Flame Spray Synthesis of WO$_3$ for No Breath Monitors

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Introduction

Nitric oxide belongs to the class of inorganic gaseous chemicals found in exhaled breath and is characterized as a signaling biomarker for disease [1-3]. The diagnostic value of exhaled NO measurements to differentiate between healthy persons with or without respiratory symptoms and patients with confirmed asthma has been established by Dupont who showed that >16 ppb of NO in lower respiratory tract could be treated as a cutoff for asthma with a 90% specificity and 90% positive predictive value [4]. This suggests that a simple and non-invasive measurement of exhaled NO may provide a reliable signal for asthma diagnosis.

Breathalyzer prototypes utilizing NO selective nanostructured sensors to detect and monitor the fractional nitric oxide concentration (FENO) in breath have been demonstrated and patented by our group [5,6]. The next challenge has been to produce the NO sensing elements (i.e. nanocrystals of γ-WO$_3$) using a scalable process that will enable the use of the NO breathalyzer and asthma monitor as a home diagnostic tool. This manuscript describes the scaled up process used to synthesize γ-WO$_3$, by means of flame spray pyrolysis.

Flame spray pyrolysis is a very effective method to synthesize nano-sized oxide particles in a large amount and an excellent quality. It has been used for dry, one-step synthesis of catalysts, sensors, biomaterials, phosphors and even nutrional supplements [7]. Furthermore, FSP is a scalable process with proven production rates over 1 kg/h [8]. FSP-made nanoparticles can also be directly deposited onto sensor substrates. This paper provides a new recipe and specific process steps for obtaining the required oxide polymorph and to optimize the particle size distribution for NO sensing.

Experimental Methods

In this work, precursor solutions were prepared from ammonium tungstate hydrate (H$_2$NCO$_3$W$_{12}$, Aldrich, purity >97%) diluted (0.4 mol/l of tungsten ions) in a 3:2 (volume ratio) mixture of diethylene glycol monobutyl ether (C$_8$H$_{18}$O, Fluka, >98.5%) and ethanol (C$_2$H$_6$O, Fluka, >99.5%). The solution was fed at 5 ml/min through the inner reactor capillary. Through the surrounding annulus, 5 l/min of oxygen (Pan Gas, purity >99%) were fed dispersing the precursor solution into a combustible spray. The methane and oxygen flow rates in the FSP-source are 1.5 and 3.2 l/min, respectively.

X-ray diffraction (XRD) patterns were obtained with a Bruker AXS D8 Advance diffractometer (40 kV, 40 mA, Karlsruhe, Germany) operating with Cu K$_\alpha$ radiation. Phase analysis is accomplished using two softwares, namely DIFFRAC$^\text{TM}$ EVA and DIFFRAC$^\text{TM}$ TOPAS. Raman scattering spectra were recorded by Renishaw InVia Reflex Raman Spectrophotometer with the excitation laser length of 514.5 nm, laser power of 300 mW and exposure time of 30s at RT. SEM images are obtained with SEM, LEO 1550 SFEG Microscope operated at a voltage of 15 kV. TEM images were obtained on a CM30ST microscope, FEI (Eindhoven), LaB6 cathode, operated at 300 kV, SuperTwin lens, point resolution ~2 Å.

Results and Discussion

As-sprayed powders

The as-synthesized powder products resulted from the reaction shown below:

$$\text{H}_2\text{NCO}_3\text{W}_{12} \xrightarrow{\text{flame}} \text{W}^{6+} \xrightarrow{\text{O}_2} \text{WO}_3$$

They were blue green in color. When a default setup without any accessories was applied, medium grain-sized WO$_3$ was obtained. (Sample A) The average surface area of such products is 63.0 m$^2$/g, (BET-determined particle diameter is 13 nm). Most peaks in the XRd spectrum shown in Figure 1a, (labeled as “middle grain size”) can be indexed in stable-phase WO$_3$ polymorphs. However, due to the small size of the particles, most adjacent peaks overlap a lot. Thus, Raman spectroscopy was used to identify the phase composition of the product, as shown in Figure 1b. In this spectrum, peaks at 272, 324, 715 and 805 cm$^{-1}$ correspond to monoclinic γ phase, the stable form of WO$_3$ at RT [9-11]. The band at 942 cm$^{-1}$ can be assigned to the stretching mode of $\text{W=O}$ terminal bonds indicating surface tungsten hydrates [10,11]. Peaks at 203, 272, 303, 370, 425, 642, 688 and 805 cm$^{-1}$ belong to the ε phase of WO$_3$. 

