SYNTHESIS OF TITANIUM OXIDE NANOPARTICLE COMPLEMENTED WITH OPTICAL PROPERTIES

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ABSTRACT

Titanium oxide nanoparticles were prepared via Sol-gel method by mixed of titanium tetra-iso-propoxide (TTIP) and nitric acid at (pH=1.85).The optical properties were studied. The wavelength and transmittance at λ=260 nm were 84.17 nm and 1.6% respectively. Maximum reflective (R) at λ=410 nm was 20% and decrease with wavelength increase; moreover the indirect allowed energy gap (E_g) was 3.2 eV. Optical constant such as absorption coefficient (α), extinction coefficient (k) are calculate and the reflective index (n) was 1.3438.

Keywords: titanium dioxide (TiO_2) nanoparticle, Sol-Gel method, optical properties, optical constant, (DLS) for TiO_2-sol nanoparticle).

1. INTRODUCTION

Theoretical and experimental studies had performed on the electronic transport properties of semi-conducting oxide thin films. Titanium dioxide or titania (TiO_2) is a high band gap semiconductor that exhibits high transparency to visible and near infrared light [1]. TiO_2 is economically available, safes, white, and undegradable material. It has high (refractive index, dielectric constant), semiconductor properties and chemical stability. Titana exists in various phases; rutile, anatase and brookite. Titania phases have got different optical and structural properties [2]. Brookite is one of the orthorhombic structures and both anatase and rutile are tetragonal. Rutile is the most thermodynamically stable phase of TiO_2. Its refractive index and density are high as compared to anatase phase. Anatase is one of the low-temperature polymorphs with an optical band gap 3.25 (eV). Anatase is thermodynamically unstable and it can be transformed into rutile upon the annealing temperature [3]. Although rutile has lower optical band gap it is not effective as a photocatalyst due to high rate of electron–hole recombination. Most desirable phase in the case of photocatalyst is anatase, however, because of higher band gap; it works in UV range [4]. The physiochemical properties of titania depend on phase composition, grain size and dispersity [5]. TiO_2 hydrosols consisting of highly crystallized nanoparticles have been widely studied in the fields of photocatalytic degradation of pollutants [6], self-cleaning windows [7], sensors [8], solar cells [9] water purification, air purification, anti-bacteria [10], optical filters [11], ceramic membranes [12], wave-guides [13] and electron chromic devices [14]. In this work a synthesis of the TiO_2 NPs Sol-Gel and study the optical characterizations were studied.

2. EXPERIMENTAL

Sol -gel method was used to prepare TiO2 NPs by mixing (3.5 ml) titaniumtetera isopropoxide (TTIP), $Ti[OCH(CH_3)_2]_4$, purity 99% from Sigma-Aldrich in (40 ml) deionization water (DW). Then added (0.2-0.3) (ml) of nitric acid (HNO_3), purity 65% from Merck to the solution until reach the PH to 1.85. The solution was put on a magnetic stirrer for (24 h) then the sol was aged for (6 h) at (50 Č) yielding a transparent sol.

3. RESULT AND DISCUSSIONS

Study the optical properties and optical constant of nanoparticles TiO_2 sol -gel then used the nanoscale devices for the purpose of measurements:

### 3.1 The optical properties and optical constant of TiO_2-Sol

The absorption (A) spectrum of TiO_2 NPs was nanoparticle measure by Lambada spectrophotometer to find the wavelength peak (λ_{max}=384.17 nm) the absorption spectrum shown in Figure-1.

