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Preparation and characterization of copper doped titanium dioxide thin film by sparking process

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Abstract

The advantages of copper (Cu) doping into Titanium Dioxide (TiO_2) semiconductor could reduce the band gap energy of TiO_2 and enhance visible light absorption. Pure and Cu-doped TiO_2 nanoparticles thin films of about 900 – 1200 nm thickness were successfully deposited onto glass substrates by sparking process. To obtain a uniform film thickness, the substrate was moved rotate around an area of 1 × 1 cm^2. The films were annealed at 500 °C for 60 min. The doping ratios of Cu-doped TiO_2 were 2, 7, 12, 18 and 23 atomic%. The effects of dopants content on optical properties were investigated. Scanning electron spectroscopy (SEM) images indicated agglomerated particle size decrease with increasing the Cu content after annealing treatment, and energy dispersive X-ray spectroscopy (EDS) analysis confirm contents of copper into TiO_2. Raman spectra reveal the annealed samples at 500 °C are anatase combined with rutile phase. Ultraviolet-visible (UV-Vis) spectroscopy study is used to characterize the effect of copper dopant with different concentrations on the band gap energies of TiO_2 nanoparticles. The absorbance spectra indicated increase visible region and the band gap energy decreased with increasing copper contents.

Keywords: Cu-doped TiO_2; thin films; nanoparticles; sparking process

1. Introduction

Titanium dioxide (TiO_2) is an interesting semiconductor oxide material because of low cost, good chemical stability, strong photocatalytic ability and non-toxic. The main TiO_2 is a wide band gap of 3 to 3.20 eV. According to their chemical and physical properties, it has been used to be a candidate material for many applications such as photoanode for dye sensitized solar cell [1], photocatalyst for hydrogen production [2] and disinfection of bacteria [3] as well as self-cleaning and anti-biofouling in water and air [4]. In the past of decade, TiO_2 mostly had been advantage of photocatalysis in ultraviolet region because they performed in good chemical stability and strong photocatalytic ability. The band gap of TiO_2 exhibits that this metal-oxide semiconductor can only manifest photocatalytic properties in UV light with shorter wavelength. However, UV light only accounts for 4% of sunlight, so the utilization rate of sunlight is very low. To fully make use of solar energy and develop new photocatalysts that can react in visible light with stable structure and performance, In order to improve their photocatalytic property, TiO_2 has been doped many impurity elements such as Cu, Ce, Fe, La, Al, Tb, Mg, Zn, Ag, Eu and Pt [5 – 8]. Among these elements, Cu-doped TiO_2 has been studied due to the Cu doping result can affect to reduction the energy band gap by increasing red shift and absorption in ultraviolet-visible region which can improve more absorption efficiency and photocatalytic property [2, 8]. There are various methods to synthesize TiO_2, which are included DC-sputtering [8], sol-gel [9], spray pyrolysis [6], ammonia-evaporation-induced synthetic [3], hydrothermal [1], flame aerosol reactor [10] and detonation [11]. A sparking process is a material preparation method which is easy to use, low cost, rapid and uses non-toxic starting materials (e.g. Ti wire). This method produced semiconductor material in size of nanoparticle that made more surface area and is suitable for photocatalytic property. The sparking technique also was used widely for many applications, for example, photoelectrode and counterelectrode for dye-sensitized solar cell [12], photocatalyst [13] and self-cleaning [14].

In this recent work, we aim to study and synthesize titanium dioxide thin films on glass substrate prepared by sparking process. Effect of Cu-doped TiO_2 on morphologies, chemical structure and optical properties were investigated. The Cu-doped TiO_2 thin films were characterized by Scanning electron microscope (SEM), Energy Dispersive X-ray spectroscopy (EDS), Raman spectroscopy and Ultraviolet-visible spectroscopy.

