

Optical Properties and Photo Stability of Different Nanomaterials

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Abstract: TiO₂ is one of the common materials used for solar cells, diodes, different types of gas sensors, optoelectronic devices, etc., TiO₂ is widely used in photovoltaic devices due to interesting optical and electrical properties. In this research, there are different types of nano materials were synthesized by different methods, Firstly, TiO₂ nanoparticle has been prepared by sol-gel techniqu. Secondly, TiO₂ nanord and TiO₂ nanowire were synthesized by a hydrothermal method. The thin films of these samples (TiO₂ NP_s-TiO₂ NRA_s-TiO₂ NWA_s) were synthesized on glass substrates via. doctor-blending method. The as-prepared samples were characterized by x-ray diffraction, HR-TEM, FE-SEM and UV-Visible spectrophotometer. X-ray diffraction pattern showed the phase structures of these samples, the Scanning Electron Microscopy (SEM) is used for analysis of morphology and Ultraviolet Visible spectroscopy (UV-Vis) was used to get the degradation degree, the light intensity and the optical absorbance.

INTRODUCTION

With the advent of nanotechnology, in recent past metal oxides nanoparticles, in particular Titanium Oxide (TiO₂) nanoparticles have become a promising material due to their unique properties. TiO₂ besides having wide range of applications such as dye-sensitized solar cells and QD-sensitized solar cells. TiO₂ nanoparticles have been recognized as an important candidate for multiple applications. TiO₂ has good stability under irradiation in solution and low toxicity but there are two serious disadvantages that limit the efficiency of photocatalytic activity of TiO₂ using the light source in the solar spectrum (with 3-5% UV light) they are: the large band gap (3.0 eV of rutile, 3.2 eV of anatase) which suppress its photo-response in visible range due to this it is only

active in the ultraviolet range and the fast recombination rate of photoinduced electron (e⁻)/hole (h⁺) pairs and cannot absorb visible light due to wide band gap of ~3.2 eV. Variety of techniques have been adopted by researchers to synthesize TiO₂ nanoparticles such as chemical vapour deposition (18), sol-gel (19), hydrothermal (20), hydrolysis (21), solvothermal (22), ball milling (23), solution combustion method (24) and many more. These methods provide various morphologies like nanosphere, nanorods and nanowires which having different photocatalytic efficiency. In previous studies, researchers have reported the preparation of TiO₂ nanoparticles using Titanium Tetrachloride (TiCl₄) and titanium (IV) isopropoxide as a precursor. The physical properties of TiO₂ depend on many factors such as crystal structure, size, morphology and the preparation methods.

TiO₂ exists in three crystallographic phases namely rutile, anatase and brookite. In general, anatase phase of TiO₂ NPs is found to be active and possess high photocatalytic efficiency compared to rutile phase due to electron hole pair recombination rate. Photocatalytic process involves the electron in the Valance Band (VB) were excited towards the Conduction Band (CB) by illuminating the UV light. The photocatalytic effect of TiO₂ nanorods were studied on the degradation of Methyl orange in aqueous solution. They also synthesized single-crystal TiO₂ nanowire arrays on FTO glass under mild hydrothermal conditions. The functional nanostructured photoanodes such as one-dimensional nanostructures (nano rods (2), nanowires (3)). In this study, the sol-gel method uses a titanium (IV) isopropoxide and ethanol absolute which is based mainly on the hydrolysis and condensation of metal alkoxides at low temperature (12). The sol-gel dip coating is the simplest, economical method and has advantages such as TiO₂ is easily deposited on the glass substrates. In this research, (rutile/anatase) TiO₂ nanorod/ nanowire arrays were synthesized via the hydrothermal method. The main objective of this paper is to study the crystallization of TiO₂ thin films of different nanomaterials (TiO₂ NP_s, TiO₂ NRA_s and TiO₂ NWA_s) deposited by doctor-blending technique as a function of calcination temperatures. Structural, morphological and optical properties with annealing temperature are investigated by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM), Photo Stability (PS), High Resolution Transmission Electron Microscope (HR-TEM) and UV-VIS spectrophotometer.

