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ABSTRACT

Tungsten oxide (WO₃) and tungsten oxide hydrate (WO₃·H₂O) nanoparticles were synthesized via microwave-assisted solution combustion in comparison with the acidic precipitation method. Oxalic acid was used as a surfactant and forming agent in the acidic precipitation method. In addition to oxalic acid, glycine and citric acid were also used as fuels in the microwave-assisted combustion method. The synthesis process was investigated by thermogravimetric (TG) and Differential Thermal Analysis (DTA) analysis. The obtained nanoparticles were analyzed using the scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The sample synthesized via the acidic precipitation method showed an orthorhombic crystal structure. One of the samples synthesized via the microwave-assisted solution combustion method was monoclinic and the two others were amorphous. The acidic precipitation method resulted in uniform plate-like structures while the combusted samples indicated irregular spherical morphology. Fourier-transform infrared (FTIR) analysis revealed stretching-vibrating bands relating to W-O bonds in the synthesized tungsten oxide nanoparticles. The bandgap energy of the nanoparticles calculated using UV-Vis spectra and Tauc plot extrapolation increased with decreasing the particle size. The data of reflectance and colorimetry had good agreement with the maximum peak position in the absorption spectra. The results indicated that the acidic precipitation method controls the particle's morphology as well as the size distribution. Although the combustion of fuels releases a lot of heat, the synthesis by solution combustion can control the size and shape of the nanoparticles, which can be an appropriate method for mass production of nanoparticles.

1. INTRODUCTION

Transition metal oxides have attracted the attention of researchers due to their high-temperature stability, controllable mechanical, and electronic properties as well as photonic and electronic transitions [1,2]. Tungsten oxide can tolerate low pH values and have promising physical and chemical properties, which can be used in electrochromic [3], photocromatic [4], photocatalytic [5], and gas sensing [6] applications that is an n-type intrinsic semiconductor with 2.6-3.6 eV bandgap, which can be modified through doping or manipulation [1,2]. Phase transitions from monoclinic II (α-WO₃, ≈-43°C) to triclinic (β-WO₃, ≈-43 to 17°C), monoclinic I (γ-WO₃, 17-330°C), orthorhombic (β-WO₃, 330-740°C), and tetragonal (α-WO₃, > 740°C) occur in tungsten oxide through increasing the temperature under the ambient pressure [1,2,7]. Phase transitions in nanomaterials can be completely different from those in bulk counterparts and depend mostly on the morphology and the crystal structure (i.e. the synthesis method). Tungsten oxide has a perovskite-type structure and its phase classification is performed according to the distortion angels and rotation direction of WO₆ octahedrons relative to the ideal ReO₃ cubic structure [1,2]. Tungsten oxide (WO₃) and tungsten oxide hydrate (WO₃·H₂O) nanostructures have been synthesized via different experimental procedures including aqueous sol-gel [8], acidic precipitation [9] hydrothermal [10], sputtering [11], etc. The synthesis methods should have the ability to control the morphology and crystal structure of the nanoparticles because the shape, size, and crystal structure of tungsten oxide nanoparticles significantly affect its electrical, magnetic, and optical properties [12]. Moreover, the large scale and cost-effective synthesis

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methods are required for industrial applications. In wet chemical methods, the morphology and crystal structure are controlled by using surfactants and reducing the surface energy of the particles [13]. The particle’s morphology and size distribution are usually homogenous because closed and homogenous media are used in the wet chemical methods, which in fact, is not suitable for mass production. In contrast, the combustion method yields large quantities of the products in shorter times, but it is more difficult to control the morphology in the combustion method because of its higher reaction rate and temperature than wet chemical methods.

The Self-Propagating High-temperature Synthesis (SHS) method was first introduced by Merzhanov et al., which is a high-temperature solid-state combustion method and results in coarser particles [14]. Patil et al. innovated the Solution Combustion Synthesis (SCS) method in which the combustion starts from a metal nitrate solution and the size and morphology of the particles are controllable by altering the combustion fuel [15].

