SUPERCAPACITORS BASED ON FUNCTIONALIZED CARBON MATERIALS

by

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B.S., Chemical Engineering, Marmara University, 2013

Submitted to the Institute for Graduate Studies in Science and Engineering in partial fulfillment of the requirements for the degree of Master of Science

Graduate Program in Chemical Engineering Boğaziçi University 2022

ACKNOWLEDGEMENTS

The path of life has not been the same for everyone, but everyone's path is beautiful. Being an engineer has been always exciting for me. For the whole process in this path, I can mention to Charles Dickens: "It was the best of the times, it was the worst of the times". I am very grateful to my mom and dad, for their unconditioned love, patience, being unofficial advisors, and first engineers in my life.

It is not an easy to trust, believe, and support someone without knowing anything about her/him. I would like to thank first and foremost to my advisor Asst. Prof. Betül Uralcan for infinite support, trust, and patience in addition to sharing the experiences. I have been very fortunate to know and to work with her, which is great honor for me. She did not give up believing to me to achieve the goals which we determined in the beginning. In every step that I fell down, she held my hands and gave the energy to go on. To say thank you will not be enough. I am really excited for the next years we will achieve a lot of things together.

Then, I am very lucky for being a member of Soft Matter Lab. I am very thankful especially Dilara Saadetnejad for the support, patience, and being always generous to me not only her experience but also her friendship. I would like to say also thank you Can Koban for sharing all the notes he took and preparatory class with me. I am also grateful to work and carry out some experiments with Kerem Kamitoğlu. I hope our paths will cross again. I am very appreciative to Hakan Sakalhoğlu for being always there. I knew that it would not be only a friendship for the ChE642 project. I feel also lucky to ask for help from Duygu Kaya first time, which I never forget. From the beginning of this journey, she has always been with me, with her infinite support along days and nights. Knowing that we will not be alone in next years is the best gift for me.

I would like thanks a lot to Akarun Ayça Ersoy for not only academic support but

also giving colors and happyness. Sometimes, one cup of coffee is not just a coffee. In the pandemic condition, there are a few people who did not leave me alone. I am very grateful to Seymen İlke Kaykanat for sharing the life, experiences, and laughter and supports. I am also very lucky to be friend with PhD. Pmar Eribol who shared with me the experiences, time-outs, and the life . I am also appreciative to Özge Selçuk for her support, kindness, help, a timeless-cup of tea and forming a long-lasting friendship with you. I also thank a lot to Assoc. Prof. Kurtul Küçükada who support me in every part of life. You all are my protective factors in my life, encouraging me for the best. I knew that there are hard times. How you get out of it, that is how your spine is shaped. My spine is stronger than before thanks to the fellows I have, anymore. If you were not, I would not have witnessed how the worst times could turn into the best.

I would like to thank also Sercan Altundemir and Selma Başıbüyük for their support and encouragements in this period. I am also thankful to Esra Ulgev and Ozlem Ozbek for not only their help in my work but also their friendships. I also thank to Kübra Kaya from the beginning of this adventure whom I will not forget the night we talked about being engineer and being on the way. I am also grateful to Tuba Değerli and Yasemin Kocaman for being the witness of the beginning of this journey and being always there. I am happy to come by and being a part of the Preschool Education Department. I would like to thank my teachers Assoc. Prof. Zeynep Erdiller, Asst. Prof. Ersoy Erdemir, and Assoc. Prof. Mine Göl Güven for their efforts and contributions in my academic life. If you did not send to me the message, I could not write these words: Zeynep Çakır. I am very appreciative to Cemile Eslem Bakkal, especially for drawings and being always kind and positive. I am very thankful to Amine Dilara Güneren and Fulya Melis Özdemir. Being close with you for years and finding a secret corner always to talk about everything, I am lucky to have such good friends. I appreciate to Gökçen Ağca, Zeynep Bozkuş, Hilal Çiçekfidan, Beyza Bah, and Melisa Yordanlı for their supports.

I would like also to thank a lot to Yakup Bal and Fırat Aydın for their support. I acknowledge the financial support of TUBITAK (T118C220) and Boğaziçi University Research Fund (17841).

Time carries on passing but there is always a music that accompanies with the life. After all the hard times, I am appreciative to the Adamlar the band due to being a facilitating force in writing this thesis. Finally, if I had a chance to choose my siblings, I would choose them. It is not easy to say to be with you that how grateful I am, sisters Esra and Duygu, my brothers Yusuf and Harun, and also my lazy cat, Mayıs. My family, life is beautiful with you.

ABSTRACT

SUPERCAPACITORS BASED ON FUNCTIONALIZED CARBON MATERIALS

Electrical double layer capacitors store energy in the form of electrical charges at the interface between an electrolyte and a high surface area electrode. As their energy storage mechanism relies on physical interactions, EDLCs have high power densities, unlike batteries, which are often limited by the slow charge- and mass- transfer kinetics. Additionally, EDLCs can sustain millions of charging/discharging cycles. Nevertheless, they suffer from low energy densities. For a high energy density EDLC, it is critical to maintain a compact architecture with large ion-accessible surface area while also ensuring low ion transport and electrical resistance. We incorporate carbon quantum dots into thermally exfoliated graphene oxide sheets in the presence of a room temperature ionic liquid to form conductive carbon networks with improved ion transport networks, enhancing ion transport kinetics and storage. This yields an electrode in which both the carbon quantum dots and the ionic liquid serve as spacers to effectively separate the thermally exfoliated graphene oxide sheets, while the ionic liquid also functions as the electrolyte and carbon quantum dots provide a conductive network. Using this approach, we achieve a gravimetric capacitance of 165 F/g at 30/70 wt% CQD/TEGO composition with 4.5 M EMIM-BF4 electrolyte at 20 mV/s. The electrodes demonstrate 70 % capacitance retention at 500 mV/s. When a 3.4 M EMIM-BF4 electrolyte is used instead, capacitance reaches 206 F/g, and the electrodes retain 70% of its capacitance at 500 mV/s. This demonstrates that we can simultaneously improve both energy and power density by tailoring the electrolyte composition.

ÖZET

İŞLEVSELLEŞTİRİLMİŞ KARBON MALZEME TEMELLİ SÜPERKAPASİTÖRLER

Elektrikli çift katmanlı kapasitörler, bir elektrolit ve yüksek yüzey alanlı eletktrot arasında bulunan arayüzde elektrik yükleri şeklinde enerji depolamaktadırlar. Enerji depolama mekanizmaları fiziksel etkileşimlere dayandığı için EDLC'ler, genellikle yavaş şarj ve kütle transfer kinetiği ile sınırlanan pillerin aksine yüksek güç yoğunluğuna sahiptirler. Bunlara ek olarak EDLC'ler milyonlarca şarj/deşarj döngüsünü sağlayan enerji depolama cihazlarıdır. Ancak, düşük enerji yoğunluklarından muzdariptirler. Yüksek enerji yoğunluğuna sahip olan bir EDLC için, iyonların ulaşabileceği geniş bir yüzey alanına sahip kompakt bir yapının sürdürülmesi, aynı zamanda düşük iyon taşınımı ve elektrik direncini sağlaması kritik bir önem taşımaktadır. Bu noktada, karbon kuantum noktalarını termal olarak pul pul dökülmüş grafen oksit tabakalarına oda sıcaklığında iyonik sıvıların varlığında dahil ederek, iyileştirilmiş iyon taşıma ağlarına sahip iletken karbon ağlarını, iyon taşıma kinetiğini ve depolamayı güçlendiriyoruz. Bu durum, iyonik sıvının elektrolit olarak, karbon kuantum noktalarının da iletken bir ağ olarak görev almasını sağlarken, termal olarak pul pul dökülmüş grafen oksit tabakaları arasında birer aralayıcı olarak görev almasına yol açmaktadır. Bu yaklaşımı kullanarak, ağırlıkça %30/70 CQD/TEGO bileşimi, 20 mV/s'de 4.5 M EMIM-BF4 elektrolit ile 165 F/g'lık bir gravimetrik kapasitans elde ediyoruz. Elektrotlar, 500 mV/s tarama hızında %70 oranında bir kapasitans tutma göstermektedir. Bunun yerine 3.4 M EMIM-BF₄ kullanıldığında, kapasitans değeri 206 F/g'a ulaşırken, elektrotlar 500 mV/s'de kapasitansının %70 oranında korunmasını sağlıyor. Bu durum, elektrolit bileşimini uyarlayarak hem enerji hem de güç yoğunluğunu aynı anda geliştirebileceğimizi göstermektedir.

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LIST OF SYMBOLS

C_{DL}	Double layer capacitance
\mathcal{C}_G	Gravimetric capacitance
C_{int}	Intrinsic capacitance
d_{0002}	Space between graphene layers
d	Thickness of double layer
E	Energy density
f	Fraction
Р	Power density
\mathbf{R}_{ele}	Electrical resistance
R_{ct}	Charge transfer resistance
SSA_{IA}	ion accesible surface area
U	Potential window
ϵ_0	Permittivity of vacuum
ϵ_r	Electrolyte dielectric constant

LIST OF ACRONYMS/ABBREVIATIONS

2D	Two dimensional
3D	Three dimensional
А	Electrode's surface area
AB	Acetylene black
AC	Activated carbon
ATR	Attenuated total reflectance
BWF	Breit Wigner Fano
CE	Counter electrode
CQD	Carbon quantum dot
CV	Cyclic voltammetry
EDL	Electrical double layer
EDLC	Electrical double layer capacitor
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series of resistance
F	Farad
FWHM	Full width half maximum
FWHM GCS	Full width half maximum Gouy-Chapman-Stern
FWHM GCS GNP	Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets
FWHM GCS GNP GO	Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide
FWHM GCS GNP GO I	Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide Intensity
FWHM GCS GNP GO I OCV	Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide Intensity Open circuit voltage
FWHM GCS GNP GO I OCV RE	Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide Intensity Open circuit voltage Reference electrode
FWHM GCS GNP GO I OCV RE rGO	 Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide Intensity Open circuit voltage Reference electrode Reduced Graphene Oxide
FWHM GCS GNP GO I OCV RE rGO RTIL	 Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide Intensity Open circuit voltage Reference electrode Reduced Graphene Oxide Room temperature ionic liquid
FWHM GCS GNP GO I OCV RE rGO RTIL SCE	Full width half maximum Gouy-Chapman-Stern Graphene nanoplatelets Graphene oxide Intensity Open circuit voltage Reference electrode Reduced Graphene Oxide Room temperature ionic liquid Saturated calomel electrode
FWHM GCS GNP GO I OCV RE rGO RTIL SCE SSA	Full width half maximumGouy-Chapman-SternGraphene nanoplateletsGraphene oxideIntensityOpen circuit voltageReference electrodeReduced Graphene OxideRoom temperature ionic liquidSaturated calomel electrodeSpecific surface area
FWHM GCS GNP GO I OCV RE rGO RTIL SCE SSA TEGO	Full width half maximumGouy-Chapman-SternGraphene nanoplateletsGraphene oxideIntensityOpen circuit voltageReference electrodeReduced Graphene OxideRoom temperature ionic liquidSaturated calomel electrodeSpecific surface areaThermally exfoliated graphene oxide

WE	Working electrode
XPS	X-ray photon spectroscopy
XRD	X-ray diffraction

1. INTRODUCTION

Climate change, high energy demand due to increasing population, and limited availability of fossil fuels are the driving forces of utilizing electrical energy from renewable energy resources such as wind and solar [1–3]. As renewable energy sources are intermittent in nature, cost-effective and efficient energy storage plays a key role in facilitating the widespread adoption of renewable energy technologies [1]. Electrical energy can be stored directly as electrical charges (e.g. capacitors and supercapacitors), or can be converted into other forms such as chemical (e.g. batteries), kinetic (e.g. flywheels) or potential (e.g. pumped hydro, compressed air) energy [2,4]. For portable energy storage, at the forefront of these are chemical and electrical energy storage systems, such as batteries and supercapacitors [2].



Figure 1.1. Ragone plot of energy storage systems.

The Ragone plot presented in Figure 1.1 depicts the energy density versus power density profiles for electrochemical energy storage devices [1]. Batteries dominate the

electrochemical energy storage market due to their high energy densities in Figure 1.1, [5,6] and they likely will dominate the market for a long time. Nevertheless, low power densities and cycle life limitations of batteries due to their charge storage mechanism that involves electrochemical redox reactions pose fundamental challenges [5,7].

