Research Article

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Modification of Energy Band Gap in Natural Dye-Sensitized Tio_2 Nano Particles

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Abstract

The photovoltaic devices have been fabricated using conventional semiconductor materials such as silicon (Si) which are quite expensive and difficult to manufacture. Dye-sensitized solar cells (DSSCs) are attractive alternative to Si-based solar cells as they can be inexpensive, portable, thermally stable, light in weight and flexible. The pure TiO2 nano particles have been prepared by sol gel method for DSSC in this project. The anatase phase of TiO2 has been confirmed using XRD. Transmission Electron Microscopy has been used to the nano particle size of the TiO_2 nano particles. The coating of natural dyes extracted from spinach and marry gold has been done on TiO_2 nano particles. The Scanning Electron Microscope and EDX study reveals the morphology and elemental composition of the pure and natural dye coated TiO2 nano particles. Tauc's Plots confirmed decrease in band gap with the natural dye coating. The natural dye coated nano particles are found to be better candidates for DSSCs.

Keywords: Dye-sensitized solar cells, Nano particles, Titanium butaoxide, Acetyl Acetonate.

Introduction

In the last decade, the photovoltaic devices have been fabricated using conventional semiconductor materials such as silicon (Si) [1]. Dye-sensitized solar cells (DSSCs) are attractive alternative to Si-based solar cells as they can be inexpensive, portable, thermally stable, light in weight and flexible [2-4]. In general, there are three major components of DSSCs: an n-type semiconductor, a sensitizer (i.e. dye), and a redox electrolyte [5-6]. TiO_2 is the one of the most commonly used n-type semiconductor with an energy band gap of 3.2 e V [7]. Because of its high brightness, it is commonly used as pigments for paints, coatings, papers and plastics. The dielectric constant and refractive index of TiO_2 is very high which makes it an excellent optical coating or dopant for dielectric materials.

Related literature

These days, nanosized TiO_2 has attracted much attention because of its wide applications as a base material for dye-sensitized solar cells, photo catalyst and sensors [8-9]. Different nanostructured TiO_2 have been utilized as photo anodes to fabricate DSSCs, including one dimensional (1D) nano-rods, two dimensional (2D) nanotubes and three dimensional (3D) materials. Furthermore, TiO_2 nano crystals are non-toxic materials and commonly used in biological applications [10]. To enhance the chemical and physical properties of TiO_2, some additives or modifiers are applied as coatings on the pure nanosized TiO_2. These additives generate more active photo catalytic sites in TiO_2 and increase the thermal stability of nanosized TiO_2 through the realization of high specific area, enhanced interface quality, and fast electron transport [11-12]. These applications of nanosized TiO_2 are basically determined by its physico-chemical properties such as structure of crystal, grain size, surface to volume ratio, porosity and thermal stability. Furthermore these physic-chemical properties depending upon the different synthesize techniques [13].

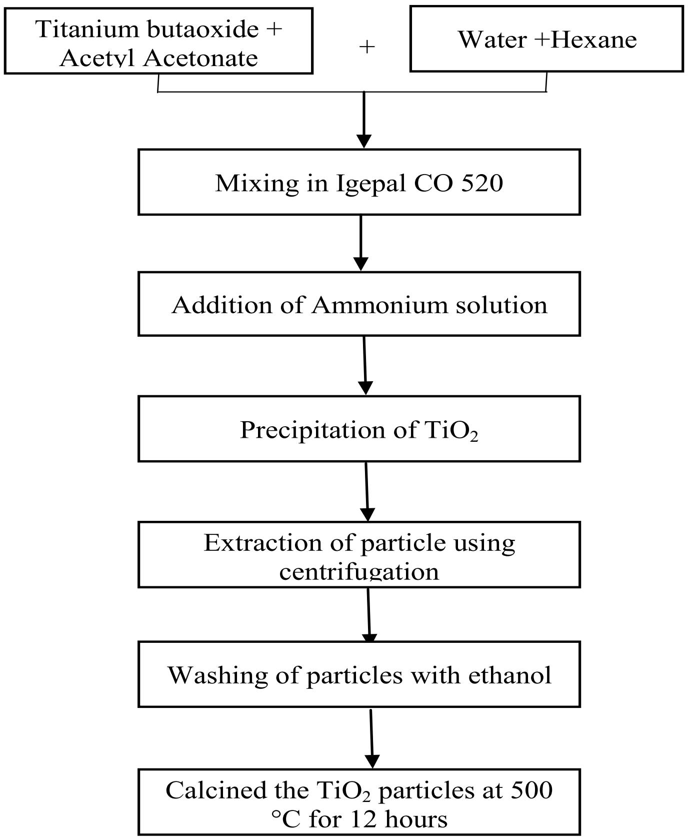
Sol gel process is a most commonly used technique to synthesize nano particles of TiO_2. This is very simple means of synthesizing the nano particles at room temperature under atmosphere pressure. Surface modification of TiO_2 semiconductor particles has an attractive potential because of the application of these materials in electro chromic and photochromic devices and dye-sensitized solar cells [14-15].

