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PREPARATION AND CHARACTERIZATION OF LOW COST PRUSSIAN BLUE SENSITIZED SOLAR CELL

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TiO_2 nanopowders of Anatase phase with high porosity have been synthesized by simple precipitation method. The X-ray diffraction studies revealed that the prepared TiO_2 sample exhibit Anatase phase. The Tunneling electron microscope images showed that the TiO_2 samples are highly porous in nature. Photoelectrochemical solar cell was fabricated by Prussian blue sensitized TiO_2as photo anode and graphite as counter electrode, Iodide /Triiodide solution is used as redox electrolyte. The TiO_2 thin films were prepared by doctor blade method on FTO substrate having a sheet resistance of 10 Ω. Prussian blue was sensitized on TiO_2 using electro deposition technique. The photovoltaic performance for the constructed cell show that the open circuit voltage is 0.63V, the short circuit current is 1.7mA, fill factor is 0.69 and its efficiency was 0.73%. This indicates that Prussian blue can be used as an effective sensitizer.

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1. Introduction

Dye sensitized solar cell is an attractive field of solar energy conversion. Its advantages are easy to fabricate and the production cost is low. Recently highest efficiency of 13% was achieved through molecular engineering of porphyrin sensitizers [1]. Ruthenium based dyes showed an efficiency of 12%. Prerequisites for photo sensitizers to function in DSSCs are the absorption in the visible or near-infrared regions of the solar spectrum and the binding to the semiconductor TiO_2 [2]. Various methods have been tried to increase the efficiency and reduce the cost of cell by replacing ruthenium. Instead of using molecular dye, natural dyes were also been tried. But the efficiency was not improved to a high extent. In order to increase the efficiency quantum confinement were also been tried using CdS, PbS, PbSe quantum dots. Irrespective of various efficiencies the stability of this type of solar cell was still unsolved. Instead of using a molecular dye, a semiconductor absorber can be used as light absorber [3]. In our present work TiO_2 a photo catalyst itself has been utilized in a quantum dot state. The sensitization is done with Prussian blue a highly stable structure and having a band gap of 1.4eV. Prussian blue (PB) is the traditional inorganic dye and it is still the subject of considerable research interest. This intense blue colored pigment is used in the preparation of paints, printing inks, laundry dye, etc. [4]. It has wide industrial applications such as in removal of heavy metal ions in wine production [5], electrochemical application as battery building [6], electronic switching and electro chromic devices [7]. With the high insolubility and ion exchange properties, PB was also used to remove the 137Cs from radioactive waste solutions [8] Prussian blue was selected due to its photo stability and electrochemical activity [9-13]. The selection of redox electrolyte is restricted with KI instead of LiI because of excellent cyclability response of Prussian blue to potassium ions. In order to maintain simplicity and to reduce the cost Prussian blue and KI redox electrolyte has been selected.

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2. Preparation method

2.1. Preparation of TiO_2 Nanopowders

The TiO_2 nanopowders were prepared by simple precipitation method. Precipitation method involves a combination of obtaining a precipitate and its drying process. Precipitation occurs through hydrolysis processes, the reactions starting from titanium (IV) butoxide are as follows:

$$Ti(O(CH_2)_3CH_3)_4 + 4H_2O \longrightarrow Ti(OH)_4 + 4CH_3(CH_2)OH \quad (1)$$

$$Ti(OH)_4 \longrightarrow TiO_2 + 2H_2O \quad (2)$$

In order to prepare the solution, titanium(IV)butoxide ($Ti(OC4H9)4$, (97%,AldrichChem.) was used as starting material. The reaction was necessary to take place in an acid environment, so HCl (conc.38%) was added drop wise into titanium butoxide until the solution reached a pH~2. According to the reactions to obtain TiO_2, the molar ratio of titanium butoxide:distilled water was respected,being1:5, adding distilled water under continuous stirring using a magnetic stirrer. In the presence of water, the alkoxide hydrolyzes, forming a white precipitate. After adding the entire amount of water, the precipitate obtained was left to dry at 80°C for 24 hours, then calcinated at a temperature of 300°C for 2 hours.

2.2. Preparation of Photoanode

The TiO_2 layer is coated onto FTO substrate by doctor blade method. Adding a few drops of very dilute acetic acid to 1 gram of prepared $TiO_{2,}$ the resulting mixture was grinded in a mortar and pestle until a colloidal suspension with a smooth consistency was observed. Then 2-3 drops of the TiO_2 suspension was dropped on the conductive side of FTO substrate and spread out evenly on the surface of the plate with glass rod. Then the substrate was dried at 200°C for 30min. and naturally cooled down to room temperature.

