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Development of Novel Materials with Photocatalytic Effect

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Abstract

For capturing solar energy and for converting it into electric power, it is utmost essential to design materials that can be used for this purpose. Generally, the materials deployed for converting solar energy into electric energy are sensitive to UV-radiation. If the material used for this purpose are sensitive to visible light, it will be the breakthrough research. It has been a challenge to design materials with novelty of being sensitive to visible light. The present paper deals with designing novel materials, sensitive to visible light. For this, UV-sensitive, Titanium dioxide (TiO_2) was doped with Cadmium and Tungsten by two different methods. First method involved Ex-situ modification of nanoparticles of the anatase form of titanium dioxide, carried out by doping with cadmium sulphide and tungsten trioxide. Second method involved in-situ simultaneous synthesis of nanoparticles of titanium dioxide and the dopants, using the precursors tetra butyl titanate for titanium dioxide, cadmium chloride for cadmium and sodium tungstate for tungsten. The doped materials were evaluated for characteristics demonstrating their sensitivity to visible light. Results obtained for ex-situ method showed reduction in the band gap energy of TiO_2 from 3.2 eV to 2.82 eV and 2.81eV by doping with 1% by wt. of cadmium sulfide and 4% by wt. of tungsten trioxide, respectively, at 400°C. For in-situ method, reduction in band gap energy of TiO_2 was observed, from 3.2eV to 2.73eV and 2.81eV with cadmium precursor and tungsten precursor, respectively. In both the cases, doped material exhibited photocatalytic effect in visible light.

Keywords: Titanium dioxide, Photocatalytic activity, band gap, ex-situ, in-situ

INTRODUCTION

It is because of such attributes that one aims to exploit TiO_2 as much as possible, for capturing and converting solar energy into electric energy. Since TiO_2 is sensitive only to UV light, it is utmost essential to modify TiO_2 for making it sensitive to visible light. If this drawback of being sensitive only to UV light is taken care of, by modifying TiO_2 into a material sensitive to visible light, it will serve a great purpose. In other words, by eliminating limitations of TiO_2 (from being UV sensitive to becoming visible-light sensitive), it will be possible to exploit complete potential of this material for capturing a wide spectrum of solar light. It will be a novel work which will help in making solar cells highly efficient, productive and cost effective.

In the present study, the aim is to overcome main limitation of TiO_2, by making the latter sensitive to visible region of solar spectrum. To be able to render the desired changes at the molecular level of

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TiO_2 so that it exhibits photocatalytic effect in the visible region of the solar spectrum, innovative approaches were required.

The inherent features of titanium dioxide (TiO_2) are of value, making the latter suitable for various applications by virtue of its photocatalytic effect [1, 2]. As a result, TiO_2 is used as:

1. A semiconductor, with high activity in UV range,
2. Completely inert nature, making it highly stable and compatible.
3. Easy and abundant availability
4. Low cost.

From the survey of the literature published so far, it is evident that it is possible to modify TiO_2 to render its effectiveness in the visible region of light. There are several leads from the literature which suggest that it is feasible to convert the UV-active TiO_2 into the visible active titanium dioxide. In the first place, it may be noted that the anatase form of TiO_2 exhibits better activity, absorbing significantly higher amounts of radiation in the complete solar spectra including visible light as compared to the rutile form of titanium dioxide. This means that the starting material to be taken for the modification will have to be anatase form of titanium dioxide. In case, there exist a significant fraction of rutile, the material should be subjected to sintering at an appropriate temperature to obtain the anatase form with little content of rutile. Secondly, the modification of TiO_2 has to done at the molecular level in such a manner that its crystalline structure gets changed. The crystal lattice parameters should be changed in a manner that the modified TiO_2 absorbs solar light in the visible region. In other words, the band gap energy has to be brought down to a level where the visible region of solar light can affect transitions when it falls on the crystal surface of modified titanium dioxide. In brief, it can be said that the naturally available TiO_2 must be subjected to modification by way of converting anatase form to rutile and followed by the modification by way of affecting changes within the crystal lattice. Of the several approaches tried so far, the incorporation of materials with low band gap energy along with heat treatment has been adopted here to achieve modifications in titanium dioxide. This was done by doping the low band gap energy material onto the lattice of TiO_2 (anatase) by heat treatment. A novel approach of in-situ doping has also been attempted in one of the cases.

There are certain materials of lower band gap energy tried and tested for their use for designing materials sensitive to visible region of sunlight. The literature review provides leads based on which further research may help in development of composites capable of converting even the visible light into electricity of the materials known for low band gap energy, salts of cadmium and tungsten were chosen for this purpose.

MATERIALS

The raw materials used in each step for the preparation of novel photocatalytic materials by ex-situ and in-situ methodologies have been described as follows:

1. *Ex-situ methodology:* The modification of band gap energy of titanium dioxide by ex-situ methodology involves the doping of nanoparticles of titanium dioxide. The materials used are as follows:
    i. *Titanium dioxide:* Anatase form of titanium dioxide was procured from Sigma Aldrich of 99 % purity having particle size in the range of 25 nm to 100 nm. Since the band gap energy of titanium dioxide lies on the border line of the UV-Visible region, therefore, it was found to be the most suitable material to be used as a base for the preparation of a novel photocatalytic material or device. Also, easy availability, cost effectiveness and its environment friendliness make it the most appropriate candidate to be used for the present study.
    ii. *Cadmium sulfide as dopant 1:* Cadmium sulfide (CdS) was used for the modification of band gap energy of titanium dioxide from the UV-region to visible region. Cadmium sulfide was procured from CDH of LR grade and used for the doping studies.

   iii. *Tungsten trioxide as dopant 2:* Tungsten trioxide was used for the modification of band gap energy of titanium dioxide from the UV region to visible region. Tungsten trioxide, procured from CDH of LR grade was used for the doping studies.

