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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Outline

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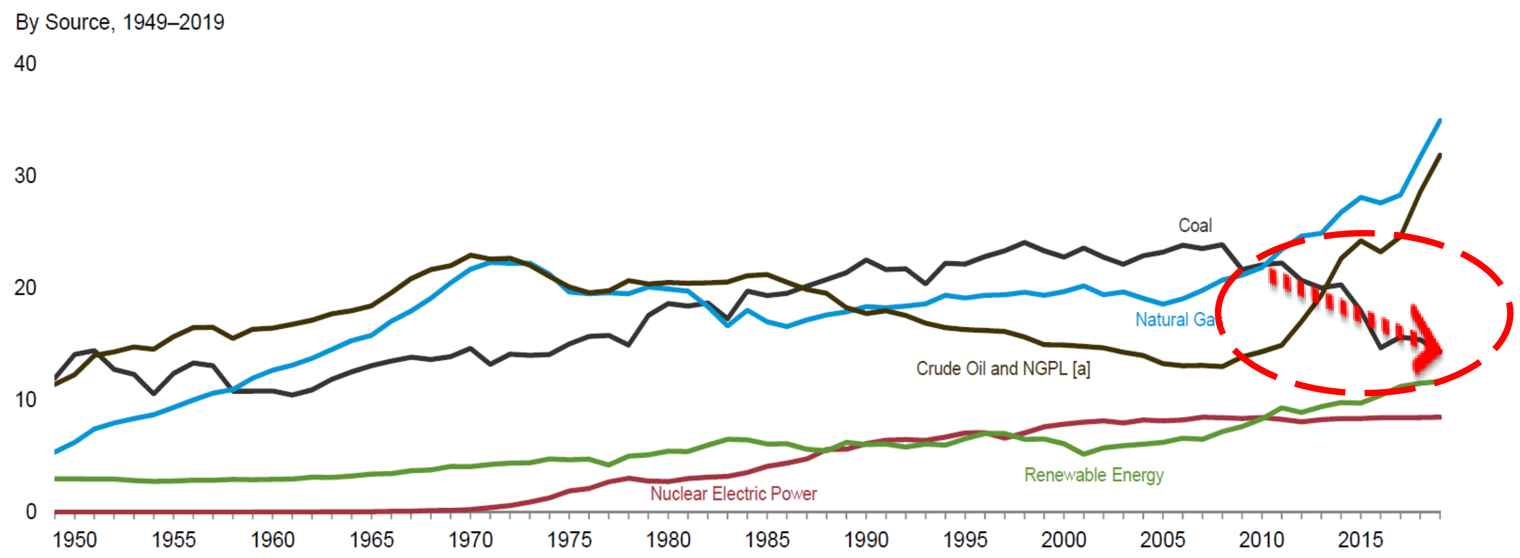
- Concluding remarks

U.S. Coal: Current and Future Use

- Coal is the most abundant energy/hydrocarbon resource in U.S.
- U.S. coal is expected to last >200 years if used at a rate of ~1 billion tons/yr
- Coal is primarily used for power generation, but it has a declining trend
- New markets for domestic coal must be generated
- The production of high-value carbon nanomaterials (e.g., graphene and graphene oxide) from coal may generate new markets

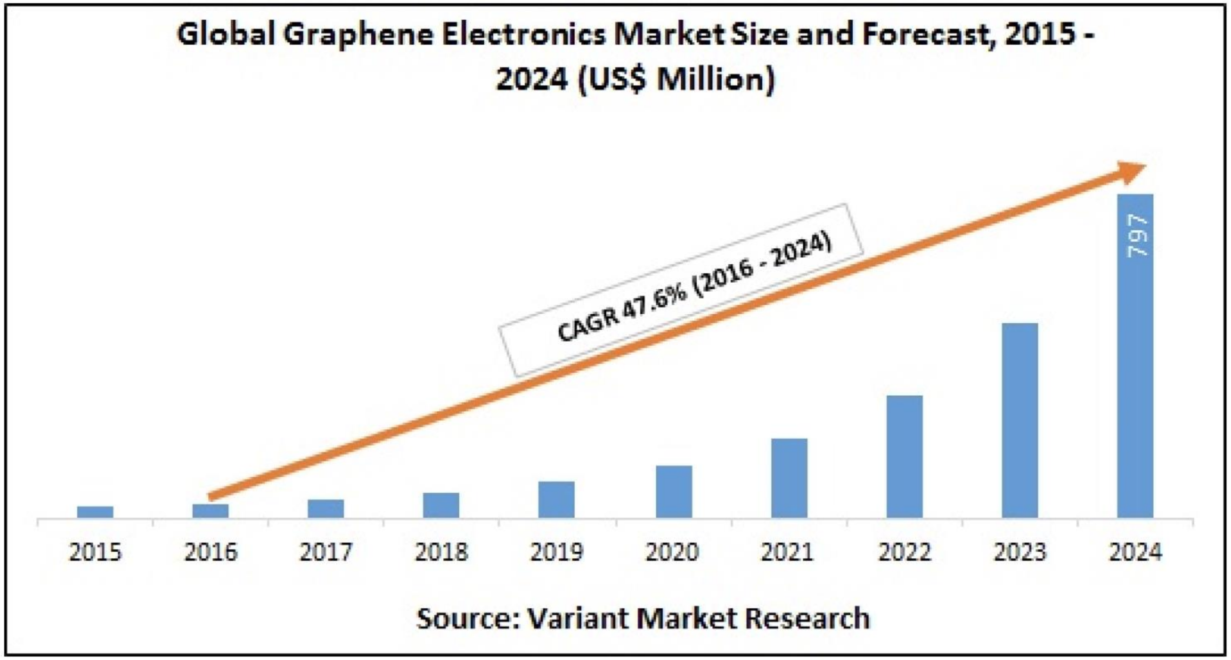
Figure 1.2 Primary Energy Production
(Quadrillion Btu)



Source: EIA, Monthly Energy Review, September 2020

Price and Market of Graphene Materials

- Current price of graphene materials: $50–$200/kg (or ~$100,000/ton)
- Current market: ~$100 million (1,000 ton/yr), expected to grow to ~$390-$800 million by 2024 (or higher)
- Low-cost graphene could capture the market for conventional carbon materials or create new markets such as those for composites and functional coatings
- Production of graphene materials from coal can potentially lower graphene's cost by 1 to 2 orders of magnitude from $100,000/ton to $1,000-10,000/ton

