

Evaluating the Impact of Tailored Water Wettability on Performance of CO₂ Capture

Adil Majeed Rather,¹ Pillalamarri Srikrishnarka,¹ Avijit Baidya, Arpita Shome, Thalappil Pradeep,* and Uttam Manna*



Cite This: *ACS Appl. Energy Mater.* 2020, 3, 10541–10549



Read Online

ACCESS |



Metrics & More



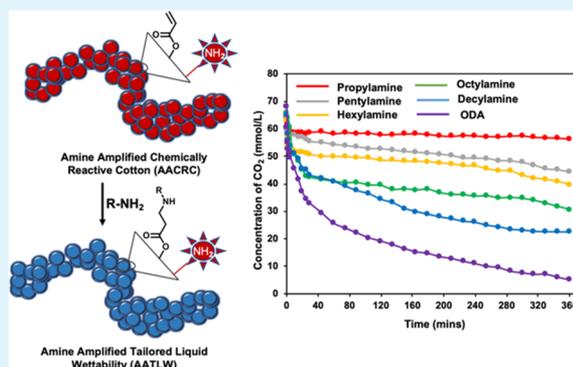
Article Recommendations



Supporting Information

ABSTRACT: The growing emission of CO₂ is a severe cause of concern due to its adverse impact on the environment and climate change worldwide. In the past, various approaches, including synthesis of porous materials and amino modifications, were adopted for efficient and direct separation of CO₂ from flue gas. Recently, hydrophobicity has been introduced to protect some of the highly potent porous materials and membranes from high humidity and aqueous exposures. While these approaches remained successful in removing CO₂ from flue gas, the exact role of hydrophobicity towards CO₂ separation is not yet validated in the literature. In this current study, an amine-amplified chemically reactive coating on fibrous cotton has been unprecedentedly developed for facile tailoring of different water wettability through the 1,4-conjugate addition reaction under ambient conditions. Further, these amine-amplified interfaces having tailored water wettability were extended to investigate independently the role of: (a) amine amplification and (b) hydrophobicity on the performance of CO₂ separation at room temperature and atmospheric pressure. The increased hydrophobicity on the amine-amplified interface played an important role in improving the CO₂ uptake from 24 mmol/L (water contact angle (WCA) of 86°) to 63 mmol/L (WCA of 151°). However, superhydrophobic coating that lacked the amine amplification process displayed a poor (7 mmol/L) CO₂ separation performance. Thus, controlled amalgamation of amine amplification and bioinspired superhydrophobicity in fibrous cotton lead to a synergistic impact towards efficient CO₂ separation at ambient temperature and pressure, irrespective of the level of humidity present during the course of the experiments. Thus, this current study would allow to design a more potent CO₂ removal material by strategic association of porosity, amine modulation, and liquid wettability.

KEYWORDS: reactive superhydrophobicity, amine amplification, chemically reactive, CO₂ separation, tailored wettability



INTRODUCTION

Industrial revolution remains instrumental for the advancement of human civilization; however, the uncontrolled management of different forms of industrial wastes leads to various severe environmental pollutions, which has an adverse impact on climate and different ecosystems. For example, the rapidly growing emission of CO₂ due to excessive burning of fossil fuels, deforestation, vehicular and industrial exhausts, etc., has an immense catastrophic impact on the environment and climate.^{1,2} In the past, various approaches were adopted to combat this existing severe challenge.^{3–6} However, the direct capture of CO₂ from flue gas appears to be a more practical and promising approach.⁶ In this process, different porous organic/inorganic nanomaterials were commonly decorated with amines for increasing the efficiency of CO₂ removal from air due to the strong and inherent affinity of the amines towards CO₂ gas.^{7–12} However, the performance of many such materials varied depending on the level of humidity present during the proof of concept demonstrations.^{9–11} In fact, the

amine modifications rendered the reported materials highly hydrophilic, which is likely to promote condensation of humid air in the reported material. Thus, the performance of CO₂ separation is expected to vary depending on the humidity in the surroundings.^{12–14} For instance, a humidity-dependent swing in the CO₂ capture has been reported in the literature.¹⁵ Thus, the design of a material for direct capture of CO₂ at ambient pressure and temperature, irrespective of the level of humidity, would be important for practical applications.

In the past, the design of highly porous materials remained an obvious strategy to separate CO₂ from flue air.^{16–19} In this context, metal–organic frameworks (MOFs), which are

Received: July 7, 2020

Accepted: October 5, 2020

Published: October 19, 2020



developed by integrating water-sensitive coordination bonds, emerged as a prospective approach for capturing CO₂ at high pressure.^{16–19} However, the poor durability of such materials under humid conditions and other practically relevant circumstances is a major concern.^{13,14} Recently, few special designs were introduced to improve the stability of the MOF, where hydrophobicity was adopted following modification of ligands and depositing a protective layer on top.^{20–29} Another important material, that is, a CO₂ capturing membrane,^{30–35} has been rationally decorated with bioinspired superhydrophobicity to prevent unwanted blocking of active absorption sites, where the extreme water repellence restricted the wetting of membranes by liquid water even in the presence of high humidity.^{30–35} However, a detailed and systematic investigation of (a) amine modification and (b) tailoring hydrophobicity on the CO₂ separation performance is unprecedented in the literature. Moreover, such comprehensive investigation is likely to pave the way for designing a sustainable and eco-friendly approach for direct and unperturbed capture of CO₂ at ambient temperature and pressure, irrespective of the level of relative humidity.

Recently, a clay-based superhydrophobic coating was introduced on a fibrous filter paper, where 3-(2-aminoethylaminopropyltrimethoxysilane) was used to decorate the coating with residual amine groups.³⁶ The adsorption capacity was found to be around 10.90 mmol/L/g after 8 h of CO₂ exposure under ambient conditions; however, this separation performance varied depending on the level of humidity during the course of the experiment.³⁶ In this current study, a naturally abundant fibrous substrate, that is, cotton ball, has been decorated with a porous and chemically reactive polymeric coating to tune the water wettability through the 1,4-conjugate addition reaction between amine and residual acrylate moieties under ambient conditions. The chemically reactive coating (CRC) loaded with residual acrylate groups was first treated with the polymer, i.e. branched polyethylenimine (BPEI) for amine amplification, prior to treat with primary amine-containing small molecules (e.g. propylamine, pentylamine, hexylamine, octylamine, decylamine, and octadecylamine), where the length of the hydrocarbon tail of primary amine-containing small molecules allowed to tune the water wettability in the synthesized material. The amine-amplified chemically reactive coating (AACRC) that was post-modified with octadecylamine (ODA) yielded amine-amplified superhydrophobic cotton (AASHC). The synthesized AASHC lowered the CO₂ level with an adsorption capacity of 63 mmol/L over 6 h at room temperature and pressure. Interestingly, a very similar superhydrophobic cotton that lacked the amine amplification process displayed poor CO₂ separation performance under the same experimental conditions. Thereafter, the controlled tailoring of water wettability on the amine-amplified interface through the 1,4-conjugate addition reaction allowed to examine the impact of hydrophobicity on CO₂ separation performance under ambient conditions. The efficiency of CO₂ separation was compromised on lowering the hydrophobicity. Moreover, the CO₂ separation performances for hydrophobic and superhydrophobic amine-amplified cotton were noticed to be completely different at high humidity. Furthermore, the CO₂ separation ability of amine-amplified superhydrophobic cotton remained independent of the initial concentration of CO₂ present in the model flue air.

