



Research article

Facile microwave synthesis of pine cone derived C-doped TiO₂ for the photodegradation of tetracycline hydrochloride under visible-LED light



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ABSTRACT

Pine cone derived carbon was doped into TiO₂ via a facile microwave procedure at different powers, different from other conventional synthesis methods. The materials were adequately characterized and applied in the photodegradation of 5 mg/L tetracycline hydrochloride (TA) under visible-LED light. The XRD results showed that all materials exist as both anatase and rutile phase. However, both the microwave power and the carbon content of the composite material inhibited the conversion of anatase into rutile. The composite material synthesized at a microwave power of 800 W (CT800), displayed the highest band gap energy (3.14 eV) but showed the least electron-hole recombination rate. Hence, CT800 exhibited the highest apparent rate constant of $9.9 \times 10^{-3} \text{ min}^{-1}$ and a half-life of 70 min. An inverse relationship between OH[•] radical scavenger (isopropanol) and the percentage degradation by CT800 suggests that OH[•] is majorly responsible for the degradation of TA. Recyclability studies revealed that after 4 cycles of photocatalytic degradation reactions, CT800 retained approximately 83% performance confirming its stability and reusability.

1. Introduction

Titanium dioxide (TiO₂) due to its relatively high chemical stability, benign, oxidation-reduction potential, cost effectiveness is a preferred and well investigated photocatalyst (Chen and Mao, 2007). However, it has drawbacks of high photogenerated electron-hole recombination rate and wide band gap (3.0–3.2 eV) (Daghrir et al., 2013). The problem of wide band gap makes it efficient only under ultraviolet light which is approximately 5% of the total solar energy (Wu et al., 2018). Currently trending are efforts to improve the photocatalytic efficiency of TiO₂ under visible light. Efforts such as modifying TiO₂ by doping/loading with metals, noble metals, non-metals and by functionalizing with different substrates (Elsellami et al., 2017; Fagan et al., 2016; Jia et al., 2017; Oseghe et al., 2015; Yang et al., 2016; Zhang et al., 2012). These dopants help to improve the photocatalytic efficiency of TiO₂ under visible light by reducing its band gap and serves as electron acceptors to slow down the electron-hole recombination rate (Rather et al., 2017; Saud et al., 2015). Modification by non-metallic materials, particularly carbon material, demonstrates a relatively significant enhanced photocatalytic efficiency under visible light compared to the other forms of modifications. Carbon has been reported to have successfully extended the absorption spectrum of TiO₂ into the visible region. For example, Cheng et al. (2016), reported on an enhanced

adsorption and photocatalytic efficiency of different carbonaceous materials loaded on TiO₂ under visible light. The remarkable improvement was attributed to an improved surface area and electron-hole separation efficiency of the composite materials caused by the presence of carbon. Carbon can be obtained from several sources such as carbonization of plant biomass or by chemically fusing small aromatic molecules. Recently, the focus has been on the conversion of biomass to carbonaceous materials. This is because biomass is readily available, economical, accessible and recyclable (Li et al., 2017; Zhang et al., 2016a). Pine cone is naturally abundant in the environment and rich in cellulose, hemicellulose and lignin which invariably serves as carbon source (Bello et al., 2016; Fratzi and Barth, 2009). Nagaraju et al. (2017), synthesized a three-dimensional activated porous carbon from pine cone for making dye sensitized solar cells. Nunell et al. (2015), also reported on the modification of activated carbon obtained from pine cone for nitrate adsorption. To the best of our knowledge, the potentials of carbonaceous materials obtained from pine cone has not been explored in improving the photocatalytic efficiency of TiO₂. However, several works have been published on the application of C-doped TiO₂ for photodegrading organic pollutants present in waste water. The composite materials have been majorly synthesized via different route such as autoclave and by refluxing but very few if any has reported on the microwave synthetic route. Shanmugam et al.

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(2016), prepared graphene-doped TiO₂ nanocomposite by microwave and observed an improved photocatalytic efficiency. However, the synthesis was carried out at a fixed microwave power of 850 W without justification on the choice.

In this study, carbon obtained from pine cone was loaded on TiO₂ to harness its potentials in improving the physicochemical and photocatalytic properties of TiO₂. The synthesis of the composite materials was achieved by microwave method at different microwave power. All the synthesized materials were characterized and their photocatalytic performance under LED light was evaluated by monitoring the degradation trend of tetracycline hydrochloride.

2. Experimental

2.1. Materials

Commercial TiO₂ (≥99%) and tetracycline hydrochloride (≥95%) were purchased from Sigma Aldrich while ethanol (≥95%) was purchased from associated chemical enterprises (ACE).

2.2. Preparation of carbon from pine cone

Pine cones used for the experiment were collected from Vaal university of technology, Vanderbijlpark campus, South Africa. They were washed with water, dried in the oven at 90 °C for 48 h and subsequently pulverized. The pulverized sample was then sieved to obtain particles less than 300 μm. About 10 g of the sieved sample was transferred into a duran bottle and was subjected to pyrolysis by microwave (1000 W, intermittently for 1 h) in an inert atmosphere. The pyrolyzed sample upon cooling was washed by dispersing in ultra-pure water (3 × 50 mL), sonicated for 10 min in a Branson 2800 sonication water bath and was further subjected to centrifugation at 6000 rpm for 1 h to get rid of the supernatant. This same washing procedure was repeated with ethanol before drying under vacuum at 60 °C overnight.

