

Synthesis and Characteristics of Multi-walled Carbon Nanotubes Coated Nanostructure TiO₂

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Abstract. Nanostructure anatase TiO₂/carbon nanotubes (TiO₂/CNTs) were prepared by hydrothermal process using acid treated CNTs and titanium (IV) sulfate. The materials were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and Brunauer-Emmett-Teller (BET). The results showed that anatase nano-TiO₂ grew on CNTs and the TiO₂ nanoparticles had diameters in the range of 30-50 nm. It was a facile approach to grow anatase nano-TiO₂.

1. Introduction

Heavy metals are widely found in the effluents from the metallurgy, mineral beneficiation processing, electroplating, painting and other industries. Because of their non-biodegradable, highly toxic and probably carcinogen, they can be easily transported to environment and may cause serious problems to our health[1]. Many technologies have focused on the efficient elimination of the heavy metals pollutants, such as chemical precipitation, adsorption, reverse osmosis, electrodialysis, ultrafiltration, and ion exchange[2-6]. Among these technologies, Adsorption is widely applied because this method is easy to handle, relatively low cost, and simply equipment[7]. The key of adsorption technology is to improve the adsorption capacity of adsorbent. The efficiency of adsorptive removal is determined mainly by the adsorption capacity, selectivity for specific compounds, and durability and regenerability of the adsorbents[8]. In recently, the developments of nanoscience science for heavy metal removal have received remarkable attention due to their special features. Various nanosized adsorbents such as zirconium phosphate, TiO₂ nanotubes, nanozerovalent iron[9], maghemite and hematite nanoparticles[10, 11], nano MgO[7] have been used for the removal of these toxic metal ions.

During the last year TiO₂ has attracted much interest as a photo-catalytic agent, gas sensor materials and catalyst support due to its natural abundance, nontoxicity, photostability, low-cost, physical and chemical stability, and unique electronic and optical properties[9, 12-14]. In addition, TiO₂ has been demonstrated as a high capacity adsorbent for As removal from copper smelting wastewater[15] and other metal such as Se(IV), Cu, Hg, Pb [16].

Carbon nanotubes (CNTs) have brought out huge activity in composites science due to their intriguing nanoscale, low density, high specific surface area, intrinsically superior mechanical properties and excellent electrical and thermal properties[17]. Many studies have reported the production and characterization of CNT-based hybrid composites [7, 18]. CNT-based hybrid composites exhibit eminently synergistic performance. The coupling of TiO₂ with carbon nanotubes has been shown to provide a synergistic effect which can enhance the overall efficiency of a photocatalytic process. The composites of titanate nanotubes with carbon nanotubes demonstrate high adsorptive capacity for Pb²⁺ and Cu²⁺.

In this study, we utilized a hydrothermal method to synthesize carbon nanotubes coated nano TiO₂. The effects of synthesis temperature and solution pH values on the TiO₂/CNTs crystallization and TiO₂loading amount were analyzed. In addition, the as-prepared composites were used to remove heavy metal ions.

2. Experimental section

2.1 Materials

The as-produced CNTs (diameter, 30-50 nm; length, ~20 μm) were purchased from Chengdu Institute of Organic Chemicals, Chinese Academy of Science. Titanium (IV) sulfate and concentrated HNO_3 were purchased from the Beijing Chemical Reagents Company. All the other chemicals were analytical grade and used in this study without an additional purification.

2.2 Purification of CNTs

As-received CNTs (4.0 g) were dispersed in 200 mL acid mixture of concentrated sulphuric acid and nitric acid with a volume ratio of 3:1 and constantly stirred at 40 $^{\circ}\text{C}$ for 6 h. After cooling to room temperature, the black suspension was filtered and washed with water until pH neutral, and then dried at 80 $^{\circ}\text{C}$ for 6 h. The dried CNTs were milled into powder for use.

2.3 Synthesis of CNTs coated TiO_2

CNTs coated TiO_2 were fabricated using Titanium (IV) sulfate and CNTs as supporter in water by hydrothermal method. CNTs (3 g) were added to 300 mL ultrapure water and dispersed by ultrasonic wave (50 W) for 10 min. A certain amount of Titanium (IV) sulfate was added in the suspensions and adjusted to the desired pH with HCl/NaOH . The suspension was poured into stainless steel autoclave and sealed. And then the autoclave was heated to 150 $^{\circ}\text{C}$ with the speed 5 $^{\circ}\text{C}/\text{min}$ and retained the temperature for 2-4 h. The autoclave was naturally cooled in air. The precipitate was filtrated and washed with ultrapure water. Finally the resulting products were dried in vacuum oven at 80 $^{\circ}\text{C}$ for 24 h.

