

FABRICATION OF Pt/CNT/TiO₂ COMPOSITES AND THE INFLUENCE OF Pt PARTICLES ON CATALYTIC PROPERTIES

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Introduction

Titania photocatalysis advantages, such as strong resistance to chemical and photocorrosion, low operational temperature, low cost, significantly low energy consumption, have led the relevant applications to the stage of commercialization [1]. Upon band-gap excitation of TiO₂, the photoinduced electrons and positively charged holes can respectively reduce and oxidize species adsorbed on the semiconductor particles. The high degree of recombination between photogenerated electrons and holes is a major rate limiting factor controlling the photocatalytic efficiency. Attempts to increase the TiO₂ efficiency have been made by doping and coating with transition metals or noble metals, combining the effect of two semiconductors or covering the surface with dye microcrystallites to increase the optical absorption in the visible range.

Multi-walled carbon nanotubes (MWCNTs) have attracted considerable attention since their discovery. Taking advantage of the unique electronic and physical properties of the MWCNTs, we expect that the combination of MWCNTs with TiO₂ may induce interesting charge transfer and thus enhance the photocatalytic activity of TiO₂. The application of TiO₂ photocatalysts in the presence of MWCNTs has been reported to enhance chemical reactions.

In this work, we used MCPBA for oxidizing the surface of MWCNTs at first, and together with potassium hexachloroplatinate(IV) (PHCP, K₂PtCl₆) and titanium(IV) isopropoxide (TIP, Ti{OCH(CH₃)₂})₄) as Pt precursor and titanium precursor, respectively, to prepare CNT/TiO₂ composite, Pt/CNT composite and Pt/CNT/TiO₂ composite by a sol-gel method. Fourier transform infrared (FT-IR) spectroscopy was used to character the functional group on the surface of MWCNT. To determine the properties of these composites, BET surface area, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) were used. To compare the photocatalytic activity, the prepared composites were also determined by the methylene blue (MB, C₁₆H₁₈N₃S Cl 3H₂O) in an aqueous solution under UV irradiation.

Experimental

In this experimental, at first, for preparation of oxidizing agent, 0.96 g MCPBA was melted in 60 mL Benzene. And then 0.2 g MWCNT was put into the oxidizing agent. The mixture was stirred with a magnet for 6 h at 343 K. Then the MWCNT was dried at 373 K and spared. The oxidized MWCNT was mixed into 20 mL of TIP solution and then the solutions were homogenized under reflux at 343 K for 5 h using a magnetic stirrer in a vial. After the stirring, the solutions were transformed to the CNT/TiO₂ gels, and these gels were heat treated at 873 K for 1 h with a heating rate of 279 K/min. Then CNT/TiO₂ composite was obtained.

Pt/CNT composite was prepared by using K₂PtCl₆ as metal precursor. 1 g K₂PtCl₆ was dissolved in 60 mL HCl to obtain K₂PtCl₆-HCl solution. And then the oxidized MWCNT were mixed into K₂PtCl₆-HCl solution. After stirring at 403 K for 3 h, the

mixtures were dried at 373 K. Then Pt/CNT composite was obtained.

Pt/CNT/TiO₂ composite was prepared as follows: 2 mL TIP was dissolved in 50 mL benzene to get the sol. The Pt/CNT composite was put into the sol, agitating at 343 K for 5 h to get Pt-CNT-TiO₂ gels. These gels were heat treated at 873 K for 1 h with a heating rate of 279 K/min to form the Pt/CNT/TiO₂ composite.

The photocatalytic activity of prepared composites was determined by using MB decomposition in aqueous solution under an UV lamp (356 nm). The initial MB concentration was chosen 1.0×10⁻⁵ mol/L. The amount of suspended composites was kept at 1 g/L in 50 mL MB solution. Before turning on UV lamp, the solution mixed with composites was kept in the dark for at least 2 h, allowing the adsorption-desorption equilibrium to be reached. Then, the solution was irradiated with UV. The first sample was taken out at the end of the dark adsorption period (just before the light was turned on), in order to determine the MB concentration in solution, which was hereafter considered as the initial concentration (c₀) after dark adsorption. Samples were then withdrawn regularly from the reactor by an order of 10 min, 20 min, 30 min, 40 min, 50 min and 60 min, and immediately centrifuged to separate any suspended solid. The clean transparent solution was analyzed by using a UV-vis spectrophotometer. The spectra (550-750 nm) for each sample were recorded and the absorbance was determined at characteristic wavelength 660 nm for the each MB solution degraded.

