



Depletion of double-layer coated nano-TiO₂ and generation of reactive oxygen species in the presence of ethanol under simulated solar irradiation

Wei Wu, Qian Xiang, Zihao Wu, Guoqiang Shan*, Lingyan Zhu*

Key Laboratory of Pollution Processes and Environmental Criteria, Ministry of Education, Tianjin Key Laboratory of Environmental Remediation and Pollution Control, College of Environmental Science and Engineering, Nankai University, Tianjin 300350, PR China

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ABSTRACT

Nano-TiO₂ is demanded in a large quantity in pharmaceutical and personal care products. To protect human from adverse effects induced by reactive oxygen species (ROS) generated by nano-TiO₂ under solar light irradiation, it is usually coated by an inorganic layer and sometimes one additional polymeric layer. In this study, a commercial double-layer coated nano-TiO₂, named STR-100C-LP (abbreviated as STR), was used to access its transformation and restoration of photoactivity in aqueous medium, comparing with pristine P25 nano-TiO₂. The organic coating made STR surface hydrophobic, while 1% (v/v) organic solvents, such as ethanol, methanol, promoted its dispersion. A series of characterization techniques indicated that dissolution effect of solvents and solar light irradiation could damage the organic and inorganic coating layers of STR. Thus, STR regained its photoactivity and produced ROS species, such as hydroxyl radicals and superoxide radical species. The results strongly suggest that the double coating layers of nano-TiO₂ were unstable in the presence of organic solvent and solar irradiation. This would result in recovery of its photoactivity and generation of ROS, finally changing its transport and fate in aquatic environment.

1. Introduction

Ultraviolet (UV) radiation may cause many skin disorders even cancer (Afaq et al., 2005; Beasley and Meyer, 2010; Laturnus et al., 2004), and the American Cancer Society recommends to use sunscreens every two hours as a proactive measure to prevent skin damages caused by the exposure to UV radiation from sunlight. Among various UV blockers which are added as key ingredients in sunscreen products (Montazer et al., 2010; Sundarajan et al., 2010; Xiao et al., 2013), nano-titanium dioxide (nano-TiO₂) is believed to be one of the most effective components of sunscreens because it effectively reflects and scatters UVB and UVA in sunlight (Dunford et al., 1997; Hext et al., 2005). In addition, nano-TiO₂ is largely used as a pigment and thickener in cosmetics, pharmaceuticals and personal care products. Weir et al. reported that 65% of the global production of nano-TiO₂ was used in pharmaceuticals and personal care products (Weir et al., 2012). It was estimated that 2900 t nano-TiO₂ would release into the environment by 2020 (Song et al., 2017).

To inhibit generation of reactive oxygen species (ROS) produced by nano-TiO₂ under UV irradiation, which may cause hazardous effects to human skin (Buchalska et al., 2010; Virkutyte et al., 2012), a typical strategy is to protect nano-TiO₂ with inorganic, such as aluminum

hydroxide (Al(OH)₃), or/and organic coating layers, such polydimethylsiloxane (PDMS), hydrogen dimethicone (Kim et al., 2002; Labille et al., 2010; Nattaya et al., 2017). It was reported that nano-TiO₂ coated with double-layer of Al(OH)₃ and PDMS or hydrogen dimethicone was more stable than that only coated with Al(OH)₃ (Tyner et al., 2011). The combined coating of Al(OH)₃ and PDMS or hydrogen dimethicone not only make nano-TiO₂ compatible in sunscreen formulas, but also render the surface of nano-TiO₂ inert to H₂O, O₂ and organic molecules, avoiding the generation of ROS and safe to human skins.

With the increasing use of pharmaceutical and personal care products, coated nano-TiO₂ is inevitably removed from the skin during daily activities, and ends up in municipal wastewater and natural water system (Auffan et al., 2010; Tyner et al., 2011). The concentration of sunscreen residuals in swimming pool water was in the range of 21–60 µg L⁻¹ (Holbrook et al., 2013). It is hypothesized that the coating on nano-TiO₂ would significantly change the environmental behaviors of nano-TiO₂. The ecotoxicities of coated nano-TiO₂ were assessed on a variety of organisms (Fisichella et al., 2012; Foltete et al., 2011; Lapied et al., 2011), and the result indicated that coated nano-TiO₂ displayed lower biological effects than primary one (Lapied et al., 2011). After losing the coating, nano-TiO₂ may be exposed to UV-light irradiation

* Corresponding authors.

