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# Self-assembled highly crystalline $TiO_2$ mesostructures for sunlight-driven, pH-responsive photodegradation of dyes

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ABSTRACT

The development of new strategies and photocatalytic materials for practical environmental solutions remains a great challenge, particularly due to the large energy demands associated with various remediation processes. In this paper, we report the fabrication of self-assembled ordered mesoporous $TiO_2$ with highly crystalline anatase structures as well as high surface area, and characterize their photocatalytic performance on the degradation of three typical dyes, including anionic methyl orange, cationic methylene blue, and neutral rhodamine B driven merely by sunlight. The results show that the dye photodegradation strongly depends on the charging state of both mesoporous $TiO_2$ surface and dyes, which can be adjusted by the pH value of the solutions. Such charge-dependent photocatalytic functionality of mesoporous $TiO_2$ can thus be exploited for highly efficient and selective dye photodegradation.

## 1. Introduction

Dyes are common across many industries—including printing, textile, pulp and paper, and leather processing—to color products to suit customer desires, generating substantial amounts of dye wastewater that is harmful to the environment, hazardous to human health, and difficult to degrade by natural means. Their use remains problematic, an anachronism remaining among the many chemicals produced and used via sustainable processes developed in recent years. Numerous treatment technologies have been developed to treat dye wastewater, from physico-chemical to biological processes [1–6]. Among these, the solar energy-driven photodegradation of dyes in aqueous solutions has gained considerable attention due to practical and fundamental benefits alike in recognition of the impact dye-laden waste has on the environment [7–10]. Semiconductor-based photocatalysis has attracted particular attention as a suitable "green" technology for this purpose because of its chemical stability and favorable energy band structure. $TiO_2$ is considered to be one of the best material candidates for photovoltaic and photocatalytic devices in this application; its nanoparticles possess superior photocatalytic efficiency over the bulk phase and the photocatalytic activity of such nanoparticles have been extensively investigated [11–13]. However, intrinsic limitations prevent further improvement in the photocatalytic process in $TiO_2$ nanoparticles. Illuminated $TiO_2$ nanoparticles behave as short-circuited electrodes: the interfacial charge transfer competing with the charge recombination between the charge carriers is a major problem in photocatalysis and is a limiting factor in improving the photocatalytic efficiency [14]. There are further drawbacks: nanoparticles tend to aggregate, are difficult to separate and recover from solution, and the environmental impact of such nanoparticles remains an open question, greatly limiting their practical use in many commercial applications. The significant need remains, therefore, for another approach and alternative materials to solve these challenging problems inherent in $TiO_2$ and in using them in a nanoparticle morphology.

So far, little information is available on the reaction mechanisms involved in the photocatalytic degradation of dyes and on the identification of major transient intermediates which have been more recently recognized as very important aspects of these processes, especially from the viewpoint of practical application [15–17]. As the charging states of both dye and photocatalyst play

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crucial roles in the photodegradation process, investigating the prior adsorption of dyes in addition to the interactions between the dyes and the catalyst surface is crucially important to develop superior photocatalysts for efficient dye degradation. In comparison with $TiO_2$ nanoparticles, highly structured mesoporous $TiO_2$ formed using evaporation-induced self-assembly is of considerable interest [18–20]. The advantage of this technique lies in the possibility of "tuning" the symmetry of the mesostructure by adjusting the composition of the initial solution and the preparation condition [21–23]. Further, the mesoporous morphology avoids the myriad practical drawbacks of nanoparticles. To the best of our knowledge, there is no study to date on the pH-responsively selective photocatalytic activity of ordered mesoporous $TiO_2$. Here, we report the fabrication of self-assembled highly crystalline ordered mesoporous $TiO_2$ and investigate the sunlight-driven photocatalytic activity of the mesoporous $TiO_2$. The results show that the adsorption of dyes on the mesoporous $TiO_2$ surface strongly depends on the pH value of the dye solution in addition to the charging state of the dyes, and that these factors in turn have a crucial effect on the photocatalytic performance of the mesoporous $TiO_2$.

