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# Chemically modified polyurethane-$SiO_2$/$TiO_2$ hybrid composite film and its reusability for photocatalytic degradation of Acid Black 1 (AB 1) under UV light

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## ABSTRACT

In this work, we have immobilized the surface modified $SiO_2$ core/$TiO_2$ shell composite sphere into polyurethane (PU) matrix to control the leaching of $SiO_2$/$TiO_2$ composite sphere during the photodegradation of dye solution. The uniform particle shape and sizes of $SiO_2$ sphere and $SiO_2$/$TiO_2$ composite sphere are synthesized without aggregation by sol–gel method. The $SiO_2$/$TiO_2$ composite spheres are chemically bonded with polyurethane using glycidoxypropyltrimethoxy silane (GPTMS) as a coupling agent to increase the flexibility and reusability of the resulting PU-$SiO_2$/$TiO_2$ hybrid composite film for photocatalysis. The PU-$SiO_2$/$TiO_2$ hybrid film has been extensively characterized by FT-IR, XRD, TGA, FE-SEM and TEM. The sizes of the prepared $SiO_2$ sphere and $SiO_2$/$TiO_2$ composite are about 310 nm and 320 nm, respectively. Photocatalytic activity of PU-$SiO_2$/$TiO_2$ hybrid film was studied towards Acid Black 1 (AB 1) under UV irradiation. The effects of operational parameters such as the amount of $SiO_2$/$TiO_2$ photocatalyst and initial pH on photomineralization have been analyzed. PU-40 wt% $SiO_2$/$TiO_2$ hybrid film with only 2.6 wt% $TiO_2$ has achieved a very good photocatalytic activity and is reusable under cyclic tests.

## 1. Introduction

Heterogeneous photocatalysis has been extensively used for removing organic contaminants from aqueous or gaseous environment [1,2]. $TiO_2$ is one of the most important semiconductor materials, because it is easily available, inexpensive, non-toxic, and has potential applications in numerous fields, such as photocatalyst [3–6], sensors [7,8], solar cells [9,10], and lasers [11]. However, when $TiO_2$ is used as a single component, it has large band gap and high recombination rate of the photogenerated electron-hole pair that will reduce the complete utilization of UV and solar energy. The specific surface area of commercially available $TiO_2$ is about 60 $m^2/g$. To increase the photocatalytic activity of $TiO_2$, it was coated on the surface of the $SiO_2$ nanosphere to form $SiO_2$/$TiO_2$ nanocomposite sphere. Even though $SiO_2$ falls in the category of insulator material, the photocatalytic activity of $TiO_2$ increased when combined with $SiO_2$ due to its large surface area [12,13]. Several researchers used $SiO_2$ nanoparticle to reduce the recombination of photogenerated electron-hole pair and to increase the surface area of the $TiO_2$ photocatalyst for the purpose of improving the photodegradation ability of dyes [14–16].

If the $SiO_2$/$TiO_2$ powder is used as catalyst in the form of suspension, removal of catalyst after photodegradation requires a solid–liquid separation technique that consumes both money and time and the recovery loss of catalyst will be high. The floating of powder may affect the human health [17]. The separation of the floating catalyst from dye solution can be difficult. If the catalyst powder cannot be separated from the dispersion after photocatalytic testing, the concentration measurement of the degradable species by UV–vis spectra will be a problem. Moreover, reusability will also be affected by the catalyst lost during filtration or centrifugation.