Results and Discussion

FT-IR was conducted on functionalized MWCNT and their corresponding spectra are shown in Fig. 1. After oxidized by MCPBA, the MWCNT have various kinds of functional groups. The band at 2910 cm⁻¹ and 2847 cm⁻¹ ascribe to C-H stretching vibration. And the bands at 1695 cm⁻¹, 1303 cm⁻¹ and 891 cm⁻¹ ascribe to C=O, S=O and C-H stretching vibration, respectively. The above observations suggest that oxidation was promoted in all treatments, and these formed functional groups can increase the active sites on the surface of MWCNT.

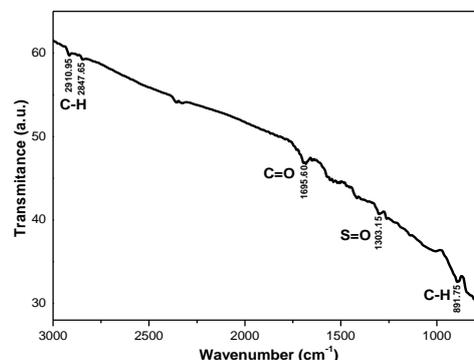


Fig. 1. FT-IR spectra of MWCNT oxidized by MCPBA.

The XRD patterns of CNT/TiO₂ composite, Pt/CNT composite and Pt/CNT/TiO₂ composite are shown in Fig. 2. Comparing the three composites, the strong (002) diffractions of the hexagonal graphite at 2θ of about 25.88° together with the weak (100) diffractions indicate that the graphite structure of the MWCNT is observed only in Pt/CNT composite, while any diffraction peak of graphite structure is not seen in the CNT/TiO₂ composite and Pt/CNT/TiO₂ composite. This indicates that the MWCNTs in these two composites are amorphous. Moreover, obvious Pt diffraction peaks can be observed in both of Pt/CNT composite and Pt/CNT/TiO₂ composite. The characteristic peaks of face centered cubic crystalline platinum at about 40° and 46° are corresponding

to Pt (111) and (200) plane, respectively. And the intensity of Pt peaks in the Pt/CNT/TiO₂ composite is obviously decreased. This indicates that the relative amount of Pt in Pt/CNT/TiO₂ composite is smaller than that in Pt/CNT composite. Furthermore, for the CNT/TiO₂ composite and Pt/CNT/TiO₂ composite, obvious anatase diffraction peaks can be observed at 25.3, 37.8, 48.0, 53.8 and 54.9 are the diffractions of (101), (004), (200), (105) and (211) planes of anatase, except the peaks at 27.4, 36.1, 41.2 and 54.3 that belong to the diffraction peaks of (110), (101), (111) and (211) of rutile in all of Pt-CNT/TiO₂ composites. This indicates that the CNT/TiO₂ composite and Pt/CNT/TiO₂ composite have a single and clear crystal structure, with type of anatase.

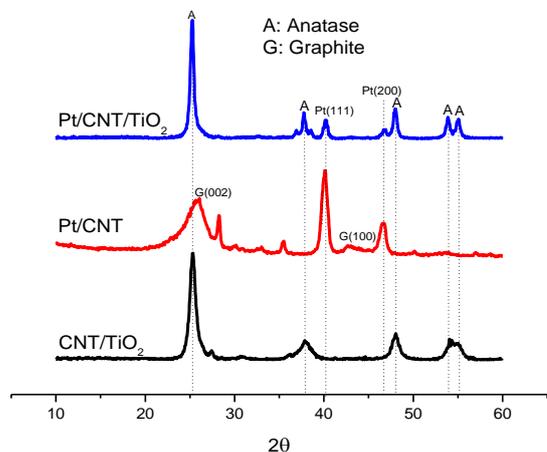


Fig. 2. The XRD patterns of samples

Fig. 3 shows the TEM images of CNT/TiO₂ composite, Pt/CNT composite and Pt/CNT/TiO₂ composite. After treatment of MWCNTs with MCPBA under reflux, the nanotubes were opened, oxidized and shortened, and exhibited regular morphology. Fig. 3 (a), CNT/TiO₂ composite, TiO₂ particles are mixed with MWCNT and dispersed on the surface of MWCNT homogeneously. Fig. 3 (b), Pt/CNT composite, Pt particles are dispersed on the surface of MWCNTs with agglomerations. Fig. 3 (c) shows TiO₂ particle agglomerations are dispersed on the surface of MWCNT with several Pt particles between them.

