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Titanium Dioxide Nanoparticles Preparation for Dye Sensitized Solar Cells Applications using Sol-Gel Method

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ABSTRACT

The dye-sensitized solar cell (DSSC) is a third generation photovoltaic device that holds significant promise for the inexpensive conversion of solar energy to electrical energy. The scope of the present investigation is to develop the novel DSSC based on TiO_2 nanoparticles. The pure titanium dioxide (TiO_2) nanoparticles were synthesized by sol-gel method using titanium isopropoxide and 2-proponal as a precursor. Structural characteristics of synthesized pure TiO_2 nanoparticles were studied by X-ray diffraction analysis. UV spectrum was observed to predict the band gap energy. Fourier transform infrared spectrum was recorded to investigate the presence of chemical composition in synthesized pure TiO_2 nanoparticles. Morphology of the synthesized pure TiO_2 nanoparticles was visualized by scanning electron microscope. In order to enhance the photocatalytic activity of synthesized pure TiO_2 nanoparticles, the natural rich banana flower dye (Inflorescence dye) was added to pure TiO_2 nanoparticles, which were characterized by the XRD, UV-Visible and FTIR spectroscopic techniques as well as SEM. To predict the photocatalytic efficiency of inflorescence dyed TiO_2 nanoparticle, dry solar cell was prepared by doctor-blade technique. The calculated efficiency was obtained as 0.78%. Hence, the present investigation paves new way to develop the DSSC.

1. Introduction

The ever increasing demand for energy requires the quick action to utilize the renewable energy sources effectively. Solar energy plays a vital type of renewable energy because of its unlimited nature, environmental friendliness and the potential for high power conversion efficiency in solar energy harvesting devices [1]. Solar cells are used to convert light photons from solar energy into electrons. Among the various solar cells, dye sensitized solar cell is an attempt to reproduce nature's photosynthesis process [2]. Improving power efficiency makes the devices more cost-competitive compared to traditional sources of energy [3].

The semiconductors can be used for DSSC are metal oxide nanoparticles such as titanium dioxide (TiO_2), ZnO, MnO_2 etc. Due to the superior properties such as nontoxic, inexpensive, good chemical stability and bio compatibility, the TiO_2 nanoparticles are widely used in DSSC [4, 5]. TiO_2 nanoparticles are prepared by several techniques such as sol gel, electro chemical anodization techniques and hydrothermal technique. The sol-gel method is a simple low cost and versatile technique which is used for the synthesis of TiO_2 nanoparticles in anatase phase.

The absorption of light by the metal oxide semiconductor is less due to its wide band gap and it affects the charge creation also. Hence, a sensitizer (Dye) is needed to coat on the surface of the metal oxide semiconductor. Natural dyes are considered as alternative photosensitizers for DSSCs because they are inexpensive, flexible, abundant, sustainable and reduce the use of noble metals [4]. The sensitizer can be natural dye or a chemical dye. The natural dyes attract high attention due to the low cost, nontoxic nature and maximum photovoltaic efficiency [6].

In the present study, pure TiO_2 nanoparticles were synthesized using the pure and natural dye mixed TiO_2 nanoparticles were subjected to powder X-ray diffraction, UV-Vis spectrum, scanning electron microscope to study the structural, optical, morphological and compositional studies. The DSSC was fabricated using natural dye mixed TiO_2 coated by doctor blade method on glass plate with iodide solution (I^+/I_3) electrolyte. The high rich dye banana flower sensitized DSSC showed a solar light energy to electron conversion efficiency of 0.78%.

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2. Experimental Methods

2.1 Synthesis of Pure

Sol-gel technique used for the synthesis of pure TiO_2 by taking titanium isopropoxide (Sigma-Aldrich) as one of the precursor solution and a mixture of distilled water with 2-propanol as another precursor solution. The synthesis process was started by the mixing 200 mL of double distilled water with 15 mL of 2-propanol. The pH of this first precursor solution was adjusted to 2 using decimolar nitric acid [11].

The second precursor titanium isopropoxide was taken as a 5 mL. The titanium precursor was added dropwise into the first precursor under continuous stirring in room temperature with equal interval of time. Formation of a white drop like precipitate was the immediate response from the reaction. After completing the drop wise addition of titanium precursor, the precipitation was allowed to settle down under a temperature 60 °C for half an hour. The white precipitation was washed several times in distilled water and then in methanol to remove the impurities. The precipitation was dried and fine white powder of TiO_2 was collected. The sol-gel processes with a simple modification was used for the synthesis of natural dye mixed TiO_2.

