METAL ADSORPTION STUDY OF CARBON NANOTUBES FUNCTIONALIZED BY CARBOXYLIC ACID GROUPS USING DIELECTRIC BARRIER DISCHARGE PLASMA

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Introduction

The pollution of water resources due to the disposal of metal ions is a worldwide concern. Due to the hazardous effects associated with these metal ions for human and environment, it is essential to be removed from wastewaters before releasing into the environment. Among various separation processes, recently adsorption and ion exchange have drawn great attention. Adsorption and ion exchange are effective and economically viable processes because of high separation efficiency and low energy consumption [1]. Carbon nanotubes (CNTs) functionalized with proper functional groups (e.g. carboxylic groups) can adsorb metal ions [2].To the best of our knowledge, functionalization of CNTs for the purpose of wastewater treatment is performed by chemical method. Oxidized nanotubes mainly have carboxylic acids as their functionality [3]. This method is tedious and time consuming.

Dielectric barrier discharge (DBD) plasma functionalization is an efficient method to functionalize surface of nanotubes rapidly without using hazardous chemicals. Adjusting plasma parameters such as power, exposure and the atmosphere used, leads to formation of different functional groups on the surface of nanotubes [4]. In this work a novel technique was used to functionalize CNTs with carboxylic acid groups by means of plasma treatment and without using any chemical.

Experimental

Multiwalled carbon nanotubes (MWNTs) were purchased from Shenzhen Nanotech Port Co. Ltd. In order to eliminate possible functional groups, the MWNTs were heated to 1000˚C in a helium atmosphere. Functionalization process is carried out using DBD plasma under humid air atmosphere. DBD plasma reactor (Fig. 1) employs high voltage of 1-10 kV with an output frequency of 0.5-10 kHz. Zero air saturated with water at 80˚C is selected as the atmosphere of plasma.

For the quantitative analysis of the plasma-functionalized sample, temperature-programmed desorption (TPD) was carried out. The details of this technique have been reported elsewhere [4]. Adsorption properties of the functionalized CNTs were studied by adding 0.025 mg of MWNTs into 50 ml of Pb^{II} solution with initial concentrations ranged from 10 to 80 ppm . After stirring for 6 h, solid phase was separated and the remained solution was measured by atomic absorption for Pb^{II} concentration.

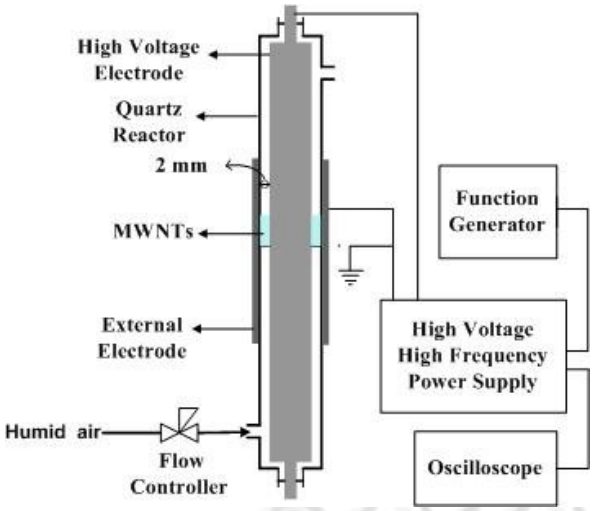

Fig. 1 Schematic of the DBD plasma functionalization set up.

Results and Discussion

Figure 2 presents SEM image of pristine MWNTs. As is shown, nanotubes are curled and entangled with each other.

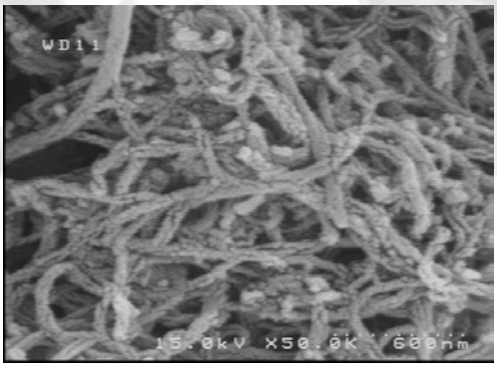

Fig. 2 SEM micrograph of pristine MWNTs.

