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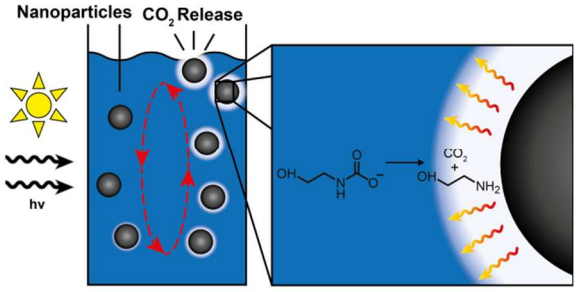

We report the use of actinic light for the photo-thermal enhanced regeneration of CO_2 from capture solutions containing nanoparticles. Regeneration efficiency increased with higher nanoparticle concentration and initial solution temperatures.

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Photothermal Release of CO_2 from Capture Solutions Using Nanoparticles

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Lowering the parasitic energy demand of CO_2 capture technologies is a basic and technical challenge. Using alternative energy sources could reduce energy costs both by lowering the energy required for regeneration and by replacing parasitic energy with renewable sources. Here we report the use of actinic light for the photo-thermal regeneration of CO_2 from capture solutions containing nanoparticles. We demonstrate an enhanced regeneration of CO_2 due to addition of carbon black nanoparticles. CO_2 regeneration efficiency increased with higher nanoparticle concentration and higher initial solution temperatures.

Introduction

In the past 25 years, the detrimental effects of CO_2 emissions have been realized. However, nearly 29 billion tons of CO_2 are still released into the atmosphere.[1] Several technologies capture CO_2 from gas streams, including metal organic frameworks, membrane-based systems, and liquid capture, but the additional energy cost of in the removal of CO_2 hinders their application for commercial CO_2 treatment.[2–8] In solution-based approaches, such as monoethanolamine (MEA), the additional energy cost is the result of the heat capacity of water (up to 120 ˚C) and the chemical bond energy between MEA and CO_2 (83 kJ/mol)[7,8]. A current challenge in the field is to either lower the energy of capture and regeneration, or harness alternative energy supplies.

Recently, the Halas group reported a nanoparticle system for photo-thermal steam generation with 80% of the absorbed light energy converting water into steam.[9,10] Intriguingly, the vapor generation was observed even when the bulk solution remained below boiling temperatures. The concept of nanoparticle heating has also been previously reported for use in amine scrubbing for microgravity environments.[11] Here we demonstrate the regeneration of CO_2 capture liquids using actinic light and light absorbing nanoparticles of carbon black (NCB), with an aqueous capture solution reaching bulk temperatures of 50 ˚C. This mechanism of regeneration is not exclusive to aqueous systems as photothermal release of CO_2 also occurred in a CO_2 binding organic liquid (CO_2BOL).[12,13] We characterized the photothermal effect by measuring the quantity of CO_2 released with respect to the incoming actinic light. The solution regeneration efficiency of CO_2 increased with higher carbon black concentration and higher initial temperatures. The largest regeneration efficiency was found to be 3.6 mol CO_2/MJ using 65 °C initial temperature, 0.1 wt% NCB, with MEA as the CO_2 capture fluid. The highly localized heat and regeneration provided by nanoparticles enables new approaches for solar energy use in carbon capture and release.

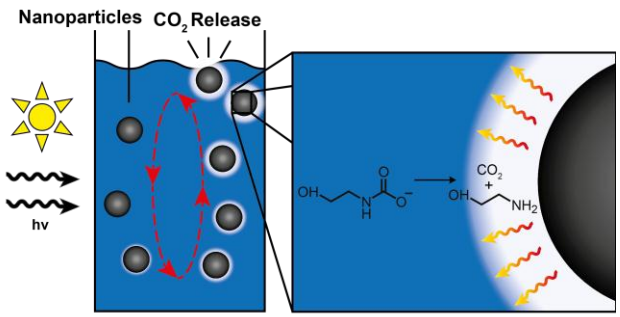

Figure 1. Carbon black nanoparticle CO_2 regeneration. Carbon black nanoparticles absorb actinic light and convert it to thermal energy, resulting in a high local temperature near the nanoparticle surface. At the surface, CO_2 is regenerated from MEA, forming a gas bubble around the nanoparticle. The bubble can grow large enough to force the nanoparticle to the surface of the fluid and release CO_2.

