Energy & Environmental Research Center (EERC)

# LABORATORY-SCALE COAL-DERIVED GRAPHENE PROCESS

DOE–NETL 2021 Integrated Project Review Meeting – Advanced Coal Processing

Webinar

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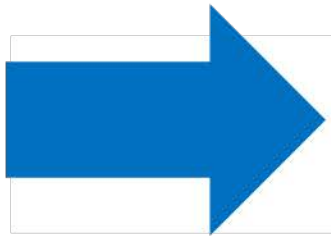
# PROJECT GOAL

The goal is to develop a technological process for converting U.S. coals into high-value solid carbon products such as graphene and high-grade graphite.



# PROJECT PARTNERS

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

NORTH AMERICAN COAL®

Lignite Energy Council

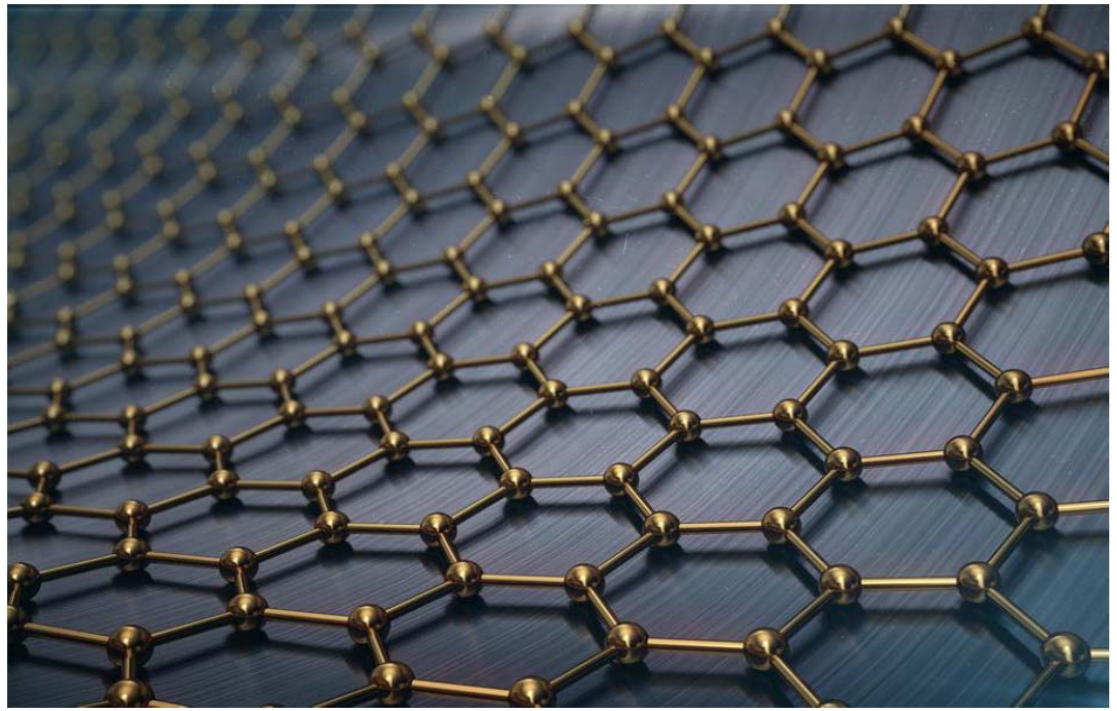
EERC

UNIVERSITY OF NORTH DAKOTA

# WHAT IS GRAPHENE?

**Graphene is a 2D carbon material with a thickness of one atom.**

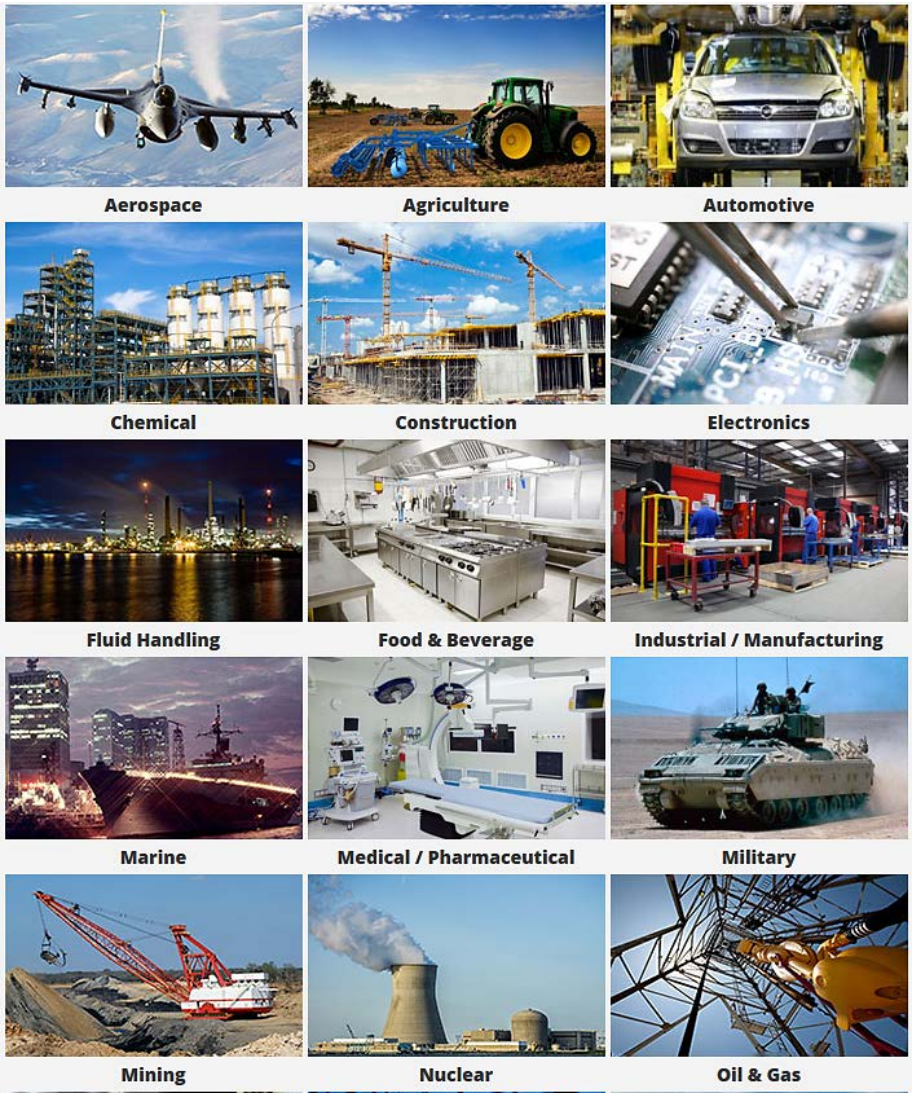
**Graphene Quantum Dots**



**Graphene sheet**

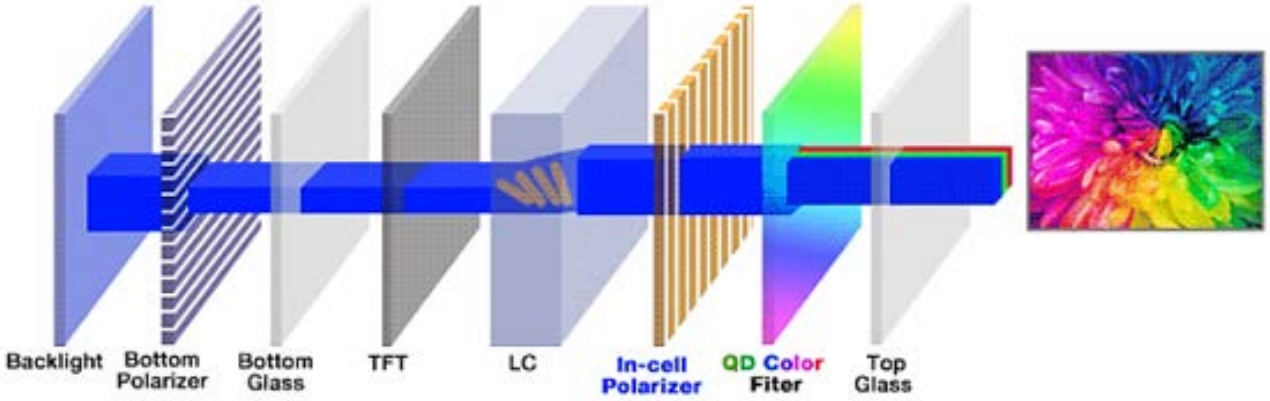
- Graphene oxide (GO)
- Reduced graphene oxide (rGO)
- Graphene nanosheets (GNS)
- Graphene nanoplatelets (GNP)
- Few-layer graphene (FLG)

# GRAPHENE APPLICATIONS BY INDUSTRY



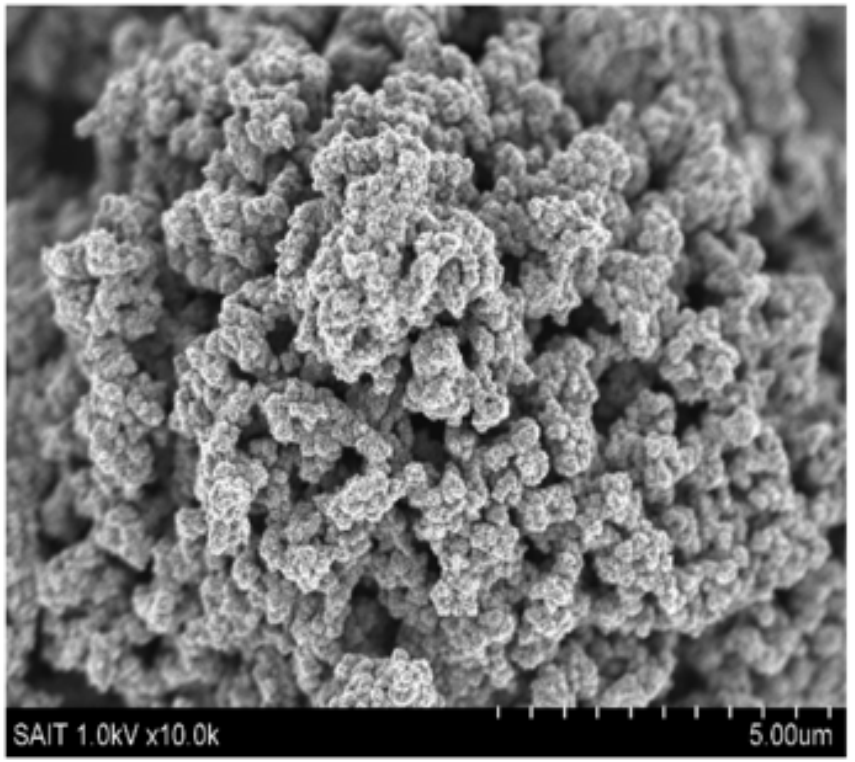

# ADVANCED SCREEN DISPLAY AND ENERGY STORAGE

## Advanced Screen Displays




Next-Generation Samsung QD-Pixel Application

## Higher-Capacity Battery Material




Samsung's "**Graphene Ball**" for Li ion batteries with up to **5x faster charging speed** and **45% more capacity.**