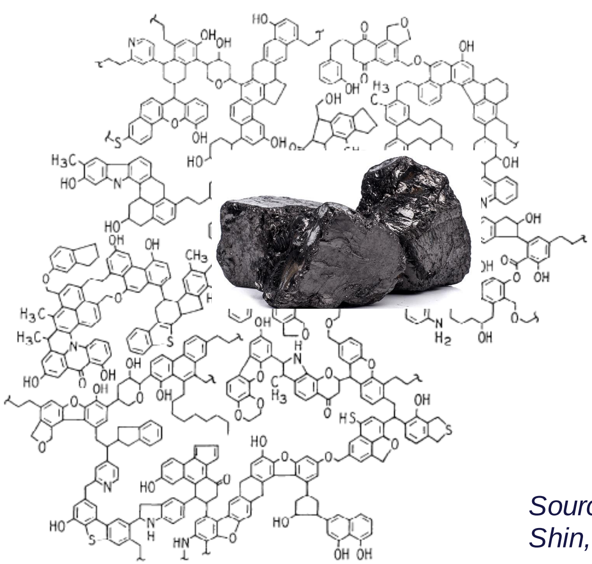


Sources: https://www.graphene-info.com/nanoxplore-plans-10000-ton-graphene-powder-facility; https://www.idtechex.com/research/articles/graphene-markets-technologies-and-opportunities-2014-2024-00006555.asp; https://www.reuters.com/brandfeatures/venture-capital/article?id=39171; https://www.variantmarketresearch.com/report-categories/semiconductor-electronics/graphene-electronics-market

Conversion of Coal to GO and RGO

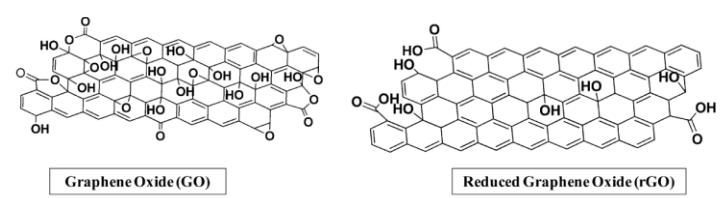
- It is possible to produce graphene oxide (GO) and reduced graphene oxide (RGO) from coal, but several R&D gaps need to be addressed (described later)
- Coal vs. graphite precursor for GO production: Opportunities
  - Low cost of precursor: ~$40/ton coal vs. ~$1,000/ton graphite
  - Availability: huge 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 → GO → 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., AC) from domestic coal resources in a cost-effective manner

Scope

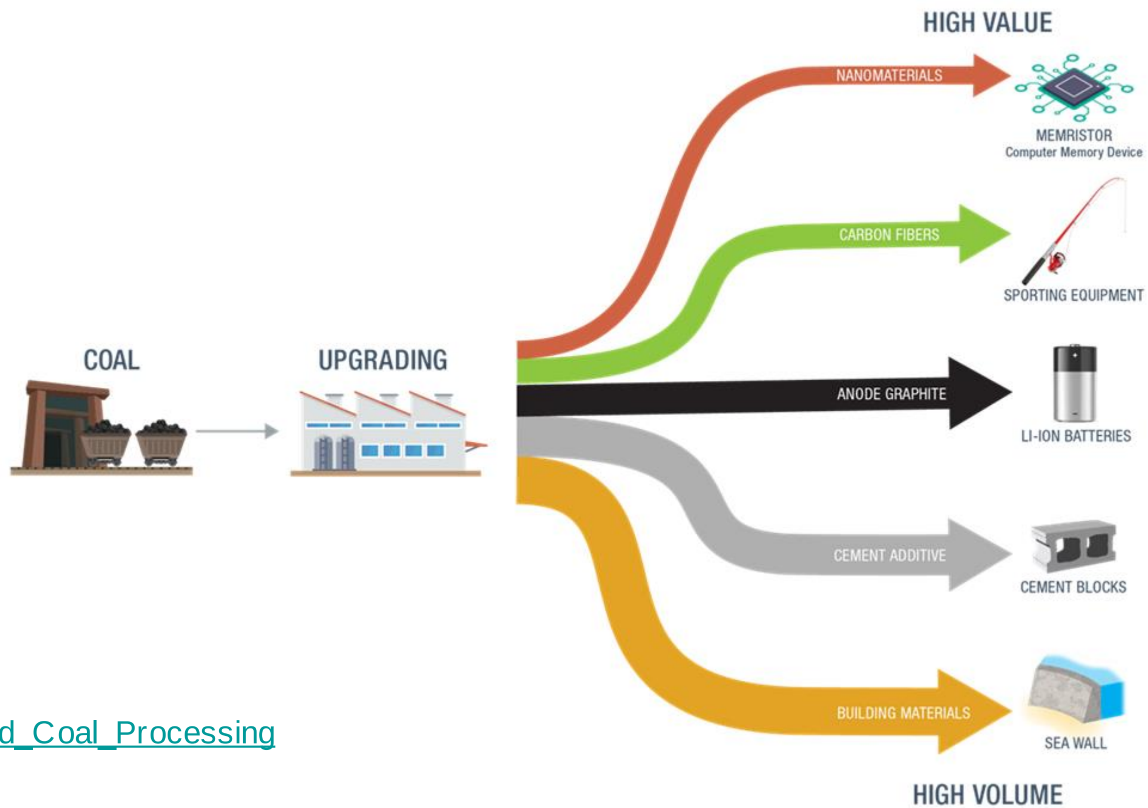
- To evaluate the feasibility of the proposed integrated approach for the production of high-value carbon materials from U.S. coal by conducting systematic experimental work and a techno-economic evaluation
  - Material preparation: 4 types of domestic coal samples will be processed at a laboratory scale 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

Strategic Alignment to DOE-FE Objectives

- DOE-FE Advanced Coal Processing R&D, "Area 1: Coal-derived carbon products enables development of new materials and manufacturing processes that utilize domestic coal to produce advanced carbon products"
- FOA-1992 AOI 2 objective: "Producing high-value solid products from domestic U.S. coal"
- Objective of this project: to produce high-value carbon nanomaterials (i.e., GO and RGO) and carbon sorbents (i.e., AC) from domestic coal resources in a cost-effective manner



