Production of Carbon Nanomaterials and Sorbents from Domestic U.S. Coal

Project DE-FE0031798
National Energy Technology Laboratory, U.S. Department of Energy

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Resource Sustainability Project Review Meeting
October 25 - 27, 2022

UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN

ILLINOIS STATE GEOLOGICAL SURVEY
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U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

Project Team, Objective, and Scope

Team

- UIUC/ISGS: S. Dastgheib, N. Haskin, T. Ilangovan, J. Mock, S. Singh.
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Objective

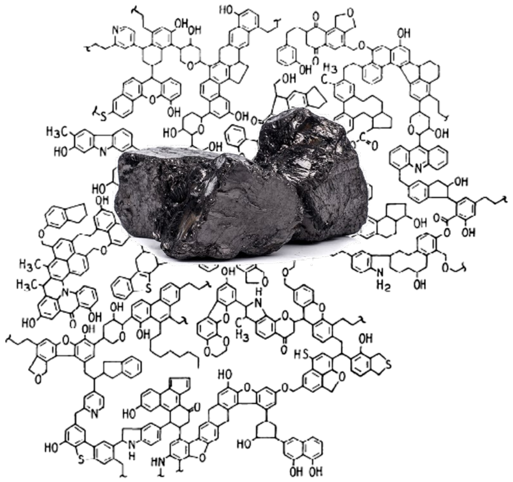
- To produce high-value carbon nanomaterials (i.e., GO and RGO) and sorbents (i.e., activated carbon (AC)) from domestic coal resources in a cost-effective manner

Scope

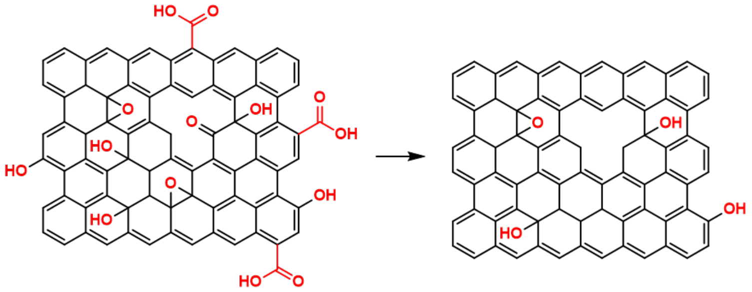
- To evaluate the feasibility of the proposed approach for the production of high-value carbon materials from U.S. coal by conducting systematic experimental work and a techno-economic evaluation
  - Material preparation: 4 types of domestic coal samples processed at a laboratory scale to produce GO, RGO, and AC products
  - Material characterization: The developed materials are extensively characterized, and the impact of the coal feedstock type on the yield and quality of each product are determined
  - Techno-economic analysis, market evaluation for graphene materials, and technology gap analysis

Conversion of Coal to GO and RGO

- It is possible to produce graphene oxide (GO) and reduced graphene oxide (RGO) from coal, but several R&D gaps need to be addressed
- Coal vs. graphite precursor for GO production: Opportunities
  - Low cost of precursor: ~$40/ton coal vs. ~$1,000/ton graphite
  - Availability: huge world coal reserves (~1,000 billion tons, ¼ in the U.S.) vs. limited graphite reserves (380 million tons, 80% in China)
  - Ease of oxidation: less dense structure of coal compared to graphite
  - Others
- Coal vs. graphite precursor for GO production: Challenges
  - Coal impurities (sulfur, various metal oxides, silica, etc.)
  - Lack of a graphitic structure
  - Quality and overall cost of the products
  - Others



$$\text{Coal} \xrightarrow{\textit{Oxidation}} \text{GO} \xrightarrow{\textit{Reduction}} \text{RGO}$$

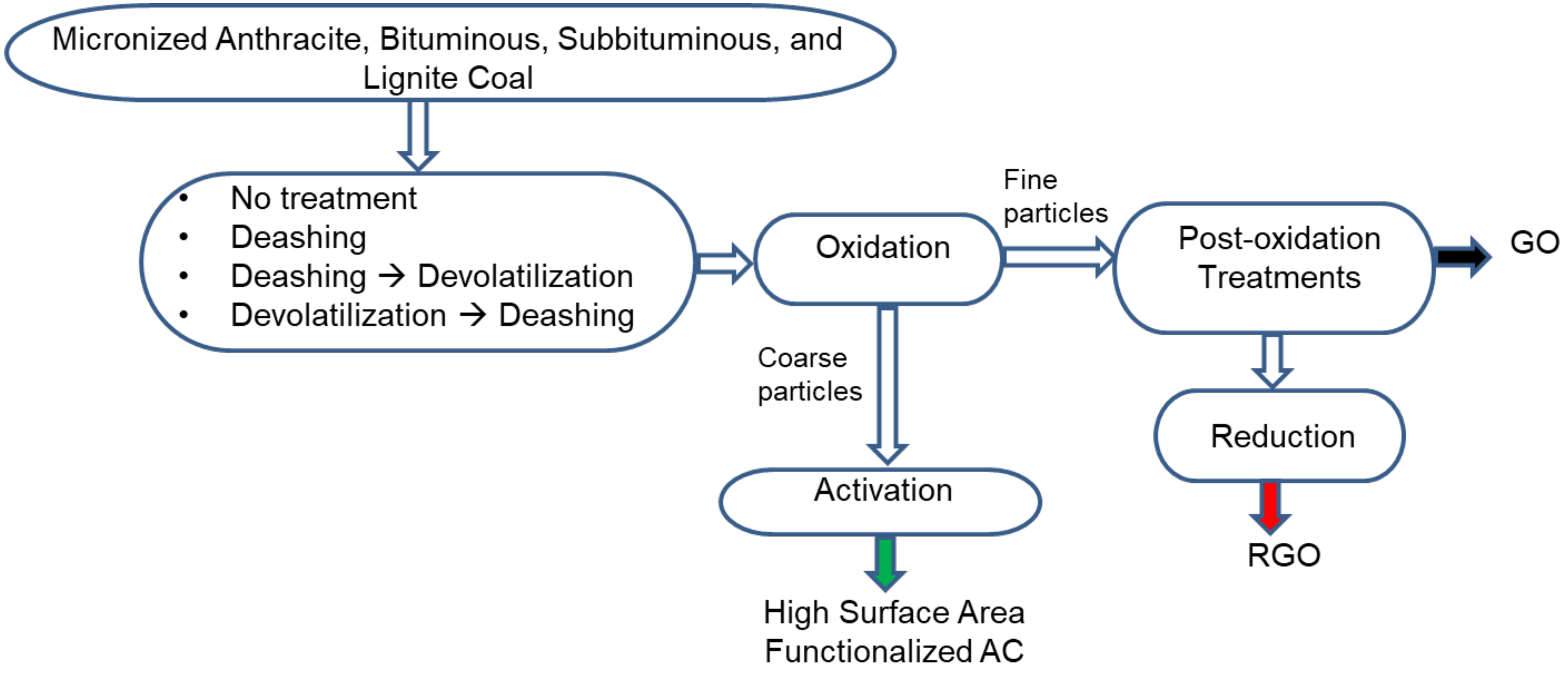


Sources: BP Statistical Review of World Energy, 2019; Crowson, Minerals Handbook 1996–97; Shin, FUEL, 1984, 63, 1187-1196; Navalon et al., Chem. Rev. 2014, 114, 6179−6212

Proposed Approach

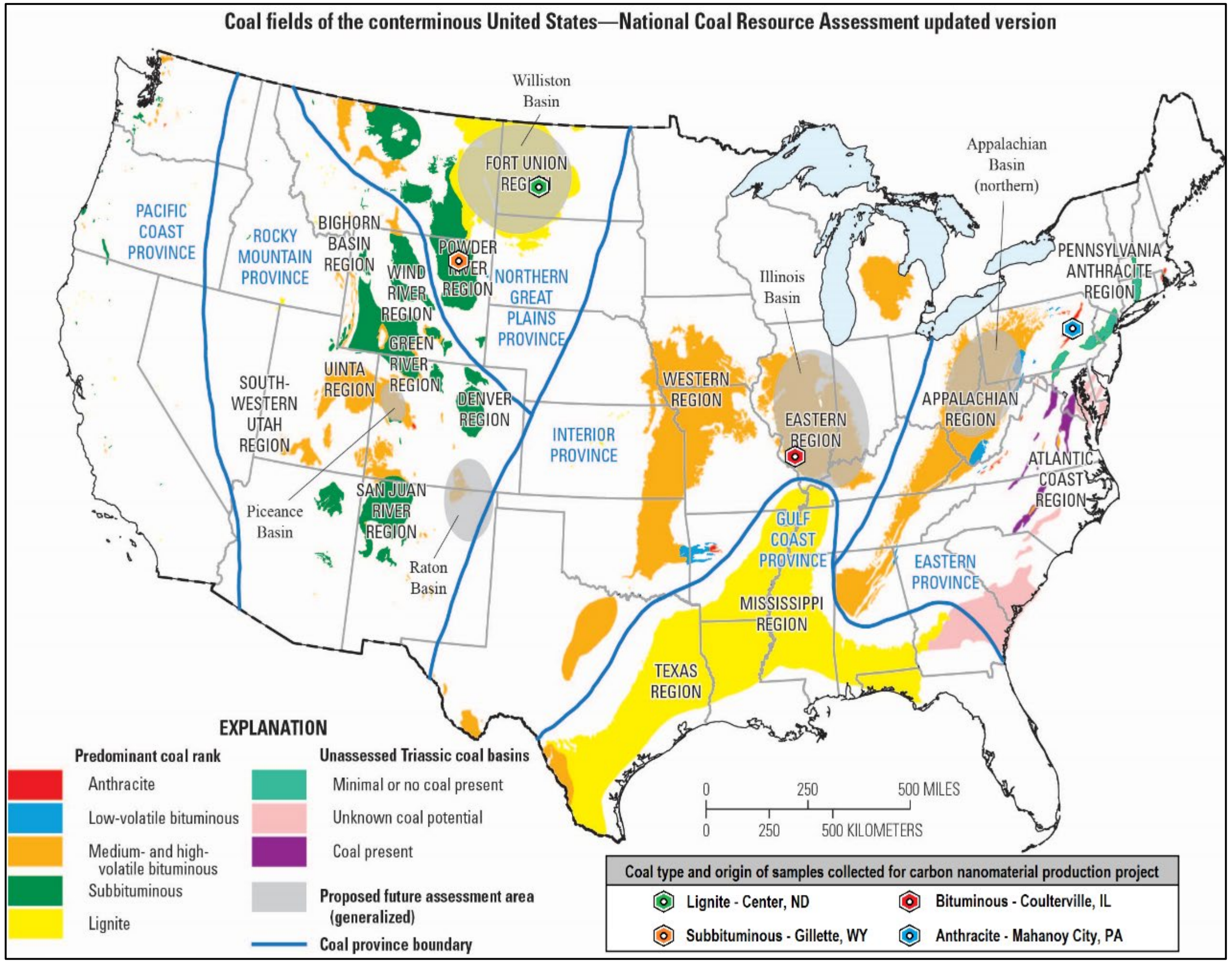
- ☐ Experimental approach
  - An integrated approach of deashing, oxidation, reduction, and activation stages to convert the coal feedstock to GO, RGO, and AC products
  - Chemicals used for deashing and oxidation are recovered and tested if they can be reused
  - Larger oxidized coal particles from the oxidation stage are activated to produce high surface area functionalized AC