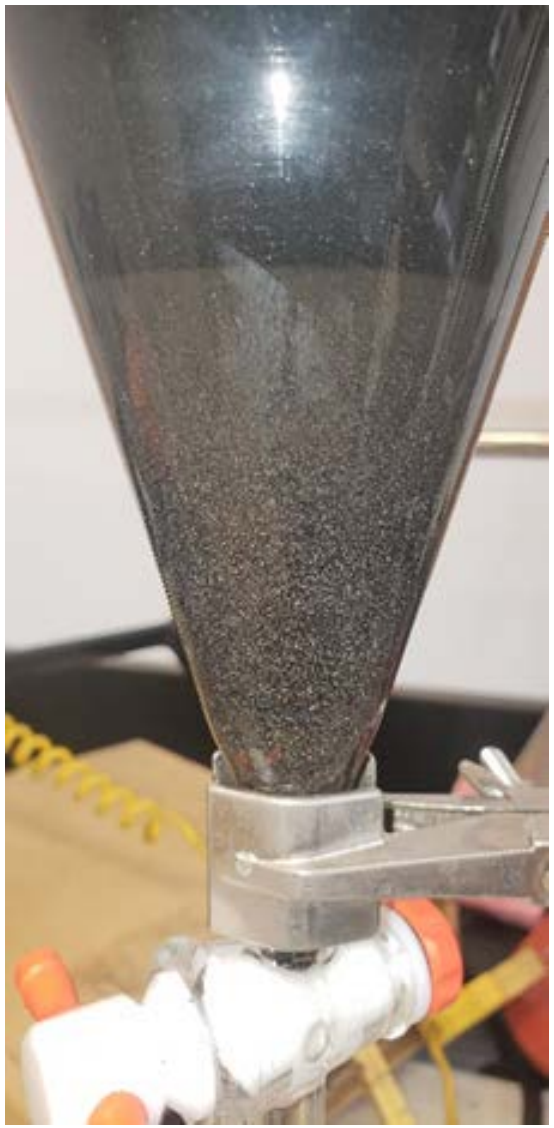
# PROJECT STRUCTURE AND SCOPE OF WORK

- **Task 1.0** – Project Management
- **Task 2.0** – Coal Pretreatment and Equipment Fabrication/Acquisition
- **Task 3.0** – Graphitization of Treated Coals
- **Task 4.0** – Exfoliation of Graphite to Graphene
- **Task 5.0** – Techno-Economic Analysis
- **Task 6.0** – Analysis of Product Target Markets and Technology Gaps

# PRELIMINARY RESULTS

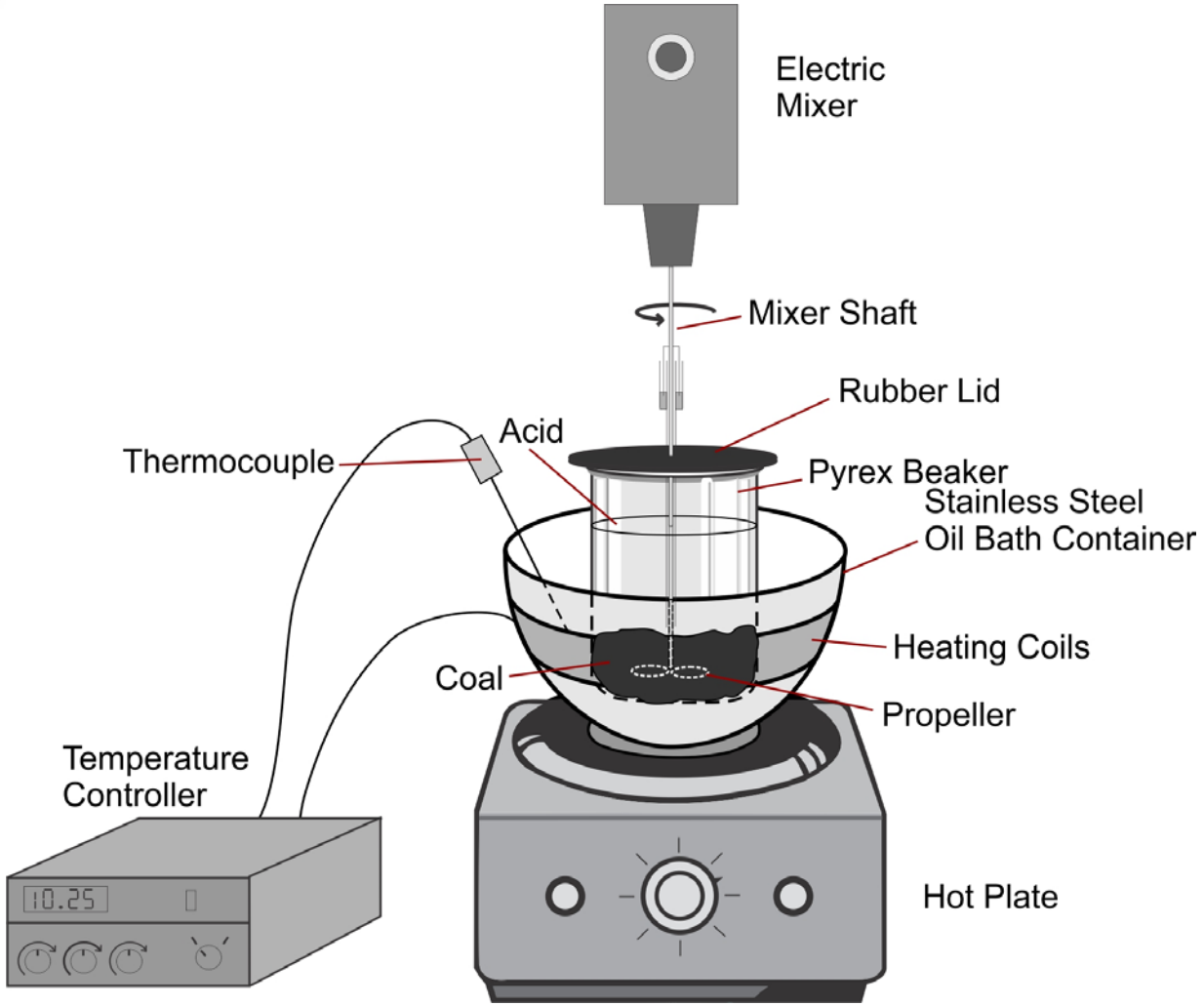
- Advanced coal cleaning
- Deoxygenation of coals
- Graphene quantum dots

# COAL DEMINERALIZATION – PHYSICAL CLEANING



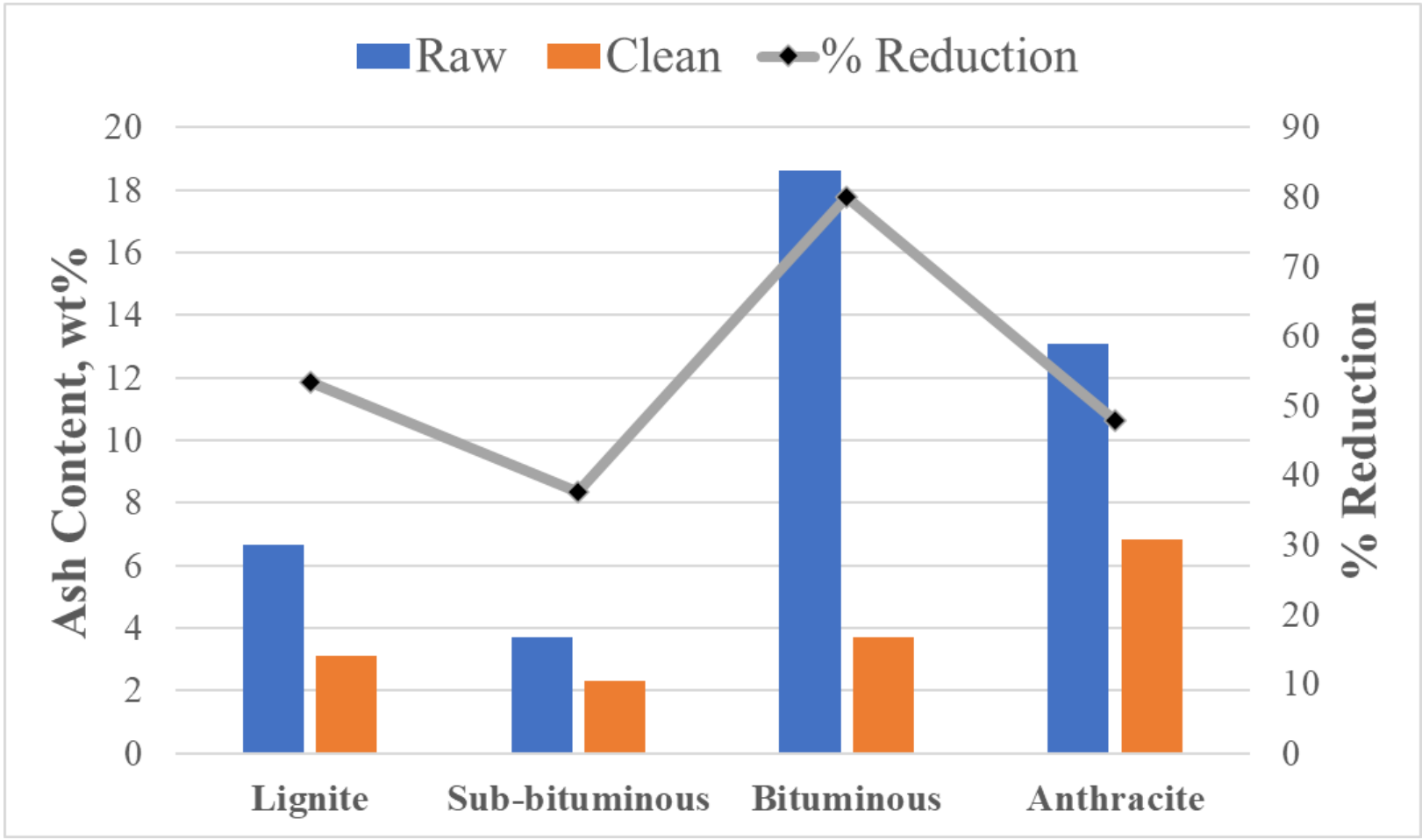
- -35-mesh crush (bituminous)
- -30-mesh crush (anthracite)
- Mix with 1.5-sg solution (bituminous)
- Mix with 1.8-sg solution (anthracite)
- Recover and rinse with DI water

