 DOI: 10.1002/masy.200750444

Modification of Performances of Various Membranes Using MWNTs as a Modifier

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Summary: The effect of multi-walled carbon nanotubes (MWNTs) incorporated for the modification of membrane performances was studied. Two different types of membranes were prepared by using MWNTs: one was polysulfone (PSf) ultrafiltration (UF) membrane and the other was polyvinyl alcohol (PVA) pervaporation membrane. The PSf UF membranes with different contents of MWNTs were prepared by the conventional phase inversion process, and used for water-treatment. On the other hand, the PVA membranes with different amount of MWNTs were prepared by the casting and drying method, and used for the pervaporation separation of water out of ethanol solution containing 10% of water. The two different types of membranes were then characterized with several analytical methods to figure out how the MWNTs were distributed through the membranes and affect on the properties of them: For the PSf membranes, the MWNTs mainly located on the surface of the membranes made them more hydrophilic and improved the selective permeation performances of the membranes. In the case of the PVA membranes, the MWNTs were distributed rather homogeneously through out the membranes, and affected on the micro-morphology of the membranes, causing them to have different pervaporation performances.

Keywords: blend membrane; multi-walled carbon nanotubes; performance; poly(vinyl alcohol); polysulfone

Introduction

Membrane separation techniques have attracted considerable attention in a wide variety of medical, food, industrial, energy, and environmental applications. Of the membranes currently being used, polymeric membranes are the most popular ones with good performances. However, still the polymeric membranes, mainly organic, polymeric membranes, have limits in their performances for various applications due to tradeoff effect between permeability and selectivity, which means that membranes more permeable are generally less selective and vice versa.[1–3] To overcome these problems, many researchers attempted to use inorganic materials as a modifier such as zeolite, silica, carbon molecular sieve to improve the performances of the organic, polymeric membranes.[4,5] Some of them have achieved positive results. Also, recently, carbon nanotubes (CNTs) have been applied for the filters and membranes to separate various gases and liquids.[6,7] For example, B. J. Hinds et al. reported that the nanotube-based membranes consisting of vertically aligned nanotubes embedded in a polymer host. The hollow nanotube cores represented the only conduction path during molecular transport through the membrane. Because of their arrangement,

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the termini of the aligned carbon nanotubes were accessible to the outer molecules from both sides of the formed membrane. From their results, it is possible for us to find possibility of CNT using the empty inner to the membrane application.

Based on this, multi-walled carbon nanotubes (MWNTs) were employed in this study as a modifier of organic, polymeric membranes. To make the MWNTs dispersion in solvent and polymer matrix, they were treated with strong acids such as sulfuric acid and nitric acid. The blend membranes prepared so were then characterized using various analytical methods to figure out the effect of MWNTs on polymer membranes. The permeation performance of the acid-treated MWNTs blended with both polysulfone (PSf) and poly(vinyl alcohol) (PVA) is being discussed through the tests with various feed solutions (1000 ppm aqueous of PVP 55,000 and water/ethanol mixture).

Results and Discussion

Characterization of the CNT Dispersions

Carbon nanotubes (multi-walled carbon nanotubes, MWNTs) manufactured by CVD process (supplied by Iljin nanotech, Korea) whose purity of greater than 95% were used for modification of performances of various membranes. First, to make well dispersed in various solvents and polymer matrix, The MWNTs were surface modified with strong acids, concentrated nitric (HNO_3) and sulfuric acids (H_2SO_4) (1:3 in vol. %).[8] Acid-treated MWNTs introduces abundant hydroxyl and carboxyl groups at the open ends and the defect sites of the nanotubes[9,10] and these functional groups will fairly stable individually by the repulsive force among the nanotubes in solvents. Furthermore, to improve the dispersability in solvents, the solution was sonicated for 80 sec using a high-power sonic tip (sonicskorea, SKB-2000, 2 kW). The dispersion properties of MWNTs in solvents were characterized using Zeta-potentiometer (Electrophoretic light scattering model ELS-8000, Otsuka, Tokyo, Japan) and UV/visible spectroscopy (UV-2550, Shimadzu).

Table 1.
Zeta potential of raw MWNTs and acid-treated MWNTs as a function of pH, in aqueous solutions.