To be a reusable photocatalyst, the photocatalytic powder needs to be embedded into a polymer matrix. The characteristic features of polymer support should control the leaching problem of catalyst, as well as the loss of catalyst during recovery. Moreover, polymer support is expected not to affect the specific surface area and activity of photocatalyst. Recently, many researchers have immobilized the $TiO_2$ photocatalyst in different polymers. Zhang and his group successfully dispersed $TiO_2$ in PMMA and PET by electrospun method to form the hydrogen bonding between $TiO_2$ precursors and PMMA matrix [18,19]. Yao et al. deposited $TiO_2$ nanoparticle on

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activated carbon fiber by sol–gel method and their photocatalytic effect is tested using phenol and methyl orange [20]. Matzusawa et al. had immobilized the $TiO_2$ nanoparticles through the pysicochemical interaction on the nonwoven polyester fibers coated with the $SiO_2$/PVC-PVA copolymer hybrid layer [21]. Hosseini et al. used highly porous perlite granules as adsorbent to adsorb $TiO_2$ nanoparticles into its pores and studied their photocatalytic activity using phenol as a pollutant [22]. Recently, Lei et al. immobilized the $TiO_2$ nanoparticle only upto 12 wt% into the polyvinyl alcohol (PVA) with hydrogen bonding [23]. In all these cases, $TiO_2$ nanoparticle has been used and is not chemically bonded with polymer substrate or matrix. Thus, the leaching of $TiO_2$ particles can be a problem, which affects the reusability of catalyst. Furthermore, they could not have high loading of $TiO_2$ nanoparticles into the polymer matrix due to the formation of high viscous polymer solution that will affect the film-making process. Chemical bonding between $TiO_2$ and polymer matrix can improve the leaching problem. Li et al. used γ-aminopropyltriethoxysilane to modify the surface of $TiO_2$ nanoparticle followed by covering a dense conductive PANI layer to form a PANI-coated $TiO_2$ through surface oxidative graft polymerization [24]. Yuranova et al. reported the photocatalytic activity of $SiO_2/TiO_2$ coated cotton textile. They have achieved the high $CO_2$ evolution during the discoloration of red wine by having the amount of $SiO_2/TiO_2$ higher than that of TiO2 coated on cotton textile [25]. They used hybrid particle for photocatalytic testing, but they did not mention the loss of catalyst during the centrifugation. The use of polymer/$TiO_2$ hybrid film always has an existing problem in the passivation of $TiO_2$ nanoparticles by the polymer matrix. Without exposing $TiO_2$ to environment, its photocatalytic ability can be limited.

Nowadays, organic dyes are one of the foremost groups of pollutants found in wastewaters fashioned from different industries. Among azo dyes used in textile industry, Acid Black 1 (AB 1) is one of the frequently used dyes in textile industries and is a potential threat to the aquatic environment due to its poor biodegradability [26,27]. Recently, Swaminathan and their group reported the photocatalytic degradation of AB 1 by differently modified photocatalysts in slurry forms [28–31].

In the present work, uniform $SiO_2$ sphere of 310 nm in size was first prepared and $TiO_2$ was coated on the surface of the $SiO_2$ sphere to form the $SiO_2$/nano-$TiO_2$ composite sphere with the size of about 320 nm. The formed composite sphere was chemically modified through silane coupling agent followed by reacting with flexible polyurethane (PU) prepolymer to form PU-$SiO_2/TiO_2$ hybrid composite without particle aggregation. The surface morphologies of $SiO_2/TiO_2$ composite sphere and PU-$SiO_2/TiO_2$ hybrid composite film were studied by using TEM and FE-SEM and the photocatalytic activity of prepared hybrid composites was tested toward the degradation of Acid Black 1 (AB 1) dye.

## 2. Experimental

### 2.1. Materials

In this study, analytical grade chemicals were used as-received without further purification. Polyurethane prepolymer (PU) (W-2907-05) was kindly supplied by Chemtura Corporation, Middlebury, Connecticut, USA. The AB 1 dye (Empirical formula: $C_{22}H_{14}N_6Na_2O_9S_2$) obtained from Aldrich was used as received. The chemical structure is presented in Figure S1 of the Supporting Information.