MATERIALS AND METHODS

Experimental: Titanium (IV) isopropoxide (97%, Aldrich), ethanol absolute (Adwic), Sodium Hydroxide (Aldrich), Triton-X100 (Aldrich), Nitric acid (Adwic), Hydrochloric Acid (Adwic) and deionized water.

Synthesis of TiO₂ quantum dots: Titanium (IV) isopropoxide (TIP) [Ti [OCH (CH₃)₂]₄] was used as the precursor for the sol-gel synthesis of nanoparticle TiO₂ catalysts. The sol-gel method include hydrolysis and condensation process of Titanium (IV) isopropoxide in aqueous media under acidic condition. The procedure used is followed by preparing two solution: in solution A, TIP added to ethanol absolute at volume ratio (1:3) under continuous stirring for 30 min until a homogenous white yellow solution produce. In solution B, deionized water added to ethanol absolute at volume ratio (1:4), nitric acid (HNO₃) as N₂ atmosphere is mixed well to solution by drop wise until the pH value approaching about (2) under magnetic stirring for 1 h at room temperature for restrain the hydrolysis process of the solution. Finally, the contents of beaker B was added slowly into beaker A and

aged under vigorous stirring for 2 h. The gel is dries at 80°C in water bath for 1 h until most ethanol evaporate, then the produced mixture is dries overnight (for 24 h) in a regular laboratory oven at 80°C. Finally, the dry amorphous gel was transformed into anatase-crystalline TiO₂ QD_s by calcination at 400°C for 2 h.

Synthesis of TiO₂ nanorod arrays (TiO₂ NRAs): The rutile TiO₂ nanorod arrays were synthesized by a hydrothermal technique using Titanium (IV) Isopropoxide (TIP) as a Ti precursor. Taking, deionized water was mixed with concentrated hydrochloric acid (37%) then, followed by stirring at standered condition for 5 minute, then titanium (IV) isopropoxide was added drop by drop to the mixture. After stirring for another 5 min, the resulting clear transparent solution was transferred to a teflon-lined stainless steel autoclave (400 mL volume) and the hydrothermal synthesis was conducted at 150°C for 20 h in a regular laboratory oven. After synthesis, the autoclave was cooled to room temperature and the white precipitate is collected then, washed using deionized water several times, dried at 80°C for 12 h and calcined at 500°C for 2 h to increase the crystallinity.

Synthesis of TiO₂ nanowire arrays (TiO₂ NWA_s): TiO₂ nanowires were prepared using hydrothermal method. In a typical preparation procedure, The prepared anatase TiO₂ white powders were dispersed in 10 m NaOH aqueous solution under ultrasonic treatment for 30 min then the mixture placed into a Teflon-lined autoclave of 400 mL capacity (the autoclave was filled with up to 80% of the total volume), sealed into a stainless steel tank and maintained at 200°C for 24 h without shaking or stirring during the heating. After the autoclave was naturally cooled to room temperature, the obtained sample was sequentially washed with dilute HCl aqueous solution and deionized water for several times until the pH value approaching about 7. Finally, the sample was dried at 80-85°C for 12 h and calcined at 400°C for 2 h.

Fabrication of TiO₂ nanoparticle films: For optical properties measurements, TiO₂ NWA_s, TiO₂ NP_s and TiO₂ NRA_s films with 0.05 g cm⁻² thickness were prepared from the various TiO₂ nanomaterials powders. The samples of TiO₂ nanomaterials films were directly deposited onto glass substrates by doctor-blading method using dispersion of 0.2 g TiO₂ powder in ethanol solution, the surfaces of the glass substrates were cleaning for 30-60 min using ultrasonicator before spreading the film then the substrates were dried in air. To control the thickness of the film the boundaries of glass substrates, adhesive tapes were used on the glass surface in order to delimit the active area of the film or were covered with scotch tape. To produce the film of TiO₂ QD_s, powder was first dispersed in Triton-X100 and ethanol but to prepared

TiO₂ NWA_s and TiO₂ NRA_s films, powder was first dispersed in Triton-X100 and acetic acid until get homogeneous pastes of these different nanomaterials. The paste was spread on the glass surface by using a glass slide, then the suspended powder was added as drops at the middle of the substrate and was spread to form a thick film. Then kept the layer at room for 30 min temperature then drying at hot plate at 300°C for 5 min.

