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Energy-Efficient Continuous Solar Desorption of CO₂ from Aqueous Amines

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CO₂ Capture; Solar Desorption; Composite Photothermal Microparticles; Microfluidics

ABSTRACT

Recovery of captured carbon dioxide (CO₂) is considered the most energy-intensive stage of post-combustion CO₂ capture strategies by aqueous amines. In response, an optically transparent, flow reactor with continuous *in operando* CO₂ collection using light-absorbing, graphite-titania composite microparticles is developed for energy-efficient solar desorption of CO₂ from saturated aqueous amine absorbents. The synthesized graphite-titania composite microparticles are demonstrated to be a more effective packing material for the continuous CO₂ solar desorption in the packed-bed flow reactor compared to other candidates, including titania and carbon black. The effect of continuous and discrete parameters, including irradiance, residence time, amine concentration, and amine chemical structure on the efficiency of the solar-enabled CO₂ desorption

using the developed continuous flow strategy with the graphite-titania composite microparticle packing are studied in detail. Furthermore, the potential for implementation of a control strategy by adjusting the aqueous amine stream flow rate to achieve constant CO₂ desorption efficiency with a dynamic solar irradiance is discussed. Finally, the continuous CO₂ desorption stability over an extended period of time (12 h) is examined with an average single-pass efficiency of 64%.

INTRODUCTION

Human activities after the second industrial revolution in the early 19th century have resulted in an increase of the atmospheric carbon dioxide (CO₂) concentration from 280 to above 400 ppm over the past 110 years, primarily due to the constant growth of population and ever-increasing worldwide energy demand.^{1,2} The unmitigated emission of CO₂ and other greenhouse gases is causing an unprecedented rapid rise in average global temperatures and an overall irreversible change in climate.^{3–5} As the concentration of atmospheric CO₂ continues to climb,⁴ it is imperative to develop and implement strategies for energy-efficient CO₂ capture, sequestration, and utilization (CCUS).⁶ Current shortcomings of mitigation efforts concerning CO₂ emission, including the high energy cost of CO₂ capture and recovery from stationary sources (*e.g.*, power plants) which can represent up to 80% of the associated CCUS cost, and the comparatively low efficiency of renewable and sustainable energy alternatives (*e.g.*, solar cells),⁷ have inhibited widespread implementation of these technologies in the energy sector.

Over the last three decades, numerous techniques have been developed for selective CO₂ capture, including adsorption,^{8,9} absorption,^{10,11} and membrane separation,^{12,13} among others. However, of these strategies, absorption with aqueous amines (*e.g.*, monoethanolamine, MEA) is one of the most widely utilized strategies for CO₂ capture in applications ranging from natural gas

sweetening¹¹ to post-combustion CO₂ removal.¹⁴ Despite groundbreaking advancements in CO₂ capture with aqueous amines, this technique suffers from a high energy penalty for the recovery of the captured CO₂. The most substantial hurdle to widespread implementation as a post-combustion capture strategy is the energy input necessary to desorb the captured CO₂ from the aqueous amine solution so it may be reused, requiring regeneration temperatures around 120 °C.¹⁵ This is further complicated by the massive quantity of absorbent necessary to fully extract the CO₂ from stationary sources of CO₂ and the requisite absorbent replacement due to degradation. This limitation, along with rising global energy demands, necessitates the development of more efficient physical and chemical absorbents for CO₂ capture from stationary sources, as well as a more sustainable strategy for its recovery.¹⁶ Among different energy-efficient CO₂ desorption strategies, solar energy is considered among the most promising candidates as a readily available source of energy to heat the solution and aid CO₂ desorption. This concept has recently been demonstrated by the addition of carbon black nanoparticles to the MEA solution, which have been shown to effectively absorb light resulting in bulk heating of the solution followed by CO₂ desorption.¹⁷ While this strategy has been demonstrated to be effective for its intended purpose, it raises additional technological challenges since the addition of particulates to the capture solution has the potential to present problems for the conventional large scale centrifugal pumps that would likely be used in such an application. Furthermore, batch techniques are prone to additional complications, including reduced light penetration (~1 mm),^{18,19} particle settling with insufficient agitation, excessively long CO₂ desorption timescales, and the presence of large concentration and temperature gradients in batch reactors. In particular, large diffusion length scales associated with conventional macroscale characterization techniques make the development of alternative CO₂ recovery routes challenging and time-consuming. For this reason, it is intriguing to consider

1
2
3 a continuous flow strategy utilizing light-absorbing microparticles for solar heating of CO₂-
4 saturated aqueous amine solutions to achieve continuous, energy-efficient CO₂ recovery while
5 removing costs associated with separating the recovered aqueous amine and light-absorbing
6 particles.
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13 Recently, microfluidic strategies have emerged as a promising tool for fundamental and
14 exploratory studies of gas-liquid reactions,^{20–22} including accelerated exploration of CO₂ capture
15 and utilization processes.^{23–31} Advantages of microscale strategies include enhanced rates of heat
16 and mass transfer, small (micro- to nano-liter) reagent volumes, controlled variation of reagent
17 concentrations in a high-throughput manner, reproducibility, and the integration of analytical tools
18 with microfluidic reactors for real-time process characterization and optimization.^{21,32,33}
19 Additionally, a continuous photothermal heating strategy is best applied using micro/milli-fluidic
20 reactors due to their excellent light transmittance, as the use of small scale channels (<1 mm)
21 results in significantly higher light absorption by the light-absorbing particles than conventional
22 batch reactors.¹⁸
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37 Here, we present a microscale fluidic strategy for continuous solar-driven desorption and
38 *in operando* recovery of captured CO₂ from aqueous amine solutions. By utilizing a membrane-
39 based flow reactor,^{27,34} the desorbed CO₂ can be continuously separated from the aqueous amine
40 solution, *in-situ*, as it is released in the flow reactor, while the liquid phase continues through the
41 packed-bed region. Using the developed continuous flow reactor, we demonstrate a single-pass
42 CO₂ desorption efficiency of 64% *via* illumination of the reactor with a light source selected to
43 emulate a solar concentrator.
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EXPERIMENTAL

Materials. Monoethanolamine ($\geq 99.0\%$, ACS Reagent), titanium n-butoxide (97%, reagent grade), toluene ($\geq 99.5\%$, ACS reagent), ethoxylated trimethylolpropane triacrylate ($M_n \sim 428$), and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (97%) were purchased from Sigma Aldrich. Carbon black was purchased from Cabot. Nitrogen (N_2 , grade 5.0) and CO_2 (industrial grade) were purchased from Messer. The graphite-titania (G-TiO₂ composite) microspheres used to pack the flow reactor were synthesized using a flow-focusing microreactor presented previously by our group.^{35–38} However, rather than annealing the microparticles at 500 °C, the in-flow synthesized microparticles were calcined under ambient atmosphere at 400 °C, which resulted in the formation of G-TiO₂ composite microparticles. Deionized (DI) water (18 M Ω -cm) was generated using the on-site facility. All chemicals were used as received.

