



Characterization and use of functionalized carbon nanotubes for the adsorption of heavy metal anions

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Abstract

The Carbon nanotubes (CNTs) have been chemically functionalized with various oxygen-containing surface groups. The feature of abundant oxygen-containing surface functional groups on the functionalized CNTs is characterized by X-ray photoelectron spectroscopy and temperature-programmed desorption analysis. Results indicate that the functionalized CNTs have a superior adsorption capacity toward anionic chromate CrO_4^{2-} , a typical toxic heavy metal ion in waste water, as compared with the unmodified ones. The excellent adsorption ability of CrO_4^{2-} is attributed to the interaction of CrO_4^{2-} with the surface oxygen-containing functional groups on the modified CNTs. The functionalized CNTs can be potentially used as an alternatively viable and promising adsorbent for the removal of heavy metal anions in waste water.

Keywords: Carbon nanotube; CrO_4^{2-} ; Adsorption; Chemically functionalization

1. Introduction

Considerable efforts have been made to focus on nanostructured carbon materials for their potential applications in numerous fields, such as microfilters, biology and medicine, nanoscale engineering and molecular electronics, hydrogen-storage devices, lithium battery, gas sensors, and catalysis [1-5]. Carbon nanotubes (CNTs), as one of the representative paradigms among nanostructured carbon materials, continue to attract tremendous attention in the past two decades due to their unique physical and chemical properties [6-7]. In particular, chemical functionalization of CNTs can modify their physical and chemical properties, leading to the improvement of their performance for specific applications [8]. Notably, some studies have indicated that functionalized CNTs are a promising candidate for the removal of trace amounts of toxic heavy metals in waste water [9], which represent an important environmental issue because of their toxic effects and accumulation throughout the food chain and hence in the human body [10-11]. It is also recognized that the adsorption of heavy metal ions from solution on CNTs is mainly dominated by the surface functional groups on CNTs [9].

However, earlier research works focused only on the adsorption of divalent cationic heavy metal ions [9]. In this

study, we demonstrate that functionalized CNTs with abundant oxygen-containing surface groups exhibit the superior adsorption capability for anionic chromate (CrO_4^{2-}), a typical heavy metal ion in waste water, from aqueous solution, as compared with the unmodified ones.

Water pollution by hexavalent chromium Cr^{6+} is of considerable concern because Cr^{6+} is a powerful epithelial irritant, is toxic to many plants, aquatic animals, and bacteria, and is confirmed to be a human carcinogenic substance [12-13]. Most of the industrial wastewater discharged into surface water contains Cr^{6+} even after a reduction treatment process to the trivalent state [14]. The disadvantage of the reduction treatment of Cr^{6+} to trivalent state is the high cost of chemicals used for the reduction process and incomplete conversion of Cr^{6+} , which may produce toxic sludge because of the surface adsorption of Cr^{6+} onto the Cr^{3+} hydroxide precipitate. Therefore, it is highly desirable to explore other viable methods to remove Cr^{6+} in waste water. From the economy and efficiency point of view, surface adsorption by choosing potential adsorbent provides a feasible and promising alternative. The results presented in this work, for the first time, reveal that the functionalized CNTs are a promising and viable adsorbent for the removal of toxic chromate from aqueous solution.

