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SYNTHESIS OF PHOTOCATALYTIC TITANIUM DIOXIDE NANOPOWDERS USING DIFFERENT ACID CATALYSERS

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Abstract- Photocatalytic titanium dioxide (TiO_2) nanoparticles were synthesized via acid assisted sol-gel process. The effects of different acids namely; acetic acid, hydrochloric acid, and nitric acid on the formation of TiO_2 nanoparticles and their photocatalytic properties were investigated. XRD, SEM, and UV-Vis spectrophotometer analyses were performed to examine the physical and chemical characteristics of the nano powders. The results showed that only anatase phase of TiO_2nanoparticleswith different crystallite size and morphology weresynthesized with respect tothe kinds of acid and the procedure applied. The TiO_2 powder synthesized from HCl exhibited highest photocatalytic activity, and its methylene blue photodegradation efficiency was 98.1% in 90 minUV irradiation.

Index of Terms: TiO_2 powder, Photocatalytic activity, Sol-gel process, Acid effect.

I. INTRODUCTION

Recently, different strategies like the ion exchange, membrane filtration, electrochemical methods, etc., have been developed to resolve the water pollution problems [1]. Many reasons including the stable state of its chemical and optical properties, as well as many other advantages such as low cost, insolubility in water, high efficiency, and its harmless property, point out the use of titania (TiO_2) as a photocatalyst in water treatment [2,3]. There are many techniques or methods employed in the production of TiO_2 films for water purification. The sol-gel process is considered one of the best methods to prepare thin oxide coating since it has multiple advantages including easiness, low-cost, and better homogeneity in the products [4,5].

Theobjectives of this study arei) to investigate the effects of different acids and different pH on the formation, morphology, and structure of TiO_2 nanoparticles, ii) to determine the effects of the developed morphology on the photocatalytic activity (PA) of TiO_2 nanoparticles synthesized, and iii) utilization of the TiO_2 nanoparticles synthesized in waste water treatment.

II. EXPERIMENTAL PROCEDURE

A. Synthesis of TiO_2 Nanoparticles

Photocatalytic TiO_2 nanoparticles were synthesized using tetra-isopropoxide (TTIP,Aldrich 97%) as a precursor. Various amount of different types of acids;acetic acid(CH_3COOH, Merck 100%), nitric acid(HNO_3, Aldrich 70%), and hydrochloric acid (HCl, Aldrich 37%) were used as catalysers.First, the acid was added to the beaker containing 0.9 mL distilled water and 23.5 mLethanol absolute (C_2H_5OH, Merck 99%). Then, 2.35 mL of TTIP was added dropwise to the solution during magnetic stirring for 30 min at room temperature. The acidity of the solution was adjusted to 4. The sol was kept at room temperature for 1 day to form a gel. After that, the gel was dried in an oven at 80 °C for 24 h to remove all moisture and volatile components. The dried agglomerate was crushed to obtain a fine powder. Next, the powders were calcined at 550 °Cfor 1 h in air. The heating and cooling rates were 2 and 6 °C/min, respectively, for all powders. Dry gels synthesized using CH_3COOH were calcined at temperatures of 450, 550, and 650 °C. The TiO_2nanoparticlessynthesizedwere coded as CH-4, HCl-4, and HN-4 for CH_3COOH, HNO_3, and HCl solutions, respectively.

A coating solution was prepared from the powder synthesized by using HCl to get a coating layer on the glass substrates by dip–coating technique. The glass substrate was cleaned by immersing it in the beaker containing ethanol for 2 h and then dried in an oven at 80 °C for 30 min. Then, the substrate was dip-coated by immersing it in the coating solution for a minute and then dried in an oven at 80 °C for 10 min. This operation was repeated one, three, and five times to increase the coated layer thickness. The coated films were calcined at 550 °Cfor 1 h.

