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Research paper

Photocatalytic microreactors based on nano TiO₂-containing clay colloidosomes

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ABSTRACT

Photocatalytic microcompartments have attracted increasing interests in the field of photocatalytic degradation. This work focused on the construction and characterization of a novel photocatalytic microsystem comprising polydopamine-modified TiO₂ nanoparticles (NPs) dispersed in clay-based colloidosomes, utilizing partially hydrophobic montmorillonite particles as building blocks for colloidosome membrane assembly. Assessment of photocatalytic activity was performed by photocatalytic degradation of methylene blue and rhodamine B, with the small molecule dyes decomposing within the compartmentalized microsystems. Encapsulation of TiO₂ NPs within the clay colloidosomes enhanced the efficiency of photocatalytic degradation. The results showed a selective degradation of methylene blue in the presence of rhodamine B, with associated $\lambda_{MB}/\lambda_{RhB}$ of 2.04. The present study indicates that photocatalytic semiconductor NPs encapsulated in clay colloidosomes form a promising microsystem with great potential for application in environmental remediation.

1. Introduction

Living systems, particularly eukaryotic cells, contain many micro-compartmentalized organelles with specific functions for synthesizing materials or transferring energy to sustain life. One challenge in materials science is to mimic subcellular organelles to construct micro-reactors with specific functions using a bio-inspired bottom-up approach (Koo and Velev, 2013; Hansen et al., 2016; Tamate et al., 2016; Buddingh and van Hest, 2017). These functions include photocatalysis, which is emerging as a new area of environmental science (Das and Srivastava, 2016). Photocatalysts that are encapsulated in microsystems have advantages over photocatalysts suspended in a liquid medium, including simple separation from aqueous conditions, controlled diffusant transport rates into or out of solutions, and enhanced reactant conversion efficiency (Rosenberg and Dan, 2011; Dan, 2012; Koo and Velev, 2013; Gao et al., 2017). As such, encapsulation has been recognized as an effective strategy for designing photocatalytic micro-reactors (Ma et al., 2014; Das and Srivastava, 2016).

Clay minerals and their derived nanocomposites have long been used as a class of effective and economically feasible materials for removal of

pollutants such as dyes, heavy metals and organic substances from wastewater (Selvam et al., 2008; Zhou and Keeling, 2013; Zhou et al., 2016). However, conventional physical adsorption methods have suffered from the limitations, including incomplete precipitation and sludge generation with further desorption treatment often required. One of most promising alternatives for the removal of various dyes from wastewater is photocatalysis, which achieves removal and decomposition of dyes in a single step under light illumination. To combine the excellent adsorptive advantages of clays with improved photocatalytic reactivity, semiconductors such as TiO₂-supported clay nanocomposites have been developed for synergistic photocatalytic adsorption of organic dyes (Ngho and Nawi, 2016; Mishra et al., 2017a,b). Several immobilization strategies have been used for preparation of such TiO₂-clay hybrid nanocomposites, including TiO₂ nanoparticles (NPs) loaded on the mineral surface (Li et al., 2009; Hajjaji et al., 2016; Szczepanik, 2017), TiO₂ NPs intercalated into pillared clay (Damardji et al., 2009; Sun et al., 2015), and TiO₂ NPs deposited on the exfoliated clay surface (Nakato et al., 2016; Tobajas et al., 2017). However, TiO₂-clay nanocomposites are generally utilized in powder form. Consequently, there are difficulties with separation and recovery of TiO₂-clay nanocomposites from aqueous suspensions.

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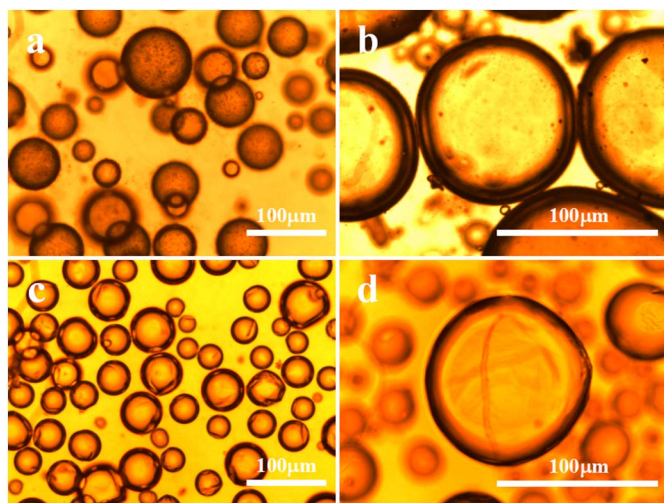


Fig. 1. The optical microscopy images of PDA-TiO₂@clay colloidosomes in water-in-oil continuous phases (a, b) and transferring into aqueous phase (c, d).

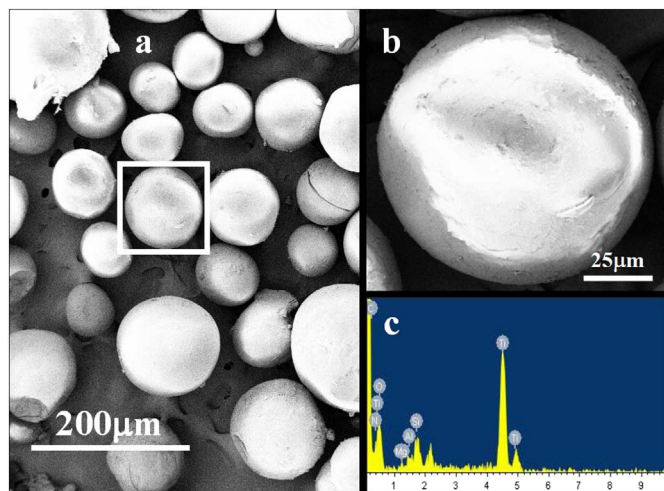


Fig. 2. SEM observations of PDA-TiO₂@clay colloidosomes. The SEM image (a), The enlarged image of selected area (b), EDS analysis of PDA-TiO₂@clay colloidosomes (c).

