

RESEARCH ARTICLE

Surface functional group-tailored B and N co-doped carbon quantum dot anode for lithium-ion batteries

Kue-Ho Kim  | Hyo-Jin Ahn 

Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul, South Korea

Correspondence

Hyo-Jin Ahn, Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 01811, South Korea.
Email: hjahn@seoultech.ac.kr

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Summary

Recently, carbon quantum dots (CQDs) have emerged as new surface modification agents for the anode materials of lithium-ion batteries (LIBs) owing to their various advantages, including high surface area, low toxicity, low cost, and chemical stability. However, CQDs intrinsically possess large amounts of nonessential oxygen-containing groups (C—O and C—OH) at the surface, which can inhibit Li⁺ accessibility and lower electrical conductivity. Owing to these limitations, CQDs have been widely studied as composite agents and not as independent active materials. Therefore, to enhance the electrical conductivity and increase the Li⁺ diffusivity of CQDs, we suggest surface functional group-tailored boron and nitrogen co-doped carbon quantum dots (BN-CQDs) for self-reliant LIB anode applications. The 0.5BN-CQD electrodes showed superior electrochemical performance, including outstanding ultrafast energy storage capability (130.4 mAh g^{−1} at 3000 mA g^{−1} with capacity retention of 88% up to 1000 cycles). This is contributed by the enhanced electrical conductivity of the boron and nitrogen co-doped structure and high Li⁺ acceptability, which facilitated the formation of C=O surface functional groups due to the boron dopant. In this regard, we believe that the fabrication of self-reliant 0.5BN-CQD electrodes could be a promising research strategy for carbon-based anode materials.

KEYWORDS

anode, carbon quantum dot, co-doped structure, Li-ion battery, ultrafast energy storage

1 | INTRODUCTION

Lithium-ion batteries (LIBs) have achieved phenomenal success worldwide owing to their extensive application in fields such as electric vehicles, portable electronics, and large-scale energy storage systems, with the increase in the demand for rechargeable batteries.^{1–3} Initially, LIBs have attracted global attention owing to their several advantages, including high energy density, stable cycle performance, and reasonable price, which make them a stable energy storage medium.^{4–6} However, the materialization of cutting-edge and multi-functional electronic

devices, which required advanced energy storage performance (high energy and power density, high cycle stability, and fast charging), have prompted the development of next-generation LIBs. Generally, LIBs comprise an anode, cathode, electrolyte, separator, and current collector within an exterior material. The LIBs performance is chiefly determined by the reactions of the electrochemical active materials during charge and discharge processes. In particular, for ultrafast (high-current density) charging conditions, the energy storage performance of LIBs, such as the specific capacity, cyclability, and rate performance, often depend on the anode owing to the

fundamental reaction mechanism limitation for the graphite anode. Numerous manufacturers have used pure graphite as an anode material because of their low cost, abundant resource, and electrochemical stability since the development of LIBs. However, graphite has two disadvantages: (a) low theoretical specific capacity (372 mAh g^{-1}), which leads to low energy density and (b) an intercalation/de-intercalation energy storage mechanism with a restricted ion diffusion pathway along the planar direction, which limits the ultrafast energy storage performance. To circumvent these limitations and develop post-graphite anode materials, many prospective strategies have been proposed, such as fabricating composite structures using two or more advantageous materials and modifying the physical or chemical characteristics of existing materials.^{7,8} Despite these efforts, the development of anode materials is gradually reaching its limits with conventional research strategies, and an alternative approach is required.