2.2 Dye Extraction

In nature, flowers, leaves, and fruits have different colors and contain several pigments that can be readily extracted and used for DSSC fabrication. The electronic structure of pigments reacts with sunlight to change the wavelengths. The specific color depends on the capacities of the viewer. Pigments can be described by the maximum absorption wavelength (λ_{max}). Natural colorants are pigmentary molecules and dyes that are mainly obtained from plants (occasionally from animals or minerals) with or without chemical treatments. Natural colorants have a hydroxyl group in their structure and are water soluble. If an alternative dye, such as a plant dye, can be made to perform as well as ruthenium

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complex dyes or organic dyes, it is interesting for both economic and environmental reasons. A goal of research on plant-based dyes for photo electrochemical solar cells is to develop a dye that can be used for the same purposes as ruthenium dyes with an acceptable efficiency. Different natural dye materials and its efficiency were calculated and given in Table 1. *Musa acuminata* (Banana flower) is one of the high content natural dye source. The clean fresh fruits and vegetables were crushed and added to Ethanol. The mixtures were centrifuged and all solutions were protected from direct light [10]. Banana flower is an important dye with good photo and electrochemical properties and sensitive to pH. Locally available fresh banana flower of 50 g was cut into small pieces and crushing the pieces, and added with 200 mL of double distilled water and ethanol. The mixture was kept for an hour to extract more dye. The extract was filtered and used for the synthesis of natural dye mixed TiO_2 [9, 10].

Table 1 Electrical parameters of measured natural DSSCs samples[20]

Dye	Jsc (mA/cm^2)	Voc (mV)	FF	η %
Red Cabbage	0.592	412	0.408	0.099
Strawberry	0.481	528	0.512	0.130
Henna	0.199	503	0.476	0.052
Mallow	0,471	550	0.527	0.140
Musa acuminata (Banana flower)	0.485	556	0.557	0.168

2.3 Dyed TiO_2 Preparation

The natural dye extracted from banana flower juice which contains Banana inflorescence as a major pigment was mixed with the first precursor solution. Since the banana inflorescence juice was extracted in water and ethanol as solvents, it got easily mixed with the precursor. Since the mixing of banana inflorescence juice varies pH of the precursor solution, nitric acid was added to maintain the pH of 2. When the two precursors were mixed in this process, instead of white precipitation, a dark brownish red precipitation was obtained. The coloration of TiO_2 was attributed to the adsorption of banana inflorescence dye on the TiO_2 nano particle. The dye aggregation on nano crystalline film produces absorptivity that may result in no electron injection and reduction in efficiency [12]. The four important parts of DSSC are dye, electrolyte, counter electrode and photo electrode.

In DSSC, the photons are converted into electric current by charge injection from excited dye molecules into the conduction band of a wide band gap semiconductor.

2.4 Solar Cell Preparation

DSSCs differ from other types of photovoltaics in both their chemical construction and the physical processes that control their operation. The performance of a solar cell depends on the performance of each of these steps and is maximized by the material and the cell design. First and second generation photovoltaic cells are based on solid semiconductor materials, while typical DSSCs combine solid and liquid phases. Fundamentally, electricity is generated on the photo electrode, which is a substrate consisting of a sintered nano porous TiO_2 film on a conducting oxide-coated glass substrate that is sensitized with a mono layer-thick dye and penetrated with electrolyte. The operation of a DSSC under illumination, lighteners through the front plate of a DSSC, and the incoming photons are absorbed by the layer of dye molecules, which leads to the excitation of the dye to an electronically excited state (S*) that lies energetically above the conduction band edge (CB) of the TiO_2 particles [20].

The dyed TiO_2 obtained by sol-gel technique was made into a paste using titanium isopropoxide solution. A thin film was coated on the glass plate using the dyed TiO_2 paced by "doctor-blade" technique with the already prepared dye mixed TiO_2 paste. The dyed TiO_2 photo anode was ready after drying. The dipping of TiO_2 film into the dye solution in the conventional process to adsorb dye is not necessary in the modified sol-gel technique due to the adsorption of dye molecules during the synthesis itself [17].

2.5 Characterization

A UV visible spectroscopy, FTIR, IR spectroscopy, Powder XRD and Scanning Electron Microscope were used to conform the surface structure and crystallinity of the sample.

