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Synergistic effect between carbon nanomaterials and ZnO for photocatalytic water decontamination

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ABSTRACT

ZnO synthesized by chemical vapor deposition (CVD) was combined with different carbon nanomaterials namely nanotubes, nanofibers, nanodiamonds, fullerene and graphene. The materials were characterized by physical adsorption of nitrogen, diffuse reflectance, UV–Vis and photoluminescence (PL) spectroscopies, transmission electron microscopy and temperature programmed desorption. The photocatalytic efficiency of the resulting carbon/ZnO composites was evaluated for phenol degradation under simulated solar light irradiation. In general, the carbon materials enhance the efficiency of ZnO, and the composite containing nitrogen-doped carbon nanotubes (N-CNT/ZnO) showed the highest photocatalytic activity. An increase of 100% in the apparent first order rate constant for phenol degradation was achieved when using N-CNT/ZnO instead of bare ZnO. PL spectra confirmed the presence of efficient electron transfer between the carbon phase and the ZnO with a maximum quenching of ZnO PL emission in the presence of N-CNT. Both ZnO and N-CNT/ZnO show high stability after four reuses.

1. Introduction

Design of active photocatalysts for heterogeneous water remediation must take into consideration three fundamental factors: (i) light flux into the system, (ii) ability of the material to absorb light, and (iii) capability of electron–hole utilization (if it is assumed that the ordinary process is heterogeneous photocatalysis). These factors can be combined in a way that they are directly proportional to the rate of a photocatalytic reaction [1,2]. Solar technologies need to take into account all these factors, but still suffer from several different complications and challenges that include inefficient photon capture, slow conversion kinetics, and unpredictable and unsolved reaction mechanisms [3–5]. Therefore, the quest to find new photocatalysts with better overlap with the solar spectrum is still open. Heterogeneous photocatalysis based on nanostructured titanium dioxide (TiO_2) has been extensively studied as an important technology for water treatment [6,7]. ZnO is an alternative to TiO_2 in photocatalytic applications due to its similar band gap (3.3 eV), its versatile morphology and lower cost [8,9]. Although ZnO is considered as highly efficient in photocatalytic applications, it also requires excitation in the near UV region. Therefore, research efforts have been devoted to design ZnO-based composite materials to increase the absorption in the visible spectral range. These attempts involve catalyst modification by metal doping [10], dye photosensitization [11], deposition of noble metals [8], combination with other semiconductors [12], or addition of nanoscale carbon materials [13–15]. The unique structure, chemical and electronic properties, and the good stability of carbon materials make the latter a very promising technique. Various studies have reported that carbon materials, such as carbon nanotubes (CNT) [13,16], few layer graphene (FLG) [17,18], fullerene (C_{60}) [19,20], and nanodiamonds (ND) [21] can provide beneficial effects on the photocatalytic activity of metal oxide semiconductors by inducing positive synergies between the two phases in the composite photocatalyst. The introduction of carbon materials favors the separation of the photo-generated electron–hole pairs by the formation of heterojunctions at the carbon/metal oxide interface, promoting faster photocatalytic reaction rates [15,22].

It has been demonstrated that surface modification of the nanocarbon material influences the performance of the composite photocatalyst [15,23,24]. Several studies have shown that the presence of oxygen species on carbon materials' surface, such as carboxylic acid and phenol groups, can enhance the dispersion of the metal oxide, thus increasing the performance of the resulting composite materials. In addition, the acid treatments, normally

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used for surface oxidation, remove residual impurities, such as amorphous carbon or metal catalyst that may be present in the carbon material [25]. Pastrana-Martínez et al. [26] have reported the use of graphene oxide(GO)–TiO_2 for diphenhydramine and methyl orange photocatalytic degradation. In this study, the high concentration of oxygen groups present on GO induced a synergetic effect between TiO_2 and GO sheets leading to a high photocatalytic performance of the GO–TiO_2 composites. In another study by some of us, on the application of TiO_2/CNT composite films for the degradation of water contaminants [27], it was proven that the presence of oxygen surface groups on CNT can act as anchoring points for TiO_2 and favor the dispersion of CNT.

The introduction of nitrogen groups on carbon materials has been also explored as an important route to improve their catalytic performance [28]. Nitrogen doping can induce the generation of free electrons on the carbon materials surface that can be transferred from its surface to adsorbed oxygen [28,29].

In the present work, we have explored the effect of coupling carbon nanotubes, nanofibers, graphene, fullerene and nanodiamonds with ZnO tetrapods in the photocatalytic degradation of phenol under simulated solar light irradiation. The effect of surface oxidation and N-doping of the nanocarbon has also been assessed for selected carbon materials.

2. Experimental

2.1. Materials

Pristine CNT sample was purchased from Nanocyl Belgium (NC-CNT, purity > 95%; diameter = 5–50 nm). Graphistrength® CNT (AK-CNT, purity > 90%; diameter = 5–50 nm) were supplied by Arkema, France. Large-diameter CNT (PYG-CNT, Pyrograph III; diameter = 60–150 nm) were supplied by Applied Sciences. Carbon nanofibers (CNF) were prepared by catalytic chemical vapor deposition (CVD) using a ternary oxide catalyst and ethylene as carbon source in a fluidized bed reactor as described elsewhere [30]. Few layer graphene samples with different average thicknesses (FLGtk and FLGtn) were synthesized by CVD, as described elsewhere [31].

