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Endodontik NiTi Eğelerden Elde Edilen TiO_2'nin Boya Duyarlı Güneş Pillerinde Kullanımının Araştırılması

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ÖZ

Artan enerji taleplerin karşılanmasında yenilenebilir enerji türleri açısından popüler olan fotovoltaik teknolojilerde verim artırmaya yönelik çalışmalar yapılmaktadır. Boya duyarlı güneş pilleri yüksek altyapı maliyeti gerektirmeyen yapılar olduğundan, verim artırmaya yönelik çalışmalar boya duyarlı güneş hücreleri (DSSC) üzerine yoğunlaşmıştır. DSSC'de ışığa duyarlı boya, TiO_2 tabakasına tutundurulmaktadır. Bu çalışmada, kullanım ömrünü tamamlamış NiTi alaşımı endodontik eğeler, farklı asitler üzerinden çözeltiye alınıp metalik değerlerine ayrıştırılmıştır. Metalik değerlerden rutil ve anataz fazı tespit edilen TiO_2'nin boya duyarlı güneş hücrelerinde kullanımı amaçlanmıştır. Çalışma kapsamında atık NiTi eğelerden elde edilen kontamine TiO_2'nin yapısı karakterize edilmiş ve N719 boya çözeltisinin yüzeye tutundurularak optik özellikleri araştırılmıştır. XRD ve Raman sonuçları farklılık göstermiş, safsızlık piklerin görülmesinde etkin bir parametre olmuştur. FTO (Flor katkılı kalay oksit) kaplı cam yüzeye geri kazanım anataz/rutil TiO_2 tatbik edilmiş, yüzeyle görünür bölge spektrumunda belirgin bir etkinlik göstermediği ortaya konulmuştur.

Investigation of the Use of TiO_2 Obtained from Endodontic NiTi Files in Dye-Sensitized Solar Cells

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ABSTRACT

Renewable energy types, particularly photovoltaic technologies, which are popular in meeting increasing energy demands, are being studied to increase efficiency. Since dye-sensitized solar cells (DSSCs) are structures that do not require high infrastructure costs, studies on improving efficiency have focused on DSSCs. In DSSCs, light-sensitive dye is attached to a TiO_2 layer. In this study, NiTi alloy endodontic files that have reached the end of their useful life were dissolved in different acids and separated into metallic values. The use of TiO_2, in which the rutile and anatase phases were detected from the metallic values, was aimed in dye-sensitized solar cells. The structure of contaminated TiO_2 obtained from waste NiTi files was characterized, and its optical properties were investigated by attaching N719 dye solution to the surface. XRD and Raman results showed differences, and impurity peaks were an effective parameter in the observation of impurities. An anatase/rutile TiO_2 recovery was applied to FTO (Fluorine-doped tin oxide) coated glass surface, and it was revealed that it did not show a significant efficiency in the visible region spectrum.

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INTRODUCTION

The need to switch from conventional energy sources to more sustainable and renewable ones is growing as they become less common. The most prevalent and advanced of these sources is the generation of electricity from the sun. Direct conversion of solar energy is possible without a solar tracker mechanism. In addition, problems like noise and environmental pollution are eliminated thanks to solar panels' lack of moving parts. In the modern era, dye-sensitized, Ga-As, Si-based solar cells and perovskite solar cells are the most popular varieties. Dye-sensitized solar cells are appealing because of their minimal infrastructural needs [1–5].

In dye-sensitized solar cells, the anode material is a layer of TiO_2. Titanium dioxide, frequently used in various sectors, from the paint industry to the health sector, from the food industry to the medical industry, is of interest due to its photocatalytic properties [6]. The light-sensitive dye transfers electrons to the conducting component through the TiO_2 layer. However, TiO_2 cannot have its valence electrons activated by visible light since it needs 3.2 eV of energy; hence this layer does not add any electrons to the system. Instead, it is a hole transporter for required electron-hole pairs to form in solar cells [7]. Therefore, the TiO_2 layer utilized as the anode material in solar cells might be chosen during the anatase phase to design a more effective solar cell. TiO_2 has a high photocatalytic activity and electron mobility because it requires a higher energy level than rutile for the excitation of electrons in the valence band from the anatase and rutile phases at room temperature [8,9]. Instead of using pure anatase phase, it was found that nanoparticle mixes with 15-20 wt. % rutile added improved the photocatalytic action. Although the cause of this phenomenon is clarified, it is hypothesized that a reduction in electron transfer at the anatase/rutile contact is to blame [10].

