Efficient removal of cationic dyes from water by a combined adsorption-photocatalysis process using platinum-doped titanate nanomaterials

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ABSTRACT

In this study, two types of titanate nanomaterials (TNMs) including titanate nanosheets (TNS) and titanate nanotubes (TNT) were hydrothermally prepared by controlling reaction times, and then the platinum (Pt)-doped TNMs were fabricated. The photocatalytic performance of as-prepared materials was compared with that of the commercially available TiO_2 P25. It was revealed that changing the morphology of TiO_2 particles could enhance their adsorption ability and photocatalytic activity for the removal of cationic dyes from water. In particular, all prepared materials displayed greater removal of methylene blue than of P25 through the synergy of adsorption and photocatalysis; however, such an effect was not so pronounced for anionic dyes. For cationic dyes (methylene blue and rhodamine B) and anionic dyes (methyl orange and naphthol blue–black), TNT presented higher photocatalytic activity than TNS. The TNMs, after Pt doping, significantly enhanced photocatalytic activity compared to the pristine ones. Remarkably, 0.5% by weight Pt-doped TNS achieved 100% removal of methylene blue and rhodamine B after 120 min and 140 min of UV irradiation, respectively, outperforming P25, although Pt-doped TNMs showed lower photocatalytic performance than P25 for anionic dyes.

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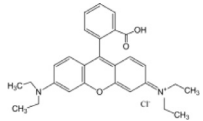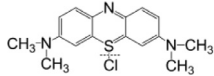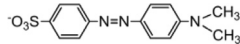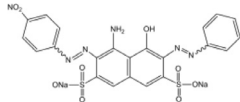
1. Introduction

In recent years, industrial development has caused many environmental problems. The treatment and reuse of wastewater have become an important issue of great interest to researchers. Commercial synthetic dyes are used as raw materials of different manufacturing processes such as textiles, paper, plastics, leather, foodstuffs, and pharmaceuticals [1–4]. Within these industries, dye production and textile manufacturing processes can discharge a large number of effluents containing toxic colored dyestuffs into aquatic systems. Worldwide, total dye production exceeds 700,000 tons annually and about 20% of this is released into waterways [5,6]. Most synthetic dyes are highly colored, toxic and carcinogenic, directly impacting human health and aquatic ecosystems [7–9]. A complete treatment of dye effluents before discharge is urgently needed.

The removal and mineralization of dyes from water have attracted considerable attention. However, until now, it has been hard to thoroughly treat discharged water bodies containing dyestuffs with traditional methods such as anaerobic/aerobic treatments, electro-coagulation, filtration, and adsorption which merely change the forms of the contamination [6,10–13]. Among the advanced methods used to reduce organic pollution, photocatalysis has been considered to be promising, one which might be achieved not only in decolorization but also in mineralization of dyes [14–19]. TiO_2 and TiO_2-based materials have been widely used in photocatalytic degradation of environmental contamination by their benefits such as cost-effectiveness, chemical stability, nontoxicity, and environmentally friendly features [20–23]. However, photocatalytic water purification using benchmark TiO_2 is limited in practical applications [24]. One restriction is the wide bandgap of TiO_2 and short lifetime of photo-induced electron-hole pairs. Another is that photocatalysis is suitable for the treatment of dyes at low concentrations only; that is, it often fails to treat high-strength solutions [25]. It is hence important to synthesize materials with the dual functions of high adsorption ability and good photocatalytic activity [13,17,26]. This combination has shown to be a viable

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Table 1
Characteristics of the dyes used in this study.

Dye	Molecular formula	Molecular weight (Da)	Class (charge)	λ_{max} (nm)	Acidity constant, pK_a	Molecular structure
RhB	$C_{28}H_{31}ClN_2O_3$	479.0	Cationic (+1)	551	3.7 [37]	
MB	$C_{16}H_{18}ClN_3S$	319.9	Cationic (+1)	665	3.8 [38]	
MO	$C_{14}H_{14}N_3NaO_3S$	327.33	Anionic (−1)	464	3.4 [39]	
NBB	$C_{22}H_{14}N_6Na_2O_9S_2$	616.5	Anionic (−2)	618	4.5 [40]	

solution [27,28]. Adsorption is applied to enrich dyes from a large volume of water body and the adsorbed dyes are then removed by photocatalysis. Consequently, the combination of adsorption and photocatalysis processes has been shown to enhance pollutant removal.