Research Design and Methodology

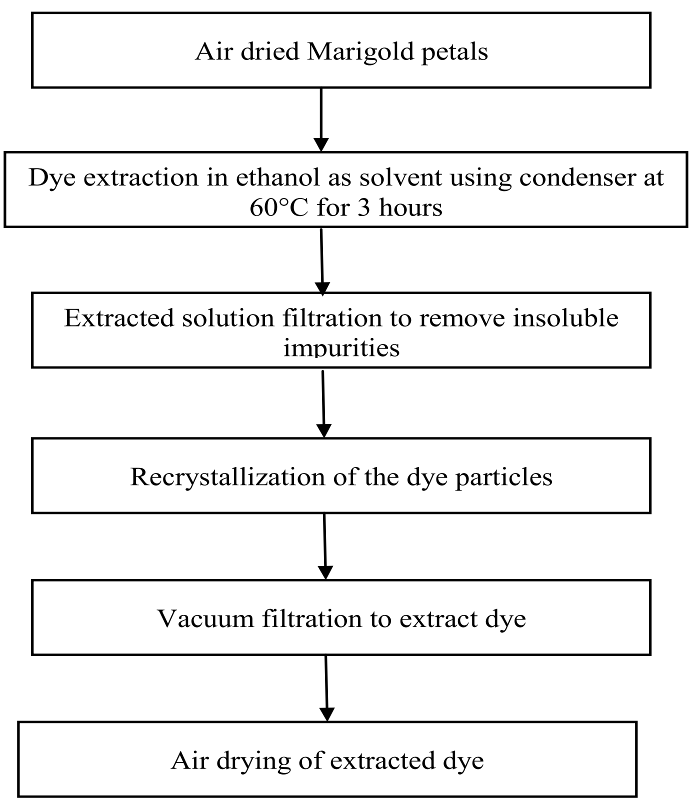
In the present study, experimentation method has been used wherein the TiO_2 nano particles were synthesized using green synthesis (sol gel) and the dyes extracted from the natural plant sources like spinach and marry gold were coated on these nano particles. The natural dye coated TiO_2 nano particles were studied for structural, micro-structural, compositional and optical properties. The main focus of the present study was to synthesize a natural dye sensitizer for solar cells. The pure TiO_2 nano particles have been prepared by sol gel method for DSSC in this project. The anatase phase of TiO_2 has been confirmed using XRD. Transmission Electron Microscopy has been used to the nano-particle size of the TiO_2 nano particles. The coating of natural dyes extracted from spinach and marry gold has been done on TiO_2 nano particles. The Scanning Electron Microscope and EDX study reveals the morphology and elemental composition of the pure and natural dye coated TiO_2 nano-particles.

Experiment Procedure

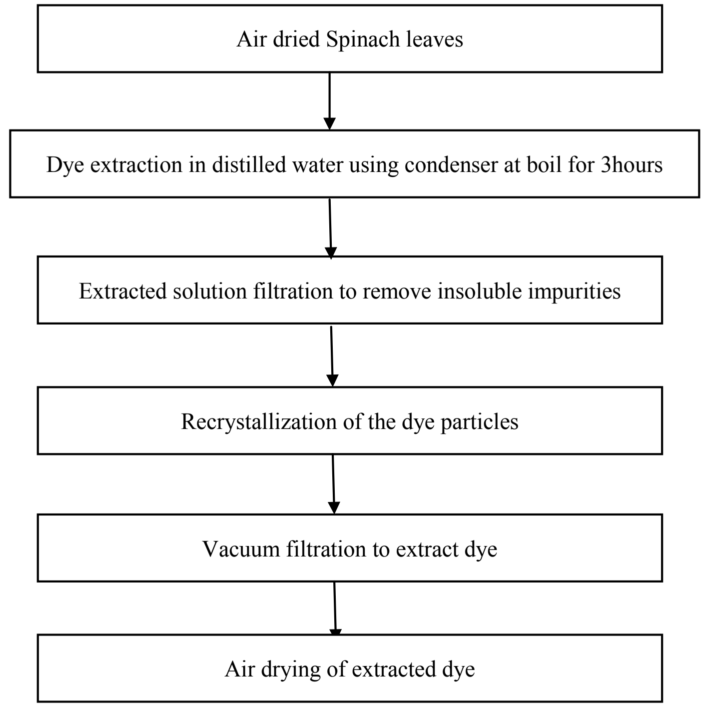
The TiO_2 nano-particles have been prepared using sol gel method. The flow chart of the synthesis is as follows.



