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Short Communication

Visible Light-Responsive TiO_2 Coated MWCNTs as a Hybrid Nanocatalysts

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Rapid synthesis of visible light responsive TiO_2/MWCNTs nanocatalyst with high surface area is demonstrated in this work. The modified microwave method was successfully used to prepare TiO_2 and TiO_2/MWCNTs nanocatalyst. The X-ray diffraction (XRD), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) were used to characterize the nanocatalysts. The photocatalytic activity of TiO_2 nanoparticles and the hybrid nanocatalysts was evaluated by degradation of methylene blue dye under UV and visible light irradiation. The XRD confirmed the formation of TiO_2 with anatase structure while TEM micrographs displayed the TiO_2 was well attached on multi walled carbon nanotubes (MWCNTs) surface. The surface area of TiO_2 nanocatalyst was dramatically increased after the attachment of MWCNTs as supported by BET analysis. Consequently, the TiO_2/MWCNTs nanocatalyst exhibited higher photocatalytic activity than that of bare TiO_2 nanoparticles. More significantly, the photocatalytics activity of the hybrid nanocatalyst under visible light irradiation was greater than under UV.
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Keywords: Hybrid nanocomposite; Microwave; Photocatalytic; TiO_2 nanoparticles

1. INTRODUCTION

As an advanced semiconducting material, TiO_2 has excellent chemical and photocatalytic properties. It has many applications particularly in electronics, magnetic, paint, solar cell and photocatalysis [1-3]. Unfortunately, photocatalytic activation of TiO_2 under visible light is very difficult because it only photoactive in the existence of UV irradiation ($\lambda \leq 384$ nm) [4].

Several methods to improve the photoactivity of TiO_2 in the visible light range have been explored such as increasing the surface area [5], creating defect structures to induce space-charge separation [6] and modification with suitable metals or other semiconductors to enlarge the absorption region [7]. Regrettably, there are several disadvantages with these methods such as thermally unstable, difficult to modify and toxic [8].

A good photocatalyst must have high photon conversion efficiency in addition to high specific surface area [9]. Currently, metal oxide/ multi walled carbon nanotubes hybrid nanocatalysts have become the subject of significance interest due to its unique photoelectronic and structural properties such as narrow band gap [10] and high surface area [11]. These characteristics are so unique hence significant enhancement in photocatalytic performance can be achieved.

The coating of multi walled carbon nanotubes (MWCNTs) with TiO_2 has been reported to enlarge the absorption region and thus improve the overall efficiency of a photocatalytic process [12]. This is because MWCNTs have an extremely high surface area and also can accept electrons from TiO_2 and reduce electron accumulation on TiO_2 nanoparticles [13, 14]. Many researchers claimed to successfully prepare TiO_2/MWCNTs using hydrothermal process. However, this method often time consuming, require multiple steps, costly due to prolong high temperature application under certain pressure and often induced structural damage on the nanotube.

Here, we presented a fast, cost-effective and clean approach to prepare hybrid materials with high surface areas by attaching TiO_2 nanoparticles on the surface of MWCNTs using a modified microwave method. The effect of the hybrid material on the photocatalytic activity was studied via the photodegradation of methylene blue (MB, $C_{16}H_{18}N_3SCl \cdot 3H_2O$) dye in aqueous solution under both ultraviolet and visible light irradiation.

2. EXPERIMENTAL

Commercially available MWCNTs (Cheap Tubes Inc., purity ≥ 95%, with length, outer diameter and inner diameter are approximately 50 μm, 10–20 nm and 5 nm respectively) were used in this work. The functionalized procedures of MWCNTs began with dispersing in 60% concentrated HNO_3 followed by 3 h sonication to prevent nanotubes agglomeration. Subsequently, the mixture was irradiated for 20 min inside a modified domestic microwave oven (Sharp model R-369T) completes with a reflux device and magnetic stirrer. The microwave power was set at 550 W. Finally, the product was rinsed with deionized water until pH 7 was achieved and dried at 80 °C for 10 h to obtain the functionalized MWCNTs (f-MWCNTs).

Next, the f-MWCNTs were dispersed in ethanol. Then few drops of titanium isopropoxide (TTIP) were added into the mixture under vigorous stirring for 20 min. The mixture was then irradiated in the microwave for 5 min with the same power as before. Subsequently, the mixture was dried in an oven at 100 °C for minimum 6 h to obtain a powder. Finally the powder was calcined at 500 °C in air for 1 h to obtain TiO_2/MWCNTs nanocatalyst. As comparison, TiO_2 nanoparticles were synthesized using the same approach but without addition of f-MWCNTs.