B. Characterization of TiO_2 Nanoparticles

The phase(s) present in the synthesized TiO_2 nanoparticles was identified using X-Ray Diffractometer (Rigaku, D/MAK/B, Tokyo, Japan). All powders were scanned continuously from 2θ of 20 to 80° at a scanning rate of 2/min with 0.02° increments. The surface morphology and particle size of the powders were examined using scanning electron microscope (SEM, Nova Nanosem 430).

C. Photocatalytic Measurement

The photocatalytic activity of TiO_2 nanoparticles synthesized was evaluatedthrough photodegradation

test of methylene blue (MB) solution under a 125 W UV lamp with a wavelength of 365 nm.To prepare the MB solution, 20 mg of MB were dissolved in distilled water to get a concentration of 20 mg/L, and then TiO_2 nanoparticles were added to this solution under continuous stirring to get the TiO_2 /MB concentration of 100 mg/20 mL. Before illumination of the UV light, the suspension aqueous solution was stirred continuously in dark for 30 min to ensure adsorption/desorption equilibrium. A 3.5 mL of the suspension was took every 30 min to check the absorptionusing the UV–Vis spectrophotometer (Shimadzu UV-1800) to determine the concentration of MB. The removal efficiency of the photocatalyst was calculated as follows:

$$\text{Degradation } \% = (C_o - C)/C_o \times 100 \quad (1)$$

where C_o and C are the concentrations of MB at initial and different irradiation time, respectively [6].

D. Photocatalytic Reactor for Water Treatment

A continuous water treatment system was designed to test the photocatalytic efficiency of the glass substrates coated with titanium dioxide. A 5000 mL glass basin with open nozzles on top and bottom was designed. Water was circulated using a pump with a speed of 150 rpm. The UV light used for irradiation of the material was placed in the center of the glass basin.

RESULTS AND DISCUSSION

A. XRDAnalyses

Fig.1 shows the XRD patterns of the powders synthesized by using different acid and then calcined at 550 °C. The peaks at the angles of 25.3, 37.8, 48, 54, 55, 62.8, 68.7, 70.3, and 75° correspond to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) planes, respectively of the anatase phase of TiO_2. All the diffraction peaks agree with the anatase phase (JCPDS 21-1272). No peaks belonging to rutile and brookite phases were detected in the powders. Similar results were reported by Zhou et al. [7] who attributed the formation of only anatase phase to the strong chemical coordination of titanium.

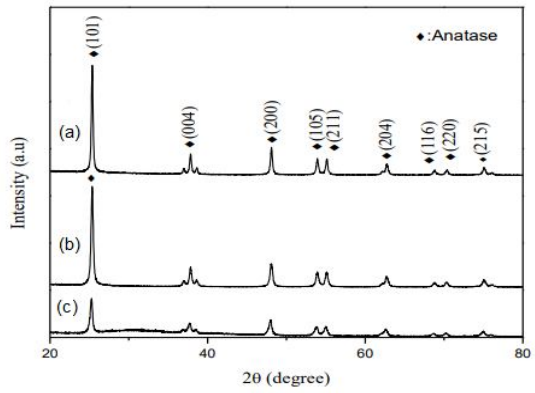

Fig.1. XRD patterns of the calcined nanoparticles synthesized by using different acids. (a) CH-4, (b) HCl-4, and (c) HN-4.

For all samples, very sharp and narrow XRD peaks indicate good crystallinity. Samples CH-4 and HCl-4 possessed no noise while sample HN-4 had low noise. A higher intensity of the peak at 2θ of 25.3°suggests that crystallinity (anatase phase) in the powders was in the order of the samples CH-4 > HCl-4 > HN-4 implying that CH_3COOH is better catalyzer than HCl and HNO_3 for the acid assisted sol-gel synthesis of TiO_2nanoparticles. This may be due to the fact that Ti has a higher affinity in the order to CH_3COO^- ions > Cl^- ions> NO_3^- ions, which promoted anatase crystallization. Here, the sol-gel formation made the rearrangement of arbitrary bonds in the precipitation process toward the defined structure of anatase. The presence of acid accelerated the formation of anatase [8]. Considering the structures of the TiO_2 polymorphs, it is obvious that linear chains can only form rutile-type nuclei, while skewed chains are restricted to forming anatase-type nuclei [9].The increase in the intensity of anatase phase due to the type of acid used during synthesis is related to the size of the crystallites present in the structure as well as the percent crystallinity of the powders. Phase composition and crystallite size are presented in Table 1.

