

# Characterization of air plasma-activated carbon nanotube electrodes for the removal of lead ion

Lingfang Yang, Zhou Shi and Wenhao Yang

## ABSTRACT

Carbon nanotube electrodes were prepared by pressing a mixture of carbon nanotubes and polytetrafluoroethylene (which acted as a binder) on a stainless steel net collector, and the electrodes were subsequently activated in our self-designed plasma apparatus, using air plasma. The morphology and surface functional groups of the electrodes were characterized using scanning electron microscopy and Fourier transform infrared spectroscopy, respectively. The results showed that the electrodes activated by air plasma possessed a rougher surface and more oxygen-containing groups than the raw electrodes, properties that were beneficial for their electrosorption performance. After 5 min of air plasma activation, the lead ion electrosorption capacity of the activated electrodes (measured at 450 mV) increased to 3.40 mg/g, which was 73% higher than the capacity of the non-activated, raw electrode, and 5.76 times the adsorption capacity of the raw electrode at 0 mV. The results of this study indicate that air plasma activation can be used to effectively enhance the electrosorption capacity of carbon nanotube electrodes.

**Key words** | activation, air plasma, carbon nanotube electrode, electrosorption, lead ion

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## INTRODUCTION

Recently increasing interest has been focused on the removal of heavy metal ion from aqueous solution due to the toxicity of heavy metal ion to human body. Among all of the heavy metal ion, lead (Pb) has been identified as one of the most toxic elements, which enters the human body via inhalation and ingestion from various sources such as contaminated air, water, soil and food. There have been cases of lead pollution reported in China recent years (Cheng & Hu 2010; Yao *et al.* 2013), and developing new methods to remove Pb from polluted water becomes a more and more urgent issue.

Capacity deionization (CDI) is a novel method for removing ion from aqueous solution; this method has received much attention because of its simplicity, and because it does not require the use of additional chemical components for regeneration (Oren 2008). When an electric field is applied between two electrodes, the charged ion in solution are electrosorbed on the surface of the counter-charged electrode. The absorption capacity strongly depends on the material properties of the electrodes. Conventionally, carbon materials such as activated carbon (Hou & Huang 2013), activated carbon cloth (Huang & Su

2010), carbon nanotubes (CNTs) (Wang *et al.* 2007; Nie *et al.* 2012), and carbon aerogel (Rasines *et al.* 2012), have been used as electrode materials. However, the reported practical electrosorption capacities of carbon-based electrodes are much lower than their theoretical absorption capacity. Thus, to improve the electrosorption capacity, the modification of carbon electrode materials – using methods including oxidation with strong acids/alkalis (Babel & Jurewicz 2008), grafting carbon nanofibers on carbon fibers (Zhan *et al.* 2011), modifying activated carbon cloth using nanoparticles (Myint & Dutta 2012), adding graphene with remarkable electrical conductivity (Wang *et al.* 2012) – has been investigated. Although these modifications did enhance the electrosorption capacity, the methods used are undesirable in other ways; specifically, use of strong acid/alkalis in the methods can produce acidic/alkaline pollution, and the methods are both costly and time consuming.

It has been reported that plasma can be applied in a solvent-free and environmentally friendly technique to improve the surface properties of carbon materials (Budou *et al.* 2000; Lee *et al.* 2005). However, there are still a few

disadvantages that result from the direct treatment of CNT powders with plasma; these disadvantages prevent the full application of this technique, and the application of the resulting materials. These disadvantages include the loss of CNT powder during vacuum processing, and the difficulty of distribution/recovery during electrosorption. To overcome the above disadvantages, we propose a method here in which CNT powder is bound with polytetrafluoroethylene (PTFE) onto current collector's surfaces to make CNT electrodes, and the CNT electrodes are then put into plasma apparatus and activated by air plasma under air pressure of 10 Pa, and radio-frequency (RF) amplifier conditions of 130 mA, 650 V at frequency of 13.56 MHz. To the best of our knowledge, no such study has yet been reported.

