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Electrical and optical properties of nanocrystalline-Cu-doped TiO_2 prepared by precipitation method

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Abstract

Electrical and optical properties of copper doped onto nanocrystalline of titanium dioxide nanoparticles (TiO_2 NPs) prepared by precipitation method were investigated. NaOH of 1 M, copper nitrate trihydrate and powder of TiO_2 NPs were used as starting materials by varying ratio of Cu-doped TiO_2 from 2 to 30 %wt. The product of precipitation process was dried at a temperature of 120 °C for 6 h and used temperature of 300 °C for 0.5 h in the calcination process. After then, the UV-Vis spectroscope was used for analyzing the electrical and optical properties of the powder. It was found that the absorbent analysis showed the wavelength in the range of 302 - 309 nm, the absorbance at 2.05 - 3.88 a.u., and 3.88 at the optimum doping of 15 %wt. The energy band gab is the indirect band gap. It was found that the energy band gap decreased with increasing the doping percent of Cu. However, the doping Cu onto TiO_2 NPs exhibits the different wavelengths and energy band gaps from pure TiO_2 NPs. The wavelength of 314 nm and the energy band gap of 3.33 eV were occurred for an only TiO_2 NPs powder whereas the only Cu powder (100 %wt. Cu-doped TiO_2) possess wavelength and energy band gap of 349 nm and 2.45 eV, respectively. Therefore, the doped Cu has affected the electrical and optical properties of TiO_2 NPs.

Keywords: Electrical properties, Optical properties, Precipitation method, Titanium dioxide nanoparticles

1. Introduction

Titanium dioxide nanoparticles (TiO_2 NPs) are semiconductors which are worldwide interesting for many applications because they are high refractive index and transparent. They can be used for photocatalytic activity in waste water and removing pollutants for air purification [1] and dye-sensitized solar cells.

In addition to optical properties, TiO_2 NPs can be also used for making capacitors, sonar transducers of submarine positioning, ultrasonic sound generators, gas sensors, components of electronics, light filter films and applying in digital displays. Earlier, majority of the research has been focused on high performance and low cost materials of doped TiO_2 NPs for improving electrical and optical properties by doping transition metals such as Co, Cr, Nb, Ta, W, V, Mn, Fe, Cu and Mo. Doping method can be done in several methods, e.g., sintering, sol-gel, spray-pyrolysis, pulsed laser, sputtering and precipitation. Precipitation method is very interesting because it can be carried out by using low cost raw materials, and is an easier manufacturing method on industrial level [2].

Physical properties of TiO_2 NPs can be changed or improved by doping some elements. Copper is common metal that is used as an electrical conductor because of its high electrical conductivity and high thermal conductivity. This research work emphasizes on the study of Cu-doped TiO_2 NPs by precipitation method and investigates their electrical and optical properties. UV-Vis spectroscopy was used to study optical properties of the powder.

2. Materials and Methods

Materials

Titanium dioxide nanoparticle powder (Degussa, P25), TiO_2 (P25) was used as main materials. Copper nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$, (Ajax, 99% purity), was used as the dopant metal precursor of 2, 5, 10, 15, 20 and 30 wt.% for the preparation methods. Glycerol (Ajax, 99.5% purity) was used as the complexing agent for copper. Sodium hydroxide, NaOH (Ajax, 95% purity) was used as the precipitating agent in the precipitation method. All materials were used without further purification.

Methods

Glycerol was added to an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (Cu:glycerol mole ratio 1:2) to generate a copper-glycerol complex [3]. This was followed by addition of TiO_2 (P25) powder to the solution with continuous stirring for 30 min to form a suspension. The copper-glycerol complex was precipitated on TiO_2 (P25) particles by adding NaOH (1 M) drop wise into the suspension with constant stirring. The precipitate formed was further stirred intensely for 30 min and prior to filtering and then drying at 120 °C for 6 h. and at temperature of 300 °C for 0.5 h in the calcination process. In addition, we compare Cu-doped TiO_2 NPs to undoped TiO_2 (P25) (TiO_2 (P25) of 100%).

3. Results and Discussion

Characterization

The structure and TiO_2 phase present of all samples were examined by X-Ray diffractometer (Bruker D2 Phaser) (Cu anode radiation of 30 kV, 10 mA). Then, the wavelength and the intensity of an absorption spectra were measured by UV-Vis spectrophotometer (GENESYS 10S). The optical energy band gab (E_g) was obtained by plotting the Kubelka-Munk function and by extrapolating the linear fit for the Tauc plot onto the photon energy axis.

