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Comparative Study of Nanostructured Zr-Fe_2O_3 and CNT Modified Zr-Fe_2O_3 Thin Films for Photo Electrochemical Generation of Hydrogen

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Abstract

Nanostructured hematite thin films are doped with zirconium successfully and also modified by introducing CNT using sol-gel method for their implementation as photo-electrode in photo-electrochemical (PEC) cell for hydrogen generation. XRD, UV-visible spectroscopy and PEC study techniques are used to characterize the thin films. The PEC responses of thin films are improved by introducing carbon nanotubes (CNT).

Keywords: Hematite; sol-gel method; photo-electrochemical cell; carbon nanotubes.

1.Introduction

Energy issue is a great challenge in the 21st century. The focus of all the researchers is to create a cost effective and more efficient way to produce hydrogen using solar energy. Among all the methods of hydrogen production photo-electrochemical (PEC) water splitting is a promising method of transforming solar energy into chemical energy stored in the form of hydrogen in an environmentally benign manner [1,2]. Metal oxide semiconductors are today the most suitable material for PEC production of hydrogen. Major research work is pursuing in this field. In the search for a better semiconductor, many oxides such as TiO_2, WO_3, ZnO, $SrTiO_3$, Fe_2O_3, Cu_2O, SiO_2, etc. have been studied as photo-electrode in PEC cell for water splitting during last 30 years. Encouraging results were obtained regarding the efficiency of photo-electrodes, by conventional semiconductors like Si, GaAs, InP, CuInSe, CdTe, etc. Unfortunately these electrodes being unstable in aqueous solutions, give photo-electrolysis operation for a very short time.
The unique properties of Fe_2O_3 make it a promising candidate as photo-electrode in the PEC cell. Its band gap (2.2 e V) lying in visible region allows the absorption of 38% of the photons of the solar spectrum. It is

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a low cost semiconductor and has long term chemical stability in many solvents over a wide pH range. But its photo response is reported quite low, due to its high resistivity and high combination rate of photo generated charge carriers at the semiconductor/electrolyte interface. Surface modifications on Fe_2O_3 films have been attempted to enhance the photo response.

2. Experiment and Synthesis Setup

2.1 Preparation of photoelectrode

2.1.1 Nanostructured Fe_2O_3 doped with Zirconium

The thin films of Zr-Fe_2O_3 are prepared by sol-gel method .The precursor comprising of 0.3 M iron nitrate, 1 at% $ZrCl_2$ (dopant) and 4-5 drops of 2-methoxyethenol in de-ionized water. The homogeneous solution is obtained after vigorous stirring. Thin films of doped iron oxide are deposited by spinning the solution on the rotating substrate (FTO) at speed of 3000 rpm using spin coating technique. To get film of desired thickness this method is repeated to get six layer deposition. The samples are sintered in furnace at temperature of 270°C.

2.1.2 Nanostructured CNT modified iron oxide doped with Zirconium

SW-CNTs (1 at% & 2 at%) is mixed to the hematite solution prepared as mentioned above and sonicated for 1 hour to make it homogenized. Thin films of CNT modified iron oxide were deposited by spinning one drop of the solution on the rotating substrate (FTO) at speed of 3000 rpm using spin coating technique. To get film of desired thickness this method is repeated to get six layer deposition. The samples are sintered in furnace at temperature of 270°C.

3. Results and discussion

Fig. 1 represents XRD patterns of nanostructured Zr doped Fe_2O_3 thin film. The Peaks obtained at 2θ values degree 24.3, 33.4, 35.8 and 54.4 are due to reflection from the planes (012), (104), (110), (024) respectively, indicating the existence of hematite phase with 1-hexagonal structure. Figure 2 shows UV-visible optical absorption spectra of different thin films prepared. The absorption spectrum shows absorption in visible region. An absorption band edge is obtained at 580 nm i.e. 2.14 eV, which is very close to the bandgap values reported by others [3]. From the I-V characteristics, presented in Fig. 3, it can be observed that current is increasing with increase in electrode potential for all the samples. The photocurrent density exhibited by Zr doped hematite thin films is enhanced after introducing CNT. It is may be due to reduction in recombination of photogenerated electrons and holes 1% CNT doped sample showed maximum photocurrent density, further it is decreased for 2% CNT doped sample.

