Original Article

Comparison between distilled water and dimethylformamid as solvent to fabricate electrodes coated with single wall carbon nanotubes

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ABSTRACT

Aims: In this study, distilled water and dimethylformamid (DMF), an organic solvent, have been compared in different characteristics to be used as the best solvent during EPD.

Materials and Methods: Electrical conductivity (EC) of both solutions was compared by dissolving electrolyte and measuring the EC. Ability of dispersion was determined after sonication in different times. Distilled water, DMF and two mixtures of them were utilized in EPD process and in deposition time of 1-5 min. The electrode weight was measured before and after the EPD and the deposit rate was estimated.

Results: Among the used solvents, DMF caused a better yield (0.4 mg/cm^2) at the optimum deposition time of 4 min. Though it did not have the ability of dissolving electrolyte and could not make an electrical field during EPD; it did not cause the electrode's oxidation. Distilled water and mixtures with water resulted in electrode oxidation with no deposition. Their yield was zero or less which indicated the electrodes oxidation.

Conclusion: According to the results, for having a good and stable dispersion through sonication, making an electrode with a homogeneous deposition via EPD process, preventing of electrode's oxidation, and better temperature control DMF is recommended.

Key words: Dimethylformamid, distilled water, electrophoretic deposition, solvent

INTRODUCTION

Development of industrial activities in the last decade endangered environment and threaten human with different kinds of anthropogenic contaminants. Water is one of the vital aspects of human life which can solve, contain, and carry different components with it. The increase in anthropogenic pollution of surface water results in bioaccumulation and biomagnification of heavy metals and organic matters in the environment and in the food chain.[1] Environmental

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pollution with different toxic substances, some with a very long biological half-life in the body, has been recognized as a public health hazard in all over the world.[2] During water treatment, several processes have been utilized for removal these kinds of material from water. Many of the unit processes which currently implemented are sand filtration, oxidation and reduction, chemical precipitation, electrocoagulation, solvent extraction, carbon adsorption, ion exchange, and membrane treatment.[3,4]

One of the novel techniques is electrosorption with different carbon material electrodes for removing dissolved inorganic contaminants from aqueous solutions such as radionuclides, metal ions, and anions.[4] Carbon is one of the most popular materials for manufacturing electrodes which possess satisfying electrical, chemical and thermal properties, relatively high capacity, and high surface area. Different type of carbon nanostructures including multi-walled carbon nanotubes (CNTs) and single-walled CNTs (SWCNTs) and graphenes have recently drawn much attention.[5] Among these types of CNTs, SWCNTs have an excellent mechanical property which can make a fixed bed in removal of contaminants.[6] One of the promising fabrication techniques for producing electrodes coated with CNTs is the electrophoretic deposition (EPD) procedure, which is mainly a combination of electrophoresis and deposition methods.[5] During EPD after voltage applied on both electrodes, ions in the water solution can move toward the oppositely charged electrode under the imposed electric field.[4] Deposition occurs only on conducting surfaces and the advantages of the method are: Low cost, simplicity of the process, uniformity of deposits, control of deposit thickness, and microstructural homogeneity.[7] The major limitation of EPD is that the deposition only occurs on conductive surfaces.[8] Dispersing CNTs homogeneously in a suitable solvent is a necessary step for controlled deposition of CNTs. Various solvent have been used to prepare CNTs suspension for EPD, including distilled water,[7] mixture of acetone and ethanol,[7,8] dimethylformamide (DMF), etc.[4,7,9] There are lots of studies that have used different solvent in electrodes fabrication through EPD. Table 1 summarizes some of these studies.

