Synthesis of Graphene Dots from Coal

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ACKNOWLEDGEMENT

I am hearty thankful to God for giving the health and potential to carry out my research on **"Synthesis of Graphene Quantum dots form coals"**.It is a good experience.

My sincere gratitude goes to my supervisor Dr. Kawaljeet Singh for his guidance, encouragement, support and understanding.

TABLE OF CONTENTS

CHAPTER 1

1.1 INTRODUCTION

Graphene Quantum dots (GQD) is creation of Nano technological. GQD's have so exciting applications which makes it pivot center for industry's requirements. It's application such as quantum computing gates, sensors for biological process which works on photonic technique, and the enhancement of photovoltaic energy conversion. These devices are being created in a laboratory at commercial scale because of ascendable demand of QD. The production material and synthesis procedure are accomplishable and less costly for the person who uses these quantum based devices.

It was observed and analyzed that graphene sheets which has range from 4 nm to 16 nm in radius naturally existing in fossil fuel possessing of carbonized vegetable thing such as coal. When graphene is separated from coal using oxidative cutting process, it shows quantum dot like photonic attribute.

Photonic attribute of GQD's are varies with the variation of contents of the coal. Coal can be differentiate with the help of moisture and carbon contents

1.2 Types of Coal

On the basis of moisture and carbon contents variations, coal can be subdivided as follow:

1 **Peat -**This coal has soft texture and brown in colour. it is made of sixty per cent organic matter such as ferns and vegetation.

2 **Lignite-** This type of coal is soft brown and it contains a large amount of water. It has high calorific value than peat

3 **Sub-Bituminous-** carbon contents are pure and the heat produced by this coal is more than lignite because this coal is formed by more pressure on lignite coal and this pressure expellees the water form lignite and turns it into Bituminous.

4 **Anthracite-**it is highest rank coal and metamorphic rock. This coal has hardness but light weight and quite black in colour. This type of coal consists of little water contents.

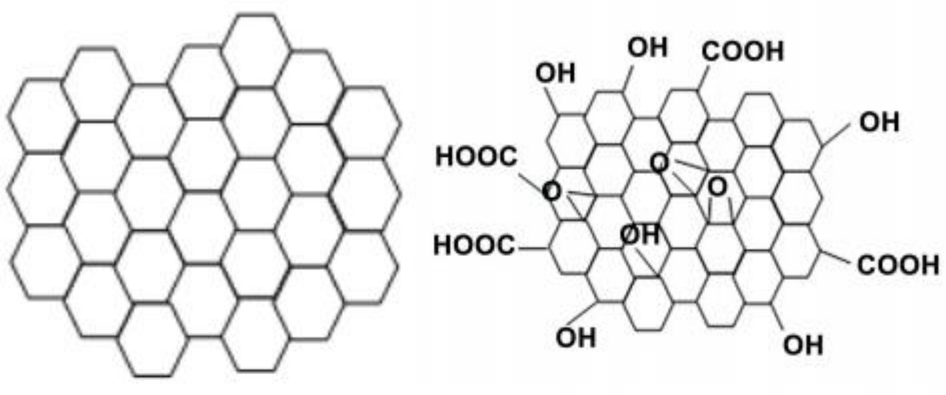
1.3 GRAPHENE

Like Diamond and graphite, Graphene is also allotropes of carbon. A single layer of carbon atoms are arranged in a hexagonal lattice. But it is basic allotropes than other allotropes of carbon.

Graphene consists of so many aromatic molecules, the ultimate case of the family of flat polycyclic hydrocarbons. Graphene is the combination of graphite and the suffix –ene.

1.4 STRUCTURE OF GRAPHENE

Graphene is a crystalline form of allotrope of carbon which has two dimensional properties. It’s carbon atoms are densely closed packed in the regular atomic scale wire pattern.



(a) (b)

Figure a is simple grpahene sheet and **figure b** is graphene oxide.

1.5 PROPERTIES OF GRAPHENE:

Graphene becomes most **stable** only for molecular larger than 24 thousands atoms.

Graphene is a zero gap semiconductor and it shows electron mobility at room temperature with values 15000 $cm^2\ V^{-1}\ S^{-1}$ and independent of temperature from 10 K to 100 K.

