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Research Article

FABRICATION OF TiO_2 BASED COMPOSITE MATERIALS BY HYDROTHERMAL METHOD

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ABSTRACT
Composite nanoparticles (nano powders) are nano-sized and can be synthesized with a wide range of organic, inorganic materials and production techniques. Titanium dioxide is one of the most commonly used materials in the production of composite materials. The reason why titanium dioxide is more preferred is that it has a minimum of any reactive step, it does not interfere with the human body and is an organic material that does not contain by-products. The photocatalytic properties of titanium dioxide can be improved by various methods. TiO_2 is the most widely used photocatalyst in air purification. In this study, titanium dioxide based composite material was fabricated by hydrothermal method. The electrical, optical and structural properties of the material were investigated with the contribution of three different compositions of cadmium oxide (CdO) for produced in the experiments. For this purpose, SEM, U-V (Vis), I-V and FTIR techniques were used for the characterization and obtained results evaluated.

Keywords: *Composite Material, TiO_2, CdO, Hydrothermal Method*

1. INTRODUCTION

Composite materials have been discovered and continue to be explored for a wide range of uses throughout human history. This process, which started with the addition of straw to mud, continues to develop in a wide range of areas from construction materials to photovoltaic nanoparticles. However, the use of the first composite word coincides with the early 1940s (Kinsinger *et al.* 2011). The purpose of producing composite materials is to gain new chemical and physical properties such as optical, electrical or mechanical, etc. to materials. There has been a rapid development in composite material technology in the near future. This rapid development has enabled them to be used increasingly in many sectors. The most preferred sector is the aviation industry (Akbulut *et al.* 2017).

Composite nanoparticles are nano-sized and can be synthesized with a wide range of organic, inorganic materials and production techniques. Titanium dioxide is one of the most used materials in the production of composite materials. The semiconductor property of titanium dioxide is used and its photocatalytic property is utilized. Inorganic metal based titanium dioxide (TiO_2) covers a wide range of catalysts, semiconductor films, etc. from the chemical industry to photovoltaic and semiconductor thin film applications. as used very often. In photovoltaic applications, it has been possible to synthesize titanium dioxide by using various additive and production methods to improve optical absorption capacity or electrical properties and researches continue along this direction.

Titanium dioxide is more preferred because it has a minimum of any reactive step, does not interfere with the human body and is an organic material (Kinsinger, Tantuccio, Sun, Yan and Kisailus 2011). TiO_2 is the most widely used photocatalyst in air purification (Zhang *et al.* 2006) and TiO_2 has been one of the most researched semiconductors since the discovery of water separation in the 1970s. TiO_2 has wide application areas such as; TiO_2 based catalyzes, cosmetics, dyes, antibacterial substances, lithium-ion cells, dye-sensitive solar cells, etc. are abundant. However, the white color and a broadband range of intact TiO_2 limit its application to the UV part of the sunlight spectrum in depth. Only a small proportion (~%5) of solar energy can be used well by copper TiO_2 and most of the solar energy is wasted. Therefore, it is necessary to reduce the recombination of electron-hole pairs to extend the absorption edge of the solar spectrum to the visible region and to increase the photocatalytic activity of TiO_2(Fang *et al.* 2017). Since titanium dioxide is a good catalyst, it can interact with different materials. The TiO_2 semiconductor can be combined with the cadmium oxide semiconductor, which has a narrow bandgap and can absorb visible light. The basic principle of this mechanism is based on the excitation of the electron in the valence band (VB) to the conductivity band (CB) by the absorption of light from the narrow band hollow semiconductor, and from there the passage of TiO_2 into the conductivity band. Thus, electrons move towards the surface of TiO_2 to form active oxidized species. There are such many studies in the literature.

