Computational analyses of graphene quantum dots for anode material in lithium-ion batteries

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Abstract. Many renewable energy technologies are underperforming due to optimal energy collection and storage. Renewable energy generation is not available all the time, it happens when the wind blows or the sun shines, storage is an essential part. Lithium-ion (LI) batteries are dominating the market as storage devices with recent advances towards the electric vehicles and renewable energy storage. Exploiting high capacity anode materials is one of the most effective ways to construct high energy density LI batteries. Energy, power, charge-discharge rate, cost, cycle life, safety and environmental impact are some of the parameters that need to be considered in adopting optimal LI batteries. As the recent development of batteries is mostly towards solid state batteries, small and high energy density materials are required. Graphene quantum dots (GQDs) have broad prospects in energy storage and conversion. First principle calculations are used to analyze optical properties of GQDs. The UV-vis spectra shows the maximum absorption peak at 750 nm within the edge of the visible region of the solar spectrum, thus favorable for renewable energy storage. Computational analyses strongly suggest the future development trend of GQDs research and its opportunities in energy storage devices.

1. Introduction

Lithium-ion (LI) batteries are one of the most used energy storage devices in many electronics to date. From small electronics, cellphones, laptops and toys to bigger machines such as electric vehicles, LI batteries play a huge role in making this machines work. LI batteries are also entering the renewable energy storage space with more pressure on the reduction of fossil fuel based energy production. This will help many countries reduce the cost of energy and can supply energy to everyone by harnessing clean natural energy from wind and solar. Renewable energy sources such as wind and solar are frequently fluctuating due to the ever-changing atmospheric conditions resulting in insufficient wind or sunshine. LI batteries have the potential to be fully utilized in various applications such as electric vehicles, renewable energy storage and electronics due to their countless advantages such as, longer life, high charge discharge rate, light weight, temperature tolerant, higher voltage and high power and energy density [1]. Currently used lithium-ion batteries contain mostly graphite as anode material.

Graphite is one of the most used materials for the manufacturing of electronics useable for their low electrical resistivity, low thermal expansion and thermal conductivity and resistant to thermal shock [2]. A relatively new carbon-based material, graphene quantum dots (GQDs) has many advantages due to its unique properties that arise from their nanoscale small size [3]. GQDs emerged as novel materials in the recent decade, and have demonstrated superiority in numerous privileged properties. GQDs are

considered superior due to facile preparation methodologies, low toxicity, high luminescent properties and high photo-stability against photobleaching and blinking, which have attracted substantial attention [4]. Several studies have evaluated different material for the anode material and yet graphite still gives a better performing energy storage device. The major anode materials used are graphite, nanostructured carbonaceous materials, metal oxides, metal nitrides, metal sulphides, metal phosphide, silicon, germanium, tin, phosphorous antimony, indium etc. [5]. Recent advancements in LI batteries include the solid-state batteries, which promotes the development of small and efficient storage devices.

Desired properties of anode material include porosity of the material, excellent conductivity, voltage match with coupled cathode material, high durability and it must be clean from impurities. Its constituent materials must be cheap and easily available. It must be light in weight and have very low current densities.

The working principle of LI batteries is shown in figure 1, the anode material used is graphite. The positive electrode receives electrons from the external circuit. The cathode stores Lithium and releases LI when the battery is charging. The electrolyte is a liquid that acts as a transporter of LI. The porous separator allows for LI to flow freely from the anode to the cathode and vice versa. The anode stores lithium and releases lithium-ions when the battery is discharging [6]. The negative electrode receives electrons from the external circuit during charging of the battery from the positive current collector. In this study, we use computational methods to analyze GQDs for application in renewable energy storage devices particularly the LI batteries. A semi-empirical molecular orbital package known as VAMP was used to carry out the calculations.