Microfluidic Platform. A schematic of the developed microfluidic platform utilizing a tube-in-tube flow reactor configuration is shown in **Figure 1**. The microreactor was constructed by attaching stainless steel T-junctions (1/8 in, Swagelok) to fluorinated ethylene propylene (FEP) tubing (outer diameter (OD): 1/8 in; inner diameter (ID): 1/16 in, IDEX Health & Science). Stainless steel reducers (1/8 in to 1/16 in, Swagelok) were then inserted into each T-junction, in line with the

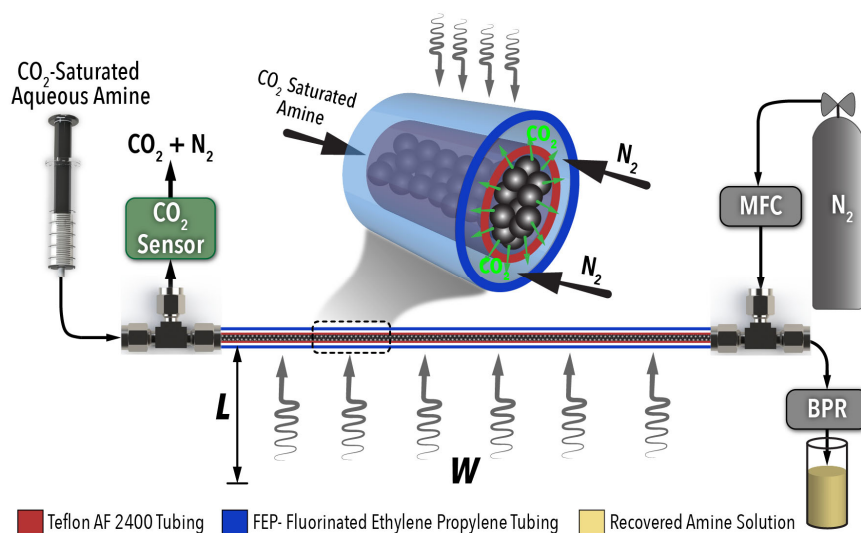


Figure 1. Schematic illustration of the developed flow chemistry platform utilizing a tube-in-tube packed bed microreactor for continuous solar-enabled CO₂ desorption from aqueous amines.

FEP tubing. Next, a tubular gas-permeable membrane (Teflon AF 2400 tubing, OD: 0.04 in, ID: 0.032 in, Biogeneral) was inserted through the reducers, T-junctions, and FEP tubing. A Teflon frit (PEEK, 2 μm pore size, IDEX Health & Science) was used to ensure the packed particles stay inside the tube-in-tube flow reactor. After closing one end of the Teflon AF 2400 tubing, light-absorbing microparticles were introduced into the inner (Teflon AF 2400) tube until the section between the T-junctions was completely packed with microparticles. Bright field images of the packed-bed flow reactor are presented in **Figure S1**. The open end of the Teflon AF2400 was then sheathed with a 4 cm segment of 1/16 in OD, FEP tubing and tightened in place with 1/16 in Swagelok fittings, while the other end was capped with a Teflon frit (PEEK, 2 μm pore size, IDEX Health & Science) and needle valve. One needle valve was attached to the 1/16 in OD, FEP tubing with a Luer-lock fitting (PEEK, IDEX Health & Science), while another 1/16 in OD FEP tubing was attached to the opposite end of the flow reactor and fed into the collection beaker. The CO₂-saturated aqueous amine solution was continuously fed to the gas-permeable inner tube using a 5 mL syringe (gas-tight, SGE) and a syringe pump (KD Scientific, KDS-100-CE).

The perpendicular ports of the stainless steel T-junctions were attached to an FEP tubing (OD:1/8 in; ID: 1/16 in) to enable gas flow through the outer annulus of the tube-in-tube flow reactor. The gas inlet, positioned in counter-flow arrangement with respect to the liquid inlet stream, was connected to a N₂ (carrier gas) mass flow controller (MFC) (Brooks), while the gas stream outlet was connected to a CO₂ sensor (Gas Sensing Solutions, SPRINTIR-WF-20). A light source (SuperPlant E40 50x40 Stucco diffuser, SuperPlant MH 600W bulb, and Lumatek Adjustable Electronic Ballast) with tunable power (250 W to 600 W), was placed at the desired distance (H) over the tube-in-tube flow reactor using a ring stand. The lamp emission spectrum can be found in **Figure S2**. Following preliminary experiments, the feed tube was partially packed

with the light-absorbing microparticles and folded aluminum strips were added to serve as solar concentrators and enhance total irradiance.

Flow Reactor Operation. Solar-enabled CO₂ desorption experiments were started by filling the packed bed flow reactor with DI water. The syringe was then filled with the desired amine solution saturated with CO₂ (prepared under inert atmosphere in a glove box, saturated by bubbling CO₂ through the solution until it returned to near ambient temperature). Next, the syringe pump was set at a high flow rate until the amine solution reached the preheating section of the flow reactor. The light source was then turned on, the liquid feed rate was set to achieve the desired residence time, t_R , and the N₂ flow rate was set to 3 mL/min. Over the course of each experiment, CO₂ concentration in the gas phase (*i.e.*, CO₂ and the carrier gas) was monitored in real time and was allowed to reach steady state operation (~4 residence times per experimental condition) before recording each data point. Each steady state CO₂ concentration was calculated from the average of 10 CO₂ sensor readings. All experiments were repeated 3 times.