Gold and carbon black nanoparticles are strong absorbers of light and can generate water vapor in the presence of sunlight.[9,10,14–18] In the hypothesized mechanism, a gas film initially forms around the nanoparticles (Figure 1). The gas film's lower thermal conductivity insulates the nanoparticle surface - increasing its surface temperature. The gas volume surrounding the nanoparticle grows until the gas is released at the bulk solution surface. Once released, the nanoparticle returns to the solution and reinitiates the process[†].

Experimental

For ease of use and cost, we chose commercially available carbon black nanoparticles (Cabot, N115) for all experiments. Many carbon blacks exist with varying particle sizes, aggregate sizes surface areas, surface chemistry, and other properties. Carbon black N115 was specifically chosen as it was previously used in nanofluid studies.[9,16] Carbon black absorbs a broad range of radiant energy wavelengths, including visible and IR radiation.[16] Before use, nanoparticles were pre-treated to increase their water solubility. 5 g of the carbon black nanoparticles were added to 100 mL of 30% H_2O_2 in a round bottom flask and boiled while stirring for 24 hours. The solution was then filtered and dried at 85 °C under vacuum for 24 hours. The pretreated carbon black was dispersed into a capture liquid (7 molal/4.9 molar/30 wt% MEA in H_2O, CO_2BOL) under ultrasonic vibration for 20 minutes, producing a capture fluid and nanoparticle dispersion, also known as a nanofluid.

The regeneration efficiency was measured using the CO_2 release rate and actinic light (Figure 2A). A 50 mL round bottom flask containing 40 mL of the NCB/capture fluid mixture was loaded gravimetrically with CO_2 by bubbling the solution with pure CO_2 to 10 wt% (0.5 mol CO_2/mol MEA) loading[††]. The flask was then connected to a constant air flow of 0.2 L/min and stirred at 500 rpm. The light source was turned on, initiating the photothermal release of CO_2 into the gas detection stream. To remove any evaporating liquids from the system, the gas stream was filtered through condensing and drying tubes. Last, to measure CO_2 concentration, the output of the system flowed through an IR CO_2 meter. Concentration and flow rate were combined to calculate the release rate of CO_2. Experiments were run in triplicate. Repeated measurements and comparisons to mass balance measurements were also conducted to validate the methodology (Supporting Information). Light sources included LED lights or photography spotlights with powers of 0.8 W and 2.6 W respectively (incident to the flask). The refraction and Fresnel reflection of light resulted in 85% of the incident light passing into the flask (Supplementary Information). The intensity output was measured using an Ambient Weather TM-206 Solar Power Meter with a spectral sensitivity range of 400 nm to 1100 nm. Each system was characterized with respect to the amount of radiant energy required per mol of CO_2 released.

Results and Discussion

More CO_2 was released when NCB was present in the solution and was confirmed by ^{13}C NMR (Figure 2B, Supporting Information).

