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Mesoporous anatase coatings for coupling membrane separation and photocatalyzed reactions

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Abstract

The main goal of the present study is the coupling of membrane separation and photocatalyzed reactions based on the use of anatase mesoporous coatings. The first type of coupled device deals with the preparation of separative photoactive anatase membranes on ceramic asymmetric supports. The intrinsic photocatalytic properties of the separative layer could be in this instance used for antifouling purposes or in photocatalytic reactors. The water permeability and the molecular weight cut-off of the prepared membranes are determined. Their photocatalytic activity is evaluated from photodegradation experiments of an organic dye in aqueous solution. A second type of configuration, based on the deposition of a photoactive anatase layer on the grains of a conventional asymmetric ceramic support, is discussed. The separative function is provided by the non-photoactive top layer, whereas the opposite side is irradiated with UV light. An example of a potential application of such a membrane involves water treatment by ultrafiltration. The retention of colloids and macromolecules would be ensured by the separative top layer whereas photodegradation of smaller organic molecules remaining in the permeate is performed by UV irradiation of the opposite side. A preliminary experiment is carried out to validate this concept.

Keywords: Anatase; Mesostructured coating; Photoactive membrane; Coupled photo-oxidation

1. Introduction

Titanium dioxide is a semiconductor oxide exhibiting very attractive photoactivity properties under UV irradiation. The two main crystalline forms, anatase and rutile, are both photoactive [1]. The gap of anatase is equal to 3.23 eV (384 nm) whereas the gap of rutile is equal to 3.02 eV (411 nm) [2]. The crystalline form anatase is known to be the most photoactive [3,4]. On the other hand, mixtures of anatase and rutile phases like for instance the standard powder P25 (from Degussa, anatase: 80%; rutile: 20%) enable to limit the recombination of charges due to the lower gap of rutile but their photocatylitic activity strongly depends on the compounds to be degraded [5,6]. In the case of anatase, it has been shown that the optimal crystallite size is in the range 6–10 nm; it is the best compromise between the electron-hole recombination rate and good accessibility to the crystallites surface [7–9]. The TiO_2 properties give rise to various technological applications like photovoltaic cells, self-cleaning layers and sensors [10–12]. In practice, most of the photocatalytic processes in liquid phase and using membranes operate with TiO_2 in suspension or immobilized in different plane supports [13–15]. An evolution proposed by Zhang et al. (2003) consists of a tubular photocatalytic reactor with the light source inside the tube, but without the idea of coupling [16]. The main problem encountered when the photocatalyst is immobilized on the support is the detachment of the photocatalyst particles by the treated liquid during its motion inside the reactor [17,18]. The photocatalytic function and the membrane separation are not coupled.

The aim of this study is to evaluate the possibility of direct coupling membrane separation and photocatalyzed reaction with the use of mesoporous anatase coatings. The coupling of these two operations for a given process of purification or a synthesis is potentially interesting from a technical and/or

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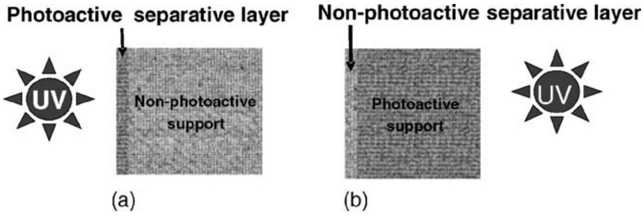

Fig. 1. Principle of direct coupling separation/photocatalysis in the case of an asymmetric ceramic membrane: (a) configuration 1: a photoactive separative top layer is deposited on a non-photoactive porous substrate. The separative side is irradiated and (b) configuration 2: a non-photoactive separative top layer is deposited on a photoactive porous support. The side opposite to the separative layer is irradiated.

an economic point of view. Only a few articles or patents have already described the use of photoactive membranes. In some cases, the photocatalyst is immobilized in a polymeric membrane for antifouling or waste water treatment [18–20]. In other cases, a photoactive TiO_2 membrane is used for the photo-oxidation of gaseous methanol [21] or VOC [22].