2. *In-situ methodology:* Nanoparticles of titanium dioxide were synthesized by in-situ method involved in the modification of titanium dioxide. Precursors of titanium dioxide and the inorganic salts were used for the simultaneous synthesis and modification of titanium dioxide. The details are as follows:
   i. *Precursor of titanium dioxide:* In the present study, tetra butyl titanate was used as an organic precursor of titanium dioxide, containing 28.02% of titanium in it. The tetra butyl titanate was procured from Synthochem Pvt. Ltd., India with purity of > 99% and was used as such without any further purification.
   ii. *Inorganic salts of cadmium and tungsten:* Inorganic salts of cadmium and tungsten were used as precursors for the modification of nanoparticles of titanium dioxide.
      - *Precursor of cadmium:* Cadmium chloride was used as a precursor for the in-situ preparation of photocatalyst. Cadmium chloride was procured from S.d. Fine Chem. Pvt. Ltd. to be used for experimental studies involved in the synthesis and modification of titanium dioxide.
        Hydrogen sulfide was also used in case of precursor 1, for the preparation of cadmium sulfide in the reaction involved for modification of titanium dioxide. Hydrogen sulphide was generated using iron sulphide (FeS) and sulphuric acid (H_2SO_4) as given in Equation 4.1. The reaction was carried in ambient conditions. Iron sulfide of 87% purity from CDH, LR grade and sulfuric acid of 98% purity from Hi-Media were used for experimental studies.
        $FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$ Equation 1
      - *Precursor of tungsten:* In-situ modification of titanium dioxide was carried out using sodium tungstate with precursor of titanium dioxide. Sodium tungstate was procured from CDH, laboratory reagent and was used in the present study.

METHODOLOGY ADOPTED

Modification of titanium dioxide for alteration of band gap energy achieved via both ex-situ and in-situ methods.

1. *Ex-situ method:* Ex-situ methodology was adopted for the modification of band gap energy of titanium dioxide. The methodology involves the doping of titanium dioxide by the use of cadmium sulfide and tungsten trioxide. In this method, nanoparticles of titanium dioxide were procured from the market to be used for the purpose. Titanium dioxide was mixed with varying weight percentages of (Table 1) the dopant salts i.e. cadmium sulfide/tungsten trioxide in a mortar pestle to prepare a homogenous mixture. The compositions were heated for two hours at various temperatures, i.e. 200°C, 300°C, 400°C and 600°C (Figure 1).
2. *In-situ method:* In-situ method was adopted for simultaneous synthesis and modification of titanium dioxide to achieve photocatalytic activity in visible region was done. In this method, organic titanate was used as a precursor for the synthesis of nanoparticles of titanium dioxide. Cadmium chloride and sodium tungstate were used as precursors for the synthesis of dopants like cadmium and tungsten, respectively.

Synthesis and Doping of Titanium Dioxide

The organic titanate i.e. tetra butyl titanate and dopant precursor were taken together in the bubbler flask. Hydrogen sulphide gas was passed through the flask containing titanate and cadmium precursors. The methodology adopted for the modification of band gap energy is shown schematically in Figure 2.

Table 1. Compositions of titanium dioxide with varying percentages of dopant i.e. cadmium sulfide/tungsten trioxide used for the doping of titanium dioxide by ex-situ method.

S.N.	Titanium dioxide (% by wt.)	Dopant (Cadmium Sulfide/Tungsten trioxide (% by wt.))

1.	100	0
2.	99.0	1.0
3.	97.0	3.0
4.	96.0	4.0
5.	95.0	5.0
6.	93.0	7.0
7.	91.0	9.0

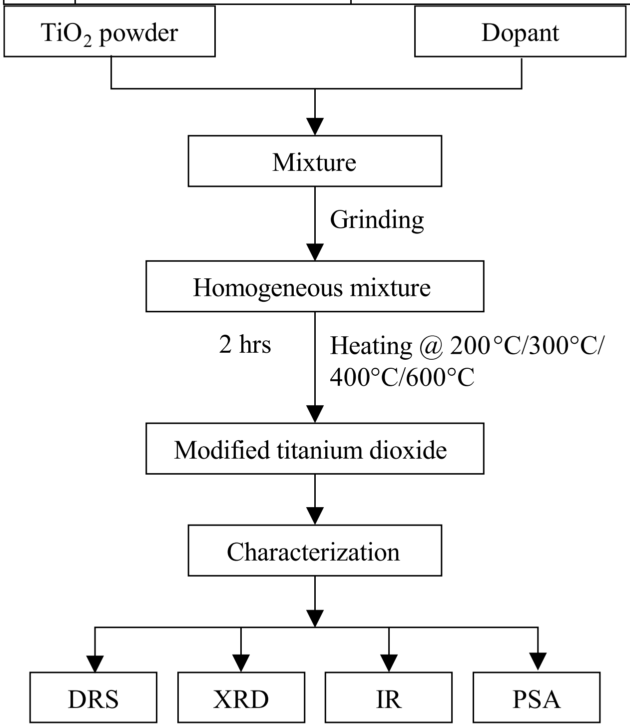

Figure 1. Flow diagram for doping of titanium dioxide using ex-situ methodology.

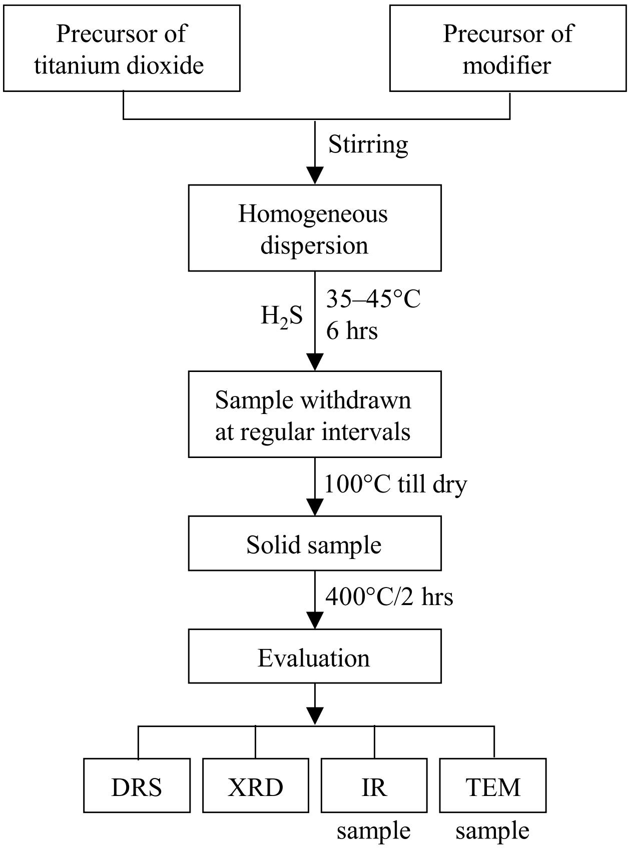

Figure 2. Flow diagram of methodology adopted of in-situ method showing simultaneous synthesis and modification of titanium dioxide.