2.4 Characterization of samples

The morphology and structure of the samples were characterized using scanning electron microscopy (SEM) (JSM-6490LV, Japan) transmission electron microscopy (TEM) (JEM-2010, Japan), and high-resolution transmission electron microscopy (HRTEM) (JEM-2010, Japan), equipped with selected-area electron diffraction (SAED). The X-ray powder diffraction (XRD) was carried out on D8 ADVANCE (Germany, Cu $\text{K}\alpha$, $\lambda = 0.15406\text{ nm}$). The textural properties of the solid adsorbent was measured in a Quantachrome Nova-1000 equipment by physisorption of N_2 at the temperature 77 K.

2.5 Adsorption measurement

The adsorption properties of the prepared TiO_2/CNT for heavy metal ions Pb^{2+} was measured in batch experiments. 200 mL of solution containing 50 mg/L Pb^{2+} were adjusted to desired pH values in the range of 5 to 11 with NaOH and H_2SO_4 . 0.10 g of TiO_2/CNT was added to solution and stirred at room temperature for 30 min. The suspension was filtered through a 0.45- μm membrane filter for Pb^{2+} analysis. The concentrations of the studied heavy metal ions in aqueous phase were determined using inductively coupled plasma mass spectrometry (ICP-MS, Thermo Fisher X Series II).

3. Results and discussion

3.1. The effect of temperature on crystallization

Fixing the volume ratio of CNTs/Titanium (IV) sulfate at 2:1 and holding reaction time for 2 h, the effect of temperatures on the crystallization was explored. Fig. 1 displays XRD patterns of the purified CNTs and samples obtained at various temperatures. As seen from Fig. 1, the diffraction peaks at $2\theta = 26.0^{\circ}$ can be indexed to the (0 0 2) reflection of CNTs. It indicated acid-oxidation pretreatment of CNTs did not damage significantly the structure of CNTs. The low intensities below 120 $^{\circ}\text{C}$ explicated TiO_2 poor crystalline. The samples exhibited diffraction peaks at 2θ values around 25.5° , 37.8° , 48.0° , 54.1° , and 62.7° when hydrothermal temperature above 120 $^{\circ}\text{C}$. This ascribed to TiO_2 characteristic diffraction peaks and can be easily indexed as the body-centered tetragonal phase of TiO_2 (PDF: 21-1271). The broad diffraction peaks indicated that the crystalline size of TiO_2 particles was quite small. The average crystal size was 30-40 nm. It was noticeable that the intensities of diffraction peaks gradually increased with increasing hydrothermal

temperature from 120 to 180 °C. When hydrothermal reaction temperature was 180 °C (t = 30 min), the TiO₂ nanoparticles increased. Accordingly, the optimal temperature was 150 °C in the present system.

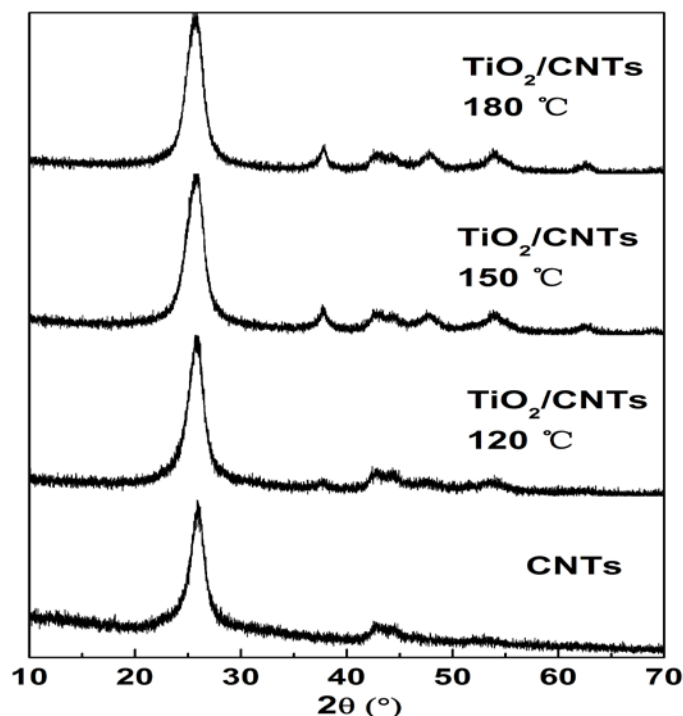
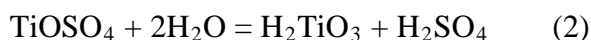


