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# **Rapid Thermally Processed Hierarchical Titania-based Hollow Fibres with Tunable Physicochemical and Photocatalytic Properties**

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## Abstract

A series of photocatalytic TiO<sub>2</sub>–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 TiO<sub>2</sub>-carbon HFs, such as TiO<sub>2</sub> 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 m<sup>2</sup>·g<sup>-1</sup>, a good mechanical strength of 11 MPa and a TiO<sub>2</sub> 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<sup>-1</sup> 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.

**Keywords:** Hollow fibre; Titanium dioxide; Rapid thermal processing; Photocatalysis; Carbon char

## 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 ( $\text{TiO}_2$ ), 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  $\text{TiO}_2$  (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,  $\text{TiO}_2$  nanoparticles are widely investigated as a well-known, effective and stable photocatalyst. As a photocatalyst in a slurry system,  $\text{TiO}_2$  nanoparticles need to be reclaimed to minimise the negative environmental influence [5]. The release of  $\text{TiO}_2$  nanoparticles to the environment will have a long-term toxicity and ecological impact on the aquatic organisms [12], even though  $\text{TiO}_2$  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  $\text{TiO}_2$  nanoparticles onto a solid support while keeping the  $\text{TiO}_2$  exposed on the surface for maximising photocatalysis efficacy. It is well documented that sol-gel syntheses using  $\text{TiO}_2$  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, TiO<sub>2</sub> 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 TiO<sub>2</sub>-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], TiO<sub>2</sub>-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 TiO<sub>2</sub>–carbon HFs, which is then subjected to a second stage RTP protocol to create the hierarchical porous TiO<sub>2</sub>–carbon HFs, where the TiO<sub>2</sub> 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 TiO<sub>2</sub> aggregation and the phase transformation during high-temperature calcination [30, 31]. 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 (TiO<sub>2</sub>) nanoparticles were reported in an earlier study [32].

### **2.2 Fabrication of HF membranes**

To prepare the HFs, a spinning-pyrolysis technique was employed [2]. Briefly, Degussa P25 TiO<sub>2</sub> 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 TiO<sub>2</sub>/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 to 7.5 min. During the two-stage RTP treatment, PEI was pyrolysed into carbonaceous char to afford the final composite TiO<sub>2</sub>–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-K $\alpha$  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.* 0.94 P/P<sub>0</sub>). 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<sup>-1</sup> 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 [33, 34]:

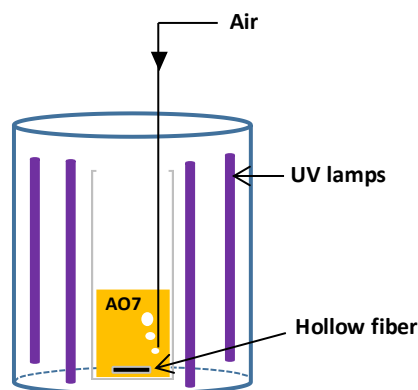
$$\sigma = \frac{8FLD}{\pi(D^4-d^4)} \quad (1)$$

where  $\sigma$  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 [35]. 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 ( $4 \times 1$  cm pieces; membrane surface area: approximately  $1.5 \times 10^{-4}$  m<sup>2</sup>) were submerged in the AO7 solution in the reactor. Scheme 1 shows the batch catalytic reactor containing HFs and AO7 solution.





**Scheme. 1.** Reactor set-up for AO7 photocatalysis.

A 30-min dark sorption experiment was performed prior to switching on the UV lamps. During the photocatalysis under UV exposure, the temperature of the reactor was gradually increased from room temperature (22 °C under air condition) to about  $40 \pm 1$  °C, of which the impact on the photodegradation of the AO7 dye was considered insignificant based on our observation, and hence, the effect was neglected in this study [2, 36]. The UV-Vis spectrum of the feed solution was recorded from 220 nm to 620 nm by a UV-Vis spectrophotometer (Evolution 220, ThermoScientific). The concentration of AO7 was determined by measuring the absorbance at 485 nm based on an established standard calibration curve. The photocatalytic activity of the membrane can be determined by the percent degradation of AO7 in the feed solution based on the equation,

