Electrospinning-based nanofiber architectures for outstanding CO₂ capture

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The worsening climate change has made the development of alternative and sustainable technologies to achieve carbon neutrality a pressing issue. Numerous strategies for carbon dioxide (CO₂) capture/conversion and relevant material preparation have been dealt with on a case-by-case basis. Therefore, a reconfigurable process to secure optimal procedures and materials is urgently required to reduce CO₂ emissions in a convenient, rapidly implementable manner. On this account, this study attempted to construct polyethylenimine (PEI)/cerium oxide (CeO₂)/activated carbon nanofibers (ACNFs) as a reliable CO₂ adsorbent from an electrospinning (ES)-based architecting as a modular process to accelerate their field applications because adsorption has outstanding advantages for CO₂ capture, such as process simplicity, wide operational range, low cost, and stable performance. By selecting ES with commercially available materials (PEI (providing CO₂ chemisorption), cerium nitrate hexahydrate (CO₂ selectivity), and polyacrylonitrile (base of porous nanofibers)), a composite nanofibrous architecture (PEI/CeO₂/ACNFs) with outstanding CO₂ capture can be achieved by simple process manipulation (manipulating the electrical polarity applied to the nozzle and concentration of the cerium nitrate for the ES). This study may provide a reconfigurable manufacture to ensure a reliable adsorbent for CO₂ capture and base materials for CO₂ conversion from electro- and photocatalysis.

1. Introduction

Climate change is recognized as a critical global issue by most people around the world [1]. Recently, it has been suggested that the carbon dioxide (CO₂) concentration is related directly to the ecosystem and biodiversity of the air and the ocean as an air filter of the world [2]. Advanced adsorption materials are essentially required as an active alternative to reducing CO₂ [3]. On the other hand, only limited data or complex approaches for highly capacitive and selective adsorption have been provided a case-by-case basis, and there is a lack of sufficient information, even for workable architectures of adsorbents. In that sense, a high-throughput screening platform is required as a priority to accelerate the utilization of reliable CO₂ adsorbents for practical applications.

As a primary viable option to capture CO₂, adsorption using porous materials, such as metal–organic frameworks (MOFs) [4], zeolites [5], porous polymer networks [6], and porous carbon [7], has been considered because of convenience, material abundance, simple facility, and low cost and energy consumption. On the other hand, surface modifications based on hydrothermal or vacuum (spattering for nanoroughness or vapor deposition for functional overlayers) reactions are required to ensure enhanced adsorption capacity considering adsorbate species, operating temperature and pressure, and space velocity [8,9]. A trade-off problem between the higher performance and process complexity may impede the practical applications of developed materials for CO₂ reduction. A convenient, modular, high-yield platform is required to screen architectures systematically for reliable CO₂ adsorption.

Because of the “mix and go” convenient configuration, electrospinning (ES) has been used extensively to produce a diverse spectrum of nanofibrous nonwovens for separation and purification purposes in the past three decades [10]. Nanofibrous structures can be installed in most environmental pollutant treatment plants because of their proper architecture, flexibility, and textural property with tolerable pressure drop. These can be extendable for energy production and storage applications [11,12]. An electric potential with polarity modulation on the spinning nozzle can control the arrangement of ionic compounds (directly added to the polymeric precursor for functionalizing/modifying purposes) in the discharging of a mixture precursor [13,14] that conveniently generates various composite nanofibers with no post-treatments under harsh hydrothermal or vacuum conditions [15].

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Subsequent thermal carbonization and activation formed textures in the resulting nanofibers to secure micro- and mesoporosity, whereas utilizing this technique is still immature for CO$_2$ adsorption.

This paper proposes an ES-based platform to build an overlayer/interlayer/base fiber (securing compositional hierarchy) architecture for highly capacitive, reliable CO$_2$ adsorption, where polyethylenimine (PEI; providing CO$_2$ chemisorption), cerium dioxide (CeO$_2$; CO$_2$ selectivity), and activated carbon nanofibers (ACNFs; base for adsorption capacity) were selected as the individual layer materials by successive ES, thermal treatment, and bath immersion (Fig. 1). The polarity of the electric potential and concentration of CeO$_2$ precursor (cerium nitrate hexahydrate (Ce(NO$_3$)$_2$$\cdot$6H$_2$O), a Ce$^{3+}$ source) were selected as vital parameters to ensure modular property and control the arrangement and density of Ce$^{3+}$ for screening optimal overlayer/interlayer/base fiber (CeO$_2$/ACNFs) architecture upon a thermal treatment for CO$_2$ adsorption. Subsequent immersion of the CeO$_2$/ACNFs in the PEI bath for impregnating amine groups (constructing a PEI/CeO$_2$/ACNFs hierarchy) was conducted to reinforce the chemisorption of the adjacent CO$_2$.

