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Synthesis of Titanium Dioxide Nanoparticles (3nm) by adding PEO

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ABSTRACT: Nanosized Titanium dioxide (TiO) powder was synthesized via hydrothermal method using titanium tetrachlorida ($TiCl_4$) as the precursor and add PEO (Mw = 600.000). The obtained nano powder was used for further characterization. The phase transformation was investigated by an X-ray diffractometer (XRD). The grain size of the TiO2 particle was found to be 3.4 nm. Experimental results have shown that the nano powders have entirely consisted with anatase crystalline phase.

KEYWORDS: Titanium dioxide (TiO_2), nanoparticles, hydrothermal method, X-ray Diffraction.

I. INTRODUCTION

Nanoparticles Titanium dioxide (TiO_2) is a very useful transition metal oxide material and exhibits unique properties such as low cost, easy handling, non-toxicity and resistance to photochemical and chemical erosion. TiO_2 also has several potential technological applications in electrochemical energy storage and conversion technology such as sensors, solar cells, photo catalysis, memory devices, fuel cell, and Lithium ion battery [1-5]. These advantages make TiO_2 a material in solar cells, chemical sensors, for hydrogen gas evolution, as pigments, self-cleaning surfaces and environmental purification applications [6]. The oxide nanoparticles synthesized by several methods appear more and more useful, because these nanoparticles have good electrical, optical and magnetic properties that are different from their bulk counterparts [7].

Titanium oxide is a semiconducting metal oxide with the band gap of 3.2eV, it can exist in three main crystallographic phases : rutile, anatase, and brookite. It is inexpensive, non-toxic and easily available [16]. The major drawback of titania is its low electronic conductivity, thus the enhancement of the electronic conductivity is desired. Generally, there are two methods to improve titania electronic conductivity, first method is by creating more oxygen vacancy, converting part of the Ti^{4+} into Ti^{3+} and the second method is by introducing dopant into titania [17].

TiO_2 nanoparticles can be synthesized using various methods such as sulphate process, chloride process, impregnation [8], coprecipitation [9], hydrothermal method [10-12], direct oxidation of $TiCl_4$ [13], metal organic chemical vapor deposition method, etc [14]. Sol-gel method [15] is one of the most convenient ways to synthesize various metal oxides due to low cost, ease of fabrication and low processing temperatures. It is widely used to prepare TiO_2 for films, particles or monoliths. In general, the sol gel process involves the transition of a system from a liquid “sol” (mostly colloidal) into a solid “gel” phase. The homogeneity of the gels depends on the solubility of reagents in the solvent, the sequence of addition of reactants, the temperature and the pH. The precursors normally used for the synthesis and doping of nanoparticles are organic alkoxides, acetates or acetylacetonates as well as inorganic salts such as chlorides. Among the classes of solvents, alcohols are largely used but other solvents such as benzene may also be used for some alkoxides.

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In the previous study, TiO_2 was synthesized with sol-gel synthesis process and the TiO_2 precursor obtained was treated with HMDS vapors at 150˚C under nitrogen atmosphere to eliminate its surface hydroxyl groups and get the nanoparticle TiO_2 with size 40 nm. In this work, the synthesis of TiO_2 with hydrothermal process was modified by adding PEO. TiO_2 was synthesized using a hydrothermal method with PEO being added at an appropriate time (determined by the temperature in the reaction vessel) to inhibit the growth of particle size. The growth of the TiO_2 grains was effectively inhibited by the addition of PEO, while aggregation of the treated TiO_2 powders could be avoided to result in a better dispersion of the particles. The characterization of particles was carried out by XRD (X Ray Diffraction).

Cool down 40 mL 95% ethanol to < 5° C

↓

Add PEO powder (Mw = 600.000), stir until complete

↓

Add $TiCl_4$ until white vapour vanish, keep stir

↓

Add urea, DI water, stir for 15 minutes

↓

Transfer to teflon-lined autoclave, hydrothermal at 200º C for

↓

Centrifuge until pH = 7-8 (use DI water)

↓

Vacuum dring at 80º C for 8 hr, grind and collect

↓

Calculate particle size from XRD data

Scheme 1. Synthesis of nano-sized TiO_2 powder

II. PROCEDURE

2.1 Materials

The materials that used in this experiment are Titanium (IV) Chloride [$TiCl_4$; MW : 189.91; 99.9% purity] Acros Organics, Ethyl Alcohol [C_2H_5OH; MW : 46.07; 99.5% purity] Shimakyu's Pure Chemicals, Urea [$Co(NH_2)_2$; MW : 60, 99.5% purity] Acros Organics, De-ionized Water (ionic resistance : 18 MΩ), Millipore and Poly Ethylene Oxide [$HO(CH_2CH_2O)_nH$; MW : 600.000) Acros Organics

2.2 Synthesize of nano-sized TiO_2 powder

TiO_2 powders were prepared by a hydrothermal process. $TiCl_4$ (Acros), DI water, Urea and ethanol (Acros) solvent were mixed, stirred for 15 minutes and kept the temperature < 5 ^oC. PEO (molecular weight = 600,000) was dissolved in ethanol and added to the previous solution and stirred for 15 minutes. The hydrothermal process was conducted at 200 ^oC, for 2 hours with a heating rate of 10 °C/minute. To separate the product, it was centrifuged and then oven dried under vacuum overnight.

