

Oxalic acid assisted synthesis of the photochromic tungsten trioxide nanostructure

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The photochromic material, tungsten trioxide nanostructure has been successfully prepared by the simple precipitation method using nitric acid with the assistance of an oxalic acid. The effect of oxalic acid as the chelating agent on the morphologies, crystal structure, the optical properties and photochromic properties were investigated. The synthesized nanostructure characterized by X-ray diffractometer consisted of orthorhombic and hexagonal phase. The results from scanning electron microscopy and transmission electron microscopy presented the flower-like shaped nanostructure formed by the growth of many nanosheets. UV-vis spectrophotometer displayed the absorbance peak at lower than 550 nm. The band gap energies of the products were decreased and the powder changed color from yellow to dark green after UV irradiation. The products prepared with oxalic acid exhibited the highest photochromic effect due to the mixed phase of orthorhombic (81%) and hexagonal (19%) crystalline which having more defect concentration in its structure and the narrow band gap energy.

Key words: Tungsten trioxide, Precipitation, Photochromic, Oxalic acid, UV light.

Introduction

Tungsten trioxide (WO_3) is an n-type semiconductor material widely uses at various applications, gas sensor, lithium-ion batteries, photocatalysts and solar energies devices. WO_3 exhibit the electrochromic and photochromic properties, band gap between 2.4 eV and 3.2 eV depended on structure [1], changed their color when active by apply voltage or light. In the photochromic mechanism, the structure and morphologies are the importance factors on photochromic performance, the nanosize enhance the surface activity of materials under the light while the hexagonal WO_3 ($h\text{-WO}_3$) show the best photochromic behavior, their nanoparticles turned blue after exposure to UV light, is trendy to use for photochromic materials [2].

The $h\text{-WO}_3$ contain the WO_6 octahedral arranged six-membered ring sharing corner oxygen along (001) plane to form many open-tunnels, empty or fulfills with water molecules, easily for intercalation of ions (Li^+ , H^+ , K^+ and Na^+) as a result of the efficiency of the photochromic properties increase from the ions transfer [3, 4]. The $h\text{-WO}_3$ with the nanostructure usually prepare by complicated method, long reaction time, high pressure, temperature and low products yield [5], like chemical vapor evaporation (CVD) [6], hydrothermal [7], solvothermal [8], thin film by using chemical method,

sol-gel [9, 10]. Although the simple way is precipitation method uses for the preparation but the product have the large size and agglomerate so the control of the structure and morphologies are important which the chemical agent widely used e.g. polyvinyl alcohol (PVA) [2], polyvinylpyrrolidone (PVP), [11] cetyl trimethyl ammonium bromide (CTAB), [12] and polyethylene glycol (PEG) [13] etc. The oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) [11, 14, 15] useful for the reducing and chelating agent in any areas, because it inexpensive strong organic acid and easily soluble in water. It used for the modification surface of the carbon nanotubes and show very good chelating properties where control structure and morphologies of the 3D metal oxide nanostructure of the fabrication of nanoplates or nanowires synthesized by sol-gel method while do not produce any residue compounds because it is simple molecules and can oxidize to CO_2 . From this result, in this work were studied the preparation of the nanostructure with metastable $h\text{-WO}_3$ phases synthesized by simple precipitation method at the mild condition which $\text{H}_2\text{C}_2\text{O}_4$ was applied for the chelating agent during the reaction. Finally, the effect of $\text{H}_2\text{C}_2\text{O}_4$ on the structure, morphology and the photochromic properties under UV light of products were studied.

Experimental Details

Precipitation of WO_3 nanostructure

1.5 g of WO_3 powder (99.5%, Sigma-Aldrich) was dissolved in 100 ml of 2.5% NH_4OH at 60 °C for 30 min, mixed with the difference concentrations $\text{H}_2\text{C}_2\text{O}_4$ (99.5%, Ajax Finechem) which were 0, 0.3,

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0.5, 0.7 and 1.0 M correlating to W, W3, W5, W7 and W10 samples, respectively. Afterward, 20 ml HNO_3 (70%, J.T. Baker) was slowly dropped to the mixture while stirring and kept at 85 °C for 60 min. As the reaction proceeded, the solution turned to yellow. The product were filtered and washed with distilled water and ethanol. Finally, after dried at 50 °C for 24 hrs, the powder was collected and kept in dark condition.

