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ZnO BASED PHOTOELECTRODE FOR WATER SPLITTING

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Greenhouse effect and depletion of the fossil fuels motivate scientific society to search for the new sources of energy. This tendency toward green energy has some issues related to choice of appropriate technology. Solar driven hydrogen production is one of the most suitable forms of energy mining. Amount a number of existing materials which can act as active centers for hydrogen extraction from water, zinc and iron oxides are the cheapest and environmental friendly. These materials were chosen to design the electrodes for study the photocurrent.

Keywords: nanosheets, nanorods, photoelectrochemical cell, electrodeposition, water splitting.

Introduction

Hydrocarbon sources of energy has two major negatives which are: bad impact on the environment and rapiddepletion. To avoid these problems with fossil fuels scientists are really interested to deal with an alternative energy sources [1, 2]. Such alternative and green energy sources have their requirements. These requirements include erenewability, friendliness to the environments, and accessibility. One of the choices of green energy sources is solar to electricity, hydrogen or heat energy production because of enormous magnitude of Sun energy, which reach Earth– approximately 10^5 terawatts per hour [3]. However, despite of huge attempts of scientific and engineering word to construct the appropriate system for harvesting photons and transfer their energy into suitable form of energy for human, there are still a lot of problems. The main ones are increasing the efficiency and stability of such systems [4, 5].

The most promising technic to use solar energy is photo-electrochemical (PEC) hydrogen production [2, 4-6]. PEC technology can convert solar energy direct to the chemical bound energy. This process is mimicking the nature's photosynthesis. Chemical energy of the hydrogen molecule can be used in hydrogen cells to produce the electricity, in ovens to produce the heat and so on [7].

Mainly the PEC consists of cathode and anode dipped in water. When photon harvested by material of anode/cathode, which is commonly a semiconductor, the half reaction of water splitting can be initiates. In detail, harvested photon can create within semiconductor an exciton. Separated exciton leaves electron and hole inside electrode, which move to the surface of structure. Such electrons and holes on the surface of cathode/anode play role as RedOx [8] centers of water splitting reactions [9].

It is obvious, that to harvest big amount of electrons and separate produced excitons band, and structural engineering are necessary. There for the semiconductors with appropriate band positions and morphology are needed. Anomalous scientific works denoted to develop the semiconducting electrodes based on TiO_2 [4], WO_3 and so forth [10]. Such materials suffer from low absorption ability and show low efficiency. That is why it is very important to develop new materials or structures with narrow band gap or wide/narrow band junctions.

The ZnO is a wide band gap material (3.37 eV) with high electron mobility (100 times higher than TiO_2), harvests only UV photons. It means, that ZnO acts as photocatalyst when it irradiated by high energetic light. But only 4-5% of solar spectrum can reach the Earth's surface. To increase

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the light absorption, the decoration of ZnO photoanode by narrow band gap semiconducting materials is applied [11].

This study focuses on the developing of wide/narrow band gap semiconducting junctions for photo-electrochemical water splitting and study of the fundamental mechanisms of enhancing photocurrent and energy/electron transfer. Design photoanode with light frontal ZnO layer, decorated by iron oxide (Fe_2O_3) whose band gap (2.2 eV) is suitable for visible spectra absorption.

6. Experimental part

Materials. The chemicals, which are $Zn(NO_3)_2$×6 H_2O,99.8% and KCl, 99.998%, $FeCl_3$and the substrate sindium-doped tin oxide(ITO) coated glass (8 Ohm/cm^2) used in electrochemical reactions were purchased from Sigma-Aldrich chemical company.

Nano-Rods (NRs) by electrochemical deposition. The NRs were synthesized by electrochemical cell (ECC) under potentiostatic condition. The ECC was consist of working, counter and reference electrodes, ITO coated glass, platinum wire and Ag/AgCl (3M KCl) respectively and electrolyte. Before using an ITO substrates were ultrasonically cleaned in acetone, alcohol and DI water for 15 min in each solution. After cleaning the ITO substrates were dried by gentle N_2 stream. Electrolyte of ECC for NRs production was consist of 0.001M $Zn(NO_3)_2$×6 H_2O and 0.1M KCl dissolved in DI water. Beaker with electrolyte was heated in water bath up to 70°C. The ECC deposition was performed under potential between the electrolyte at -1.1V during 30 minutes. After deposition the substrates were rinsed with DI water, and gently blown dry with Ar.