The organic titanate in liquid form was taken in a bubbler flask. Cadmium chloride/ sodium tungstate as precursor was added gradually at room temperature under continuous stirring to the organic titanate. The reaction mixture was stirred continuously using a magnetic stirrer for the purpose of mixing of the dopant precursor with organic titanate. Hydrogen sulfide gas was passed at a flow rate of 10ml / minute for the precipitation of cadmium sulfide from cadmium chloride and tungsten trioxide in case with sodium tungstate as the precursor dopant. Samples were withdrawn at regular intervals of 2 hrs after subjecting it to heat treatment. The samples were dried at 100°C followed by calcination at 400°C for 1 hour.

Mixtures of TiO_2 and varying amounts of dopants were subjected to heat treatment at temperatures from ambient to 200°C, 300°C, 400°C and 600°C for a period of 2 hours. It may be mentioned here that during the initial trials done for the optimization of time for heat treatment, it was established that within the period of 1 to 3 hours, maximum advantage is achieved. If the material is kept for more than 4 hours, the tendency of deterioration sets in and hence, all these studies presented here are conducted for 2 hours of heat treatment.

The prepared compositions by both the methods were further characterized by X-ray diffraction (XRD), particle size analyser (PSA) and transmission electron microscopy (TEM) and IR spectrophotometer (FTIR) was used for evaluation of various structural interactions between titanium dioxide and the dopants used in the present study. State-of-the-art instrumentation techniques were used to characterize the prepared doped compositions.

1. *Powder X-ray diffractometer (PXRD):* Powder X-ray Diffractometer (PXRD), Phillips Analytical was used to analyze the atomic structure of materials. Titanium dioxide as such and modified titanium dioxide by both methods (using cadmium and tungsten salts) were analyzed

using PXRD to identify the crystalline phase and evaluate the change in crystal lattice of titanium dioxide after its modification.

2. *Particle size analyzer (PSA):* Dynamic light scattering was used to measure the particle size of the prepared photocatalyst in the suspension. It is based on the principle of Brownian motion of the particles. Particle Size analyzer (PSA), from Metrohm Inc. Zetatrac S3000 and Microtrac S3500 were used to determine particle size distribution of the samples. This instrument is based on the laser diffraction method.
3. *Transmission electron microscope (TEM):* Transmission Electron Microscope (TEM) is a technique used for imaging solid materials at atomic resolution. Structural information can be acquired both by imaging as well as by electron diffraction. In TEM, high energy electrons are used instead of photons and electromagnetic lenses instead of glass lenses. Transmission Electron Microscope (TEM), Morgagni 268D was used to study nanoparticles by means of its size and shape. Nanoparticles of titanium dioxide modified with cadmium and tungsten salts were analyzed by transmission electron microscope for the evaluation of its size and shape.
4. *Infra-red spectroscopy (FT-IR):* Infrared spectroscopy deals with the infrared region of the electromagnetic spectrum. Infrared has a longer wavelength and lower frequency than visible light. Infrared spectroscope, FTIR-ATR BOMEM (FTLA 2000) was used to understand the structural changes taking place after modification of titanium dioxide. The results could be manifested on the basis of the characteristic of the bond formed. The FTIR Spectrophotometer in transmittance mode from 4000–400 cm^{-1} was used.

RESULTS AND DISCUSSION

The results obtained during the modification of TiO_2 using salts of cadmium and tungsten by adopting both ex-situ and in-situ approaches have been discussed here. In order to understand whether TiO_2 has been modified or not, the specimens were characterized by PXRD. Further, particle size and particle size distribution using Particle size analyzer and changes at atomic level by TEM/SEM were also carried out. For establishing modifications at the molecular level, IR spectroscopic studies were carried out. From the IR studies, it was possible to ascertain interactions between the dopant and substrate in doped compositions.

The objective of the study was to modify the photoactivity of TiO_2 from the UV region to the visible region. This was made possible by the doping of TiO_2 with cadmium sulphide and tungsten trioxide by ex-situ and in-situ methods. TiO_2 is known to have a high recombination rate of electron-hole pairs formed in photocatalytic processes and it is a major limitation because of which it is sensitive only in UV region. In order to overcome this limitation, several methods of modification have been attempted, as per the published literature, in order to increase the hole–electron separation efficiency. One of the prominent methods pertains to noble metal doping as reported by Lee, et al. 2005, Sarkany, et al. 2003 and Lai, et al. 2008 [3–5]. The other approach adopted by Lin, et al. 2008 [6], for achieving the desired goal was by coupling with other semiconductors. Dye sensitization was a unique method demonstrated by Ghicov, et al. 2009 [7]. In addition to these methods, there are some notable studies that need to be highlighted here: a) coupling TiO_2 with silica reported by Takat, et al. 1997; Fu, et al. 1996 [8-9] and b) embedding the silicon into TiO_2 matrix by Yan, et al. 2005 [10]. These studies were reported to create novel structures which exhibited excellent photocatalytic activity. Incorporation of silicon atoms into TiO_2 matrix was found to result in an increased thermal stability and decreased crystallite size of the silicon-modified TiO_2. Park and Jung, 2000 reported [11] the effect of Si-doping on photocatalytic behaviour of TiO_2 and attributed the increase in surface area and crystallinity by embedding amorphous silica into TiO_2. All these studies help in arriving at the experimental plan for the present study.

In the present work, both ex-situ and in-situ methods were tried for the preparation of titanium dioxide-cadmium sulphide (TiO_2-CdS) compositions and titanium dioxide-tungsten trioxide compositions (TiO_2-WO_3). While the ex-situ method involved heat treatment of a mixture of CdS-TiO_2 compositions in various ratios, the in-situ method involved the in-situ synthesis of nanoparticles of TiO_2 and CdS, using precursors such as polybutyl titanate and cadmium chloride, respectively. The following Equation 2 can be used to explain the reaction taking place between cadmium chloride (dopant) and tetrabutyl titanate (substrate) to result in doped compositions of TiO_2 with CdS, in the presence of Hydrogen sulphide.

$$\underset{\text{(Cadmium Chloride)}}{CdCl_2} + \underset{\text{(Tetrabutyl Titanate)}}{C_{16}H_{36}O_4Ti} \xrightarrow[\text{Equation 2}]{H_2S} CdS - TiO_2 + HCl + \text{by-products}$$

Similarly, both ex-situ and in-situ methods were used for the preparation of doped compositions of TiO_2–WO_3. The in-situ method involved the use of sodium tungstate as a precursor for WO_3 and tetrabutyl titanate as a precursor of TiO_2. The following equation can be used to explain the reaction taking place between sodium tungstate (dopant) and tetrabutyl titanate (substrate) to result in doped TiO_2 doped with WO_3 in the presence of heat.

$$\underset{\text{(Cadmium Chloride)}}{Na_2WO_4} + \underset{\text{(Tetrabutyl Titanate)}}{C_{16}H_{36}O_4Ti} \xrightarrow[\text{Equation 3}]{\text{Heat}} TiO_2 - WO_3 + \text{by-products}$$

The compositions of TiO_2-CdS and TiO_2-WO_3 prepared by both ex-situ and in-situ methods were characterized to study the effect of doping on the morphology and particle size of TiO_2. Powder X-Ray Diffraction (PXRD) analysis was carried out to identify the chemical composition and the crystalline phase obtained during ex-situ and in-situ methodologies. The results of various studies are described in the following section.

