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Nanosilica Polyamidoamine Dendrimers for Enhanced Direct Air CO\textsubscript{2} Capture

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Abstract: Exploring efficient system to recover CO\textsubscript{2} from atmosphere could be a way to address the global carbon emission issue. Herein, we report the synthesis of nanosilica (NS) functionalized with polyamidoamine (PAMAM) dendrimers (NS-PAMAM) as efficient adsorbents for CO\textsubscript{2} capture under simulated direct air capture (DAC) (400 ppm CO\textsubscript{2} in Helium at 30 °C) and indoor air (≥400 ppm, 50± 3% RH at 30 °C) condition. Results inferred, 1\textsuperscript{st} (NS-G1.0), 2\textsuperscript{nd} (NS-G2.0), 3\textsuperscript{rd} (NS-G3.0), and 4\textsuperscript{th} (NS-G4.0) generations of NS-PAMAM dendrimers exhibited distinct performance for CO\textsubscript{2} capture. Among them, NS-G3.0 demonstrated superior CO\textsubscript{2} adsorption capacity of 0.50 mmol/g under simulated dry CO\textsubscript{2} (400 ppm in He), 1.02 mmol/g under indoor air (dry) CO\textsubscript{2} (≥400 ppm, 26± 3% RH), and 1.54 mmol/g under indoor air (humid) CO\textsubscript{2} (≥400 ppm, 50± 3% RH) compared to the other generations. The study encompassed the evaluation of CO\textsubscript{2} adsorption-desorption performance of the NS-PAMAM dendrimers under varying structural and chemical parameters, kinetics, regeneration at a low temperature (80 °C), as well as CO\textsubscript{2} adsorption under humid conditions. Additionally, NS-G3.0 displayed substantial superiority with stable CO\textsubscript{2} capture during ten short temperature swing adsorption (TSA) cycles, making it a promising candidate for CO\textsubscript{2} capture from ambient air. Finally, we demonstrate the recovery and reutilization of the captured CO\textsubscript{2} for the synthesis of formate via carbonate hydrogenation and as calcium carbonate pellets.

Keywords: Direct air capture, Indoor air CO\textsubscript{2} capture, Nanosilica, PAMAM dendrimer
1. Introduction

The increasing CO\textsubscript{2} level in the atmosphere affects the planet’s natural balance, consequently bringing out a dramatic global climate change, ambiguously attributing to the rise of industrial civilization and the burning of fossil fuels.\textsuperscript{1} According to IPCC 2023 report, mitigating efforts should be accelerated to limit the warming below 2 °C.\textsuperscript{2} Therefore, carbon dioxide capture, and storage (CCS) is found to be one of the most promising and highly desirable concept to address this alarming issue. It involves various techniques like pre, post-combustion, oxy-fuel combustion, and direct air capture (DAC) to capture CO\textsubscript{2} efficiently. Post- and pre-combustion methods are identified to be vital capture routes but suffer several limitations, primarily the higher energy consumption for the release of absorbed CO\textsubscript{2} and high capital cost limits their usage further in large scale making them a less desirable option for the future.\textsuperscript{3}

Among various CCS techniques, DAC is one of the rapidly growing technologies which shows efficient carbon capture from ambient air, although the concentration of CO\textsubscript{2} in the atmosphere is very dilute and also exhibit a potential capability to convert the captured CO\textsubscript{2} to other valuable chemicals. Currently, there are over 18 operating DAC plants globally, capturing nearly 0.01 Mt\textsubscript{CO2} per year.\textsuperscript{3-5} In order to achieve the net zero emissions by 2050 goal, direct air capture needs to be expanded to capture approximately 60 Mt\textsubscript{CO2} per year by 2030. One of the key advantages of DAC is their potential to address emissions not only from point sources but also from distributed sources, thereby can be deployed anywhere as it is not location specific.\textsuperscript{3,4} For DAC application, adsorbent materials exhibiting high durability and high CO\textsubscript{2} selectivity under low CO\textsubscript{2} concentration and at atmospheric pressure could be the promising candidates.\textsuperscript{6} In direct air capture, significant attention is given to both absorption and adsorption techniques for capturing CO\textsubscript{2}.\textsuperscript{7} Despite the prominent efficiency of liquid amine solutions, such as monoethanolamine (MEA), in capturing CO\textsubscript{2} through absorption, their drawbacks include high energy consumption during regeneration, corrosive properties, and loss of amine during operation.\textsuperscript{8} Therefore, for DAC, adsorption has gained enhanced attention as a sustainable alternative for its vital role in reversible capture and release of CO\textsubscript{2}, high capacity, selectivity, and cyclic stability.\textsuperscript{5} In this context, DAC using solid amine-based sorbents were extensively studied. CO\textsubscript{2} adsorption can be achieved over several adsorbents such as zeolites, activated carbon, metal-organic frameworks (MOFs), and amine-grafted sorbents, etc.\textsuperscript{9} The adsorption capacity mainly depends on pore volume, surface area, and the degree and type of
Amine-based solid sorbents possess high CO$_2$ adsorption capacity, selectivity, and regenerability without any considerable performance loss making them an ideal sorbent for the future. Amine-based solid adsorbents used for DAC are synthesized in four ways: (i) Amine-impregnation, (ii) Amine-grafting, (iii) in-situ polymerisation and (iv) combination of impregnation and grafting.