Nano-Sheets (NSs) by electrochemical deposition. ZnO NSs were produced via ECC with applied-1V potentials between ITO glass and electrolyte. The cleaning procedure of the substrates were the same as describe in previous section. Electrolyte of ECC for NSs synthesis was consist of 0.05M $Zn(NO_3)_2$×6 H_2O and 0.1M KCl dissolved in DI water. The temperature was held around 80°C in water bath. Duration of hole synthesis was an hour. After all the produced structures were gargled with DI water, and dried with Ar.

Iron oxide nanoparticles deposition onto ZnO arrays. ZnO nanostructures decoration by Fe_2O_3 nanoparticles was proceeded using simple spin coating manner. 0.2M solution of $FeCl_3$ in ethanol was exploited for source of iron. Some drops of this Sol. were transported onto spinned substrate. To produce qualified distribution of iron oxide, spin rate and time duration of coating were selected as 3000 rpm and 10 min respectively. After deposition of iron salt, substrates were heated to 350°C for 15 min to obtain Fe_2O_3. By repetition of above described coating for 5 times, shell layer of iron oxide nanoparticles was formed.

Characterization Methods. To study the morphology and the crystallinity of produced samples, scanning electron microscopy (SEM) and X-ray diffractometer (XRD) were utilized respectively.The photocurrent investigation was carried out via P-2X Elins potentiostat under 100W Xe lamp irradiation.

7. Results and Discussion

SEM images show the morphology of obtained ZnO NRs, NSs and ZnO/Fe_2O_3 core shell structures (Figures 1–3). It can be seen from Figure 1 that diameter of ZnO NRs lays in rage of 100 – 200 nm. Unlike ZnO NRs, ZnO NSs have a smaller dimension and a dense distribution on the substrate. It means that ZnO NSs have higher surface area and hence, more active centers for oxidation reactions. Therefore, NSs are more appropriate to further investigations. It was found that the core/shell structure of ZnO/Fe_2O_3has high a quality design, and seemed has equal distribution on whole surfaces (Figure 3).

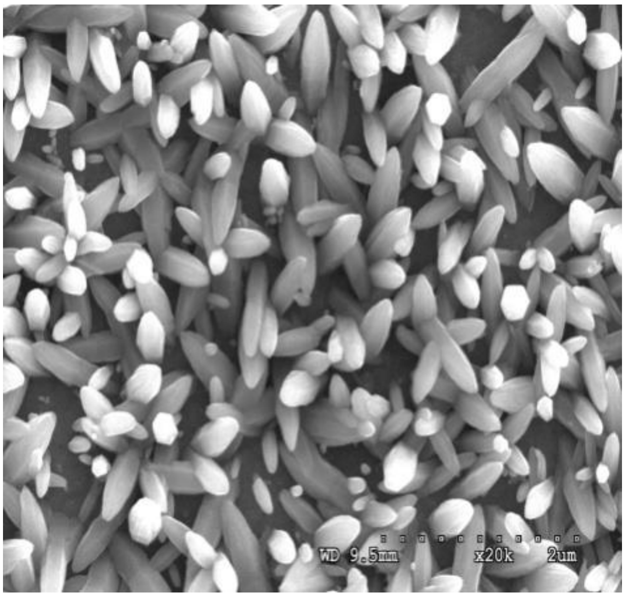


Fig.1. SEM image of ZnO nanorods arrays electrochemically deposited onto ITO glass

