Chemically Grafted Aminated Carbon Nanotubes and L-Lysine in Ultramodified Conditions for Carbon Dioxide Storage

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ABSTRACT: The study reported CO2 storage properties of single-walled carbon nanotubes (CNTs) modified by introducing amino groups onto CNT surfaces via a chemical process. Two different approaches were used to produce amino-functionalized nanotubes by adding lithium amide and L-lysine amino acid. Lithium amide was introduced on CNT surfaces, and then, it was further modified by adding amino-moiety (L-lysine amino acid) to obtain multiamino sites on the CNT surface for CO2 storage. The aminated CNT were followed by CO2 adsorption experiments, and amino group interactions with CO2 have helped CNT to achieve higher adsorption capacity. The successful modification of CNTs showed enhanced CO2 storage capacity as compared to pristine CNT. The modified CNT possessed free amine groups on the surface, which led to an enhanced CO2 adsorption capacity. The modified CNT samples were analyzed by X-ray photoelectron spectroscopy, infrared spectroscopy, and X-ray diffraction techniques.

INTRODUCTION

Carbon dioxide is anticipated as the most important greenhouse gas responsible for global warming. It is a major combustion product in many industries, ranging from energy production in power stations (fossil fuel and natural gas) to glass and cement fabrication. According to latest approximation, the level of CO2 surpassed 400 ppm. Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas CO2. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of greenhouse gases. Commercial CO2 capture technology that exists currently is very expensive and energy-intensive. Development of enriched technologies for CO2 capture is necessary to achieve low energy penalties. The recovery of carbon dioxide is an important issue, on one side, to decrease the carbon dioxide emission into the atmosphere and, on the other side, to reuse the captured carbon dioxide for industrial applications. As a means to remove CO2 from flue gases on a large-scale, several different approaches have been proposed.1 In general, there are four main approaches utilized for the separation of CO2 from other light gases: cryogenic distillation, membrane purification, absorption with liquids, and adsorption using solids.1 Cryogenic distillation, although widely used for other gas separations, is generally not considered as a practical means to separate CO2 from flue gases because of the high energy costs involved.

Absorption processes involving CO2 capture by liquid media are widely established. The liquid media are often aqueous amine (e.g., monoethanol amine) solutions or other fluids with basic character, such as chilled ammonia, that chemically absorb the acid gases.2–5 Commercial processes that are based on physical absorption exist as well, using methanol or polyethylene glycol and dimethyl ether as absorbing phases.6 Absorption-based processes are often used as the current benchmark for comparing new CO2 capture processes. Adsorption processes for gas separation via selective adsorption on solid media are also well-known.5,6 These adsorbents can operate via weak physisorption processes or strong chemisorption interactions. Solid adsorbents are typically employed in cyclic, multimodule processes of adsorption and desorption, with desorption induced by a pressure or temperature swing. Selective adsorption on microporous materials seems to provide another alternative. Accordingly, among the possible procedures, we can mention the adsorption of CO2 in the amine-based systems, currently used for the purification of natural gas on the industrial scale. However, amine plants being complex and costly to develop, the scientific community has been looking for alternative solutions for both separation/removal and storage of CO2. Therefore, a transfer from carbon dioxide absorption in liquid...
amine baths to adsorption on amine-functionalized solids may be an interesting way to overcome these mentioned disadvantages. Leal et al.\textsuperscript{7} were the first to functionalize the surface of silica with an aminoislate for its use in the adsorption of carbon dioxide. The amine-functionalized carbon nanotubes (CNTs) were also reported by Ma et al. though for different applications.\textsuperscript{11} After that, further work was carried out to investigate the adsorption of carbon dioxide on amine-functionalized materials using different amine molecules and different techniques.\textsuperscript{7–14}

In this work, we studied the carbon dioxide interaction with amine-functionalized materials. We have investigated the use of CNTs functionalized with amine groups and amine precursors for the use in solid-state CO\textsubscript{2} storage. The amine groups were functionalized on the surface of CNTs via the chemical process using dimethyl formamide (DMF) as a solvent. The aminated CNTs (ACNTs) were later functionalized with amino acid precursors such as L-lysine. Recent interests in CO\textsubscript{2} capture with solid sorbents with high CO\textsubscript{2} adsorption capacity has led to an active research in this area.\textsuperscript{13,15} Amines immobilized on high surface area materials can be used as high-capacity CO\textsubscript{2} capture sorbents. We postulate that CO\textsubscript{2} adsorption capacity can be enhanced by increasing the number of amine functional groups on the surface using diamines (an amine molecule with two amino groups). Furthermore, this sorbent can be used to capture other acid gases, such as H\textsubscript{2}S and SO\textsubscript{2}. The amine groups are particularly useful for the adsorption of CO\textsubscript{2} bonded chemically or physically on any supported materials. The ACNTs were investigated for CO\textsubscript{2} storage both before and after functionalization with amine molecules.