2. Materials and methods

Cu-doped TiO_2 films were synthesized in form of thin film on a rotating glass substrate by a pair tip sparking process. Titanium wires (purity 99.80%, diameter 0.32 mm) were placed as the main tips, while Copper wire (purity 99.99%, diameter 0.50 mm) wires were placed as the doping tips, which are shown in Fig. 1. The sparking process was done for 60 min under flowing argon (Ar) atmosphere with a flow rate 0.50 L min^{-1} at room temperature. The doping ratio of Cu to Ti was controlled by sparking energy using a different capacitor (C) paralleled Cu doping tips. The capacitances paralleled Ti was fixed at 48 nF, while the capacitance paralleled of Cu were varied by 0.50, 1.10, 1.50, 3.10 and 4.70 nF. After the sparking process, all samples were annealed at 500 °C for 60 min in normal ambient.

The surface morphology of thin films was observed by using scanning electron microscopy (SEM; JEOL JSM-6335F). The element compositions and doping rations were investigated by using energy dispersive X-ray spectroscopy (EDS; OXFORD EDS Detector). The chemical structure of Cu-doped TiO_2 films was measured by Raman spectroscopy (JOBIN YVON HORIBA) in a wavelength range of 300 – 800 cm^{-1}. Optical absorption property of thin films was recorded in a wavelength range of 100 – 700 nm using Ultraviolet-Visible spectroscopy (Perkin-Elmer Instruments).

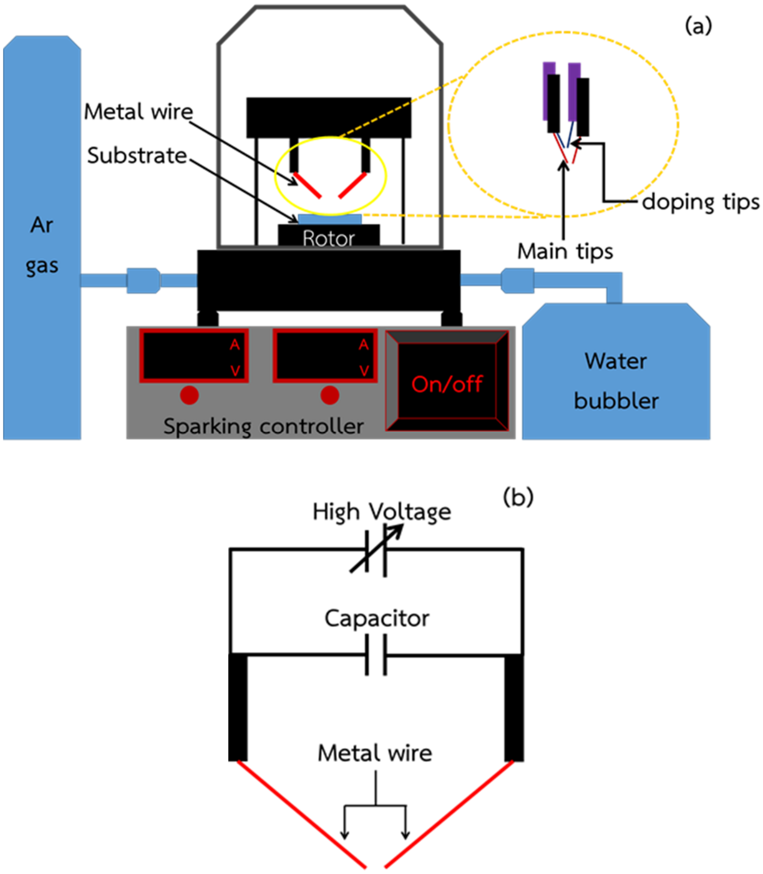

Fig. 1 (a) Systematic diagram of a pair tips sparking process was done under argon atmosphere and (b) equivalent circuit of sparking process.

