Short communication

Novel biomass-derived hybrid TiO$_2$/carbon material using tar-derived secondary char to improve TiO$_2$ bonding to carbon matrix

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ARTICLE INFO

ABSTRACT

The present paper reports on an innovative and simple route for the preparation of new hybrid materials based on TiO$_2$ and carbonaceous supports with relatively high biochar content prepared via controlled laboratory batch pyrolysis system. Pine tar was used as a precursor for secondary char (confirmed by TGA) serving as a coating and "connecting material" between commercially available Degussa P25 TiO$_2$ and biomass derived porous carbon support (biochar) produced from softwood or Lignin. The prepared hybrid materials were characterized by a series of physico-chemical characterization techniques such as XRD, XPS, TGA, UV–vis, XRF, SEM, COD and BET analysis. The results confirmed that the method used is viable and can be used to embed TiO$_2$ in the structure of biochar. In aqueous phase phenol degradation, the TiO$_2$/(secondary char-coated biochar) hybrid materials proved photocatalitically active, and especially the TiO$_2$/secondary char-coated SWP700) showed better photocatalytic performance than the commercial TiO$_2$ counterpart.

1. Introduction

Heterogeneous photocatalysis has proven to be a low-cost, environmentally friendly and sustainable technology for the purification of water, and titanium dioxide (TiO$_2$), such as Degussa (Evonik) P25, is the most commonly used photocatalyst due to its chemical stability, low cost and relative high photocatalytic activity under UV light irradiation [1,2]. Hybrid inorganic/organic materials (e.g. TiO$_2$/carbon materials derived from biomass) have attracted much attention recently as new functional nanocomposites that exhibit superior characteristics, such as optical, electrical, mechanical and thermal properties. They owe these characteristics to the synergistic effects resulting from the physical and chemical interactions that occur between TiO$_2$ and carbon materials derived from biomass [1,2]. Recently, several studies investigated the performance of TiO$_2$ deposited on carbon materials, such as TiO$_2$–loaded carbon derived from beech sawdust prepared by an original method, combining impregnation and pyrolysis (680 °C and 830 °C) and tested in the photocatalytic oxidation reaction of the azo-dye Acid Black 194 [3]. In another study, it was shown that TiO$_2$/ MWCNT (multiwall carbon nanotubes) nanocomposites could be synthesized in situ in a single step by laser pyrolysis, leading to enhanced electronic interactions between the two components. Such hybrid materials can be used as an active layer in the porous photoelectrode of

solid-state dye-sensitized solar cells [4]. Another form tested was titanium dioxide/carbon fabrics, prepared by pyrolysis of cellulosic fabrics in the presence of titanium ions. Such materials were tested for their photocatalytic properties in the photodegradation of methylene blue [5]. It should also be noted that novel TiO$_2$/carbon nanocomposites were prepared through the pyrolysis (900 °C) of TiO$_2$/poly(furfuryl alcohol) hybrid materials, which were obtained by the sol–gel method and the use of these nanocomposites as photocatalysts for photodegradation of methylene blue [6,7]. The high porosity and high surface area displayed by the carbon nanocomposites described here make it suitable for many applications, such as sorbents or materials for carbon electrodes. Uniform TiO$_2$@carbon composite nanofibers were prepared by thermal pyrolysis and oxidization of electrospun titanium (IV) isopropoxide/polyacrylonitrile (PAN) nanofibers in argon which have the unique advantages of porosity, one-dimensional nanostructure, and TiO$_2$@carbon hybrid nanofibers acts to encapsulate the TiO$_2$ nanocrystals and enhance the conductivity of the active material, which plays a critical role in the excellent lithium storage capacity and cyclability of the electrode [8]. Combining TiO$_2$ with non-toxic and abundant porous carbon materials such as lignocelluloses and raw biomass is being increasingly investigated as means to increase photocatalytic activity and conceptually new area of photocatalytic materials.

