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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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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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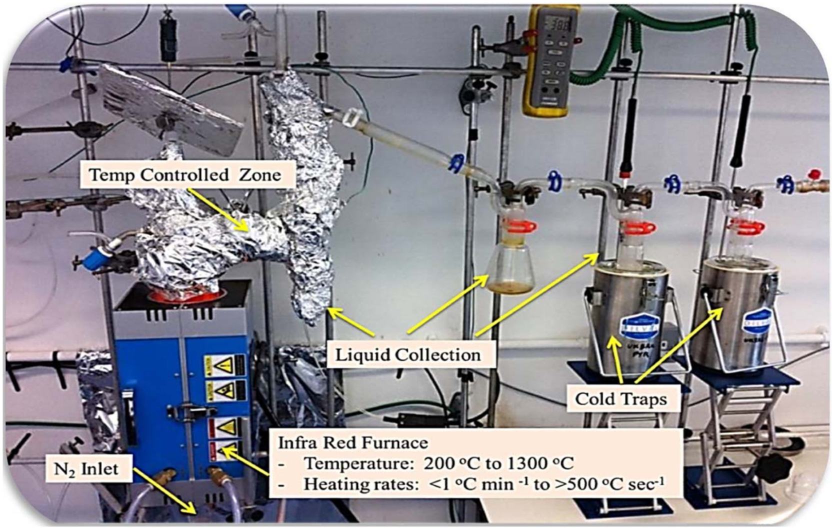

Fig. 1. Scheme of small-scale laboratory batch pyrolysis unit situated at UKBRC, The University of Edinburgh.

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,