Carbon quantum dots (CQDs) have emerged as a new surface modification agent for the anode materials of LIBs. CQDs are defined as carbon dots that exhibit quantum effects with diameters $<10 \text{ nm}$. CQDs were accidentally discovered during the treatment of single-walled carbon nanotubes by Xu's group.⁹ Originally, similar to other quantum dot-based materials, CQDs have been actively used in the sensing, photocatalysis, and biochemistry fields owing to their simple synthesis, non-toxic nature, and broad optical absorption.¹⁰⁻¹³ Recently, CQDs have also been employed as surface engineering agents for energy storage and conversion fields on their applicability to various electrode materials and advantageous functions that can support the electrical conductivity, specific capacity, and ion diffusion kinetics of conventional electrode materials.¹⁴⁻¹⁷ The various advantages of CQDs including high surface area, low toxicity, low cost, and chemical stability, facilitate their use as electrode material modification agents. However, CQDs intrinsically possess many trivial oxygen-containing groups (C—O and C—OH) at the surface, which can inhibit Li^+ accessibility to charge storage sites and induce inferior kinetic properties. Further, electron transfer is restricted due to the dislocation of sp^2 carbon, leading to a decrease in the electrical conductivity of CQDs compared to other carbon-based materials.¹⁸ The Li^+ diffusion kinetics and electrical conductivity are crucial factors for the anode performance of LIBs, particularly for the specific capacity and cycle stability at a high current density. Owing to these intrinsic limitations, CQDs have only been used as surface modification agents to ameliorate the electrochemical activity and wettability of conventional electrode materials. However, if the aforementioned issues are resolved, CQDs can be attractive anode materials

owing to their advantages, including high surface area, facile synthesis process, and structural controllability. To modify the surface functional groups of carbon-based materials, anion doping is a powerful strategy; nitrogen, sulfur, boron, and fluorine are utilized as dopant, which bond with carbon.¹⁹⁻²¹ In addition, these doped anions influence the electrical characteristics of carbon, such as increasing the charge carriers, providing additional charge storage sites, and improving the electronegativity pertaining to the bonding state and doping site within the carbon lattice.²² In this regard, tailoring the surface functional groups and enhancing the electrical conductivity of CQDs for LIB anode materials should be performed, which has not been studied in detail till date.

In this study, we first report surface functional group-tailored, boron and nitrogen co-doped CQDs (BN-CQDs) using a simple hydrothermal method for self-reliant anode materials for LIB applications. During the hydrothermal process, boron and nitrogen atoms in the doping agents successfully formed chemical bonds with carbon, preventing the formation of nonessential oxygen-related functional groups and enhancing the electrical conductivity of the CQDs. The fabricated electrode, 0.5BN-CQD exhibited excellent cycling stability compared to the other samples owing to the engineered surface functional groups, it also showed superior high-rate energy storage capability owing to the enhanced electrical conductivity with boron and nitrogen co-doping.

2 | EXPERIMENTAL DETAILS

Boron and nitrogen co-doped CQDs with tailored surface functional groups were successfully synthesized using a simple hydrothermal method. To prepare the precursor solution, 0.5 M citric acid ($\text{C}_6\text{H}_8\text{O}_7$ [99%], Sigma-Aldrich) and 0.5 M urea ($\text{CH}_4\text{N}_2\text{O}$ [99.5%] Sigma-Aldrich) as a nitrogen doping agent, were dissolved in 30 mL of deionized water with vigorous stirring. Then, to tailor the surface functional group and doping structure of CQD, various amount (0.1, 0.5, and 1.0 g) of boric acid (H_3BO_3 [99.5%], Sigma-Aldrich) were added into the solution, as boron doping agents. The homogeneous mixed solution was poured into a Teflon-lined hydrothermal bath with a stainless-steel autoclave. The autoclave was heated to 180°C for 6 hours and cooled to room temperature naturally. Subsequently, the as-synthesized CQDs were centrifuged at 10 000 rpm for 20 minutes to remove sediments and impurities. The light brown supernatant solution was dialyzed using a fixed membrane with a molecular weight cut-off of 6 to 8 kD for 12 hours. During the dialysis process, the de-ionized water was used as a solvent and mass cylinder with vibrator were adopted

to get the homogeneous solution. The resultant solution was dried in an oven at 50°C for 24 hours to obtain a bluish-black CQD powder. For comparison, CQDs without boron acid were also synthesized (denoted as N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD, respectively, according to the addition amount of boric acid).