Raw-MWNTs		Acid-treated MWNTs	
pH	Zeta-potential (mV)	pH	Zeta-potential (mV)
2.65	29.04	2.54	−33.18
3.75	45.27	3.64	−40.17
5.38	32.04	5.28	−66.37
7.10	0.88	7.00	−69.03
9.35	−24.24	9.39	−56.70

Table 1 shows that zeta potential value of raw MWNTs and acid-treated MWNTs as function of pH, in aqueous solutions. The pH values of the MWNTs solutions were adjusted from 2.0 to 10.0 by adding 10 mM hydrochloric acid or 10 mM sodium hydroxide solution. Acid-treated MWNTs have a high zeta potential value over a wide pH range (2–10); at a pH value of 2.5, 7, and 9.3, the zeta potential value of acid-treated MWNTs are −33, −69, and −56 mV, respectively. On the other hand, a zeta potential value of raw MWNTs without acid treatment is 0 mV around $pH = 7$. These results suggested strongly that acid-treated MWNTs are formed good dispersion in water. Also, the modified MWNTs which have hydroxyl and carboxyl group at the open ends and the defect sites were so well dispersed in various polar organic solvents such as N-Methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO).

As shown in Figure 1, the dispersability of acid-treated MWNTs in different solvents can be obtained from a UV/visible spectrometer, relatively. It is well known that the more stable suspension of CNTs in solvents shows increased absorption in a UV/visible spectrometer.[11,12] Thus, from the Figure 1, it was found that NMP was the best solvent for nanotubes' ability to stay in suspension. However, the acid-treated MWNTs are good enough to make good dispersion in solvents, such as DMSO, water, DMF, not precipitating for over

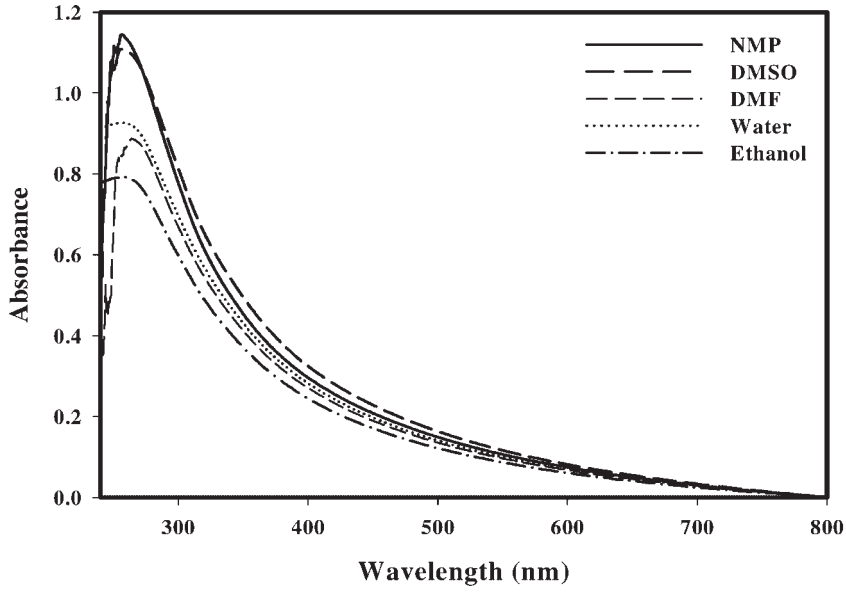

Figure 1.
UV-visible spectra of MWNTs dispersed in different solvents.

10 days without agitation. On the contrary, the MWNTs in ethanol was somewhat aggregated for the same time. Moreover, the acid-treated MWNTs turned out to be well dispersed in the polymer matrix.

Preparation of MWNTs/Polymer Blend Membranes

As explained above, before blending with polymeric materials, MWNTs were treated with strong acids such as sulfuric acid and nitric acid to make them well dispersed in various solvents such as water and NMP that would be used for the preparation of membranes. The modified MWNTs were then blended with both polysulfone (PSf) solution in NMP and poly(vinyl alcohol) (PVA) solution in water, respectively, to prepare a PSf ultrafiltration (UF) membrane for water-treatment and a PVA pervaporation membrane for the separation of water-ethanol mixtures by pervaporation. With the different content of MWNTs respect to polymer, the PSf membranes were prepared by the phase inversion process of the MWNTs/PSf blend solution, using water as a coagulant, and the PVA membranes were prepared by drying the MWNTs/PVA blend solution at a room temperature after casting the solution on a glass plate. The prepared MWNTs/polymer blend membranes show that the MWNTs are well dispersed in polymer matrix (See Figure 2 and Figure 3).