3. Results and Discussion

The morphologies and chemical structure of pure TiO_2 and Cu-doped TiO_2 films

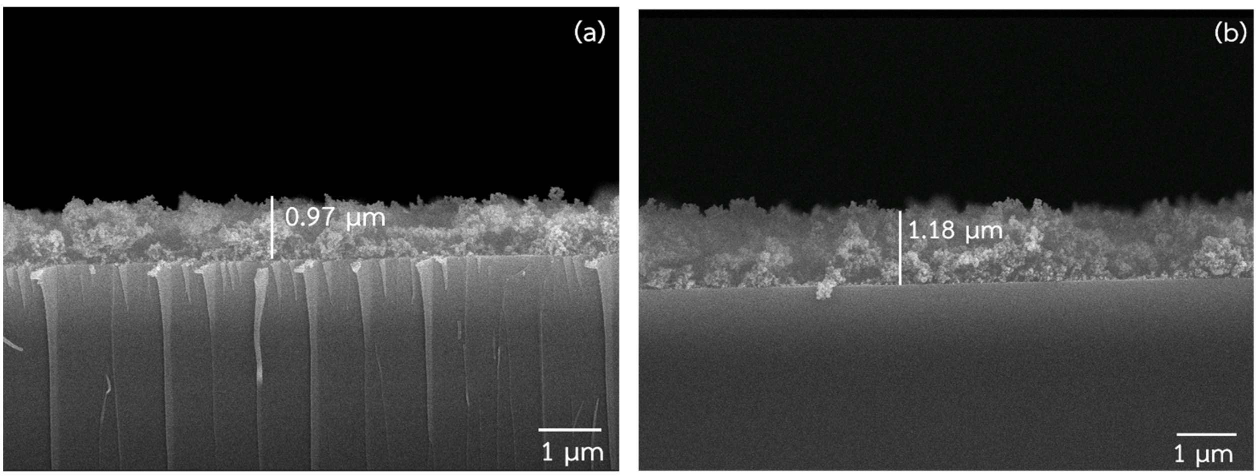

Fig. 2 SEM cross section of un-doped (a) and 23% of Cu-doped TiO_2 (b) thin films.

Fig. 2 shows the SEM cross section of un-doped and 23% of Cu-doped TiO_2 thin films prepared by the sparking process. The different energy ($E = CV^2/2$, at the same breakdown voltage (V)) of Ti and Cu resulted different Cu content and the film thickness as illustrated in Table 1.

Table 1 The Cu doping ratio and films thickness.

Capacitance Ti : Cu	Cu doping (atomic%)	Thickness (μm)
48 : –	0	0.97
48 : 0.50	2	0.99
48 : 1.10	7	1.10
48 : 1.50	12	1.01
48 : 3.10	18	0.99
48 : 4.70	23	1.18

Fig. 3 (a – f) shows the SEM surface morphologies and EDS of un-doped and Cu-doped TiO_2 at 2, 7, 12, 18 and 23 atomic%. It is noticed that the agglomerated particle size decrease with increasing the Cu content after the annealing treatment. This can be explained because dopants can replace Ti in the substitutional sites or be incorporated in the interstitial sites [15]. In some case, they may segregate on the surface [16]. The results of EDS confirmed the existence of Cu in all samples (0, 2, 7, 12, 18 and 23 atomic%).

Fig. 4 show the Raman spectra of annealed Cu-doped TiO_2 films. The peaks corresponded to the anatase and rutile phases are marked. It is noted that the anatase peaks at 148, 405 and 519 cm^{-1} and rutile peak at 448 and 612 cm^{-1}. Obviously, there is no impurity peak was obtained in Raman spectra, indicating that no CuO formed in Cu-doped TiO_2 samples.

