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Anatase-3DOM Structure for Reactive Red Dye Photocatalytic Degradation

Tanya Kiatboonyarit [1]*, Thipchanok Bowornhathai [1], Ramida Rattanakam [1], Supakit Achiwawanich [1], Sutasinee Kityakarn [1]*

[1] *Department of Chemistry, Faculty of Science, University of Kasetsart, Bangkok, Thailand, 10903.*

*Corresponding author's e-mail address: fscistsn@ku.ac.th

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ABSTRACT

Photocatalysts TiO_2-powder and TiO_2-3DOM (Three-dimensionally ordered macroporous, 3DOM) were prepared by the sol-gel method and calcined at 723 K. The TiO_2 and Ce/TiO_2 photocatalysts showed only anatase phase without CeO_2 and the particle size of the Ce/TiO_2-3DOM was smaller than the TiO_2-powder. The Poly(methyl methacrylate, PMMA) was the template for TiO_2 particle-orientation as investigated by SEM. The stoichiometry of element and the molar percentage of Ce/Ti in the sample were determined by EDS. The photocatalytic degradation of reactive red dye was evaluated by UV-Vis spectroscopy. TiO_2-powder-723 showed the highest photocatalytic activity compared to others due to their morphology and particle size.

INTRODUCTION

Wastewater from textile industrial processes generally consists of surfactants, chelating reagents, pH regulators, dyes and etc. Azo dyes are commonly used in the dyeing process. The residual dyes are biologically non-degradable compounds that contaminate wastewater. In textile wastewater treatment, color removal is a primary concern. Several methods such as electrocoagulation methods, electrochemical reduction methods, electrochemical oxidation methods, indirect oxidation methods and photo-assisted methods have been applied in order to eliminate dyes from wastewater [1-3].

The photo-Fenton process is the photoassisted method where H_2O_2, iron sulfate and UV radiation are incorporated resulting in OH· radicals which are capable of reducing harmful organic compounds. For the heterogeneous photocatalysis method, TiO_2 is used in the advanced oxidation process (AOP) for the mineralization of many organic pollutants. TiO_2 is a photoactive semiconductor, and generates electron/hole pairs (e^-/h^+) when irradiated by photons with sufficient energy. The generated e^-/h^+ pairs react with water or oxygen producing OH· or O_2^{-}· radicals, which will then react with the organic compounds to break them down to CO_2 and H_2O.

The improvement of photocatalysts is essential to reach the full potential of solar radiation because most photocatalysts are excited by UV radiation which accounts for only a small percentage of sunlight. The doping or substituting of p-block, lanthanide or actinide elements into TiO_2 such as Pt-TiO_x, B-TiO_x, CeO_x-TiO_x [4,5-14] is interesting for researchers. The application of rare earth elements like Ce (Ce^{3+}/Ce^{4+}) is able to suppress the recombination of e^-/h^+ pairs and increases the efficiency of TiO_2 photocatalysts by decreasing the band-gap energy. In addition, the morphology of photocatalysts is important to modify the efficiency of photocatalysts.

In this research, TiO_2 and Ce/TiO_2 photocatalysts with different morphologies (powder and 3DOM) were prepared by the sol-gel method. The 3DOM formation of TiO_2 was prepared using PMMA as a template. The effect of Ce addition and the morphology of TiO_2 were investigated. The photocatalytic degradation of reactive red dye (RR) was evaluated by UV-Vis spectroscopy.

METHODOLOGY

Titanium (IV) isopropoxide, ethanol and cerium (III) nitrate hexahydrate were used for sol-gel preparation. The gelation of samples was at 323 K for 24 h and heated up to 383 K for 24 h. The dry powder was calcined at 723 K and 873 K under the mixing of N_2 and O_2 (70:30), (labeled, respectively, as TiO_2-powder-723 and TiO_2-powder-823). The sample with Ce was prepared by adding 2% molar ratio of Ce to Ti into the mixture (labeled as 2%Ce/TiO_2-powder-723).

The 3DOM samples were prepared in the same manner. TiO_2-powder and the mixture of Ce/TiO_2 was prepared by the addition of cerium (III) nitrate solution with 2% molar ratio of Ce to Ti. The mixture was dropped onto the PMMA, kept at room temperature for 7 days, dried at 353 K for 12 h and calcined at 723 K under the mixing of N_2 and O_2 (70:30) and the samples were labeled as TiO_2-3DOM, and 2%Ce/TiO_2-3DOM.