There is a wide area of study with many different contributions such as; TiO_2:FeS_2,ZrO_2:TiO_2,SiO_2:TiO_2,TiO_2:CNSP etc (Rashid *et al.* 2018). Cadmium oxide is an important n-type semiconductor with a direct band gap of ~2.5 V and an indirect band gap of 1.18~1.20eV. Nonlinear materials have promising applications in catalysts. CdO nanoparticles are known to be highly reactive and have been used in processes such as energy storage systems, electrochromic thin films and heterogeneous catalyses. It forms an important component in the synthesis of nanoscience and nanotechnology. Nanomaterials produced by chemical methods have proved to be more effective by providing better control as well as providing different sizes, shapes, and functionalization than those produced by physical methods such as laser ablation, arc discharge and evaporation. Metal oxide nanoparticles can be produced by soft chemical methods such as co-precipitation, sol-gel and hydrothermal synthesis (Sayilkan *et al.* 2007).

In this study, cadmium oxide (CdO) nanoparticles are added to titanium dioxide (TiO_2), which is a good semiconductor, to improve optical absorber and electrical conductivity properties. For this purpose, using SEM, UV-Vis, I-V and FTIR measurements of unadulterated TiO_2 sample produced by hydrothermal method and also CdO: TiO_2 (10:90) and CdO: TiO_2 (20:80) composite samples with two different ratios of CdO added into TiO_2 were produced and characterized.

2. MATERIALS AND METHODS

Synthesis steps of TiO_2; first, titanium isopropoxide (Ti (OC3H7) 4) ethyl alcohol (ethanol (CH3CH2OH)) were put in a beaker, while hydrochloric acid (HCl) and ethanol were added to each other in a separate beaker. The mixtures were stirred for one hour on a magnetic stirrer and the two mixtures formed were added, too. The resulting new sample was again stirred in the magnetic stirrer for half an hour. The solution was determined as TiO_2 and in the following process, two different doped samples were obtained by adding 10% and 20% cadmium oxide (CdO) calculated as molar ratios to the solution prepared by the same experimental procedures. Thus, the samples; TiO_2, CdO: TiO_2 (10:90), CdO: TiO_2 (20:80) were produced. These mixtures were subjected to the hydrothermal process, drying and annealing, respectively, in accordance with the literature. As a result of these steps, three powder samples in powder forms were obtained.

SEM, UV-VIS, I-V and FTIR analyses of the three physical and chemical properties of the powder samples were performed to determine the physical and chemical properties.

3. RESULTS

3.1. Scanning Electron Microscope (Sem) Results

Fig. 1 shows SEM images of pure TiO_2 and TiO_2 doped with CdO as; CdO: TiO_2 (10:90) and CdO: TiO_2 (20:80), respectively. The SEM images of the samples showed that the pure sample consisted of smooth spherical structures. In CdO: TiO_2 composites, these spherical structures were not observed. In composite samples, these spherical structures were disintegrated and disrupted by CdO effect, and instead of these spheres random particle structures of large and small dimensions were formed. Based on these findings, it was found that the structural properties of the samples varied depending on the sample composition ratio.