Table 1. The crystallite size and phase composition of the powders synthesized by using different acids.

Sample code	Catalyser	Crystallite size (nm)	Phase(s)
CH-4	CH_3COOH	23.82	anatase
HCl-4	HCl	22.48	anatase
HN-4	HNO_3	15.96	anatase

Fig.2 shows the XRD patterns of the powders synthesized by using CH_3COOH and then calcined at 450, 550, and 650 °C in air for 1 h. Only anatase phase was detected in the XRD patterns for all of the powders calcined at different temperatures.

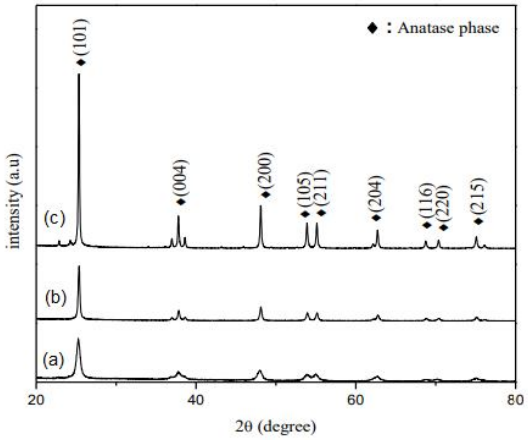

Fig.2. XRD patterns of the powders synthesized using CH_3COOH as a catalyst and then calcined at temperatures of (a) 450 °C, (b) 550 °C, and (c) 650 °C.

It was observed that as the calcination temperature increased, the intensity (accordingly the amount) of the anatase phase increased suggesting a better crystallinity. The increase in the anatase phase has reflected the increase in the crystallite size because high temperature increases the tendency of crystal growth; hence, to achieve complete crystallization [10].

B. SEM Analysis

The representative SEM images of the powders synthesized are shown in Fig.3.SEM examinations revealed that the morphology of all of the powders consisted of agglomerates of nanoparticles of various sizes. The average particle size as obtained by Image Processing analytical software was 11.8, 10.8, and 10.7 nm for the powders synthesized by using CH_3COOH, HCl, and HNO_3, respectively. The particle size as determined from SEM images is close to that calculated from XRD measurements. It is obvious that the smallest particle size belongs to the sample synthesized by using HNO_3.An irregular distribution of particles as either a single particle or a cluster of particles has been noticed. The images shown in Fig. 3 revealed that the particles synthesized by using HCl as a catalyst are agglomerated as small clusters while the particles synthesized by using HNO_3 are highly agglomerated as chunks or blocks.It was clear that when CH_3COOH was used as a catalyst, particles agglomerated as a big chunk and the agglomerates were irregular in shape. The findings agree with those reported by Golobostanfard et al. [11] who prepared TiO_2 powder by the sol-gel process using TTIP as precursor followed by calcination at 450 ºC.They reported that the formation and morphologyof TiO_2 could be affectedby the type of acid.