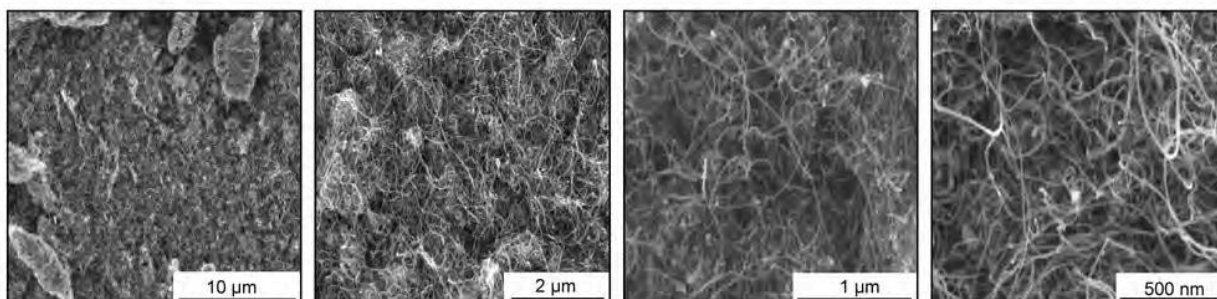


Fig. 1: SEM images of as received baytube CNTs at different resolutions

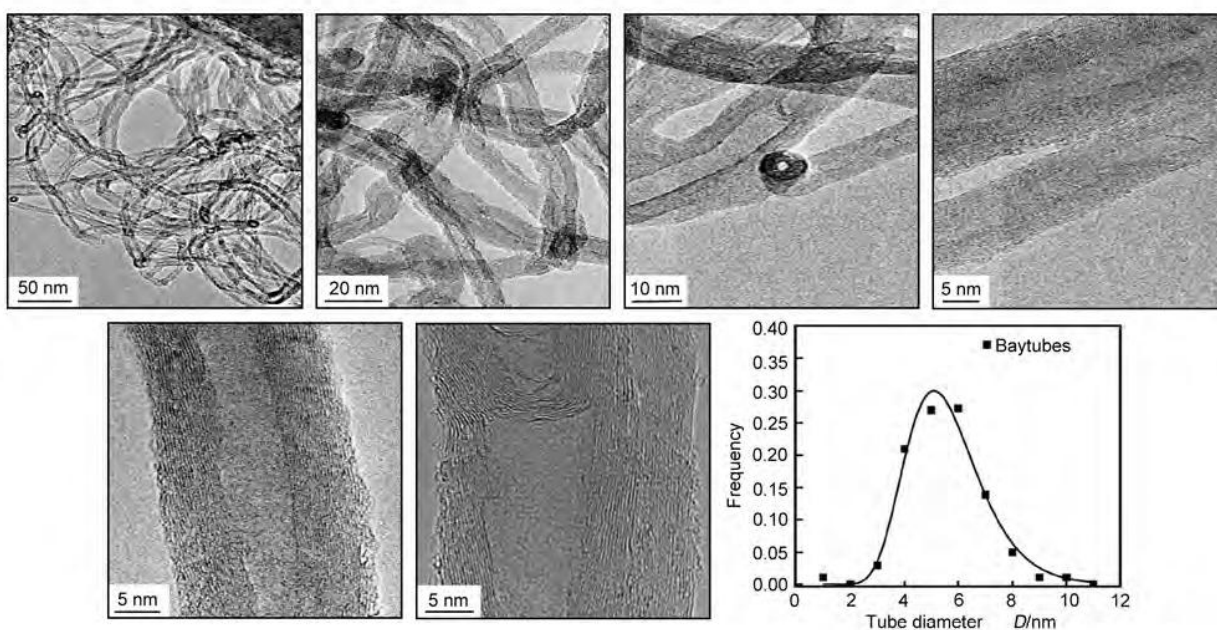


Fig. 2: TEM / HRTEM images at different resolutions and diameter distribution of as received baytube CNTs

