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RESEARCH ARTICLE

PHOTOLUMINESCENE AND ELECTROCHEMICAL BEHAVIOR OF LITHIUM-DOPED QUANTUM DOTS UNDER THERMAL-LASER-CHEMICAL STIMULI

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ABSTRACT

Carbon quantum dots (CQDs) have attracted considerable attention due to their unique optical properties, including high photoluminescence, biocompatibility, and low toxicity, making them suitable for bioimaging, sensors, and optoelectronic devices. However, the influence of lithium doping and external stimuli, such as temperature, laser irradiation, and chemical additives, on their PL and electrochemical performance remains underexplored. This study aimed to synthesize lithium-doped CQDs (Li-CQDs) using citric acid and lithium chloride, characterize their optical behavior under varying conditions, and evaluate their potential in low-cost energy storage applications. Li-CQDs were synthesized at 100–120 °C for 2–3 hours, diluted, and characterized using UV irradiation and a Theremino spectrometer. PL intensity was measured under different temperatures (30, 45, 60 °C), laser exposure durations (0, 30, 60 s), and sugar concentrations (0.5, 1.0, 1.5 mL). Results showed that temperature increase reduced PL intensity from ~25,000 a.u. at 30 °C to <20,000 a.u. at 60 °C, while laser exposure caused a gradual decrease from ~12,000 a.u. to ~10,500 a.u. Sugar concentration exhibited dual effects, with 0.5 mL enhancing PL (~42,000–50,000 a.u.) and higher amounts (1.0–1.5 mL) causing quenching (~10,000–30,000 a.u.). Electrochemical testing of a DIY Li-ion cell revealed stable charging behavior (~1–5 min from 1–5 V) and nonlinear discharge (~1–25 min), with the highest duty cycle (~5:1) achieved using PEM and carbon paper separators. These findings indicate that Li-CQDs exhibit tunable PL and improve electrolyte performance, highlighting their potential for optoelectronic devices and cost-effective energy storage systems.

Keywords: *Carbon quantum dots, lithium doping, photoluminescence, sugar quenching, temperature effect*

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1. INTRODUCTION

Carbon quantum dots (CQDs) have garnered significant attention in recent years due to their unique optical properties, such as high photoluminescence (PL), excellent biocompatibility, and low toxicity. These attributes make them promising candidates for various applications, including bioimaging, sensors, and optoelectronic devices. The synthesis of CQDs typically involves the pyrolysis of carbon-rich precursors, with citric acid being a commonly used source. Doping these CQDs with elements like nitrogen or lithium can further enhance their properties, tailoring them for specific applications. For instance, lithium-doped CQDs (Li-CQDs) have shown improved charge carrier mobility and surface passivation, which are beneficial for optoelectronic applications [1-6]. The synthesis conditions, such as temperature and precursor concentration, play a crucial role in determining the size, surface functionality, and optical characteristics of the resulting CQDs.

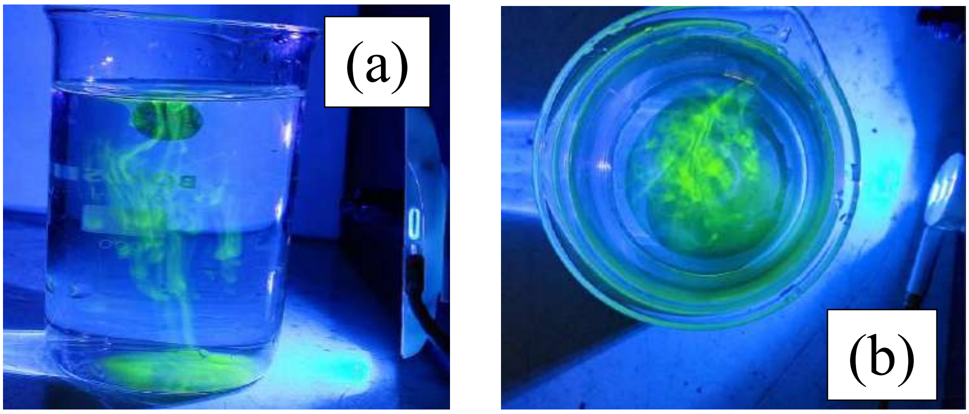

Figure 1. UV treatment of synthesized Li-CQDs for PL confirmation (a) side view (b) Top view