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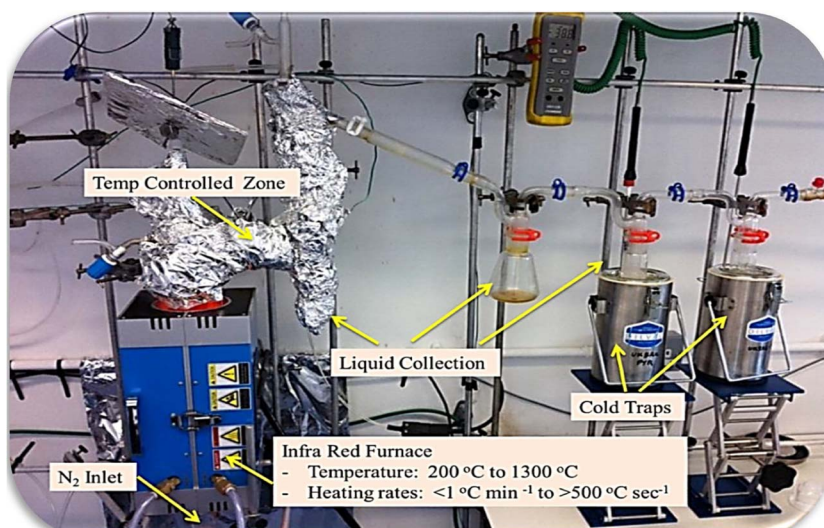
Fig. 1. Scheme of small-scale laboratory batch pyrolysis unit situated at UKBRC, The University of Edinburgh.

Another approach to synthesis is to load TiO_2 onto the already carbonized matrix, such as biochar. Biochar is a relatively low-cost carbon-rich material that can be produced from a wide variety of dedicated or waste biomass, such as wood materials, sewage sludge, and agricultural residues. Pyrolysis processes convert biomass under an oxygen-limited or inert atmosphere at temperatures typically ranging from 300 to 800 °C [1,9,10]. The advantageous properties of biochar include relatively large specific surface area and specific structure, long-term stability, and enriched surface functional groups (e.g., C═O, C─O, and OH), which present technological merits in addition to sustainability concerns [1,9,10]. Another advantage is the fact that biochar can be produced not only from the whole biomass but also from its constituents, such as lignin, a byproduct of pulping and biorefineries. The use of such residues in making added-value products such as (photo)catalysts for environmental applications is favourable and increases the efficiency of full biomass utilization [1,9,11]. Due to its carbon-rich and highly cross-linked nature, lignin is a good biochar precursor, and its use for the preparation of activated carbons has been investigated [1]. Despite its numerous advantages, the use of biochar as a support for TiO_2 photocatalysts poses the challenge of TiO_2 attachment to the surface of the carbon matrix which can be improved through increasing the carbon matrix hydrophilicity (e.g. by incorporating functional groups such as ─OH, ─COOH on its surface).

In biomass pyrolysis, there are two general processes responsible for the production of char. The so-called 'primary char' is the result of devolatilization and carbonisation of the biomass cellular structure, and as such to a large extent retains the physical structure of the starting material. In addition to this, secondary homogeneous and heterogeneous reactions of pyrolysis intermediates present in pyrolysis vapours can form so-called 'secondary char' [9]. This char deposits within pores and on surfaces of the primary char and can considerably alter the yield and structure of biochar [9]. The extent to which secondary char is formed depends on a large number of parameters but is significantly enhanced by high concentration of pyrolysis vapours and their intensive interaction with biomass char [9].

In this study, we set out to test the feasibility of using enhanced secondary char formation for binding a photocatalyst (commercial TiO_2 P25) in the porous structure of biochar. To achieve a high degree of secondary char formation, we used a precursor in the form of Pine tar (condensed vapours of pine pyrolysis). Pine Tar (http://www.pinetarworld.com) is a natural product usually used for wood preservation, surface treatment of wooden buildings and other outdoor wooden constructions to achieve better durability and protection against UV irradiation. Its pyrolysis yields solid carbon product. We

used this fact and the fact that due to its liquid nature it can be easily impregnated onto biochar supports to develop hybrid materials combining primary char matrix with the photocatalyst embedded in secondary char layer coating pores and surfaces of the support. To our best knowledge, there are no scientific and technological reports on the preparation of TiO_2-based photocatalytically active carbon-supported hybrid materials in the proposed way. The effect of production parameters on formation and photocatalyst performance of resulting materials was studied and discussed.

2. Experimental

Detailed experimental procedures for materials characterization and measurements and photocatalytic activity in the aqueous phase are available in Supplementary Information.

2.1. Fabrication of hybrid TiO_2-based carbon materials

Automated TGA/DSC instrument (Mettler-Toledo TGA/DSC-1, Leicester, UK) was used for preliminary experiments focused on biochar production with enhanced secondary char formation (see Fig. S1-S4, Supplementary Information) at four temperatures from 350 °C to 650 °C in 100 °C steps, under nitrogen, with flow rate (0.33 L min^{-1}) and residence time at highest treatment temperature of 20 min. The materials used included softwood pellets biochar (SWP700, part of the Standard Biochar set developed by the UKBRC at the University of Edinburgh For more details on the properties of the biochar, please visit ww.biochar.ac.uk/standard_materials.php and for details on production see [2]. Also, two types of lignin, **Lignin, alkali** and **Lignin, alkali – low sulphonate** supplied by Sigma-Aldrich (CAS Number: 8068-05-1) were used. Two types of pine tar **Pine Tar 773** and **Pine tar EU-832** supplied by Auson (http://www.pinetarworld.com) were used as precursors for secondary char.