Resistivity of graphene is 10^{-6} ohm-cm at room temperature.

Quantum dot are a Nano crystal dots.

Graphene quantum dots can be prepared by the oxidation cutting of graphene oxide.

But what is **graphene quantum dots** that is the main question, in simple way it can be said that it is layer of graphene oxide one and only one layer to ten layer of graphene oxide with size less than 30 nm and it has unique properties such as optical ,spin, electronic and photoelectric and so many more.

Chapter 2

2.1 Literature Review

1. C**lois Powell (2015)** ***et al***

C**lois Powell (2015)** ***et al*** **.**have been performed a way to synthesis graphene oxide. For preparation of graphene oxide they under carbon source (lignite coal) and chemical Humic Acid (HA) that are eco-friendly and not much costly. Graphene oxide can produce by lignite source and Humic acid which has large number of ether group compare to repotted graphene oxide. Graphene film produced by HA has less conductive and its practical importance for current display device.[1]

2. **Ruquan Ye (2013)** ***et al***

Ruquan Ye (2013) ***et al*** reported a approach to synthesize tunable graphene quantum dots from various types of coal, and establish that the unique coal structure has an advantage over pure sp^2-carbon allotropes for producing quantum dots. The crystalline carbon within the coal structure is easier to oxidatively displace than when pure sp^2-carbon structures are used, resulting in nanometer-sized graphene quantum dots with amorphous carbon addends on the edges. The synthesized graphene quantum dots, produced in up to 20% isolated yield from coal, are soluble and fluorescent in aqueous solution. Characterization of coals is done by scanning electron microscope (for size and shape), X-ray Photoelectron Spectroscopy (for rate of carbons oxidation for coal), solid-state Fourier transform infrared (ssFTIR) spectra (for bond presence). They have observed that anthracite and coke contain certain amount of graphite-like stacking domains, while bituminous coal has a higher proportion of aliphatic carbon and smaller polyaromatic domains [2].

3. GokiEda ***et.al*** **(2009)**

GokiEda(2009) ***et al*** have been observed blue photoluminescence (PL) with chemical procedure. They derived graphene oxide. The PL of graphene oxide is associated to radiative recombination of electron-hole pairs in isolated “molecular” sp^2 domain, which are present within the carbon-oxygen sp^3 matrix in chemically derived graphene oxide. They also observed that during reduction of sp^2 domain make correlation with PL intensity.[3]

4. **JianhuaShen et al (2010)**

JianhuaShen et al. (2010) prepared GQDs by hydrazine hydrate using reduction method on graphene oxide(GO) with their surface passivized by polyethylene glycol (PEG). Photo Luminescence (PL) was observed under 365nm (blue shift)and 980nm (green shift) wavelength. Spectra of photo luminescence vary with excitation of wavelength. They observed that peaks of photo luminescence with maximum intensity and longer wavelength. They observed that peaks of photo luminescence with maximum intensity and longer wavelength, it happened when excitation wavelength varied from three hundred to four hundred nanometer .it can be used in bioscience and electrical technology. [4]

5. **Yiging Sun et al (2013)**

Yiging Sun et al. (2013) reported a method where how they could be able to synthesis graphene quantum dots (GQDs). They used graphite powder for oxidizing and etching. This method produced graphene quantum dot in large amount. Raman spectroscopy and ultraviolet spectroscopy revealed that emission peak of GQD is tunable where they vary the conditions of reaction range of emission peak goes 440 to 510nm.GQD are less toxic to biological cells and it is useful for medical application.[5]

6. Shenghai Zhou et al (2013)

Shenghai Zhou *et al* (2013) have summarized recent progress in fluorescent Graphene Quantum Dot(GQD) research. They focused on their synthesis and fluorescence sensing applications for the presence sign of inorganic ions, small organic molecules and large biomaterials. In this research, they discussed the preparation of GQDs, both top-down and bottom-up methods have been developed that use hydrothermal/solvothermal, microwave, ultrasound, CVD and electrochemistry. This article will helpful for my research project on graphene quantum dots.[6]