2.3. Preparation of C-TiO₂

The as-prepared carbon (1 g) was dispersed in 200 mL of solvent (ethanol and deionize H₂O in the ratio of 2:3) by sonication. After 10 min of sonicating, 10 g of the commercial TiO₂ was added to the solution and was further sonicated for 10 min before it was stirred for 1 h at room temperature. The 200 mL of stirred solution was then transferred into three different 250 mL duran bottles, each containing 40 mL and were thereafter subjected to microwave radiation at different power (600, 800, and 1000 W) for 5 min. The materials obtained after microwave treatment were allowed to cool and then washed with 2 × 50 mL of distilled H₂O and 50 mL ethanol and then allowed to dry in a vacuum oven at 60 °C overnight. The composite materials were labelled CT600, CT800, and CT1000.

2.4. Characterization of the materials

The morphology of the samples was examined on a scanning electron microscope (ZEISS Ultra/Plus FEG-SEM) and transmission electron microscope (JEOL JEM-2010). The phase and crystallinity of the materials were obtained by powder x-ray diffraction analysis (Shimadzu XRD-7000 X-ray diffractometer with a Cu K α radiation (λ = 0.15406 nm)). N₂ sorption analysis on the samples were carried out using the ASAP 2020 micrometrics instrument after degassing under N₂ flow at 90 °C for 1 h, and then increased to 200 °C for approximately 12 h. Perkin Elmer LS 55 fluorescence spectrophotometer was used to obtain the photoluminescence spectra of the samples when excited at 310 nm. Infrared measurement of the samples was achieved using Fourier transmission infrared (FTIR) spectrometer (PerkinElmer spectrum 100 series attached to a universal ATR accessory). The UV–vis diffused reflectance spectra of the samples were recorded using a 2540

Shimadzu UV spectrophotometer with BaSO₄ as a reference. The surface properties and binding energies of the samples were investigated by X-ray photoelectron spectroscopy (Thermo ESCALab 250Xi) using monochromatic Al Kα (1486.7 eV) source.

2.5. Photocatalytic tests

Photocatalytic degradation studies were carried out in a quartz photochemical reactor with a 25 W flexible white vis-LED light strip (≈450 nm, 46 W/m²) as light source. Prior to irradiation 300 mg/L of the catalyst was dispersed in a 200 mL tetracycline solution (5 mg/L) by sonicating for 5 min. The mixture was then stirred in the dark for 45 min to attain sorption equilibrium before commencing the photocatalytic experiment which lasted for 2 h. At specific time intervals (20 min), 2.5 mL was sampled, immediately filtered using a 0.45 μm filter and the absorbance taken on a T80 + UV–vis spectrophotometer at 360 nm.

3. Results and discussion

3.1. Morphology and composition

The morphology and composition (qualitative) of the materials are shown in Fig. 1. The SEM and TEM micrographs shows that the shapes of the particles are irregular and possess characteristics interparticle voids resulting from aggregation and agglomeration of the particles. The degree of agglomeration increased as the microwave power increased hence the decrease in the BET surface area (Table 1) as the microwave power increased. The commercial TiO₂ was subjected to N₂ sorption analysis and the outcome shows that it possesses BET surface area of 7 m²/g. The surface area of the composite materials irrespective of the microwave power for their synthesis were observed to be higher than the commercial TiO₂. Hence, results of the BET surface area also show the effect of carbon on the surface area of TiO₂. The diameter of the particles as obtained from TEM micrograph shows that it ranges from 50 – 53 nm. A qualitative study on a representative material (CT1000) was carried out to confirm the composition and distribution of the elemental composition. Fig. 1d and h are mapping micrograph and EDX spectrum respectively. The figures reveal that the materials consist of titanium, carbon and oxygen only, confirming the purity of the material. The mapping micrograph shows that the composite elements are well distributed. Therefore, an inference can be made on the efficiency of the synthesis procedure for making the composite material.

3.2. Structural analysis

Powder X-ray diffraction (PXRD) analysis was carried out on the samples in order to obtain information on their phases, percentage composition of the phases, and crystallite sizes. The diffractograms of the samples are presented in Fig. 2. It is observed from the diffractogram that all the materials possess peaks typical for polycrystalline materials. However, no peak for carbon was seen in the diffractogram. This is probably due to the low amount of carbon in the composite material or it is amorphous. The peaks showed that it has both anatase and rutile TiO₂ phase. The peaks for anatase TiO₂ appeared at 26.08°, 37.62°, 38.58°, 39.46°, 48.89°, 54.73°, 55.73°, 55.96°, 63.55°, 69.52°, 71.17°, and 75.91° which according to JCPDS 21-1272, corresponds to (101), (103), (004), (112), (200), (105), (211), (204), (116), (220), and (215) reflections respectively. Rutile phase had just a peak at 28.25° which corresponds to (110) reflection (JCPDS 21-1276). The crystallite sizes, D, for both the anatase and rutile TiO₂ phase were estimated by Scherrer's equation (equation (1)).

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

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