Source: NETL/DOE
https://netl.doe.gov/Advanced_Coal_Processing

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

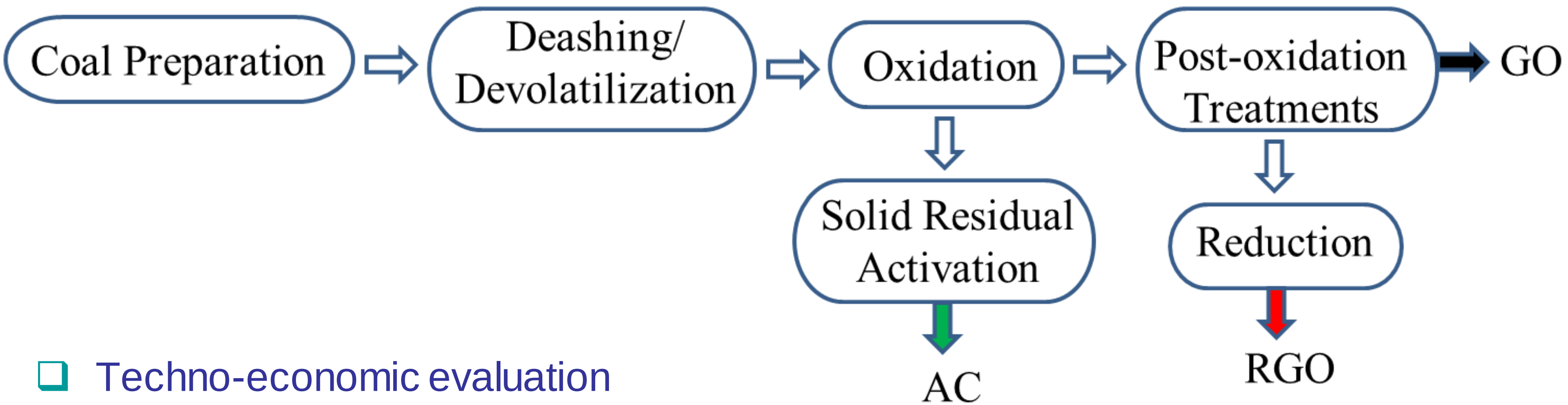
Current main gaps in coal-to-graphene R&D	Proposed approach to advance the state of the art
1. Lack of systematic work on GO and RGO production from different types of coal with different compositions	• Four types of coal (lignite, subbituminous, bituminous, and anthracite) will be systematically treated 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

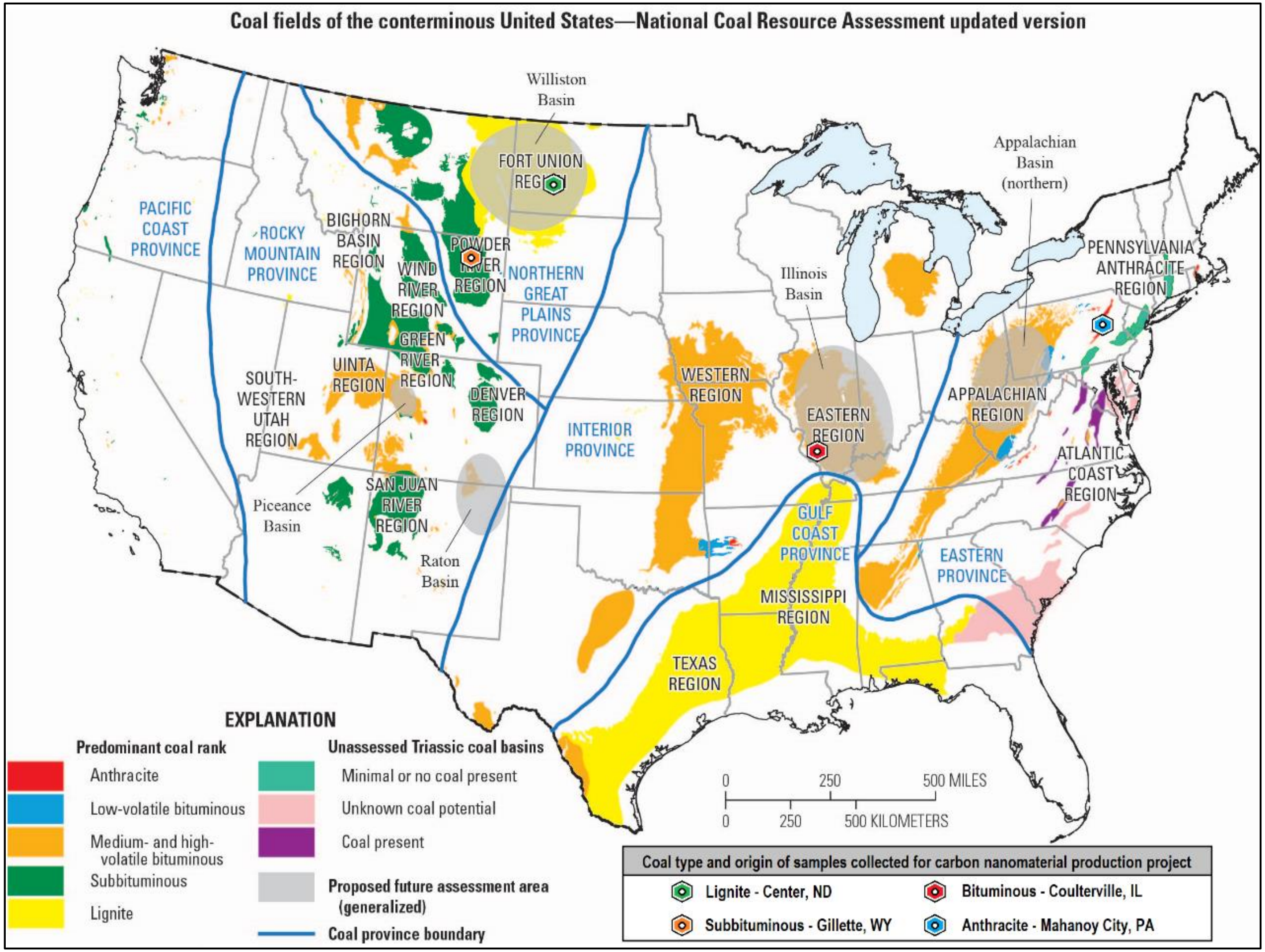
- Experimental approach
  - An integrated approach of deashing, oxidation, reduction, and activation stages to convert the coal feedstock to GO, RGO, and AC products
  - Chemicals used for deashing and oxidation are planned to be recovered and recycled to the process
  - Solid residuals from the oxidation stage are activated to produce AC



