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PH Tester Gauge Repeatability and Reproducibility Study for WO_3 Nanostructure Hydrothermal Growth Process

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Abstract. PH value is one of the important variables for tungsten trioxide (WO_3) nanostructure hydrothermal synthesis process. The morphology of the synthesized nanostructure can be properly controlled by measuring and controlling the pH value of the solution used in this facile synthesis route. Therefore, it is very crucial to ensure the gauge used for pH measurement is reliable in order to achieve the expected result. In this study, gauge repeatability and reproducibility (GR&R) method was used to assess the repeatability and reproducibility of the pH tester. Based on ANOVA method, the design of experimental metrics as well as the result of the experiment was analyzed using Minitab software. It was found that the initial GR&R value for the tester was at 17.55 % which considered as acceptable. To further improve the GR&R level, a new pH measuring procedure was introduced. With the new procedure, the GR&R value was able to be reduced to 2.05%, which means the tester is statistically very ideal to measure the pH of the solution prepared for WO_3 hydrothermal synthesis process.

1. Introduction

Tungsten trioxide (WO_3) nanostructure is one of the metal oxide nanostructures that can be used as a functional element in various gas sensor applications [1] to detect gases such as ethylene, hydrogen, nitrogen oxide and others. WO3 is a n-type indirect band gap semiconductor and possesses a band gap energy range from 2.4 – 2.8EV that results in a higher utilization of the solar spectrum [2]. Nanostructure of WO3 can certainly enhance the performance of functional material and provide unique properties that are absent in its bulk form, hence it becomes rapidly expands in the field of materials chemistry [3].

There are few methods to grow WO3 nanostructure includes sol gel, chemical vapor deposition (CVD) and hydrothermal process [4]. Among them, the hydrothermal method received heavy interest due to fact that the preparation and equipment used for this process is relatively simple and less complicated. Hydrothermal is defined as the method to produce different chemical compounds and materials at temperatures above 100°C and pressures above 1 ATM by using physical and chemical processes flowing in aqueous solutions [5]. Typically, hydrothermal treatment begins with the preparation of a precursor solution [6]. The pH precursor is then added with appropriate amount acid or alkaline agent until the desired value is achieved. Depends on final nanostructure required, additional additive such as capping reagents or directive agents was mixed with the prepared solution and heated in a dedicated reactor to certain temperature ranges from 120 – 300 °C for a desired period of time. This allows the nucleation and growth of the crystallites took place.

Previous studies have established a few treatment parameters such as precursor concentration, pH, temperature, and growth duration significantly influence the morphological properties of the nanostructure [7]. Out of those variables, pH alone was discovered as a very important parameter which dictates the shape of the WO3 nanostructures, leading to a modification of the morphology from rod-like to prism-like and flower-like structures as illustrated in Figure 1.

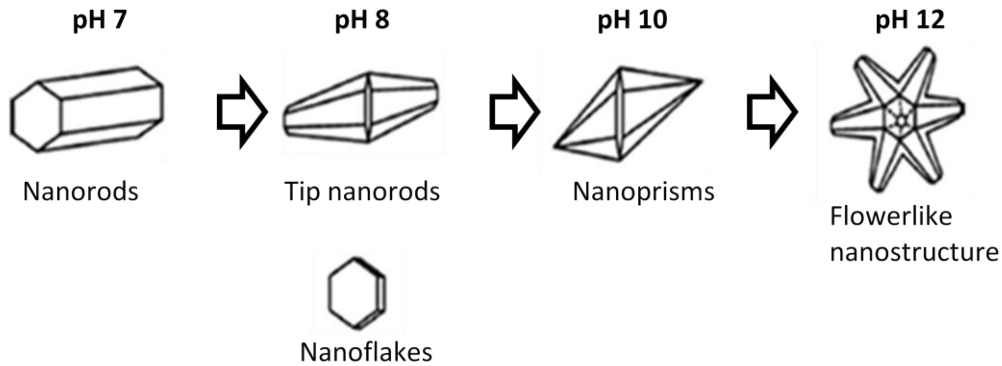
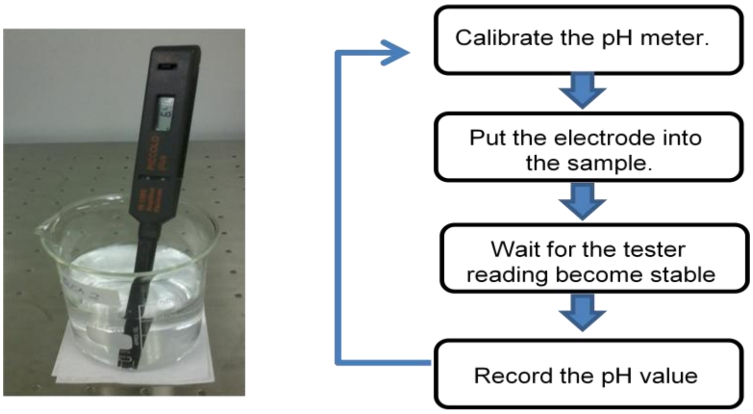


Figure 1. Illustration of different WO_3 morphology synthesis using hydrothermal with different pH value [8].