Material characterization

The X-ray diffraction (XRD) using X'Pert MPD, Philips CuK ($\lambda = 1.5405 \text{ \AA}$) radiation. UV-vis absorption spectra were obtained by UV-2450, Shimadzu. Fourier transform-infrared spectrophotometer (FT-IR) were recorded by Vertex70, Bruker, using the KBr Pellet technique. Scanning electron microscopy (SEM) was performed on FEI Quanta 400 at accelerating voltage of 25 kV. Transmission electron microscopy (TEM) was carried out with JEOL 2010 microscopy with the acceleration voltage of 200 kV.

Photochromic property test

The powder was irradiated in UV box (10W $\times$ 6 UV lamps) for 360 min. The coloration between irradiation was measured by the colorimeter, SC80B, SADT then the color differences calculated by Eq. 1: [16, 17]

$$\Delta C = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

where ΔC is the color differences of powder before and after being irradiated, ΔL^* is being the lightness difference, Δa^* is being the red/green difference and Δb^* is being the yellow/blue difference.

Results and Discussion

XRD analysis

To study the effect of $\text{H}_2\text{C}_2\text{O}_4$ on the structure of the precipitate powder, the XRD pattern of all samples were characterized and displayed in Fig. 1. The XRD pattern of powder fabricated by using $\text{H}_2\text{C}_2\text{O}_4$ less than 0.7 M display the peak at $2\theta = 16.5, 25.6, 34.1$ degrees of planes (020), (111), (202) and (040), (200), (002) and at 34.9 degrees of $o\text{-WO}_3$ suggested that tungsten oxide monohydrate ($\text{WO}_3 \cdot \text{H}_2\text{O}$) [18]. Similarly, the peak in the system of $\text{H}_2\text{C}_2\text{O}_4$ more than 0.7 M show

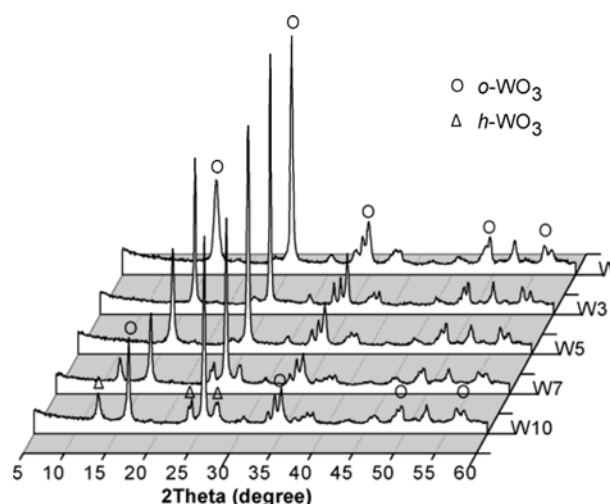


Fig. 1. XRD patterns of WO_3 samples prepared at difference $\text{H}_2\text{C}_2\text{O}_4$ concentrations.

the recrystallization that has mix phase of $o\text{-WO}_3$ and $h\text{-WO}_3$. or $h\text{-WO}_3 \cdot 0.33\text{H}_2\text{O}$ peaks at $2\theta = 14, 23, 27$ and 36 degrees of planes (010), (001), (110), (011), (020) and (021), respectively [2]. The percentage of $h\text{-WO}_3$ determined from the peak was increased in the powder added $\text{H}_2\text{C}_2\text{O}_4$ to 26% and 19% in W7 and W10. The crystallite size calculated from Scherer's equation shown in Table 1 that decreased from 41.4 nm to 33.1 nm since increasing $\text{H}_2\text{C}_2\text{O}_4$ in reaction.

