

***In-situ* Dressing of MWNTs with TiO₂ nanoparticles: Microwave-Assisted Synthesis towards Water Treatment**

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.Abstract. A facile method for *in-situ* dressing of multi-walled carbon nanotubes (MWNTs) with TiO₂ nanoparticles was achieved using modified microwave technique. TiO₂/MWCNT nanocatalyst was formed using titanium (IV) isopropoxide as the precursor in the presence of MWCNTs and constantly irradiated for 5 min. FE-SEM micrographs suggested that TiO₂ nanoparticles were well attached on the outer sidewall of MWCNTs. XRD measurement revealed that the TiO₂ exist in anatase form with the calculated crystallite size of approximately 5 nm. XPS results show that TiO₂ contacts closely with MWCNTs via Ti-O-C bonds. The photocatalytic activity of the nanocomposite was evaluated based the degradation of methylene blue under visible light irradiation. The results showed that 1 mg of TiO₂/MWCNTs hybrid nanocatalyst efficiently degraded the dye.

Introduction

Owing to its' excellent chemical and photocatalytic properties, TiO₂ has many applications in electronics, magnetic, paint, solar cell and photocatalysis [1, 2]. Unfortunately, the application of TiO₂ in photocatalysis is limited to short wavelength irradiation (UV region of solar spectrum) [3]. Thus to improve the photoactivity of TiO₂ in the visible light range, several strategies have been suggested such as increasing the surface area [4], creating defect structures to induce space-charge separation [5] and modification with suitable metals or other semiconductors to enlarge the absorption region[6]. Unfortunately, there are several disadvantages with using these method for photocatalytic activity such as thermally unstable, difficult to modify and toxic [7].

It's important to know that the good photocatalyst material must have high photon conversion efficiency in addition to high specific surface area. One of the recent methods to achieve these demand involve enlarge of the absorption region and thus improve the overall efficiency of a photocatalytic process by dressing MWCNTs with TiO₂ nanoparticles. This is due to MWCNT can act as a photosensitising agent when excited under visible-light irradiation in addition with the high surface area of MWCNTs [8].

Materials and Methods

A modified microwave method was used to synthesise the hybrid nanocatalysts. Initially, a 35 mm hole was drilled through the top of a household microwave oven. A reflux condenser was subsequently installed in the microwave oven to enable continuous synthesis at ambient pressures. Several additional modifications have been conducted inside the microwave cavity including remove the glass turntable plate and electric motor with terminated their electrical connections. Aluminum plate was subrogating the microwave bottom side in order to allow the operating of magnetic stirring.

The microwave oven was safely insulated for protection purposes by location and operating it in a fume hood. In addition, the wavelength limitation of the microwave to 12 cm where prevent the microwaves radiation escaping from the upper hole or from the glass door which attached with mesh since they have much smaller perforations. Unlike the conventional microwave oven where

the on-off method was used [1-min on then 1-min off] to allow the mixture to cool down, this modified microwave allow to run constantly as well as operates properly, simple and very easy to utilization, thus, it was expected to be appropriate to most of the samples preparation.

In order to synthesised the hybrid nanocatalysts, commercially available MWCNTs (Cheap Tubes Inc., USA, 10–30 nm and 5 nm outer and inner diameter) was initially functionalized as described in the previous work [9]. The functionalized MWCNTs (f-MWCNT) were then dispersed in ethanol. 75 μ L of titanium isopropoxide (TTIP) representing a TiO₂/ MWCNTs weight ratio of 10% was added slowly under vigorous stirring for 20 min. The mixture was then irradiated inside the microwave for 5 min using 550 W power and continuously stirred. Subsequently, this mixture was dried in oven and then the dried samples were calcined at 500 °C in air for 1 h to obtain TiO₂/MWCNTs nanocomposites. The sample was characterized by X-ray powder diffraction (XRD) (Bruker model D8 Advance), field-emission scanning electron microscopy (FESEM) (ZEISS model SUPRA 55VP) and X-ray photoelectron spectra (XPS) (AXIS ULTRA from Kratos). Crystallite size of the material was determined based on Scherrer equation using Topas (Version 4) software after considering instrumental contribution. The photocatalytic activity of the hybrid nanocatalyst was evaluated by monitoring the degradation of methylene blue (MB) in an aqueous solution under visible light irradiation (VL, 20 W commercial halogen tungsten lamp) at distance 20 cm from the sample. A control MB degradation measurement under UV irradiation (UV, 12 W VL-6.LC lamp at 365 nm) was also conducted for comparison. Small amounts (1mg) of the hybrid nanocatalyst were used for this evaluation.

