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

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National Energy Technology Laboratory, U.S. Department of Energy

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Project Review Meeting
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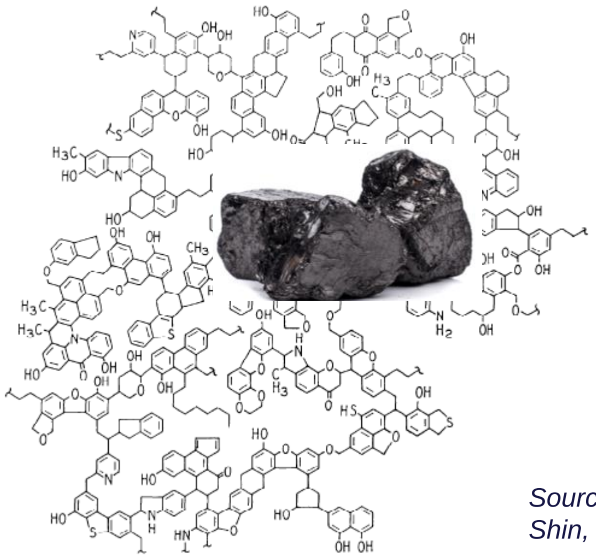
Outline

- Background
- Project description and objectives
  - Objective and scope
  - R&D gaps
  - Description of the proposed approach
- Project update
  - Results
  - Accomplishments and challenges
- Project next steps
  - Experimental work
  - Techno-economic analysis
  - Market evaluation and technology gap assessment
- Concluding remarks

Conversion of Coal to GO and RGO

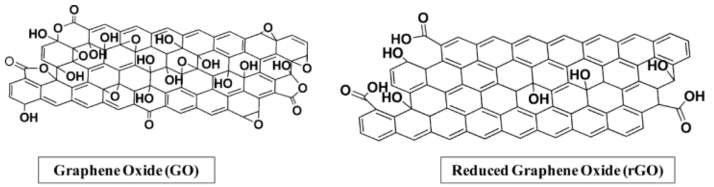
- ❑ It is possible to produce graphene oxide (GO) and reduced graphene oxide (RGO) from coal, but several R&D gaps need to be addressed
- ❑ Coal vs. graphite precursor for GO production: Opportunities
  - ➢ Low cost of precursor: ~$40/ton coal vs. ~$1,000/ton graphite
  - ➢ Availability: huge world coal 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
  - ➢ Others

Reactive model of coal structure: J. H. Shinn



Oxidation *Reduction*

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

Project Objective, Scope, and Collaboration with Industry

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 will be extensively characterized, and the impact of the coal feedstock type on the yield and quality of each product will be determined
    - Techno-economic analysis, market evaluation for graphene materials, and technology gap analysis

Industry Collaboration

- Peabody Energy collaborates with the UIUC team on selection/collection of coal samples and by providing insight on commercial advice and support

Research Gaps in Coal-to-Graphene Materials R&D

Current main gaps in coal-to-graphene R&D	Proposed approach to advance the state of the art
1. Lack of systematic work on GO and RGO production from different types of coal with different compositions	• Four types of coal (lignite, subbituminous, bituminous, and anthracite) will be systematically treated according to the proposed oxidation and reduction stages to produce GO, RGO, and AC
2. Lack of a clear strategy for removing coal ash and preventing the contamination of graphene products with ash impurities	• A deashing process before the oxidation stage is included in the proposed approach
3. Absence of any work on the benefit of removing volatile matter from coal before oxidation in the manufacturing process of graphene materials	• Coal samples will be devolatilized or used without devolatilization before oxidation to understand the impact of volatile matter on product yield and quality

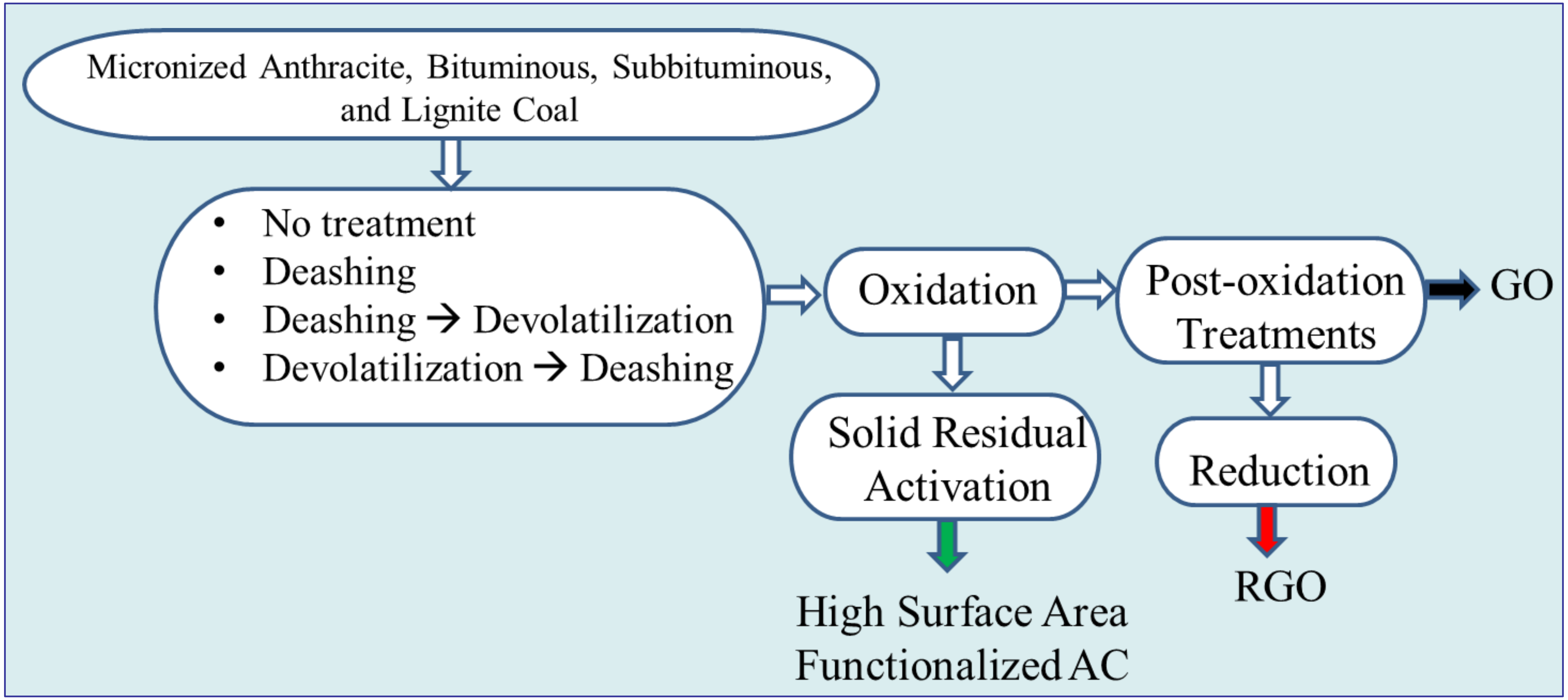
Research Gaps in Coal-to-Graphene Materials R&D