7. SuelaKellici *et al* (2017)

SuelaKellici *et al* (2017) provided evidence of an innovative, rapid and environmentally benign synthetic process for making calixarene functionalized GQD with tunable physical properties. The level of PL can be managed by calibrating the level of calixarene assisted fragmentation and functionalization onto graphene. The characterization of sample has been investigated by Transmission Electron Microscopy (TEM) images (revealed a mean particle size of used sample). X-ray photoelectron spectroscopy (XPS) analysis was employed to determine the changes in the chemical states of all synthesized GQD. Raman spectroscopy lends further insight to study the structure and defects on the carbon structure of GQD and to confirm the presence of p-tetrasulfonic acid calix[4]arene SCX4. These materials have inherent capacity to be applied in a broad range of applications including photovoltaic, biological and light emitting devices. `Furthermore, this work has potential for the continuous production of large scale quantities of GQD. [7]

Rishi Kumar have performed the experimental work on coal sample for investigating the Coal samples of the same type exhibit nearly identical properties, despite being from geographically different areas of origin. It is clear that by oxidative separation, the properties of graphene quantum dots synthesized can be predicted by the type of coal being used. Supplemented with the extremely low cost of materials and synthesis steps, our study shows promise for the use of coal-based quantum dots as a cheap source for scalable quantum dot device fabrication. Optimizing the synthesis procedure, further analysis of lignite as a source of graphene quantum dots have been done. In this research it was found that the evaporation step was a problem area for the synthesis, and must be replaced with a less volatile procedure in order to preserve graphene structures in solution. Lignite did not show any sign of producing graphene, but more trials would be needed to fully rule out lignite as a possible GQD source. This review will help for preparation for graphene quantum dots.

8. Zhenyu Li *et al*

Zhenyu LI *et al* (2008) have done some calculations which show that an oxidative cut of graphene by forming carbonyl pairs after forming epoxy. It is witnessed that if they form carbonyl pair direct bypassing epoxy formation to layer graphene up from an edge position they can't get that much energy. The proposed epoxy pairs may be related to some long puzzling experimental observations on graphene oxide. This atomic picture is valuable for effective means of graphene manipulation. [8]

9. Shoujun Zhu (2011) *et al*

Shoujun Zhu (2011) *et al* used a one-step solvent thermal method. They have produced fluorescent graphene Quantum dots (GQD) from graphene oxide by one step solvent thermal method. They acquired green fluorescent and Photo Luminescence (PL) quantum value was high near 11.4%.Spectroscopy (Ultraviolet V)-vis absorption of the GQDs provided absorption peak at ca. 320 nm, this absorption peak value is comparable to reported GQD. It is also evidence of low cytotoxicity as well as good compatible with biological tissue; GQDs are made clear to be friendly with environment along with bio-labeling agent. By using of a one-step method ore colorful fluorescent GQD will be exploring future. [9]

10. Dan li (2008) *et al*

Dan li (2008) et al suggested a new way to from aqueous graphene dispersion by chemical reaction of Graphene Oxide (GO) without need of polymeric or any stabilizers. They treated graphene with chemical and converted graphene as a water soluble and conducting small molecule. This treatment enhanced the Graphene property and it achieved new functionalities. Graphene sheets are improved in terms of chemical stability, thermal and mechanical strength. The production cost is also reduced. [10]

11. Daniela C. Marcano (2010) *et al*

Daniela C. Marcano (2010) *et al* has improved method for producing Graphene Oxide (GO) over Hummers method. It is not any toxic gas and there is not any exothermic reaction. Moreover, with the improved method they were succeeded to obtain carbon materials with higher fraction oxidized and strong affinity for water. This IGO is more oxidized with regular structure than HGO. The improved method might interfere less the basal plane of the graphite than old Hummers 'method. Further analysis, it is cleared that the improved method is more beneficial for big scale production of GO. [11]