# COAL DEMINERALIZATION – CHEMICAL CLEANING

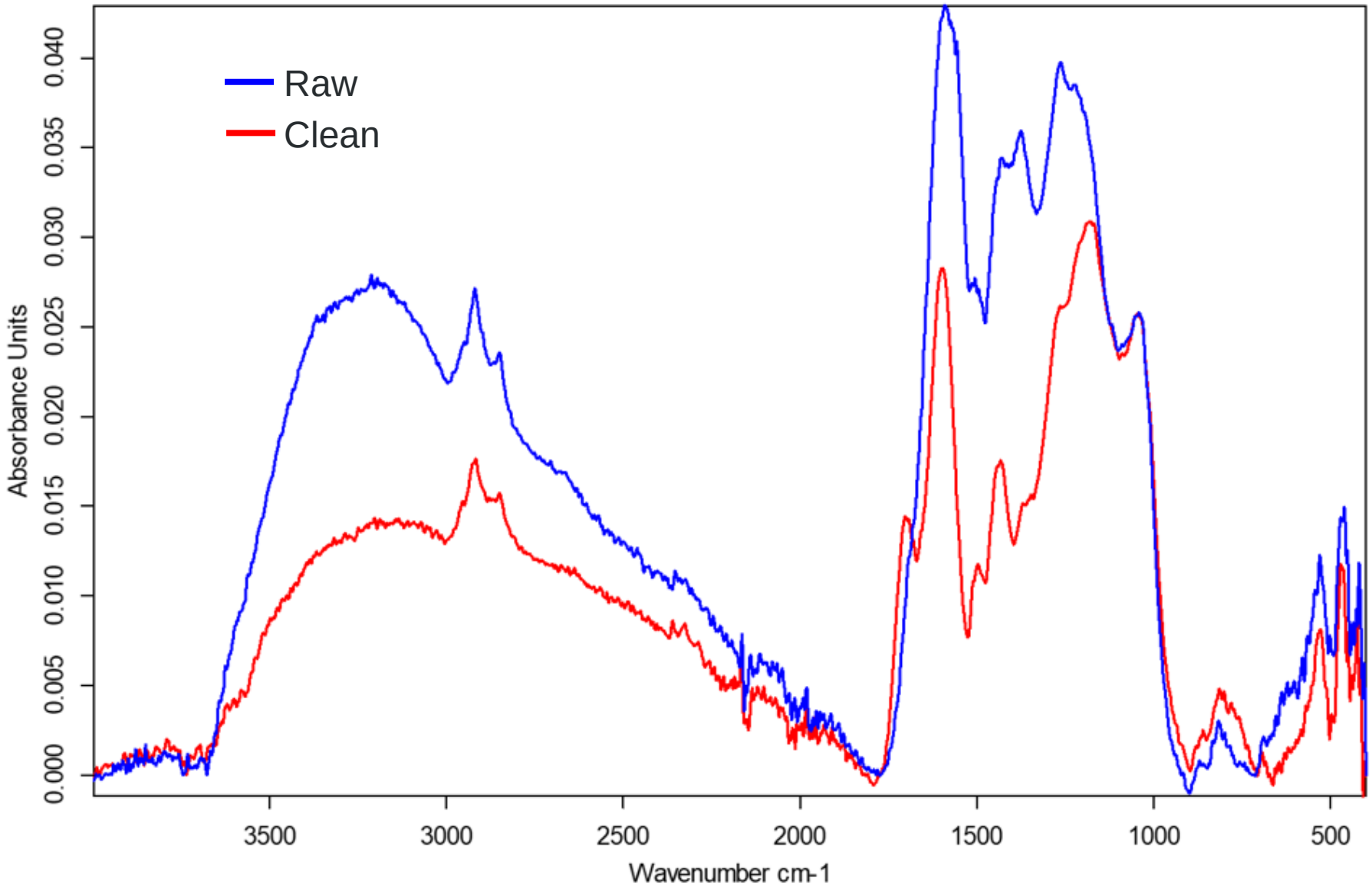



- ¼-inch crush (lignite, subbituminous)
- -35-mesh crush (bituminous)
- -30-mesh crush (anthracite)
- Treat with HCl at 70$^{o}$C overnight
- Recover and rinse with DI water

