



Rapid thermally processed hierarchical titania-based hollow fibres with tunable physicochemical and photocatalytic properties

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ABSTRACT

A series of photocatalytic TiO₂–carbon composite hollow fibres (HFs) was prepared in this study by a wet-dry phase inversion spinning method followed by a rapid thermal processing (RTP). The RTP method consists of two stages: (1) calcination at 800 °C for 15 min encased in a quartz tube followed by (2) a short open heating exposure at 800 °C for 0 to 7.5 min in air. The innovative two-stage RTP method led to a time saving of more than 90%. Results revealed that the pyrolysis conditions during the second stage of HF fabrication were essential to the final physical and chemical properties of resultant TiO₂–carbon HFs, such as TiO₂ crystallinity and carbon content, mechanical, textural and electronic properties, as well as photocatalytic reactivity. The best results show that HFs pyrolysed for a short duration (< 2 min) in the second stage produced a high microporous surface area of 217.8 m²·g⁻¹, a good mechanical strength of 11 MPa and a TiO₂ anatase-to-rutile (A/R) ratio of 1.534 on the HF surface. The HFs also achieved a 68% degradation of acid orange 7 dye with a k_{app} of 0.0147 min⁻¹ based on a Langmuir–Hinshelwood model during the photocatalysis under UV light. Thus, this work provides a new synthesis protocol with significant time and cost savings to produce high-quality HFs for wastewater treatment.

1. Introduction

A tremendous, concerted research effort in designing advanced, integrated technologies for wastewater treatment and water purification while reducing energy and environmental footprint has gained momentum. Pollution arising from the wastewater effluents of the dye industry leads to the destruction of ecosystems and to the detriment of human health. Without adequate and proper treatment of these dye-containing effluents to remove the harmful toxic dyes before discharge, these effluents can cause short-term acute ecotoxicity and long-term bioaccumulation in ecosystems.

In the last decade, photocatalytic membranes in various geometry and size have been reported [1,2]. There are several technological and environmental challenges relating to the use of photocatalytic nanomaterials for water treatment. Titanium dioxide, or titania (TiO₂), an n-type transition metal oxide semiconductor, has been widely utilised as a

photocatalyst to initiate the degradation of organic pollutants. It has been applied to photocatalytic oxidation of several industrial and pharmaceutical effluents, such as 4-methoxybenzyl alcohol [3], ciprofloxacin [4], reactive dyes [5,6], nitrobenzene [7,8] and benzylparaben [9]. When a higher photon energy than the band gap of TiO₂ (anatase 3.20 eV and rutile 3.02 eV) is absorbed, electrons will be excited from the filled valence band (VB) to the empty conduction band (CB), leaving negative electrons in the CB and positive holes in the VB. The energy of excited electron–hole pairs will either react with oxygen or water and eventually generate highly reactive hydroxyl radicals to decompose hazardous organic compounds [10,11]. Therefore, TiO₂ nanoparticles are widely investigated as a well-known, effective and stable photocatalyst. As a photocatalyst in a slurry system, TiO₂ nanoparticles need to be reclaimed to minimise the negative environmental influence [5]. The release of TiO₂ nanoparticles to the environment will have a long-term toxicity and ecological impact on the aquatic organisms [12], even

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though TiO₂ is considered to be biocompatible and FDA approved as a colour additive for human use [13–15].

To satisfy these requirements, it is essential to immobilise TiO₂ nanoparticles onto a solid support while keeping the TiO₂ exposed on the surface for maximising photocatalysis efficacy. It is well documented that sol–gel syntheses using TiO₂ precursors, including tetrabutyl orthotitanate [16], titanium isopropoxide [17,18], titanium tetrachloride [19], and titanium glycolate [20], followed by dip-coating [21] and a calcination process can be used to construct the photocatalytic devices for environmental applications. However, the conventional thermal calcination is time-intensive and requires a high-temperature sintering process to coalesce the inorganic oxides together to confer desired properties such as mechanical strength and photoactivity. Despite this, TiO₂ is known to undergo grain growth and usually a phase transformation from the anatase to rutile phases during the high-temperature thermal process at 400–600 °C for powders [22] or at 700–800 °C for non-powders [2,23–25]. Such changes will significantly decrease the photocatalysis efficiency for the intended purposes. Therefore, a new protocol is urgently needed to avoid not only the energy penalty but also the undesired morphological changes.

Thus, in this paper, an innovative two-stage rapid thermal processing (RTP) protocol is developed for the synthesis of TiO₂-supported hollow fibres (HFs). This technology was firstly applied in the preparation of glass-carbon HFs by sintering particle-polymer–solvent systems to pyrolyse the polymer [26]. As the HF configuration has an extremely high surface area to volume ratio and a sponge-like, porous inner structure [27], TiO₂-carbon HFs can create a reactor that has an increasing selectivity and efficiency by combining photocatalysis and phase separation processes in one step [15,28,29]. The new RTP protocol takes the advantage of partially carbonizing the polymer binder with a very short heating duration (in minutes) under a constant temperature of 800 °C.