2. Experimental

2.1. ES-based construction

Cerium nitrate hexahydrate (CAS#10294–41–4; Ce(NO$_3$)$_2$$\cdot$6H$_2$O) with different doses (0.05, 0.10, 0.15, and 0.20 g) was dissolved in 10 mL of N,N-dimethylformamide (CAS#68–12–2; DMF) and stirred for 1 h at 60 °C. The solution was then incorporated with 1 g of poly(acrylonitrile) (PAN; CAS#25014–41–9; $M_w$ = 150,000 g/mol) for one day with magnetic stirring at room temperature to form Ce(NO$_3$)$_2$/PAN composite precursors. The resulting precursor solutions were fed into a plastic syringe for ES at a flow rate of 5 μL min$^{-1}$, which was regulated using a syringe pump (Fig. S1). The metal nozzle (inner diameter = 0.67 mm) was connected to an electric potential of −12 kV, where the distance between the tip of the nozzle and the revolving drum collector (200 rpm) was 15 cm. The diameter and length of the drum collector were 10 and 20 cm, respectively. As shown in Fig. S2, the as-spun NFs were put in an alumina tube and treated thermally through the following steps: (1) stabilization (250 °C), (2) carbonization (250–900 °C), (3) activation (900 °C), and (4) oxidation (250 °C). The thermally treated NFs were denoted as CeO$_2$/ACNFs (1–4). For comparison, analogous NFs were synthesized without cerium nitrate (ACNFs) or under the opposite electric polarity (+12 kV; +CeO$_2$/ACNFs).

To prepare PEI-impregnated samples, 2 g of vacuum-dried (at 150 °C for 12 h) ACNFs was immersed in a PEI ($M_w$ = 800 Da) solution (10 g PEI dissolved in 200 mL of ethanol for 1 h under magnetic stirring) and stirred magnetically at room temperature for 3 h to ensure the PEI impregnation on the sample surfaces (approximately 0.85 g of PEI/1.00 g of ACNFs). The treated sample was placed in a vacuum oven at 100 °C for 5 h to secure dried PEI/ACNFs. An analogous procedure was carried out for CeO$_2$/ACNFs and +CeO$_2$/ACNFs to provide PEI/CeO$_2$/ACNFs and PEI/+CeO$_2$/ACNFs.

2.2. CO$_2$ adsorption

A static volumetric analyzer (TriStar II 3020, Micromeritics, USA) was used to obtain the capacities of CO$_2$ adsorption for the resulting samples. Before the test, the samples were degassed for 12 h at 150 °C to remove moisture (ensuring the residual pressure of <1 × 10$^{-3}$ mbar). A steady flow of CO$_2$ (0.015 L/min) was used to test each sample (0.1 g), while different temperatures (0, 25, 50, and 75 °C) were conducted to examine the adsorption capacity. The nitrogen (N$_2$) adsorption capacity was also examined under identical conditions to identify the selectivity of CO$_2$ adsorption. The CO$_2$ desorption was conducted at 100 °C for 2 h under pure nitrogen (as desorption gas) atmosphere.

2.3. Characterization

The samples were examined by field-emission scanning electron microscopy (SEM; 7800F, JEOL, Japan) and transmission electron microscopy (TEM; JEM-F200, JEOL, Japan). Elemental maps were obtained using an energy-dispersive X-ray spectroscopy (EDS) included in the TEM. To prepare the samples, ethanol was used to disperse each sample before placing it on a carbon-coated copper grid. The crystallinity of the samples was analyzed by X-ray diffraction (XRD; SmartLab, Rigaku, Japan) with a Cu Kα radiation source. X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo Scientific, USA) was used to obtain the Ar$^+$ depth profiles with an etching rate of 0.1 nm/s for quantifying the surface elements of the samples. The surface chemistry and pyrolysis characteristics were examined using Fourier transform infrared (FTIR) spectroscopy (VERTEX 70, Bruker, USA) and thermogravimetric analysis (TGA; LABSYS evo, Setaram Instrumentation, France), respectively. The textural properties of the samples were analyzed using a porosimeter (Autosorb-iQ 2ST/MP, Quantachrome, Austria).