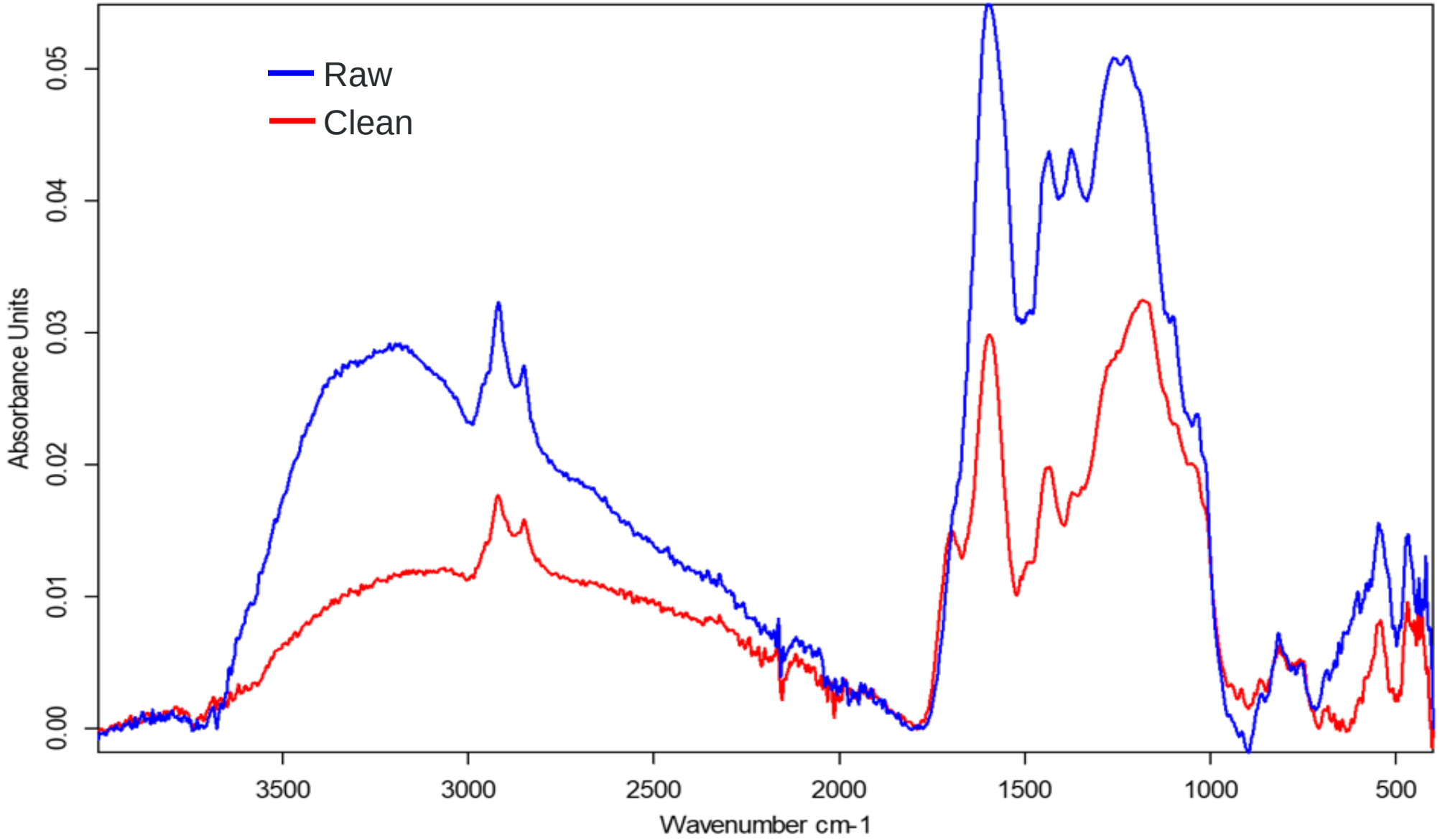
# COAL ASH REDUCTIONS



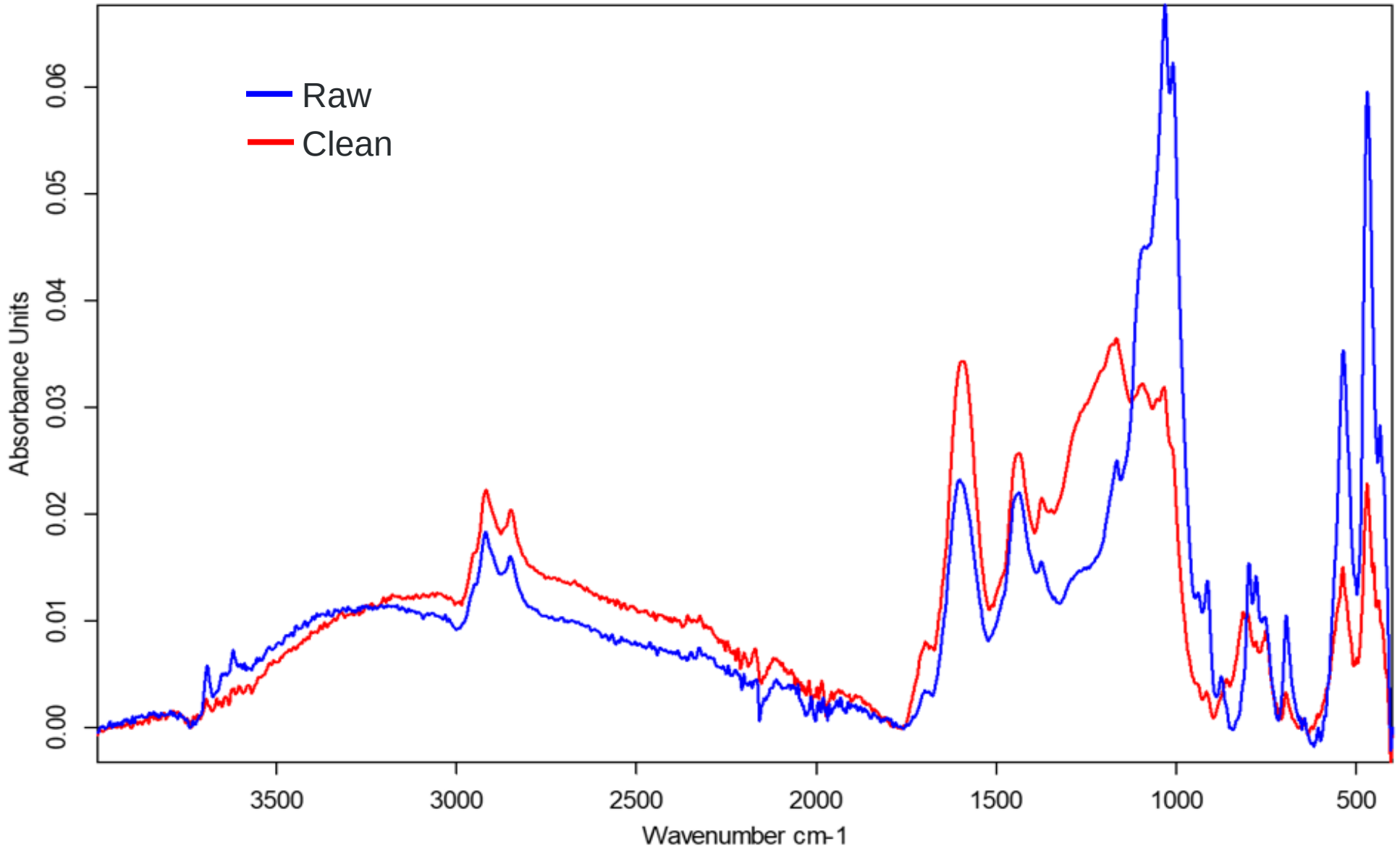

# FTIR SPECTRA FOR LIGNITE



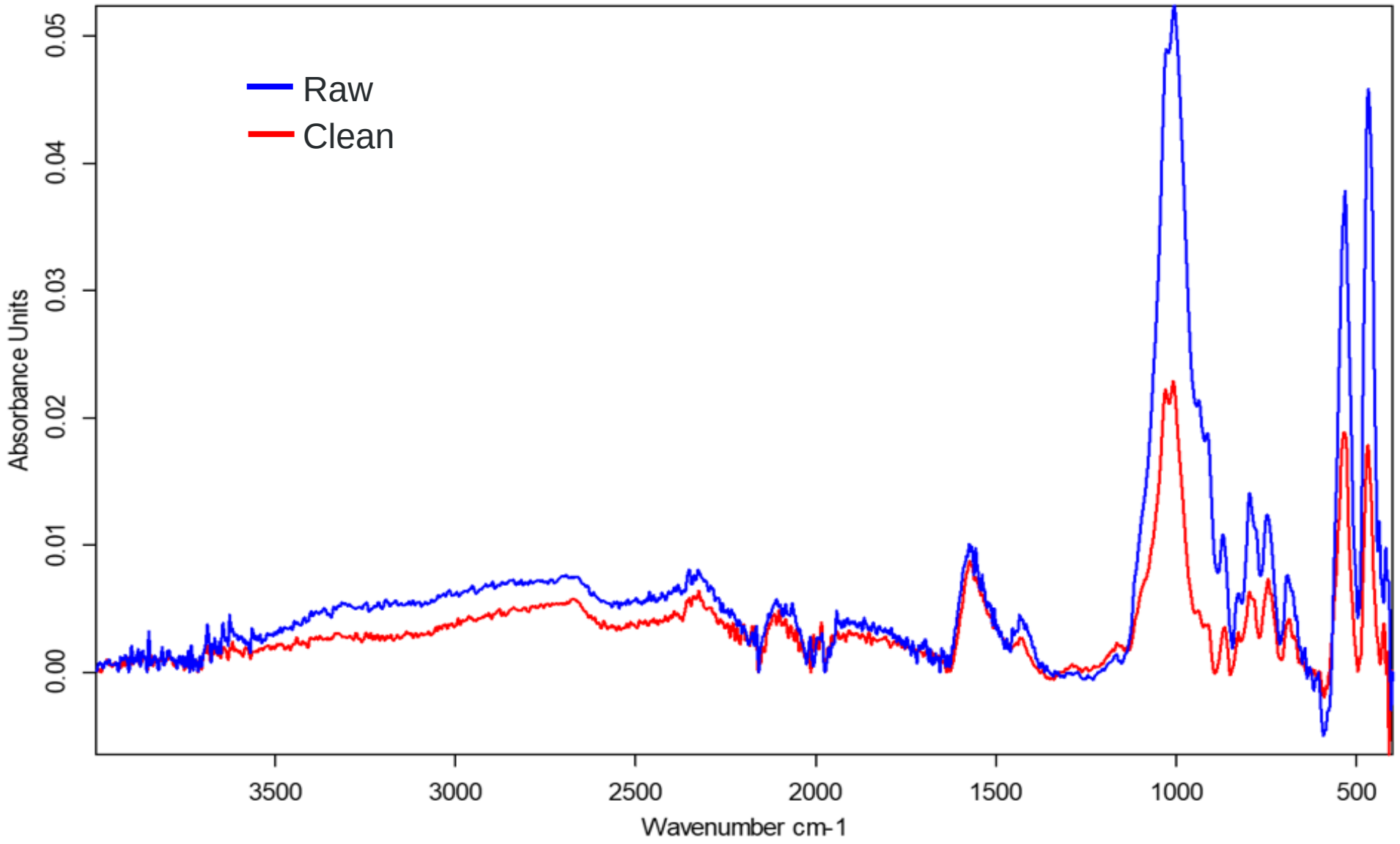
# FTIR SPECTRA FOR SUBBITUMINOUS COAL



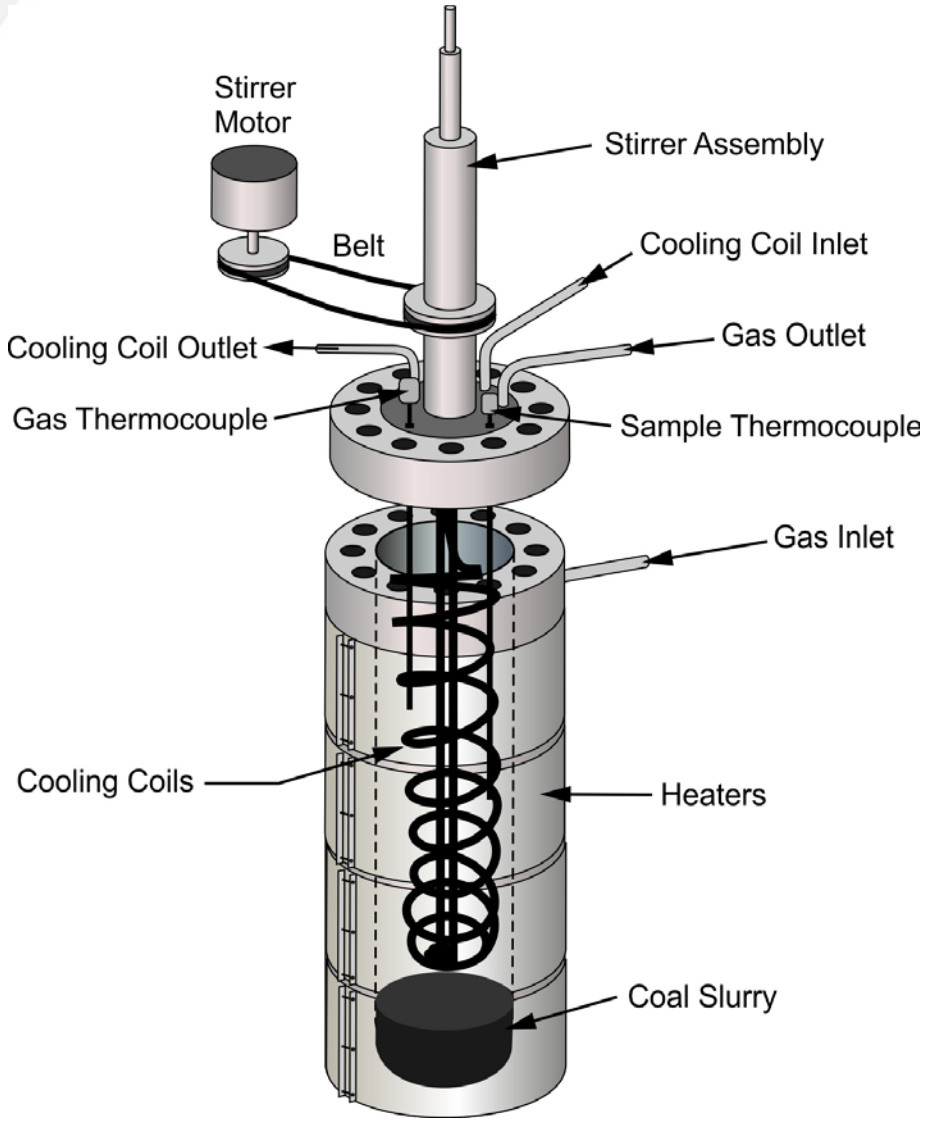
# FTIR SPECTRA FOR BITUMINOUS COAL



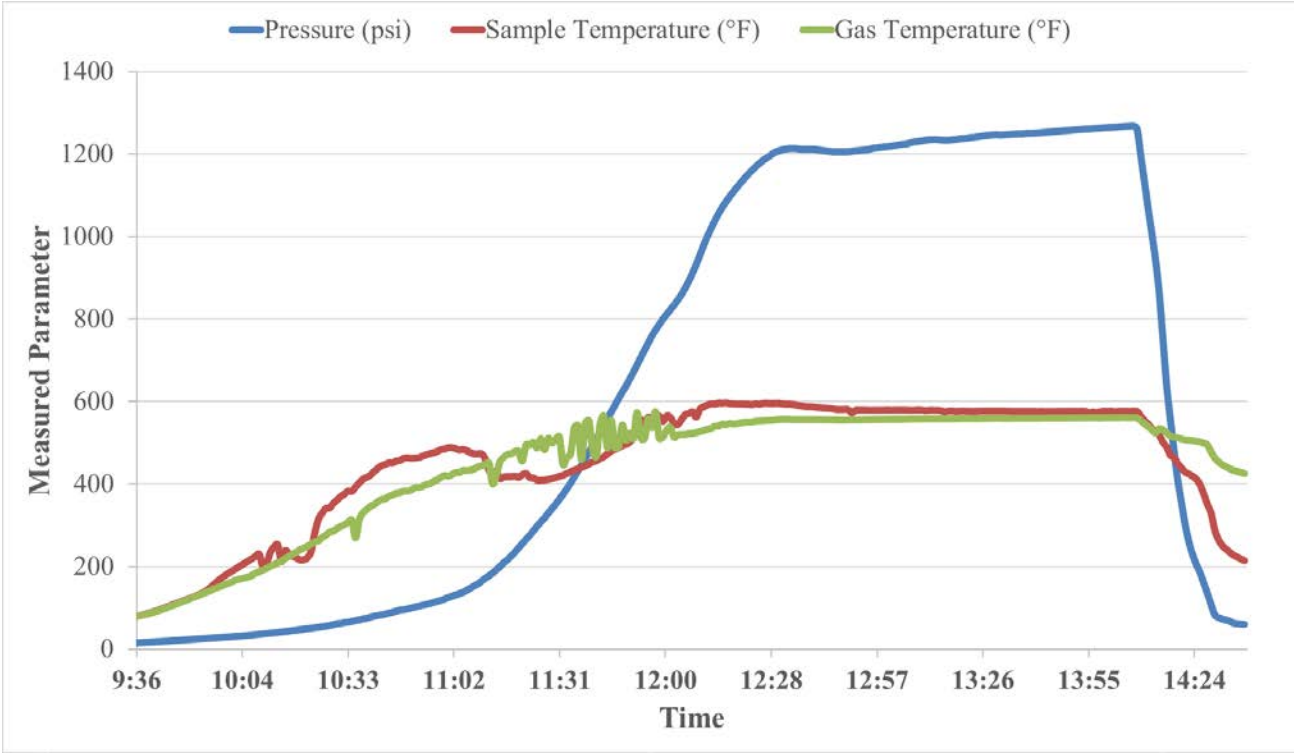
# FTIR SPECTRA FOR ANTHRACITE



# COAL DEOXYGENATION OF REACTIONS

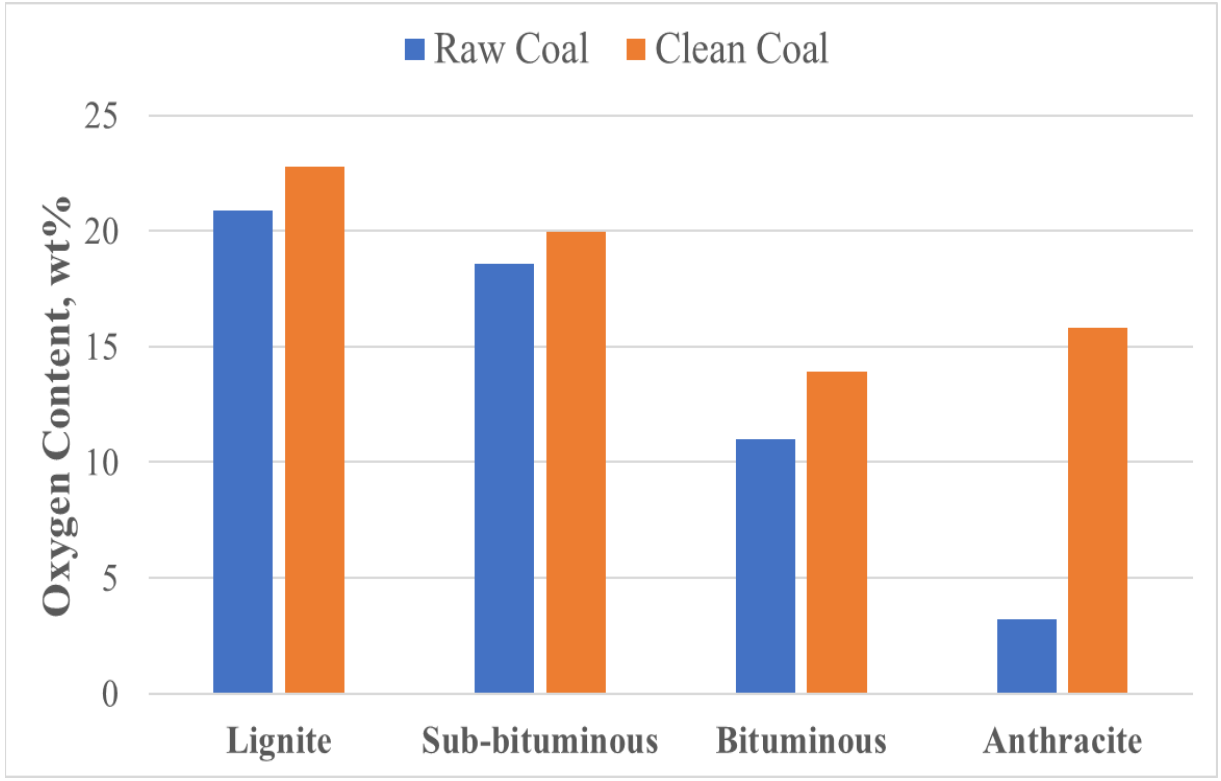



## Typical Test Run Profile

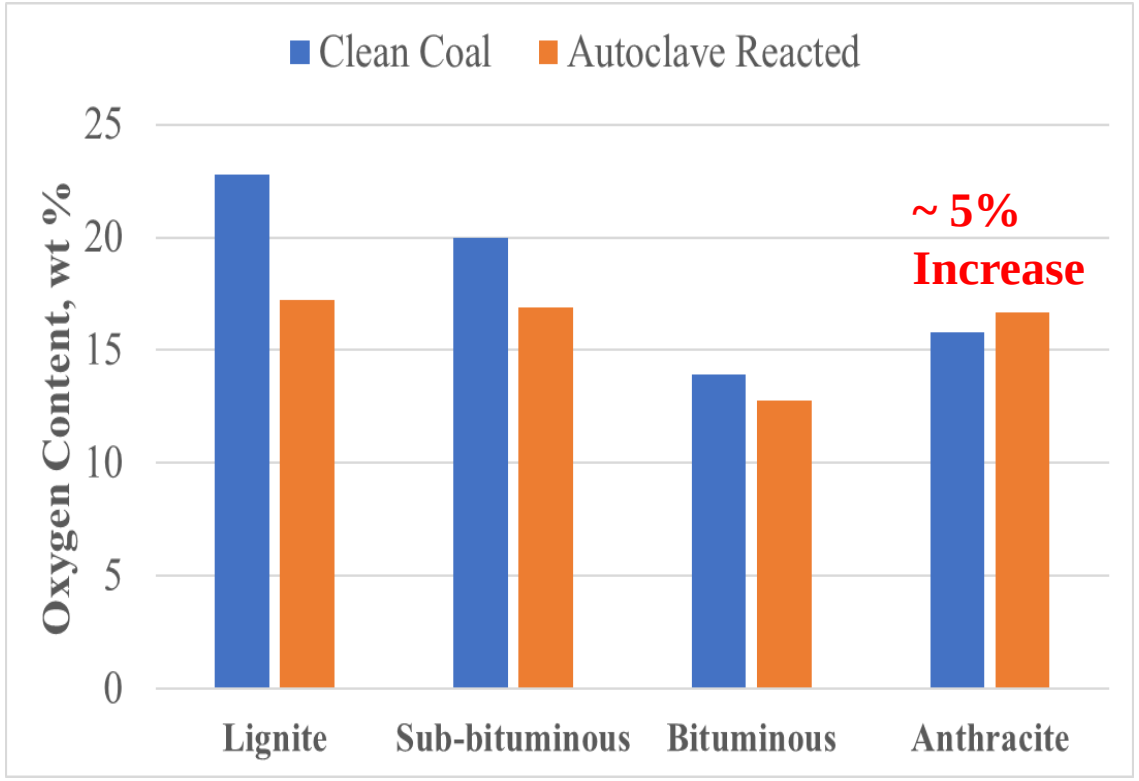