In this study, lead ion, an aquatic environmental pollutant, were selected as a model ion to evaluate the feasibility of electrosorption using CNT electrodes activated by air plasma. The electrodes were then characterized using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy.

## EXPERIMENTAL

### Preparation of CNT electrodes

CNTs used in the study were purchased from Nanotech Port Co. Ltd in Shenzhen, China. Specifications of the CNTs are as follows: length  $<2\ \mu\text{m}$ , diameter 20–40 nm, surface area 130–160  $\text{m}^2/\text{g}$ , purity  $>97\%$  and ash content  $<3\%$ .

The CNTs were physically mixed with KOH powder at the KOH/CNT mass ratio of 4:1. The mixtures were then calcined for 2 h at  $850\ ^\circ\text{C}$  under a nitrogen atmosphere. Afterwards, the samples were washed with deionized water until pH of the washing water showed no change

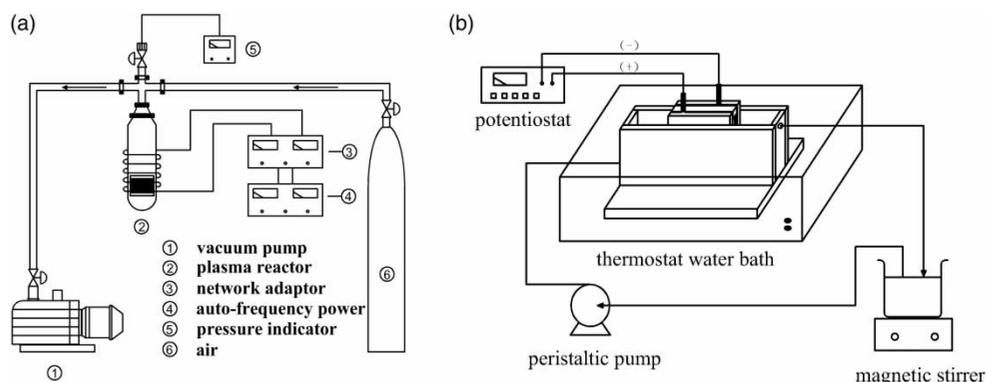
and then dried at  $110\ ^\circ\text{C}$  for 24 h. The CNTs were then mixed with PTFE (density 1.48–1.53 kg/L, purity  $60 \pm 2\%$ , Guangdong Chemical Reagent Inc., China) at a weight ratio of 80:20. To make the CNT electrodes, after the CNTs/PTFE mixture (50 mg) was applied on to each current collector (nets made of stainless steel wire with a shape of  $30\ \text{mm} \times 50\ \text{mm}$ ), the collector was pressed with a hydraulic cylinder at 10 MPa for 10 min, and it was then dried in an oven for 24 h at  $120\ ^\circ\text{C}$ .

### Activation of CNT electrodes using air plasma

The apparatus used for the air plasma activation is shown in Figure 1(a). Radio-frequency (RF) inductively coupled plasma was used in this study. The plasma treatment was carried out in a cylindrical reactor of quartz glass with dimension of 30 mm (outer diameter)  $\times$  100 mm (length). The spiral coil was fixed outside the reactor. Prior to ignition, the reactor was evacuated to a pressure of 10 Pa. Air was then flowed into the reactor via a needle valve to maintain the constant pressure. Plasma ignition started at 10 Pa, and the RF amplifier was adjusted to 130 mA, 650 V with frequency of 13.56 MHz. The CNT electrodes were activated with the air plasma in the reactor for 1–7 min, as required. The activated electrodes are named here as P-air electrodes.

### Characterization

The surface morphology of the electrodes was examined using a scanning electron microscope (Hitachi S-4800, Japan). FTIR spectra were measured for the electrodes using an FTIR spectrophotometer (Shimadzu FTIR-8400s, Japan). Pore size distribution was obtained using  $\text{N}_2$  adsorption–desorption method (Quanta NOVA4000, USA).