The purpose of this research is to synthesize tungsten oxide (WO₃) and tungsten oxide hydrate (WO₃.H₂O) nanoparticles via the acidic precipitation and a novel microwave-assisted solution combustion synthesis method. Different morphologies and crystal structures were obtained based on the applied method and fuel.

2. EXPERIMENTAL PROCEDURES

All the chemicals were purchased and used without further purification. Tungsten metal powder (analytical grade, 99.99%) was purchased from Sigma Aldrich. Sodium tungstate (Na₂WO₄.2H₂O, >99%), HCl (30%), hydrogen peroxide (H₂O₂, 30%), HNO₃ (67%), H₂SO₄ (37%), oxalic acid (C₂H₂O₄, >99%), glycine (C₂H₄NO₂, >99%), and citric acid (C₆H₈O₇, >99%) were provided from Merck.

2.1. Acidic Precipitation

Sodium tungstate dihydrate (Na₂WO₄.2H₂O) was dissolved in 50mL deionized water to obtain a transparent solution (0.5M). The same molar ratio of HCl was added into the solution under magnetic stirring as the sodium tungstate until light yellow precipitates appeared. Then, the reaction vessel was transferred into the oil bath at 90°C. Oxalic acid was subsequently added into the reaction system with the sodium tungstate solution/oxalic acid (W/C) ratio of 1:1.6. The final yellow precipitates of WO₃·H₂O nanoplates were washed with deionized water and air-dried at 60°C. WO₃·2H₂O first forms under the acidic condition, and then, transforms to WO₃·H₂O in the presence of oxalic acid according to reaction (1) and (2) [16,17]:

\[ \text{WO}_3^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{WO}_3 + 2\text{H}_2\text{O} \]  
(1)

\[ \text{WO}_3 + 2\text{H}_2\text{O} \rightarrow \text{WO}_3\cdot\text{H}_2\text{O} + \text{H}_2\text{O} \]  
(2)

2.2. Microwave-Assisted Solution Combustion Synthesis

Tungsten oxide nanoparticles synthesis by microwave-assisted solution combustion was done through two simultaneous processes [18]. In this method, the tungstic acid was formed through reactions (3) and (4):

\[ \text{W}(s) + 2\text{H}_2\text{O}_2(l) \rightarrow \text{H}_2\text{WO}_4(aq) + \text{H}_2\text{O}(l) \]  
(3)

\[ \text{H}_2\text{WO}_4(aq) \xrightarrow{\text{Δ}} \text{WO}_3 + n\text{H}_2\text{O}(s) ; \quad n=0 \text{ or } 1 \]  
(4)

The tungsten powder (4.0g) was dissolved in a certain amount of H₂O₂ to obtain a transparent solution through Equation (3). In parallel, a combustion reaction produce the required heat (Δ) for the synthesis of tungsten oxide and the formation of the final structure. The combustion reaction is theoretically described based on the propellant chemistry and stoichiometric amounts of the reactants according to reactions (5) to (7) [19,20]:

\[ 2\text{HNO}_3(aq) + 5\text{C}_2\text{H}_2\text{O}_4(s)(\text{Oxalic acid}) \rightarrow 10\text{CO}_2(g) + 6\text{H}_2\text{O}(g) + \text{N}_2(g) \]  
(5)

\[ 18\text{H}_2\text{O}_2(aq) + 5\text{C}_2\text{H}_2\text{O}_4(s)(\text{Citric acid}) \rightarrow 30\text{CO}_2(g) + 29\text{H}_2\text{O}(g) + 9\text{N}_2(g) \]  
(6)

\[ 9\text{HNO}_3(aq) + 5\text{C}_2\text{H}_2\text{NO}_2(s)(\text{Glycine}) \rightarrow 10\text{CO}_2(g) + 17\text{H}_2\text{O}(g) + 7\text{N}_2(g) \]  
(7)

Typically, 9.0mL nitric acid and 7.5g citric acid (C₆H₈O₇·H₂O) was introduced to the tungsten solution. After heating the solution on a hotplate at 80°C, the obtained viscous gel was transferred to a microwave oven (rotating sample at 900 watts) to complete the one-step combustion reaction in 60s. The same procedure was used for oxalic acid and glycine fuels. The samples were named WO, MO, MC, and MG according to Table 2. The combustion of all the fuels was done with flame in the microwave oven.