## RESULTS AND DISCUSSIONS

Figure 1 presents the X-ray diffraction (XRD) profiles of CNT, CNT–LiNH\textsubscript{2}, and CNT–LiNH\textsubscript{2}–Lys, indicated as (a–c), respectively. The curve (a) gives the typical peaks of CNT at around 2θ = 27.0 and 44.0, representing the ordered structure and amorphous phases of carbon in the sample. Similarly, the profile (b) shows the peaks from the lithium amide-functionalized CNTs, where the aminated peaks dominated over the CNTs peaks. These composite peaks provide information that the amine groups are adsorbed to CNT surfaces in the form of –NH\textsubscript{2}. There is a sharp peak at 2θ = 29.5, which indicated that a part of LiNH\textsubscript{2} phase is also present on the CNT surface. CNT peaks significantly decreased in the aminated sample and new peaks emerged with good crystallinity as shown in Figure 1b. In addition, CNT–NH\textsubscript{2}–Lys showed various peaks in the spectrum with high intensity and crystallinity. The peaks belong to the composite material of CNT–NH\textsubscript{2} and lysine chemically mixed for several hours. The new peaks were emerged because of the functionalized product of CNTs, which include the formation of N–C bond between amine groups of CNT–NH\textsubscript{2} and that of the carboxyl group present in lysine as shown in spectrum (c), thus giving rise to a new composite or grafted product containing two amine groups in addition to the one attached directly to CNTs. These amine groups are believed to be effective binding sites for the CO\textsubscript{2} storage under favorable conditions.\textsuperscript{6–18} Moreover, a negligible amount of lithium amide is also present in the sample even after washing several times by using DMF. However, all the samples did not show any peak which belong to any impurity or byproduct particularly in ACNTs and functionalized ACNTs. Thus, this development was significant to conclude that the functional-ization of CNT–NH\textsubscript{2} to form CNT–NH\textsubscript{2}–Lys occurred during the process.\textsuperscript{19}

Figure 2 presents the surface morphology of samples prepared for this study. The field-emission scanning electron microscopy (FESEM) micrographs (a–f) indicated raw CNTs, CNT–NH\textsubscript{2}, and CNT–NH\textsubscript{2}–Lys, respectively. The morphologies of pure CNT at two different magnifications indicated their diameter approximately 50–100 nm and length over 500 nm Figure 2a,b. The addition of LiNH\textsubscript{2} to the CNTs however provided different morphology as shown in (c,d). The nanotubes were not similar in shape and size compared to that of pure CNT in panel (b), instead a scattered and long nanotube covered with bonded amine groups could be observed in the micrographs. It is believed that CNT’s functionalized with amine groups could possibly change their
shape during the process. Mostly, the amine groups are adsorbed on the CNT surface through chemisorptions or physisorption depending on the experimental conditions. During this interaction between the CNT and amine group, some traces of lithium ion (Li⁺) separated from the LiNH₂, which paved way for amine groups to adsorb on the CNT surface. The remaining ions of amine (NH₂⁻) and lithium (Li⁺) were washed out from the sample through DMF repeatedly, and the adsorbed amine groups were observed from the FESEM image as shown in Figure 2d. Similarly, the addition of Lys to the ACNTs covers more surface because of the interactions between amine groups of ACNTs and carboxylic group (−COOH) of Lys. The amine group of ACNTs involved in chemical bonding with alpha carbon (−C=O) of −COOH of Lys released a H₂O molecule. The resulted H₂O molecule from the −OH of −COOH and H⁺ from the amine group was removed after the sample was heated at 100−110 °C for 2−4 h in a vacuum oven.