EXPERIMENTAL SECTION

Materials. Branched polyethylenimine (PEI; MW ≈ 25 kDa), dipentaerythritol penta-acrylate (5AcI, MW = 524.21 g/mol), propylamine, pentylamine, hexylamine, octylamine, decylamine, and octadecylamine were purchased from Sigma-Aldrich (Bangalore, India). Absolute ethyl alcohol (CAS 64-17-5; lot 1005150) was purchased from Tedia Company (United States of America). Reagent-grade THF was purchased from RANKEM (Maharashtra). Methylene blue was acquired from Sigma-Aldrich (Bangalore, India). A Lab Companion vacuum desiccator, UV blocking (Amber 6 L) was purchased from Tarson (India). CO₂ concentration was measured using a CO₂ meter Chauvin Arnoux (C.A 1510, Air Quality Measurement). Cotton was obtained from a local medical shop in Guwahati City (Assam, India). Milli-Q grade water was used for all experiments.

General Considerations. Glass vials that were used for preparing the polymer solutions were washed with acetone and ethanol prior to use. FTIR spectra were recorded using a PerkinElmer instrument under ambient condition by preparing the KBr pellets. Scanning electron microscopy images were obtained using a Sigma Carl Zeiss scanning electron microscope (samples were coated with a thin layer of gold prior to imaging). The water contact angles were measured using a KRUSS drop dhape analyzer-DSA25 instrument with an automatic liquid dispenser under ambient conditions. Change in the CO₂ concentration was measured using a CO₂ meter. Digital pictures were acquired using a Canon PowerShot SX420 IS digital camera.

Preparation of Amine-Amplified Superhydrophobic Cotton. First of all, the naturally abundant medical cotton (1 gram) was rinsed with ethanol and acetone to remove the deposited contaminants. Next, the precleaned cotton was placed in BPEI solution (10 mg/mL ethanol) for 2 h. Afterward, the BPEI-modified cotton was placed in the chemically reactive nanocomplex (CRNC) solution, which was prepared by mixing ethanolic solutions of 5-AcI (132.5 mg/mL) and BPEI (50 mg/mL) with an appropriate composition (5AcI/BPEI = 10:3) for 1 h. The deposition of the CRNC on the fibrous cotton yielded a chemically reactive coating (CRC). Next, the CRC was washed with ethanol to remove the unreacted and loosely bound nanocomplexes and was dried under ambient conditions. Thereafter, the CRC was post-modified with BPEI for amine amplification. The BPEI-treated CRC is denoted as amine-amplified chemically reactive coating (AACRC). Finally, the AACRC was exposed to solution (5 mg/mL in THF) of octadecylamine (ODA) for 8 h for adopting superhydrophobicity. After the ODA treatment, the synthesized material was washed thoroughly with THF for 1 h to remove the unreacted ODA molecules and allowed to air-dry under ambient conditions. Then, the water wettability of the as-modified cotton pieces was examined with digital images and contact angle measurement. This post-covalent modification of AACRC provided the amine-amplified superhydrophobic cotton (AASHC).

Similarly, AACRC was post-modified with lower analogues of ODA, including propylamine, pentylamine, hexylamine, octylamine, and decylamine for tailoring water wettability. After post-modification with these selected amine-containing small molecules, cotton pieces were rinsed with THF for 1 h and were dried under ambient conditions. After successful post-modification with different amines, the wettability of the cotton pieces was examined by measuring the water contact angle. Meanwhile, in the absence of the amine amplification process, the direct post-covalent modification of CRC with octadecylamine yielded another superhydrophobic interface, which is labeled as without amine-amplified superhydrophobic cotton (WOAASHC).

Carbon Dioxide (CO₂) Separation. To understand the CO₂ adsorption capability of the AASHC, a Tarson 6 L desiccator was taken in which 1 g of uncoated and modified cotton along with the CO₂ sensor was placed. Thereafter, a desired amount of 99% pure CO₂ was introduced into the desiccator using a syringe and the change in CO₂ concentration was monitored using a CO₂ sensor for 24 h. These changes were recorded using a data logger present inside

Scheme 1. (A) Chemical Reaction of the 1,4-Conjugate Addition Reaction between Representative Amine and Acrylate Groups. (B) Chemical Structure of Branched Polyethylenimine (BPEI). (C) Schematic Illustration of Chemically Reactive Nanocomplex (CRPNC) Loaded with Residual Acrylate, Which Was Synthesized by Mixing BPEI and Dipentaerythritol Penta-acrylate (5Acl). (D, E) Illustrating the Deposition of CRPNC on the Fibrous Cotton That Yielded The Chemically Reactive Coating (CRC). (E, F) Schematic Representation Depicting the Amine Amplification Process of CRC through the 1,4-Conjugate Addition Reaction for Achieving Amine-Amplified Chemically Reactive Coating (AACRC; F). (G) Post-Covalent Modification of AACRC with Octadecylamine (ODA) Yielded Amine-Amplified Superhydrophobic Cotton (AASHC). (E, H) Post-Modification of CRC (E) with ODA Provided Superhydrophobic Coating that Lacked the Amine Amplification Step, and Such a Material Is Denoted as Without Amine-Amplified Superhydrophobic Cotton (WOAASHC, H)