While amine loading is a crucial factor for CO$_2$ adsorption capacity under ultra-dilute conditions, the morphology of amine molecules within the support and the interaction between gas and solid surfaces can greatly influence the overall efficiency of CO$_2$ capture. Though amine-impregnated adsorbents modified with PEI, a polymeric amine (e.g. TEPA), and linear amines (e.g. PEHA) are widely explored to exhibit high CO$_2$ adsorption capacity, they often show poor CO$_2$ adsorption kinetics and stability compared to amine-grafted adsorbents and in-situ polymerised adsorbents. Generally, amine-grafted materials show higher adsorption rates and higher stability during adsorption/desorption cycles than impregnated adsorbents. At the same time, they are strongly resistant to leaching even under harsh reaction conditions such as high temperature and moisture. Recently, we reported hierarchical silica functionalized with 3-Aminopropyltriethoxysilane (APS) and N$_1$-(3-trimethoxysilylpropyl)diethylenetriamine (TMPTA) for DAC. These modifications resulted in enhanced kinetics, CO$_2$ uptake under both dry and humid conditions, and stable cyclic adsorption-desorption performance, but required a temperature of 110 °C during the regeneration process.

Additionally, silica nanoparticles modified with branched polymers, such as dendrimers, have garnered significant attention due to their unique topological features. Dendrimers are a class of organic compounds known for their highly branched three-dimensional arrangement, typically presenting a spherical shape with abundant reactive terminal groups that have been widely explored for surface modification and adsorption applications. Among dendrimers, poly(amidoamine) (PAMAM) dendrimers have gained prominence due to their unique properties such as nano spherical construction, solubility, reactivity, and abundant surface terminal groups, thus providing an increased number of active sites resulting in improved performance. The increase in nitrogen-containing groups, such as amines (the practical binding sites for CO$_2$) with higher dendrimer generations makes PAMAM suitable for achieving enhanced CO$_2$ adsorption capacities. In particular, the PAMAM dendrimers with primary amine terminals interact with
CO₂, forming reversible carbamate species analogous to those formed by liquid amines such as monoethanolamine (MEA). Notably, such interaction mechanism contributes to the superior performance and stability of PAMAM dendrimer-based adsorbents in CO₂ capture applications. Due to the structure uniqueness, PAMAM dendrimers offer higher amine loading, enhanced stability, and superior CO₂ uptake, effectively overcoming the drawbacks of other adsorbents. Unlike PEI and similar amine molecules, which often degrade and require higher regeneration temperatures, PAMAM dendrimers maintain their performance over multiple cycles, operate efficiently under humid conditions, and necessitate lower regeneration temperatures. Moreover, the versatile structure of PAMAM allows its easy modification with varying terminal groups, making them ideal for environmental remediation.