Powder X-Ray Diffraction (PXRD) Studies

The results of PXRD studies for doped composition of TiO_2 with cadmium sulphide by ex-situ method and in-situ method are presented in Figure 3. The diffraction patterns of TiO_2 doped with WO_3 by ex-situ and in-situ methods are given in Figure 4. The PXRD of reference TiO_2 was taken from JCPDS 21-1272.

From the results of PXRD diffraction pattern, it can be seen that 2θ value of 25.3°, seen in the reference sample was obtained in Figures 3 and 4 confirming that the anatase form of TiO_2 was formed

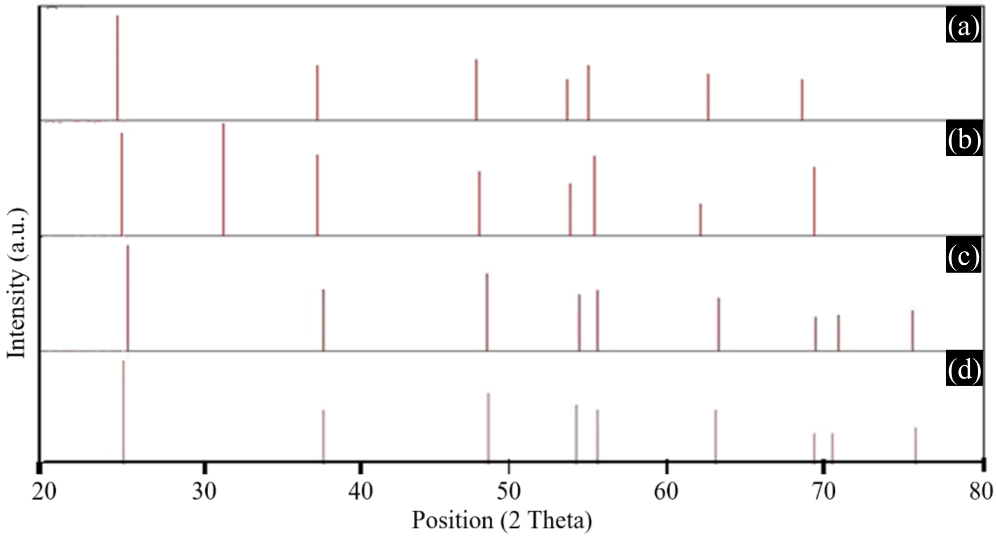

Figure 3. PXRD pattern of (a) reference-TiO_2 (b) TiO_2 used for doping studies (c) Cd-doped composition by ex-situ method and (d) Cd-doped composition by in-situ method. PXRD results for in-situ method confirm that there is formation of TiO_2 as evident from 2θ value of 25.3° matching with that of standard anatase TiO_2.

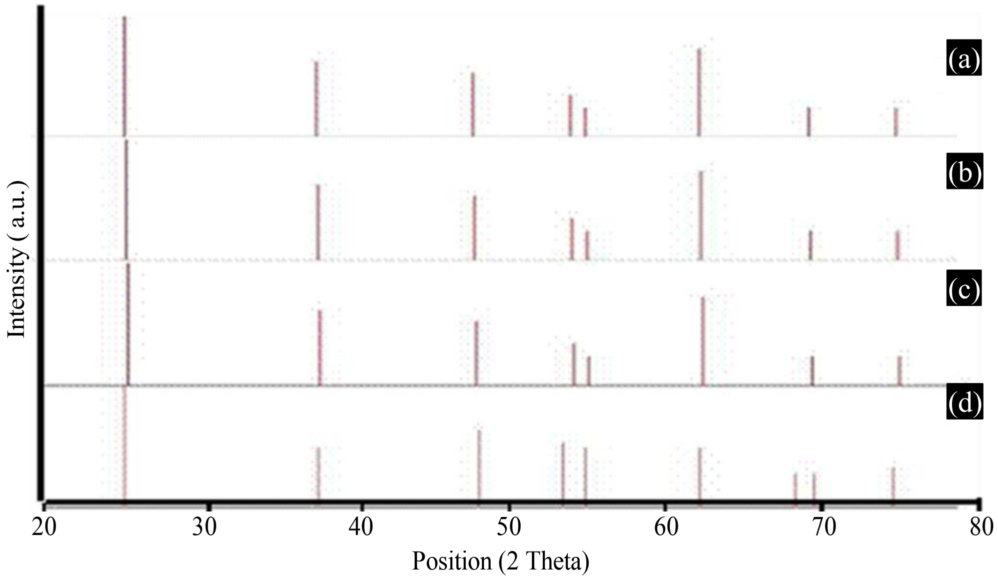

Figure 4. PXRD pattern of (a) reference-TiO_2 (b) TiO_2 used for doping studies (c) W-doped composition by ex-situ method and (d) W-doped composition by in-situ method. PXRD results for in-situ method confirm that there is formation of TiO_2 as evident from 2θ value of 25.3° matching with that of standard anatase TiO_2.

in the methodology involving in-situ synthesis of titanium dioxide. From spectral pattern (Figure 3) of the ex-situ composition, it can be concluded that the doped composition has anatase form of TiO_2 as the substrate on which dopant is attached. It can be seen that the PXRD patterns of the samples formed by ex-situ and in-situ methods agreed closely with the PXRD pattern of the anatase form of TiO_2 which was taken as the reference.

Here it may be noted that the presence of cadmium in the doped composition was not detected in the PXRD pattern in both the in-situ and ex-situ methods, because of the fact that the content of cadmium in the composition was well below the detection limit of the PXRD.