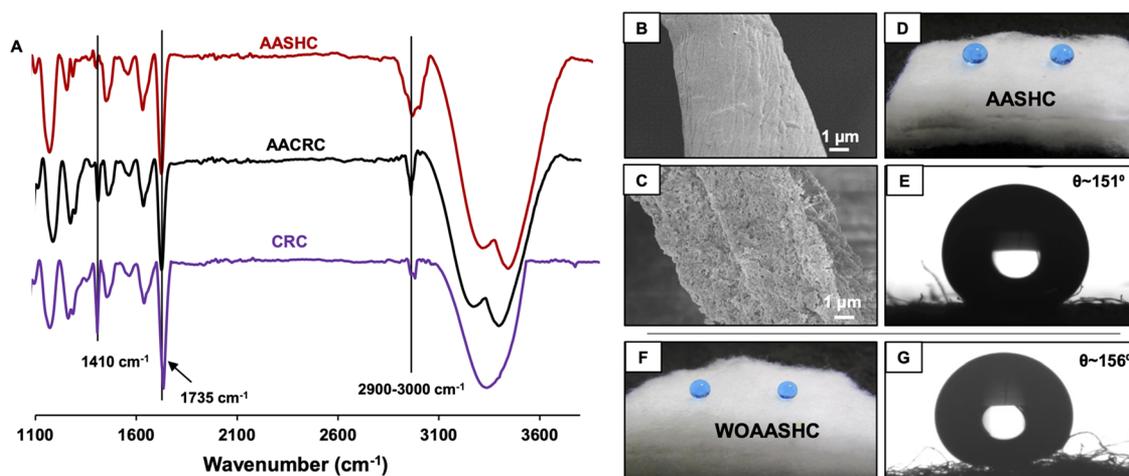
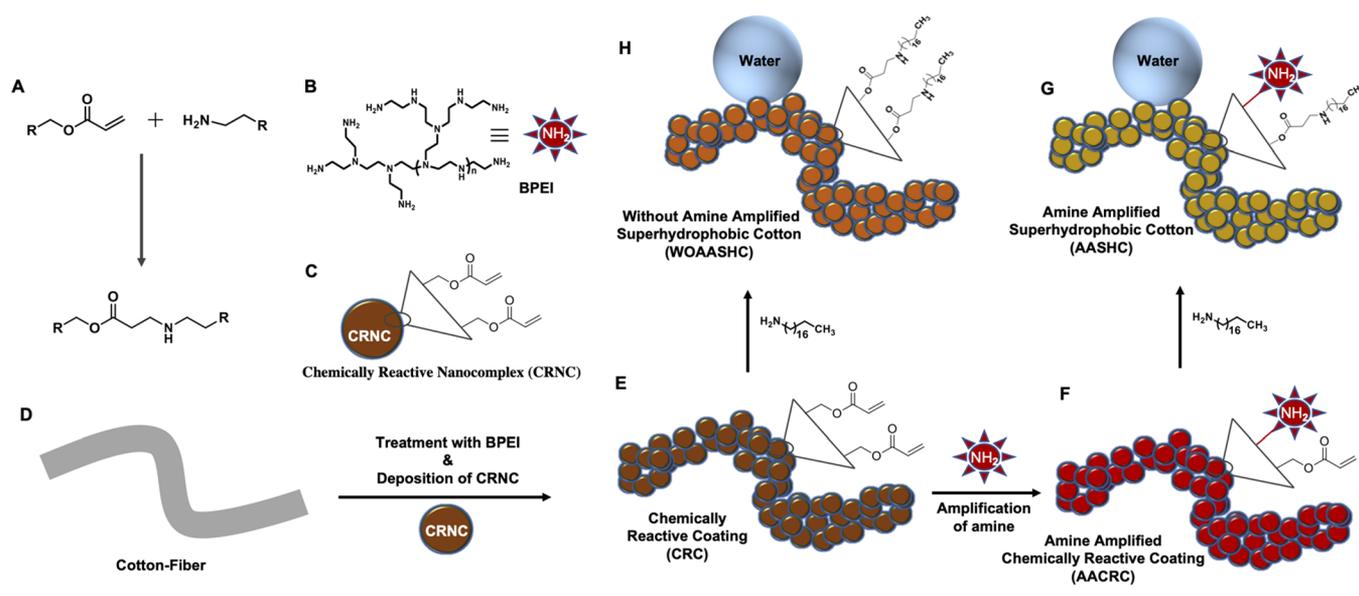


Figure 1. (A) FTIR spectra of chemically reactive coating (CRC: violet), amine-amplified chemically reactive coating (AACRC: black), and amine-amplified superhydrophobic cotton (AASHC: red). The peaks at 1409 and 1735 cm^{-1} correspond to symmetric deformation for the C–H bond of the β -carbon of the vinyl group and the carbonyl stretching, respectively. (B, C) FESEM images of pristine cotton (B) and chemically reactive coating (C) on fibrous cotton. (D–G) Digital images (D, F) and contact angle images (E, G) of amine-amplified superhydrophobic cotton (AASHC; D, E) and without amine-amplified superhydrophobic cotton (WOAASHC; F, G) respectively.

the sensor and later transferred to PC. Afterwards, this cotton piece was placed at 60 °C in a conventional oven for 2 h for desorption of the adsorbed CO_2 gas. Moreover, the CO_2 separation studies for other cotton pieces including pristine cotton and superhydrophobic cotton were performed in a similar manner.

RESULTS AND DISCUSSION

Synthesis of Amine-Amplified Chemically Reactive Coating (AACRC). In the recent past, interfaces consisting of residual amine groups were found to be an effective approach

for separating CO_2 from flue air.^{16–19} In this context, branched polyethyleneimine (BPEI) has been widely used for modifying various metal oxides and zeolites for demonstrating the CO_2 separation performance.^{16–19} However, the controlled tailoring of hydrophobicity on amine-modified interfaces and its impact on the CO_2 separation process at practically relevant settings are rare in the literature. In our current design, an amine-amplified chemically reactive coating has been introduced for (a) tailoring of water wettability and (b) investigating its impact on CO_2 separation performance. In the recent past, our