Methods of analysis: Several techniques were used to characterize the surface of prepared materials.

X-Ray Diffraction (XRD): X-ray diffraction patterns were recorded with a Pan Analytical Model X' Pert Pro which was equipped with CuK α radiation ($\lambda = 0.1542$ nm), Ni-filter and general area detector. An accelerating voltage of 40 kV and an emission current of 40 mA were used. The diffractograms were recorded in the 2θ range of 0.5-70°.

Fourier Transform Infrared spectroscopy (FTIR): Fourier Transform Infrared (FTIR) spectroscopy Fourier Transform Infrared spectroscopy (FT-IR) of the prepared samples was measured using Nicolet Is-10 FT-IR spectrophotometer adopting KBr technique; thermo fisher scientific. For all samples, the KBr technique was carried out approximately in a quantitative manner since the weight of sample and that of KBr, were always kept constant.

High Resolution Transmission Electron Microscopy (HR-TEM): High Resolution Transmission Electron Microscopy (HR-TEM) images for the prepared samples were recorded on a JEOL JEM-1230 electron microscope operating at an acceleration voltage of 120 kV. The samples for TEM measurements were prepared by dropping a carbon-coated copper grid with suspended of materials in methanol HPLC which was pre-sonicated for 15 min.

Field Emission Scanning Electron Microscope (FE-SEM): Field Emission Scanning Electron Microscope (FE-SEM) s used to analyze the morphology, particle size and shape of the materials. For the prepared samples were recorded on a JSM-7500F electron microscope operating at an acceleration voltage of 30 kV.

UV-Vis absorption spectroscopy: Optical absorption spectra of the samples were measured using Ultraviolet-Visible absorption spectroscopy (Spectro UV-Vis 2800, USA). Barium sulfate solution was used as a reference material.

RESULTS AND DISCUSSION

Figure 1 shows the X-Ray Diffraction (XRD) spectra of the titanium oxide nanoparticles at 400°C, Copper sulfide and Copper Nickle nanoparticles. XRD spectrum of TiO₂ QD_s sample, shows that the anatase phase is formed with the broad peaks. All diffraction peaks for the sample, show the anatase phase with tetragonal structure is formed and all diffraction peaks were in good agreement with JCPDS No. 21-1272. The diffraction peaks located at 2θ are 25.21°, 37.60°, 47.94°, 51.45°, 53.92°, 55.01°, 62.59° and 65.42° corresponding to the (101), (004), (200), (105), (211), (204), (116) and (215) lattice planes, respectively. Further, we have observed that without recrystallization results into amorphous polymorphs of TiO₂. The estimated value of crystalline size of the sample is 7.23 nm. The crystallite size was calculated using Sherrer equation as follows^[1]:

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

Where:

- D : The crystallite size
- K : A dimensionless shape factor has a typical value of about 0.9
- $\lambda = 1.54\text{\AA}$: The X-ray wavelength
- β : The line broadening at half the maximum intensity (FWHM)
- θ : The Bragg's diffraction angle

Figure 2 shows the FTIR spectra of TiO₂ QD_s, TiO₂ NR and TiO₂ NW. Curves a represent FTIR spectra for sample TiO₂ QD_s calcined at 400°C. The absorption band observed in the ranges of 400-800 cm⁻¹ is associated to the bending vibration (O-Ti-O) bonds in the TiO₂ lattice^[2-4] which confirms the presence of TiO₂ as crystalline phase. The sharp peak at 1620 cm⁻¹ refer to characteristic bending vibration of -OH group^[3-5]. A broad absorption peak observed in the ranges 3200 to 3800 cm⁻¹ is due to the interaction of hydroxyl group of water molecule with TiO₂ surface^[3-6]. The intensity of higher absorption bands decreases with calcination temperature which is inferred that the removal of water molecules from sample and particle growth.