The synthesis of ordered, anatase-based mesoporous coatings and membranes allows us to suggest two different types of configuration. The first one consists of the preparation of a photoactive and mesoporous membrane. With such a pore size, as a filtering barrier, the probability for a molecule to be in contact with the photoactive walls is close to 1. On the other hand, ordered mesoporosity like the one obtained by mesophase templating offers an opportunity to optimize two main characteristics of the separative layers [23]: their permeability and their permselectivity. For these membranes, the irradiation must be applied on the separative and photoactive layer side which is generally in contact with the feed solution (Fig. 1a). A second configuration should be also considered. It consists of the use of a conventional asymmetric membrane, without photoactive separative layer, but presenting a photoactive coating on the grain surface of the membrane support (Fig. 1b). In this case, the irradiation should be applied on the opposite side of the membrane, in contact with the permeate. Such a configuration could be applied for the waste water treatment with a low ultrafiltration membrane allowing the retention of the colloids or of the macromolecules, and allowing the permeation of small molecules like organic volatile compounds (VOC) which would be photo-oxidized on the other side of the membrane (Fig. 2).

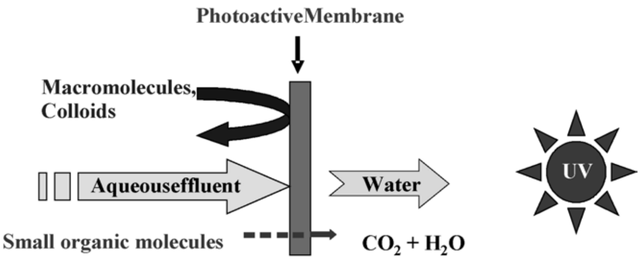

Fig. 2. Schematic representation of a potential use of configuration 2 in the case of ultrafiltration of waste water: the separative layer in contact with the feed enables the retention of macromolecules and colloids; the small organic molecules which are not retained by the membrane are degraded by UV irradiation of the opposite side of the membrane consisting in a photocatalytic porous support.

A method has recently been developed for the preparation of layers with ordered mesoporous structure obtained via templating effect [24,25]. It is here applied to prepare photoactive coatings and membranes. The permeability, the selectivity and the photoactivity of these anatase mesoporous layers will be described in this study.

2. Experimental

2.1. Material preparation

The mesoporous thin layers and membranes have been synthesized from an anatase hydrosol obtained from the acidic hydrolysis of titanium isopropoxide and the use of the templating effect of liquid crystal mesophases. The synthesis conditions are already detailed in previously published papers [24,25]. The selected amphiphilic molecules are triblock copolymers poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide): $EO_{20}PO_{70}EO_{20}$ and $EO_{106}PO_{70}EO_{106}$, labeled P123 and F127, respectively, and provided by BASF. After the precursor hydrolysis, the structuring agent is introduced or not into the anatase sol. The samples obtained without surfactant will be labeled WS and those obtained with the copolymer P123 or F127 will be later labeled P70 and F67, respectively, in reference to the copolymer molar fraction in the layers after drying [24,25]. These compositions correspond to optimized materials in terms of quality and stability of the mesostructure. The layers have been deposited by dip-coating on one side of glass slides for the photoactivity characterization (layer surface: 5 cm^2, withdrawal rate 5 cm min^{-1}). The photoactive membranes have been prepared by slip-casting (emptying rate 5 cm min^{-1}) on asymmetric tubular supports (length 25 cm, internal diameter 0.7 cm) in alumina with a 5 nm pore-sized gamma alumina top layer. For the preparation of photoactive supports, alumina disks (diameter 4.7 cm) with a 1.8 μm average pore size, have been immersed in the anatase sols and removed with a withdrawal rate of 5 cm min^{-1}. In parallel sols were dried as thick layers in large beakers to obtain equivalent powders for additional analyses. After drying at room temperature and controlled humidity during one day, the samples were treated at 150 °C during 2 days and then thermally treated up to 350 °C because this temperature gives rise to the best compromise between the required anatase crystallite size and a high specific surface area [24].

2.2. Characterization

The layers have been studied using transmission electron microscopy (TEM; JEOL JEM 2010). For this purpose, TEM samples were prepared by scrapping the films and deposition of chips on copper grids. Scanning electron microscopy