Applied Catalysis A: General 453 (2013) 80–91

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Preparation and characterization of TiO_2 coated with a thin carbon layer for enhanced photocatalytic activity under fluorescent lamp and solar light irradiations

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ARTICLE INFO

Article history:
Received 1 June 2012
Received in revised form
22 November 2012
Accepted 28 November 2012
Available online 13 December 2012

Keywords:
Carbon coated TiO_2
Epoxidized natural rubber
Reactive red 4 dyes
Ethylene blue and phenol

ABSTRACT

Carbon (C) coated TiO_2 with C content between 0.20% and 1.09% were prepared by calcination of various mixtures of TiO_2 and epoxidized natural rubber (ENR-50) under N_2 atmosphere between 470 °C and 620 °C. The optimum calcination temperature and C content was 560 °C and 0.25 ± 0.01%, respectively with the estimated C coating thickness of 0.68 nm. The process did not change its BET surface area and induce any phase transformation. Photocatalytic activity of C coated TiO_2 was better than pristine TiO_2 for the degradation of anionic reactive red 4 (RR4) dye by more than 3 times, phenol by 1.1 times and cationic methylene blue (MB) by 1.5 times under a 45-W household fluorescent lamp irradiation while under solar irradiation, its photocatalytic activity with respect to pristine TiO_2 improved by 5.5, 3.5 and 2 times, respectively. Coating of more than 1% C on TiO_2 changed its photocatalytic activity either at par or less than that of the pristine TiO_2. The observed photocatalytic improvement was due to the significant decrease in the electron–hole recombination process as observed for the optimum C coated sample.

1. Introduction

Wastewater from industrial discharges or agrochemical products such as dyes, pesticides etc. contain chemicals that are non-biodegradable and harmful to the environment [1]. Titanium dioxide (TiO_2) photocatalysis is among the most promising methods for application in wastewater detoxification since it can lead to complete mineralization of pollutants to CO_2, water and mineral acids [2]. Unfortunately, TiO_2 is less effective under visible light region [3]. Many efforts have been done to improve the photocatalytic efficiency of TiO_2. One of the promising methods involves doping of TiO_2 with elements such as N [4,5], S [6] and C [7]. Combination of TiO_2 with C had been reported to give favorable results [7–16]. There are at least four ways of combining TiO_2 with C that had been tested in the literatures namely (i) direct mixing of TiO_2 with activated carbon either prior to treatment or within the reactors [10], (ii) TiO_2 coated activated carbon [8,9] (iii) carbon (C) doped TiO_2 [17,18] and (iv) carbon (C) coated TiO_2 [11,12]. The first two modes of combinations were reported to produce synergistic effects with improved rate of pollutants removal as compared to the pristine TiO_2. This is due to the role of carbon that acts as accumulation sites for pollutants through adsorption which is then eventually transferred to the surface of TiO_2 for photodegradation [14]. The latter two modes of combination seem similar but actually differ from one another. For the C doped TiO_2, the C dopant has been described either as an anion that replaces oxygen substitutionally in the lattice [11–14] or as a cation that occupies an interstitial lattice site [15,16,19,20]. Generally C doped TiO_2 is yellow in color with C content less than 1% while C coated TiO_2 contained C above 2% and black in color [21]. For C coated TiO_2, a layer of C covers the TiO_2 particles whereby the contaminant molecules have to be adsorbed into the C layer and then diffuse through the C layer to reach the surface of the photocatalyst TiO_2 and be decomposed under light irradiation. Several advantages of C coated TiO_2 had been listed in the literatures such as suppression of phase transformation from anatase to rutile at high temperatures, improvement of anatase crystalline structure resulting in higher photocatalytic activity, improved adsorption of pollutants [22] and better rate of sedimentation of the photocatalyst particles [16].

It is obvious that the thickness of the C coating is critical. A thicker C layer gives higher adsorptivity, but at the same time makes the intensity of UV rays arriving at the surface of the anatase photocatalyst weaker, and the apparent diffusion rate of contaminant molecules may also be reduced. On the other hand, too thin a coating layer would reduce adsorptivity of the pollutant into the system. Therefore it is not surprising that in a number of cases, prepared C coated TiO_2 had poorer photocatalytic

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http://dx.doi.org/10.1016/j.apcata.2012.11.047

activities compared to the pristine TiO_2 [15,16,19,20] which could be due to the reduced intensity of light reaching the TiO_2 surface. Therefore in order to have high rate constants in the removal of pollutants, a critical balance between these different effects of C layers is required. Since the light intensity reaching the surface of TiO_2 particles would decrease greatly due to the absorption and scattering of light by the C layer, a thin C layer should be beneficial to the transmission of charge carriers and the improvement in the photocatalytic properties of the coated catalyst [11].