$$\text{AO7 degradation (\%)} = (C_0 - C_t) / C_0 \times 100\% \quad (2)$$

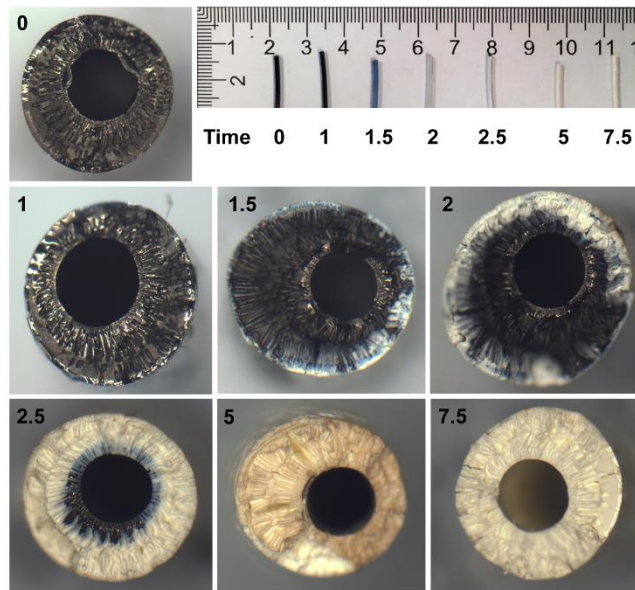
where  $C_0$  and  $C_t$  are the AO7 concentration in the reactor solution before photocatalysis (after dark sorption) and at a reaction time  $t$ , respectively. The UV absorbance of the AO7 solution was measured every 15 min until the experiment was stopped at 75 min.

### 3. Results and Discussion

#### 3.1 HF morphology and properties

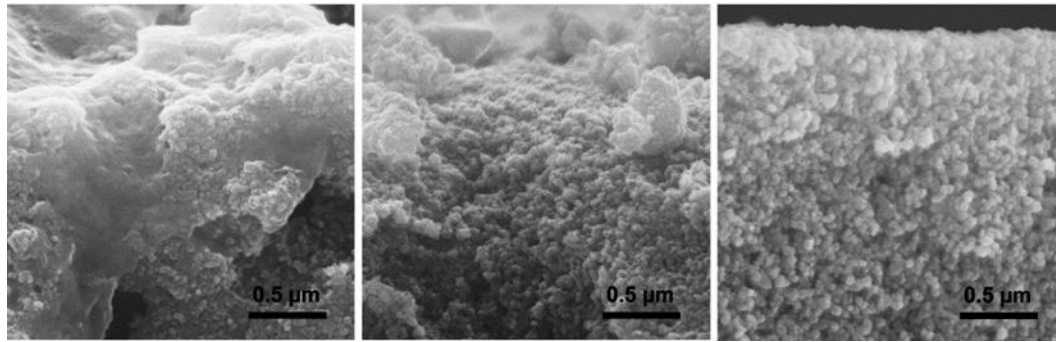
In the first stage, partial pyrolysis of HFs was carried out in an encased quartz tube to minimise direct heat transfer that would otherwise decompose the polymer binder completely. Instead, the HFs were pyrolysed for 15 min under this condition without any need of speciality gases and formed a homogeneous composite of TiO<sub>2</sub>-char HFs. As shown by the digital micrographs in Fig. 1, all the HFs had an average outer diameter and an inner diameter of  $1.40 \pm 0.10$  mm and  $0.67 \pm 0.07$  mm, respectively. When the HF was only exposed to the first-stage calcination (0 min), the appearance of the HFs was completely black, which is attributed to the characteristic colour of the carbonaceous char. After this stage, the 0-min HF lost 27% of its original mass as a result of the pyrolysis. As the time of the second-stage RTP calcination was extended from 1 to 7.5 min, the HFs (without the quartz sleeves) were exposed to the high temperature in an oxidative environment, which resulted in a systematic loss of the char as the black colour diminished from the outside inward progressively. As shown in Table S1, the HF mass also decreased rapidly to the minimum of 42 wt% due to the decomposition of the char.

Unsurprisingly, the white colour attributed to the TiO<sub>2</sub> nanoparticles emerged as the char was decomposed. It is interesting to note that the second-stage RTP heat treatment was predominately governed by the surface heat transfer from the outside to the inside of the HFs instead of a homogeneous heat treatment. This is a hallmark feature of the RTP technique which undertakes the adiabatic heating process [37]. As a result of this, with low calcination times (< 2 min), the HFs possessed a TiO<sub>2</sub>-exposed surface whilst keeping the bulk of the HFs a composite architecture at its inner luminal core. From this treatment protocol, one can appreciate that RTP is generally a surface treatment confined to the top layer of a thin film to reach the desired temperature with the char support experiencing only a mild temperature gradient [37, 38].