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AXS D8 Advance diffractometer (40 kV, 40 mA, Karlsruhe, Germany) operating with Cu K$_\alpha$ radiation. Phase analysis is accomplished using two softwares, namely DIFFRAC$^\text{TM}$ EVA and DIFFRAC$^\text{TM}$ TOPAS. Raman scattering spectra were recorded by Renishaw InVia Reflex Raman Spectrophotometer with the excitation laser length of 514.5 nm, laser power of 300 mW and exposure time of 30s at RT. SEM images are obtained with SEM, LEO 1550 SFEG Microscope operated at a voltage of 15 kV. TEM images were obtained on a CM30ST microscope, FEI (Eindhoven), LaB6 cathode, operated at 300 kV, SuperTwin lens, point resolution ~2 Å.
Tungsten hydrates are common by-products during the synthesis of WO₃. However, the appearance of ε-WO₃ is surprising here since it was typically reported as a phase only stable below -40°C. Although not quantitative, the relative intensity of 642 cm⁻¹ and 688 cm⁻¹ bands compared to 715 cm⁻¹ band indicates the content of ε-WO₃ in the products. It is clear that the as-synthesized product contains a fairly high percentage of ε-WO₃. Computer-assisted phase analysis based on the XRD spectrum enables us to quantitatively determine the fraction of either phase.

By using a cooling oxygen gas sheath around the flame, smaller grain-size particles were able to grow. As the quenching sheath diameter shrinks from 10 cm (Sample B2) to 5 cm (Sample B1), the particle diameter decreases from 12 nm ($S=66.3$ m²/g) to 9 nm ($S=97.0$ m²/g). Figure 1 shows the XRD and Raman spectra of the powders obtained having different grain sizes. For example, for Sample B1 (labeled as "small grain size") the shapes of the spectra obtained are similar to those of medium-sized particles, except that all the peaks in the XRD result are a little bit broader resulting from the smaller grain size of this batch. Besides, ε-WO₃ becomes a dominant phase in the material, as concluded from the enhanced intensity of ε-WO₃ peaks in the Raman result. In addition, the W=O bond peak is also intensified, showing a more active surface in this material, which can be attributed to the "nano effect".

On the other hand, the use of a glass tube on top of the flame enables the growth of particles. The diameters are 16 nm ($S=52.5$ m²/g), 20 nm ($S=40.5$ m²/g) and 27 nm ($S=30.5$ m²/g) when the tube lengths are 10 cm (Sample C1), 20 cm (Sample C2) and 30 cm (Sample C3), respectively. Figure 1 also provides the structural information of Sample C3 (labeled as "large grain size"). Quite different from those of the other two products, the peaks in both XRD and Raman spectra become very sharp and easy to identify due to the large grain size of the material. The peaks that are unique to ε-WO₃ (JCPDS No.: 872386) become distinguishable from γ-WO₃ (JCPDS No.: 830950) for the first time. Its Raman spectrum reveals a much smaller fraction of ε-WO₃ in this product. Besides, the surface hydrate almost disappears in this product. As the grain size increases, a larger fraction of ε phase of WO₃ will appear in the as-synthesized products.

Figure 2 shows TEM images illustrating the morphology and crystal structures of the as-synthesized WO₃ products. Most particles share a spherical shape in (a) and (b). Their SAED patterns (d) and (e) are composed of a series of continuous diffraction rings per their nanocrystalline character. Those rings can be indexed in stable phases of WO₃. Since γ-WO₃ and ε-WO₃ are structurally similar, it is impossible to distinguish the rings from either phase. Compared to (e), the rings in (d) are more ambiguous due to the smaller size of the product. In Image (c), we can clearly observe two major shapes in "large-grain-size" product. One is small round-shaped particles with an average diameter of 50 nm and the other is huge square monocrystals whose sizes varying from 60 nm to 300 nm. SAED patterns reveal the small particles are polycrystalline WO₃ (Image (f)) and the huge crystals are single crystalline γ-WO₃ with crystal planes either (100) or (110) (Image (g)).

Heat-treated powders

All the synthesized products were heat treated at 500°C for 8 hours to let them stabilize. Heat treatment had a profound effect on the products. First of all, the color of the products changed to yellowish green as is typical of pure γ-WO₃ powders. Second, the particles sizes increased and grew almost twice the size of the as-sprayed products. Such variation is also reflected in the XRD and Raman spectra in Figure 3 in which most peaks became much sharper.

Finally and most importantly, following heat treatment, all pure WO₃ undergoes a phase transition, in which the ε-WO₃ phase transforms to γ phase. This is clearly shown in Figure 3. In the Raman spectra, the intensities of ε-WO₃ peaks were reduced. In large-grain-size products, they even disappeared. Figure 3 also provides evidence that the surface hydrates have also diminished after heat treatment. The color change results from the disappearance of both ε-WO₃ and surface hydrates.

Table 1 summarizes the structural and morphological features of the flame-sprayed powders obtained under variable processing conditions and before/after heat-treatment. The highest content of γ-phase is obtained for a larger particle size of about 60 nm. Since this polymorph is the NO-selective phase, C3 is expected to be the optimum material for developing gas sensing films for NO detection.
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### Conclusion

Scalable synthesis of nanostructured powders of tungsten trioxide was accomplished by flame spray pyrolysis. Process maps that determine the relative phase content and particle sizes were obtained. Pure $\gamma$-WO3 powders may be obtained in this manner. These are targeted as sensing elements for the detection of NO in exhaled breath for personalized asthma monitors.

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