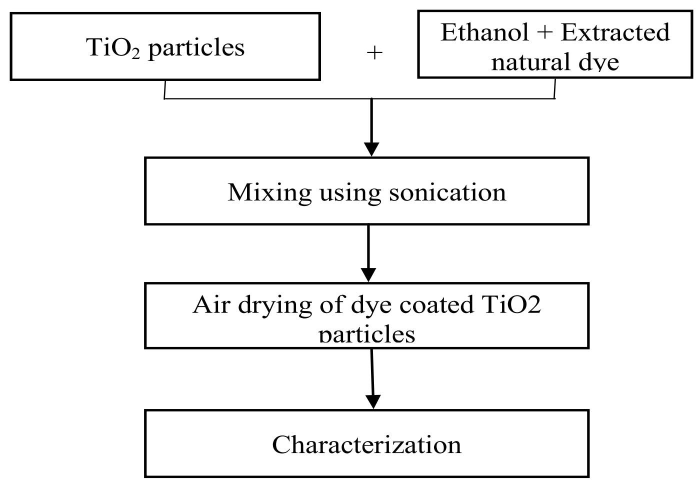
The extraction of the natural dyes has been done as follows.



Extraction of Spinach Dye



Coating of the dyes on the TiO_2 nano particles



Results and Discussions

The X-ray diffraction is an important tool to analyze the crystal structure of the materials. The X-Ray diffraction pattern of TiO_2 is shown in figure 1.1. The XRD pattern clearly reveals the crystalline nature of the sample. All the peaks in TiO_2 nanoparticles are indexed according to the Anatase phase of TiO_2.

No secondary phase has been detected in the XRD pattern. The crystal structure of the sample is tetragonal with large "c/a" ratio. All the peaks of the above diffraction pattern were indexed using space group I41/amd (space group number 141).

The crystallite size of the TiO_2 powder has been calculated using Scherer equation.

$$\tau = K\lambda/\beta Cos\theta$$

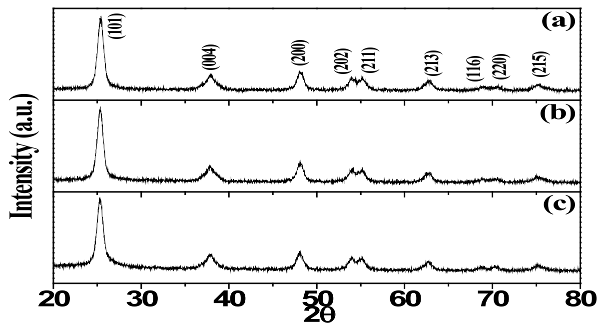


Figure 1: X-Ray diffraction patterns for the pure TiO_2 nano particles, spinach dye coated nano particles and marry gold flower TiO_2 nano particles using Cu kα radiations.

Where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. λ is the X-ray wavelength. β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. θ is the Bragg angle. The typical value of the crystallite size was calculated for the TiO_2 powder from XRD pattern is ~12nm.

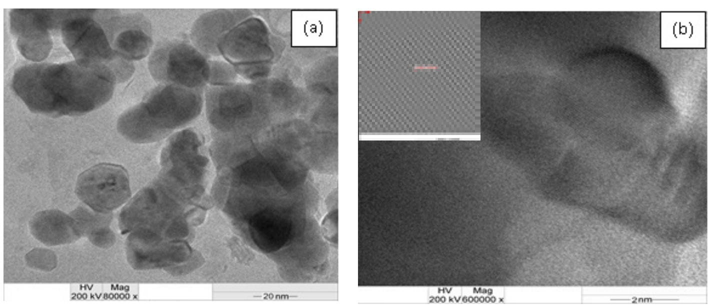


Figure 2: (a) TEM image of the TiO_2 nano particles. The average size of the particle is found to be ~17 nm. (b) HRTEM images of the TiO_2 particle clearly evident the crystal planes. The FFT image of the crystal planes (inset).

