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Synthesis, Characterization and Application of Nanoporous TiO_2 as Photoanode for DSSC Sensitized by a Natural Dye Extracted from "Mesua Ferrea"

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Abstract :
Nanoporous TiO_2 is preferred as the wide band gap semiconductor in dye sensitized solar cells (DSSC) due to its high photo catalytic activity, high adsorption potential, anticorrosion properties, chemical stability and eco-friendliness. The key difference of the DSSC over traditional single junction solar cells is the use of a sensitizer dye, which broaden the absorption frequency of the wide band gap semiconductor and thereby increase the efficiency of the photo electrode. Natural dyes as photosensitizer are getting prime importance in recent years due to their availability, low cost and environmental friendliness. In this work, we have reported the synthesis of nanoporous TiO_2 thin film on a transparent conducting oxide (TCO) glass substrate by a modified sol-gel technique using titanium isopropoxide as the precursor. The as synthesized films were characterized by UV-vis spectroscopy, X - diffraction (XRD) and transmission electron microscope (TEM) for the investigation of their optical, structural and morphological properties. One natural dye was extracted from locally available young red leaves of "Mesua ferrea using water and alcohol as solvents at different temperatures. For the fabrication of the TiO_2 photoanode, the as synthesized films were dipped into the dye extracts and the sensitization efficiency as well as the HOMO-LUMO interaction between the dye and TiO_2 was investigated through UV –vis spectroscopy.

Keywords: *DSSC, nanoporous TiO_2, natural dye, photoanode*

1. Introduction

Dye sensitized solar cells (DSSC) being the third generation solar cell is getting prime attention as an alternative source of clean and green energy due to its low cost, easy fabrication and environment friendliness[1] The most significant part of a DSSC is the photoanode which consists of a wide band gap semiconductor nanoparticle and a sensitizer dye . Although many works have been done regarding the application of wide band gap semiconductor such as ZnO, , TiO_2, ZrO_2, ZnS, CdS, CdSe, WO_3, Fe_2O_3, etc., TiO_2 has been preferred most frequently in a DSSC due to its favourable properties like high photo catalytic activity, anticorrosion, chemical stability, high adsorption capability and eco-friendliness[2-5]. As the semiconductor nanoparticle plays an important role regarding the efficiency of the cell many techniques have been used so far to improve the performance of TiO_2 by increasing its optical activity through shifting the response from UV to visible region. One of the way is the sensitization of TiO_2 by inorganic or organic dyes where anchorage of the dye to the surface of the semiconductor are important parameters for determining the efficiency of the photoanode. [6].Although, in the past few years, the most efficient cells have been obtained by using inorganic and organic dye, but owing to the high cost and non-benign nature of these complexes as well as the complicated synthetic routes, low efficiency and use of toxic chemicals, a quest for green alternatives as natural dyes (containing natural pigments) extracted from fruits, flowers and plants is getting prime importance in terms of easy availability, cost efficiency, nontoxicity and environment friendliness.[7-9]. Even though, a numerous efforts have been made by several research groups all over the world to utilize these natural dyes as sensitizers in a DSSC, but regarding the efficiency and stability of the dye , there is still more to explore in this area [10-15]. Moreover, as the properties of TiO_2 are a function of the crystal structure, particle size, and morphology of the nanoparticle, the synthesis process also play an important role. Various techniques are available for the synthesis of TiO_2 nanoparticle such as sol gel, chemical vapour deposition (CVD) , sputtering, hydrothermal and peptization. [16-20]. However, sol-gel process is a suitable method for preparing anatase TiO_2 nanoparticle since the composition, particle size, film thickness, and phase transformation can be controlled by controlling the parameters like concentration, growth temperature, and sintering condition. [21].

In this work, we have reported the synthesis of TiO_2 nanoparticles by a modified sol-gel process using titanium isopropoxide as the precursor . The as synthesized nanoparticles are used to prepare TiO_2 thin films on a glass plate coated with a transparent conducting oxide (TCO) using Triton-X .as binder material . The morphology and optical properties of TiO_2 thin films were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-Vis absorption spectroscopy. The natural dyes were extracted from locally available young red leaves of "Mesua ferrea, using water and alcohol as solvents and were characterized by UV-vis spectroscopy. The extracted dyes were then adsorbed onto the as synthesized optimised TiO_2 thin films for the formation of the photoanode for application in DSSC. The effects of changing extraction temperature and extracting solvent were investigated through UV-vis spectroscopy. The performance of the as fabricated photoanode as well as the interaction between TiO_2 nanoparticle and the natural dyes were investigated through absorption spectroscopy for the evaluation of the optimised photoanode. The effects of changing extraction temperature and extracting solvent are also analyzed.