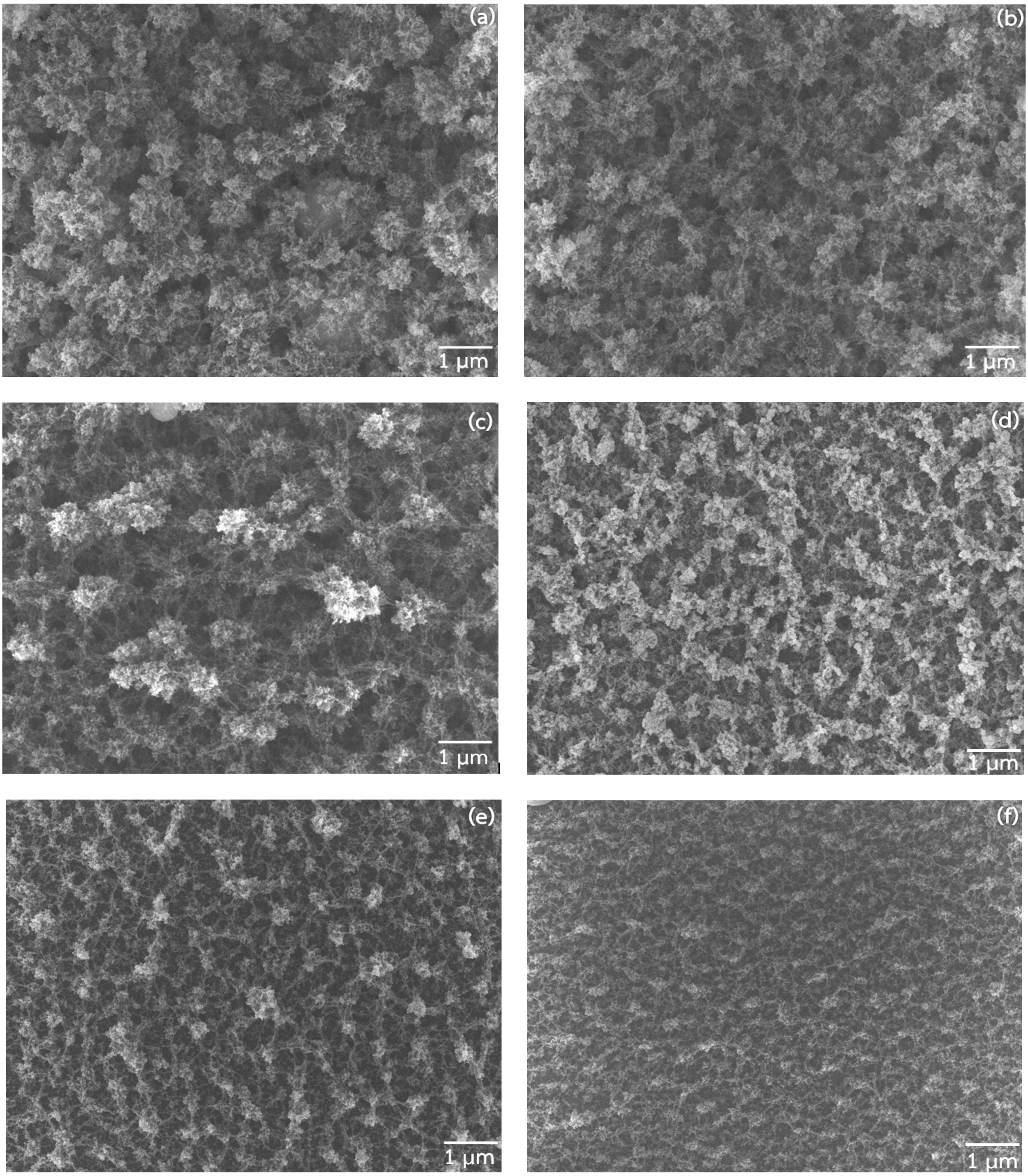

Fig. 3 SEM images of (a) un-doped, (b) 2% Cu-doped, (c) 7% Cu-doped, (d) 12% Cu-doped, (e) 18% Cu-doped and (f) 22% Cu-doped TiO_2 films.