Result and Discussion

The presence of diffraction peaks at 25.28°, 37.81°, 42.82°, 47.70° and 54.04° in the X-ray diffractogram of the synthesised hybrid nanocatalyst indicated the existence of pure anatase TiO₂ phase in the sample as shown in Fig. 1. The (200) reflection plane of anatase structure was selected for crystallites size calculation which was approximately 4.6 nm.

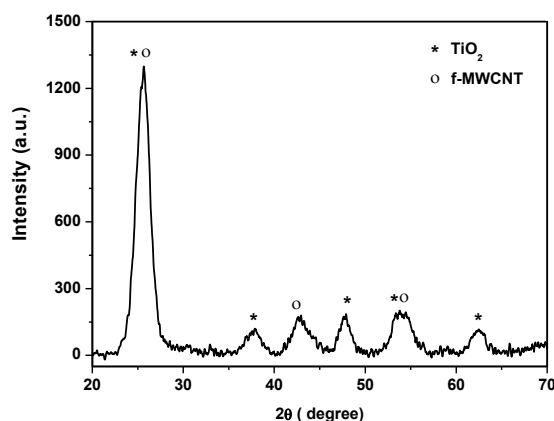


Fig. 1: X-ray diffractogram of the TiO₂/MWCNT hybrids nanocatalyst.

Fig. 2 depicts the FE-SEM images of the hybrid nanocatalyst. The images confirmed the strong adhesion of TiO₂ nanoparticles on the MWCNTs surface. The attached TiO₂ nanoparticles which were produced *in situ* have a mean particle size of approximately 10 nm. The interface connection

between MWCNTs and TiO_2 can clearly be observed, indicating that TiO_2 nanoparticles were well attached on the surface of the MWCNTs.

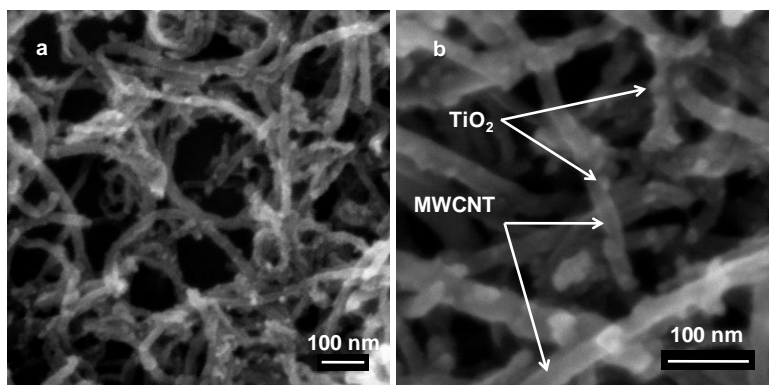


Fig. 2 FE-SEM micrograph of MWCNTs decorated with 10% TiO_2 anoparticles at different magnification: (a) 50,000 \times and (b) 100,000 \times

The narrow scan of XPS spectra for the C 1s region of the sample hybrid nanocatalyst deconvoluted into a complex peaks at 284.5, 285.5, 286.4 and 287.4 eV, as shown in Fig. 3. The peaks are assigned to (C-C), (C-O), (C=O) and (-COOH), respectively [10]. The existence of (-COOH) functional group on the MWCNTs surface which formed after functionalisation processes confirmed that the surface was dressed with very thin TiO_2 layer, where such functional groups act as active sites for directed deposition of TiO_2 nanoparticles around the MWCNTs surface [11, 12]. For example, the -COOH groups on the MWCNTs surface possibly reacted with the -OH groups on the Ti precursor via esterification reaction to form $\text{O}=\text{C}-\text{O}-\text{Ti}$ bonds [13, 14].