3. Results and discussion

Different doses of the inorganic salt (Ce(NO$_3$)$_3$$\cdot$6H$_2$O) were mixed individually with PAN in DMF to produce precursor solutions for constructing CeO$_2$/ACNFs-1, CeO$_2$/ACNFs-2, CeO$_2$/ACNFs-3, and CeO$_2$/ACNFs-4. An external electric potential with different polarities (+, −) was applied to derive the electrohydrodynamic movement of the ionic compounds in the precursor solution during its discharging through the ES nozzle. For the negative potential, Ce$^{3+}$ and NO$_3^-$ ions migrated toward the outer and inner regions of the nozzle, respectively, while the ions moved in opposite directions with the positive potential (Fig. 2A and 2B). The figures also present representative SEM images of the electrosprun Ce(NO$_3$)$_3$/PAN fibers under negative and positive electric potentials. Both fibers showed smooth surfaces with a diameter range from 250 to 300 nm.

The concentrations of Ce$^{3+}$ (C$_3$) as a function of the distance from the center of the nozzle (x) were determined analytically using the Boltzmann distribution and zeta potential profile equations (Eqs. S1 and S2 [16]). Ce$^{3+}$ was distributed narrowly with distance from the center of the nozzle, where the concentrations were dependent on the electrical discharging precursor solution (Ce(NO$_3$)$_3$/PAN in DMF). The dose of was Ce(NO$_3$)$_3$ regulated in the four stages to ensure optimal distribution of CeO$_2$ particles and pore size of ACNFs. The as-spun nanofibers (Ce(NO$_3$)$_3$/PAN NFs) were thermally treated to produce CeO$_2$ particles on porous nanofibers (CeO$_2$/ACNFs), and subsequently immersed in PEI solution to form PEI-impregnated CeO$_2$/ACNFs (PEI/CeO$_2$/ACNFs) for their use in CO$_2$ adsorption tests.

Fig. 1. Schematic of the ES-based process to construct hierarchical composite nanofibers for reliable CO$_2$ adsorption from a combined physi- and chemisorption. To ensure a proper distribution of Ce$^{3+}$ ions within PAN, different polarities (+ and −) of electric potential were applied to the ES nozzle, where the ion pairs (Ce$^{3+}$ and NO$_3^-$ from the dissolution of Ce(NO$_3$)$_3$) were oppositely moved by switching the polarity that generates different distributions of the ion pairs within
polarity and strength, as shown in Fig. S3A and S3B. In particular, the ions were densely distributed (>450 M) at a distance of 160 to 180 nm for the negative potential. Longer distances (i.e., closer to the fiber surface) were obtained at higher electric strengths because of the stronger electrostatic attractions between the Ce$^{3+}$ and the negatively charged nozzle surface. By contrast, relatively negligible amounts of ions were distributed at these distances because of electrostatic repulsion, showing that modulating the electric polarity was the driver for the concentrated distribution of Ce$^{3+}$ at the outer or inner region of the fibers. The atomic depth profiles Fig. S3C from argon ion (Ar$^+$) etching matched the surface concentrated distribution of Ce$^{3+}$ (6.6%) for the negative potential (i.e., nearly zero % for the positive potential), supporting the adjustability of the ES for the site-selective distribution of Ce$^{3+}$. FTIR spectroscopy showed a significantly greater surface distribution of NO$_3^-$ (absorption band at 1380–1350 cm$^{-1}$) for the positive potential (i.e., closer to the fiber region of CeO$_2$) compared to those of CeO$_2$/ACNFs-3, which was induced by oxidation of the outermost Ce$^{3+}$ ions (forming CeO$_2$), while the characteristic lattice spacing (0.318 nm) for CeO$_2$ (111) was identified by high-magnification TEM (Fig. 2L). XRD (Fig. 2M) revealed the characteristic 2θ bands at 28.6°, 33.1°, 47.6°, and 56.3°, which were indexed to the (111), (200), (220), and (311) lattice planes of CeO$_2$, respectively [18]. A broad diffraction band at approximately 25° was assigned to amorphous carbon formed from the thermal treatment of PAN [19]. The intensity of the characteristic CeO$_2$ bands was also proportional to the Ce(NO$_3$)$_3$ dose, which is consistent with the size increases in TEM images (Fig. 2G–2J) by estimating the average crystal sizes using the Scherrer equation (Table S1). For comparison, the morphologies of ACNFs and +CeO$_2$/ACNFs-3 were observed by SEM and TEM, where no dark dots on the fiber surfaces were identified (Fig. S5). There were no significant differences in appearance between ACNFs (Fig. S5A) and +CeO$_2$/ACNFs-3 (Fig. S5C). On the other hand, the TEM image of +CeO$_2$/ACNFs-3 exhibited fine dark dots in the core region, which may be caused by the inside-concentrated distribution of Ce$^{3+}$ ions for the positive potential. The dots were smaller than those of CeO$_2$/ ACNFs-3 probably due to limited oxygen exposure to the inner region located Ce$^{3+}$ ions to form CeO$_2$ particles that generate weak intensities of the characteristic CeO$_2$ bands compared to those of CeO$_2$/ACNFs-3 despite the differences between the ACNFs and +CeO$_2$/ACNFs-3 (Fig. S6). This represented that the inside-dominant distribution of Ce$^{3+}$ could retain surface texture of ACNFs likely due to the confined oxidation of Ce$^{3+}$ ions to form CeO$_2$ particles.