Based on the previous studies, DMF was chosen as the solvent to obtain a stable SWCNT suspension and it was used to make an electrode coated with SWCNTs for removal chromium from aqueous solutions.[4] Besides coated electrodes, another study used DMF as a solvent to prepare solid-phase microextraction fiber coated with SWCNTs by EPD.[9] However, as it is shown in Table 1 different studies preferred to use water for making electrodes through EPD. For example, Tomas *et al*., used water for deposit CNTs on metallic surfaces.[10] Besides making a good dispersion, some other characteristics are important in solvent selection, including the ability of dissolving electrolytes, and making a constant conductivity for EPD. In this study for the 1st time in a sole experiment, we aimed to compare two different solvent, distilled water and DMF, as an organic solvent, in various aspects including dispersion of CNTs, electrical conductivity (EC), and dissolving of reagents.

MATERIALS AND METHODS

Reagent and materials

The reagents utilized in this study were sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), nitric acid (HNO_3), and sodium sulfate (Na_2SO_4) which all purchased from Merck Co., N,N-dimethylformamide (≥99%) was purchased from Aldrich Co., and SWCNTs with 1-2 nm diameter were obtained from Research Institute of Petroleum Industry, Tehran, Iran. The scanning electron microscope image of SWCNTs is shown in Figure 1. Stainless steel net (SSNs) of 100 meshes was purchased from the local store.

Determination of the electrical conductivity

First, 30 ml of distilled water and 30 ml of DMF prepared separately and then <0.1 mol (350 mg) Na_2SO_4 was added to each of the liquids. Both of them were placed on the stirrer for 15 min and, therefore, their ability of dissolving electrolyte was compared.

In the second step, EC of both solutions was determined by using an EC meter (Senceion 5, Hach Co., Germany)

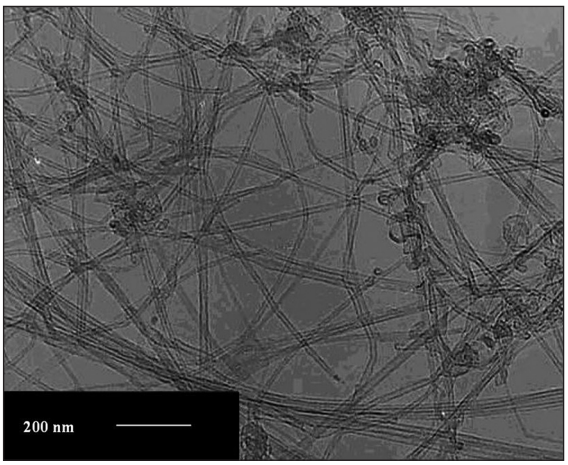

Figure 1: Scanning electron microscope image of single-walled carbon nanotubes

Table 1: Overview of used solvents for EPD of CNTs

CNTs type	Solvent type	References
MWCNTs	Water	[5,10,12]
SWCNTs	N,N′-dimethylformamide	[4,6,9,13]
SWCNTs	1,2-dichloroethane	[14]
SWCNTs	Methanol	[13]
MWCNTs	N-methylpyrrolidone + methanol	[15]
Carbon nanofibers	N,N′-dimethylformamide	[16]

CNTs: Carbon nanotubes, EPD: Electrophoretic deposition, SWCNTs: Single-walled carbon nanotubes, MWCNTs: Multi-walled carbon nanotubes

and EC of distilled water and DMF after dissolving the added electrolyte was compared. For accuracy, the test was repeated; therefore 0.35 g of Na_2SO_4 mixed completely with DMF, and after 15 min stirring the salts were settled at the bottom of the beaker. The sedimentation was separated and dried at 100°C for 15 h. They were perfectly dried and then weighted.

Preparation of single-walled carbon nanotubes and electrophoretic deposition

In case of fictionalizing SWCNTs, 100 mg of them were added to 10 mg of the mixture of H_2SO_4: HNO_3 (3:1) and placed in an ultrasonic bath (BANDELIN, DT 156, Germany) for 2 h. After this period of time, the suspension was washed with pure water to remove any residual acidic solution from SWCNTs. Washing continued until pH was reached to 7 using a pH meter (CyberscanpH1500-Thermo Fisher Scientific Inc., Netherland). Then, SWCNTs were put in an oven for 48 h in a constant temperature about 50°C. During this process, the carboxylic functional groups were added to the defect and end sites of SWCNTs. These functional groups were determined using FT-IR test.

