

Preparation and characterization of new photocatalyst combined MWCNTs with TiO₂ nanotubes

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Abstract: A new type of photocatalysts MWCNTs/TiO₂-NTs nanocomposites prepared by combining multi-walled carbon nanotube (MWCNTs) with TiO₂-derived nanotubes were synthesized by a modified hydrothermal method. The SEM, XRD, UV-Vis and TG-DTG were used to characterize its property. The produced MWCNTs/TiO₂-NTs nanocomposites were used as the catalysts for photo-degradation of aquatic humic substances. Their photocatalytic efficiency was evaluated by the photodegradation of humic acid in an aqueous solution under ultraviolet light irradiation. The results show MWCNTs could enhance the activity of the photocatalysts; the best degradation efficiency was obtained by using MWCNTs/TiO₂-NTs nanocomposites containing 20% MWCNTs as the photo-catalyst.

Key words: carbon nanotubes(CNTs); titanium dioxide; photocatalysis; humic acid

1 Introduction

How to combine carbon nanotubes(CNTs) with TiO₂ and let them become a new photocatalyst is of great interesting work due to it concerns with serious pollution problems. The CNTs has many special characteristics, such as high chemical stability, extraordinary mechanical and unique electronic properties[1-2]; furthermore, it can absorb organic substance strongly with particular π -electron structure[3]; TiO₂ has been widely used in solving various environmental problems such as wastewater treatment, air clean, as a photocatalyst[4-6]. Provided that CNTs is used as support material and all those advantages of both CNTs and TiO₂ are utilized a powerful photocatalyst could be produced.

There are some endeavors to combine CNTs with TiO₂ to form nanocomposites. LI et al[7] has reported TiO₂ nanoparticle could chemically absorb at single-walled carbon nanotubes(SWCNTs) defeat sites via an ester-type linkage between carboxylic acid group at the defeat sites and hydroxyl groups at the surface of the TiO₂ nanoparticle. LEE et al[8] reported that anatase TiO₂ nanoparticles with a size range of 2–10 nm had

been formed on CNTs by control hydrolysis and condensation of TALH (titanium bis-ammonium lactate dihydroxide). SUN et al[9] reported that amine-terminated TiO₂ nanoparticles were coated on SWCNTs using TiCl₄ as starting materials. JI TIANU et al[10] reported that anatase TiO₂ were coated on MWCNTs by sol-gel method using Ti(OEt)₄ and Ti(OPr)₄ and by hydrothermal hydrolysis of TiOSO₄.

The common characteristics of the above nanocomposites are the TiO₂ nanoparticles linked or coated on CNTs, in this work, we establish a new type of photocatalyst, the MWCNTs is coupled with TiO₂-derived nanotubes(TiO₂-NTs) to form MWCNTs/TiO₂-NTs nanocomposite, which can be used as a photocatalyst to degraded humic substances in environmental protection and water supply industry. To our best knowledge, this is the first report dealing with the use of MWCNTs/TiO₂-NTs nanocomposite to eliminate aquatic humic substance.

2 Experimental

2.1 Catalyst preparation

Titania nanoparticles were produced by sol-gel

method similar with Refs.[11–12].

MWCNTs(made by Sigma-Aldrich Inc., outer diameter is 20–50 nm, length 200 nm–2 μ m) was modified as following procedure: 1.0 g MWCNTs were suspended in 40 mL concentrated sulfuric acid and concentrated nitric acid ($\text{H}_2\text{SO}_4\text{:HNO}_3=3\text{:}1$), sonictreated for 2 h, refluxed for 8 h in oil bath at 80 $^\circ\text{C}$, then filtered (by Millipore 0.45 μ m membrane filter) and washed with deionized water until its pH value is adjusted to about 7; then put into 100 mL deionized water, and used in synthesis of CNTs and TiO_2 nanocomposites.

The 0.6 g titania nanoparticles, different amount of modified MWCNTs (MWCNTs/ TiO_2 mass fraction being controlled at 5%–30%), and 10 mol/L NaOH were transferred to a Teflon lined stainless steel autoclave of 100 mL capacity, then heated in oven at 125 $^\circ\text{C}$ for 24 h, similar to previous reports[13–14]. After cooled down to room temperature, filtered by Millipore 0.45 μ m membrane filter, washed with 0.1 mol/L HCl aqueous solution and then with deionized water until its pH value equal to about 7, dried at 105 $^\circ\text{C}$ for 6 h and calcined at 350 $^\circ\text{C}$ for 8 h in atmosphere ambient, obtained the black MWCNTs/ TiO_2 -NTs nanocomposite samples.