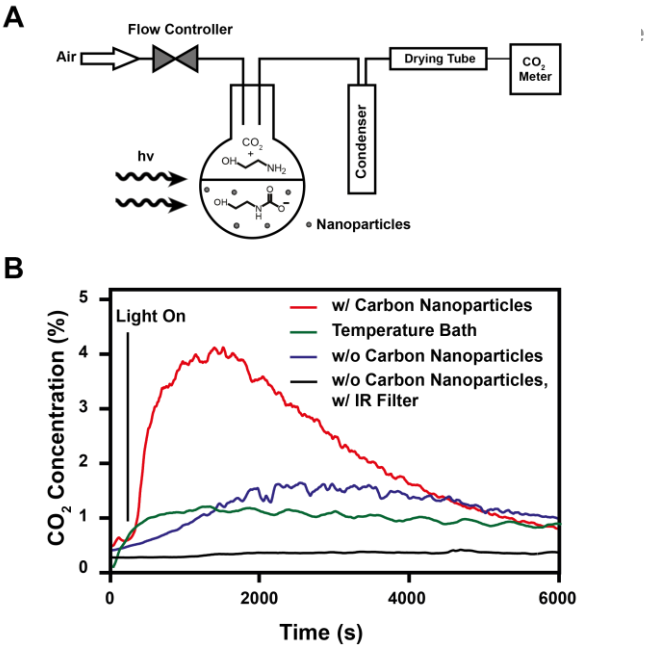

Figure 2. CO_2 regeneration measurements. (A) Experimental schematic. Carbon black nanoparticles added to a carbon capture fluid, such as MEA. Air flows through the flask, across a condenser and drying tube, finally reaching a CO_2 meter. Light shines through the flask, releasing CO_2 - measured by the CO_2 meter. The concentration of CO_2, light irradiance, and flow rate are used to calculate the regeneration efficiency. (B) Representative data. Release of CO_2 is triggered by light in MEA. After 2,000 sec, the maximum amount of CO_2 is released and the release rate of CO_2 slows. Some CO_2 is released without carbon black due to the IR transmittance of the light source, resulting in increased bulk fluid temperatures.

Some CO_2 was also released when NCB was absent from the solution. The release of CO_2 without NCB can be explained by two factors. First, water and glass absorb IR radiation (inherent in both solar and actinic light). This absorption results in a bulk solution temperature increase (up to 50 °C) that releases detectable amounts of CO_2. Second, the stream of air, used for measurements, has a low partial pressure of CO_2. The low partial pressure shifts the vapor equilibrium, further releasing CO_2. When an IR filter was applied, the CO_2 concentration within the detection stream was reduced to < 0.5% indicating that IR is largely responsible for background release. For further experiments, to simulate potential use, IR filters were not applied as solar energy includes IR wavelengths.

As a comparison to the photothermal method, a 50 °C water bath was also used to induce the release of CO_2. The total regeneration of CO_2 was similar to the solution without carbon black, though the profiles were distinctive. To support that photothermal release of CO_2 was not due to bulk heating or the low partial pressure of CO_2 in our apparatus, we compared release profiles of a bulk temperature bath to a computational model of CO_2 solubility in MEA (Supplementary Information).[19]

As the nanoparticles enhanced release of CO_2, we examined CO_2 release as a function of NCB concentration in solution. MEA was used as the capture fluid and was illuminated by the 2.6 W light