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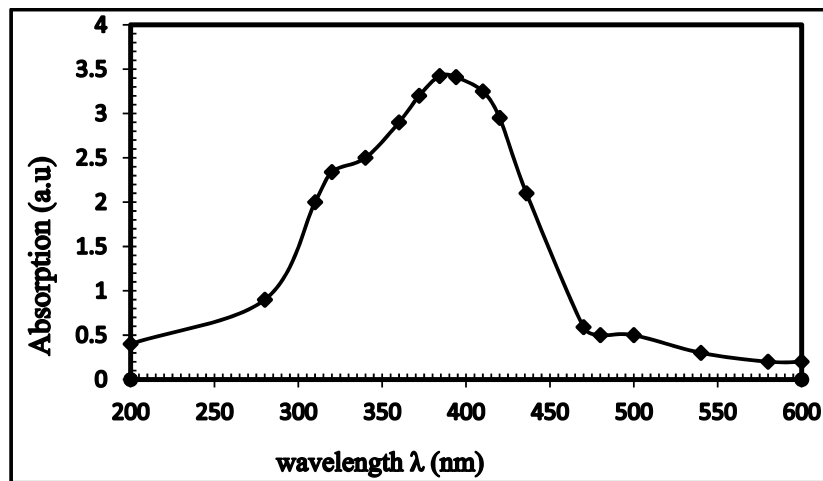
Figure-1. The absorption spectrum for TiO$_2$- sol nanoparticles and the maximum
absorption wavelength in λ_{max}=384 (nm).

The transmittance (T%) increases with increasing of the incident photons wavelength (λ) that shown in Figure-2. The high transmittance inferred that TiO$_2$-sol could be used for optical coating application. In ultraviolet light the transmittance (T_{max}=1.6% in λ=260 nm).
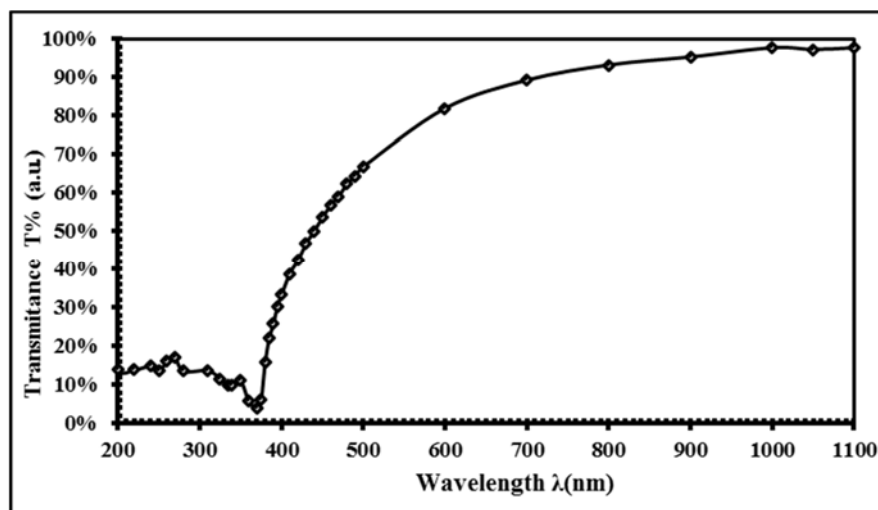
Figure-2. The transmittance spectrum for TiO2- sol.

Both T and reflective (R) as-prepared TiO$_2$-sol as a function of λ into two main parts. The first one at λ<1000 nm is called high absorption region, and is characterized by drastic change of both T and R as a function of λ in which T+R<1 where the optical constants were determined. The second one is non absorption region at λ>1000 nm; both T and R are characterized by stability through the whole wavelength range of T+R=1 where refractive index was determined. The maximum reflective was 20% at the wavelength equal to 410 nm and its decrease when wavelength increase as shown in Figure-3.

