Title: Surface modification of carbon black nanoparticles enhances photothermal separation process

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Abstract: Carbon black nanoparticles (CB) were covalently modified to improve the photothermal regeneration of a CO₂ capture nanofluid through decarboxylation. Photothermal release of CO₂ addresses the high energy costs associated with regenerating capture fluids. By incorporating sulfonamides on the surface of CB, we enhance the photothermal separation of CO₂ from MEA by approximately 70% more than the unmodified CB. In contrast, with an anionic sulfonate on the surface, the total CO₂ released fell by 60%. We verified the chemical composition and structure of surface modification using complementary techniques including FT-IR, TGA, XPS, and Raman spectroscopy.

Main Text:

Nanoparticle mediated photothermal phase transitions and chemical reactions have the potential to improve many fields of energy harvesting [1-12]. The efficiency of a nanoparticle photothermal process in a liquid medium requires surface interactions between particle and solution, however these interactions have received little study. Previously, we observed that oxidized nanoparticles enhanced photothermal regeneration of an aqueous monoethanolamine (MEA) CO₂ capture fluid [13]. This occurs when carbon black nanoparticles (CB) activated by light convert photo energy into thermal energy, resulting in breaking the C-N bond between CO₂ and MEA. These results show how a photothermal process might be used to drive chemical reactions in solution with high energy efficiencies. Here, we show the effect of surface modification on photothermal efficiency of regenerating MEA by releasing CO₂. Modification of the CB surface changes the: (1) dispersability in solution, or aggregate size and (2) the amount of released CO₂ from chemically bound MEA. We modified the surface of CB particles using sulfonation with sodium nitrite, followed by an additional sulfonamide bond formation, both of

which form stable nanofluids. Anionic sulfonate and neutral amine surface functionality on CB can improve, or suppress, the total amount of CO₂ released from MEA indicating the surface properties control the efficiency of chemical reactions activated by a photothermal effect. While the chemical release of CO₂ from MEA depends on the surface modification of the CB, the photothermal vaporization of water was not effected by the same modifications. This suggests that the surface modification does not affect the photothermal process, but rather enhances only the subsequent chemical reactions. We conclude that the efficiency of decarboxylation in a heterogenous solution is influenced by the surface functionality of a photothermal nanoparticle rather than an effect of physical dispersion or aggregate size.

We are interested in using CB to release CO₂ from capture solutions to lower the high cost and limitations of traditional methods for regenerating carbon capture solutions. Recently, Halas and Nordlander showed that under solar illumination, NPs in water convert light to thermal energy and generate steam [7-8, 18], concentrating light energy into mesoscale volumes near the illuminated surface of the liquid resulting in extreme heating at the nanometer scale without heating the bulk fluid to its boiling point [19]. We reported that the same phenomenon regenerates a MEA capture solution using CB to release CO₂ from a chemically bound state [13]. A representation of this is shown in Fig. 1.

Fig. 1 – Decarboxylation of MEA using the photothermal effect of CB nanoparticles. CB concentrates actinic light, resulting in a high local temperature near the nanoparticle surface. As CO₂ is released from MEA, a gas bubble grows around the nanoparticle, and forces it to the surface of the fluid. The initiation of bubble growth and rate of decarboxylation may both be effected by the surface properties of CB.

To prepare a stable CB-MEA nanofluid with enhanced CO₂ release efficiency, the CB surface was modified to achieve desired interactions between the CB nanoparticles and the solution. To study the role of the covalent surface modification of CB, we probed how surface charge and chemical functionality of the nanoparticles change the amount of CO₂ released, providing initial mechanistic understanding of release.

CB has promising applications ranging from pharmaceutical drug-delivery vectors and bio-sensing devices to harvesting solar-energy, alongside use as conductive fillers in the rubber and electronic industries, such as fuel cells and lithium batteries [14]. In these applications, the highly irregular hydrophobic surface of nanopores is modified to influence acidity/basicity, wetting, and reactivity of CB [15-17]. We modified CB particles using sulfonation with sodium nitrite, followed by an optional sulfonamide bond formation resulting in CB with either anionic sulfonate or neutral amine groups. The covalent surface functionality was confirmed by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and Raman spectroscopy. Dispersion studies using dynamic light scattering (DLS) techniques showed that particle or aggregate size does not influence the photothermal effect.