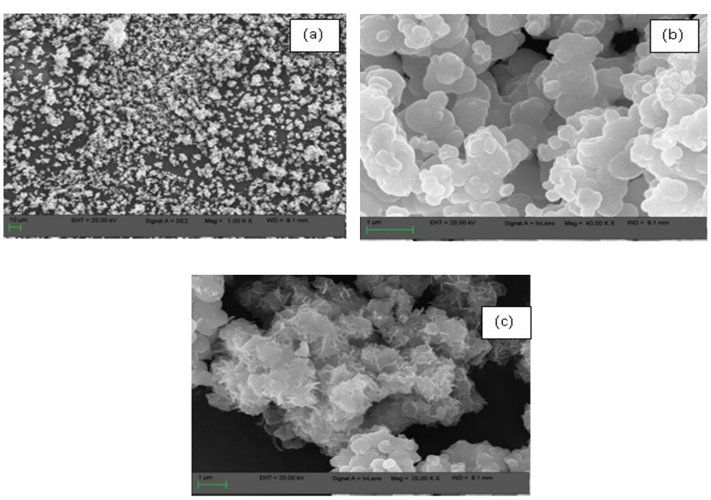


Figure 3: The SEM micrographs for the pure TiO_2 powder at various magnifications.

The transmission electron micrograph of the TiO_2 particles has been observed (Figure 2(a)). It is clearly evident from the image that the uniform particles have been formed by this synthesis method. The average particle size is found to be ~ 17 nm. HRTEM image of the particle has been taken at very high magnification ~ 6,00,000 X. The fringes are clearly seen from the figure 2(b).

The FF transform of the fringes were done to find out the distance between the fringes. The distance of one black fringe is ~0.099nm, which is in good agreement with the XRD data.

The morphology of the powder samples was studied using Scanning Electron Microscope (Carl Zeiss, Germany). The micrographs were taken by spreading the powder particles on the carbon tape. The micrographs were taken at various magnifications and at different locations to analyze the same extensively. Figure 4.2 shows various micrographs. Figure 4.2(a) shows the morphology of the samples at low magnification ~1000 X. The overview of the sample shows that the morphology is same and uniform. As the magnification was increased two different kinds of morphologies are observed. The figures 4.2(b) and (c) show both types of morphologies. In the sample the morphology which is shown in figure 4.2(c) is predominant in the sample as compared to the figure 4.2(b). So it can be concluded that there may be mixing of rutile and anatase phase of the TiO_2 in the sample. Due to very less amount of the rutile phase the Anatase phase is clearly evident in the XRD whereas some cluster of the particles show rutile phase formation on SEM micrographs.

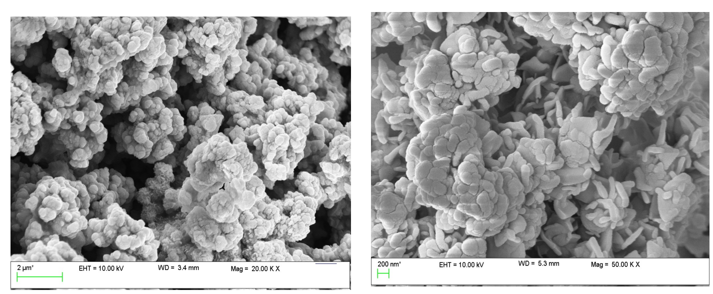


Figure 4: The Scanning electron micrographs of Dye Coated TiO_2 Nano Particles (a) Spinach dye coated TiO_2 nano Particles, (b) Marry gold dye coated TiO_2 nano particles.

The TiO_2 nano particles coated with extracted dyes from spinach and marry gold flowers show some different morphology as compared to pure TiO_2 nano particles. In figure 1(a) it is clearly evident that the spinach dye coated TiO_2 nano particles are larger as compared to the pure TiO_2 nano particles. The morphology of the spinach dye coated TiO_2 nano particles is uniform throughout the sample and the particles are more agglomerated.

