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Excellent photocatalytic degradation activities of ordered mesoporous anatase TiO_2–SiO_2 nanocomposites to various organic contaminants

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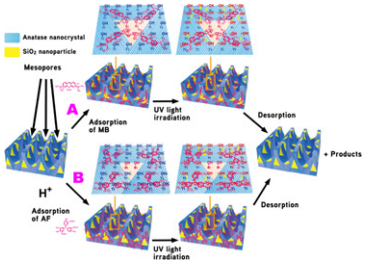
HIGHLIGHTS

- Mesoporous TiO_2–SiO_2 nanocomposites highly efficiently degrade various dyes, MC-LR.
- The degradation activities of mesoporous TiO_2–SiO_2 are much higher than that of P25.
- The mesoporous TiO_2–SiO_2 nanocomposites are considerably stable and reusable.
- The dyes are not only decolorized promptly but degraded readily as well.
- Mesoporous TiO_2–SiO_2 nanocomposites exhibit extensive and promising application.

GRAPHICAL ABSTRACT



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ABSTRACT

Ordered 2-D hexagonal mesoporous TiO_2–SiO_2 nanocomposites consisted of anatase TiO_2 nanocrystals and amorphous SiO_2 nanoparticles, with large mesochannels and high specific surface areas, have been extensively and detailedly evaluated using various cationic dyes (methylene blue, safranin O, crystal violet, brilliant green, basic fuchsin and rhodamine-6G), anionic dyes (acid fuchsin, orange II, reactive brilliant red X3B and acid red 1) and microcystin-LR. We use mesoporous $80TiO_2$–$20SiO_2$-900 for the degradation of cationic dyes and MC-LR, due to the dominant adsorption of Si—OH groups and synergistic role of coupled adsorption and photocatalytic oxidation. For anionic dyes, due to the adsorption results predominantly from Ti—OH groups, our strategy realizes the enhanced photocatalytic oxidation by strong surface acids and larger available specific surface area. Based on this, we prepared $90TiO_2$–$10SiO_2$-700 to degrade them. The results show that our samples exhibit excellent degradation activities to all the contaminants, which are much higher than that of P25 photocatalyst. The dyes are not only decolorized promptly but degraded readily as well. It is strongly indicated that our mesoporous nanocomposites are considerably stable and reusable. These results demonstrate that our mesoporous TiO_2–SiO_2 nanocomposites present extensive and promising application in the fast and highly efficient degradation of various organic pollutants.

1. Introduction

One of the most pervasive problems afflicting people throughout the world is inadequate access to clean water. Problems with

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water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich [1]. Dyestuffs and microcystins (MCs) are two main contamination sources. About 700,000 tons of dyes are annually produced in the world [2,3], and about 400 tons per day are released into the environment during manufacturing, processing and using [4,5]. The presence of dyes in wastewaters has been recognized as one of the most important environmental hazardous substances, and the discharge of dyes in the wastewaters is a matter of concern for both toxicological and esthetical reasons [6–8]. It is well-known that some xanthene, azo, fluorine dyes, *etc*. are highly carcinogenic and mutagenic [9–11]. In addition, the existence of MCs in water is another major threat to human health. MCs, a family of potently cyclic heptapeptides hepatotoxins and tumor promoters, are the most common cyanotoxins produced by cyanobacterial harmful algal blooms occurring in eutrophic water such as lakes, ponds, reservoir and rivers, *etc*., and are frequently responsible for poisoning animals and humans who come into contact with toxic blooms and contaminated water [12–14]. MCs are extremely toxic and acute exposure to high levels of which will result in lethal liver hemorrhage or liver failure [12]. A well-documented incident of MCs water contamination occurred in a hemodialysis clinic in Brazil in 1996, resulting in the deaths of over 50 patients [13,15]. While chronic exposure to low levels of MCs presents tumor promoting activity and is possibly carcinogenic [12,16]. MCs possess more than 80 derivatives, among which microcystin-LR (MC-LR) is the most abundant and commonly detected, and also the most toxic microcystin (LD_{50} 50 $\mu g\,kg^{-1}$, mouse i.p.) in natural blooms [12,17]. Accordingly, the World Health Organization (WHO) has proposed a guideline value for a maximum concentration of 1.0 $\mu g\,L^{-1}$ for MC-LR in drinking water [18]. The size of MC-LR is 1.4–2.9 nm [19].

Conventional methods such as coagulation, flocculation, sand filtration, *etc*. have been used to deal with waters containing dyes or/and MCs. However, many shortcomings still exist in these methods due to the increasing number of refractory materials in effluents, difficulties in the complete removal of color or/and dissolved MCs, and expensiveness [12,20,21]. Conventional biological processes also do not treat dye wastewater effectively because of the large degree of aromatics present in the molecules, the stability of modern dyes to light and oxidizing agents, and the inherent reluctance to biodegradation [10,22,23]. Biological methods require a long reaction time in treating MCs and are thus not viable [24]. Although activated carbon adsorption is an effective means for the removal of dyes and MCs [10,12,21,25], it is still considered as an expensive method mainly due to the non-renewable use [12,25] and the deficiency of accessible mesopores for adsorption of large MCs [26]. Therefore, the highly effective removal of dye effluents and MCs remains a challenge.