Titanate nanomaterials (TNMs) fabricated based on precursor TiO_2 P25 with various morphologies such as titanate nanosheets (TNS), titanate nanotubes (TNT), titanate nanorods, and titanate nanofibers have been used previously and proved the synergistic effect of adsorption ability and photocatalytic activity on the degradation of several dyes [20,29–32]. However, the titanate nanomaterials still exhibit the drawbacks as other TiO_2 nanoparticles. To improve photocatalytic activity of TNMs via enhancing separation of electron-hole pairs, doping them with noble metals such as Pt, Ag, and Au is commonly used [31,33–36]. To the best of our knowledge, effects of dye structures and TNMs morphologies on photocatalytic removal of dyes have seldom been explored. Simultaneous photodegradation of both cationic and anionic dyes using TNMs is rarely reported. In addition, most research therefore far has focused on solving single dye solutions with very little attention having been paid to dye mixtures in photocatalysis. The effect of interaction between two dyes in the solution on photocatalytic mechanisms has not been elucidated systematically. In this work, four model dyes with different structures and charges were used for evaluating photocatalytic activity of TNMs, before and after Pt doping, for single and binary dye solutions.

2. Materials and methods

2.1. Materials

Titanium dioxide (TiO_2) Degussa P25, hydrogen hexachloroplatinate ($H_2PtCl_6 \cdot xH_2O$, 99.8%), and sodium hydroxide (NaOH, 98%) were obtained from Sigma-Aldrich Co. (St. Louis, MI, USA). The characteristics of the four dyes (Table 1) used in this study, including methylene blue (MB), naphthol blue black (NBB), methyl orange (MO), and rhodamine B (RhB) were also provided by Sigma-Aldrich Co. All chemicals were analytical reagent grade and were utilized without further purification.

2.2. Materials preparation

2.2.1. Preparation of titanate nanomaterials (TNMs)

TNMs with different morphologies were prepared by a facile hydrothermal process for various reaction times as described previously [41]. In brief, 1.6 g of TiO_2 (P25) was dispersed in 100 mL of 10 mol/L NaOH solution under vigorous stirring and sonication for 30 min. Afterward, the suspension was transferred into a Teflon-lined stainless-steel autoclave and kept in an oven at 130 °C for 3 and 24 h. Pure TNS and TNT were obtained after 3- and 24-h hydrothermal processing, respectively. After the reaction was completed, the autoclave was cooled to ambient temperature, and the solids were then filtered and washed by 0.1 mol/L HCl and distilled several times until the pH reached around 6.5–7.5. The resulting white powders were dried in a vacuum oven at 70 °C for 24 h.

2.2.2. Preparation of Pt-doped TNMs

The Pt-doped TNS and TNT catalysts were prepared by photodeposition as follows: 3.0 g of the pristine TNMs was introduced to 450 mL of 33.3 vol% ethanol solution; to this mixture, an appropriate volume of H_2PtCl_6 aqueous solution (0.1 mmol/L) was then added to obtain a nominal Pt loading with a weight percent of 0.5. They were illuminated under an ultraviolet lamp and stirred for 3 h. Light intensity on the pristine surface materials was approximately 6.5 mW/cm^2 for Pt photodeposition. The catalysts were subsequently separated by centrifugation and washed several times by distilled water. The resulting powders were dried in an oven at 70 °C for 24 h to remove moisture. Photoreduction of Pt^{+4} ions to platinum nanoparticles (Pt^0) occurred and then highly dispersed Pt particles were deposited onto the TNS and TNT surfaces. The as-prepared catalysts were denoted as Pt$_{0.5}$-TNS and Pt$_{0.5}$-TNT, corresponding to the sample containing 0.5 wt% Pt.

2.3. Characterization of structure and morphology of as-prepared materials

Transmission electron microscope (TEM, JEOL JEM1230, Tokyo, Japan) was used for the morphological investigation of all samples. The X-ray powder diffraction (XRD) measurements were performed by a diffractometer (Bruker D2 PHASER, Germany) with a CuKα radiation source. Fourier transform infrared spectroscopy (FT-IR) was carried out on a Bruker Tensor 27 IR spectrophotometer (Germany). The XPS analysis was conducted on a Fison VG ESCA210 spectrometer with Mg-Kα radiation. Diffuse reflectance spectra of as-prepared samples were recorded using a Jasco V650 spectrophotometer (Japan). Zeta potentials of as-prepared materials and dye solutions were determined using a zeta potential analyzer (Zetasizer Nano-ZS, UK). The solution pH was determined by a digital pH meter (Horiba F-23, Japan). The Brunauer-Emmett-Teller (BET) surface area and pore size distribution based on the Barret-Joyner-Halender (BJH) theory of the sample was calculated from an N_2 adsorption-desorption isotherm at −196 °C, performed