- ☐ Techno-economic evaluation
  - Process simulation and cost estimation
  - Market analysis
  - Technology gap assessment



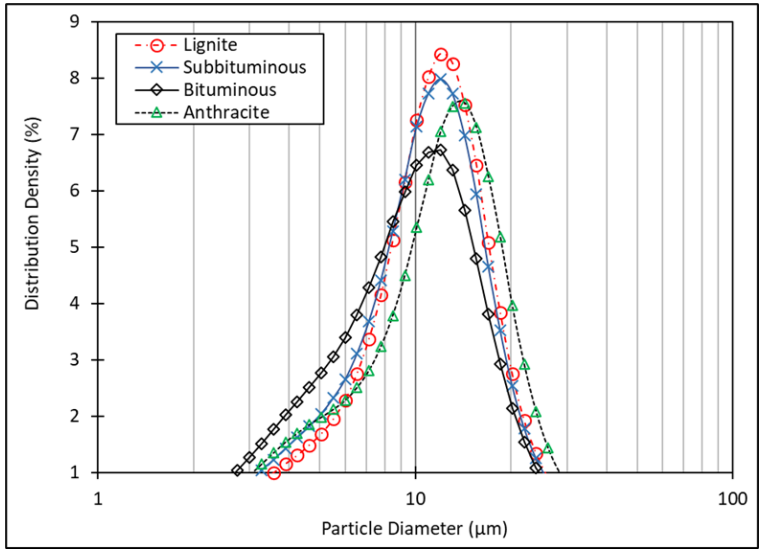
Coal Selection, Preparation, and Characterization

- Four coal samples (lignite, sub-bituminous, bituminous, and anthracite) are selected, prepared, and characterized



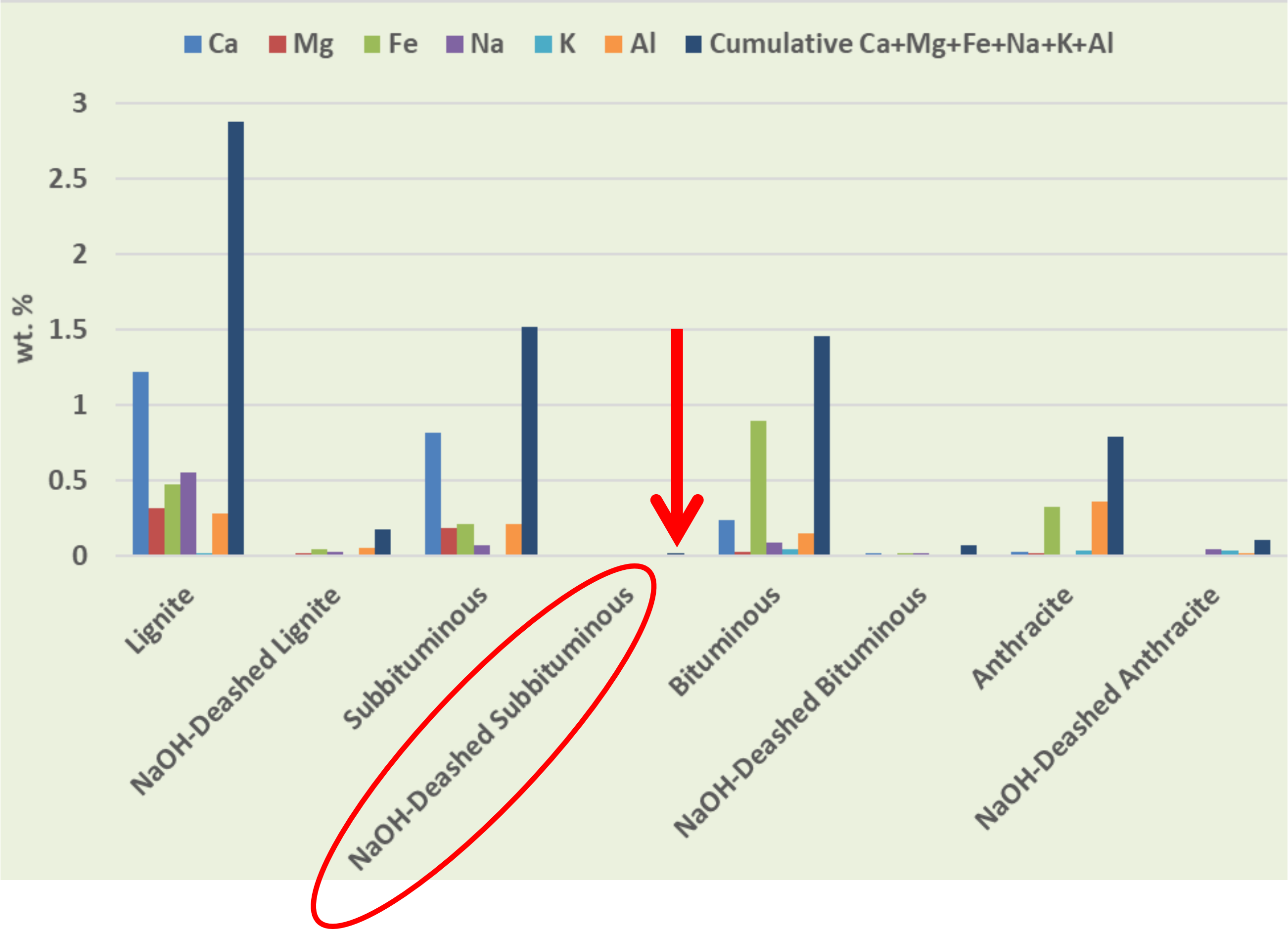
Sources of anthracite, bituminous, subbituminous, and lignite coal samples obtained from different U.S. coal mines are shown on the USGS coal resources map.

	Anthracite	Bituminous	Subbituminous	Lignite
Proximate Analysis (%) - Dry Basis				
Ash	9.5	10.5	6.1	10.3
Volatile	5.0	42.0	43.2	46.3
Fixed Carbon	85.5	47.5	50.7	43.3
Heating Value - Dry Basis				
BTU/lb	13,300	12,740	12,115	11,013
Ultimate Analysis (%) - Dry Basis				
Carbon	84.65	70.50	71.20	68.42
Hydrogen	2.00	5.00	4.90	4.49
Nitrogen	0.70	1.40	1.00	1.04
Sulfur	0.55	3.26	0.29	1.42
Ash	9.50	10.50	6.10	10.34
Oxygen	1.70	9.30	16.60	14.28
Chlorine	NA	0.08	< 0.01	< 0.01