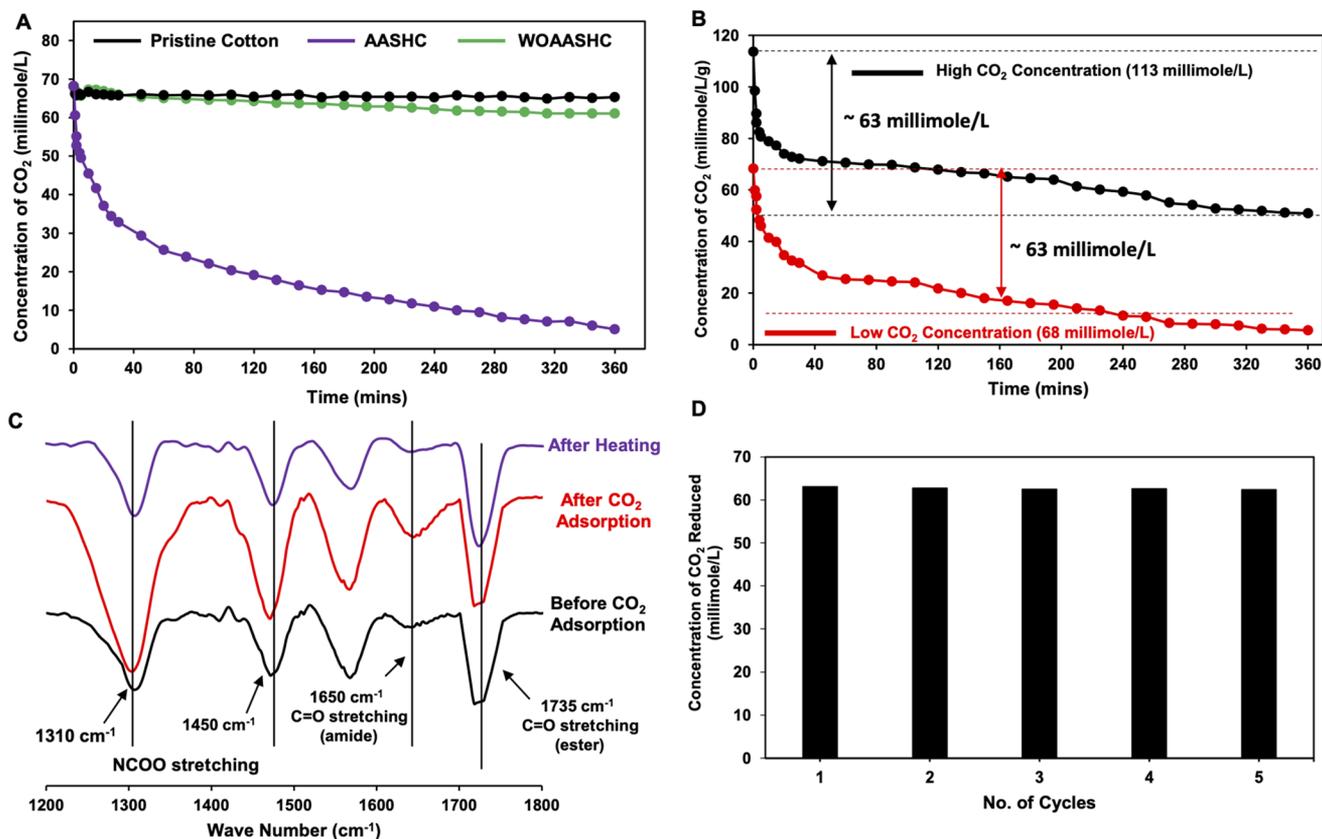


Figure 2. (A) Plot illustrating the reduction in the concentration of CO₂ by pristine cotton (black), without amine-amplified superhydrophobic cotton (WOAASHC: green), and amine-amplified superhydrophobic coating (AASHC: violet). (B) Plot displaying the CO₂ separation performance using AASHC at high (black) and low (red) concentrations of CO₂. (C) FTIR spectra of amine-amplified superhydrophobic cotton before (black) and after (red) performing CO₂ separation, whereas the violet curve accounts for the IR spectrum after desorption (violet) of CO₂ at 60 °C for 2 h. (D) Plot illustrating the recyclability of AASHC in separating CO₂ for five consecutive cycles.

research group has extended the 1,4-conjugate addition reaction (Scheme 1A) between BPEI (Scheme 1B) and dipentaerythritol penta-acrylate (5AcI) to synthesize chemically reactive polymeric nanocomplex (CRPNC, Scheme 1C) loaded with residual acrylate group.^{37,38} In the past, the spray deposition and layer-by-layer deposition of this CRPNC provided chemically reactive coatings for customizing different water and oil wettability through appropriate post-covalent modification with the selected small molecules.^{39–42} Further, this CRPNC was successfully deposited on fibrous cotton to develop a chemically reactive coating (CRC, Scheme 1D,E), where the post-covalent modification of the coating with octadecylamine (ODA) provided durable superhydrophobicity, which was extended for remediation of oil spillages following an environment-friendly selective absorption and filtration approach.⁴³ In contrast to these earlier designs, a facile and covalent amine amplification process has been integrated to this CRPNC-derived chemically reactive coating through post-covalent modification with BPEI polymer (Scheme 1E,F). This coating is labeled as AACRC in the rest of the text. Next, the synthesized AACRC was modified with a hydrophobic small molecule (i.e. ODA) through the 1,4-conjugate addition reaction, to achieve amine-amplified superhydrophobic cotton (AASHC, Scheme 1G). The deposition of CRPNC on a fibrous substrate followed by the amine amplification process prior to ODA treatment was characterized through FESEM and FTIR analysis, as shown in Figure 1A–C and Figure S2. The characteristic IR peaks at

1410 cm⁻¹ and 1735 cm⁻¹ represent the symmetric deformation of the β-carbon of the vinyl group and the carbonyl stretching, respectively, revealing the presence of residual acrylate groups in the CRPNC deposited cotton, as shown in Figure 1A (violet spectrum). Further, the FESEM images of the uncoated (Figure 1B) and coated (Figure 1C) fibrous cotton confirmed the successful deposition of CRPNC, where the random aggregation of granular domains in CRC provided the essential hierarchical topography to achieve the bioinspired water wettability. The residual acrylate groups in the CRC further allowed the covalent immobilization of BPEI polymer, as confirmed with FTIR analysis. After the treatment of CRC with BPEI polymer, a significant change in the IR peak was observed in the region of 3200–3600 cm⁻¹, where two prominent humps indicate the inclusion of primary amines from BPEI. Further, the IR peak intensity at 1410 cm⁻¹, which corresponded to the symmetric deformation of the β-carbon of the vinyl group, decreased significantly with respect to the normalized carbonyl stretching at 1735 cm⁻¹, as shown in Figure 1A (black spectrum). During this amine amplification process, ~28% of the total residual acrylate groups in CRC is consumed on the reaction with the amines of BPEI polymer through the 1,4-conjugate addition reaction. The remaining acrylate groups in AACRC were post-modified with selected small molecules for adopting the desired extreme water repellency. The FTIR analysis after the reaction of AACRC with ODA revealed the significant depletion of the IR signature for the β-carbon of the vinyl group at 1409 cm⁻¹ with respect