1. Experimental

2.1. Materials

Reagents were purchased from Sigma-Aldrich and used as received without further purification unless otherwise noted. VULCAN[®] 9 N115 carbon black nanoparticles (CB), donated from Cabot Corporation, was dried *in vacuo* at 90 °C for 48 hrs before use. Dichloromethane (DCM) was dispensed under argon from a glass solvent purification system custom manufactured by Jorg Meyer (Univeristy of California, Irvine). Reagent grade carbon dioxide was purchased from Airgas.

2.2. Sample Preparation

2.2.1 Sulfonation of CB

Fig. 2 – Reaction scheme for the anionic surface modification of CB.

Carbon black was covalently modified using 4-aminobenzenesulfonic acid and sodium nitrite. The introduction of anionic groups ($-\text{SO}_3\text{Na}$) onto the surface of CB nanoparticles was achieved via generation of a diazonium salt in situ [20]. 0.5 g of CB, and 5.0 g of 4-aminobenzenesulfonic (sulfanilic) acid in 6 mL of H_2O were heated to $80\text{ }^\circ\text{C}$ while stirring under normal atmospheric conditions for 10 mins where 2.0 g of sodium nitrite (dissolved in 1 mL H_2O) was added dropwise. After 6 hrs of stirring and heating at $85\text{ }^\circ\text{C}$, the reaction was cooled to RT, and diluted with H_2O where the insoluble black material was then centrifuged and rinsed thoroughly twice with H_2O (20 mL). The desired product **1** was isolated by evaporation of water under vacuum at $80\text{ }^\circ\text{C}$ for 24 hrs.

In order to clarify the nature of the $-\text{SO}_3\text{Na}$ attachment onto CB, a control experiment was made using a sample of the reaction described above without sodium nitrite. A mixture of 100 mg of crude CB, 1.0 g sulfanilic acid (SA) and 1 mL H_2O was heated to $80\text{ }^\circ\text{C}$ in an oil bath and maintained at this temperature for 6 hrs. The insoluble black material was then centrifuged and rinsed with H_2O . This material referred to hereafter as a blank sample was dried in an oven at $85\text{ }^\circ\text{C}$ for 24 hrs.

2.2.2. Surface modification of $\text{CB-SO}_3\text{Na}$ with EDA

Fig. 3 – Reaction scheme for the amination of $\text{CB-SO}_3\text{Na}$.

Carbon black was covalently modified by transforming the sulfonyl chloride into a series of sulfonamides. The introduction of amine groups ($-\text{NH}_2$) onto the surface of CB nanoparticles was achieved by first activating the sulfonate with thionyl chloride, then adding ethylene diamine [21]. 0.25g of $\text{CB-SO}_3\text{Na}$ (**1**) in 15 mL of dichloromethane (DCM) was sonicated for 20 mins in a round bottom flask where it was sparged with argon gas, and cooled to $0\text{ }^\circ\text{C}$. Under constant

stirring, 3 mL of thionyl chloride was added to the black suspension and the reaction mixture was warmed to RT and maintained at this temperature for 3 hrs. Excess thionyl chloride was removed under rotary evaporation, whereupon 0.25 g of **2** was resuspended in 7 mL of DCM. The reaction mixture was sonicated for 20 mins, sparged with argon, and cooled to 0 °C. Under constant stirring, 3.0 mL of ethylenediamine was added to the black suspension. The reaction mixture was warmed to RT and allowed to stir for 8 hrs. A black solid was collected by Büchner filtration, washed with 1 M hydrochloric acid (20 mL), and water (20 mL), and dried under vacuum at 80 °C for 24 hrs to yield **3** as a black crystalline powder.

2.2.3. Oxidation of CB

Fig. 4 – Reaction scheme for the oxidation of CB.