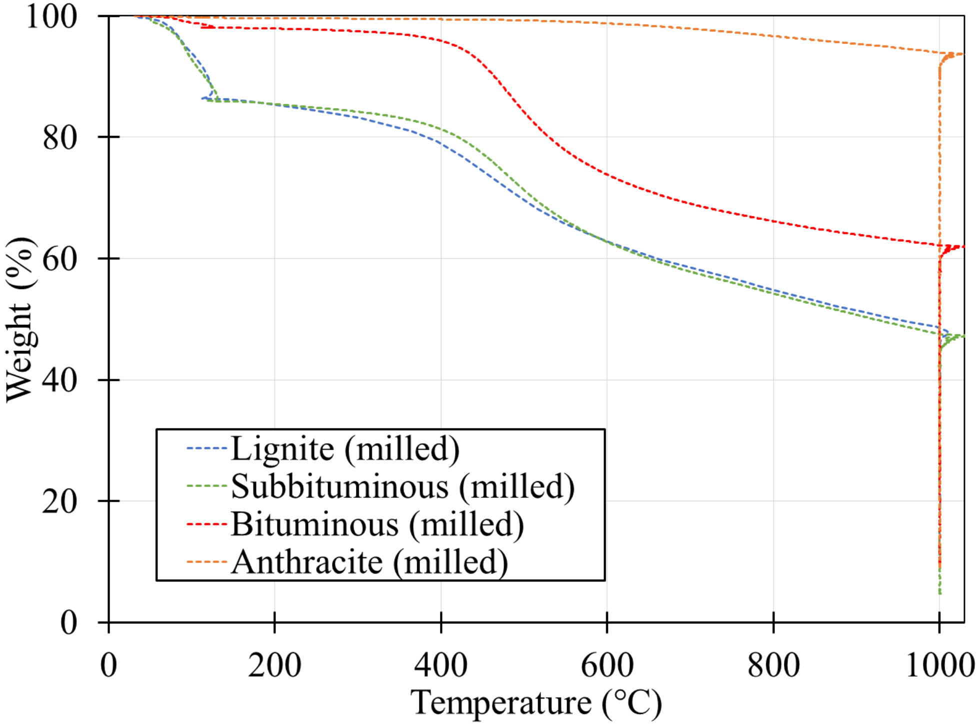
Coal Deashing by Molten NaOH

- As-received or devolatilized coal samples were deashed
- The effectiveness for removal of each major metal (i.e., Ca, Mg, Fe, K, Na, and Al) was up to 100%
- Cumulative removal of <u>Ca+Mg+Fe:</u> 96%-100%, exceeding 90% removal goal
- Cumulative removal of <u>Ca+Mg+Fe+K+Na+Al:</u> 86%-98%
- Sulfur removal: 65% to 100%.



Coal Devolatilization

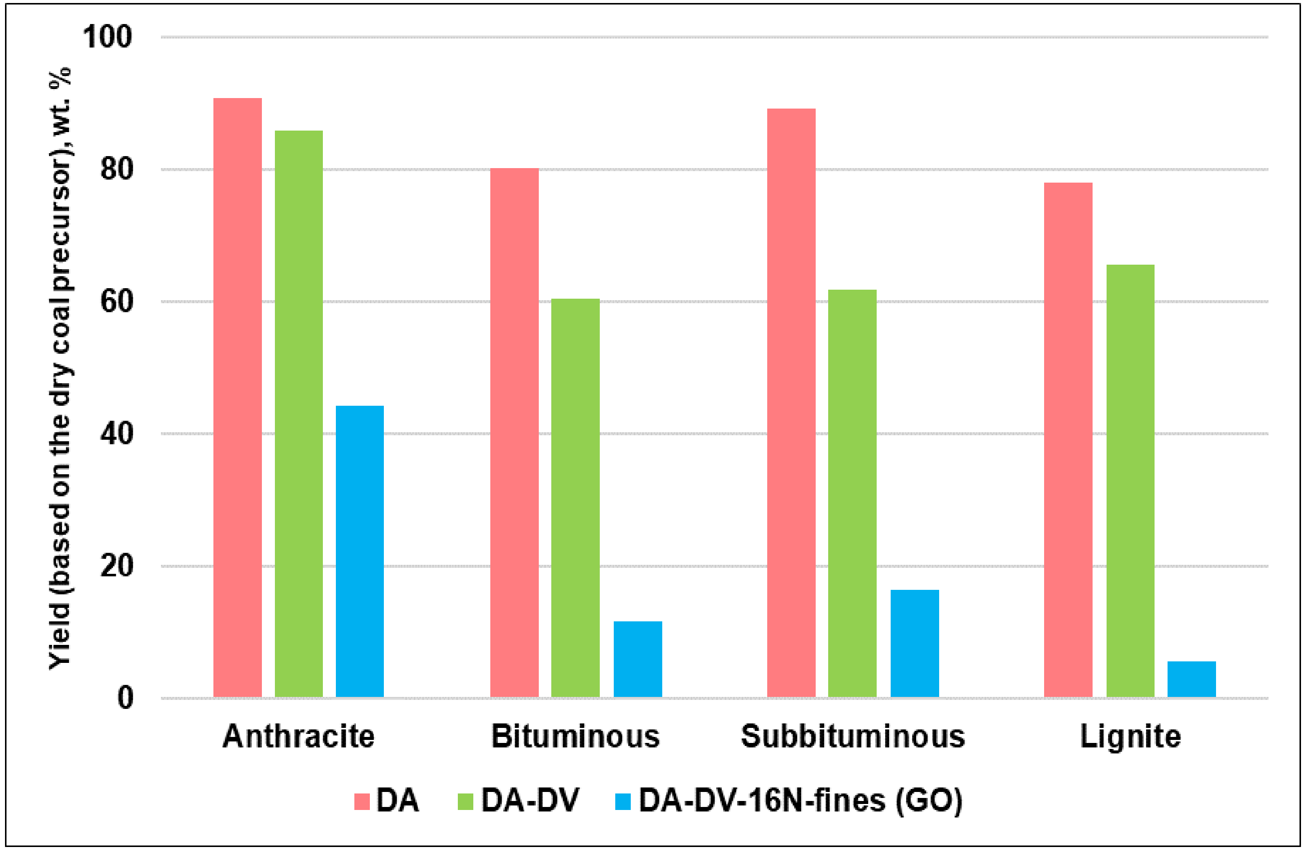
- TGA profiles of as-received coal samples showed a weight loss of ~ 7-47% (DB) for coal samples when heated to 1000 ºC (due to removal of volatile matter and decomposition of surface functionalities)
- As-received or deashed coal samples were devolatilized by pyrolysis under N_2 at 900 ºC
- Pre-oxidation treatment with air was performed for as-received bituminous coal
- Devolatilization resulted in development of porosity and a significant surface area for some samples (> 200 m^2/g)



Coal precursor	Thermal treatment	BET surface area (m^2/g)
Anthracite	None (as-received)	0.1
Anthracite	Devolatilization at 900 °C	13.0
NaOH-deashed anthracite	None	3.9
NaOH-deashed anthracite	Devolatilization at 900 °C	21.2
Lignite	None (as-received)	2.6
Lignite	Devolatilization at 900 °C	228.7
NaOH-deashed lignite	None	17.2
NaOH-deashed lignite	Devolatilization at 900 °C	142.9
Bituminous	None (as-received)	24.4
Bituminous	Oxidation at 250 °C followed by devolatilization at 900 °C	176.5
NaOH-deashed bituminous	None	9.8
NaOH-deashed bituminous	Devolatilization at 900 °C	40.4
Subbituminous	None (as-received)	23.5
Subbituminous	Devolatilization at 900 °C	204.3
NaOH-deashed subbituminous	None	10.3
NaOH-deashed subbituminous	Devolatilization at 900 °C	26.3

Coal Oxidation with Nitric Acid

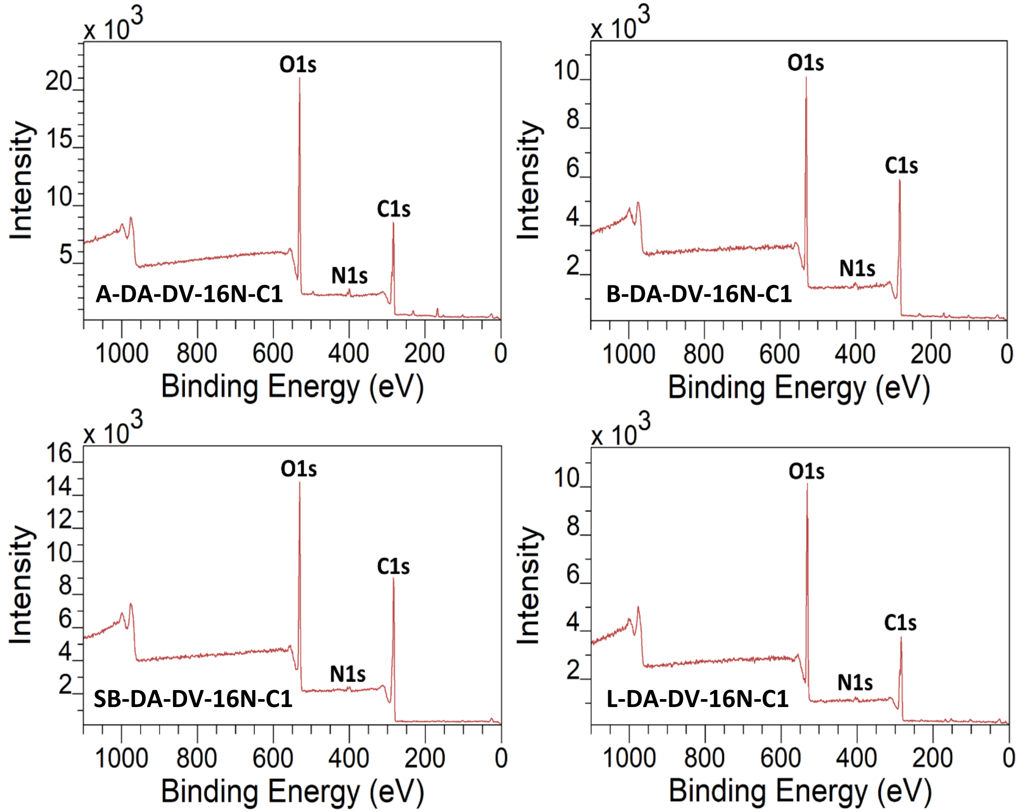
- Nitric acid oxidation
  - Simple approach to use just one oxidant and one-stage oxidation (vs. Hummers method that uses several oxidants with several oxidation steps) to reduce cost and address other safety or environmental concerns
  - The objective is to develop coal-based GO materials with surface chemistry similar to the graphite-based GO (as characterized by Raman spectra and XPS for oxygen functionalities)
  - Yield values of deashed-devolatilized (DA-DV) coal precursors oxidized with concentrated nitric acid (16N) varies based on the coal type