### 2.2. Synthesis of $SiO_2$ sphere

A mixture of 2 mL TEOS, 0.6 mL dodecane, 10 mL anhydrous ethanol, and 2 mL of water was stirred at room temperature for 30 min followed by addition of 0.4 mL of ammonia solution and continued the stirring for 10 min. Then add 6 mL of anhydrous ethanol to this mixture and continued the stirring for 2 h at room temperature, the $SiO_2$ spheres were separated by centrifugation and washed three times with ethanol. Finally, the $SiO_2$ sphere was dried under vacuum oven at 60 °C for 6 h.

### 2.3. $TiO_2$ coating on $SiO_2$ sphere

The $SiO_2$ sphere (1 g) dispersed in anhydrous 2-propanol (50 mL) was ultrasonicated for 30 min. To this, 0.5 mL of $Ti(iOBu)_4$, 0.2 mL of dodecane, and 0.1 mL of water was added and stirred for 4 h at room temperature. The $TiO_2$-coated $SiO_2$ spheres were separated by centrifugation and washed three times with ethanol and dried in vacuum oven at 60 °C for 6 h. The $SiO_2/TiO_2$ composite sphere was calcined at 450 °C for 4 h to get the anatase phase for $TiO_2$. The total amount of $TiO_2$ nanoparticle coated on the $SiO_2$ porous sphere was 4 wt%. The schematic diagram for the $TiO_2$ coating procedure to form $SiO_2/TiO_2$ sphere is shown in Scheme 1.

### 2.4. Surface modification of $SiO_2/TiO_2$ sphere

The $SiO_2/TiO_2$ sphere (40 mg) and ethanol (4 mL) was ultrasonicated for 30 min followed by adding glycidoxypropyltrimethoxy silane (GPTMS, 40 mg) to this solution. After 4 h ultrasonication, the unreacted GPTMS was removed by centrifugation. The GPTMS-modified $SiO_2/TiO_2$ sphere was further washed three times with ethanol to completely remove the unreacted GPTMS then re-dispersed in 4 mL THF under ultrasonication. The schematic diagram for the GPTMS-modified $SiO_2/TiO_2$ composite sphere is shown in Scheme 1.

### 2.5. Preparation of PU-$SiO_2/TiO_2$ hybrid film

Three different concentrations i.e., 25, 50 and 75 wt% of GPTMS-modified $SiO_2/TiO_2$ spheres were dispersed in THF and respective amount of PU prepolymer was added into the above solutions. The reaction mixture was stirred at 50 °C for 3 h. The solution of PU-$SiO_2/TiO_2$ hybrid was poured into petri-dishes and dried in a hot air oven at 50 °C for 6 h. The prepared PU-$SiO_2/TiO_2$ hybrid film was kept in a vacuum oven at 60 °C for 12 h to remove the solvent. The reaction of GPTMS-modified $SiO_2/TiO_2$ with polyurethane is also given in Scheme 1.

### 2.6. Characterizations

The surface modification of $SiO_2/TiO_2$ by GPTMS was confirmed by Fourier Transform Infrared Spectrometer (FT-IR) (FTS-1000; Digilab, Holliston, MA, USA). Surface morphologies of the $SiO_2$ and $SiO_2/TiO_2$ spheres were examined by a transmission electron microscope (TEM, H-7000, equipped with a CCD camera, Hitachi, Tokyo, Japan) and the cross-sectional view of PU-$SiO_2/TiO_2$ hybrid film by a field-emission scanning electron microscope (FE-SEM, JSM 6500F, JEOL, Tokyo, Japan). Powder X-ray diffraction (XRD) patterns were recorded with a Bruker D2-phaser diffractometer using CuKα radiation ($\lambda = 1.5418$ Å). The weight losses of PU and its composites were analyzed using a thermogravimetric analyzer (TA Instrument Q500, New Castle, DE, USA) at a heating rate of 10 °C $min^{-1}$ up to 600 °C in air. UV–vis diffuse reflectance spectra were recorded on Shimadzu UV-2450 UV–visible spectrophotometer equipped with an integrated sphere assembly using $BaSO_4$ as a reflectance sample. The degradation of AB 1 dye was monitored by Jasco V-670 UV spectrophotometer.