Based on these preliminary tests, conditions with the highest yield of biochar, Lignin, alkali – low sulphonate and pine Pine Tar 773 (see Fig. S1-S4, Supplementary Information), and SWP700 were selected for further studies of the preparation of new hybrid materials in a small-scale laboratory batch pyrolysis system [12,13] – referred to as stage I (Fig. 1).

The typical preparation procedure involved several steps: firstly, Pine Tar 773 was placed into a glass container and heated (to lower its viscosity) to a temperature of about 50 °C by magnetic stirrer with heating plate, and then different carbon materials were added (SWP700 or Lignin, alkali – low sulphonate) in weight ratio Carbon material: Tar,

80:20, and after that commercial TiO_2 P25 powder was added to get 25 wt.% TiO_2(P25)/secondary char + LIGNIN and 25 wt.% TiO_2(P25)/ secondary char + SWP700. A further process involves the thorough mechanical mixing of the materials using a spatula until a uniform preparation has been obtained. Glass containers (~10 mL) with metal grid to protect the container from damage with the resulting mixture were placed in a quartz tube and pyrolyzed in the small-scale batch pyrolysis system (Fig. 1) at 400 °C and maintained for 20 min. [13,14] before gradual cooling (with continued N_2 flow (0.33 L min^{-1})) until below 100 °C (about 1 h). Some key parameters (e.g. TiO_2 loading) were adapted from our previous work [2] where new inorganic−organic hybrid materials based on 25 wt.% TiO_2 and new biochar-based supports like SWP700 were thermally modified at 400 °C, and such prepared hybrid materials exhibited very high phenol degradation (64.1%) under UV light after 240 min of illumination. It's also well known that phase composition of TiO_2 depends significantly on its preparation temperature, therefore the new composites of TiO_2/secondary char + carbon material derived from biomass were prepared at 400 °C to avoid the phase transformation of TiO_2 to the less photocatalytically active rutile phase appearing in an extensive temperature range from 450 to 700 °C.

The TGA/DSC instrument was also used to carry out proximate analysis of the composite carbon materials. The proximate analysis method used consisted of the materials first being heated up to and then kept for 10 min at 105 °C under N_2 to determine moisture content; the temperature was then raised at 25 °C min^{-1}–900 °C where it remained for a further 10 min to determine volatile matter content. Finally, air was introduced to the system combusting the sample (also at 900 °C) for 20 min to determine the ash content. Fixed C was then calculated on a weight percent basis by subtracting moisture, volatile matter and ash values from the original starting mass.

3. Results and discussion

3.1. Brunauer–Emmett–Teller (BET) specific surface area analysis

BET specific surface area of the prepared materials are summarized in Table 1. Comparing the specific surface area of pure carbon material like SWP700 (254 m^2 g^{-1}), it can be seen that the most significant decrease in the surface area is for 25 wt.%TiO_2/secondary char + SWP700 (60.3 m^2 g^{-1}) in contrast to pure Lignin and 25 wt.% TiO_2/secondary char + Lignin (16.6 and 11.5 m^2 g^{-1} respectively). Nitrogen adsorption isotherms of all prepared hybrid materials do not show any signs of porosity in the materials, being predominantly non-porous with the very low specific surface area. This is likely to be the result of pore blockage by tar and resulting carbons after pyrolysis. Another contributing factor may be the higher amount of inorganics (i.e. ash content) in the prepared materials (see SI, Fig. S2 and S3, Table S4) that may partially fill or blocks the pores [15,16,17], thereby decreasing accessible surface area.