E-mail addresses: yunongshan@nankai.edu.cn (G. Shan), zhuly@nankai.edu.cn (L. Zhu).

and generate ROS and singlet oxygen, leading to genotoxicity and/or phototoxicities to organisms (Fouqueray et al., 2012; Lapied et al., 2011; Santaella et al., 2014). Under some specific environmental conditions, the integrity of the surface coating could be affected. It was reported that chlorine (HOCl/OCl^-) in swimming pool water could damage the $\text{Al}(\text{OH})_3$ layer of single-coated nano-TiO₂, leading to enhanced photocatalytic activity which was accessed by ROS generation (Al-Abed et al., 2016; Virkutyte et al., 2012). Nevertheless, little efforts have been done to evaluate the integrity of inorganic and organic double coated nano-TiO₂ and the following influences on the co-existing organic pollutants.

Ethanol (EtOH) has found its wide applications in a variety of fields, such as chemical and energy industries, hospitals, and brewery industries. Especially, a large amount of EtOH is applied in personal care products such as mouth and hand washes, cosmetics, sunscreens (especially sunscreen spray) with proportion as high as tens percent, where coated nano-TiO₂ is also present (Lachenmeier, 2008; Patil and Sandewicz, 2013; Reid et al., 2011; Somboon and Sansuk, 2018). Thus, large amount of EtOH might be released to the sewage flow of municipal wastewater treatment plants, the compositions of which are very complex with many organic pollutants. It was reported that EtOH was 3.12 g/L in the alcohol wastewater obtained from the Saphip Lopburi Co., Ltd., Thailand (Intanoo et al., 2012). As a consequence, there is a high potential that EtOH coexist with coated nano-TiO₂ particles in cosmetics as well as wastewater at relatively high concentrations. It is unclear if the coating of the double-layered nano-TiO₂ is affected in the presence of EtOH and sunlight irradiation, which is crucial for comprehensive assessment of its final fates and risks, as well as the consequent impacts on the fate and transformation of other co-present organic pollutants.

The current study aimed to investigate if a double coated nano-TiO₂ could recover its photoactivity in the presence of low content of EtOH. To fully understand the impacts of EtOH, other organic solvents, such as methanol, acetone, acetonitrile, were also tested. Pristine P25 nano-TiO₂ was used for comparison. Rhodamine B (RhB), was selected to probe the photoactivity of the nano-TiO₂ under simulated solar irradiation (Aarhi and Madras, 2007; Bian et al., 2012; Silva et al., 2006; Sun et al., 2011; Sun et al., 2014). A variety of characterization techniques were applied to comprehensively characterize the change of the coated materials and the fate of co-existing pollutants.

2. Materials and methods

2.1. Chemicals and reagents

Coated nano-TiO₂ with a commercial name of STR-100C-LP (abbreviated as STR) was purchased from Sakai chemical industry Co., Ltd., Fukushima, Japan. The main component of STR provided by the supplier, was TiO₂ (79.0–89.0%) and the percentage of aluminum hydroxide was 6.0–8.0% and that of hydrogen dimethicone was 3.5–5.5%. Uncoated nano-TiO₂ P25 particles (Degussa P25) were purchased from Degussa Corporation, Essen, Germany. RhB was purchased from J&K Scientific Ltd., Beijing, China. EtOH was supplied by Concord Technology Co. Ltd., Tianjin, China. Methanol (MeOH), acetonitrile (ACN) and acetone (DMK) were provided by ANPEL Scientific Instrument, Co., Ltd., Shanghai, China. Acetic acid (HOAc) and formic acid were purchased from CNW Technologies GmbH, Germany. Na₂HPO₄·12H₂O and benzoquinone (BQ) were bought from Guangfu chemical technology Co., Ltd., Tianjin, China. H₃PO₄ was got from Tianjin chemical technology Co., Ltd., Tianjin, China. NaOH was from Jiangtian chemical technology Co., Ltd., Tianjin, China. Terephthalic acid (TPA) was supplied by J&K Scientific Ltd., Beijing, China.