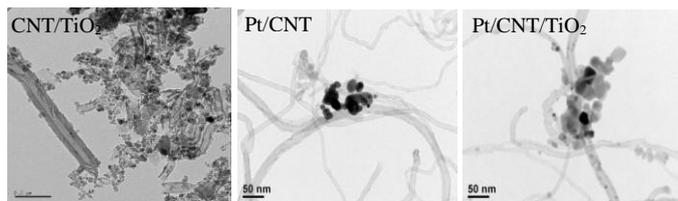


Fig. 3. TEM images of samples.

Fig. 4 shows the changes in relative concentration (c/c_0) of MB in the aqueous solution on time of UV irradiation for CNT/TiO₂ composite, Pt/CNT composite and Pt/CNT/TiO₂ composite. After irradiation under UV lamp, the concentration of MB solution is decreased with an increase of UV irradiation time for all of composites. Furthermore, for Pt/CNT composite, the concentration of MB solution is only decreased 17%. However, the concentration of MB solution is decreased 25% and 61% by CNT/TiO₂ composite and Pt/CNT/TiO₂ composite.

However, the use of semiconductors as photocatalysts is limited mainly to the recombination of generated photo-holes and photo-electrons. So increase the efficiency of the photodegradation of dye, we may increase the amount of electron (e^-) and prevent the recombination of the electron-hole. As studied in our previous

works [2,3], MWCNTs can act as an electron sensitizer and donor in the composite photocatalysts to accept the photo-induced electron (e^-) into the conduction band of the TiO₂ particles under UV irradiation, thus increase the amount of electron. So CNT/TiO₂ composite and Pt/CNT/TiO₂ composite could have more photocatalytic activity than Pt/CNT composite. However, in the case of TiO₂ upon its band-gap excitation the high degree of recombination between photogenerated electrons and holes is a major ratelimiting factor controlling the photocatalytic efficiency. Deposits of Pt metal particles on the surface of the TiO₂ leads to an efficient charge separation of the light generated electron-hole pairs in a semiconductor and increasing the lifetime of the photogenerated pairs allowing longer time intervals to diffuse to the surface. Pt metal particles are very effective traps for the electrons due to the formation of a Schottky barrier at the metal-semiconductor contact. Thus it can prevent the recombination of the electron-hole in the TiO₂ particles. So the Pt/CNT/TiO₂ composite could have more photocatalytic activity than CNT/TiO₂ composite.

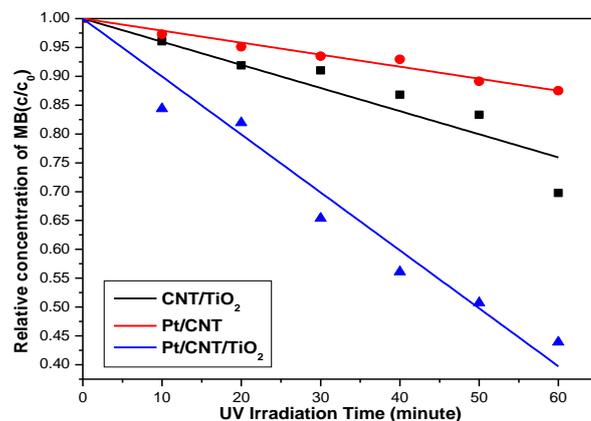


Fig. 4. Comparing to the decomposition of MB in the aqueous solution between Pt-CNT catalyst and Pt-CNT/TiO₂ composites; MB: 1.0×10^{-5} mol/L.

Conclusions

In this study, we successfully prepared the CNT/TiO₂ composite, Pt/CNT composite and Pt/CNT/TiO₂ composite and determined their photocatalytic activity for MB solution by irradiation under UV light. According to the results it could be suggested that the photodecomposition of MB solution is increased by photo-induced-electron absorption effect by MWCNTs and electron trap effect by Pt metal, thus Pt/CNT/TiO₂ composite have best photocatalytic activity among the three kinds of composites.

References

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