2.2 Characterization

The morphology and microstructure of TiO_2 nanoparticles, modified MWCNTs, and samples of MWCNTs/ TiO_2 -NTs nanocomposites were characterized with SEM (scanning electron microcopy, HITACHI S-4800 instrument, Japan).

XRD patterns were analyzed by using X-ray diffractometer (i.e. SIEMENS Diffraktometer D5000, Germany)using Cu K_α radiation source at 35 kV, with a scan rate of 0.02 $^\circ$. Crystallite size of anatase TiO_2 can be determined from the line broadening by using Scherrer's formula.

The UV-Vis spectra were measured by a JASCO V-570 UV/Vis/NiR spectrophotometer (made by JASCO Corporation, Japan).

The thermogravimetry-differential thermogravity analysis(TG-DTG) was conducted in N_2 and O_2 at a heating rate of 10 $^\circ\text{C}/\text{min}$ on a Labsys TM 1600 (Setaram Scientific & Instrument Equipment, France).

2.3 Photodegradation experiment

The photodegradation experiments were carried out in closed box, whose UV radiation source is 100 W high-pressure mercury lamp, its wavelength range is 290–450 nm, the peak intensity is 365 nm (Model B 100 A, UVP. Inc, USA); a photoreactor is installed on the inside. The photoreactor consisted of two 100 mL beakers, which filled with 80 mL aqueous humic acid

solution and photocatalysts suspension (including TiO_2 nanoparticles, modified MWCNTs and samples of MWCNTs/ TiO_2 -NTs), and magnetically stirred. No pure oxygen was supplied because it has enough oxygen for oxidation photodegradation under continuously stirring in atmosphere in previous experiment[15].

The initial humic acid concentration(ρ) was 30 mg/L, the photocatalyst concentration was 1 g/L, and the pH of the solution was adjusted to 4.0 with ammonia and nitric acid solution. Before mercury lamp switched on, the mixture solution of humic acid and photocatalyst was sonic treated for 5 min and then magnetically stirred in a dark condition for 30 min to achieve adsorption-desorption balance, then take out sample, centrifuged (Eppendorf, Centrifuge 5417, Germany) and filtrated with 0.45 μ m Millipore membrane filters, and measured clear solution concentration(ρ_0) by JASCO V-570 UV/Vis/NiR spectrophotometer at 436, 400, 365, 280 and 254 nm wavelength, the ρ_0 was considered as beginning concentration after dark adsorption[16]. The samples were withdrawn regularly (in general, every 30 or 1 h for each sample) from the beakers. The humic acid concentrations(ρ_i) in different times were obtained and the removal rate could be expressed as following formula.

$$\text{Removal rate: } R = \rho_i / \rho_0 \times 100\%$$

3 Results and discussion

3.1 Catalyst characterization

The SEM images of CNTs and TiO_2 nanocomposite are given in Fig.1. There are two kinds of nanotubes in the nanocomposite, one is TiO_2 nanotube whose diameter is about 10 nm (Fig.1(a)), and another is carbon nanotube Fig.1(b). The TiO_2 nanotubes have much higher specific surface area than TiO_2 nanoparticles and many hydroxyl group excelling in ion absorption[17], but in general, the TiO_2 nanotubes is composed of $\text{H}_2\text{Ti}_3\text{O}_7$ [18], and $\text{H}_2\text{Ti}_n\text{O}_{2n+1} \cdot x\text{H}_2\text{O}$ ($3 < n < 6$)[19] as well as $\text{H}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ [20], which are amorphous with poor photocatalysis activities; if calcined at 350 $^\circ\text{C}$ in air, a parts of them would changed into anatase and maybe used to be a photocatalyst[21], meanwhile, if temperature is larger than 493 $^\circ\text{C}$, the MWCNTs could be disappear[22], so in our experiment, 350 $^\circ\text{C}$ was chosen as the calcinations temperature, and the samples obtained has photocatalysis activities.

