Contemporary Engineering Sciences, Vol. 10, 2017, no. 31, 1539 - 1549
HIKARI Ltd, www.m-hikari.com
https://doi.org/10.12988/ces.2017.711182

Effect of Cu on Optical Properties of TiO_2 Nanoparticles

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Abstract

Cu-doped TiO_2 nanoparticles were prepared; the effect of Cu on optical properties of TiO_2 nanoparticles to shift its absorption edge toward visible light region was studied. By using a green synthesis mechanism were obtained TiO_2 nanoparticles, and trough wet - impregnation method using copper sulfate as precursor were obtained Cu-TiO_2 nanoparticles. The synthesized material was characterized by Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDS), UV-VIS diffuse reflectance spectroscopy (UV-Vis/RDS). FTIR characterization have been made to confirm the formation of TiO_2. Through EDS analysis was determined the ion dopant percent in each sample. Morphological properties and particle size were identified by SEM micrographs, which disclose a spherical shape with an average size between 70 and 27.3 nm. UV-VIS/RDS spectrum showed that the band gap energy decreases with the increase of Cu concentration in TiO_2, for that reason, doped nanoparticles had activity under visible light irradiation.

Keywords: Titanium dioxide, doping, band gap, UV- light, visible light

1 Introduction

Titanium dioxide is a photosensitive semiconductor, it can be excited to produce electron–hole pair under ultraviolet light irradiation, through photoinduced processes that take place in TiO_2 [1]. Due to its chemical stability, non-toxicity, high photochemical resistance and abundance, has attracted a lot of interest in the scientific community [2]. It has been widely researched and numerous applications

have been developed in different areas, including photocatalysis, photovoltaic and photoelectrochemical devices and painting industry [3-5]. Photoinduced processes on TiO_2 are originated from its band gap (Eg), when photons emitted by a light source have a higher energy than band gap energy of TiO_2, they are absorbed and an electron (e^-) is promoted from the valence band to the conduction band, leaving a hole (h^+) in the valence band [6]. The photoexcited electron can be used directly to produce electricity in photovoltaic solar cells or to drive chemical reactions.

TiO_2 is a semiconductor with a large band gap, Eg = 3.2 eV and 3.0 eV for more common polymorphs of TiO_2 rutile and anatase, respectively [6-7], due to this, photoinduced reactions in TiO_2 take place under ultraviolet irradiation at 387 nm [8], which comprises around 3-5 % of solar light energy. To overcome this limitation, different ways have been investigated to extend its activity to visible region, making a better use of solar resource. Modification of electronic structure (doped) through insertion of non-metal ions, transition metal ions or rare earth elements has been an important alternative [6-9]. Metal transition doped has demonstrated to be an effective alternative to reduce the band gap of TiO_2 because it creates impurity levels that allow the electronic transitions within the conduction band and valence band, and simultaneously reduces the recombination rate of photogenerated charges [10]. In water photoelectrolysis, extending the TiO_2 photoresponse from the ultraviolet to the visible light region using Fe, Co, Mn, and Cu has been reported [11-13], leading also the increase of photocurrent density and the incident photon to current efficiency (IPCE) in relation to non-doped material [12].

This work aims to reduce the band gap energy of TiO_2 nanoparticles obtained from a green synthesis mechanism based on the Lemon Grass extract, in which organic solvents are replaced and natural extracts are used as reducing agent of the precursor alcoxide. Through impregnation wet were doped TiO_2 nanoparticles with copper sulfate as an ion precursor and their potential use under visible light irradiation was investigated.

2 Materials and Methods

2.1 Materials

Pure TiO_2 nanoparticles obtained from a green synthesis mechanism based on the Lemon Grass extract. Titanium isopropoxide IV ($C_{12}H_{28}O_4Ti$) – 95%, manufactured by AlfaAesar was used as a TiO_2 precursor, ethanol (CH_3CH_2OH) manufactured by Panreac was used for washing nanoparticles. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was used as a source of Cu for doping.