12. Jingzhi Shang et al

Jingzhi Shang et al used resolved spectroscopic techniques to studied fluorescence of Graphene Oxide (GO) in H_2O in steady state. . They confirmed that main reason for fluorescence of Graphene oxide is attributed to recombination of electrons and holes from the lower level of Conduction band and neighbor of localized states to wide range valence band. They observed the fluorescence dependent on excitation wavelength decays kinetics at 500 to 800 nm. They came to know lifetime of carrier at the bottom is about 2 Nano seconds with the help of transient absorption and TRF measurements. They observed that functional groups with carbon to oxygen with single or double bond and carbon with hydroxyl group are involved in the fluorescence of GO. [12]

13. Daniel R et al

Daniel R et al have completed chemically conversion of Graphene Oxide (GO). We get material similar to graphene by using powerful reducing agent (such as hydrazine or borohydrazine) either thermally or electrochemical. Raman spectroscopy is used to check properties of the materials. Graphene oxide is used for synthesis of functionalized graphene platelets which potentially obsolete improved electronic, mechanical or thermal properties. [13]

14. Guoqing Xin et al

Guoqing Xin et al have studied the Photoluminescence (PL) property of graphene oxide (GO).they have performed hydrazine (N_2H_4) reduction for shifting ultraviolet region to blue region. They observed that by increasing hydrazine concentration to 0.3M, there is a shift of peak from 341nm to 421nm. the size of sp2 domains increased when they increased the concentration, reducing the band gap and red shifting the PL. in the next step, they performed activity of reduction of the GO as a result the density of small sp^2 nucleuses increased and enhanced the interconnectivity of localized sp^2 sites. If we further increased concentration, large density of sp2 nucleus sites increased interconnectivity of sp2 cluster in GO, resulted hopping and tunneling effect that restricted further red shifting of PL and terminate PL.[14]

15. Wei Luo et al

Wei Luo et al found a new fabrication plan that gives a way to prepare graphene from Graphene Oxide (GO) with the help of a microwave radiation and a Magnesiothermic. They are using two-step reduction method. This method gives as-prepared graphene. The prepared graphene has ratio of carbon to oxygen is

165.7 and comparable to the reported ratio of carbon and oxygen 246.X ray diffraction has been used for structural information. They have found a new for fabrication of graphene products from GO. [15]

CHAPTER 3

MATERIALS & ACTING TECHNIQUE

3.1 STUFF USED FOR TECHNIQUE:

To synthesize the quantum dots, the two types of coals such as anthracite and coke are used.

Anthracite

Anthracite- However, it's still a type of coal and can be used as an energy source. This type of coal consists of little water contents

Prominent attribute of Anthracite Coal

- Anthracite has 80 to 95 percentages of contents of carbon.
- It has very low value of sulfur and nitrogen which is less than one percent each.
- It consists of moisture content five to fifteen percent.
- It has high density so that it burns so slowly and difficult to ignite.
- Anthracite burns then raise 900 degree Celsius temperature.

3.2 Coke

Coke is a type of fuel which has few impurities and high carbon contents; it can be made from coal. Method of **destructive distillation** is done on low-ash and low-sulphur **bituminous coal**. It is typically grey, hard, and porous. While coke can be formed naturally, synthetic from is commonly used.

Prominent attribute of Anthracite coke

- It is highly porous.
- It has less content of sulphur.
- It has less contents of water nearly 3 to 6 per cent.

3.3.Technique:

Take 3oo mg coal and it is crushed to smallest pieces such as fine powder. This powder is dissolved into an eighty mL with raio3:1 solution consisting of sixty mL concentrated H_2SO_4 and twenty mL H_2NO_3.

This solution is kept for sonication bath for two hours for maximum disclosure of all surfaces of the amorphous coal powder to acid. After the sonication process, solution is kept to heat for hundred degrees Celsius which allowing the oxidative separation reaction to rush to completion

Now there is need of neutralize the strong acidic prepared solution. It is done by using sodium hydroxide solution for pH value 7 of resulting solution. This step is known as oxidative separation

Oxidative separation provides the solution of graphene oxide, salt crystals and amorphous carbon from the neutralize step. Teflon with pores sizes of 650nm, 450nm and 220nm is used filter the solution via vacuum filter. Dialysis process is done on the solution using dialysis tubing for 5 days. Each day Concentration of solution is maintained across the membrane by changing the aqueous solution.