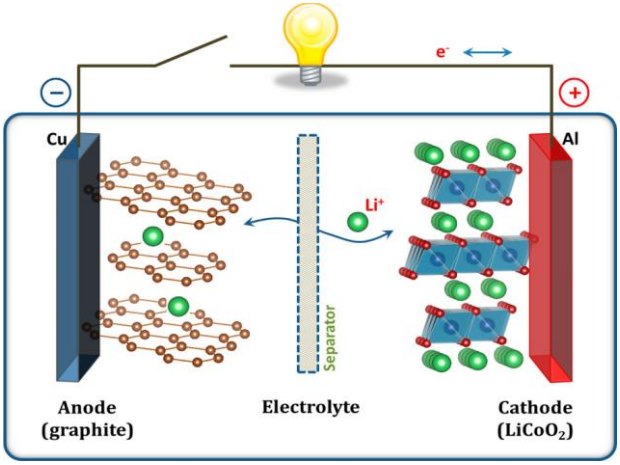

Figure 1. Working principle of LI batteries [7]. The anode material used is graphite.

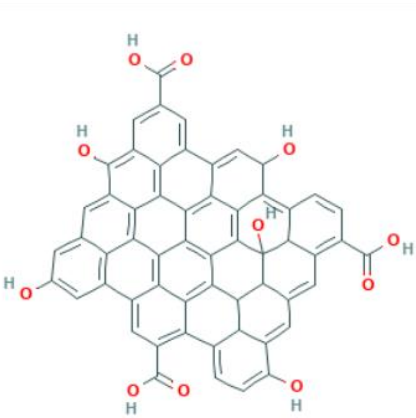

Figure 2. Chemical structure of GQDs obtained from PubChem database.

2. Computational methodology

GQDs are considered among the recent research interest in carbon based nanomaterials. Very few studies have been done with most being done experimentally [2]. Computational calculations are done using VAMP, a semi-empirical molecular orbital program that has been optimized to be highly numerically stable and fast. It contains many enhancements in comparison with normal geometry optimization methods so that it even optimizes problematic systems successfully. Other features of VAMP are transition state optimization, solvent models, and the calculation of many electronic properties. VAMP is used to determine the UV-vis spectrum and the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy orbitals of GQDs.

Since the chemical structure of GQDs is non-periodic, we had to use another computational package that accommodates calculation of density of states (DOS) and partial density of states (PDOS). The DOS and PDOS are determined by the density functional tight binding module (DFTB+) of material studio simulation package. DFTB+ is a semi-empirical tight binding method based on a two-centered approach

to density functional theory (DFT), it uses approximations for large and complex structures to make calculations faster [8].

3. Results and discussion

3.1. Density of states

The density of states is determined by using a unique function, DFTB+ as implemented in the material studio package. Figure 3 shows the contribution of atoms of the GQDs in the Fermi region, the highest occupied and semi occupied orbitals are shown. The dominant states as expected come from the contribution of carbon atoms denoted by the 2p orbital. The highest peak is located at -4 eV of energy followed by a shoulder peak at -3.24 eV and 0 eV. The O-H groups take a small portion with oxygen having the highest peak at -3 eV, which is 17.5 electrons/eV less than the maximum peak of carbon atoms. Between energy regions of -2 to 9 eV, no contributions from hydrogen are observed. The Fermi region is therefore dominated with carbon atoms. The dominant carbon based peak at the centre of the DOS spectrum was also observed by Ortega *et.al* and their study suggested that just like graphene, the DOS vanishes at Fermi level [9]. This is observed through the contribution of the states from the hydrogen atom. The oxygen based states also exhibit this behaviour in the conduction band region, with very small peaks rising very close to the Fermi region.