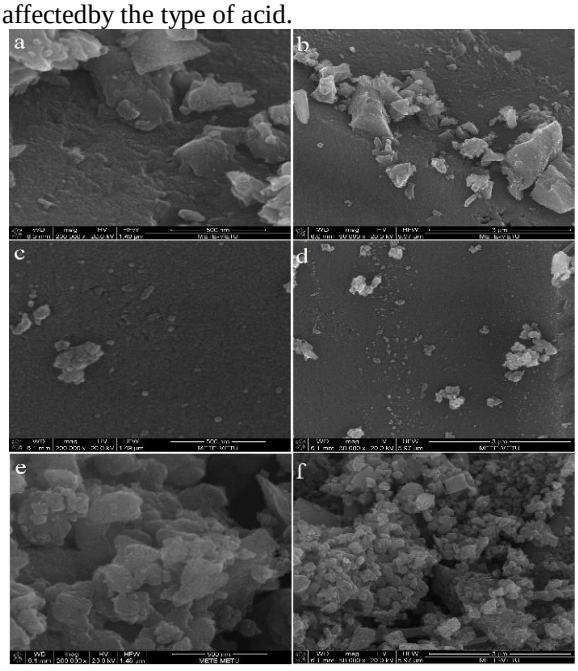

Fig.3. SEM images of the calcined powders synthesized using different acids. (a) CH_3COOH; 500X, (b) CH_3COOH; 3000X, (c) HCl; 500X, (d) HCl; 3000X, (e) HNO_3; 500X, and (f) HNO_3 ; 3000X.

C. Photocatalytic Activity

The blue color of MB solution was completely removed after 90 min of UV illumination for all of the powders synthesized by using CH_3COOH, HCl, and HNO_3. The degradation percentages were fairly close to each other although little differences that emerged after 30 and 60 min of illumination, where the photocatalysis efficiency for the prepared samples was HCl-4 > HN-4 > CH-4. The degradation was almost the same after 90 min of illumination as shown in Fig.4. It was inferred that there is a little effect on the activity of photocatalysis when the acid type is changed. However, in order for the material to have a good photocatalytic efficiency, it should have a high surface area and good crystallinity [12]. An increase in crystallinity lead to enhancement of photocatalytic activity but, at the same time reduces the surface area which eventually decreases photocatalytic activity due to increase in crystallite size.

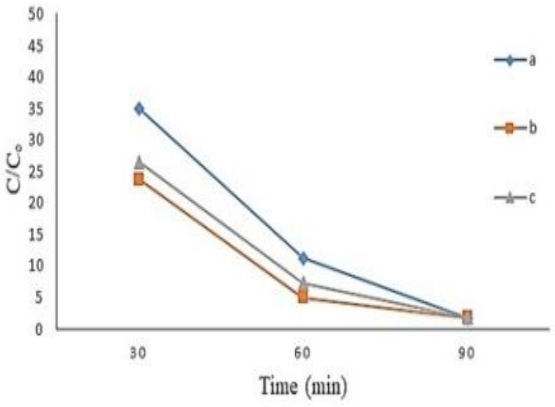

Fig.4. Time-dependentphotodegradation of MB under UV illumination of the powders synthesized by using different acids. (a) CH_3COOH, (b) HCl, and (c) HNO_3.

D. TiO_2 Layer Coated on Glass Substrate

The glass pillars used in the monitoring system have been coated by using the TiO_2nanoparticles having the highest PA. 30 of glass pillars was coated for 1 time, 3 times, and 5 times using 150, 450, and 750 mg of TiO_2nanoparticles synthesized, respectively. Before starting the system to measure PA using a catalyst, the MB was examined without using the catalyst for 7 h to ensure that light used in the system does not affect the dye. After that, the examination was carried out on the coated pillars for 7 h. Percent MB degradation of the coated layers was noted at 1 h interval. The results showed that increasing the number of coating layers, hence increasing the amount of TiO_2, lead to increase in PA. The photocatalytic efficiency of TiO_2 could be affected by the crystalline structure and the surface morphology of films [13]. It is clear that the rate of photodegradation depends on the thickness of the substrate, the decay rate was found to increase with film thickness.

CONCLUSIONS

The kind of acids strongly influences the crystallinity, crystallite size, and morphology of TiO_2nanoparticles. The crystallization of the anatase phase depended on the ions, where Ti has a higher affinity in the order ofCH_3COO^- ions > Cl^- ions> NO_3^- ions. Also, calcination temperature affects the crystallinity and the size of the crystals. TiO_2nanoparticlesynthesized using HCl has the highest photocatalytic activity. TiO_2 coated glass was successfully prepared with different cycles and found that the cycle influence on the photodegradation rate by increasing the coating layer of TiO_2.

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