RESULTS AND DISCUSSION

Light-Absorbing Composite Microspheres. With the adoption of the packed-bed flow reactor strategy, there were two primary considerations for the selection of the packing material, namely light absorption over the ultraviolet and visible region of the solar spectrum, and pressure drop across the flow reactor (ΔP). These characteristics were tested for four different light-absorbing material candidates, including carbon black powder (both as-received and isostatically pressed/sieved), white titanium dioxide microparticles (synthesized according to the procedure discussed in Ref. 33), batch-synthesized carbon/TiO₂ (C/TiO₂) particles, and G-TiO₂ composite

microspheres. Each of the packing candidates, (I) white TiO₂, (II) as received carbon black, (III) isostatically pressed carbon black, (IV) batch-synthesized C/TiO₂, and (V) G-TiO₂ composite particles were characterized with scanning electron microscopy (SEM) (**Figure 2A**). The UV-Vis absorption spectra for each of the material candidates is presented in **Figure S3**. The packing materials were loaded into an FEP tube (0.04" ID, 1/16" OD), and the pressure drop was measured by flowing DI water at 100 μ L/min through each packed bed flow reactor using an ISCO high pressure syringe pump (**Figure 2B**). The pressed carbon black and batch-synthesized C/TiO₂ particles resulted in pressure drops greater than 175 psi/cm and ruptured reactors (**Figure S4**) due

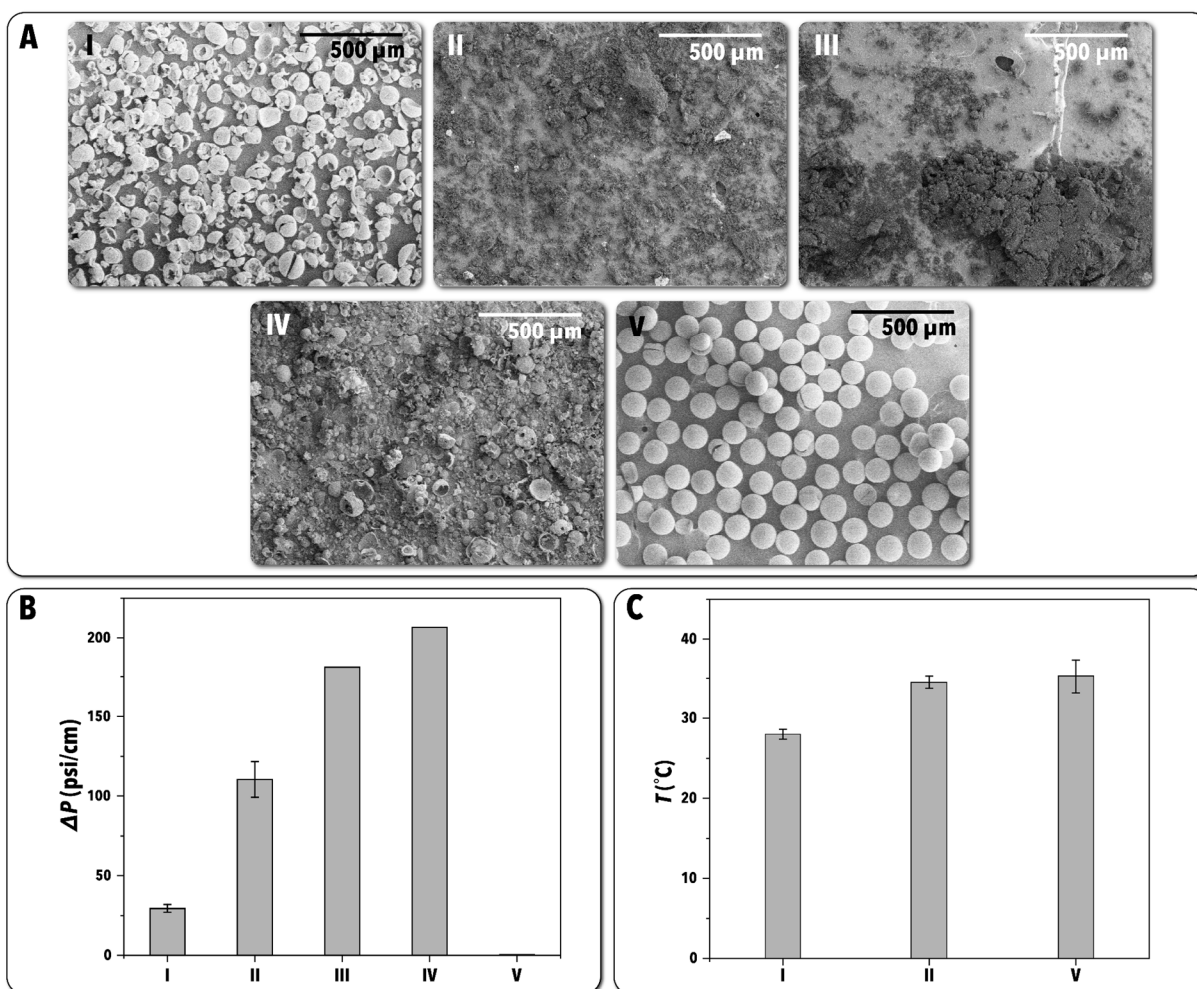


Figure 2. Characterization of the light-absorbing material candidates. (A) SEM images of the (I) flow-synthesized TiO₂ microparticles, (II) as-received carbon black, (III) isostatically pressed carbon black, (IV) batch-synthesized C/TiO₂, and (V) flow synthesized G-TiO₂ particles. (B) Pressure drop measurements for packed bed flow reactors fabricated with the materials shown in panel A. (C) The DI water temperature leaving the packed bed flow reactors constructed using the materials shown in panel A under constant illumination.

to polydisperse particle sizes and settling in the flow reactor. Meanwhile, the flow reactor packed with the highly monodisperse G-TiO₂ composite particles was observed to have a relatively low pressure drop of 0.5 psi/cm, due to the large average size (120 μm) and monodispersity of the flow-synthesized G-TiO₂ microspheres.

Following the pressure drop tests, the photothermal heating of the materials that did not cause mechanical failure of the flow reactor (*i.e.*, flow-synthesized white TiO₂, as received carbon black, and G-TiO₂ microparticles) was studied, under the same irradiance. The packed bed flow reactors (6-cm long) were illuminated using a solar simulator (A4 Lightline, Sciencetech), and the exit DI water temperature was measured by inserting a thermocouple into the exit stream. The G-TiO₂ and the as-received carbon black particles resulted in the greatest DI water temperature increase, reaching 35 °C and 34.5 °C, respectively (**Figure 2C**). As the G-TiO₂ composite microparticles resulted in the greatest inlet/outlet temperature difference for DI water and the lowest pressure drop across the four different materials tested, they were selected as the optimal light-absorbing material for the energy-efficient, continuous solar-desorption of CO₂.