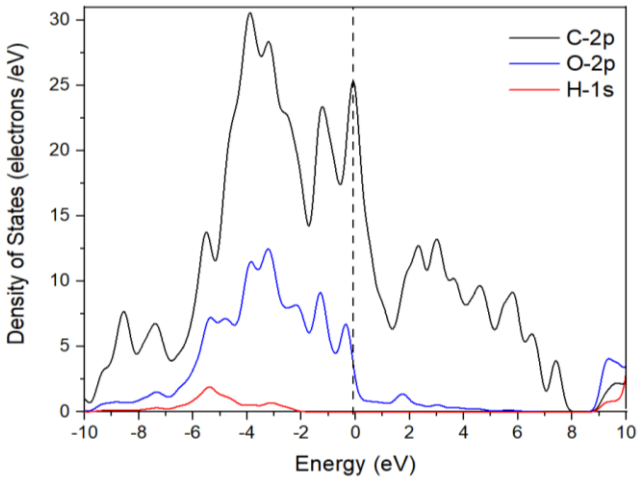

Figure 3. Density of states for GQDs calculated from material studios DFTB+ Energy module. The atoms and their highest occupied states are shown with their orbitals.

3.2. UV-vis spectrum

Figure 4 shows the UV-vis spectrum of GQDs. The UV-vis clearly shows the optical and electronic response of the material with longer wavelengths indicating less energy than shorter wavelengths. The absorption peak is located at 750 nm which lies at the edge of the visible spectrum hence motivating further investigation of the material. There are very few computational works to compare with this study but a very reasonable number of experimental works such as calculation of electronic absorption spectra by Timofeeva *et.al* [10]. In the study by Changzang *et.al*, there are no peaks observed on the spectrum in the visible region with the highest located at 200 nm, however, the photoluminescence give rise to peaks within the visible region of the solar spectrum [11]. Jauja-Ccana *et.al*, in their molecular dynamics study observes absorption band between 200 and 250 nm caused by electronic transition of the C=C bonds and between 300 and 400 nm corresponding to the electronic transition related to the C=O bonds [12]. These electronic transitions are characteristic of a graphemic materials. The isodensity surfaces of the quantum dot suggests a good absorbing material applicable to battery anode materials. Many studies of GQDs for applications in various fields are recent and thus lack conclusive findings and methodologies as studies are still carried out in this material.

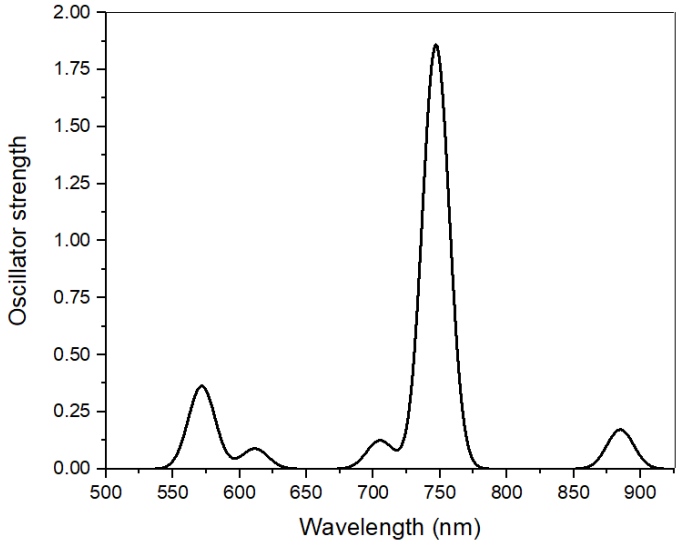

Figure 4. UV-vis spectrum of GQDs. It shows the wavelengths of UV or visible light that are absorbed or transmitted through the material of interest. The highest peak is located at 750 nm of wavelength with two located at 575 and 885 nm.