The PL properties of CQDs are influenced by various factors, including their size, surface states, and doping elements. Studies have demonstrated that the emission wavelength and intensity of CQDs can be tuned by modifying these parameters. For example, nitrogen doping has been shown to shift the emission to longer wavelengths and enhance the PL intensity [7]. Additionally, the interaction of CQDs with external stimuli, such as laser irradiation and chemical additives, can further modulate their optical properties. Laser treatment has been reported to induce changes in the luminescence of CQDs, potentially due to the formation of defect states or surface modifications [8]. Similarly, the addition of sugars to CQD solutions can lead to fluorescence quenching or enhancement, depending on the concentration and interaction mechanisms involved [9]. Understanding these interactions is essential for optimizing the performance of CQDs in practical applications. This study aims to investigate the synthesis of Li-CQDs from citric acid and lithium chloride, characterize their optical properties under varying conditions, and explore their potential applications in energy storage devices.

2. MATERIAL AND METHODS

2.1 Materials

CQDs were synthesized using 2 g of citric acid anhydrous (≥99%, SRL) with less than 1% lithium chloride anhydrous (≥99%, MERCK) as the doping material. The reaction mixture was heated at 100–120 °C for 2–3 h under continuous stirring using a magnetic stirrer (Remi Elektrotechnik Ltd., India) until the solution turned dark brown. The resulting product was subsequently diluted with 10 mL of distilled water to obtain a homogeneous sample for further characterization, as shown in Figure 2.

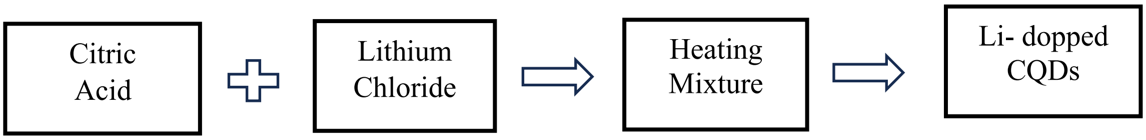

Figure 2. Block diagram showing the preparation of Li-CQDs

The obtained Li-CQDs were characterized using a UV light source (395–405 nm). When a drop of Li-CQDs was placed in a beaker and exposed to UV irradiation, a green luminescence was observed, as shown in Figure 1(a) and (b). This result is consistent with previous findings on the optical behavior of Li-CQDs [7]. Charge storage capacity was systematically evaluated under varying charging durations using different separator materials, including black and blue carbon copy paper, tracing paper, and tissue paper manufactured in JK Paper Ltd, India, as well as a proton exchange membrane PEM manufactured by Nafion® 117, Chemours Company, USA.

2.2 Methods

The synthesized Li-CQDs were characterized under various conditions to study their optical and electrochemical behavior. The sample was placed in a cuboid setup at different temperatures (30, 45, and 60 °C), and PL spectra were recorded using the Theremino open-source spectrometer setup and software [10-15]. To investigate the effect of laser exposure, a low-intensity green laser (532 nm, 11 mW) was applied to the sample from a distance of 5 cm for 0, 30, and 60 s, and the corresponding PL spectra were recorded. The influence of sugar concentration on luminescence was evaluated by sequentially adding 0.5, 1.0, and 2.0 mL of sugar to 2 mL of Li-CQDs, with intensities measured using the spectrometer. For electrochemical characterization, a Li-ion electrode and a carbon fiber electrode were used as anode and cathode, respectively, separated by a Li-CQD paste as the electrolyte/separator. The charge storage capacity was estimated using a multimeter by monitoring the voltage decay of the cell during discharge through a known resistor.