From the literature, the structure formation start from precursor species in aqueous solution usually depended on pH where the monotungstate ions (WO_4^{2-}) was created at pH higher than 7.5 and polytungstate Y ions ($\text{W}_{10}\text{O}_{32}^{4-}$) at the pH range of 1 to 3. Similarly, in this work as the precursor WO_3 powder dissolved with ammonium solution, pH was higher than 8 that raise the WO_4^{2-} ions. As $\text{H}_2\text{C}_2\text{O}_4$ solution was added into the system, pH was decreasing to the range of 1 to 3 where the $\text{W}_{10}\text{O}_{32}^{4-}$ ions were arisen since reacted of WO_4^{2-} and H^+ ions from $\text{H}_2\text{C}_2\text{O}_4$, their ions are the growth species of the $h\text{-WO}_3$ by combine with other H^+ ions. If pH less than 1, the $o\text{-WO}_3$ crystal structure can be generated.[11] Meanwhile, between HNO_3 dropping into the mixture, the $\text{WO}_3/\text{H}_2\text{C}_2\text{O}_4$ solution was reacted with HNO_3 as pH less than 1 then H^+ combines with WO_4^{2-} to produce $o\text{-WO}_3$ so mix polymorphs crystals

Table 1. The properties of samples synthesized at various concentrations of oxalic acid.

Samples	Oxalic acid (M)	Hexagonal phase (%)	Crystallite size (nm)	Band gap energy (eV)	Defect concentration (E_0)
W	–	–	41.4	2.85	1.64
W3	0.3	–	27.6	2.80	1.55
W5	0.5	–	33.1	2.45	3.76
W7	0.7	26	33.1	2.43	3.82
W10	1.0	19	33.1	2.45	3.94

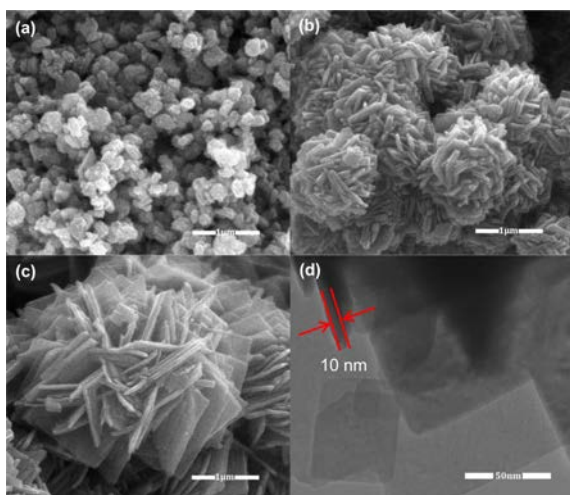


Fig. 2. SEM Image of samples generated at various $\text{H}_2\text{C}_2\text{O}_4$: (a) W, (b) W5, (c) W10 and (d) TEM image of W10.

were fabricated. However, if more than 1.0 M $\text{H}_2\text{C}_2\text{O}_4$ is used, the solution cannot be precipitated [19-21].

SEM & TEM Images

The effect of $\text{H}_2\text{C}_2\text{O}_4$ on the morphologies of products was recorded by SEM and TEM, the SEM images presented morphologies of powder in Fig. 2. W prepared without $\text{H}_2\text{C}_2\text{O}_4$ assistance in Fig. 2(a). The image displayed the irregular shape with an average size of 250 nm and agglomeration similarly to the powder with 0.3 M $\text{H}_2\text{C}_2\text{O}_4$ of W3. In contrast, samples were added at higher than 0.5 M $\text{H}_2\text{C}_2\text{O}_4$ of W5 in Fig. 2(b), the powder exhibited growth and formed to nanosheets with their thickness of 50 nm and agglomerated to nanoflowers with 1.3 μm in diameter while the nanosheets grew and the diameter of nanoflowers increased to 3 μm for using the higher $\text{H}_2\text{C}_2\text{O}_4$ concentration at 1 M as shown in Fig. 2(c), but the nanosheets thickness only about 10 nm from the lateral surface of W10 nanoflowers displayed on TEM image in Fig. 2(d). The fabrication and decreasing of thickness of nanoflower, it is due to the action of the oxalic acid as a chelating agent, when it is put in the precursor solution, the carboxyl groups ($-\text{COOH}$) of $\text{H}_2\text{C}_2\text{O}_4$ can form strong bonding with $-\text{OH}$ groups on the colloidal surface of particles, leading to slow down the growth of particles. It is noted that the nucleation of particles in forms of the nanosheets which finally formed as nanoflowers can be controlled by $-\text{COOH}$ functional group of oxalic acid [15, 20]. The nanostructure leads to the higher specific surface area that is most sensitive areas for the light excitable and enhances the photochromic effect.

