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Synthesis of TiO_2 thin films on different substrates by chemical vapor deposition method

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ABSTRACT

TiO_2 thin films were synthesized by using Chemical Vapor Deposition (CVD) method on different substrates, such as glass, aluminium foil , and ceramic. The samples had been characterized by microscopy analysis, SEM, and EDS. The results show that TiO_2 thin films were successfully fabricated and TiO_2 nanocrystals with size of 50-100 nm loaded uniformly on surface of different substrates. The photocatalytic activities of all samples were investigated in photo-degradation of methyl orange (MO) under UV light irradiation and was followed by the UV-Vis diffuse reflectance spectroscopy, showing that the conversion of methyl orange achieved the highest percentage of 91% with TiO_2 thin film synthesized on the ceramic substrate over 270 minutes of reaction. The hypothetical mechanism explaining this observation is that the surface morphology of ceramic plays a major role in the augmentation of MO molecules adsorption onto the surface of material, thus, improves the dye degradation process.

Introduction

Titanium dioxide (TiO_2), nowadays, has been proven as an outstanding semiconductor due to its numerous advantages as nontoxic nature, photochemical stability, biologically inert,...[1-4] Recently, this typical material was used in the application of environmental protection sector through the decomposition of waste pollutants [5-7].

There are many methods to create TiO_2 catalyst particles such as sol-gel, hydrothermal, sputtering. Basically, photocatalytic reactors can be classified into two types based on the catalytic state of suspension and immobilization. Meanwhile, the suspension form is being studied widely, however, it has two basic disadvantages [8-11]: (i) the high density suspension catalysts cause the phenomena such as light scattering, reflection, and occlusion lead to reduce the photocatalytic activity, (ii) after the reaction that photocatalyst needs to be recovered from the treated mixture and reused. These disadvantages can be solved through the use of immobilized catalysts, and the TiO_2 thin films have attracted more attention [12,13]. Various methods can be used to prepare thin films, including chemical vapor deposition (CVD), chemical bath deposition, spin coating, dip coating, pulse laser deposition (PLD), electrochemical and oblique angle deposition methods [14-16]. Among these, CVD is flexible and useful because this method allows the control of various parameters that affect products and the selection of precursors [17-19].

The CVD is a synthesized method in which a thin film of material is fabricated by binding in the form of diffusion, as a result of reaction between the gas

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phases and the heated surface [20-22]. The CVD process provides good control of composition, microstructure, and thickness of the TiO_2 film [23,24]. The application of the CVD method is due to several advantages, including uniform films, complex surface area, good homogeneity and high deposition rates [25]. The layer is in the form of a coating, a powder or a single crystal. By changing the experiment's condition, such as substrate materials, reaction temperature, composition of gas phase, pressure, etc. that different properties of the final films can be achieved [26,27].

In this research, several TiO_2 thin films were prepared using the chemical vapor deposition (CVD) method, which TiO_2 layer of material is coated on different kinds of substrates: glass, aluminum foil, and ceramic by using titanium tetraisopropoxide (TTIP - $Ti[OCH(CH_3)_2]_4$) as the main precursor for reactions. Photocatalytic efficiency of the as-prepared catalysts was determined by studying the degradation of methyl orange (MO - $C_{14}H_{14}N_3NaO_3S$) under ultraviolet light irradiation.

Experimental

Preparation of catalysts

TTIP (98%) was analytical reagent grades and purchased from Sigma Aldrich. The weight composition of the aluminum substrate was 52.94% Al, 47.06% O, while the ceramic one was prepared in accordance with the proportion of cordierite ($2MgO.2Al_2O_3.5SiO_2$) with %wt. composition was 71.55% Kaolinite, 7.33% MgO, 4.31% $Al(OH)_3$ and 16.81% $CaMg(CO_3)_2$.