Current main gaps in coal-to-graphene R&D	Proposed approach to advance the state of the art
4. Absence of any approach for the conversion of solid by-products (e.g., residual chars) to other high-value products	• Solid by-products will be converted to AC sorbents to eliminate the generation of a carbon solid waste and to generate additional income for the plant
5. Absence of any approach for recycling and reusing oxidants or chemicals in the process	• Chemicals used for coal deashing and oxidation will be recovered and recycled for reuse
6. Lack of data on the performance of domestic U.S. coals for graphene production	• The focus of this work is on all four types of domestic U.S. coal
7. Lack of a techno-economic evaluation and market assessment	• A technoeconomic evaluation and market analysis are included in this work
8. Lack of a feasibility study on large-scale production	• A process simulation and cost estimation will be conducted for a 20 ton of coal/day plant

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
  - Solid residuals 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


Micronized Anthracite, Bituminous, Subbituminous, and Lignite Coal

- No treatment
- Deashing
- Deashing → Devolatilization
- Devolatilization → Deashing

Oxidation

Post-oxidation Treatments

GO

Solid Residual Activation

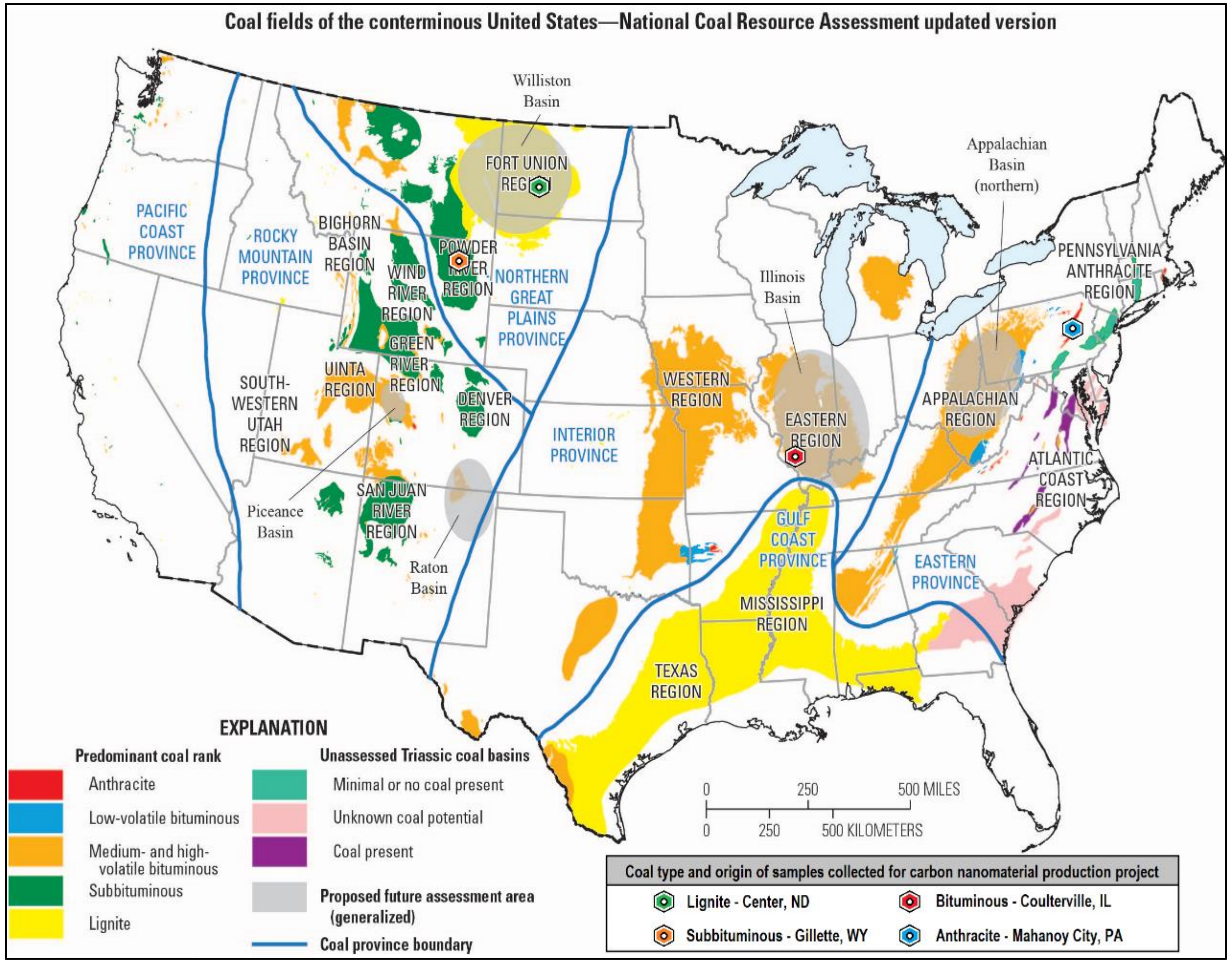
Reduction

RGO

High Surface Area Functionalized AC

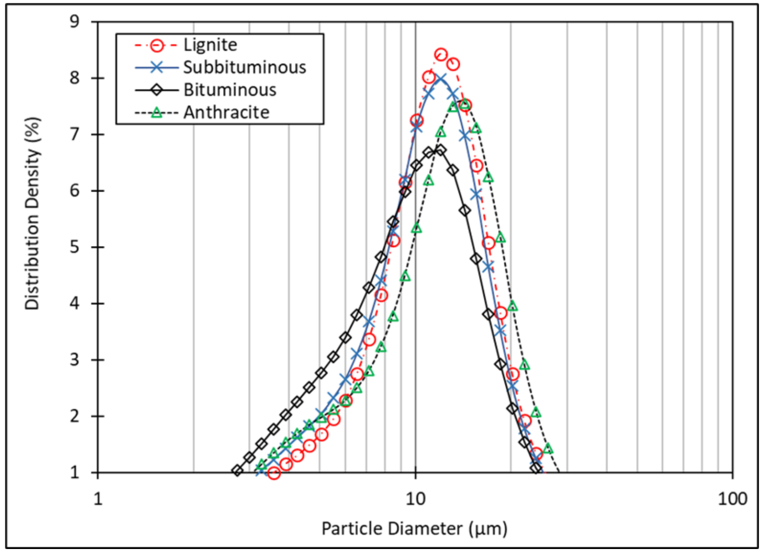
Coal Selection, Preparation, and Characterization

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



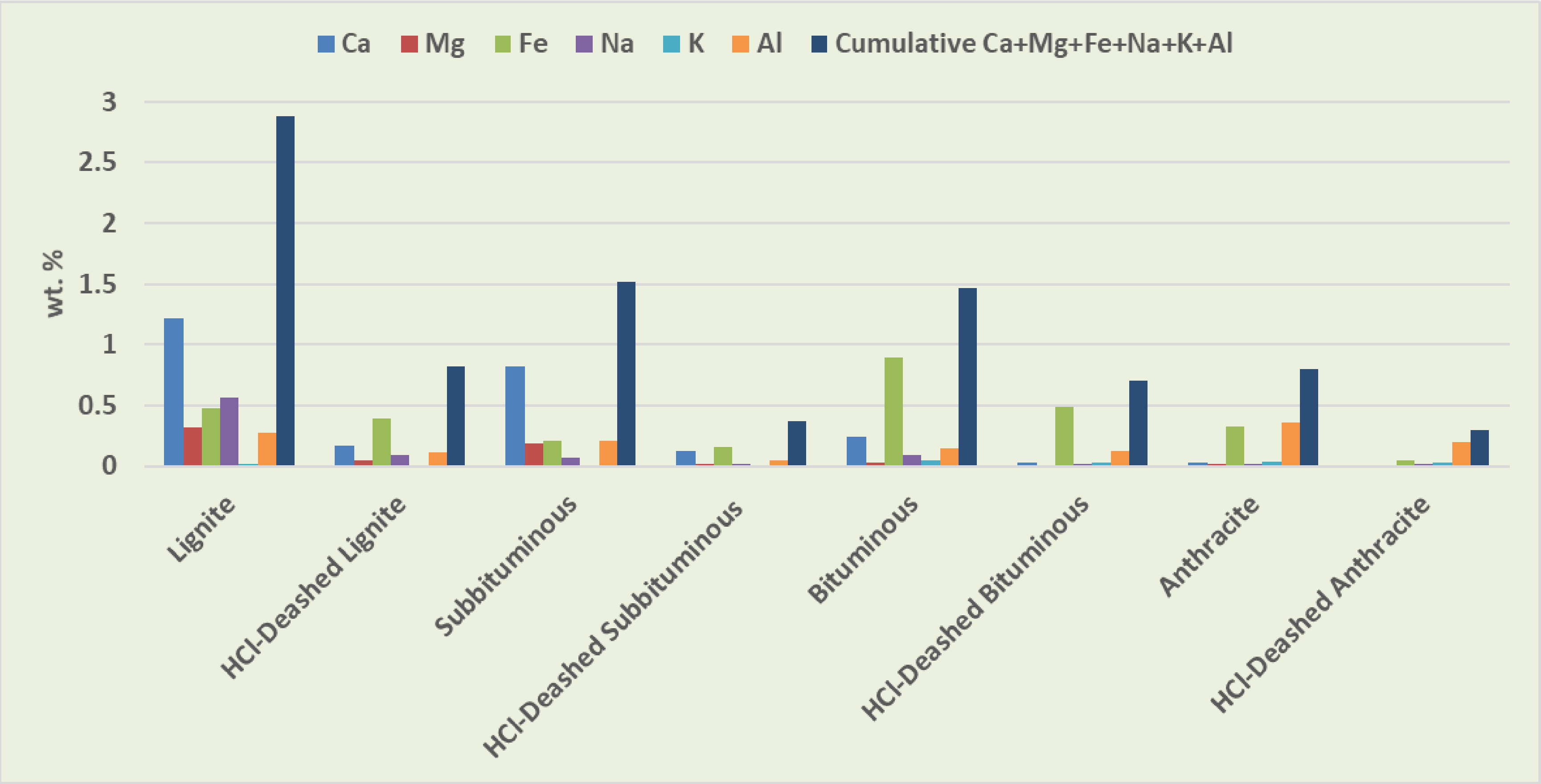
Sources of anthracite, bituminous, subbituminous, and lignite coal samples obtained from different U.S. coal mines are shown on the USGS coal resources map.