Meanwhile, the fast energy storage capability, durability $(10^6 \text{ charge/discharge} \text{ cycles})$, and safety of supercapacitors make them attractive candidates for use in high power applications such as pitch-control systems and back-up power for windmills, regenerative braking technologies and battery-assist devices for electric/hybrid cars, and replacements for truck, bus, crane and lifting vehicle engine starts [8–10]. Despite these advantages, the widespread adoption of supercapacitor technology has been restricted due to their limited energy storage capability [1,8,9,11]. Mainly, they complement batteries providing bursts of energy for short times i.e., when batteries fail to deliver power at such high rates [12,13]. The next section describes supercapacitors in three main categories: electrical double layer capacitors, pseudocapacitors and hybrid supercapacitors.

Based on their charge storage mechanisms, supercapacitors are categorized into three groups: i) pseudocapacitors, ii) hybrid capacitors, and iii) electric double-layer capacitors (EDLCs) [13]. Electrostatic double-layer capacitors (EDLCs) store energy in the form of electrical charges through separation of charges at the interface between the surface of a conductive electrode and an electrolyte [14]. Pseudocapacitors store charge primarily via faradaic charge transfer in addition to double-layer [15]. Distinct from batteries, in pseudocapacitors, redox reactions take place near the electrode/electrolyte interface, hence they are not restricted by solid-state diffusion limitations [16,17]. Metal oxides (RuO₂, MnO₂, Fe₃O₄, Fe₂O₄, PbO₂, MoO₃), metal hydroxides (Ni(OH)₂), and conductive polymers are some examples of commonly utilized pseudocapacitive electrode materials (PANI and PPY) [5,14,15,18–21]. Although pseudocapacitive behavior can potentially improve the energy density, widespread use of these devices is hindered by the narrow potential windows of aqueous electrolytes used in pseudocapacitors, expensive electrode active materials such as RuO₂, as well as the low capacitance and electrical conductivity of metal oxides and conductive polymers [1]. Hybrid capacitors combine a faradaic battery electrode with a supercapacitor electrode to simultaneously utilize the high energy density of batteries and power density of supercapacitors [22]. While high energy densities can be obtained with hybrid capacitors, they cannot replace EDLCs or pseudocapacitors as their charge/discharge rates and cycle lives are still limited compared to the latter [23]. As the focus of this thesis is EDLCs, we next describe the working principles of EDLCs in details.

1.1. Working Principles of EDLCs

In a very simple definition, EDLCs are composed of two, typically carbonaceous, high specific surface area (SSA) electrodes deposited onto metallic current collectors imbibed with an electrolyte consisting of a solvent and a salt, and separated by an ionpermeable membrane, as shown in Figure 1.2. When a potential difference is applied between the electrodes through the metal current collectors, ions in solution quickly redistribute forming an electrical double layer (EDL) of electronic and ionic charges accumulated at the electrode/electrolyte interphase to balance the charges on the electrodes [17, 19, 24].



Figure 1.2. Charging and discharging mechanism of EDLCs.

The properties of EDL play a major role in energy storage applications as the potential distribution in the EDL determines the capacitance of the electrode/electrolyte interface. Below we present classical analytical continuum models that describe charge and potential distribution at the EDL. The first EDL model by Helmholtz describe the double layer capacitance can be represented as,

$$\mathbf{C} = \frac{\epsilon_r \epsilon_0 A}{d} \tag{1.1}$$

where ϵ_r is the electrolyte dielectric constant, ϵ_0 is the permittivity of vacuum (8.85.10⁻¹² F/m), d is the thickness of the double layer (m), and A is the electrode's surface area (m^2) [1,25].

According to this model, potential decreases linearly with distance from electrode surface as depicted in Figure 1.3a.

The second model explaining EDL is Gouy-Chapman as in Figure 1.3b. Although Helmholtz's concept was revolutionary at the time, it had a weakness in that it did not account for entropic concerns that prevented the EDL from being one layer thick [26]. Gouy (1910) suggested that the ions in solution generate a three-dimensional (3D) diffuse cloud of anions and cations with a net charge which is equal and opposite to the charge at the electrode's surface [27, 28]. This 3D region extends outer part of Helmholtz to the bulk solution [24]. Chapman advances this model considering thermal conditions [24, 26]. However, overrating the double layer capacitance is the main drawback of the second model of EDL [26, 28]. The ions are regarded as pointcharges in this model. As a result, as the surface potential rises, the concentration of counterions near the surface rises to unphysical levels, and the model eventually fails at high potentials [28].

The last model of EDL is proposed by Stern (1924) which combines Helmholtz and Gouy-Chapman models [24, 28, 29]. In the last version of EDL in Figure 1.3c, the ionic layer nearest to the electrode surface or the inner region of the electrolyte, could be handled by using an adsorption process that coexisted with the diffuse ionic cloud [28]. As the surface potential rises, a subset of ions attaches to the surface in a similar way to the Helmholtz model, which prevent the capacitance from reaching unphysically high values [26, 28]. Thus, overestimated double layer become more accurate form which is connected in series. The capacitance of Gouy-Chapman-Stern (GCS) model [28], can be shown as,

$$\frac{1}{\mathbf{C}_{\mathbf{d}}^{\mathbf{GCS}}} = \frac{1}{C_d^H} + \frac{1}{C_d^{GC}}.$$
(1.2)



Figure 1.3. Schematic diagrams of diffuse layers by a) Helmholtz, b) Gouy-Chapman,c) Gouy-Chapman-Stern model.

Grahame developed Stern's concept by splitting the Helmholtz layer into two layers: the inner Helmholtz layer, which contains specific adsorbed ions and solvent molecules, and the outer Helmholtz layer, which includes solvated ions [28,30]. For the first time, his contribution accounted for the distinct existence of the solvent within the double-layer, rather than treating the solvent as a continuum [28].

1.2. Performance Metrics

An EDLC is evaluated based on two predominant performance metrics: energy density (E) and power density (P) [16]. Energy density refers to the quantity of energy that is stored in a device per unit mass, and is defined as,

$$\mathbf{E} = \frac{1}{2}C_G U^2 \tag{1.3}$$

where C_G is the gravimetric capacitance and U is the operating voltage. The C_G of the device can be further broken down into,

$$\mathbf{C}_{\mathbf{G}} = C_{int}SSA_{IA} \tag{1.4}$$

where C_{DL} is the double layer capacitance per unit surface area, often referred to as the intrinsic capacitance, and SSA_{IA} is the ion-accessible specific surface area of the electrode. Power density describes how fast the device can be charged and discharged and is defined as,

$$\mathbf{P} = \frac{U^2}{ESR} \tag{1.5}$$

where ESR is the equivalent series resistance of the whole device. The ultimate goal in EDLC research would then be to create a device with maximum energy and power density.

1.3. Carbon-based Electrode Materials

Electrically conductive and electrochemically stable carbonaceous materials with a large surface area have been considered desirable for EDLC applications [31–33]. Consequently, engineering EDLCs is often regarded synonymous to engineering the porous structure of the electrodes [34]. Activated carbon (AC) is commonly used in commercial EDLCs as a low-cost material with a large surface area (1000-2000 m²/g), although a significant portion of AC's surface area is composed of nanopores that are too small for ion penetration [32,33]. In an attempt to improve upon activated carbon, other carbonaceous materials such as carbon black, carbon nanotubes (CNT), carbidederived carbon and graphene-based materials have also been studied [1,3,35]. In this study, thermally exfoliated graphene oxide and carbon quantum dots were used.

1.3.1. Thermally Exfoliated Graphene Oxide (TEGO)

Two-dimensional (2D) sheet-like materials and their hybrid structures are among the most promising electrode materials for EDLCs owing to their large surface area and superior electronic, thermal, and mechanical properties. In particular, thermally exfoliated graphite oxides (TEGO), a class of defective graphene materials, produced via the thermal reduction and exfoliation of graphite oxide, are particularly promising due to their exceptionally high intrinsic capacitance, SSA ($\sim 2630 \text{ m}^2/\text{g}$), and flexible 2D (sheet-like) structure as opposed to the rigid pore structure of most high surface area carbon materials [31–33]. While TEGO share many similarities to pristine graphene, such as high surface area and 2D morphology, and can exhibit high electrical conductivity, its honeycomb lattice is disrupted by oxygen-containing functional groups and lattice defects, the concentration of which depends on the specific reduction treatment. Pope et. all showed that these functional groups increase intrinsic capacitance in a conventional dilute electrolyte (0.1 M TEABF₄ in acetonitrile), reaching a maximum at C/O ratio between 10-100 [36]. A major challenge with TEGO-based electrodes is that upon consolidation into an electrode, only a small fraction of its high theoretical surface area remains electrode-accessible. This is caused by aggregation and significant restacking when the sheets are processed into dense electrodes.

1.3.2. Carbon-based Quantum Dots

Carbon-based quantum dots, in general, refer to zero-dimensional materials, generally on the order of a few nanometers, mainly composed of carbon atoms. Recent research has been focused on CQDs due to their good solubility and good luminescence [37]. Based on their precise structure, they are categorized into three groups: carbon dots (CDs), graphene quantum dots (GQDs) and carbon quantum dots (CQDs).

<u>1.3.2.1.</u> Structural and Electrical Properties. CDs differentiate themselves from the other two groups by lacking the quantum confinement phenomenon. Although they are sized in the range 1-20 nm, the electronic band gap of CDs is not strongly correlated with particle size. The electronic properties of CDs can be easily tuned by modifying the surface functional groups. They mainly exhibit sp³ hybridization and a small sp² hybridization core.

GQDs, on the other hand, are zero-dimensional graphene sheets on the order of 1-10 nm size and show quantum confinement phenomenon. They have sp² carbon core and good crystallinity.

CQDs are also spherical nano-size carbons with a crystalline structure and exhibit quantum confinement phenomenon. Their size distribution is wider than GQDs, in the range 1-20 nm. Furthermore, heir crystallinity is lower than that of GQDs as they possess a lower amount of crystalline sp² carbon. Their band gap energy is related to the quantum confinement effect as fall as surface functionalization. CQDs surface functional groups, namely carbonyl, carboxyl, carboxyl groups as well as nitrogen containing sites, all contribute to supercapacitor's energy storage performance. In particular, oxygen-containing surface functional groups increase water solubility and enhance dispersibility in polar solvents. Their presence can also potentially improve wettability, hence enhance capacitance in water-based electrolytes. N-containing functional groups can also improve the pseudocapacitive contribution.

The electronic properties of all carbon-based quantum dots rely on the electronic energy states of the surface functional groups, dopants (e.g. nitrogen, boron) and carbon cores [38,39]. Their highly crystalline structure with a small amount of intrinsic defects enhance electronic transfer in carbon-based quantum dots. In particular, GQDs are considered to be the most advantageous type due to their higher order of crystallinity [40, 41]. CQDs can also function as a conducting electron transport medium or a bridge for electron transfer due to its π electron network from sp² hybridization [42]. In particular, their presence is proven to be beneficial in maintaining electrical conductivity after cycling, that would otherwise diminish due to the cracking of the primary active electrode material [43].

<u>1.3.2.2. Preparation Methods.</u> Aggregation prevention, size control, uniformity and surface properties are important aspects during preparation. CQDs can be synthesized via a top-down or a bottom-up approach. In the top-down approach, higher dimensional carbon materials such as graphite, graphene, CNTs and fullerene are used as the carbon source. The bottom-up approach is used to mainly synthesize CQDs from smaller carbon-based molecules via chemical reactions [44–46].

Laser ablation, chemical-oxidation induced method and electrochemical exfoliation are considered as top-down methods. Laser ablation method involves using a nanosecond-pulsed laser with a set wavelength directed at the target. As a result of this process, a dense plasma is obtained. The CQDs are synthesized by shearing the carbon structure of the target and simultaneously incorporating the dopant atoms (e.g., nitrogen, oxygen, sulfur) in the precursor solution [47–49]. Although this method is highly tunable and yields high purity material through modifying laser pore, precursor type and concentration and target material, it is not necessarily scalable as it requires highly sophisticated equipment and high-vacuum conditions. Chemical-oxidation induced method involves using an acidic oxidation agent and yields CQDs with controllable size in a relatively facile process [50]. In this method, carbon nonosheets are first chemically exfoliated into several carbon nanosheets and are subsequently reduced to yield CQDs. The main disadvantage of this method is the fact that it is time-consuming. Electrochemical exfoliation uses chemical oxidation and chemical exfoliation under a potential difference [51, 52]. It is considered to be more environmentally friendly as it does not involve an acidic-based oxidation agent. The carbon source (e.g., graphite, graphene, graphene oxide [53] is dipped into an ionic liquid and used as the anode. When a potential difference is applied between the anode and the cathode,

the electrolyte is oxidized at the anode resulting in anionic intercalation. Meanwhile, the applied potential disrupts the carbon chemical bonding and leads to the exfoliation of the carbon nanostructure.