**Figure 1** | (a) Diagram of plasma activation apparatus. (b) Schematic of CDI unit cell and experimental device.

## Electrosorption

Electrosorption experiments were carried out in a CDI device (Figure 1(b)) under the following conditions: four pairs of capacitor units were assembled in series in the CDI device, with electrode spacings of 3 mm, and an applied voltage of 0 or 450 mV. Lead solution was obtained from lead standard solution (1,000 mg/L, Fluka, Switzerland) diluted to desired concentration. The lead ion solution (200 mL) was pumped into the electrosorption tank, and the solution was circulated using a peristaltic pump operating at a flow rate of 4 mL/min. The concentration of Pb ion was measured using an atomic absorption spectrophotometer (Shimadzu AA-7000). The electrosorption capacity ( $q_e$ , mg/g) of the electrodes was calculated using the following equation:

$$q_e = \frac{(C_0 - C_t)V}{m}$$

where  $C_0$  (mg/L) and  $C_t$  (mg/L) are the initial and final lead ion concentrations, respectively,  $V$  (mL) is the volume of the lead solution used, and  $m$  (g) is the net mass of CNTs in the working electrodes.

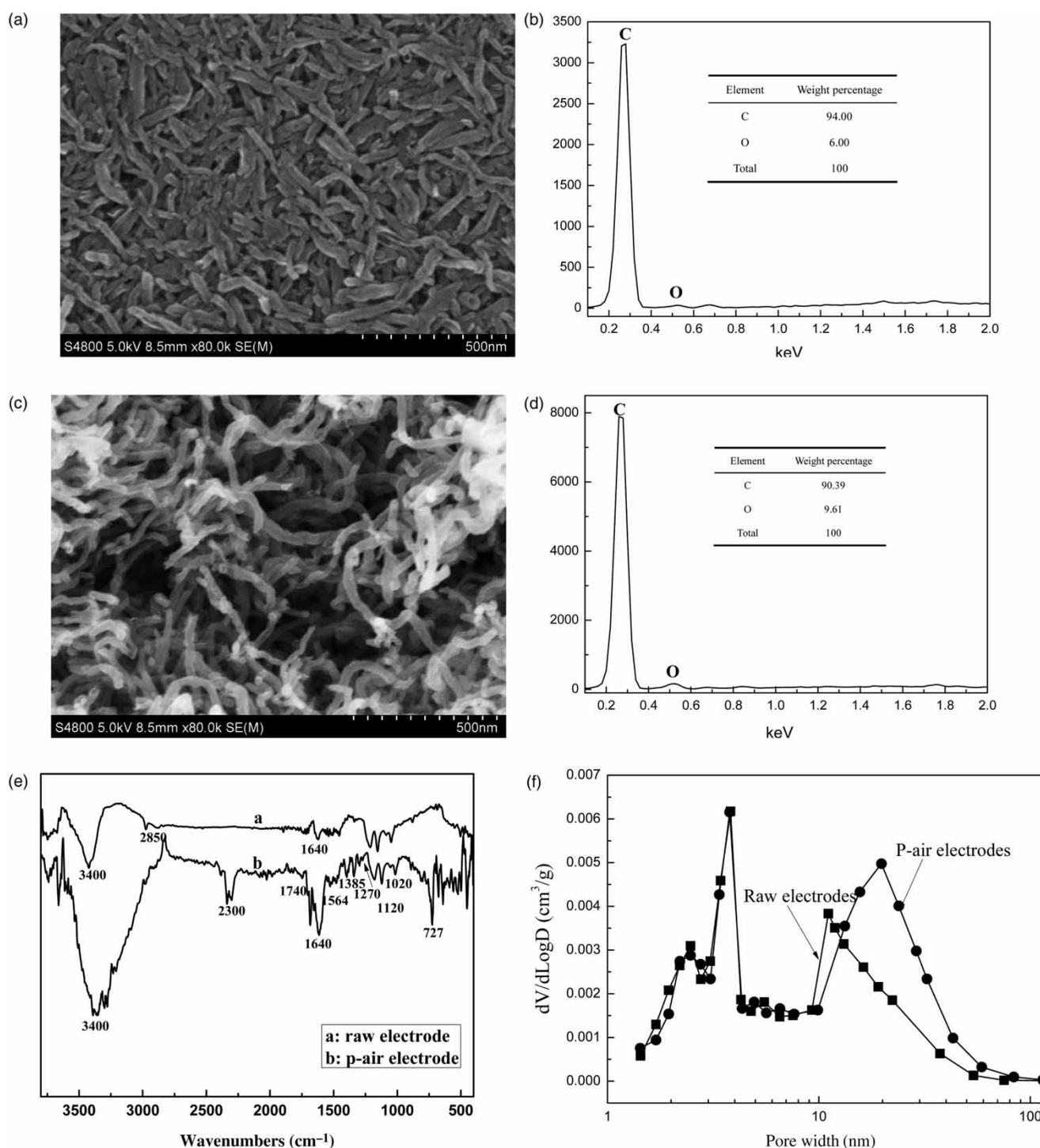
## RESULTS AND DISCUSSION

### Characterization of surface morphology and surface functional groups of the electrodes

SEM images and energy-dispersive X-ray spectroscopy (EDXS) spectra are shown in Figure 2 for the raw and air plasma-activated electrodes. The differences between the surface morphologies of the raw electrodes (without plasma treatment) and the P-air electrodes were determined by comparing the images shown in Figures 2(a) and 2(c); after the air plasma activation, the originally smooth and homogeneous surfaces of the raw CNT electrode become rougher, and the pores on the surface became larger due to partial burning of CNTs and binders. Further measurement demonstrated that the volume quantity of pores in the size range of 10 to 90 nm increased after air-plasma treatment, and the center of distribution of the pore diameter in the size range was enlarged from 10 to 20 nm after air-plasma treatment (Figure 2(f)). Further EDXS analysis indicated that the weight percentage of oxygen increased from 6 to 9.61 after the air plasma activation (Figures 2(b), (d)). The weight percentage here is defined as the ratio of the mass of the counting element over the sum mass of all elements. This

result suggested that oxygen-containing groups were formed on the CNT surfaces, as was reported when multiwalled CNT powders were activated using  $O_2$ -plasma (Yu *et al.* 2011).