3.2. X-ray diffraction (XRD) and UV−vis diffuse reflectance spectroscopy

XRD analysis was used to characterize all prepared hybrid materials (25 wt.% TiO_2/secondary char + Lignin, 25 wt.% TiO_2/secondary char + SWP700 photocatalysts, and Degussa (Evonik) P25 TiO_2 for comparison) and the patterns are shown in Fig. S5 (see Supplementary Information). For each photocatalyst presented in Table 1, the XRD data indicated that TiO_2 was mainly composed of anatase (ca. 77%) and rutile (ca. 23%) phases (common composition of commercial TiO_2 P25). The average size of anatase and rutile crystallites for our hybrid photocatalysts, estimated by using the Scherrer equation, was about 13 and 25 nm, respectively (Table 1). The results indicated that the TiO_2 particles and secondary char + carbon materials derived from biomass integrate well. In addition, at the pyrolysis temperature of 400 °C, the diffraction peaks from Degussa (Evonik) P25 TiO_2 phase are only present on the surface of prepared materials and haven't changed the composition and ratio of anatase and rutile phases which present almost the same profile observed in the pure Degussa (Evonik) P25 TiO_2. The UV–vis DRS spectra of the hybrid photocatalysts were recorded as shown in Fig. S6 (see Supplementary Information). The results obtained (Table 1) indicated that light absorption of Degussa (Evonik) P25 TiO_2 was improved by depositing TiO_2 on hybrid support surfaces (secondary char + Carbon materials) and decreased the typical anatase TiO_2 (E_{gap} = 3.20 eV) band gap energy (E_{gap} = 3.18 and 3.06 for 25 wt.% TiO_2/secondary char + Lignin and 25 wt.% TiO_2/secondary char + SWP700, respectively). Recently, published discussions on TiO_2/"C"-biomass hybrid materials [1,2] and graphene based materials [18,19,20,21,22] provide more information about the structure and optical properties, and the reader is cordially invited to explore them.

3.3. Scanning electron microscopy (SEM)

To obtain more detailed information about the microstructure and morphology of the synthesized materials, Scanning Electron Microscopy technique was used. The results are shown in Figs. 2 and 3. SEM images of materials showed that many small spherical particles were closely attaching with bigger particles forming particle agglomerates (Lignin (Fig. 2a), secondary char + Lignin (Fig. 2d), and 25 wt.% TiO_2/secondary char + Lignin (Fig. 3a)). Materials such as SWP700, secondary char + SWP700, and 25 wt.% TiO_2/secondary char + SWP700 (Figs. Fig. 22 b, e and Figure 3c) were composed of irregular plate-like structures and agglomeration tendency is rather small. The results indicated that the integration of secondary char (Fig. 2 c) changed the morphology of prepared materials. It is believed that pine tar-derived secondary char coated the surfaces of the primary char (Lignin and SWP700), and many small mineral particles on the surface of carbon materials tended to agglomerate. As can be seen in Fig. 3b and d, the structure of the surface of each hybrid material (after 20 h of illumination, photocatalysis) is different, and the roughness varies in each material. Additionally, it has been shown that the main elements (see SI, Table S4) for TiO_2/secondary char + SWP700 before illumination and after 20 h of illumination (photocatalysis) are Ti (92.5 and 91.0% respectively), Ca (3.49 and 2.59% respectively) with trace
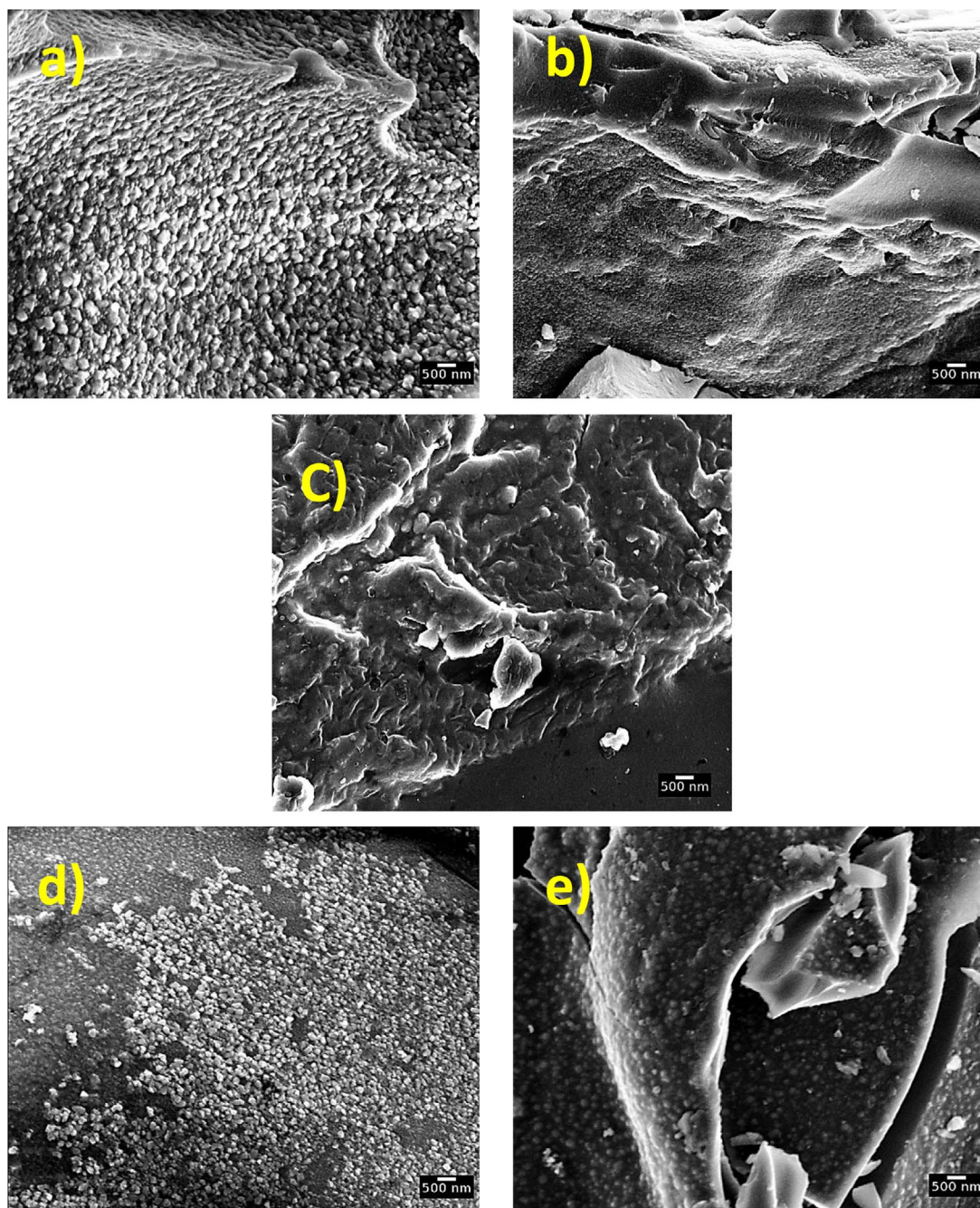
Table 1
Results of BET specific surface area, crystallite size, crystal phase, band gap energy and absorption threshold over all tested photocatalysts.