Therefore, it is very important that the measurement tools used to measure the pH value is accurate and reliable. One of the techniques largely used to access the measurement tool capability is gauge repeatability and reproducibility (GR&R) method. GR&R is a statistical tool that measures the amount of variation in the measurement system arising from the measurement device and the people taking the measurement [9]. Using this method, we can determine the uncertainty of the measurement systems before we can compare, control or optimize the manufacturing processes. Based on analysis of variance (ANOVA) method, the GR&R value of less than 10% is considered ideal while value of 10 - 20% is acceptable but there should be some plan to review the system for improvement. The GR&R value more than 30% indicates that the measurement system under the study is unacceptable which require either more accurate tool to be used or improvement of the measurement procedure is required.

2. Methodology

GR&R study on the PICCOLO pH tester (Hanna Instruments, USA) was conducted according to the process flow illustrated in Figure 2. Using MINITAB software, metrics for three operators measuring different buffer solution was generated. The 10 sample measurement was repeated by the operators in random order to minimize the bias in the analysis. To determine the GR&R value, analysis of variance (ANOVA) method which is also available in MINITAB software was used to analyze the data obtained from the study.



(a) (b)

Figure 2. Positioning of the tester to measure pH value (a) and the repeated process flow to conduct the pH measurement (b).

3. Result & Discussion

ANOVA analysis was done on the collected pH data from the experiment and the distribution of the variation component as shown in Figure 3 (a). It can be seen that the part-to part is the majority that contributes to the variation due to different pH value used as part of the experiment.

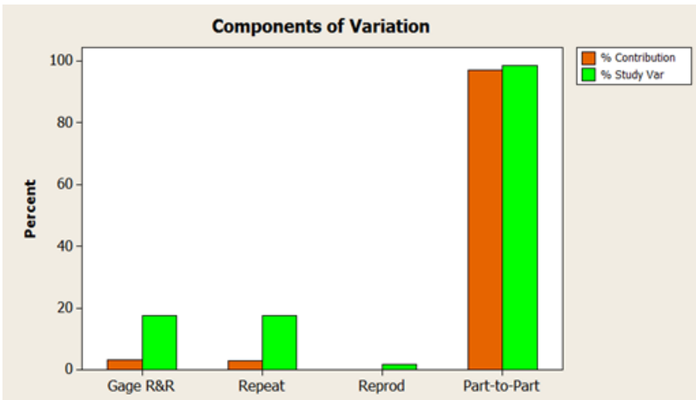


Figure 3. Histogram of variations components

Table 1 shows the ANOVA analysis, which indicates the total GR&R value of 17.55 %. Even though this value is considered acceptable because it is well below the 30 % range, but it is worth to revise the pH testing process to further improve the reliability and consistency of the measurement process.

Table 1. ANOVA analysis results of GR&R study

	StdDev (SD)	**Study Var (6 * SD)**	**% Study Var (% SV)**
Total Gage R&R	0.41445	2.4867	17.55
Repeatability	0.41235	2.4741	17.46
Reproducibility	0.04175	0.2505	1.77
Operator	0.04175	0.2505	1.77
Part-to-part	2.32437	13.9462	98.45
Total Variation	2.36103	14.1662	100.00

Base on observations and further discussion, the same GR&R study was carry out again but this time, two simple steps was included as illustrated in Figure 4.

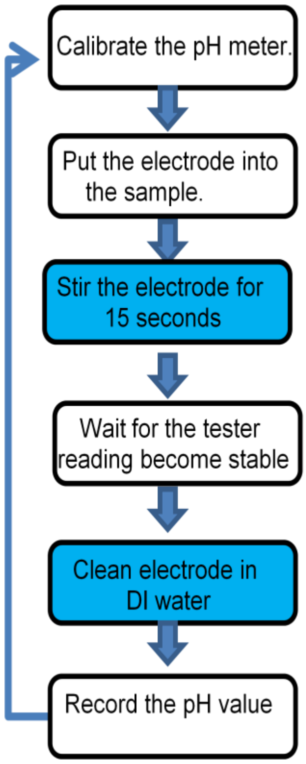


Figure 4. Additional two process steps (highlighted in blue) included in the process flow

The new ANOVA analysis in Table 2 confirms that the new GR&R value has been further reduced to 2.5%. With such low percentage of variation, the pH tester used and in the measurement process is statistically ideal to produce reliable and consistence pH value.

Table 2. ANOVA analysis results with the new additional measurement steps.

	StdDev (SD)	**Study Var (6 * SD)**	**% Study Var (% SV)**
Total Gage R&R	0.05413	0.3248	2.05
Repeatability	0.05280	0.3168	2.00
Reproducibility	0.01192	0.0715	0.45
Operator	0.01192	0.0715	0.45
Part-to-part	2.64508	15.8705	99.98
Total Variation	2.64564	15.8738	100.00

4. Conclusion

The GR&R of the pH tester and measurement procedure was successfully assessed. Based on ANOVA analysis, the initial pH tester GR&R was found to be 17.55 % which is statistically in acceptable condition. By introducing new pH measurement process step, the GR&R was able to further reduce to 2.5 %. The result proved that the tester and method is fit to be used and provides a higher certainty that the pH value measured is accurate. This will contribute to minimize the overall process variation of the synthesized nanostructure produced via hydrothermal method.

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