The large amount of volume of aqueous GQD solution is left after the completion of dialysis

3.4.Proposal:-

This experiment connotes to synthesize graphene quantum dots with the help of coal. Graphene sheet will be pulled apart from coal by an oxidative process. Aim of this project to show the various samples of anthracite/coke coals will synthesis GQDs with identical photonic properties. Graphene sheet will be described for quantum dot like optical aspects.

3.5 Objective:-

To synthesis the Graphene dots from the coal with facile method and characterized GQD's the optical properties where this study target to increase and varying the fluorescence quantum yield by improving the preparation of quantum dots where preparation may be possible at minimum cost.

3.6.Expected outcomes:-

Anthracite is used which has higher content of carbon by weight. Higher content increases the chance of fruitful synthesis. Study on this project shows ground of expectation for the formation of quantum dots synthesis from coal. It may less expensive for ascendable quantum dot synthesis. Further study can be directed in two direction-, the optical data will be examined carefully to the fulfill expectation of finding relation between the coal and the optical observation from the result by optimizing the synthesis technique.

3.7.Application

From the time of discovery of quantum dots, it is being observed that Qds has highly properties which are capable of being tuned. Among the researcher and application developers, Qds is the attracting interest. Qds took place in various applications such as diode lasers, displays, solar cells, Medical imaging, transistors and quantum computing etc. Qds is also used in inkjet printing and have role in spin coating because of small sizes of Qds which make it capable for suspending in solution. Fabrication of semiconductor is done with less time and less expensive now due to Qds processing technique.

It is suitable for optical applications because it emit so many colors, longer lifetime and high efficiencies with high extinction coefficient. Electronics devices perform faster due to small size of Qds. Small size means electrons have no need to travel as far as with larger particles.

There are so many examples of electronics devices which have better performance now such as solar cells, transistor, quantum computing and further more. LED screen has been improved with higher peak brightness along high accuracy and saturation of color.

CHAPTER 4

4.1.CHARACTERIZATION TECHNIQUES

4.1.1 FOURIER TRANSFORM-INFRARED SPECTROSCOPY (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a dependable and practically logical instrument for recognizable proof of functional group and evaluation of the nature of material. When we treated organic material with infrared light in a simple manner in an intermediate area we will get subsequent range that give a unique mark which can be used to effectively screen as well as for various other applications. The productivity and execution of organic matter relates with nature of organic materials utilized and assembling. Thus affirmation, character and quality of material is basic.

4.1.2 APPLICATIONS

The following are the important applications of FTIR spectroscopy:

1. **IR spectroscopy used to detect coal**
   Various methods like reflectance or transmission are used to detect coal by comparing against unearthly database. It can be performed fast and compelling ID contemplates for test of a wide range of different polymers matters including almost whole size pellets, hazy specimens, filaments, and fluid.

2. **Analysis of polymers by FTIR**
   This method is a very useful to identify polymers and quality of plastics. When infrared rays specially mid-range rays passes through plastics, it absorbs and form a spectrum(transmittance or absorbance) that viewed on screen and further used for various other applications.

3. **Techniques for polymer analysis**
   There are various other techniques like NMR, GC/MS,DRIFTS, TGA which are used with Infrared Spectroscopy .FTIR consolidated with these procedure give huge corresponding information in regards to a polymer particle's sub-atomic structure. FTIR, when utilized together with these other diagnostic system resulted to be very effective to detect unknown plastics and other polymers.

RESULTS:

FTIR AND UV spectroscopy of anthracite has been recorded. It will help for preceding my expected outcome.