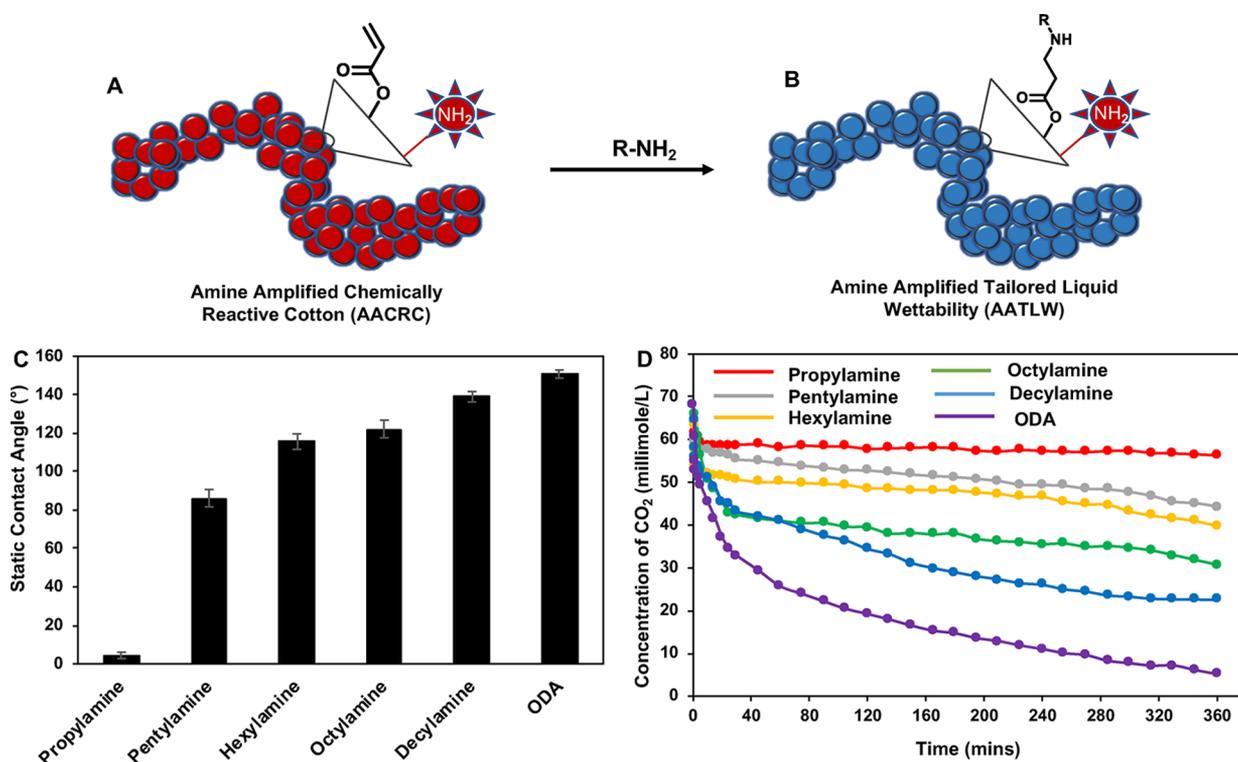


Figure 3. (A, B) Schematic illustration of amine-amplified chemically reactive cotton (AACRC; A) that was post-modified with amine-containing small molecules (B) through the 1,4-conjugate addition reaction for tailoring water wettability. (C) Plot displaying the static contact angle of beaded water droplets on amine-amplified chemically reactive coating after post-modification with different amine-containing small molecules including propylamine, pentylamine, hexylamine, octylamine, decylamine, and ODA. (D) Plot accounting for the CO₂ separation performance of AACRC after post-modification with different amine-containing small molecules including propylamine (red), pentylamine (gray), hexylamine (yellow), octylamine (green), decylamine (blue), and ODA (violet).

to the normalized carbonyl stretching at 1735 cm^{-1} . This simple study confirmed the successful post-chemical modification of AACRC with selected small molecules, as shown in Figure 1A (red spectrum). The water wettability was monitored at each step, and AACRC remained superhydrophilic with a water contact angle of 0° as similar to uncoated cotton, as shown in Figure S1. However, after ODA treatment, the same AACRC displayed superhydrophobicity, where water droplets were beaded with a contact angle of 151° , as shown in Figure 1D,E. This coating on fibrous cotton will be denoted as amine-amplified superhydrophobic cotton (AASHC) for further discussion. During this amine amplification process, CRC was exposed to different concentrations of BPEI, prior to treatment with ODA. Beyond a certain concentration (125 mg/mL) of BPEI treatment, AACRC failed to display superhydrophobicity, as shown in Figure S3. The amine amplification was performed with 125 mg/mL concentration of BPEI polymer solution for the rest of the CO₂ separation experiments. As expected, after ODA treatment, the as-synthesized CRC, without any amine amplification, also displayed superhydrophobicity with a water contact angle of $\sim 156^\circ$, as shown in Figure 1F,G; and this coating on fibrous cotton was denoted as without amine-amplified superhydrophobic cotton (WOAASHC).

Investigation on CO₂ Separation Performances by AASHC and WOAASHC. In this current study, two distinct superhydrophobic coatings with (AASHC) and without (WOAASHC) amine amplification were extended to examine the role of embedded biomimicked superhydrophobicity on the performance of CO₂ separation. For direct comparison,

uncoated cotton, WOAASHC, and AASHC, with the same weight (1 g), were individually exposed to a constant concentration (68 mmol/L) of CO₂ gas at a relative humidity of 40% and ambient temperature and pressure. Over time, AASHC gradually lowered the concentration of CO₂ in the experimental system, and after 6 h, the concentration of CO₂ reduced from 68 to 5 mmol/L (Figure 2A). However, under similar experimental conditions, both uncoated cotton and WOAASHC failed to perform, as evident from Figure 2A. Further, the CO₂ separation performance of AASHC was compared at settings having different initial concentrations of CO₂. As a proof of concept demonstration, AASHC was separately exposed to two different concentrations of CO₂ including 68 and 113 mmol/L. After 6 h of exposure, AASHC lowered the CO₂ concentration with equal efficiency (63 mmol/L), irrespective of differences in the initial concentration of CO₂, as shown in Figure 2B. Further, AASHC continued to separate CO₂ over 24 h, in contrast to WOAASHC, as shown in Figure S4. After 24 h, the reduction values in the concentration of CO₂ by WOAASHC and AASHC were 10 and 87 mmol/L, respectively. To understand the mechanism of the efficient separation of CO₂ by AASHC, an FTIR analysis was performed on AASHC before and after conducting the CO₂ capture, as shown in Figure 2C. With respect to the normalized IR signature at 1735 cm^{-1} for the ester carbonyl stretching, prominent appearance of IR peaks for the C–N (1310 cm^{-1}) and amide C=O stretching (1650 cm^{-1}) revealed chemisorption of CO₂ on AASHC through a mutual reaction between the residual amine and CO₂ gas. Further, these intense IR signatures for the C–N (1310 cm^{-1})