2.3. Sensitization of Prussian blue on TiO_2Thin Film

The Prussian blue was deposited on to TiO_2 film by simple electrochemical deposition process. In the process, the 0.01M of $FeCl_3$ solution was taken in a beaker and then 0.1M KCl and 0.1M HCl were added stepwise with constant stirring. Further, $K_3Fe(CN)_6$ 0.01 M was added into the reaction constant. TiO_2 coated FTO substrate is connected to negative terminal and graphite electrode is connected to positive terminal of the regulated power supply. The deposition was carried out at 2.5 V for 15 minutes leading to the formation of very smooth film of PB on TiO_2.Since the TiO_2nanopowder is having high porosity the Prussian blue completely covers the TiO_2 molecule.

2.4. Solar cell Fabrication

Dye sensitized solar cell is assembled with Graphite coated FTO glass as a counter electrode, Prussian blue sensitized Tio_2electrode as photo anode and KI/I_2 solution as electrolyte. First the graphite coated counter electrode is placed over the photo anode and it is sealed with 25mm thick thermal adhesive film. The electrolyte solution was filled between the electrodes through the hole made in the counter electrode. After the electrolyte is filled the hole is closed using an adhesive. The active area of the cell was $1cm^2$.

3. Result and discussion

3.1 XRD Analysis

Fig.1 shows the XRD image of TiO_2 prepared by precipitation method. The peak positions at 12.54, 18.825 and 23.85 confirm the structure as Anatase phase. The crystallite size has been calculated using Scherrer's formula. The broadening of peaks is due to smaller particle size. The average crystallite size of the nanopowders is found to be 4 nm.

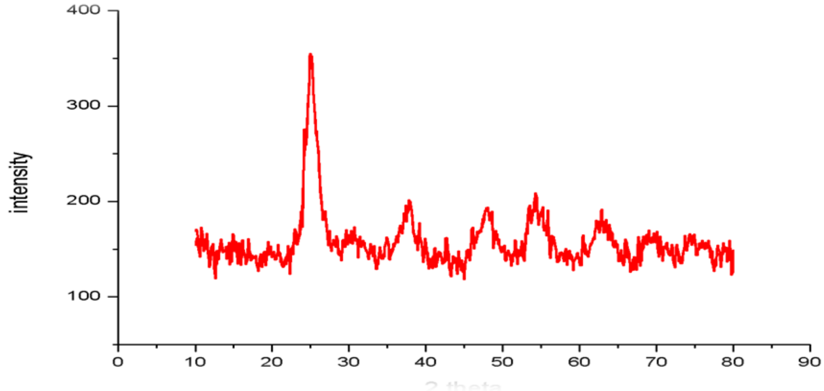


Fig. 1. XRD image of TiO_2

Peak width(degree)	Peak position(theta)	Particle size(nm)	Average particle size
1.884	12.54	4.43	3.99(nm)
2.100	18.825	4.01	
2.400	23.85	3.54	

$$D = \frac{K\lambda}{\beta cos\Theta}$$

3.2 TEM analysis

Fig.2 shows TEM image of as prepared TiO_2, which reveals the synthesized nanopowder is porous in nature. The porous nature provides a large surface area for adsorbing dye [14]. The porosity is achieved without any templates the photo excitation of dye increases with increase in porosity of TiO_2. The particle size is in the range of 30 nm to 40 nm. The variation of the particle size is due to the agglomeration of TiO_2 particles.

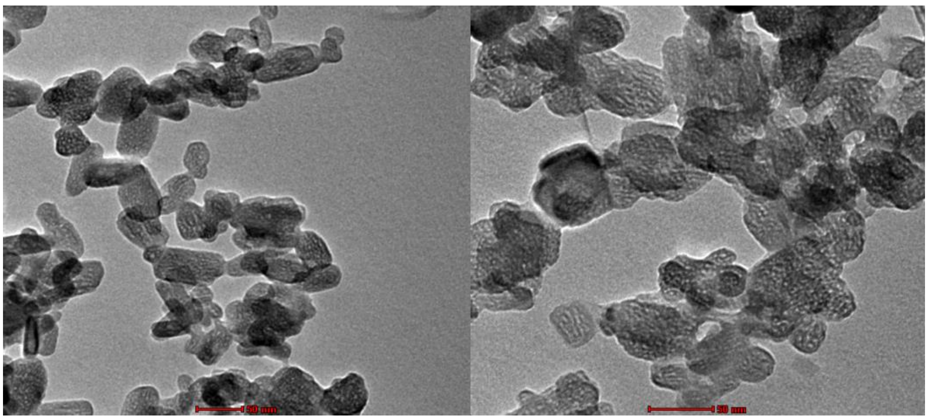
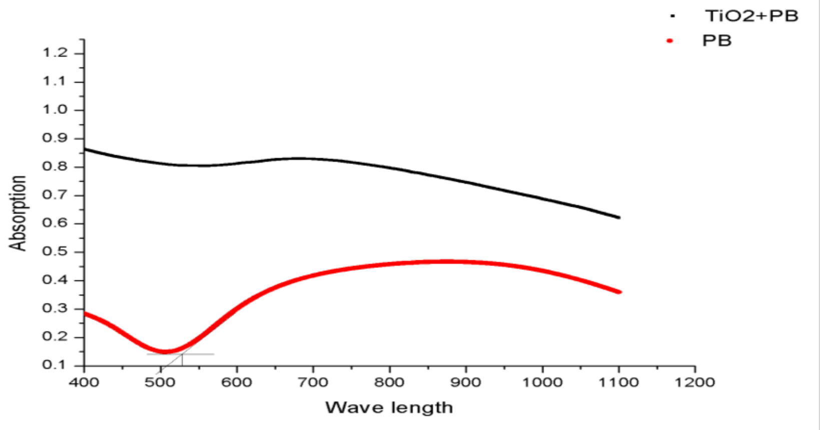