The structure of all the samples was characterized by X-ray diffraction spectrometer (XRD, D8 Advance Bruker). The Cu K_a x-ray is generated by an x-ray tube operated at 40 kV and 30 mA. The XRD patterns were recorded in the range of 10-80 degree. The XRD patterns were indexed by comparison with the JCPDS file. The morphology of the samples and the chemical composition in the prepared samples were investigated by Scanning Electron Microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDS), Quanta 450FEI. The samples were sputtered with Au and imaged at 10k and 30k magnification. The photocatalytic dye degradation by TiO_2 catalysts was evaluated using UV-Vis spectroscopy. The suspended TiO_2 photocatalysts in the 12 ppm RR dye solution were irradiated by UV source (B-100YP, UVP lamp). The adsorption at 541 nm was used to determine the photocatalytic degradation of RR dye.

RESULTS AND DISCUSSION

The XRD patterns of all samples in Figure 1 showed the pattern of TiO_2 anatase (PDF No. 01-075-2545) without other TiO_2 phases and CeO_2 (PDF No. 01-078-3080). The TiO_2-powder-823 showed highly sharp intensity indicating the high crystallinity of the TiO_2 anatase. The TiO_2-commercial, TiO_2-powder-723 and 2%Ce/TiO_2-powder-723 showed broad XRD peaks indicating the small crystalline size of the TiO_2 anatase. The TiO_2-3DOM-723 and 2%Ce/TiO_2-3DOM-723 showed boarder peaks and lower intensity of anatase phase due to the small crystalline size of TiO_2 anatase forming in 3DOM structure. The addition of Ce in the TiO_2 structure did not deform the anatase phase, however it suppressed the growing of TiO_2 crystal, resulting in the small crystalline size. The XRD peak intensity was affected by Ce addition. The high percentage of Ce showed a low XRD intensity indicating that the cerium ions dissolved in anatase phase [12]. This means that the Ce addition percentage represented the cerium ion solubility in anatase.

The morphology and chemical composition of TiO_2 photocatalysts were evaluated by SEM- EDS (Figure 2 and Table1). The SEM

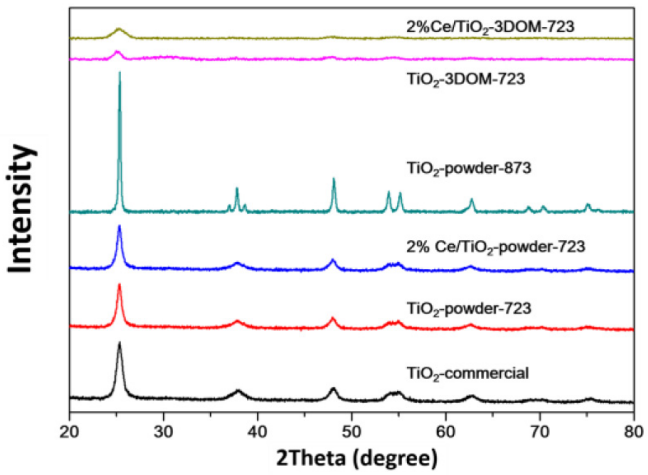

Figure 1 XRD patterns of TiO_2-commercial, TiO_2-powder-723, 2%Ce/TiO_2-powder-723, TiO_2-powder-873, TiO_2-3DOM-723 and 2%Ce/TiO_2-3DOM-723.

images presented the small particle size of TiO_2-commercial and TiO_2-powder-723 which correspond to the board XRD peaks (Figure 2 (a) – (b)). 2%Ce/TiO_2-powder-723 showed smaller, compact particles compared to the other powders (Figure 2 (c)). The percentage molar ratio of Ce to Ti in 2%Ce/TiO_2-powder-723 was 2.2 %.

The particles of PMMA were spherical with size of approximately 0.25 mm, Figure 2 (d). PMMA was used as the template for 3DOM formation for TiO_2 prepared by the sol-gel method. After the mixture of TiO_2 precursor was dropped onto the surface of PMMA and the coated TiO_2 precursor decomposed at 723 K, TiO_2 anatase with 3DOM structure and small particles TiO_2 anatase formed on the 3DOM structure as shown in Figure 2 (e) – (f).