The particle size and morphology of the synthesized samples were investigated by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) and a dynamic light scattering measurement system (Malvern, zetasizer nano S90). To characterize the crystallographic and chemical bonding states, X-ray diffraction (XRD, Rigaku D/Max-2500) patterns with Cu K α source and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) with Al K α source were performed. The optical properties of all samples were analyzed by ultraviolet-visible (UV-vis) spectroscopy (Perkin-Elmer, Lambda-35) using deionized water as a dispersion state. Fourier transform infrared (FT-IR) spectroscopy (Thermo Scientific, Nicolet-iS50) was utilized to demonstrate the chemical bonding state of the samples. Each synthesized sample was prepared as an anode to examine the energy storage performance. The weight ratio of electrode slurries were 6 (CQD): 1 (ketjen black): 3 (poly[vinylidene fluoride]) and a 1-methyl-2-pyrrolidinone was used as a solvent. The homogeneous slurries were spread on Cu current collector using doctor blade equipment and dried for 10 hours at 100°C oven. CR2032 Coin-type cells were prepared using the fabricated CQD anode and Li metal (Honjo Chem. Corp., 99.999%) counter electrode with

polypropylene separator (Celgrad 2400) and a 1.6 M LiPF₆ in a mixture of dimethyl carbonate and ethylene carbonate(EC) (3:7) as the electrolyte. To evaluate the electrochemical kinetic properties, electrochemical impedance spectroscopy (EIS) was measured with 10⁵ to 10⁻² Hz frequency range. The energy storage performances were examined using a battery cycler (WonATech Corp., WMPG 3000) in the potential range of 0.05 to 3.0 V (vs Li/Li⁺). The cycling stability was evaluated at a current density of 100 mA g⁻¹ up to 100 cycles, and the rate capability was investigated at current densities of 100, 300, 700, 1000, 1500, 2000, and 3000 mA g⁻¹. Further, the ultrafast cycling stability was examined at a high current density of 2000 mA g⁻¹ up to 1000 cycles.

3 | RESULTS AND DISCUSSION

We synthesized surface functional group-tailored boron and nitrogen co-doped carbon quantum dots (BN-CQDs) using a hydrothermal method. Figure 1 presents a schematic of the experimental procedure for preparing N-CQDs and BN-CQDs. As shown in Figure 1A, citric acid and urea were used as CQD formation agents and nitrogen doping sources, respectively, which constructed the N-CQD structure during the hydrothermal process. For BN-CQDs, various amounts of boric acid (0.1, 0.5, and 1.0 g) were added as the boron doping source, maintaining all other experimental factors precisely for reliable comparison (see Figure 1B). Interestingly, boron

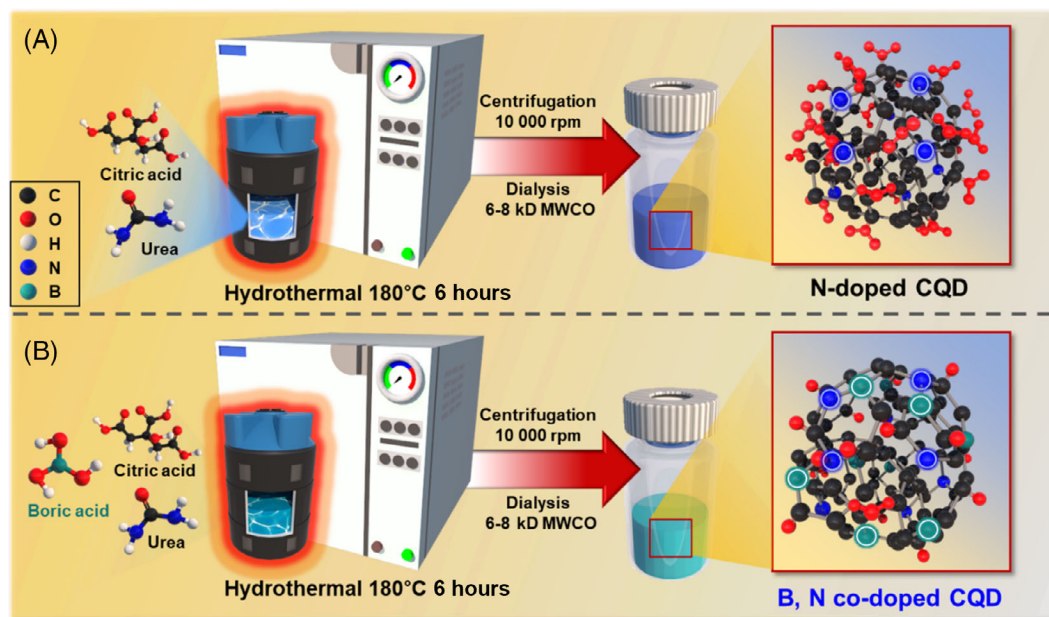


FIGURE 1 Schematic of the experimental procedure for preparing (A) N-CQD and (B) BN-CQD. BN-CQD, boron and nitrogen co-doped carbon quantum dots; N-CQD, nitrogen co-doped carbon quantum dots