In the next step, 4 suspensions of SWCNTs were prepared. The solvent for these 4 trials were different, including; DMF, distilled water, a mixture of DMF with 30% distilled water and a mixture of DMF with 60% distilled water. The experiments were done from 1 to 5 min and were triplicate. Hence, the sample size was approximately 60 trials.

After 15 mg of functionalized SWCNTs were added to each solution, they ultrasonically dispersed. Subsequently, after 4 h a suspension of 0.5 mg/mL of SWCNTs was obtained. During all steps, pH was adjusted on 10 by adding 1 M NaOH solution. Consequently, two pieces of clean SSNs (6 cm^2 × 1 cm^2), one used as cathode and the other as anode, were parallel immersed into each suspension of SWCNTs. However, only parts of them (2 cm^2 × 1 cm^2) were placed in the suspension. The distance between the two SSNs was kept at 1 cm. A direct current voltage of 30 V was applied. The experiment was done in different periods of times ranging from 1 to 5 min. During the first experiment in the 1st min, no amount of electrolyte was added. However, for the next tests which were carried out from 2 to 5 min, a constant amount of electrolyte was added to each suspension. The test was done for all suspensions and the produced current was illustrated and compared. The amount of deposited SWCNTs was determined by weighting the SSN anode before and after each trial.

For the last experiment with DMF, another suspension of 0.5 mg/ml SWCNTs was prepared after 4 h dispersion. The solution of 10 g/L Na_2SO_4 was prepared. Optimum time was determined after the first experiment with DMF, and the experiment carried out in that time for several times. Before EPD, 10 ml of Na_2SO_4 solution was added to the suspension and the changes in amount of deposits and also electrical current was recorded. The experiment repeated for 3 more times and during each test, 2 ml of Na_2SO_4 solution was added to the suspension and the changes were compared.

Experiment with DMF repeated for 23 times in constant voltage and different amount of electrolytes. The difference and changes in amount of deposit was recorded in each step.

RESULTS

During the first step of the experiment, it was determined that DMF cannot dissolve the electrolyte (Na_2SO_4) completely. After the test was repeated and dried salts weighted, it was illustrated that 0.346 g of 0.35 g Na_2SO_4 was remained and was not dissolved. EC was measured before and after dissolving the reagent. The result of the experiment and measuring is shown in Table 2. The test showed that DMF has the ability of dissolving salt in a very little amount, which is responsible for making low electrical field in the slurry.

In the next step of the experiment, after all the suspensions were ultrasonically dispersed for 4 h, all of them showed a good dispersion similarly. It should be noted that, if the sonication occurs for a shorter time, for example for 30 min, DMF will show a better dispersion than distilled water with no agglomerated particle in the suspension.

During the EPD process in a constant voltage of 30 V, as it is mentioned in the method, the experiment took place in five stages in different time intervals. The results of all the tests are presented in Table 3. According to this table, the test for water did not complete in all mentioned deposition times. The reason is that when the electrolyte was added to the DMF, no great change in the electrical field was appeared and it was <0.1 mA. Besides, the suspension remained dispersed after the test was terminated. However, after adding electrolyte in the suspension with water, the electrical current rose up and had an ascending rate, however after the current turned off, the dispersion turned to an agglomerated situation. In addition, any amount of SWCNTs did not deposit on the SSN anode. The electrolyte weight was less than it was prior to the test and the yield was negative. The photo of distilled water and DMF just after the second trial is shown in Figure 2.

Table 2: Results of adding electrolyte to both solvents

Solvent	EC (1)* (ms/cm)	EC (2)** (ms/cm)
DMF	0.0022	13.21
DW	0.0018	0.0027

*Before adding electrolyte, **After adding electrolyte. DMF: Dimethylformamid, EC: Electrical conductivity, DW: Distilled water

The results of the experiment with a different mixture of DMF and distilled water are also presented in Table 3. It can be understood from the table that in comparison with DMF and the amount of deposits through the experiment with the other used solvents, other mixtures were not successful in making an electrode.