	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



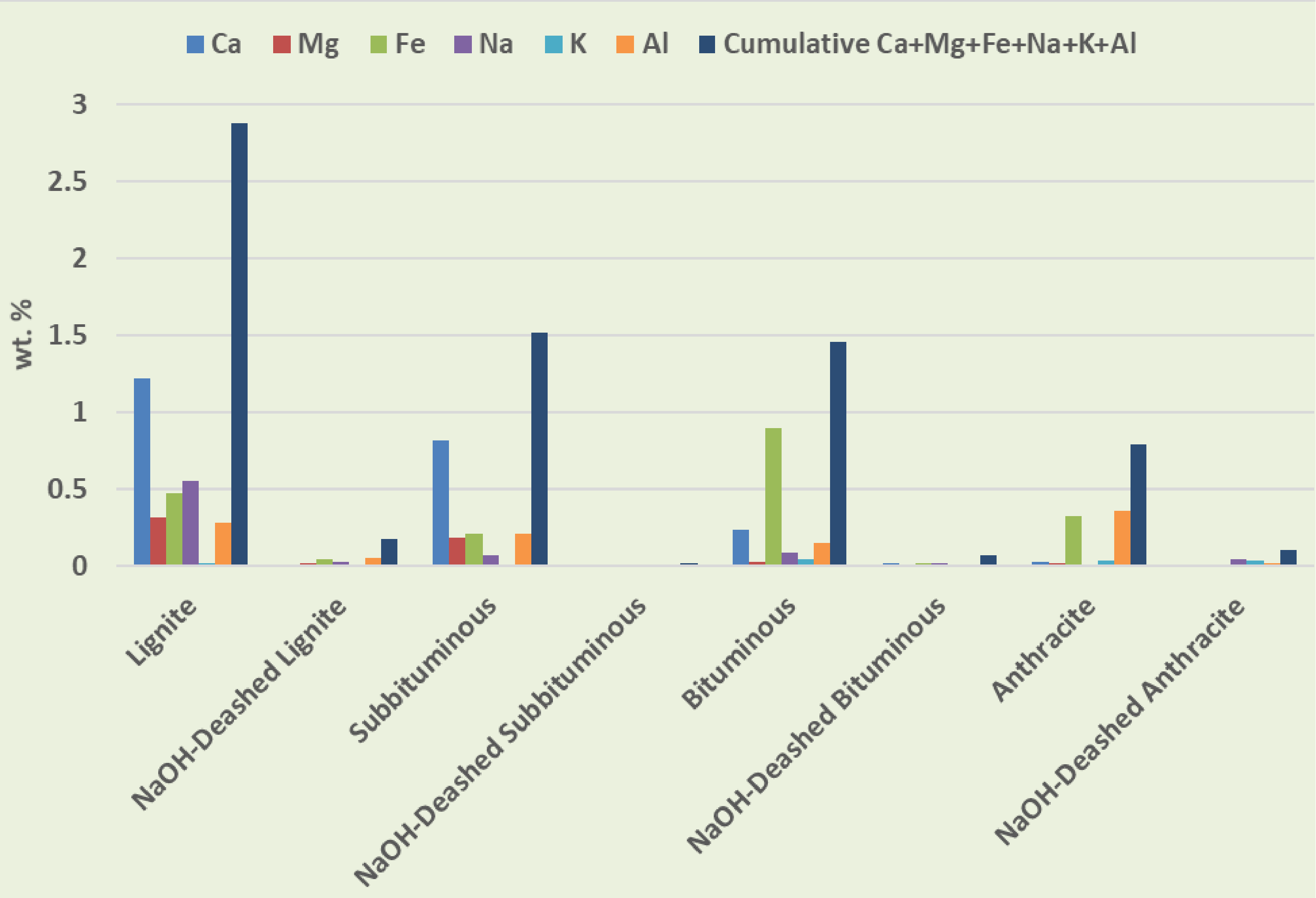
Coal Deashing (HCl Treatment)

- HCl deashing effectiveness for removing each major metal (i.e., Ca, Mg, Fe, K, Na, and Al) varied in a range of 19-100%
- Cumulative removal of major metals ranged from 52% to 75%

