

## Synthesis of amino-functionalized carbon nanotubes with plasma activation followed by chemical treatment

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### Introduction

Removal of heavy metal ions from water and wastewater has become an important problem with increasing in application of metal species in industries. Among the various separation methods for removal of heavy metal ions from water and waste water, adsorption and ion exchange are considered to be the most attractive processes due to their advantages such as low energy consumption and regeneration capability of adsorbents. In recent years a large number of studies have been devoted to exploit the adsorption capabilities of carbon nanotubes for removal of heavy metal ions from water [1]. According to some of the reports [1], adsorption sites are mostly acidic and basic functional groups which are formed by chemical treatment of the CNTs. It has been shown that materials carrying iminodiacetic, thiol or amine functional groups may be utilized for removal of heavy metal ions [2]. In particular, adsorbents with nitrogen-containing functional groups have been widely explored. Since these functional groups are found to be one of the most effective functionalities in adsorption or removal of heavy metal ions. Among the chelating ligands, linear polyamine in the forms of  $H_2N(CH_2CH_2NH)_{n-1}H$ , i.e. ethylenediamine (EDA,  $n=2$ ), diethylenetriamine (DETA,  $n=3$ ), triethylene tetramine (TETA,  $n = 4$ ), etc., can form stable metal complexes with a variety of metal ions [3,4].

In this investigation we used chlorination of CNTs as an intermediate step for increasing the reactivity of nanotubes in reaction with DETA and application of these functional CNTs in removal of lead ions from water.

### Experimental

MWCNTs (Shenzhen Nanotech Port Co., Ltd, China), DETA and chloroform (Merck) were used to prepare the DETA-functionalized MWCNTs. CNTs were annealed in helium atmosphere at  $1000^\circ\text{C}$  in order to remove any possible functional groups which are likely to be formed during synthesis and purification of the CNTs. MWNTs were placed in a direct barrier dielectric (DBD) reactor for plasma chlorination treatment. A high voltage amplifier (TREK 10/40A) was used to generate DBD plasma. A HAMEG 20 MHz oscilloscope was used for monitoring the generated current and phase shift. The DBD plasma reactor consisted of a 4.0 mm thickness quartz tube as a dielectric barrier and a stainless steel rod inner electrode. The plasma processing gas was provided with a saturated stream of helium with chloroform at  $25^\circ\text{C}$ . CNTs were exposed to plasma for 4 min

and then were dried at  $80^\circ\text{C}$  to remove the physically adsorbed chloroform onto the CNT surface. These samples are labeled as Cl-CNT. In the next step the chlorinated samples were reacted with DETA according to the following procedure. Cl-CNTs were located in an autoclave and a solution of ethanol and DETA were added. After the suspension was mixed with an ultrasonic homogenizer for 20 min, the autoclave environment was purged with nitrogen to provide an inert medium. The autoclave was placed at  $100^\circ\text{C}$  for 72 h. Afterwards the solid content of the autoclave was washed several times with deionized water and then dried overnight at  $80^\circ\text{C}$ . The final product was labeled as Cl-DETA-CNT. To have a basis for comparison, some of the annealed MWCNT was treated in a concentrated nitric acid for 4 h under reflux conditions. The solution was then centrifuged and its solid was collected, resuspended in deionized water, centrifuged several times and finally dried overnight. This sample was reacted with DETA by the same procedure described above and were labeled as COOH-DETA-CNT.

Functional groups of each sample were identified via IR spectroscopy. Further characterization of functional groups was studied by a temperature programmed desorption method (TPD) and the evolved gases were detected with an IR spectrometer.

For adsorption studies 0.025 g of each sample was mixed with a 100 ppm solution of lead and then was stirred for 6 h. Following adsorption of lead on surface of the samples, the concentration of lead in the solution was measured with atomic adsorption spectrometer.

### Results and Discussion

Figure 1 shows the FTIR spectrum of Cl-CNTs and annealed CNTs.

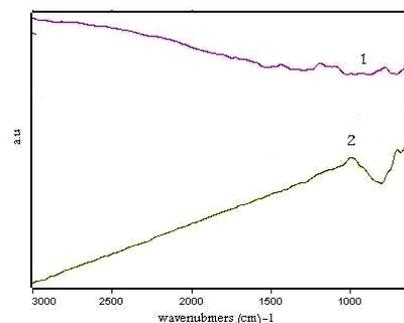
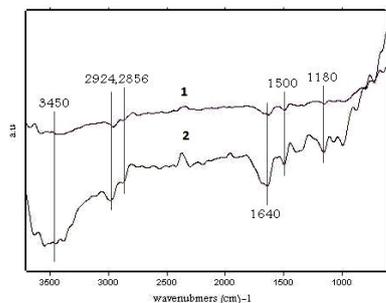


Fig. 1 FTIR spectrum of (1) annealed CNTs (2) Cl-CNTs.