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

Coal Selection and Preparation

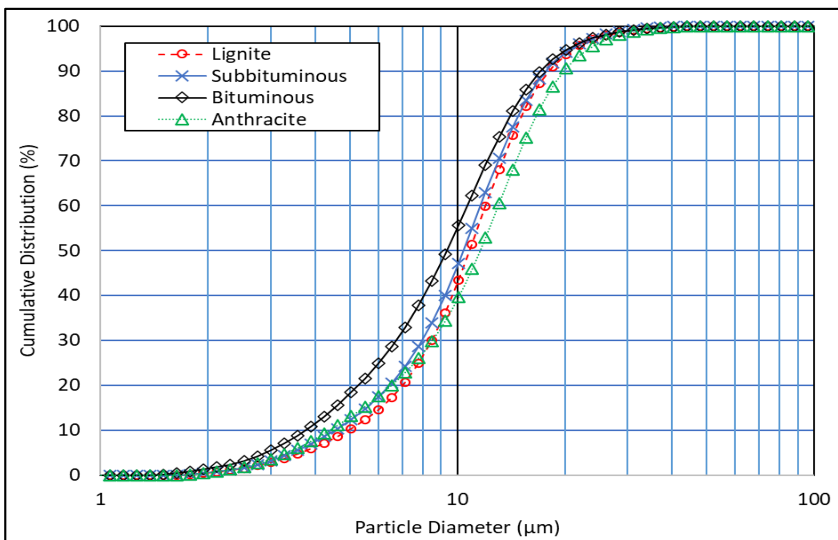
- Four coal samples (lignite, sub-bituminous, bituminous, and anthracite) are selected and obtained from coal companies

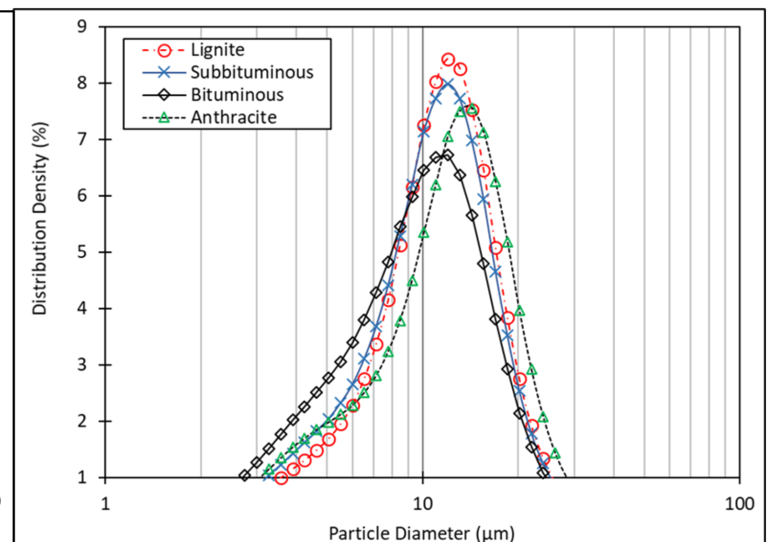


Sources of anthracite, bituminous, subbituminous, and lignite coal samples obtained from different U.S. coal mines are shown on the USGS coal resources map.

Coal Preparation and Characterization

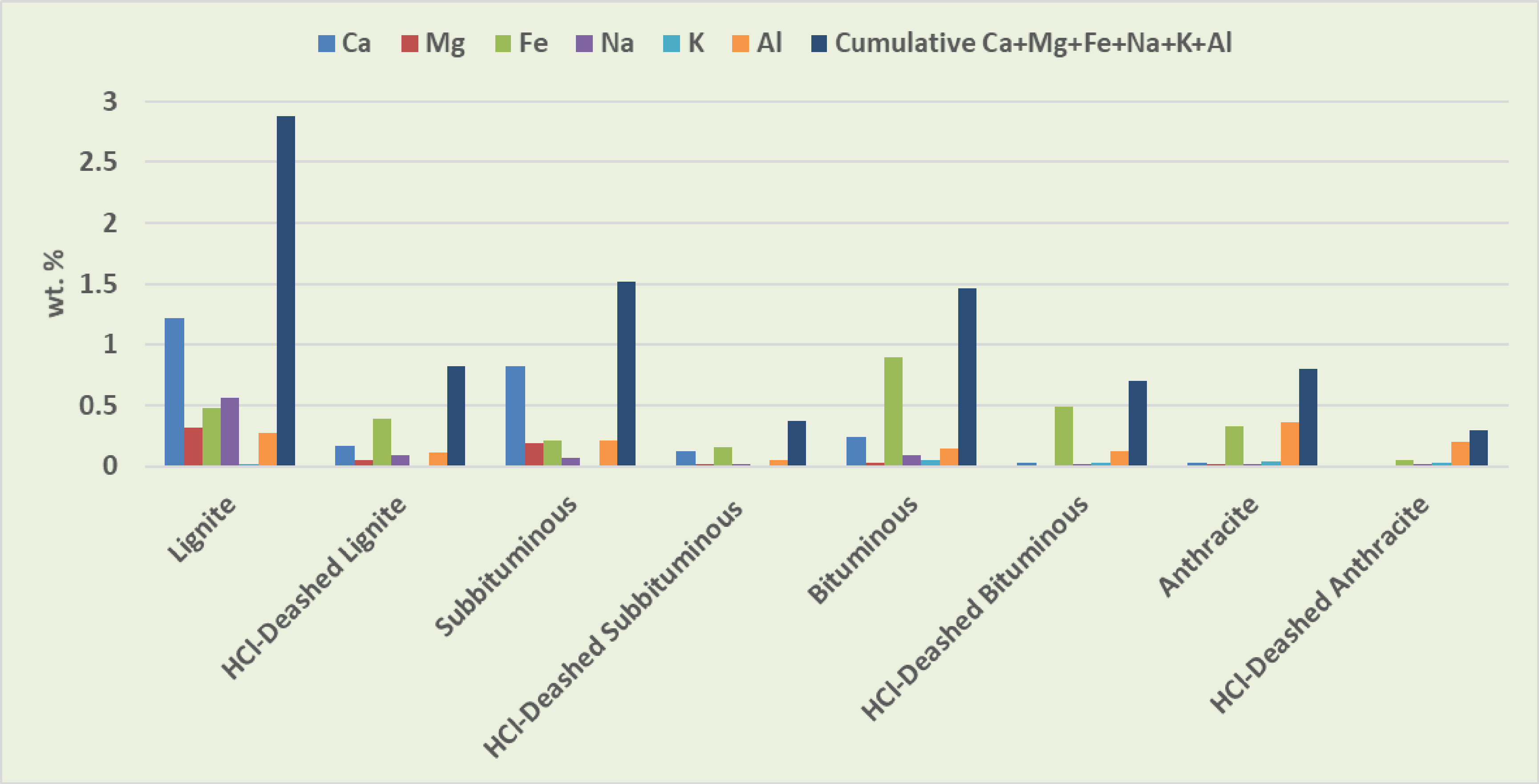
	Anthracite	Bituminous	Subbituminous	Lignite
Proximate Analysis (%) - Dry Basis				
Ash	9.5	10.5	6.1	10.3
Volatile	5.0	42.0	43.2	46.3
Fixed Carbon	85.5	47.5	50.7	43.3
Heating Value - Dry Basis				
BTU/lb	13,300	12,740	12,115	11,013
Ultimate Analysis (%) - Dry Basis				
Carbon	84.65	70.50	71.20	68.42
Hydrogen	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