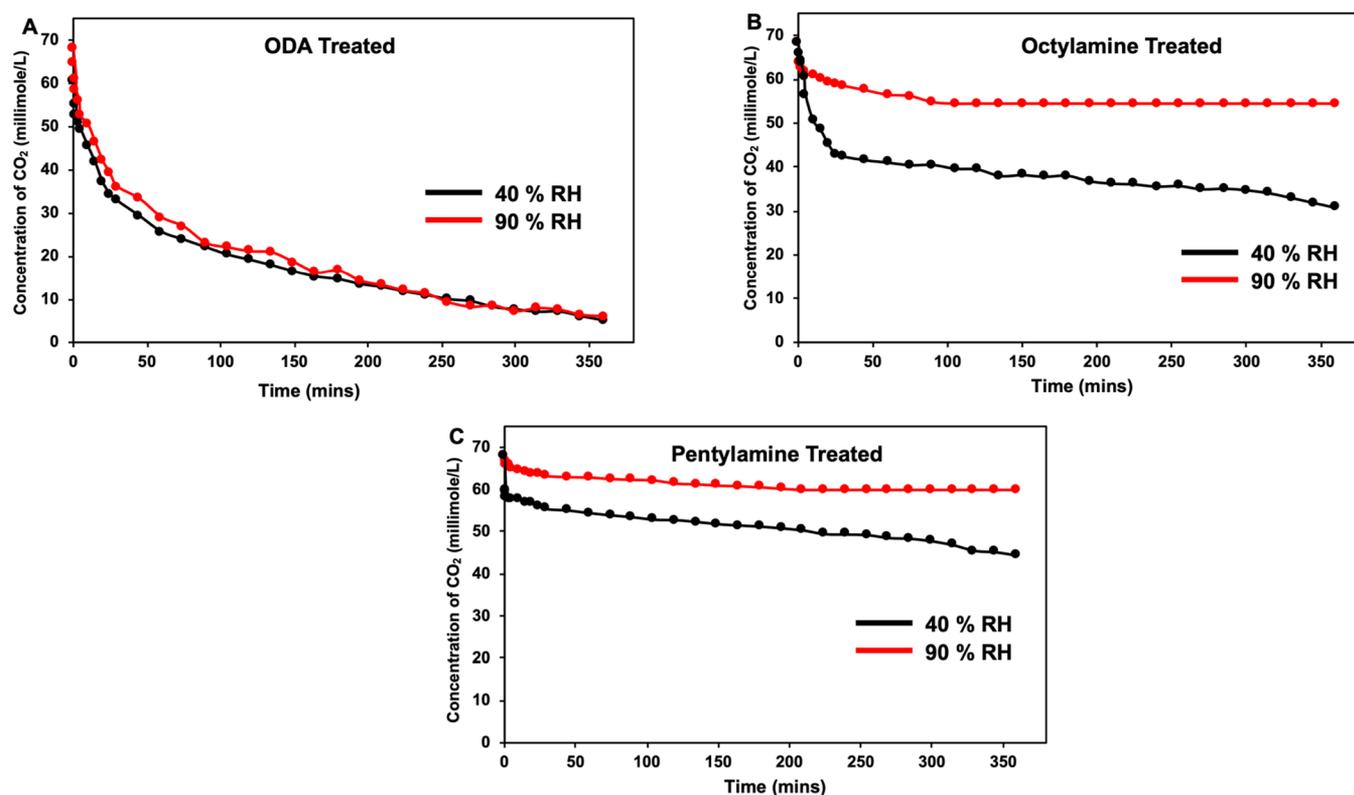


Figure 4. (A–C) Plots illustrating the reduction in the concentration of CO₂ in different humid conditions including 40% (black) and 90% (red) for amine-amplified chemically reactive coatings (AACRC) that were post-modified with ODA (A), octylamine (B), and pentylamine (C).

and amide C=O stretching depleted significantly with respect to the ester carbonyl stretching at 1735 cm⁻¹ after heating cotton at 60 °C for 2 h (violet spectrum; Figure 2C). This study suggested the successful desorption of CO₂ from AASHC. Interestingly, the same AASHC was successfully and repetitively used for separating CO₂ for five consecutive cycles, as shown in Figure 2D, without compromising its separation performance. At the end of each cycle, the AASHC was treated at 60 °C for 2 h for the desorption of CO₂ gas. Further, this repetitive adsorption and desorption of CO₂ has no impact on the integrity and antiwetting property of the AASHC. Hence, this study implies that the as-synthesized AASHC could be a potential candidate for practical applications owing to its highly durable and recyclable property.

Effect of Change in Water Wettability on CO₂ Separation Performance. In the past, few reports have focused on the extremely liquid-repellent interfaces to improve the CO₂ separation performance, where the extreme water repellence emphasized on protecting the CO₂ separating interface from unwanted wetting by the liquid phase.^{30–35} However, the impact of different liquid wettability on CO₂ separation performance is yet to be demonstrated in the literature. The residual acrylate groups in the amine-amplified chemically reactive cotton (AACRC) allowed to tailor the liquid wettability by post-modification with various alkyl amines through the 1,4-conjugate addition reaction, as shown in Figure 3A,B. The extent of hydrophobicity was tailored by selecting appropriate alkylamines (i.e., propylamine, pentylamine, hexylamine, octylamine, decylamine, and octadecylamine). The water contact angle gradually enhanced on increasing the hydrocarbon chain length in the selected

alkylamine, as shown in Figure 3C. Afterward, these amine-amplified interfaces having different water wettability were explored for examining the CO₂ separation performance. Interestingly, the CO₂ separation ability significantly compromised on decreasing the hydrophobicity in the amine-amplified interface. For instance, the propylamine-treated AACRC, which is extremely hydrophilic, reduced the concentration of CO₂ by 12 mmol/L over 6 h, whereas the octylamine-treated AACRC, which displayed moderate hydrophobicity with a water contact angle of 122°, reduced the concentration of CO₂ by 38 mmol/L over the same time duration (6 h), under an identical experimental setup. However, under similar experimental conditions, the concentration of CO₂ was depleted significantly (63 mmol/L) by AASHC (ODA-treated AACRC) that embedded with biomimicked superhydrophobicity, as shown in Figure 3D. The initial concentration (68 mmol/L) of CO₂ and relative humidity (40%) were kept identical for examining the performance of CO₂ separation by amine-amplified cotton (1 g each) with tailored water wettability. Thus, the reduction in the concentration of CO₂ significantly changed with variation in the water wettability (Figure 3D). Therefore, this study affirms that the change in water wettability indeed has a significant impact on the CO₂ adsorption capability for the amine-amplified interface.

When evaluating CO₂ separation performance for flue gases, the presence of water vapor cannot be overlooked. In the past, various materials including zeolites, ionic liquids, carbon-based materials, and MOFs were explored for CO₂ adsorption. However, many synthesized materials explored in the past for CO₂ adsorption failed to perform on exposure under moist/humid conditions. The adsorption of water vapors into the adsorbent material is known to reduce the CO₂ adsorption

capacity under humid conditions. Therefore, the CO₂ separation performance of AASHC derived from AACRC was compared under low (RH: 10%; Figure S5), moderate (RH: 40%), and high (RH: 90%) humid conditions. The CO₂ separation ability of AASHC at three distinct RH values was found to remain unperturbed, as shown in Figure 4A and Figure S5. However, the same AACRC, that is, post-modified with octylamine, displayed moderate hydrophobicity and became inefficient for separating CO₂ at high relative humidity (RH: 90%), as shown in Figure 4B. Moreover, such depletion of the CO₂ separation performance was observed for pentylamine-treated AACRC (that is, embedded with an even lower WCA \approx 86°) at high relative humidity (RH: 90%), as shown in Figure 4C. Hence, under a highly humid environment, the CO₂ separation performance is tremendously affected on decreasing the hydrophobicity in the amine-amplified interfaces. Such compromise of CO₂ separation at high humidity is likely due to the easy penetration of moisture in the less and moderately hydrophobic amine-amplified cotton; however, the long hydrocarbon tail of the covalently immobilized ODA in the AASHC restricts the condensation of moisture. Thus, the embedded superhydrophobicity merely has any impact on separation of CO₂ (see Figure 2A), but this extreme water repellence displayed an immense impact on the CO₂ uptake—once it is integrated with the amine-amplified interface. Further, the AASHC continued to perform under practically relevant high humid conditions. Therefore, the coexistence of bioinspired superhydrophobicity and amine amplification is important for efficient and uninterrupted CO₂ separation at practically relevant diverse settings.

CONCLUSIONS

In conclusion, an amine-amplified chemically reactive cotton (AACRC) has been introduced through strategic use of the 1,4-conjugate addition reaction between residual acrylate of CRC and amines of BPEI polymer. The residual acrylate groups in CRC provided facile basis for both (i) associating amine amplification and (ii) tailoring various water wettability, including bioinspired superhydrophobicity. The performance of CO₂ separation was compared for amine-amplified coating that embedded with different water wettability. The CO₂ separation performance was observed to improve with increasing hydrophobicity in the amine-amplified interface, where AASHC that displayed superhydrophobicity was found to be the most efficient in separating CO₂ at ambient temperature and pressure. Thus, improved hydrophobicity on the amine-amplified interface has a positive impact on CO₂ uptake. However, without amine amplification, the superhydrophobicity has merely any impact on CO₂ uptake. Further, this CO₂ separation performance of AASHC remained unperturbed at high relative humidity, irrespective of the initial concentration of CO₂ present in the experimental system. Such a material would be useful in developing a more effective green house facility. Further association of AASHC with an appropriate catalytic component would allow to convert the separated CO₂ to useful chemicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.0c01603>.