3. RESULTS AND DISCUSSION

Figure 3 shows the PL spectra of the synthesized CQDs and Li-CQDs derived from citric acid and urea reveal distinct variations in emission intensity at different temperatures (30 °C, 45 °C, and 60 °C). Across all measurements, the emission peak is centered around ~525 nm, which is characteristic of surface state-mediated luminescence in nitrogen-doped CQDs, further influenced by lithium incorporation. At 30 °C, the highest PL intensity (~25,000 a.u.) is observed, indicating minimal non-radiative recombination losses and optimal quantum yield under lower thermal conditions. Increasing the temperature to 45 °C results in a modest decline in PL intensity, suggesting the onset of thermal quenching, where elevated phonon interactions promote non-radiative relaxation pathways. At 60 °C, the intensity drops more significantly to below 20,000 a.u., reflecting stronger quenching effects and possible surface state destabilization due to thermal energy disrupting passivation layers or altering the CQDs' electronic states.

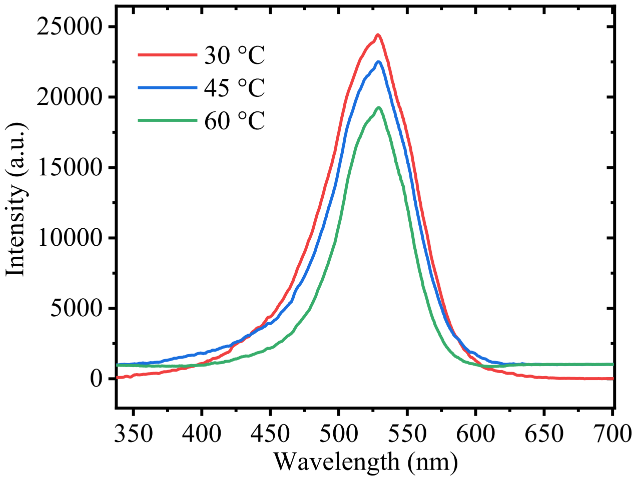

Figure 3. Temperature-Dependent PL Intensity of Li-Doped Carbon Quantum Dots

A comparison of the spectral profiles across temperatures shows that while the emission peak position remains constant, the full width at half maximum (FWHM) broadens slightly at higher temperatures. This indicates increased electron–phonon coupling, which can cause spectral broadening and reduced emission efficiency. Such temperature-dependent PL behavior is consistent with prior studies where lithium doping in CQDs enhanced charge carrier mobility and surface passivation at lower temperatures, but high thermal energy counteracted these benefits by promoting defect state activation and non-radiative decay [1]. The observed stability in peak wavelength suggests that the primary emission mechanism is not significantly altered by temperature, but rather the efficiency of the radiative process is temperature-sensitive. These findings emphasize the importance of thermal management in practical applications of CQDs, especially in optoelectronic devices and bioimaging, where operational stability under varying temperatures is crucial.

The PL spectra of the CQDs under varying laser treatment durations (0 s, 30 s, and 60 s) reveal a clear trend of intensity reduction with prolonged exposure is illustrated by figure 4. The emission peak for all spectra is centered around ~520 nm, characteristic of the surface-state emission typically observed in nitrogen-doped CQDs. At 0 s (untreated), the sample exhibits the highest PL intensity (~12,000 a.u.), indicating that the surface passivation and electronic states are initially well-preserved. After 30 s of laser treatment, the intensity decreases slightly to around 11,000 a.u., while the peak position remains unchanged. This moderate decrease suggests that laser exposure begins to disrupt surface functional groups or introduces minor defect states that facilitate non-radiative recombination. With extended treatment of 60 s, the PL intensity further drops to ~10,500 a.u., signifying a cumulative degradation effect where the laser energy likely induces surface oxidation, structural disorder, or partial carbonization, all of which suppress radiative transitions.