Consequently, after the EPD process was accomplished, the suspension with DMF had a better deposition. Figure 3 shows the results of the test with DMF in different deposition times. As it is illustrated in Figure 3, the best time interval for EPD process was known as 4 min which showed a better deposition of SWCNTs on the SSN anode. This time was chosen as the optimum time for the last test. During the last test, electrolyte was dissolved in water and then added to the suspension. There was no change in the amount of deposits on the anode. The result of this experiment was similar with the trial of DMF and 60% water.

Table 3: The experiments with different mixture of DMF and DW

Solvent	Time (min)	Electrolyte (g)	Yield (mg/cm²)
DMF	1	0	0.15
	2	0.3	0.30
	3	0.6	0.25
	4	0.9	0.40
	5	1.2	0.25
DW*	1	0	0.7
	2	0.3	−2.4
60% DMF + 30% DW*	1	0	0
	2	0.3	−0.05
	3	0.6	−0.05
	4	0.9	−0.05
	5	1.2	0
30% DMF + 60% DW*	1	0	0
	2	0.3	−0.25
	3	0.6	−4.25
	4	0.9	−8.6

*DW: Distilled water, DMF: Dimethylformamid

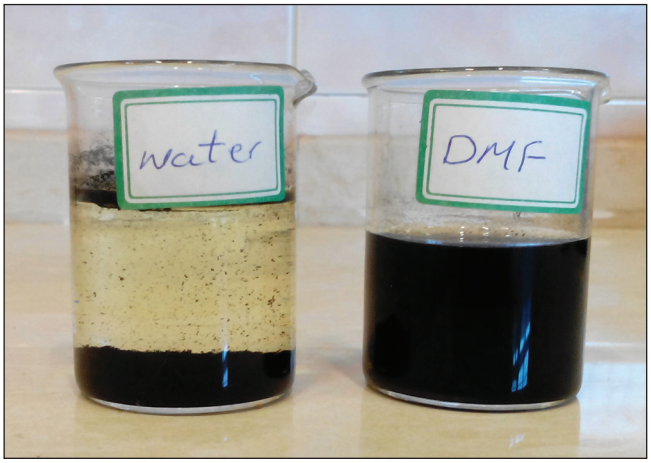

Figure 2: Photograph of single-walled carbon nanotubes dispersion in dimethylformamid and distilled water after the second trial

DISCUSSION

During EPD process, the applied voltage should make a good current in the suspension and consequently results in migration of charged particles to the opposite electrode. However, it has been said that the deposition rate is not simply related to the current.[11] If there was no EC, no particle movement would appear. In addition, different studies demonstrated that conductivity of the suspension is a key factor and needs to be taken into account in EPD process.[14] Randall and Van Tassel have proved in their study that for electrophoretic migration in the suspension, electrical fields should exist.[12] It is illustrated from the results that DMF, as an organic solvent, and water have some advantages and disadvantaged in comparison to each other. Water is cheaper, healthy, and environmental friendly and produces a constant electrical field during the EPD. However, using water as the sole solvent will cause a number of problems. Electrochemical reaction in the electrodes when an electrical current is passed through is one of the main problems, which seriously affects the efficiency of the process and the uniformity of the deposit. Electrolysis of water comes about at low voltages and results in gas evolution at the electrodes; therefore, to prevent such changes, deposition time should be shortening enough. It is an emphasis on Besra and Liu study; in that study they acclaimed that when the current density is high, Joule heating of the suspension occurred and the deposit will electrochemically attacked. In the other hand, in metallic electrodes the normal potential of the electrode is largely overpassed. This phenomenon causes oxidation of the electrodes and metallic impurities and so their migration in the slurry. In most cases, these impurities are retained in the deposit.[11] On the other hand, adding more electrolyte will cause an intensive electrical field in the suspension, whereas the existence of charger salts can play a significant role in improving the adhesion of CNTs the surface and in aggregating the deposition rate. The salts will associating a charge to the CNT surface and, therefore, make the suspension to be stable.[18]

As experiment showed, for having a homogeneous deposit on the electrode, a good dispersion is needed, but water is not able to have a good dispersion in a shorter time.