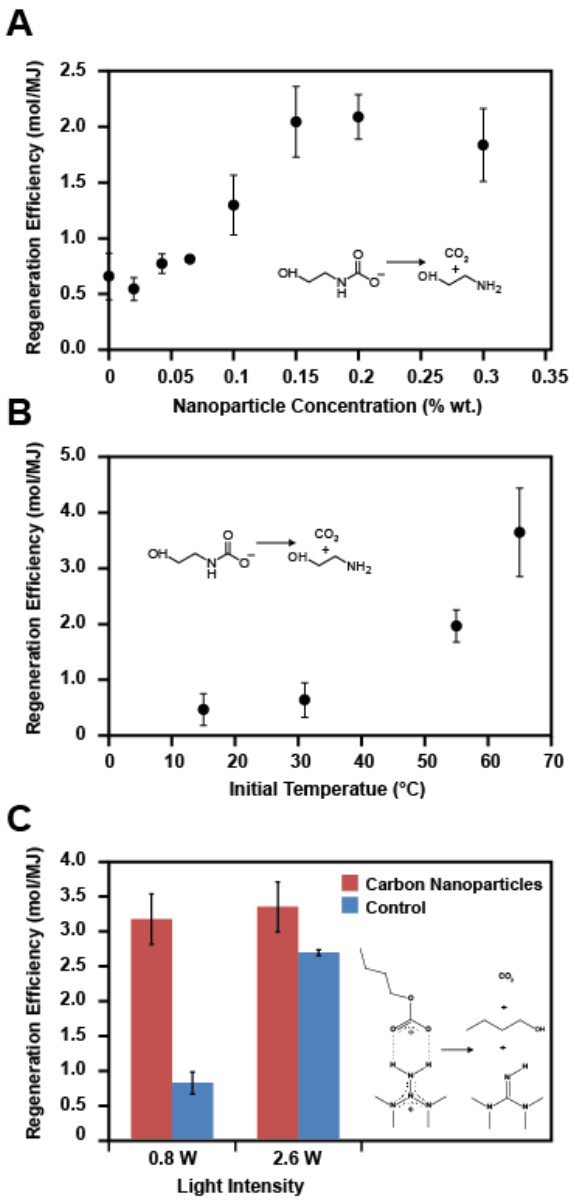

Figure 3. Regeneration efficiencies. (A) Carbon nanoparticle concentration. Regeneration efficiency increased with increasing nanoparticles concentration. Bulk temperatures reached 50 °C (B) Initial temperature. As the initial temperature of the capture fluid increased, an increase in the regeneration efficiency was found. This might influence applications as regenerators contain capture fluids at elevated temperatures. 0.1 wt% NCB concentration was used (C) CO_2BOL. The carbon black nanoparticles also released CO_2 in non-aqueous systems. Due to the lower desorption temperature profile of the CO_2BOL, the higher intensity light source was sufficient to remove CO_2 with and without nanoparticles. A lower intensity LED light source increases CO2 regeneration only with nano-particles present.

source. We found that higher concentrations of nanoparticles resulted in higher regeneration efficiencies (Figure 3A). Solutions with no nanoparticles still released some CO_2, but at lower levels due to IR absorption. Bulk solution temperatures reached ~50 °C (Supplementary Information). A possible hypothesis for the enhanced solution regeneration is that the increased concentration, and therefore number of nanoparticles, created greater surface area for the localized heating and nucleation of CO_2. Concentrations of nano-particles above 0.15 wt% did not result in higher regeneration efficiencies. Above this concentration, all light was absorbed by the nanofluid and no further absorption occurred. The addition of the NCB to the solution also increased the working capacity of the fluid within the examined region from 1wt% CO_2 in solution (with no NCB) to 2.3 wt% CO_2 in solution (at 0.2 wt% NCB).

Next, we examined the effects of the bulk solution temperature on regeneration efficiency. In most solution regeneration configurations, the temperature of the incoming CO_2 rich solution is elevated above room temperature as the reaction with CO_2 is exothermic. The bulk temperature of the solution was modulated by flowing preheated water through the solution via a stainless steel tube. This internal heating method was used to minimize the shading of the nanoparticle solution. The NCB concentration was 0.1 wt%. As expected, higher initial temperatures resulted in increased regeneration efficiency (Figure 3B). At higher temperatures, the energy difference between the initial state and the regeneration state is lower. The high initial temperature allows more of the photo-thermal energy to release CO_2 and regenerate the fluid since less energy is spent heating the solution to the higher temperatures. The largest efficiency in the scope of this report was found at 65°C (3.6 mol CO_2/MJ).