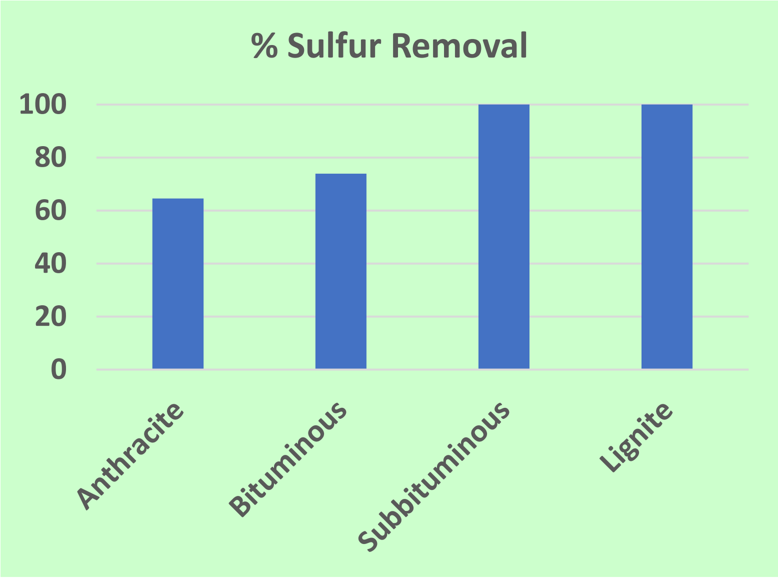


Coal Deashing by Molten NaOH

- 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 Ca+Mg+Fe: 96%-100%, Cumulative removal of Ca+Mg+Fe+K+Na+Al: 86%-98%
- Sulfur removal: 65% to 100%.

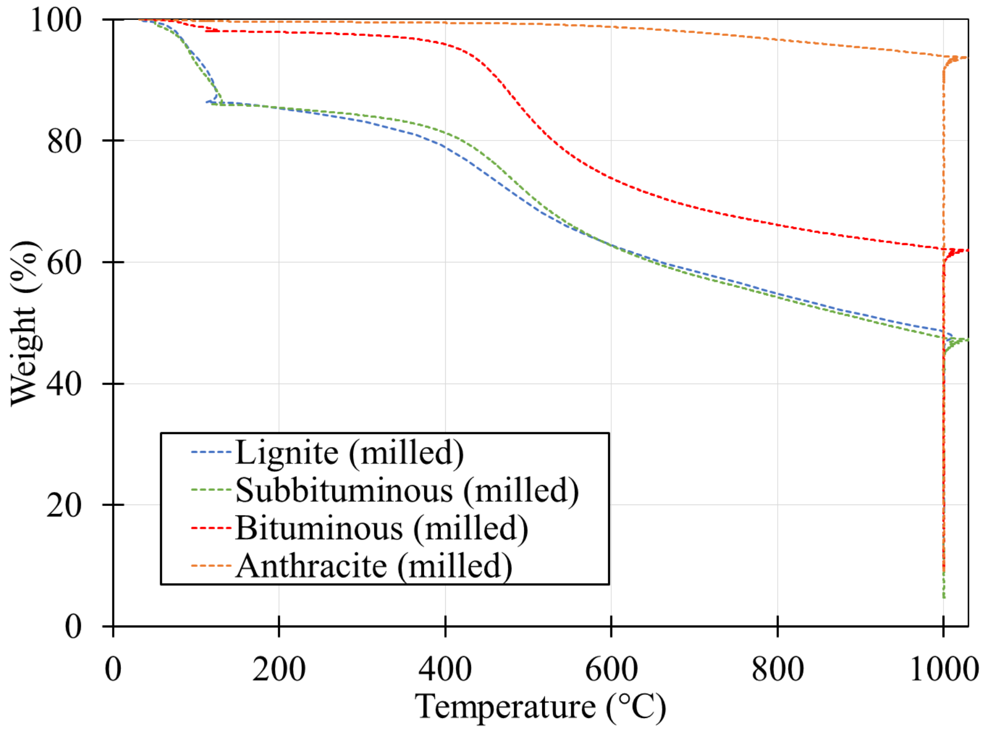


	S % (As-received)	S% (Deashed)
Anthracite	0.55	0.195
Bituminous	3.26	0.851
Subbituminous	0.29	< 0.001
Lignite	1.42	< 0.001



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)
  - Feasibility of reuse and recycling nitric oxide is evaluated

- Experimental approach
  - Samples are oxidized using concentrated nitric acid
  - Precursors: as-received coal, deashed, deashed-devolatilized, and devolatilized-deashed
  - Nitric acid is recovered by distillation and reused for Cycle 2, then Cycle 3
  - Fine particles are separated from larger particles by centrifugation/filtration
  - Solid residuals from the oxidation stage are activated to produce functionalized AC

- Characterization
  - X-ray Photoelectron Spectroscopy (XPS)
  - Raman Spectroscopy
  - X-Ray Diffraction (XRD)
  - CHN Elemental Analysis
  - Surface Area and Pore Size Distribution Analysis

Coal Oxidation with Nitric Acid

4 Coal samples:
Anthracite (A),
Bituminous (B),
Subbituminous (SB),
Lignite (L)

Deashing/Devolatilization

4 pre-oxidation treatments

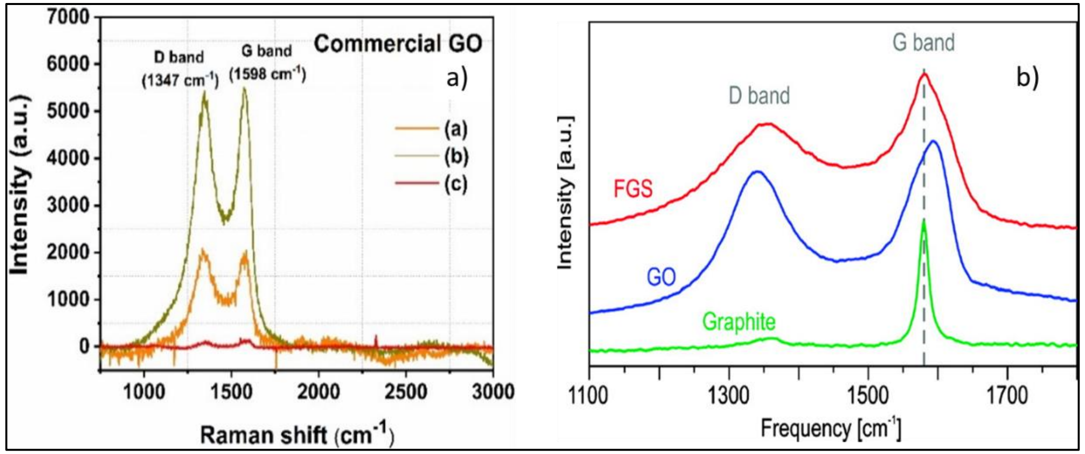
- No treatment
- Deashing (DA)
- Deashing → Devolatilization (DA-DV)
- Devolatilization → Deashing (DV-DA)