2.3. Characterization

Thermal analysis was carried out using a thermogravimetric analyzer (PYRIS DIAMOND) under the air atmosphere. The samples were placed in an open Al pan and heated from room temperature to a maximum temperature of 600°C at a rate of 10°C.min⁻¹. The crystal structure of the synthesized samples was examined by X-ray powder diffraction using a
PHILIPS-PW1730 X-ray diffractometer with Cu-Kα radiation (λ=1.54056Å) at 2θ range of 10-80 degree and step size of 0.02 degree. The SEM image (LEO 1455 VP apparatus) was used to determine the surface morphology of the nanoparticles. The information on the functional group and bonding of samples were provided by Fourier-transform infrared (FTIR) spectroscopy using a Perkin-Elmer spectrometer in a KBr matrix. The UV-Vis spectra for the powder samples were recorded at room temperature with a double beam (Perkin Elmer UV-Vis Lambda 20) spectrophotometer over the wavelength range of 200-800nm. The reflectance spectra of synthesized samples were measured by an xrite i1Pro 2 spectrophotometer in the wavelength range of 380-730nm.

3. RESULTS AND DISCUSSION

3.1. Theoretical Combustion Thermodynamics

In general, the formation of crystal structure, agglomeration, and particle growth and the final state of the system highly depends on the combustion reaction enthalpy, which is calculated according to the heat produced by the combustion of the fuels [15,21]. In an adiabatic system, the reaction heat is used to increase the reaction temperature. Therefore, the maximum reaction temperature T_{ad} is calculated through Equation (8) [15,22,23]:

$$\Delta H^{T_{ad}} = \int_{T_{ad}}^{T_{ad}} C_p dT$$

(8)

Where $\Delta H^{T_{ad}}$ is the reaction enthalpy at $T_{ad}$ and $C_p$ is the specific heat capacity of the products. The theoretically calculated thermodynamic values for different fuels are listed in Table 1. The amount of exhaust gases during the combustion reaction affects the porosity of the final product. The amount of the exhaust gases from reactions (5), (6), and (7) is 25, 68, and 34mol, respectively. The combustion heat of these reactions is $-826\text{kJ.mol}^{-1}$, $-7364\text{kJ.mol}^{-1}$, and $-3539\text{kJ.mol}^{-1}$ which, results in the increase of the $T_{ad}$ temperature to 1025.8K, 2526.7K, and 2438.2K, respectively by considering the amount of the exhaust gases. According to the amount (mol) of the reactants in reactions (5), (6) and (7), the oxidizer to fuel ratio was 0.4, 3.6, and 1.8, respectively.

3.2. Thermal Analysis

The combustion precursors were characterized by using thermogravimetry (TG), differential thermal analysis (DTA) to obtain a better understanding of the auto-combustion process. TG and DTG curves were obtained, however, a mass spectrometer was not available for the analysis of evolved gases. Generally, the DTA profile can be identified with four different stages for a SCS precursor: (a) endothermic loss of water, (b) combustion reaction, (c) removal of carbonaceous materials, and (d) final product formation with constant mass [24].

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Oxalic acid (C$_2$H$_2$O$_4$)</th>
<th>Citric acid (C$_6$H$_8$O$_7$)</th>
<th>Glycine (C$_2$H$_4$NO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^\circ_{combustion}$ (kJ/mol)</td>
<td>-826</td>
<td>-7364</td>
<td>-3539</td>
</tr>
</tbody>
</table>

| Oxidizer to fuel ratio | 0.4 | 3.6 | 1.8 |

| amount of exhaust gases (mol) | 25  | 68  | 34  |

| $T_{ad}$ (K) | 1025.8 | 2526.7 | 2438.2 |

Figures 1(a) and (b) illustrate the TG-DTG and DTA analysis results of the MO sample, respectively.

