



Carbon nanotube/titanium nanotube composites loaded platinum nanoparticles as high performance photocatalysts

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ABSTRACT

The multi-walled carbon nanotubes, titania nanotubes, and Pt metal (Pt/TNT-MWCT) hybrids; synthesized via hydrothermal-deposition methods, were tested toward photocatalytic degradation of methylene blue (MB) dye under visible light ($\lambda > 420$ nm) in comparison with the binary hybrid Pt/TNT and Pt/graphene photocatalysts. These catalysts were characterized using X-ray diffraction (XRD), UV–vis diffuse reflectance (DRUV–vis), Fourier transform infrared spectroscopy (FTIR), N₂ sorptometry, photoluminescence (PL) spectroscopy and transmission electron microscopy (TEM) attached with energy dispersive X-ray spectroscopy (EDX). DRUV–vis analysis confirmed the enhancement in the absorption of Pt/TNT following MWCNT incorporation. TEM images showed the coverage of MWCNTs by brookite TNT that has been substantiated by EDX. The higher photo-activity of Pt/TNT-MWCNT (100% degradation in 140 min under visible irradiation) was attributable to the better contact between MWCNT and TNT; exhibited via formation of the Ti–O–C bond, which promoted the charge separation and electron transportation. Reduced charge recombination was evidenced for Pt containing samples and a further reduction was existed following MWCNTs incorporation; as investigated by PL measurements. The adsorption of MB by MWCNTs played major role in the removal efficiency. On the other hand, Pt/graphene presented appreciable activity, however, lower than Pt/TNT-MWCNT both in UV and vis light spectral regions due to decreasing the photocatalytic effect of the former than that of the latter. A mechanism for the MB oxidation was proposed based on the obtained results.

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1. Introduction

TNT is one of the promising nanostructured oxides with tubular structure but has no absorption in the visible light region [1]. Researchers have fabricated a variety of geometric structures of TiO₂ nanoparticles including spherical nanoparticle, nanowire, nanorod and nanotubes [2–6]. TNTs are useful in dealing with waste-water due to the large surface to volume ratio. Most of synthesized TNTs are anatase in nature however, brookite is sometimes observed as a by-product when precipitation is carried out in an acidic medium [7]. Classically, brookite is obtained as large crystals by hydrothermal methods either in aqueous or in organic media [8] as well as when sodium cation content increases [9]. Brookite nanoparticles used to exhibit higher activity toward some reactions; such as methanol photooxidation and acetaldehyde degradation, than anatase nanoparticles [10]. This difference

is explained by considering the crystallinity and the conduction band position, which is more negative than anatase. Generally, one main drawback of the TiO₂ nanostructure, when used in the practical application comes from their easy loss during water treatment. Attempts have been employed to improve the reuse efficiency of TiO₂, via the immobilization onto some supports such as carbon nanotube (CNT), glass, ceramic and activated carbon [11–14]. CNTs were chosen as support to increase remarkably the photoactivity of TiO₂ [15,16] through hindering electron–hole pair recombination. Accordingly, the aim of this work is to prepare a novel brookite TNT of nanospindle structure coating an oxidized MWCNT to study their effects as hybrid nanostructures toward photocatalytic degradation of the MB dye. Assembling metal particles either in the wall of TNT and/or CNTs or both will indeed enhance their photoelectricity and catalytic properties. Therefore, Pt loaded TNT and TNT-MWCNT was synthesized; and tested as well, and the obtained results are discussed in relation to the factors contributing to the enhanced photoactivity. For comparison purposes, Pt/graphene was synthesized to figure out the effect of graphene higher conductivity and surface area values [17] than CNT, on the photoactivity performance.

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2. Experimental methods

2.1. Synthesis of titanium nanotube supported platinum

1.5 g of TiO₂ anatase (Aldrich) was refluxed at 423 K with 100 ml 10 M NaOH solution for 24 h. This milky suspension was then filtered and washed with aqueous HCl (0.1 M) and distilled water till pH 7. It was then dried at 373 K for 10 h and finally heated at 350 °C for 6 h. The produced TNT was dispersed in 50 ml H₂O together with 2 ml of 0.5 M/L acetone. An adequate amount of H₂PtCl₆ solution; to prepare 3 wt.% Pt, was added drop-wisely onto the above suspension during stirring for 1 h. Accordingly, hydrazine hydrate that acts as reducing agent was dropped into the above mixture. This mixture was then evaporated at 324 K for 4 h and finally heated at 623 K for 6 h.

2.2. Synthesis of Pt/MWCNT-TNT nanostructures

MWCNTs (average diameter 3–10 nm and length 5–20 μm) were first oxidized [11] via refluxing at 393 K using mixed acids (H₂SO₄:HNO₃ = 3:1) for 30 min. It was then diluted with water, filtered and washed till pH 7 followed by drying in an oven at 343 K for 12 h. The hybrid nanostructures were prepared by slowly dropping TiO₂ anatase (Aldrich) dissolved in 75 ml NaOH of 10 M concentration into the acid-treated MWCNTs dispersed in water with the aid of ultrasonication to give composite containing 30% CNTs/TNT. This dark suspension was loaded into Teflon-lined stainless steel autoclave and stored at 423 K for 60 h. The produced precipitate was separated by centrifugation followed by washing with ethanol-water mixture. The collected materials were left to dry at 393 K and heated at 623 K for 6 h. A desired amount of the MWCNTs/TNT composite was dispersed in water followed by ultrasonication at 318 K for 30 min. An adequate amount of H₂PtCl₆ solution; to prepare 3 wt.% Pt, was added onto the above suspension during stirring for 1 h. Accordingly, hydrazine hydrate was dropped into the above mixture followed by evaporation at 324 K for 4 h and heating at 623 K for 6 h.