atoms acted as dopants in the carbon structure, and in addition, adjusted the ratio of oxygen-related surface functional groups by facilitating the formation of C=O bonds. This BN-CQD structure with engineered surface functional groups can contribute to the energy storage performance of LIB anodes, particularly under ultrafast charging/discharging conditions with enhanced electrical conductivity and improved Li⁺ acceptability.

Figure 2A,B show TEM images of as-synthesized N-CQD and 0.5BN-CQD, wherein, a dark carbon lattice area appears, implying the successful synthesis of CQD. The particle size distributions of N-CQD and 0.5BN-CQD were in the range of 2 to 7 nm (see Figure 2C,D). Further, both samples showed the same lattice fringe spacing of 0.21 nm, corresponding to the (100) plane for graphitic carbon. This indicates that boron and nitrogen doping may not affect the particle size and *d* spacing of CQD owing to the similar atomic radii of carbon (77 pm), boron (85 pm), and nitrogen (70 pm).²³ Figure S1 show the dynamic light scattering measurement results, which confirm the average particle size of N-CQD (3.69 nm) and 0.5BN-CQD (3.51 nm). Since the electrochemical reactions predominantly depend on the surface area, the nano-sized particles of CQD with a high surface area can provide abundant and efficient charge storage sites compared to the bulk carbon-based anode materials.

To investigate the chemical bonding state and verify the formation of CQDs, absorbance spectra were recorded by UV-vis spectroscopy. Figure 3A shows the absorbance spectra of all the synthesized samples in the

range of 200 to 600 nm. The absorbances of the samples were measured in a dispersion state of deionized water at the same concentration (see Figure S2). The UV-vis spectra of all samples showed two distinguishable absorption peaks at 230 (λ_1) and 324 nm (λ_2), corresponding to the π - π^* transition of aromatic C=C bonds in the sp² hybridized domains and the n- π^* transition of aromatic C=O bonds in the sp³ hybridized domains, respectively.²⁴ The amount of boron doping agent increased from that in 0.1BN-CQD to that in 1.0BN-CQD, accordingly, the absorbance peak intensities at λ_1 decreased owing to the generation of carbon-boron bonds. In particular, 1.0BN-CQD exhibited low C=C bond peaks due to the excessive amount of boric acid, which impedes the formation of C=C bonds of the CQD structure. Further, Figure S3 shows deionized water (transparent) and dispersed solution of N-CQD (dark blue) and 0.5BN-CQD (dark blue) under daylight. Compared to the deionized water, the N-CQD and 0.5BN-CQD solutions exhibited bright blue fluorescence under UV light at 365 nm, confirming the quantum effects of CQD, as reported previously.²⁵ The FT-IR spectra of N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD were recorded to identify the chemical bonding states and the spectra are shown in Figure 3B. All samples showed CQD characteristic features with stretching vibrational peaks at approximately 3180.5, 2941.2, 1661.9, 1558.0, 1400.9, 1309.7, 1167.7, and 772.2 cm⁻¹, signifying the bonding states of N-H, C-H, C=O, C-C, C-N, C-OH, C-O, and O-C=O, respectively.²⁶ In addition, the boron-doped samples (0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD) showed peaks, corresponding to B-C and B-O bonds at ~1053.3 and ~917.2 cm⁻¹, respectively. Therefore, the successful preparation of N-CQD and BN-CQD structures using boric acid and urea as boron and nitrogen doping sources, respectively, via a simple hydrothermal method is verified.