FT-IR analysis

To study the water molecule as the photon donor in the coloration mechanism of the nanostructures, FT-IR spectra of precipitated WO_3 samples were recorded and

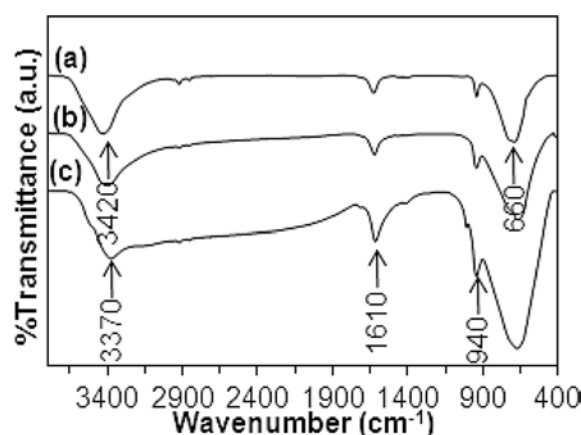


Fig. 3. FT-IR spectra (a)W, (b)W5 and (c)W10 samples.

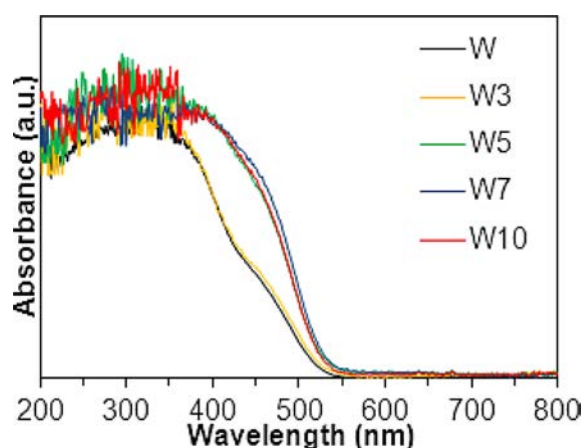


Fig. 4. The optical absorbance spectra of samples synthesized at various oxalic acid concentrations.

given in Fig. 3. All samples displayed the broad absorption band at $\sim 3400\text{ cm}^{-1}$ and the small band at $\sim 1610\text{ cm}^{-1}$ which were the stretching and bending vibrations of $-\text{OH}$ groups from water molecules [22]. The low intense absorption broad at $\sim 940\text{ cm}^{-1}$ referred to $\nu(\text{W}=\text{O})$ vibrations and the strong absorption broad at $\sim 660\text{ cm}^{-1}$ corresponded to $\nu(\text{O}-\text{W}-\text{O})$ vibrations. In addition, W10 exhibited the increased absorption band at $\sim 660\text{ cm}^{-1}$ suggested that highly degree of hydration since increased water molecules as a result of increase $h\text{-WO}_3$ in powder that have more open-tunnel contained water molecules [2].

Optical properties

The factor of photochromic efficiency including optical properties, band gap energies and the vacancies of the powder were studied. The absorbance spectra of powder from UV-vis spectrophotometer displayed in Fig. 4. The absorbance spectra of sample increase with increasing of $\text{H}_2\text{C}_2\text{O}_4$ in the preparation process. W as non-added $\text{H}_2\text{C}_2\text{O}_4$ product show the absorbance peak wavelength at lower than 525 nm and increase to 550 nm in products added $\text{H}_2\text{C}_2\text{O}_4$ more than 0.5 M indicated that photochromic properties can be excited