Fig. 1. The XRD patterns of purified CNTs and TiO₂/CNTs prepared at various temperatures

3.2. The effect of solution pH value on TiO₂ loading amount

The solution pH value influenced the TiO₂ loading on the CNTs. Fig. 2 depicts the samples prepared at various pH values. The TiO₂ nanoparticles aggregated when solution pH 3.0. While the solution pH increased to 9.8, the nanoparticles became small and the loading amount decreased. However, when the solution pH 12.1, the TiO₂ nanoparticles were not loaded adequately. The TiO₂ did not adhere to CNTs, but formed independently nanoparticles. Therefore, an increase in pH is unfavourable to the formation of TiO₂/CNTs.

The formation of TiO₂/CNTs hybrids involved basically two steps: Step 1) Titanium (IV) sulfate can hydrolyze easily to form H₂TiO₃. The reaction process probably involves the following chemical reactions:



Step 2) To some extent, the CNTs serves as a nuclei for TiO₂ epitaxial growth via heterogeneous nucleation. Defects and organic groups on CNTs surface facilitate the binding of metal atoms.

The experiments demonstrated that the p*H*_iep (isoelectric point) of oxidation CNTs is 2.1, and the absolute value of the zeta potential increased with the increased pH values. The surface potential of CNTs increases with increasing pH of the solution. The metatitanic acid radical is very difficulty to access CNTs due to electrostatic repulsion. Accordingly, the optimal pH value was 5 in the present system.

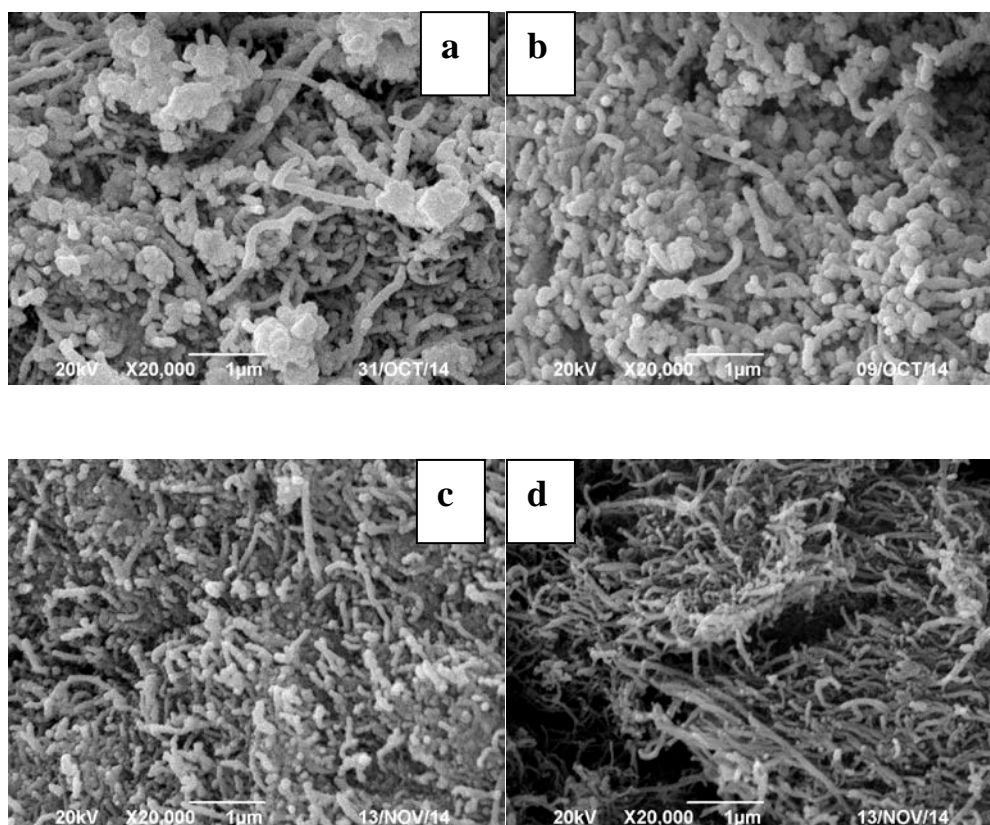


Fig. 2 The SEM image of TiO₂/CNTs prepared at various pH, 3.0(a), 6.3(b), 9.8 (c), 12.1(d)

3.3. Specific surface area characteristics of TiO₂/ CNTs

Fig.3 depicts nitrogen adsorption-desorption isothermal curves and pore size distribution of TiO₂/CNTs. It can be seen clearly all isotherms are type IV curves, confirming their mesoporous character. The sharp increase of sorption at $P/P_0 > 0.8$ is mainly attributed to nitrogen condensation between the entangled nanotubes and to a lesser extent in the central canal of the nanotubes with open tips, in accordance to Jurewicz's report [19]. The total surface area of TiO₂/CNTs was measured to be 159.2 m²/g.