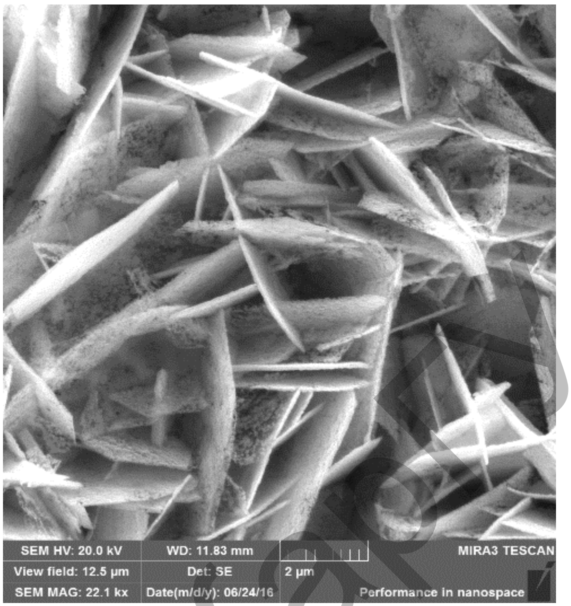


Fig.2. SEM image of ZnO NSs electrochemically deposited onto ITO glass

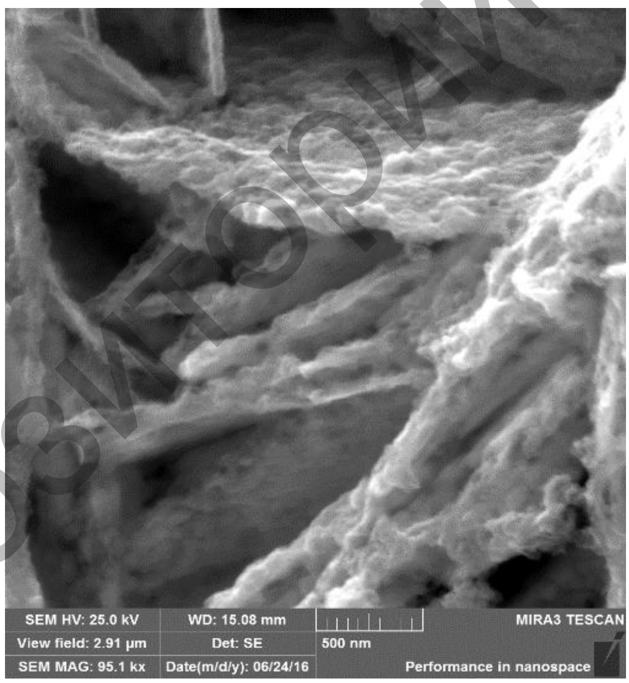
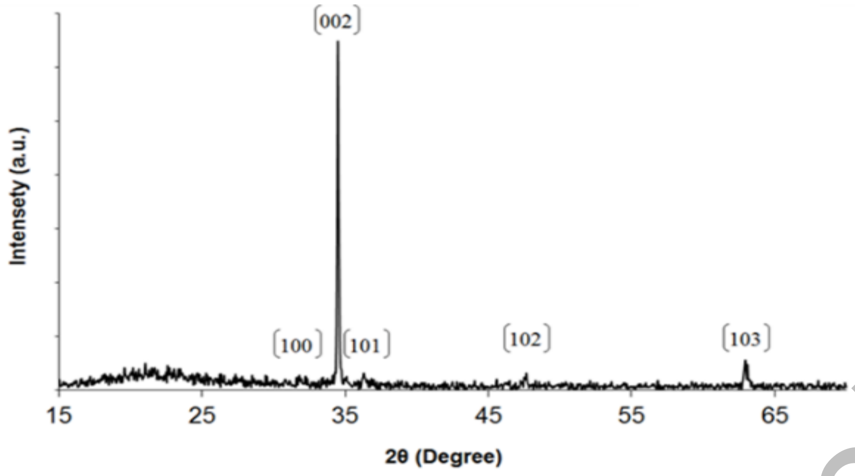
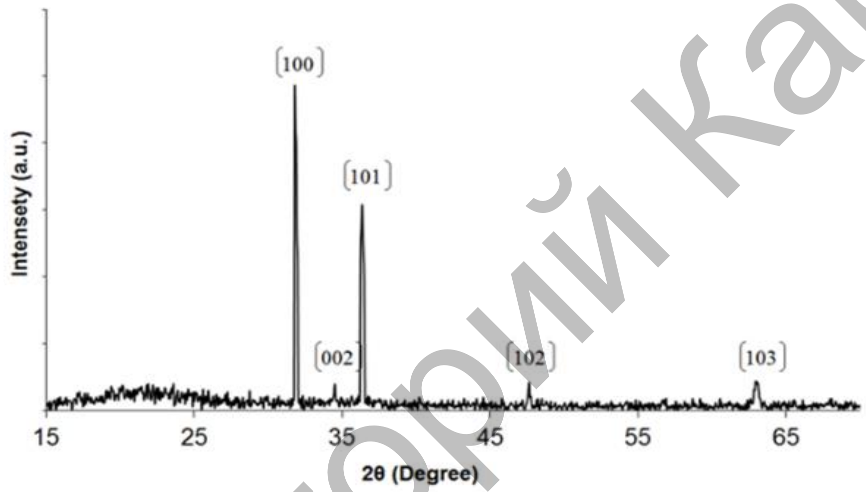