Oxidation with HNO_3

- 16 samples prepared using concentrated HNO_3 (16N)
- Selected samples prepared with 8N and 4N acid concentrations
- 8 additional samples prepared using recycled acids in 2 additional cycles

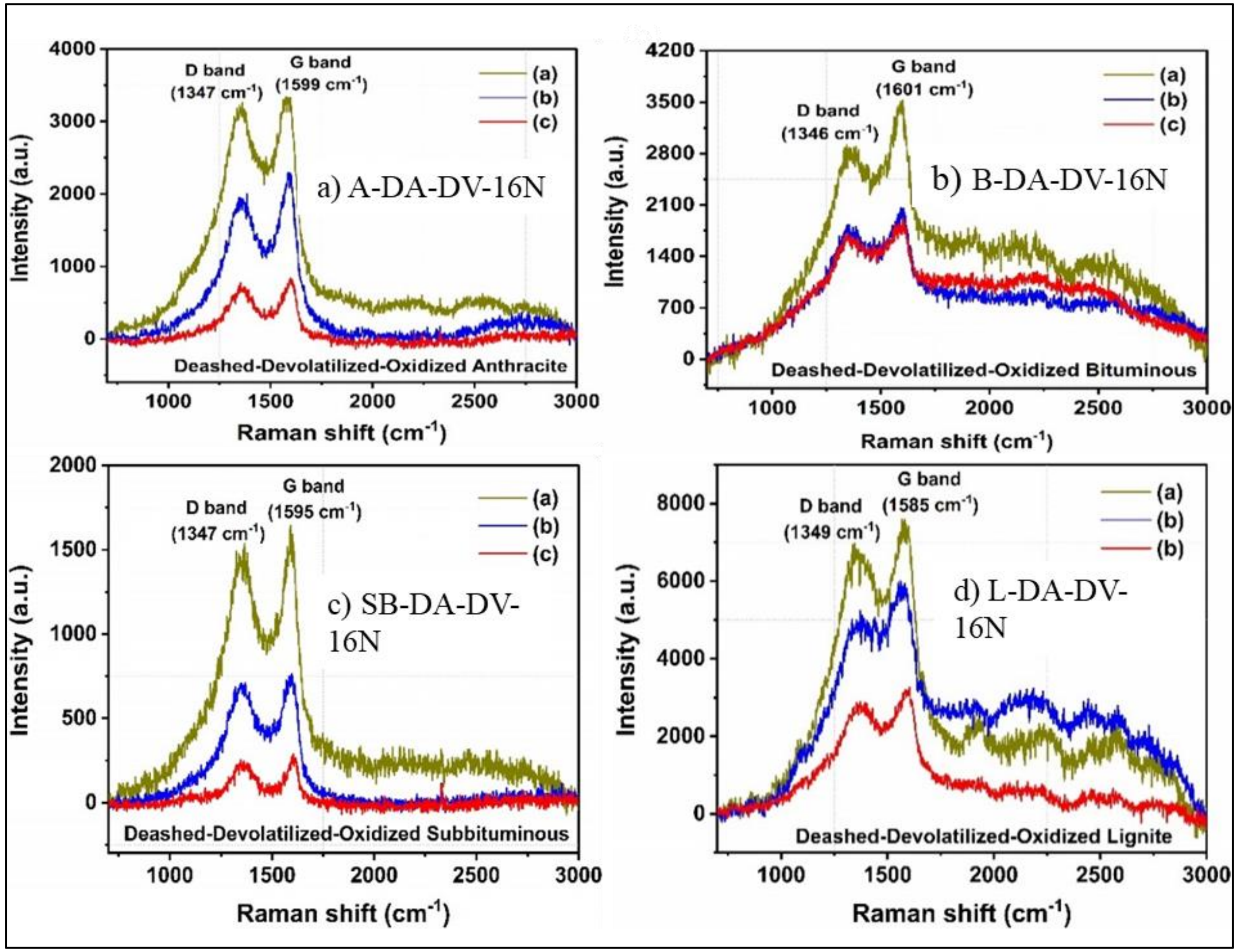
Characteristics of Oxidized Coal Samples (Raman Spectroscopy)

- 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 graphite-based GO



Raman spectra of a single-layer graphite-based graphene oxide (GO) powder obtained from Graphene Supermarket (Calverton, NY) (a), and Raman spectra of GO, functionalized graphene oxide (FGO), and graphite reported by Kudin et al (b).