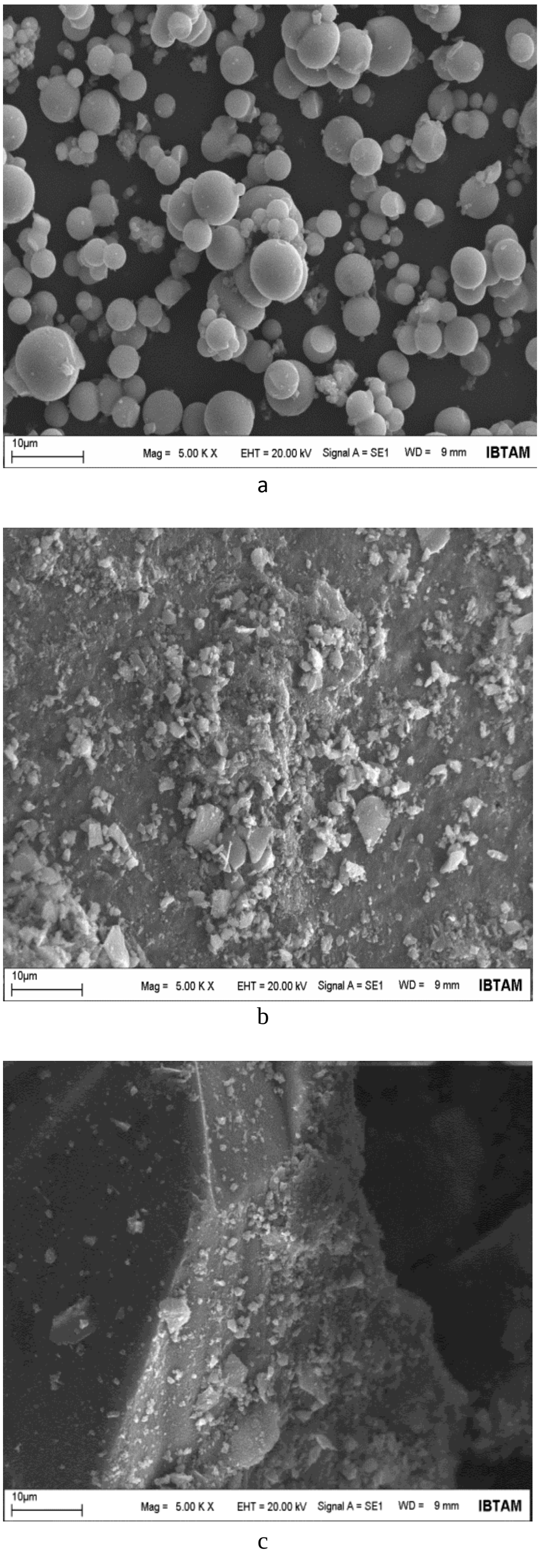

Fig 1. SEM images of the specimens; a)TiO_2, b) CdO:TiO_2(10:90), c) CdO:TiO_2(20:80).

3.2. Optical Analysis Results

Optical band intervals of pure TiO_2, CdO: TiO_2 (10:90) and CdO: TiO_2 (20:80) samples were investigated. The samples were pelletized and optical measurements were taken. The transmittance method was not used because the samples were not transmissible and instead of this diffuse reflectance method was used. According to this method, reflectance measurements of the samples were taken and optical band intervals were calculated. The Kubelka-Munk function developed for this is expressed as follows (Morales *et al.* 2007);

$$F(R) = \frac{(1-R)^2}{2R} \quad (1)$$

Here, F (R) is the Kubelka-Munk function and corresponds to absorbance and R is reflectance. The most important feature of the Kubelka-Munk function is that the samples with weak absorbance coefficients convert the measured reflectance values into absorbance values.

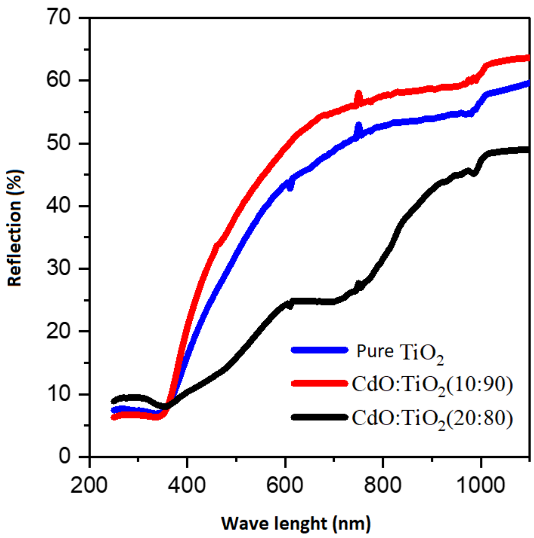

Fig 2. Reflection spectra of samples

Reflection spectra of pure TiO_2, CdO: TiO_2 (10:90) and CdO: TiO_2 (20:80) samples are given in Fig. 2. Variations of the reflection spectra with wavelength can be seen in the figure. Looking at all three samples, around 400 nm is seen as the reflection limit. Reflection increases with increasing wavelength. When the reflection properties of the three samples are examined, it is seen that they exhibit similar behaviors. As shown in the figure, it has been observed that as the doping ratio increases, the percentage of reflection of the sample first increases and then decreases(He *et al.* 2002; Sun *et al.* 2009; Wojcieszak *et al.* 2015).