The thermal decomposition behavior of Ce(NO$_3$)$_3$/PAN NFs (as-spun prior to ACNFs, +CeO$_2$/ACNF-3, and CeO$_2$/ACNFs-3) was investigated by TGA in steps 1 and 2 of the thermal treatment (Fig. S2). As shown in Fig. S7, the weight losses in the temperature range (25–250 °C) in the air atmosphere resulted from the cyclization of nitrile groups and dehydrogenation of PAN (i.e., the stabilization of PAN) [20]. Until the temperature reached 250 °C, the as-spun fiber samples exhibited weight losses of 1.17%, 2.52%, and 3.95%, respectively. Additional weight losses (2.42%, 2.96%, and 4.29%) were observed when the temperature was maintained at 250 °C for 30 min. The highest weight loss of Ce(NO$_3$)$_3$/PAN may be caused by the catalytic oxidation of adjacent PAN molecules, which was induced by oxidation of the outermost Ce$^{3+}$ to CeO$_2$. The higher loss of +Ce(NO$_3$)$_3$/PAN than PAN reflected this hypothesis. This is consistent with a previous report where a significant shrinkage of PAN was observed upon oxidation of transition metal to metal oxide in PAN during thermal treatment [21]. Over 250 °C with a nitrogen atmosphere, the samples exhibited nearly identical weight loss profiles, where the losses were mostly driven by pyrolytic carbonization of PAN. The weight differences between the samples were similar during the temperature increase, suggesting that no more catalytic oxidation of the PAN occurred because of a lack of oxygen molecules. After the temperature reached 900 °C, the residues of the PAN, +Ce(NO$_3$)$_3$/PAN,
and Ce(NO$_3$)$_3$/PAN were 32.65%, 31.19%, and 29.53%, respectively, which were probably due to pyrolysis-induced shrinkage in the absence of oxygen.

Textural properties of the thermally treated CeO$_2$/ACNF samples (1–4), including ACNFs and +CeO$_2$/ACNF-3, were obtained from N$_2$ adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method. As shown in Fig. 3A, all samples exhibited a substantial increase in N$_2$ adsorption at a low relative pressure (<0.05), representing a significant portion of micropores. In particular, ACNFs demonstrated type-I isotherms, whereas the others (CeO$_2$-containing configurations) exhibited type-IV isotherms with H$_4$ hysteresis loops in the range of 0.5–1.0 (P/P$_0$) due to the mesoporosity of slit-shaped pore channels owing to CeO$_2$ formation [22]. The N$_2$ adsorption capacity of the samples was observed in the following order: CeO$_2$/ACNFs-4 < ACNFs < CeO$_2$/ACNFs-1 < CeO$_2$/ACNFs-2 < CeO$_2$/ACNFs-3. Even though increasing Ce(NO$_3$)$_3$ content in PAN led to improvement of the adsorption performance, an excessive dose of Ce(NO$_3$)$_3$ caused the formation of unfavorable architecture (forming large CeO$_2$ particles and their blocking the pore channels) for transport within the microstructure and interaction with CeO$_2$ and ACNF surface of CO$_2$ molecules. The lowest capacity of CeO$_2$/ACNFs-4 may be due to the blockage of slit-shaped pores by the densest distribution of CeO$_2$ particles on the fibers, which could be confirmed by the modulation of Ce(NO$_3$)$_3$ doses.