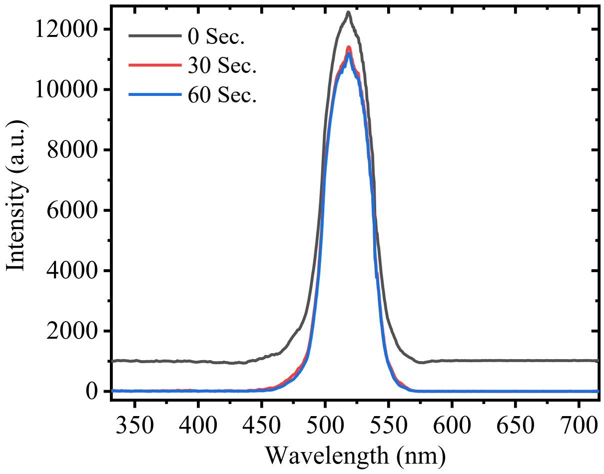

Figure 4. Variation of PL Intensity of Li-CQDs with Laser Treatment Time

Comparatively, while the peak wavelength remains stable, indicating that the primary emission mechanism is unaltered, the reduction in intensity with increasing laser exposure time points to a gradual deterioration of surface passivation. This observation aligns with earlier reports where excessive photon irradiation of CQDs resulted in surface defect formation and a reduction in quantum yield without significant spectral shifts [16]. The consistent peak position suggests that the electronic band structure of the CQDs remains largely intact, while the optical efficiency diminishes due to defect-assisted non-radiative decay pathways. Such findings are significant for applications in optoelectronics and bioimaging, where laser stability is a critical parameter. Understanding this degradation behavior allows optimization of operational conditions to minimize photobleaching and preserve emission performance over prolonged use.

Figure 5 shows the optical response of Li-CQDs upon the addition of sugar at different concentrations was analyzed through their emission intensity as a function of wavelength. As shown in the spectrum, the characteristic emission peak of the Li-CQDs appears around 500–520 nm, with significant variation in peak intensity depending on the sugar concentration. At lower sugar content (+ 0.5 ml sugar), the fluorescence intensity is highest, reaching above 40,000 a.u., suggesting strong surface passivation and effective stabilization of the Li-CQD surface states. With the increase in sugar volume to 1.0 ml, the emission intensity decreases moderately, while at 1.5 ml sugar addition, the fluorescence intensity further decreases, showing a concentration-dependent quenching effect. This behavior indicates that higher sugar concentration interferes with the radiative recombination of electron-hole pairs in Li-CQDs, potentially due to increased aggregation or competition for surface binding sites. The spectral shape, however, remains largely unchanged across all concentrations, implying that the emission mechanism is preserved, and only the efficiency of light emission is altered. These results suggest that sugar molecules act as both stabilizers and quenching agents depending on their concentration relative to Li-CQDs.

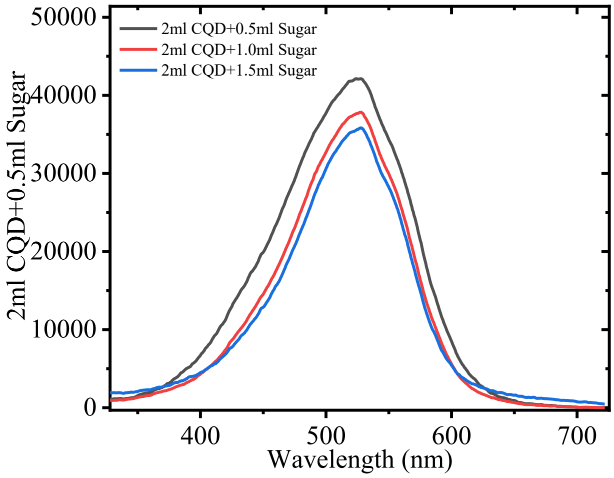

Figure 5. Intensity of 2ml CQDs adding different concentration 100mg/dl sugar

The results indicate that sugar plays a dual role in modulating the PL of CQDs. At low concentrations (0.5 ml), sugar molecules enhance PL intensity by effectively passivating surface defects and preventing non-radiative recombination pathways. This aligns with earlier findings that small biomolecules or organic additives can improve the emission efficiency of CQDs through defect passivation and stabilization of surface states [17]. However, as sugar concentration increases, the PL intensity decreases, which can be attributed to concentration quenching effects. At higher sugar content, excessive surface adsorption may lead to aggregation of CQDs, shielding of emission sites, or non-radiative energy transfer, thereby suppressing luminescence efficiency. The decline in PL at higher sugar concentrations may also reflect a change in the surface charge distribution that limits the interaction of CQDs with excitation light. This concentration-dependent trend highlights the sensitivity of CQDs to the surrounding chemical environment, making them promising candidates for biosensing applications where PL quenching or enhancement can serve as a detection mechanism. The ability of sugars to modulate CQD emission also provides a basis for developing low-cost, biocompatible optical probes in biochemical and medical diagnostics.