2. Experimental

All reagents and solvents, viz. titanium isopropoxide, isopropyl alcohol, acetic acid, nitric acid, ammonia, ethanol , Triton-X, etc. used in this work were of ACS grade and obtained from Aldrich and Merk (India) Ltd and used as received unless otherwise stated Deionised water was used throughout the experiments. The crystal structures of the films were analyzed by using a X-ray diffractometer (Make: Seifert, Model 003 T/T) with CuKα radiations operated at 40 kV and 30 mA. For optical studies, optical absorbance spectra in the vicinity of absorption edge were recorded using Perkin–Elmer spectrophotometer. Surface morphology and particle size was examined by LEO 1430VP Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

2.1. Synthesis of TiO_2 nanoparticle

In a typical reaction, 6.3 ml of TTIP was added drop wise to a 25 ml 1:10 mixture of methanol and ethanol and was stirred continuously. 1 ml of conc. HNO_3 and 25 ml of distilled water was added drop wise to this mixture with continuous stirring at 50^0C until a homogeneous mixture was obtained. The white precipitate formed finally was dried at 100^0C in an oven for 10 hours. The powder was then subjected to calcinations at 450^0C in a muffle furnace for 4 hours and the white crystalline nano powder was further used for preparation of TiO_2 thin film.

2.2. Preparation of TiO_2 thin film

For the preparation of the thin film, 2g of the synthesized TiO_2 nano powder was mixed with 25 ml ethanol, 1ml of Triton-X and a few drops of surfactant. The paste formed was layered onto a chemically cleaned glass substrate coated with a transparent conducting oxide (TCO) by dip- coating technique using a single dip coater (Model N0.-SDC 2007C, Apex Instruments Co.). The films were dried in air and then annealed at 400^0C for 30 min. A blue white transparent film was obtained which indicates the formation of TiO_2 film.

2.3. Extractions of Natural Dyes

The natural dyes were extracted from young red leaves of "Mesua ferrea" using water and alcohol as solvents. For both aqueous and alcoholic extraction of the dyes, the extraction was done at three different temperatures viz. 50^oC, 75^oC and 100^oC. For aqueous extraction of the dyes, 100gm of finely crushed fresh young leaves of "Mesua ferrea " (sample A) and 100gm of dry young leaves of "Mesua ferrea (sample B) were transferred into two conical flasks containing 100 ml of deionised water and then boiled for 30 minutes at desired temperatures. The extracts were kept in dark for 24 hour and then filtered with a whatman 40 no. filter paper. Similarly, the alcoholic extraction of the dyes were prepared following same procedure on a soxhlet apparatus for two hours. The extracts were kept in dark for 24 hours and then filtered with a whatman 40 no. filter paper.

Finally, all the filtrates were collected and stored in an air tight bottle at 0^oC until its anchorage on the semiconducting surface.

3. Results and Discussion

3.1. Optical studies for the TiO_2

The optical absorption spectra of the as synthesized TiO_2 nanoparticle prepared are shown in Fig.1(a) which shows absorption in the UV-region indicating the formation TiO_2, as it is sensitive to the UV- region.