Sample ID	I_D/I_G ratio
Commercial graphite-based single-layer GO (GO)	*1.06 ± 0.07*
A-DA-DV-16N	0.92 ± 0.05
B-DA-DV-16N	0.88 ± 0.05
SB-DA-DV-16N	0.90 ± 0.01
L-DA-DV-16N	0.89 ± 0.03



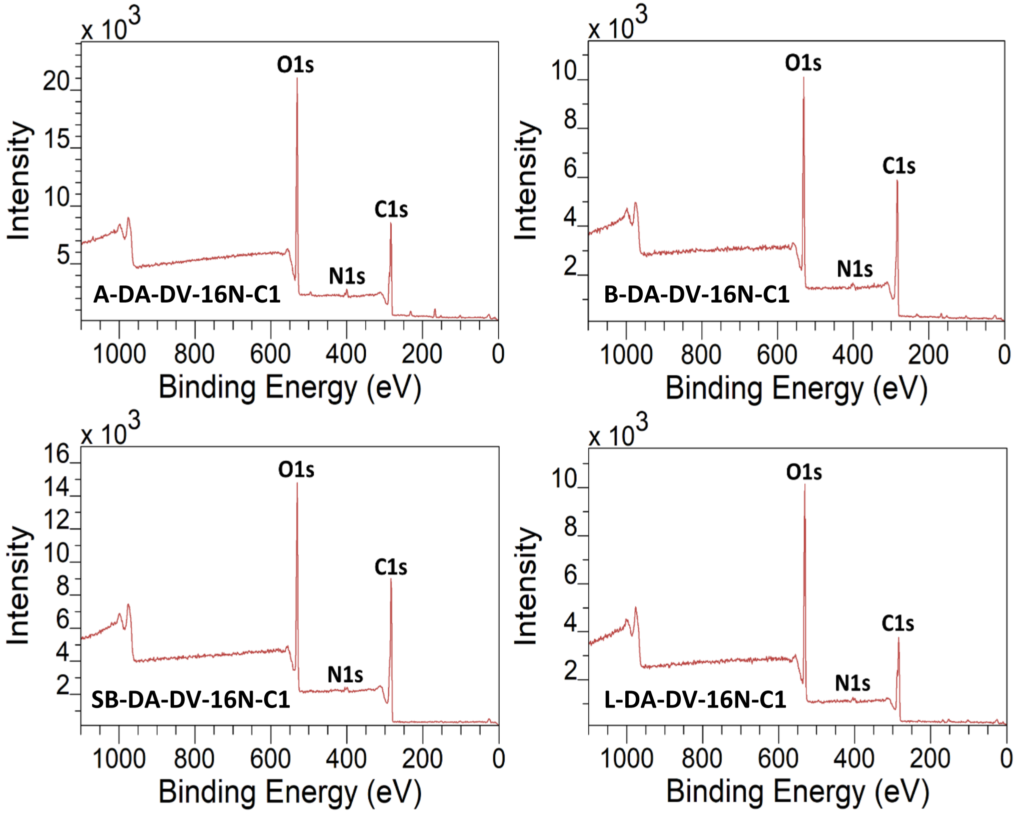
Raman spectra of deashed-devolatilized coal samples oxidized by concentrated nitric acid.

Characteristics of Oxidized Coal Samples (XPS)

- ❑ Several coal-based samples had similar or higher surface oxygen contents compared to a graphite-based GO sample
- ❑ Based on the characterization results, reuse of less concentrated acid (i.e., 12N or 10N), recovered from each cycle and reused for the next cycle, is not as effective as using the concentrated acid
- ❑ Fine particles obtained from coal oxidation have significantly higher oxygen contents than coarse particles

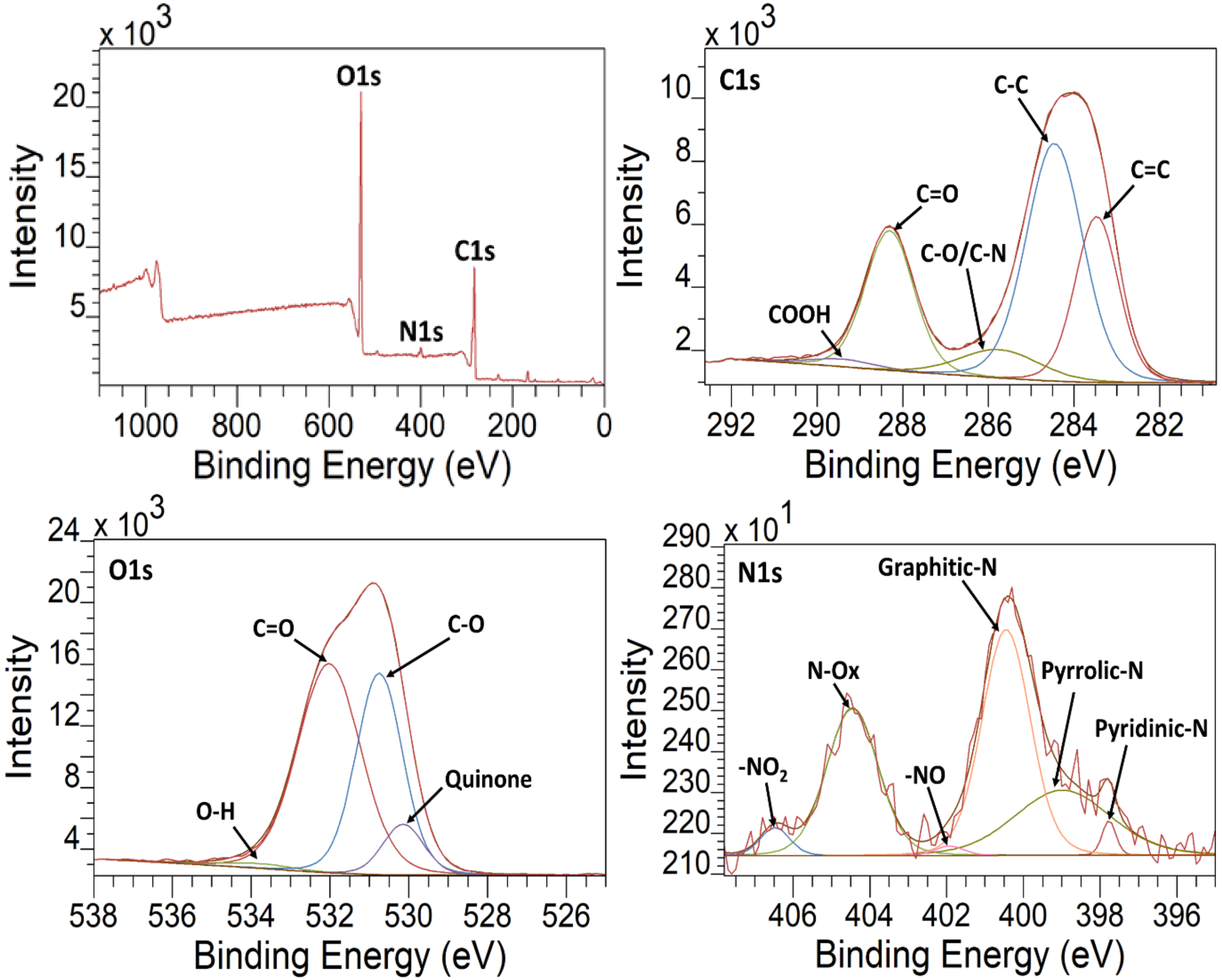
Sample ID	Elemental composition* (at.%)			
	O	C	N	C/O
Graphite-based graphene oxide (GO)	*28.72*	*70.59*	*0.69*	*2.46*
A	11.14	87.81	1.05	7.88
A-16N	18.79	78.40	2.81	4.17
A-DA-16N	26.31	71.39	2.30	2.71
A-DA-DV-16N-C1	33.61	63.40	2.99	1.88
A-DA-DV-12N-C2	20.88	77.23	1.89	3.69
A-DA-DV-10N-C3	20.62	77.63	1.75	3.76
A-DV-DA-16N	39.97	54.31	5.72	1.35
A-DA-DV-16N-Coarse	18.89	80.37	0.74	4.25
A-DA-DV-16N-Coarse (duplicate)	19.41	79.73	0.86	4.10