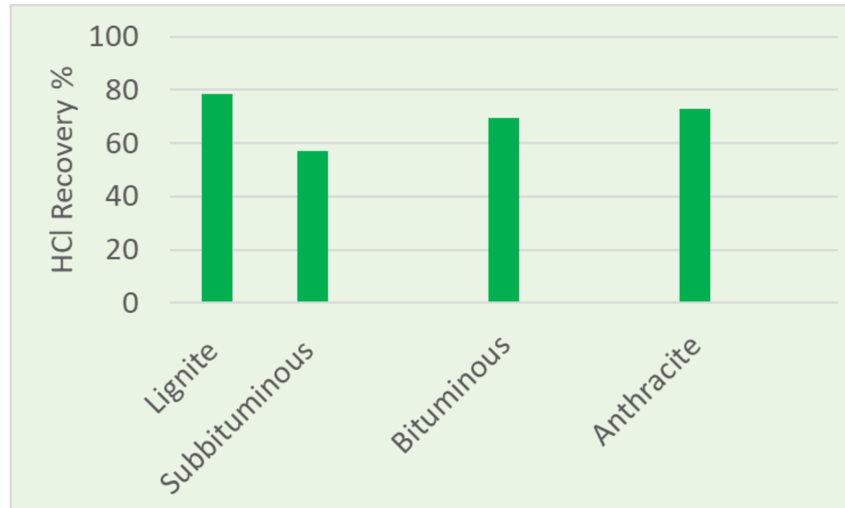
Coal Deashing (HCl Treatment)

- 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 (HCl Recovery)

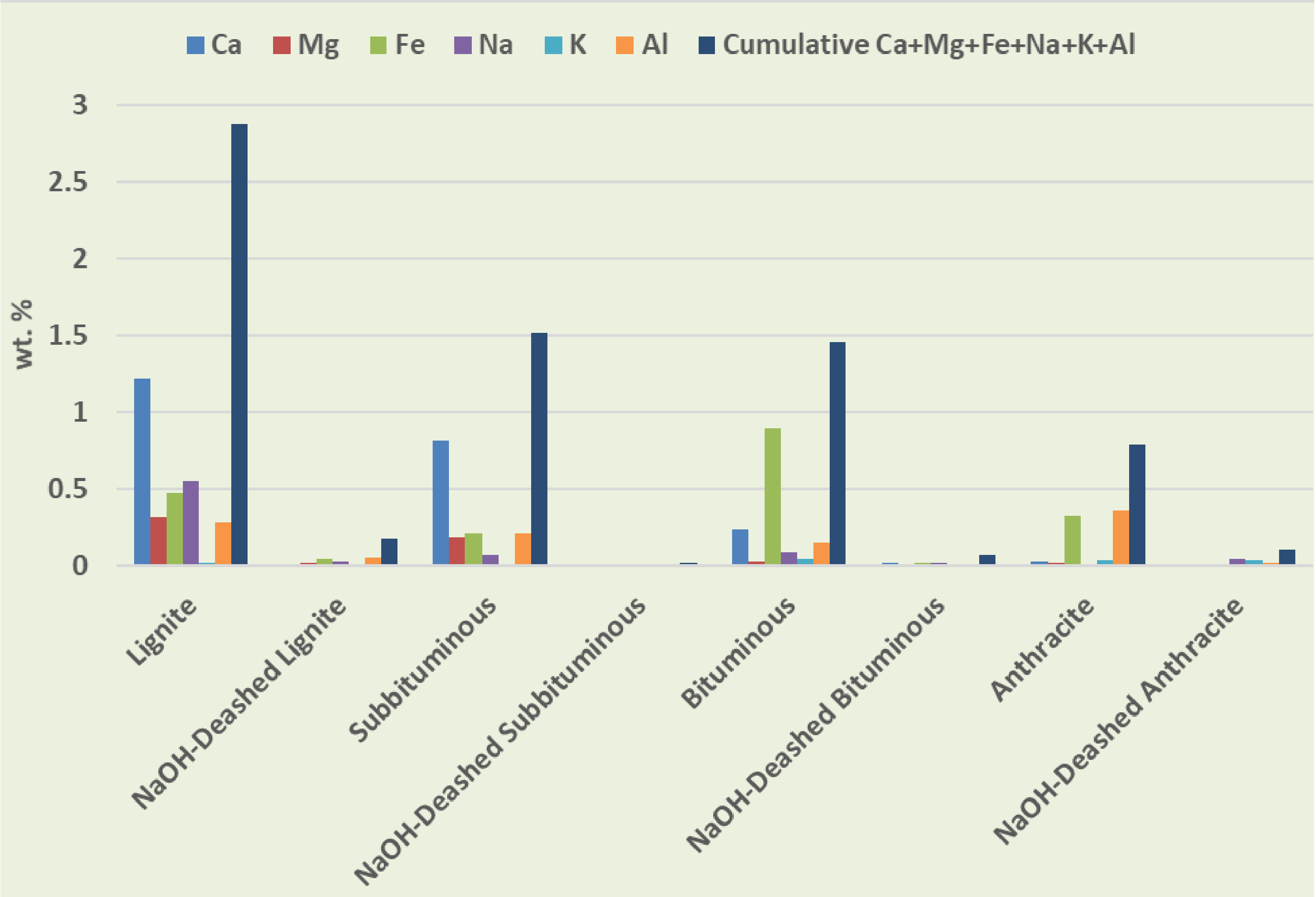
- About 52-79% of HCl was recovered by distillation
- Minerals extracted by HCl treatment from different coal samples had different characteristics



Photographs a, b, c, and d show separated impurities (i.e., solid residuals after acid evaporation) from lignite, subbituminous, bituminous, and anthracite coal samples, respectively.

