Hydrothermal Synthesis Of Tungsten Oxide (WO_3) Nanostructures Using Sodium Chloride As Structure Directing Agent

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***Abstract*—Tungsten oxide (WO_3) nanostructure were synthesized by a facile hydrothermal method at 150° C using tungstate dehydrates ($Na_2WO_4.2H_2O$) as the precursor. Without any additive, scanning electron microscopy revealed a rhombus shaped WO_3 nanostructures while with the addition of sodium chloride, the morphology changes to nano-dagger bundles that formed flower-like structure. Furthermore, the size of the nano-dagger can be controlled by changing the amount of NaCl additive. The Raman spectrum analysis suggested the fundamental modes of crystalline h-WO_3 has been maintained among the different NaCl concentration groups despite of noticeable changes in their morphology structure.**

Keywords—hydrothermal; WO_3; Directing Agent; Nano-dagger structure

I. INTRODUCTION (*Heading 1*)

Metal oxides (MOx) have drawn much attention as a functional element for various types of nanotechnology applications due to their unique electronic properties [1]. Tungsten oxide is one of the materials that have been studied for applications such as field emission, phototcatalysts, electrochromic devices, and nanoscale electronic gas sensors [2-5]. There are many methods available to synthesis WO_3 which includes thermal evaporation [6], laser pyrolysis [7], sol-gel [8] and hydrothermal [9].

Among them, hydrothermal has become more preference method to synthesis WO_3 due to simplicity, cost-effective and environmental friendly [10]. Furthermore, this process require relatively low power and non-sophisticated equipment which is a suitable route to achieve mass and economic of scale production system requirement [11].This study reports the effect of NaCl as the directing agent in producing dagger-like nanoflowers via facile hydrothermal process. The morphology of the nanoflower can also be controlled by having different NaCl concentration in the precursor solution. Through this dimension control capability, the final morphology of the as-synthesized WO3 nanostructure can be tailored to meet the specific design requirement; for example as ultra-sensitive sensing element in gas sensor applications.

II. METHODOLOGY

Precursor for WO_3 nanoflower synthesis was prepared by dissolving tungstate dehydrates ($Na_2WO_4.2H_2O$) purchased from Sigma-Aldrich without further purification in DI water. Unlike 2 steps pH modification proposed by [9,12], the pH of the solution was directly bring down to 2.4 by mixing with oxalic acid ($C_2H_2O_4.2H_2O$) while the solution been stirred continuously at 300 r.p.m. This solution then transferred into teflon-lined stainless steel autoclave and maintained at 150° C for 5 hours.

To investigate the effect of NaCl to the WO_3 morphology, the same process steps were repeated with additional step of mixing the prepared solution with NaCl just before heating in the autoclave. Different amount of NaCl been dissolved into the solution to achieve 0.3 M, 0.6 M and 0.85 M concentration accordingly. The duration of 5 hours and 150° C temperature was fixed throughout the hydrothermal process.

Once the process is completed, the autoclave was cooled down to room temperature naturally. The nanostructures obtained were washed in DI water and later dried in air for further characterization. The morphology of as-synthesis WO_3 nanostructure was examined using scanning electron microscopy (SEM, 7500 JEOL JSM). Raman scattering spectroscopy was performed on Integra NT-MTD with diode laser at 473nm.

III. RESULTS AND DISCUSSION

Morphology of the WO_3 nanostructure produced by single step hydrothermal synthesis as shown in Figure 1. It can be seen that without NaCl additive, the WO_3 nanostructure reassemble rhombus shape nanoflower shown in Figure 1 (a) similar to structure reported by [11].With the present of directing agent, the rhombus shape of WO_3 has been directed into multi-direction dagger-like nanoflower originated from the center as shown in Figure 1 (b) . This nano-daggers [13] with sharp tips and length up to several micron was realized when 0.3 M NaCl was added to the precursor solution. When higher NaCl concentration was used, the dagger size is getting smaller in size as shown in Figure 1 (c) and (d). Boxplot graph on Figure 2 helps to illustrate the statistical comparison of the nano-dagger size between the groups.

In general, the box-plot shape indicates that the measured data are reasonably symmetrical except for group 0.85 M which plotted with few outlier points perhaps from from a measurement or data entry error. Different median line position of each boxplot confirms the significant data from each populations; hence they can be clearly associated with their concentration grouping.