The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) surface area measurement. The photocatalytic activities of the synthesised samples were evaluated by monitoring the degradation of methylene blue (MB) solution. The degradation rate of MB by TiO_2 nanoparticles and hybrid TiO_2/MWCNTs nanocatalyst was estimated from the change in absorbance during photodegradation [15]. The experiment was conducted at room temperature with initial pH of 7.0. Two different radiations were used in this study: a 20 W commercial halogen tungsten lamp as the visible light (VL) source and a 12 W VL-6.LC lamp at 365 nm as the ultraviolet (UV) source. A small loading amount of nanocatalyst (1 mg) was suspended in 100 ml of aqueous MB (10 mg/L) in a 250 ml beaker. Prior to light irradiation, the solution was sonicated for 10 min and preserved in a dark room for at least 1 h to ensure adsorption-desorption homogeneity of the dye on the catalyst surface. The flask was mechanically shaken at 400 rpm for 120 min under constant irradiation by a light source located axially to the container. The distance between the light source and container is fixed at 20 cm. To monitor the MB degradation, the clean solution was analysed using UV-Visible spectrometry (Perkin Elmer Lambda 900 UV/Vis) in the range 450–750 nm.

3. RESULTS AND DISCUSSION

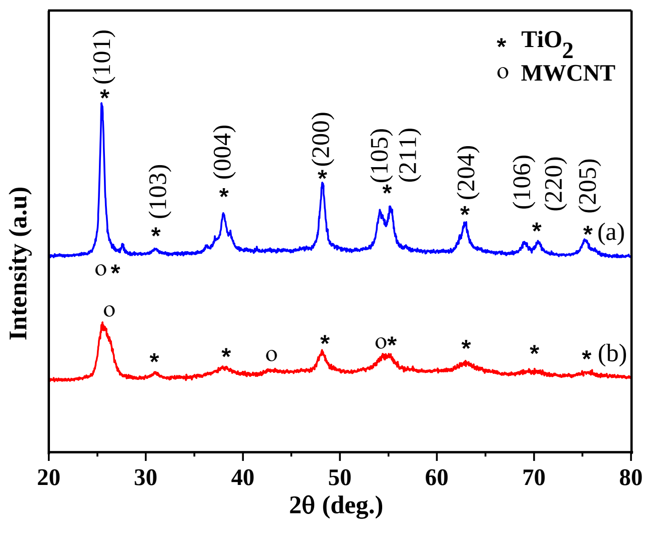

Figure 1. X-ray diffractograms of: (a) TiO_2 and (b) TiO_2/MWCNTs.

The X-ray diffractograms of the prepared samples are presented in Figure 1. TiO_2 nanoparticles displayed several sharp, intense crystalline peaks correspond to anatase phase. The coexistence between MWCNTs and TiO_2 was indicated by broader peaks for the hybrid nanocatalyst which were due to the overlap reflections between MWCNTs and TiO_2.

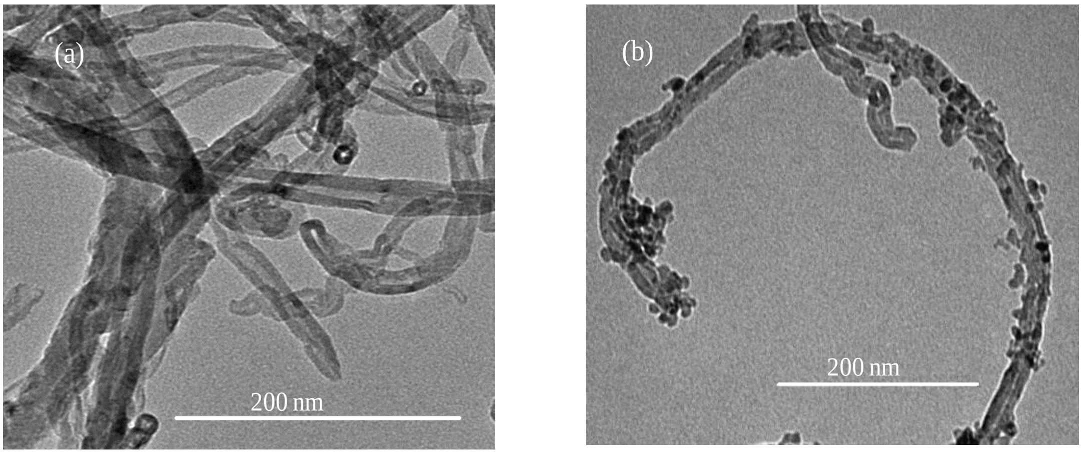

Figure 2. TEM images of (a) functionalized MWCNTs and (b) coating MWCNTs with TiO_2 nanoparticles.

Figure 2 shows the TEM images of f-MWCNTs and the hybrid material. The defects on the surface of f-MWCNTs due to acid treatment can be clearly observed in Figure 2(a). These defects acted as an anchor to hold TiO_2 nanoparticles close to the tube surface. Figure 2(b) shows the TEM micrographs of MWCNTs coated with TiO_2. 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. The diameter of the coated MWCNTs significantly increases and consequently the inner core of MWCNTs is hardly visible.