**Fig. 1.** Light microscopic images of TiO<sub>2</sub>-char composite HFs with increasing RTP calcination time (0-7.5 min) at 800 °C.

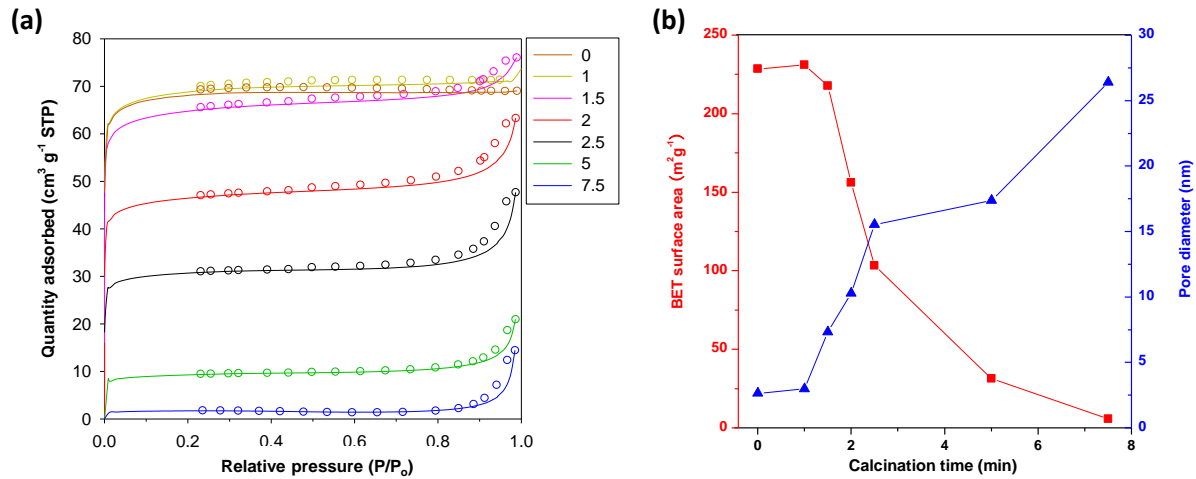
Further visual examination of the HFs was carried out by SEM. Fig. 2 shows the cross-sectional SEM images of the 1, 2 and 7.5-min HFs at the outer edge near the surface. With a short calcination time, the 1-min HF displayed a large quantity of PEI-derived char matrix, which bound TiO<sub>2</sub> nanoparticles. For the 2-min sample, the carbonaceous matrix was seen to be partially removed at the outer edge and TiO<sub>2</sub> nanoparticles were partially exposed. This SEM observation is in agreement with the light microscopic images. Further RTP treatment (7.5 min) removed all the carbonaceous char in the HFs and only the regular TiO<sub>2</sub> nanoparticles with approximately 50 nm in size remained after the calcination.



**Fig. 2.** Cross-sectional SEM images of composite TiO<sub>2</sub>-char HFs treated for different RTP calcination times (1, 2 and 7.5 min, left to right).

The textural property changes of the calcined HF during RTP processing were supported by the N<sub>2</sub> physisorption data. Fig. 3(a) shows the N<sub>2</sub> physisorption isotherms while Fig. 3(b) displays the results of surface area and average pore diameter of the HF as a function of RTP calcination time (0-7.5 min). From Fig. 3(a), at 0 min, the HF possessed a highly microporous texture as shown by a rapid increase in N<sub>2</sub> adsorption at a relatively low partial pressure of 0.2 P/P<sub>0</sub> and without any hysteresis at 0.9 P/P<sub>0</sub>. As the RTP time increased, the microporous portion derived from the char decreased sharply from 1 min to 7.5 min as depicted by the loss in surface area in Fig. 3(b). Concurrently, the average pore size of the HF increased as the char was decomposed leaving only the voids between TiO<sub>2</sub> nanoparticles, which is in good agreement with the SEM images. This can also be inferred from the increasing pore diameter of the HF from 2.7 to 26.4 nm as the RTP time increased, which demonstrates a systematic enlargement of the mesopores in the bulk. Based on the microscopic examination and the physisorption results, these mesopores are therefore found to be located mostly at the outer part of the HF but as the RTP time increased, the mesopores and macropores completely ensued the entirety of the HF due to the removal of microporous char. Moreover, it can be concluded that the textural property of the HF was hierarchical and asymmetric with shorter RTP times (< 2 min). From the N<sub>2</sub> adsorption/desorption isotherms and pore size distribution, hierarchical macro-