The G-TiO₂ composite microparticles were then characterized using energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS). **Figure 3A** shows a bright-field image of the flow-synthesized G-TiO₂ composite microparticles as well as EDS maps of a single cut microparticle. The EDS maps (**Figure 3A II-IV**) illustrate the presence of an outer TiO₂ shell surrounding a carbon core containing a smaller amount of Ti atoms. The observed core-shell structure is formed by slight hydrolysis of the titanium n-butoxide trapped at the surface of the photocured particles as they are collected in DI water, while the graphite core (containing Ti atoms from the unhydrolyzed precursor) is formed as the photocured ethoxylated trimethylolpropane triacrylate is heated sufficiently to dehydrogenate the carbons but not high

enough to begin their oxidation. Graphite formation is also likely aided by the presence of the TiO_2 shell, which inhibits oxygen diffusion to the carbon core, thus preventing oxidation. The presence of the peaks at 26.5° and 55° in the XRD pattern (**Figure 3B**) indicates the presence of graphite, while the low, broad peak at 25° is indicative of the presence of anatase TiO_2 in the composite microparticles. Meanwhile, the XPS spectrum (**Figure 3C**) possessed Ti 2p and C 1s peaks with

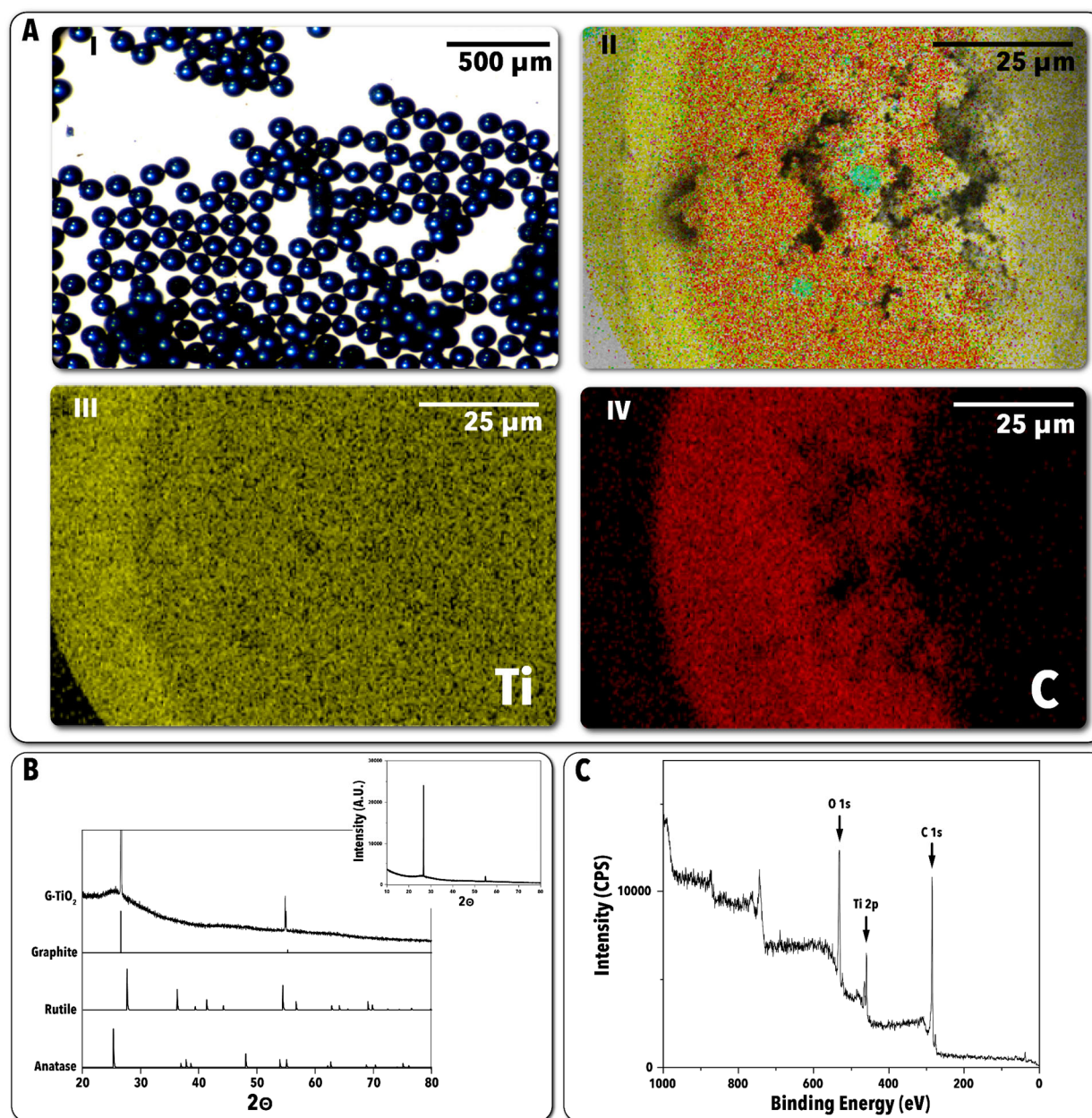


Figure 3. (A) (I) A bright-field image of the flow-synthesized G-TiO₂ particles. (II) EDS map of a cut G-TiO₂ microparticle. (III) Ti and (IV) C EDS maps. (B) XRD and (C) XPS spectra of the flow-synthesized G-TiO₂ microparticles.

binding energies of 460 eV and 285 eV, respectively. The Ti 2p peak is consistent with the presence of TiO₂, while the C 1s peak indicated the presence of elemental carbon.^{39–41}

