

# PHOTOCATALYTIC PROPERTIES OF POLYOXOMETALATE SUPPORTED ON TITANATE NANOTUBE

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## Summary

This research studies the photocatalytic property of polyoxometalates (POMs) on titania supports by using hydrothermal technique. It is desirable to develop the photocatalytic materials into the easy recoverable form. Therefore, the water-tolerant solid POMs were prepared by combining POMs with heterogeneous supporting materials. The POM,  $H_4(SiW_{12}O_{40})$ , was incorporated with titania powders via a hydrothermal method. It was found that POM on titania support was more active than pure POMs by that it could accelerate the deterioration of methylene blue solution for 70 % of initial concentration after leaving for reaction under UV for 1 hour.

## Keywords

Titanate nanotube, Hydrothermal, polyoxometalate, photocatalysis

## Introduction

Polyoxometalates (POMs) are early well-defined transition metal–oxygen clusters with unique structural characteristics and multiple functions, which have been significantly impacting the development of materials with catalytic, photochemical, electrochromic and magnetic properties [1]. In addition, POMs are becoming of interest owing to its photocatalytic reaction to decompose organic compounds such as alcohol, aldehyde and proteins which hydrogen gas was also generated [2]. The photooxidative behaviors of POMs mainly occurred in homogeneous aqueous solution. However, to recover POMs from the process, it is desirable to develop the photocatalytic materials with easier recoverable form. Therefore, water-tolerant solid POMs were prepared by combining POMs with photoactive or inactive supporting materials (e.g., silica, mesoporous molecular sieve MCM-41 or MCM-48, NaY zeolite, activated carbons, layered double hydroxide,  $TiO_2$  in amorphous or anatase phase, and polymeric membranes) [3]. These materials can be prepared by many soft chemical synthesis techniques including sol–gel chemistry, intercalation chemistry, colloidal crystal templating, cluster chemistry and hydrothermal process [4].

In this research, POM of  $H_4(SiW_{12}O_{40})$  were loading to anatase phase of  $TiO_2$  particle via hydrothermal process. The synergistic photocatalytic properties of both POMs and titanai were expected. Here, the  $H_4(SiW_{12}O_{40})/TiO_2$

composites with different  $H_4(SiW_{12}O_{40})$  doping levels, pH levels and time for synthesis were investigated. Furthermore, their photocatalytic property was investigated via the decomposition of methylene blue.

## Experimental

The  $H_4(SiW_{12}O_{40})/TiO_2$  composites were prepared by hydrothermal method., Silicotungstic acid 26-water ( $SiO_2.12WO_3.26H_2O$ , analytical grade and purchased from KANTO CHEMICAL CO., Inc) was dissolved into 50 ml of DI water. The acidity of the mixture was adjusted to pH 1–14 by using hydrochloric acid or sodium hydroxide solution.  $TiO_2$  powder (>98%, TAYCA CORPORATION) (50 g) was added into the silicotungstic acid solution in order to obtain a series of catalysts with different mass ratio of  $H_4(SiW_{12}O_{40}) : TiO_2$  (i.e., 0.5:1.0, 1.0:1.0, 2.0:1.0). The suspension was sonicated for 6 minutes. This suspension was transferred into an autoclave and kept at 90 °C for 120 hours. After cooling the suspension to room temperature, the precipitates were filtered and washed by distilled water several times until the pH of washing water reached 7. The final product is obtained by drying at 70 °C overnight in an oven.

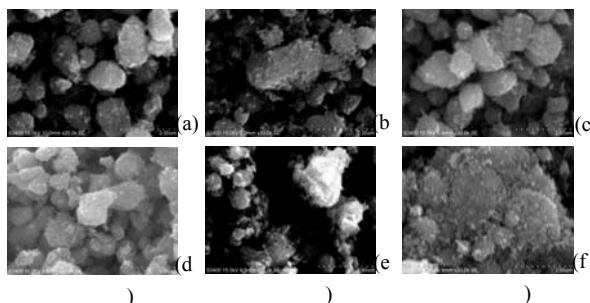
The photocatalytic activity of  $H_4(SiW_{12}O_{40})/TiO_2$  was tested by photo-decomposition of methylene blue solutions. In a typical reaction, the catalyst (0.02 g) was