NiTi alloys (NiTi-60) can be recovered using hydrometallurgical techniques over a variety of mineral acids to produce TiO_2 particles (HCl and H_2SO_4 (sample to acid ratio 1:7)) [11]. TiO_2 powders made from waste NiTi alloy files with various acid types were studied for their photocatalytic capabilities and suitability for dye-sensitized solar cells. Recycled TiO_2 powders used in dye-sensitized solar cells were not subjected to intermediate operations like grinding and another heat treatment because they were outside the study's purview.

MATERIALS AND METHODS

The solution obtained from the hydrothermal leaching of NiTi alloy endodontic files recycled for the investigation is shown in Figure 1, together with the TiO_2 powders produced after dehydration at 450ºC for 1-2 hours by precipitation around pH 3. In addition, AEROXIDE® TiO_2 P25 brand reference material was obtained from Evonik GMBH. Two different TiO_2 powder groups produced over HCl and H_2SO_4 acidic solutions were characterized, the recovery TiO_2 powder groups and the reference TiO_2 material were compared, and the amount of absorption was tested in the visible spectrum region in a dye-sensitized solar cell.

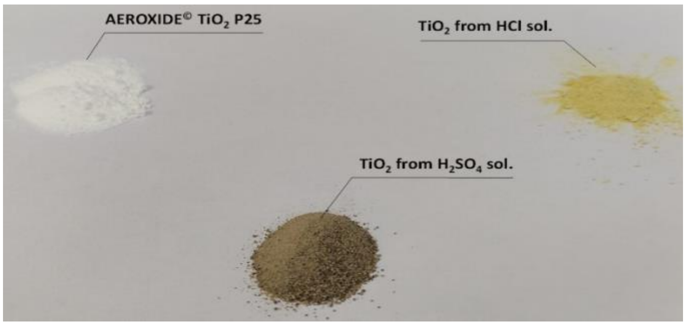

Figure 1. *TiO_2 powders used in the production of dye-sensitized solar cells*

TiO_2 powders produced from the reference material AEROXIDE© P25 and HCl and H_2SO_4 acid solution were subjected to SEM-EDS analysis (Hitachi - SU 1510), particle size distribution (Cilas 1190), Confocal Raman analysis (Renishaw inVia Reflex) and XRD analysis (PANalytical EMPYREAN) for crystallographic determination. Following the characterizations, the recycled two TiO_2 powder group was compared to the AEROXIDE© P25 reference material.

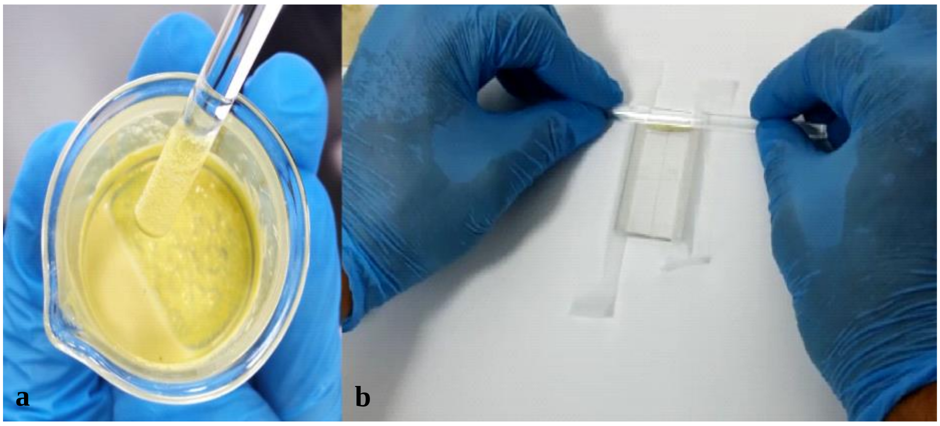

Figure 2. *a) Preparation of TiO_2 paste b) Application of TiO_2 paste on FTO glass by doctor blade technique*