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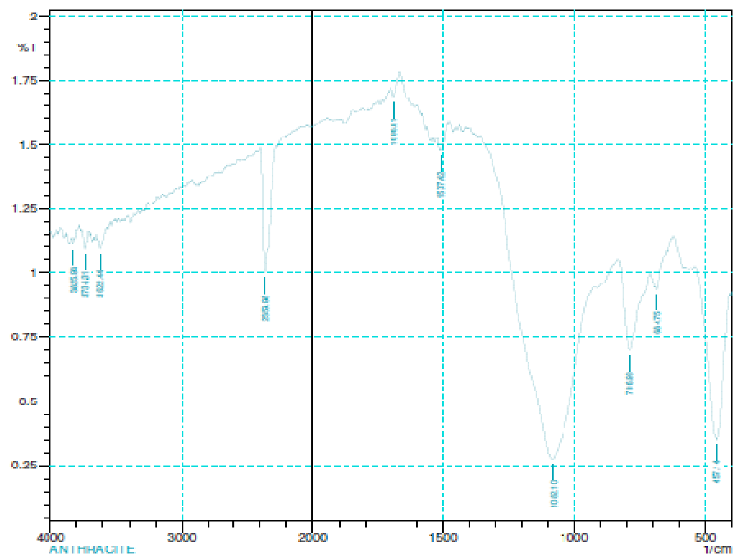

No.	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	457.14	0.3516	0.6062	541.05	406.99	293.8752	24.0847
2	664.75	0.935	0.0305	690.54	654.85	71.3905	0.0958
3	786.98	0.6935	0.3327	832.31	708.86	254.5236	8.8728
4	1082.1	0.2759	0.004	1083.07	922	363.0332	-6.0817
5	1507.42	1.4751	0.0224	1511.28	1485.24	47.3867	0.1343
6	1686.81	1.6832	0.0484	1696.45	1661.73	61.2066	0.1764
7	2359.98	1.0003	0.2366	2395.67	2339.73	108.1188	2.1701
8	3622.44	1.0939	0.0092	3634.01	3619.54	28.2881	0.0199
9	3734.31	1.0921	0.0203	3756.49	3729.49	52.6576	0.0996
10	3825.93	1.1101	0.0262	3831.72	3814.36	33.8512	0.0956

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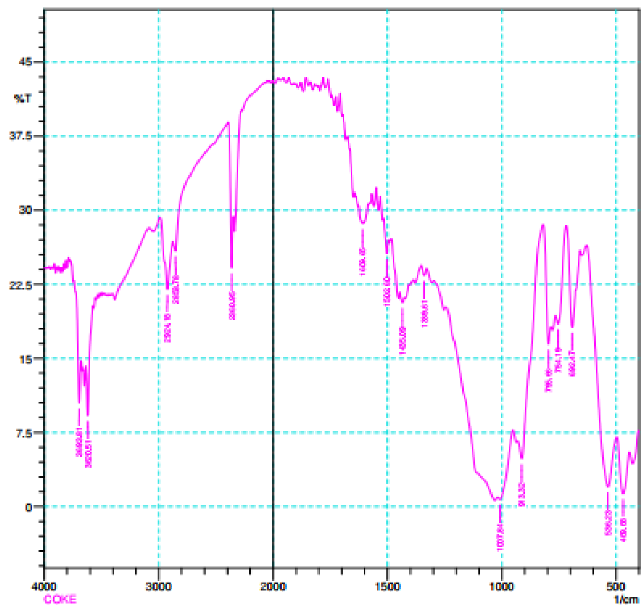

No.	Peak	Intensity	Corr. Inte	Base (H)	Base (L)	Area	Corr. Are
1	469.68	1.309	4.967	497.65	441.71	84.411	16.972
2	536.23	2.003	10.746	628.81	497.65	145.161	31.709
3	692.47	18.171	6.139	717.54	678	26.055	2.228
4	754.19	18.49	3.022	765.77	717.54	31.716	1.332
5	795.66	16.438	4.915	819.77	785.05	23.649	1.347
6	913.32	4.853	5.192	930.68	819.77	96.279	0.668
7	1007.84	0.745	1.272	1018.45	951.9	107.822	3.267
8	1339.61	23.412	0.851	1352.14	1329	14.429	0.198
9	1435.09	20.655	0.757	1446.66	1425.44	14.389	0.197
10	1502.6	25.623	1.991	1517.06	1496.81	11.528	0.349
11	1609.65	28.672	0.159	1612.54	1605.79	3.656	0.01
12	2360.95	24.186	8.043	2392.78	2347.45	23.401	2.059
13	2853.78	25.876	1.551	2877.89	2392.78	225.646	-12.365
14	2924.18	22.011	5.82	2989.76	2877.89	66.908	5.083
15	3620.51	9.241	6.661	3637.87	3575.18	52.23	3.975
16	3693.81	10.488	6.541	3725.63	3678.37	38.855	3.548