![Figure 1. (a) TG-DTG and (b) DTA analysis of MO sample](image-url)
and exothermic over 100°C (Figure 1a). The first weight loss was observed at 85°C in TG analysis. Nevertheless, it can be safely assumed that it corresponds to the removal of weakly absorbed water from the external surface of the prepared gel due to the low temperature of this feature. The exothermic nature of the weight loss over the 100°C can be assigned to the decomposition of oxalic acid that released the CO₂ and H₂O during the combustion of oxalic acid by nitric acid [25,26].

The combustion behavior of the MC sample was studied by TG-DTG and DTA, and the results are shown in Figures 2(a) and (b). The first endothermic peak at 82°C can be assigned to the evaporation of the remaining water in the gel and the other weak weight loss at 135.5°C arises from desorption of chemically absorbed [27]. A broad exothermic peak is observed between 100°C and 600°C, accompanied by a weight loss of about 32%, which is assumed to correspond to the combustion process of citric acid and exit of residuals [23,24,28].

The results of TG-DTG and DTA of combustion reaction for producing the MG sample are exhibited in Figures 3(a) and (b), respectively. As can be observed in the DTA graph, the reaction has an exothermic peak at 137 that can be attributed to the solution of glycine that forms the amine and carboxyl groups by an endothermic peak at 154. The abrupt weight loss at 100-300 shows the exothermic peak at 197 that can be corresponded to the combustion of glycine and decomposition of the carboxyl group and exiting the adsorbed water. While the combustion of glycine has a broad peak from 100-600, the second sharp exothermic peak is seen at 528 that can be attributed to the decomposition of the amine group of glycine [23,24,28].

The results indicate that glycine combustion is more severe than citric acid and oxalic acid. Although thermodynamic calculations show high-temperature production rates, however, it produces relatively low temperature combustion as the reaction proceeds from the soluble state, which results in the production of nanoparticles.
3.3. Crystal Structure

XRD patterns of the synthesized samples are shown in Figure 4. The sample synthesized via acidic precipitation using oxalic acid contains fully crystallized orthorhombic tungsten oxide hydrate (WO₃•H₂O) nanoparticles according to JCPDS card no. 01-084-0886 [16,29]. The crystallite sizes of the samples calculated based on Scherrer in Equation (9) are listed in Table 2.

$$D = 0.9 \lambda / \beta \cos \theta$$  \hspace{1cm} (9)

Where $D$ is the crystallite size, $\lambda$ is the wavelength of the incident radiation CuKα line, $\theta$ is the Bragg's angle, and $\beta$ is the full width in half maximum (FWHM) [30].

![XRD patterns of WO, MO, MC, and MG samples](image)

**Figure 4.** XRD patterns of WO, MO, MC, and MG samples

Microwave-assisted combustion synthesis in the presence of oxalic acid and citric acid has resulted in amorphous nanoparticles. It seems that there has not been enough time for MC and MO samples to crystallize because of the high intensity as well as the combustion reaction rate. The XRD pattern of the MG sample shows monoclinic tungsten oxide (WO₃) according to JCPDS card no. 01-072-0667. This difference in crystallization can be due to the higher reaction heat in the case of glycine fuel and the formation of amine groups during the reaction.

<table>
<thead>
<tr>
<th>Sample by band position (cm⁻¹)</th>
<th>Band assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO</td>
<td>3368</td>
<td>$\nu_{\text{as}}$ and $\nu_{\text{sym}}$ of OH</td>
</tr>
<tr>
<td></td>
<td>2850</td>
<td>$\nu_{\text{as}}$ and $\nu_{\text{sym}}$ of (CH₃)</td>
</tr>
<tr>
<td></td>
<td>1688</td>
<td>$\nu_{\text{sym}}$ (COO)</td>
</tr>
<tr>
<td></td>
<td>1615</td>
<td>$\delta$ (H-O-H)</td>
</tr>
<tr>
<td></td>
<td>1442</td>
<td>1393</td>
</tr>
<tr>
<td></td>
<td>1251</td>
<td>1175</td>
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<td></td>
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<td>1079</td>
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<tr>
<td></td>
<td>820</td>
<td>814</td>
</tr>
<tr>
<td></td>
<td>721</td>
<td>723</td>
</tr>
<tr>
<td></td>
<td>672</td>
<td>603</td>
</tr>
</tbody>
</table>