To demonstrate the structure statement of the samples in detail, XRD and XPS analyses were performed. Figure S4 displays the XRD curves for N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD. All samples showed only one broad peak at ~25.00°, signifying the structure of graphite (002) plane.²⁷ A less intense and broadened graphite peak was observed for 1.0BN-CQD compared to other samples, which implies decreased C-C bonds due to the excessive amount of boron. Figure 4 shows the results of XPS measurement, which were aligned by the 284.5 eV C 1s reference peak. Figure 4A appears the XPS spectra of C 1s for all samples, showing identical peaks at approximately 284.5, 285.1, 286.9, 287.9, and 289.2 eV. Each peak is related to the binding energies of C-C, C-N, C-O, C=O, and C-OH bonds, forward order.²⁸ The common C-N bond represents the nitrogen-doped

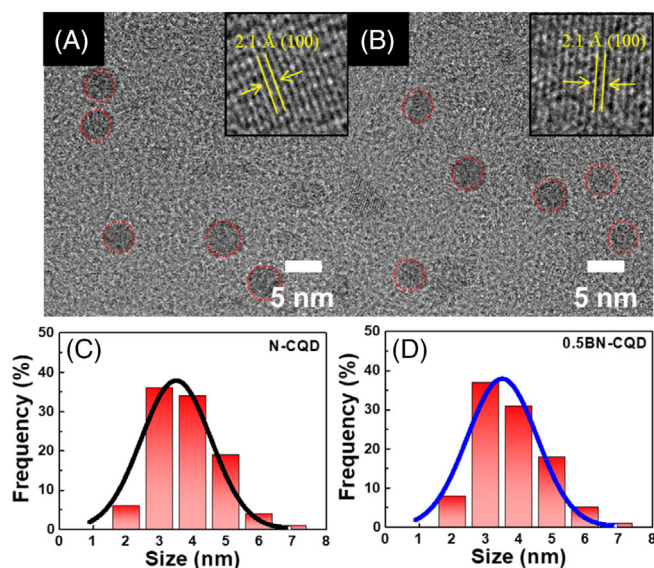


FIGURE 2 Transmission electron microscopy images and particle size distributions of (A,C) N-CQD and (B,D) BN-CQD. BN-CQD, boron and nitrogen co-doped carbon quantum dots; N-CQD, nitrogen co-doped carbon quantum dots

FIGURE 3 (A) Absorbance spectra in the range of 200 to 600 nm and (B) Fourier transform infrared spectra in the range of 500 to 4000 cm^{-1} obtained from N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD, respectively. BN-CQD, boron and nitrogen co-doped carbon quantum dots; N-CQD, nitrogen co-doped carbon quantum dots

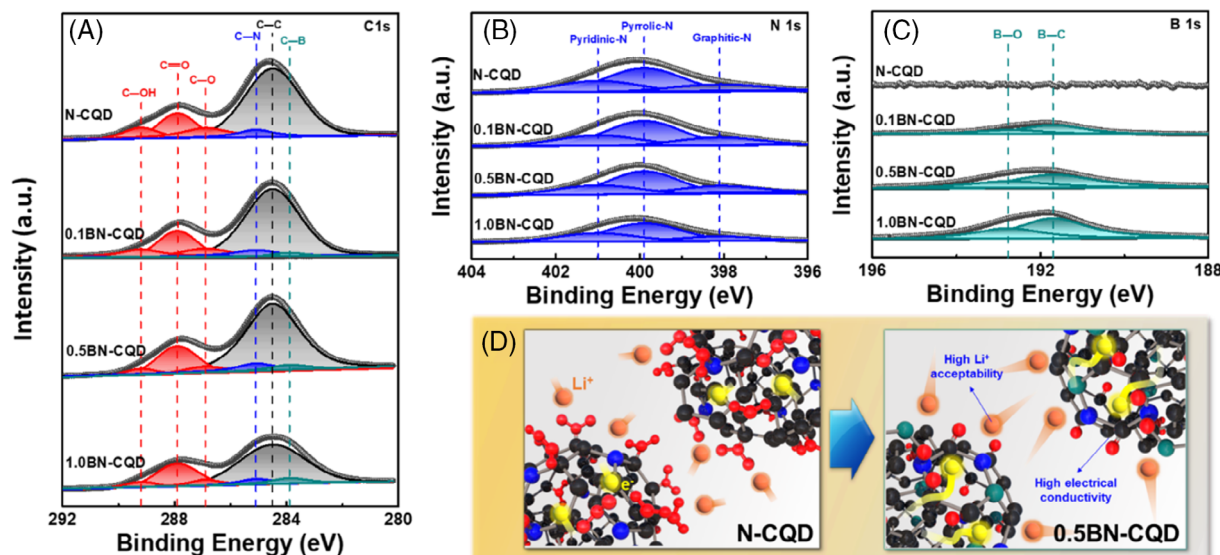
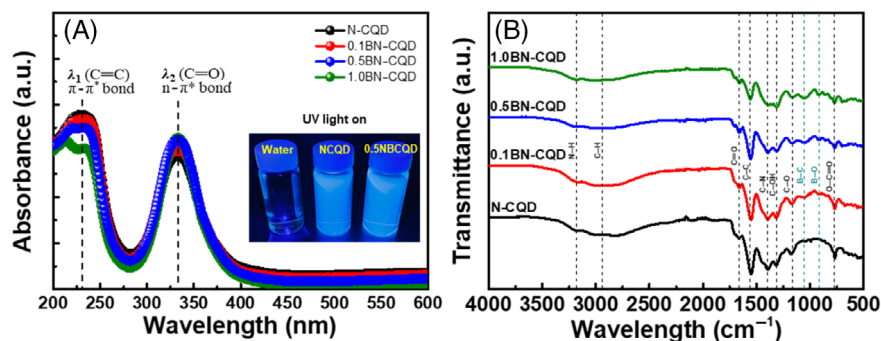