Continuous Solar-Enabled CO₂ Desorption. In the next set of experiments, the developed flow reactor packed with G-TiO₂ composite microparticles was utilized to investigate the in-flow bulk fluid photothermal heating using a metal halide lamp. DI water was loaded into a 5 mL syringe and only fed through the tube-in-tube flow reactor (*i.e.*, no preheating sections or aluminum “concentrators”) illuminated by the lamp suspended at a height of 32 cm above the flow reactor. To conduct the temperature measurements, the needle from the exit-side needle valve was removed and a thermocouple was inserted in its place, while additional thermocouples were utilized to determine the inlet temperature of the DI water fed to the flow reactor and the external temperature under the lamp. In the first test, the effect of irradiance variation on exit bulk fluid temperature was evaluated (**Figure 4A**) using a liquid flow rate corresponding to a 0.5 min residence time (3.7 mL/h) in the illuminated tube-in-tube flow reactor segment and lamp power settings of 250 W, 400 W, and 600 W. For each tested lamp power, the feed inlet temperature remained constant, while higher temperatures were observed at higher lamp powers for both the exterior temperature and the exit bulk fluid temperature (**Figure 4A**). Furthermore, the DI water exit temperatures were higher than the exterior temperatures. It was found that the 400 W lamp power resulted in an average external temperature of 28 °C and an average DI water exit temperature of 32 °C, while the temperatures measured at the 600 W lamp power were 37 °C and 51 °C, respectively. The increased bulk fluid temperature above the ambient temperature upon increasing the irradiance (controlled by the lamp power) was a result of the photothermal heating of the packed G-TiO₂ particles in the flow reactor. Next, we evaluated the effect of residence time under a constant irradiance on the fluid photothermal heating in the packed bed flow reactor. The irradiance was

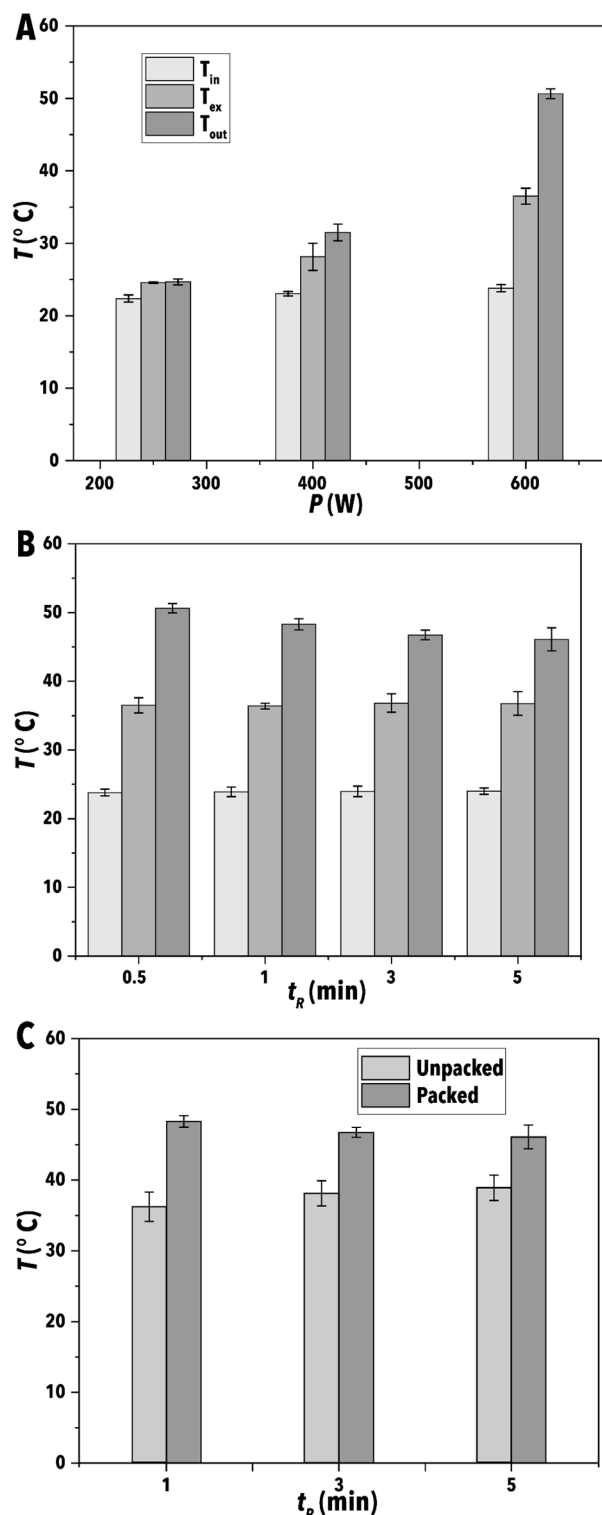


Figure 4. (A) Graph of temperature vs. lamp power for the inlet flow (T_{in}), reactor exterior (T_{ex}), and exit flow (T_{out}) of the packed reactor. (B) Graph of temperature vs. residence time for inlet flow, reactor exterior, and exit flow of the packed reactor. (C) Control experiments for the exit flow temperature without packing by residence time at 600 W compared to the same conditions with packing.

held constant (with the lamp power of 600 W), while t_R was varied from 0.5 min (3.7 mL/h) to 5 min (0.37 mL/h) (**Figure 4B**). As expected, the reactor inlet and external temperatures remained constant, while higher fluid exit temperatures were observed at lower residence times, contrary to expectations. However, this is explained by the presence of a “dead zone” between the illuminated flow reactor segment and the thermocouple, as the thermocouple could only be inserted as far as the PEEK frit installed to keep the packing in place (**Figure S5A**). The lower flow rates corresponding to higher t_R result in greater time spent in the “dead zone”, where the fluid cools prior to contacting the exit thermocouple. In the next set of packed bed flow reactor characterization experiments, we conducted a control experiment with an unpacked flow reactor at a similar irradiance to the packed bed flow reactor (600 W lamp power) and 32 cm lamp height and different residence times (**Figure 4C**). The measured temperatures followed the expected pattern,

with the highest temperature, 38 °C, observed at a 5 min residence time, and the lowest temperature, 36 °C, observed at the highest flowrate (*i.e.*, lowest residence time in the flow reactor). The difference in the observed temperature pattern (*i.e.*, negative T vs. t_R correlation in the packed bed flow reactor, positive T vs. t_R correlation in unpacked reactor) is explained by the location of the thermocouple in the unpacked reactor, as the absence of packing materials enabled the thermocouple to be placed at the end of the illuminated section, eliminating the “dead zone.” The temperatures were consistent with the previously measured external temperatures, indicating that the presence of the packing dramatically improves the in-reactor photothermal heating. It should be noted that the temperatures achieved in the illuminated region of the packed-bed flow reactor should be substantially higher than those measured, as the temperature measurements in the packed-bed flow reactor were taken at the exit valve rather than the interior of the illuminated section due to the additional packing and the frit used to keep the reactor packing in place (**Figure S5B**).