Two doping mechanisms of TiO_2 with cadmium sulphide are possible i.e. substitutional and interstitial. Because of the relatively large size mismatch with Ti^{4+} (0.68 Å) cations, Cd^{2+} (0.97 Å) is not expected to occupy the titanium sites in the lattice of anatase. It is more likely that they stay on the particle surfaces, at grain boundaries and grain junctions. These relatively large Cd^{+2} cations at the grain boundaries and grain junctions inhibit growth of crystals of titania through the formation of Cd-O-Ti bonds which increase the diffusion barrier at the titania grain junctions [12]. The higher photocatalytic activity of cadmium doped TiO_2 was attributed to the trapping of conduction band electrons by cadmium, which prevents the electron-hole recombination, thereby enhancing the redox reactions on the surface of TiO_2. This may be responsible for partial contraction of anatase structure thereby decreasing ‘d’ value. Therefore, Cd doped TiO_2 exhibit a decreasing crystallinity with increasing level of cadmium in the material [13].

Compositions of TiO_2 with tungsten trioxide prepared by ex-situ and in-situ methods were analyzed by X-ray diffractometer. PXRD pattern (Figure 4) was used to identify the crystal phase present in the system and to determine the influence of tungsten doping on TiO_2 structure.

In the case of PXRD pattern of anatase titanium dioxide, a high reflex at 2θ = 25.3° and the lower ones at 37.8°, 47.9°, 53.9° and 54.9° are observed. In the present case of tungsten doping, substitutional doping is more likely to occur due to the radius of Ti^{4+} (0.68 Å) being almost equal to that of W^{6+} (0.65 Å) [14,15]. This will in turn result in the increment in the lattice parameters and cell volume. As a result, the positions of diffraction peaks for WO_3-TiO_2 shifted to lower diffraction angles. A 2θ value of 25.3° was obtained which is similar to the anatase form of titanium dioxide. This confirms the formation of anatase form of titanium dioxide. PXRD pattern also indicates the absence of peak due to tungsten attributed to the low content of tungsten doped at the lattice of Ti^{4+} which is below the detection limit of the instrument. The other reason could be that the dopant was incorporated into the structures of TiO_2 and substituted the lattice titanium and oxygen atoms or located at the interstitial site.

However, the changes that are taking place at the crystal level such as the lattice parameters are evident from the results presented in Table 2 for TiO_2-CdS and Table 3 for TiO_2-WO_3 system. The effect of doping on the crystal lattice of TiO_2 was determined by studying the change in lattice parameters ‘a’ and ‘c’ of TiO_2 (Table 3).

From the results, it is evident that there is a change in the lattice parameters ‘a’ and ‘c’ of TiO_2 prepared by both ex-situ and in-situ methods and hence further confirms doping of TiO_2 to have taken place.

Table 2. Effect of doping on TiO_2 and its lattice parameters ‘a’ and ‘c’, by both ex-situ and in-situ methods indicating a change in lattice parameter ‘a’ and ‘c’ of TiO_2 confirming the doping using Cadmium ions.

Influence factor	TiO_2 (Reported)	TiO_2 (Experimental)	Doped TiO_2 (ex-situ)	Modified TiO_2 (in-situ)
a/nm	3.78	3.03	3.30	3.35
c/nm	9.51	9.57	11.42	11.25

Table 3. Effect of doping on TiO_2 and its lattice parameters ‘a’ and ‘c’, change in lattice parameter of TiO_2 confirms the doping using tungsten ions at the surface of titanium dioxide.

Influence factor	TiO_2 (Reported)	TiO_2 (Experimental)	Doped TiO_2 (ex-situ)	Modified TiO_2 (in-situ)
a/nm	3.78	3.03	3.73	3.20
c/nm	9.51	9.57	10.08	10.24

The parameters ‘a’ and ‘c’ were calculated using the Braggs Law equation. The experimental values of titanium dioxide achieved were closely similar to the reported value. From these results, following conclusions can be drawn:

1. For the samples synthesized by ex-situ methodology, the lattice parameters ‘a’ of 3.30 and lattice parameter ‘c’ of 11.42 were obtained. In the case of in-situ method, formation of TiO_2 in anatase form with a value of 3.35 for ‘a’ and 11.25 for ‘c’ was obtained. The change in lattice parameters confirmed that the doping of TiO_2 has taken place
2. Because of the presence of the dopant, for titanium dioxide-cadmium sulphide compositions, the ‘a’ and ‘c’ parameters have undergone a shift from 3.03 to 3.30 in the case of ex-situ method and from 3.03 to 3.35 in the case of in-situ method. The ‘c’ parameter shifts from 9.57 for undoped TiO_2 to 11.42 in the case of TiO_2 prepared by ex-situ methods and 11.25 in the case of in-situ methods.
3. Because of the presence of the dopant, for titanium dioxide-tungsten trioxide compositions the ‘a’ and ‘c’ parameters had undergone a shift from 3.03 to 3.30 in the case of ex-situ method and from 3.03 to 3.35 in the case of in-situ method. The ‘c’ parameter shifted from 9.57 for undoped TiO_2 to 11.42 in the case of TiO_2 prepared by ex-situ methods and 11.25 in the case of in-situ methods.
4. The change in ‘a’ and ‘c’ parameters was more pronounced in the case of in-situ incorporation of dopant as compared to ex-situ incorporation.

From the above results, it is evident that the doping is taking place by virtue of the heat treatment causing the dopant to get into the lattice replacing the titanium atoms (ions). Since the in-situ method of preparation involved the interactions of atoms in solution and at the scales in the region of much less than nanoscale, the doping must have taken place more efficiently in the in-situ method.

Particle Size Analysis

Results of analysis of particle size and particle size distribution, of doped compositions of TiO_2 prepared by ex-situ as well as in-situ methods, are presented in Figure 5. In the case of specimens of ex-situ doping of TiO_2, it may be noted that the average particle size of doped TiO_2 was reduced from 100nm (in the case of TiO_2 as such) to 65 nm when the doping was done with 1% by weight of Cadmium sulphide at 400°C. Looking at the results of particle size distribution for doped composition of TiO_2 by ex-situ, it is evident that particle size range is much narrower than that of TiO_2 as such. In the case of in-situ doping, both the average particle size and distribution of particle size are much lower and narrower in comparison to the results of ex-situ doped compositions. For example, the particle size ranged from 25 nm to 100 nm for composition doped by ex-situ, whereas for a similar composition prepared by the in-situ method, particle size ranged from 25 to 87 nm.