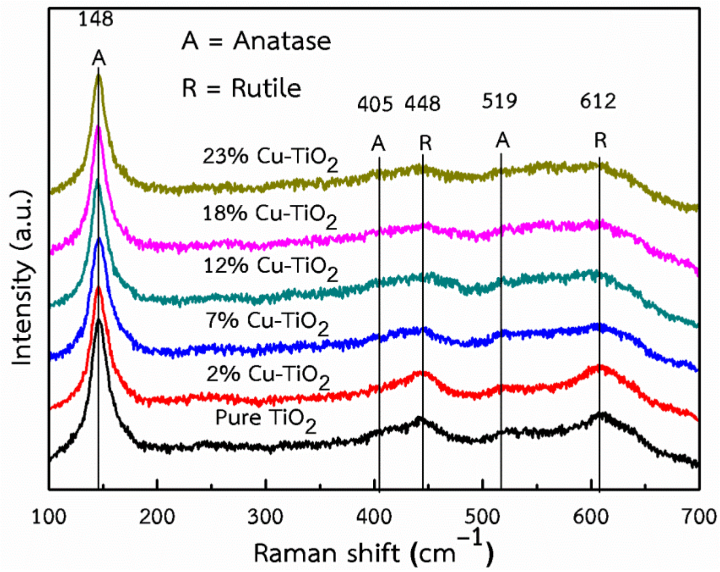

Fig. 4 Raman spectra of pure TiO_2 and Cu-doped TiO_2 films.

The optical property of pure TiO_2 and Cu-doped TiO_2 films

Fig. 5 shows the optical absorbance spectra of samples in wavelength range of 300 – 800 nm at room temperature. It is clear that the absorbance increased with increasing the doping ratio of Cu. Moreover, a red shift of the absorption edge was observed in the doped films [1]. It probably caused by the band gap energy turning that resulting from Cu content in TiO_2. The change in the optical absorption is due to the defect centers created by the substitution of Ti^{+4} by Cu^{+2} atoms. Earlier studies indicated that doping with aliovalent ions change the local lattice symmetry and defect characteristics, which could change the absorption properties and the material properties. In Cu-doped TiO_2, when copper ions are either located inside TiO_2 or on the surface sites, a rearrangement of the neighbor atoms take place to compensate the change deficiency, resulting in lattice deformation. The lattice deformation affects the electronic structure causing the band gap shift [17].

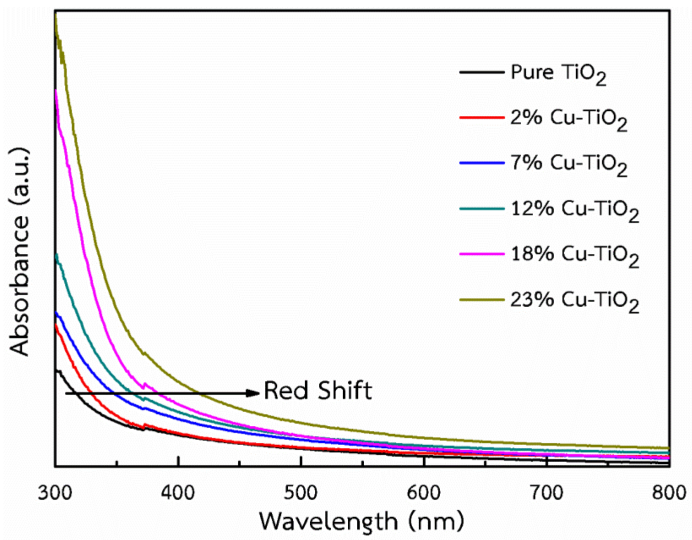

Fig. 5 Absorbance spectra of pure TiO_2 and Cu-doped TiO_2 films.

For calculation the energy gap (E_g), Tauc Method is used to evaluate the energy gap of the samples using as equation (1);

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (1)$$

Where C is a constant, E_g is the optical band gap energy, hv is photon energy. α is absorption coefficient and can calculate from absorbance by α = 2.30 A/d, where A is the absorbance and d is the film thickness. The relation curves of $(\alpha h\nu)^2$ and hv were plotted. A linear extrapolation, the point value of fitted line and x axis is E_g, as shown in Fig. 6(a). The optical band gaps of the film were 2.55 to 3.34 eV as show in Fig. 6(b). It is clearly seen that optical band gap decrease with increasing the Cu doping ratio. Consequently, it was according to a reported of Thimsen *et al*. say the estimated E_g for pristine TiO_2 was 3.31 eV. With increasing dopant concentration, the band gap energy decreased and was estimated to be 2.51 eV at the highest dopant concentration of 15 wt.%. This change of approximately 0.79 eV was due to the incorporation of Cu^{2+} ions into structure of TiO_2 [18].