added in a solution of methylene blue ( $C_0 = 5$  ppm, 20 ml) and then sonicated for 6 minutes to make the catalyst well disperses in the reaction solution. Before UV-light irradiation, the suspension was shaken in the dark for 30 minutes to ensure establishment of adsorption-desorption equilibrium between the organic molecules and the catalyst surface. The test sample was irradiated with UV-C light for 15, 30, 60, 120 and 240 minutes. This experimental unit consists of 8 quartz tube photoreactors (each with 50 ml effective volume), six of them contained 2 mg each of the interested catalyst dispersed in 20 ml of methylene blue solution and two blank reactors contained only the methylene blue solution without any catalyst. The concentration of methylene blue was analyzed by a UV-vis spectrophotometer at wavelength of 665 nm. Before the measurement, the suspended catalyst powder in the aqueous sample was separated by centrifuging at 4000 rpm for 15 min.

## Results and Discussion

### *Effect of pH on the morphology and amount of final POM on the titania supporter*

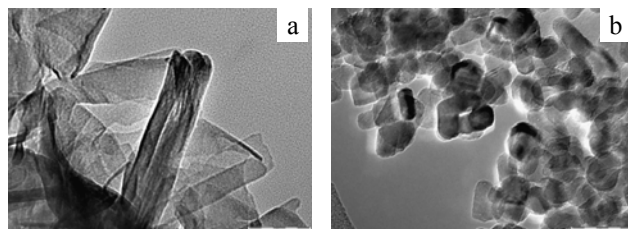
Fig. 2 shows the SEM images of samples synthesized by hydrothermal process with various pHs of solution adjusted by HCl (Figs. 4a, 4b, and 4c) or NaOH solution (Figs. 4d, 4e, and 4f). The morphology of all samples were not different; that was, with the sphere of 5 – 10 um clustering and when analyzing by EDX technique, peak of tungsten (W) would be found at position of 1–3 keV in all conditions of experiment.



**Fig. 2** SEM picture of catalyst  $H_4(SiW_{12}O_{40})/TiO_2$  different synthesis condition: (a) pH 1 (b) pH 2 (c) pH 3 (d) pH 12 (e) pH 13 (F) pH 14

The XRD patterns of sample synthesized were compared with that of pure  $TiO_2$ . It was found that sample synthesized at position  $25^\circ$ ,  $37^\circ$ ,  $48^\circ$  and  $55^\circ$  without finding characteristics of such peak in the sample synthesized under alkaline condition; this corresponded to XRD patterns of synthesis of Titania nanotube which was the result of adding NaOH into the reaction and caused the inductance to titania to form into sheet and gradually rolled to one another to be look like pipe. This could be found when analyzing by TEM technique. According to Fig. 3 (a), TEM image of sample synthesized under a strong alkaline condition (pH14) was shown, it was found that sample obtained had 2 shapes that were, some looked like film and some looked like pipe. It was expected that if

this took longer in hydrothermal, the entire film would roll and form cylinder. It was also found that 1 substance was inside such cylinder, this can be observed from the light which was permitted to pass differently and can see another layer of surface as shown in Fig. 3(a). For sample synthesized under acid condition, there would not be form into cylinder or film. It still remained in shape of small sphere as in Fig. 3(b).



**Fig. 3** TEM picture of catalyst  $H_4(SiW_{12}O_{40})/TiO_2$ . different synthesis condition : (a) Added NaOH (pH14) (b) without NaOH

### *Photocatalytic properties of POM on the titania supporter via methelene blue decomposing reaction*

The test on removal efficiency in photocatalytic deterioration of methylene blue over as-prepared catalyst showed that after leaving for reaction under UV for 1 hour, the  $H_4(SiW_{12}O_{40})/TiO_2$  could catalyze the deterioration of methylene blue at about 70 % removal efficiency. The catalyst sample can be separated from the solution by centrifugal.

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