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Regular Article

Bifunctional supported ionic liquid-based smart films for dyes adsorption and photodegradation

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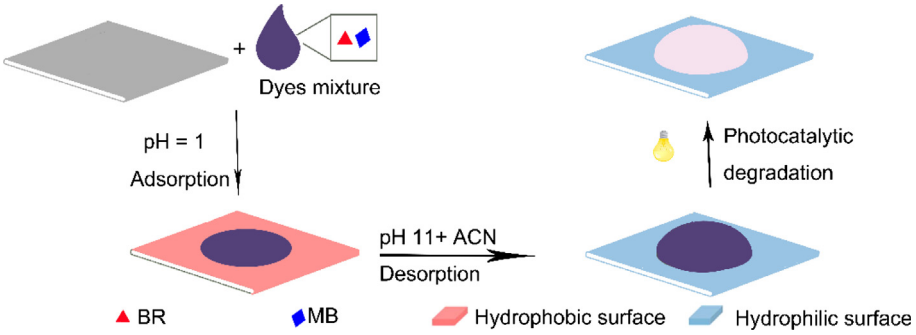
GRAPHICAL ABSTRACT



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ABSTRACT

Herein, novel bifunctional smart films containing poly(styrene-butyl acrylate-ionic liquids) (P(S-BA-ILs)) and TiO_2 were first prepared by a simple cast method and then used to demonstrate a superior bifunction of adsorption/desorption for dyes due to the property of reversible wettability switching and photodegradation under ultraviolet (UV) irradiation due to the addition of TiO_2. The glass transition temperature (Tg) of P(S-BA-ILs) latex was characterized using a differential scanning calorimeter (DSC). The surface properties of films (P(S-BA-ILs)-TiO_2) were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), attenuated total (internal) reflection Fourier transform infrared spectroscopy (ATR-FTIR), and water contact angle (WCA) measurements. The results showed that the films displayed reversible wettability switching of hydrophobicity (124.5 ± 2°)/hydrophilicity (10.5 ± 2°) and hydrophobicity (35.1 ± 2°)/hydrophilicity (93.1 ± 2°) triggered by pH and temperature, respectively. Additionally, the films exhibited large adsorption capacities for pollutants at different pH: brilliant red (BR) (6.6 mg cm^{-3}) at pH 1, methylene blue (MB) (12.4 mg cm^{-3}) and phenol (1.1 g cm^{-3}) at pH 11, and metal ions As, Mo and Sb (1.11, 1.57, and 1.25 mg cm^{-3}) at pH 1, as well as superior reusability and excellent in situ photodegradation performance. The convenient preparation of the smart films as well as the good bifunction of adsorption and photodegradation for dyes predicts potential for application to curb water pollution.

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1. Introduction

Stimuli-responsive films, also termed smart films, prepared by natural inspiration have aroused great interest due to their intelligent controllable potential. According to the constituents, smart films are classified as hydrogel thin films with a swelling and shrinking three-dimensional network, or grafted polymer layers [1]. By adjusting the small changes in environmental triggers such as pH [2], temperature [3], light irradiation [4,5], solvent/solute [6], electrical potential [7], and molecular interaction (chirality, biomolecule, CO_2, and so on) [8–11], their physicochemical properties can be significantly regulated in a controlled fashion, which can not only help replace human labor but also realize some functions [12]. Smart films have been widely used for applications such as (1) smart coatings (bioadhesion, antibacterial properties, self-cleaning and self-healing) [11,13–15]; (2) chemical gates for the regulation of flow and permeability [16]; (3) loading and control of the release of proteins, cells, carbon nanotubes and fluorescein [8,17–19]; (4) sensors for selective detection of analyte [20]; and (5) water/oil mixture separation [21,22]. For example, Zhao et al. synthesized a CO_2-responsive polymer brush for the capture and release of proteins. When the film was incubated with a solution saturated with nitrogen (N_2), the chains in the film collapsed (hydrophobic) and the protein was adsorbed; after the film was wetted with solution saturated with CO_2, the film became extended (hydrophilic), with the protein released from the surface [8]. Light responsive smart films or self-cleaning smart coatings have been used to realize switchable wettability via photocatalytic degradation of a hydrophobic coating, or degradation of the organics staining the coating [14,23]. However, the current study of such smart films has been centered on only single function films, with no reports of bifunctional smart films. As is known, compared with single-functional materials, bifunctional materials show many advantages in practical applications, such as simple preparation processes, reduced cost and phase transfer secondary pollution, and a favorable commonality [24]. Therefore, more bifunctional smart films are urgently needed to achieve environmentally friendly and highly efficient industrial processes.