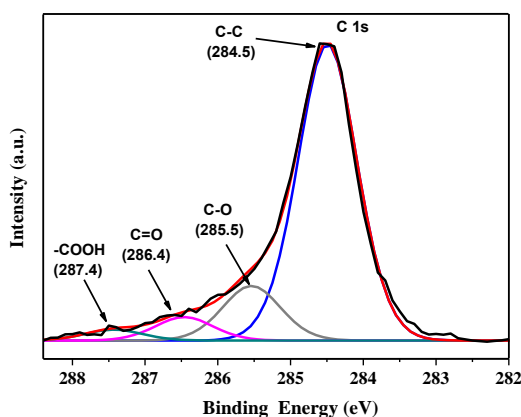


Fig. 3 Deconvoluted XPS spectra of the C 1s region for the $\text{TiO}_2/\text{MWCNT}$ hybrids nanocatalyst.

The narrow scan analyzing of XPS spectra for the O 1s region of nanocomposites was shown in Fig. 4. The O 1s region can be deconvoluted into three different peaks. The peak at around 530 eV is attributed to the (Ti-O-Ti) bond of TiO_2 , which means that the chemical state of oxygen is main lattice oxygen in TiO_2 . The others peaks which located at the banding energy around 531 and 533 eV are assigned to the (C=O) and hydroxyl group (C-OH), respectively.

Combining the XPS spectra and the fitting curves of C1s and O1s assume that Ti-O-C bond presents, which is formed from the close contact and reaction of TiO_2 nanoparticles with MWCNTs [15]. It was suggested that the decrease in the band gap can be attributed to the formation of Ti-O-C

bonds [16]. Although the easily adsorbed of H₂O on the surface of the sample, the physically adsorbed water on the nanocomposite surface is mostly desorbed due to the ultra-high vacuum (10⁻⁹ torr) situation of the XPS system. Therefore, XPS spectra only show chemisorbed H₂O on the surface of the sample.

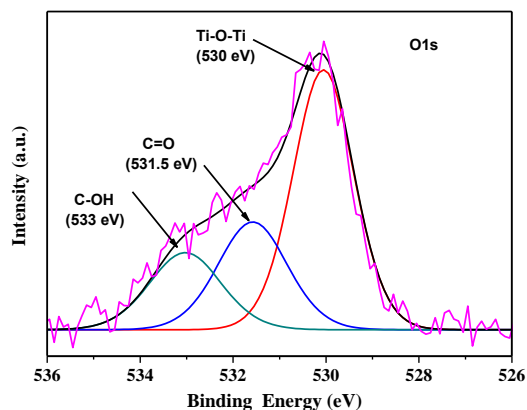


Fig. 4 Deconvoluted XPS spectra of the O 1s region for the TiO₂/MWCNT hybrids nanocatalyst.

As can be seen from Fig. 5, the binding energies of Ti 2p_{3/2} and 2p_{1/2} were centered at 458.9 and 464.4 eV. It was observed that Ti 2p peaks position were slightly shifted toward higher binding energy compared with those of the pure anatase TiO₂ (not show in this work). This indicates that the chemical environment of Ti atom which presented in TiO₂ dressed MWCNTs is different from that of pure anatase, which is probably due to the strong interaction between TiO₂ nanoparticles and the MWCNTs through the formation of Ti-O-C bond at the interface [15, 17, 18]. The splitting between the bands was found 5.63 which consistent with presence of the normal state of Ti⁴⁺ in the anatase TiO₂.

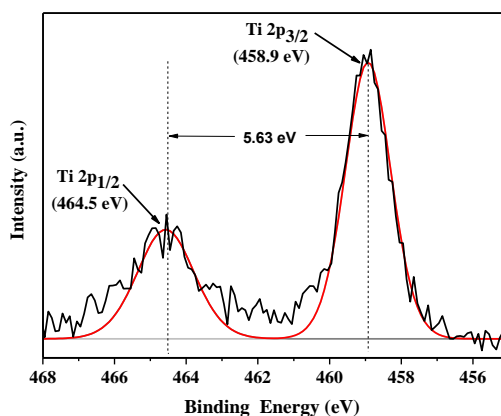


Fig. 5 Deconvoluted XPS spectra of the Ti 2p region for the TiO₂/MWCNT hybrids nanocatalyst.