The CNT samples were purified with 50 vol.% sulfuric acid (99.9 wt.%, H_2SO_4, Sigma–Aldrich, 120 °C, 3 h), while nanofibers and FLG samples were purified with hydrochloric acid (37 wt.%, HCl, Sigma–Aldrich, 12 h). The CNT (NC-CNT, AK-CNT and PYG-CNT), CNF and graphene (FLGtk and FLGtn) samples were oxidized with nitric acid (65 wt.% HNO_3, Sigma–Aldrich) at 120 °C for 3 h under reflux. After cooling, the suspensions were washed with distilled water and dried at 130 °C for 12 h.

Nanodiamonds (ND) were obtained by diamond (Carbodeon) disaggregation as follows. Briefly, 1 g of the diamond sample was added to a sodium chloride aqueous solution and the suspension was sonicated for 6 h in a cooled bath. The suspension was centrifuged to recover the ND powder. The collected powders were then oxidized by boiling with nitric/sulfuric acid mixture (1:3, HNO_3:H_2SO_4) for 24 h. After cooling, the suspension was washed up to neutral pH and dried overnight at 130 °C.

Nitrogen doped carbon nanotubes (N-CNT) were synthesized by catalytic-CVD in a fluidized bed reactor using ethylene as carbon source and acetonitrile/N_2 as carbon/nitrogen source, as described elsewhere [28]. The fullerene (C_{60}) sample was purchased from Sigma–Aldrich and used as received.

2.2. Synthesis of ZnO and carbon/ZnO composites

ZnO tetrapods were synthesized by CVD according to a previously described procedure [32]. Briefly, Zn metal powder (Alfa Aesar) was allowed to melt under argon flow atmosphere at 900 °C and oxidized by maintaining a controlled flow of air in the opposite direction. Nanoparticles of ZnO produced in the mixing zone were collected using cold traps and used without further purification.

The carbon/ZnO materials were prepared by adding the required amount of ZnO to a suspension of the carbon material in THF under vigorous stirring followed by sonication for 30 min and stirring of the resultant suspension for 1 h. The composite material was filtered, washed with water and dried at 130 °C for 12 h. The photocatalysts are denoted as X/ZnO, where X corresponds to the carbon material used. Based on previous results using CNT, the carbon phase [16,27] was fixed at 16.7 wt.% for all materials.

2.3. Catalyst characterization

The thermal behavior of the composites was investigated by thermogravimetric (TG) analysis, using a STA 490 PC/4/H Luxx Netzsch thermal instrument. The runs were performed by heating the sample from 50 °C to 900 °C at 10 °C min^{-1} under air flow.

The specific surface area (S_{BET}) of the powder catalysts was obtained by N_2 adsorption–desorption isotherms at −196 °C using a Quantachrome Nova 4200e apparatus. Temperature programmed desorption (TPD) analysis was carried out by heating the samples to 1100 °C at 5 °C min^{-1} under helium flow using an AMI-300 Catalyst Characterization Instrument (Altamira Instruments).

The diffuse-reflectance UV–Vis spectra (DR UV–Vis) of the materials were measured on a JASCO V-560 UV–Vis spectrophotometer equipped with an integrating sphere attachment (JASCO ISV-469). The DR UV–Vis data were transformed by the instrument software (JASCO) to equivalent absorption Kubelka–Munk units. Photoluminescence measurements were carried out at room temperature on a Hitachi 4500 Fluorescence spectrometer with a 150 W Xenon lamp as light source. Excitation spectra were taken in the synchronous mode with the simultaneous variation of the excitation and emission wavelengths.

Transmission electron microscopy (TEM) images were taken using a TEM-FEI Tecnai-G2-20-FEI 2006 microscope. X-ray photoelectron spectroscopic (XPS) analysis was performed using a VG Escalab MKII spectrophotometer operating with a non-monochromatized Mg Kα source (1253.6 eV).

2.4. Photocatalytic activity tests

The photocatalytic efficiency of the carbon/ZnO materials was evaluated in the degradation of an aqueous solution of phenol 20 mg L^{-1}, under natural pH conditions (pH = 6.1) and simulated solar light irradiation. The experimental setup is described in detail elsewhere [8]. The irradiation source consisted of a 1500 W xenon lamp equipped with a cutoff soda–lime glass UV filter with infrared reflection coating, to simulate outdoor exposure (30.9 mW cm^{-2} irradiance, determined with an Ocean Optics USB2000+ spectroradiometer).

To avoid an excess of catalyst and to ensure a total absorption of efficient photons, a preliminary study on the effect of ZnO load was performed. The optimum load found was 0.83 g L^{-1} of metal oxide (see supplementary data, SD1). Thus, the amount of composite catalyst was kept at 1.00 g L^{-1}, leading to a ZnO amount of 0.83 g L^{-1} for all the experiments. A dark period of 30 min before switching on the lamp was maintained to allow the system to attain the adsorption–desorption equilibrium condition.

The concentration of phenol was evaluated by High Performance Liquid Chromatography (HPLC) with a Hitachi Elite LaChrom apparatus equipped with a Lichrocart Purospher Star RP-18 endcapped column (250 mm × 4.6 mm, 5 μm particles), using a mobile phase consisting of a water:methanol mixture in