



Facile template free method for textural property modulation that enhances adsorption and photocatalytic activity of aperiodic titania supported silica materials

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ABSTRACT

A series of aperiodic titania–silica photocatalysts were prepared in ethanolic solutions of co-solvents such as ethyl acetate (EtOAc), acetonitrile (ACN), acetone (ACT), and *N,N'*-dimethylformamide (DMF) using a combination of sol–gel chemistry and mild hydrothermal conditions. Extensive structural characterization emerged critical in demonstrating that the incorporation of such polar aprotic solvents is a viable approach for the enhancement and modulation of textural properties such as surface areas and pore sizes without the use of expensive templates. These studies revealed that the dark adsorption capacities of Rhodamine B (RhB) dye were dependent on the pore volume, and had minimal role on the photocatalytic degradation of the dye molecules. However, photocatalysts with large pore diameters exhibited improved initial degradation rates, suggesting that the sizes of the pores through which organics can diffuse in and out of the mesostructure are vital for their effective photocatalytic degradation under visible light irradiation. This work provides an insight into the use of facile preparation methods for the design of photocatalysts of desired porosities that are optimal for application in areas such as persistent organic pollutant remediation in waste water management.

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1. Introduction

Increased mismanagement of wastewater from industrial processes exacerbates contamination and pollution of the ecosystem, and exposes living organisms to carcinogenic toxins, xenobiotics, biocides, and other organ disrupting agents [1–3]. Organic dyes are common components of effluents from such processes and have also emerged as persistent pollutants owing to their high chemical stability that is facilitated by the fused aromatic ring structures [4].

Conventional methods for the treatment of effluents such as coagulation–flocculation and precipitation, electrocoagulation, and ion-exchange are still limited by high energy costs, the use of expensive organic solvents, and uncontrollable sludge production. Other techniques such as physical adsorption are limited by mere transfer of the effluent from one phase to another (for *e.g.* adsorption of dye solution onto a solid matrix) incapable of degradation, and may require subsequent tertiary treatments thus rendering the remediation processes long and tedious. Such concerns present an urgent need for the creation of more cleanup programs composed of facile techniques that curb dye pollution in an efficient and economically sustainable approach.

More sustainable alternatives for wastewater treatment that have emerged in recent years are based on advanced oxidation processes (AOPs), such as ozonation, photocatalysis, photo-Fenton reaction, cavitation, and electrolysis [5]. AOPs are specifically designed for the removal of dissolved organics using highly reactive oxidative species (ROS) such as hydroxyl radicals that are believed to be primary actors in the degradation process [6,7]. These ROS are photogenerated under favorable semiconductor band-gap magnitudes that match or exceed the redox potential requirements [8]. Of the aforementioned technologies, heterogeneous semiconductor photocatalysis is an attractive option as it promises energy sustainability *via* the use of cheap light sources for the mineralization of highly refractory compounds such as organic dye pollutants, without the production of noxious by-products [9–11].

Titania based materials have proven to be the mainstay of recent research efforts owing to their high activity and low cost of production, for use in advanced oxidation processes such as the reduction of contaminants in order to provide clean drinking water [7,12,13]. In particular, an extensive review of aperiodic titania–silica (TiO₂–SiO₂) mixed oxides demonstrated their relevance and versatility in for environmental remediation [14]. Such mixed oxide photocatalysts have been explored for the degradation of methylene blue [15–17], methyl orange [18–20], and azo dyes [21] *etc.* The few existing literature reports employing such photocatalysts specifically for RhB dye degradation, implicate crystallinity

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[22], sufficient exposure of active titania [23], high photoinduced charge carrier separation ability [24], and small anatase crystallite sizes [25]. Some literature reports purposely allude to the premise that the silica phase in the mixed oxide plays a significant role in increasing the adsorption capacity of organics [23,26,27], and improves the proximity between the organic substrate and the active sites (titania phase) thus facilitating their intimate interaction during the photocatalytic reaction [28–30]. However, such interactions need not necessarily imply improved photocatalytic activity, and some investigators have indeed indicated that adsorption is not always a pre-requisite for the photocatalytic reaction [31,32]. These existing studies, however, are limited by one or more of the following drawbacks: (1) the use of expensive surfactant templates for pore size and surface area expansion, (2) lack of detailed dark adsorption studies, (3) lack of a detailed and comprehensive physico-chemical characterization of the photocatalysts that preclude a clear understanding of structure-activity relationship that is essential for understanding dye degradation, (4) absence of studies pertaining to the role of polar aprotic solvents in the modulation of textural properties of mixed oxides, and (5) the misconstrued role of the silica phase that presumes that the higher activity of TiO_2 - SiO_2 mixed oxides over TiO_2 is primarily due to the high adsorptivity of organics facilitated by the silica surface. Most vividly, the major drawback of existing literature is that the structure-activity relationships between the photocatalyst and dye degradation still remains unclear in the absence of a thorough characterization, and this work is a contribution to address these incongruences and provide much needed clarity.