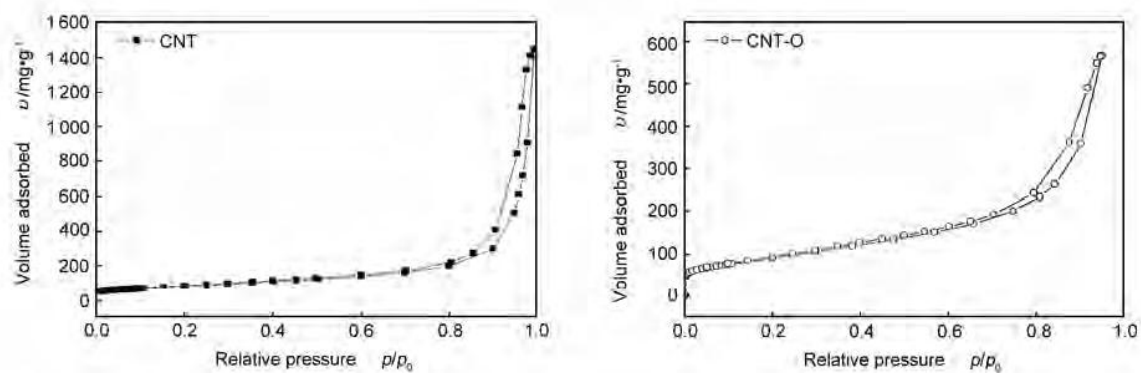


Fig. 3: BET adsorption isotherms of CNT and CNT-O

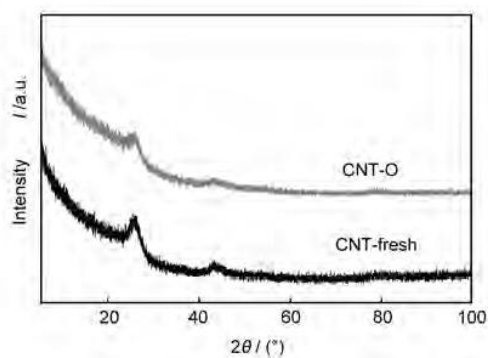


Fig. 4: XRD patterns of CNT and CNT-O

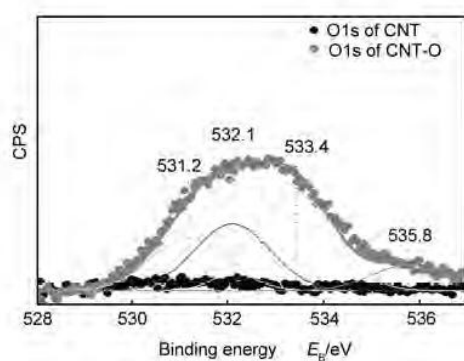


Fig. 5: XPS O1s spectra of CNT and CNT-O and fitting of O1s spectra of CNT-O using a multiple Gaussian function

2. Experimental section

CNTs are commercial multiwalled CNTs supplied by Bayer Material Science Company. Chemical functionalization of the as-received CNTs was carried out by introducing oxygen-containing functional groups with concentrated nitric acid (HNO_3). The as-received CNTs were refluxed in the concentrated HNO_3 for 10 h under continuous stirring, followed by washing with distilled water completely and drying at 373 K overnight in a furnace. This method is also well utilized for oxidation of other carbon allotropes, such as activated carbons and fullerenes[15]. Such oxidation treatment of CNTs not only introduced different oxygen-containing functional groups onto the surface or inner matrix of CNTs but also removed the metal impurities inherently present in the as-received CNTs. For clarity, the as-received CNTs are denoted as CNT and the functionalized ones as CNT-O.

Temperature-programmed desorption (TPD) were carried out in a quartz reactor connecting with a Quadrupole Mass Spectrometer 200 M2. Sample (20 mg) was loaded between two quartz wool plugs with helium flow at room temperature for 2 h. After that, the temperature was increased to 830 °C with a ramp rate of 10 °C/min and a helium flow rate of 15 mL/min.