Last, as many capture and release schemes do not use aqueous amines, we examined if the photothermal CO_2 release was compatible with a non-aqueous alkyl guanidinium CO_2 capture fluid, referred to as CO_2BOL.[12,13] Specifically, a combination of tetramethylguanidine and 1-butanol in dimethylformamide was used (0.5 M each). CO_2BOLs bind CO_2 as an alkylcarbonate salt and does not require water as a solvent. In the nanoparticle regeneration system, the CO_2BOL had a greater regeneration efficiency than MEA (Figure 3C). The solvent for the CO_2BOL, dimethylformamide, has a lower heat capacity and lower thermal conductivity than water, which results in increased local temperatures and higher regeneration efficiencies. We found that the 2.6 W light source induced CO_2 release in CO_2BOL both with and without the NCB. The lower regeneration temperature of the CO_2BOL allowed the solution to obtain similar regeneration efficiencies between the solution without nanoparticles and the solution with nanoparticles. The enhanced regeneration efficiency was observed by using the lower intensity, 0.8 W LED lights. At higher intensities, nucleation boiling may be a larger driving force for desorption rather than high localized temperatures since the bulk solution temperatures reach regeneration temperatures. The regeneration efficiency of the CO_2BOL increased 380% between the CO_2BOL with and without carbon black, when illuminated with the 0.8 W light source.

We examined the potential performance of solar energy regeneration with a nanofluid system by estimating the surface area of incident

solar light required to regenerate MEA used in a 500 MW coal-fired power plant. In such a plant, on average, 2500 mol CO_2/sec are emitted.[20] With an average solar insolation of 561 W/m^2, an estimated 1.22 km^2 of surface area would be required to regenerate MEA, assuming 0.1 wt % NCB and an initial temperature of 65 °C.[21] The average solar insolation value was based on the average daytime direct normal solar insolation in Ward County, Texas which was reported by *Cohen et al.* as a comparative value for estimating the use of solar thermal energy for post-combustion CO_2 capture.[21] Our calculation assumes a flat surface as the interaction area between sunlight and the capture fluid. As a comparison, the Solar Energy Generating System in California[22] covers a total of ~2.3 km^2 of field area, with the largest plant covering a field area of 0.48 km^2. Further optimization such as improved geometries, light collection, and thermal insulation could result in higher regeneration efficiencies and lower land usage. However, energy would still be required to pump the MEA and to compress the released CO_2 for storage. The physical effects of NCP on process equipment was not examined as part of this study. A potential incorporation platform could be the use of parabolic troughs with the CO_2 capture nanofluid. Detailed process conditions, simulations, and cost analysis have yet to be performed and are beyond the scope of this initial publication.

Conclusions

In conclusion, we demonstrate a new potential energy source for carbon capture and release technologies by regenerating capture fluids using actinic light and carbon black nanoparticles. We report that increased nanoparticle concentration and increased initial capture fluid temperatures resulted in higher regeneration efficiencies. The carbon black nanoparticles demonstrated capture fluid regeneration in both aqueous and non-aqueous systems including MEA and CO_2BOL. These photothermal nanoparticles could be incorporated, at low loading levels, into CO_2 capture fluids without affecting chemical absorption. Fossil fuels remain inexpensive and this approach might serve as a temporary stop-gap as renewable energy technologies continue to mature. The use of photothermal nanoparticles might aid in the integration of solar energy with CO_2 capture technologies as an economical intermediate. The incorporation of the nanoparticles enables the use of sunlight, instead of steam, to regenerate the capture fluid as the nanoparticles rapidly reach regeneration temperatures. Our future work will focus on exploring the surface properties of the nanoparticles, effect of particle size, understanding the basic phenomenon of photothermal gas regenerate, reducing the aggregation of nanoparticles, exploring other photothermal nanoparticles, and optimizing system geometry for light absorption.

Notes and references

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† In an alternative hypothesis, the collective heating effect of the nanoparticles raises the liquid temperature to the boiling point.[23] Nucleation centers, such as small gas bubbles or NCB, can diffuse through the liquid and enter a superheated area which initiates the vapor formation.

†† After bubbling, aggregates of the nanoparticles on the order of microns in diameter were found. These aggregate can settle in a stationary solution after 8 hours. All experiments were conducted with the aggregated particle distribution. While this may have a negative effect on the regeneration efficiency, we continued with the experiments to demonstrate whether or not using the nanoparticles could be used for CO_2 capture fluid regeneration.