After it was established that the presence of the flow-synthesized G-TiO₂ particles and illumination resulted in substantial photothermal heating of the liquid fed into the packed-bed flow reactor, a preheating section (packing of the light-absorbing microparticles in the feed tube) was incorporated and folded strips of aluminum were added under the heating segments of the flow reactor to enhance illumination from all directions. The effect of irradiance (I) on the CO₂ desorption efficiency (E_D = mol CO₂ desorbed/mol CO₂ in amine) was then investigated by varying I (lamp power and height) with a CO₂-saturated 5 M aqueous MEA solution at a constant residence time. **Figure 5A** presents the measured I at different power and height combinations using a pyranometer (Tenmars TM206 Handheld Solar Power Meter). The highest I was observed at the highest lamp power, as measurements of 1013 W/m² and 857 W/m² were recorded at 29 cm and

32 cm lamp heights, respectively. As expected, lowering the lamp power substantially decreased I substantially. **Figure 5B** shows that E_D increased with increasing I . Increasing I results in greater light absorption by the G-TiO₂ composite microparticles within the packed-bed flow reactor, and thus greater bulk fluid photothermal heating. While it was possible to further increase the irradiance by decreasing the lamp height, $\sim 1000 \text{ W/m}^2$ was selected as the maximum value to be consistent with maximum solar irradiance. Furthermore, additional experiments were completed outdoor on a sunny day (31°C , approximately $1000 \text{ W/m}^2 I$) to compare natural solar irradiation to the metal halide lamp used for the indoor screening experiments. Using a 5 M MEA solution at a 3 min residence time, the solar irradiance experiment resulted in an average single-pass CO₂ desorption efficiency of 22% compared to the 25% obtained using the metal halide lamp. This result indicates reasonable agreement between the experiments conducted in the lab using the metal halide lamp and the actual solar irradiance. The lower desorption under actual solar irradiation is likely attributable to slightly lower external temperatures compared to those observed with the metal halide lamp ($\sim 31^\circ\text{C}$ vs. $\sim 35^\circ\text{C}$). Additionally, we conducted control experiments without packing the flow reactor at a 3 min

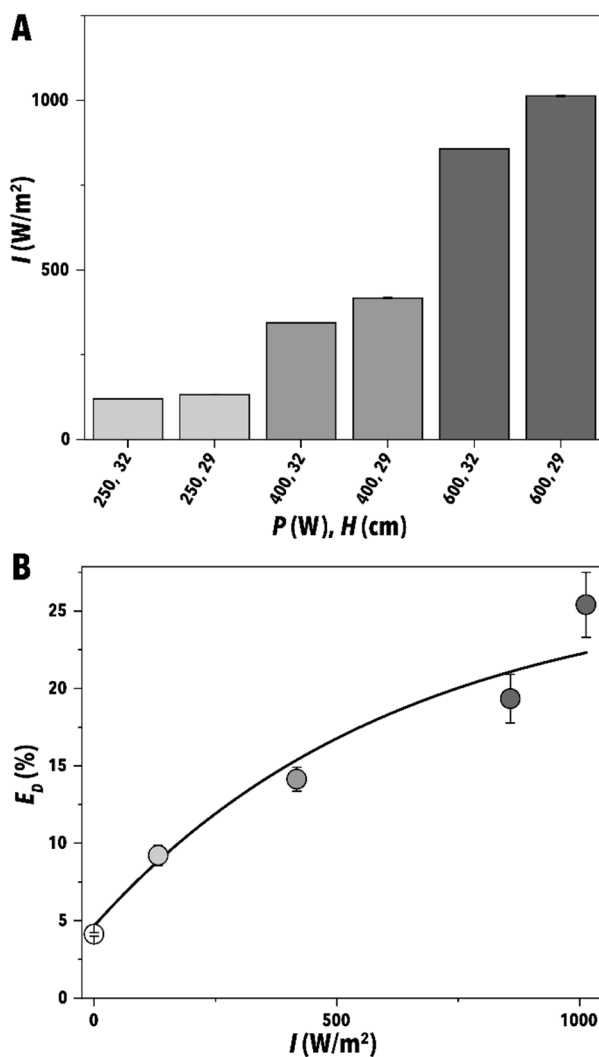


Figure 5. (A) Measured irradiance vs. lamp power and height. (B) CO₂ desorption efficiency vs. irradiance at a 5 min t_R using 5 M MEA.

residence time using a 5 M MEA solution at an irradiance of $\sim 1000 \text{ W/m}^2$. The illuminated, unpacked flow reactor produced an average CO_2 desorption efficiency of 9%, which is attributable to the heat produced by the lamp ($\sim 35^\circ\text{C}$) causing a small amount of CO_2 desorption.

Following the determination of reasonable agreement between indoor and outdoor CO_2 desorption efficiency results using the developed continuous flow reactor, in the next set of experiments we evaluated the effect of residence time, amine concentration, and amine type on the solar-enabled CO_2 desorption efficiency. **Figure 6A** presents the effect of residence time on the solar-enabled CO_2 desorption using 5 M MEA and an irradiance of $\sim 1000 \text{ W/m}^2$. As can be seen in **Figure 6A**, increasing the residence time increases the measured CO_2 desorption efficiency, which is expected as the aqueous amine solution spends more time in the microreactor, allowing the bulk fluid to reach higher local temperatures