The obtained TiO_2 powders were mixed with acetic acid, ethanol, and deionized pure water to form a TiO_2 anode layer mortar and mixed with a glass baguette, as shown in Figure 2a, to be dispersed in this mixture for 50 minutes. This mixture added 0.4 mL acetic acid, 2 mL deionized distilled water, and 10 mL ethanol for 2 g TiO_2 powder. Then the slurry mixture was taken into 100 mL ethanol, 5 g terpineol, and 10 g of 10 wt. % ethylene cellulose and ethanol mixture were added to this ethanol medium and stirred for 50 minutes. After this process, an area of 25 mm^2 was created with the help of 25 µm thickness Scotch tape on FTO (Fluorine doped Tin Oxide) glass samples cleaned in an ultrasonic bath for 10 minutes, and TiO_2 paste prepared by previous processes was applied with the doctor blade technique as shown in Figure 2b. Subsequently, the Scotch tapes were removed, and the FTO glass with the paste applied was dried at 100ºC for 1 hour and then sintered at 450ºC for 1 hour, and the samples in Figure 3a were produced.

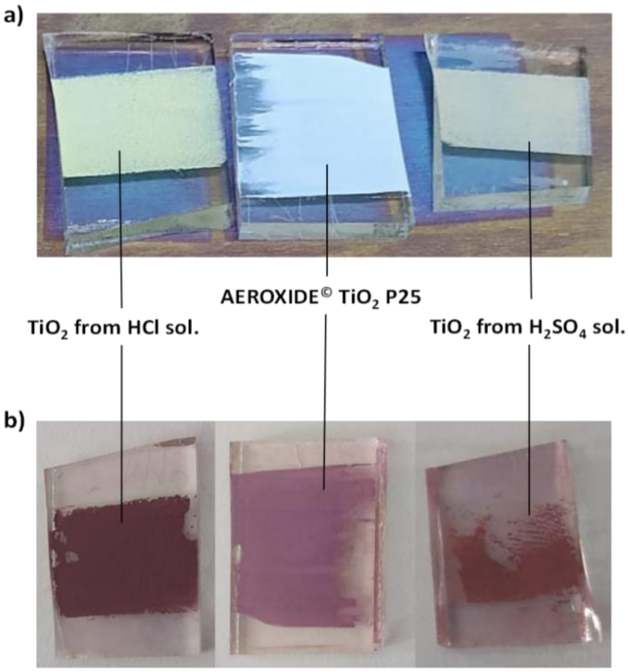

Figure 3. *a) Sintered TiO_2 applied FTO glass b) After N 719 dye immersion*

The TiO_2 layer applied as an anode material on FTO (fluorine-doped tin oxide) coated glass in solar cell production was immersed in 10^{-3} M N719 (Aldrich) ruthenium-containing dye solution. The absorbance values in the visible region were analyzed with a UV-Vis-NIR instrument (Shimadzu UV-3600 Plus).

RESULTS

SEM (scanning electron microscopy) was used to analyze microphotographs of TiO_2 particles recovered from HCl and H_2SO_4 acid solutions, and EDS (energy dispersive spectrometry) was used to evaluate the elemental distribution. Figure 4 displays SEM microphotographs, while elemental distribution is given in Figure 5. The SEM picture of the samples applied to and sintered on FTO glass is shown in Figure 6. Commercially used Aeroxide © TiO_2 particle morphology is similar to TiO_2 obtained over HCl acid. However, the TiO_2 structure produced over H_2SO_4 exhibits a sharp angular structure.