The pore size distributions of the samples were determined using the Barrett-Joyner-Halenda (BJH) and Horvath-Kawazoe (HK) models. As shown in Fig. S8, drastic increases in pore volume were observed for the diameters smaller than 3 nm in all samples, showing that the thermal treatment induced a significant portion of micropores. On the other hand, CeO$_2$/ACNFs-2, 3, and 4 included relatively larger portions of the pores with diameters >3 nm because of the coexistence of the mesoporous CeO$_2$ particles (Table S1). The highest volume of CeO$_2$/ACNFs-3 matched the N$_2$ adsorption capacity, suggesting that modular coordination of Ce$^{3+}$ is required to ensure optimal textural properties. The pore size distributions for diameters <1 nm were also analyzed to identify the portion of pores with diameters of 0.5 to 0.6 nm (Fig. 3B) because these diameters (close to the kinetic diameters (<1 nm) of CO$_2$) are favorable for physical adsorption of CO$_2$ (increasing adsorption energy of CO$_2$ due to van der Waals potential field formed by the pore walls) [23,24]. Compared to the others, CeO$_2$/ACNFs-3 exhibited a prominent portion of the pores for CO$_2$ selectivity, showing the requirement of the modular approach to derive a favorable effect of the simultaneous oxidation of Ce$^{3+}$ ions and PAN molecules for constructing optimal textural properties.

The textural properties of PEI-impregnated (for reinforcing CO$_2$ chemisorption) CeO$_2$/ACNFs-3 (PEI/CeO$_2$/ACNFs-3), including PEI/ACNFs and PEI/+CeO$_2$/ACNFs-3 were also investigated. All samples exhibited significantly reduced N$_2$ adsorption after impregnation, reflecting that the PEI was loaded on the nearly entire pore walls through the simple immersion (Fig. S9A). The lower N$_2$ adsorption levels at low relative pressures represented the PEI loading on most of the micropore region upon impregnation. The CeO$_2$-included samples still exhibited type-IV isotherms even after PEI incorporation, suggesting that the loading was performed uniformly along the pore walls. The stronger hysteresis intensity at >0.5 P/P$_0$ for PEI/CeO$_2$/ACNFs-3 than PEI/+CeO$_2$/ACNFs-3 was related to the higher amount of CeO$_2$ particles on the fiber surfaces. On the other hand, the loading changed the type of the hysteresis loop from H$_4$ to H$_3$, which followed the existence of non-rigid aggregates of CeO$_2$ particles, according to a previous report [25]. Although CeO$_2$/ACNFs retained the CO$_2$ selective microporosity after the loading, the micropore volumes in both BJH (Fig. S9B) and HK (Fig. S9C) models were reduced significantly. PEI/+CeO$_2$/ACNFs showed a similar pore size distribution to PEI/ACNFs than PEI/CeO$_2$/ACNFs, suggesting that the insufficiently developed CeO$_2$ on the fiber surface cannot generate favorable textures for CO$_2$ adsorption. The PEI loading was analyzed further by FTIR (Fig. S10), where the C=O and C-N stretching vibrations of the amide were observed at 1620 and 1575 cm$^{-1}$, respectively, as an amine-grafted architecture [26]. Unlike the Ce(NO$_3$)$_3$/PAN NFs, the strong adsorption bands at 1581 cm$^{-1}$ and 1251 cm$^{-1}$ were assigned to C–C and C–C bonds instead alkyl, nitrile, carbonyl, and other groups, also proving successful carbonization of PAN NFs through the thermal treatment [27].