3.3. *HOMO and LUMO energy orbitals*

To analyse the stability of GQDs, molecular orbitals are determined. Figure 5 and 6 shows the HOMO and LUMO energy levels respectively. The HOMO and LUMO densities clearly shows the strength and stability of the material, with clusters of orbitals appearing on the top part and very few around the center. Clusters of orbitals appear to be attached to the carbon atoms, signaling very strong possibities of containing only one type of atoms thus further studies can lead to GQDs that are clean from impurities. The HOMO eigenvalue is -7.349 eV while we have energy of -4.641 eV for the LUMO. In determining the HOMO and LUMO energy states of single layered quantum dots (SLGQDs), Bayat *et.al* obtained -7.15 eV and -4.25 eV for the HOMO and LUMO orbitals respectively [13]. The difference between the HOMO and LUMO gives an energy gap of 2.708 eV suggesting properties of semiconductor that can be tuneable to enhance its optical and electronic properties.

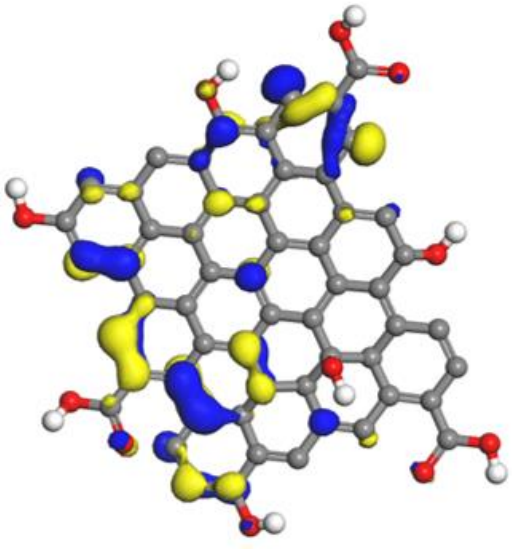

Figure 5. HOMO energy levels.

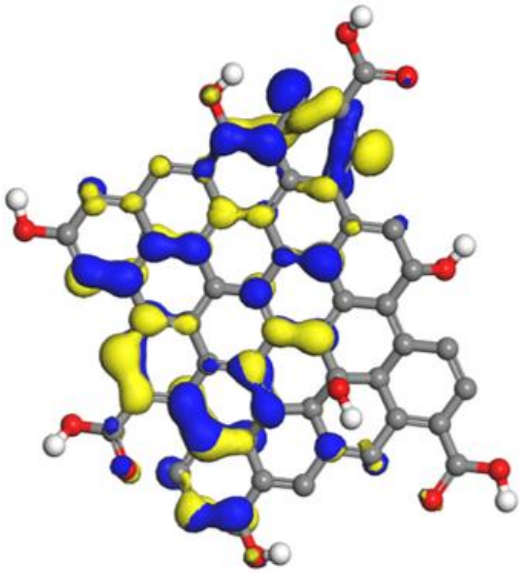

Figure 6. LUMO energy levels.

4. Conclusion

The result shows strong probability of graphene quantum dots to be applied in storage devices. The results generally show good optical, excitation and spectral properties. GQDs have broad prospects in energy storage and conversion. First principle calculations are used to analyze optical properties of

GQDs. The UV-vis spectra shows the maximum absorption peak at 750 nm within the edge of the visible region of the solar spectrum with one visible peak in the visible region at 575 nm, thus favorable for renewable energy storage. The HOMO and LUMO energy levels suggests an energy gap of 2.98 eV and hints at the stability of the structure with properties that can be tuneable to obtain GQDs that are clean form impurities. The density of states shows the possibilities of obtaining a pure GQDs structure through proper methods. The highest states around the Fermi region are due to the dominant carbon atoms in the structure. For GQDs to be applicable in LI batteries, one needs to consider a wide range of properties some not presented in this paper. Our results show the existence of tuneable properties to improve optical response of GQDs through the UV-vis spectrum in conjunction with the HOMO and LUMO orbitals, the DOS informs on the stability of the material. Computational analyses strongly suggest the future development trend of GQDs research and its opportunities in energy storage devices. This is due to GQDs satisfying several desired characteristics for anode materials.

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