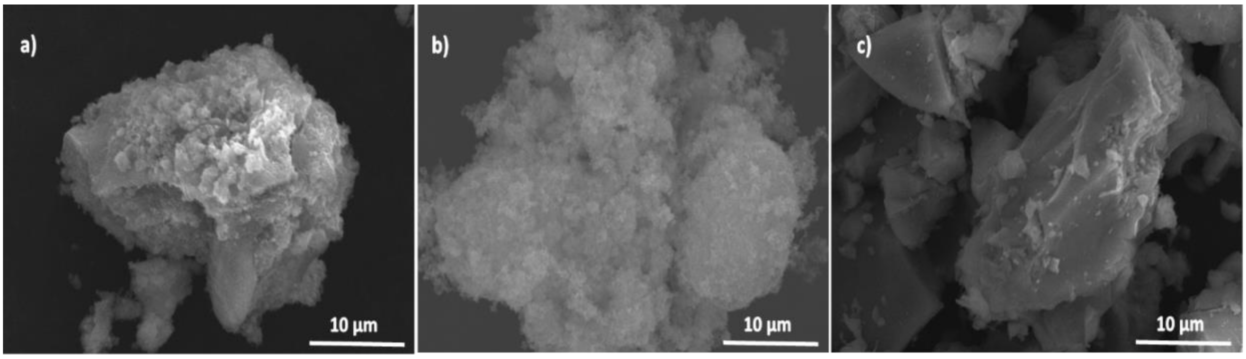

Figure 4. *SEM micrograph of powder particles at 3Kx magnification a) TiO_2 powder from HCl solution b) Aeroxide© TiO_2 P25 c) TiO_2 powder from H_2SO_4 solution*

In the elemental mapping shown in Figure 5, in addition to Ti and O, chlorine and nickel are in Figure 5a, and sulfur and nickel are in Figure 5c because these elements come from the production processes. However, nickel is more abundant in TiO_2 produced by H_2SO_4 acid leaching and less abundant in TiO_2 produced by HCl acid leaching.

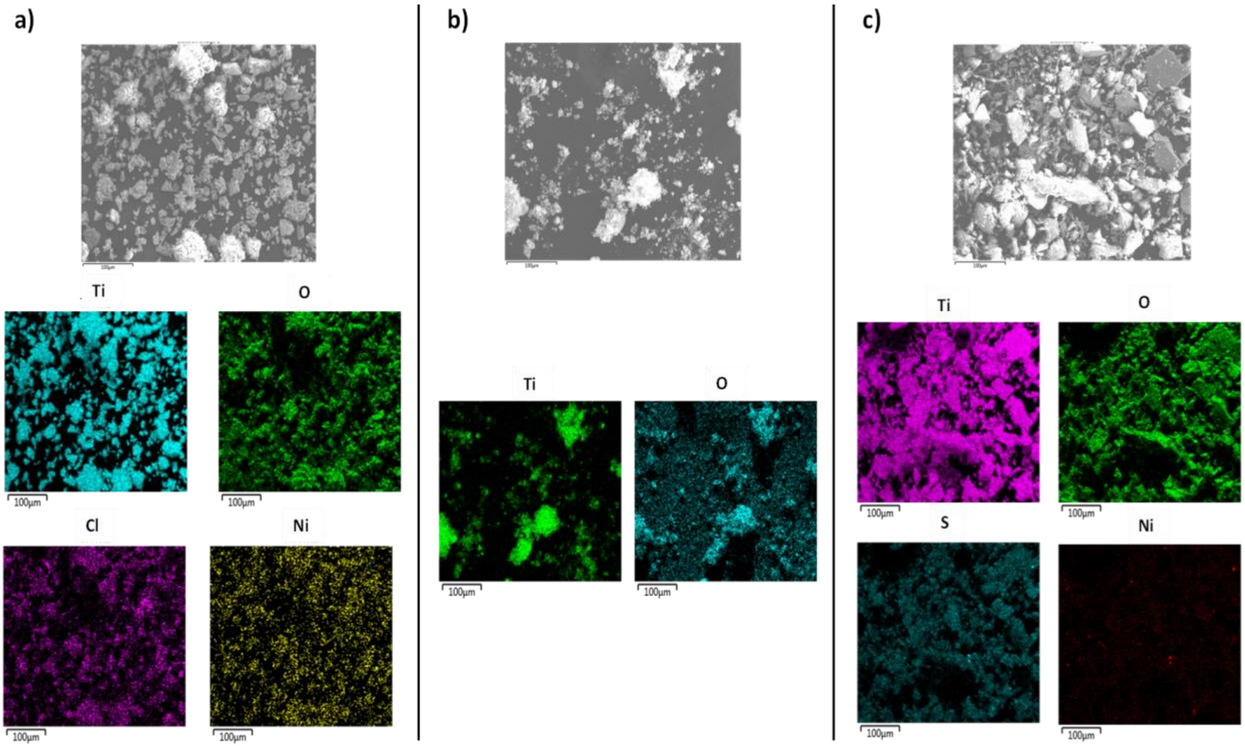

Figure 5. *SEM-EDS mapping of powder particles a) TiO_2 powder from HCl solution b) Aeroxide© TiO_2 P25 c) TiO_2 powder from H_2SO_4 solution*