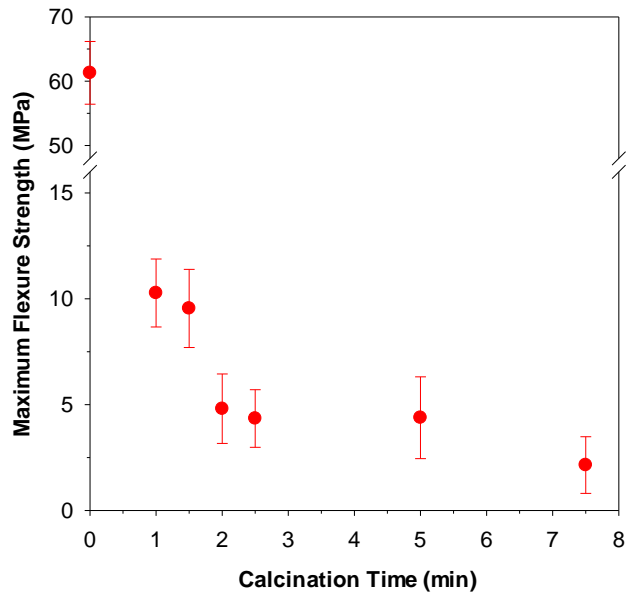
meso-microporous characteristics were shown in these HF samples in the cross-sectional, radial direction along the fibre axis, which might indeed enhance the mass transport in chemical reactions due to the increased surface area, and thus improve its overall catalytic efficiency [39, 40].



**Fig. 3.** (a) Nitrogen adsorption (line) and desorption (open circles) of the composite HF samples and (b) BET surface area and average pore diameter as a function of RTP time (0-7.5 min).

The mechanical property of the composite HF samples in terms of fracture strength was also examined by three-point bending tests. In previous studies, it was found that the carbonaceous matrix in silica composites can significantly enhance the mechanical strength due to an increased structural integrity formed by carbon-silica interconnection [41, 42]. Also, high mechanical properties have been demonstrated in metal-carbon nanotubes composites [43]. Similarly, the maximum bending stress results in Fig. 4 show that the removal of the carbonaceous matrix led to a reduction in flexure stress. With increasing RTP calcination time from 0 to 7.5 min, the maximum bending stress declined dramatically from 61 MPa to 2 MPa. Moreover, the bending stress of the 2-min sample reduced to half those of the 1-min and 1.5-

min samples. Therefore, it is necessary to use a short RTP time to maintain superior mechanical properties since the carbonaceous matrix acts as an important physical support to the overall HFs.



**Fig. 4.** Mean of maximum bending stress (MPa) plus two standard deviations of the composite HFs as a function of RTP calcination time.

The crystal morphology and phase composition of the  $\text{TiO}_2$  photocatalyst are also significant factors directly affecting the photocatalytic property of the HFs. Fig. 5(a) displays the XRD results of the  $\text{TiO}_2$  crystallinity on the HF surface with respect to RTP time. The 0-min sample showed mixed anatase and rutile phases as indicated by highly intense XRD peaks at  $25.4^\circ 2\theta$  (1 0 1) and  $27.4^\circ 2\theta$  (1 1 0), respectively. These peaks in the spectra match the JCPDS files 89-4921 and 89-4202 of tetragonal systems for the pure anatase phase and the pure rutile phase, respectively [44]. A clear trend can be seen that the disappearance of the anatase phase was offset by the emergence of the rutile phase. In general,  $\text{TiO}_2$  turns into the anatase

phase by calcination between 300 °C and 400 °C and transforms into the rutile phase when the temperature reaches above 600 °C [45]. However, this change was not found in this current study where the RTP temperature was set at 800 °C, which is significantly above this phase transition temperature. Regarding this, we propose that the TiO<sub>2</sub> nanoparticles were thermally shielded by a sacrificial layer of carbonaceous matrix. Hence, the anatase phase of TiO<sub>2</sub> was still predominantly preserved in the 0 to 2-min samples. This fact was most evidenced by the different crystalline composition of the surface versus interior layers of the 2-min HF as shown in Fig. 5(b). As the HF surface was continuously exposed to heat, the anatase TiO<sub>2</sub> rapidly turned into the rutile phase yet the lumen of the HFs still possessed a high degree of anatase TiO<sub>2</sub>.