2.3. Synthesis of graphene supported Pt

Graphitic oxide was prepared from purified natural graphite using modified methods [18,19]. Briefly, 2 g graphite was added to 46 ml of concentrated H₂SO₄ under continuous stirring in an ice bath. 1 g NaNO₃ and 6 g KMnO₄ were then added slowly and successively. The ice bath was removed and the suspension was allowed to cool to room temperature. 92 ml of water was then added to above mixture. After 15 min, the above mixture was diluted to 280 ml using warm water. Following this, 30% H₂O₂ was added till the solution turned bright yellow. The suspension was filtered and the filter cake was washed with warm water, repeatedly. The residue was diluted using water and the resulting suspension was centrifuged. The product was dried under vacuum and stored in vacuum desiccators, until further use. One pot modified polyol method [20] was adopted to disperse Pt nanoparticles onto reduced graphene oxide (RG-O), using H₂PtCl₆ as a Pt source and polyethylene glycol and hydrazine hydrate as reducing agents for Pt precursor and G-O, respectively. 3 wt.% Pt metal loading prepared by the modified polyol process i.e. Pt ions [H₂PtCl₆–6H₂O (40% Pt based, Sigma–Aldrich)] dissolved in PEG solution (2 g/100 ml), was added drop wise to the graphite oxide dispersed in 20 mL H₂O and ultrasonicated for 30 min at 318 K solution. The solution was continuously stirred while adding hydrazine hydrate in a stepwise way and increasing the reaction temperature to 60 °C. The reduction product was separated by filtration and then washed with large amounts of water several times to remove residual ions. The

product was finally dried in an oven at 100 °C for 12 h and calcined at 623 K for 6 h.

2.4. Catalyst characterization

2.4.1. X-ray diffraction

The X-ray powder diffraction patterns of various solids were carried out using a Philips 321/00 instrument. The patterns were run with Ni-filtered Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) at 36 kV and 16 mA with scanning speed of 2° in 2 θ min⁻¹. The XRD phases present in the samples were identified with the help of ASTM powder data files.

2.4.2. N₂ adsorption

The surface properties namely BET surface area, total pore volume (V_p) and mean pore radius (r) were determined from N₂ adsorption isotherms measured at 77 K using conventional volumetric apparatus. The samples were out-gassed at 473 K for 3 h under a reduced pressure of 10⁻⁵ Torr before starting the measurement. The total pore volume was taken from the desorption branch of the isotherm at $P/P^0 = 0.98$, assuming complete pore saturation. The amount of chemisorbed H₂ was measured using the same apparatus. The sample was first reduced with H₂ at 673 K for 1 h and then cooled to room temperature in flowing He. H₂ gas was introduced into the sample at 298 K until no more adsorption was observed. The Pt dispersion was calculated considering a dissociative adsorption of H₂ on a Pt surface atom leading to a stoichiometric ratio, Pt:H equal to 1.

2.4.3. UV-vis diffuse reflectance and photoluminescence spectroscopy techniques

UV-vis diffuse reflectance spectra of various samples in the 700–300 nm range were obtained using a Jasco V-570 (serial number, C 29635) spectrophotometer, which attached to a diffuse reflectance accessory unit. The photoluminescence (PL) excitation and emission spectra were measured on a FL/FS 900 time-resolved fluorescence spectrometer.

2.4.4. Transmission electron microscope (TEM)

TEM micrographs were measured using a Philips; model Tecani Feil2, at an accelerating voltage of 200 kV. The powder samples were put on carbon foil with a microgrid. TEM images were observed with minimum electron irradiation to prevent damage to the sample structure. The elemental compositions of the composite material were investigated by energy-dispersive X-ray attached to the TEM equipment. The average particle diameter (d) was calculated by the following formula: $d = \frac{\sum n_i d_i}{\sum n_i}$, where n_i is the number of particle, d_i is the diameter in a certain range, and $\sum n_i$ is more than 100 particles on TEM images of the sample. Computer-assisted counting of nanoparticle images and automated image analysis based software package including KONTRON KS 400 (Zeiss–Kontron) was used.

2.4.5. Fourier transform infrared spectra (FT-IR)

The infrared spectra of the samples were recorded in the range of 400–1000 cm⁻¹. The method includes mixing few milligram of a fine powder of the sample with KBr powder in an agate mortar. The mixture was then pressed by means of hydraulic press. The transmission was automatically registered against wavenumber (cm⁻¹) using a PerkinElmer instrument (Spectrum GX), made in USA.

2.5. Measurements of photocatalytic activity

Dark (adsorption) experiments were carried out for 60 min under continuous stirring for better adsorption equilibrium of the

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