Hydrothermal method, microwave-assisted synthesis and pyrolysis are typical bottom-up approaches involving synthesizing the CQDs from smaller carbon-based molecules. Hydrothermal method uses small carbon-based molecules such as citric acid and urea typically in an aqueous dispersion to synthesize CQDs. This method is advantageous as it is low-cost, environmentally friendly and scalable [54–58]. CQD properties can be controlled by tuning reaction temperature, heating rate and reactant concentration. In the microwave assisted method, microwave irradiation is used to synthesize CQDs. Using solvents with different polarities facilitate controlling the structure and energy gap of the CQDs. The disadvantage of this method is the broad size distribution of the particles. Pyrolysis involves a carbonization process that is responsible from CQD synthesis [59].

1.3.2.3. Applications in Supercapacitors. Carbon-based quantum dots have been recently used as both electrode and electrolyte materials for supercapacitors. In these applications, carbon-based quantum dots are utilized either as the primary active electrode material with their high electrical conductivity and capacitance, or as an additive to the primary electrode material [60–63]. Recently, Qing et al. incorporated carbon-based quantum dots into graphene microfibers and observed an enhancement in mechanical strength as well as the specific surface area [60]. This resulted in a three times increase in the areal capacitance of the system. Incorporating CQDs into supercapacitors has been also recently investigated by Zhao et al. (2014) where rGO/CQDs electrodes are utilized in supercapacitor fabrication [64]. They have demonstrated CQDs prevent the aggregation and restacking of graphene nanosheets. They found that high specific capacitance, good rate capability, and excellent cycling stability were obtained as compared to rGO without CQDs [65].

1.4. Electrolytes

Electrolytes are critical in the transfer and balancing of charges between the two electrodes [8]. They are also divided into different groups. In all electrochemical processes, the interaction between the electrolyte and electrodes has a substantial impact on the electrode–electrolyte interface state and internal structure of active materials [8]. Thus, the choice of electrolyte is important for performance of supercapacitors to have high power and energy density, longer cycle life, and safety [8]. Ionic mobility and conductivity are also significant aspects to consider when evaluating electrolyte performance [8].

Commonly used electrolytes in supercapacitors can be grouped as liquid and solid-state electrolytes. Liquid electrolytes can be further classified as aqueous electrolytes, organic electrolytes, and room temperature ionic liquids (RTILs), while solid state electrolytes can be broadly grouped as organic electrolytes and inorganic electrolytes [66]. Aqueous electrolytes have higher ionic conductivity compared to organic and RTIL electrolytes. While this lowers the equivalent series resistance, leading to high power rates, their low electrochemical stability limit device working potential [67, 68]. Meanwhile, organic electrolyte-based supercapacitors take a significant part of the commercial market thanks to their high operation potential window typically in the range of 2.5 to 2.8 V. The high operation cell voltage can provide a significant improvement in energy and power densities. Typical organic electrolytes for the commercial supercapacitors consist of conductive salts (e.g., tetraethylammonium tetrafluoroborate (TEABF₄) dissolved in the acetonitrile or polycarbonate. However, organic electrolytes are more expensive and have lower conductivity compared to aqueous electrolytes, and pose safety concerns related to the flammability, volatility, and toxicity [66, 69].

RTILs, with their attractive tunable properties, have recently received significant interest as alternative electrolytes for supercapacitors. Ionic liquids (ILs) are organic salts made up of bulky organic cations and a variety of charge-delocalized inorganic/organic anions that typically remain liquid at temperatures below 100°C or even at room temperature [70]. The cation/anion bulk asymmetry in ILs tends to mask the intermolecular force and prevent ionic aggregation into the low-energy crystalline form, lowering the beginning points of their liquids to substantially lower temperatures than inorganic salts. ILs are unique in that they have a minimal vapor pressure, as well as a wide liquids range, a strongly ionized environment, good thermal and electrochemical stability, and universal solubility/affinity toward natural and synthesized molecules [70]. Their physical and chemical properties are highly tunable due to the large variety of cations and anions. This property is very attractive due to the fact that the electrolyte composition can be optimized to meet certain requirements of supercapacitor performance such as cell voltage, working temperature range and equivalent series resistance of the device [70].

As described above, the goal in EDLC research is to improve the energy density of EDLCs while maintaining their other attractive properties, such as high power densities, long cycle lives and safety. As discussed earlier, energy and power density are two competing performance metrics in EDLC design. The focus of this dissertation is to improve the energy density of EDLCs.

The main goal of the proposed work is to rationally design and manufacture electrical double layer capacitors with superior energy density that will maintain high power density, cycle life, and safety while simultaneously lowering production costs. In this endeavor, I incorporate thermally exfoliated graphene sheets enriched with carbon quantum dots with room temperature ionic liquids by molecularly self-assembling them into lamellar electrode-electrolyte nanocomposites. The remainder of this dissertation is organized as follows. Section 2 begins by explaining the experimental work which comprises materials and methods I applied. All the materials and methods during the study is explained in a detailed way in this chapter. Section 3 outlines the results and discussions of this work. This part contains firstly structural characterization results of the electrode materials. Then, the electrochemical characterization results are given. Finally, Section 4 includes conclusions of the study.

2. MATERIALS AND METHODS

2.1. Materials and Equipments

All the chemicals that were used in this study are summarized in Table 2.1. Table 2.1. Materials that were used during the study.

Name	Abbreviation/ Formula	Source
(N-Methyl-2-pyrrolidone)	$\rm NMP/~C_5H_9NO$	Merck
Poly(1,1,2,2-tetrafluoroethylene)	PTFE/ $(C_2F_4)_n$	Nanografi
Acetylene black	AB	Nanografi
Potassium chloride	KCl	Merck
1-Ethyl-3-methylimidazolium tetrafluoroborate	EMIMBF_4	Proionic
Sulphuric acid	H_2SO_4	Merck
Graphene nanoplatelets	GNP	Graphitena
Phosphoric acid	H_3PO_4	Merck
Hydrogen peroxide	H_2O_2	Merck

All the equipment used in this study is summarized in Table 2.2.

After this section, all the methods applied in this study is explained in a detailed way. After the preparation of materials and electrodes used in this thesis, how characterization methods were carried out in both structural and electrochemical will be explained, in an order. Structural characterization methods include Raman Analysis, X-ray Photon Spectroscopy, UV-Vis Spectroscopy, Fourier Transformed Infrared Spectroscopy, and X-ray Diffraction Analysis, while electrochemical methods constrain Cyclic Voltammetry and Electrochemical Impedance Spectroscopy measurements.

Equipment Name	Source
Ultrasonicator	Bandelin Sonoplus HD 4400
UV-Vis Spectrophotometer	Agilent Technologies Cary Series
FTIR Spectrometer	Bruker Vertex 80v
Potentiostat	BioLogic SP300
Centrifuge	NÜVE 400
Freeze Dryer	Labconco Freezone 4.5
Tubular Furnace	Protherm
Coin Cell Crimping Machine	Tico
Vacuum pump	KNF N 022 AN 18

Table 2.2. Equipment that were used during the study.

2.2. Preparation of Electrode Materials

2.2.1. Preparation of Graphene Oxide

The GO fabrication process is depicted in Figure 2.1. GO was produced according to the modified Hummers method [71]. 120 mL of sulphuric acid and 13 mL of phosphoric acid were mixed. 1 g of graphene nanoplatelets and 6 g of potassium permanganate were added to the mixture and mixed using a magnetic stirrer. The oxidation reaction nanoplatelets to GO was allowed to proceed at 50 °C for approximately 16 h. The mixture was cooled down to room temperature and 130 g of ice was added to the mixture. Upon the addition of 2 mL of hydrogen peroxide to the slurry, the mixture turned from purple/brown to bright yellow. The suspension was distributed into two 500 mL centrifuge tubes and centrifuged for 15 min at 1800 rpm (NÜVE 400, Unit Operations Laboratory, Chemical Engineering, Bogazici University). The supernatant was discarded, and the material was re-suspended in water. This washing procedure was then repeated with 250 mL of hydrochloric acid and again with ethanol three times. The filtrate was dried in a 40 °C vacuum oven for 24 h.



Figure 2.1. The fabrication process of GO.

2.2.2. Preparation of Thermally Exfoliated Graphene Oxide

The TEGO synthesis is depicted in Figure 2.2. The as-prepared GO suspension (80 mL) with a concentration of 0.5 mg/mL in water was dried using a freeze dryer (Labconco Freezone 4.5, Center for Life Sciences and Technologies, Bogazici University) and subjected to thermal annealing at 700 °C using a tubular furnace (Protherm) in Ar atmosphere for 1 h. Finally, the obtained black powder was washed with hot (70°C) distilled water and filtered and then this procedure was repeated three times. The filtrate was dried in a 70°C vacuum oven for 12 h.

2.2.3. Preparation of Carbon Quantum Dots

CQDs were obtained ed by our collaborators in Prof. Haluk Bingöl's group at Necmettin Erbakan University, Department of Education of Chemistry.



Figure 2.2. The fabrication process of TEGO.

2.3. Electrode Preparation Methods

Electrode preparation steps are given in next two sections.

2.3.1. Preparation of TEGO electrode

10 mg thermally exfoliated graphene oxide-TEGO (75 wt%), 2 mg acetylene black (15 wt%), and 1.3 mg polytetrafluoroethylene-PTFE (10 wt%) were mixed mechanically with a glass stick for 15 minutes. 2 ml N-methyl-2-pyrrolidone-NMP was added. Then, the suspension was mixed in a magnetic stirrer for 15 minutes. It was ultrasonicated (Bandelin Sonoplus, HD 4400) at 20% amplitude for 30 minutes.

The solution was dripped onto nickel foam $(1\text{cm}^*1.5\text{cm})$ by using a micropipette. The main goal was to achieve 1 mg/cm^2 as a density of active material during preparation of the electrode. It was also put into oven at 80°C overnight to evaporate the solvent. After that, the electrode was pressed under 1000 kg/cm² for one minute via the help of coin cell crimping machine (Tico). The connection was carried out by using solder and copper wire.

2.3.2. Preparation of TEGO-CQDs electrodes

There are three kinds of CQDs utilized in the electrode preparation. All three CQDs are dissolved in dimethylformamide-DMF with a density of 5 mg/ml. 9.75 mg RGO (65 wt%), 2.25 mg acetylene black (15 wt%) and 1.5 mg PTFE (10 wt%) were mixed mechanically for 15 minutes with a glass stick. The CQDs solution (5mg/ml) was added as 3 ml or 1.5 mg (10 wt%). 1.4 ml NMP was added, and the solution was mixed at 300-400 rpm in a magnetic stirrer at room temperature for 30 minutes. It was also ultrasonicated at 20% amplitude for 30 minutes in an ice bath.

The solution was dripped onto nickel foam (1cm*1.5cm) by using a micropipette. The main aim was to achieve 1 mg/cm² as a density of active material during preparation of the electrode. It was also put into oven at 55 °C overnight to evaporate the solvent. The electrode was pressed under 1000 kg/cm² for one minute via the help of coin cell crimping machine (Tico). The connection was accomplished by using solder and copper wire. Additionally, two more electrodes were fabricated by using two concentrations of CQD3 which are 20 and 30 wt%.

2.4. Structural Characterization Methods

We applied structural characterization methods to analyze the properties of active material (GO and TEGO), CQDs and TEGO-CQD3.

2.4.1. Raman Spectroscopy

We perform Raman spectroscopy (Reinshaw inVia, laser: 532 nm, laser power: 50 mW, exposure time: 10s, lens 5X, Bogazici University Advanced Research and Development Center) on pressed powders of GO and TEGO. It is a powerful and nondestructive technique which has been widely used to characterize the structure and electronic properties of carbon materials. For this analysis dense and smooth pellets of TEGO-based materials were prepared by compression of approximately 10 mg of material. In the Raman spectra of the samples, we look for two common peaks: The D band (between ca. 1272-1406 cm⁻¹) and G band (between ca. 1593-1629 cm⁻¹). The D peak is the characteristic of lattice defects, edge imperfections, and low-symmetry graphitic structure, and the second peak, i.e., G peak, demonstrates the occurrence of C=C stretching vibrations [72].

2.4.2. X-Ray Photon Spectroscopy

This technique provides insight into the surface elemental composition such as C, O, B, N. In other words, the surface chemistry of the materials is analyzed via this technique. Particularly, XPS analysis gives information about the types and relative amounts of organic functional groups (e.g., C-O, C=O, O-C=O, C-N, etc.) present on carbon surfaces and the presence of surface impurities which can affect material performance [73].