The particle sizes of TiO_2-3DOM-723 and 2%Ce/TiO_2-3DOM-723 were small and their morphology was more regular

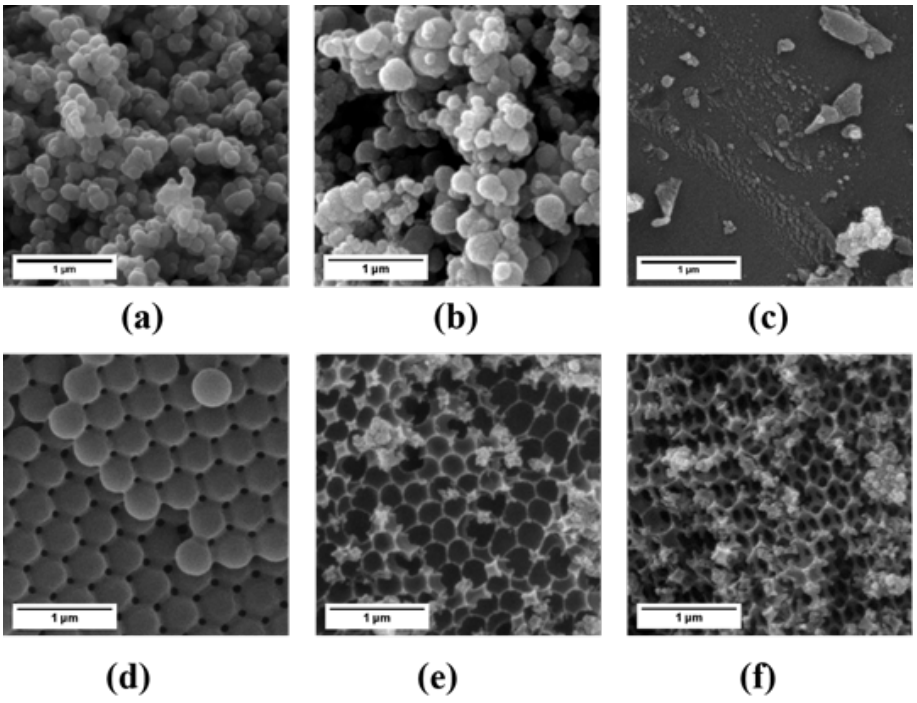

Figure 2 SEM images of (a) TiO_2-commercial, (b) TiO_2-powder-723, (c) 2%Ce/TiO_2-powder-723, (d) PMMA, (e) TiO_2-3DOM-723 and (f) 2%Ce/TiO_2-3DOM-723. The magnification of all sample was 30k and scale bar was 1 µm.

Table 1 Chemical composition of photocatalysts measured by EDS.

Photocatalysts	Elemental (weight %)			Elemental (atomic %)		
	Ti	Ce	O	Ti	Ce	O
TiO_2-commercial	56.92		43.08	30.62		69.38
TiO_2-powder-723	57.34		42.66	30.98		69.02
2%Ce/TiO_2-powder-723	54.70	3.65	41.65	30.28	0.69	69.03
TiO_2-3DOM-723	61.63		38.37	34.91		65.09
2%Ce/TiO_2-3DOM-723	56.12	5.25	38.63	32.33	1.03	66.64

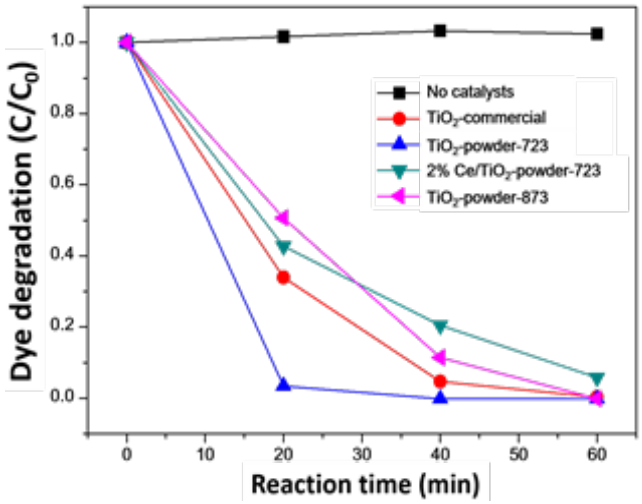

Figure 3 Photocatalytic activity of non-catalysts, TiO_2-commercial, TiO_2-powder-723, 2%Ce/TiO_2-powder-723, TiO_2-powder-873.