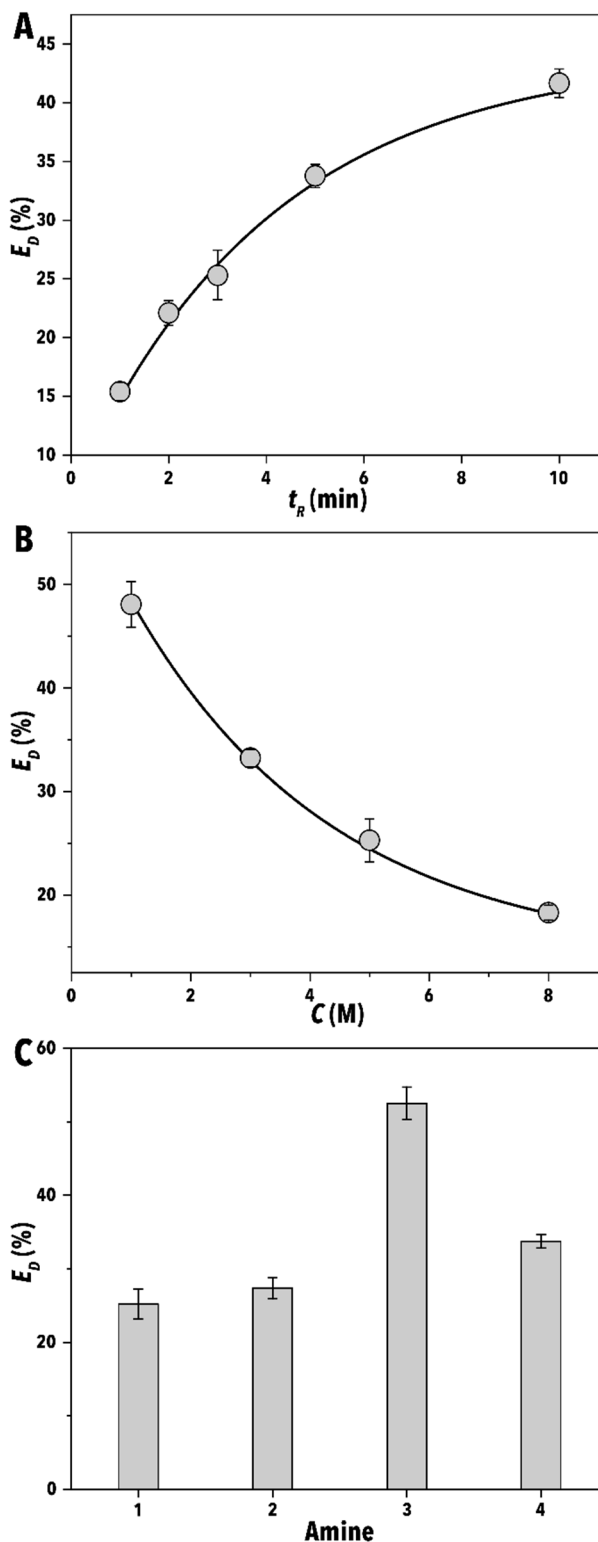
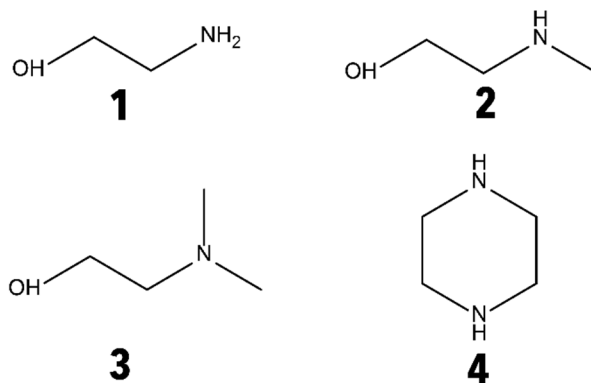


Figure 6. (A) Measured E_D for different residence times at $I \sim 1000 \text{ W/m}^2$, using a 5 M MEA solution. (B) Measured E_D for different MEA concentrations at $I \sim 1000 \text{ W/m}^2$ and $t_R = 3 \text{ min}$. (C) Measured E_D for various amines at $I \sim 1000 \text{ W/m}^2$ and $t_R = 3 \text{ min}$; 1, 2, and 3 were 5 M concentrations, 4 was 3 M.

and desorb larger amounts of CO₂. The largest single-pass CO₂ desorption efficiency of MEA was obtained for a residence time of 10 min (~42%). After exploring residence time effects, we explored the effect of saturated amine feed parameters on the CO₂ desorption efficiency. **Figure 6B** shows the effect of MEA concentration (*C*) on the CO₂ solar-desorption efficiency. Decreasing *E_D* was observed with increasing *C*, with the highest single-pass efficiency (48%) obtained at 1 M concentration. This pattern is attributable to the high heat capacity of the CO₂-saturated MEA, as well as the fact that CO₂ desorption is an endothermic reaction. The additional energy required to sufficiently heat the saturated amine absorbent due to the increased mixture heat capacity coupled with the greater quantity of CO₂ absorbed in higher concentration MEA solutions explains the lower desorption efficiencies observed. Furthermore, it was observed that the fraction of CO₂ absorbed per mole of MEA decreased as the MEA concentration increased, which may be attributable to the reaction exothermicity resulting in a lower CO₂ equilibria or reduced CO₂ mass transfer coefficients at higher amine concentrations.⁴²

In order to demonstrate the versatility of the developed solar-enabled CO₂ desorption strategy, in the next set of experiments we utilized the developed fluidic platform to evaluate the performance of other potential CO₂ absorbers under a constant irradiance of ~1000 W/m² (**Figure 6C**). **Scheme 1** illustrates the amines utilized in this study: **1** MEA, **2** N-methyl monoethanolamine (MMEA), **3** N,N- dimethyl monoethanolamine (DMEA), and **4** piperazine (PIP). Of the tested amines, MEA demonstrated the lowest CO₂ desorption efficiency in the packed-bed flow reactor, followed by MMEA



Scheme 1. Amines tested: **1** monoethanolamine (MEA), **2** N-methyl monoethanolamine (MMEA), **3** N,N-dimethyl monoethanolamine (DMEA), **4** piperazine (PIP).

(Figure 6C). PIP exhibited the second highest CO₂ desorption efficiency (34%) with the highest fraction of CO₂ absorbed per mole (0.83), but required the use of a 3 M solution due to solubility issues at 5 M concentration. DMEA possessed the highest CO₂ desorption efficiency (53%) with the lowest fraction of CO₂ absorption (0.22). The observed trend is explained by the degree of amine functionalization, as more energy is required to desorb CO₂ from amines with fewer substituents (*i.e.*, primary > secondary > tertiary).⁴³

Dynamic Solar Irradiance. To implement a solar-driven packed-bed flow reactor strategy for energy-efficient CO₂ capture and desorption processes using chemical absorbents, the system must be robust enough to deal with natural fluctuations of the solar irradiance. Therefore, we evaluated the effect of irradiance variation on the amount of CO₂ desorbed in the packed-bed flow reactor by repeatedly changing the lamp height during a continuous CO₂ desorption process. Figure 7A illustrates the variation in the irradiance and the corresponding changes in CO₂ release caused by varying the irradiance through changing the lamp height between 29 cm and 32 cm. Since CO₂ production from point source applications (*e.g.*, power plants) will remain relatively constant, it is necessary to ensure that other process parameters may be tuned to maintain a constant CO₂ desorption efficiency, especially if combined with a controller for real-time control