Fig.2 TEM images of TiO_2 nanoparticles at different resolution

3.3 Optical properties

Fig.3(a) and 3(b) Shows the absorption spectrum of Prussian blue dye(red line) and Prussian blue sensitized Tio_2(black line). The red line is the absorption spectrum of Prussian blue, shows the absorption peak is at 869 nm, which is at Infrared region. From the absorption peak the band gap of Prussian blue dye is calculated as 1.4 eV.



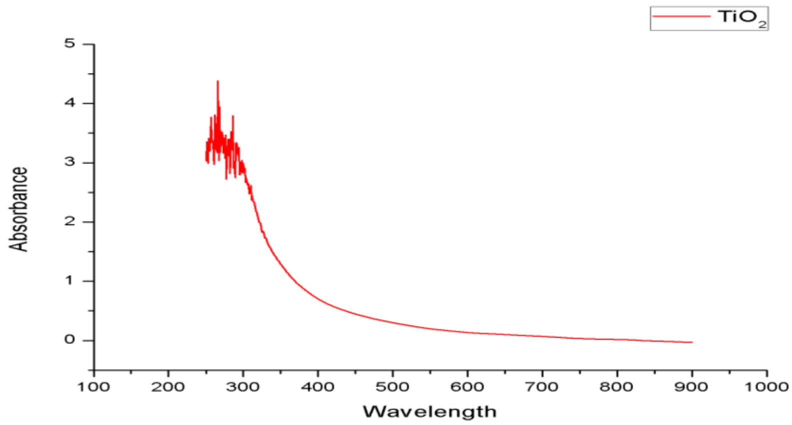


Fig.3 (a) Absorption spectra of Prussian blue and Prussian blue sensitized TiO_2.
Fig3(b) Absorption spectra of TiO_2

The absorption peak of Prussian blue sensitized TiO_2 is at 684 nm and which indicated the band gap as 1.8 eV. The absorption of light increases in Prussian blue TiO_2 combination which in turn increases the conversion efficiency. This combination utilizes the longer wavelengths of solar spectrum.

3.4 J-V Characteristics

Fig. 4 shows the J-V characteristics of Prussian blue sensitized solar cell. The solar cells conversion efficiency can be calculated from the relation.

$$\eta = \frac{Jsc * V_{OC} * Fill\ Factor}{Input\ Power}$$

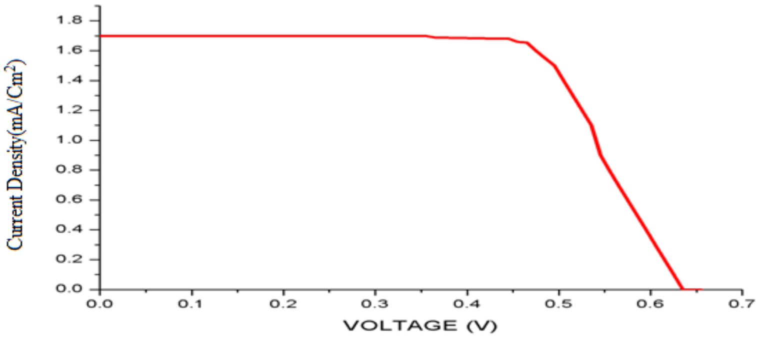


Fig.4 J-V characteristics of prussian blue sensitized solar cell

The above graph shows the open circuit voltage is 0.63V, the short circuit current density is 1.7mA/cm^2, fill factor is 0.69 and its efficiency is 0.73%. The efficiency can be improved with platinum counter electrode.

4. Conclusion

Simple and cost effective solar cell has been constructed. Highly porous Anatase phase TiO_2 nanopowders were prepared by precipitation method. The Anatase phase determination is done with XRD and porosity is determined with TEM images. The photo electrochemical properties were studied with J-V characteristics, which reveal the conversion efficiency is 0.73%. The limitation in efficiency can be increased by replacing platinum counter electrode.

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