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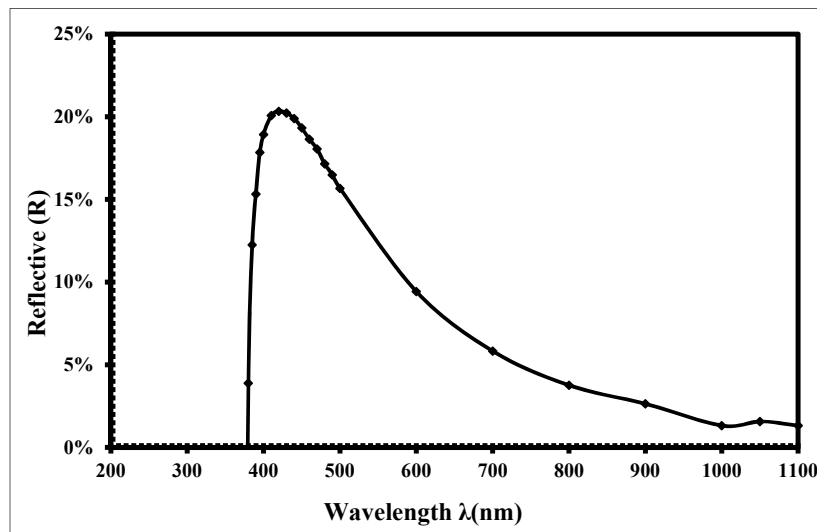
Figure-3. The reflective spectrum for TiO_2- sol nanoparticle.

The refractive index was measure by refractometer-AR4 from Germany and its equal (n=1.3438) for TiO_2 –sol nanoparticle was prepare in the laboratory.

Both of T, A and thickness of the cavity spectrophotometer) were used to determine the absorption coefficient (α) according [20] shown in Figure-4.

$$\alpha = 2.303 \frac{A}{T} \qquad \qquad ...(4)$$
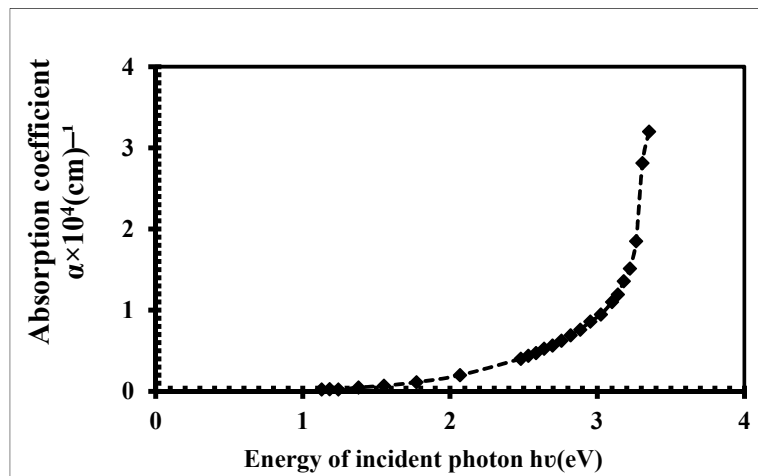
Figure-4. Absorption coefficient (α) vs photon energy (hν) for TiO2- sol nanoparticle.

The estimated absorption coefficient (α) versus photon energy (hν) is depicted in Figure-4. One can observe that α increases with the increasing of photon energy through the whole range of high absorption region while it decreases through the non- absorbing region. One can observe that both arrow and circle distinguish the end term of Urbach tail region ($\alpha \leq 10^4$ cm^{-1}) and high absorption region ($\alpha \geq 10^4$ cm^{-1}). Extinction coefficient of TiO_2-sol was calculated by [21]

$$k = \frac{\alpha\lambda}{4\pi} \qquad \qquad ...(5)$$

The calculated values of extinction coefficient, k vs λ for TiO_2 are shown in Figure-5. It could be noticed that k decreases with increasing of λ.