During the past decades, many new approaches have been investigated for removing the pollutants of dyes or/and MCs worldwide, including photocatalytic oxidation [2–4,9–11,13,14,20,22,23,27–33], photoelectrocatalytic oxidation [5], coupled photocatalytic oxidation and biofilm process [22], integrated microwave/UV-illuminated method [34], Fenton and photo-Fenton processes [35,36], adsorption and fast separation of Fe_3O_4@$n$$SiO_2$@$m$$SiO_2$ microspheres [37], ultrasonically induced degradation [38], *etc*. Among those approaches, photocatalytic oxidations have attracted great attention as emerging successful technologies [39]. Up to now, TiO_2 heterogeneous photocatalytic technology has been regarded to be the most efficient, environmentally benign and promising method, and numerous researches are focusing on it [39,40]. However, one of the main drawbacks is very poor adsorptive power to some dyes [27,29] and other organic pollutants [41,42]. Accordingly, the supported TiO_2 particles with activated carbon [41], alumina [42], silica [41,42], mesoporous silica shell [43], MCM-41 [44] and SBA-15 [45], respectively; the TiO_2 surfaces modified with Al_2O_3 [30], SiO_x [46], MgO_x [47], respectively; TiO_2–SiO_2 and TiO_2–Al_2O_3 composites [27,48,49], *etc*. have been extensively studied in order to improve their adsorption performances and photocatalytic activities. Although most of the above-mentioned photocatalysts exhibited enhanced activities, but none of them was reported to exhibit highly efficient degradation to various organic contaminants such as cationic and anionic dyes, MC-LR, *etc*. in the literature.

In this study, the ordered 2-D hexagonal mesoporous TiO_2–SiO_2 nanocomposites, with large pore channels and high specific surface areas, very unique and unprecedented mesoporous frameworks consisted of anatase TiO_2 nanocrystals and amorphous SiO_2 nanoparticles by linking mutually, partitioning off from each other and coexisting, are extensively and detailedly evaluated using six cationic and four anionic dyes with different structures and anchoring groups, and MC-LR. We use mesoporous $80TiO_2$–$20SiO_2$-900 nanocomposite to degrade the cationic dyes and MC-LR, due to the synergistic role of coupled adsorption and photocatalytic oxidation. Whereas for the anionic dyes, due to the considerably strong adsorbability of TiO_2, our strategy realizes the enhanced photocatalytic oxidation by strong surface acid through increasing Ti/Si ratio, the number of strong surface acid sites, available surface area of TiO_2, *etc*. Based on this, we prepared mesoporous $90TiO_2$–$10SiO_2$-700 nanocomposite to degrade them. Our results show that mesoporous TiO_2–SiO_2 nanocomposites exhibit excellent degradation activities to all the contaminants, which are much higher than that of P25. This study demonstrates that our samples display extensive and promising application in the fast and highly efficient removal of various organic pollutants.

2. Experimental and characterization

2.1. Initial materials and preparation

Titanium isopropoxide [≥97%] and tetraethyl orthosilicate [≥96%] were purchased from Fluka. Pluronic P123 $[HO(CH_2CH_2O)_{20}(CH_2CHCH_3O)_{70}(CH_2CH_2O)_{20}H]$ was received from Aldrich. Ethanol (absolute), concentrated HCl (36.5 wt.%), NaCl (99.5%, AR grade) were purchased from Shanghai Chemical Corp. P25 photocatalyst was kindly supplied by Degussa Corp. Methylene blue (MB) was from Sinopharm. Safranin O (SO), crystal violet (CV), brilliant green (BG), basic fuchsin (BF), rhodamine-6G (Rh6G), acid fuchsin (AF), orange II (OII), acid red 1 (AR1), acetonitrile (CH_3CN, ≥99.9% for HPLC) were purchased from Sigma–Aldrich Inc. Reactive brilliant red X3B (RX3B) was from Jining dye manufacture of China. MC-LR (≥95% by HPLC) was purchased from Agent Technology Co., Ltd and stored at −25 °C. Trifluoroacetic acid (TFA, 99.5+%, HPLC grade) was purchased from Alfa Aesar. NaOH (96%), $HClO_4$ (71%) are AR grade and were purchased from Shanghai Chemical Corp. All the chemicals were used as received without any further purification. The molecular structures and related information of various dyes and MC-LR are shown in Fig. 1 and Table 1, respectively. The highly ordered mesoporous TiO_2–SiO_2 nanocomposites, pure TiO_2 and SiO_2 were synthesized according to our previous procedure [50,51] (see Supplementary materials).

2.2. Preparation of the dyes and MC-LR aqueous solutions

The aqueous solutions of the dyes and MC-LR were prepared using deionized and Milli-Q water, respectively, and their concentrations are presented in Table 1. The pH values of cationic dyes and MC-LR solutions were not adjusted and buffered, while the pH values of anionic dyes solutions were adjusted to 2.0 by addition of diluted $HClO_4$ and NaOH solutions, and measured with PHS-3C meter.