# OXYGEN CONTENT OF COAL RESIDUE

## $O_2$ Increase During Cleaning Process



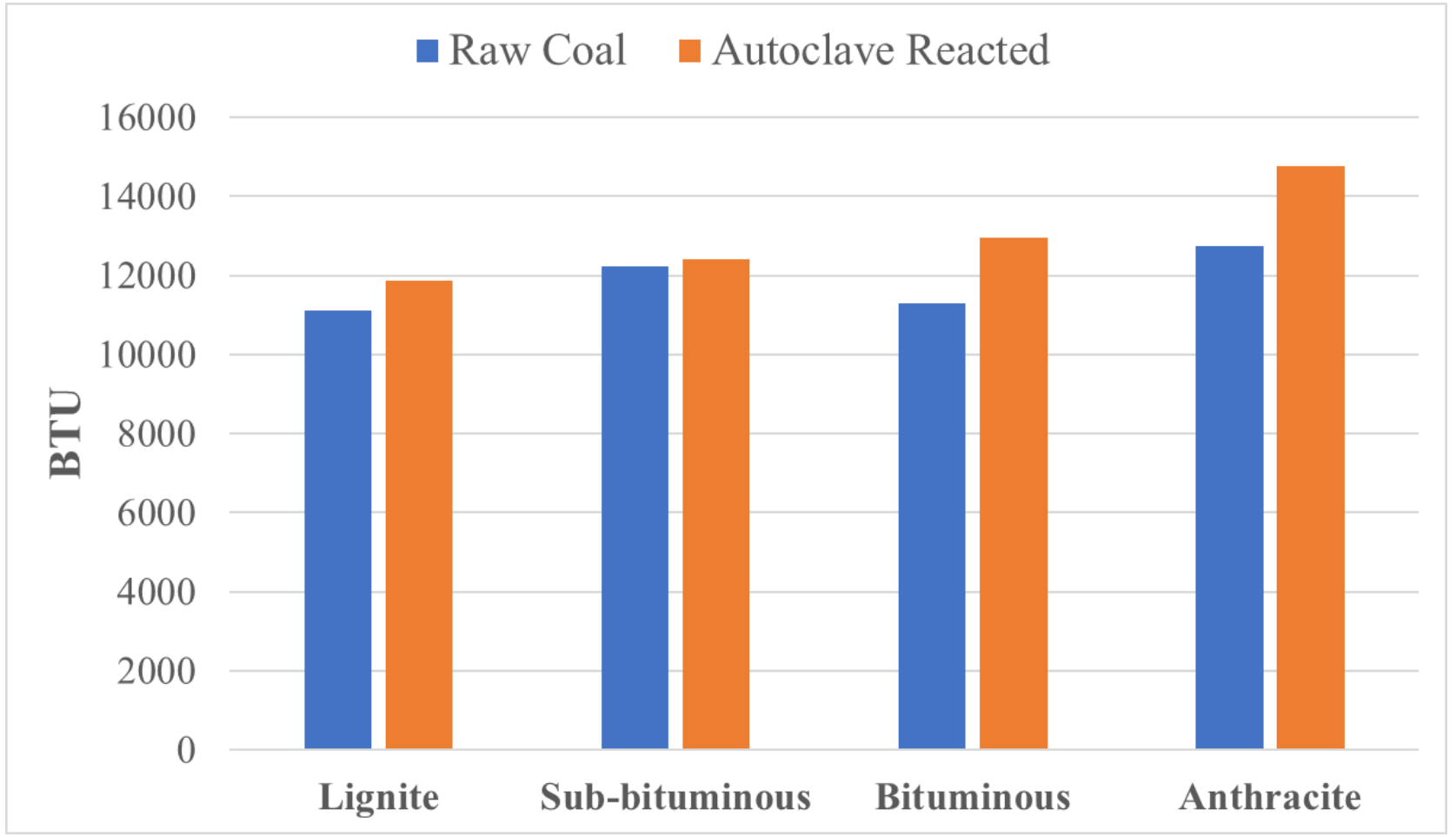

## $O_2$ Reduction During Autoclave Reactions



# ANALYSIS OF GASES FROM AUTOCLAVE REACTIONS

| Component, % | Lignite | Subbituminous | Bituminous | Anthracite |
|---|---|---|---|---|
| $H_2$ | 11.3 | 9.3 | 52.7 | 80.9 |
| $H_2S$ | 0.4 | tr | tr | tr |
| **$CO_2$** | **87.6** | **86.9** | **45.6** | **19.0** |
| CO | 0 | 2.2 | 0 | 0 |
| $CH_4$ | 0.2 | 0.8 | 0.9 | 0 |