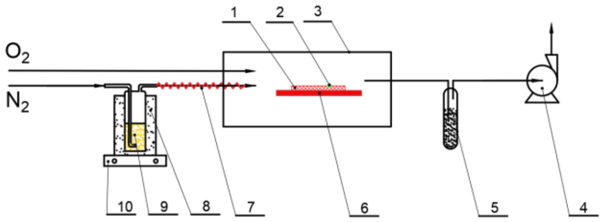

Figure 1: Schematic diagram of CVD system

The CVD reaction system using to synthesize TiO_2 thin films was shown schematically in Figure 1, where:

1.Substrate; 2.Thermocouple;
3.Furnace; 4.Vacuum pump;
5.Cooling trap; 6.Electric heating plate;
7.Heating tape; 8. Glycerol;
9. Precursor solution; 10.Magnetic stir

Firstly, 10 mL of TTIP solution as TiO_2 precursor was added into a bubbler. Then, this bubbler was placed into a beaker containing 300 ml of glycerol and heated up to 80 °C with magnetic stirrer. The precursor solution was vaporized and carried into the furnace, by using 225 mL/min nitrogen (N_2, 99.99%) flow as carrier gas, to interact with the suface of substrates. Glass, aluminium foil and ceramic were used as substrates with the dimension was 20×10×2 mm and placed on the surface of the heating plate. The reaction temperature was kept at 300 °C [28], including with 500 mL/min oxygen (O_2, 99.99%) flow as oxidation agent. After total 30 min of CVD reaction, the excess products were seeped through cooling trap and taken to the outside by vacuum pump, then, these samples was calcined at 450 °C [14] for 3 hours to crystallize TiO_2. The final samples of TiO_2 coating on glass, aluminium foil and ceramic was named as Ti/Gl, Ti/Al, and Ti/Cer, respectively.

Characterization

The images of materials' surface was observed using microscopy from Kruss, Germany. The morphology and chemical characterization of prepared samples was studied using a JEM-1010 field emission scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDS) (Hitachi S-4800).

Photocatalytic experiments

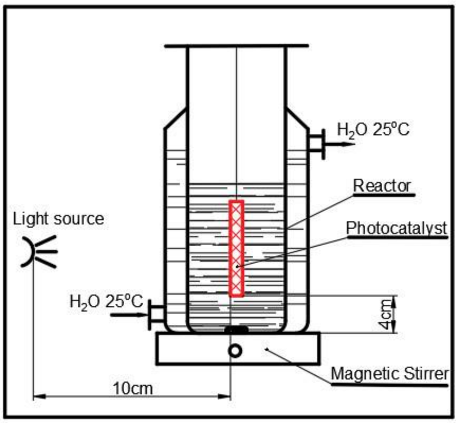

Figure 2: Schematic diagram of photocatalytic experiments

The experiments were carried out in a quartz tube as the reactor and placing on a magnetic stirrer (Figure 2). The solution was irradiated with a 500W Xenon lamp (LOT, Germany) with wavelength 172-1299 nm, placed next to the reaction mixture. The catalyst plate was located in a distance of 10 cm from the light source.

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The reaction temperature was maintained at 25°C. The pre-prepared catalyst plate was immersed into 100 mL solution MO (10 mg/L) (85%, Sigma Aldrich, maximum absorbance in the visible region at 464 nm) and placed 4 cm from the bottom of the quartz tube, facing the incident UV light. The reactor system was placed in a black box to avoid the effect of ambient light. Prior to exposure to the radiation, the TiO_2 coating sample and MO containing system was stirred in the dark for 30 min [29] to reach equilibrium adsorption. In order to monitor MO concentration during irradiation, 5 mL aliquots of the solution were regularly withdrawn from the reactor and analyzed by the UV/Vis diffuse reflectance spectroscopy (Avantes Ava-Raman, Netherlands) at the wavelength of 464 nm.

The conversion of the dye photo-degradation was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{C_0 - C}{C_n} \times 100\%$$

where:

C_0 is the concentration of MO solution at the beginning of UV illumination (mg/L),
C is the concentration of MO solution at the time *t* of reaction (mg/L)