2.2 Synthesis of Titanium Dioxide Nanoparticles

Fresh leaves of Lemon Grass (Cimbopogon Cytratus) were washed with distilled water to remove the dust or any other dirt of the environment and dried at 40°C in a furnace, after that the leaves were cut into fine pieces and grinded. Aqueous extract was prepared by immersion of 100 g of lemon grass in 500 ml of distilled water at 90°C. This extract was filtered several times and concentrated by

evaporation heating it at 60°C. For synthesis of pure TiO_2 nanoparticles, an aqueous solution of 5mM of titanium isopropoxide was stirred by ultrasound during 30 min, 15 ml of the aqueous extract of lemon grass was added in 85 ml of isopropoxide solution with continuous stirring at 175 rpm and room temperature for 24 h [14]. After the reduction reaction, nanoparticles synthesized were removed by centrifugation and dispersed in ethanol and then in distilled water to wash out impurities. Finally, TiO_2 nanoparticles were dried in an oven at 100°C and then they were calcined in a muffle furnace for 3 h, starting at 300°C until 550°C, this heat treatment also allows the removal of organic matter without reacting [15].

2.3 Preparation of Fe doped TiO_2 Nanoparticles

TiO_2 nanoparticles were doped by using wet impregnation method [10]. Wet impregnation is a used technique where the precursor material is dissolved in a solvent and mixed with the support, and then the solvent is removed by evaporation when the precursor gets deposited on the bas material. An amount of TiO_2 was added in distilled water, the TiO_2 slurry was stirred (by ultrasound) for 30 min (to break up the loosely attached aggregates). After, an aqueous solution of Copper sulfate pentahydrate (precursor of Cu) with the required amount of precursor for doping was added to TiO_2 suspension (1, 3, and 5 wt % of copper was introduced as the dopant). It was subject of stirring by ultrasound at room ambient during 1 h, and subsequently stirring with heating at 60°C to evaporate the solvent, dried at 120°C and finally doped nanoparticles were calcined in a muffle furnace at 400°C for 1 h.

2.4 Characterization methods

The FTIR spectra of the samples, in the range of 400 to 4000 cm^{-1}, were recorded as the percentage of transmittance (%T) versus wavenumber. This analytic method is useful for the determination of the functional groups present in the nanoparticles synthesized identified by its characteristic peaks in the spectrum. The morphology, dimension and surface characteristics of the TiO_2 nanoparticles synthesized were determined with a scanning electron microscopy, Tescan model Vega 3, the sample was analyzed at 18°C. Determination of Cu presence and the chemical composition in TiO_2 samples were determined by using Energy Dispersive X-ray Spectroscopy, the amount of Cu introduced into the structures as a percentage of mass of Cu in relation to the mass of TiO_2 may be obtained with this. This analysis was carried out using a scanning electron microscope with a probe EDX Bruker Nano GmbH Berlin. The optical measurements were carried out to determine the band gap of pure TiO_2 and Cu doped TiO_2 to recognize the relative position of the absorption edge as an important indication whether the absorption edge has been shifted toward visible region, to find a relationship between the band gap energy and the amount of Cu used for doping the semiconductor.

UV-Vis spectroscopy in mode diffuse reflectance spectra were recorded on a spectrophotometer UV/VIS Evolution 600 Thermo Scientific in the wavelength range of 200 to 800 nm.

3 Results and Discussions

3.1 Fourier Transform Infrared – FTIR

FTIR analysis was performed to identify the role of the lemon grass leaf extract in the reduction reaction to produce titanium dioxide nanoparticles. Figure 1 shows the infrared spectra of green synthesized TiO_2. In Figure 1.a, a broad band located at 3278.98 cm^{-1} is observed, which is assigned to the stretching vibration of the hydroxyl bond (-OH) and the band around 1630 cm^{-1} is attributed to the bending mode of hydroxyl vibrations (-OH), this vibration band is related to protons of the physisorbed water into the synthesized material [16]. According to [17] titanium oxide retains adsorbed undissociated water due to the strong Lewis acidity of the co-ordinatively unsaturated Ti^{4+} surface sites. The descent band absorption at 1000 - 400 cm^{-1} is due to vibration modes of Ti-O, which indicates the formation of TiO_2 [16-17]. The chemical bonding of the Cu doped TiO_2 nanoparticles were also scrutinized. Figure 1.b, shows the IR spectra of the Cu/TiO_2 nanoparticles, all the doped samples show similar spectra to pure TiO_2, the intensities of these signals decrease according to undoped TiO_2, indicating water desorbed [18]. It is not detected bands in the low frequency regions that can be attributed to Cu-O vibration bond [19]. The absence of evidence of oxides generated from the dopant implies that the ions were incorporated within the TiO_2 lattice.