Digital images and contact angle images of pristine cotton and amine-amplified superhydrophobic cotton; FESEM images of uncoated cotton, WOAASHC, and AASHC at lower and higher magnifications; digital images and contact angle images of amine-amplified reactive coating after ODA treatment with different concentrations of BPEI; plots illustrating the decrease in concentration of CO₂ by WOAASHC and AASHC over 24 h; and plots illustrating the decrease in concentration of CO₂ by AASHC in different humid conditions (PDF)

AUTHOR INFORMATION

Corresponding Authors

Thalappil Pradeep – Department of Chemistry, DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/0000-0003-3174-534X; Email: pradeep@iitm.ac.in

Uttam Manna – Department of Chemistry and Centre for Nanotechnology, Indian Institute of Technology-Guwahati, Guwahati, Assam 781039, India; orcid.org/0000-0003-3204-158X; Email: umanna@iitg.ac.in

Authors

Adil Majeed Rather – Department of Chemistry, Indian Institute of Technology-Guwahati, Guwahati, Assam 781039, India

Pillalamarri Srikrishnarka – Department of Chemistry, DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/0000-0001-5187-6879

Avijit Baidya – Department of Chemistry, DST Unit of Nanoscience (DST UNS) and Thematic Unit of Excellence (TUE), Indian Institute of Technology Madras, Chennai 600036, India; orcid.org/0000-0001-5215-2856

Arpita Shome – Department of Chemistry, Indian Institute of Technology-Guwahati, Guwahati, Assam 781039, India

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsaem.0c01603>

Author Contributions

[†]A.M.R. and P.S. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge the financial support from Board of Research in Nuclear Sciences (BRNS) (34/20/31/2016-BRNS, DAE-YSRA) and Ministry of Electronics and Information Technology (grant no. 5(9)/2012-NANO), Government of India. We thank CIF and Department of Chemistry, Indian Institute of Technology-Guwahati, for their generous assistance in executing various experiments and for the infrastructure. A.S. thanks the institute for the Ph.D. scholarship. P.S. thanks IIT Madras for his Ph.D. fellowship.