Results and discussion

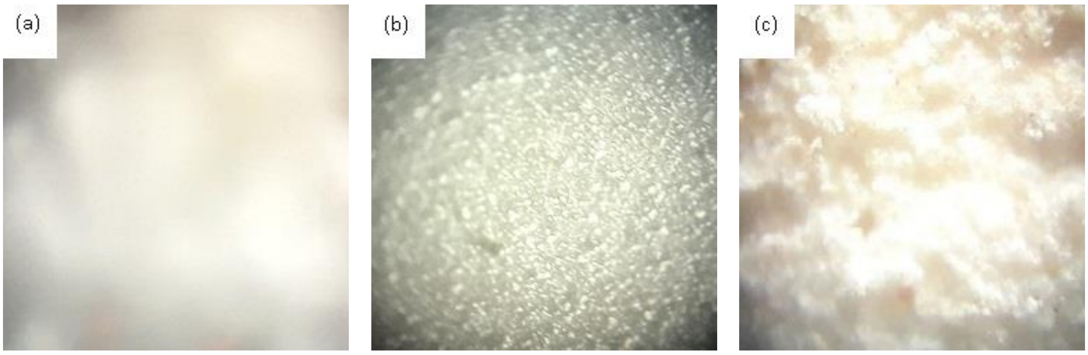

Figure 3: Microscope images of a) Ti/Gl, b) Ti/Al, and c) Ti/Cer

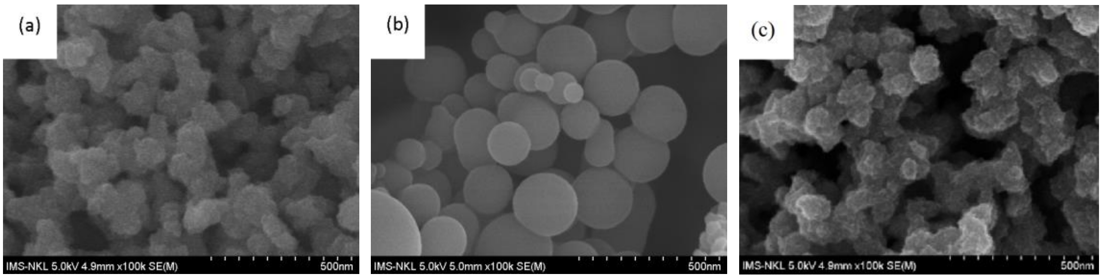

Figure 4: SEM images of a) Ti/Gl, b) Ti/Al, and c) Ti/Cer

Charaterization of materials

TiO_2 coating on substrates observed by microscope at 10 times magnification in Figure 3 showed different kinds of TiO_2 nanoparticles formations. Generally, all the samples obtained a white thin layer of TiO_2 on the surfaces. However, by using CVD method, these layers are considerably affected by the the original morphology of substrate themselves [26,30]. As the results, the catalyst films on glass and ceramic was rough and rugged (Figure 3a and 2c), meanwhile, the TiO_2 particles seem to locate and arrange uniformly on the surface of aluminium foil (Figure 3b). To evaluate more detailed the particle size and morphology, all samples were analyzed by SEM method, as shown in Figure 4. On the glass substrate, TiO_2 nanoparticles, about 50 nm in size, were very uniform and aggregated to form clusters containing small pores (Figure 4a). This phenomenon was also observed with the ceramic-substrate sample, morever, nanopores appeared in higher quantity with lager size comparing to Ti/Gl material (Figure 4c). It could be explained by the initial morphology of ceramic was uneven and had directly significant impact on the crystalliztion of TiO_2 in a very disorderly way. Meanwhile, the appearance of catalyst on aluminium foil was dissimilar with the others with the presence of TiO_2 nanosphere particles, which were in range from 50 nm to 100 nm of diameter.

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Specified peaks corresponding to Ti and O elements were found in EDS spectra of all materials (Figure 5). Those high and sharp peaks indicated that the catalyst was synthesized with high purity and deposited successfully on all three kinds of substrate. The atomic percentage of Ti element in Ti/Gl, Ti/Al, and Ti/Cer was 16.43%, 14.94%, and 12.13%, respectively. The minor differences in those values showing that the vaporization and crystallization process of TiO_2 played an important role in controlling the catalyst's percent during the CVD synthesis. Besides that, all peaks of elements corresponding to each substrate's components were presented in EDS spectras, proving that coating TiO_2 by CVD method had high effectiveness without damaging based materials.