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



Characteristics of Oxidized Coal Samples (XPS)

- XPS spectra were deconvoluted to characterize different oxygen and nitrogen functionalities



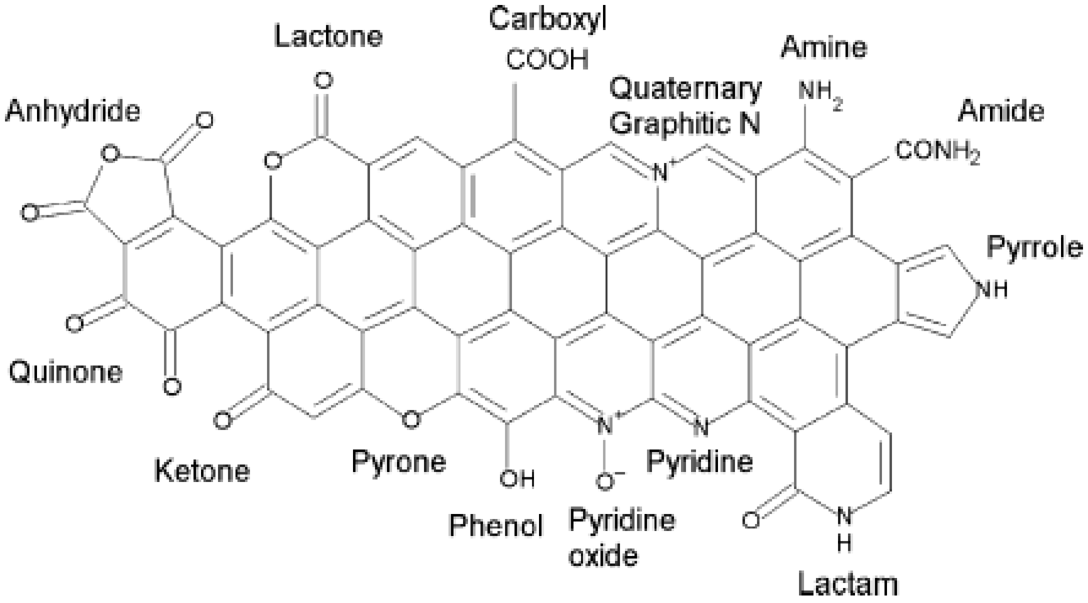
Full survey, C1s, O1s and N1s XPS spectra of A-DA-DV-16N sample

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.

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)
- Work is in progress to characterize surface chemistry of functionalized ACs
- 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.

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

Project Next Steps

- Graphene oxide preparation and characterization
- Reduced graphene oxide production from graphene oxide
- Reduced graphene oxide and activated carbon characterization
- Process simulation and cost estimation
- Market analysis for the graphene and activated carbon products
- Technology gap assessment

Summary and Conclusions

- ❑ It is possible to produce GO and RGO materials from coal, but several R&D gaps including removal of coal impurities, recycling of chemicals used in the process, improving product quality, techno-economic evaluation, and other gaps need to be addressed.
- ❑ Experimental work performed included coal preparation, removal of coal impurities, coal devolatilization (to prepare several precursors for oxidation and GO preparation), coal oxidation, AC preparation, and an extensive physicochemical characterization.
- ❑ 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 graphite-based GO.
- ❑ Based on the XPS characterization, several oxidized coal samples had similar or higher surface oxygen contents compared to a graphite-based GO sample.
- ❑ Work is in progress to further process coal-based GO materials from coal and prepare RGO. Project next steps also include a techno-economic analysis.
- ❑ Through conducting both experimental work and techno-economic analysis, this project and other similar projects can address coal-to-graphene R&D gaps and help to achieve DOE-FE goal to “utilize domestic coal to produce advanced carbon products”.

Acknowledgement and Contact Information

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