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One-pot solvothermal synthesis of dual-phase titanate/titania Nanoparticles and their adsorption and photocatalytic Performances

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ABSTRACT

Dual phase titanate/titania nanoparticles undergo phase transformation gradually with the increase of solvothermal synthesis temperature from 100 °C to 200 °C, and eventually are fully transformed into anatase TiO_2. The crystal structure change results in the changes of optical absorption, sensitizer/dopant formation and surface area of the materials which finally affect the overall dye removal ability. Reactions under dark and light have been conducted to distinguish the contributions of surface adsorption from photocatalytic degradation. The sample synthesized at 160 °C (S160) shows the best performances for both adsorption under dark and photocatalytic degradation of methylene blue (MB) under visible light irradiation. The adsorption mechanism for S160 is determined as monolayer adsorption based on the adsorption isotherm test under dark condition, and an impressive adsorption capacity of 162.19 mg/g is achieved. For the photocatalytic application, this sample at 0.1 g/L loading is also able to degrade 20 ppm MB within 6 hours under the visible light (> 420 nm) condition.

1. Introduction

Environmental contamination is one of the great challenges we are facing nowadays [1–4]. Photocatalysis is a promising technology making use of solar energy to break down toxic organic pollutants into neutral CO_2 and H_2O, which doesn't require extra chemical and energy input [5,6]. An ideal photocatalyst needs to fulfill several criteria [7–13]: (1) effective absorption of solar energy by extending its absorption range to visible light; (2) efficient charge separation to prevent photogenerated electron-hole recombination; (3) high surface area allowing easy adsorption of reactants and providing more reactive sites; (4) chemically stable under light irradiation, robust against photo-corrosion and low in toxicity. To date, the full potential of photocatalysis in practical applications has not been reached as these challenges have yet to be overcome. Most stable photocatalytic materials studied so far such as TiO_2 and $SrTiO_3$, are capable of absorbing UV light that only covers 5% of solar spectrum [14], while some visible light active photocatalysts, such as CdS, undergo photo-corrosion during irradiation [15–18]. In addition, these materials often have poor surface adsorption for organic species. Much work has been focused on extending the light absorption of TiO_2 related materials into the visible light range but the visible light adsorption and photocatalytic performance is not so ideal [19].

Titanates are a new family of photocatalytic materials that were introduced in the late 1990s and the research in this work only grew active in the recent years [16,20–22]. They combine the properties of conventional TiO_2 with properties of layered materials that make them favorable for ion exchange [23,24]. A unique property of titanates is their strong physical adsorption capacity. Nanostructured titanates possess large surface areas and can adsorb organic species such as dyes on their surfaces [25–28]. Good interfacial contact between photocatalyst and adsorbed species enhances electron-hole interaction and reduces the possibility of charge recombination. Despite these advantages, titanates are responsive only to UV light as they have been reported to possess wide band-gaps between 3.4 to 3.8 eV [16,29]. In addition, the synthesis of such materials often involves complex processes which require intense acidic/alkaline conditions and high temperatures [21,22,30,31].

We have previously reported a unique dual phase photocatalyst that displays excellent degradation of methylene blue and phenol under visible light [32,33]. The material comprises of a hydrated layered titanate and anatase TiO_2 with visible light sensitivity due to nitrogen doping and surface sensitization. However, little was known about the influence of synthesis condition on the phase transformation, crystallinity and performance of this class of mixed phase TiO_2-based materials. Particularly, there has been no systematic investigation on the differentiation between surface

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adsorption and photocatalytic degradation. In this paper, we explore the variation of synthesis temperature and its influence on crystal structure, optical absorption, dopant formation and the specific surface area. In particular, this temperature study allows an observation of phase transition across the samples and its effect on overall photocatalytic activity. Importantly, reactions under dark and light were conducted to distinguish the contributions of surface adsorption from light degradation. The adsorption isotherm and kinetics of the best performing material were investigated to understand the adsorption mechanism. The visible light photocatalytic degradation kinetics was also studied.

2. Experimental

2.1. Sample preparation

Chemicals and materials used for synthesis were titanium isopropoxide [Ti $(OC_3H_7)_4$, 99.5%, Aldrich], ethanol [technical grade, 95%], acetylacetone [$C_5H_8O_2$, 99.5%, Fluka], triethylamine [$N(CH_2CH_3)_3$, 99.5%, Aldrich] and deionized water. Ethanol and acetylacetone (ACAC) were mixed in molar proportion of 20: 1. Next, titanium isopropoxide (TI) and triethylamine (TE) were added simultaneously dropwise in molar ratio of 1:4. Lastly, 3 mol of deionized water were added and the mixture was allowed to stir for 30 minutes. Following this, 50 mL of this clear yellow solution was measured into a 125 mL capacity stainless steel autoclave for hydrothermal reaction. The autoclave was then heated in an ambient oven for duration of 3 hours at temperatures varying from 100 to 200 °C. The as-prepared samples were labeled as SX, where X denotes the synthesis temperature. The autoclave was cooled under ambient conditions. Thereafter, the gel was dried in an oven at 80 °C. The extracted powder was cleaned repeatedly with ethanol and deionized water via centrifuging process to remove traces of organic waste. Lastly, the powder was re-dried in ambient oven at 80 °C and collected.