We conducted the XPS analyses in two parts. The first one (Thermo Scientific K-Alpha XPS, lens: standard, source gun type: Al K Alpha, spot size: 400 μ m, acquisition time:80.4 s, Bogazici University Advanced Research and Development Center) on dust form of GO and TEGO. It is used provide insight into the surface elemental composition (C and O) of GO, TEGO. As second part, for TEGO-CQD3 and CQDs, we applied Koç University (KUYTAM) to analyze the materials. Since CQDs are dissolved in a solvent, they were dripped onto the silicon wafer and put into oven. Gradually, three films were obtained after a few times of dripping. TEGO-CQD3 solution was prepared by using distilled water and it was frozen. Lyophilizer (Life Sciences and Technologies, Bogazici University) was applied to get the dust form and to get rid of water.

2.4.3. FTIR Spectroscopy

FTIR spectra were taken (Bruker Vertex 80v spectrometer) with 4 cm-1 resolutions in a spectral region 400 to 4000 cm-1 in the ATR cell at room temperature (Bogaziçi University, Chemical Engineering, KB430). FTIR is a very effective analytical technique that can identify a wide variety of frequency components at the same time [74]. FTIR stands for Fourier transform infrared spectroscopy and is a universal analytical instrument for evaluating a wide range of materials, particularly for identifying unknown materials [75]. Pure compounds, mixes, impurities, and compositions of diverse materials have all been identified using this approach [75].We performed this analysis to three kinds of CQDs in solution form. The samples were dripped about 0.5ml and then measured.

2.4.4. UV-Vis Spectroscopy

The UV-Visible absorption spectra of three kinds of CQDs were taken (SHI-MADZU UV-2600, Bogazici University KB441). UV-Vis spectroscopy is a helpful absorption or reflectance spectroscopy for determining the quantity of analytes by detecting a sample's absorptivity or reflectance in the ultra-violet to visible light wavelength range [76]. The dissolved forms of CQDs were diluted as 1:15 with DMF. Then the measurements were taken.

2.4.5. Powder X-ray Diffraction Spectroscopy

To analyze the distance between graphene oxide sheets (d0002), X-ray diffraction spectra measurements were taken in two parts. Firstly, GO, TEGO, and their composites with RTIL were analyzed (Rigaku D/MAX-Ultima+/PC, Bogazici University Advanced Research and Development Center). The second part is carried out by using diffractometer (PANalytical X'Pert PRO) to monitor how the interlamellar spacing is tuned with the incorporation of TEGO and CQD3 into TEGO electrodes as thin films (Yıldız Technical University, BİTUAM). TEGO and CQD3 (5 mg/ml) were solved with NMP, then it was tip-sonicated (Bandelin Sonoplus HD 4400) in 20% amplitude for 30 minutes. Finally, the solution (0.3 mg/ml) was vacuum filtered via the help of vacuum pump (KNF, N 022 AN 18). The fabrication way of thin film TEGO-CQD3 with RTIL was same with TEGO. The only difference was to add 10 μ l RTIL after filtration was over to prevent restacking of graphene sheets. Herein, the lowest detectable angle of $2\theta = 5^{\circ}$ corresponds to an upper limit in the observable d-spacing of Å. Larger spacing between the sheets leads to peaks at lower scattering rate [26]. Bragg's Law is utilized for calculating d-spacing or d₀₀₀₂,

$$\mathbf{d_{0002}} = \frac{\lambda n}{2sin\theta} \tag{2.1}$$

where n=1.

2.5. Electrochemical Characterization

After the structure of active materials were analyzed, electrochemical characterization methods were conducted. To understand and define the parameters of these electrodes, two-, three-, and four-electrode setup can be used. Three electrode setup is generally utilized for electrochemical characterizations [15]. After the cell structures are introduced, how the three- electrode cell is prepared will be explained in new section.

2.5.1. Three-Electrode Cell Preparation

Two-electrode setup is utilized in order to measure of the cell as a whole in Figure 2.3a. During the flow of current between the working and counter electrodes in a fourelectrode configuration which can be seen in Figure 2.3b, the potential between the reference electrode and the sense electrode is monitored [15].

On the contrary of two and four electrode types, three electrode setup is used to understand the electrochemistry of the electrode material in Figure 2.4b. It includes working electrode (WE), counter electrode (CE), and reference electrode (RE). RE behaves like a reference potential to measure and control the potential of WE. In this setup, current flows between CE and WE. For this reason, in the cell they should be see each other. While the current flows in this direction, RE senses and measures the potential between them [15].



Figure 2.3. Cell configurations of a) two electrode and b) four electrode system.

In all the electrochemical characterization experiments, three-electrode cell was used, Figure 2.4a. A platinum plate was chosen as counter electrode. As reference electrode, Ag/AgCl-SCE (Ionode 005) was used containing 3 M KCl solution. For electrolyte, $[EMIM^+][BF_4^-]$ (Proionic) was used in five different concentrations. The counter electrode and working electrode should see each other from two sides of reference electrode. The position orders of these electrodes were WE, RE, and CE as in Figure 2.4a. Firstly, three electrodes were connected by using crocodiles to computer-controlled digital potentiostat (BioLogic SP300). Then, these electrodes were dipped into electrolyte. After the cell was ready, it was waited for 15 minutes to absorption of electrolyte by working electrode. Two methods applied are given in next two sections,
respectively.



Figure 2.4. a) Three electrode cell used during the electrochemical characterization and b) three-electrode cell figuration.

2.5.2. Cyclic Voltammetry

The most extensively used approach for obtaining qualitative information about electrochemical reactions is cyclic voltammetry [24, 77]. It results from scanning linearly the potential of stationary working electrode. Herein, potentiostat measures the current, the result of applied potential, while potential sweep happens. Thus, cyclic voltammogram occurs [24].



Figure 2.5. Representation of Cyclic Voltammetry.

A cyclic voltammogram or current/ voltage (I-V) curve is pictured in Figure 2.5. In three electrode electrochemical cell, current is observed while working electrode is applied by changing applied potential in reverse and forward directions [78]. Between the working and counter electrode, CV technique includes a cyclic variation of electrode potential, in a operating potential window while flowing current is measured between two electrodes (WE and CE) [78,79]. Herein, scan rate controls the time scale [79]. At the end of each cycle, working electrode's potential returns to the initial value and a cycle is obtained which can be repeated many times [78,79].

In three electrode cell, capacitance is calculated by utilizing the obtained area from CV curve, which can be represented as,

$$\mathbf{C} = \frac{1}{m\nu(V_b - V_a)} \int_{V_b}^{V_a} I dV \tag{2.2}$$

where V_b and V_a are the final and initial potential, m is the mass of active materials, and ν is the scan rate. The The obtained area from a cycle is the integrated area of the I-V curves [80–82]. All CV measurements were taken in the potential window of -0.9 and 0 V. The measurement protocol included of the following: (1) a 15 min rest to stabilize for reference potential (open circuit voltage-OCV), (2) CV from the OCV, started at 20 mV/s 20 times and turn to OCV for 5min, (3) 50 mV/s 20 times and turn to OCV for 5 min, (4) 100 mV/s 20 times and turn to OCV for 5 min, (5) 250 mV/s 20 times and turn to OCV for 5 min, (6) 500 mV/s 20 times and turn to OCV for 5 min.

The capacitance values are calculated via the help of the integrated areas of I-V curves by using Equation (2.2). The obtained values will be given in the Results and Discussion part.

2.5.3. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a useful tool for examining the characteristics of chemically modified electrodes and determining electrochemical reaction rates [24, 83, 84]. Following the CV measurements, EIS data were taken. The protocol followed in this characterization; (1) 30 min rest at the OCV, (9) EIS measurement carried out, scanning the potential from OCV to positive potentials in 10 mV increments with a 5 min rest at the potential of interest before the impedance (200 kHz to 50 mHz) was recorded.

At the end of the electrochemical impedance measurement, a Nyquist plot (presented in Figure 2.6) composed of imaginary impedance measurement as a function of real impedance measurement is obtained. EIS is generally utilized to estimate the ion kinetics on the porous media [85].

The Nyquist plots begin to occur in higher frequency and continues to lower frequency. the point of the plot which intersects with x-axis is attributed to the electrical resistance (R_{ele}) [86]. The diameter of semicircle is ascribed to the charge transfer resistance (R_{ct}) [86]. The EIS results will be given in the form of Nyquist plots. (R_{ele}) and (R_{ct}) values are obtained via the help of these figures which will be explained in Results and Discussion part.



Figure 2.6. Representation of a Nyquist plot.

3. RESULTS AND DISCUSSION

For a high performance EDLC, it is critical to maintain a compact architecture for keeping the energy density high, while also sustaining the ability to fast charge/discharge with minimal ohmic losses. Taking these into account, the energy density of EDLCs can be enhanced by maximizing the intrinsic capacitance (C_{int}), potential window (U) and ion accessible surface area (SSA_{IA}). The first objective of this thesis is to study the intrinsic properties of the electrolyte and electrode materials motivated by the need to develop promising materials with high intrinsic capacitance and electrochemical stability for device applications. The second objective deals with improving ion transport through EDLC electrodes and developing processing strategies for enhanced EDLC performance. The work towards achieving these goals is summarized below.

3.1. Structural Characterization of Graphene Oxide and Thermally Exfoliated Graphene Oxide

Raman spectra collected for the series of GO and TEGO are given in Figure 3.1. GO presents two Raman features, which are assigned to D and G peaks. The D-peak in the region between 1272-1406 cm⁻¹ is the result of the breathing mode of aromatic rings with six-fold symmetry [72]. This mode is only active in the presence of lattice disorder hence the peak intensity also depends on the characteristic distance between defects which is a measure of the average lateral crystallite size of pristine graphene domains [87].

Meanwhile, the G-peak between 1593-1629 cm⁻¹ corresponds to the in-plane oscillations of sp² carbon pairs in the form of chains or rings of any order [72]. Consequently, the ratio of the intensities of the D- and G- peaks (ID/IG), the peak positions and the width of the peaks (given by the full width at half maximum, FWHM) all provide insight into the structure of the graphene-based materials that evolve after doping and activation treatments.



Figure 3.1. Raman spectra of GO and TEGO.

To quantify the evolution of these characteristics of the D- and G- peaks, spectra were fit using the Breit- Wigner-Fano (BWF) line shape for the G-peak and Lorentzian fit for the D-peak Figure 3.2 [16]. This was found to best fit the spectra compared to fitting both peaks with either Gaussian or two Lorentzian shapes. The BWF fit is described as,

$$\mathbf{I} = I_P \frac{(1 + (x - x_P)/q\gamma)^2}{1 + (x - x_P)^2/\gamma^2}$$
(3.1)

where x is frequency, I_P is the maximum intensity, γ is peak width, and q is utilized the asymmetry of G peaks. As shown in Table 3.1, the ID/IG ratio of TEGO is higher than that of GO while the D-peak FWHM (69.7 cm⁻¹) and the G-peak FWHM (73.6 cm⁻¹) are smaller than those of GO. The narrower peaks suggest that the thermally exfoliated material's graphitic domains are more uniform in size/shape and/or contain fewer non-6 member rings compared to GO [72]. The D peak is activated by defects, i.e., in-plane substitution heteroatoms, vacancies, or grain boundaries/ edges. The larger ID/IG ratios of TEGO indicates that reduction is carried out successfully.



Figure 3.2. Raman spectra of TEGO and GO, fitting curves. Dashed red lines indicate the Lorentzian fit to the D-peak and the BWF fit to the G-peak and the solid red line is the sum of the two fits.

Table 3.1. Estimating the degree of defectiveness of TEGO-based materials.

Materials	Intensity Ratio	Peak Po	ositions (cm^{-1})	$FWHM (cm^{-1})$	
	ID/IG	G-Band	D-band	G-Band	D-band
GO	0.95	1582.14	1343.02	72.4	86.1
TEGO	1.06	1580.51	1343.02	69.7	73.6

Raman analysis does not give information about the sp³ carbon content or the relative number of functional groups because the sp² signals are thought to be resonantly enhanced and effectively draw out any sp³ contributions to the spectrum [72]. To obtain further information about the capacitive features of GO and TEGO, XPS is applied to the materials to analyze functional groups and electronic states of elements on the surface of the materials [88]. The elemental analysis includes C1s and O1s groups, and XPS survey analysis of GO and TEGO are given in Figure 3.3 and Figure 3.4, respectively.



Figure 3.3. XPS survey spectra of GO and the deconvoluted spectra of b) C1s and c) O1s peaks.