3.2 Scanning Electron Microscopy – SEM

The size and morphology of the nanoparticles with different contents of Cu-TiO_2 were determined by a scanning electron spectroscopy (SEM). The SEM image of pure and doped TiO_2 are presented in Figure 2a-d. The morphology is not uniform in these samples but prevails spherical shape in the nanoparticles. The particle size is not uniform for pure and doped TiO_2 nanoparticles, and there is a propensity to form aggregates, especially in Cu doped TiO_2, according to [20], the temperature of calcination affects the size and agglomeration of crystalline particles. The particle size was measured by using ImageJ software, for pure TiO_2 70 nm was determined, conversely, Cu doping produced a decreased in the particle size around 27.3 nm – 28.5 nm. These results are in agreement with the results obtained by [21], in this investigation the decrease in the particles size of commercial Degussa P-25 TiO_2 is attributed to the suppression of particle growth by the introduction of Cu atoms into the TiO_2 crystal structure.

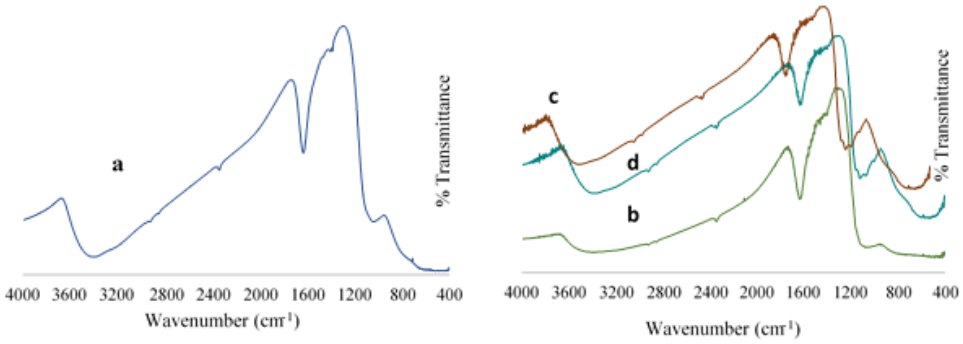

Figure 1. FTIR spectrum of pure TiO_2 nanoparticles synthesized, (a) pure TiO_2, (b) 1%wt Cu doped TiO_2, (c) 3%wt Cu doped TiO_2, (d) 5%wt Cu doped TiO_2