CB was oxidized according to the method described by Li et al [22]. 20 mL of a 2 M solution of ammonium persulfate (9.1 g) in 1 M HCl was added to a 1.0 g mass of dried CB, then the reaction was heated to 55 °C and maintained for 6 hrs. The oxidized CB (**4**) was subsequently washed with water until a neutral pH was established. The material was isolated via centrifugation, and dried at 80 °C for 24 hrs.

2.3 Characterization

TGA measurements were performed on a TA Instruments TGA Q5000 thermogravimetric analyzer. The samples were analyzed at a heating rate of 10 °C min⁻¹ from 30 to 800 °C under an atmosphere of inert air flowing at 40 mL min⁻¹. X-ray photoelectron spectroscopy was performed using an Axis-Supra analyzer (Kratos Analytical Ltd., Manchester, UK) equipped with a monochromatic Al X-ray source. The pressure of the analysis chamber during acquisition was lower than 5x10⁻⁹ torr. The X-ray spot size used for these experiments was 300 x 800 μm². Survey spectra used to determine surface elemental composition were recorded with a pass energy of 160 eV, in the binding energy range from 0 – 1200 eV in 0.5 eV steps. At least two spots on one or more replicates were analyzed for each sample type. Photoelectron lines were recorded. The high resolution of the main constituent elements, i.e., O1s, N1s and C1s, spectra were acquired at an analyzer pass energy of 20 eV in 0.01 eV steps with a 300 ms dwell time.

Quantitative analysis, based on peak area intensities after removal of the Shirley-type background, was performed by CasaXPS using the Kratos elemental library. The solar simulator was custom designed and manufactured by Lee Moritz (University of California, Irvine Machine Shop). Desorbed CO_2 was measured for flow rate using a Cole-Parmer Gas Mass Flowmeter (32707-02), and for CO_2 concentration using a COZIR Wide-Range CO_2 Sensor that uses NDIR, fitted with Gold-plated optics (GC-0016). FTIR spectra were obtained with a Perkin-Elmer Frontier spectrometer (L1280034) under ambient conditions. Test samples were prepared by uniformly dispersing the CB in KBr and compressing the powder into pellets. The spectra were obtained in the wavenumber range $4000 - 600 \text{ cm}^{-1}$, typically 64 scans at a resolution of 4 cm^{-1} were accumulated for each spectrum. Hydrodynamic diameter measurements were recorded using a Malvern Zetasizer ZS Nano dynamic light scattering instrument equipped with NIBS optics (ZEN 3600). Raman spectra were recorded with all analyses collected at a single point on the CB samples, performed using lens with 50x and 532 nm laser with a low laser power to avoid any heating effect using a Renishaw inVivo Raman microscope (H14087).

2.4 Gas desorption and detection system to quantify capture fluid regeneration efficiency

To a round bottom flask was added CB (40 mg, 0.1 wt %) and aqueous monoethanolamine (40 mL, 30% monoethanolamine in water (v/v)) respectively. The reaction mixture was sonicated for 20 mins, weighed, and saturated with 4 g of CO_2 , 10 wt %, gravimetrically (sparged for approximately 20 mins). To ensure the aqueous monoethanolamine is fully saturated, the headspace of the flask was pressurized with CO_2 by use of a balloon. The following parameters were kept constant for all trials. See Fig. 2 for schematic of reaction setup.

Fig. 5-Schematic of photothermal regeneration. In a roundbottom flask filled aqueous MEA saturated with CO_2 and CB nanoparticles, a solarsimulator initiates the release of CO_2 which is analyzed by means of an airflow meter and CO_2 meter.