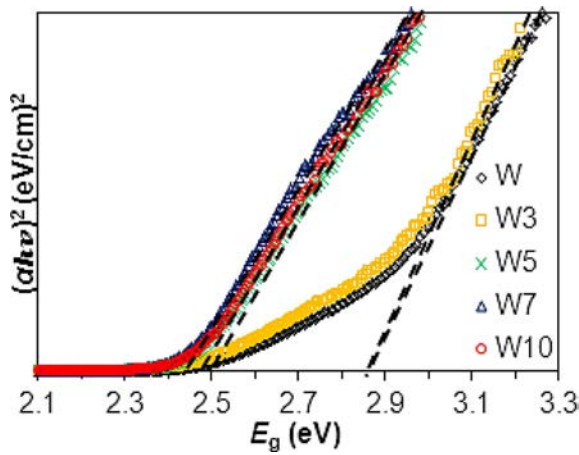


Fig. 5. The plot $(\alpha h\nu)^2$ as a function E_g (band gap energies) of sample synthesized at various oxalic acid concentrations.

from visible to UV light.

The direct band gap energy of products was calculated from the relationship of Eq. 2 below: [16]

$$\alpha E = A'(E - E_g)^m \quad (2)$$

Where E_g , A , E are the direct band gap, a constant and the photon energy ($E = hc/\lambda$), respectively. $m = 1/2$ for direct band gap and $m = 2$ for indirect band gap. The absorption coefficient (α) was estimated by Eq. 3,

$$\alpha = A/d' \quad (3)$$

Where A is the measured absorbance, d' is the thickness of samples in UV-vis cell (0.4 cm) and E were approximated by Eq. 4,

$$E = 1240/\lambda \quad (4)$$

Where λ is the measured wavelength in nanometer.

The direct band gap energies of products at difference $H_2C_2O_4$ were estimated by intercept X of the linear portion of $(\alpha h\nu)^2$ as a function of E to $\alpha E = 0$ (where $E = E_g$), show at Fig. 5 and Table 1. The band gap energy of WO_3 that prepared without $H_2C_2O_4$ was 2.85 eV. Meanwhile, the band gap energies of $H_2C_2O_4$ modified powder was decreased from 2.85 eV to 2.45 eV at increasing acid concentration more than 0.5 M. The sample which has a narrow band gap made the optical absorption edge shifted to the visible light region and its photochromic effect can be excited by the visible light.

The defect or vacancies concentration (E_0) were determined by the slope of the linear graph that plot $\ln \alpha$ as a function of E from Eq. 5. where α is the absorption coefficient calculated from absorbance, α_0 is a constant, E_0 is the photon energy and E_0 is an empirical parameter that depended on defect concentration, temperature and structure disorder [23].

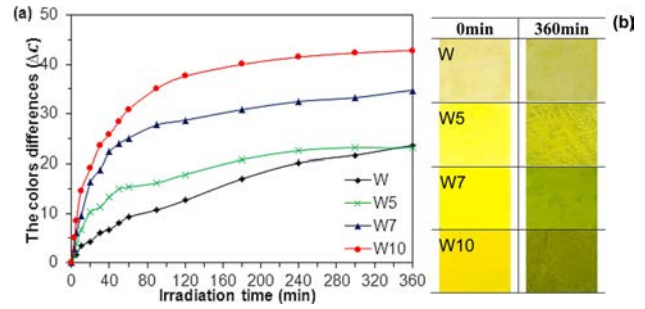


Fig. 6. (a) The colors differences (ΔC) and (b) the images of the coloration of the photochromic powder of samples synthesized at various oxalic acid and irradiated under UV light 360 min.

$$\alpha E = \alpha_0 \exp(E/E_0) \quad (5)$$

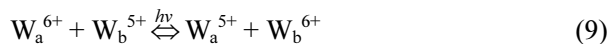
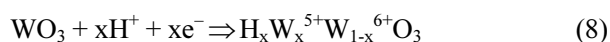
The E_0 of samples prepared via $H_2C_2O_4$ assistance displayed in Table 1 that increased with the increasing $H_2C_2O_4$ concentration. The high vacancies of 3.82 and 3.94 were found in W7 and W10 modified with 0.7 and 1.0 M $H_2C_2O_4$, respectively. As the result of the effect of the $H_2C_2O_4$ on the fabrication of the structure increased h - WO_3 phase that low degree of crystallinity risen in a sample, a large surface area and many tunnels coming from six oxygen atoms corner linked arrangements in structure [3].