Essentially, RTP involves a simple, short, rapid firing/dwell time during the calcination process to significantly reduce the fabrication time. As RTP is an emerging technique for fabricating inorganic thin film membranes, the main principle of RTP is to heat the top layer with a short isothermal hold before rapidly cooling the HFs to room temperature. This method allows only the top layer to be heat-treated to achieve the desired structure/properties whilst keeping the support relatively intact. The first stage involves a short partial pyrolysis of the polymer binder to form composite of TiO₂–carbon HFs, which is then subjected to a second stage RTP protocol to create the hierarchical porous TiO₂–carbon HFs, where the TiO₂ is surface-exposed for photocatalysis whilst the carbonaceous char offers mechanical strength and microporosity as a structural support. In addition, the presence of carbonaceous material has previously been demonstrated to reduce TiO₂ aggregation and the phase transformation during high-temperature calcination [24,25]. Therefore, this study systematically investigates the effect of RTP (fast and short temperature-heating protocol) on the mechano-physicochemical and photocatalytic properties of the final composite HFs for the decomposition of organic pollutants in wastewater.

2. Experimental

2.1. Chemicals and materials

In this study, all the chemicals and reagents were from Sigma Aldrich (ACS grade) and used without further purification. The specific details of the Degussa P25 titanium dioxide (TiO₂) nanoparticles were reported in an earlier study [30].

2.2. Fabrication of HF membranes

To prepare the HFs, a spinning-pyrolysis technique was employed [2]. Briefly, Degussa P25 TiO₂ powder was mixed with poly(ether

imide) (PEI) and 1-methyl-2-pyrrolidinone (NMP) as a solvent at an 18:25:75 ratio (w/w) for 24 h until a homogenous state was achieved, and then degassed under vacuum for another 24 h. The spinning dope was then extruded through a tube-in-orifice spinneret (OD = 2.5 mm and ID = 0.8 mm). The pressure in the spinning dope and airgap was maintained at 4 bars and 50 mm, respectively. Phase inversion was induced from the inner side of the HFs using deionised (DI) water as a bore fluid followed by the outside in a DI water bath, where the green fibres were left immersed for 24 h. Then, the TiO₂/PEI green fibres were dried for 24 h at 60 °C. A muffle furnace was used for the calcination without the introduction of any specialised gases, which was preheated to 800 °C. Before pyrolysis, the green fibres were placed inside a double open-ended quartz tube (length = 20 cm; OD = 8 mm) to minimise the geometric curvature. In the first-stage calcination, the HFs were directly placed into the preheated furnace for a fixed 15 min holding time followed by cooling for 15 min outside of the furnace until reaching room temperature. Then in the second-stage RTP calcination, the HFs were removed from the quartz tube and calcined again in a preheated furnace (800 °C) for a pre-determined time of 0–7.5 min. During the two-stage RTP treatment, PEI was pyrolysed into carbonaceous char to afford the final composite TiO₂–char HFs.

2.3. Characterization techniques

The morphological structure of the pyrolysed composite HFs was examined using a field-emission scanning electron microscope (FESEM JEOL 7001F operating at 10 kV). The crystal structure and phase composition of the HFs (after grinding) were analysed by a powder X-ray diffraction system (XRD, Bruker AXS D8 advance, Cu-Kα radiation). Nitrogen sorption measurement of the HFs was performed using Micromeritic TriStar 3000 instrument after degassing the samples at 200 °C overnight under vacuum on a VacPrep061 (Particle and Surface Sciences Pty). The specific surface area was determined using the Brunauer, Emmett and Teller (BET) method and the total pore volume was taken from the last point of the adsorption isotherm (*ca.* 0.94P/P₀). The cumulative pore volume distribution was determined from the adsorption branch of isotherms using the Density Functional Theory (DFT) model of cylindrical pores with oxide surfaces. Dubinin-Astakhov and Barrett-Joyner-Halenda methods were taken to determine the average pore diameter of microporous and mesoporous materials, respectively. A three-point bending test was performed using an Instron 5543 universal machine with a set strain rate of 1 mm·min⁻¹ to measure the mechanical strength of the composite HFs. The maximum bending strength was calculated using the following expression for a simple tube adapted from previous studies [31,32]:

$$\sigma = \frac{8FLD}{\pi(D^4 - d^4)} \quad (1)$$

where σ is the bending strength (MPa), F is the load applied (N), and L , D and d are the span, the outer diameter and the inner diameter (mm) of the HFs, respectively. The UV–visible diffuse reflectance spectra of the HFs were recorded by a UV–Vis spectrophotometer (Evolution 220, Thermo Scientific) from 185 to 700 nm.

2.4. Photocatalysis evaluation of the HFs

The photocatalytic activity of the composite HFs was evaluated using four UV-A lamps (SYLVANIA Blacklite F8W/BL350, 330–370 nm emission; 8 Watt each) as the UV source. Acid Orange 7 (AO7) was used as a model colour dye due to its excellent stability under UV irradiation [33]. 25 mL of AO7 (5 ppm; pH 6.5) in a quartz reactor vessel was placed concentrically at 15 cm away from the UV lamps in the UV chamber to minimise the heating effect of the UV lamps. HF membranes weighing about 50 mg (4 × 1 cm pieces; membrane surface area: approximately 1.5 × 10⁻⁴ m²) were submerged in the AO7 solution in the reactor. Scheme 1 shows the batch catalytic reactor containing HFs and

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