- Halogen projector bulb light source, irradiance between 2800-3000 W/m² (~65 °C bulk heating)
- No purge line into flask, only out-flow of CO₂ from flask upon desorption
- CO₂ is flushed through empty head space of flask, condenser, and instruments prior to each trial
- Out-flow of CO₂ is monitored with a mass flow meter and a CO₂ meter
- 40 mL scale
- Stirring rate: 500 rpm
- Total stripping time: 3 – 3.5 hrs

2.5 Mathematica analysis

Reaction results are recorded in voltage by the mass flow meter, and in percent CO₂ by the CO₂ meter. Using Mathematica, the flow-rate data and the CO₂ percentage are converted to a plot of CO₂ release (mL/s) vs. time (s). Based on the shape of the flow rate data, the photothermal-enhanced rate of CO₂ release is evident. After converging the flow data with the percentage of released CO₂, two absolute parameters are recorded: the total mass of CO₂ release and the time it takes to reach half the maximum of CO₂ released. By integrating the area under the curve as shown in Fig. S1, the total amount of CO₂ released.

3. Results and Discussion

3.1 Chemical Composition

Characterization of surface modification on CB is complicated due to the highly disordered surface, and multiple characterization techniques were employed to confirm covalent modification. Initially, the covalent modification of CB was confirmed by TGA, and FTIR.

Fig. 6- TGA curves for CB, SA+CB, and CB-SO₃Na. The loss of surface functional groups at 511 °C (9.6 wt loss %) and 678 °C (6.2 wt loss %) indicate covalent modification of CB with –SO₃Na.

The presence of covalent functional groups on CB was analyzed by TGA and masses were recorded as a function of temperature. TGA curves show a mass loss corresponding to the covalent sodium sulfonation of the CB surface as shown in Fig. 6. The loss of surface functional groups occurred in two stages. The mass losses at 511 °C (9.6 wt loss %) and at 678 °C (6.2 wt loss %) are associated with the decomposition of -SO₃Na from the CB surface. A control of the blank sample of mixed sulfanilic acid and CB-raw showed decomposition at a much lower temperature (250 °C) than the CB-SO₃Na.

In the trace of CB-SO₂-EDA, approximately 25 mass percentage was lost at 275 °C which is attributed to the covalent sulfonamide attached to CB (Fig. 7). The formation of covalent sulfonamide bonds to the surface of CB is apparent by the free ethylenediamine (EDA) decomposed at a lower temperature of 70 °C than did the EDA in CB-SO₂-EDA.

Fig. 7- TGA curves for CB, EDA, and CB-SO₂-EDA. The loss of surface functional groups at 275 °C (25.0 wt loss %) indicate covalent modification of CB from –SO₃Na to –SO₂EDA.

As shown in Fig. 8, the FTIR spectra of CB-raw (unmodified) and modified CB-SO₃Na, and CB-SO₂-EDA differs significantly.

Fig. 8 – Overlapped FTIR spectra of CB, CB-SO₃Na, and CB-SO₂-EDA. Differences in bands present in spectra of CB samples indicate successful covalent modification of CB with desired functionality.

The absorption bands were of weak intensity because of the black-body absorbing nature of carbon black [23]. However, normalized FTIR spectra provide useful relative information on

surface modifications. A broad band centered at approximately 3450 cm^{-1} were observed in the spectra of all samples, and is likely due to O-H stretching of water absorbed in the KBr pellet. The band at 1630 cm^{-1} also observed in all spectra is attributed to C=C stretching of the CB [24, 25]. As Fig. 8 shows, after modification the FTIR spectrum of CB differs significantly from that of CB-SO₃Na and CB-SO₂-EDA. Differences are also observed in the $1700 - 1000\text{ cm}^{-1}$ region and in the intensity of C-H bond stretching at 2919 and 2850 cm^{-1} attributable to C-H asymmetric and symmetric stretches, respectively [24, 26-27]. Fig. 8 also shows the difference in spectra of CB-SO₃Na and CB-SO₂-EDA. Bands from approximately $1200-1100$, and 620 cm^{-1} are attributed to the S=O stretch [28, 29] from the sulfonate in CB-SO₃Na and sulfonamide in CB-SO₂-EDA. Surface modification from the -SO₃Na to -SO₂-EDA induces a slight loss of S=O bonds on the surface, as observed from the reduced spectral intensity of the peaks around 1200 cm^{-1} . There is also an increased spectral intensity of the peak at 3434 cm^{-1} in the CB-SO₂-EDA spectrum attributable to the N-H stretch. The new band appearing as a shoulder at 3180 cm^{-1} corresponds to N-H bond stretching [30]. The C-N stretching vibration is present at 1486 and 1034 cm^{-1} also appears in the CB-SO₂-EDA spectrum [31]. The bands present in both the spectra of sulfonate and sulfonamide surface modified CB along with the TGA data suggests that desired functionality was introduced onto the surface covalently, and was further confirmed with the following described techniques.