C1s electronic state of TEGO displays a single, symmetrical peak at approximately 285 eV while two peaks are observed at 285 eV and 287.2 eV for GO. The obtained peaks are deconvoluted to understand the bond structure of GO and TEGO. Fitting of the C1s spectra was performed with considerations for relative sensitivity factors to identify and quantify the various carbon interactions present on the materials' surfaces. C1s peaks of all materials were fitted to give a C=C bond [89,90] at 284.5 eV, a C-C bond [90] at 285.5 eV, a C-O bond [89] at 286.7 eV, and a C=O bond [91] at 288.2 eV.



Figure 3.4. XPS survey spectra of TEGO and the deconvoluted spectra of b) C1s and c) O1s peaks.

GO and TEGO contain 7.67%, 36.19 of C=C bonds, 32.97%, 27% of C-C bonds, 49.69%, 8.14% of C-O bonds, 9.68%, 28.66% of C=O bonds. The C/O ratios obtained for the materials are given in Table 3.2. For GO and TEGO, only carbon and oxygen species are detected. TEGO has lower oxygen content compared to GO, suggesting that GO has more oxygen functional groups.

O1s electronic states of GO is deconvoluted to 3 bonds which are C-O bond [90] at 530.4eV, O=C-OH bond [92] at 531.7eV, and C=O bond [89] at 532.4eV. TEGO's electronic state of O1s is deconvoluted to C-O bond [89] at 533.1 eV, O=C-OH bond [92] at 531.2 eV, and C-OH bond [92] at 533.5 eV.

3.2. Structural Characterization of Carbon Quantum Dots

The elemental structure of CQDs were analyzed via using X-ray Photon Spectroscopy. The results show that CQD1, CQD2, CQD3, and CQD3/TEGO are mainly composed of C1s, O1s, and N1s which are given in Figure 3.5 and Table 3.2. Additionally, S2p is observed in both the survey spectra of CQD2 and CQD3 during characterization and the peak is observed around 165 eV. CQD3 was chosen as optimum CQDs to understand the effect of increase in C/O. When CQD3 was added to TEGO, C/O increased from 3 to 6.3.

Table 3.2. Atomic weight of CQD1, CQD2, CQD3, and CQD3/TEGO from XPS survey spectra.

	C %	0%	N%	S %	C/O
CQD1	72.7	18.5	8.8	0	3.9
CQD2	65.5	22.5	11.9	0.2	2.9
CQD3	68	23.1	6	2.9	3
CQD3/TEGO	84.3	13.3	1.65	0.7	6.3

After C/O ratio was determined, C1s, O1s, N1s and S2p peaks were deconvoluted. XPS analysis results of CQD1 is shown in Figure 3.6. C1s peak was deconvoluted into three peaks (Figure 3.6a), C=C at 284.5 eV [93], C-O at 285.6 eV [94], and C=O at 287.9 eV [95]. O1s peak was also fitted by two bonds (Figure 3.6b), as C=O at 531.4 eV [93] and C-O at 533 eV [94]. Although N1s is relatively low in the survey spectra, four peaks were fitted (Figure 3.6c). They were assigned to bonds of N-H at 398.5 eV [96], pyridinic N at 399.9 eV [94], pyrrolic N at 400.8 eV, and pyridinic-N oxide at 403.2 eV [95].



Figure 3.5. XPS survey spectra of a)CQD1, b)CQD2, c)CQD3, and d)TEGO/CQD3.

Figure 3.7 indicates the XPS analysis of CQD2, which also mostly includes C, O, and N from the survey spectra (Figure 3.5b). C1s peak (Figure 3.7a) was deconvoluted in three peaks, i.e. C=C at 284.5 eV [93], C-O at 285.9 eV [94], and C=O at 287.8 eV [95]. In Figure 3.7b, O1s was also deconvoluted in two peaks C=O at 531.2 eV [93] and 532.8 eV [94]. Although the rate of N1s is lower than others, the peak was assigned to pyridinic N at 399.6 eV [94] and graphitic N at 403.5 eV [95]. Finally, although the atomic rate of S2p is the lowest, it was deconvoluted in two peaks, i.e. C-S-C at 163.4 eV [97] and S=O at 167.4 eV [98].



Figure 3.6. CQD1 deconvolution peaks of a) C1s, b) O1s, c) N1s, and d) S2p.

C1s peak of CQD3 was deconvoluted into three peaks (Figure 3.8a), C=C at 284.5 eV [93], C-O at 285.9 eV [94], and C=O at 288.3 eV [95]. O1s peak was also fitted by two bonds (Figure 3.8), as C=O at 531.47eV [93] and C-O at 533.4 eV [94]. Furthermore, N1s deconvoluted peaks (Figure 3.8c) were assigned to pyridinic N at 400 eV [94], C-N at 401.8 eV [96], and graphitic N at 403.3 eV [95]. The existence of carbon atoms assigned to N1s peak can be attributed to the increase of C/O in CQD3/TEGO. Although atomic weight is the lowest in S2p (Figure 3.8d), it was also deconvoluted in C-S-C at 163.2 eV [97]) and S=O at 167.8 eV [98].



Figure 3.7. CQD2 deconvolution peaks of a) C1s, b) O1s, c) N1s, and d) S2p.

Then, the XPS results of CQD3/TEGO is given in Figure 3.9. The peaks assigned to C1s deconvolution (Figure 3.9a) are C=C at 284.5 eV [93], C-O at 285.4 eV [94], C=O at 286.7 eV [95], and O-C=O at 288.6 eV [99]. As a difference from CQD3 C1s deconvolution, there is an extra peak including carbon bond.



Figure 3.8. CQD3 deconvolution peaks of a) C1s, b) O1s, c) N1s, and d) S2p.

In Figure 3.9b, O1s deconvolution peaks were assigned to the C=O at 531.8 eV [93], C-O at 533.3 eV [94], O=C-O at 535.3 eV [96], and O=C-OH at 530.5 eV [92,100]. Although the oxygen containing bonds increase when compared with CQD3, these bonds are mainly composed of carbon containing bonds. Thus, they leaded to increase in C/O ratio. N1s peaks are seen in Figure 3.9c. As CQD3 and CQD3/TEGO

results are compared, the number of deconvolution peaks decreased. These peaks are ascribed to pyrrolic N at 400.3 eV and graphitic N at 402.2 eV [95]. The atomic weight decrease in N1s is also a reason to the increase of C/O ratio. The atomic weight of S also decreased in CQD3/TEGO (Figure 3.9d).



Figure 3.9. CQD3/TEGO deconvolution peaks of a) C1s, b) O1s, c) N1s, and d) S2p.

The UV-Vis spectra of CQDs are shown in Figure 3.10. CQD1 displays two stronger peaks at 281 and 274 nm. CQD2 shows a peak at 274 nm. CQD3 has also a sharp peak at 267 nm. Generally, CQDs' optical absorption peak is observed in ultraviolet region with a maximum absorption around 283 nm, resulting from $n-\pi^*$ transition of C=O [101–103]. The stronger peaks of CQDs are also associated with the π - π^* transition of C=O bonds over the surface of quantum particles [103, 104].Furthermore, around 245 nm all the CQDs has a weaker peak, which is attributable to the π skeletons that contain C=C/C=O groups [105].



Figure 3.10. UV-Vis spectra of CQDs.

The FTIR spectra of CQDs are depicted in Figure 3.11. The broad peak around 3500 cm^{-1} and 2970 cm^{-1} can be ascribed to OH and C-H stretching, respectively [100, 106]. There is another peak appearing in the spectra around 1651 cm⁻¹ which can be attributed to C=O stretching vibration [72] while the bands around 1413 cm⁻¹ are assigned to C=C vibrational stretch [107, 108]. The samples of CQDs were solved in DMF; therefore, there is a peak around 1250 cm⁻¹ can be attributed to the C-O-C vibrational stretching [108]. The last peak around 1250 cm⁻¹ can be attributed to the C-O-C vibrational stretching [106]. The FTIR results and assigned peaks validate of XPS analysis of CQDs. The presence of –OH groups with their reducing activity on the surface of CQDs verifies the ability of CQDs to donate electrons during electrochemical

reaction [92].



Figure 3.11. FTIR spectra of CQDs.

3.3. Electrochemical Characterizations

Gravimetric capacitance (C_G) depends on intrinsic capacitance (C_{int}) and ion accessible surface area (SSA_{IA}). Meanwhile, the essential metric for energy storage performance, energy density (E), is linearly correlated with both C_G and packing fraction (f). Simultaneous optimization of these parameters is essential for improving energy storage performance in supercapacitors: A material with only a high intrinsic capacitance does not necessarily yield a competitive energy storage performance. For instance, graphite has a large intrinsic capacitance albeit a very small gravimetric capacitance because ions cannot access the interlamellar space between graphene sheets as the spacing between graphene layers is too small to be accessible to electrolyte ions (distance between two graphene sheets in graphite is ~0.34 nm). Meanwhile, a material with high C_G but low packing fraction is also not preferable in designing a high energy density supercapacitor.

In this work, we aim to improve ion absorption and diffusion through channels in electrodes comprised of gaps between TEGO sheets by increasing the ion accessible surface area while keeping the packing fraction high. In this respect, we use the ions in the electrolyte and CDQs as spacers between TEGO sheets to increase the ion accessibility of the electrodes, while avoiding using inactive spacers during electrode consolidation.

3.3.1. TEGO/RTIL Composite Films

First, we investigate the effect of incorporating the room temperature ionic liquid $[\text{EMIM}^+][\text{BF}_4^-]$ in between TEGO sheets. Figure 3.12 shows the dry TEGO film in the absence of RTIL and CQDs has a diffraction peak at 24.8° corresponding to a d-spacing of 0.36 nm. Meanwhile, when the TEGO film is solvent exchanged with pure $[\text{EMIM}^+][\text{BF}_4^-]$ in the final step of vacuum filtration, the peak shifts to 21.8° (0,41 nm). Here, we observe an increase in sheet-to-sheet distance, indicating the penetration of the ionic liquid between the layers.



Figure 3.12. XRD spectra of TEGO and TEGO/RTIL.

Capacitance performance of the three-electrode setups for dried TEGO electrode and TEGO/RTIL composite in 4.5 M [EMIM⁺][BF⁻₄] electrolyte are depicted in Figure 3.13. The TEGO/[EMIM⁺][BF⁻₄] composite shows superior capacitance and scan rate dependence compared to the dry TEGO electrode. In particular, at a scan rate of 20 mV/s, TEGO/[[EMIM⁺][BF⁻₄] composite yield a capacitance of 132 F/g, while dried TEGO film yielded only a capacitance of 81 F/g.



Figure 3.13. Specific capacitance of TEGO and TEGO/RTIL as a function of scan rate.

More importantly, when scan rate is increased to 500 mV/s, the capacitance of the TEGO/[EMIM⁺][BF⁻₄] composite decreased by 65% corresponding to 46 F/g, while the dried TEGO film showed an extremely small capacitance of 15 F/g. with more than 80% decrease in capacitance. The particularly enhanced superior performance of TEGO/RTIL composites at higher scan rates further shows the incorporation of [EMIM⁺][BF⁻₄] into the electrodes improves ion transport through the channels between TEGO sheets.

The enhanced ion transport, as well as improved conductivity in the composites of TEGO/[EMIM⁺][BF₄⁻] is also supported by the Nyquist plots Figure 3.14. The points that the Nyquist plots cross the real axis are nearly the same for dried TEGO and TEGO/[EMIM⁺][BF₄⁻] composites, indicating the electrodes have similar electrical resistance. Meanwhile, the Nyquist plot for the TEGO/[EMIM⁺][BF₄⁻] composite electrode presents a much smaller semicircle (0.7 Ohm) in the high frequency region compared to the dried TEGO electrode (3.7 Ohm) Since the active electrode material is identical in both electrodes, the improved performance of the TEGO/[EMIM⁺][BF₄⁻] composite is attributable to the enhanced ion diffusion channels in the composite material that are formed through the incorporation of EMIM⁺ and BF₄⁻ ions between TEGO sheets during the vacuum filtration process.



Figure 3.14. Nyquist plots of TEGO and TEGO/RTIL composite.

We note that although the incorporation of the ionic liquid into the electrodes during the electrode consolidation process improves ion diffusion and C_G in the composite films of TEGO/[EMIM⁺][BF⁻₄], in these films the TEGO sheets are still not arranged in a flat, face-to-face orientation, are partially corrugated and not evenly wetted by the electrolyte. Particularly, the XRD profiles of the TEGO and TEGO/RTIL composite films (Figure 3.12) display a nearly amorphous structure. If stacking of the TEGO sheets were perfectly flat face-to-face type, we would have observed a sharp XRD peak for the TEGO/[EMIM⁺][BF⁻₄] composite, reflecting an evenly distributed inter-sheet spacing.