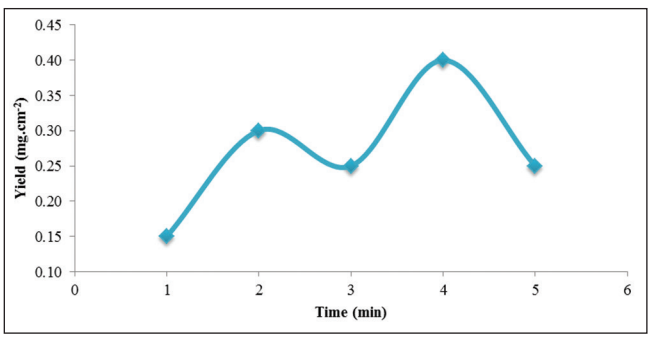

Figure 3: Electrophoretic deposition process with dimethylformamid as the only solvent

Another problem in using water as the solvent is that, water cannot get used for several times in the EPD process. The experiment showed that water solely or in a mixture with organic solvent will oxidize the electrode and after adding more electrolytes the fabricated deposits will completely demolish. During the tests which had water as solvent the electrolyte weight after the experiment was even less than before the trial. This is an emphasis on Besra and Liu study which ascertain that EC of the suspension is not simply related to the EPD process.[11] However, Boccaccini *et al*., utilized water for EPD process. In that experiment, they acclaimed that after EPD and when the electrodes were dried EPD can repeated to make a thick film.[10] Nevertheless, the present study showed that, if the thicker film on the anode is needed, the new suspension should be used. It is better to avoid adding electrolyte because the electrolysis of water will speed up and consequently not only the deposits but also the electrode will damage.

For EPD process and for having a better dispersion, organic liquids are preferable. Using DMF reduced electrolytic gas evolution, joule heating, and electrochemical attack of the electrodes and in lower deposition times omit these adverse effects. Different studies have mentioned DMF as the best solvent for EPD of SWCNTs.[4,6,7,9] In another study, DMF solution compared to ethanol and acetonitrile for electrodeposition of carbon nanofiber. In that study, the suspension with DMF showed a better dispersion and stability.[19] However, for having an electric field in the bulk suspension a higher voltage is required. Likewise flammability, cost, and toxicity of organic solvents should be considered. Besides, with respect to all these facts, some studies tended to use more healthy and environmental friendly liquids as a solvent.[11]

In case of deposition of SWCNTs by using DMF, the EC was very low. However, it did not affect the migration of particles. As the experiment showed and as it can be illustrated from the Table 3, the yield of SWCNTs on the anode was better when DMF was used as the only solvent. This is probably due to the low EC of the solvent. As the DMF cannot dissolve the salt, therefore, no electrical field appeared in the slurry and so electrolysis of the solvent did not occurred. Therefore, the structure of the electrode was not damaged and the deposit in different stages remained stable.

In different experiments with water as the only solvent and deposition time of 30 min, after adding enough electrolyte a relatively higher EC appeared. In the end of EPD time, a great deposit conducted on the electrode. However, the deposition was not homogeneous at all and the opposite electrode was oxidized. In contrary, in the same experiment with DMF electrical field remain constant and the deposit was not thick but it was homogenous. The test which was repeated for 23 times had the same result; a homogeneous thin film, but constant in amount in all the intervals. Furthermore, evaporation in the suspension with water is higher and the temperature increase faster but it is more controllable in the organic solvent.

CONCLUSION

With respect to the mentioned facts, for making an electrode with a homogeneous deposition through EPD process, having a good dispersion, preventing of electrode's oxidation, and better temperature control DMF is recommended. However, it is suggested that electrodes with different dielectric constant should be tested with DMF to obtain the better deposit on the anode.

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Conflicts of interest

There are no conflicts of interest.

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