

Impact of Coal-Borne Impurities on Coal-Derived Graphene Quantum Dots

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ABSTRACT

The impact of coal-borne impurities on coal-derived graphene quantum dots (GQDs) has been investigated on four U.S. coal ranks: lignite, subbituminous, bituminous, and anthracite. Preliminary characterization of the GQDs has been done using ultraviolet-visible spectroscopy (UV-vis) and UV fluorescence spectroscopy. GQDs produced from raw and clean coal samples exhibit differences in their optical properties. Higher UV-vis absorbances were observed from GQDs obtained from clean coal samples compared to those obtained from raw coal samples. In all cases, the photoluminescence emission spectra show an increasing redshift from lowest to highest coal rank. Excitation of anthracite-derived GQDs in the UV region produced little to no fluorescence signal, but a maximum emission signal was observed when excited in the visible region. These studies are relevant in tailoring specific optical applications of GQDs derived from different coal ranks.

Keywords: coal, coal-borne impurities, graphene, graphene quantum dots, optical properties

1 INTRODUCTION

Technological advances in new materials development are increasingly incorporating two-dimensional, high-value materials from carbonaceous feedstocks. Graphene and its derivatives such as graphene oxide, reduced graphene oxide, and graphene quantum dots (GQDs) are increasingly being used in thermal and electrically conductive devices [1] and composite materials applications [2]. Most of the current approaches use natural graphite as the feedstock for graphene products. This route is hindered by the limited natural reserves and, thus, high cost for such raw materials. As a result, greater attention is being directed to finding new ways to harness the rich carbon content of abundant and relatively cheap coal. The goal of this study is to develop methods to improve the quality of coal as a precursor for graphene and other high-value carbon materials.

2 METHODS

The four U.S. domestic coal samples used in this study include southern Pennsylvanian anthracite from Schuylkill County, Pennsylvania; bituminous coal from Sufco Mine in Sevier County, Utah; subbituminous coal from the Northern Antelope Rochelle Mine (NARM) in Campbell County,

Wyoming; and lignite coal from Center Mine in Oliver County, North Dakota.

The methods employed in the cleaning of these coal samples include physical [3] and chemical [4] cleaning to remove ash constituents. Portions of the raw coals were crushed to about -30-mesh (~595 μm) particle size and mixed with a salt solution to separate the coal-rich fraction from the mineral-rich fraction by a specific gravity separation technique. The coal-rich fraction was further treated chemically with mineral acids such as hydrochloric acid (HCl) or nitric acid (HNO_3) to remove additional mineral content. The cleaned coal residues were subsequently reacted with proprietary chemical agents in an autoclave reactor to reduce the heteroatom content. The upgraded coal residues were then treated with an acid mixture consisting of 3 parts sulfuric and 1 part nitric acid overnight at 70°C to digest the coal [5]. The resultant solution was neutralized by adding a 3M sodium hydroxide solution. The neutral solution was filtered through a 5- μm polytetrafluoroethylene (PTFE) filter, and the filtrate was dialyzed in 3.5-kD dialysis bags for 72 hours to obtain purified GQD solutions.

3 RESULTS

The inorganic ash impurity reductions ranged from 37% to 80% (Fig. 1), with residual ash content of 3.1 wt% for lignite, 2.3 wt% for subbituminous, 3.7 wt% for bituminous, and 6.8 wt% for anthracite. The oxygen content reductions of the autoclave-reacted coal residues (Fig. 2) were 24%, 15%, and 8% for lignite, subbituminous, and bituminous coals, respectively. In the case of anthracite, there was a marginal increase in oxygen content of about 5%.