However, the Lys-functionalized ACNTs presented interesting results as shown in Figure 2e,f, where a small fractions of Lys is attached to the ACNTs through chemical bonding as confirmed by Fourier-transform infrared spectroscopy (FTIR) results presented in the later section. The images also showed that the ACNTs contain bulk particles of impurities remaining in samples in the form of LiNH₂ and unreacted lysine. However, this impurity is smaller than that of ACNTs (Figure 2d) as confirmed by XRD results.

Figure 3 presents the X-ray photoelectron spectroscopy (XPS) spectra of CNT, CNT−LiNH₂, and CNT−LiNH₂−Lys indicated as (a−c), respectively. The spectrum (a) provided a typical peak of graphitized C 1s carbon with binding energy 284.5 eV. There was no other peak present except a small peak (286.1 eV) probably because of the atmospheric oxidation or residual oxides resulting from the CNT purification. The XPS spectra of ACNT and ACNT−Lys however showed the peaks of nitrogen (N 1s) and lithium (Li 1s) elements in addition to the C 1s and O 1s peaks as observed from the spectra (b,c) of Figure 3. The percentage of lithium was low in spectra (c) as compared to (b) because of the remaining of small part of LiNH₂ as confirmed by XRD analysis. This was also related to the C 1s peak in trace (c) where a less intense peak is observed as compared to traces (a,b). The functionalization of Lys on ACNTs probably covers the most of the CNT surface, which led to the decrease in peak intensity for C 1s. In addition, this effect was also observed for the O 1s peaks. This observation clearly shows that the surface of CNT is occupied by the amine groups (−NH₂) in ACNTs and by −NH₂ and −Lys in ACNT−Lys samples. Hence led to low CNTs surface exposed for core-level electrons in XPS measurements.

Further investigation of the XPS data was carried out through convolution of core level electrons of different elements present in the samples. The details of each element including carbon, oxygen and nitrogen, lithium and their core level states are presented in Figures 4 and 5, respectively.

Figure 3. XPS spectra of samples CNT and ACNTs: (a) CNT, (b) CNT−LiNH₂, and (c) CNT−LiNH₂−Lys.

Figure 4. (A) XPS convolution of C 1s and O 1s core level electron analysis of CNT (a,d), CNT−LiNH₂ (b,e), and CNT−LiNH₂−Lys (c,f). (B) XPS convolution of Li 1s and N 1s core level electron analysis of CNT−LiNH₂ (a,c) and CNT−LiNH₂−Lys (b,d).
Li\textsubscript{2}) probably belonged to Li functionalized ACNT showed only two XPS peaks (Li, and \textsubscript{1} \textsubscript{H} \textsubscript{N} \textsubscript{H}) that there was little or negligible amount of Li\textsubscript{NH\textsubscript{2}} present prepared samples for this study. The simple mechanistic routes contributed to the covalent bonding with the C\textsubscript{4} in Figure 4b) which could be assigned to C=O, C\textsubscript{1}, C\textsubscript{2}, and C\textsubscript{3} in Figure 4A(c). The C\textsubscript{2} peak confirmed the presence of C=O, which is from the lysine molecule added to ACNT for the functionalization. Because there were not many carbon peaks in ACNT\textsubscript{Lys}, there was no impurity present in the form of inorganic or organic materials other than lithium and L-lysine. However, the presence of H\textsubscript{2}O and LiOH were observed as indicated in Figure 4A(f). This confirmed that the surface of CNT was occupied by both amine groups and by L-lysine through chemical bonding, corresponding to the different functionalities of different carbons as well as oxygen. In addition to this, a detailed XPS core electron analysis of nitrogen and lithium was investigated to find out their exact contribution toward the surface modifications of the samples.