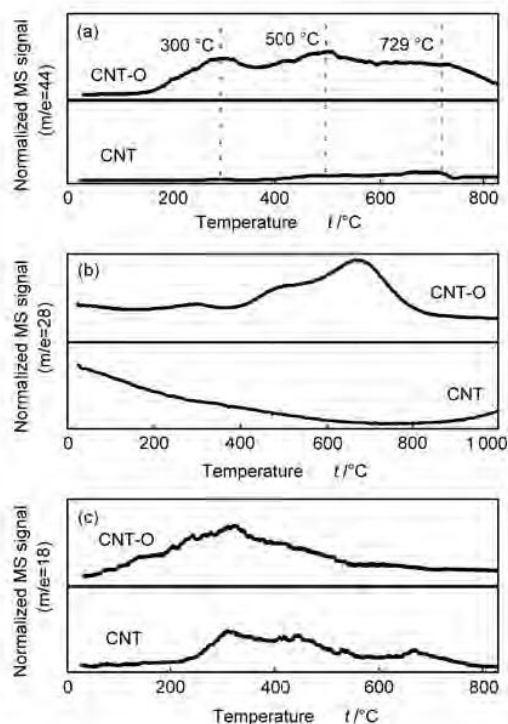


Fig. 6: (a): CO_2 TPD profile and (b, c): CO and H_2O TPD profiles of CNT and CNT-O

The powder X-ray diffraction (XRD) analysis was performed on a STOE STADI-P transmission diffractometer equipped with a focusing primary Ge (111) monochromator and a position sensitive detector, using $\text{Cu-K}\alpha 1$ radiation. Specific surface areas were measured by nitrogen adsorption at 77 K using an AUTOSORB-1-C physisorption/ chemisorption analyzer (Quantchome). X-ray photoelectron spectroscopy (XPS) was measured at beam line U49/2-PGM1 at BESSY in Berlin. Scanning electron microscopy (SEM) analysis was performed on a Hitachi S-4800 at an acceleration electron voltage of 15 kV. Micrographs from transmission electron microscope (TEM) were taken on a Philips CM 200 LaB6 at an acceleration voltage of 200 kV. Zeta-potential measurement was performed in a Malvern zetasizer. Approximately 10 mg of CNTs was dispersed in 10 mL water and ultrasonicated for 10 min. Then, zeta potential was measured at 25 °C from pH 1.5 to 12, which was adjusted by using 0.25 mol/L HCl or NaOH.

Adsorption isotherms of heavy metal ions at room temperature were obtained by adding 10 mg CNT or CNT-O to a 2 mL Eppendorf tube containing 1.5 mL of the appropriate adsorbate solution with different concentrations. The pH calculated for CrO_4^{2-} (not adjusted with additional buffer) is around 7.8, which ensures that the sole species adsorbed was bianionic CrO_4^{2-} during the adsorption experiments. The suspensions were kept for 5 days to ensure an equilibrium adsorption of heavy metal ions on the carbon. The pH at the adsorption equilibrium is about 5.9. The

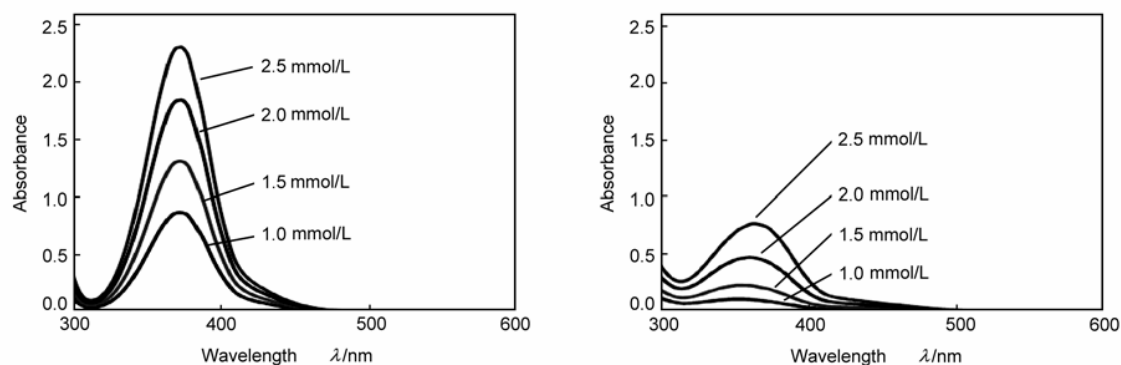


Fig.7: UV-Vis adsorption spectra of the chromate solution after adsorption by the samples of CNT (left) and CNT-O (right)