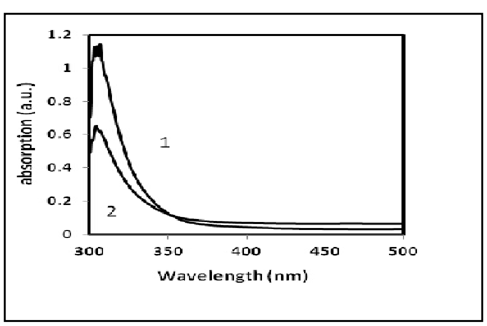

Figure 1(a) : UV-vis spectra of TiO_2

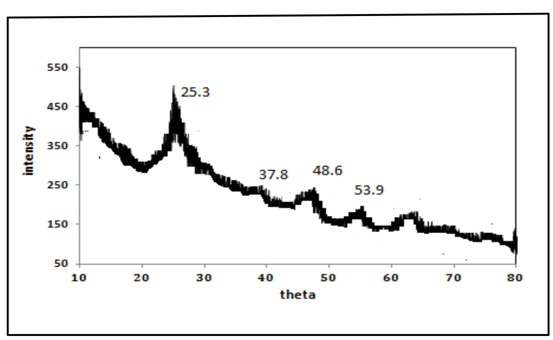

Figure 1(b): X-ray diffraction pattern for TiO_2

3.1.1. Surface morphology and structural studies

3.2. XRD image of TiO_2

Fig. 1(b) shows the XRD patterns of the TiO_2 thin film. The XRD patterns of the sample consisted of five distinctive TiO_2 peaks at 25.30^o, 37.80^o, 48.60^o and 53.98^o corresponding to (1 0 1), (0 0 4), (2 0 0), (1 0 5) crystal planes (JCPDS 21-1272) respectively which confirms the anatase phase.

3.2.1. SEM and HRTEM images of TiO_2 thin films

The SEM micrographs of the synthesized TiO_2 nanoparticles is shown in Fig.2 (a), from which, it is observed that the TiO_2 nanoparticles are spherical and nanoporous in nature thus being suitable for adsorbing the dye on its surface. From the HRTEM images of the prepared TiO_2 thin films in Fig 2 (b), it can easily be implied that the films are well crystalline and are nanoporous also.

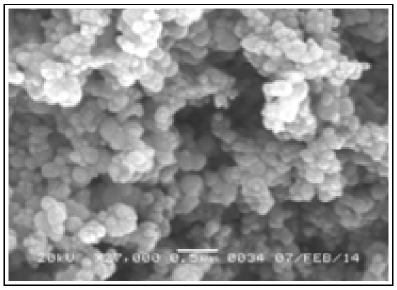

Figure 2 (a) SEM images of TiO_2 nanoparticle

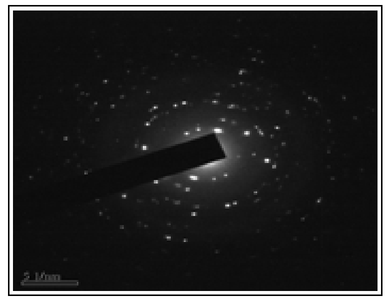

Figure 2(b) : HRTEM image of TiO_2 thin films

3.3. Optical Studies

3.3.1. Absorption Spectra of Natural dyes

The optical absorption spectra of the dyes extracted at three different temperatures (25^{o}C, 50^{o}C and 100^{o}C), from the fresh leaves of "Mesua ferrea"using water and alcohol as solvent are shown in the Fig 3 (a) and Fig. 3(b) respectively. From the spectra, it is observed that the absorption pattern of all the samples show good absorption in the visible region with an absorption edge around 540 nm and 690 nm respectively

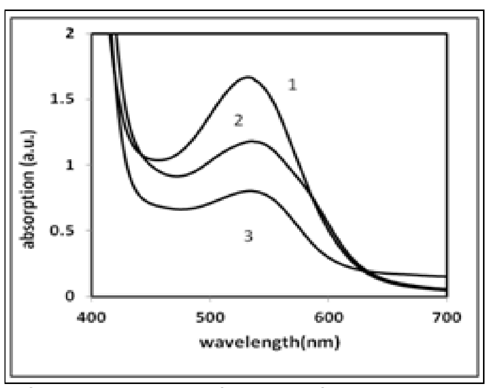

Figure 3 (a) : UV-Vis absorption spectra of aqueous extract of "Mesua ferrea"at three different temperatures (1) 25^{0}C, (2), 50^{0}C and (3) 100^{0}C.

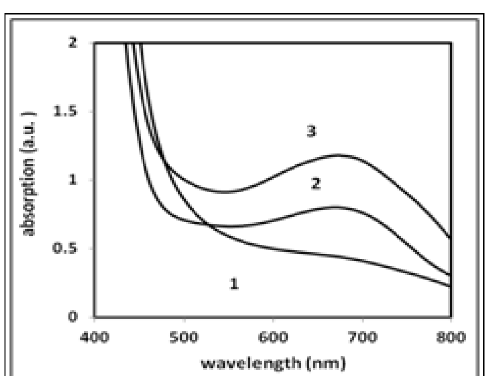

Figure 3(b): UV-Vis absorption spectra of alcoholic extract of "Mesua ferrea" at (1) 25^{0}C, (2), 50^{0}C and (3) 100^{0}C

The aqueous extract prepared at 100^0C showed better absorption in the visible region in comparison to that extracted at 25^0C and 50^0C. However, a much higher absorption was observed for the alcoholic extract as shown in Fig 3(b). The difference in the absorption characteristics is attributed due to the complicated mixed composition (viz. chlorophyll, anthocyanins etc) of the extracts.