The morphology of marry gold dye coated TiO_2 nano particles has been shown in figure 1(b). The morphology of the sample is almost similar to the pure TiO_2 nano particles. The two morphologies have been clearly evident from the SEM micrographs.

Element	Weight %
Ti	44.72
O	55.28

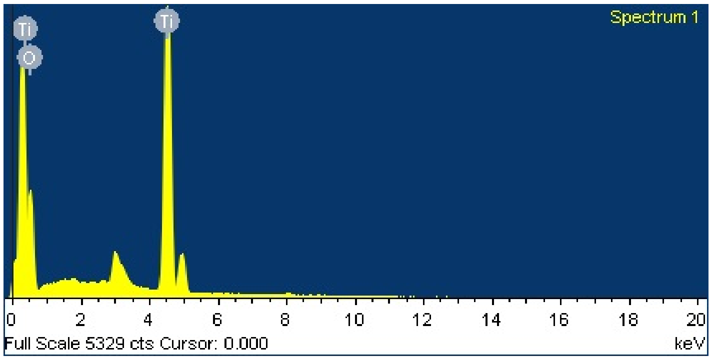
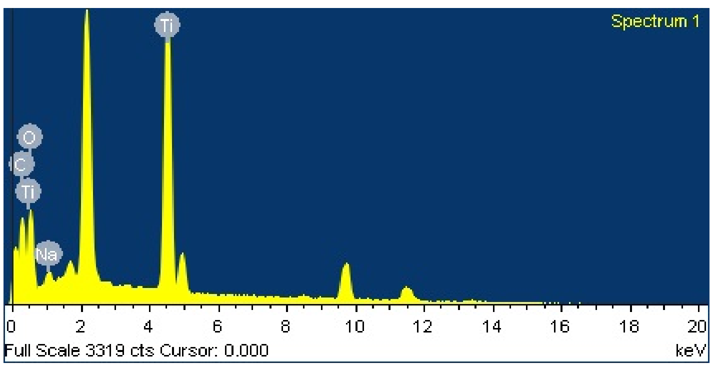


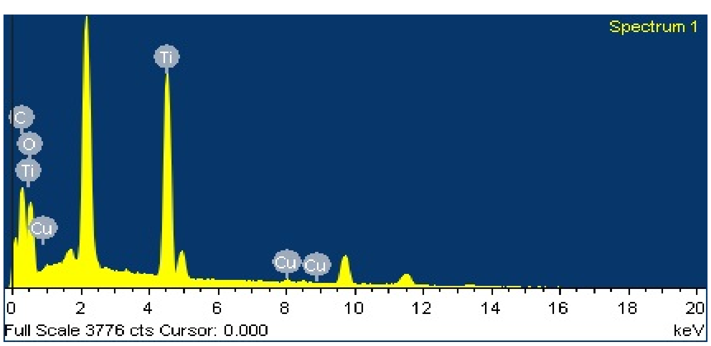
Figure 5(a): Energy dispersive X-ray analysis of pure TiO_2 nano particles.

Element	Weight %
Ti	35.55
O	47.17
Na	1.64
C	15.64



Figrue 5(b): Energy dispersive X-ray analysis of spinach dye coated TiO_2 nano particles.

Element	Weight %
Ti	30.85
O	47.15
Cu	1.57
C	20.42



Figrue 5(c): Energy dispersive X-ray analysis of marry gold flower dye coated TiO_2 nano particles.

The energy dispersive X-ray analysis of the pure TiO_2 nano particles, spinach dye coated nano particles and marry gold flower TiO_2 nano particles have been shown in figure 2,3 and 4. It is clearly evident that the pure TiO_2 nano particles does not have any other element except Ti and O, whereas the presence of Na and Cu have been found in spinach dye coated nano particles and marry gold flower TiO_2 nano particles respectively. So the EDX analysis clearly indicates the compositions of elements present in the sample.