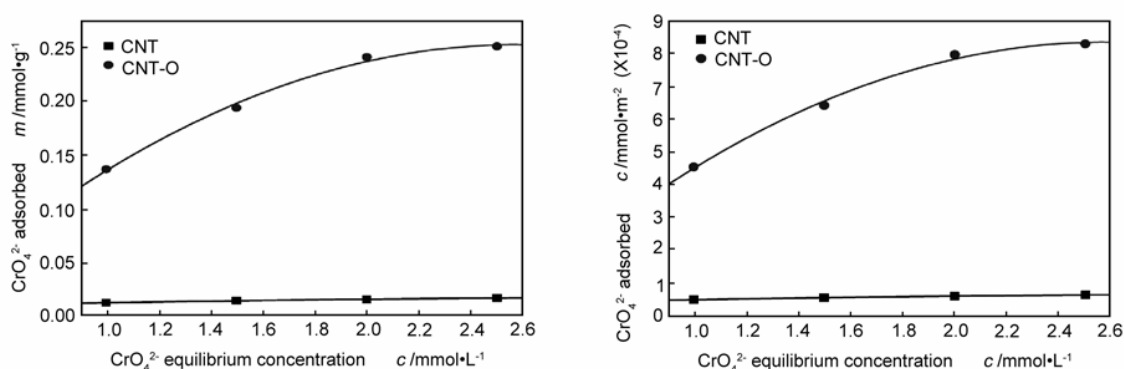


Fig.8: Adsorption isotherms of CrO₄²⁻ per unit mass (top) and per unit surface area (bottom) in aqueous solution on the samples of CNT and CNT-O

concentration of CrO₄²⁻ after adsorption was measured by Perkin-Elmer Lambda 650 UV/Vis spectrometer.

3. Results and discussion

Fig.1 shows the SEM images of the as-received CNTs. It is found that CNTs are evenly and well distributed, and no amorphous carbon is detected. Details of the microstructure of the wall and surface structure of CNTs are revealed by TEM and high-resolution TEM images, as shown in Fig.2. Clearly, the walls of these CNTs exhibit well-graphitized structure, and no amorphous carbon is present. The distribution of outer diameters is shown in Fig.2, illustrating that the average diameter of the CNTs is around 5 nm.

Fig.3 shows the nitrogen adsorption-desorption isotherms and pore size distribution of the original CNTs and the functionalized CNT-O. The specific Brunauer-Emmett-Teller(BET) surface area and micropore volume of CNTs are 293 m²·g⁻¹ and 0.12 cm³·g⁻¹, respectively. After oxidation treatment, the specific BET surface area of CNT-O is increased to 301 m²·g⁻¹ and the micropore volume is 0.13 cm³·g⁻¹. XRD patterns shown in Fig.4 indicate no significant difference observed between CNTs and CNT-O.

The remarkably increased amount of oxygen-containing functional groups on the CNT-O as compared with the unmodified CNTs has been illustrated by XPS analysis. Based on the areas of the O1s and C1s peaks in the spectra, the surface composition of the original CNTs and the as-functionalized CNT-O can be quantified. Results showing the difference in surface functional groups of the CNTs and the CNT-O are shown in Fig.5, which clearly suggests that the CNT-O be loaded with oxygen-containing surface functional groups. The surface oxygen content on the CNT-O is calculated to be 22%, whereas the original CNTs has a surface oxygen content of only ca. 3%. Further deconvolution of the O1s peaks in the spectra is depicted in Fig.5. The O1s spectra of the CNT-O can be deconvoluted into four peaks [16-18]. The peak at around 531.2eV corresponds to carbonyl/C=O species and the peaks at 532.1eV and 533.4eV to the C-O and hydroxyl/ C-OH moiety. The small peak at 535.8eV is assigned to adsorbed water.