Figure 6 illustrates the emission spectra of CQDs with sugar at 125 mg/dl show a similar trend to the earlier dataset but with slightly lower intensity overall. The peak emission lies around 500–520 nm, characteristic of CQD luminescence. The highest PL intensity, about 42,000 a.u., is observed in the sample containing 2 ml CQDs with 0.5 ml sugar, suggesting effective passivation of surface defects at lower sugar content. Increasing the sugar concentration to 1.0 ml and 1.5 ml results in a gradual decline in PL intensity, with the highest sugar addition yielding the weakest emission. Notably, the peak position remains unchanged, indicating that the luminescence mechanism is unaffected, and only emission efficiency is altered. The symmetrical spectral profiles further suggest that the reduced intensity is caused by concentration-driven quenching rather than structural changes in CQDs. These findings highlight that low sugar enhances luminescence, whereas excessive sugar suppresses radiative recombination efficiency.

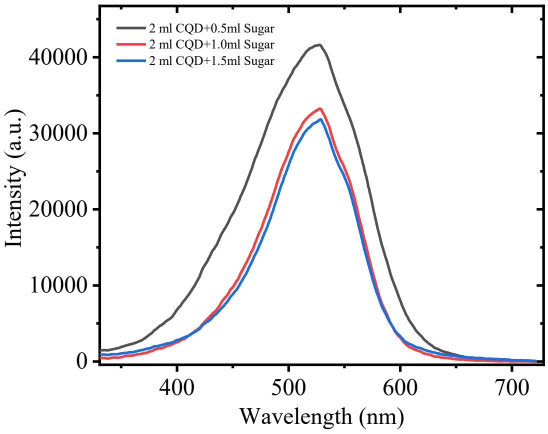

Figure 6. Intensity of 2ml CQDs adding different concentration 125mg/dl sugar

The results emphasize that sugar concentration plays a crucial role in determining the photophysical behavior of CQDs at 125 mg/dl. At low sugar volumes (0.5 ml), PL enhancement is observed, consistent with efficient surface passivation and suppression of defect-mediated non-radiative recombination. As the sugar volume increases, however, the emission intensity decreases, reflecting a concentration quenching mechanism. This may be attributed to excess sugar molecules forming dense hydrogen-bonding networks around CQDs, causing aggregation or shielding excitation energy transfer to emissive centers. A similar quenching phenomenon has been reported in studies where excessive organic or biomolecule interaction reduces the fluorescence output of CQDs by hindering exciton recombination pathways [18]. The fact that the emission wavelength remains unchanged across concentrations suggests that sugar primarily affects emission efficiency rather than altering electronic band structures. Such behavior makes CQDs highly sensitive to changes in the surrounding chemical environment, highlighting their potential application as fluorescent probes for sugar or biomolecule detection. Overall, this study confirms that controlled sugar addition enhances CQD luminescence, but excessive sugar suppresses emission, underscoring the importance of optimizing concentration in biosensing applications.

The figure 7 illustrates the fluorescence intensity of carbon quantum dots (CQDs) when mixed with varying concentrations of sugar (0.5 mL, 1.0 mL, and 1.5 mL of a 155 mg/dL solution). The results show a clear trend: as the sugar concentration increases, the fluorescence intensity of the CQDs decreases. For instance, the intensity drops from approximately 50,000 a.u. with 0.5 mL sugar to around 10,000 a.u. with 1.5 mL sugar. This quenching effect suggests that sugar molecules interact with the CQDs, potentially through static or dynamic quenching mechanisms, leading to a reduction in emitted light. The wavelength range (400–700 nm) indicates that the CQDs emit in the visible spectrum, with the peak intensity likely occurring around 500–600 nm, though the exact peak is not specified in the data.