The removal activity of MB by the nanocomposites was studied under UV (Fig. 6 a) and VL (Fig. 6 b) irradiations. The intensities of the absorption peaks were gradually decreased with increasing irradiation time, indicating progressive decomposition for MB dye. However, VL irradiation recorded faster MB degradation suggesting that the photocatalytic activity of the hybrid nanocatalyst was enhanced.

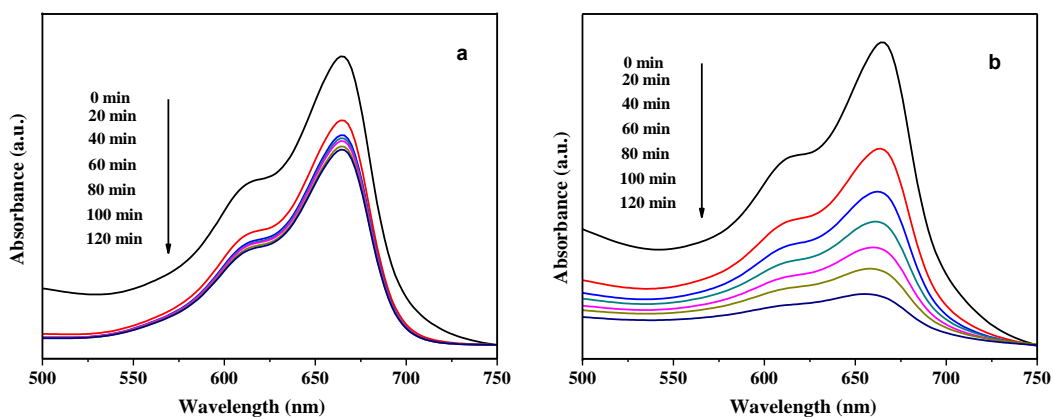


Fig. 6 UV–Vis absorption spectra of MB solutions after photocatalysis for different illumination times with nanocatalysts under (a) UV and (b) VL irradiations.

The residual concentration ratio of MB for duration up to 120 min under UV and VL irradiation were presented in Fig. 7. Under both irradiation conditions, insignificant reduction of the blank MB (without the catalyst) was observed which confirmed that MB cannot be degraded without a catalyst. Under UV illumination, the total degradation of MB solution was 32.2%. The surprising result was obtained when the solution was irradiated with VL in which a total of 83.2% of MB was removed. This result indicated that the hybrid nanocatalyst prepared in this work is extremely photoactive under VL irradiation. The dramatic photocatalytic activity improvement of the hybrid nanocatalyst is believe to result from the fact that MWCNTs can act as a photosensitising agent under VL irradiation [19]. Importantly to note that, the amount of nanocomposite used in this work is significantly less than the previous reports [20-22], suggesting the great future for this material and the synthesis technique employed.

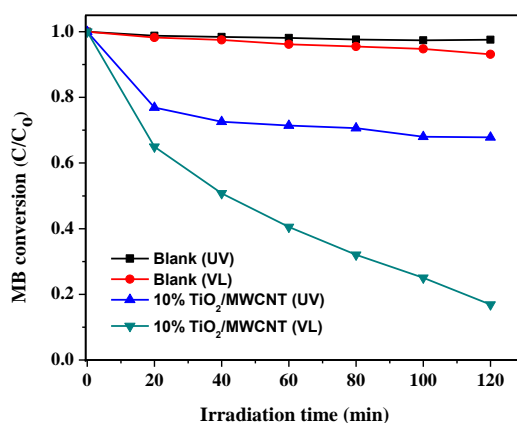


Fig. 7 Residual concentration ratios of MB versus irradiation time.

Conclusions

The in-situ dressing of MWCNT with 10 wt% of TiO₂ nanoparticles was successfully conducted using microwave technique. The hybrid nanocatalyst exhibited excellent photocatalytic activity under VL irradiation. Moreover only a small amount of the hybrid nanocatalyst is required for MB

removal compared to earlier studies. This great improvement point towards great future for this material and the synthesis technique employed.

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