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Enhanced photocatalytic activity of MWCNT/TiO_2 heterojunction photocatalysts obtained by microwave assisted synthesis

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ABSTRACT

Herein reported are the synthesis and the photocatalytic activity of MWCNT/TiO_2 heterojunction photocatalysts obtained by microwave-assisted method using titanium butoxide as precursor. The obtained materials were characterized by XRD, Raman, SEM, TEM, UV–vis, FTIR, surface area (BET) and photoluminescence. The characterization results showed that the addition of MWCNT did not provide structural changes on TiO_2. The photocatalytic activities of the synthesized materials were investigated using acid blue 9 dye as a model molecule. The results indicate an enhancement on photocatalytic activity by the addition of low amount of MWCNT (1 and 3 wt%). The improvement is attained to the synergic effect between TiO_2 and MWCNT which reduces the electron–hole pair recombination according with the photoluminescence study. In this way, a proposed schema for the enhanced photoactivity of the MWCNT/TiO_2 heterojunction photocatalyst is discussed.

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1. Introduction

Toxic, recalcitrant, and/or dyed organic compounds can be eliminated by various advanced oxidation processes. They are based on reactive oxygen species (ROS) production as hydroxyl radicals ($OH^{\bullet}$), which are effective for organic contaminants degradation [1]. The production of ROS in heterogeneous photocatalysis is based on the irradiation of semiconductors. The preferred semiconductor used in photocatalysis is titanium dioxide (TiO_2) [2–4], due to its chemical stability, superhydrophilicity, long durability, nontoxicity and low cost [5]. Unfortunately, the rapid recombination of photogenerated electron–hole pairs in the bulk semiconductor decreases the efficiency of photocatalytic reactions [6,7]. Several attempts have been made to increase the photocatalytic activity of semiconductors such as: controlling the morphology and crystal phase; doping with transition metals or nonmetal elements; or coupling with secondary semiconductors/conductors [6,8–10]. Unfortunately, these methods involve compounds that are either thermally unstable, difficult to modify or even toxic. Another possible approach is by coupling TiO_2 with multiwall carbon nanotubes (MWCNTs), which provide a synergistic and cooperative effect that leads to enhancement of the overall photocatalytic performance [6,7,9,11]. In this regard, the improvement is attributed to the enlarged absorption region of TiO_2, the increment of surface area and the enhancement of electronic transfer; therefore, a reduction of electron in the TiO_2 bulk is achieved [12–15]. Different synthesis methods have been used to obtain the TiO_2–MWCNT materials (composites, hybrids, heterojunctions) [3,7,9,16–19]. Nevertheless, most of these methods require long preparation times (several hours or a day), involve multiple steps and have high thermal costs, which often result in structural damage in the MWCNT [14,15]. Moreover, microwave assisted synthesis is a novel technique that offers several advantages, such as simple and fast synthesis procedures, reduces the reaction time, offers faster kinetics, higher yield, uniform heating and minimal structural damage [20,21]. This method has been widely used to obtain pure TiO_2; nevertheless, there are few reports where microwave

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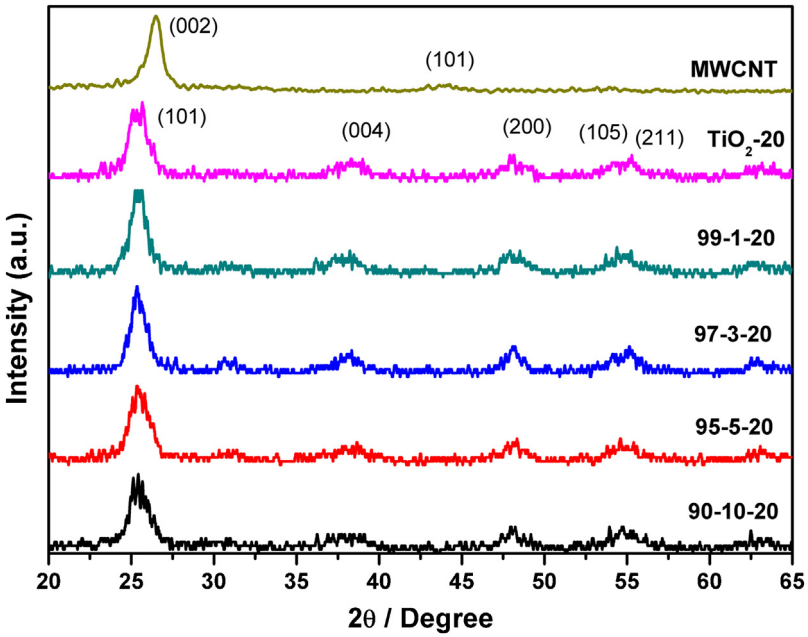