X-Ray Diffraction Data

The XRD patterns of TiO_2 (P25) and 2, 5, 10, 15, 20, 30 and 100 %wt of Cu-doped TiO_2 are shown in Fig. 1. The peaks at 2θ = 25.43 ° and 48.20 ° can be indexed to the (101) and (200) crystal faces of anatase TiO_2 (JCPDF 89 -4921) and 2θ = 27.55 ° and 36.28 ° corresponding to the crystal faces of rutile TiO_2 (PDF 72-1148) which appear in all samples, except 100 %wt of Cu-doped TiO_2 powder [4 - 5]. CuO (tenorite) diffraction peaks appeared near 2θ = 35.63 ° and 38.95 °, indexed to the (-111) and (111) for X-ray diffraction planes (PDF 41-0254) for all the powder samples, except pure TiO_2 (P25). It is also observed that the CuO peak intensities increased for higher Cu doping from 10-30 %wt of Cu-doped TiO_2 powder samples, but the peaks intensities of the crystalline form of TiO_2 (P25) are decreased. The CuO peak intensities for 100 %wt of Cu-doped TiO_2 powder sample are also found.

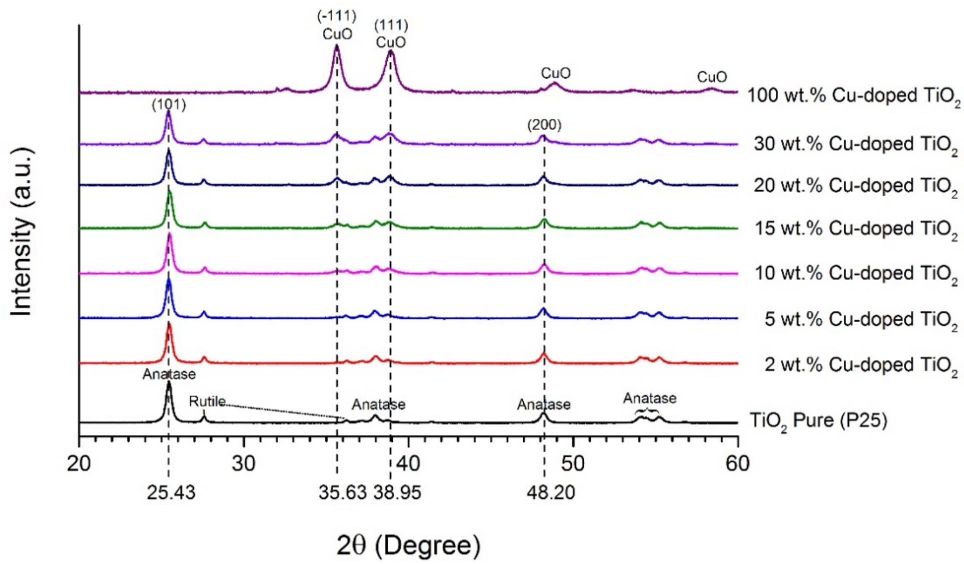

Fig. 1 XRD diffractograms for powder samples

Absorption spectra of all samples

The UV-Vis spectra of TiO_2 (P25), CuO nanoparticles of 100 % and the Cu-doped TiO_2 powder samples are depicted in Fig. 2. It was found that the wavelength and absorption intensity of TiO_2 nanoparticles possess 314 nm and 3.64 a.u., respectively. CuO nanoparticles of 100 % possess the wavelength and the absorption intensity of 349 nm and 1.32 a.u., respectively. Cu-doped TiO_2 nanoparticles have wavelength in the range of 302-309 nm and possess the absorption intensity in the range of 2.05-3.88 a.u. The increasing absorption intensity was found between 2 %wt and 15 %wt of Cu doped. However, the decreasing absorption intensity was found from 20 to 30 %wt. It is noted that an optimum absorption intensity was found at 3.88 a.u. of 15 %wt Cu doped TiO_2