REFERENCES

- (1) Anderegg, W. R. L.; Prall, J. W.; Harold, J.; Schneider, S. H. Expert credibility in climate change. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, *107*, 12107–12109.
- (2) Hansen, J.; Ruedy, R.; Sato, M.; Lo, K. Global Surface Temperature Change. *Rev. Geophys.* **2010**, *48*, RG4004.
- (3) Nielsen, C. J.; Herrmann, H.; Weller, C. Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS). *Chem. Soc. Rev.* **2012**, *41*, 6684–6704.
- (4) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO₂ from Ambient Air. *Chem. Rev.* **2016**, *116*, 11840–11876.
- (5) Wang, S.; Li, X.; Wu, H.; Tian, Z.; Xin, Q.; He, G.; Peng, D.; Chen, S.; Yin, Y.; Jiang, Z.; Guiver, M. D. Advances in high permeability polymer-based membrane materials for CO₂ separations. *Energy Environ. Sci.* **2016**, *9*, 1863–1890.
- (6) Bui, M.; Adjiman, C. S.; Bardow, A.; Anthony, E. J.; Boston, A.; Brown, S.; Fennell, P. S.; Fuss, S.; Galindo, A.; Hackett, L. A.; Hallett, J. P.; Herzog, H. J.; Jackson, G.; Kemper, J.; Krevor, S.; Maitland, G. C.; Matuszewski, M.; Metcalfe, I. S.; Petit, C.; Puxty, G.; Reimer, J.; Reiner, D. M.; Rubin, E. S.; Scott, S. A.; Shah, N.; Smit, B.; Trusler, J. P. M.; Webley, P.; Wilcox, J.; Mac Dowell, N. Carbon capture and storage (CCS): the way forward. *Energy Environ. Sci.* **2018**, *11*, 1062–1176.
- (7) Chaikittisilp, W.; Kim, H.-J.; Jones, C. W. Mesoporous Alumina-Supported Amines as Potential Steam-Stable Adsorbents for Capturing CO₂ from Simulated Flue Gas and Ambient Air. *Energy Fuels* **2011**, *25*, 5528–5537.
- (8) Dutcher, B.; Fan, M.; Russell, A. G. Amine-Based CO₂ Capture Technology Development from the Beginning of 2013—A Review. *ACS Appl. Mater. Interfaces* **2015**, *7*, 2137–2148.
- (9) Flaig, R. W.; Popp, T. M. O.; Fracaroli, A. M.; Kapustin, E. A.; Kalmutzki, M. J.; Altamimi, R. M.; Fathieh, F.; Reimer, J. A.; Yaghi, O. M. The Chemistry of CO₂ Capture in an Amine-Functionalized Metal–Organic Framework under Dry and Humid Conditions. *J. Am. Chem. Soc.* **2017**, *139*, 12125–12128.
- (10) Zhao, X.; Yuan, Y.; Li, P.; Song, Z.; Ma, C.; Pan, D.; Wu, S.; Ding, T.; Guo, Z.; Wang, N. A polyether amine modified metal organic framework enhanced the CO₂ adsorption capacity of room temperature porous liquids. *Chem. Commun.* **2019**, *55*, 13179–13182.
- (11) Lashaki, M. J.; Khiavi, S.; Sayari, A. Stability of amine-functionalized CO₂ adsorbents: a multifaceted puzzle. *Chem. Soc. Rev.* **2019**, *48*, 3320–3405.
- (12) Brandani, F.; Ruthven, D. M. The Effect of Water on the Adsorption of CO₂ and C₃H₈ on Type X Zeolites. *Ind. Eng. Chem. Res.* **2004**, *43*, 8339–8344.
- (13) Liu, J.; Wang, Y.; Benin, A. I.; Jakubczak, P.; Willis, R. R.; LeVan, M. D. CO₂/H₂O Adsorption Equilibrium and Rates on Metal–Organic Frameworks: HKUST-1 and Ni/DOBDC. *Langmuir* **2010**, *26*, 14301–14307.
- (14) Bien, C. E.; Chen, K. K.; Chien, S.-C.; Reiner, B. R.; Lin, L.-C.; Wade, C. R.; Ho, W. S. W. Bioinspired Metal–Organic Framework for Trace CO₂ Capture. *J. Am. Chem. Soc.* **2018**, *140*, 12662–12666.
- (15) Yang, H.; Singh, M.; Schaefer, J. Humidity-swing mechanism for CO₂ capture from ambient air. *Chem. Commun.* **2018**, *54*, 4915–4918.
- (16) Hu, Z.; Wang, Y.; Shah, B. B.; Zhao, D. CO₂ Capture in Metal–Organic Framework Adsorbents: An Engineering Perspective. *Adv. Sustainable Syst.* **2019**, *3*, 1800080.
- (17) Espallargas, G. M.; Coronado, E. Magnetic functionalities in MOFs: from the framework to the pore. *Chem. Soc. Rev.* **2018**, *47*, 533–557.
- (18) Zhao, X.; Wang, Y.; Li, D.-S.; Bu, X.; Feng, P. Metal–Organic Frameworks for Separation. *Adv. Mater.* **2018**, *30*, 1705189.
- (19) Ding, M.; Flaig, R. W.; Jiang, H.-L.; Yaghi, O. M. Carbon capture and conversion using metal–organic frameworks and MOF-based materials. *Chem. Soc. Rev.* **2019**, *48*, 2783–2828.
- (20) Jasuja, H.; Huang, Y.-g.; Walton, K. S. Adjusting the Stability of Metal–Organic Frameworks Under Humid Conditions by Ligand Functionalization. *Langmuir* **2012**, *28*, 16874–16880.
- (21) Ding, M.; Cai, X.; Jiang, H.-L. Improving MOF stability: approaches and applications. *Chem. Sci.* **2019**, *10*, 10209–10230.
- (22) Nguyen, J. G.; Cohen, S. M. Moisture-Resistant and Superhydrophobic Metal–Organic Frameworks Obtained via Post-synthetic Modification. *J. Am. Chem. Soc.* **2010**, *132*, 4560–4561.
- (23) Sun, Q.; He, H.; Gao, W.-Y.; Aguila, B.; Wojtas, L.; Dai, Z.; Li, J.; Chen, Y.-S.; Xiao, F.-S.; Ma, S. Imparting amphiphobicity on single-crystalline porous materials. *Nat. Commun.* **2016**, *7*, 13300.
- (24) Fukushima, T.; Horike, S.; Kobayashi, H.; Tsujimoto, M.; Isoda, S.; Foo, M. L.; Kubota, Y.; Takata, M.; Kitagawa, S. Modular Design of Domain Assembly in Porous Coordination Polymer Crystals via Reactivity-Directed Crystallization Process. *J. Am. Chem. Soc.* **2012**, *134*, 13341–13347.
- (25) DeCoste, J. B.; Denny, M. S., Jr.; Peterson, G. W.; Mahle, J. J.; Cohen, S. M. Enhanced aging properties of HKUST-1 in hydrophobic mixed-matrix membranes for ammonia adsorption. *Chem. Sci.* **2016**, *7*, 2711–2716.
- (26) Qian, X.; Sun, F.; Sun, J.; Wu, H.; Xiao, F.; Wu, X.; Zhu, G. Imparting surface hydrophobicity to metal–organic frameworks using a facile solution-immersion process to enhance water stability for CO₂ capture. *Nanoscale* **2017**, *9*, 2003–2008.
- (27) Chen, Y.; Li, S.; Pei, X.; Zhou, J.; Feng, X.; Zhang, S.; Cheng, Y.; Li, H.; Han, R.; Wang, B. A Solvent-Free Hot-Pressing Method for Preparing Metal–Organic-Framework Coatings. *Angew. Chem., Int. Ed.* **2016**, *55*, 3419–3423.
- (28) Zhang, W.; Hu, Y.; Ge, J.; Jiang, H.-L.; Yu, S.-H. A Facile and General Coating Approach to Moisture/Water-Resistant Metal–Organic Frameworks with Intact Porosity. *J. Am. Chem. Soc.* **2014**, *136*, 16978–16981.
- (29) Yang, S.; Peng, L.; Sun, D. T.; Asgari, M.; Oveisi, E.; Trukhina, O.; Bulut, S.; Jamali, A.; Queen, W. L. A new post-synthetic polymerization strategy makes metal–organic frameworks more stable. *Chem. Sci.* **2019**, *10*, 4542–4549.
- (30) Lv, Y.; Yu, X.; Jia, J.; Tu, S.-T.; Yan, J.; Dahlquist, E. Fabrication and characterization of superhydrophobic polypropylene hollow fiber membranes for carbon dioxide absorption. *Appl. Energy* **2012**, *90*, 167–174.
- (31) Hou, J.; Ji, C.; Dong, G.; Xiao, B.; Ye, Y.; Chen, V. Biocatalytic Janus membranes for CO₂ removal utilizing carbonic anhydrase. *J. Mater. Chem. A* **2015**, *3*, 17032–17041.
- (32) Yu, X.; An, L.; Yang, J.; Tu, S.-T.; Yan, J. CO₂ capture using a superhydrophobic ceramic membrane contactor. *J. Membrane Sci.* **2015**, *496*, 1–12.
- (33) Geyer, F.; Schönecker, C.; Butt, H.-J.; Vollmer, D. Enhancing CO₂ Capture using Robust Superomniphobic Membranes. *Adv. Mater.* **2016**, *29*, 1603524.
- (34) Lin, Y.-F.; Wang, W.-W.; Chang, C.-Y. Environmentally sustainable, fluorine-free and waterproof breathable PDMS/PS nanofibrous membranes for carbon dioxide capture. *J. Mater. Chem. A* **2018**, *6*, 9489–9497.
- (35) Wu, X.; Zhao, B.; Wang, L.; Zhang, Z.; Li, J.; He, X.; Zhang, H.; Zhao, X.; Wang, H. Superhydrophobic PVDF membrane induced by hydrophobic SiO₂ nanoparticles and its use for CO₂ absorption. *Sep. Purif. Technol.* **2018**, *190*, 108–116.
- (36) Baidya, A.; Yatheendran, A.; Ahuja, T.; Sudhakar, C.; Das, S. K.; Ras, R. H. A.; Pradeep, T. Waterborne Fluorine-Free Superhydrophobic Surfaces Exhibiting Simultaneous CO₂ and Humidity Sorption. *Adv. Mater. Interfaces* **2019**, *6*, 1901013.
- (37) Rather, A. M.; Manna, U. Facile Synthesis of Tunable and Durable Bulk Superhydrophobic Material from Amine “Reactive” Polymeric Gel. *Chem. Mater.* **2016**, *28*, 8689–8699.
- (38) Rather, A. M.; Manna, U. Stretchable and durable superhydrophobicity that acts both in air and under oil. *J. Mater. Chem. A* **2017**, *5*, 15208–15216.
- (39) Parbat, D.; Manna, U. Synthesis of ‘reactive’ and covalent polymeric multilayer coatings with durable superoleophobic and

superoleophilic properties under water. *Chem. Sci.* **2017**, *8*, 6092–6102.

(40) Maji, K.; Manna, U. Hierarchically featured and substrate independent bulk-deposition of ‘reactive’ polymeric nanocomplexes for controlled and strategic manipulation of durable biomimicking wettability. *J. Mater. Chem. A* **2018**, *6*, 6642–6653.

(41) Das, S.; Das, A.; Parbat, D.; Manna, U. Catalyst-Free and Rapid Chemical Approach for in Situ Growth of “Chemically Reactive” and Porous Polymeric Coating. *ACS Appl. Mater. Interfaces* **2019**, *11*, 34316–34329.

(42) Das, A.; Maji, K.; Naskar, S.; Manna, U. Facile optimization of hierarchical topography and chemistry on magnetically active graphene oxide nanosheets. *Chem. Sci.* **2020**, *11*, 6556–6566.

(43) Rather, A. M.; Jana, N.; Hazarika, P.; Manna, U. Sustainable polymeric material for the facile and repetitive removal of oil-spills through the complementary use of both selective-absorption and active-filtration processes. *J. Mater. Chem. A* **2017**, *5*, 23339–23348.