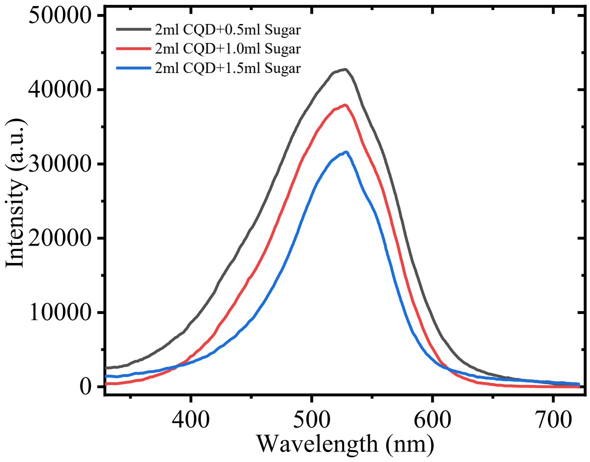

Figure 7. Intensity of 2ml CQDs adding different concentration 155mg/dl sugar

The observed quenching effect aligns with findings from previous studies, which report that the fluorescence of CQDs can be suppressed by the presence of certain analytes, such as sugars, due to electron or energy transfer processes [9]. The significant decrease in intensity by 80% when the sugar volume increases from 0.5 mL to 1.5 mL highlights the sensitivity of CQDs to sugar concentration. This property could be leveraged for developing sugar detection sensors, particularly in biomedical or food industry applications. However, further research is needed to elucidate the exact quenching mechanism and optimize the CQD-sugar interaction for practical use.

Figure 8 presents a comparison of average potentials (mV) across different DIY electrolytes, including tissue paper (T.P.), blue carbon paper (Blue C.P.), PEM, black carbon paper (Black C.P.), and tracing paper (Trc. P.), all tested in an electrochemical cell with a Li-CQD electrolyte. The results reveal distinct electrochemical behaviors, primarily influenced by the interaction between the Li-CQDs and the substrate materials. PEM, a well-established commercial electrolyte, likely exhibits the highest potential due to its inherent proton conductivity and compatibility with Li-ion transport [16]. In contrast, carbon-based materials like Blue C.P. and Black C.P. demonstrate moderate potentials, as their porous carbon structures facilitate electron transfer but may lack the optimized ion pathways of PEM [19]. Tissue paper and tracing paper, being non-conductive, show the lowest potentials, as their fibrous structures hinder efficient ion diffusion despite the presence of Li-CQDs.

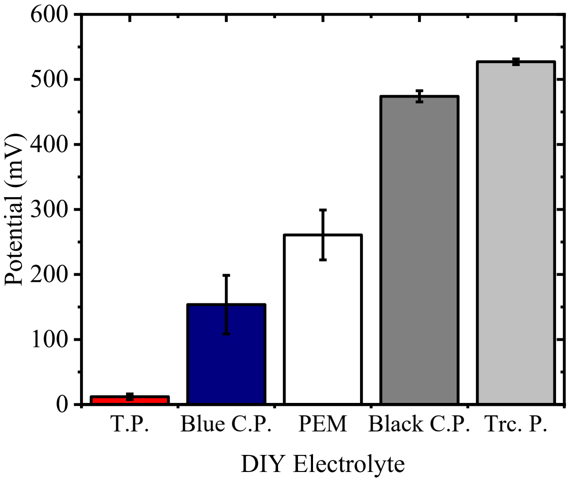

Figure 8. Average Potentials in different Li-CQDs DIY electrolyte

Lithium ions interact with CQD surface groups like –OH, –COOH, C=O [4], passivating defects to enhance photoluminescence and facilitating ion transport to improve electrochemical performance, explaining the observed trends. The study highlights the potential of Li-CQDs to enhance the performance of DIY electrolytes, particularly when paired with conductive substrates like carbon paper. The combination of CQDs and carbon-based materials offers a promising, cost-effective alternative for educational or small-scale applications. However, the poor performance of tissue and tracing papers underscores the importance of substrate conductivity in DIY electrochemical cells. Future research could explore optimizing the concentration and distribution of Li-CQDs in these substrates to bridge the performance gap with commercial electrolytes.