In recent decades, room-temperature ionic liquids (ILs), referred to as "designer liquids", have emerged, which are a novel, extremely large class of molten salts composed of large asymmetric organic cations and inorganic or organic anions [25]. Supported ILs (SILs), an important branch in the IL community, *refer to ILs immobilized on solid, polymer, liquid or aerogel supports by either covalent or noncovalent bonds using various methods, including simple physisorption, self-assembly or polymerization* [26]. SILs present some of the unique properties of ILs (intrinsic low surface tension, thermal, chemical and photocatalytic stability, nonflammability, and functionalization properties) [27–32], along with the intrinsic properties such as prevention of leaching and good recovery due to the synergistic effect of the supports and ILs, which makes it possible to produce new functional materials. Recently, ILs and SILs have been widely applied to catalytic reactions, separation technologies, electrochemistry, antibacterial study, surface modification, and the self-cleaning field [33–35]. In particular, due to their ability to form strong electrostatic and hydrogen bonding interactions with dissolved molecules, ILs and SILs have been widely used to prepare separation and adsorption materials. In our laboratory, a series of SIL materials have been developed for the separation and adsorption of a biomacromolecule [36–38]. As far as we know, bifunctional smart-film-based SILs for dye adsorption and photodegradation have not yet been reported.

Herein, bifunctional smart films containing TiO_2 nanoparticles and P(S-BA-ILs) latex produced by soap-free emulsion polymerization were first produced by a simple cast approach. The wettability switching of the smart films was evaluated by measurements of the water contact angle (WCA). The films showed a good reversible wettability transition between hydrophobicity and hydrophilicity triggered by pH and temperature, respectively (Fig. 1(1)). Given the properties of reversible wettability switching and the addition of the photocatalyst TiO_2, it is possible to construct bifunctional films that can both adsorb and photodegrade dyes. As a proof of concept, the resultant bifunctional smart films were used to both separate and photodegrade dyes, which demonstrated their advantage for applications and potential for dye treatment and water purification (Fig. 1(2)).

2. Experimental section

2.1. Chemicals and materials

Styrene (S, 99%), *n*-butyl acrylate (BA, 99%), ammonium persulfate (APS, 98%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AIBA, 98%), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol (EtOH), acetonitrile (ACN) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. Ltd.

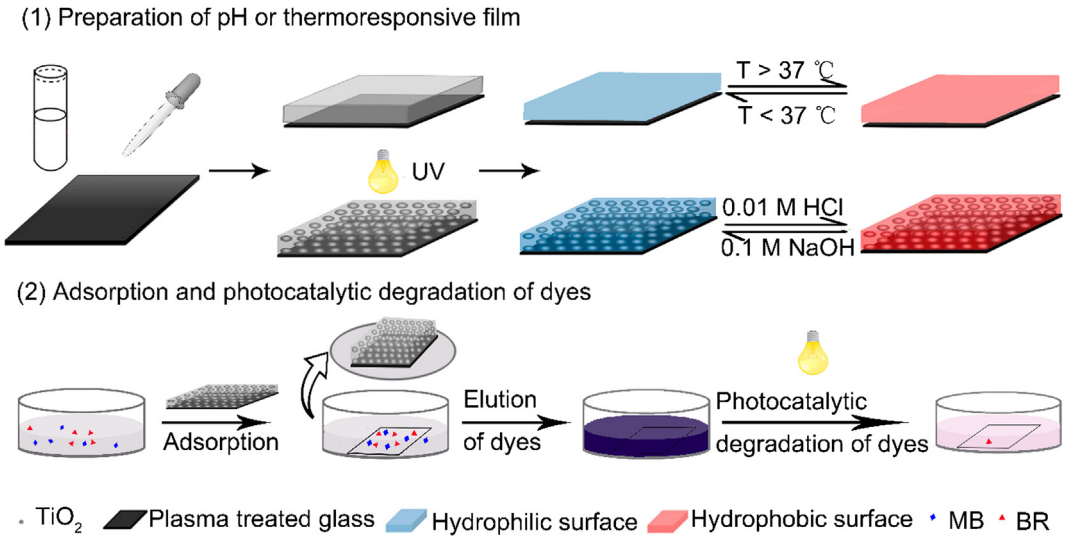

Fig. 1. Schematic illustration showing the preparation of the pH and thermoresponsive film and its application for dye adsorption and photodegradation.

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