The relationship between absorbance and optical band is expressed in the following equation.

$$\alpha h\nu = A (h\nu - E_g)^n \quad (2)$$

The α value in this equation corresponds to the value of F (R) / d (d = sample thickness). A is a constant, Eg is a forbidden energy (optical band) range, n is a constant and determines the type of optical transition. The forbidden energy ranges (αhν) of the samples were obtained from the $(\alpha h\nu)^2$–hν graph.

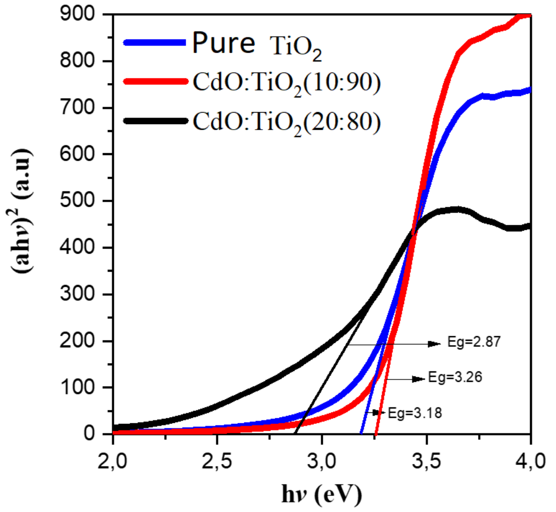

Fig 3.Specimens $(\alpha h\nu)^2$–hν spectrum

$(\alpha h\nu)^2$–hν spectra were plotted to calculate the forbidden energy range of the obtained samples and are given in Fig. 3 (Lebukhova *et al.* 2017). Eg values were obtained from linear parts of the$(\alpha h\nu)^2$–hν spectra. Eg values were calculated as 3.18 eV for pure TiO_2 sample, 3.26 eV for CdO: TiO_2 (10:90) sample and finally 2.87 eV for CdO: TiO_2 (20:80) sample(A.Aadim *et al.* 2016; Laatar *et al.* 2017; Kamil *et al.* 2018). The optical band spacing of the composite materials produced varies depending on the composite ratio of the material.

3.3. Electrical Conductivity Results

In order to determine the electrical characteristics of the prepared samples, their electrical conductivity was measured by 2-probe method and I-V graphs were obtained and the results were given in Fig. 4.

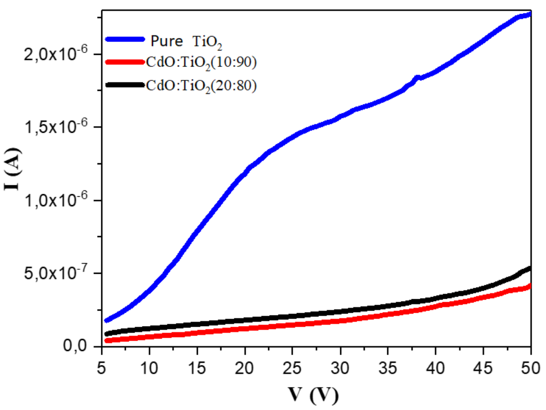

Fig. 4. Specimens I-V curves

The following equation was used to calculate the electrical conductivity of the samples.

$$\sigma = \frac{I}{V} \cdot \frac{d}{A} \quad (3)$$

Where σ is the electrical conductivity, I current, V potential difference, d is the thickness of the sample and A is the cross-sectional area of the sample ($A = \pi r^2$ r radius of contact point).

The calculated electrical conductivity of the samples are; $6{,}08\times10^{-7}\ \Omega^{-1}cm^{-1}$ for pure TiO_2 sample, $1{,}29\times10^{-7}\ \Omega^{-1}cm^{-1}$ for CdO: TiO_2 (10:90) sample and CdO: TiO_2 (20:80) for sample and $1{,}58\times10^{-7}\ \Omega^{-1}cm^{-1}$.