3.3.2. Incorporation of CQDs into the Electrodes

Next, to improve ion diffusion channels in the electrodes and obtain a more even distribution of sheet-to-sheet distance between TEGO sheets, we incorporate CQDs into the electrodes. Increasing the ion accessible surface area of electrodes by using spacers is not a new approach: several studies have previously used spacers to prevent collapsing of graphene sheets into graphite-like structures [109–111]. However, these studies have commonly used inactive spacers to prevent stacking: While this increases the ion accessible surface area, a significant increase in energy density cannot obtained as inactive spacers add dead weight to electrodes, lowering f. Alternatively, metalbased spacers are also used but they are not ideal as they decrease electrochemical stability [112]. As opposed to inactive spacers, CQDs are conductive materials, and have been previously successfully used in conjunction with metal oxides and conductive polymers in supercapacitor applications [111, 113].

Here, we use CQDs to improve the ion accessible surface area and at the same time to construct a conductive network by evenly distributing CQDs on TEGO surface as a spacer. Figure 3.15 shows the capacitance profiles of CQDs/TEGO/RTIL composite electrodes in 4.5 M $[EMIM^+][BF_4^-]$ electrolytes. Clearly, introduction of 10 wt% CQD3 improves capacitance, while CQD1 and CQD2 have more subtle impact on capacitive performance. The superior performance of CQD3 could be attributable to the improved electrical conductivity of the CQD3/TEGO/RTIL composite and its continuous ion transport network.



Figure 3.15. Specific capacitance of CQDs/TEGO/RTIL films in 4.5 M $[\text{EMIM}^+][\text{BF}_4^-]$ as a function of scan rate.

Figure 3.16b shows both the electrode resistance (R_{ele}) and charge transport resistance (R_{ct}) for the three electrodes computed from the Nyquist plots (Figure 3.16a). The semicircle diameter (R_{ct}) is the smallest for the CQD3/TEGO/RTIL composite compared to TEGO, CQD1/TEGO/RTIL, and CQD2/TEGO/RTIL electrodes.



Figure 3.16. a)Nyquist plots of TEGO and CQDs/TEGO/RTIL and b)electrical resistance (R_{ele}) and charge transfer resistance (R_{ct}) as a function of CQDs amount in the electrodes.

After choosing CQD3 as the ideal candidate among the three types of CQDs, we next optimize the CQD3/TEGO composition of the electrodes. Figure 3.17 shows that in the composition space considered in this work, C_G increases with increasing CQDs amount in the electrodes. Furthermore, capacitance retention with increasing scan rate is also improved in at higher CQDs content. To further characterize the ion diffusion kinetics in the CQDs/TEGO composites with varying CQDs content, we look at the Nyquist plots (Figure 3.18).



Figure 3.17. Specific capacitance of different concentrated CQD3/TEGO/RTIL films in 4.5 M $[\text{EMIM}^+][\text{BF}_4^-]$ as a function of scan rate.

Figure 3.18b shows that for CQD3_{30wt%}/TEGO/RTIL composite the intersection of the real axis is the smallest, indicating electrical resistance is the smallest for the CQD3_{30wt%}/TEGO/RTIL composite.



Figure 3.18. a) Nyquist plots of CQD/TEGO/RTIL composites, and b) electrical resistance (\mathbf{R}_{ele}) and charge transfer resistance (\mathbf{R}_{ct}) as a function of CQDs amount in the electrodes.

Meanwhile, the diameter of the semicircle in the high frequency range is substantially smaller for 20wt% and 30wt% compared to 10wt%, demonstrating the largest charge transfer resistance is obtained with the CQD3_{10wt%}/TEGO/RTIL composite. Figure 3.19 shows the XRD profiles of the CQD3_{20wt%}/TEGO/RTIL and CQD3_{20wt%}/TEGO composites compared to dried TEGO. While the CQD3_{20wt%}/TEGO film alone does not have a sharp peak, indicating an amorphous structure, the peak of CQD3_{20wt%}/TEGO/RTIL is significantly more distinct at $2\theta \approx 19.6^{\circ}$ corresponding to a d-spacing of ~ 0.46 nm.



Figure 3.19. XRD profiles of TEGO, CQD3/TEGO, and CQD3/RTIL/TEGO.

The detectable diffraction peak of $CQD3_{20wt\%}TEGO/RTIL$ suggests that the TEGO sheets tend to align flat, more face-to-face type compared to the TEGO/RTIL composite profile in Figure 3.12.

3.3.3. Effect of Electrolyte Composition

Using the optimum electrode configuration identified in the previous section, we next test the performance of CQD3_{30wt%}/TEGO/RTIL composite electrode in different electrolytes. In particular, Figure 3.20 shows capacitance as a function of electrolyte composition. While pure $[EMIM^+][BF_4^-]$ exhibits the smallest capacitance values and poor scan rate dependence, electrolytes in the range 2.5 to 5.9 M exhibit all comparable performance. This indicates among these options, identifying the best electrolyte composition depends on the practical application requirements.



Figure 3.20. Specific capacitance (C_G) CQD3_{30wt%}/TEGO/RTIL composite electrode as a function of electrolyte concentrations at different scan rates.

Meanwhile, when the ultimate goal is to reduce cost, 2.5 M is likely more preferable as it contains only 33 wt% [EMIM⁺][BF⁻₄] compared to the 5.9 M electrolyte with 54 wt%. After optimum concentration of CQD3_{30wt%}/TEGO/RTIL is determined, the ion diffusion kinetics is summarized in Figure 3.21. The real part of Nyquist plots showing that electrical resistance is higher in 6.5 M than other concentrations. The diameter of the semicircle obtained from plots indicating charge transfer resistance is higher in 6.5 M. Intermediate dilution levels of electrolyte have lower resistance values.



Figure 3.21. Nyquist plots of CQD3 $_{30wt\%}$ /TEGO/RTIL composite electrode as a function of electrolyte concentrations at different scan rates.

4. CONCLUSION AND RECOMMENDATIONS

4.1. Conclusion

Energy storage technologies are important both with regards to storage and transportation solutions for renewable energy and consumer electronics. Although batteries dominate the energy storage market, supercapacitors with attractive properties like longer cycle life, fast charge and discharge rates and durability have gained prominence among energy storage technologies. However, they have lower energy density than more conventional electrochemical energy storage devices like batteries. The main goal of this thesis is to help improving the role of supercapacitors in the energy storage market by improving their energy density while sustaining high power density.

To reach this objective, we first synthesized TEGO sheets and analyze their structural properties. Raman and XPS analysis results show that the reduction of GO was carried out successfully. Structural properties of CQDs were studied by utilizing XPS, UV-Vis, and FTIR spectroscopy. Three types of CQDs were incorporated into TEGO electrodes with room temperature ionic liquids to facilitate fast ion transport through electrodes and improve ion accessible surface area. The optimum kind and amount of CQDs to enhance capacitive behavior was determined via CV and EIS measurements.

In particular, CQD3 was determined as the optimum CQD that yields the highest capacitance. CQD3/TEGO/RTIL composite with 30 wt% CWD yielded the largest capacitance. XRD profiles of the CQD3/TEGO/RTIL films showed incorporation of CQD into the electrode increased sheet-to-sheet distance between TEGO sheets and provided an ion transport network. EIS results supported the reduction in charge transfer and electrical resistance.

Finally, the effect of electrolyte composition on capacitance and cell resistance was studied. The highest gravimetric capacitance was obtained with the CQD3 30 wt% /TEGO/RTIL composite in 3.4 M [EMIM⁺][BF⁻₄]as 206 F/g at 20 mV/s. The films exhibited good scan rate dependence, retaining 70% of their capacitance at 500 mV/s.

4.2. Recommendations

The method described in this thesis can be further improved in several ways. The present work experimented with only one type of room temperature ionic liquid, $[EMIM^+][BF_4^-]$. The electrode consolidation process can be improved by experimenting with various types of ionic liquids. Specifically, ion accessible surface area and ion transport in TEGO/CQD/RTIL electrodes can be improved by tuning ion size and polarity. We expect to obtain more efficient ion transport by incorporating ionic liquid cocktails comprised of multiple ion types in the electrode films. In the current study, RTIL-based aqueous solutions are used as electrolytes. To improve the electrochemical stability of the systems and operate at higher potentials, mixtures of ionic liquids with organic solvents can be substituted as electrolytes. Furthermore, functionalization of TEGO with elements such as boron or nitrogen can be considered to improve intrinsic capacitive performance. As a next step, the cyclic stability of the devices should be studied to assess the performance of TEGO/CQD/RTIL electrodes in practical applications.

REFERENCES

- Simon, P. and Y. Gogotsi, "Materials for Electrochemical Capacitors", Nature Materials, Vol. 7, pp. 845–855, 2008.
- Saikia, B. K., S. M. Benoy, M. Bora, J. Tamuly, M. Pandey and D. Bhattacharya, "A Brief Review on Supercapacitor Energy Storage Devices and Utilization of Natural Carbon Resources as Their Electrode Materials", *Fuel*, Vol. 282, 2020.
- Béguin, F., V. Presser, A. Balducci and E. Frackowiak, "Carbons and Electrolytes for Advanced Supercapacitors", *Advanced Materials*, Vol. 26, pp. 2219–2251, 2014.
- Vatamanu, J., O. Borodin, M. Olguin, G. Yushin and D. Bedrov, "Charge Storage at the Nanoscale: Understanding the Trends from the Molecular Scale Perspective", *Journal of Materials Chemistry A*, Vol. 5, pp. 21049–21076, 2017.
- Winter, M. and R. J. Brodd, "What are Batteries, Fuel Cells, and Supercapacitors?", *Chemical Reviews*, Vol. 104, pp. 4245–4269, 2004.
- Badwal, S. P., S. S. Giddey, C. Munnings, A. I. Bhatt and A. F. Hollenkamp, "Emerging Electrochemical Energy Conversion and Storage Technologies", *Frontiers in Chemistry*, Vol. 2, 2014.
- Zhang, L. and X. S. Zhao, "Carbon-Based Materials as Supercapacitor Electrodes", *Chemical Society Reviews*, Vol. 38, pp. 2520–2531, 2009.
- Miller, J. R. and P. Simon, "Materials Science: Electrochemical Capacitors for Energy Management", *Science*, Vol. 321, pp. 651–652, 2008.
- Ismanto, A. E., S. Wang, F. E. Soetaredjo and S. Ismadji, "Preparation of Capacitor's Electrode from Cassava Peel Waste", *Bioresource Technology*, Vol. 101,

pp. 3534–3540, 2010.

- Burke, A., "Ultracapacitors: Why, How, and Where is the Technology", Journal of Power Sources, Vol. 91, pp. 37–50, 2000.
- Huang, S., X. Zhu, S. Sarkar and Y. Zhao, "Challenges and Opportunities for Supercapacitors", APL Materials, Vol. 7, 2019.
- Smith, T. A., J. P. Mars and G. A. Turner, "Using Supercapacitors to Improve Battery Performance", *PESC Record - IEEE Annual Power Electronics Specialists* Conference, Vol. 1, pp. 124–128, 2002.
- Ahmed, S., A. Ahmed and M. Rafat, "Nitrogen Doped Activated Carbon from Pea Skin for High Performance Supercapacitor", *Materials Research Express*, Vol. 5, 2018.
- Zhai, Y., Y. Dou, D. Zhao, P. F. Fulvio, R. T. Mayes and S. Dai, "Carbon Materials for Chemical Capacitive Energy Storage", *Advanced Materials*, Vol. 23, pp. 4828–4850, 2011.
- Kar, K. K., Handbook of Nanocomposite Supercapacitor Materials I Characteristics, Springer Series in Materials Science, 2020.
- Pope, M. A., Electrochemical Double-Layer Capacitors Based on Functionalized Graphene, Ph.D. Thesis, Princeton University, 2013.
- Jiang, Y. and J. Liu, "Definitions of Pseudocapacitive Materials: A Brief Review", *Energy and Environmental Materials*, Vol. 2, pp. 30–37, 2019.
- Conway, B. E., Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Springer US, 1999.
- 19. Roldán, S., C. Blanco, M. Granda, R. Menéndez and R. Santamaría, "Towards

a Further Generation of High-Energy Carbon-Based Capacitors by Using Redox-Active Electrolytes", *Angewandte Chemie - International Edition*, Vol. 50, pp. 1699–1701, 2011.