In this investigation of elements of nitrogen and lithium from the ACNT and ACNT\textsubscript{Lys}, we observed peaks of Li \textsubscript{1}s and N \textsubscript{1}s as in Figure 4B. It was analyzed that the peaks of lithium comes from Li=O, Li=\textsubscript{N}, and Li=\textsubscript{C} assigned as Li\textsubscript{1}, Li\textsubscript{2}, and Li\textsubscript{3} in Figure 4B(a), respectively. However, the functionalized ACNT showed only two XPS peaks (Li\textsubscript{1} and Li\textsubscript{2}) probably belonged to Li=O and Li=\textsubscript{N}, which indicated that there was little or negligible amount of Li\textsubscript{NH\textsubscript{2}} present after the functionalization of the ACNT with lysine. This also confirmed that the \textsubscript{NH\textsubscript{2}} group on the CNT surface has contributed to the covalent bonding with the \textsubscript{COOH} group of L-lysine, resulting in the loss of H\textsubscript{2}O and formation of the C=\textsubscript{N} bond between \textsubscript{COOH} and \textsubscript{NH\textsubscript{2}} groups. This development provided two \textsubscript{NH\textsubscript{2}} groups present in the lysine molecule to the ACNT for CO\textsubscript{2} storage through chemical bonding between \textsubscript{NH\textsubscript{2}} and CO\textsubscript{2}. Finally, the XPS study showed that the modifications carried out on the CNT surface were successfully achieved for higher CO\textsubscript{2} adsorption. The important development however was the grafting of the \textsubscript{NH\textsubscript{2}} group of ACNT with that of the \textsubscript{COOH} group of lysine, which was clearly observed from the Figure 4A(c), where only three peaks of carbon were obtained.

Figure 5 provides the schematic representation of the prepared samples for this study. The simple mechanistic routes suggested that the CNT acted as a support for the amine precursors for CO\textsubscript{2} absorption. The other functionalized supports previously used for the CO\textsubscript{2} adsorption were silica or titania. This functionalization of N\textsubscript{H\textsubscript{2}} on CNTs usually takes place through chemical bonding or sometimes as a physisorption in nature and thus gives rise to C=\textsubscript{N} bonding as confirmed by XPS results. Furthermore, the ACNTs were treated with an organic compound lysine, which includes one \textsubscript{COOH} group and two \textsubscript{NH\textsubscript{2}} groups in a single molecule. The \textsubscript{NH\textsubscript{2}} group of the ACNT is free to bond with the \textsubscript{COOH} group of lysine, thus releasing a H\textsubscript{2}O molecule. After the functionalization on the ACNT, two amine groups were available for two or more CO\textsubscript{2} molecules to adsorb as shown in the Figure 5. The substitution of water actually occurs when an electron rich amine group interacts with the carbonyl of the carboxyl group present in lysine. This interaction leads to form a new bonding between carbon and nitrogen, thus giving a grafted product with multiamine groups attached on the CNT support. This would help to enhance the adsorption of CO\textsubscript{2} on CNTs or ACNTs under modified conditions.

In order to know the chemical nature of the modified samples, FTIR measurements were carried out for CNTs and functionalized CNTs assigned as CNT, CNT=NH\textsubscript{2}, and CNT=NH\textsubscript{2}–Lys in Figure 6, respectively. The IR spectrum of raw CNT showed a typical peak at around 1600–1650 cm\textsuperscript{-1}, which belongs to the C=C of ordered phase. There was a weak and broad band present at wavenumber approximately 3400 cm\textsuperscript{-1}, which was attributed to O–H groups on the surface of CNT. Similarly, the IR spectrum of CNT=NH\textsubscript{2} showed the band at 1250 cm\textsuperscript{-1} assigned to that of C=\textsubscript{N} bond stretching as shown in Figure 6. Furthermore, weak and broad bands between wavenumbers 2950–3100 cm\textsuperscript{-1} were attributed to N=H stretching bands. In addition, a weak band that appeared at 3700 cm\textsuperscript{-1} corresponds to the O–H stretching bands. This O–H band was emerged because of absorption of moisture or OH by the lithium ion (Li\textsuperscript{+}), thus forming LiOH during the process. In addition, an IR of CNT=NH\textsubscript{2}–Lys has shown number of bands for different functionalities present within the material. A band at 1610 cm\textsuperscript{-1} is attributed to the C\textsubscript{=O} group, which is at lower frequency because of the bonding with the amine group of ACNT, thus reducing its band toward lower wavenumbers. However, the actual frequency of C\textsubscript{=O} in the \textsubscript{COOH} group is approximately 1700–1785 cm\textsuperscript{-1}. This result is in consistent with the XPS findings explained above. Small bands of C=\textsubscript{N} and N–H at
1230 and 1570 cm\(^{-1}\) were observed related to the formation of new amide in ACNT–NH\(_2\)–Lys. Furthermore, weak stretching bands at wavenumbers 2800–3000 cm\(^{-1}\) were assigned to that of N–H and C–H functionalities, respectively. These IR results were consistent with the XPS results explained in the above section, thus confirming the functionalization of ACNT–NH\(_2\) and ACNT–NH\(_2\)–Lys.