TPD spectra of MWNT samples are presented in Fig. 3. TPD of the pristine nanotubes (Fig. 3a) shows relatively low gas evolution at high temperature. In other word, pristine nanotubes have slight amount of functional groups on their surfaces. These functional groups might be produced during purifying process in acidic media. Heat treatment of pristine nanotubes in the presence of helium mostly removes these functional groups. The TPD of the functionalized MWNTs (Fig. 3b) shows a low-intensity peak at 320˚C, a broad peak at 550˚C and a sharp peak at 840˚C. In accordance with other studies [2,3], desorption of oxygen-containing groups leads to release of H_2O, CO_2 and CO. Evolution of H_2O occurs at about 300˚C, which originates from formation of carboxylic

anhydride from two adjacent carboxyl groups. CO_2 release at low temperatures is mainly due to the decomposition of carboxylic acid and at higher temperatures as a result of decomposition of lactone groups. CO is derived from the decomposition of anhydrides, carbonyl and quinine groups [4]. However, two adjacent carboxylic groups may be first dehydroxylated to the anhydride which decomposes at higher temperatures than those of free carboxylic groups. Diffusion of the evolved gases through narrow pores of nanotubes is rather slow and CO molecules may react with surface-bound oxygen and oxidize to CO_2.

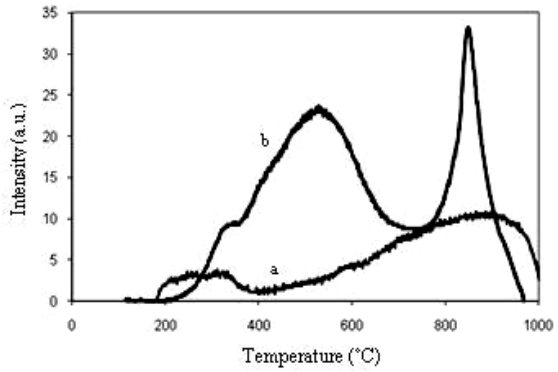

Fig. 3 TPD profiles of a) pristine and b) functionalized MWNTS.

Functionalized CNTs were used in lead ion adsorption experiments to further evaluate the quantity of functional groups on the surface. Figure 4 shows adsorption isotherm of plasma functionalized MWNTs.

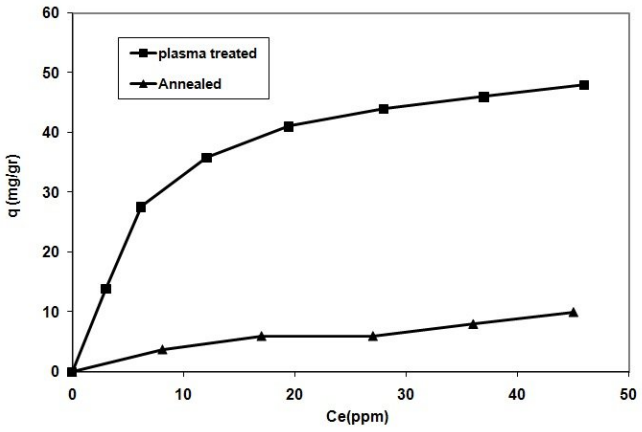

Fig. 4 TPD profiles of a) pristine and b) functionalized MWNTS.

As can be seen lead ions are adsorbed onto the CNT surface with an adsorption capacity of 50 mg/g. As the CNTs were annealed before functionalization and according to the isotherms the annealed samples do not show any considerable adsorption, the adsorbed metal ions can be attributed to formation of carboxylic acids during the plasma treatment. It must be noted that plasma functionalization can introduce less functional groups onto the surface. Therefore the observed capacity cannot be compared to the chemically treated nanotubes with strong oxidizers. Further investigation for increasing the yield of functionalization is ongoing.

Conclusions

Plasma treatment in humid air mainly functionalizes the surface of the nanotubes with oxygen-containing groups (e.g. carboxylic and carbonyl groups). Desorption of these functional groups leads to evolution of H_2O, CO_2 and CO. Metal adsorption study revealed successful functionalization of CNTs with oxygenated groups.

References

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