- Snook, G. A., P. Kao and A. S. Best, "Conducting-Polymer-Based Supercapacitor Devices and Electrodes", *Journal of Power Sources*, Vol. 196, pp. 1–12, 2011.
- Bélanger, D., T. Brousse and J. W. Long, "Manganese Oxides: Battery Materials Make the Leap to Electrochemical Capacitors", *The Electrochemical Society Interface*, pp. 49–52, 2008.
- Zhong, C. and W. Hu, *Electrolytes for Electrochemical Supercapacitors*, pp. 31– 254, CRC Press, 2016.
- Inagaki, M., H. Konno and O. Tanaike, "Carbon Materials for Electrochemical Capacitors", *Journal of Power Sources*, Vol. 195, pp. 7880–7903, 2010.
- 24. Wang, J., Analytical Electrochemistry, pp. 1–28, John Wiley Sons, Inc., 2006.
- Shao, H., Y. C. Wu, Z. Lin, P. L. Taberna and P. Simon, "Nanoporous Carbon for Electrochemical Capacitive Energy Storage", *Chemical Society Reviews*, Vol. 49, pp. 3005–3039, 2020.
- Bozym, D. J. I., The functionalized Graphene-Ionic Liquid Interface for Electrochemical Double-Layer capacitors, Ph.D. Thesis, Princeton University, 2015.
- 27. Gouy, M., "Sur la constitution de la charge électrique à la surface d'un électrolyte", Journal de Physique Théorique et Appliquée, Vol. 9, pp. 457–468, 1910.
- Uralcan, B., Computer-Aided Understanding of Perturbations in Soft Matter Systems, Ph.D. Thesis, Princeton University, 2019.

- Stern, O., "Zur Theorie der Elektrolytischen Doppelschicht", Zeitschrift für Elektrochemie, Vol. 30, pp. 508–517, 1924.
- Grahame, D. C., "The Electrical Double Layer and the Theory of Electrocapillarity.", *Chemical Reviews*, Vol. 41, No. 3, pp. 441–501, 1947.
- Ratajczak, P., M. E. Suss, F. Kaasik and F. Béguin, "Carbon Electrodes for Capacitive Technologies", *Energy Storage Materials*, Vol. 16, 2019.
- 32. Wong, S. I., J. Sunarso, B. T. Wong, H. Lin, A. Yu and B. Jia, "Towards Enhanced Energy Density of Graphene-Based Supercapacitors: Current Status, Approaches, and Future Directions", *Journal of Power Sources*, Vol. 396, pp. 182–206, 2018.
- Liu, T., F. Zhang, Y. Song and Y. Li, "Revitalizing Carbon Supercapacitor Electrodes with Hierarchical Porous Structures", *Journal of Materials Chemistry A*, Vol. 5, pp. 17705–17733, 2017.
- Simon, P. and Y. Gogotsi, "Capacitive Energy Storage in Nanostructured Carbon-Electrolyte Systems", Accounts of Chemical Research, Vol. 46, pp. 1094–1103, 2013.
- Stoller, M. D., S. Park, Z. Yanwu, J. An and R. S. Ruoff, "Graphene-Based Ultracapacitors", *Nano Letters*, Vol. 8, pp. 3498–3502, 2008.
- Pope, M. A. and I. A. Aksay, "Four-fold Increase in the Intrinsic Capacitance of Graphene Through Functionalization and Lattice Disorder", *Journal of Physical Chemistry C*, Vol. 119, pp. 20369–20378, 2015.
- 37. Yuan, F., Z. Wang, X. Li, Y. Li, Z. Tan, L. Fan and S. Yang, "Bright Multicolor Band Gap Fluorescent Carbon Quantum Dots for Electroluminescent Light-Emitting Diodes", Advanced Materials, Vol. 29, 2017.
- 38. Qie, L., W. Chen, H. Xu, X. Xiong, Y. Jiang, F. Zou, X. Hu, Y. Xin, Z. Zhang

and Y. Huang, "Synthesis of Functionalized 3D Hierarchical Porous Carbon for High-Performance Supercapacitors", *Energy Environment Science*, Vol. 6, pp. 2497–2504, 2013.

- Li, L. and T. Dong, "Photoluminescence Tuning in Carbon Dots: Surface Passivation or/and Functionalization, Heteroatom Doping", Journal of Material Chemistry C, Vol. 6, pp. 7944–7970, 2018.
- 40. Yan, X., X. Cui and L.-s. Li, "Synthesis of Large, Table Colloidal Graphene Quantum Dots with Tunable Size", *Journal of the American Chemical Society*, Vol. 132, No. 17, pp. 5944–5945, 2010.
- Tian, P., L. Tang, K. Teng and S. Lau, "Graphene Quantum Dots from Chemistry to Applications", *Materials Today Chemistry*, Vol. 10, pp. 221–258, 2018.
- Essner, J. B. and G. A. Baker, "The Emerging Roles of Carbon Dots in Solar Photovoltaics: a Critical Review", *Environmental Science: Nano*, Vol. 4, pp. 1216–1263, 2017.
- 43. Ma, Y., W. Yuan, Y. Bai, H. Wu and L. Cheng, "The Toughening Design of Pseudocapacitive Materials via Graphene Quantum Dots: Towards Enhanced Cycling Stability for Supercapacitors", *Carbon*, Vol. 154, pp. 292–300, 2019.
- 44. Wang, Y. and A. Hu, "Carbon Quantum Dots: Synthesis, Properties and Applications", *Journal of Materials Chemistry C*, Vol. 2, pp. 6921–6939, 2014.
- Li, Z., L. Wang, Y. Li, Y. Feng and W. Feng, "Frontiers in Carbon Dots: Design, Properties, and Applications", *Materials Chemistry Frontiers*, Vol. 3, pp. 2571– 2601, 2019.
- Wang, X., Y. Feng, P. Dong and J. Huang, "A Mini Review on Carbon Quantum Dots: Preparation, Properties, and Electrocatalytic Application", *Frontiers in Chemistry*, Vol. 7, 2019.

- 47. Calabro, R. L., D.-S. Yang and D. Y. Kim, "Controlled Nitrogen Doping of Graphene Quantum Dots through Laser Ablation in Aqueous Solutions for Photoluminescence and Electrocatalytic Applications", ACS Applied Nano Materials, Vol. 2, No. 11, pp. 6948–6959, 2019.
- 48. Kang, S., Y. K. Jeong, J. H. Ryu, Y. Son, W. R. Kim, B. Lee, K. H. Jung and K. M. Kim, "Pulsed Laser Ablation Based Synthetic Route for Nitrogen-Doped Graphene Quantum Dots Using Graphite flakes", *Applied Surface Science*, Vol. 506, p. 144998, 2020.
- 49. Kang, S., Y. K. Jeong, K. H. Jung, Y. Son, W. R. Kim, J. H. Ryu and K. M. Kim, "One-Step Synthesis of Sulfur-Incorporated Graphene Quantum Dots Using Pulsed Laser Ablation for Enhancing Optical Properties", *Optics Express*, Vol. 28, No. 15, pp. 21659–21667, 2020.
- 50. Yang, S., J. Sun, X. Li, W. Zhou, Z. Wang, P. He, G. Ding, X. Xie, Z. Kang and M. Jiang, "Large-Scale Fabrication of Heavy Doped Carbon Quantum Dots with Tunable-Photoluminescence and Sensitive Fluorescence Detection", *Journal* of Material Chemistry A, Vol. 2, pp. 8660–8667, 2014.
- Iskandar, F., U. Hikmah, E. Stavila and A. H. Aimon, "Microwave-Assisted Reduction Method under Nitrogen Atmosphere for Synthesis and Electrical Conductivity Improvement of Reduced Graphene Oxide (rGO)", *RSC Advanced*, Vol. 7, pp. 52391–52397, 2017.
- Iskandar, F., O. B. Abdillah, E. Stavila and A. H. Aimon, "The Influence of Copper Addition on the Electrical Conductivity and Charge Transfer Resistance of Reduced Graphene Oxide (rGO)", New Journal Chemistry, Vol. 42, pp. 16362– 16371, 2018.
- 53. Ahirwar, S., S. Mallick and D. Bahadur, "Electrochemical Method to Prepare Graphene Quantum Dots and Graphene Oxide Quantum Dots", ACS Omega,
Vol. 2, No. 11, pp. 8343–8353, 2017.

- 54. Permatasari, F., A. Aimon, F. Iskandar, T. Ogi and K. Okuyama, "Role of C–N Configurations in the Photoluminescence of Graphene Quantum Dots Synthesized by a Hydrothermal Route", *Scientific Reports*, Vol. 6, p. 21042, 2016.
- 55. Ogi, T., H. Iwasaki, K. Aishima, F. Iskandar, W.-N. Wang, K. Takimiya and K. Okuyama, "Transient Nature of Graphene Quantum Dot Formation via a Hydrothermal Reaction", *Royal Society of Chemistry Advanced*, Vol. 4, pp. 55709– 55715, 2014.
- 56. Hess, S. C., F. A. Permatasari, H. Fukazawa, E. M. Schneider, R. Balgis, T. Ogi, K. Okuyama and W. J. Stark, "Direct Synthesis of Carbon Quantum Dots in Aqueous Polymer Solution: One-Pot Reaction and Preparation of Transparent UV-Blocking Films", *Journal of Material Chemistry A*, Vol. 5, pp. 5187–5194, 2017.
- 57. Ogi, T., K. Aishima, F. A. Permatasari, F. Iskandar, E. Tanabe and K. Okuyama, "Kinetics of Nitrogen-Doped Carbon Dot Formation via Hydrothermal Synthesis", New Journal Chemistry, Vol. 40, pp. 5555–5561, 2016.
- Permatasari, F. A., H. Fukazawa, T. Ogi, F. Iskandar and K. Okuyama, "Design of Pyrrolic-N-Rich Carbon Dots with Absorption in the First Near-Infrared Window for Photothermal Therapy", ACS Applied Nano Materials, Vol. 1, No. 5, pp. 2368–2375, 2018.
- Lai, C.-W., Y.-H. Hsiao, Y.-K. Peng and P.-T. Chou, "Facile Synthesis of Highly Emissive Carbon Dots from Pyrolysis of Glycerol; Gram Scale Production of Carbon Dots/mSiO2 for Cell Imaging and Drug Release", *Journal Material Chemistry.*, Vol. 22, pp. 14403–14409, 2012.
- 60. Li, Q., H. Cheng, X. Wu, C.-F. Wang, G. Wu and S. Chen, "Enriched Carbon

Dots/Graphene Microfibers towards High-erformance Micro-Supercapacitors", Journal of Materials Chemistry A, Vol. 6, pp. 14112–14119, 2018.

- Zhang, L. L., X. Zhao, H. Ji, M. D. Stoller, L. Lai, S. Murali, S. Mcdonnell,
 B. Cleveger, R. M. Wallace and R. S. Ruoff, "Nitrogen Doping of Graphene and its Effect on Quantum Capacitance and a New Insight on the Enhanced Capacitance of N-Doped Carbon", *Energy Environmental Science*, Vol. 5, pp. 9618–9625, 2012.
- Liu, W.-W., Y.-Q. Feng, X.-B. Yan, J.-T. Chen and Q.-J. Xue, "Superior Micro-Supercapacitors Based on Graphene Quantum Dots", *Advanced Functional Materials*, Vol. 23, No. 33, pp. 4111–4122, 2013.
- Hassan, M., E. Haque, K. R. Reddy, A. I. Minett, J. Chen and V. G. Gomes, "Edge-Enriched Graphene Quantum Dots for Enhanced Photo-Luminescence and Supercapacitance", *Nanoscale*, Vol. 6, pp. 11988–11994, 2014.
- 64. Zhao, N., X. N. Cheng, J. Yang, M. X. Yang, S. H. Zheng and Y. Z. Zhou, "Experimental Study on the Preparation, Characterization and Conductivity Improvement of Reduced Graphene-Oxide Papers", *Journal of Physics and Chemistry of Solids*, Vol. 75, pp. 1141–1146, 2014.
- Zhao, X., M. Li, H. Dong, Y. Liu, H. Hu, Y. Cai, Y. Liang, Y. Xiao and M. Zheng, "Interconnected 3D Network of Graphene-Oxide Nanosheets Decorated with Carbon Dots for High-Performance Supercapacitors", *ChemSusChem*, Vol. 10, pp. 2626–2634, 2017.
- Zhong, C., Y. Deng, W. Hu, J. Qiao, L. Zhang and J. Zhang, "A Review of Electrolyte Materials and Compositions for Electrochemical Supercapacitors", *Chemical Society Reviews*, Vol. 44, pp. 7484–7539, 2015.
- 67. Jiang, L., L. Sheng, X. Chen, T. Wei and Z. Fan, "Construction of Nitrogen-Doped

Porous Carbon Buildings Using Interconnected Ultra-Small Carbon Nanosheets for Ultra-High Rate Supercapacitors", *Journal of Materials Chemistry A*, Vol. 4, pp. 11388–11396, 2016.