Characteristics of Oxidized Coal Samples (XPS)

- Several coal-based samples had similar or higher surface oxygen contents compared to a commercial graphite-based GO sample (CGO)
- Fine particles obtained from coal oxidation have significantly higher oxygen contents (about 10% higher) than coarse particles

Sample ID	Elemental Compositions (atom%)*			
	O	C	N	C/O
CGO	31.75	67.77	0.48	2.13
CGO-140°C	19.93	79.77	0.31	4
A-DA-DV-16N	33.61	63.4	2.99	1.88
B-DA-DV-16N	26.68	70.69	2.63	2.64
SB-DA-DV-16N	26.22	72.09	1.69	2.75
L-DA-DV-16N	34.53	63.2	2.27	1.83



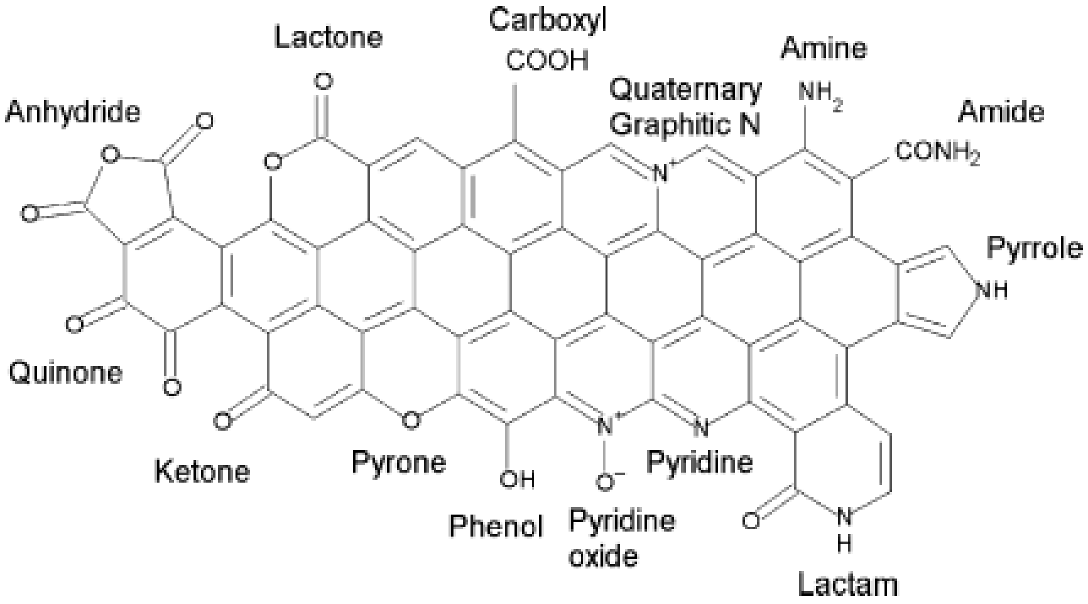
*Based on XPS surveys for O, C, and N elements only

Characteristics of Oxidized Coal Samples (XPS)

- An example of distributions of oxygen- and nitrogen-containing functionalities is shown below
- Coal-based nitrogen-doped GO samples may have different applications as advanced functionalized materials

Sample ID	O1s peak			
	Quinone	C-O	C=O	O-H
A-DA-DV-16N	7.37 %	39.55 %	51.54 %	1.54 %

Sample ID	N1s peak					
	Pyridinic-N	Pyrrolic-N	Graphitic-N	-NO	N-Ox	-NO_2
A-DA-DV-16N	2.73 %	22.83 %	41.09 %	1.97 %	27.55 %	3.83 %

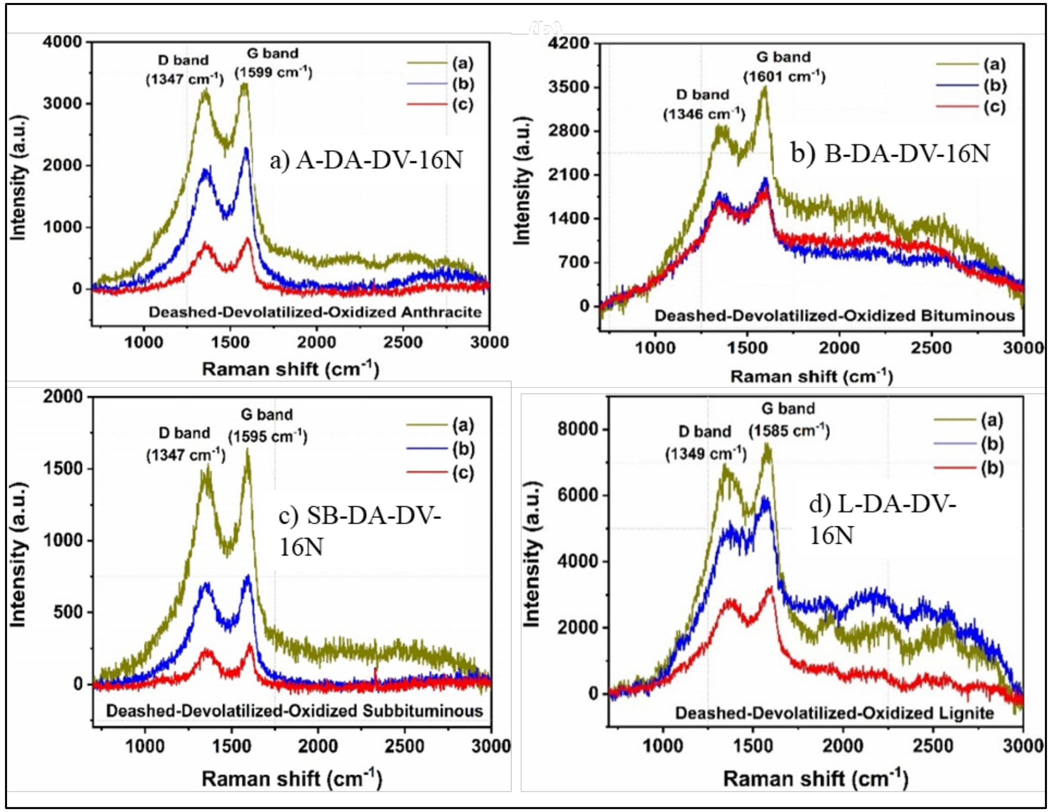


Arrigo et al. J. Am. Chem. Soc. 2010, 132, 9616-9630.

Characteristics of Oxidized Coal Samples (Raman Spectroscopy)

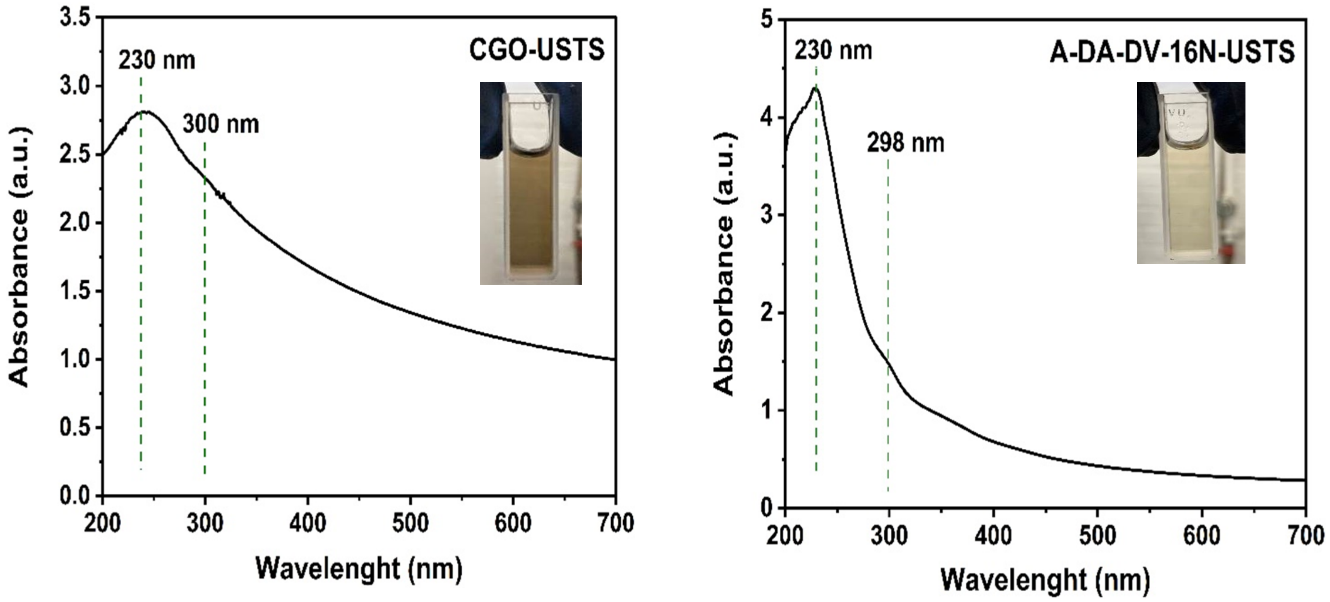
- Raman spectra of oxidized coal samples prepared by nitric acid oxidation showed characteristic D and G bands and I_D/I_G ratios similar to those of the baseline graphite-based GO
- Coal-based GO samples had oxygen contents of ~26-34%, well above the oxygen contents of similar graphite-based GO sample