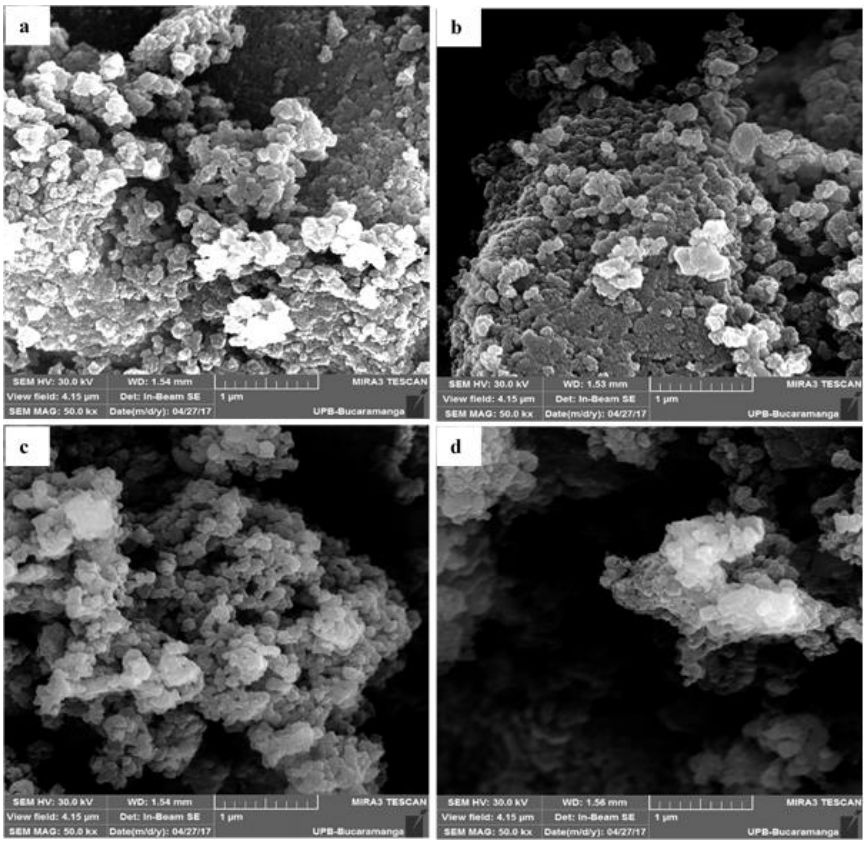

Figure 2. SEM micrographs of TiO2 synthesized, a. Pure TiO_2, b. 1%wt Cu doped TiO_2, c. 3%wt Cu doped TiO_2, d. 5%wt Cu doped TiO_2

3.3 Dispersive X-ray Spectroscopy – EDS

Figure 3 shows the elemental composition of each sample evaluated through energy dispersive X-ray spectroscopy**.** In these spectrum, the characteristic X ray energy emitted from Ti are observed on 4.508 (Kα) and 0.452 (Lα) keV, and O are on 0.525 (Kα) keV, in doped samples the characteristic signals of Cu are observed

on 8.040 (Kα) and 0.930 (Lα) keV [22]. In doped samples, the presence of S is identified on 2.307(Kα) keV, which is due to the $CuSO_4$ used by the Cu precursor [23]. There are peaks associated with K (Kα), Ca (Kα), Mg (Kα), Si (Kα) and P (Kα); these lines are attributed to the equipment used for the analysis or impurities (Varma et al, 2014). The percentage real of Cu incorporated into the TiO_2 structure was 0.78, 2.98 and 4.59% wt., with respect to the initial amount of Cu added during the doping process 1, 3 and 5% wt., so the amount of impregnated material was similar as was taken for impregnation.