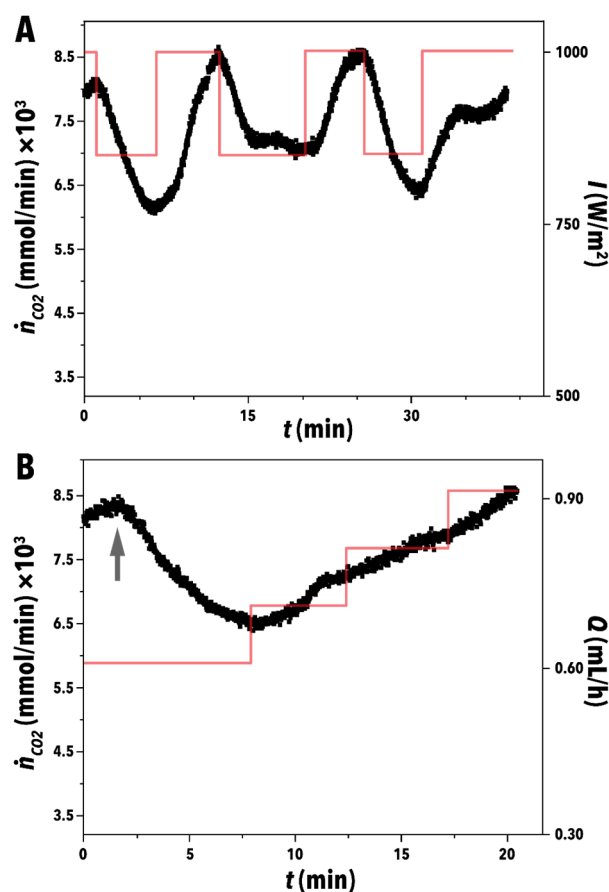


Figure 7. (A) Fluctuations in CO₂ release caused by variation in I between ~ 1000 W/m² and ~ 860 W/m². (B) Proof-of-concept for feedforward control based on irradiance. CO₂ release is returned to its original value by varying the aqueous amine feed flow rate.

based on measured irradiance and ambient temperature. **Figure 7B** shows the decrease in CO₂ release caused by the change in the irradiance from $\sim 1000 \text{ W/m}^2$ to $\sim 860 \text{ W/m}^2$ at the point indicated by the arrow. After 7.5 min, the flow rate was increased in stepwise increments of 0.1 mL/h to increase the total amount of CO₂ released back to its initial value. This proof-of-concept result demonstrates the possible implementation of a real-time controller to maintain constant CO₂ desorption throughput a day using the packed-bed solar desorber.⁴⁴

Next, we studied stability of maximum CO₂ desorption within the developed continuous packed-bed flow reactor for PIP, due to its comparatively high CO₂ absorption and superior desorption efficiency. **Figure 8** shows the stability test conducted using 1 M PIP (0.934 mol CO₂/mol PIP) over the course of 800 min at a constant 10 min residence time and an irradiance of $\sim 1000 \text{ W/m}^2$. Under these conditions, the measured E_D remained relatively stable, at an average single-pass efficiency of 64%. However, it is apparent that some instability is present, as seen with the oscillation between $\sim 55\%$ and $\sim 75\%$, which may be attributable to flow inconsistencies caused by the syringe pump or the formation of CO₂ bubbles in the preheating section. As the tests were conducted using a 10 min residence time with a single-pass through the flow reactor, it is conceivable that the overall E_D could be increased further by using a longer residence time and/or recycling the partially regenerated absorbent through the same packed-bed flow reactor.

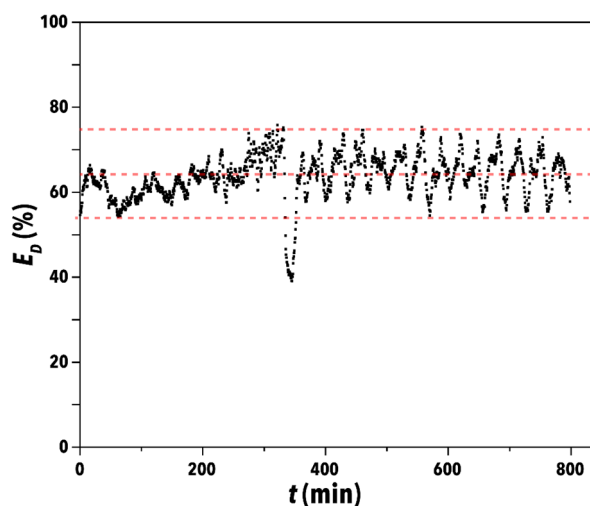


Figure 8. Measured E_D stability tests at 10 min residence time under $I \sim 1000 \text{ W/m}^2$, and 1 M concentration of PIP.

CONCLUSION

In conclusion, we demonstrated the design and utilization of a continuous flow strategy equipped with a packed-bed flow reactor to enable rapid, energy-efficient *in operando* solar desorption and recovery of CO₂ from aqueous amines. Among different tested light-absorbing materials, including standard TiO₂ microparticles, G-TiO₂ composite microparticles, batch-synthesized C/TiO₂ microparticles, as-received carbon black, and isostatically pressed and sieved carbon black, the composite microspheres demonstrated to be the most effective material candidate for continuous photothermal fluid heating with minimal pressure drop across the flow reactor (*i.e.*, low capital cost). CO₂ desorption efficiency was then tested as a function of irradiance and aqueous amine residence time, as well as amine concentration and structure, where it was demonstrated that the desorption efficiency increased with higher irradiance and residence time, lower concentration, and the presence of more electron-donating groups bonded to the nitrogen. The potential for integration of a real-time controller into the solar-enabled CO₂ desorption process was also demonstrated, enabling the amount of solar-desorbed CO₂ by the continuous flow reactor to remain constant with dynamic solar irradiance. Finally, maximum desorption efficiency stability tests were conducted using piperazine, where a maximum average single-pass desorption efficiency of 64% was achieved for a residence time of 10 min, with the opportunity for higher desorption with increased residence time and/or absorbent recycling. The results of this work demonstrated that continuous flow reactors packed with highly monodisperse, light-absorbing microparticles may be effectively implemented to efficiently desorb CO₂ from aqueous amine absorbents with minimal energy input. Additional studies are needed to scale up the developed technique for utilization in industrial scale CO₂ capture.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at DOI:

Images of the packed bed microreactor with and without the outer tube, emission spectrum of the metal halide lamp used to carry out the desorption experiments, image of a packed bed ruptured during the pressure drop tests, and UV-Vis spectra of the various packing candidates characterized in this work.

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