The N\(_2\) isotherms of samples at 273 K were obtained and shown in the Figure 7. The CNT, CNT–NH\(_2\), and CNT–NH\(_2\)–Lys showed different curves from type II for CNT and type IV for CNT–NH\(_2\)–Lys, respectively. The samples of modified CNT did not show any micropores and there was no N\(_2\) adsorption at lower pressures. The nitrogen adsorption increased at higher relative pressures (\(P/P_0\) 0.7–0.9) up to 350 and 175 cm\(^3\)/g for CNT–NH\(_2\) and CNT–NH\(_2\)–Lys, respectively. The N\(_2\) adsorption for CNT was approximately 170 cm\(^3\)/g under similar conditions. The reduction in N\(_2\) adsorption in CNT–NH\(_2\)–Lys as compared to CNT–NH\(_2\) was due to the large CNT surface occupied by Lys molecules through chemical interaction with amine groups present on the CNT surfaces. The addition of lysine precursors as led to the blocking of pores thus reduced the overall pore volume, which reduced the N\(_2\) adsorption onto the CNT–NH\(_2\)–Lys. However, the surface of CNT–NH\(_2\) was not covered fully by the amine precursor used, but there was less effect on the porosity of CNTs. Another reason for high N\(_2\) adsorption could be the lithium ions (Li\(^{+}\)) present on the surface of CNT–NH\(_2\) which came from the amine precursor LiNH\(_2\) used for the amination of CNTs. The Li\(^{+}\) being electron-deficient can easily attract the electron-rich nitrogen to form a complex. Subsequently, this adsorption by Li\(^+\) could lead to further increase in the adsorption of nitrogen onto the CNT–NH\(_2\). Interestingly, this phenomenon was not found in the CNT–NH\(_2\)–Lys sample, where there was negligible amount of Li\(^+\) present on the surface because of the extra washing and lysine functionalization of the CNT–NH\(_2\) sample. Thus, the lysine functionalization reduced the surface area of CNT–NH\(_2\)–Lys, which proved to be insignificant for the N\(_2\) adsorption. However, the CO\(_2\) adsorption in CNT–NH\(_2\)–Lys was still better than CNT in N\(_2\) adsorption by a small factor of approx. 5 cm\(^3\)/g. This showed that the N\(_2\) adsorption in CNT–NH\(_2\)–Lys was probably through different factors. First, the N\(_2\) adsorption might be due to the spaces originated from the functionalization of lysine on the CNT–NH\(_2\). These channels between two functionalized groups can adsorb nitrogen chemically and/or physically on the surface of CNT–NH\(_2\)–Lys. The second reason for the adsorption of N\(_2\) might be the presence of a small amount of Li\(^+\) onto the surface as confirmed from XPS results. Thus, these results showed that the nitrogen adsorption of CNT was effective by amine and lysine functionalization, which produced higher adsorption capacity as compared to raw CNT.

Carbon dioxide adsorption experiments were performed at 273 K and a pressure of 750 mmHg. The results are presented in Figure 8, where each sample was analyzed under similar conditions for CO\(_2\) adsorption at 273 K. The unmodified CNT adsorbed 150 cm\(^3\) of CO\(_2\) at a given pressure. The adsorption of CO\(_2\) in CNT was the result of the high porosity and surface area of CNT. The CO\(_2\) adsorption of CNT showed its active nature toward the free CO\(_2\) molecule. However, the percentage of CO\(_2\) was increased after the medication of CNT with amine precursors. The ACNT–NH\(_2\) sample further enhanced the CO\(_2\) storage to 178 cm\(^3\) at similar pressure as that of the CNT sample. The increase in CO\(_2\) storage was related to the –NH\(_2\) groups, which are very active for CO\(_2\) adsorption because of the free electrons present on the nitrogen atom. Subsequently, the –NH\(_2\) groups interact with CO\(_2\) under pressure and gave rise to the formation of some intermediates such as carbamate or carboxylic acid species as reported in the literature. Some CO\(_2\) was also adsorbed on the vacant space of the CNT surface, thus helping to maintain the pure CNT storage capacity. Thus, additional modified ACNT–NH\(_2\) with lysine provided a much higher CO\(_2\) quantity than unmodified and ACNT–NH\(_2\) samples. The total capacity of CO\(_2\) adsorbed by ACNT–NH\(_2\)–Lys was estimated to be 230 cm\(^3\) with similar conditions. This ameliorated capacity was significant toward the CO\(_2\) storage. It showed that the amine groups had played a greater role in the enhanced CO\(_2\) storage as reported previously by many studies.

