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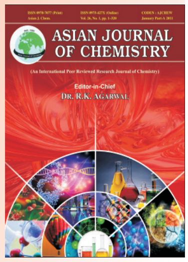

Microwave-Assisted Synthesis of Pd-MWCNT/TiO_2 Catalysts and its Application in the Photodegradation of Reactive Black B†

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MWCNT-TiO_2 and Pd-MWCNT/TiO_2 composites were prepared *via* a controlled and energy efficient microwave assisted method and their high photocatalytic activity was evaluated by the degradation of reactive black B solutions (RBB) under visible light. The surface structure, crystal phase and elemental identification of these composites were characterized by SEM, TEM, XRD, EDX and UV-visible, respectively. The degradation of reactive black-B solution was determined using UV-visible spectrophotometry. These as-prepared photocatalysis were used for H_2 evolution under visible light irradiation. An increase in photocatalytic activity was observed and it may attribute to the increase of the photo-absorption effect by the MWCNT and the cooperative effect of Pd element.

Keywords: Microwave, MWCNT, Visible light, UV-visible, Pd, TEM, Reactive black-B.

INTRODUCTION

Photocatalytic processe is a promising class of advanced oxidation technologies used for environmental remediation[1]. TiO_2 has excellent photocatalytic properties with applications in medicine, buildings and environmental remediation[2,3]. TiO_2 has been studied intensively as a photocatalyst for the complete degradation of organic pollutants[3-5] because it is easily available, nontoxic, low cost and chemically stable. However, TiO_2 has some shortcomings preventing its widespread applications. TiO_2 is difficult to separate from aqueous phase and has relatively low quantum yield due to the rapid recombination of electron/hole pairs and can only used under ultraviolet (UV) light.

In this study, we combined Pd nanoparticles on an MWCNT matrix to design an effective catalyst. To improve the catalysis activity, TiO_2, MWCNT/TiO_2 and Pd-MWCNT/TiO_2 as composites were prepared by the microwave-assisted method. The prepared catalysts were characterized by XRD, EDX, SEM and TEM techniques. The catalytic efficiency of the Pd-MWCNT/TiO_2 composite was evaluated by the photo degradation of commercial industrial dye (reactive black B) under visible light.

EXPERIMENTAL

Multiwalled carbon nanotubes are very stable. They need to be treated with strong acids to introduce active functional groups on their surface. In this experiment, 6.0 g MCPBA was suspended in 200 mL of benzene as a solvent. Then 3 g of MWCNTs powder was put into the solution and the mixture was treated by magnetic stirring for 6 h at 353 K. The resultant solution was filtered and continuously washed with deionized water and ethanol 5 times. The sample was dried at 393 K and fully milled.

One beaker containing 20 mL of ethanol (95.0 %) was prepared; 2 mL of TNB was then added to the solution, followed by magnetic stirring for 5 min; 10 mL distilled water was added dropwise to the solution with constant stirring. From the above, after added 10 mL distilled water into the TNB (2 mL) and ethanol (20 mL) solution, 50 mL volume fraction of 5 % hydrochloric acid solution; 0.5 g as-prepared oxidized MWCNT powder and 0.5 g $PdCl_2$ yellow powder were added into the solution, respectively with microwave irradiation for 20 min in a domestic microwave oven for 4 h. After that, use the same process to wash the black solution 5 times as above, dried at 373 K. Then heat treated at 773 K for 1 h. This sample was named Pd-MWCNT/TiO_2 (Fig. 1).

Measurement of photocatalytic activities: The photocatalytic activities of the MWCNT/TiO_2 and Pd-MWCNT/TiO_2 were determined by the decomposition of reactive black-B in aqueous solution under visible light. The catalysts (0.05 g) were suspended in 100 mL of reactive black-B solution with a concentration of 0.002 g/L in a glass vessel. Prior to irradiation,