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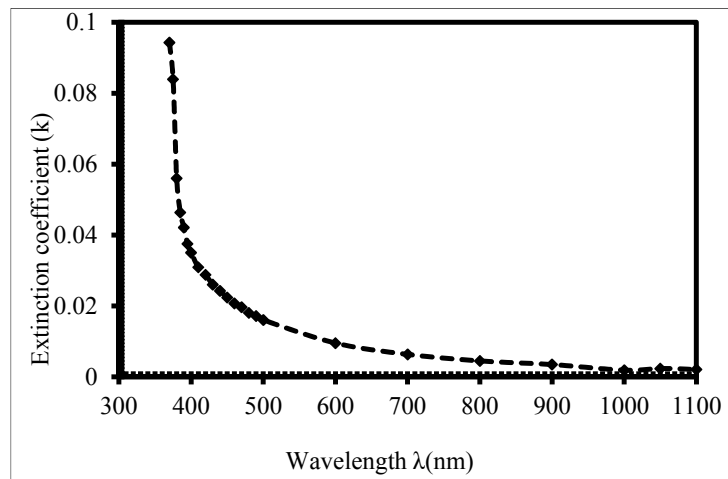
Figure-5. Extinction coefficient (k) vs λ for TiO$_2$- sol nanoparticle.

3.2 The optical band gap calculation

An absorption edge of semiconductors corresponds to the threshold of charge transition between the highest nearly filled band and the lowest nearly empty band.

According to inter-band absorption theory, the optical band of the films of can be calculated using the following relation [22]:

$$\alpha \, h\nu = B(h\nu - E_g)^r \tag{3}$$

where B is the probability parameter for the transition, also the constant B is a measure of the disorder of the material [22].

$$B = 4\pi\lambda_{min}/nc\Delta E \tag{4}$$

where λ_{min} is the minimum metallic conductivity, n is the refractive index, c is the light-velocity, and $\Delta E = \Delta E_c - \Delta E_v$ represents the band tailing E_g is the optical band gap of the material, $h\nu$ is the incident photon energy; r is the transition coefficient.

The reported value of r is 2 for the measurement of indirect allowed band gap, r=3 for indirect forbidden band gap, r=1/2 for direct allowed band gap and r=3/2 for forbidden direct band gap. All the possibility for r direct and indirect band gaps of TiO$_2$-sol were found, and the indirect optical band gap is evaluated by extrapolating the straight line part of the curves $(\alpha h\nu)^{1/2}$ with energy axes ($h\nu$) i.e $(\alpha h\nu)^{1/2}$=0 according to [22].

$$(\alpha \, h\nu)^{1/2} = B(h\nu - E_g) \tag{5}$$

Same way:

$$(\alpha \, h\nu)^{3/2} = B(h\nu - E_g) \tag{6}$$

Due to phonon energy assisting the indirect transition, Equation (5) could be written as;

$$(\alpha \, h\nu)^{1/2} = B(h\nu - E_g \pm E_{ph}) \tag{7}$$

where E_{ph} is the phonon energy assisting the indirect transition. Direct optical band gap was evaluated by extrapolating the straight line part of the curves $(\alpha h\nu)^2$ with energy axes ($h\nu$) i.e. $(\alpha h\nu)^2$ =0 according to