From the XRD results, it can be seen that the transition from the anatase to rutile phase was easily controlled by the RTP time. By further analysing the anatase and rutile phase mass fractions from the intensities, the anatase-to-rutile (*A/R*) ratio of the HF samples can be calculated using Spurr's equation [46, 47]:

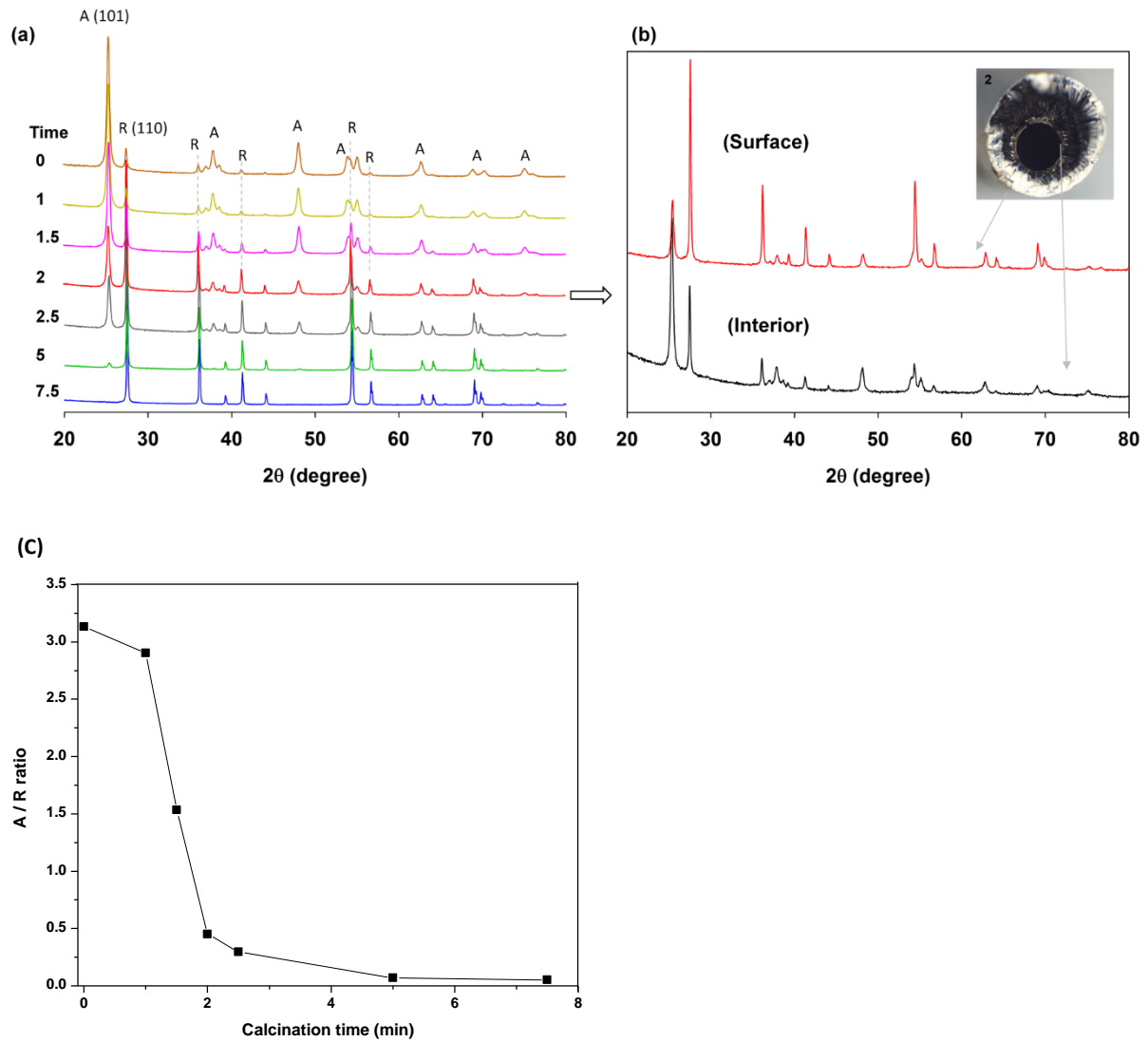
$$f_a = (1 + 1.26 I_r / I_a)^{-1} \quad (3)$$

$$f_r = (1 - f_a) \quad (4)$$

$$A/R \text{ ratio} = (f_a / f_r) \quad (5)$$

where  $f_a$  and  $f_r$  are the anatase and rutile fractions and  $I_a$  and  $I_r$  are the integrated intensities of the most intense peaks of anatase (1 0 1) and rutile (1 1 0), respectively. Fig. 5 (c) shows that the *A/R* ratio on the HF surface decreased systematically from 3.13 (0 min) to 0.30 (2.5 min) and then the ratio almost became nil (0.05). The *A/R* ratio of TiO<sub>2</sub> crystalline morphology once

again confirms that a shorter RTP time is desirable for an optimal balance between the anatase/rutile TiO<sub>2</sub> phases.