Characterization of MWNTs/Polymer Blend Membranes

MWNTs/PSf blend membrane: Figure 2 shows that the PSf membrane modified with MWNTs and prepared by phase inversion process showed a finger-like structure and porous structure through exchange between the solvent (NMP) and non-solvent (water). In addition to, as shown in Figure 2(b), the MWNTs were found to be positioned mainly on the surface layer of the membrane affecting hydrophilicity of membranes and pore size.

First, the surface hydrophilicity of the blend membranes, one of the characteristics of the blend membranes, was measured based on the dynamic water contact angle of the membrane using contact angle goniometer (SEO 300A). The contact angle

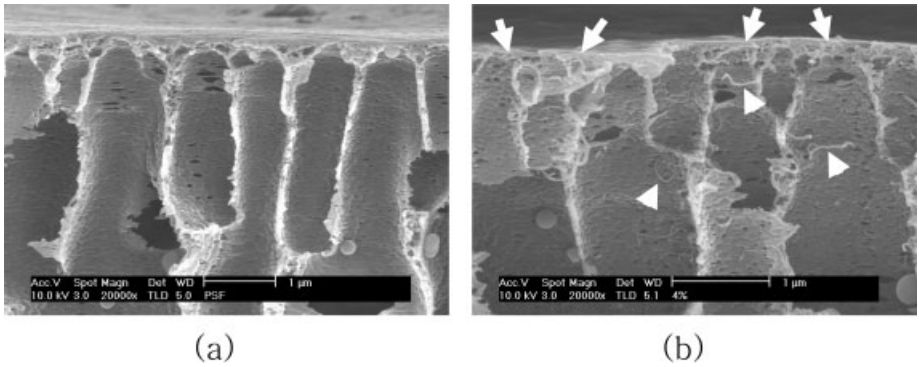

Figure 2.
FESEM photographs of the cross-sections of the MWNTs/PSf blend membranes: (a) just PSf membrane, (b) 4.0 wt. % of MWNTs.

decreased with increasing content of MWNTs from 71.8° to 55.4°, since the hydrophilic MWNTs migrated to the membrane surface during the phase inversion process in water, making the membrane surface hydrophilic. This result might be explained by the fast exchange of solvent and non-solvent in the phase inversion process due to the hydrophilic MWNTs.

Table 2 also shows the variation in solution viscosity and pore size of blend membranes with adding MWNTs in the casting solution. With increasing contents of MWNTs, the casting solution viscosity increased; in particular, the viscosity significantly added up at 4 wt% MWNTs content. It was found that the rheological percolation threshold of MWNTs/PSf blend solutions was between 2 and 4 wt. % due to the combined nanotube-polymer network.[13,14] This phenomenon induced that the higher solution viscosity is formed with a smaller pore size because of a delayed exchange between solvent and non-solvent. The order of the pore size with maximum distribution according to the contents of MWNTs of the blend membrane was $1.5\% > 1.0\% > 2.0\% > 0.5\% > 0.0\% > 4.0\%$, with the result from Capillary Flow Porometry (Model CFP-1500-AEL, Porous Materials Inc., NY, USA) (See Table 2). It can be concluded that the pore size of the blend membranes increased gradually with the content of MWNTs up to 1.5 wt. % and then decreased, probably due to the combined effect of increased viscosity and lowered thermodynamic stability of the

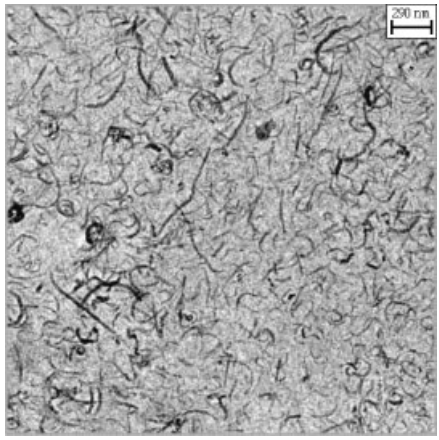

Figure 3.
TEM images of a specimen from the crossectional microtomy of the MWNTs/PVA (10/90) blend membrane.