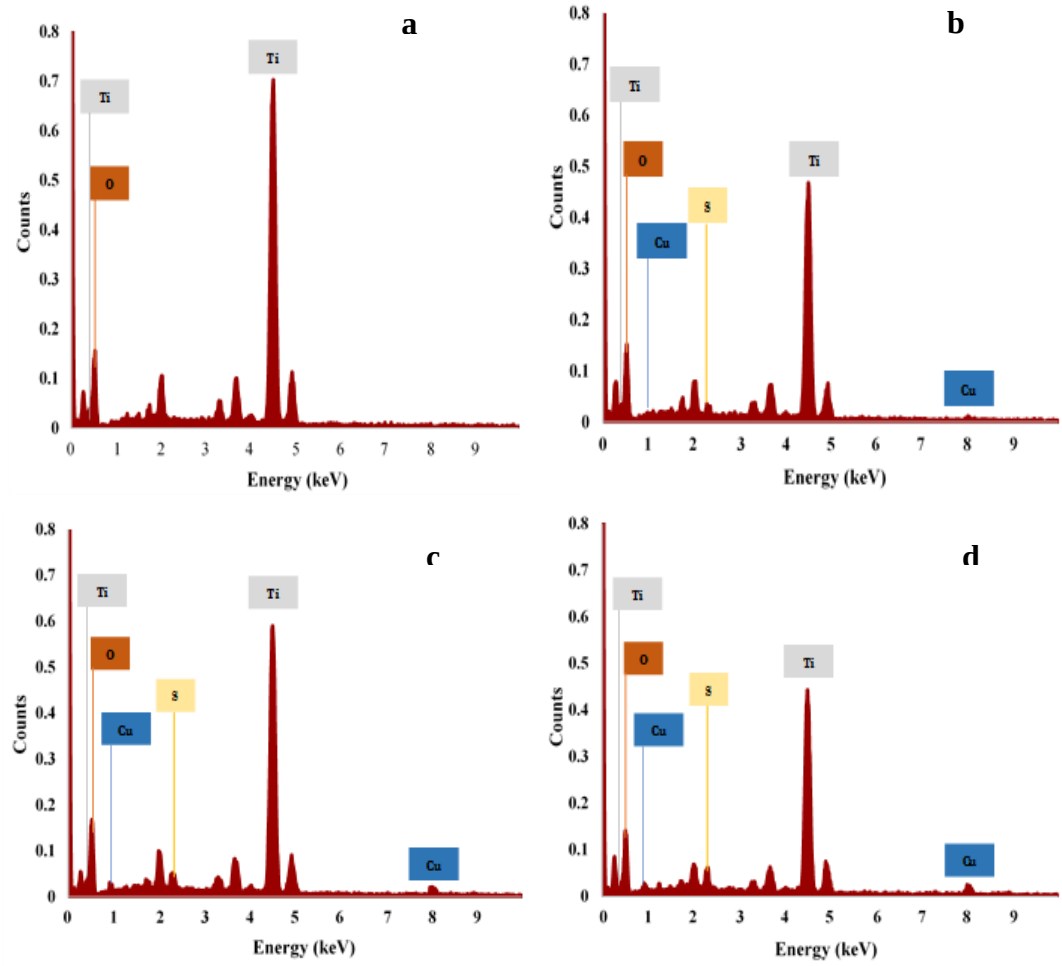

Figure 3. Energy Dispersive X-ray Spectroscopy spectrum, a. Pure TiO_2, b. 1%wt Cu doped TiO_2, c. 3%wt Cu doped TiO_2, d. 5%wt Cu doped TiO_2

3.4 UV-VIS Diffuse Reflectance Spectroscopy – UV-VIS/DRS

The UV-VIS/RDS spectra of pure and doped TiO_2 are depicted in Figure 4. The optical electronic excitation from valence band to conduction band is generally showed through an increase in the absorbance band in a specific wavelength in a UV-VIS spectrum [24]. All samples in this figure have a sharp absorption band in the region comprised by wavelength less than 400 nm, which may be attributed to

the band structure of original TiO_2. However in doped samples is observed the increase of the absorbance in wavelengths higher than 400 nm, therefore, the valence band in doped samples can be excited with photons of lower energy than pure TiO_2. Figure 4 reveals that incorporation of copper ions leads to shift of optical response toward visible region of the spectra, in the same way, increasing the amount of dopant, increases the intensity of those absorbance peaks in the visible region. Based on the spectrum in figure 4, the optical energy band gap of pure TiO_2 and Cu doped TiO_2 was determined by using the Tauc plot relation. Starting with the equation $\alpha h\upsilon = B(h\upsilon - E_g)^n$, where α is the absorption coefficient, which is proportional to the absorbance, h is the Planck's constant (J.s), υ is the light frequency (s^{-1}), B is the absorption constant, E_g the band gap energy and n is a constant related to the electronic interband transition. n = 2 for an indirect allowed transition (plotted as $(\alpha h\upsilon)^{1/2}$ versus E), n = 3 for an indirect forbidden transition (plotted as $(\alpha h\upsilon)^{1/3}$ versus E), n = 1/2 for a direct allowed transition (plotted as $(\alpha h\upsilon)^{2}$ versus E), n = 3/2 for a direct forbidden transition (plotted as $(\alpha h\upsilon)^{2/3}$ versus E) [24]. Plotting $(\alpha h\upsilon)^{1/n}$ as a function of E (photon energy), the band gap energy value is obtained by extrapolating until $(\alpha h\upsilon)^{\frac{1}{n}} = 0$ the linear section of this spectra. Considering in TiO_2 an indirect allowed transition, the band gap energy obtained for pure TiO_2 and doped TiO_2 samples are plotted on Figure 5.