## 2. Experimental

Mesoporous $TiO_2$ was synthesized by using a mixture of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer (P123), ethanol, concentrated HCl, and tetrabutyl titanate (TBT) [24]. The mass ratio of P123/TBT/EtOH/HCl was 1:2.8:30:2. For a typical synthesis, 1.0 g of P123 was dissolved in 30 g of ethanol, and then 2 g of concentrated HCl was slowly added with stirring. Then 2.8 g of TBT was added, and the solution was stirred for 4 h. The resulting solutions were transferred into Petri dishes and subsequently sealed and aged at room temperature for 1 week. Then the samples were calcined at 400 °C in air for 2 h with a 1 °C $min^{-1}$ temperature ramp to obtain the mesoporous $TiO_2$ thin films with thickness of about 2 μm. All chemical reagents used in this study were of analytical grade and were supplied by Sigma–Aldrich (Australia). Nitrogen adsorption–desorption experiments were performed at 77 K with a Micromeritics ASAP 2020MC. The samples were degassed at 300 °C for 5 h prior to measurement. The pore volume was estimated from the desorption branch of the isotherm at $P/P_o = 0.98$ assuming complete pore saturation. The morphology and microstructure of the mesoporous $TiO_2$ were investigated using an X-ray diffractometer (XRD, PW1140/90) with CuKa radiation (25 mA and 40 kV), and a transmission electron microscope (TEM, JEOL-2011).

Three typical dyes including rhodamine B (RB), methyl orange (MO), and methylene blue (MB) were studied for photodegradation. The molecule structures of the dyes are shown in Fig. 1. The concentrations of the dye solutions were 50 mg/L. 10 mg of the mesoporous $TiO_2$ samples were added into 20 mL dye solution and the muddy solution was dispersed with an ultrasonic instrument for 30 min, and then irradiated by sunlight. The temperature was in the range of 22–26 °C and the average sunlight intensity was about 6.5 kW h $m^{-2}$. The pH of the samples was adjusted by using 0.1 mol/L HCl or 0.1 mol/L NaOH. After the photocatalytic experiment, the remaining dye solutions were collected and analyzed. A UV-240 UV–vis spectrometer was used to record the change of the absorbance of the dye solution.

## 3. Results and discussion

The $TiO_2$ mesostructures were formed using the evaporation induced self-assembly (EISA) approach, which has been established as an efficient process for the preparation of mesostructured oxide with controlled morphologies [24]. The wide-angle X-ray diffraction pattern of the sample is shown in Fig. 2a. The main diffraction peaks correspond to the tetragonal structure of anatase $TiO_2$. Fig. 2b exhibits the small angle X-ray diffraction spectrum, clearly showing the principle diffractional peak (1 0 0) and suggesting a well-defined hexagonal mesostructure. The $N_2$ sorption isotherms of mesoporous $TiO_2$ show type-IV curves with clear condensation steps, indicating uniform mesopores (Fig. 2c). The Langmuir surface area which is calculated from nitrogen sorption results to be 172.2 $m^2/g$. Fig. 2d shows the derived pore size distributions. The pore size distributions of the samples are observed to be narrow and the corresponding peak is located at about 4.8 nm, confirming the formation of the mesostructure [25].

The mesostructure of the $TiO_2$ was further investigated by transmission electron microscopy (TEM). The TEM images of the ordered mesoporous structure of the $TiO_2$ are displayed in Fig. 3. As shown in Fig. 3a, the cross-sectional view of the mesoporous $TiO_2$

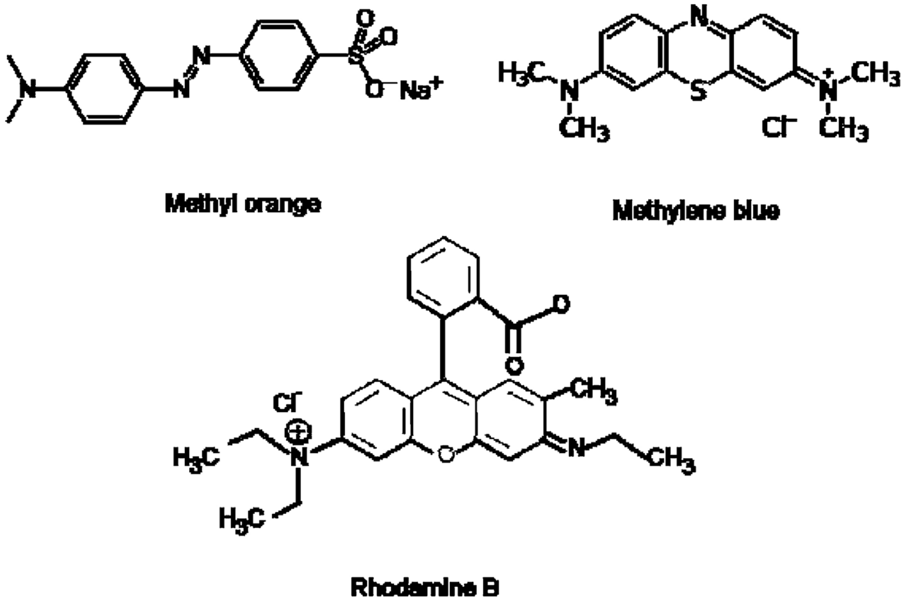

**Fig. 1.** The molecule structures of dyes.