- Chang, J., Z. Gao, X. Wang, D. Wu, F. Xu, X. Wang, Y. Guo and K. Jiang, "Activated Porous Carbon Prepared from Paulownia Flower for High Performance Supercapacitor Electrodes", *Electrochimica Acta*, Vol. 157, pp. 290–298, 2015.
- Pal, B., S. Yang, S. Ramesh, V. Thangadurai and R. Jose, "Electrolyte Selection for Supercapacitive Devices: A Critical Review", *Nanoscale Advances*, Vol. 1, pp. 3807–3835, 2019.
- 70. Miao, L., Z. Song, D. Zhu, L. Li, L. Gan and M. Liu, "Ionic Liquids for Supercapacitive Energy Storage: A Mini-Review", *Energy and Fuels*, Vol. 35, pp. 8443–8455, 2021.
- Marcano, D. C., D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev,
 L. B. Alemany, W. Lu and J. M. Tour, "Improved Synthesis of Graphene Oxide", *American Chemical Society Nano*, Vol. 4, pp. 4806–4814, 2010.
- Ferrari, A. C. and J. Robertson, "Interpretation of Raman Spectra of Disordered and Amorphous Carbon", *Physical Review B*, Vol. 61, 2000.
- Strohmeier, B., J. Piasecki, K. Bunker, J. Sturgeon, B. Stitch and J. Marquis, "XPS and FESEM/STEM Surface Characterization of Activated Carbon, Carbon Black, and Carbon Nanotubes", *Microscopy and Microanalysis*, Vol. 16, pp. 442– 443, 2010.
- Singh, M. K. and A. Singh, "Fourier Transform Infrared (FTIR) Analysis", Characterization of Polymers and Fibres, pp. 295–320, 2022.
- 75. Kowalczuk, D. and M. Pitucha, "Application of FTIR Method for the Assessment of Immobilization of Active Substances in the Matrix of Biomedical Materials",

Materials, Vol. 12, 2019.

- Skoog, D., F. Holler, J. Leary and T. Nieman, *Principles of Instrumental Analysis*, Saunders golden sunburst series, Saunders College Pub., 1998.
- 77. Helseth, L., "Comparison of Methods for Finding the Capacitance of a Supercapacitor", Journal of Energy Storage, Vol. 35, p. 102304, 2021.
- 78. Joshi, P. and D. Sutrave, "A Brief Study of Cyclic Voltammetry and Electrochemical Analysis", *International Journal of ChemTech Research*, Vol. 11, No. 9, p. 77, 2018.
- Evans, D., K. O'Connell, R. Petersen and M. Kelly, "Cyclic Voltammetry", Journal of Chemical Education, Vol. 60, pp. 290–293, 1983.
- Zhang, Z. J., D. H. Xie, P. Cui and X. Y. Chen, "Conversion of a Zinc Salicylate Complex into Porous Carbons Through a Template Carbonization Process as a Superior Electrode Material for Supercapacitors", *RSC Advances*, Vol. 4, pp. 6664–6671, 2014.
- Shi, Y., M. Zhang, D. Yang and J. Li, "Study on Preparation of High Performance Manganese Dioxide Supercapacitor by Cyclic Voltammetry", *Ionics*, Vol. 27, 2021.
- Kulova, T. and A. Skundin, "Cyclic Voltammetry of Supercapacitors with the Simplest Equivalent Circuit", *Russian Chemical Bulletin*, Vol. 69, pp. 1672–1678, 2020.
- Park, S.-M. and J.-S. Yoo, "Peer Reviewed: Electrochemical Impedance Spectroscopy for Better Electrochemical Measurements", *Analytical Chemistry*, Vol. 75, pp. 455–462, 2003.
- 84. Basri, N., A. Awitdrus, M. Suleman, N. Syahirah, M. Nor, B. Nurdiana, M. Dolah,

M. Sahri and S. A. Shamsudin, "Energy and Power of Supercapacitor Using Carbon Electrode Deposited with Nanoparticles Nickel Oxide", *International Journal of Electrochemical Science*, Vol. 11, pp. 95–110, 2016.

- Uchaikin, V., R. Sibatov and A. Ambrozevich, "On Impedance Spectroscopy of Supercapacitors", *Russian Physics Journal*, Vol. 59, pp. 845–855, 2016.
- Mei, B.-A., O. Munteshari, J. Lau, B. Dunn and L. Pilon, "Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices", *The Journal of Physical Chemistry C*, Vol. 122, pp. 194–206, 2017.
- Tuinstra, F. and J. L. Koenig, "Raman Spectrum of Graphite", Journal of Chemical Physics, Vol. 53, pp. 1126–1130, 1970.
- Zhang, W., Y. Zhang, Y. Tian, Z. Yang, Q. Xiao, X. Guo, L. Jing, Y. Zhao, Y. Yan, J. Feng and K. Sun, "Insight into the Capacitive Properties of Reduced Graphene Oxide", ACS Applied Materials and Interfaces, Vol. 6, pp. 2248–2254, 2014.
- Guan, Y., K. P. Meyers, S. K. Mendon, G. Hao, J. R. Douglas, S. Trigwell, S. I. Nazarenko, D. L. Patton and J. W. Rawlins, "Ecofriendly Fabrication of Modified Graphene Oxide Latex Nanocomposites with High Oxygen Barrier Performance", *ACS Applied Materials and Interfaces*, Vol. 8, pp. 33210–33220, 2016.
- 90. Rivera, L. M., A. F. Betancur, D. G. Zarate, D. Torres, L. Hoyos and A. García, "Simultaneous N Doping and Reduction of GO: Compositional, Structural Characterization and its Effects in Negative Electrostatic Charges Repulsion", *Diamond and Related Materials*, Vol. 97, 2019.
- 91. Wang, R., Y. Wang, C. Xu, J. Sun and L. Gao, "Facile One-Step Hydrazine-Assisted Solvothermal Synthesis of Nitrogen-Doped Reduced Graphene Oxide: Reduction Effect and Mechanisms", *RSC Advances*, Vol. 3, pp. 1194–1200, 2013.

- 92. Gupta, B., N. Kumar, K. Panda, V. Kanan, S. Joshi and I. Visoly-Fisher, "Role of Oxygen Functional Groups in Reduced Graphene Oxide for Lubrication", *Scientific Reports*, Vol. 7, 2017.
- 93. Dager, A., T. Uchida, T. Maekawa and M. Tachibana, "Synthesis and Characterization of Mono-Disperse Carbon Quantum Dots from Fennel Seeds: Photoluminescence Analysis Using Machine Learning", *Scientific Reports*, Vol. 9, 2019.
- 94. Guo, Y., L. Zhang, F. Cao and Y. Leng, "Thermal Treatment of Hair for the Synthesis of Sustainable Carbon Quantum Dots and the Applications for Sensing Hg2+", *Scientific Reports*, Vol. 6, 2016.
- 95. Ilnicka, A., M. Skorupska, M. Szkoda, Z. Zarach, P. Kamedulski, W. Zielinski and J. P. Lukaszewicz, "Combined Effect of Nitrogen-Doped Functional Groups and Porosity of Porous Carbons on Electrochemical Performance of Supercapacitors", *Scientific Reports*, Vol. 11, 2021.
- 96. Li, Y., Y. Q. Wang, D. Liu, Y. Gao, S. N. Wang and H. Qiu, "Dual-Emission Ratiometric Fluorescent Probe Based on Lanthanide-Functionalized Carbon Quantum Dots for White Light Emission and Chemical Sensing", ACS Omega, Vol. 6, pp. 14629–14638, 2021.
- 97. Hu, Q., M. C. Paau, Y. Zhang, X. Gong, L. Zhang, D. Lu, Y. Liu, Q. Liu, J. Yao and M. M. Choi, "Green Synthesis of Fluorescent Nitrogen/Sulfur-Doped Carbon Dots and Investigation of Their Properties by HPLC Coupled with Mass Spectrometry", *RSC Advances*, Vol. 4, pp. 18065–18073, 2014.
- 98. Das, R. K. and S. Mohapatra, "Highly Luminescent, Heteroatom-Doped Carbon Quantum Dots for Ultrasensitive Sensing of Glucosamine and Targeted Imaging of Liver Cancer Cells", *Journal of Materials Chemistry B*, Vol. 5, pp. 2190–2197, 2017.

- 99. Ang, W. L., C. A. B. Mee, N. S. Sambudi, A. W. Mohammad, C. P. Leo, E. Mahmoudi, M. Ba-Abbad and A. Benamor, "Microwave-Assisted Conversion of Palm Kernel Shell Biomass Waste to Photoluminescent Carbon Dots", *Scientific Reports*, Vol. 10, 2020.
- 100. Hou, H., C. E. Banks, M. Jing, Y. Zhang and X. Ji, "Carbon Quantum Dots and Their Derivative 3D Porous Carbon Frameworks for Sodium-Ion Batteries with Ultra Long Cycle Life", Advanced Materials, Vol. 27, pp. 7861–7866, 2015.
- 101. Zhu, S., S. Tang, J. Zhang and B. Yang, "Control the Size and Surface Chemistry of Graphene for the Rising Fluorescent Materials", *Chemical Communications*, Vol. 48, pp. 4527–4539, 2012.
- 102. He, M., J. Zhang, H. Wang, Y. Kong, Y. Xiao and W. Xu, "Material and Optical Properties of Fluorescent Carbon Quantum Dots Fabricated from Lemon Juice via Hydrothermal Reaction", *Nanoscale Research Letters*, Vol. 13, 2018.
- 103. Chunduri, L. A. A., A. Kurdekar, S. Patnaik, S. Aditha, C. Prathibha and V. Kamisetti, "Keywords Single Step Synthesis of Carbon Quantum Dots from Coconut Shell: Evaluation for Antioxidant Efficacy and Hemotoxicity", *Journal* of Materials Sciences and Applications, Vol. 3, pp. 83–93, 2017.
- 104. Chaudhary, S., S. Kumar, B. Kaur and S. K. Mehta, "Potential Prospects for Carbon Dots as a Fluorescence Sensing Probe for Metal Ions", *RSC Advances*, Vol. 6, pp. 90526–90536, 2016.
- 105. Park, S. Y., N. Thongsai, A. Chae, S. Jo, E. B. Kang, P. Paoprasert, S. Y. Park and I. In, "Microwave-Assisted Synthesis of Luminescent and Biocompatible Lysine-Based Carbon Quantum Dots", *Journal of Industrial and Engineering Chemistry*, Vol. 47, pp. 329–335, 2017.
- 106. Alarfaj, N. A., M. F. El-Tohamy and H. F. Oraby, "CA 19-9 Pancreatic Tumor

Marker Fluorescence Immunosensing Detection via Immobilized Carbon Quantum Dots Conjugated Gold Nanocomposite", *International Journal of Molecular Sciences*, Vol. 19, 2018.

- 107. Zhao, X., J. Zhang, L. Shi, M. Xian, C. Dong and S. Shuang, "Folic Acid-Conjugated Carbon Dots as Green Fluorescent Probes Based on Cellular Targeting Imaging for Recognizing Cancer Cells", *RSC Advances*, Vol. 7, pp. 42159– 42167, 2017.
- 108. Kepić, D., Z. Marković, S. Jovanović, I. H. Antunović, D. Kleut and B. T. Marković, "Novel Method for Graphene Functionalization", *Physica Scripta Topical Issues*, Vol. T162, 2014.
- 109. Wang, Y., Y. Wu, Y. Huang, F. Zhang, X. Yang, Y. Ma and Y. Chen, "Preventing Graphene Sheets From Restacking for High-Capacitance Performance", *Journal* of Physical Chemistry C, Vol. 115, pp. 23192–23197, 2011.
- 110. Zhu, Y., S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach and R. S. Ruoff, "Carbon-Based Supercapacitors Produced by Activation of Graphene", *Science* (*New York, N.Y.*), pp. 1536–1542, 2011.
- 111. Kim, T. Y., H. W. Lee, M. Stoller, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff and K. S. Suh, "High-Performance Supercapacitors Based on Poly(Ionic Liquid)-Modified Graphene Electrodes", ACS Nano, Vol. 5, pp. 436–442, 2011.
- 112. El-Kady, M. F., V. Strong, S. Dubin and R. B. Kaner, "Laser Scribing of High-Performance and Flexible Graphene-Based Electrochemical Capacitors", *Science*, Vol. 335, pp. 1326–1330, 2012.
- 113. Yang, X., J. Zhu, L. Qiu and D. Li, "Bioinspired Effective Prevention of Restacking in Multilayered Graphene Films: Towards the Next Generation of High-

 $\label{eq:performance Supercapacitors", Advanced Materials, Vol. 23, pp. 2833-2838, 2011.$