III. RESULTS AND DISCUSSIONS

X-Ray Diffraction (XRD), also known as powder diffraction is a technique to characterize the crystallographic structure, crystallite size (grain size) and preferred orientation in polycrystalline samples. XRD is commonly used to identify unknown substances or to determine the purity of crystalline material by comparing diffraction data against a database maintained by the International Centre for Diffraction Data (ICDD).

In this particular study, XRD was used to characterize the crystallinity and the grain size of Tio_2. XRD analysis in this study was performed using desktop Bruker D2 Phaser XRD machine with Cu K_α irradiation as photon source, λ= 1.5406 Å, Ni filter, 40 kV and 100 mA. All samples was analyze in the range of 2θ= 20° –60°, scanning speed 1°/min and 0.05°/point scanning step.

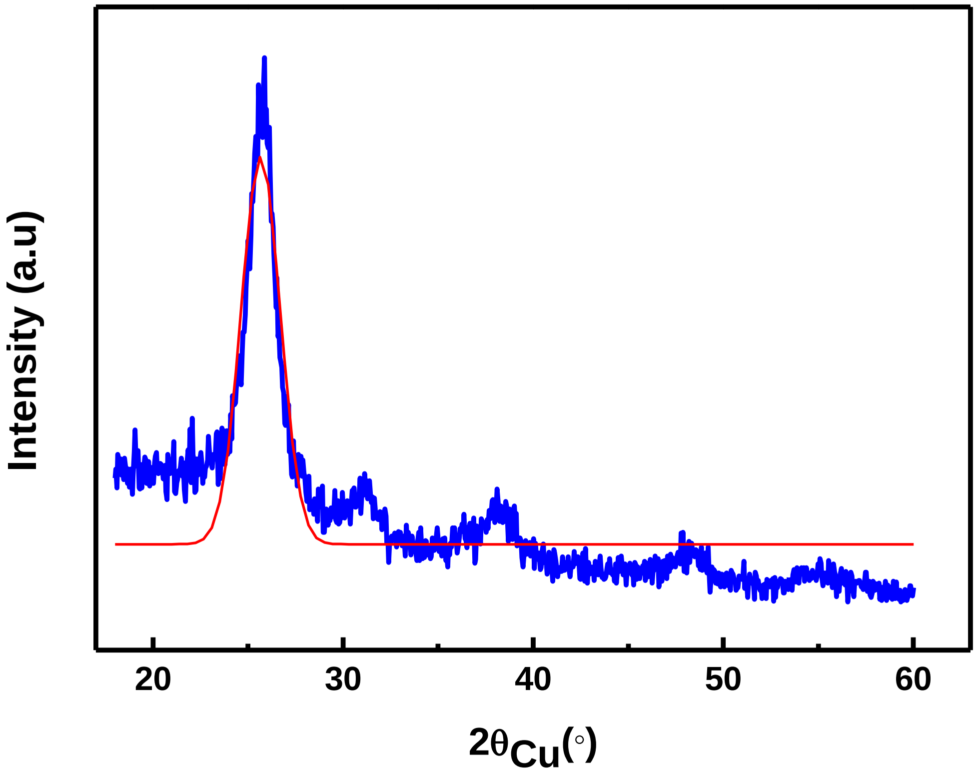

Figure 1. Fitting curve of XRD Pattern for TiO_2

Obtained XRD patterns were then compared with JCPDS reference from ICDD. EVA DIFFRAC 2.0 software was used to access JCPDS references. For the crystallite size estimation, Debye-Scherrer equation (eq. 1) was applied.

$$t = \frac{K \cdot \lambda}{B \cdot \cos\theta} \quad (1)$$

where :

K = shape factor (throughout this study K = 0.9)

t = crystallite size (Å)

λ = X-ray wavelength (Cu K_α = 1.5406 Å)

B = full width at half height maximum, FWHM

θ = angle (degree)

The FWHM was estimated by using OriginLab 8.0 software based on the strongest intensity XRD peak, this peak was fitted by using PsigVoigdt1 function.

Figure 1 shows the XRD pattern of nano sized TiO_2. The peak appeared at 2θ value ranging the diffraction peak at 2θ with 25.3˚, 38.3˚, 48˚, 54˚, indicate to the formation of anatase phase of TiO_2. The phase of nanosized TiO_2 is pure anatase phase, agree with our previous result [5]. The smallest particle size after optimazion is 3.4 nm. This smallest particles size due to adding PEO during synthesize process and PEO inhibit the growth of particle size.

The avarage size of the particles was calculated using Debye-Scherrer's formula. By following (1) equation, we can calculate and get the particle size (t) is 3.4 nm.

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