Sample	Raman G band, cm^{-1}	Raman D band, cm^{-1}	Raman I_D/I_G ratio	O atm % (from XPS)
Commercial graphite-based GO (CGO)	**1347**	**1598**	**1.06 ± 0.07**	**31.75**
Commercial graphite-based GO dried at 140 °C (CGO-140°C)	**1348**	**1590**	**1.03 ± 0.04**	**19.93**
Anthracite-based GO (i.e., A-DA-DV-16N-fines dried at 140 °C)	**1347**	**1599**	**0.92 ± 0.05**	**33.61**
Bituminous-based GO (i.e., B-DA-DV-16N-fines dried at 140 °C)	**1346**	**1601**	**0.88 ± 0.05**	**26.68**
Subbituminous-based GO (i.e., SB-DA-DV-16N-fines dried at 140 °C)	**1347**	**1595**	**0.90 ± 0.01**	**26.22**
Lignite-based GO (i.e., L-DA-DV-16N-fines dried at 140 °C)	**1349**	**1585**	**0.89 ± 0.03**	**34.53**



Characteristics of Oxidized Coal Samples (UV-vis)

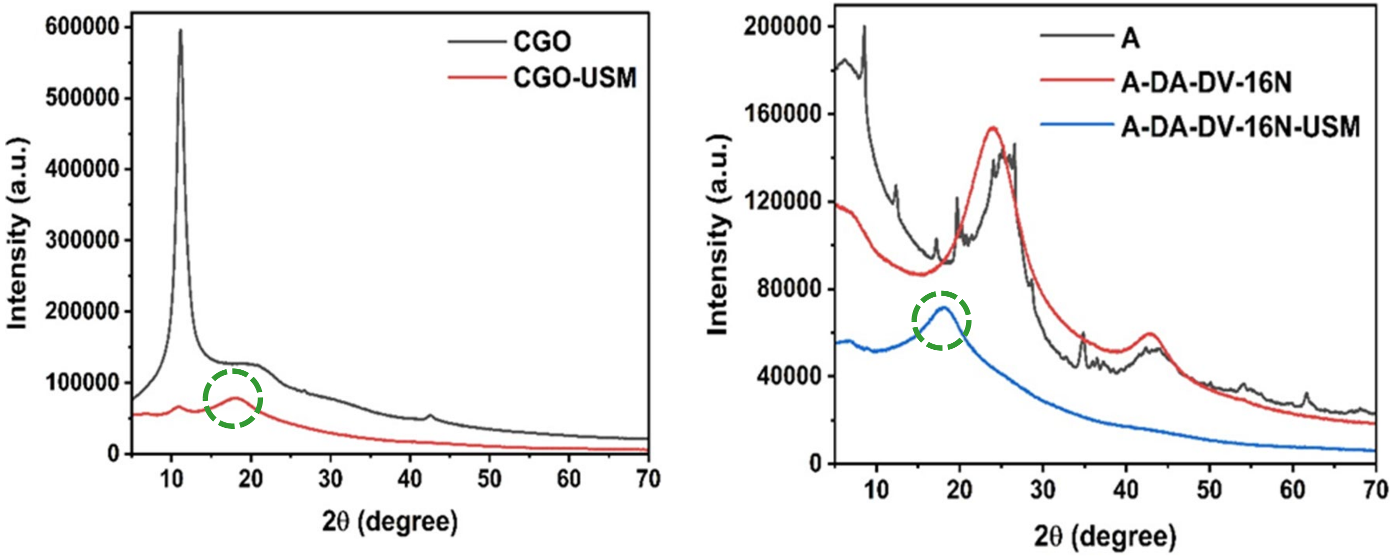
- The UV/Vis spectra of the majority of coal-based or graphite-based GO samples showed similar absorption peaks exhibiting the similarity of coal-based and graphite-based GO samples.
- The first and main peak at ~230 nm is attributed to the π-π* transitions of aromatic C-C bonds. The second minor peak at ~298 nm that is observed in some samples is assigned to the n-π* transitions of C=O bonds.



UV-Vis profiles of anthracite coal-based (A-DA-DV-16N) and graphite-based (CGO) GO samples obtained after ultrasonication of the samples in water.

Characteristics of Oxidized Coal Samples (XRD)

- XRD profiles of a graphite-based commercial GO (CGO), anthracite coal, coal-based GO (A-DA-DV-16N) and ultrasonicated GO samples (USM) samples were compared. The interlayer spacing (d) was evaluated using Bragg's equation. The crystallite size (D) was calculated according to the Scherrer's equation.
- The main peak of CGO was observed at ~11º while for the coal-based GO the main peak was at ~24º.
- Ultrasonicated graphite-based and coal-based samples showed similar XRD profiles.

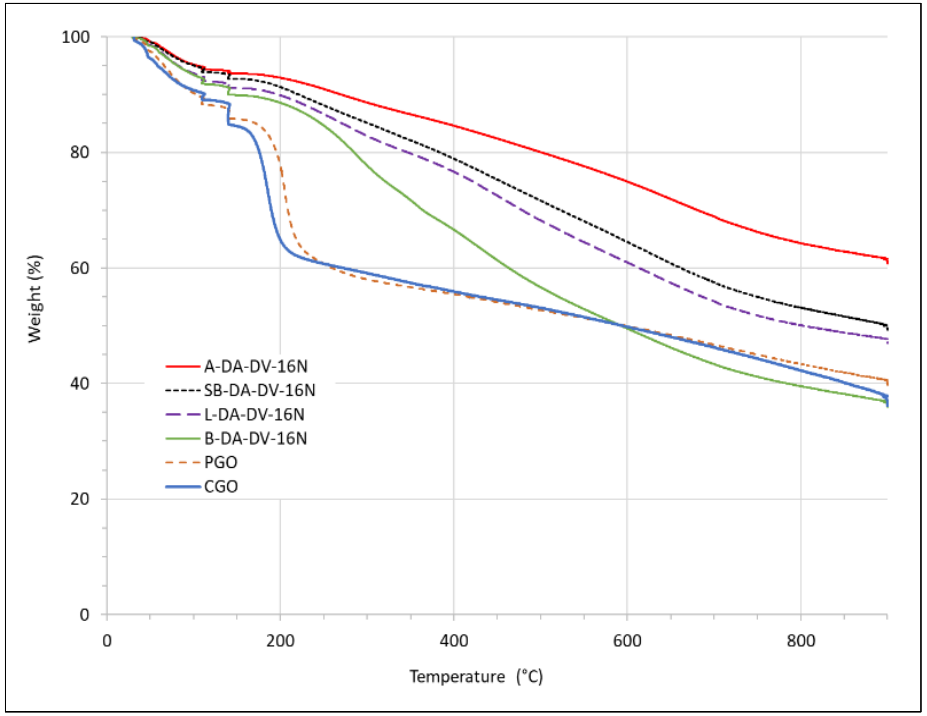


XRD profiles of anthracite coal-based (A-DA-DV-16N), graphite-based (CGO), and ultrasonicated (USM) GO samples.

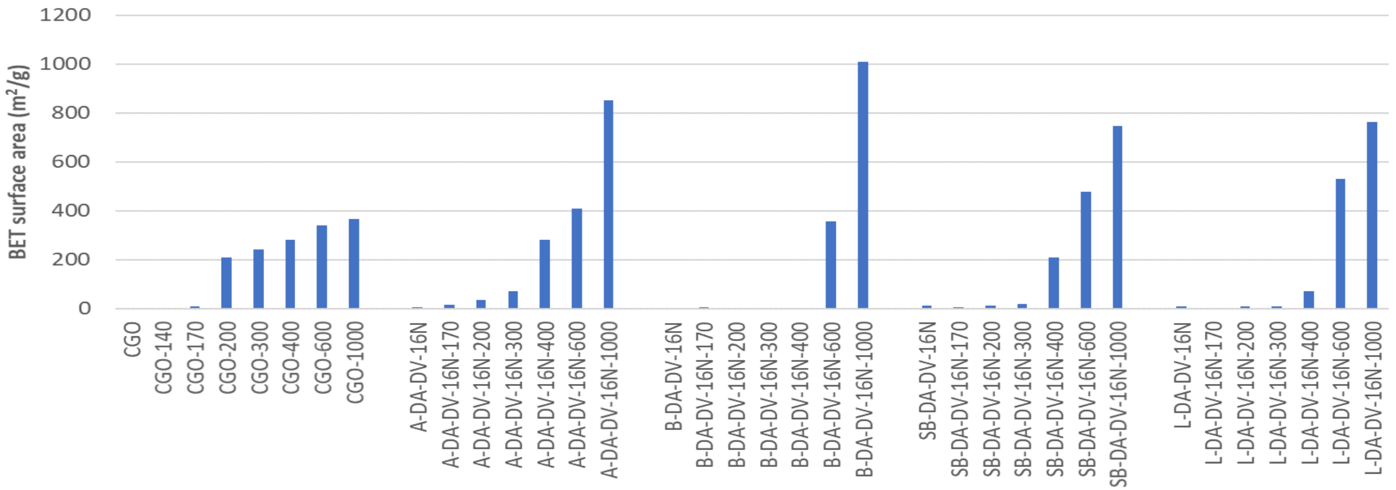
Sample ID	2θ angle for 002 peak (º)	Interlayer distance, d (nm)	Crystallite size, D (nm)	Number of layers, N
CGO	11.15	0.792	6.06	9
CGO-USM	18.15	0.488	1.26	3
A (Anthracite coal)	26.6	0.334	2.68	9
A-DA-DV-16N	24.25	0.366	2	6
A-DA-DV-16N-USM	18.1	0.489	1.37	4

Reduction of GO to RGO

- RGO samples were prepared by reduction of coal-based or graphite-based GO (CGO) under nitrogen at 170-1000 ºC.
- Thermogravimetric analysis (TGA) showed the extent of decomposition of surface functionalities suggesting that the coal-based and graphite-based GO samples have different distribution of surface oxygen functionalities that are removed at different temperatures.
- The BET surface area of coal-based RGO samples prepared at 1000 ºC were ~750-1000 m^2/g, more than twice the surface area of the graphite-based RGO prepared at the same condition.