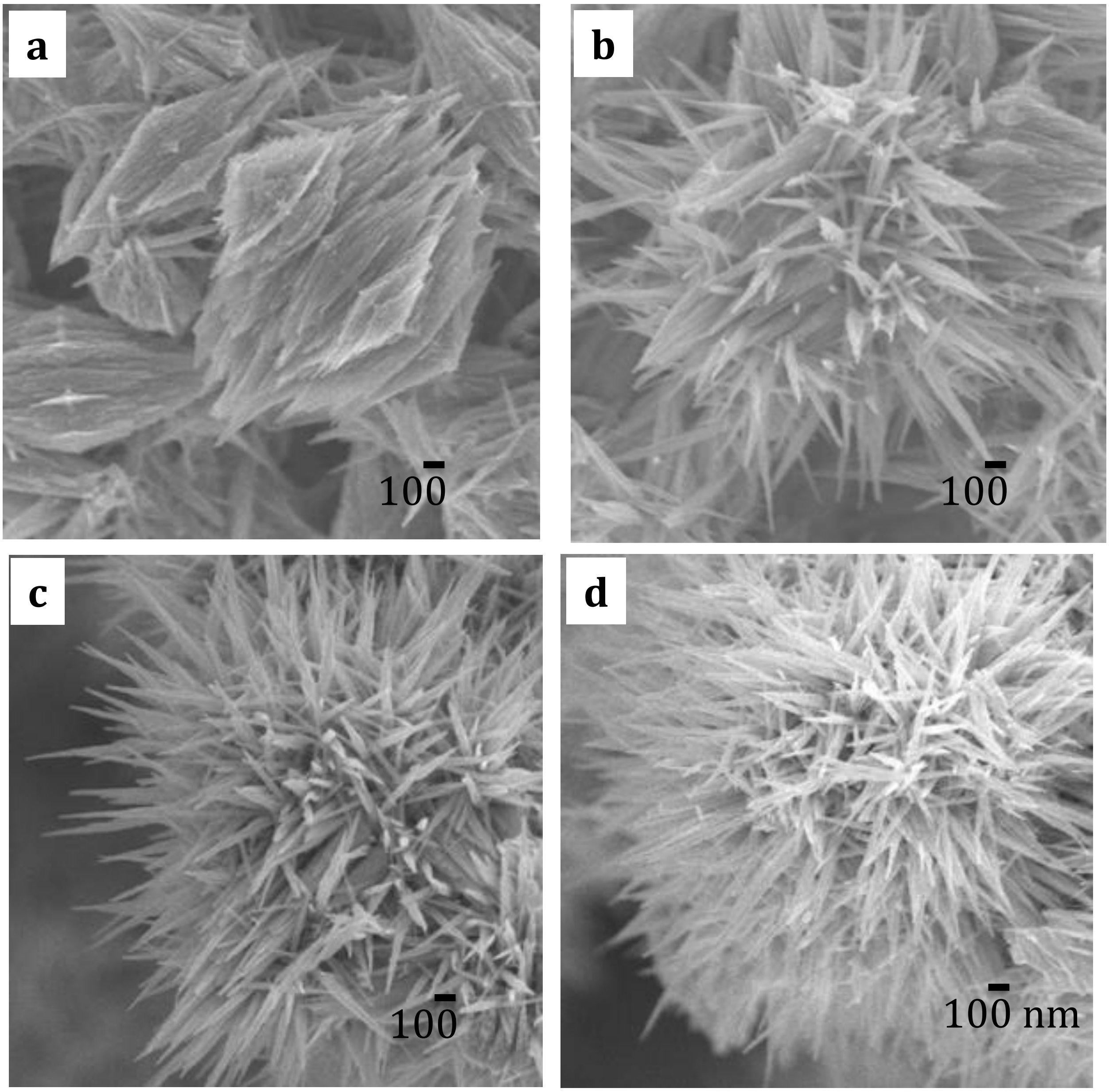

Fig. 1. *SEM image of rhombus shaped as-synthesized WO3 nanoflower w(a) and with 0.3 M (b) 0.6 M (c) and 0.85 M (d) NaCl as directing agent.*

The median line which represent the average diameter of the measured nano-dagger were 70 nm , 53 nm and 35 nm for 0.3 M, 0.6 M and 0.85 M respectively.