The feature of the more abundant oxygen-containing functional groups on the CNT-O than that on CNTs has been also corroborated qualitatively by the TPD profile obtained under helium atmosphere. It can be seen from Fig.6 that the intensity of CO₂, CO, and H₂O in TPD profiles of CNT-O is much higher than that of CNTs. Further deconvolution of the CO₂ in TPD profile gives three main

peaks located around 300 °C, 500 °C, and 700 °C, which can be attributed to anhydride, carboxylic, carbonyl, and lactone groups [19]. Clearly, all of these types of acidic functional groups have been significantly increased after the functionalization by oxidation, thereby making CNTs more active for capturing heavy metal ions from aqueous solution. Adsorption of heavy metal ions on CNTs or activated carbon is generally related to the surface functional groups [9, 20–22].

The functionalized CNT-O and original CNTs have been used for testing their capability for adsorption of anionic chromate (CrO_4^{2-}), a typical heavy metal ion in waste water. Figs. 7 and 8 show the UV-Vis spectra of solution after the adsorption equilibrium is reached and the corresponding CrO_4^{2-} adsorption isotherms on CNTs and CNT-O in aqueous solution. Obviously, the sample CNT-O with the abundant oxygen-containing surface functional groups, particularly the OH groups, has the excellent CrO_4^{2-} adsorption capacity because the adsorption of CrO_4^{2-} occurs mainly via ion exchange with acidic surface OH groups [23–25].

In addition, the adsorption isotherm of CrO_4^{2-} on the CNT-O fits well with Langmuir model, from which a maximum adsorption capacity of 249 $\mu\text{mol/g}$ can be extracted for CNT-O. In contrast, the original CNTs exhibit a poor maximum adsorption capacity of 16 $\mu\text{mol/g}$, which can be accounted for by the very low oxygen-containing surface functional groups in the original CNTs. In other words, the adsorption capacity of CrO_4^{2-} from aqueous solution on the CNT-O is 15 times as large as that on the CNTs. Similar results are obtained if the adsorption capacity is based on surface area. The estimated maximum adsorption capacity per unit surface area on the CNT-O is 0.83 $\mu\text{mol/m}^2$, which is pretty higher than 0.06 $\mu\text{mol/m}^2$ on the CNTs. Therefore, based on both the adsorption capacity per unit mass and per unit surface area, the CNT-O exhibits the superior performance for capturing CrO_4^{2-} from aqueous solution. Zeta-potential analysis demonstrates that the CNT-O is negative-

ly charged on the surface in the range of $\text{pH} > 3.5$, and bianionic CrO_4^{2-} is the predominant species in this pH range [25]. Hence, these exclude the electrostatic effect as the main contribution to the adsorption of CrO_4^{2-} from aqueous solution using the functionalized CNT-O as adsorbent. However, the contribution of BET surface area and micropore volume to the difference in adsorption capability of CrO_4^{2-} for the original CNTs and functionalized CNT-O can also be excluded because of negligible change of their BET surface area and micropore volume as mentioned above. Thus, the superior adsorption capability of chromate on the CNT-O as compared with the CNTs can be ascribed to the interaction of chromate with the abundant surface oxygen-containing functional groups on the CNT-O.

4. Conclusion

We have investigated the adsorption of anionic chromate, a typical heavy metal ion in waste water, using functionalized CNTs as adsorbent. The features of abundant oxygen-containing surface functional groups on the functionalized CNT were characterized by the XPS and TPD analyses, which are ascribed to the excellent adsorption capacity of chromate as compared with the unmodified CNTs. The results herein have demonstrated that functionalized CNTs with abundant oxygen-containing surface functional groups have the significant potential as a viable adsorbent for the removal of chromate from aqueous solution.

Acknowledgement

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