Table 2.
Viscosities of the MWNTs/PSf blend solutions and pore size with maximum distribution of the MWNTs/PSf blend membranes.

	Viscosity (cP)	Pore Size with Maximum Distribution (μm)
PSf	311.3	0.0607
MWNTs/PSf (0.5/99.5)	327.2	0.1048
MWNTs/PSf (1.0/99.0)	337.4	0.1185
MWNTs/PSf (1.5/98.5)	356.0	0.1680
MWNTs/PSf (2.0/98.0)	365.3	0.1116
MWNTs/PSf (4.0/96.0)	473.2	0.0494

blend solutions by the addition of hydrophilic MWNTs.

MWNTs/PVA Blend Membrane

Figure 3 shows that the modified MWNTs are well dispersed in the PVA matrix despite the fairly large amount of MWNTs. This is indicated that the functional groups of MWNTs provide stronger interaction with hydroxyl groups of PVA. Furthermore, their interactions between the functional groups developed at the open ends and the defect sites of the MWNTs and hydroxyl groups of PVA affect the mobility of PVA polymer chains. The effect of MWNTs on the morphology of the blend membranes is from the Figure 4 presenting the DSC data of the blend membranes.

From the DSC results, it was found that with increasing contents of MWNTs, the glass transition temperature (T_g) of the blend membranes increased from 69.21 °C to 78.53 °C due to interaction between the functional groups of MWNTs and the hydroxyl groups of PVA. The increase of T_g indicated that segmental motions of the chains are restricted owing to a reduction of free volume in the membrane matrix, with increasing the MWNTs loading. On the other hands, except for the 1.0 wt. % of MWNTs, the crystallinity of the blend membranes decreased gradually from 41% to 36%, with increasing contents of MWNTs. When small amount of MWNTs, such as 1 wt. %, was added, it acted as if a nucleating agent, and then induced little increase in the crystallinity. However, as the content of MWNTs increased further, the effect that the MWNTs in strong interaction with PVA molecules made PVA molecules not to be easy to pack together to form crystals became dominant, resulting in the decrease in the crsytallinity. These characteristic of the MWNTs/PVA blend membranes affected on the performance of the membranes that will be explained in the following section.

Effect of the MWNTs Loading on Performance of the MWNTs/Polymer Blend Membranes

MWNTs blended with PSf turned out to increase the hydrophilicity of the surface of the PSf membranes, while affecting the pore size of the membranes. Then again, MWNTs blended with PVA were well dispersed in the PVA matrix, making the membranes have higher T_g and changing the crystallinity of the membrane. In the based on the characteristic of MWNTs/polymer blend membranes, their membrane performaces were determined by testing them under different testing conditions;

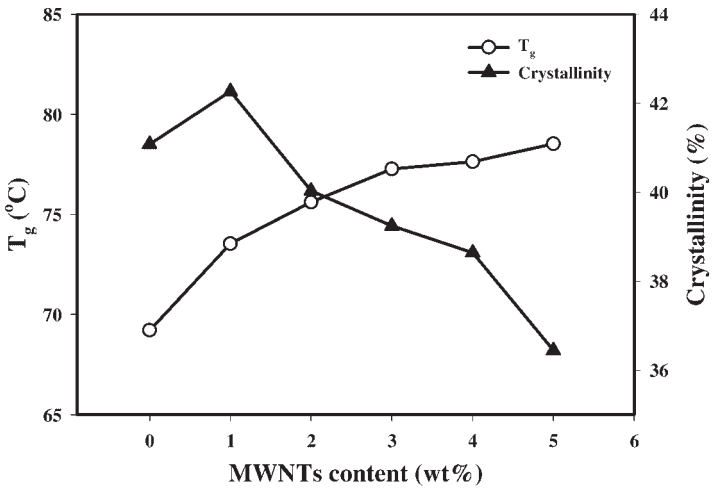

Figure 4.
Effect of the amount of MWNTs on the T_g and crystallinities of MWNTs/PVA blend membranes.

For MWNTs/PSf blend membranes, the separation of PVP 55,000 out of water were carried out, and using MWNTs/PVA membranes, water was separated from water/ethanol mixture whose composition was 10/90 in wt. %.