As can be seen the FTIR spectrum of annealed nanotubes do not show any characteristic peaks while in Cl-CNTs a peak at about  $800\text{ cm}^{-1}$  is observed which is attributed to C-Cl stretching in CNT framework []. In Figure 2 FTIR spectra of DETA functionalized CNTs are presented. In both spectra symmetric and asymmetric stretching of methylene groups at  $2920$  and  $2850\text{ cm}^{-1}$ , C-N stretching at  $1180\text{ cm}^{-1}$  and in-plane stretching of N-H at  $1640\text{ cm}^{-1}$  are observed []. A broad peak at  $3450$  is assigned to  $\text{NH}_2$  stretching in Cl-DETA-CNT while in COOH-DETA-CNT sample this peak is overlapped with

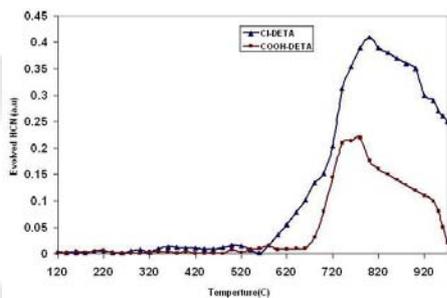
hydroxyl groups which may be assigned to none-reacted carboxylic acid functional groups of CNTs in addition to NH<sub>2</sub> stretching.

As the amine molecules are expected to decompose to nitrogenated species, further confirmation of amine linkage to carbon nanotubes were accomplished by TPD method. NH<sub>3</sub> and HCN are two major components which are expected to be

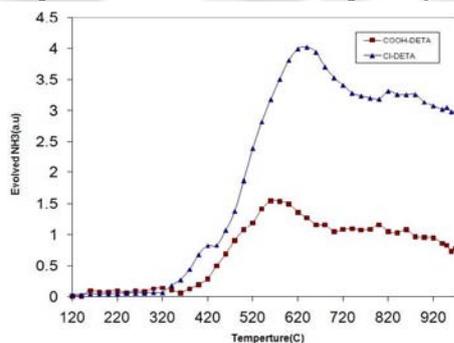


**Fig. 2** FTIR spectra of (1) COOH-DETA-CNT (2) Cl-DETA-CNT.

released during the TPD experiments. Desorption of these two compounds were detected by IR spectroscopy. Figures 3 and 4 show desorption of NH<sub>3</sub> and HCN for the corresponding samples.



**Fig. 3** Desorption of HCN from the corresponding samples.



**Fig. 4** Desorption of NH<sub>3</sub> from the corresponding samples.

Ammonia is mainly desorbed at 600°C and its desorption continues to 1000°C. HCN desorption starts at higher temperatures and similar to ammonia desorption continues to higher temperatures. Larger amount of NH<sub>3</sub> and HCN in Cl-DETA-CNT samples desorbed is due to larger amount of chlorinated functional groups on the CNTs surface and higher reactivity of them with DETA. It is possible that in COOH-DETA-CNT samples, there are many unreacted carboxyl sites.

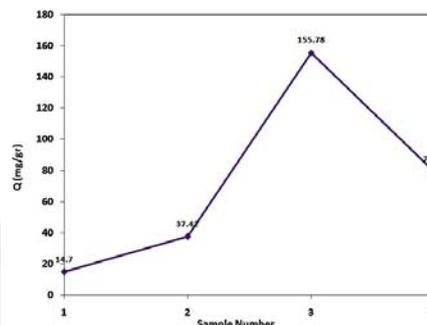
If the desorbed gases are considered as an index representing the quantity of DETA linked to CNTs, we may conclude that plasma chlorinated samples have higher affinity to react with DETA than acidified sample.

As mentioned earlier DETA ligands are believed to have considerable adsorption affinity toward heavy metal ions. In this respect adsorption behavior the functionalized sample, as listed in Table 1, for lead ions in water were studied.

**Table 1. Sample labels for adsorption experiment.**

Sample 1	Annealed CNTs
Sample 2	Chlorinated CNTs
Sample 3	Cl-DETA-MWNT
Sample 4	Acidified CNTs

As can be seen in Figure 4, sample 3 shows enhanced adsorption of lead ions in comparison with acidified CNTs. Cl-DETA-MWNT sample has an adsorption capacity of 155 mg/g which is significantly higher than that of the acidified CNTs. This adsorption capacity reveals both high quantity of functional groups and formation of stable metal complexes in the adsorption sites.



**Fig. 5** Adsorption capacity of various samples for a solution of 100 ppm lead ions

## Conclusions

DETA linked carbon nanotubes were successfully synthesized via a new method utilizing plasma functionalization. Both FTIR and TPD studies confirmed the reaction of DETA ligand with MWNTs. Adsorption properties of the amino functionalized CNTs show their enhanced capability in removal of heavy metal ions which can be promising in water and wastewater treatment.

## References

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