Optical properties: The FT-IR spectra of TiO₂ nanorod is shown these figure. It is believed that the broad absorption peak at 3000-3600 cm⁻¹ is attributed to the fundamental O-H stretching vibration of hydroxyl group^[5] The weak band occurs at 1615-635 cm⁻¹ correspond to O-H bending vibration of hydroxyl

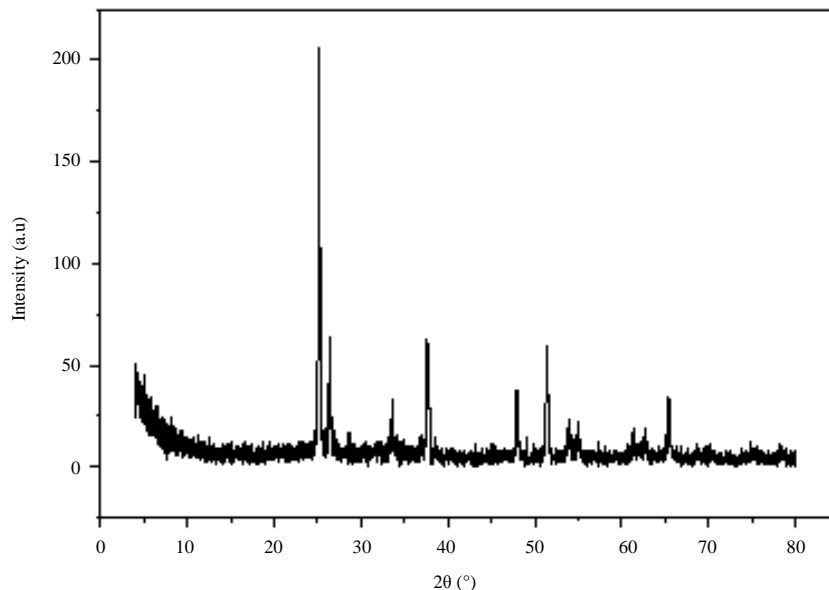


Fig. 1: XRD spectra of TiO_2 QDs at 400°C (TiO_2 at 400°C)

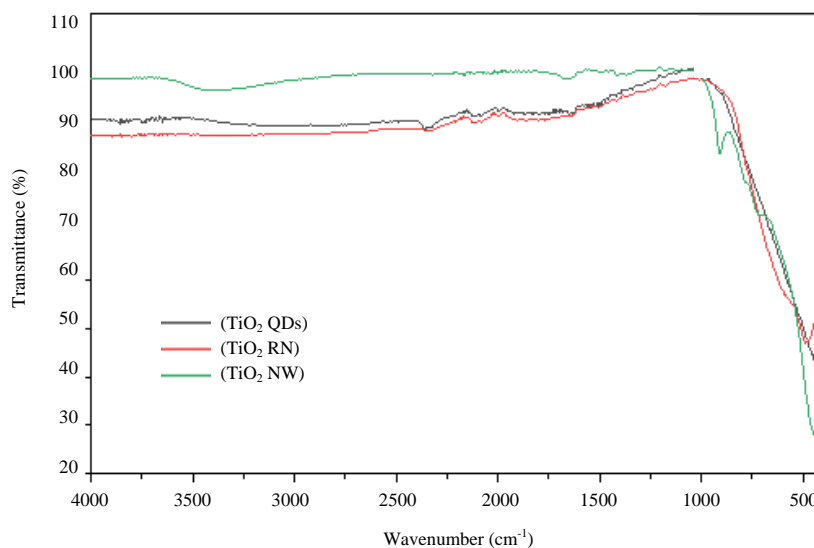


Fig. 2: FTIR spectra of TiO_2 QD, TiO_2 NRA_s and NWA_s

group due to chemically adsorbed water molecules^[6]. The peak around 800 cm^{-1} was assigned to the Ti-O stretching band^[7] confirms the formation of TiO_2 ^[8].