# INCREASE IN COAL Btu



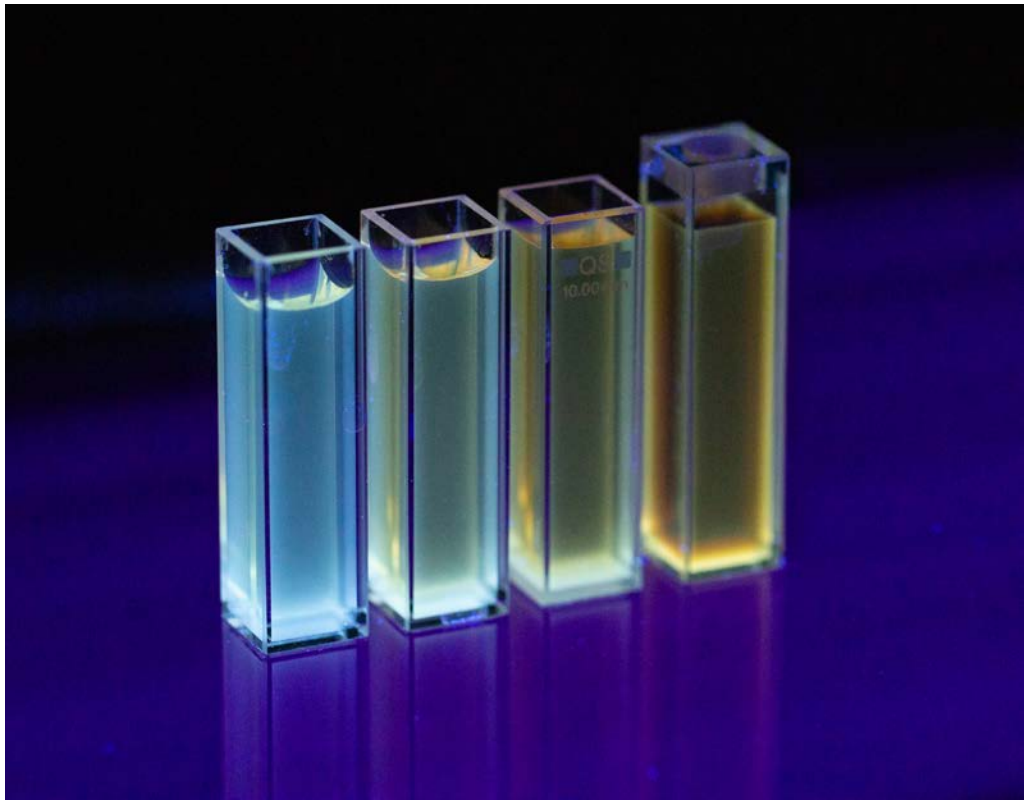

Side benefit from coal deoxygenation is increase in Btu.

# GRAPHENE QUANTUM DOTS (GQDs) FROM RAW AND CLEAN COAL SAMPLES

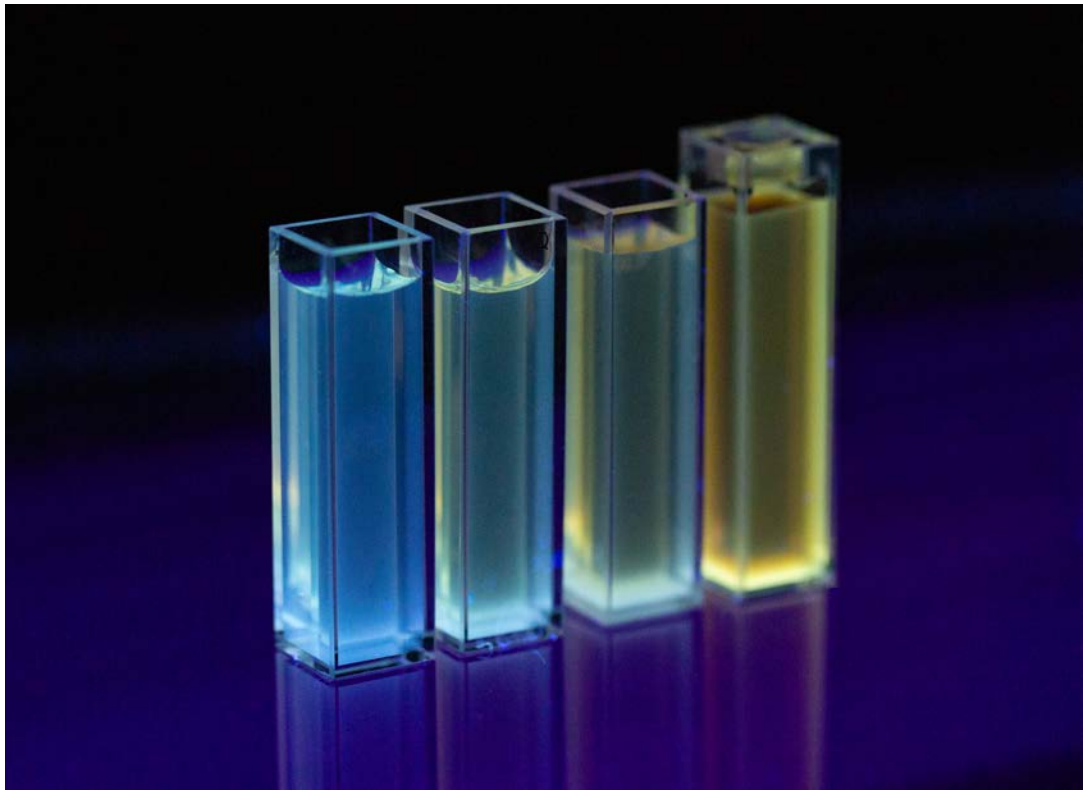
**Samples from left to right**: lignite, subbituminous, bituminous, anthracite.
**Pairs**: raw, clean.