**CONCLUSIONS**

In summary, we have investigated the CNTs and modified CNTs for the use in CO\(_2\) adsorption. The CNTs were modified by using amino group-containing precursors via a chemical process. The functionalization of CNT with amino precursors has significantly improved the CO\(_2\) storage capacity of CNTs. First, the CNT was treated with LiNH\(_2\) under appropriate conditions to get the ACNT or the amine-functionalized CNT. The part of this prepared ACNT was further modified with organic amine precursor, L-lysine. The CNT and ACNT interactions with LiNH\(_2\) and l-lysine were confirmed through XPS and FTIR measurements, respectively, and related these results with previously reported amino-
carboxylic interactions. The unmodified CNT and modified CNT showed a significant CO$_2$ adsorption at STP. The CO$_2$ adsorption capacity of CNT was observed to be approximately 150 cm$^3$/g, and this adsorption capacity was further increased significantly after the CNT was modified with amide and lysine precursors. The ACNT and ACNT-Lys produced higher CO$_2$ storage (178 cm$^3$/g) and (250 cm$^3$/g) under similar conditions, respectively. These results provide an opportunity to extend these adsorptive application areas of high standard CNTs in large quantity.

**EXPERIMENTAL SECTION**

Materials and Methods. The single-walled CNT, lithium amide (LiNH$_2$), i-lysine, and DMF were procured from Aldrich and were used without any further purification. The first step in the process was the preparation of the ACNT or the amine-functionalized CNT in DMF for 12 h. The prepared solution of LiNH$_2$/DMF (1 g/10 g) was added to the CNT/DMF (1 g/20 g) solution at 50 °C and was stirred constantly for 8–12 h until the homogeneous solution was obtained. The solution was then filtered and washed several times with DMF to remove unreacted amide molecules. The sample was dried in a vacuum oven at 100 °C for 6 h. After drying, the sample of ACNT was taken for the further characterization and analysis.

Functionalization of the ACNT. The remaining ACNT was further dissolved in DMF and constantly stirred for 1 h. A predissolved i-lysine (Lys) was added to ACNT solution once and was kept under vigorous stirring for further 8 h. The solution was filtered and washed several times to remove impurities and unreacted materials in the reaction mixture. The product was dried in a vacuum oven at 100 °C for 6 h and finally followed by detailed characterization and analysis. The prepared samples were collected in air-tight sample vials to protect them from the oxidation or atmospheric moisture. The use of lysine for functionalization was performed because of the presence of additional number of amine groups in it, particularly significant for CO$_2$ interactions. Lysine also contains one carboxylic group (–COOH), which is involved in the reaction with the amine group of ACNT to form the nitrogen–carbon bond (N–C) as the functional group from carboxylic to amide formation.

Characterization. The surface morphology of the prepared samples was investigated using FESEM (Hitachi, S-5500). The samples were examined without any of the coatings usually used in FESEM measurements. XRD measurements were performed using a D/Max-2200 Ultima/PC apparatus (Rigaku, Japan) to analyze the elemental phases and the crystalline structures in the materials. XPS spectra of the samples were obtained using a MultiLab 2000 spectrometer (Thermo Electron Corporation, UK) to investigate the chemical nature and oxidation states of the samples. FTIR of samples was conducted to identify the chemical nature of each precursor after grafting. To study the CO$_2$ adsorption of the samples, the BET analyzer Micromeritics ASAP 2020 instrument was used. The measurements were performed at 273 K.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by grants from the Development Program of MOTIE/KEIT (Grant No. K10077357, Development of activated carbon fiber materials with very low cost and high functional property for removing sick house syndrome gas).

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