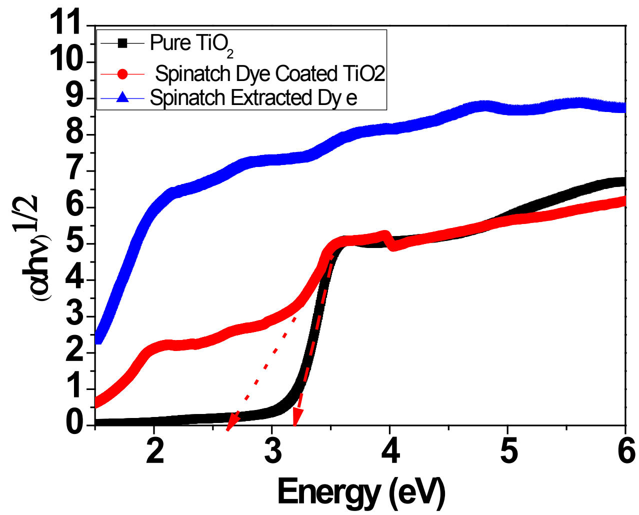


Figure 6: The Tauc's plot for the pure TiO_2 nano particles, spinach dye coated nano particles and pure extracted spinach dye.

The UV Visible spectrum has been observed for the pure TiO_2 nano particles, spinach dye coated nano particles and marry gold flower TiO_2 nano particles with UV Visible spectrometer in the wavelength range 200nm-900nm. The Tauc's plots ((αhω) 1/2 vs. energy) are derived from the absorption vs. wavelength graphs. The pure TiO_2 nano particles clearly show that a sharp absorption edge at ~400 nm and the band gap calculated from the Tauc's plots is 3.2 e V. However the Tauc's plots of spinach extracted dye and spinach dye coated nano particles show a different behavior. There is no absorption edge and band gap has been found for the pure Dye. The absorption edge for the spinach dye coated nano particles is very week and broad. The band gap calculated for the spinach dye coated nano particles is around 2.6 e V. It is clearly evident the band gap decreases with the coating of spinach organic dye to the pure TiO_2 nano particles, which makes the spinach dye coated nano particles suitable for the solar cell applications. The Tauc's plots of marry gold dye and marry gold dye coated TiO_2 nano particles has been shown in the fig.6. For the comparison the Tauc's plot for pure TiO_2 nano particles have also been given in the figure. Marry gold dye also does not show any absorption edge in the whole range of spectra. However the marry gold dye coated nano particles show a decreased band gap ~1.94 e V. This decreased band gap may be due to the presence of Cu in marry-gold dye coated TiO_2 nano particles. So it is also evident that these dye coated nano particles are good materials for the application of solar cell.

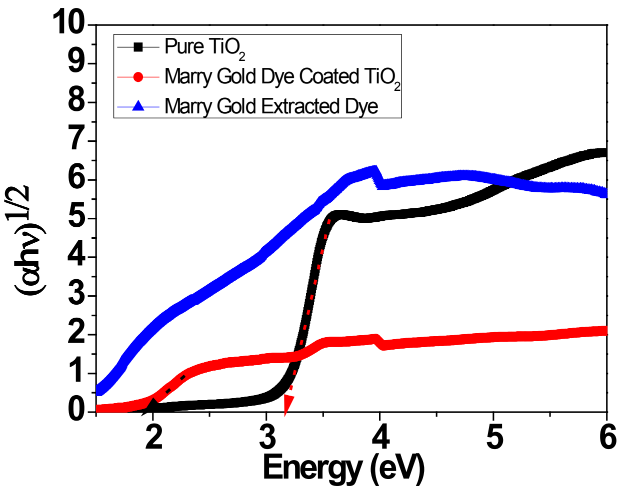


Figure 7: The Tauc's plot for the pure TiO_2 nano particles, marry gold dye coated TiO_2 nano particles and pure extracted marry gold dye.

Findings and Recommendations

The pure TiO_2 nano particles are synthesized by using green synthesis (Sol gel method). The pure TiO_2 nano particles are found of the size of ~11nm - 20 nm. The optical properties of TiO_2 nano particles has been observed and found that TiO_2 nano particles as a band gap of 3.2 e V. The dye extracted from spinach and marry gold flower has been coated on the TiO_2 nano particles and the physical properties of these particles has been recorded. The elemental composition with the dye coating has been changed and the presence of Na and Cu has been found in the spinach and marry gold dye coated TiO_2 nano particles. Dye-sensitized solar cells (DSSCs) prepared through this experiment are recommended to be attractive alternative to Si-based solar cells as they can be inexpensive, portable, thermally stable, light in weight and flexible.

Conclusion

The pure TiO_2 nano particles have been successfully prepared by sol gel method for DSSC in this project. The optical properties of dye coated particles clearly give the evidence of decrease in band gap; which makes the dye coated TiO_2 nano particles as the suitable materials for solar cells and provide and effective alternative for solar cells.

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