The XRD patterns of MWCNTs, raw material TiO_2 , and MWCNTs/ TiO_2 -NTs were given in Fig.2. The most intense two peaks of MWCNTs correspond with (002) and (100) reflection, respectively. The raw material TiO_2 was in anatase phase; the successful conversion of

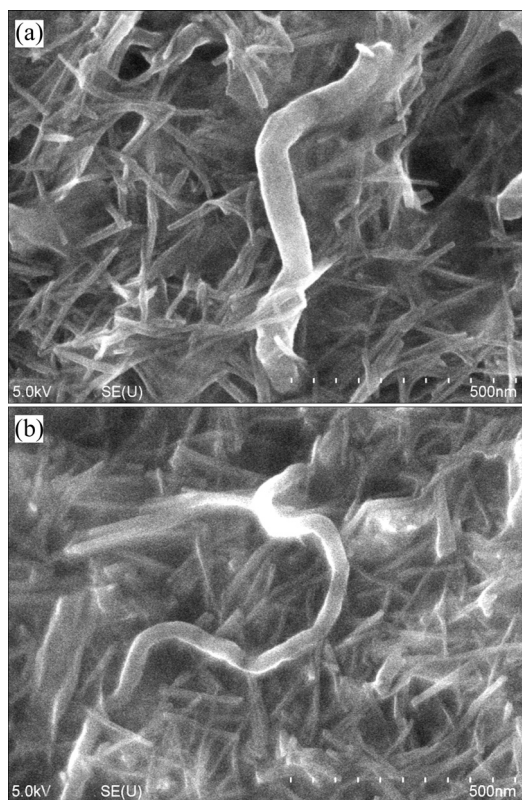


Fig.1 SEM images of MWCNTs/TiO₂-NTs nanocomposite (Bar full size: 500 nm, MWCNTs of 20%)

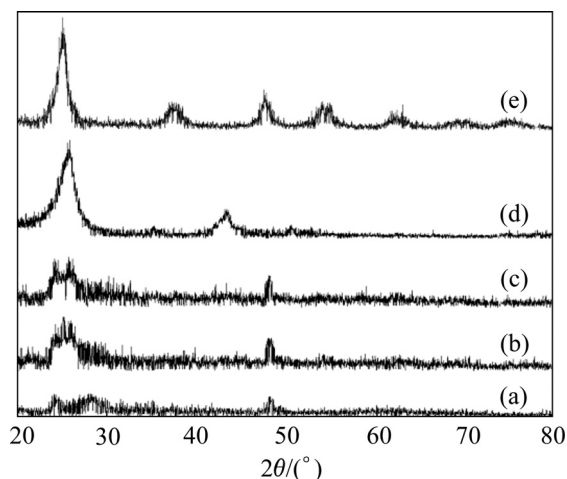


Fig.2 XRD patterns of MWCNTs, raw material TiO₂, and nanocomposites of MWCNTs/TiO₂-NTs: (a) 5% MWCNTs/TiO₂; (b) 20% MWCNTs/TiO₂; (c) 30% MWCNTs/TiO₂; (d) MWCNTs; (e) TiO₂

MWCNTs/TiO₂-NTs composites to anatase was demonstrated by XRD analysis using the calcined MWCNTs/TiO₂-NTs composites.

The TG-DTG curves of MWCNTs, MWCNTs/TiO₂-NTs in O₂ ambient are given in Figs.3 and 4. Pure MWCNTs in Fig.3 exhibit a sharp mass loss at 500–620 °C, indicating carbon nanotube disappeared, Note

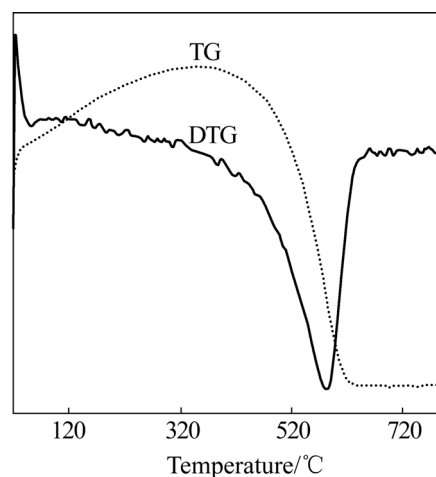


Fig.3 TG-DTG curve of pure MWCNTs in O₂ ambient

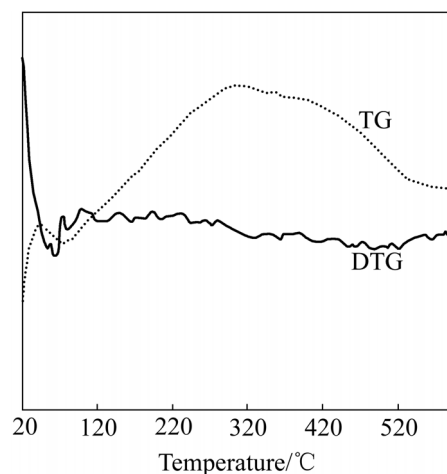


Fig.4 TG-DTG curves of 20% MWCNTs/TiO₂-NTs in O₂ ambient

that MWCNTs disappeared at the calcination temperature higher than 495 °C.