Photochromic properties

To study the effect of $H_2C_2O_4$ added in the preparation of the nanostructure on the photochromic properties, the colors difference before and after illumination were tested and shown in Fig. 6(a). The colors difference increased with increasing the irradiation time and $H_2C_2O_4$. The colors difference after 360 min irradiated for W and W5 samples which both exhibited in o - WO_3 phase were nearly the same of 24%. However, the mixed phase of W7 and W10 samples demonstrated higher the color differences of 35% and 43%, respectively. W10 with 1.0 M $H_2C_2O_4$ exhibited the highest photochromic properties and its color difference was higher than those of W and W5 samples about 1.8 folds due to the effect of a large amount of the acid were added that created the mixed phase of hexagonal with the best photochromic sensitivity and orthorhombic phase.

The coloration images before and after 360 min UV irradiation of W, W5, W7 and W10 were added $H_2C_2O_4$ at the difference concentration and presented in Fig. 6(b). The W sample changed color from yellow to dark yellow while W5 was added 0.5 M $H_2C_2O_4$ changed to greenish yellow. In the same way, W7 and W10 were added 0.7 and 1.0 M $H_2C_2O_4$, respectively that have mixed phase (o - WO_3 and h - WO_3) made a difference color, W7 turned green while W10 changed to dark green after irradiated. This explains that W10 sample has higher photochromic sensitivity than W7 due to the higher defect concentration in W10 structure and its more specific surface area as a result of the

chelating agent control the fabrication of the nanoflowers.



The photochromic mechanism of WO_3 arises under the UV light irradiation. When the WO_3 photochromic sample exposure to the photon energy as higher than band gap energy of WO_3 then the electron from valence band (VB) was excited and awoken to conduction band (CB), hole (h^+) were produced at VB (Eq. 6), can be reacted with water molecules produced photon ions (H^+) (Eq. 7 and Eq. 8) and diffused into tunnels of lattice to form Hydrogen Tungsten Bronze ($\text{H}_x\text{W}_x^{5+}\text{W}_{1-x}^{6+}\text{O}_3$) [2, 24]. The valence of W changed from 6^+ to 5^+ and occurred the inter charge transfer of the electron from W^{5+} atom to the nearly W^{6+} atom then the color turned blue (Eq. 9). The importance parameters have an effect on photochromic performance, for example, the band gap energy, vacancies, surface area and water molecules. In the metastable $h\text{-WO}_3$ phase having low crystallinity and narrow band gap energy were easily excited by light to create a lot of the active electrons and holes, electrons transferring between adjacent molecules, electron holes reacted with water and generated many protons which diffused to the tunnels or inserted into the vacancies of the $h\text{-WO}_3$ structure where $\text{H}_x\text{W}_x^{5+}\text{W}_{1-x}^{6+}\text{O}_3$ in a large amount was formed and led to the enhancement of color change [11, 24].

Conclusions

The photochromic WO_3 nanostructures have been successfully synthesized by precipitation method at low temperature with a short time. The oxalic acid was introduced to the precursor solution for controlling the microstructure, shape and size of the prepared samples. The effects of the oxalic acid on the properties of the products were studied. The study found that the precipitated powder added oxalic acid in the fabrication process contained mixed structure ($o\text{-WO}_3$ and $h\text{-WO}_3$) which had nanoflowers shape generated by many nanosheets when using an oxalic acid as the control structure reagent more than 0.5 M and the nanosheets had the thickness only about 10 nm in W10 added 1.0 M oxalic acid. After irradiated, the result showed that the W10 sample exhibited the highest photochromic property due to the effect of the chelating agent controlled the structure to the mix phase with $h\text{-WO}_3$ that having the narrow band gap energy, high defect vacancies and

contains more water molecules content which the precipitated powder turned dark-green and displayed the result of the color difference higher than pure orthorhombic structure powder.

Acknowledgments

Financial supported from Center of Excellence in Nanotechnology for Energy (CENE) is acknowledged. The authors are thankful to the Department of Chemistry, Faculty of Science, Prince of Songkla University for the use of UV-vis Spectrophotometer. The authors also wish to acknowledge the Center of Excellence in Materials Engineering (CEME) and Department of Mining and Materials Engineering, Faculty of Engineering, The Graduated School, Prince of Songkla University.

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