$$(\alpha \, h\nu)^2 = B(h\nu - E_g) \tag{8}$$

Same way

$$(\alpha \, h\nu)^3 = B(h\nu - E_g) \tag{9}$$

Relationship of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^{3/2}$, $(\alpha h\nu)^2$ and $(\alpha h\nu)^3$, and $h\nu$ is depicted in Figure-6. It reveals the simultaneous existence of direct and indirect band gaps in TiO$_2$-sol. direct and indirect band gaps of TiO2-sol nanoparticles are shown in Table-1.
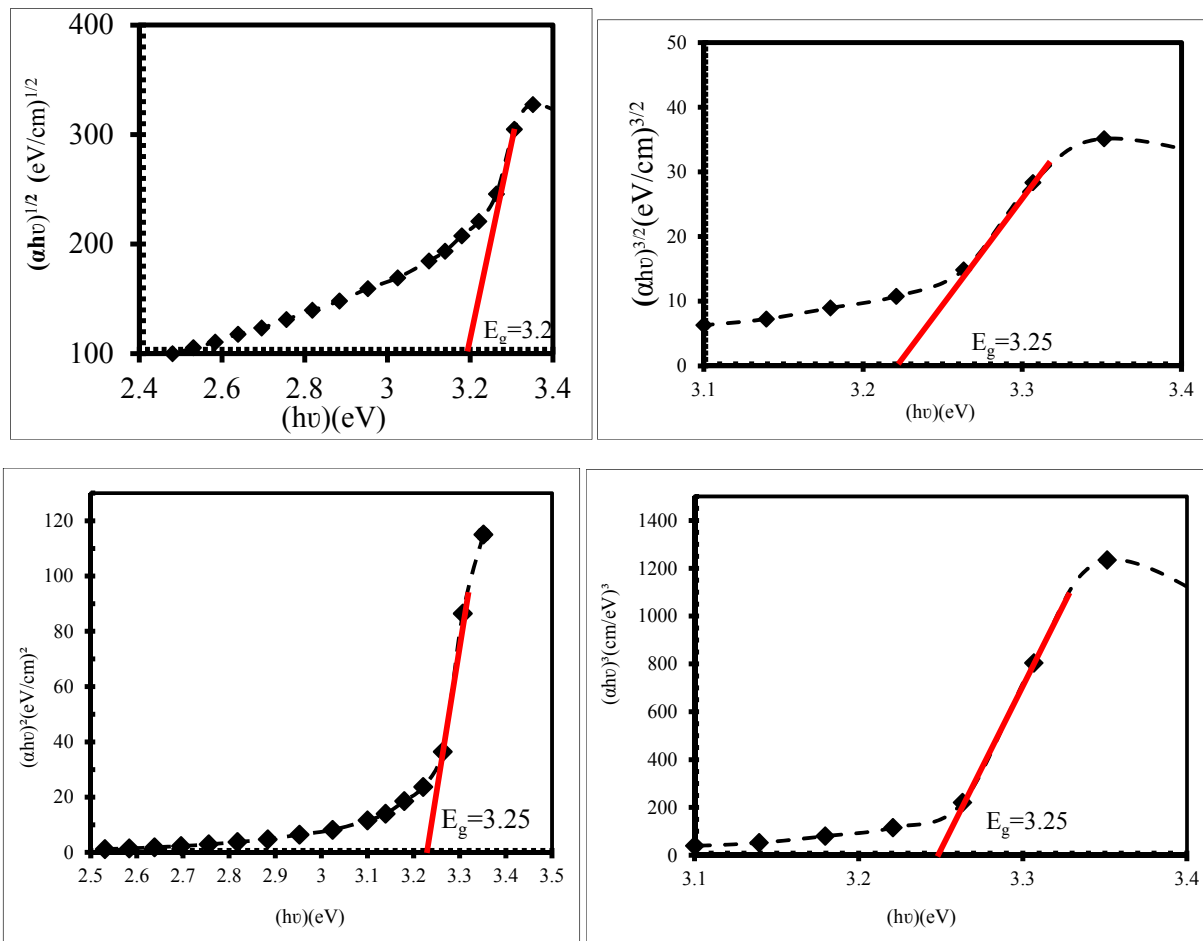
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Figure-6. $(\alpha\ h\upsilon\ )^2$, $(\alpha\ h\upsilon\ )^3$, $(\alpha\ h\upsilon\ )^{1/2}$ and $(\alpha\ h\upsilon\ )^{3/2}$ vs photon energy.

Table-1. Direct and indirect band gaps of TiO_2-sol nanoparticles.

Transition coefficient (r)	Transition mode	Energy gap according to Figure-5
1/2	Direct allowed	3.20
3/2	Direct forbidden	3.25
2	Indirect allowed	3.25
3	Indirect forbidden	3.25

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