Recently, Goncalves et al. reported the successful incorporation of PAMAM dendrimers inside Zr-based MOF (NU-1000), achieving a CO₂ adsorption capacity of up to 3.2 wt% at 1 bar, which is higher than that of dendrimer-free NU-1000. The primary amines in the polyamidoamine dendrimers facilitated chemically reversible CO₂ adsorption through carbamate formation, along with enhanced uptake likely due to dendrimer-amide-based physisorption. Therefore functionalizing/polymerising PAMAM dendrimers over amine functionalized nanoporous silica holds a great promise for CO₂ capture applications, offering tailored surface functionalities and controlled porous structures conducive to efficient adsorption and desorption processes. Herein, we have initially synthesized Nanosilica (NS) functionalized with 3-Aminopropyltriethoxysilane (APS). The terminal amine group in APS is polymerised and dendrimers are formed using methyl acrylate (MA) and ethylene diamine (EDA) till generation four (G4.0). While conventional silica-based adsorbents demonstrate appreciable capacity for ambient CO₂ capture, our research showcases that our reported modified NS exhibits remarkable CO₂ capture capacity not only in ambient air but also in indoor air environments. Moreover, our engineered surface functionalization strategy facilitates rapid CO₂ adsorption kinetics, particularly notable at 80 °C for efficient regeneration. Despite the steric hindrance from dendrimers, the densely concentrated amine functional groups ensure ample accessibility and favourable CO₂-amine interactions, leading to enhanced CO₂ capture performance at such lower temperatures compared to typical amine-silica based adsorbents reported in the literature. We extensively investigated the CO₂ adsorption performance of these amine-functionalized NS adsorbents, along with the evaluation of crucial parameters such as adsorption kinetics, facile regeneration at low temperature, cyclic stability, moisture stability, and others. Furthermore, the
CO₂ performance of these adsorbents were also evaluated under both realistic indoor air (dry and humid) conditions. For a further application, we investigated the use of PAMAM dendrimer-modified NS for hydrogenating CO₂ to formate. Even though there are various articles reporting the capture and conversion of CO₂,⁴⁰,⁴¹ there are only a few reports describing the catalysed transformation of captured CO₂ from indoor air into formate where either a high CO₂ pressure, liquid amines,⁸ or a co-catalyst was required for the reaction.⁴²,⁴³ Herein, we employed the best-performing adsorbent NS-G3.0 as a CO₂-capturing source from indoor air, and the captured CO₂ from this adsorbent was further hydrogenated to formate using (para-cymene)Ru-pyridyloxime [Ru]-1 catalyst in water. We also showed that the desorbed CO₂ can be captured in Ca(OH)₂ solution and converted to solid CaCO₃ pellets that can be used for further applications.⁴⁴

2. Results and discussion

2.1. Synthesis and characterization of PAMAM modified NS

Typically, the synthesis of NS-PAMAM dendrimers with varying generations (NS-G0 – NS-G4.0) was initiated by the synthesis of nanosilica and its further modification by 3-aminopropyltriethoxysilane (APS), to obtain NS-G0 with free-NH₂ terminals over the surface of NS. Further modification of NS-G0 to NS-G1.0 – NS-G4.0 was achieved by following a sequential two-step procedure for each generation. The two-step procedure involved, step-1: Michael addition reaction between methyl acrylate (MA) and the amino groups of NS-G0 (or NS-G1.0, NS-G2.0, and NS-G3.0), to form the respective NS-G0.5 (or NS-G1.5, NS-G2.5, and NS-G3.5) followed by step-2: the amidation of resultant terminal ester groups of NS-G0.5 (and NS-G1.5, NS-G2.5, and NS-G3.5) using ethylenediamine (EDA) to obtain NS-G1.0 (and NS-G2.0, NS-G3.0 and NS-4.0).⁴⁵ The detailed procedure for the synthesis of the four generations of NS-PAMAM dendrimers is outlined in the supporting information (Scheme 1).
Scheme 1. Simplified illustration for the synthesis of NS-PAMAM dendrimers-based adsorbents for CO$_2$ capture under DAC and indoor air condition.

Structural and chemical characteristics of NS-PAMAM dendrimers were investigated by P-XRD, FTIR, TGA, FE-SEM, EDX, and N$_2$ physisorption. P-XRD patterns of NS and NS-PAMAM dendrimers were analogous, suggesting the amorphous nature of NS was retained even after functionalisation of NS (Figure S1). The FTIR spectrum (as depicted in Figure 1a-b) of NS-PAMAM dendrimers (NS-G1.0, NS-G2.0, NS-G3.0 and NS-G4.0) showed distinct absorption bands at 1640 and 1543 cm$^{-1}$, which are attributed to the primary C=O stretching...
vibrations and a combination of N–H bending/C–N stretching vibrations, respectively, which is consistent with the formation of amide bonds.\textsuperscript{47,44} Moreover, the band observed at 2951 cm\textsuperscript{-1} is due to C–H stretching in the dendrimer (Figure S2a). Further, the absorption band observed at 1743 cm\textsuperscript{-1} for the NS-PAMAM dendrimers corresponds to the C=O stretching of the ester groups (Figure S2b).\textsuperscript{48,49} The TGA thermogram (Figure S3) of NS-PAMAM dendrimers displayed prominent weight loss as compared to NS, which corroborated well with the elemental analysis of the NS-PAMAM dendrimers (Table S1).\textsuperscript{48} The observed slight deviations in the theoretical and actual N content can be attributed to the incomplete branch extensions or cross-linked structures during dendron growth due to steric hindrance. This observation is consistent with the analogous literature reported system, such as PAMAM-functionalized organotalc dendron (PAMAM-talc-G).\textsuperscript{48,50,51}