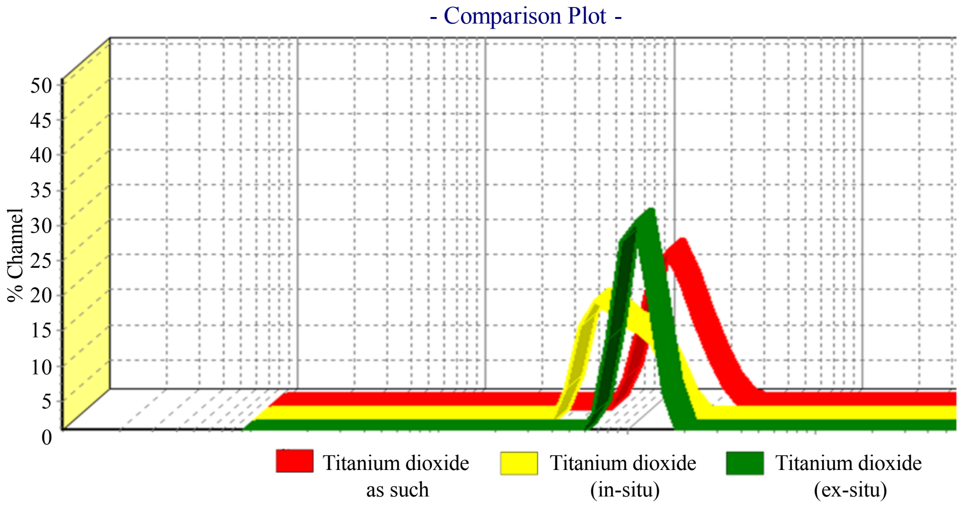

Figure 5. Particle size analysis of TiO_2 as such TiO_2 synthesized by ex-situ and TiO_2 synthesized by in-situ indicates particle size in the range of 25-100 nm.

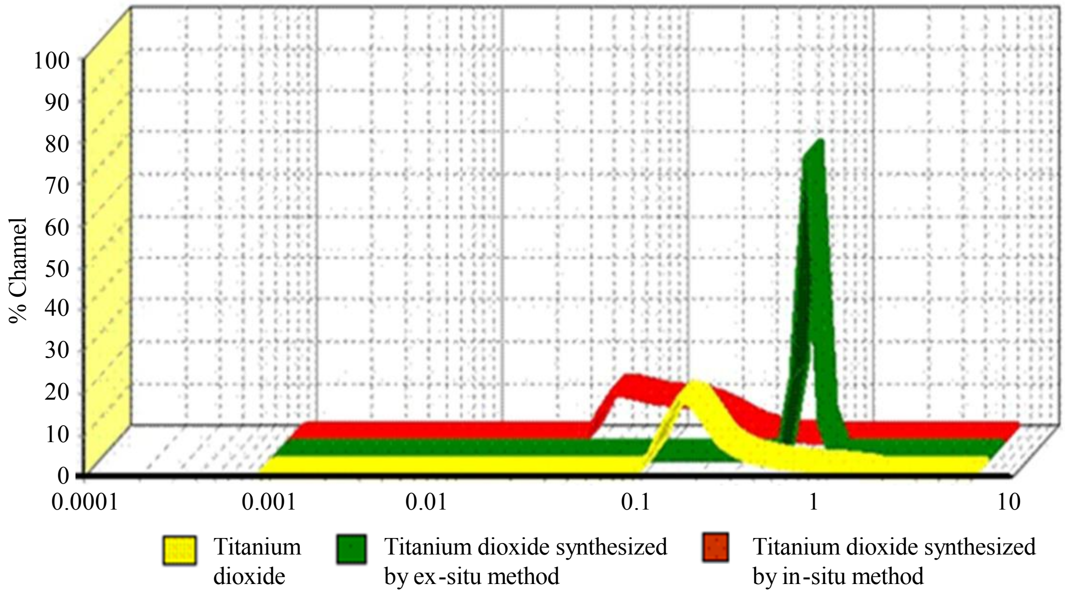

Figure 6. Particle size analysis of TiO_2 as such TiO_2 synthesized by ex-situ method and TiO_2 synthesized by in-situ method indicates particle size in the range of 25-150 nm.

Results of particle size analysis of doped composition of TiO_2 with tungsten are presented in Figure 6. Looking at the results of particle size distribution for doped composition of TiO_2 by ex-situ and in-situ method, it is evident that the particle size lies in the range of 25 nm to 150 nm.

In the case of in-situ doping, both the average particle size and distribution of particle size are much lower in comparison to the results of ex-situ doped compositions, ranged from 25 to 75 nm. Whereas, by ex-situ method of doping does not affect the initial particle size of the TiO_2. The particles size ranged from 100 nm to150 nm for composition doped by ex-situ method.

The particle size obtained in the in-situ method is attributed to the particle size of TiO_2, CdS and WO_3 confirming the fact that the in-situ methodology adopted in the present study resulted in synthesizing nanoparticles of doped compositions.

Transmission Electron Microscopy (TEM) Analysis

The TEM images in Figure 7 show the morphology of cadmium doped titanium dioxide using ex-situ and in-situ methods. Figure 7(a) shows that Cd-doped TiO_2 prepared by ex-situ method and Figure 7(b) shows the Cd-doped TiO_2 by in-situ method. The particles were found to be in the range of 25 nm – 65 nm spherical in the shape when prepared by both the methods, but it was observed that agglomeration was negligible in case of doped TiO_2 prepared by in-situ method. In-situ method was found to be more effective in synthesis and dispersion of nanodoped TiO_2 with an average particle size of 25 nm – 65 nm.

The TEM images in Figure 8 show the morphology of tungsten doped TiO_2. Figure 8(a) shows that W-doped TiO_2 prepared by ex-situ method and Figure 8(b) shows the W-doped TiO_2 by in-situ method. The particles were found to be in the range of 15 nm to 30 nm spherical in the shape when prepared by both the methods, but it was observed that agglomeration was negligible in case of doped TiO_2 prepared by in-situ method. The in-situ method was found to be more effective in synthesis and dispersion of nanodoped TiO_2 with an average particle size of 15 nm–30 nm.

Results of TEM analysis therefore, corroborate findings of particle size analyser used for the study, confirming that the in-situ method for doping is superior to ex-situ method.