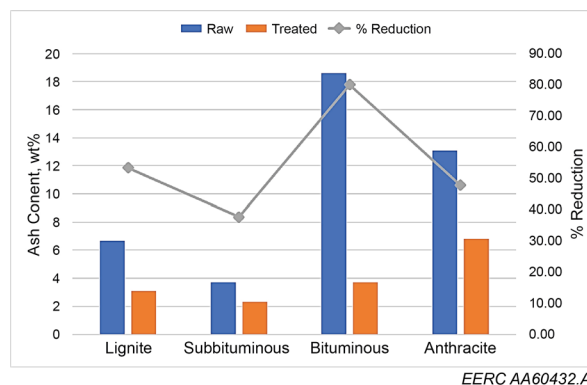


Figure 1: Raw and chemically treated coal residual ash contents and corresponding percent reductions.

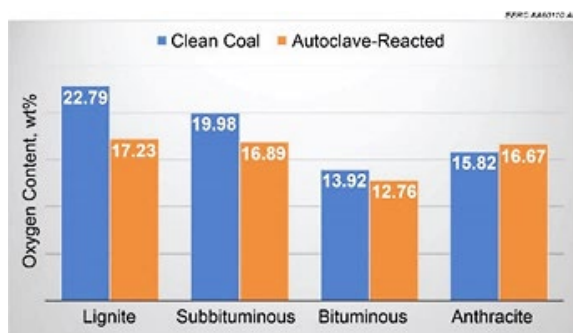


Figure 2: Oxygen content of clean and autoclave-reacted coal residues.

Bright light images of the GQD solutions made from raw and clean coal residues are shown in Fig. 3 and their corresponding photoluminescence images under ultraviolet (UV) radiation are shown in Fig. 4. A comparison of the UV-vis (visible spectroscopy) absorption spectra of the GQDs prepared from the raw and clean coals is shown in Fig. 5. A similar comparison for the UV photoluminescence spectra excited at 395 nm is presented in Fig. 6. The fluorescence spectrum of anthracite-derived GQDs excited at 550 nm is presented in Fig. 7 and compared to the corresponding spectrum excited at 395 nm.



Figure 3: Photos of GQDs from raw and clean coal samples. Image pairs (left to right): lignite, subbituminous, bituminous, and anthracite. In each pair, the left sample is from raw coal and the right sample is from clean coal.

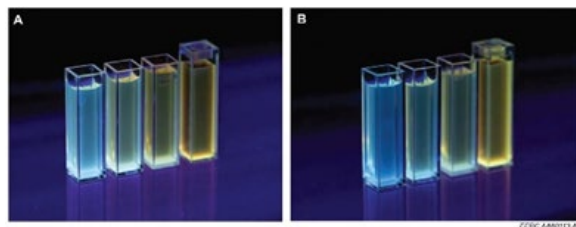


Figure 4: Photoluminescence images of GQDs from A) raw and B) clean lignite, subbituminous, bituminous, and anthracite coals, respectively.

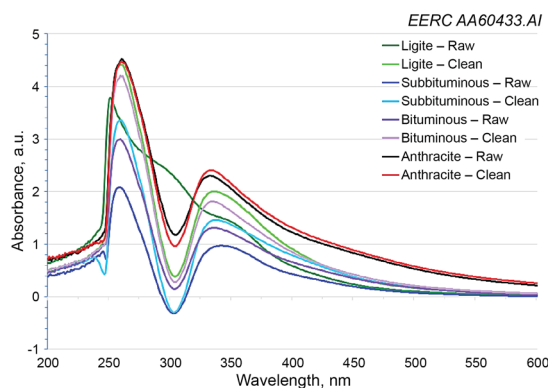


Figure 5: Comparison of UV-vis absorbance spectra of GQDs made from raw and clean coals.

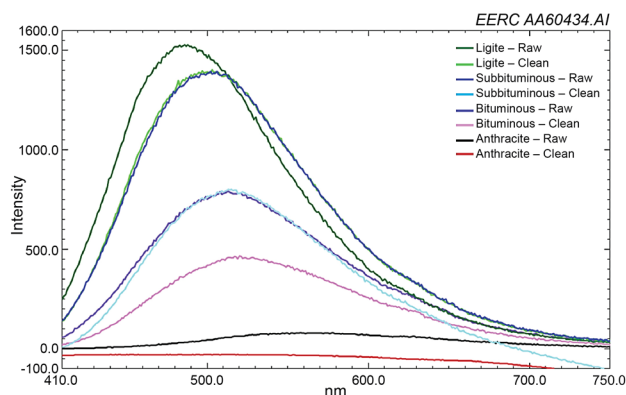


Figure 6: Comparison of photoluminescence spectra of GQDs made from raw and clean coals excited at 395 nm.