The preparation of mixed oxide systems containing equimolar amounts of titania and silica that are used to degrade Rhodamine B (RhB) as a model xanthene cationic dye is detailed. Our studies revealed that the TiO_2 - SiO_2 exhibited equilibrium adsorption capacities of RhB that are in some cases comparable to that of bare titania. However, the same photocatalysts demonstrate different photocatalytic performances indicating that properties responsible for catalytic activity are not governed by the adsorption. Thus, an optimal choice of the support and anatase loading is relevant for the minimization of radiation scattering by the “inert” phase and diffusion impediments in the porous structure that may limit the photocatalytic activity [33,34]. Specifically, catalysis practitioners that use porous materials have demonstrated that pore sizes are of significant influence on the resulting activity of TiO_2 -based photocatalysts [35,36]. Enhanced activities appeared to be favored by the larger pore sizes [37,38] and in some cases, optimum average sizes were attained, beyond which the activities began to decline [39].

In this work, the TiO_2 - SiO_2 photocatalysts were prepared using polar aprotic solvents including Drying Control Chemical Additives (DCCAs) such as acetonitrile and DMF that have proven essential for the production of crack free materials [40–42]. We recently demonstrated the applicability of polar protic co-solvents in tuning the crystallinity of such photocatalysts [43]. In contrast, polar aprotic solvents of varying dielectric constants and viscosities were chosen with care (ensuring dissolution in ethanolic TEOS), to alter the hydrolysis and condensation reactions that affect the resultant physico-chemical properties. The effect of polar aprotic solvents on the physico-chemical properties of TiO_2 - SiO_2 is lacking in the literature. It is imperative to observe that the hydrolysis and condensation reactions are dependent on several competing factors that are not limited to the viscosity, degree of solvation, dielectric constants, boiling points, surface tension, and steric factors of the solvent media in the sol-gel reactions [44,45]. This article demonstrates that larger pores permit the diffusion of substrate molecules and products to access and leave the active sites most efficiently. The results provide practitioners in catalysis with fundamental information pertaining to the design of more improved low cost photocatalysts used in the areas of textile

dye removal and the degradation of persistent organic pollutants (POPs).

2. Experimental

2.1. Materials and reagents

Commercially available titanium isopropoxide ($\text{Ti}[\text{OPr}^i]_4$, Acros, 98 + %), tetraethylorthosilicate (TEOS, Fisher, 98%), ethanol (Pharmco-AAPER, ACS/USP grade, anhydrous), acetonitrile (Acros, ACS grade), *N,N'*-dimethylformamide (Acros, ACS grade), acetone (Pharmco-AAPER, ACS/USP grade), ethyl acetate (Fisher, ACS grade), conc. nitric acid (Acros, ACS grade), triethanolamine (TEA, Acros, ACS grade), and isopropyl alcohol (IPA, Acros, ACS grade) were used as received. Ultrapure water (resistivity > 18 $\text{M}\Omega\text{cm}$) was used throughout the experiments, and for the dilution of Rhodamine B (Alfa Aesar) to desired concentrations.

2.2. Preparation of photocatalysts

TiO_2 - SiO_2 mixed oxide sols were prepared by simultaneous hydrolysis and condensation of alkoxide precursors, $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, followed by hydrothermal treatment in order to accelerate the sol-gel reactions and induce crystallization. In a typical synthesis, 1.65 mL of $\text{Si}(\text{OC}_2\text{H}_5)_4$ was added slowly into a solution containing 9 mL of co-solvent that was dissolved in 9 mL of $\text{C}_2\text{H}_5\text{OH}$ (200 Proof, anhydrous) under vigorous stirring in a Teflon liner. The hydrolysis process was initiated by the introduction of 1 mL of H_2O and the reaction was catalyzed by the addition of 100 μL of conc. HNO_3 . $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ was added dropwise to ensure homogenous distribution and the suspension left to stir until gelation. Gelation was usually achieved in less than 3 h. The resultant gels were subjected to hydrothermal treatment in a Thermolyne autoclave reactor furnace and heated to a temperature of 120 °C for 14 h, filtered, and dried overnight at 70 °C. These powders were then ground and calcined in air at 500 °C for 6 h at a heating rate of 3 °C/min. in order to expel the organics. Thermogravimetric analyses, TGA (not shown) indicate that this calcination temperature and conditions were sufficient for the complete removal of solvent from the mixed oxide powder materials.

2.3. Characterization

The calcined samples were characterized by powder X-ray diffraction using a Rigaku Ultima IV with PDXL software. The diffraction patterns were recorded at room temperature employing Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 0.15408\text{ nm}$), an accelerating voltage of 40 kV, and emission current of 44 mA. The angle regions were scanned from 10° to 80° (2θ) with a step size of 0.02°. The textural properties such as specific surface area and pore size distribution of the mixed oxide materials were determined by using N_2 physisorption analysis. After the samples were dried overnight at 70 °C and degassed extensively at 100 °C, N_2 adsorption-desorption isotherms were obtained at -196 °C using a Surface Area and Pore Size Analyzer, NOVA 2200e (Quantachrome Instruments). The Brunauer-Emmett-Teller (BET) equation was applied within a relative pressure range (P/P_0) of 0.05–0.30 for the calculation of the specific surface areas. The pore volume was determined from the amount of nitrogen adsorbed at the highest relative pressure of $P/P_0 \sim 0.99$. The pore diameter and pore size distribution plots were obtained by applying the Barrett-Joyner-Halenda (BJH) model to the desorption isotherm. The UV-vis diffuse reflectance (DR) spectra of the samples were recorded in the range of 210–600 nm using a Cary 100 Bio UV-Vis spectrophotometer equipped with a Harrick DR praying mantis accessory. Transmission electron microscopy (TEM) images were recorded on a Tecnai G² instrument operating

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