Photocatalyst	XRD		UV–vis		BET Surface Area [m^2 g^{-1}]
	Crystallite size (nm)	Crystal phase	E_{gap} (eV)	Absorption threshold (nm)	
25 wt.% TiO_2/secondary char + LIGNIN	12	Anatase (76)	3.18	389	11.5
	24	Rutile (24)			
25 wt.% TiO_2/secondary char + SWP700	13	Anatase (78)	3.06	404	60.3
	25	Rutile (22)			
TiO_2(P25)	12	Anatase (80)	3.20	385	56.0
	23	Rutile (20)			

Fig. 2. SEM images of (a) Lignin, (b) SWP700, (c) Secondary char after pyrolysis (400 °C), (d) secondary char + Lignin, (e) secondary char + SWP700.

amounts (< 1%) of minerals and inorganic alkalis. In the case of TiO_2/secondary char + Lignin before illumination and after 20 h of illumination (photocatalysis) we have a similar situation with Ti (88.4 and 87.6% respectively) and also detected S (9.25 and 6.09% respectively) with trace amounts (< 1%) of minerals and inorganic alkalis.

3.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) analyses were carried out to determine the chemical and electronic surface structure of prepared materials and pure Lignin, alkali – low sulphonate (see SI, Table S1 and S2). It can be stated that the surface of lignin prepared by laboratory batch pyrolysis has more functional groups located at binding energies of 291.2 eV and 531.8 eV which clearly correspond to Carbonates and C=O in comparison with pure Lignin, alkali – low sulphonate which