Figure 6 shows the SEM photographs of TiO_2 powder structures produced by leaching NiTi files at 50x magnification after sintering and before dye immersion after applying TiO_2 powder structures to the

FTO glass surface with the specified procedure. In Figure 6b, the Aeroxide © TiO_2 P25 structure has a more integrated morphology with the surface than in Figure 6a and Figure 6b.

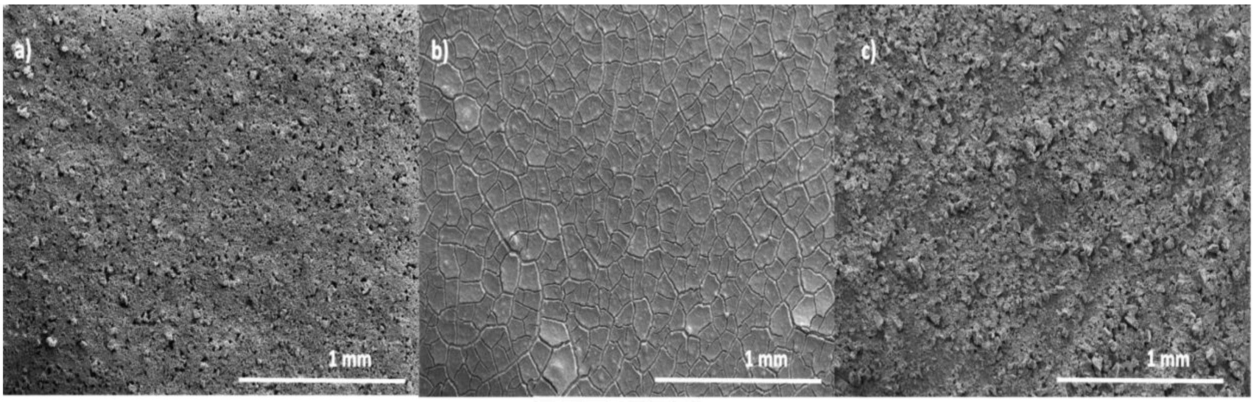

Figure 6. *SEM micrograph of samples after sinter process at 50x magnification a) TiO_2 powder from HCl solution b) Aeroxide© TiO_2 P25 c) TiO_2 powder from H_2SO_4 solution*

Figure 7 shows the results of Raman analysis of Aeroxide© TiO_2 P25 used as a reference and TiO_2 powders produced on HCl and H_2SO_4 acids. In these analysis results, Raman spectra were obtained for the vibrational modes of bonds at the molecular level. Raman analysis was performed at 785 nm, 100% power for 250 repetitions. The TiO_2 structures formed by the leaching of Aeroxide TiO_2 P25 and H_2SO_4 are anatase-dominated, while the TiO_2 structure produced by the leaching of HCl is in the rutile phase, as can be seen when the Raman shifts shown in Figure 7 are studied. In his research, Tuchel observed that the Raman spectrum may exhibit shifts based on the impurities present in the material. The bands observed at 143, 197, 397, 516, and 638 cm^{-1} are consistent with those expected for anatase TiO_2. However, the presence of bands at 241, 445, and 610 cm^{-1}, which correspond to the reference rutile phase, indicates that the sample is not solely composed of either anatase or rutile. Specifically, he noted that commercial TiO_2 tends to have a smaller crystallite size and is purer, while TiO_2 with impurities tends to have a larger crystallite size [12].