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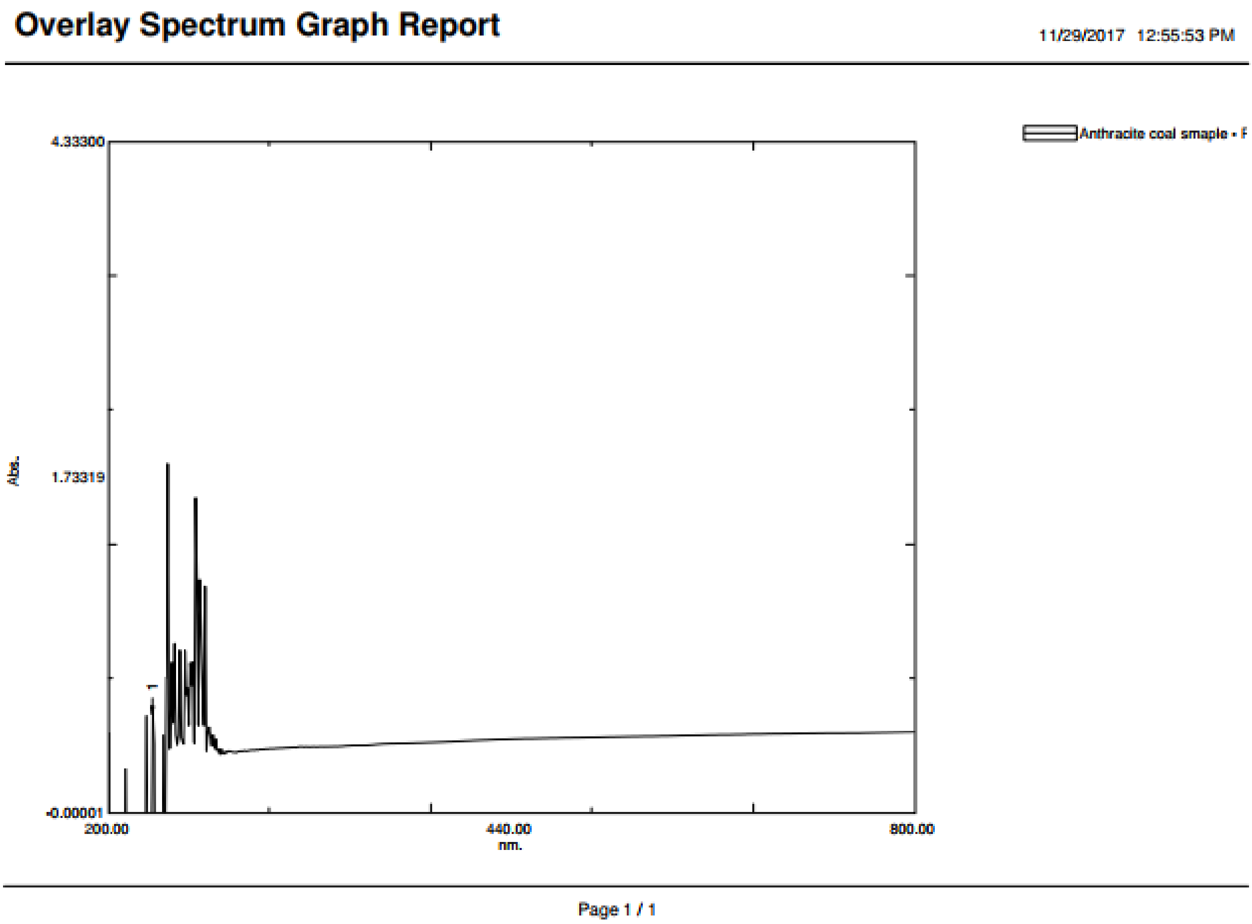

Analysis:

Anthracite "Anthracite coal sample - Raw Data varies form 200.00 values 0.51274nm to 800.00values 0.51826 nm

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