3. Results and Discussion

3.1 UV-Vis Analysis

The UV-Vis absorption spectra of pure TiO_2 and dyed TiO_2 are given in Fig. 1. The absorption spectrum shows that the pure TiO_2 does not absorb the solar radiation above 320 nm. Hence TiO_2 needs a dye sensitizer to become a good solar cell photo anode material. An ideal sensitizer for a single junction photo voltaic cell converting standard global A.M.1.5 sunlight to electricity should absorb all light below a threshold wavelength of about 920 nm [3]. The natural dyed TiO_2 exhibits a good absorption peak between the end of UV region and the beginning of visible region. It exhibits a good absorption peak in visible region at 530 nm [8] which gets suppressed when mixed with TiO_2. This implies that these types of dye molecules are strongly bound to the oxide surface. The UV cutoff wavelength of pure TiO_2 nano particle is 361 nm and the band gap is calculated as 3.43 eV. The band gap of TiO_2 in anatase phase is 3.2 eV [15, 16].

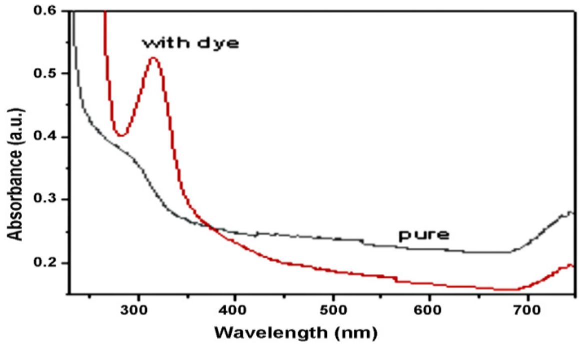

Fig. 1 UV visible patterns of (a) pure TiO_2, (b) dyed TiO_2

3.2 Powder XRD

TiO_2 nano particles prepared by sol-gel process were characterized from powder X-ray diffraction (PXRD) patterns. The PXRD of pure TiO_2 nano particles which are prepared from an acidic solution of pH 2 is shown in Fig. 2(a). The broadened diffraction peak at 2θ = 25° indicates the less crystallized anatase structure [13].

The PXRD pattern of natural dye mixed TiO_2 nano particles with similar growth conditions is shown in Fig. 2(b). From these two PXRD patterns, it is clear that the mixing of natural dye during synthesis of TiO_2 has improved the crystalline nature of the anatase phase TiO_2. Fig. 2(c) shows the PXRD of the dyed TiO_2 after calcined at a temperature of 250 °C for about 2 hrs. The nano crystalline anatase structure was confirmed by the existence of (1 0 1), (0 0 4), (2 0 0), (2 1 1) and (0 0 2) diffraction peaks. The lack of orientation corresponding to the plane (1 1 0) confirms the absence of rutile phase and complete presence of anatase phase.

Particle size was obtained by Scherrer equation,

$$D = K\lambda / (\beta \cos\theta)$$

Where, 'D' is the particle size, 'λ' is the wavelength.

X-ray radiation (λ = 0.15406 nm), 'K' is the shape factor, a dimensionless constant (0.94 in case of spherical shaped particles) and β is the full width at half-maximum height (FWHM) of the respective diffraction peaks [14]. The average particle size of the synthesized TiO_2 nano particles in anatase phase is approximately 50 nm.

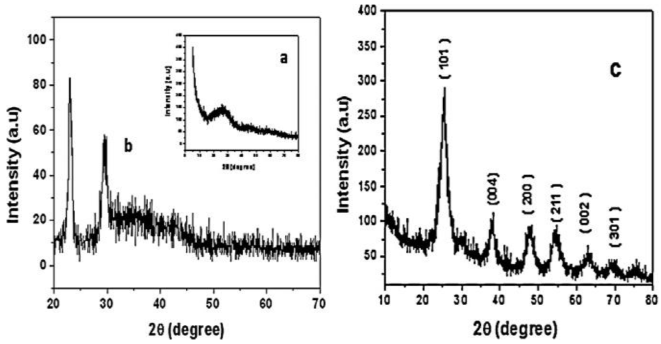

Fig. 2 PXRD patterns of (a) pure TiO_2 (b) dyed TiO_2 (c) dyed TiO_2 after calcinations at 250 °C

3.3 Scanning Electron Microscope

The mixing of natural dye during synthesis yielded uniform adsorption of dye molecules on TiO_2 and prevented the formation of nano clusters.