3.4. Fabrication of TiO_2 photoanode

For the fabrication of the photoanode, the optimized dyes (sample-A aquous extract at 100^oC and sample–B alcoholic extract at 100^oC) were adsorbed onto the surfaces of as prepared optimized TiO_2 thin films by continuous dip coating technique. The films were withdrawn after 24 hour of dip time, washed in distilled water and dried in an oven at 40^oC for 5 h. It was observed that, after immersion in the extracts, the colours of the TiO_2 films changed indicating the anchorage of the dyes on the surface of TiO_2 thin film.

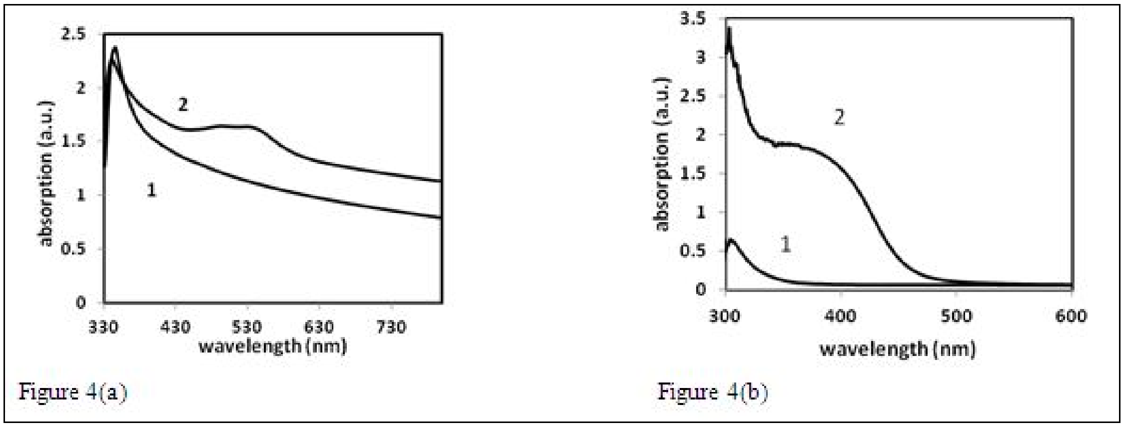

Figure 4: (a)-4(b) show the comparison of UV-Vis absorption spectra of the TiO_2 thin film (1) and dye loaded (2)TiO_2 thin film (soaked with dye A and B respectively).

From the spectra it is observed that, the percentage of absorption in the dye loaded TiO_2 thin film increases significantly in comparison to unloaded TiO_2 thin film. This indicates the good anchorage of the dye on the surfaces of TiO_2 thin film . The spectra also reveal that compared to the alcoholic extract , the aqueous dye extract show a better sensitization of TiO_2 and thus a better HOMO- LUMO interaction between the dye and TiO_2 establishing them more suitable for the fabrication of photoanode for DSSC.

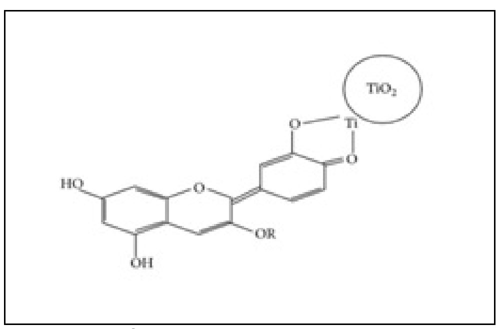

Figure 4(c): Anchorimg of TiO_2 with the anthocyanin composition of the dye

4. Conclusion

Nanoporous TiO_2 thin film deposited on a transparent glass substrate coated with conducting oxide (TCO) was prepared and was characterized by UV, XRD, SEM and HRTEM analysis to be used as the wide band gap semiconductor .Two photoanodes were fabricated by adsorbing the dye extracted from "Mesua ferrea onto the prepared TCO/TiO_2 thin films and their efficiency was investigated with the help of UV-vis absorption spectroscopy which shows that aqueous dye extract will be a better suitable sensitizer for application in DSSC.

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