Coal Deashing (NaOH Treatment)

- The effectiveness of deashing by the molten NaOH method 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 ranged from 96% to 100%
- Cumulative removal of Ca+Mg+Fe+K+Na+Al ranged from 86% to 98%



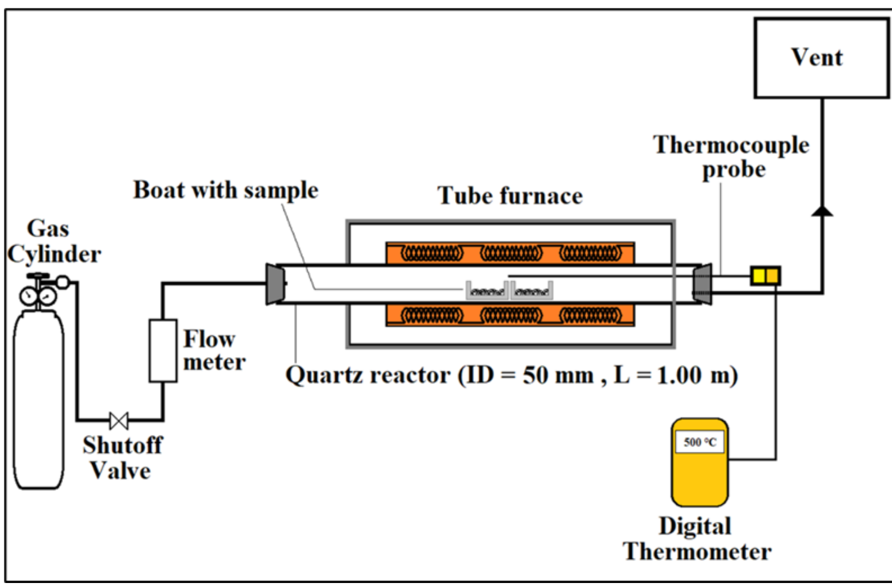
Coal Deashing

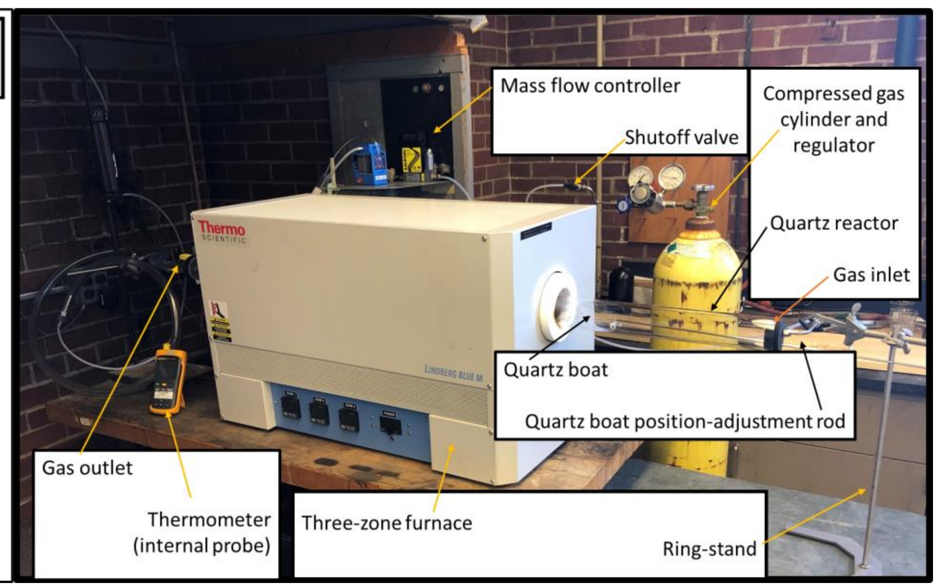
- Coal deashing is required to convert coal to a high-purity carbon source for production of high-value carbon materials

- A high level of purification can be achieved by the molten NaOH deashing method which might be needed for different applications of coal-based nanomaterials
- Cost of NaOH might be a significant factor in the overall cost of the coal-based nanomaterials
- Work is in progress to perform multicycle deashing using the recovered alkali solution from the first cycle of NaOH-deashing
- Other alkali deashing methods such as mixed NaOH-KOH molten method were also explored but appear to be less promising
- Other approaches for integration deashing and oxidation stages are being considered

Coal Devolatilization and Heat Treatment

- Coal devolatilization with and without air peroxidation
  - Pre-oxidation treatment was performed for caking coal samples.
  - Deashed coal samples were devolatilized by pyrolysis under an inert atmosphere.
  - Devolatilized or deashed-devolatilized coal samples will be also used as precursors for GO production. The impact of coal volatile matter on GO production will be investigated.





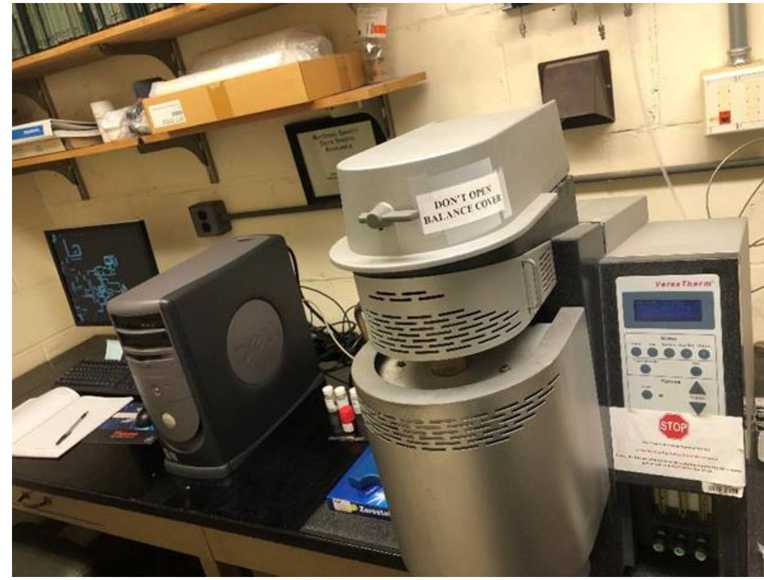
Coal and Char Characterization

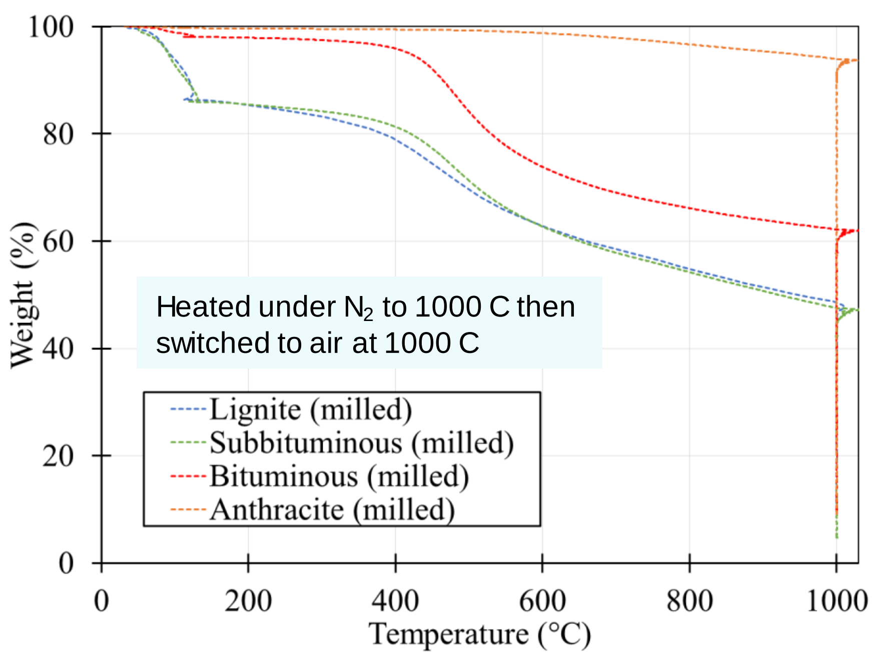
- Surface area measurement and pore size distribution