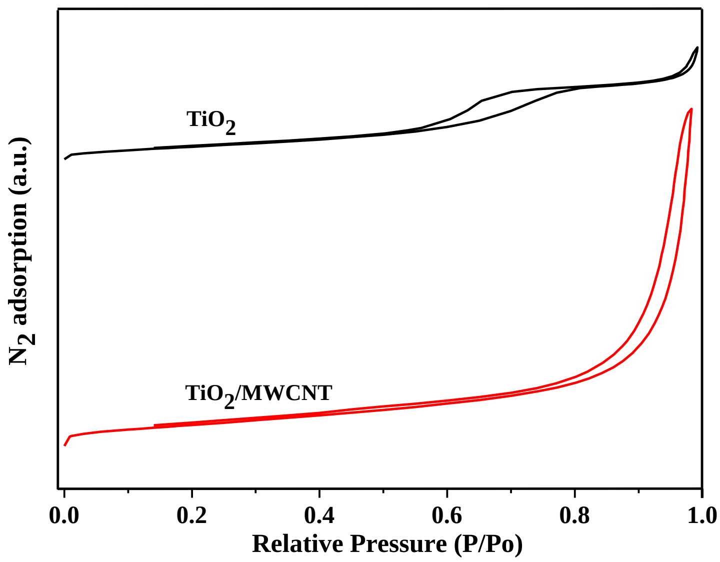

Figure 3. Adsorption isotherms of N_2 on the TiO_2 composites and TiO_2/MWCNTs.

The results for BET surface area measurements are shown in Figure 3. At low pressures the surface is partially occupied by the gas. Then as pressure increased the monolayer was filled and the isotherm reaches a plateau. All N_2 adsorptions ranges show characteristics of type IV isotherms according to the IUPAC classification which is typical for a mesoporous texture. The estimated surface areas for TiO_2 was 122.19 m^2/g while the surface area of the hybrid nanocatalyst was approximately 189.68 m^2/g. It had been considered that the invading TiO_2 nanoparticles blocked the micropores of MWCNTs surface resulted in formation of hybrid nanocatalyst with higher surface area.

The photocatalytic activities for blank MB, bare TiO_2, and TiO_2/MWCNTs nanocatalyst studied by the degradation of MB were shown in Figure 4. The blank run shows 2.7% and 6.2% MB degradation after 120 min under UV and VL irradiation respectively which was insignificant since it could not be decomposed without use of catalyst. The MB removal with TiO_2 nanoparticles recorded 23.2 % and 58.6% for the same measurement period under UV and VL irradiation, respectively. As comparison, about 32.5% and 96.5% MB was degraded by the TiO_2/MWCNTs nanocatalyst under UV and VL irradiation respectively. It is clear that the hybrid nanocatalyst exhibited the highest photodegradation efficiency of MB which is due to higher specific surface area. This observation correlated the surface area with strong adsorption ability. Unlike in other studies [16,17], the measurement in this work used smaller loading amount of nanocatalyst. Moreover, the results obtained in this work is promising compared to the previous report [18]. More importantly, the MB degradation under VL irradiation for both nanocatalysts was significantly higher than it those under UV irradiation.

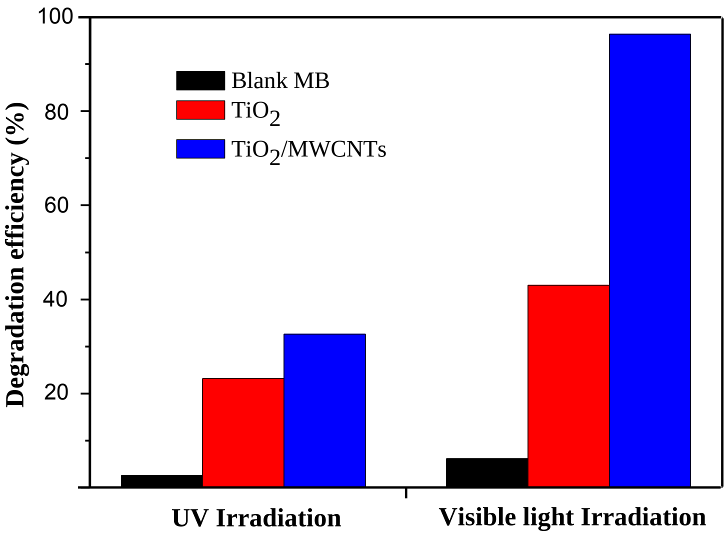

Figure 4. photocatalytic degradation behaviors of MB over TiO_2 and TiO_2/MWCNTs nanocomposites under UV and visible light

4. CONCLUSIONS

A hybrid nanocatalyst active in VL was successfully synthesised by attaching TiO_2 nanoparticles with MWCNTs using modified microwave method. It was found that TiO_2/MWCNTs nanocatalyst has higher surface area than bare TiO_2. The results showed that TiO_2 nanoparticles were well attached on the surface of the MWCNTs. In addition, the efficiency of MB degradation under both UV and VL light range was highest for TiO_2/MWCNTs nanocatalyst compared to bare TiO_2 nanoparticles.

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