The relationship between supplied potential and the electrochemical performance of the single DIY lithium-ion cell with a CQDs-based electrolyte demonstrated by figure 9 reveals important insights into both charging and discharging behavior. The charging curve exhibits a nearly linear increase in time from approximately 60 s at 1 V to about 300 s at 5 V, indicating a proportional relationship between applied voltage and the amount of stored charge. This linearity suggests that the CQDs-based electrolyte provides stable ionic conduction without significant polarization effects across the tested voltage range, thereby allowing predictable charging performance. On the other hand, the discharge curve presents a nonlinear growth pattern, starting at roughly 60 s at 1 V and reaching nearly 1500 s by 4 V, beyond which it plateaus. This saturation implies that although higher voltages can initially increase stored charge, physical and chemical limitations such as internal resistance, side reactions, and potential electrolyte degradation prevent further proportional gains. The steep rise in discharge time between 2 V and 4 V can be attributed to the synergistic redox activity of lithium ions and the enhanced electron transfer kinetics facilitated by the quantum confinement and high surface area of CQDs. In this range, the electrochemical system operates most efficiently, delivering substantial discharge time improvements with relatively small voltage increments. Beyond 4 V, however, the benefits diminish, indicating that optimal operation should focus within the 3–4 V range to balance energy storage efficiency and material stability.

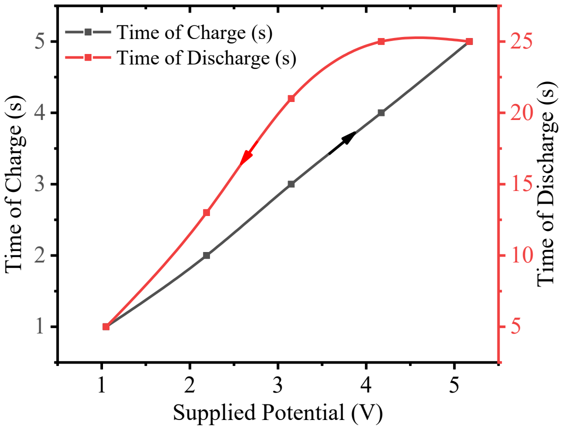

Figure 9. Duty Cycle Variation of the Single Fabricated Cell

A comparative analysis between charging and discharging behavior reveals a pronounced disparity that defines the duty cycle of the device. At voltages ≥ 4 V, the ratio of discharge time to charge time an indicator of how effectively the cell retains and delivers energy reaches approximately 5:1. This high ratio signifies strong charge retention and minimal self-discharge, comparable to the performance enhancements observed in other lithium-ion systems incorporating carbon nanostructures, where improved conductivity and surface chemistry stability significantly extended operational lifetimes [20]. In contrast, at lower voltages, the duty cycle is markedly reduced, highlighting that insufficient charging potential fails to fully exploit the cell's energy storage capacity. Furthermore, when compared with conventional lithium-ion systems lacking quantum dot additives, the CQDs-based electrolyte shows superior discharge duration, aligning with previous research where carbon quantum dots improved electrode–electrolyte interface stability and accelerated electron transfer rates, thereby increasing cycle life and energy density (Guan et al., 2020). The plateau in discharge time beyond 4 V also aligns with known voltage thresholds in advanced lithium-ion cells, where excessive potentials risk initiating side reactions or electrolyte breakdown, reducing long-term performance. The observed trends strongly support the role of CQDs as an effective electrolyte additive in DIY-scale lithium-ion devices, combining rapid charging, extended discharge, and a favorable duty cycle. These findings underscore the potential of low-cost, nanomaterial-enhanced electrochemical systems for practical applications in energy storage, especially where performance-to-cost optimization is essential.

4. CONCLUSION

This study demonstrates that Li-CQDs synthesized from citric acid exhibit tunable PL and promising electrochemical behavior, highlighting their potential for optoelectronic and energy storage applications. The PL intensity was highest at lower temperatures (30 °C), decreasing with thermal elevation due to non-radiative recombination and surface state destabilization. Laser exposure induced gradual intensity reduction without shifting emission peaks, indicating surface defect formation while preserving electronic band structures. Sugar addition revealed a dual effect: low concentrations enhanced PL through surface passivation, whereas higher concentrations caused quenching via aggregation or energy transfer, underscoring the sensitivity of CQDs to the chemical environment. Electrochemical testing of DIY Li-ion cells showed stable charge storage and enhanced duty cycles when Li-CQDs were paired with conductive substrates like carbon paper. Overall, controlled doping and environmental modulation effectively optimize the optical and electrochemical performance of CQDs.

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