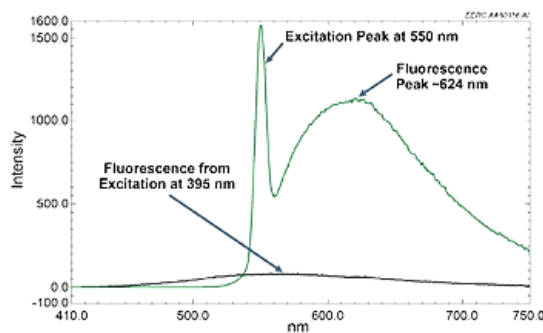


Figure 7. Photoluminescence spectrum of anthracite GQDs excited at 395 and 550 nm.

4 DISCUSSION

Results of coal-borne impurities removal, primarily ash and heteroatoms, are promising. Residual ash content in the coals of about 3 wt% obtained by hydrofluoric acid-free procedures are encouraging. Additional refinements are planned to achieve ultraclean coal residues with residual ash content of 0.5 wt% or less to further improve the coal-derived carbon precursors for high-end applications such as synthetic graphite. The key heteroatom that was targeted for removal in this study is oxygen, and reductions of 8%–24% were achieved. Anthracite samples showed a marginal oxygen content increase of about 5%, due to the cleaning

process. Removal of oxygen is important, especially in cases where the target product is synthetic graphite, where oxygen tends to form cross-linked isochar that limits the extent of graphitization of the coal residues. In addition, ash impurities in coal-derived graphite can create defects that limit the application of synthesized graphite in fast-charging lithium ion-battery [6] applications.

GQDs produced from raw and clean coal samples exhibited differences in their optical properties. Higher UV-vis absorbances were observed from GQDs obtained from clean coal samples compared to those obtained from raw coal samples (Fig. 5). The increase in absorbances suggests an increase in the concentration of photabsorbers following a reduction of the ash impurities in the samples. In all cases, the photoluminescence emission maxima showed an increasing redshift from lowest to highest coal rank, which is consistent with an expected increase in the aromatic ring content and an increase in the degree of ring condensation that correlates with coal maturity. Lignite produces the bluest-color UV fluorescence, and anthracite fluoresces orange when exposed to UV radiation. Excitation of anthracite-derived GQDs in the UV region produced little to no fluorescence signal, but a maximum emission signal at 624 nm was observed when excited in the visible region at 550 nm. These studies are relevant in tailoring specific optical applications of GQDs derived from different coal ranks and for producing high-value carbon materials from abundant coal natural resources.

5 CONCLUSIONS AND FUTURE WORK

GQDs have been made from four different U.S. coal ranks (lignite, subbituminous, bituminous, and anthracite) after cleaning to remove coal-borne impurities. The results of the cleaning show ash reductions in the range of 37% to 80%, with residual ash content as low as 2.3 wt%. Additionally, the oxygen content of the coals was reduced by 8%–24%. UV-vis spectra show that the GQDs made from clean coal residues have higher optical absorbances than those made from raw coals. UV photoluminescence emission spectra are increasingly redshifted from lowest coal rank (lignite) to highest coal rank (anthracite). Hence, lignite coal produces the bluest emission of the four coal ranks and anthracite produces an orange-colored emission. Furthermore, anthracite is the only coal type that can be excited efficiently in the visible region.

Future work is planned to refine the coal-cleaning methods to make ultraclean coals with residual ash content of about 0.5 wt% or less for high-end applications such as synthetic graphite. In addition, further characterization of the GQDs will be conducted to explore different applications as well as provide useful insights into the development of tailored optical applications using GQDs from different types of coal and/or by coal rank.

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