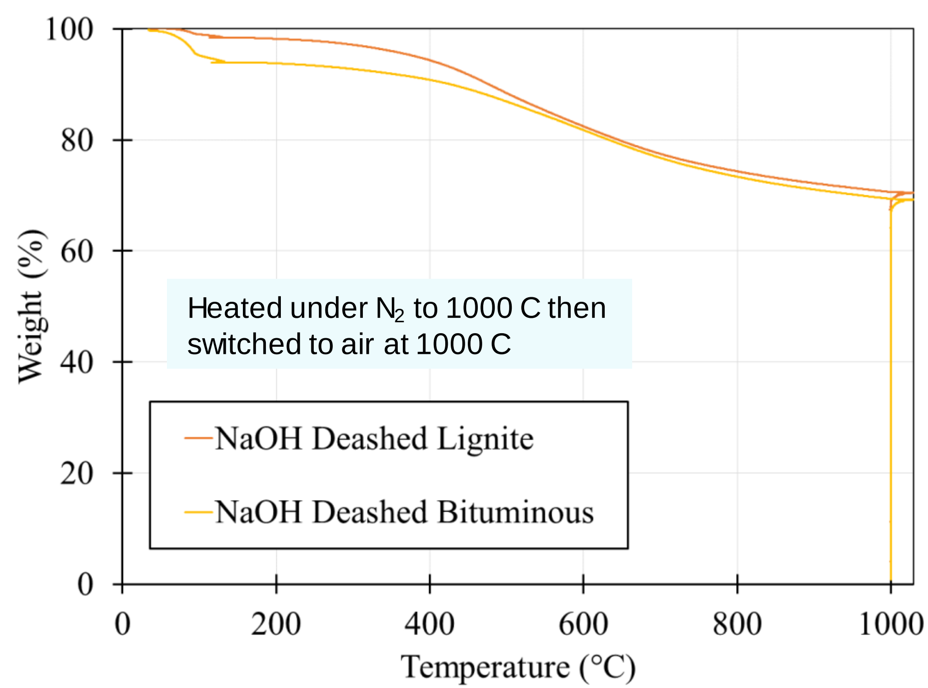
Coal precursor	Thermal treatment	BET surface area (m^2/g)
Anthracite	None (as-received)	0.1
Anthracite	Devolatilization at 700 °C	~0
NaOH-deashed anthracite	None	3.9
NaOH-deashed anthracite	Devolatilization at 900 °C	21.2
Lignite	None (as-received)	2.6
Lignite	Devolatilization at 700 °C	46.1
NaOH-deashed lignite	None	17.2
NaOH-deashed lignite	Devolatilization at 900 °C	144.1
Bituminous	None (as-received)	24.4
Bituminous	Oxidation at 250 °C followed by devolatilization at 700 °C	155.9
NaOH-deashed bituminous	None	9.8
NaOH-deashed bituminous	Devolatilization at 900 °C	40.4
Subbituminous	None (as-received)	23.5
Subbituminous	Devolatilization at 700 °C	150.7
NaOH-deashed subbituminous	None	10.3
NaOH-deashed subbituminous	Devolatilization at 900 °C	26.3

Coal and Char Characterization

- Thermogravimetric analysis
  - Measurement of sample moisture, volatile matter (VM), and ash content
  - After NaOH deashing, ash content reduced to ~ 0.6-4% for different coals
  - VM content of coal samples varied in a range of ~ 7-47% (DB)
  - VM content of alkali-deashed samples varied in a range of ~ 7-29% (DB)