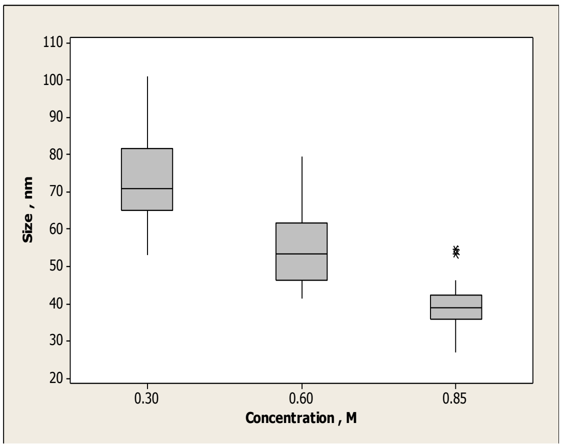

Fig. 2. *Boxplot of nano-dagger diameter distribution for different amount of NaCl.*

This phenomena most likely due to the increase of cation in the hydrothermal solution through NaCl mix that actively create weaker bond among W hence create less possibility for the dagger to bundled together and cause the nano-dagger become smaller in diameter. Base on experimental observations , it is also suggested that the transformation from rhombus like nanoflower towards nano-dagger shape go through few stages , including aggregation of small W particles, crystal growth, splitting and breaking to become nano-dagger as schematically illustrated in Figure 3.

At the begining of the reaction, the W particle nucleates (Fig. 3(a)). The aggregation and the cystal orientation of W particle with respect to each other is determined by the minimization of the highest energy surfaces. The morphology of the particle is obtained through attachments of primary particles as building blocks in a highly oriented fashion [14]. The surface of the WO3 particle contains high index crystallography planes, through which the particles connect to each other to decrease

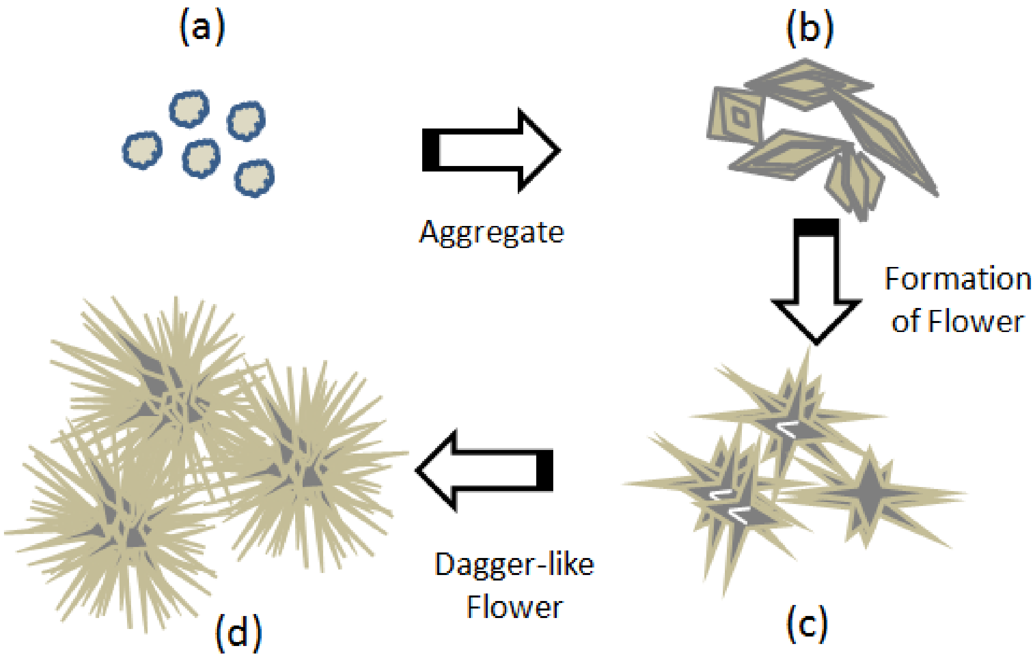

Fig. 3. *Formation of WO3 dagger-like nanoflower via hydrothermal syntheis with high cation concentration oxplot of nano-dagger diameter distribution for different amount of NaCl.*

When a small amount of NaCl presents in the the reaction system, the morphology of the nanoflower change from rhombus like shape to nano-dagger like shape (Fig. 3 (c-d)). According to Bai et al. [15], NaCl retarding the formation of WO_3 grow in the [110] direction and promoting the WO_3 grow in the [001] direction.Furthermore, chloride ions play a major role in giving one-dimensional shape through adsorbtion of chloride ions to the surface of the seed crystals of WO_3 and thereby decrease the surface energy of the WO_3 seed crystals in all directions except one direction.

Therefore, with the assistance of NaCl, as the reaction prolonged, further crystal growth takes place by means of agglomeration/attachment with other seed layers in this particular undisturbed direction.Finally, this process continues to give one dimensional dagger-likes nanostructures [16].