![Figure 1](image-url)

**Figure 1.** (a) FTIR spectra (zoomed-in view) and (b) N\textsubscript{2} adsorption-desorption isotherm at -196 °C of NS and NS-PAMAM dendrimers.

The N\textsubscript{2} adsorption-desorption isotherms at -196 °C of NS, (NS-G0–NS-G4.0), showed type IV isotherm (Figure 1b), which is characteristic of mesoporous materials with narrow pore size distributions.\textsuperscript{48} The observed hysteresis loop for NS, corresponding to the capillary condensation in mesopores decreased significantly with the increase in the dendrimer formation (NS-G0–NS-G4.0) (Figure S4).\textsuperscript{52} Notably, the BET surface area and pore volume of NS were
912 m²/g and 1.43 cm³/g, respectively, which decreased upon the formation of dendrimers.\textsuperscript{36,48,52}
Moreover, the average pore diameter showed a decrease in trend from NS-G0 to NS-G4.0 as compared to NS, which is in line with the dendrimer formation.\textsuperscript{48} However, very less pore volume was observed for NS-G4.0, presumably due to the denser dendrimer. Detailed textural properties of NS and NS-G0 − NS-G4.0 are provided in Table 1.

**Table 1.** Textural properties and CO\textsubscript{2} adsorption results of NS-PAMAM dendrimers.

<table>
<thead>
<tr>
<th>Material</th>
<th>N content\textsuperscript{a} (mmolN/g)</th>
<th>S\textsubscript{BET}\textsuperscript{b} (m²/g)</th>
<th>V\textsubscript{total}\textsuperscript{c} (cm³/g)</th>
<th>Particle size\textsuperscript{d} (nm)</th>
<th>Pore diameter\textsuperscript{e} (nm)</th>
<th>q\textsubscript{CO2}\textsuperscript{f} (mmol/g) 30 °C, 400 ppm CO\textsubscript{2}</th>
<th>q\textsubscript{CO2}\textsuperscript{g} (mmol/g) 30 °C, indoor air</th>
</tr>
</thead>
<tbody>
<tr>
<td>NS</td>
<td>2.7</td>
<td>912</td>
<td>1.43</td>
<td>103</td>
<td>3.79</td>
<td>0.09</td>
<td>0.15</td>
</tr>
<tr>
<td>NS-G0</td>
<td>4.2</td>
<td>178</td>
<td>0.84</td>
<td>120</td>
<td>3.77</td>
<td>0.16</td>
<td>0.24</td>
</tr>
<tr>
<td>NS-G1.0</td>
<td>6.6</td>
<td>32</td>
<td>0.09</td>
<td>124</td>
<td>3.77</td>
<td>0.19</td>
<td>0.45</td>
</tr>
<tr>
<td>NS-G2.0</td>
<td>7.1</td>
<td>25</td>
<td>0.09</td>
<td>128</td>
<td>3.74</td>
<td>0.30</td>
<td>0.61</td>
</tr>
<tr>
<td>NS-G3.0</td>
<td>8.6</td>
<td>24</td>
<td>0.07</td>
<td>130</td>
<td>3.43</td>
<td>0.50</td>
<td>1.54</td>
</tr>
<tr>
<td>NS-G4.0</td>
<td>9.6</td>
<td>22</td>
<td>0.02</td>
<td>134</td>
<td>3.09</td>
<td>0.27</td>
<td>0.84</td>
</tr>
</tbody>
</table>

\textsuperscript{a}N content calculated from TGA analysis.
\textsuperscript{b}Specific surface area calculated using BET method (P/P\textsubscript{0} = 0.05-0.30).
\textsuperscript{c}Total pore volume calculated from N\textsubscript{2} adsorption at P/P\textsubscript{0} = 0.99.
\textsuperscript{d}Particle size calculated from FE-SEM image analysis.
\textsuperscript{e}Pore diameter calculated using NLDFT method.
\textsuperscript{f}CO\textsubscript{2} adsorption capacity measured using TGA for 400 ppm CO\textsubscript{2} (simulated air).
\textsuperscript{g}CO\textsubscript{2} adsorption capacity measured using TGA for ≥400 ppm CO\textsubscript{2}, 50±3% RH (indoor air).