# UV FLUORESCENCE IMAGES OF GQDs

GQDs from Raw Coal Samples

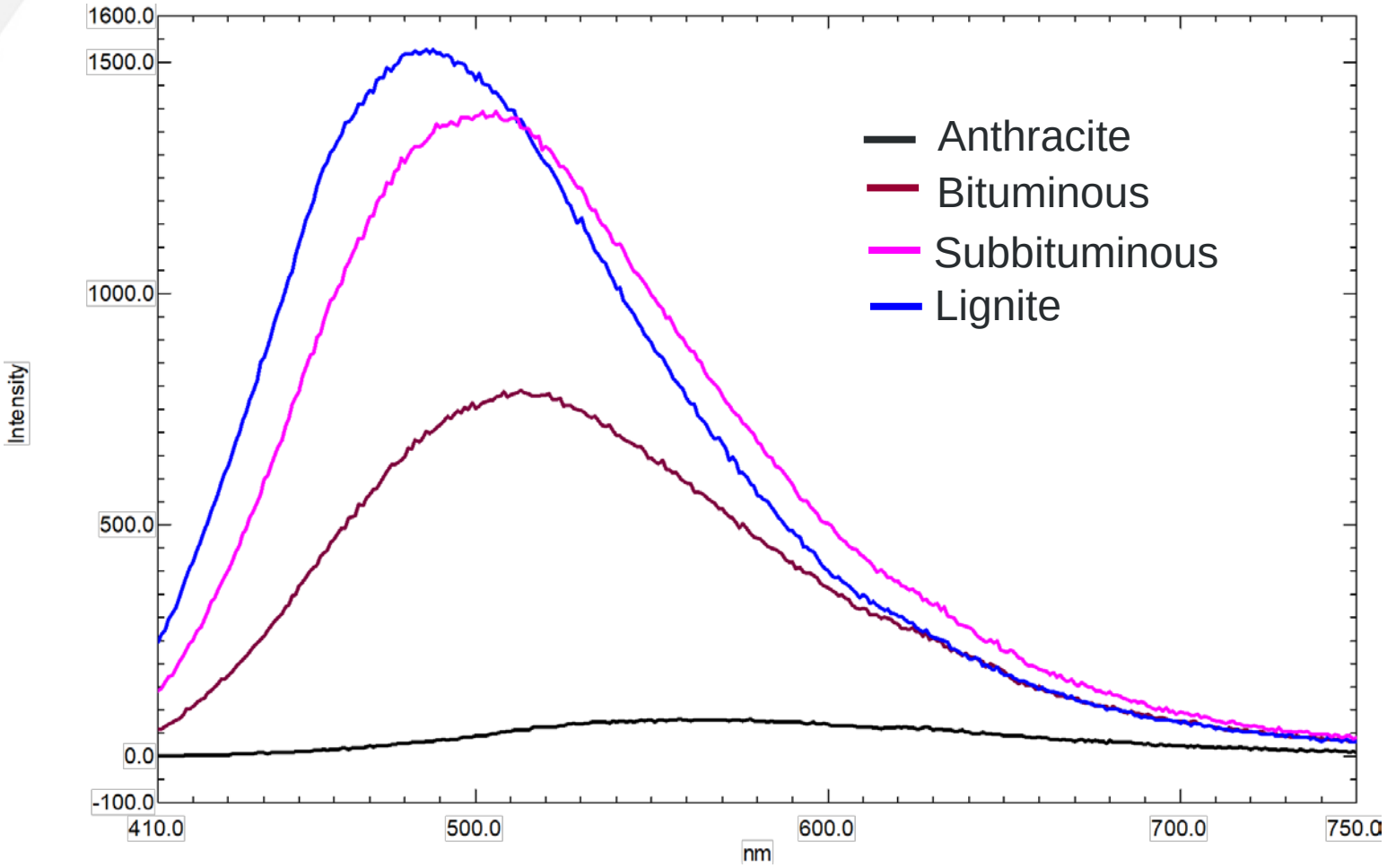


GQDs from Clean Coal Samples



**Samples from left to right**: lignite, subbituminous, bituminous, anthracite.

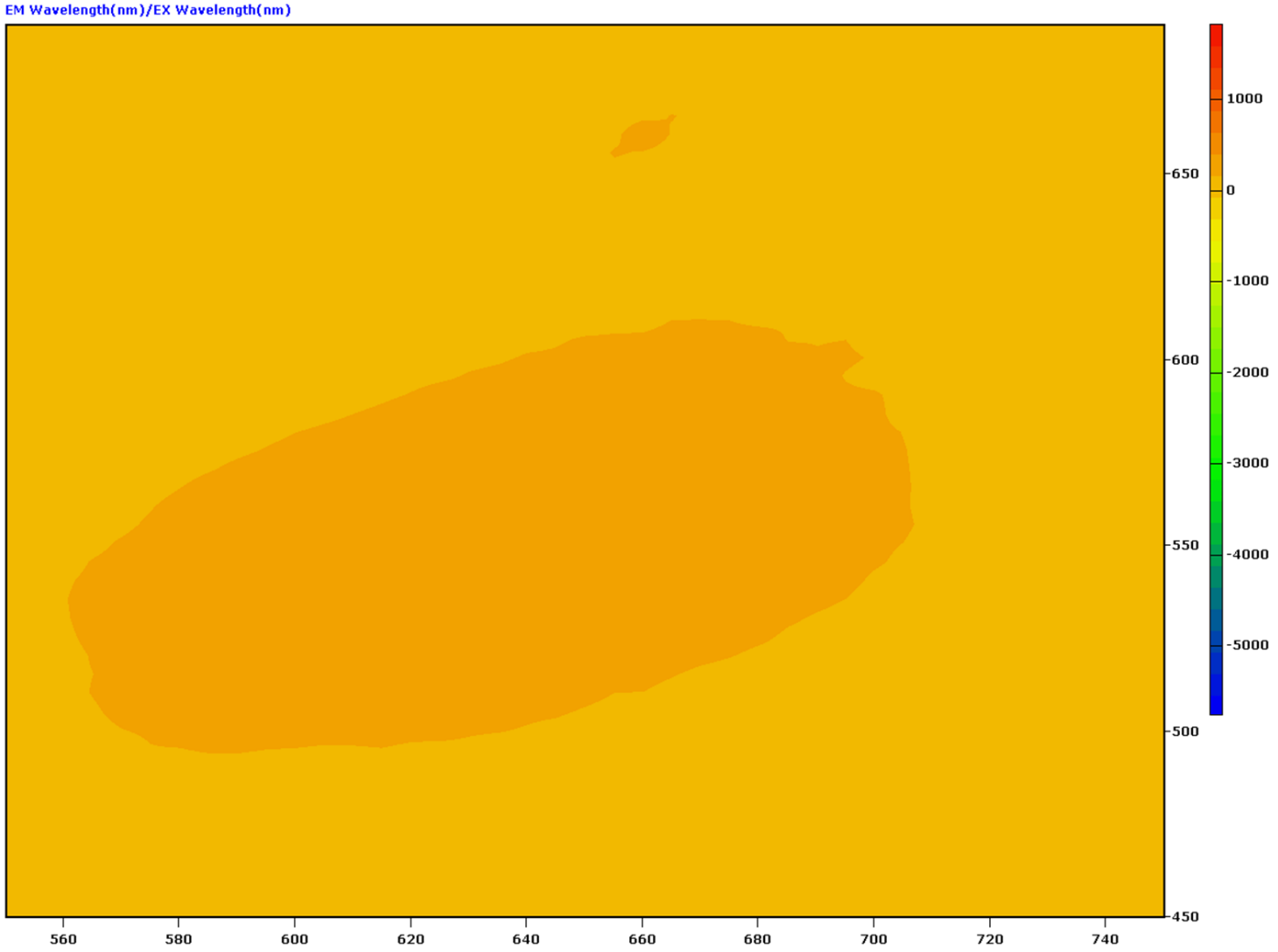
# UV FLUORESCENCE SPECTRA OF GQDs




| Sample | Raw $\lambda_{max}$ | Clean $\lambda_{max}$ |
|---|---|---|
| Lignite | 488 | 503 |
| Subbituminous | 502 | 515 |
| Bituminous | 513 | 520 |
| Anthracite | 621* | 624* |

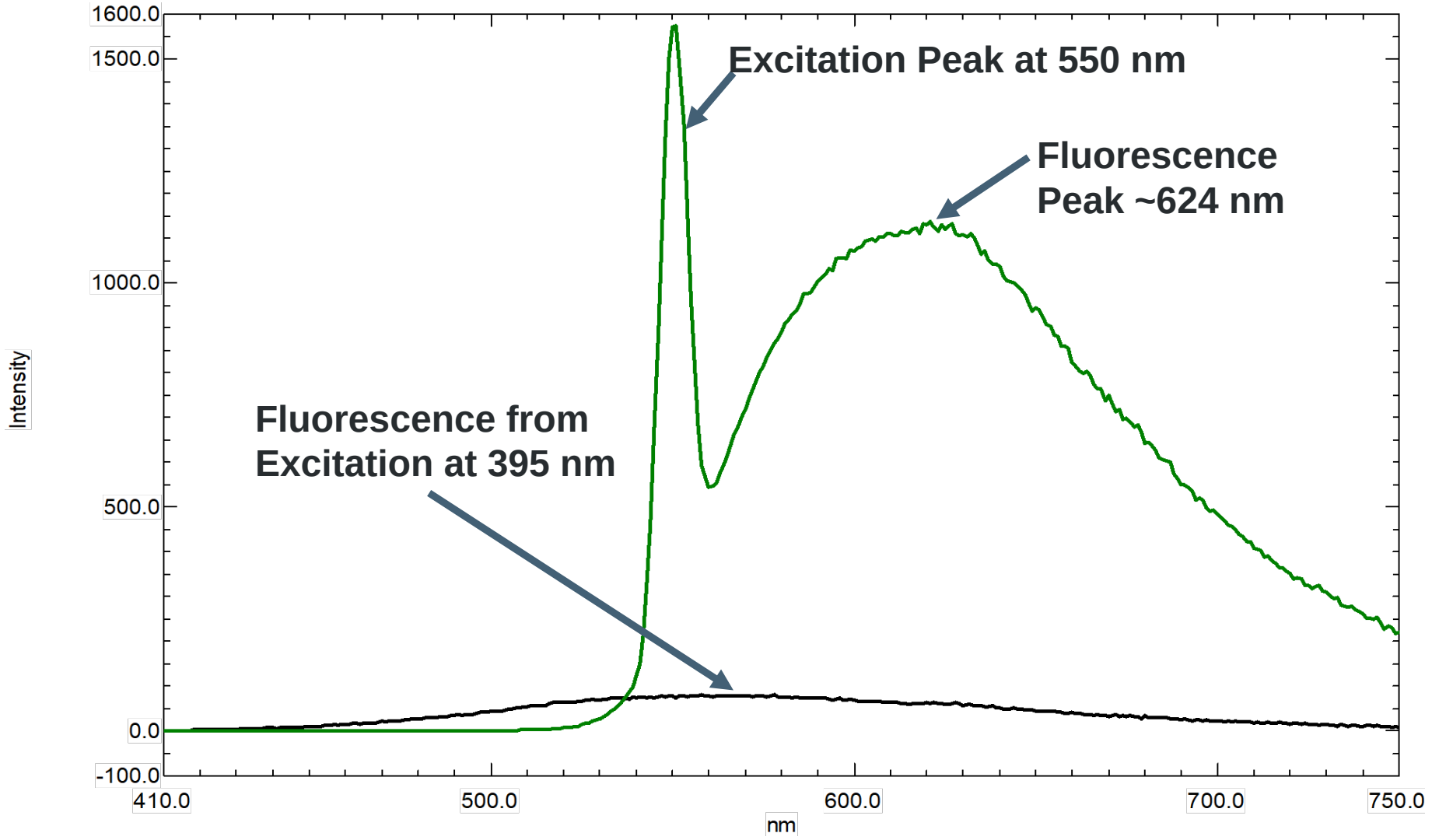
- Excitation at 395 nm
- No peak for anthracite
- *Excited at 550 nm

# 3D UV FLUORESCENCE MAP FOR ANTHRACITE

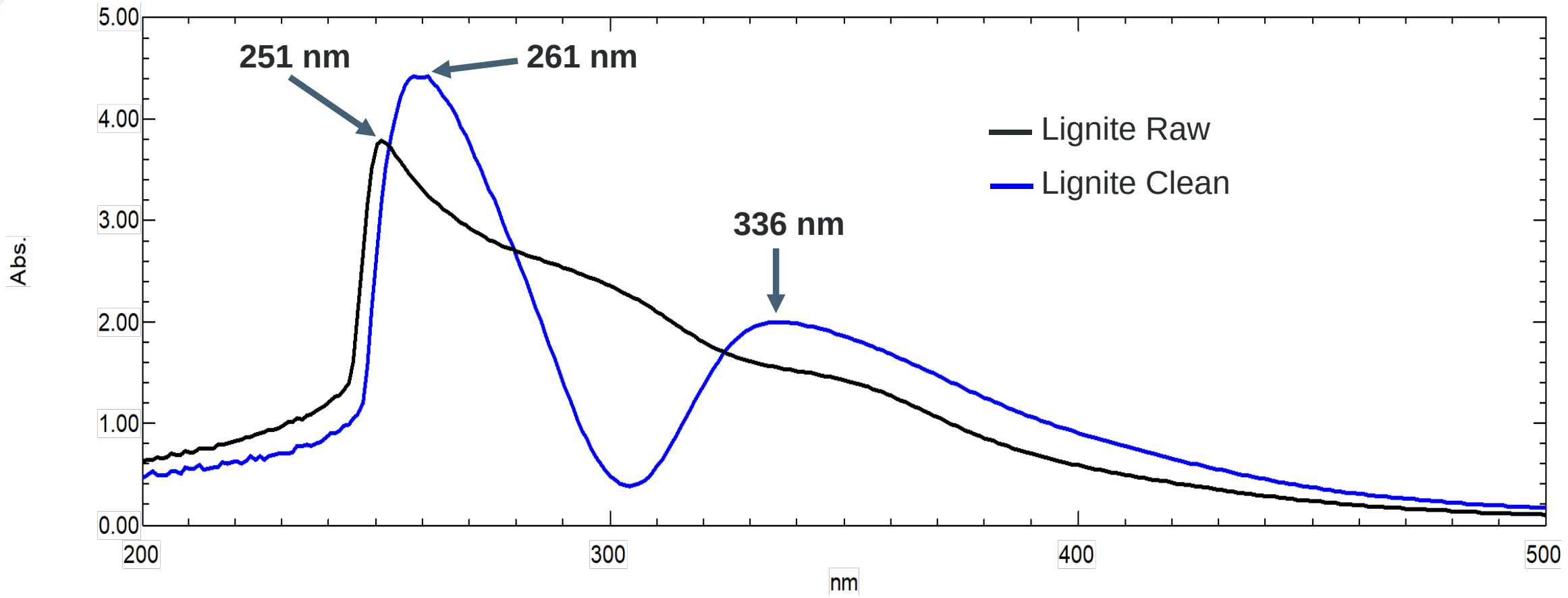



Anthracite needs to be excited in the visible region between 500 and 600 nm to observe maximum fluorescence intensity.