The UV-Vis spectra of nanocomposites of MWCNTs/TiO₂-NTs are given in Fig.5. The absorption edge shifted to a shorter wavelength (Blue shift) corresponding to the order: (d)>(c)>(b)>(a); which means more higher percent MWCNTs, more stronger shift ability.

3.2 Photocatalysis result

The percent of removal rate of humic acid at different UV light irradiation time over MWCNTs, raw material TiO₂, and MWCNTs/TiO₂-NTs with different ratios were shown in Fig.6. The MWCNTs shows high adsorbing capacity at the beginning of irradiation time, which has some connection with its special structure[23]; but has poor removal rate because of without photocatalysis ability. The TiO₂ particles has a higher

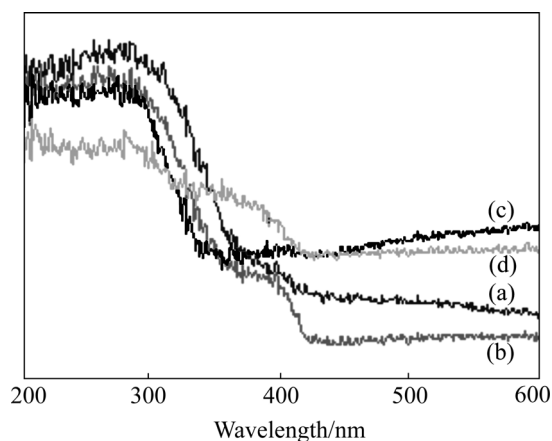


Fig.5 UV-Vis spectra of MWCNTs/TiO₂-NTs: (a) 5% MWCNTs/TiO₂; (b) 10% MWCNTs/TiO₂; (c) 20% MWCNTs/TiO₂; (d) 30% MWCNTs/TiO₂

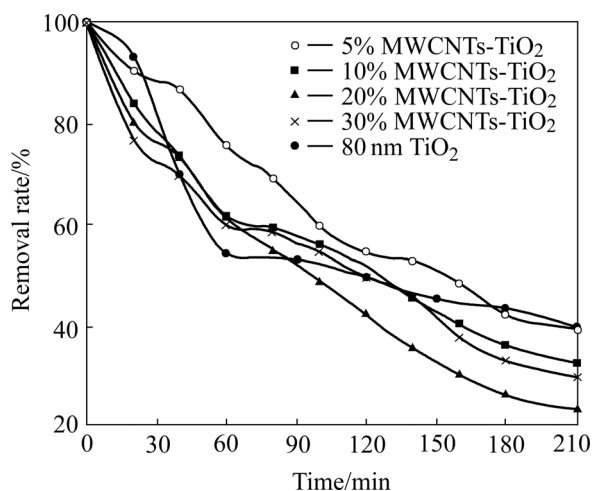


Fig.6 Removal rate of humic acid by using different catalysts

removal rate than MWCNTs, but lower than all MWCNTs/TiO₂-NTs, because the TiO₂ nanotubes are more active than pure TiO₂ nanoparticles for photodegradation of organic substance[24]. At the same time, the diffuse reflectance UV-vis spectra of the MWCNTs/TiO₂-NTs composites gives new insights into the photo-degradation mechanism, they show the characteristic spectrum of anatase with its fundamental absorption edge rising at 400 nm. The MWCNTs/TiO₂-NTs composites, on the other hand, can absorb at higher wavelength than the sole TiO₂. The absorption is observed even totally over the whole range of the UV-vis spectrum for the MWCNTs/ TiO₂-NTs composites of 20% and 30% of MWCNTs. It is noticeable that the MWCNTs/TiO₂-NTs composites of 20% MWCNT provides the largest change of the UV-vis spectrum, and be followed by 30%, 10%, and 5% MWCNTs.

4 Conclusions

1) The UV-Vis spectra of the nanocomposites samples indicates the enhancement of absorption increase with MWCNTs percent from 5% to 30%.

2) The synergetic effect has observed for nanocomposites of MWCNTs/TiO₂ on the photocatalytic degradation of humic acid, which increases with MWCNTs percent from 5% to 20%, the 20% MWCNTs/TiO₂ has optimum synergetic effect and has the highest removal rate.

3) The MWCNTs/TiO₂-NTs could be utilized with success in other removals of organic pollutants and further studies should be carried out.

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