does not have these surface functional groups on the surface. Generally, it may be noted that pyrolysis process can cause an increase of the surface activity of carbon functional groups present on the surface of Lignin and SWP700. Additionally, TiO_2(P25)/secondary char + SWP700 after 20 h of illumination in water exhibited new functional group on the surface (O=C−O located at 289.3 eV and 534.2 eV). It can also be stated that the surfaces of 25 wt.% TiO_2/secondary char + Lignin and 25 wt.% TiO_2/secondary char + SWP700 before illumination and after 20 h of illumination (photocatalysis) have strong bands at 458.8 ± 0.3 eV clearly corresponding to TiO_2. Furthermore, there are significant differences between 25 wt.% TiO_2/secondary char + Lignin before illumination and after 20 h of illumination (photocatalysis) in the case of TiO_2 on the surface (0.88 and 3.75% respectively) which may be associated with surface agglomeration and accumulation of minerals and inorganic alkalis on the surface
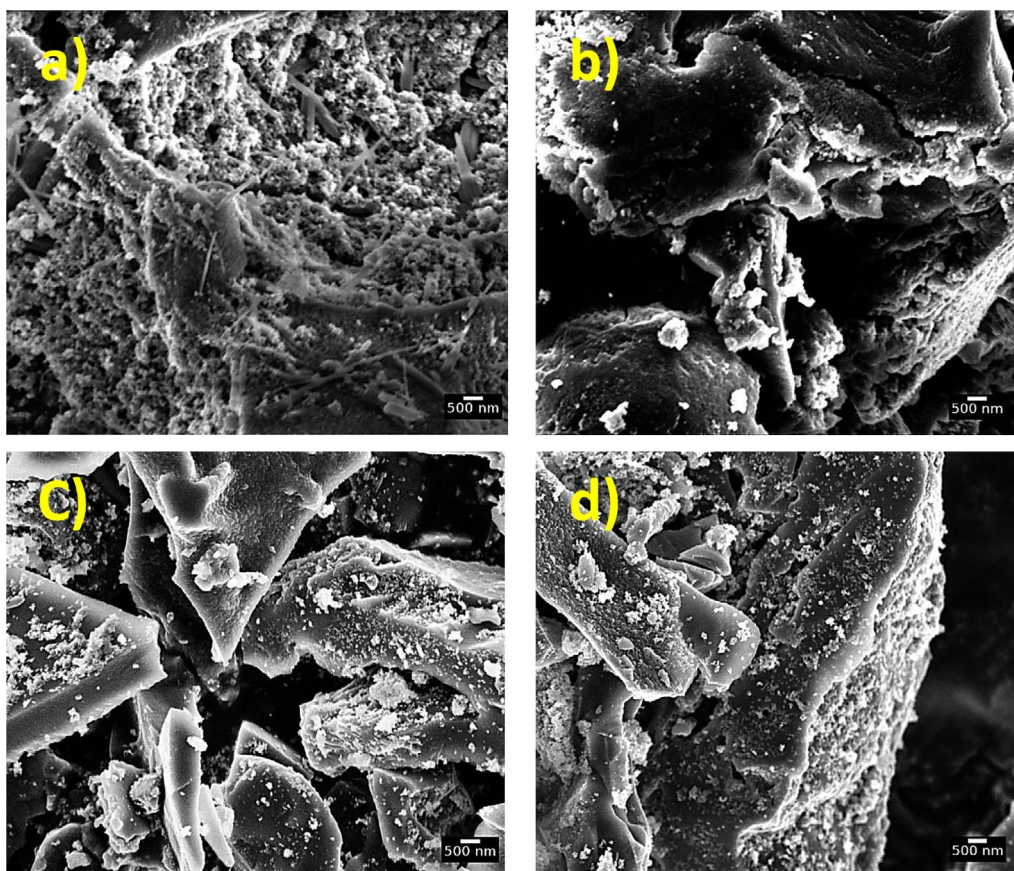
Fig. 3. SEM images of (a) TiO$_2$/secondary char + Lignin, (b) TiO$_2$/secondary char + Lignin after 20 h of illumination (photocatalysis) (c) TiO$_2$/secondary char + SWP700, (d) TiO$_2$/secondary char + SWP700 after 20 h of illumination (photocatalysis).
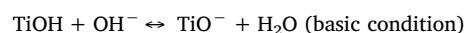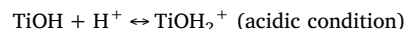
of lignin-based hybrid material and relatively high pH ($>$ 10) that will be discussed in the next section. On the contrary, 25 wt.% TiO$_2$/secondary char + SWP700 showed very similar quantity of TiO$_2$ on the surface (2.10 and 2.27%, respectively) which may reveal a better integration (less agglomeration) of pine tar-derived secondary char coated the SWP700 surface. It should be also noted that integration of secondary char with Lignin and SWP700 to get 25 wt.% TiO$_2$/secondary char + Lignin/SWP700 (before illumination and after 20 h of illumination (photocatalysis)) during controlled laboratory batch pyrolysis system changed the presence of O 1 s bands at 529.8 $\pm$ 0.3 eV clearly corresponding to Ti−O and minerals and inorganic alkalis like Ca−O Si−O, Na$_2$O which is in good agreement with the results of XRF technique (see SI, Table S4).