Fig. 4A and S11 show the CO$_2$ and N$_2$ adsorption capacities and the equilibrium isotherms of ACNFs, CeO$_2$/ACNFs-3, PEI/ACNFs, PEI/+CeO$_2$/ACNFs-3, and PEI/CeO$_2$/ACNFs-3 at different temperatures for pressure up to 850 mmHg (1.13 bar), respectively. The adsorption capacities of all samples were proportional to pressure, which were due to the forced deep diffusion of CO$_2$ into the pores regardless of PEI incorporation. In the absence of PEI (ACNFs and CeO$_2$/ACNFs-3), CO$_2$ adsorption was inversely proportional to the operating temperature, showing exothermic physisorption to be the main driver of the CO$_2$ uptake (Fig. S11A and S11B). The higher uptake for CeO$_2$/ACNFs-3 than ACNFs proved that the formation of CeO$_2$ particles on the surface of activating NFs could provide a favorable pore structure and selectivity for enhanced CO$_2$ adsorption. The microstructure of the resulting CeO$_2$ particles may also have oxygen basic and vacant sites as active surfaces that enable the storage of extra oxygen. These oxygen vacancies may act as active sites for the chemisorption and activation of CO$_2$, leading to the reduction to CO or other products from intermediate carbonates [28]. Owing to the presence of the active sites with adjacent hydroxyl groups, adsorbed CO$_2$ onto the active sites was reacted with surface oxygen ions or hydroxide species to be formed as carbonates [29,30]. This suggests that CeO$_2$/ACNFs-3 may provide greater selectivity to CO$_2$ than N$_2$ (<5 cm$^3$/g at 0 °C, 850 mmHg) owing to its large quadrupole moments and polarizability to CO$_2$ molecules [31]. In the presence of PEI
from the optimal CeO$_2$ adsorption capacity (reached 185.79 cm$^3$/g at 75 °C, 850 mmHg; derived the highest $Q_{\text{max}}$ in the Langmuir–Freundlich model (Table S2 and Eqs. S3 and S4)), even better than those in most recent relevant studies [32]. This highest performance was probably due to a combinatorial effect of chemical and physical CO$_2$ affinities of PEI and CeO$_2$ from the optimal CeO$_2$ particle and pore size distributions that confers enhanced bindings to adjacent CO$_2$ molecules, even under lower operating pressures (<100 mmHg) [33]. Other bindings from electrostatic (between the positively charged groups in PEI and negatively charged CeO$_2$), Lewis acid (CeO$_2$)–base (PEI), and π–π stacking (between the aromatic groups on PEI and ACNF) interactions might also derive the enhancement in CO$_2$ adsorption [34–36]. In the case of PEI/ACNFs, the higher capacities than those of ACNFs alone at higher temperatures were related to the strong interactions between the CO$_2$ and amine groups of PEI on the microporous channels of ACNFs. The temperature-dependent uptake manner was attributed to the increased molecular flexibility and intermolecular distance of the branched chain of PEI molecules, promoting the reactivity with CO$_2$ [37–39]. The PEI-impregnated CeO$_2$/ACNFs-3 also exhibited the temperature-dependent manner, suggesting that the PEI/CeO$_2$/ACNFs hierarchical architectures may be a viable option even for post-combustion CO$_2$ capture [7,32]. As shown in Fig. S11A–S11E, the Freundlich and Langmuir–Freundlich models were well fitted ($R^2 > 0.99$) to the experimental results of CO$_2$ adsorption for all tested samples (Table S2). In particular, the operating temperatures were relevant (inversely or directly proportional) to the value of $n$ (determined by the slope of the plot in the Freundlich model) [40], while all of the $n$ values in the Freundlich model were >1, representing the favorable multilayer adsorption of CO$_2$ [41].