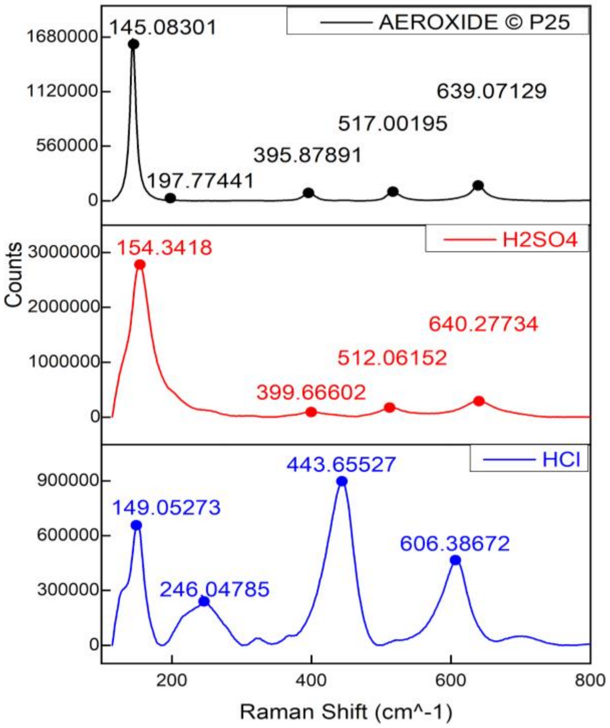

Figure 7. *Raman spectrum of powder particles*

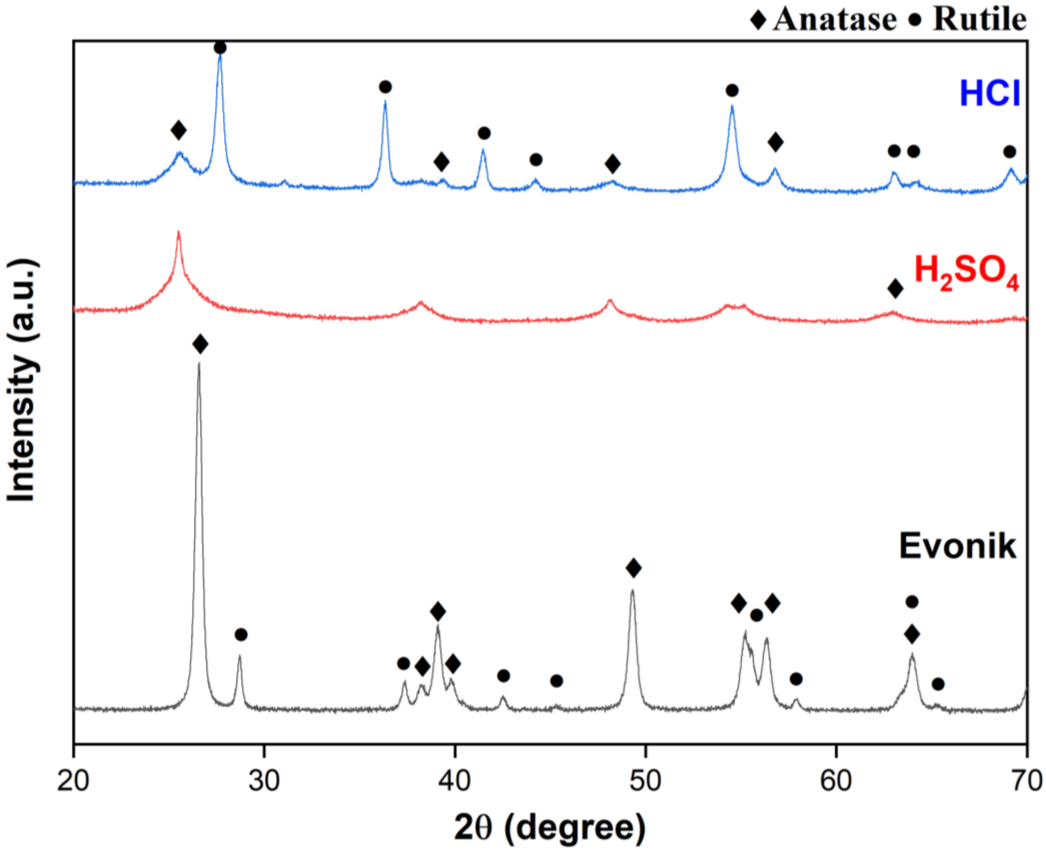

Figure 8. *XRD analysis of powder particles*

XRD analysis results are given in Figure 8. It is supported by the literature that the Raman spectra given in Figure 7 are compatible with the XRD patterns shown in Figure 8. X-ray diffraction (XRD) analyses were conducted using a copper (Cu) Kα tube with a step size of 0.013, within range of 20 to 70 degrees. The phases of TiO_2 used in the anode material of the dye-sensitized solar cell were determined. The XRD patterns provide peaks on the anatase and rutile phases of TiO_2 [13]. The XRD findings indicate that the peaks have shifted, which can be attributed to the presence of impurities within the structure.