3.5. Photocatalytic activity in aqueous phase

To evaluate the photocatalytic activity of all prepared hybrid composites, phenol degradation in H$_2$O after 240 min of illumination was carried out under UV light irradiation (Fig. 4). Slight degradation ($<$ 6%) of phenol was observed in the presence of pure SWP700, LIGNIN, secondary char + SWP700 and secondary char + LIGNIN under UV light after 240 min of illumination. The highest phenol degradation was achieved with 25 wt.% TiO$_2$/secondary char + SWP700 material (UV light: 52.5%) followed by 25 wt.% TiO$_2$/secondary char + LIGNIN (UV light: 35.8%) compared to TiO$_2$ (25 wt.% TiO$_2$, UV light: 32.4%) after 240 min of irradiation. It might be worth mentioning and discussing the fact that the introduction of secondary char and TiO$_2$ significantly reduced phenol adsorption in the dark by SWP700, supporting the claim about pores blocked by secondary char and minerals.

The pH of the phenol solution (50 mg L^{-1}) with hybrid materials in Millipore water was measured (pH$_{PhOH}$ = 7.29, pH$_{Water}$ = 7.34) before

irradiation with light (pH = 8.55 for TiO$_2$(P25)/secondary char + SWP700 and pH = 10.39 for 25 wt.% TiO$_2$/secondary char + LIGNIN), and it turned out to be 8.53 and 10.27 respectively for hybrid materials after 4 h of illumination. It is well-known that pH on the degradation of organic compound assisted by the TiO$_2$ is influenced by the acid-base equilibrium governing the surface chemistry, according to the following reactions [23]:

TiOH + H$^+$ $\leftrightarrow$ TiOH$_2$$^+$ (acidic condition)

TiOH + OH$^-$ $\leftrightarrow$ TiO$^-$ + H$_2$O (basic condition)

It is also worth mentioning that at pH $>$ 10 (especially for 25 wt.% TiO$_2$/secondary char + LIGNIN), the repulsive forces between phenol molecules as negatively charged phenolate species and TiO$_2$ are expected [24], and most of the adsorbed phenolate species are not in direct contact with the active site of prepared material surface [25,26], thereby may decreasing photocatalytic activity.

3.6. Long-term materials stability test

The composite materials produced showed 51.6% (25 wt.% TiO$_2$/secondary char + SWP700) and 35.7% (25 wt.% TiO$_2$/secondary char + LIGNIN) performance in single cycle tests (see Fig. 4). However, the stability of the prepared hybrid materials in cyclic and long-term operation is an important practical factor in photocatalytic processes, particularly for industrial usages. To evaluate the stability and reusability of prepared hybrid materials, successive cycles of the photocatalytic phenol degradation were carried out (Fig. 5) under the same reaction conditions with significant loss of activity in 25 wt.% TiO$_2$/secondary char + SWP700 (from 51.6% to 13.4% after 20 h of illumination (Run 5)) and 25 wt.% TiO$_2$/secondary char + LIGNIN (from
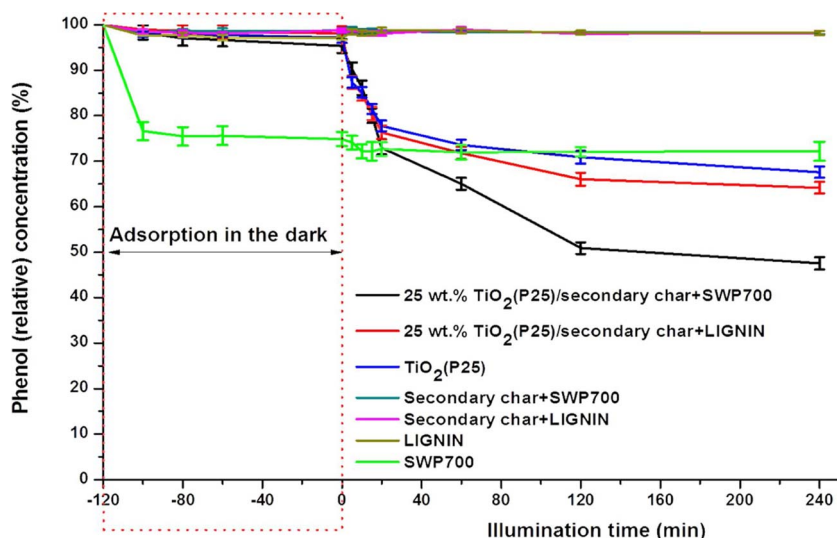
Fig. 4. Photocatalytic phenol degradation under UV over all tested photocatalysts.