Fig. S11F and Table S3 (with Eqs. S5 and S6) present the van’t Hoff plot and thermodynamic parameters of $\Delta H^\circ$, $\Delta S^\circ$, and $G^\circ$ of the samples, respectively. The negative values of $\Delta H^\circ$ in the absence of PEI (ACNFs and CeO$_2$/ACNFs-3) confirmed the exothermic nature of the adsorption process, driven by a net decrease in entropy. The higher $\Delta H^\circ$ level of CeO$_2$/ACNFs-3 than ACNFs indicated that CeO$_2$/ACNFs-3 has a greater portion of chemisorption. The inversely proportional adsorption capacity of ACNFs and CeO$_2$/ACNFs-3 to the operating temperature reflected the increase in $\Delta G^\circ$ with increasing temperature, which matched the CO$_2$ uptake results (Fig. S11A and S11B). In the presence of PEI, the positive $\Delta H^\circ$ values of the samples represented an endothermic adsorption process for CO$_2$, indicating better performance at high temperatures. On the other hand, the momentum to offset the CO$_2$ adsorption will be strengthened due to the exothermic nature of CO$_2$ adsorption that accelerates the desorption of CO$_2$ as the temperature increases. This induced relatively lower $R^2$ levels (dependence on the van’t Hoff equation in the CO$_2$ adsorption) for PEI/ACNFs ($R^2 = 0.8051$) and PEI/CeO$_2$/ACNFs-3 ($R^2 = 0.4883$) that that of PEI/CeO$_2$/ACNF-3 ($R^2 = 0.9432$), proving the robust performance of PEI/CeO$_2$/ACNF-3 in a temperature-dependent manner.

Fig. 4B shows a comparison in CO$_2$ adsorption capacity between the present and previous studies in the absence and presence of PEI [42–48]. The developed CeO$_2$/ACNFs-3 and PEI/CeO$_2$/ACNFs-3 in this study demonstrated the highest specific surface area and CO$_2$ adsorption capacity within each category. The consecutive CO$_2$ adsorption–desorption tests were also carried out at different temperatures (25 °C and 75 °C) to investigate the cycling behavior and stability of PEI/CeO$_2$/ACNFs-3 (Fig. 4C). The adsorption capacity of PEI/CeO$_2$/ACNFs-3 exhibited relatively constant capacities at 25 °C (130–134 cm$^3$/g) and 75 °C (185–187 cm$^3$/g) after the five adsorption–desorption cycles. This stability was probably due to PEI overlayers as protective coatings to suppress the deactivation of CeO$_2$ particles on the fiber surface, further suggesting that the overlay (PEI)/interlayer (CeO$_2$)/base fiber (ACNFs) hierarchical architecture warrants further investigation for its practical applications. In the light of practical implementation, the necessary expense for the proposed method was estimated based on a previous study [49], which was compared to that from chemical surface etching of Ce(NO$_3$)$_3$/PAN NFs for surface distribution of Ce components. Even though the cost reduction by adopting the proposed method was marginal for PEI/CeO$_2$/ACNFs production, wastewater generation and chemicals to
consumed for the chemical etching can be reduced by switching the electrical polarity for electrospinning. Nevertheless, the cost issue of Ce (NO$_3$)$_3$ needs to be compromised through mass production and improving supply chain stability to secure an actual competitive advantage in practical implementation [50].

4. Conclusion

To ensure an optimal compositional hierarchy of nanofibrous adsorbents for CO$_2$ emissions, an ES-based assembly with polarity modulation of electric potential was developed and utilized to build composite architectures. In particular, the location of Ce$^3+$ in the Ce(NO$_3$)$_3$/PAN precursor (inner distribution at positive potential while outer at a negative potential) was conveniently manipulated by switching electrical polarity when the precursor was discharged through the nozzle with electric potential. At a negative potential, in particular, CeO$_2$ particles were densely distributed on the surface of the nanofibers as CeO$_2$/ACNFs further enhanced CO$_2$ adsorption even at increased temperature probably because of the capacity of CO$_2$ chemisorption to ACNFs. Switching polarity of the electrical potential for electrospinning was effective to distribute conveniently CeO$_2$ particles on ACNFs to maximize CO$_2$ adsorption capacity while only an immersion of CeO$_2$/ACNFs in PEI dissolved solution was required to anchor PEI molecules for improving chemisorption of CO$_2$ in spite of the porosity reduction. A repetitive adsorption–desorption of CO$_2$ proved the stability in high temperature and long-term operation. This work may provide a reliable architecture of highly capacitive composite nanofibers for CO$_2$ capture and modular preparation platform to screen optimal hierarchies of base adsorbents for various types of CO$_2$ capture and conversion applications.

CRediT authorship contribution statement

Sangmo Kang: Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft. Jungho Hwang: Methodology, Validation, Funding acquisition, Writing – review & editing, Project administration, Supervision. Jeong Hoon Byeon: Methodology, Validation, Data curation, Conceptualization, Writing – review & editing, Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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