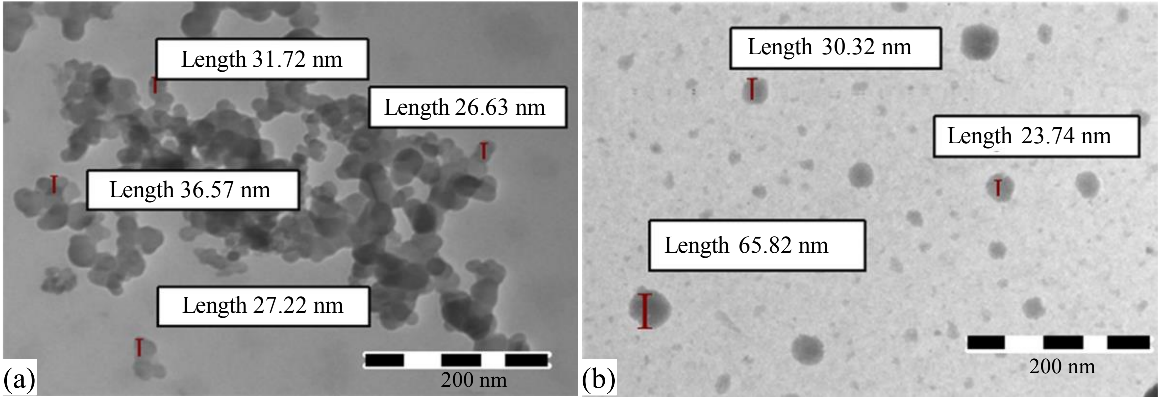

Figure 7. TEM pictures of TiO_2 – CdS compositions prepared by (a) ex-situ method and (b) in-situ method, confirming the formation of spherical particles with an average particle size of 27.22 nm to 31.72 for ex-situ method and 23.74 nm to 30.32 nm by in-situ method.

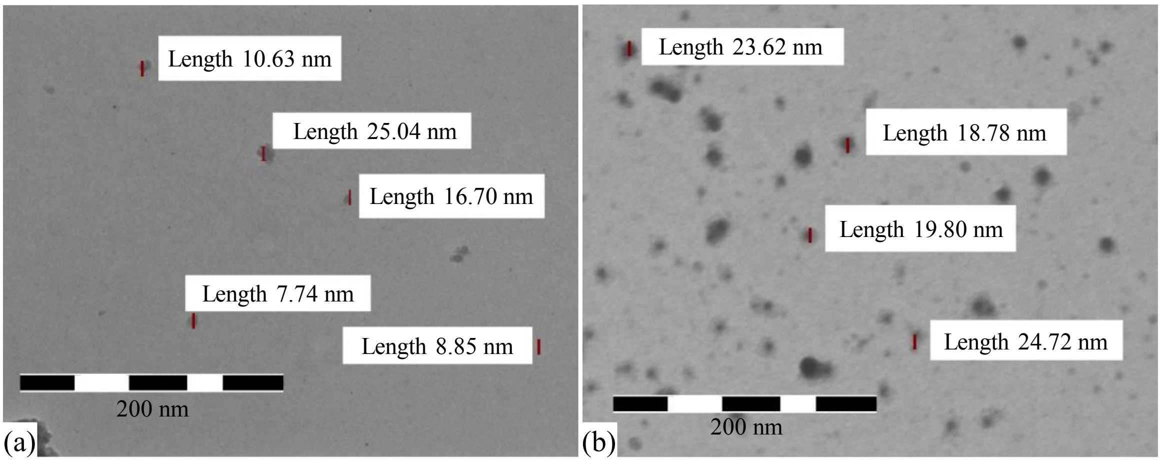

Figure 8. TEM pictures of TiO_2-WO_3 compositions prepared by (a) ex-situ method and (b) in-situ method, confirming the presence of spherical particles in the size range of 15 nm to 30 nm.

Infra Red Spectroscopy (IR)

The IR analysis of TiO_2 and CdS used for the ex-situ preparation of the TiO_2-CdS compositions along with the IR spectra of the final composition, in the transmittance mode ranging from 400 to 4000cm^{-1} are presented in Figure 9(a).

The IR analysis of TiO_2 and tungsten trioxide used for the ex-situ preparation of the TiO_2–WO_3 compositions along with the IR spectra of the final composition, in the transmittance mode ranging from 400 to 4000cm^{-1} are presented in Figure 9(b).

The spectra of TiO_2 exhibit a broad intense band below 1200 cm^{-1} and 500-900 cm^{-1} attributed to Ti-O-Ti; at 920 cm^{-1} and 490 cm^{-1} attributed to Ti-O and at 860 cm^{-1} attributed to Ti-O-Ti. The presence of some weak transmittance bands between 3400 and 3600cm^{-1} and at 1625cm^{-1} are seen, which are attributed to the stretching vibrations of the O-H groups and the bending vibrations of the adsorbed water molecules, respectively [16-20]. A band between 650 and 830cm^{-1} is seen which is attributed to different vibrational modes of TiO_2. Anatase and rutile phases of TiO_2 exhibit strong FT-IR absorption bands in the regions of 850-650 and 800-650 cm^{-1}, respectively [21, 22].

In the case of IR spectra of CdS, the absorption peak at 3404 cm^{-1} corresponds to the -OH group of water absorbed by the sample. The weak absorption band at 1630.5 cm^{-1} was attributed to CO_2 adsorbed on the surface of the particles, which is common for all powder samples exposed to the atmosphere [23].

For the compositions of CdS-TiO_2 prepared at ambient temperatures, characteristic peaks of cadmium sulphide and TiO_2 as such were observed at 401 cm^{-1}, 555 cm^{-1} and 3490 cm^{-1} due to TiO_2 as such and peaks at 1153 cm^{-1}, 1284 cm^{-1}, 1654 cm^{-1} and 2430 cm^{-1} due to CdS were observed confirming the fact that at ambient temperature no interactions take place between CdS and TiO_2. The IR spectra of the composition heated at 400 °C is shown in Figure 9(a) where the presence of prominent peaks at 2379 cm^{-1}, 2927 cm^{-1}, 2981 cm^{-1} and 3490 cm^{-1} were seen confirming interactions between CdS and TiO_2.

For the composition of titanium dioxide-cadmium sulphide prepared in-situ, shift in the absorbance frequency of the peaks obtained at ambient temperature is obtained. Peak shift from 401 cm^{-1} and 555 cm^{-1} to 412 cm^{-1} and 505 cm^{-1} respectively followed by a peak shift from 3490 cm^{-1} to 3417 cm^{-1} was obtained. It can also be seen from the IR spectra that the in-situ method adopted has led to the simultaneous synthesis and modification of nanoparticles of TiO_2.

For the compositions of WO_3- TiO_2 prepared at ambient temperatures (Figure 9(b)), peaks due to tungsten trioxide as such were observed at 405 cm^{-1} and at 1674 cm^{-1} due to cadmium sulphide.