There are various methods of preparations of C coated TiO_2. These involved hydrolysis of organic titanium complexes such as titanium tetraisopropoxide on polymers followed by calcinations at high temperatures exceeding 400 °C [24]. Successful synthesis was also obtained via direct mechanical mixing of TiO_2 particles with precursors such as polyethylene glycol (PEG) and calcinations at high temperatures exceeding 700 °C [11]. Other works involved mixing of TiO_2 with polyvinyl alcohol (PVA) at 1100 °C under inert atmosphere [12] or carbonization of TiO_2 in the presence of organic vapor supplied by hexane or ethanol at high temperatures [15]. Other approaches involved controlled oxidation of C containing titanium compounds such as TiC [13] and sol–gel auto combination of titanium isopropoxide with citric acid and ethylene glycol [24]. In most cases, the final C content exceeds 1.4% [19,20,23] while low C content just slightly below 1% were obtained at temperatures between 400 °C and 500 °C using either n-hexane or ethanol vapor as the C precursors [15,16]. However, the preparation of a C coated TiO_2 with low C content below 0.5% is rarely reported in the literatures.

The objective of this work was to produce a C coating method that would be highly reproducible and predictable in terms of the C contents of the products. The second objective was to produce a thin C coated TiO_2 that would consistently perform better than the pristine TiO_2 in the photocatalytic degradation of various types of pollutants. The final objective was to assess the effectiveness of the synthesized C coated TiO_2 against several types of organic pollutants under the irradiation of benevolent low energy light sources in the form of a compact 45-W household fluorescent lamp and solar light. For these purposes, a natural biopolymer in the form of epoxidized natural rubber (ENR-50) was selected as the C precursor since C coating of TiO_2 via a natural biopolymer-based C precursor has not yet been exploited within the literatures.

2. Experimental

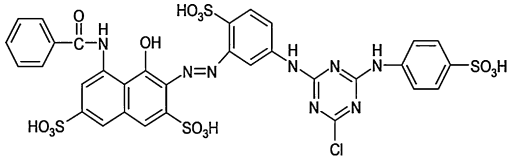
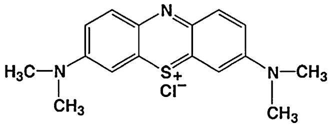
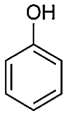
2.1. Material

A 99% TiO_2 anatase powder (Sigma–Aldrich) was used as the starting material in the preparation of C coated TiO_2. Epoxidized natural rubber (ENR-50, Kumpulan Guthrie Sdn. Bhd.) dissolved in toluene to make an 11.4% solution (w/v) was used as the C precursor. Acetone solvent (R&M chemicals) was used for dilution of sample mixtures for the homogenization process via ultra-sonication. Reactive Red 4 (RR4) or otherwise commonly known as Cibacron Brilliant Red (Color Index Number: 18,105, with 50% dye content) was provided by Aldrich Chemical, Methylene Blue dye (~98%, Color Index Number: 52,015,) was purchased from Unilab and Phenol (99.5%) was obtained from Scharlau. Table 1 summarized chemical structure, molecular weight and λ_{max} for RR4, MB and phenol respectively. Ultra pure water (18.2 MΩ cm^{-1}) was used to prepare all solutions in this work.

2.2. Preparation of C coated TiO_2 samples

C coated TiO_2 samples were prepared by calcinations process using a custom made reactor which was placed in a muffle furnace. The reactor was either made from pyrex glass or stainless steel depending on the temperatures used. The overall experimental setup is shown in Fig. 1. For a typical preparation, a series of 12 g TiO_2 powder were suspended in 60 mL of acetone and mixed with various amount of 11.4% solution of ENR-50 in toluene (0.5, 1, 3, 5 and 8 g), respectively. The solution mixtures were then sonicated for 8 h at 50 Hz using Crest Ultrasonicator. After drying off the solvent in an oven at 100 °C, the ENR coated TiO_2 samples were calcined under a series of temperatures ranging from 470 °C to 620 °C under N_2 flow for 5 h. Each temperature setting of the furnace was verified using a Cole-Palmer type K thermometer (EW-90225-10). The samples were then cooled down to room temperature again under N_2 flow. Finally the products were cleaned by sonicating them in ultrapure water and eventually centrifuged to isolate the fine particles giving

Table 1
Summary of organic pollutants.

Chemical structure & organic pollutant	Properties		
	Chemical formula	Molecular weight (g mol^{-1})	Absorption max (nm)
 Reactive red 4 dye (RR4)	$C_{32}H_{23}ClN_8O_{14}S_4$	995.23 g	517 nm
 Methylene blue dye (MB)	$C_{16}H_{18}ClN_3S{\cdot}2H_2O$	319.85	661 nm
 Phenol	C_6H_6O	94.11	270 nm