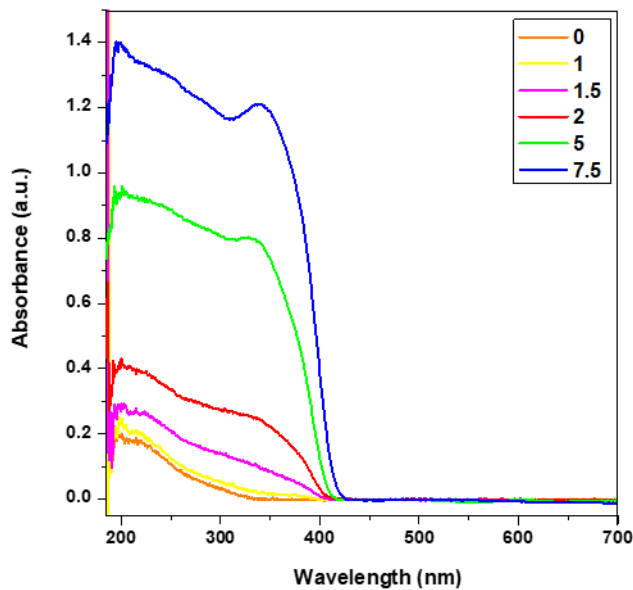


**Fig. 5.** (a) XRD patterns of the composite TiO<sub>2</sub>-char HF samples as a function of RTP calcination time; (b) XRD analyses of the surface and interior section of the 2-min HF sample; and (c) A/R ratio of the HF surface with increasing RTP time.

The effect of RTP calcination time on the optical property of grounded composite HF samples was also investigated by diffuse reflectance spectroscopy. The results after baseline correction are



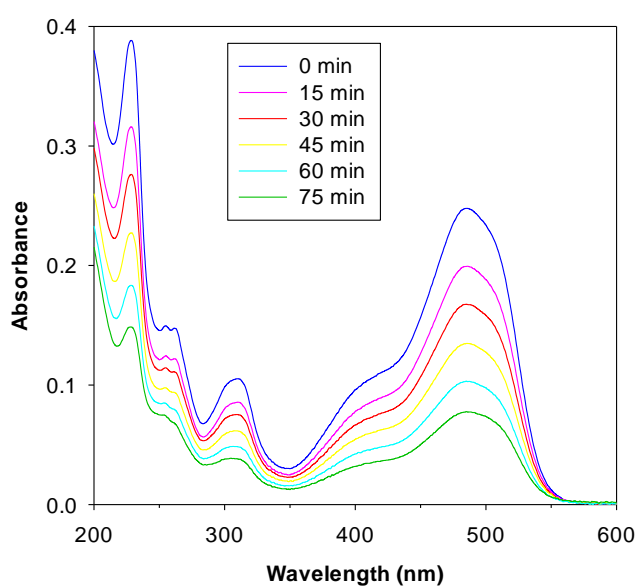
shown in Fig. 6. At a first glance, the absorbance scales significantly with increasing RTP time, while the spectra for the 0 and 1-min samples mostly overlap. It is well known that  $\text{TiO}_2$  has a strong UV absorption capability as a semiconductor [22, 48, 49], while those of carbonaceous char is considered to be relatively non-UV absorbing [50, 51]. As the carbonaceous matrix enveloped the  $\text{TiO}_2$  nanoparticles, the UV-visible light was hindered from reaching the  $\text{TiO}_2$  surface. This was especially the case for the 0 and 1-min HF. However, as the calcination time increased, the char matrix decomposed rapidly to expose the  $\text{TiO}_2$  surface, whilst changing the  $\text{TiO}_2$  phase from predominantly anatase to pure rutile. Hence, as the calcination time was extended, the surface of  $\text{TiO}_2$  nanoparticles was increasingly exposed leading to an increasing UV absorption, which corroborates our previous characterization results.