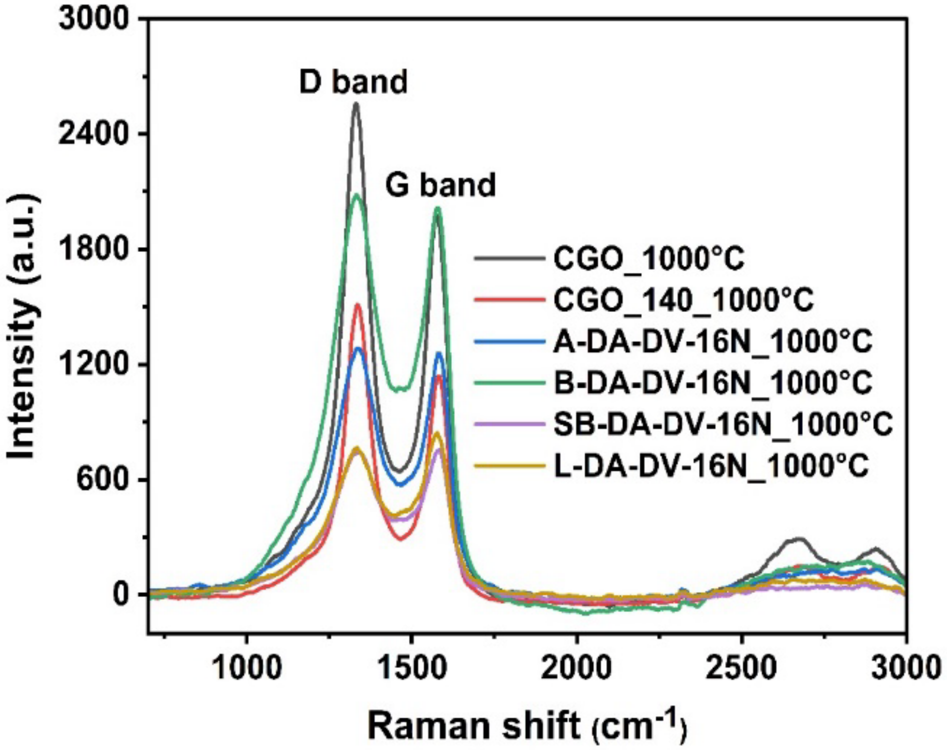


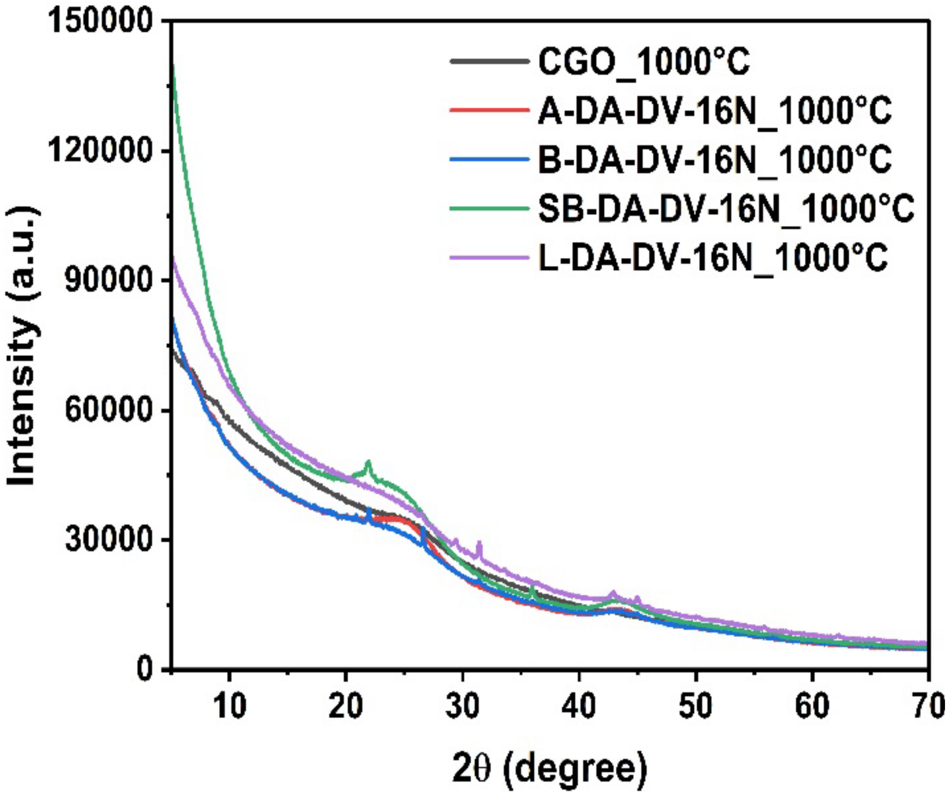
TGA profiles of coal-based and graphite-based GO samples under N_2 with a heating rate of 4 ºC/min. Samples were hold at 110 ºC and 140 ºC for 30 min.



Reduction of GO to RGO

- ❑ Raman spectra revealed similar D and G bands for RGO samples prepared from reduction of coal-based or graphite-based GO. Similar broad 2D bands were also observed for these samples.
- ❑ XRD samples of both graphite-based and coal-based samples also showed similar profiles.

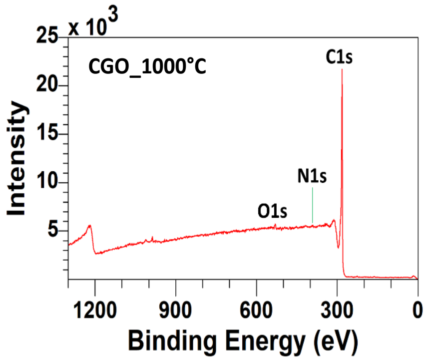


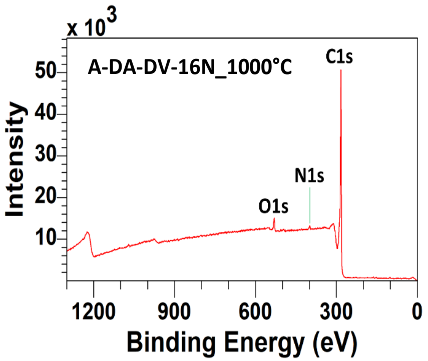


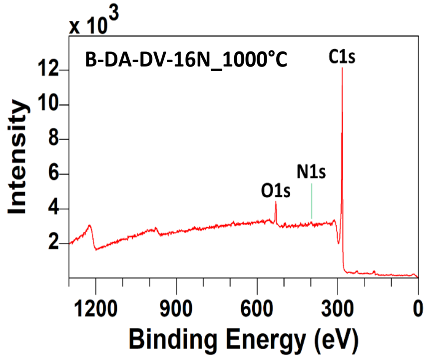
Reduction of GO to RGO

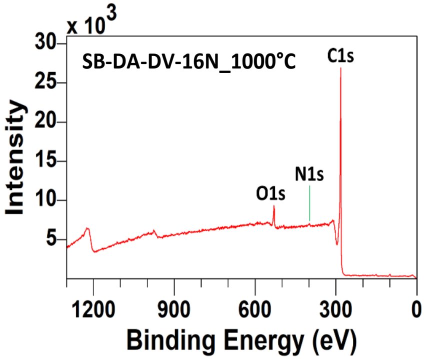
- XPS results show that the carbon content of four coal-based RGO prepared at 1000 ºC under nitrogen was ~95-97%, well above the 85% target level. In comparison the graphite-based baseline sample (i.e., CGO-1000 ºC) had a carbon content of ~ 99%.
- Nitrogen content of coal-based samples reduced significantly from 1.7-3% (before reduction) to 0.5-0.9% after reduction but the nitrogen contents of coal-based RGO samples were 3-6 times higher than that of the graphite-based RGO.
- Additional experimental work is planned to perform reduction under a reducing atmosphere.