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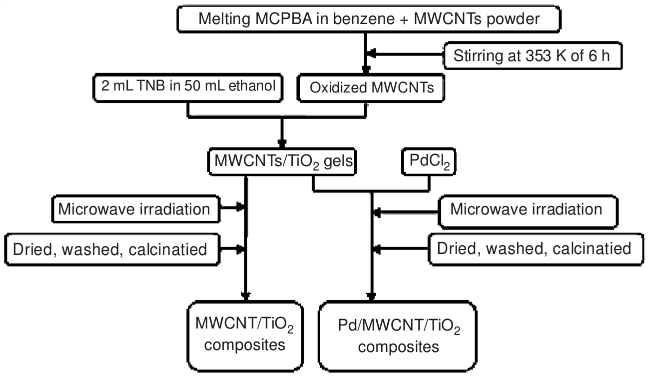

Fig. 1. Procedure for the preparation of MWCNT/TiO_2 and Pd-CNT/TiO_2 composites

the suspensions were magnetically stirred in the dark for 0.5 h to ensure the establishment of an adsorption/desorption equilibrium among the photocatalyst, reactive black-B and atmospheric oxygen, which was hereafter considered as the initial concentration. Photocatalytic degradation was tested using the MWCNT/TiO_2 and Pd-MWCNT/TiO_2 catalysts under visible light irradiation. The reactions were carried out in an open cylindrical stainless glass vessel. The light irradiation of the reactor was done for 30, 60, 90 and 120 min and the removal of the dispersed powders through centrifuge. The clean transparent solution was analyzed using a UV-visible spectrophotometer. The spectra (450-700 nm) for each sample were recorded and the absorbance was determined at the characteristic wavelength of 597 nm. As the catalytic properties of Pd-MWCNT/TiO_2 composition absorption and degradation the black colour of the solution faded gradually with time. For the recycling, MWCNT/TiO_2 and Pd-MWCNT/TiO_2 photocatalysts were recycled three times.

RESULTS AND DISCUSSION

SEM and EDX analysis: The X-ray diffraction (XRD) patterns of Anatase TiO_2,MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites are shown in Fig. 2. It could be confirmed that the TiO_2 in the as-prepared photocatalysts is anatase-phase. For these three samples, (101), (004), (200), (105), (211) and (204) crystal planes are originated from the anatase TiO_2 phase while (111), (112), (121), (103), (031), (200), (213) and (134) crystal planes are originated from the Pd element phase[17]. After refinement, the cell constants are calculated to a = 4.2261 Å, b = 6.9238 Å, c = 7.8547 Å (JCPDS card No. 14-0072). No impurity phase is detected. The broadening of these diffraction peaks indicates that the sample is nanosized. The crystalline size of the sample is estimated to be 15 nm from the Scherrer equation.

Moreover, these nanocomposite particles were further characterized by EDX which showed the expected peaks for Pd element, as well as the peak of Ti due to TiO_2 and other impure elements such as Cu and Zn are also existed which might get from the experimental process. he elemental contents of MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composite photocatalysts were listed in Table-1.

TEM analysis: The TEM images of the MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites are shown in Fig. 3. From Fig. 3(a) and (b), it could be observed that the TiO_2 particles were well dispersed on the surface of MWCNT with a few

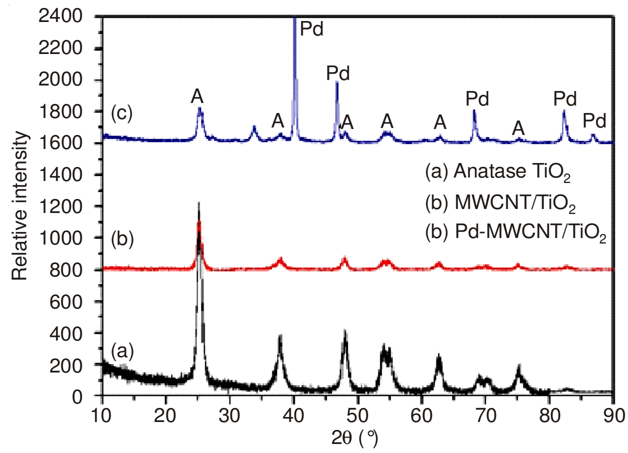

Fig. 2. XRD patterns of pure anatase TiO_2 (a), MWCNT/TiO_2 (b) and Pd-MWCNT/TiO_2 (c)