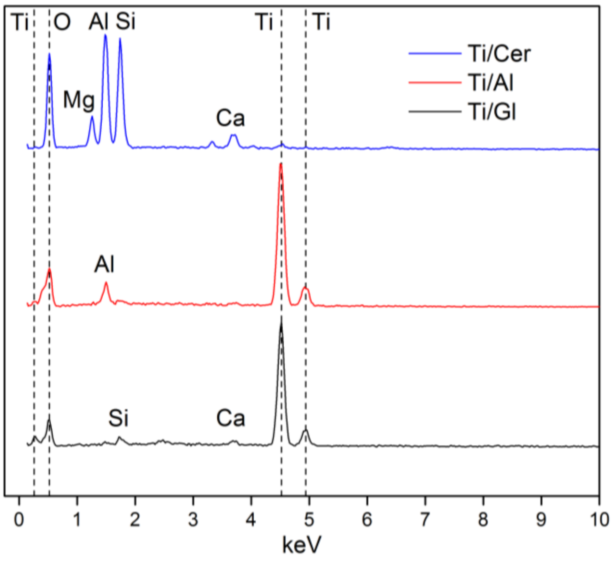

Figure 5: EDS spectra of elements in all specimens

Photocatalytic activities

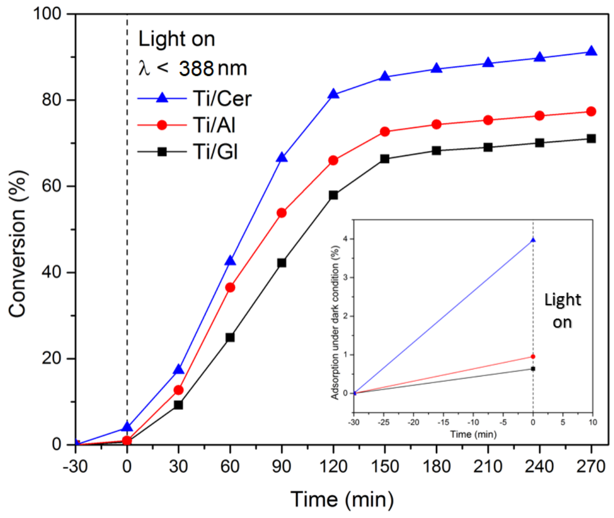

Figure 6: Conversion of MO solution with TiO_2 thin fims coated on different substrates

The photocatalytic activities of TiO_2 thin films coated on different substrates were evaluated by MO degradation under ultraviolet light (UV light) irradiation (λ < 420 nm). All experiments were followed by the UV-Vis spectra analysis and the conversion of dye molecules is shown in Figure 6. Firstly, the catalyst material was immersed into 10 ppm MO solution and stirred in dark condition for 30 min to attain adsorption - desorption equilibrium. It could be seen from Figure 5 that, during 30 min stirring in dark, the MO concentration decreased approximately 4% when using the Ti/Cer material, in contrast to the Ti/Gl and Ti/Al. This could be explained by the specified morphology of ceramic substrate leading to the deposition of TiO_2 nanoparticles containing more and larger pores over the surface, thus, increasing the adsorption dye molecules ability of prepared material.

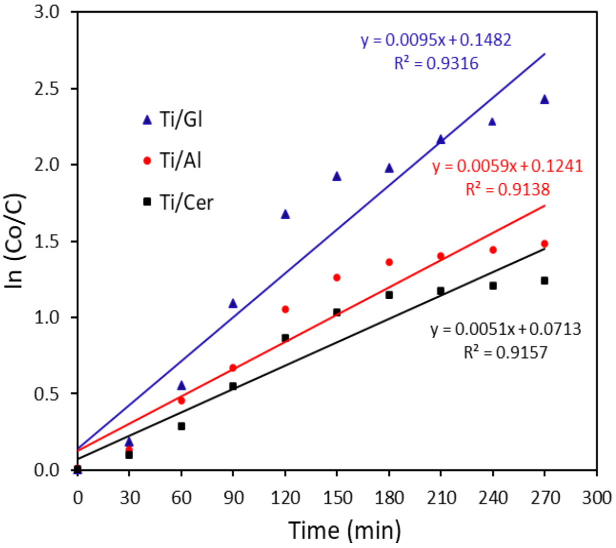

Figure 7: Kinetic analysis of MO degradation

The MO solution was then irradiated at different time intervals up to 270 min. Figure 7 illustrated the relationship between ln (C_o/C) and reaction time using three kinds of material, the degradation reactions of MO solution can be described by the pseudo-first-order kinetic model $\ln(C_o/C)=kt$. The reaction rate constant k can be estimated from the slope of the equation:

$$y = kx+b$$

All of the experiments are followed by the pseudo-first-order equation with the correlation coeficients between the model and experimental values are acceptable ($R^2>0.91$). Form the Figure 7, the Ti/Cer showed the best degradation reaction with $k_1 = 0.0095$, followed by 0.0059; 0.0051 with Ti/Al and Ti/Gl respectively. For the photocatalytic activity, according to Figure 6, the final conversion percentage of MO solution with Ti/Cer attained the value at about 91% and the dye colour was almost disappeared after 270 min, in the opposite of Ti/Gl. The reason for this phenomenon might relate to the noteworthy adsorbability of Ti/Cer material comparing to the others. This result claimed that almost MO molecules were converted into intermediates under UV light irradiation when using Ti/Cer as photocatalyst.

Mechanistic considerations

After the calcination step at 450 °C, titania particles coated on the ceramic substrate were experienced a phase changing from amorphous to anatase form (with the bandgap energy is approximately 3.2 eV) [31,32]. Hereby, under UV light irradiation, a typical photodegradation procedure possibly occurs to dye molecules, as shown in Figure 8. After photons' energy absorption, electrons will separate and move from the valence band (VB) to the conduction band (CB) of TiO_2 molecule. Therefore, at the CB, an oxidation process of dissolved O_2 in solution to form $O_2^{\bullet}$ radicals occur by photo-induced electrons.

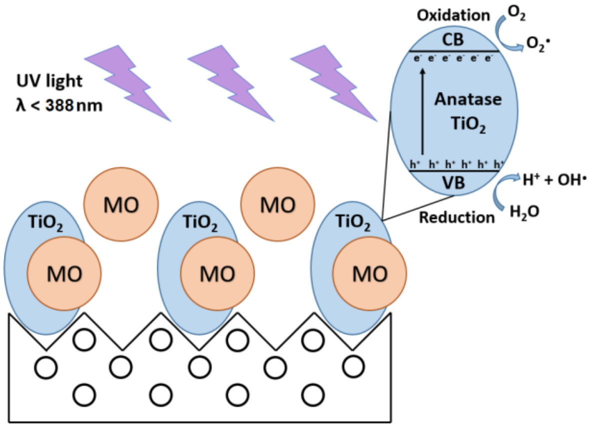

Figure 8: Photocatalytic mechanism of TiO_2 nanoparticles deposited on ceramic substrate

On the other hand, a reduction reaction of water to generate $OH^{\bullet}$ was performed at the VB of titania [33,34]. The MO molecules are adsorbed to the surface of pre-prepared catalyst, and here, oxidized by $O_2^{\bullet}$ and $OH^{\bullet}$ radicals and degraded into by-products. However, a major drawback of original anatase titania is the fast recombination of photo-induced electron and hole pairs [34,35], directly affect the photocatalytic efficiency in negative way even under UV light irradiation. With the large bandgap energy, these factors not only prolong the reaction time but also inhibit the oxidation of dye molecules by free oxidized radicals, leading to intermediates mixture but not the final desired products as CO_2, N_2, and H_2O.

Conclusion

This study proposed a method to synthesize TiO_2 thin layer on different substrates using CVD method. The morphology analytical results showed that the titania nanoparticles were successfully fabricated on the surface of glass, aluminium foil, and ceramic. The photocatalytic activities of pre-prepared materials were investigated by methyl orange treatment under UV light, indicating positive potential of the TiO_2 deposited on the ceramic substrate with 91% of MO was degraded over 270 min due to its high dye molecules adsorbability. These obtained results have opened opportunities in developing more advanced photocatalysts, including titania doped with transition metals or non-metal elements coating on abundant substrates to expand the application in dealing with practical wastewater problems.

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