**Table 3.** Band positions of FTIR spectra

3.4. FTIR Spectra

All peaks of samples have corresponded to their band assignment in Table 3 as band positions. There are obvious differences in the FTIR spectra of the synthesized samples. As can be seen from Figure 5, unlike amorphous samples, the crystalline samples show distinct peaks at different wavelengths. Peaks at 1650 cm⁻¹ and 3400 cm⁻¹ are related to the O-H bond, which has a higher intensity in MO and MC samples in comparison with MG and WO samples [31]. This is indicative of more water adsorption in MO and MC samples. Peaks in the range of 500-1000 cm⁻¹ are attributed to different bonds between oxygen and tungsten; mostly belong to stretching-vibrating bands in WO₃ octahedral structures [18]. Some obvious differences in FTIR spectra of MG and WO samples are more broad peaks at 1650 cm⁻¹ and 3400 cm⁻¹, peak shift from 800 cm⁻¹ to 650 cm⁻¹, in WO sample, the appearance of a peak at 1000 cm⁻¹, and disappearing of peaks at 1100 cm⁻¹ and 1500 cm⁻¹ [21-24].

3.5. Microstructure and Morphology

All WO yellow powder contained plate-like particles with cubic shapes due to the presence of oxalic acid as
a surfactant (Figure 6). According to SEM images, the plates are rather uniform in length, width, and height (about 100nm in thickness), which demonstrates the capability of acidic precipitation method for high accurate controlling of the morphology.

**Figure 5.** FTIR spectra of WO, MO, MC and MG samples

The schematic structure of WO₅₂H₂O is shown in Figure 7a. The layers of corner-sharing WO₄(OH₂) octahedron and interlayer water built the WO₅₂H₂O [16]. The octahedrons of WO₄(OH₂) consists of four W–O bonds, one W=O bond, and one W–OH₂ (structural H₂O) [31,33,34].

**Figure 6.** SEM images of WO powder

Hydrogen bonds connect the interlayer water to WO₄(OH₂) octahedron. Thus removal of interlayer water from WO₅₂H₂O produces WO₅.H₂O (Figure 7b) [16].

**Figure 7.** Schematic representation of (a) layered WO₅₂H₂O, (b) dehydrated WO₅.H₂O from WO₅₂H₂O, and (c) the role of oxalic acid in dehydration process of WO₅₂H₂O to WO₅.H₂O [16]

The process is illustrated in Figure 7(a,b) in which C₃H₂O₄ destroyed the hydrogen bonds between the structural water and interlayer water. The electron-rich organic molecules of C₃H₂O₄ involve four O atoms that can form hydrogen bonds with four different interlayer H₂O molecules in WO₃.2H₂O, as schematically shown in Figure 7c. The hydrogen bonds between interlayer water and WO₄(OH₂) octahedron are destroyed by strong interactions of C₃O₄²⁻ ions with interlayer water. Thus, C₃H₂O₄ plays
a key role in the dehydration process of $\text{WO}_3\cdot\text{H}_2\text{O}$ to $\text{WO}_3\cdot\text{H}_2\text{O}$ at low temperatures (70-90°C) [16]. SEM images represent the nanoplates of WO were stacking side by side following the above-mentioned procedure. Unlike the WO sample, microwave-assisted synthesized samples showed irregular structures with less particle size than the WO sample (Figure 8). The MO powder is in yellowish-green and contains 50nm size particles with mostly spherical morphology. Black MC powder contained rock-like particles with irregular shape and size, which also confirms their amorphous nature as was shown in XRD patterns. MG sample is in navy blue and its SEM image shows spherical particles with a uniform particle size distribution of about 300nm. These differences in morphology are related to the applied materials and different synthesis methods. The results of TG-DTA analysis showed the intensity of the reaction, hence the final structure and morphology used in the combustion reaction depending on the fuel.