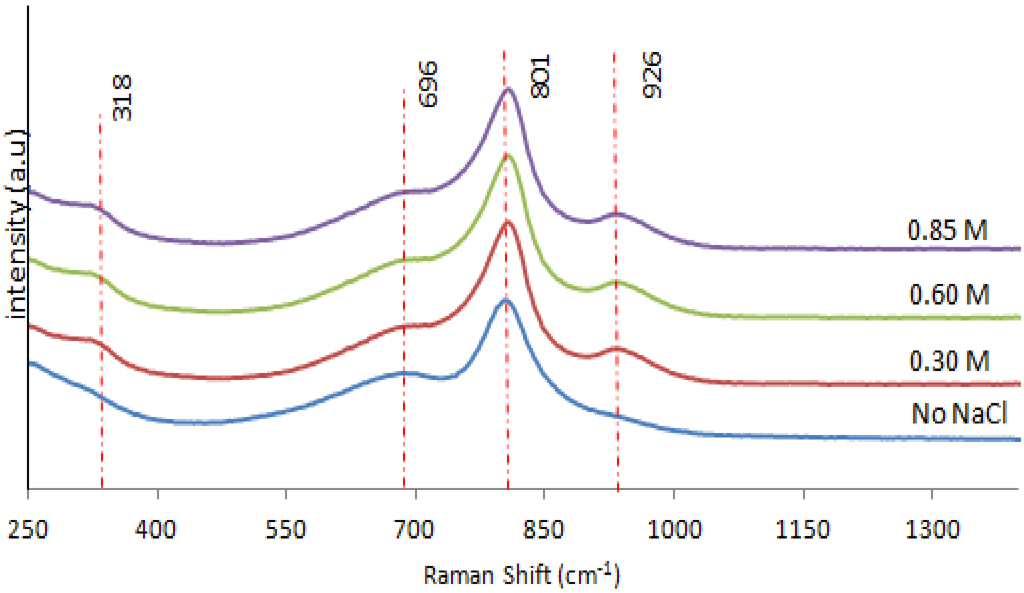

Fig. 4. *Raman spectra of as-synthesized WO_3 (a) and with NaCl directing agent at different concentration ; (b) 0.3M; (c) 0.6M and (d) 0.85 M.*

From the result, high NaCl concentration produces finer and tighter distribution of nano-dagger. Liu et al. observed that addition of sodium chloride salt greatly increases the ionic strength of the growth solution and higher ionic strength favors the formation of smaller crystals through electrostatic screening. The higher ionic strength, the smaller the particle size and size distribution width will be, because the ionic strength screening the repulsive forces between particles thus results in changes in the shape of the size distribution of aggregates. Furthermore ions next to the nano-dagger form a diffusion barrier and inhibit surface access, thus, slowing the crystal growth [17].

Since inorganic compounds have vibrational bands mainly below 1200 cm-1, an investigation of Raman spectroscopies of WO3 to obtain chemical structure details was done in the range 250~1200 cm^{-1} [18, 19]. In Fig. 4(a), Raman spectra of WO3 nanostrucutre without NaCl additive only observed at two peaks; a weak intensity at 696 cm^{-1} and well define peak at 801 cm^{-1}. Based on literature, these bands can be assigned to the fundamental modes of crystalline h-WO3 [20,21].

For groups added with NaCl additive, additional two small intense at 318 cm^{-1} and 926 cm^{-1} were noticed regardless of different concentration (Fig. 4(b-d)). The latter peak correspond to the –W=O bonds due to the presence of nanocrystalline structure [22]. This result suggests that the synthesized material have slightly different phase structure affected by the morphology changes with the existence of oxygen deficiency while the majority features of raman is identical.

IV. Conclusion

Monoclinic WO_3 nanostructure was successfully synthesized by facile hydrothermal process. The introduction of NaCl as the structure directing agent into the reaction solution induced the formation of dagger-like nanoflowers was also demonstrated. It has been shown that finer dagger size of the flower can be achieved by simply tuning the concentration of NaCl. This finding presents an alternative approach to control the growth direction and morphology dimensions of WO3 nanostructure synthesized via facile hydrothermally method.

Acknowledgement

The authors wish to thank MIMOS Berhad for facility accessibility to perform this experiements, Universiti Teknologi MARA (UiTM) and the Ministry of Higher Education Malaysia (MOE) for the financial support under the Exploratory Research Grant Scheme (File No : 600-RMI/ERGS 5/3(18/2013)).

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