Figure 5 shows the flux and the rejection as a function of operating pressures when 1,000 ppm aqueous solution of PVP 55,000 was used as a feed. The membrane with 0.5 wt. % MWNTs showed the highest flux, while the membrane with 1.5 wt. % MWNTs showed the larger pore size. To explain this, the fouling pattern has to be considered. For large pores, it would relatively for the PVP 55,000 to get into

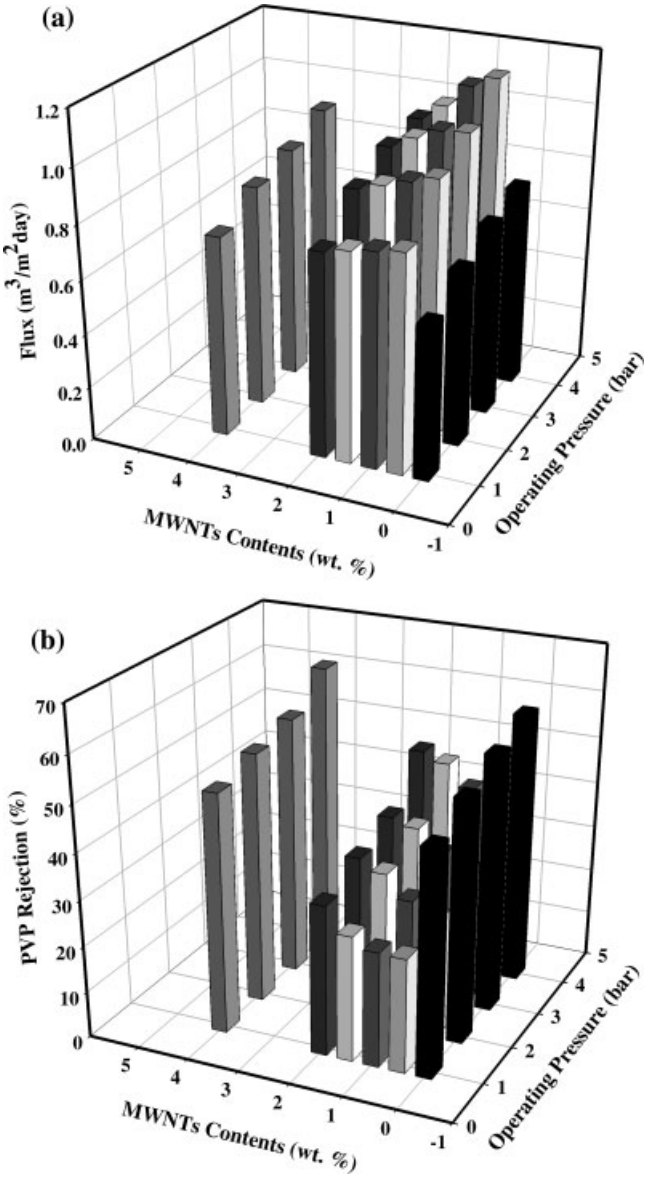

Figure 5.
Permeation properties of the MWNTs/PSf blend membranes as a 1,000 ppm aqueous solution of PVP 55,000 was used as a feed solution: (a) flux, (b) rejection.

the pore inside, plugging pores, but when pore is small, the molecules of PVP 55,000 are not easy to get into the pores, and just cumulating on the surface of the membrane. Because of such kind of fouling behavior, the membrane with 1.5 wt. % MWNTs composed with relatively large pores was fouled more and showed less flux than the membrane with smaller pores such as the membranes of the MWNTs of 0.5 and 1.0 wt. %. However, the blend membrane with 4 wt. % MWNTs shows higher flux than the pure PSf membranes despite the smaller pore sizes. Also, generally, the membrane showed high flux exhibits low rejection, but, in this case, the blend membrane with 4 wt. % MWNTs obtained higher rejection at all operating pressure than the PSf membranes. As explained above, that is probably due to the improve hydrophilicity of the blend membrane by the added MWNTs. From these results, for the PSf membranes, the MWNTs are possible to control the surface hydrophilicity and the pore size of the PSf membrane. On the other hand, for the MWNTs blended with PVA, affecting the performance of the membranes was different from the MWNTs/PSf blend membrane.