35.7% to 0.5% after 20 h of illumination (Run 5)). We believe that the following reasons (each of them in different magnitude) are responsible for such decrease in phenol degradation (especially in the case of a lignin-based hybrid material with the most pronounced photocatalytic deactivation):

a 25 wt.% TiO$_2$/secondary char + SWP700 and 25 wt.% TiO$_2$/secondary char + LIGNIN after 240 min of UV illumination showed Ti leaching (1.01 and 8.61 wt.% Ti respectively) confirmed by ICP-MS. We would assume that 400 °C may not have been a high enough temperature to form resistant enough char from Pine Tar 773. In case of LIGNIN, 400 °C would probably not be a high enough temperature to yield stable char. Longer holding times may reduce these negative effect.

b Integration of pine tar-derived secondary char coated the surfaces of the primary char (Lignin and SWP700) changed the morphology of prepared hybrid materials, and many small mineral particles on the surface of carbon materials tended to surface agglomeration and accumulation of these small ash particles (i.e. minerals and inorganic alkalis) on or inside the catalyst surface (especially in TiO$_2$/secondary char + LIGNIN) which was confirmed by SEM (Fig. 2), XRF (Table S4) and XPS analysis (Table S1 and S2).

c The suspensions containing 25 wt.% TiO$_2$/secondary char + SWP700 and 25 wt.% TiO$_2$/secondary char + LIGNIN before illumination and after 20 h of illumination (photocatalysis) showed relatively high pH (especially the hybrid material with LIGNIN, pH > 10)

which suggested that phenol molecules as negatively charged phenolate species are scarcely adsorbed, and these phenolate species may be repelled away from the photocatalyst surface thereby opposing adsorption of contaminant molecules and decreased photocatalytic activity.

Chemical Oxygen Demand (COD) measurements were carried out to check the amount of "carbon species" dissolved in water after 240 min of UV-light illumination (Table S3, SI). It was observed that secondary char alone showed the highest COD values of organic species compared to other prepared materials or carbon-based composites. It is worth mentioning that our hybrid materials (TiO$_2$/secondary char + SWP700 and 25 wt.% TiO$_2$/secondary char + LIGNIN) before illumination and after 20 h of illumination (photolysis) gave very comparable results in the case of "carbon species" in water and provided a promising stability of the hybrid materials prepared by controlled laboratory batch pyrolysis system. This is likely a result of incomplete carbonization of the tar precursors, yielding secondary char with high volatile content, as can be seen in Figs. S2 and S3.

4. Conclusions

We have successfully prepared composite materials with TiO$_2$ imbedded on biochar support by controlled laboratory batch pyrolysis with enhanced secondary char formation. Pine tar was used as a precursor for secondary char serving as a coating and "connecting
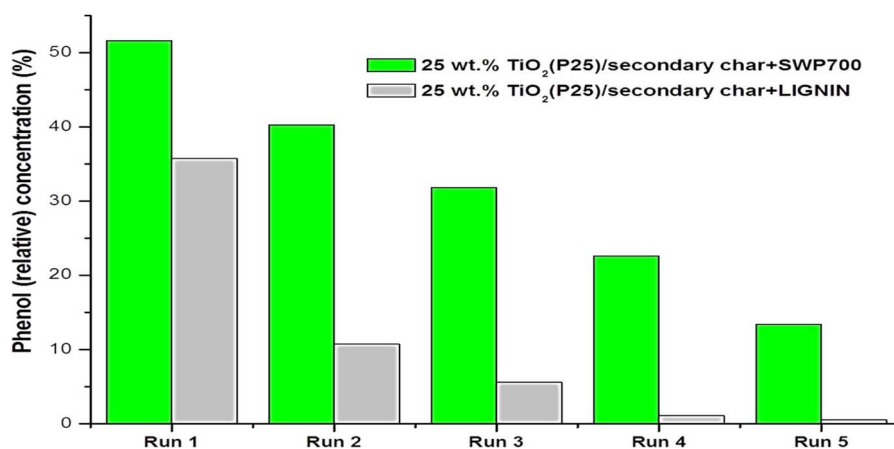

Fig. 5. Multi-cycle performance of hybrid photocatalyst in degradation of phenol in the aqueous phase.

material" between TiO_2 and biomass-derived carbon support (biochar) produced from softwood (SWP700) and Lignin. We demonstrated the feasibility of using such novel approach utilizing low-cost waste materials to attach TiO_2 to carbon matrix. These results can be used to establish sustainable utilization routes of biomass for composite production with good physical and chemical stability and should open new opportunities to develop more innovative, efficient and straightforward methodologies for the preparation of composite photocatalysts.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jaap.2018.02.013.

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