The FTIR spectra are shown in Figures 2(e), and lines *a* and *b* are for the electrodes before and after the plasma activation, respectively. A comparison of the FTIR spectra showed that some new absorption bands appeared after the activation. Following Jia & Thomas (2000), Charlier (2002), Hao *et al.* (2007) and Zhang *et al.* (2009) some of the bands associated with the functional groups could be assigned: specifically, the new absorption bands at 2,300 and 1,385–1,270  $cm^{-1}$  were assigned to C=N and C–N vibrations, respectively. It is likely that the C=N and C–N bonds were produced because the activation of the gas phase by the RF energy predominantly created  $N_2^+$  ion, excited molecules, and electrons, and these highly energized particles provided sufficient energy for the covalent attachment of nitrogen to the electrodes, resulting in the formation of the surface functional groups. It was also found that the intensity of the band at 1,740  $cm^{-1}$  increased after the plasma treatment. Because the band at 1,740  $cm^{-1}$  was associated with the C=O bonds in the carbonyl acid groups (–COO), this result indicated that the plasma created more –COO groups on the activated carbon surface of the electrodes. The presence of two peaks in particular indicated large increases in the adsorption: the first was at 3,400  $cm^{-1}$ , and the second was at 1,640  $cm^{-1}$ . These two peaks were assigned to O–H stretching vibrations and bending vibration peaks, respectively. The band at 1,640  $cm^{-1}$  could also correspond to the stretching vibrations of the C=O groups of the amide functionality (Gao *et al.* 2006). The new adsorption peaks at 730–640  $cm^{-1}$  were assigned as O–H bending vibration peaks. To eliminate the undesired OH groups from adsorbed  $H_2O$  on the sample surface, samples were placed in a 120 °C oven for 24 hours, and then heated with Hg lamp irradiation when prepared for FTIR measurement. Thus, we might conclude that increase of the hydroxyl groups on the electrode surface mainly resulted from the air plasma activation. During the plasma discharge process, electrons, UV and reactive species such as O,  $O^+$ ,  $O_2^{2+}$ ,  $O_2^+$  and –C free radicals are generated. These species react with each other, thus producing OH and other oxygen functional groups (Naseh *et al.* 2010). The increase of these groups could enhance the interactions such as complexation with lead ion (Yu *et al.* 2011). A few oxygen groups existing on the surface of the raw electrodes were formed during pre-treatment when the electrodes were calcined with KOH (He *et al.* 2010).