Figure 6 shows the pervaporation performance of the blend membranes as a function of the contents of MWNTs of the membranes with different contents of MWNTs, water/ethanol (10/90 in wt. %) mixture was used as a feed. The total flux of the membranes increased with increasing content of the MWNTs, whereas separation factor of over all blend membranes decreased. This result tendency is generally in membrane performance. However, in this case, as the contents of the MWNTs increased, the acid-treated MWNTs strongly affect membrane properties. In general case, with increase in T_g, the free volume of the membrane usually decreases so that the permeation flux decreased and the selectivity increased. However, in the present study, with the MWNTs content increasing from 0 to 5 wt. %, the T_g of the membranes increased, and the total flux of the membranes was also increased. These phenomena were explained as two factors.

First, as explained in the DSC result above, the decrease of crystallinity in PVA matrix has influence on the flux increase of the membranes. As PVA is a semicrystalline polymer, the presence of crystalline regions is inaccessible to the penetrant, and permeability increases with the decrease of crystallinity in the membrane matrix. A different reason, the hollow cores of nanotube have influence on the performance of membranes. In other words, as the inner core diameter of nanotubes has

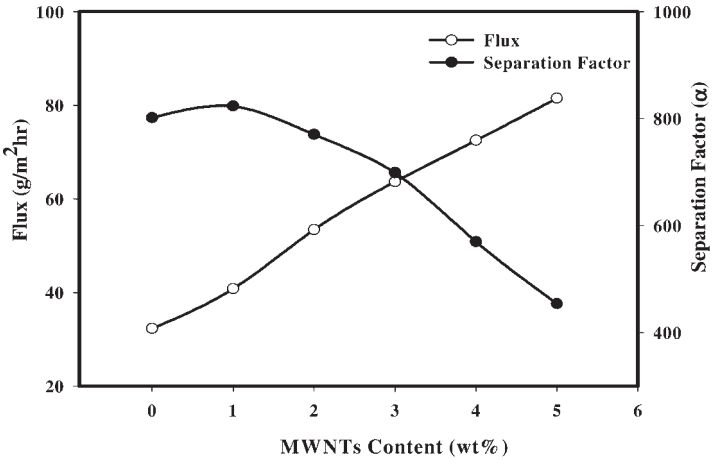

Figure 6.
Total fluxes and separation factors of the MWNTs/PVA blend membranes in the pervaporation separation of water/ethanol mixture (10/90 in wt. %) at 40 °C as function of the contents of MWNTs used.

4.3 ± 2.3 nm, the diameter is larger than the kinetic diameter of water molecule (0.30 nm) and ethanol molecule (0.430 nm).[15] Thus, both water and ethanol molecular transports across the membrane matrix are accessible through the inner cores of nanotubes. So, as the contents of the MWNTs increased, the more MWNTs particles in the membrane, the more chances of diffusing penetrant molecular through the nanotube diameter can occur. From these results, it became clear that the increase of total flux and decrease of separation factor with increasing MWNTs content is due to the its the crystallinity of membrane and molecular transport take place through the inner cores of MWNTs.

Conclusions

Acid-treated MWNTs were used to modify the performance of the membranes such as PSf ultrafiltration (UF) membranes and PVA membranes. The PSf membrane modified with MWNTs and prepared by phase inversion process showed finger-like and porous structure, but the PVA membrane prepared by drying MWNTs/PVA blend solution at room temperature showed a homogeneous and non-porous structure. The performance properties of the MWNTs/polymer blend membranes were appeared to be very dependent on the contents of the MWNTs used. The following conclusions can be drawn from this study:

(1) The MWNTs blended with PSf are observed increase the hydrophilicity of the surface of the PSf membranes, controlling the pore size of the membranes due to the thermodynamic stability and viscosity of the dope solution with different contents of MWNTs.

(2) The addition of MWNTs into the PVA membranes has increased the permeation flux and decreased the selectivity in the separation of water/ethanol mixture (10/90 in wt. %), suggesting that the crystallinity change of membrane and the molecular transport take place through the inner cores of MWNTs and MWNTs have an important role in affecting the membrane performance.

Acknowledgements: This research was supported by a grant (code #: 05K1501-01210) from 'Center for Nanostructured Materials Technology under 21st Century Frontier R&D Programs' of the Ministry of Science and Technology, Korea.

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