**Fig. 6.** Diffuse reflectance UV-vis spectra of HF samples treated for different RTP times (0-7.5 min).

### 3.2 Photocatalytic properties

The photocatalytic degradation of AO7 (5 ppm) dye by the HFs (50 mg) was studied by measuring the UV-Vis absorbance of the solution every 15 min up to 75 min. Prior to the experiment, 30 min of dark absorption was carried out to reach a stable AO7 concentration. No concentration change was found before and after dark adsorption showing negligible physical adsorption of AO7 on the HFs. As shown in Fig. 7, the UV-vis spectra of the AO7 solution with the 2-min HF sample between 200 and 600 nm displayed several characteristic absorption bands of AO7 molecules. The decrease in intensity of UV bands at 485 nm (hydrazine form) and 432 nm (azo) is characteristic of the N=N azo bond cleavage because of the photocatalytic degradation of AO7 molecules [52-54]. At the same time, the intensity of peaks at 310 nm and 230 nm increased, indicating the production of small molecules with naphthalene and benzene ring, such as *p*-phenolsulfonic acid, 1,2-naphthaquinone and phenol, from the AO7 photo-degradation process [52, 55].



**Fig. 7.** Representative UV-Vis spectra during AO7 degradation process by the 2-min TiO<sub>2</sub>-char HF sample.

Fig. 8(a) displays the AO7 photo-degradation percentage as a function of time for all the HFs under UV light with five repeated measurements. The highest AO7 removal percentage (68%) was obtained by the 1.5-min HF at the end of the photodegradation experimental period (75 min). Interestingly, it can be observed the maximum photodegradation increased first and then decreased with increasing RTP calcination time. Fig. 8(b) illustrates the AO7 degradation rate (%) produced by the HFs as determined by a logarithm equation with the AO7 initial and final concentrations ( $C/C_0$ ) with respect to the photocatalysis time. In this figure, the trends of the AO7 photodegradation by different HF samples can be clearly seen whereby the 1.5-min HF again produced the fastest degradation rate.

To evaluate the photoreactivity of HF samples, the Langmuir-Hinshelwood (L-H) model has been applied to interpret the photocatalytic degradation of AO7, which is often used for the photocatalytic reaction kinetics for organic pollutants. The relationship of the degradation rate ( $r$ ) and the concentration of the pollutant ( $C$ ) can be expressed as below:

$$r = -\frac{dC}{dt} = \frac{k_r k_{ad}}{1 + k_{ad}C} \quad (6)$$

$$\frac{1}{k_{ad}} = \frac{1}{k_r} C + \frac{1}{k_r k_{ad}} \quad (7)$$

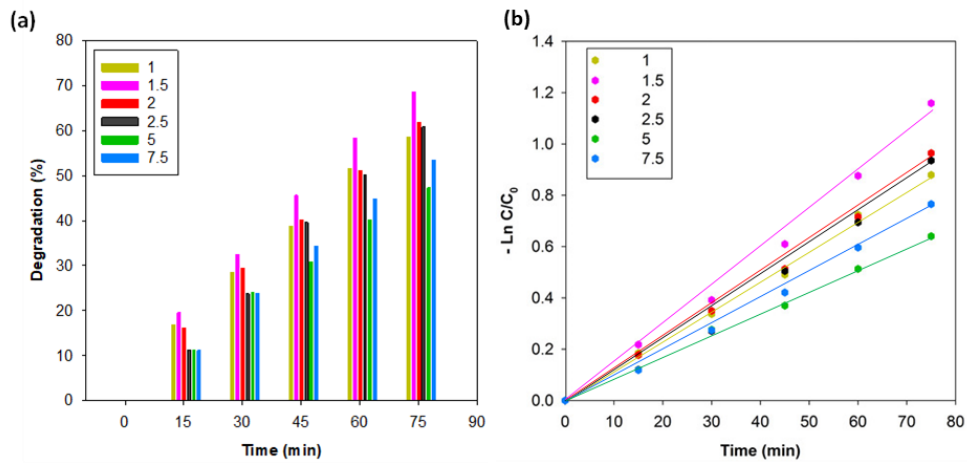
where  $k_r$  is the intrinsic rate constant and  $k_{ad}$  is the adsorption equilibrium constant.