Accordingly, it was observed that the electrical conductivity of the samples varied depending on the ratio of TiO_2 and CdO in the material. The results obtained are similar to the results of the previous study. (Nagashima *et al.* 2012).

3.4. FTIR Results of Samples

Variations of FTIR spectra with the number of waves for chemical structure analysis of the samples are given in Fig. 5. Characteristic vibration bands were observed in the FTIR spectrum of TiO_2 at 1200cm^{-1} and 1700 cm^{-1}. The presence of these bands confirms the chemical structure of titanium dioxide. The change in peak intensities indicated the presence of cadmium oxide but also showed good addition.

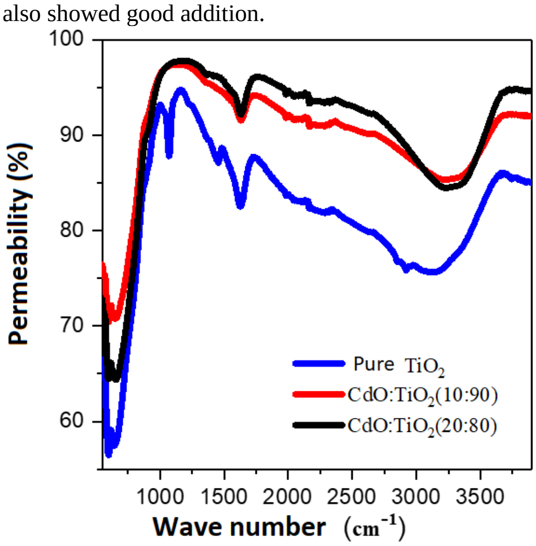

Fig 5.Specimen FTIR spectrums

When the curves given in Fig. 5 are examined, it is observed that the permeability is maximum between 900–1300 cm^{-1}. This increase can be said to be typical bands of TiO_2 and similar results can be found in the literature. (A.Aadim *et al.* 2016). In the figure, the wide vibration bands observed in the range of 500-700cm^{-1} were caused by vibrations in the Ti-O-Ti bonds in the TiO_2 mesh. 598 cm^{-1} Ti-O vibration band and 1638cm^{-1} Ti-O-Ti stretch band corresponded to(Nithya *et al.* 2013; Mashkour *et al.* 2017).

4. DISCUSSION

In this study, cadmium oxide (CdO) doped titanium dioxide (TiO_2) composites and pure titanium dioxide (TiO_2) were produced as semiconductor materials. The samples produced; additive titanium dioxide (TiO_2) and CdO: TiO_2 (10:90) and CdO: TiO_2 (20:80) are composite materials. Structural, electrical, optical and chemical, properties of the three samples were analyzed by SEM, I-V, UV-VIS and FTIR measurements.

When the SEM images of composite materials were evaluated; The structure of pure TiO_2 sample was observed as spherical particles and these spherical structures were determined to be uniform. In composite samples, spherical structures disappeared and instead of the particles of different sizes formed in varying sizes and shapes depending on CdO contribution ratio. The dielectric property was increased by adding CdO into TiO_2. The electrical conductivity of the samples was calculated from the current-voltage (I-V) plots drawn by electrical measurements. Accordingly, the electrical conductivities were found as $6{,}08x10^{-7}\Omega^{-1}cm^{-1}$ for pure TiO_2 sample, $1{,}29x10^{-7}\ \Omega^{-1}cm^{-1}$ for CdO: TiO_2 (10:90) sample and $1{,}58x10^{-7}\Omega^{-1}cm^{-1}$ for CdO: TiO_2 (20:80) sample. The forbidden energy ranges of the samples were calculated from the absorbance spectrum. It was found to be 3.18 eV for pure TiO_2 sample, 3.26 eV for CdO: TiO_2 (10:90) and finally 2.87 eV for CdO: TiO_2 (20:80). FTIR analyses were performed to examine the structural properties of the samples and the average characteristic band of the samples was around 1300 cm^{-1}.

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