2.2. Preparation of the suspensions of nano-TiO₂

The suspensions of STR and P25 in EtOH were prepared by adding

2 mL of EtOH to the test tubes containing 0.2 g of STR or P25 particles, and then diluted with water to 200 mL. The concentration of EtOH was 1% (v/v). The suspensions were labeled as STR + EtOH and P25 + EtOH, respectively. The suspension of P25 without EtOH was prepared by dispersing 0.2 g of P25 particles in 200 mL of pure water. All the stock suspensions were sonicated in water bath at 20 °C for 1 h before photocatalytic degradation experiments, and the concentrations of STR and P25 were 1.0 g/L. The suspensions of STR in MeOH, ACN and DMK were prepared following the same procedures. The RhB stock solution at a concentration of 0.1 g/L was prepared by dissolving 0.05 g RhB with pure water and diluting to 500 mL.

2.3. Photocatalytic degradation experiments

Photolysis degradation experiments were performed in a XPA-7 photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) with 12 quartz tubes and a 800 W xenon lamp in the center. The light intensity was 132 W/m², and the emission spectrum of the lamp is shown in Fig. S1. The lamp was immersed in a quartz immersion well, and the reaction system was cooled by circulating water and maintained at room temperature. The reaction solution was stirred using a magnetic stirring bar to prevent the settling of the particles. STR or P25 at 0.75 g/L and RhB at 0.025 g/L were added in the reaction tubes and the total volume of the reaction solution was 40 mL.

Prior to irradiation, the reaction solution was stirred for 1 h to reach adsorption/desorption equilibrium of RhB on the surface of STR or P25. Then the reaction was initiated by turning on the light. Approximately 0.8 mL of aqueous solution was withdrawn at predetermined time intervals and centrifuged under 10,000 rpm. The supernatant was withdrawn for analysis of RhB in the solution.

2.4. Analytical and characterization techniques

The XRD patterns of STR and P25 were analyzed on a RigakuD/Max 2500 PC diffractometer with CuKα radiation ($\lambda = 0.154184$ nm).

The RhB and HOAc concentrations were measured on a high performance liquid chromatograph (HPLC) instrument (Agilent Technologies 1260, USA) equipped with a C18 column (Agilent, Eclipse XDB-C18, 4.6 mm × 150 mm, 5 mm). For detection of RhB, an Ultraviolet detector (VWD) at 550 nm was used, and mobile-phase was methanol/water (75/25, v/v) at a flow rate of 0.3 mL/min. The column temperature was kept at 35 °C and injection volume was 10 μL (Sun and Yang, 2011). The detection of HOAc was measured at 210 nm. Mobile-phase was 98:2 (v/v) methanol/water (with 4 mmol/L, pH~3 Na₂HPO₄·12H₂O) at a flow rate of 0.3 mL/min. The column temperature was kept at 30 °C and injection volume was 10 μL (Li et al., 2013). The degradation of RhB was described by a pseudo first-order reaction kinetic model: (Chang et al., 2013)

$$\frac{C_t}{C_0} = e^{-K_{\text{obs}}t} \quad (1)$$

C_t and C_0 are the RhB concentrations (mg/L) in the solution at reaction time t (min) and at the beginning of the reaction, K_{obs} is the pseudo-first-order rate constant (min^{-1}). The results were reported as the averages of three replicates.

The difference between the systems of P25 + EtOH with RhB (as P25 + EtOH + RhB) and P25 + EtOH without RhB (as P25 + EtOH) on the generation of HOAc, was evaluated by independent t -test performed with IBM® SPSS® Statistics version 19 (Chicago, IL, USA).

The pH of the solutions before and after simulated solar irradiation was measured using a digital pH meter (SevenEasy Plus, S20P, Mettler Toledo, Inc., Switzerland).

The surface morphologies of STR and the samples in the presence of EtOH after dark reaction and irradiation, respectively, were characterized on a field emission scanning electron microscopy (FE-SEM, LEO, 1530vp, Germany), and a high-resolution transmission electron

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