2.2. Materials characterization

X-ray diffraction was used to study the crystal structure and phase transition across the increasing synthesis temperatures. The XRD patterns of the powders were recorded using a Shimadzu LabX-6000 diffractometer of CuKα radiation (λ=0.15418 nm) equipped with a secondary graphite monochromator. A step size of 0.02° over 2θ ranging from 5 to 80° was used with scanning rate set at 0.2° per minute. Optical absorption of the bulk powders were measured on Perkin Elmer Lambda 900 UV-Visible spectrometer in diffuse reflectance spectroscopy mode over the spectral range of 200–800 nm. The nature of dopant species and bond integrity across the samples were analyzed using X- ray photoelectron spectroscopy, XPS (Kratos Axis ULTRA). Specific surface area and pore size was determined using a Micromeritics ASAP 2020 surface analyzer based on the Brunauer Emmett Teller, BET theory. The samples were outgassed under vacuum and heated to 100 °C. JEOL 2100-F transmission electron microscopy (TEM) with a field emission gun was used to observe the morphology of the synthesized samples. The accelerating voltage was 200 kV. The synthesized powders were dispersed in ethanol and ultrasonicated for 5 min. The dispersion was then dropped onto a holey-carbon-copper grid for imaging.

2.3. Adsorption and photocatalytic degradation of methylene blue under visible light

Methylene blue (MB) dye was chosen as primary candidate for photocatalytic degradation activity of the prepared powders in order to study both adsorption and degradation effects. Solutions of the dye were prepared by mixing with deionized water at 20 ppm concentration. 10 mg of photocatalyst powder was dispersed in 100 mL of each MB solution. An adsorption isotherm test was carried out by varying concentrations of methylene blue from 5 to 50 ppm. For each test, 10 mg of adsorbent was added to 100 mL of MB solution. The equilibrium concentration was measured after adsorption saturation of each test was reached.

Control experiments were performed for mixtures in the dark as well as blank MB solutions under light irradiation. In addition, reference photocatalyst powder Degussa P25 TiO_2 was also tested as a platform for comparison of photocatalytic activity. The irradiation source was a 450 W Newport Xenon Arc lamp with spectral range from 200–2500 nm. A short wave light filter was used to cut off the transmission below 420 nm. A cooling water filter was also attached to block IR-rays and prevent excessive heating. MB suspension was placed directly under the light source so that the irradiation was uniform over the surface of the solution. During the experiment, the suspension was kept under stirring to ensure an aerobic environment for complete dye mineralization reaction [34]. Samples were taken at regular time intervals and underwent centrifuging. The spectral intensity measurements of the degraded dye were performed on a Shimadzu 2500 UV- Visible spectrometer.

3. Results and discussion

3.1. XRD and TEM analyses

Fig. 1 presents the XRD patterns of the samples synthesized with varying hydrothermal temperatures from 100 to 200 °C. Across curves (a) to (c), broad peaks with relative low intensities appear. Samples S100, S130 and S160 display low angle diffraction at 8.56°, 17.01° and 26.39°. These peaks correspond to a layered hydrogen titanate $H_2Ti_3O_7 \cdot xH_2O$. We shared in previous report about the crystal structure of this titanate in detail [33]. In that report, S160 was found to be a dual phase structure containing titanate and anatase phase in approximately 50:50 weight ratio. It is believed that S100 and S130 possessed dual phases where titanate existed in greater proportions at lower temperatures albeit having poorer crystallinity. As the hydrothermal temperature increases, the peaks grow sharper; an indication of improving crystallinity and nano-particle growth. Additional peaks at 37.78°, 48.77° and 62.86° also emerged in samples S130 (curve b) and S160 (curve c). Curve (d) of Fig. 1 shows the crystal structure underwent

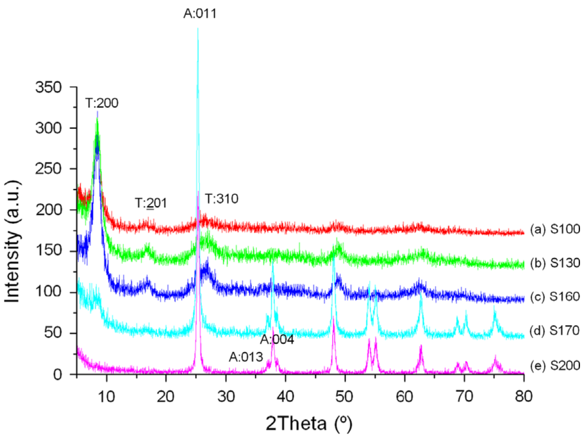

Fig. 1. X-Ray diffraction patterns of samples treated at various temperatures (a) S100, (b) S130, (c) S160, (d) S170 and (e) S200. T denotes titanate and A denotes anatase phases.