Shows the FTIR spectra of TiO_2 nanowire has vibration bands at $800\text{--}1200\text{ cm}^{-1}$ which are characteristic of the O-Ti-O network. The TiO_2 nanowire showed one broad band near 3400 cm^{-1} which correspond to the water molecules and hydroxyl groups adsorbed on the surfaces and another peak at 1650 cm^{-1} is due to O-H bending vibrations of adsorbed water molecules. TiO_2 nanowire was prepared totally in anatase phase, so, The Ti-O-Ti

stretching vibration band near 895 cm^{-1} for TiO_2 nanowire^[9]. Figure 3 shows High Resolution Transmission Electron Microscopy (HR-TEM) of the as-prepared and calcined samples. Figure 3a, b the as-prepared TiO_2 QD contains amorphous structure as indicated by XRD. TiO_2 QD after calcination to 400°C the particle size distribution assembled to aggregates; the crystallite size ranged $7.36\text{--}9.50\text{ nm}$. Figure 3c, d TiO_2 NRA_s after calcination to 500°C the crystalline width ranged $31.48\text{--}81.48\text{ nm}$ and the crystalline length ranged from $202.31\text{--}900.63\text{ nm}$ and TiO_2 NWA_s was calcinated

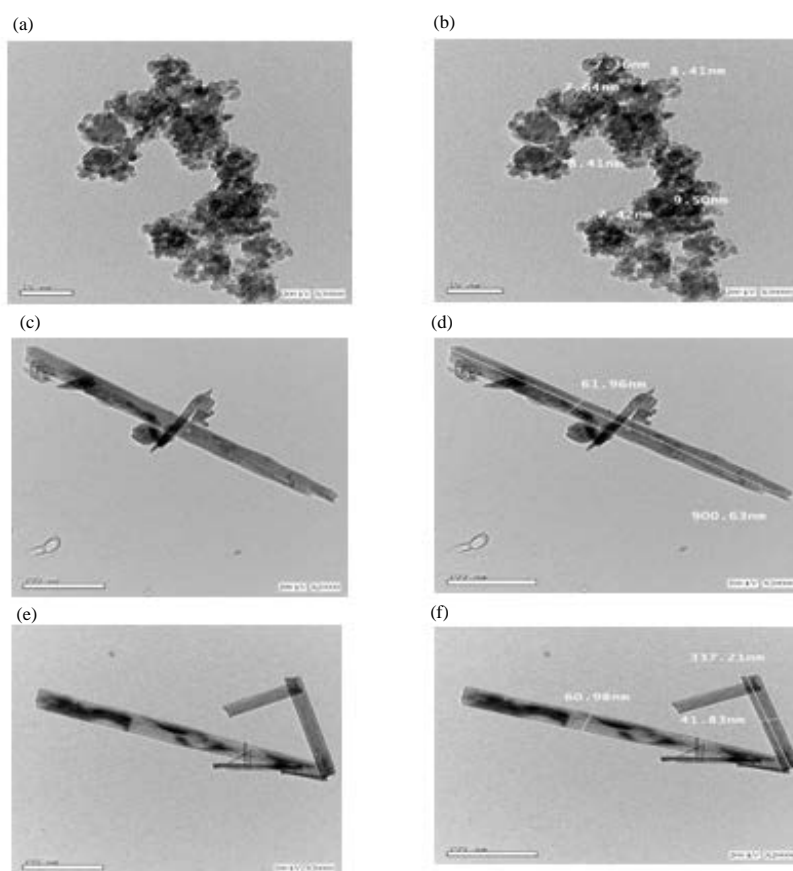


Fig. 3(a-f): HR-TEM of (a-b) TiO_2QD_s , (c-d) TiO_2NRA_s and (e-f) TiO_2NWA_s

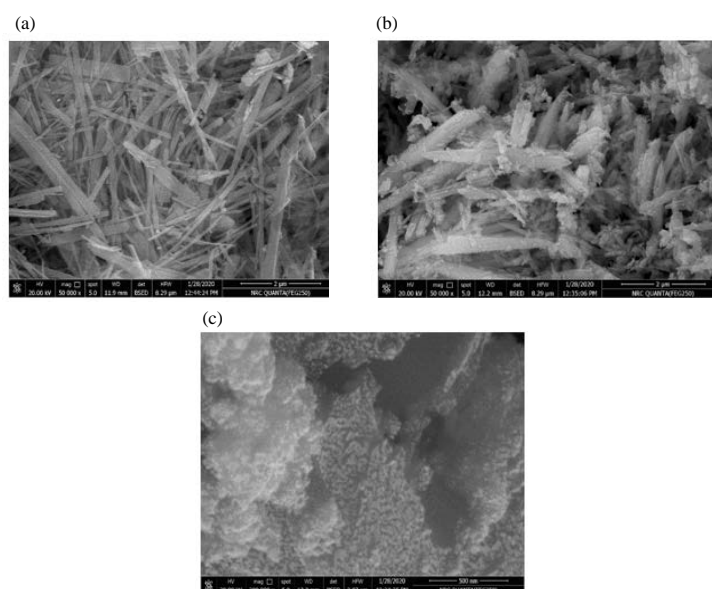


Fig. 4(a-c): FE-SEM of (a) TiO_2 NWA_s, (b) TiO_2 NRA_s and (c) TiO_2 QD_s

at 400°C shows clear wires structures and the wires have a length of 735.20 and 40.18 nm diameter shown

in Fig. 3e, f. Figure 4 shows the FE-SEM images for the TiO_2 QD, TiO_2 NRA_s and TiO_2 NWA_s. From FE-SEM