When the compositions were heated to 400°C, peak shift of the compositions prepared at ambient temperature were observed i.e. from 408cm^{-1} to 405cm^{-1}, 578 cm^{-1} to 520 cm^{-1}, from 1512cm^{-1} to 1465cm^{-1}, from 1650 cm^{-1} to 1654 cm^{-1} and from 3498 cm^{-1} to 3475 cm^{-1} were obtained confirming the modification of the structure of TiO_2 due to interactions with CdS.

For the composition of titanium dioxide-tungsten trioxide prepared in-situ, peaks at 474 cm^{-1} and 550 cm^{-1} were observed which were attributed to Ti-O interactions. Peaks at 686 cm^{-1} and 898 cm^{-1} attributed to W-O-W was observed. Peaks at 1674 cm^{-1} and 2430 cm^{-1} due to –OH-W are observed and at 3517 cm^{-1} and 3737 cm^{-1} due to interactions W-OH and water. The IR spectra confirm the simultaneous formation of nanoparticles of TiO_2 and its modification during the in-situ synthesis [24].

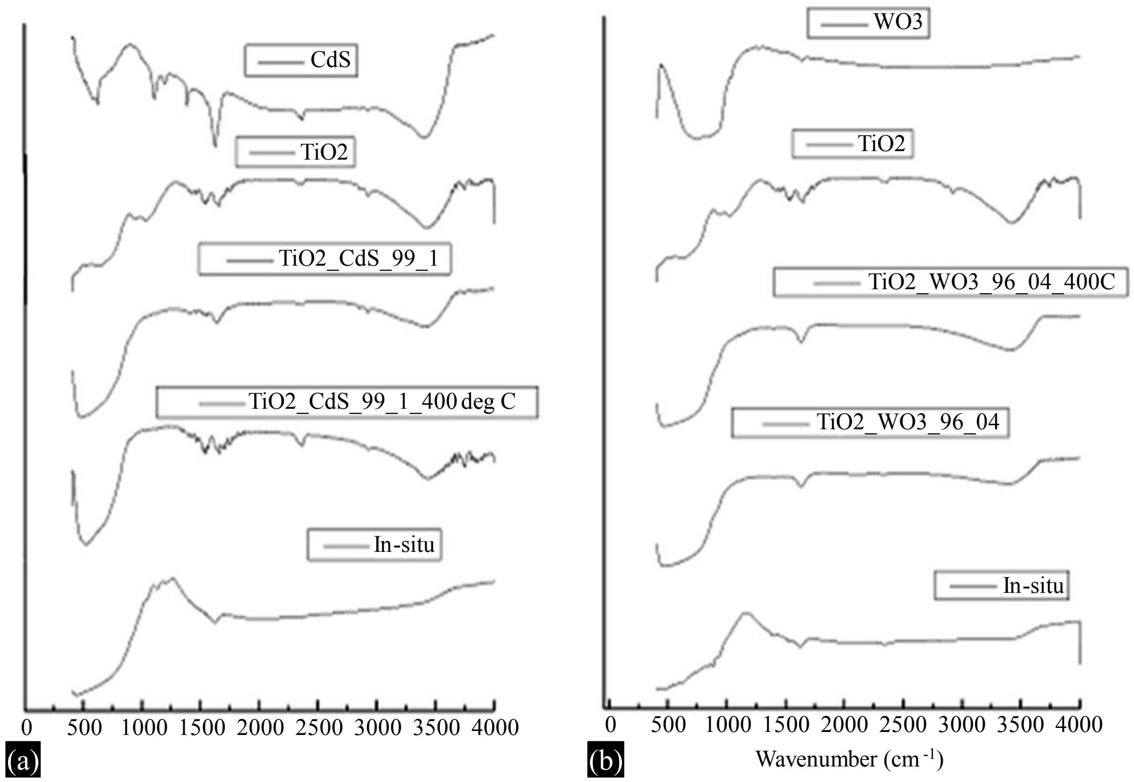

Figure 9. FTIR spectra of (a) TiO_2-CdS compositions and (b) TiO_2-WO_3 compositions prepared by ex-situ method and in-situ method.

From the IR spectra of TiO_2-CdS and TiO_2-WO_3 compositions it can be concluded that the presence of CdS and WO_3 lead to modifications in the lattice structure of TiO_2.

CONCLUSION

In the present study, doping of TiO_2 was done by ex-situ as well as in-situ methods using Cadmium and tungsten salts. Doped samples were evaluated by X-Ray Diffractometer (PXRD), particle shape and size by Transmission electron microscope (TEM) and particle size analyser (PSA). IR spectroscopy was used to understand the interactions between the various constituents. From the present study, following conclusions can be drawn:

1. The band gap energy of titanium dioxide (3.2eV) which lies in the UV region was modified to extend the photoactivity of titanium dioxide from the UV region to UV-visible region of electromagnetic spectrum.
2. Photocatalysts having band gap energies in the visible region such as cadmium sulphide (2.8eV) and tungsten trioxide (2.4eV) were used to modify the band gap energy of titanium dioxide from UV region to UV-visible region.

3. The modification in the spectral activity of titanium dioxide was carried out by two methodologies i.e. Ex-situ method and In-situ method.
4. Synthesis and doping of nanoparticles of TiO_2 with CdS and WO_3 can be successfully done by both ex-situ as well as in-situ methods.
5. In case of ex-situ method, the band gap energy of titanium dioxide was modified from 3.2 eV to 2.82 eV and 2.81eV by doping with 1% by wt. of cadmium sulfide and 4% by wt. of tungsten trioxide, respectively, at 400°C.
6. In-situ method was used as a novel methodology for modification of titanium dioxide.
7. The in-situ method resulted in the simultaneous synthesis of nanoparticles of titanium dioxide and the dopants. It involved the use of precursors such as tetra butyl titanate for titanium dioxide, cadmium chloride for cadmium sulfide and sodium tungstate for tungsten trioxide.
8. Powder X-Ray Diffraction (PXRD) analysis confirms the successful incorporation of cadmium sulphide salt /tungsten trioxide onto the surface of TiO_2 by both methods as confirmed by changes in the ‘a’ and ‘c’ lattice parameters of titanium dioxide.
9. X-Ray Diffraction studies confirmed the synthesis of titanium dioxide, where the 2 theta value of the synthesized material was found to be similar to the 2 theta value of the reference sample of titanium dioxide
10. The in-situ formation of nanoparticles of titanium dioxide and cadmium sulfide was confirmed by Particle size analysis and transmission electron microscopy
11. FTIR Spectroscopy was used to confirm the interactions between the dopants and titanium dioxide.

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