FESEM images (Figures 2a-f) of NS-PAMAM dendrimers, infer the presence of highly ordered and uniform nanospheres, where the particle size is increasing from 100 to 135 nm with the increase in generations of dendrimers. Thus, it can be inferred that, NS-PAMAM dendrimers have a denser structure than nanosilica particles due to the presence of increasing polymeric groups on their surface.\textsuperscript{49} Moreover, EDS analysis of NS, NS-G0, NS-G1.0, NS-G2.0, NS-G3.0, and NS-G4.0 confirmed the presence of nitrogen and constituent element (Si) in the framework, therefore, suggesting the morphological and structural features of NS remain intact even after dendrimer modification (Figure S5). Additionally, TEM images (Figures 2g-h) confirmed the presence of similar morphology in NS and NS-G3.0 (Figures S6-S7).
Figure 2. FESEM images of (a) NS, (b) NS-G0, (c) NS-G1.0, (d) NS-G2.0, (e) NS-G3.0, (f) NS-G4.0, (g-h) TEM images of (g) NS and (h) NS-G3.0 and their corresponding particle size distribution graphs (inset).
2.2. CO$_2$ adsorption performance of NS-PAMAM dendrimers under simulated dry and indoor air conditions.

The CO$_2$ capture performance of NS-PAMAM dendrimers was studied using TGA in the presence of simulated dry air conditions (400 ppm CO$_2$ in He), as well as indoor air conditions (≥400 ppm CO$_2$), under dry (26 ±3% RH) and humid conditions (50 ±3% RH). It was observed that the NS-PAMAM dendrimers provide numerous sites for CO$_2$ adsorption, due to the abundance of surface amine terminals facilitating CO$_2$ capture at lower pressure for DAC application. Results inferred that with the increase in dendrimer formations (NS-G0 to NS-G3.0), the CO$_2$ adsorption capacity also increased (Table 1, Figure 3a, and Figure S8) owing to the increasing amine loading (as can be seen from Figure S9 and Table S1). A volcano curve is observed when correlating CO$_2$ uptake with amine loading (mmol N/g) for PAMAM modified NS dendrimers (Figure S9). Initially, as amine loading increases, the CO$_2$ uptake also increases until it reaches a peak, after which it decreases. For instance, the CO$_2$ adsorption capacity increases from 0.16 mmol CO$_2$/g (for NS-G0: amine loading of 4.2 mmol N/g) by three-folds to 0.50 mmol CO$_2$/g (for NS-G3.0: amine loading of 8.6 mmol N/g). Since amino groups interact with CO$_2$, an increase in the number of amino groups provides more active sites, thereby enhancing the CO$_2$ adsorption capacity. However, further increasing the amine loading to 9.6 mmol N/g (for NS-G4.0) resulted in a lower CO$_2$ uptake (0.27 mmol CO$_2$/g), attributed to a decrease in both pore volume (0.02 cm$^3$/g) and specific surface area due to pore blockage (Table S2). Hence, above and over the optimum amine loading (NS-G3.0), any additional amine grafting does not contribute to further increasing the CO$_2$ uptake. Consistent with previous reports, our findings also inferred that the impact of grafted amine loading becomes more pronounced on pore volume and specific surface area with the increase in the number of amine moieties per branch. In addition, as the NS-PAMAM dendrimer generations increased sequentially from NS-G0 to NS-G4.0, slower adsorption kinetics was observed, presumably due to the overcrowding of carbamate. Nevertheless, the CO$_2$ adsorption capacities of NS-PAMAM dendrimers are comparable to those of other amine-modified materials, as summarized in Table S3 for CO$_2$ capture. The observed trend can also be compared with literature reports on mesoporous silica, wherein Reynhardt et al. and Acosta et al. also found that the growth of PAMAM on PE-MCM-41 and triazine-diamine dendrimer on SBA-15, respectively was limited to G4.0. Additionally, Shah et al. reported that the CO$_2$ adsorption on PAMAM dendrimer-loaded organoclays and observed a CO$_2$ capacity of 0.45 mmol/g on G4-PAMAM dendrimer.
loaded organoclay laponite at 30°C, and TEMPO-oxidized cellulose nanofiber (Den-TCPP-TOCNF) at room temperature and 100% CO₂. In another work, reported by Wang et al.,⁵⁷ the CO₂ capture performance of PAMAM dendrimer functionalized cellulose nanocrystals (CNCs) of different generations (CNC-G1 to G4) was evaluated under dry conditions at 25–45°C and 100% CO₂ by TGA. The second generation of PAMAM functionalized CNCs (CNC-G2) exhibited a CO₂ capture capacity of 0.30 mmol/g at 25°C, 0.22 mmol/g at 35°C, and 0.21-0.24 mmol/g at 45°C, respectively, prevailing amongst all the samples. Similarly, Jing et al.,⁵¹ reported CO₂ uptake of 0.45 mg/g on G3-PAMAM dendrimer functionalized SBA-15 at 30°C and 90% CO₂.