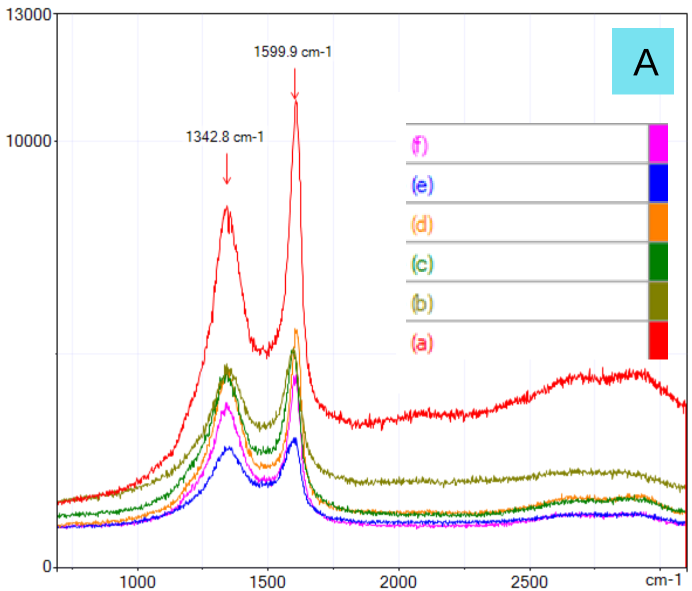


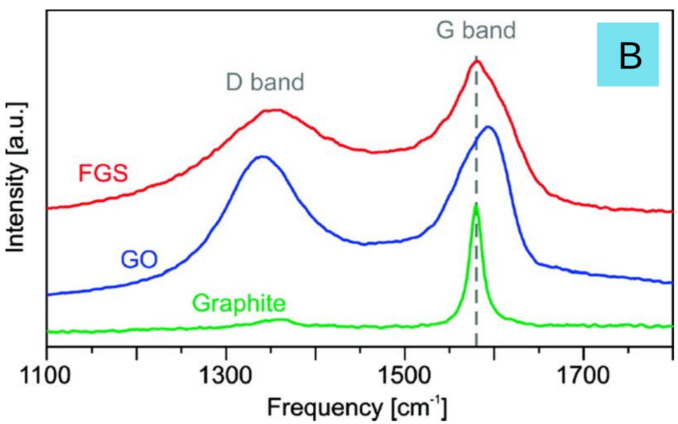


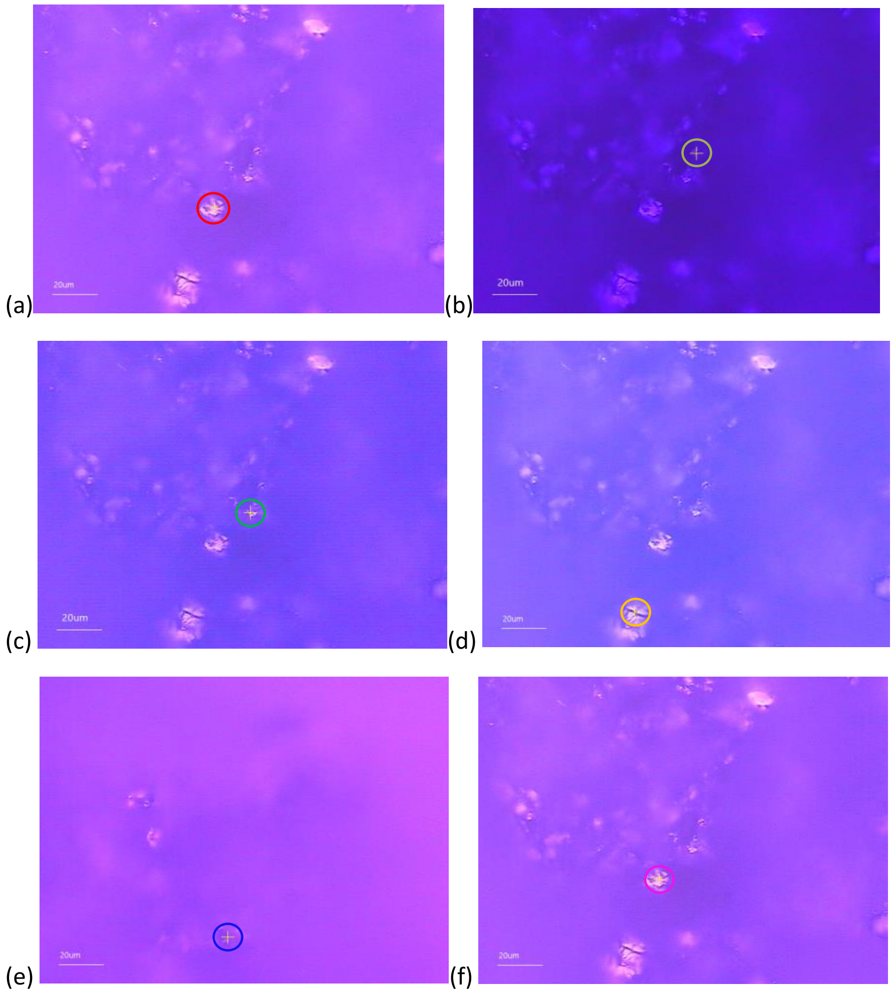


Characteristics of Oxidized Samples (Preliminary Results)

- Raman spectra of oxidized coal samples prepared by nitric acid oxidation showed characteristic D and G bands similar to those reported in the literature for GO





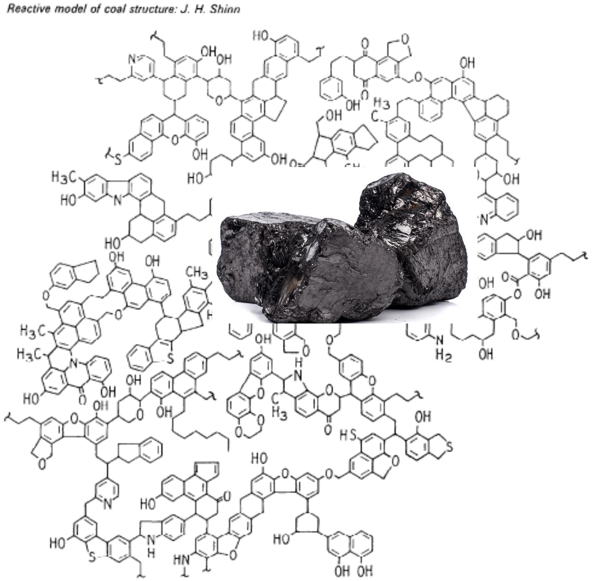


Raman spectra of a GO sample produced from coal and comparison with the literature data. (A) Replicate analyses of a coal-based sample prepared in our lab, along with a sample photograph. (B) Raman spectra of GO materials or graphite from the literature (Kudin et al., Nano Lett., 2008, 36-41).

Project Next Steps: Experimental Work

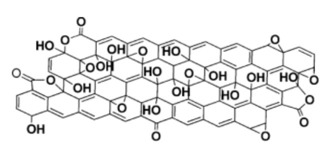
- Oxidation of deashed coal
- Oxidation of deashed–devolatilized coal
- Recovery and reuse of oxidizing agent
- Graphene oxide preparation and characterization
- Reduced graphene oxide production from graphene oxide
- Activated carbon preparation from residual solids
- Reduced graphene oxide and activated carbon characterization

Reactive model of coal structure: J. H. Shinn

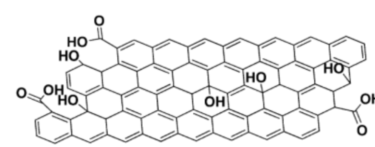


Oxidation *Reduction*

Coal → GO → RGO



Graphene Oxide (GO)



Reduced Graphene Oxide (rGO)

Project Next Steps: Techno-economic Analysis, Market Evaluation, and Technology Gap Assessment

- Process simulation and cost estimation
  - A process flow diagram will be developed.
  - A conceptual process simulation will be conducted. Simulation outputs will be used for equipment sizing and for capital and operating cost estimates.
- Market analysis for the graphene and activated carbon products
  - A market analysis for the graphene products and AC will be conducted to assess the present and future market size and market value for different applications.
- Technology gap assessment
  - Both the experimental results and technoeconomic analysis of this project will be analyzed to identify the main technology gaps of our proposed technology.
  - Additional R&D related to process or product improvement will be identified and proposed to enable scale-up of the proposed technology to the pilot or commercial scale.

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, and other gaps need to be addressed.
- The cost-effectiveness of the process at a commercial scale should be demonstrated through a techno-economic evaluation and market analysis.
- In the first year of the project we focused on coal preparation and removal of coal impurities to prepare a suitable precursor for coal oxidation and GO preparation. A cumulative removal of 86%-98% was achieved for the major metal impurities for different coal samples.
- Work is in progress to prepare GO materials from coal. Preliminary results from Raman Spectroscopy showed characteristic D and G bands similar to those reported in the literature for GO.
- 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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