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The morphology of TiO_2 improved as nearly spherical particles due to the adsorption of the dye rich in inflorescence. So natural dye takes an additional role of a capping agent. The average crystalline size of TiO_2 nano particles is 50 nm and it agrees well with the value obtained from PXRD (Fig. 3).

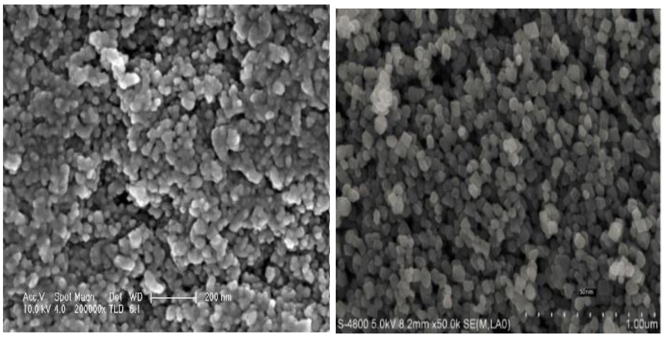

Fig. 3 SEM image of (a) pure TiO_2 and (b) dyed TiO_2

3.4 FTIR Analysis

FTIR spectrum was used to calculate the various functional groups present in titanium dioxide nanoparticles. Fig. 4 represents the FT-IR spectra of sol-gel derived comparison of pure TiO_2 and dyed TiO_2 in the range of 400-4000 cm^{-1}. The peaks at 3438.70 and 1640.26 cm^{-1} in the spectra are due to the stretching and bending vibration of the -OH group. In the spectrum of pure TiO_2, the peaks at 823.88 cm^{-1} show stretching vibration of Ti-O and peaks at 1416.38 cm^{-1} shows stretching vibrations of Ti-O-Ti. Peaks at 3438.70 cm^{-1} indicates the presence of amines, 3287.11 cm^{-1} indicates the presence of alkynes, 3011.35 cm^{-1} indicates the presence of aromatic rings, and 1712.28 cm^{-1} indicates the presence of pyridines, 1243.18 cm^{-1} indicates the presence of thiophenes.

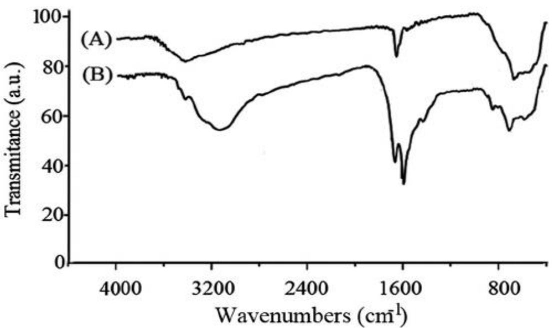

Fig. 4 FTIR image of (a) pure TiO_2 and (b) dyed TiO_2

3.5 Efficiency Studies

The fill factor (FF) was found using the equation [18]:

$$\text{Fill Factor} = (I_{max} \times V_{max}) / (I_{sc} \times V_{oc}) \quad (1)$$

where I_{max} and V_{max} denote the maximum output value of current and voltage respectively, and I_{sc} and V_{oc} denote the short circuit current and open-circuit voltage, respectively.

The values of J_{sc} = 1.64 $mAcm^{-2}$, V_{oc} = 0.65 V and the calculated value of FF=0.50.

The total energy conversion efficiency was calculated using the following equation [19]:

$$\eta = (J_{sc} \times V_{oc} \times FF) / P_{in} \quad (2)$$

where P_{in} denotes the energy of incident photon. The efficiency was calculated as 0.78% which is a good value for a natural dye sensitized DSSC and for a modified sol-gel synthesis.

4. Conclusion

Pure and dye mixed TiO_2 nano particles were synthesized using sol-gel technique. The direct mixing of natural dye is a promising method for uniform adsorption of dye and hence light to electron conversion efficiency can be improved. The structural, optical and morphological properties of pure and dye rich inflorescence mixed TiO_2 were analyzed using XRD, UV visible spectroscopy, SEM and FTIR analyses. The TiO_2 nano particles prepared are crystalline and comparatively smaller particle size having spherical morphology. The band gap of the synthesized TiO_2 nano particles is 3.43 eV and it was reduced to 3.29 eV due to the adsorption of dye. The FTIR study confirms the purity of TiO_2 and the presence of natural dye's functional group. The light to electron conversion efficiency under standard conditions is 0.78%.

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