![Figure 3](image)

**Figure 3.** CO₂ uptake profiles of NS-PAMAM dendrimers under (a) dry CO₂ (400 ppm CO₂ in He, 30 °C) (b) under humid indoor air conditions (≥400 ppm CO₂, 50 ±3%, RH, 30 °C), (c) FTIR spectra of NS-G3.0 obtained after treating with dry (400 ppm CO₂ in He) and humid indoor air conditions (≥400 ppm CO₂, 50 ±3%, RH, 30 °C) conditions, and (d) CO₂ adsorption-desorption performance up to 10 cycles of PAMAM dendrimer (NS-G3.0) under indoor air conditions.
conditions (≥400 ppm CO₂, 50 ±3% RH, adsorption period: 0.5 h at 30 °C, and desorption period: N₂, 0.5 h at 80 °C).

Developing adsorbents with enhanced capacity and stability under humid conditions, especially at low CO₂ concentrations, is one of the key areas of exploration.¹⁸ The CO₂ concentration in indoor air is typically ≥400 ppm, and therefore we examined the CO₂ uptake performance of NS-PAMAM dendrimers under indoor air conditions under dry (26 ±3% RH) and humid conditions (50 ±3% RH) (Figure S10). Results showed that NS-G3.0 exhibited a high CO₂ uptake 1.54 mmol/g (Figure 3b), under humid indoor air conditions (50 ±3% RH) as compared to 1.02 mmol/g under dry air condition (26±3 % RH) at 30 °C (Figure S10).

FTIR spectroscopy was employed to understand the CO₂ capture mechanism in both dry and humid conditions (Figure 3c). NS-G3.0 exhibits peaks at 1557 and 1635 cm⁻¹ corresponding to COO⁻ of carbamate and bicarbonate, respectively, indicating the favourable interaction of CO₂ with the NH₂ groups of NS-G3.0.⁶⁰,⁶¹ The increased CO₂ capacity under humid indoor air conditions as compared to the dry conditions, can be attributed to the involvement of water molecules in the formation of bicarbonate along with carbamate,⁶²–⁶⁴ while under dry CO₂ conditions, two molecules of amine react with CO₂ to form alkyl ammonium carbamate ion pairs (eq. 1–3).

Zwitterion formation:

\[ \text{CO}_2 + R_1R_2\text{NH} \rightarrow R_1R_2\text{NH}^+\text{CO}_2^- \]  
(1)

Zwitterion deprotonation through amine group (anhydrous condition):

\[ R_1R_2\text{NH}^+\text{CO}_2^- + R_1R_2\text{NH} \rightarrow R_1R_2\text{NH}_2^+ + R_1R_2\text{NCO}_2^- \]  
(2)

Formation of bicarbonate (hydrous condition):

\[ R_1R_2\text{NCO}_2^- + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow R_1R_2\text{NH}_2^+ + 2\text{HCO}_3^- \]  
(3)

where, \( R_1 = \text{H} \) for primary amines, \( R_1, R_2 = \text{alkyl/aryl} \) for secondary amines.