Fig. 1. XRD patterns of MWCNT, pure TiO_2 and TiO_2–MWCNT materials synthetized via microwave.

assisted synthesis have been used to prepare TiO_2–MWCNT materials. In all cases, the synthesis of this material is carried out to obtain the decoration of MWCNT with TiO_2. Nguyen et al. [22] synthesized TiO_2–MWCNT composites using titanium isopropoxide as a precursor and an ionic liquid as a solvent. They report an enhancement in the photoelectrodegradation of methylene blue by increasing the TiO_2 content in composite. Moreover, Liu et al. [23] used the commercial TiO_2 (Degussa P25) and zinc sulfate as precursors to prepared Zn–TiO_2–MWCNT composite. In that study, they used only a ratio Zn/TiO_2/MWCNT and reported the photocatalytic reduction of Cr(VI). In the case of Alosfur and co-workers [14,15,24], they synthesized TiO_2–MWCNT composites using titanium isopropoxide as a precursor and reported an enhancement to photodegrade methylene blue with UV and Visible light irradiation. The improvement in the photocatalytic activity, they indicated that the MWCNTs could act as an electron sensitizer and donator in the composite photocatalysts, contrary to that reported by [6,12,13,25]. Taking in consideration these previous finding, herein is reported the synthesis of the MWCNT/TiO_2 heterojunction photocatalysts by microwave assisted method. The titanium butoxide was used as Ti precursor with ethanol as solvent. The loads of MWCNT were varied in such a way that the surface of TiO_2 was decorated with MWCNTs. The photocatalytic activity of material is evaluated in the degradation of dye acid blue 9 (AB9) under UV-A light irradiation, and compared with the commercial photocatalyst Sigma–Aldrich. A schema is proposed for the enhanced photoactivity of the MWCNT/TiO_2 material and is discussed and supported by the characterization results.

2. Material and methods

2.1. Preparation of MWCNT

MWCNT was synthetized by the spray pyrolysis process; a vycor tube was attached to a pneumatic device used as a solution atomizer. The overall tube dimensions were 0.9 cm of internal diameter and 23 cm of length. A cylindrical furnace (modele Thermolyne 1200) equipped with a high precision temperature controller (±1 K) was used to achieve the desired reaction temperature. α-Pinene (Aldrich, 98.00%) was used as a carbon source. 25 mL of the selected carbon feedstock and 1000 mg of ferrocene (Aldrich, 98.00%) were placed in a glass container and carried through the pneumatic device with Argon (99.99%, Praxair) at 83.3 $cm^3\ s^{-1}$ flow rate for 30 min at 800 °C. The MWCNT films produced during each reaction at the inner surface of the vycor tubing were removed from the substrate, purified and functionalized by a conventional acid treatment in order to achieve both the iron removal and their dispersion in water.

2.2. Preparation of MWCNT/TiO_2

MWCNT/TiO_2 materials were prepared by microwave assisted synthesis. Initially 4 different amounts of MWCNT (10 wt%, 5 wt%, 3 wt% and 1 wt% of the final amount of material) were dispersed in deionized water (25 mL) in an ultrasound BRANSON (model 2510) during 30 min and then, added to 82 wt% of ethanol (Industrial grade), 15.5 wt% of titanium butoxide (Sigma–Aldrich, 97.00%) and 2.5 wt% nitric acid (J.T. Baker, 65.00%) mixture. The suspension was irradiated in a commercial microwave reactor Anton Paar (model Synthos 3000) during 20 min at 120 °C. The precipitates were dried in a Felisa oven (model FE-2910) at 100 °C for 24 h. Each sample received a thermal treatment in a Felisa furnace (model FE-340) at 400 °C for 1 h. The nomenclature used to identify the materials obtained by microwave assisted synthesis was: 99-1-20, 97-3-20, 95-5-20 and 90-10-20 respectively. The first number corresponds to the wt% of TiO_2, the second number refers to the wt% of MWCNT and the last number refers to the synthesis time. TiO_2-20 corresponds to pure titanium dioxide synthetized by the same method (without MWCNT) at 20 min.

2.3. Characterization of MWCNT/TiO_2

Characterization was performed using X-ray diffraction (XRD) in an XRD SIEMENS (model D5000) diffractometer using CuKα radiation. Crystallite size was calculated using the Scherrer equation and the (1 0 1) anatase peak as reference. Raman spectroscopy was performed using a Labram system (model Dilor micro-Raman) equipped with a 20 mW He–Ne laser emitting at 514.5 nm. A Fourier Transformed Infrared spectrophotometer BRUKER (model TENSOR 27) equipped with a Pike ATR (attenuated total reflection)

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