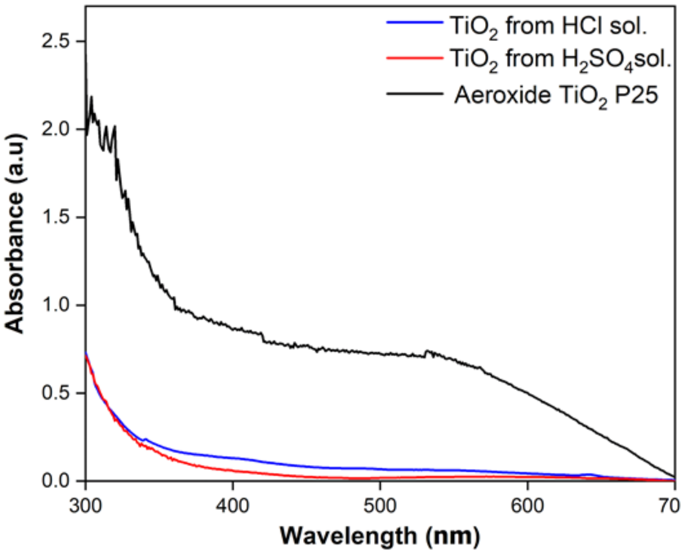

Figure 9. *Uv-Vis-NIR analysis of powder particles*

Following the application of N719 dye, the anode material samples used to construct solar cells were tested in the visible region of the spectrum in Figure 9. TiO_2-coated FTO samples were subjected to measurements. Examining the test findings reveals that commercially available Aeroxide© TiO_2 P25 produced absorbance in the visible spectrum (380–700 nm). On the other hand, no absorbance was present in this location in TiO_2 powder samples produced via H_2SO_4 and HCl acids.

Table 1 shows the particle size analysis results of TiO_2 powders used to produce anode material for dye-sensitized solar cells. When the results are examined, it is seen that the particle sizes are slightly larger than the literature values for Aeroxide© TiO_2 P25 reference material [14]. The reason for this may be the need for sufficient dispersion.

Table 1. *Particle Size distribution of powder particles*

Materials	***Total Particle Size (µM)***			
	D (10%)	**D (50%)**	**D (90%)**	**Mean D**
Aeroxide© TiO_2 P25	4.19	21.41	53.21	25.58
TiO_2 from H_2SO_4 solution	12.02	39.75	144.47	65.99
TiO_2 from HCl solution	8.60	36.09	75.47	57.88

DISCUSSION AND CONCLUSIONS

The TiO_2 powders produced over HCl and H_2SO_4 did not give a satisfactory result compared to the commercially used Aeroxide© TiO_2 P25 material. The material used in dye-sensitized solar cells should contain rutile and anatase phases, and the particle size should be small enough and excited by the visible spectrum (380-700 nm) [10,12–14]. The rutile and anatase phases in the materials obtained over HCl and H_2SO_4 acids were not as crystalline as the reference material compared to the commercial Aeroxide© TiO_2 P25 in XRD analysis. This is thought to be due to the lack of crystal structure, large surface area, and fast electron transport capability with appropriate electronic configuration, as mentioned in the literature. In the materials obtained over HCl and H_2SO_4 acids, contaminations from production (S, Cl, Ni) reduced electron transport [15].

TiO_2 powders obtained from the study should be produced under optimum conditions using dye-sensitized solar cell anode material. These conditions should be investigated with the support of literature studies. TiO_2 powder production parameters should be determined by examining the properties of the reference material in detail. In this context, grinding, washing with pure water, desulfurization (for sulfur contamination), and dechlorination (for chlorine contamination) of the materials obtained from HCl and H_2SO_4 acids should be performed. In the production of powder materials obtained from HCl and H_2SO_4 acids, intermediate processes are required due to contamination.

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