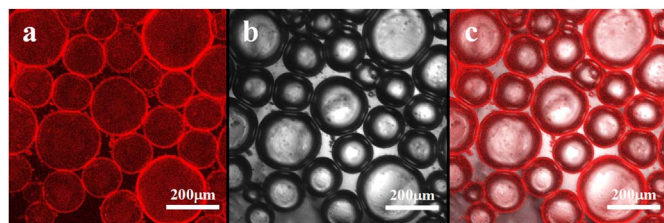


Fig. 3. CLSM images of PDA-TiO₂@clay colloidosomes. The fluorescence image (a), the optical transmission microscopy image (b), the overlay image of (a) and (b) (c). Rhodamine B was used of 100 μg mL⁻¹.

Bio-inspired photocatalytic microsystems based on semi-permeable colloidosomes (microcapsules) have been reported using various embedded photocatalysts, including TiO₂, ZnO, and Pt/ZnO (Hanczyc et al., 2003; Li et al., 2009; Subramaniam et al., 2011; Huo et al., 2014; Das and Srivastava, 2016; Nakato et al., 2016). In our previous work, we successfully prepared novel cross-linked water-in-water clay-based colloidosomes using modified montmorillonite particles as a building

block to produce Pickering emulsion droplets (Sun et al., 2016). Here, a novel light-driven mimetic microreactor system has been demonstrated, in which where photocatalytic TiO₂ NPs are encapsulated in clay-based colloidosomes to combine the hybrid advantages of clay-based colloidosomes and wide band-gap semiconductors. The photocatalytic activities and stabilities of the TiO₂ NP-containing clay colloidosomes (TiO₂@clay colloidosomes) were investigated in detail. The photocatalytic performance of the TiO₂@clay colloidosomes was further tested via degradation experiments with methylene blue (MB) and rhodamine B (RhB) using TiO₂@clay colloidosomes as photocatalysts.

2. Materials and methods

2.1. Materials

The octadecyl trimethyl ammonium bromide (OTAB)-modified montmorillonite (HFGEL-310, organic bentonite) was provided by Zhejiang Fenghong New Materials Co., Ltd. (see detailed XRD pattern in Fig. S1, Supporting information). P25-type TiO₂ NPs were purchased from Degussa, Germany. Dopamine hydrochloride, MB and RhB were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tris (hydroxymethyl)aminomethane hydrochloride (Tris-HCl), hydrochloric acid, toluene, and tetraethoxysilane (TEOS) were purchased from Chengdu Kelong Chemical Reagent Company. All chemical reagents were of analytical grade unless otherwise specified. All solutions were prepared with ultrapure Milli-Q water (resistance > 18.2 MΩ·cm).

2.2. Surface modification of TiO₂ NPs

The surfaces of the TiO₂ NPs were modified with polydopamine (PDA), formed by the polymerization of dopamine under alkaline conditions, in order to improve their hydrophilicity and photocatalytic activity (Mao et al., 2016). TiO₂ NPs (0.5 g) and dopamine hydrochloride (0.05 g) were added to 100 mL of 0.1 M Tris buffer solution (pH 8.0). The pH of the suspension was slowly adjusted to 8.5 by the addition of ammonium hydroxide (NH₃·H₂O). The reaction mixture was kept in the dark for 24 h at room temperature with magnetic stirring (1300 rpm). The PDA-coated TiO₂ NPs (PDA-TiO₂ NPs) were isolated by centrifuging the reaction mixture at 8000 rpm for 5 min. The collected TiO₂ NPs were washed 3 times with water and 3 times with ethanol.

2.3. Preparation of PDA-TiO₂@clay colloidosomes

The PDA-TiO₂@clay water-in-oil colloidosomes were prepared by a Pickering emulsion method (Sun et al., 2016). Typically, an aqueous solution containing a PDA-TiO₂ NPs dispersion was added to 10 mL toluene containing 1 mg·mL⁻¹ of modified montmorillonite dispersion, with a TiO₂/clay weight ratio of between 0.4 and 20 and a water/toluene volume fraction of 0.5. The mixture was homogenized for 1 min using a homogenizer (Fluko, F10) at 10,000 rpm. Following cross-linking by hydrolytic reaction with 60 μL of TEOS, the water-in-oil PDA-TiO₂@clay colloidosomes were transferred into a continuous water phase to prepare water-in-water PDA-TiO₂@clay colloidosomes.

2.4. Photocatalytic dye degradation

Photocatalytic dye degradation experiments were performed by mixing 300 μL of a stock solution of MB (0.5 mg·mL⁻¹, Abs_{max} = 668 nm) or RhB (0.5 mg·mL⁻¹, Abs_{max} = 555 nm) with 29.7 mL of Milli-Q quality (18.2 MΩ·cm) water and adding 100 mg of PDA-TiO₂@clay colloidosome dispersion, followed by exposure to an ultraviolet (UV) lamp (365 ± 10 nm at 18 W). At 10 min intervals, 2 mL aliquots were

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