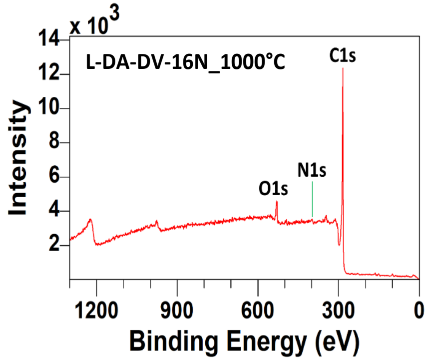
Sample ID	**Elemental Compositions (at.%)**			
	O	C	N	C/O
CGO_1000°C	0.80	99.05	0.15	123
A-DA-DV-16N_1000°C	2.52	96.62	0.86	38.34
B-DA-DV-16N_1000°C	3.60	95.48	0.92	26.52
SB-DA-DV-16N_1000°C	4.13	95.35	0.52	23.08
L-DA-DV-16N_1000°C	4.50	94.82	0.68	21.07











Preparation of Functionalized Activated Carbon

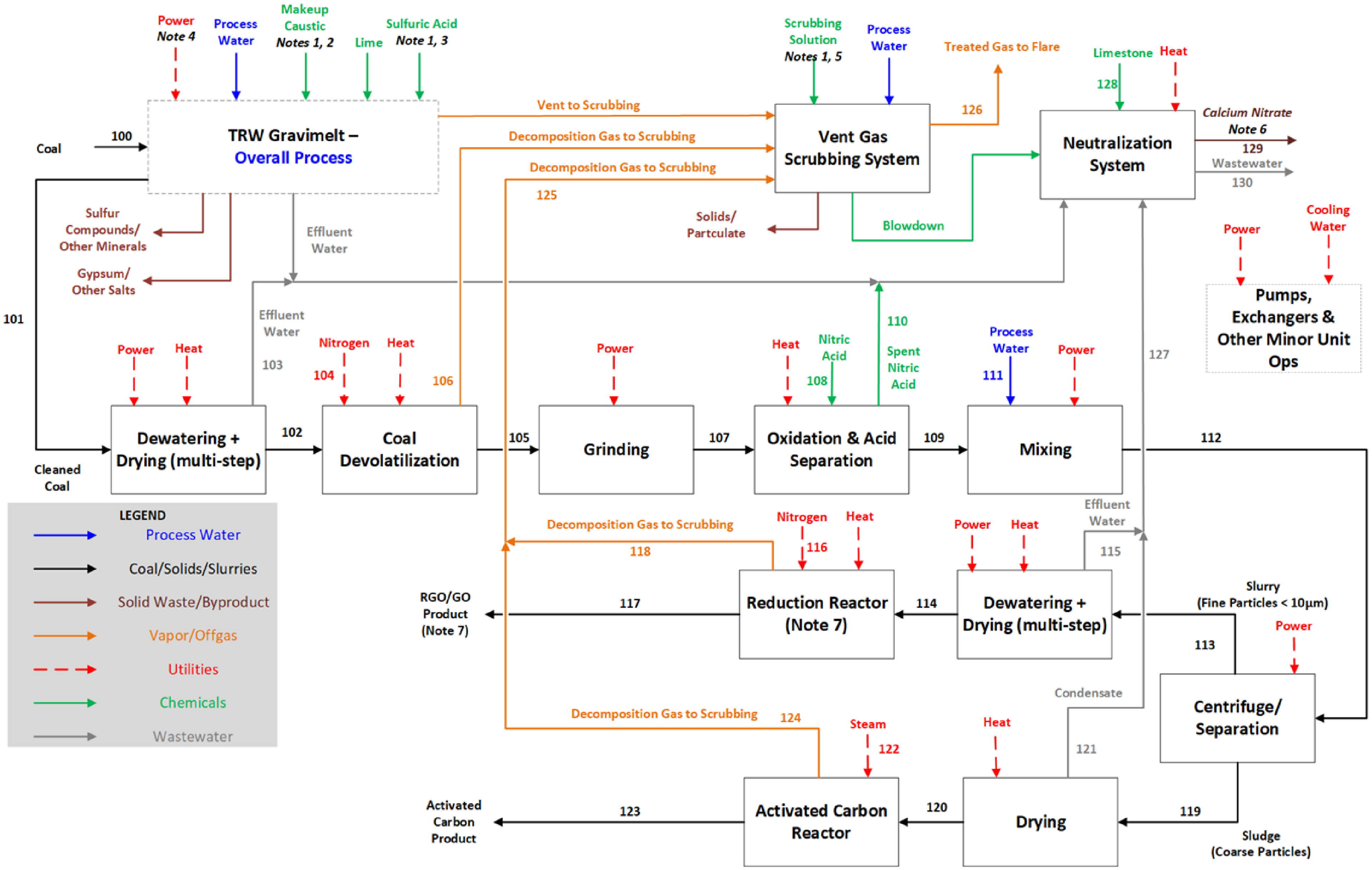
- Larger particles of oxidized coal samples are activated under different conditions to produce high surface area functionalized activated carbon.
- Depending on the precursor type and activation conditions, some ACs had surface areas exceeding 1500 m^2/g and pore volumes more than 1 cm^3/g with different pore size distributions (e.g., highly microporous or different combinations of micro- and mesoporosity).
- High surface area functionalized activated carbons prepared from oxidized coal may have different applications in gas or liquid filtration, water treatment, catalyst applications, supercapacitors, etc.
- The high performance of some of developed materials for supercapacitor application was confirmed through charge storage experiments and comparison with baseline commercial materials.

Activated carbon precursor	**Surface area and porosity of activated carbons developed from oxidized coal samples**			
	BET surface area (m^2/g)	**Total pore volume (cm^3/g)**	**Micropore volume (cm^3/g)**	**Meso+macropore volume (cm^3/g)**
SB-16 N-C	1440.7	0.670	0.568	0.102
A-16 N-C	811.9	0.362	0.346	0.016
B-16 N-C	1147.5	0.548	0.455	0.094
SB-DA-16 N-C	1038.2	0.491	0.443	0.048
B-DA-16 N-C	1145.0	0.522	0.479	0.044
B-DA-DV-16 N-C	1169.1	1.171	0.454	0.717
L-DA-DV-16 N-C	1056.8	0.631	0.418	0.213
SB-DA-DV-16 N-C	1556.3	1.029	0.604	0.425

Technoeconomic Analysis

- Develop design basis.
- Develop block flow diagram, table of input/output streams, and associated material balance table.
- Develop process flow diagram and equipment list.
- Develop heat and material balance tables (including any necessary process simulation).
- Perform sizing and capital cost estimation.
- Generate overall process economics results for all cases.

Process Block Flow Diagram



Power *Note 4*

Process Water

Makeup Caustic *Notes 1, 2*

Lime

Sulfuric Acid *Note 1, 3*

Coal

100

TRW Gravimelt – Overall Process

101

Sulfur Compounds/ Other Minerals

Gypsum/ Other Salts

Effluent Water

Vent to Scrubbing

Decomposition Gas to Scrubbing

Decomposition Gas to Scrubbing

125

Scrubbing Solution *Notes 1, 5*

Process Water

Treated Gas to Flare

126

Vent Gas Scrubbing System

Solids/ Partculate

Blowdown

Limestone

128

Heat

Neutralization System

Calcium Nitrate Note 6

129

Wastewater

130

Cooling Water

Power

Pumps, Exchangers & Other Minor Unit Ops

127

Effluent Water

103

Power

Heat

Cleaned Coal

Dewatering + Drying (multi-step)

102

Nitrogen

104

Heat

106

Coal Devolatilization

105

Power

Grinding

107

Heat

Nitric Acid

108

110

Spent Nitric Acid

Oxidation & Acid Separation

109

Process Water

111

Power

Mixing

112

Effluent Water

115

Decomposition Gas to Scrubbing

118

Nitrogen

116

Heat

Power

Heat

RGO/GO Product (Note 7)

117

Reduction Reactor (Note 7)

114

Dewatering + Drying (multi-step)

Slurry (Fine Particles < 10µm)

113

Power

Centrifuge/ Separation

Condensate

Decomposition Gas to Scrubbing

124

Steam

122

Heat

121

Activated Carbon Product

123

Activated Carbon Reactor

120

Drying

119

Sludge (Coarse Particles)