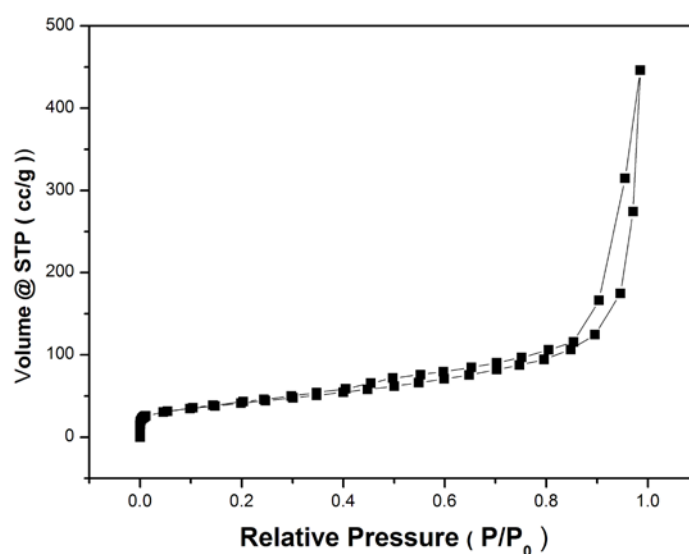


Fig. 5. Nitrogen adsorption-desorption isothermal curves of the sample.

3.4. Adsorptive characteristics of TiO₂/ CNTs for Pb

Fig. 4 shows the influence of pH of test solution on the adsorption of Pb²⁺ by TiO₂/CNTs at pH 2.8–11.3. As it is seen, there are significant increases in removal efficiency with increasing pH values. At pH 2.8–4, the removal efficiency was low. It was probably TiO₂/CNTs surface groups

adsorb H^+ , which competed with Pb^{2+} . The significant enhancement in removal efficiency with increasing pH values from 7.9 to 11.3 is most probably due to formation $Pb(OH)_2$. Hence, at pH 5.1-6.2, it exhibited actually removal efficiency of $TiO_2/CNTs$. The removal efficiency was 83.2%.

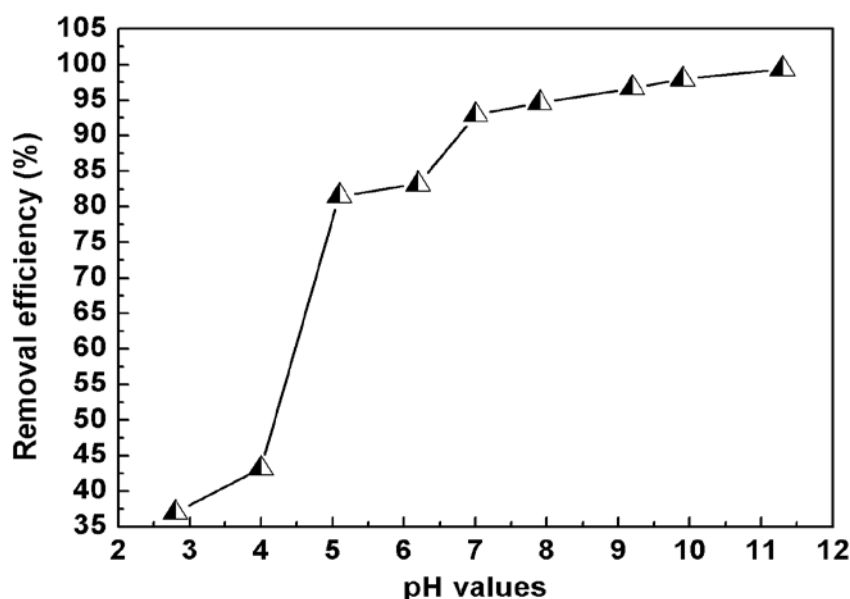


Fig. 4 pH values effect on removal efficiency

4. Conclusions

In summary, a facile process has been successfully employed to prepare $TiO_2/CNTs$. The hydrothermal temperature influenced eminently TiO_2 crystallation. The solution pH influenced TiO_2 loading amount. $TiO_2/CNTs$ displayed high removal efficiency for Pb^{2+} .

Acknowledgements

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