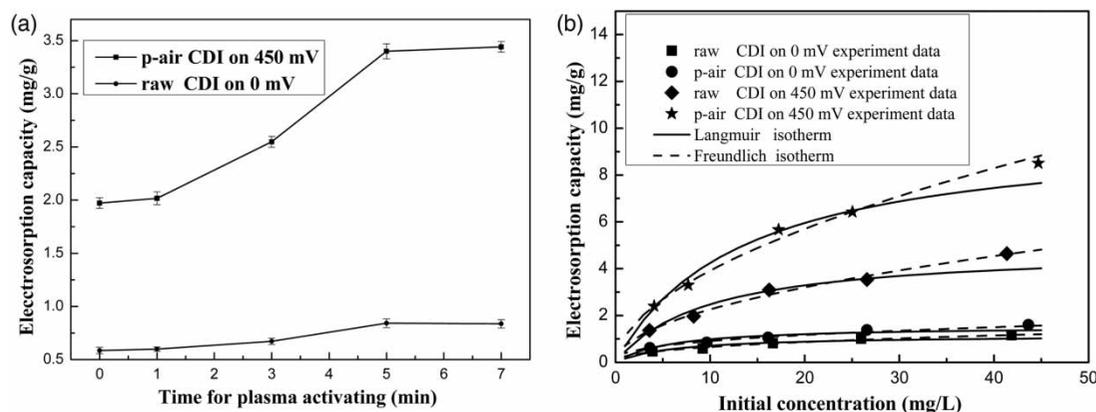


**Figure 2** | (a), (c) SEM images of raw and p-air electrode. (b), (d) EDXS spectrum of raw and P-air electrode. (e) FTIR spectra. (f) Pore size distribution of raw electrode and p-air electrode.

### Influence of plasma activation on the electrosorption capacity

The relationship between the electrosorption capacity of the electrodes for lead ion and the activation time is shown in

**Figure 3(a)**. The adsorption capacity of the raw electrode at 0 mV was approximately 0.59 mg/g; it increased to 0.84 mg/g after activation with the air plasma for 5 min. The adsorption capacity changed very little when the activation time was extended further. To explain, the electrode weight loss



**Figure 3** | (a) Influence of plasma activation time on lead ion removal ( $C_0 = 10$  mg/L). (b) Electrosorption/adsorption isotherms of CNT capacitor for removal of lead at 0 and 450 mV.

was measured. It was found to be approximately 5% after 5 min of activation, and 12.5% after 7 min of activation. This fact implies that, in terms of the total function groups on the surface, the decrease of the function groups due to mass loss of CNTs or PTFE during the plasma activation may have been offset by the increased porosity of the electrode surface, and/or increase in functional groups on the surface of the material; thus the electro-sorption capacity changed little when plasma activation time extended.

