S QDs. This shows that the QDs increase the absorption of electromagnetic spectrum considerably. As the deposition cycles increase, the absorption edge of the spectra of Photoanodes are red-shifted and the absorbance increase in both UV and visible light spectrum region. The reason behind red-shift is the increased size of Ag_2S quantum dots due to agglomeration, because of increasing SILAR cycles.

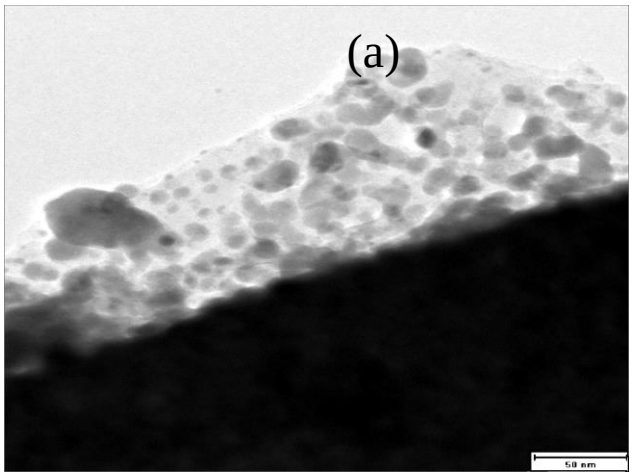

Fig.3: TEM images showing closer view of quantum dots deposited on a single ZnO Nanorod.

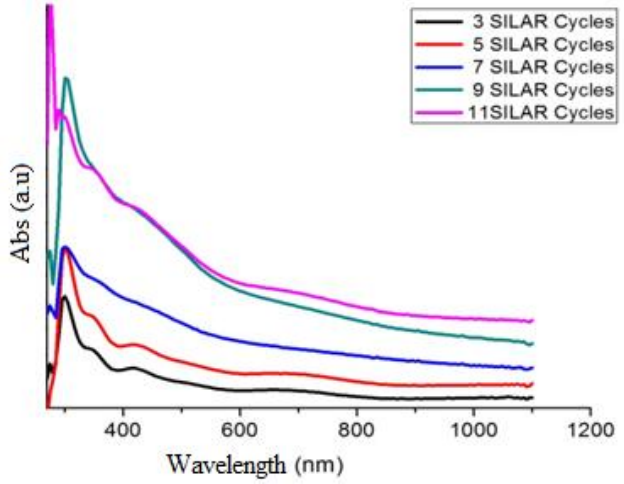

Fig 4: UV-Vis sspectra of Photoanodes.

To study the effects of Ag_2S quantum dots content on the performances of working photoelectrode electrochemical activity of the series of working electrodes which are prepared by varying the SILAR cycles of Quantum dots is studied. Polysulphide electrolyte (0.5 M sodium sulphide (Na_2S), 2 M Sulphur (S), 0.2 M Potassium chloride (KCl) and 0.5 M Sodium hydroxide (NaOH), dissolved in methanol/water (7:3 v/v)) [3] is used for this purpose.

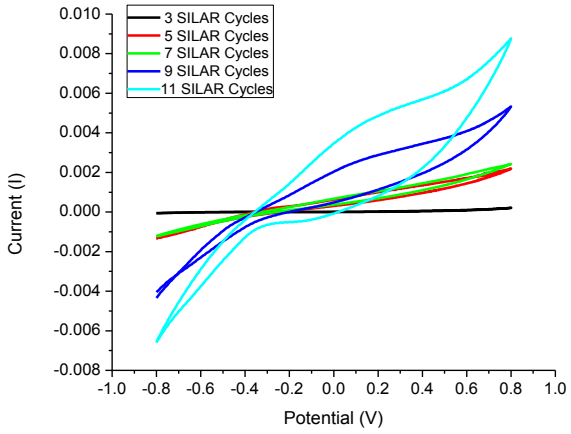

Fig.5: Electrochemical activity of working photoelectrode with varying (3, 5, 7, 9, and 11) SILAR cycles at scan rate 50 mVs^{-1}.

When the deposition cycles are increased from 3 to 11 in regular odd intervals, more and more Ag_2S Quantum dots are adsorbed on the surface of ZnO Nanorods, they are packed together and much more uniform, more photogenerated carriers are produced and electron transport is enhanced. Consequently, bottom of the conduction band of Ag_2S gets close to the ZnO and electrons transfer to the electrolyte rapidly and swiftly, resulting in the gradual increase in the anodic current from 0.20mA to 0.875 mA with increasing SILAR cycles.

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