3.2 Chemical Structure

Raman spectroscopy was used to determine the degree of surface functionalization, as shown in Fig. S7. Chemical structure and surface composition was independently confirmed with XPS analysis. Surface modification was confirmed by comparing high-resolution region XP spectra of elements respectively present in the unmodified and modified CB samples. The XPS survey scan for CB is shown in Fig. S3.

The C1s peaks of CB-raw displayed a main peak at 284.2 eV , which is attributed to the sp²-hybridized carbon atoms present in the CB structure [32]. Fig. 9 compares the wide-survey XP spectra for CB before and after CB-SO₃Na, and CB-SO₂-EDA functionalization.

Fig. 9 – XPS wide-scan spectra of CB, CB-SO₃Na, and CB-SO₂-EDA. Differences in elements present in spectra of CB samples confirm desired chemical surface functionality.

In a wide-survey scan for CB-SO₃Na, elements not present in the unmodified CB appeared, such as S2p centered at 168.5 eV, and Na1s at 1072.1 eV. Similarly for the XP spectrum of CB-SO₂-EDA, elements not present in the unmodified CB appeared, such as S2p centered at 168.5 eV, and N1s at 401.1 eV. Following the reaction with EDA, the Na1s peak is reduced indicating the conversion from –SO₃Na to –SO₂-EDA. The modification on the surface of CB changes the chemical state of the respective elements. This change was monitored by the changes in the envelope shape of the high-resolution C1s, S2p, and N1s XP spectra recorded in the modified nanoparticles. Deconvoluted high-resolution C1s, O1s, Na1s, S2p, and N1s XP spectra for these carbon samples are shown in Fig. S3-S6.1.

In the case of CB-SO₃Na, the deconvoluted S2p spectrum confirms the formation of sulfonic acid and oxidized sulfur species (Fig S5.1). In the case of CB-SO₂-EDA, the deconvoluted N1s spectrum confirms the formation of amine and amide groups on the CB-SO₂-EDA surface (Fig S6.1).

3.3 Carbon capture regeneration efficiency

After confirming that the surface of CB was covalently modified with the desired surface functionality, we assessed the application of the modified particles as nanofluids by measuring

the efficiency of a decarboxylation reaction (and subsequent CO₂ solvent regeneration) due to photothermal heating. To measure the release of CO₂ using the photothermal effect, we used our previously developed gas desorption and detection system to characterize the regeneration of CO₂ capture fluids [13]. All reactions were run as 0.1 wt % CB nanofluids in 30 wt % MEA with 2945 W/m² input light irradiance resulting in a low bulk temperature of ~65 °C. A plot of total mass of CO₂ released for each modified CB nanofluid is shown in Fig. 10. With the inclusion of an amine on the surface, CB-SO₂-EDA released the highest amount of CO₂, ~70% more CO₂ than the unmodified CB. While in contrast, CB-SO₃Na released the lowest amount of CO₂, ~60% less than the unmodified CB.

Fig. 10 – Effect of surface modification on CO₂ decarboxylation. Solvent regeneration, assessed as CO₂ release, varies from CB samples signifying an effect of surface functionality.