TABLE-1
EDX ELEMENTAL MICROANALYSIS (wt %) OF MWCNT/TiO_2 AND Pd-MWCNT/TiO_2 COMPOSITES

Sample	Elements (wt %)				
	C	O	Ti	Pd	Impurity
MWCNT/TiO_2	5.44	42.72	49.63	0	2.21
Pd-MWCNT/TiO_2	5.67	41.33	26.34	22.33	4.33

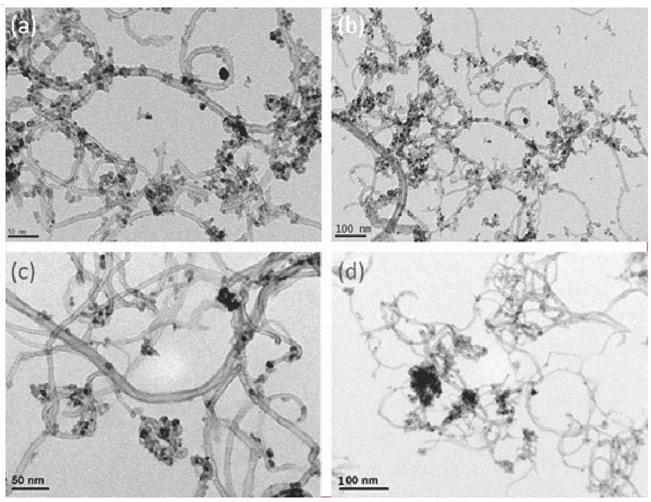

Fig. 3. TEM images of composite photocataysts: (a) and (b) MWCNT/TiO_2, (c) and (b) Pd- MWCNT/TiO_2

TiO_2 particles agglomerated together due to the formation of large grains. The difference in the particle size distribution between the images in Fig. 3(c) and (d) was clearly observed. A few regular black dots were observed, which correspond to Pd particles. The mean size of the Pd nanoparticles was approximately 8-10 nm, as obtained from the TEM image. In other words, the Pd particles with a small size were attached uniformly to the surface of the MWCNT. The size of the TiO_2 particles was 10-20 nm and they were distributed uniformly on the surface of the MWCNT. A generally precipitate-free and smooth interface was observed among the Pd, TiO_2 and the MWCNT matrix.

Degradation procedure

Adsorption ability: To obtain an accurate degradation data of the MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites, pure adsorption experiments were performed under dark conditions and the results are shown graphically in Fig. 5. From Fig. 5, the level of reactive black-B adsorption by Pd-MWCNT/ TiO_2 shows better adsorption ability than MWCNT/TiO_2 composite (from -30 min to 0 min).

Photocatalytic activities: After irradiation for 2 h, both of the samples exhibit good degradation efficiency of reactive black-B solution. The degradation results of the two samples were shown in Fig. 4. From overall results shown in Fig. 4 the Pd-MWCNT/TiO_2 catalyst showed better degradation ability not only in terms of its adsorption, but also its photocatalytic degradation. The result of recycle experiments were shown in Fig. 5, 46 % of reactive black-B was degraded when Pd-MWCNT/TiO_2 was used for the first time. After three times recycles, a small decrease of photocatalytic activity with Pd-MWCNT/TiO_2 was found, 41 % of reactive black-B was degraded in 150 min, respectively as shown in Fig. 4.