Fig.3. SEM image of ZnO/Fe_2O_3 core/shell structure

The XRD analysis proved that obtained by electrochemical synthesis of sought-for materials allows to produce predetermined structures of ZnO (Figures 4 a, b). The reaction of water splitting was studying using three electrode installation with 0.1M NaOH aqueous solution. Figures 5 and 6 represent the photocurrent of beard ZnO NRs and ZnO NSs. It is obvious by comparison of Figures 5 and 6, that ZnO NSs have higher photocurrent than ZnO NRs. The reason for high current in NSs based electrode can be resulted by high surface development of NSs. Last criteria affect to the total surface area, and hence the total active part. Since the NSs have more photocurrent, that structure was chosen to more suitable to further investigation of photo response after decoration.



a)



b)

Fig.4. XRD analysis of ZnO NRs (a) and ZnO NSs (b)

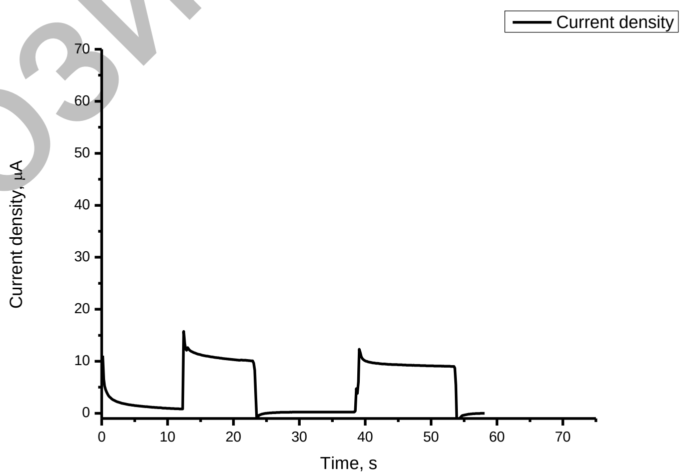


Fig.5. Photocurrent of bare ZnO nanorods. 100W UV Xenon lamp was exploited as light source

Figure 7 shows 4 times increasing the photocurrent of decorated ZnO by iron oxide. The emergence of electron current within an electrode after light irradiation gives the theoretical premises for overall water splitting reactions.

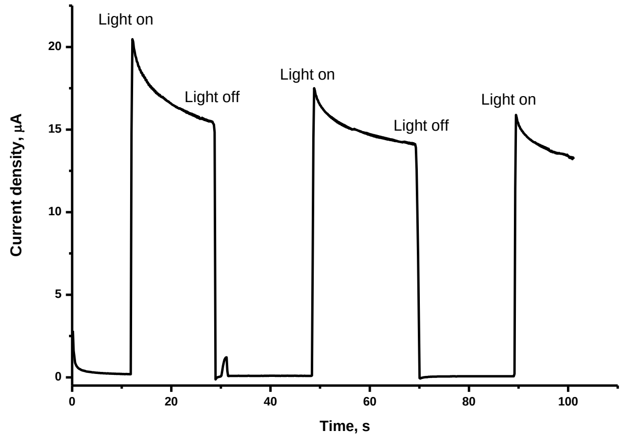


Fig.6. Photocurrent of bare ZnO nanosheets. 100W UV Xenon lamp was exploited as light source.

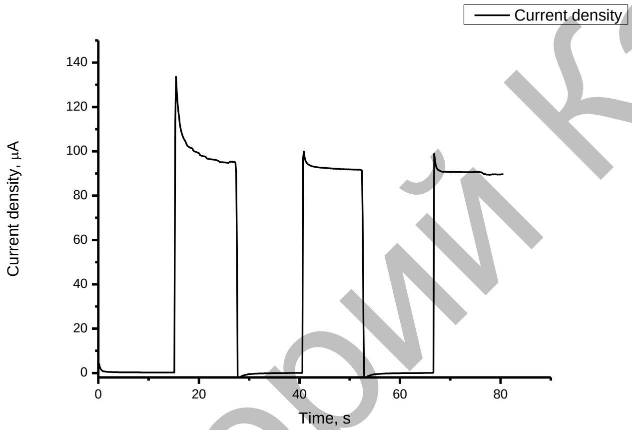


Fig.7. Photocurrent of ZnO/Fe_2O_3 nanocomposites. 100W UV Xenon lamp was exploited as light source

Conclusion

In conclusion, ZnO NRs, NSs and ZnO/Fe_2O_3arrays were assembled onto ITO glass. This development is useful to understanding and creation the fundamental issues in green energy development. Synthesis of various nanostructures by ECC and spin coating technics helps us to design the artificial photosynthetic system. It was shown that high developed morphology of wide band gap materials possesses high light absorption and therefore high solar–to-chemical energy conversion. The decoration of ZnO by iron oxide plays the great role for enhancing photocurrent in a cell.

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