LEGEND

Process Water

Coal/Solids/Slurries

Solid Waste/Byproduct

Vapor/Offgas

Utilities

Chemicals

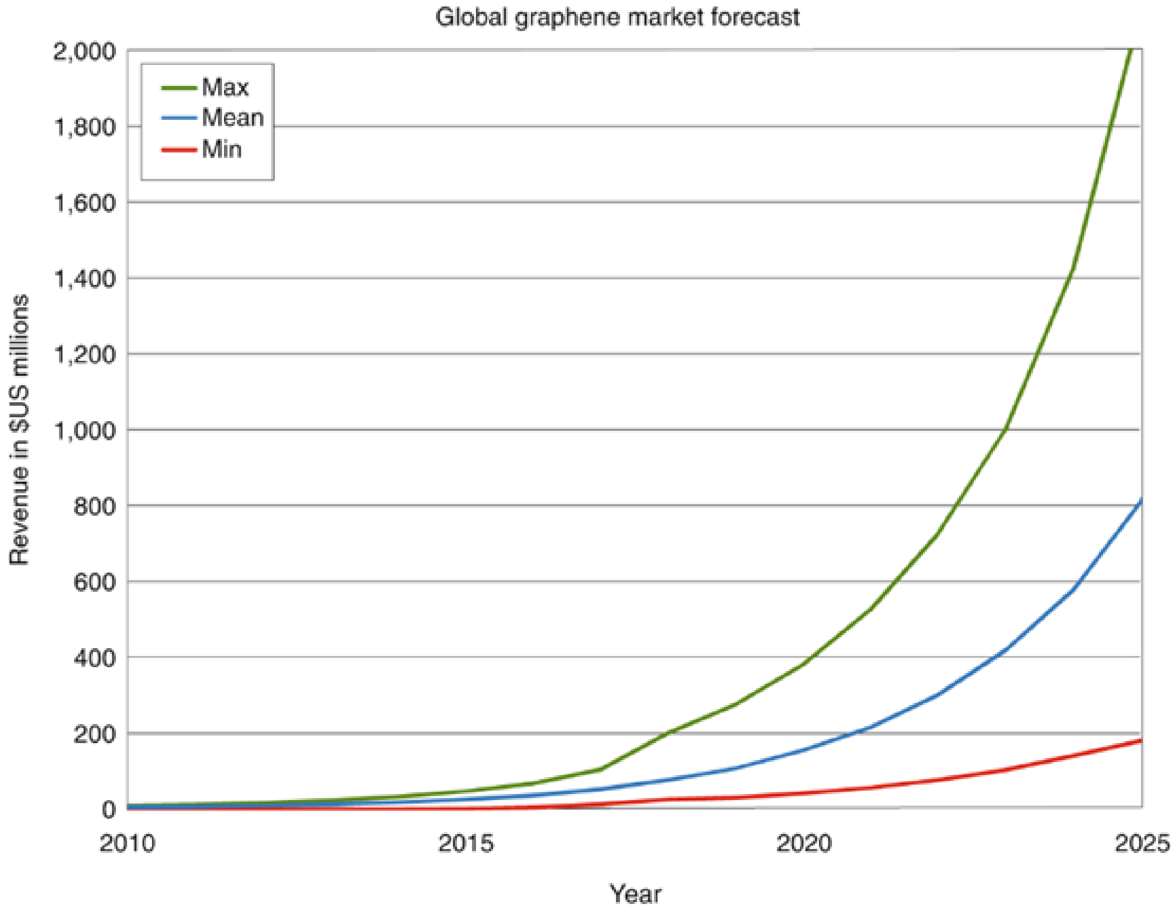
Wastewater

Main Input/Output Streams

ITEM	INPUT/OUTPUT	UNIT OPERATION/PROCESS
Utilities		
Power	Input	TRW Gravimelt (multiple unit ops)
Power	Input	Cleaned Coal Dewatering
Power	Input	Coal Grinding
Power	Input	Oxidized/Washed Coal Centrifuge
Power	Input	Slurry Dewatering Upstream of RGO Reactor
Power	Input	Other unit ops (pumps, conveying, etc.)
Heat	Input	Cleaned Coal Drying Step
Heat	Input	Coal Devolatilization
Heat	Input	Oxidation Reactor
Heat	Input	Coarse Coal Sludge Drying Step
Heat	Input	Fine Coal Slurry Drying Step
Heat	Input	Reduction Reactor
Heat	Input	Neutralization System
Steam	Input	Activated Carbon Reactor
Nitrogen	Input	Coal Devolatilization
Nitrogen	Input	Reduction Reactor
Cooling Water	Input	TBD
Process Water		
Process Water	Input	Gravimelt (water wash and acid wash steps)
Process Water	Input	Mixing/downstream of Oxidation
Process Water	Input	Vent Gas Scrubbing
Chemicals		
Caustic	Input	Gravimelt (Caustic Concentration Section)
Lime	Input	Gravimelt (Caustic Regeneration Section)
Sulfuric Acid	Input	Gravimelt (Acid Wash)
Limestone	Input	Acid Neutralization
Scrubbing Solution	Input	Vent Gas Scrubbing
Solid Waste		
Sulfur Compounds/Mineral Matter	Output	Gravimelt (Caustic Regeneration Section)
Gypsum/Other Salts	Output	Gravimelt (WW Treatment Section)
Solids/Particulate	Output	Vent Gas Scrubbing System
Liquid Effluent		
Gravimelt treated water	Output	Gravimelt (WW Treatment Section)
Wastewater	Output	Cleaned Coal Dewatering/Drying
Wastewater	Output	Fine Particle Slurry Dewatering/Drying
Wastewater	Output	Cleaned Coal Dewatering/Drying
Wastewater	Output	Neutralization System
Vent Gas Streams		
Scrubbed vent to flare	Output	Vent gas scrubbing
Products/Co-Products		
Activated Carbon (AC)	Output	Activated Carbon Reactor
Graphene Oxide (GO)/Reduced GO	Output	Reduction Reactor
Calcium Nitrate	Output	Acid Neutralization

Market Analysis

- ❑ Properties and applications of graphene and related materials (GRM)
  - ➢ Properties and production methods
  - ➢ Current and short-term GRM applications: composites, inks and coatings
  - ➢ Emerging and future GRM applications: batteries, energy storage, etc.
- ❑ Economics analysis of GRM
  - ➢ Current global market conditions (~200 million $US)
  - ➢ Projected market conditions (expected compound annual growth rate of ~40%)

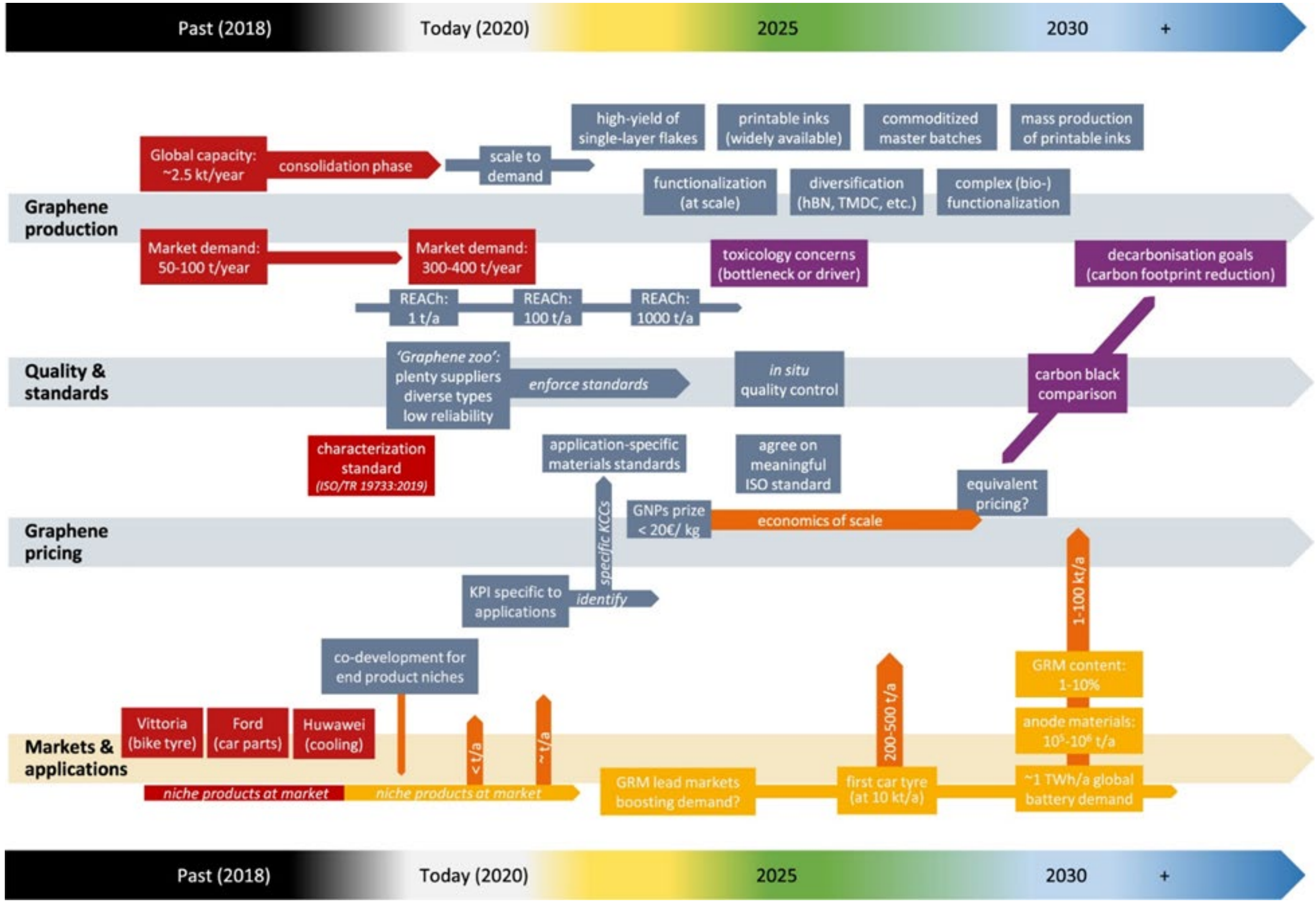


Graphene market growth estimations from 20 different market reports (Source: T. Reiss et al. Nature Nanotechnology 2019,14, 904-910)

Technology Gap Assessment

- Major general gaps in GRM
  - High material cost
  - Immature industry standards for quality of GRM
  - Lack of demand, killer application

- Major gaps in coal-based GRM
  - Process development and optimization for different types of coal
  - Product quality
  - Side-by-side comparison of coal-based and graphite-based GRM for different applications
  - Technoeconomic analysis, cost estimation, and pilot (and higher level) implementation



Roadmap for the industrialization of GRM (Source: H. Doscher et al. 2021 2D Mater. 8 022005)

Tasks to be completed

- Process simulation and cost estimation
- Market analysis for the graphene and activated carbon products
- Technology gap assessment
- Additional experimental work

Summary and Conclusions

- ☐ Experimental work performed includes coal preparation, removal of coal impurities, coal devolatilization, coal oxidation, AC preparation, reduction, and an extensive physicochemical characterization.
- ☐ Coal-based materials and a baseline graphite-based commercial GO were extensively characterized side-by-side.
- ☐ A one-step oxidation method by concentrated nitric acid produces materials with similar or higher oxygen contents but significantly higher nitrogen contents than those of the graphite-based samples prepared by Hummers' method.
- ☐ Coal-based and graphite-based samples had similar Raman spectra (D and G bands) and exhibited similar UV-Vis absorption peaks.
- ☐ The carbon content of four coal-based RGO prepared at 1000 ºC under nitrogen was ~95-97%, well above the 85% target level. Coal-based and graphite-based RGO samples exhibited similar Raman and XRD profiles.
- ☐ A TEA work is in progress to estimate the cost of coal-based nanomaterials production.
- ☐ Market analysis reports suggest a CAGR of 40% for GRM. Short-term applications include composites, inks and coatings but energy storage application appears to be a potential long-term application.
- ☐ Several gaps need to be filled to secure a reliable market for GRM.

Acknowledgement, Disclaimer, and Contact Information

- Acknowledgment: This material is based upon work supported by the Department of Energy Award Number DE-FE0031798.

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