It was necessary to determine if the increased and decreased rates of CO₂ release were related to the chemical process of decarboxylation, wherein the surface functionality affected the release, or if the modification changed the efficiency of the photothermal process by altering aggregate sizes of the particles. To test if the change seen in photothermal CO₂ release profiles was a result of the chemical reactivity of modified CB, and not aggregate size, DLS was employed to monitor how surface functionality affects aggregate sizes. Simultaneously, we conducted experiments analogous to the work of Halas [7], where a photothermally active nanoparticle in water produced steam when stimulated with light. If the nanofluids had similar

dispersivity (measured as aggregates sizes), or produced the same amount of steam, then the result was not a physical effect of the surface modification. CB nanofluids were formulated in double distilled water in an identical manner to the CO₂/MEA experiments above. Fig. 11A compares mass loss of CB samples in 30 wt % aqueous MEA saturated with and without CO₂. This experiment allowed us to conclude whether the surface modification affects the physical photothermal process of steam generation, or the chemical reaction and solvent regeneration by decarboxylation. Fig. 11B compares mass loss of CB samples in 30 wt % aqueous MEA without CO₂ and in water. In nanofluids without CO₂, the photothermal energy conversion drives a phase change to produce steam rather than the chemical decarboxylation reaction of CO₂. This experiment determined if the mass loss in 30 wt % aqueous MEA differed from the mass loss due to steam (in the 100% water nanofluids) indicating that aggregate size would change the photothermal effect.

Fig. 11 – Mass loss as a result of CB surface functionality. (a) CB samples are prepared as nanofluids in 30 wt % aqueous MEA, saturated with and without CO₂. (b) CB samples are prepared as nanofluids in H₂O and unsaturated 30 wt % aqueous MEA.

A difference in mass loss due to surface functionalization is presented in Fig. 11. There is no similar trend between CB samples in 30 wt % aqueous MEA, saturated with and without CO₂. We conclude from this data that the differences in mass loss due to vaporization and CO₂ release should be considered independent from each other. The surface modification affects the chemical process, CO₂ release via decarboxylation, rather than the physical steam generation caused by altered aggregate sizes of the particles. Fig. 11 also shows the mass loss of CB samples in unsaturated aqueous MEA are similar between nanofluids. A comparable trend exists in 100%

water CB samples. There is no increased mass loss due to surface functionality, as seen in CO₂ saturated 30 wt % aqueous MEA.

To clarify that the nanofluid dispersity, nanoparticle aggregate size, was not responsible for increased CO₂ release, we compared mass loss against hydrodynamic radii between chemical and physical effects on the photothermal release of CO₂ (Fig. 12).

Fig. 12 – Mass loss as a result of nanofluid dispersivity. (a) CB samples are prepared as nanofluids in H₂O, mass loss as a result of steam generation. (b) CB samples are prepared as nanofluids in unsaturated aqueous MEA, without CO₂. (c) CB samples are prepared as nanofluids in aqueous MEA saturated with CO₂, mass loss due to decarboxylation.

Although surface modification does change aggregate sizes in both H₂O and aqueous MEA, there is no trend indicating that aggregate size influences steam generation or CO₂ release. There is also no similarity in efficiency of steam generation and CO₂ release between surface functionality. Therefore, surface functionality does not affect the photothermal process itself; and we conclude it must change the rate of reaction in CO₂ release, similar to how a change in ligand functionality can change the reactivity of a catalyst.

4. Conclusions

This study demonstrates that the surface of CB can be covalently modified to incorporate sulfonamides which improve the release of CO₂ from MEA ~70% more than the unmodified CB. Covalently modifying the surface of CB was confirmed by the loss of organic groups at high temperatures (>250 °C) as indicated by TGA, and as identified by both FTIR and XPS analysis.

The incorporation of nanofluids into carbon capture and release would enable the use of sunlight, rather than steam, to regenerate the capture fluid at lower bulk temperatures. Photothermal release of CO₂ addresses the high energy costs associated with regenerating capture fluids, which prohibit widespread commercial implementation. Because this method has great potential for industrial applications, as it uses economically available materials and alternative energy sources, it is important to understand this process. By investigating surface functionality of CB, we make progress in exploring how photothermal nanofluids can be enhanced to more efficiently perform separations processes. Carbon capture nanofluids with modified CB showed increased total release of CO₂. Surface modification affected dispersion properties as a nanofluid, yet there was no influence of changes in aggregate sizes on the photothermal release of CO₂. Our future work focuses on understanding the basic phenomenon and mechanism of photothermal gas release, and optimizing system geometry for light absorption in a scaled implementation.

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