EXPERIMENTAL DESIGN FOR DETERMINATION OF EFFECTIVE PARAMETERS IN HYDROTHERMAL SYNTHESIS OF TiO_2-DERIVED NANOTUBES

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The synthesis of titanate nanotubes (TNT) which offers a very high specific surface area, high aspect ratio, better electrical contact, and transport of charge carrier has attracted particular interests in creating as a new kind of nanostructure materials due to various applications of photocatalysts, high effect solar cell, gas sensor, semiconductor devices, and new generation electrodes for lithium batteries [1-4]. Currently, there are developed methods for synthesis of titanate nanotubes including chemical synthesis with template, electrochemical synthesis, and alkaline hydrothermal synthesis. Among the aforementioned synthesis approaches, hydrothermal treatment received wide investigations, owing to their cost-effective, easy route to obtain nanotubes, the feasibility and availability of widespread applications [5-7].

Statistical experimental design methodology is an established and proven methodology for product and process improvements. The Plackett-Burman design was demonstrated to be powerful tools for identifying significant process parameters with relatively few experiments. A Plackett–Burman design can examine up to N−1 parameters ($f \leq N-1$) in N experiments, with N being a multiple of 4 [8]. Therefore, in this work, a screening approach, involving the use of Plackett-Burman experimental design, permitted the evaluation of the effects of 8 parameters from hydrothermal synthesis of TiO_2-derived nanotubes such as raw material surface area, m_{TiO2}, filling factor, temperature, time, aging, stirring, and HCl concentration on surface area of synthesized samples. The selection of levels of the different parameters was carried out based on preliminary experiments results. A matrix with 11 parameters (eight real parameters A-H and three fictitious parameters I-K) was used. Each synthesis was performed based on the conditions generated from Plackett–Burman design to obtain twelve different products.

The initial TiO_2 powders have the purity of >99.5 % and a BET surface area of 50 and 10 m^2/g, respectively. Pore structure of the TiO_2-derived nanomaterials was characterized by N_2 adsorption at –196 °C using an adsorption apparatus (Micrometrics, ASAP2010). The external features and morphology of the TiO_2 were analyzed by using a high-resolution transmission electron microscope (HR-TEM, Philips CM 200 FEG). In preparation, a commercial TiO_2 powder was dispersed in an aqueous solution of NaOH (10N) under vigorous magnetically stirring for about 1 hr to form a white suspension, followed by placing into a Teflon container. After hydrothermal processing, in each case the mixture was allowed to cool then aged at room temperature without stirring. The precipitate was repeatedly centrifuge and rinsed with distilled water and HCl solution until ~pH =6-7. The powder was dried in air at 100 °C for 24 hrs to give the as-synthesized product.

Since all the parameters were coded on a +1 to -1 scale, the absolute magnitude of the resulting coefficients (t_{obs}) can be used to rate the relative importance of the parameters. A parameter is considered significant if the value of the t-test is above a tabulated student's t-value (t_{tab}). The number of degrees of freedom and the applied significance level, α, will determine t_{tab}. A tabulated student's t-value around ± 4.3 is a guide to predict the important reveal effects. Standardized Pareto plot (Fig. 1) represents the absolute value of t_{obs} on surface area. For each parameter, give rapid visual information on the magnitude of t_{obs}. The length of the bar is proportional to the significant of parameter. If the magnitude of bar is more than the t_{tab} value, parameter is significant. Regarding to $t_{obs} < t_{tab}$, the most significant parameter is filling factor that enhanced their amounts. In addition to, temperature, stirring, raw materials surface area, and time are of relative significance parameters on surface area of synthesized samples, respectively but other parameters have little effects on these responses in the ranges tested. The last three lowest surface area responses related to the higher surface area raw material and stirring condition. TEM micrographs (Fig. 2) showed that the morphology for high, medium, and low surface areas of products is nanotubes, nanowires, and nanospheres, respectively.

References:

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Figures:

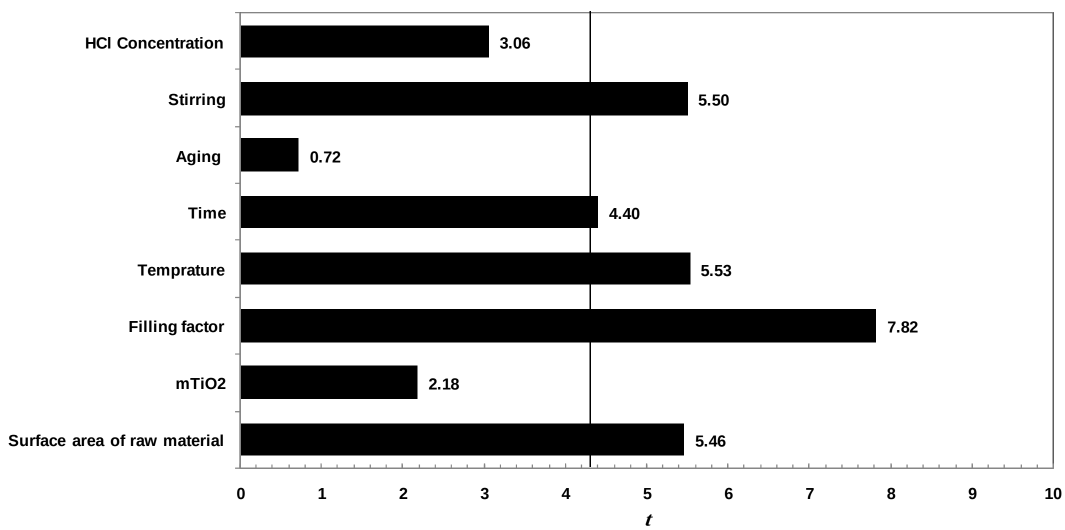

Fig. 1: Standardized Pareto chart of effects on surface area of synthesized samples (α=0.05)

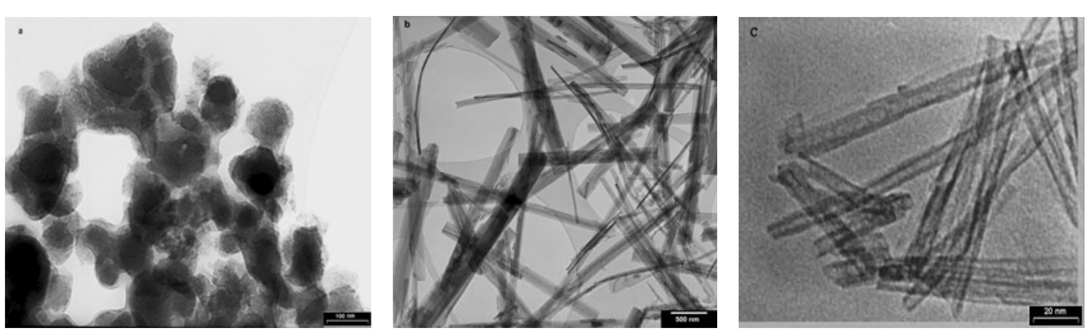

Fig. 2: TEM images of synthesized samples (a) nanospheres (b) nanowires (c) nanotubes