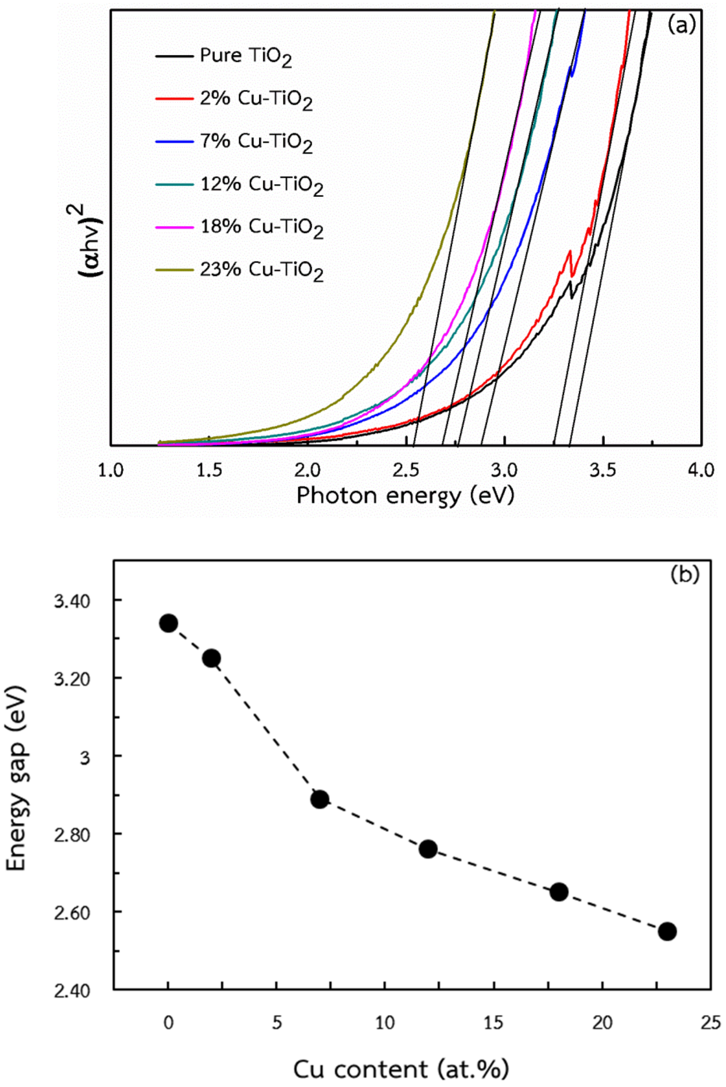

Fig. 6 Variation of $(\alpha h\nu)^2$ Vs (hv) (a) and energy gap (b) of pure TiO_2 and Cu-doped TiO_2 thin films.

4. Conclusion

Pure TiO_2 and Cu-doped TiO_2 thin films were deposited on glass substrate by double tip sparking process. The morphologies, chemical structure and optical properties were investigated. Scanning electron spectroscopy (SEM) images indicated agglomerated particle size decrease with increasing the Cu content after annealing treatment, and energy dispersive X-ray spectroscopy (EDS) analysis confirm contents of copper into TiO_2. Raman spectra reveal the annealed samples at 500 °C are anatase combined with rutile phase. Ultraviolet-visible (UV-Vis) spectroscopy study is used to characterize the effect of copper dopant with different concentrations on the band gap energies of TiO_2 nanoparticles. The absorbance spectra indicated increase visible region and the band gap energy decreased with increasing copper contents.

5. Suggestions

This technique is easy to use, low cost, rapid and uses non-toxic starting materials (e.g. Ti wire). Using this sparking process, films can be deposition directly onto a substrate without the need for a vacuum system. Moreover, the sparking apparatus is easily portable, which means that windows/glass walls can be coated in situ.

6. Acknowledgement

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7. References

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