![Figure 8. SEM images of (a, b) MO, (c, d) MC, and (e, f) MG samples](image)

3.6. Optical Analysis and Band Gap
UV-Vis absorption spectra of the synthesized samples are shown in Figure 9. It can be seen that all the samples show adsorption edges at different wavelengths, which may arise from the quantum effects due to the size, crystal structure, and other influencing parameters. The bandgap was calculated according to the Tauc method by plotting $(\alpha h\nu)^{1/\alpha}$ versus $h\nu$ using Equation (10):

$$(\alpha h\nu)^{1/\alpha} = k(h\nu - E_g)$$  \hspace{1cm} (10)$$

Where $h$ is the Planck constant, $\nu$ is the frequency of the incident photon, $k$ is constant, $\alpha$ is the adsorption coefficient, and $E_g$ is the bandgap energy [36,37].

![Figure 9. UV-Vis spectra of WO, MO, MC, and MG samples](image)
Assuming a direct bandgap for synthesized nanoparticles, i.e. \( n = 1/2 \), the bandgap is calculated by extrapolating the Tauc plot on the energy axis, as shown in Figure 10. It was observed that the band gaps were increased due to the quantum confinement effect arising from size reduction. The calculated band gaps for WO, MO, MC, and MG samples were 2.7, 3.2, 3.46, and 3.5 eV, respectively.

![Figure 10. Tauc plot and bandgap calculation of (a) WO, (b) MO, (c) MC, and (d) MG samples](image)

The CIE diagram of different samples is seen in Figure 11. The appearance of the samples is changed from the grey color of MG and MC samples to pale green in MO and greenish-yellow in WO samples. It seems that the black color of MG and MC samples is related to the residual carbonaceous matters from combustion reactions. There is a good agreement between the appearance of the samples (inset images of figures 7 and 8) and the colorimetric diagram. The reflectance spectra of the samples are illustrated in Figure 12. There is also a good agreement between the appearance (Figure 11) and the visible reflectance of the samples. There is an obvious decrease in reflectance intensity because of the residual carbonaceous matters in MC and MG. The maximum peak positions in the reflectance spectrum showed that the samples have absorption below 550 nm, which illustrates the yellow color of samples with the various tendency to other colors. The maximum peak position in the reflectance and absorption spectra is in good agreement with reflectance and shows the complementary absorption spectra.

![Figure 11. CIE diagram of WO, MO, MC, and MG samples](image)
Moreover, the absorption edges illustrated by the rods in the figure have good compatibility with the Tauc formula.

It seems that the formation of crystalline WO$_3$ with maximum crystallite size of 24 nm and maximum particle size of 300 nm causes the quantum confinement and thus, increases the bandgap in comparison with the pure WO$_3$ sample (485 nm) [28].

4. CONCLUSION

Acidic precipitation and microwave-assisted solution combustion methods were used for the synthesis of tungsten oxide hydrate (WO$_3$.H$_2$O) and tungsten oxide (WO$_3$) nanoparticles. The particles showed orthorhombic, monoclinic, and amorphous structures. Thermodynamic calculations demonstrated that the fuels provide different reaction energies. Microwave-assisted combustion in the presence of oxalic acid yielded spherical particles while citric acid resulted in irregular shaped particles and glycine produced uniform fine spherical particles. Vibrating-stretching bands of W-O bonds in FTIR spectra also confirmed the formation of tungsten oxide. The influence of fuel type and synthesis method on the crystal structure can be obviously verified by the FTIR peaks in the range of 500-1000 cm$^{-1}$. The largest bandgap (3.5 eV) calculated based on the Tauc relation as well as the adsorption and reflectance spectra belonged to the combustion in the presence of glycine fuel, which was about 1 eV higher than the bulk WO$_3$, leading to the finest particle size. According to the results, the acidic precipitation method is suitable for morphology control while the combustion method can be used for mass production. CIE diagram showed that the WO$_3$ sample has the purest yellow color. Purification can be done by sintering the microwave-synthesized samples at 400°C to remove the residual carbonaceous matters without any phase change. The SCS method can be assumed as a fast technique to mass production of nanoparticles.

REFERENCES