The energy band gap energy

The energy band gap of the optimum absorption intensity (15 %wt Cu doped TiO_2), TiO_2 (P25) and CuO NPs can be obtained by plotting a relation between $[Ah\nu]^2$ against $h\nu$ which is referred from the Kubelka-Munk formalism and the Tauc plot, as shown in Fig. 3. An indirect band gap was calculated and used a constant as n = 2 [6-7]. Therefore, the relationship can be described as;

$$[Ah\nu]^2 = K(h\nu - E_g) \tag{1}$$

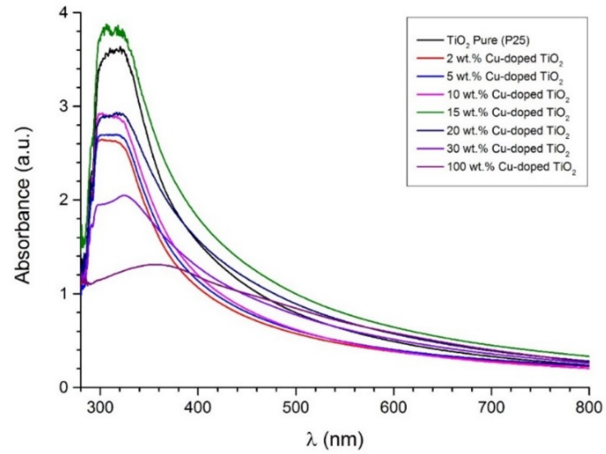

Fig. 2 Wavelength and absorbance of powder samples

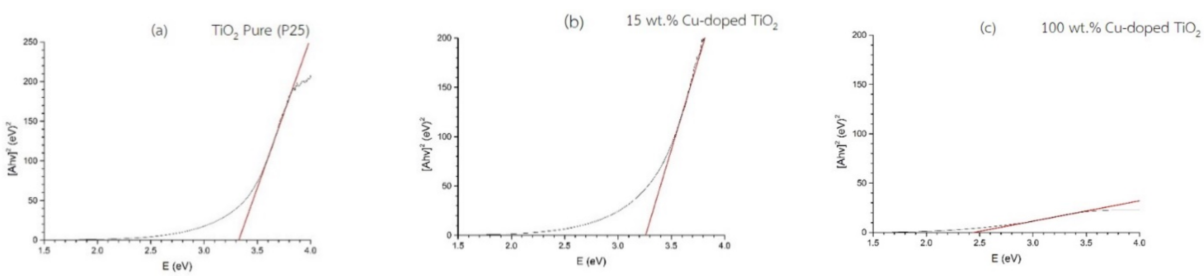

Fig. 3 A plot of $[Ah\nu]^2$ against $h\nu$ (a) TiO_2 Pure (P25), (b) 15 %wt Cu-doped TiO_2 and (c) 100 %wt Cu-doped TiO_2

It was found that the band gap energy of TiO_2 (P25) was 3.33 eV. Undoped CuO NPs possess the energy band gap of 2.45 eV [8]. However, 15 %wt Cu-doped TiO_2 NPs possess the energy band gap of 3.26 eV. It was noted that the doping Cu into TiO_2 had been affected to the energy band gap of TiO_2 which occurred from the quantum size effects, electronic excitation consisting of a loosely bounded electron-hole pair (the Mott-Wannier exciton), usually delocalized over a length much longer than the lattice constant. As the diameter of the semiconductor crystallite approaches this exciton Bohr diameter; its electronic properties start to change. It can be observed as a blue shift in the optical bandgap or exciton energy [9] which agrees with the data experiment of Robabeh [10], found that the absorption peak of TiO_2 is generally related to the transition of the electrons from valence band (VB) (O-2p state) to conduction band (CB) (Ti-3d state) in the UV region. Also In Fig. 3 (b) 15 %wt Cu-doped TiO_2 shows highest absorption intensity due to presence of Cu^{2+} sub-band state in the middle of band gap energy for indirect transition of the excited electrons from VB to CB. The different absorption bands in Cu-doped TiO_2 were the result of the charge transition from ligand to metal ($O^{2-}_{(2p)} \longrightarrow Cu^{2+}_{(3d)}$) at 302-309 nm and the broadband absorbance range of 400-600 nm due to existence of Cu^{+} from the reduction of CuO as well as $(Cu\text{-}O\text{-}Cu)^{2+}$ [10].

Copper doped nanocrystalline of titanium dioxide (0-30% Cu-doped TiO_2) nanoparticles were prepared by precipitation method. The structure of the samples was characterized by the XRD diffraction technique. UV-VIS spectroscopy was used to determine optical band gap. It was found that the structure of the Cu was found at 10 - 30 %wt. The maximum absorption intensity occurred at 15 %wt Cu doping level. The energy band gabs were 3.28 eV for Cu-doped TiO_2 powder, and 3.33 eV of TiO_2, and 2.91 eV for Cu NPs. Therefore, the doping Cu has an effect on the electrical and optical properties of TiO_2.

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