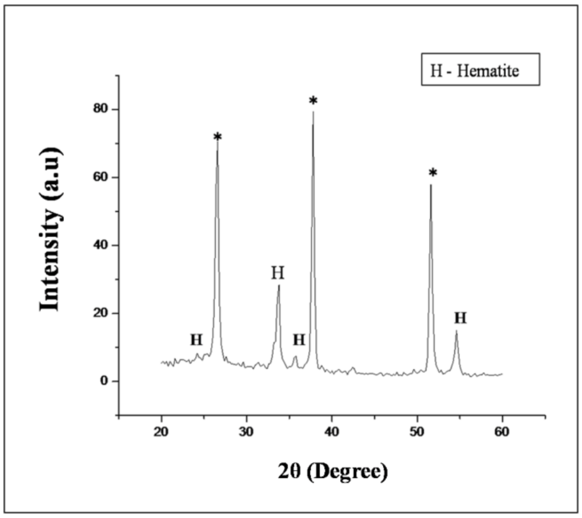

Figure 1: XRD pattern of different thin films prepared (*corresponds to peaks of underlying SnO_2: In coating of substrate).

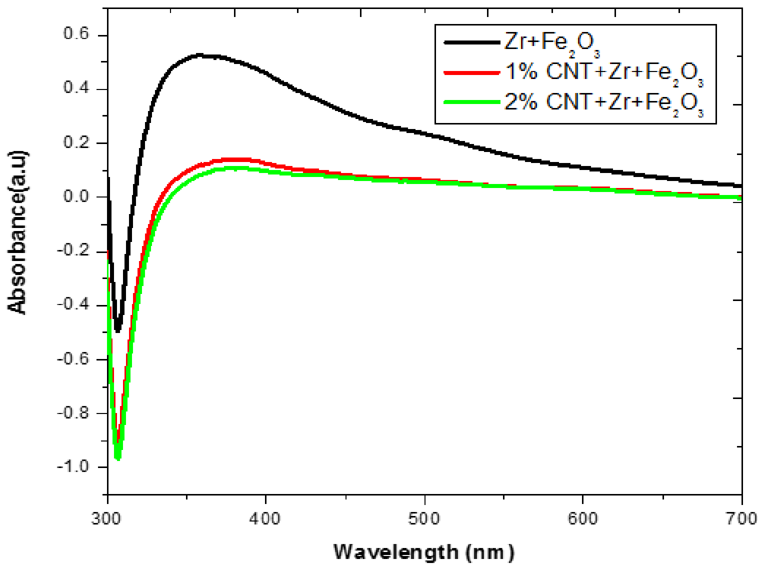

Figure 2: Absorption vs wavelength curve of different thin films prepared.

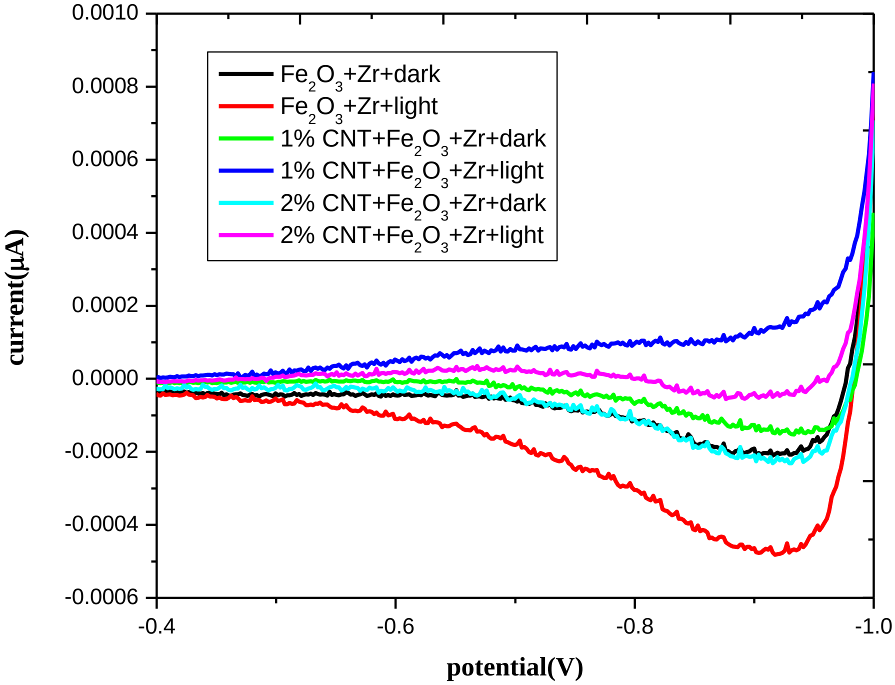

Figure 3: I-V characteristics for different prepared samples in darkness and under visible light illumination.

4. Conclusion

In conclusion, nanostructured Zr doped hematite and CNT modified Zr doped hematite thin films were successfully synthesized by using simple and economical method (sol-gel spin coating method). PEC responses of thin films were improved by introducing CNT. 1% CNT based Zr doped hematite thin film exhibited PEC response better than the Zr doped hematite thin films.

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