Further, to assess the regenerability of NS-G3.0, temperature swing adsorption/desorption (TSA) cycles were conducted under indoor air (≥400 ppm CO₂, 50 ±3% RH, adsorption period: 0.5 h at 30 °C, and desorption period: 0.5 h at 80 °C) (as depicted in Figure 3d). Optimizing the temperature of both CO₂ adsorption and desorption is of utmost importance to enhance the
efficiency of this process. For instance, Choi et al. presented findings on an aziridine-modified SBA-15 adsorbent, referred to as hyperbranched amino silica, achieving a CO$_2$ uptake of 1.72 mmol/g under fully humidified conditions. In comparison, Chaikittisilp et al. functionalized SBA-15 with Z-Lysine + 3-Aminopropyltrimethoxy silane (APTMS), resulting in a dry CO$_2$ uptake of 0.60 mmol/g but necessitating regeneration at 110 °C during adsorption-desorption cycles. Similarly, Liu et al. utilized macroporous silica functionalized with L-alanine, achieving a CO$_2$ capture of 2.65 mmol/g at 50 °C. Despite the high uptake, cyclic studies required a temperature of 110°C as also was reported by other amine-modified adsorbents shown in Table S4. Advantageously, our findings showed that the adsorbent NS-G3.0 can be regenerated at a much lower temperature of 80 °C in 0.5 h. In addition, NS-G3.0 exhibited remarkably high CO$_2$ capture performance during ten consecutive adsorption-desorption cycles, where the adsorption capacity of 1.54 mmol/g was found to be consistent for ten consecutive cycles with no significant loss in the adsorption capacity (Figure 3d), inferring the high regeneration performance of NS-G3.0 at a low temperature of 80 °C, as compared to the literature reported systems (Table S4). Notably for the spent NS-G3.0, the XRD peak at (2θ = 23°) was retained even after ten cycles, indicating no significant loss in the structural framework of NS-G3.0 (Figure S11). The lower regeneration temperature of NS-G3.0 is probably due to its engineered surface functionalization facilitating optimized CO$_2$-to-amine interactions. The dense concentration of amine groups ensures effective CO$_2$ capture and release, despite some steric hindrance from dendrimers. Hence, the optimized dendrimer structural characteristics of NS-G3.0 reduces energy barriers for CO$_2$ desorption, allowing efficient regeneration at lower temperatures for enhanced CO$_2$ adsorption-desorption behavior.

2.3. Recovery and reutilization of the captured CO$_2$

To enhance the sustainability and economic viability of CO$_2$ capture, the reutilization of desorbed CO$_2$ is critical. Here, we illustrate the conversion of CO$_2$ recovered during the desorption step from NS-G3.0 into valuable products such as formate and CaCO$_3$ (Figure 4).

2.3.1 CO$_2$ Capture Process

Initially, the CO$_2$, as recovered from the desorption of NS-G3.0 (0.1 g), was captured by passing the gas through an aqueous KOH (1 mmol, 5 mL). The CO$_2$ then captured in KOH was confirmed by the presence of a peak at 168.2 ppm corresponding to CO$_3^{2-}$ in the $^{13}$C NMR.
spectra (Figure S12). Notably, the effluent gas, after passing through the aqueous KOH solution, showed only N$_2$ gas (as confirmed by GC-TCD, Figure S13), confirming the complete capture of CO$_2$ released during the desorption process. This method aligns well with the findings of other studies where CO$_2$ capture efficiency using alkaline solutions has been reported to be high.$^{71-73}$

### 2.3.2 Conversion of recovered CO$_2$ to Formate

Further, the captured CO$_2$, as K$_2$CO$_3$, was subjected to hydrogenation over a ruthenium-catalyst ([Ru]-1), developed previously by our group,$^{74}$ under 20 bar H$_2$ pressure for 6 h at 80 °C, resulting in the formation of formate (yield: 0.99 mmol, $^1$H NMR peak at ~8.4 ppm and $^{13}$C NMR peak at 171 ppm) (Figure 4, Figure S14), suggesting that the recovered CO$_2$ can be successfully hydrogenated to formate.$^{75,76}$ Conversion of CO$_2$ to formate/formic acid offer various advantages as formic acid/formate is a potential C1-based feedstock with a wide range of applications across various fields, including agriculture, leather, textile and pharmaceutical industries.$^{75,76}$ Also, with a 4.4 wt% of hydrogen, FA is considered as important liquid organic hydrogen carrier (LOHC) for reversible hydrogen storage and delivery.$^{74}$ Furthermore, formate/formic acid play a vital role as intermediates in the production of essential oxygenated compounds, such as alcohols, esters, and acids, within the domain of syngas catalysis.$^{77,78}$