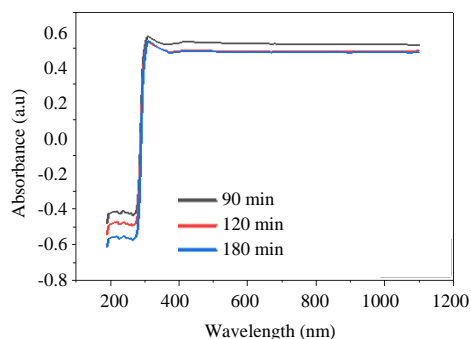


Fig. 5: Absorbance spectra of synthesized TiO_2 QDs at 90, 120 and 180 min

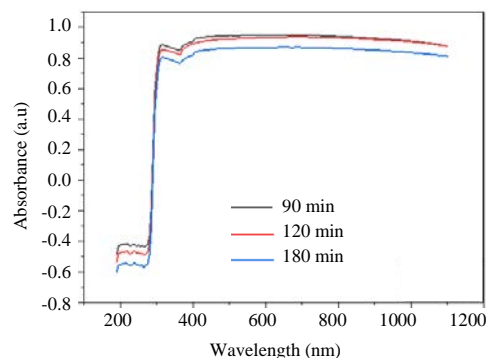


Fig. 7: Absorbance spectra of synthesized TiO_2 NWA_s at 90, 120 and 180 min

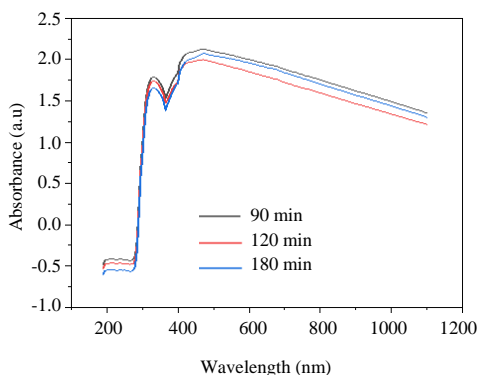


Fig. 6: Absorbance spectra of synthesized TiO_2 NRA_s at 90, 120 and 180 min

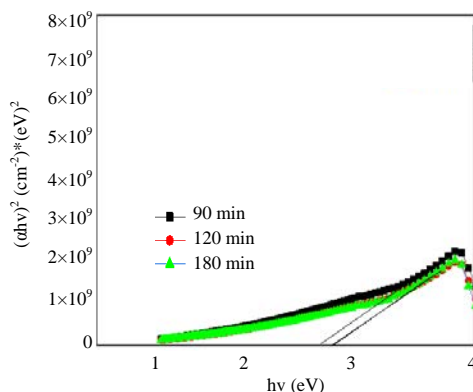


Fig. 8: Optical band gap of synthesized TiO_2 QD at 90, 120 and 180 min

images of samples, Fig. 4c it is found the particles for TiO_2 QD are homogeneous and almost irregular in shape. From the sample at 400°C , it is found that particle size is increased and is highly agglomerated^[9]. Figure 4b show that particle size of the sample in the range (7.36-9.50 nm), shows the micrographs of TiO_2 nanorods, TiO_2 nanorods are reunited together and the uniform diameters of nanorods is about 281.4 nm with length of about 500 nm and Fig. 4a show that TiO_2 NWA_s morphology and indicates both variable lengths ~ 510 nm and uniform diameters in range 49.55-80.21 nm.

Figure 5a shows the UV-vis absorption spectra and photostability for samples at different exposure time of light. It is seen that absorption edge of TiO_2 QDs calcined at 400°C , TiO_2 NRA_s and TiO_2 NWA_s. The absorption edges for TiO_2 QDs calcined at 400°C were decreasing by increasing exposure time to 180 min but samples at 120 and 180 min have the same absorption edge due to photostability of samples. Figure 6 shows the UV-vis absorption spectra and photostability for samples at different exposure time of light. It is seen that absorption edge of TiO_2 NRA_s. The absorption edges for TiO_2 NRA_s were decreasing by increasing exposure time to 180 min

due to photostability. Figure 7 shows the UV-vis absorption spectra and photostability for samples at different exposure time of light. It is seen that absorption edge of TiO_2 NWA_s. The absorption edges for TiO_2 NRA_s were decreasing by increasing exposure time to 180 min due to photostability. To know the nature of band gap, we have made detailed calculation of band gap using Tauc formula:

$$(\alpha h\nu)^n = A (h\nu - E_g)$$

Where:

- α : The absorption coefficient
- $h\nu$: The energy of photon
- E_g : The energy gap
- n : The nature of the transitions

The term n is taken 2 for direct transition and $\frac{1}{2}$ for an indirect transition. The band gap is determined by plotting $(\alpha h\nu)^n$ versus energy of photon and tangent drawn to the curve intersect the energy axis at $\alpha = 0$. Figure 8 shows the Tauc plot of TiO_2 QDs calcined at 400°C for direct band transition and the estimated direct band gaps of TiO_2 QDs calcined at 400°C at exposure times 90, 120