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Electronic Supplementary Information (ESI) available: Nanoparticle characterization, light source emission spectra, optical simulation, CO_2 solubility in MEA model . See DOI: 10.1039/c000000x/

1. P. Friedlingstein, R. A. Houghton, G. Marland, J. Hackler, T. A. Boden, T. J. Conway, J. G. Canadell, M. R. Raupach, P. Ciais, and C. Le Quéré, *Nat. Geosci.*, 2010, **3**, 811–812.
2. R. P. Lively, R. R. Chance, B. T. Kelley, H. W. Deckman, J. H. Drese, C. W. Jones, and W. J. Koros, *Ind. Eng. Chem. Res.*, 2009, **48**, 7314–7324.
3. D. Camper, J. E. Bara, D. L. Gin, and R. D. Noble, *Ind. Eng. Chem. Res.*, 2008, **47**, 8496–8498.
4. H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, *Nature*, 1999, **402**, 276–279.
5. H. J. Herzog, *Environ. Sci. Technol.*, 2001, **35**, 148A–153A.
6. D. M. D'Alessandro, B. Smit, and J. R. Long, *Angew. Chem. Int. Ed.*, 2010, **49**, 6058–6082.
7. B. A. Oyenekan and G. T. Rochelle, *Ind. Eng. Chem. Res.*, 2006, **45**, 2457–2464.
8. S. Freguia and G. T. Rochelle, *AIChE J.*, 2003, **49**, 1676–1686.
9. O. Neumann, A. S. Urban, J. Day, S. Lal, P. Nordlander, and N. J. Halas, *ACS Nano*, 2013, **7**, 42–49.
10. O. Neumann, C. Feronti, A. D. Neumann, A. Dong, K. Schell, B. Lu, E. Kim, M. Quinn, S. Thompson, N. Grady, P. Nordlander, M. Oden, and N. J. Halas, *Proc. Natl. Acad. Sci.*, 2013, **110**, 11677–11681.
11. J. Cole, PhD Thesis, Rice University, 2009.
12. D. J. Heldebrant, C. R. Yonker, P. G. Jessop, and L. Phan, *Energy Environ. Sci.*, 2008, **1**, 487–493.
13. D. J. Heldebrant, C. R. Yonker, P. G. Jessop, and L. Phan, *Energy Procedia*, 2009, **1**, 1187–1195.
14. H. Zhang, H.-J. Chen, X. Du, and D. Wen, *Sol. Energy*, 2014, **100**, 141–147.
15. R. A. Taylor, P. E. Phelan, T. Otanicar, R. J. Adrian, and R. S. Prasher, *Appl. Phys. Lett.*, 2009, **95**, 161907.
16. D. Han, Z. Meng, D. Wu, C. Zhang, and H. Zhu, *Nanoscale Res. Lett.*, 2011, **6**, 457.
17. A. O. Govorov and H. H. Richardson, *Nano Today*, 2007, **2**, 30–38.
18. *Nanoparticle heat transfer and fluid flow*, CRC Press/Taylor & Francis Group, Boca Raton, 2013.
19. D. Tong, J. P. M. Trusler, G. C. Maitland, J. Gibbins, and P. S. Fennell, *Int. J. Greenh. Gas Control*, 2012, **6**, 37–47.
20. K. S. Fisher, C. Beitler, C. Rueter, K. Searcy, G. Rochelle, and M. Jassim, *Integrating MEA Regeneration with CO2 Compression and*

Peaking to Reduce CO2 Capture Costs, USDOE Office of Fossil Energy (FE) Report DOE/ER/84111, 2005.
21. S. M. Cohen, M. E. Webber, and G. T. Rochelle, *J. Energy Power Eng.*, 2011, **5**, 195–208.
22. H. Price, E. Lüpfert, D. Kearney, E. Zarza, G. Cohen, R. Gee, and R. Mahoney, *J. Sol. Energy Eng.*, 2002, **124**, 109–125.
23. S. Baral, A. J. Green, M. Y. Livshits,, A. O. Govorov, and H. H. Richardson, *ACS Nano*, 2014, **8**, 1439–1448.