### 2.3.3 Conversion of recovered CO$_2$ to CaCO$_3$

Furthermore, conversion of CO$_2$ to CaCO$_3$ is one of the prominent ways for CO$_2$ sequestration. The CO$_2$ recovered during the desorption step from NS-G3.0 (0.1 g), was passed through an aqueous Ca(OH)$_2$ solution, resulting in the formation of CaCO$_3$ (Figure 4). The obtained precipitate was subsequently washed, centrifuged, and dried to form small pellets and the crystalline structure was further analysed by P-XRD, which corroborated well with that of commercial CaCO$_3$ (Figure 4). Advantageously, the total CO$_2$ recovered from the precipitation was estimated to be around 91.62%. Notably, CaCO$_3$ has numerous applications, including in the construction industry, as a filler material in plastics, and in paper manufacturing.$^{79}$ Hence, through this approach, we demonstrated a practical and efficient method for repurposing desorbed CO$_2$ into a valuable product, consistent with efficiencies reported in other studies of CO$_2$ mineralization processes.$^{44}$
Figure 4. Scheme depicting the capture, recovery, and reutilization of CO$_2$: (a) hydrogenation of captured CO$_2$ (in aqueous KOH, 1 mmol, 5 mL) to formate over [Ru]-1 catalyst, along with $^{13}$C NMR spectrum (in D$_2$O) of captured CO$_2$ and further hydrogenated to formate, and (b) conversion of desorbed CO$_2$ to CaCO$_3$ pellet, and the P-XRD of CaCO$_3$ (obtained from recovered CO$_2$, inset: image of CaCO$_3$ pellet) and commercial CaCO$_3$. 
3. Conclusions

We demonstrated the synthesis of nanosilica (NS) functionalized polyamidoamine (PAMAM) dendrimers (NS-PAMAM) with varying generations (NS-G0 – NS-G4.0) as efficient adsorbents for CO$_2$ capture under Direct Air Capture (DAC) conditions. While screening these generations of NS-PAMAM dendrimers, NS-G3.0 exhibited the highest CO$_2$ uptake, reaching 1.02 mmol/g under indoor air conditions (≥400 ppm CO$_2$, 26 ± 3% RH, 30 °C). Notably, under humid indoor air conditions (50 ± 3% RH), NS-G3.0 displayed even higher CO$_2$ capacity, reaching 1.54 mmol/g at 30 °C. This increased capacity under humid conditions is attributed to water molecules aiding in the formation of bicarbonate along with carbamate. The studied adsorbents demonstrated remarkable recoverability, retaining ≥99% CO$_2$ capacity after ten thermal swing adsorption (TSA) cycles under indoor air conditions (≥400 ppm CO$_2$, 30 °C, and 50 ±3% RH) at a low regeneration temperature of 80 °C. The engineered surface functionalization of NS-G3.0 facilitated fast CO$_2$ adsorption kinetics compared to other generations. Despite the steric hindrance introduced by dendrimers, the dense concentration of amine functional groups ensured sufficient accessibility and favourable CO$_2$ to amine interaction to achieve enhanced CO$_2$ capture. These findings underscore the potential of PAMAM dendrimer-modified NS adsorbents for high-capacity, fast CO$_2$ capture from diluted mixtures (400 ppm in He) and directly from indoor air (≥400 ppm CO$_2$). Moreover, we demonstrated that the captured CO$_2$ was successfully utilized for the formation of formate and sequestered in the form of CaCO$_3$ pellets. Overall, this research highlights the promising attributes of these adsorbents, including high thermo-cyclic stability, regenerability at low temperatures, and their applicability for indoor air CO$_2$ capture.

Supporting Information

Experimental section, evaluation of CO$_2$ adsorption performance, characterization (P-XRD, FE-SEM, TEM and EDS) for studied NS-PAMAM dendrimers, TGA, N$_2$ sorption isotherms, comparative chart of CO$_2$ adsorption performance of PAMAM dendrimer modified NS adsorbents under DAC condition, GC-TCD analysis, $^1$H NMR, $^{13}$C NMR, comparative chart of cyclic stability of reported aminosilane and amine-based adsorbents for DAC is given in the Supporting Information.
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References


Nanosilica Polyamidoamine Dendrimers for Enhanced Direct Air CO$_2$ Capture

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