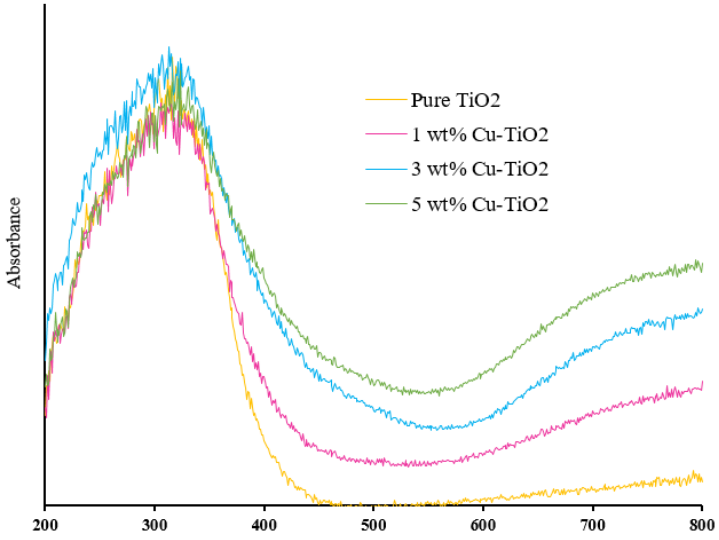

Figure 4. UV-VIS/RDS spectrum of TiO_2 samples

Figure 5 illustrates the estimation of band gap energy for all samples by extrapolation the straight line to the E (eV) axis. The band gap energy (Eg) obtained for TiO_2 nanoparticles synthesized by green synthesis method is 2.98 eV, the calculated Eg values for Cu doped TiO_2 with 1%, 3%, and 5% are 2.6 eV, 2.23 eV and 1.99 eV, respectively. Figure 5 shows that the band gap energy decreases with Cu doping and with the increasing of the Cu concentration, furthermore, these results suggest that Cu doping certainly causing absorbance of visible light by TiO_2.

The band gap energy values obtained in this investigation are similar to those reported by [25], in which have reported a reduction in band gap of TiO_2 from 3 eV for pure samples to 1.6 eV for 7.5 % Cu doped TiO_2 by using a different doping mechanism. Doping with transition metals can extend the absorption edge of TiO_2 to visible light due to its electronic characteristics, through inserting new electronic states into the original band gap, which is why electrons can be excited from the defect state to the TiO_2 conduction band by photons less energy [26]. According to the work developed by Guo and Du [27], Cu doping can induce some doping states near the top of valance band, and thus enhance the visible absorption in the range of 400–1000 nm by Cu 3d–Ti 3d optical transition.

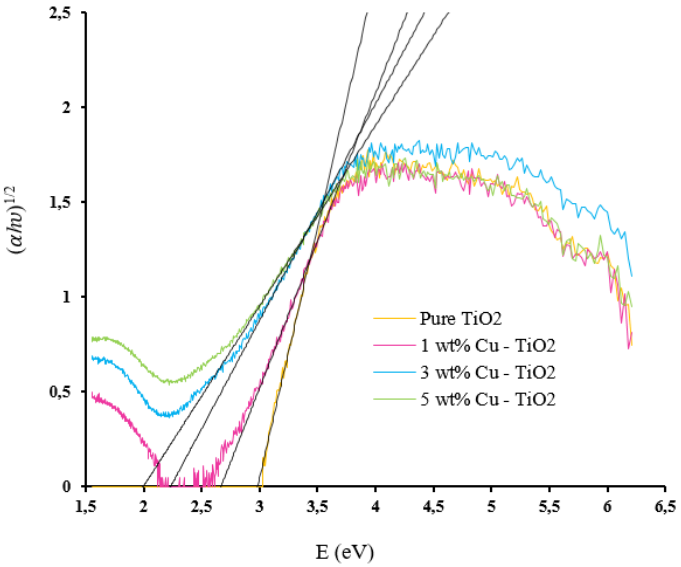

Figure 5. Tauc plot of pure TiO_2 and doped TiO_2

4 Conclusions

Titanium dioxide and Cu doped TiO_2 particles have been synthetized, the biosynthesis mechanism leaded to obtain particles with nanometric size. The size decreased in Cu doped TiO_2 nanoparticles. The metal doping in titanium dioxide has been carried out by wet impregnation process, Cu doped TiO_2 showed a reduction in the band gap from 2.98 eV to 1.99 eV, shifting the absorption edge of TiO_2 toward a region of lower energy, which improve the photoactive process in the material.

Acknowledgements. Authors of this paper would like to express their gratitude to University of Cartagena for providing the recourses and the space to perform this project through the resolution No. 031-2017.

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Received: December 1, 2017; Published: December 19, 2017