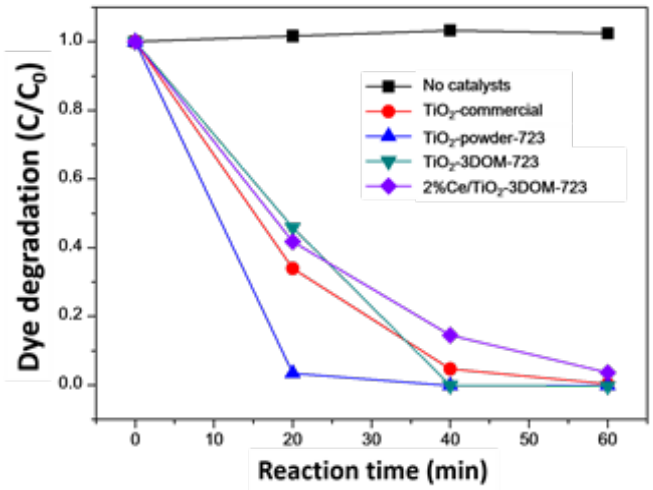

Figure 4 Photocatalytic activity of non-catalysts, TiO_2-commercial, TiO_2-powder-723, TiO_2-3DOM-723, 2%Ce/TiO_2-3DOM-723.

than the 2%Ce/TiO_2-powder-723. The SEM image of TiO_2-3DOM showed agglomeration of TiO_2 on the 3DOM structure. The number of agglomerated particles increased with the addition of Ce resulting in deformation of 3DOM structure as observed in Figure 2 (f). The percentage molar ratio of Ce to Ti in 2%Ce/TiO_2-3DOM was 3.1%.

The photocatalytic degradation of reactive red dye (RR) by TiO_2-anatase under irradiation was investigated by sampling 2 mL of solution every 20 min; the results are shown in Figure 3 and Figure 4. The RR dye did not degrade under irradiation without catalysts. The TiO_2-powder-723 showed the highest dye photodegradation due to its small regular particles. The TiO_2-powder-873 showed low catalytic activity compared to the TiO_2-powder-723 despite having the highest crystallinity of anatase phase. It is well known that the agglomeration of TiO_2 particles take place at high calcination temperature, resulting in large particle size and decreased surface area of catalysts. The photocatalytic activity of Ce added into TiO_2 was not significantly different from the TiO_2-powder-873. However, the photocatalytic activity of Ce/TiO_2 was lower than the TiO_2-powder-723 and TiO_2-commercial. This was due to the small compact particles of Ce/TiO_2-powder-723, which lead to decreased surface area of catalysts and lower catalytic activity.

To study the effect of morphology of TiO_2, photocatalysts with different morphology were used. The photodegradation of RR by TiO_2-3DOM-723 and 2%Ce/TiO_2-3DOM-723 showed similar photocatalytic activity that was lower than the TiO_2-powder-723 due to smaller photocatalysts particle sizes.

In further research, the preparation of 3DOM at high calcination temperature will be considered and the photocatalytic activity of high temperature calcined 3DOM will be investigated. The decrease in cerium percentage will be studied in order to evaluate the threshold of cerium present in the TiO_2 structure, which can enhance the photocatalytic activity of TiO_2.

CONCLUSION

The anatase-3DOM was prepared by sol-gel method and PMMA was used as a template for 3DOM formation. The addition of Ce suppressed the growing of TiO_2 particles, resulting in small particles of Ce/TiO_2 for both powder and 3DOM. The TiO_2-powder-723 showed the highest photocatalytic activity due to its small regular particles. The addition of Ce into TiO_2 did not improve the photocatalytic activity of TiO_2 catalysts. The anatase 3DOM structure exhibited low photocatalytic activity due to the smaller particle size of the catalyst and lower degree of TiO_2 crystallinity. Increased calcination temperature was considered to enhance the photocatalytic activity of TiO_2-3DOM.

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