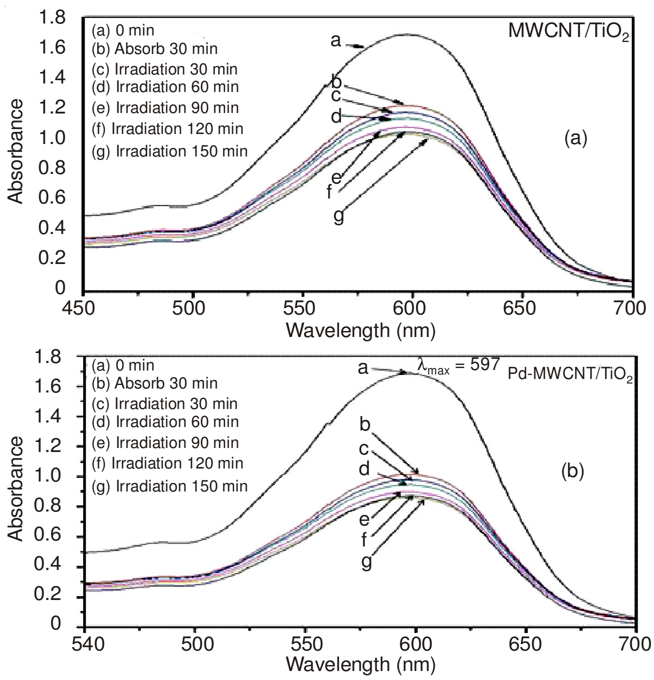

Fig. 4. Photodegradation of reactive black-B solution under visible light irradiation: (a) MWCNT/TiO_2; (b) Pd-MWCNT/TiO_2

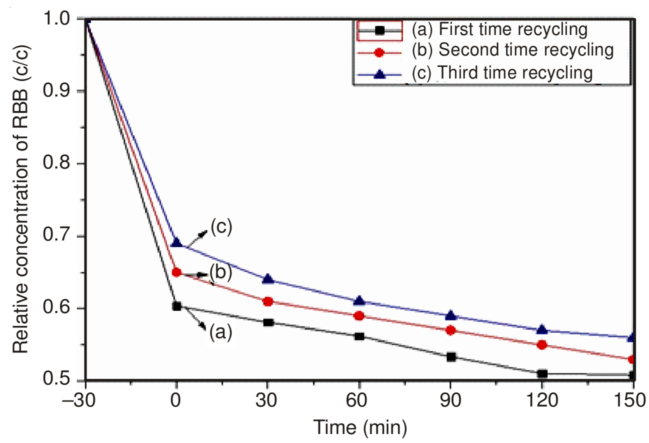

Fig. 5. Relative concentration of reactive black-B(c/c_0) under visible light irradiation; (a): first time recycle; (b): second time recycle; (c): third time recycle

Photo-degradation mechanism: The Pd-MWCNT/TiO_2 composites have a narrower band gap and can increase the level of photo-degradation under both UV and visible light. This whole process is clearly described in Fig. 6.

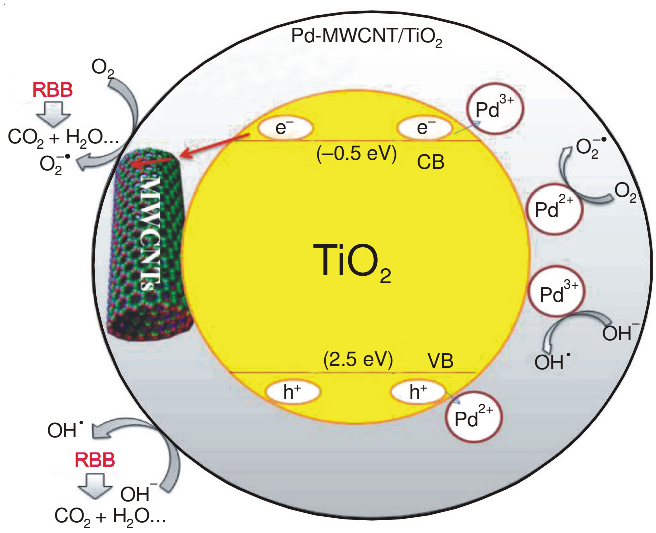

Fig. 6. Simple mechanism of degradation of reactive black-B by Pd-MWCNT/TiO_2 composite

Conclusion

MWCNT/TiO_2 and Pd-MWCNT/TiO_2 composites were synthesized by microwave assisted method. Compared with the pristine MWCNT, though the surface areas of MWCNT/ TiO_2 and Pd-MWCNT/TiO_2 were greatly decreased, they showed good adsorption effects. Under visible light irradiation, reactive black-B, which is a typical standard dyestuff, was easily and efficiently degraded by the Pd-MWCNT/TiO_2 composite. Meanwhile, sample Pd-MWCNT/TiO_2 showed better photocatalytic activity than MWCNT/TiO_2 sample. After the third time recycling, the sample still remains relative stable degradation efficiency of reactive black-B solutions.

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