If adsorption is relatively weak or if the concentration of the targeting pollutant is relative low (5 ppm in this work), then two microscopic constants ( $k_r$  and  $k_{ad}$ ) can be integrated as one computed constant ( $k_{app}$ ), which can be used to express the reaction by a simplified form of pseudo-first order kinetics [56, 57]:

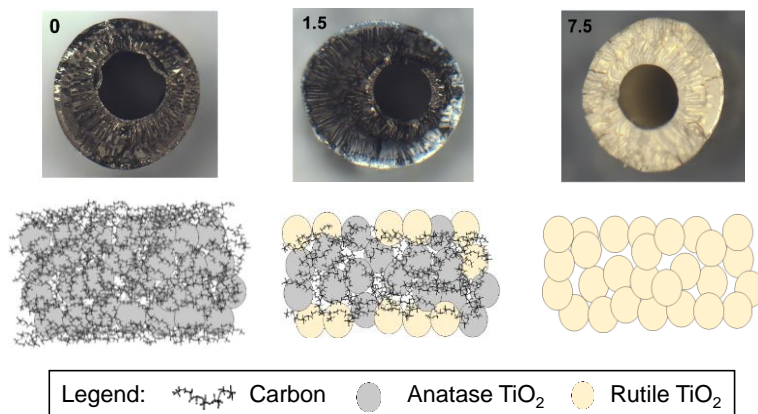
$$\ln\left(\frac{C}{C_0}\right) = -k_r k_{ad} t = -k_{app} t \quad (8)$$

The linear fitting of  $\ln(C/C_0)$  with respect to time ( $t$ ) is plotted in Fig. 8(b), while the first order constant  $k_{app}$  and the coefficient of fitting,  $R^2$ , are calculated and listed in Table S2. From Fig. 8(b),  $k_{app}$  increases from 1 to 1.5 min and then gradually decreases as the RTP time increases. It is found that the 1.5-min HF offered the highest efficiency of photocatalysis with a  $k_{app}$  constant of  $0.0147 \text{ min}^{-1}$ . Although the 7.5-min sample had the greatest amount of the exposed  $\text{TiO}_2$  photocatalyst according to the SEM results, the AO7 degradation rate only reaches a  $k_{app}$  of  $0.0099 \text{ min}^{-1}$ . This is because that all the  $\text{TiO}_2$  anatase phase was transformed into the rutile phase which can be seen in Fig. 5(c). This result is consistent with the earlier report of the trend of photocatalytic efficiency and  $\text{TiO}_2$  crystal morphology [10, 58].

As shown in the schematic in Fig. 9, even though the  $A/R$  ratio of the 1.5-min sample (1.534) is lower than the 1-min sample (2.904) on the HF surface, the former performed much better as the  $k_{app}$  value is 25% greater than the 1-min HF ( $0.0117 \text{ min}^{-1}$ ). This suggests that the presence of the carbonaceous matrix hindered the access of both UV light and AO7 molecules from reaching the  $\text{TiO}_2$  nanoparticle surface. The thermal decomposition of the char matrix in the second stage exposed the photocatalyst and revealed the  $\text{TiO}_2$  active surface, leading to an increase in photoactivity. However, by over-extending the RTP time to 7.5 min, the removal of the char matrix led to a total transformation of the  $\text{TiO}_2$  crystalline morphology and a 35% loss of the photocatalytic efficiency. Hence, a balance of all these important properties of the HFs is critical and can be achieved by a relatively short RTP duration using the dual-stage protocol.



**Fig. 8.** Photodegradation of AO7 by TiO<sub>2</sub>-char composite HF under UV light irradiation: (a) using HF with various calcination times during the second stage; (b) reaction kinetics and linear line of best fit was obtained with  $R^2$  correlation of  $> 0.979$ .



**Fig. 9.** Schematic representation of HF formation by the RTP process with different second-stage calcination times.

## Conclusions

In this work, an innovative, effective rapid thermal treatment method was developed to construct photocatalytic TiO<sub>2</sub>-char composite HFs by partial pyrolysis at 800 °C in less than 30 min. The results show the mechanical strength of HFs mainly depends on the RTP pyrolysis time while the photocatalytic reactivity and efficiency are based on the A/R ratio in TiO<sub>2</sub> crystalline morphology as well as the degree of char decomposition of the HF surface. A promising HF sample was achieved having a reasonable mechanical strength of 11 MPa and an AO7 removal percentage of 68% with a  $k_{app}$  of 0.0147 min<sup>-1</sup> for the photodegradation of AO7 under UV light. This work provides a rapid and simple calcination protocol for the thermal processing of photocatalytic composite materials and hollow fibres as well as for other interesting material geometries for wastewater treatment and environmental applications.

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