After 5 min of air plasma activation, the lead ion electro-sorption capacity of the activated electrodes increased from 1.97 to 3.40 mg/g; this final value was 73% higher than that of the non-activated, raw electrode at 450 mV, and 5.76 times higher than the adsorption capacity of the raw electrode at 0 mV. These results indicated that the air plasma activation was an effective method to improve the electrode capacitance. Comparing with chemical activations which usually take several hours and use pollution-causing strong acid/alkalis, the air-plasma activation possesses the advantages of little pollution and short activation time.

### Electrosorption isotherms

To investigate the adsorption/electrosorption behavior of the air plasma-activated electrodes, experiments were

carried out using lead nitrate solutions with different initial concentrations (5, 10, 20, 30, and 50 mg/L), at voltages of 0 and 450 mV. The results are shown in Figure 3(b). The Langmuir (Equation (1)) and Freundlich (Equation (2)) isotherms were used to fit the experimental data for the lead adsorption/electrosorption of the CNT electrodes:

$$q = \frac{q_m K_L C}{1 + K_L C} \quad (1)$$

$$q = K_F C^{1/n} \quad (2)$$

where  $C$  is the lead concentration (mg/L),  $q$  is the amount of adsorbed lead at equilibrium (mg/g),  $q_m$  is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g),  $K_L$  is a constant related to the heat of adsorption,  $K_F$  is the Freundlich constant related to the adsorption capacity of adsorbent,  $n$  is constant and  $1/n$  is the indication of the tendency of the adsorbate to be adsorbed. Table 1 shows the parameters for the two isotherms. The regression data demonstrated that the Freundlich model was more accurate than the Langmuir model for modeling the lead electro-sorption isotherm. As discussed in 'Characterization of surface morphology and surface functional groups of the electrodes', there were

**Table 1** | Isotherm parameters of lead adsorption/electrosorption on electrodes at different conditions

CNT electrodes	Potential (mV)	Langmuir			Freundlich		
		$q_m$	$K_L$	$r^2$	$K_F$	$1/n$	$r^2$
Raw	0	1.16	0.16	0.9131	0.26	0.40	0.9833
Plasma activated		1.56	0.17	0.9928	0.39	0.36	0.9897
Raw	450	4.88	0.10	0.9671	0.71	0.50	0.9910
Plasma activated		9.94	0.07	0.9824	1.13	0.54	0.9928

multiple functional groups on the surfaces of electrodes. Lead can be easily adsorbed to the electrode by forming various complexes of Pb-functional group (Ren *et al.* 2011; Yu *et al.* 2011). It conforms to the mechanism of the Freundlich model that the adsorption took place with multiple adsorption groups, and with multiple interactions between these groups and the adsorbate. Thus, the Freundlich isotherm described the electrosorption isotherm of the lead ion better than the Langmuir isotherm. These results were different from what was reported in the literature, where the Langmuir model fitted the electrosorption isotherms better than the Freundlich model when sodium was used as a model ion (Wang *et al.* 2007, 2012; Zhan *et al.* 2011). Generally, the stability constants for the Pb-functional group complex are much greater than that for the Na-functional group complex; for example, the stability constants of Pb-EDTA and Na-EDTA are  $10^{18.3}$  and  $10^{1.6}$  respectively (John 1992). Comparing with Pb, the interactions between Na and various function groups are much less and weaker, resulting in little difference in the interactions identified; thus, the isotherm of the electrosorption might be approximately homogeneous and uniform, and the Langmuir model could be applied.

## CONCLUSIONS

The results of SEM and FTIR experiments demonstrated that the CNT electrodes activated by air plasma had a rougher surface with larger holes and more oxygen-containing functional groups than the raw electrode. These plasma-produced changes were beneficial for the electrosorption performance. The results of the experiments demonstrated that after only 5 min of air plasma activation, the lead electrosorption capacity of the activated electrodes increased by 73% at a voltage of 450 mV. This study showed that the air plasma-activated CNT electrodes enhanced the electrosorption of metal ion. Compared with electrosorption performed using chemically modified electrodes or CNT powder electrodes, this method holds the advantages of a faster and more convenient operation, as well as less secondary pollution.

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