# ANTHRACITE FLUORESCENCE SPECTRA AT 395 AND 550 nm

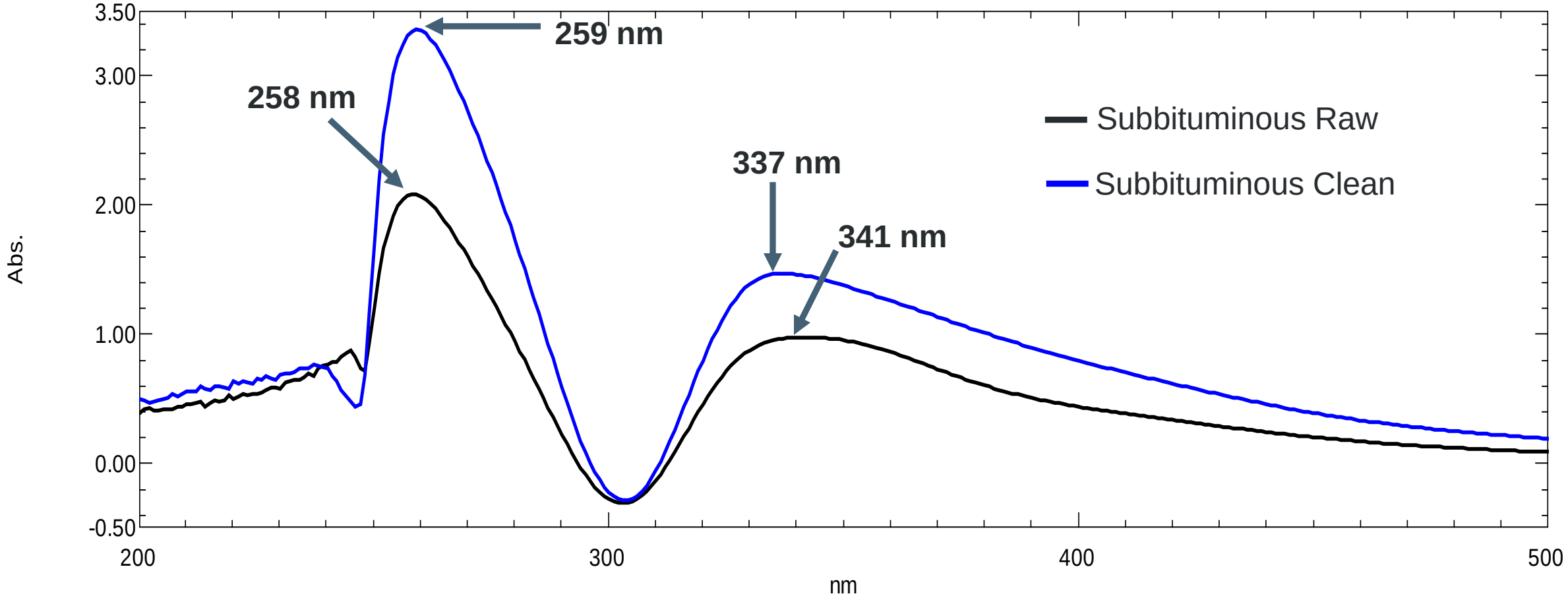


# UV-Vis SPECTRA OF GQDs FROM LIGNITE

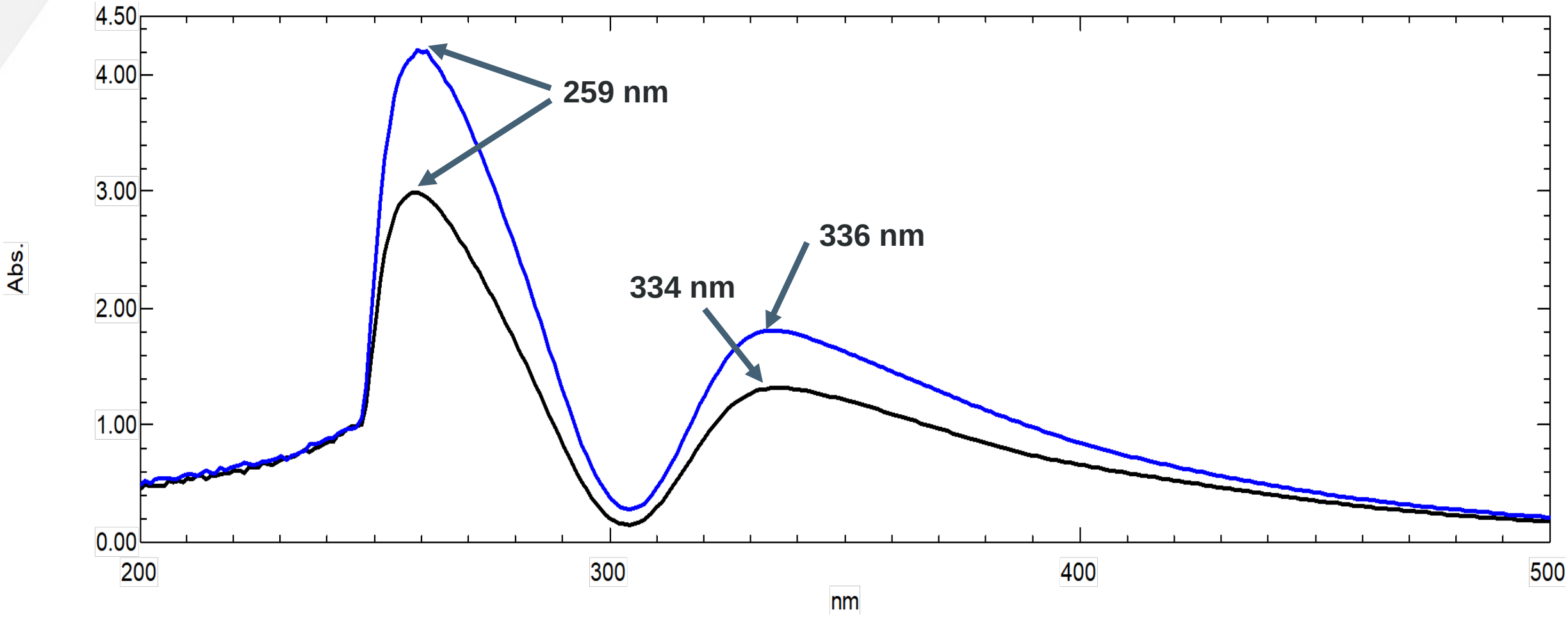



Poorly developed second peak in raw compared to clean sample.

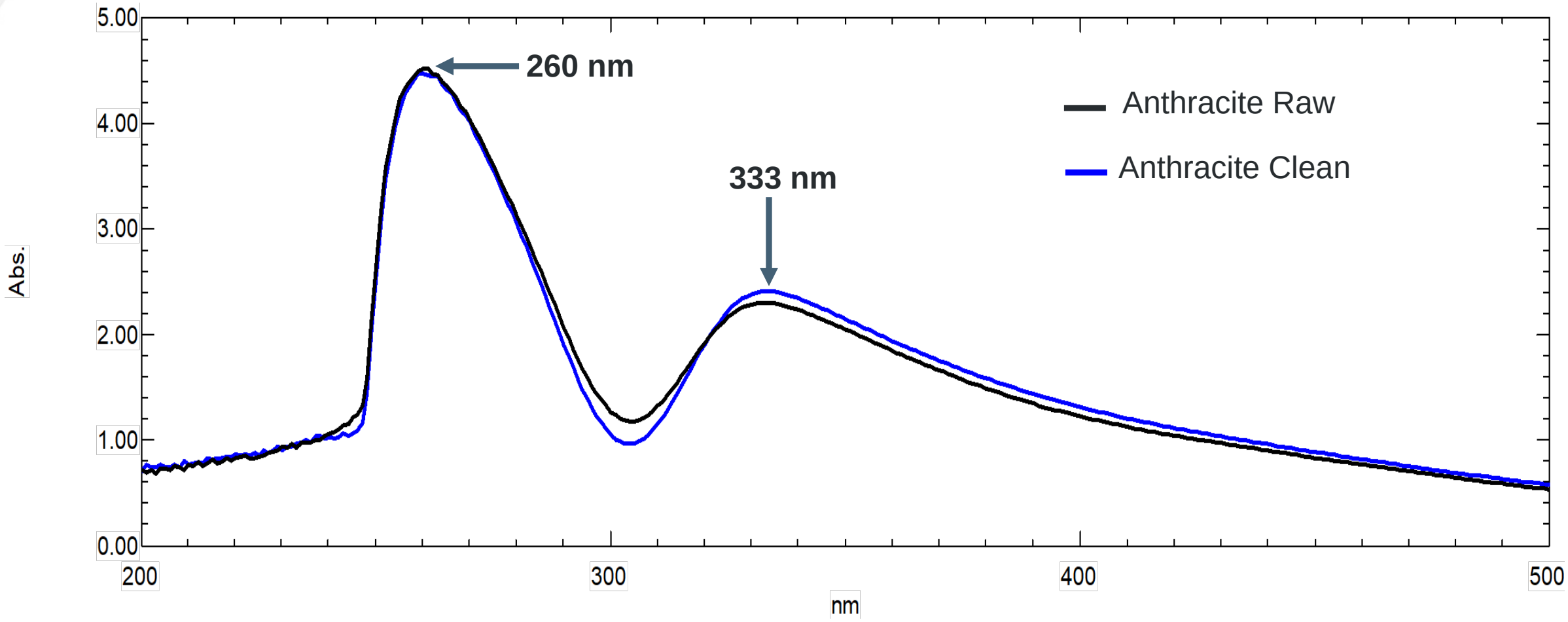
# UV-Vis SPECTRA OF GQDs FROM SUBBITUMINOUS COAL



# UV-Vis SPECTRA OF GQDs FROM BITUMINOUS COAL



# UV-Vis SPECTRA OF GQDs FROM ANTHRACITE



# CONCLUSIONS AND LESSONS LEARNED

- Coal ash has an impact on the quality of GQDs, with more serious effects on lignite-derived GQDs.
- Coal oxygen content reductions of 8%–25% have been demonstrated, with a corresponding increase in Btu.
- UV fluorescence of GQDs shows a progressive red shift from lignite-derived GQDs to anthracite.
- Anthracite GQDs can be excited by visible radiation.
- Lignite produces the bluest-emitting GQDs.

# ACKNOWLEDGMENTS

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# THANK YOU

Critical Challenges. Practical Solutions.