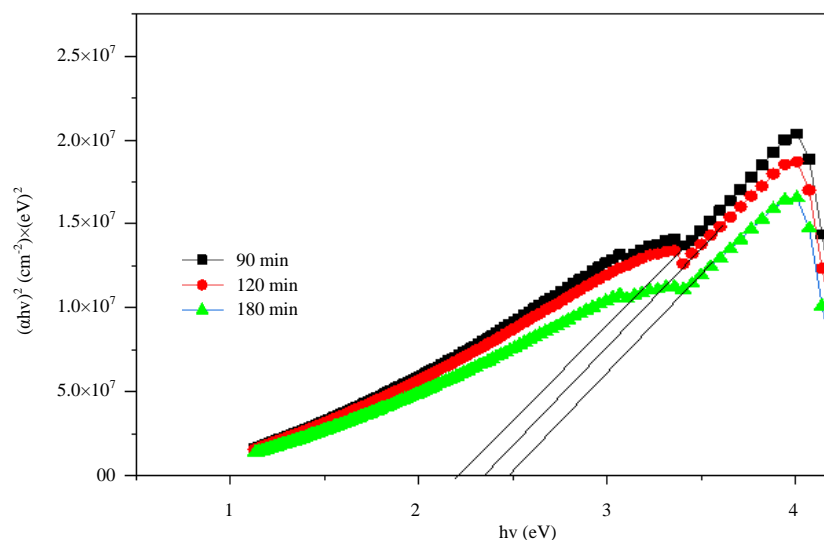


Fig. 9: Optical band gap of synthesized TiO_2 NRA_s at 90, 120 and 180 min

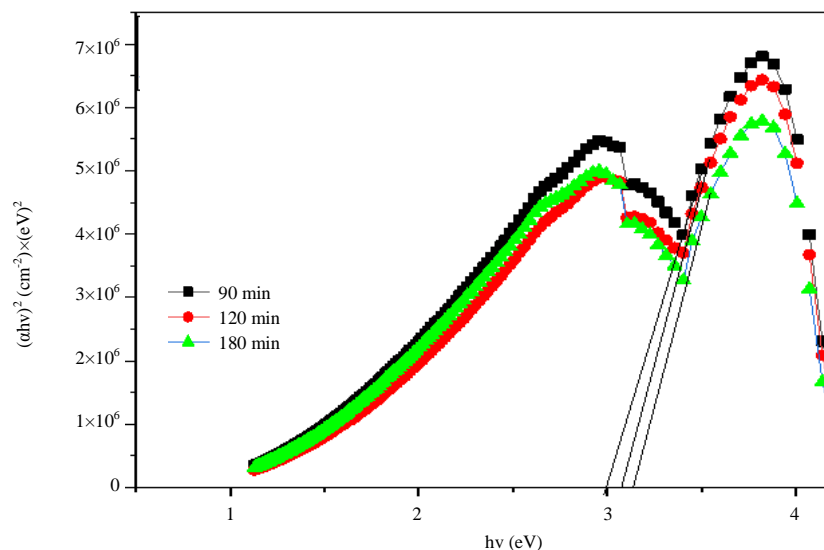


Fig. 10: Optical band gap of synthesized TiO_2 NWA_s at 90, 120 and 180 min

and 180 min are 2.68, 2.8 and 2.8 eV, respectively. Figure 9 shows the Tauc plot of TiO_2 NRA_s for direct band transition and the estimated direct band gaps of TiO_2 NRA_s at exposure time's 90, 120 and 180 min are 2.19, 2.34 and 2.47, eV respectively. Figure 10 shows the Tauc plot of TiO_2 NWA_s for direct band transition and the estimated direct band gaps of TiO_2 NWA_s at exposure time's 90, 120 and 180 min are 3, 3.07 and 3.13 eV, respectively.

CONCLUSION

Titanium dioxide nanoparticle was synthesized by sol-gel method. Titanium dioxide nanorod and

Titanium dioxide nanowire were synthesized by a hydrothermal method. Absorbance spectra for TiO_2 NRA_s and TiO_2 NWA_s is decreasing by in increasing exposure time from (90-180 min) under light of photostabilizer.

Optical band gap in direct allowed transition for TiO_2 NRA_s and TiO_2 NWA_s increasing by increasing exposure time from (90-180 min) under light of photostabilizer. Absorbance spectra for TiO_2 QD_s is remains stable by increasing exposure time at 120 and 180 min under light of photostabilizer.

Optical band gap in direct allowed transition for TiO_2 QD_s and is remains stable by increasing exposure time at

120 and 180 min which are 2.8 and 2.8 eV, respectively under light of photostabilizer. TiO_2 QDs is more stable than TiO_2 NRAs and TiO_2 NWAs. TiO_2 QDs can be used as a working electrode in solar energy conversion due to it has a higher stability and higher efficiency than other nanomaterials.

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