FIGURE 4 X-ray photoelectron spectroscopy core-level spectra of (A) C 1s, (B) N 1s, and (C) B 1s of N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD and (D) illustration the advantage of surface functional group-tailored BN-CQD structure. BN-CQD, boron and nitrogen co-doped carbon quantum dots; N-CQD, nitrogen co-doped carbon quantum dots

carbon structure with urea. A C—B bond was detected at a binding energy of ~ 283.9 eV for boron-doped samples (0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD), and the peak intensity increased as the amount of added boron increased.²⁹ Interestingly, among the oxygen-related functional groups, the ratio of C=O bonding in 0.5BN-CQD increased compared to that in N-CQD, contrary to the decreasing tendency of C—O bonding and C—OH bonding. Based on the binding intensity area in the C 1s XPS spectrum, we calculated the respective ratios of oxygen-related functional groups, which are summarized in Table 1. The 0.5BN-CQD sample showed the largest C=O bonding ratio of 72.9% with the smallest C—O bonding (16.2%) and C—OH bonding (10.9%) ratio, which is attributed to the catalytic effect on oxygen chemisorption by boron dopant.³⁰ This increased ratio of C=O bonding facilitates redox-mediated Li^+ storage with high Li^+ acceptability, resulting in the enhancement of the energy storage performance of LIB anodes.³¹ Further, the

TABLE 1 Respective ratios of oxygen-related functional groups for N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD

Samples	C—OH (%)	C=O (%)	C—O (%)
N-CQD	19.6	45.5	34.9
0.1BN-CQD	20.1	54.2	25.7
0.5BN-CQD	10.9	72.9	16.2
1.0BN-CQD	11.3	68.4	20.3

estimated atomic percentages of B and N within all samples were also calculated using the C 1s XPS data. Owing to the fixed dopant concentration, the atomic percentage of nitrogen was similar in all the samples (2.1% for N-CQD, 2.0% for 0.1BN-CQD, 2.2% for 0.5BN-CQD, and 2.0% for 1.0BN-CQD), and the atomic percentage of boron increased from 0.7% to 1.9% and 3.3% for 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD, respectively as the amount of boric acid increased. Figure 4B shows a

similar N 1s XPS spectrum for all samples with three peaks at ~ 401.0 , ~ 399.9 , and ~ 398.1 eV, corresponding to pyridinic-N, pyrrolic-N, and Graphitic-N, respectively.³² In particular, the bonding positions of pyridinic-N and pyrrolic-N are edges of graphite, offering one (pyridinic-N) or two (pyrrolic-N) p-electrons to the aromatic π -system.³³ Figure 4C shows the B 1s XPS spectrum and the boron-doped samples show two peaks at ~ 192.8 and ~ 191.7 eV, representing B—O and B—C bonding. Boron doping in the carbon lattice can create additional charge carriers through the carbon structure, resulting in enhanced electrical conductivity.³⁴ In addition, the boron dopant generates extrinsic defects and active sites, which can affect the specific capacity enhancement.³⁵ We demonstrated the advantages of engineering surface functional groups in BN-CQD concerning boron and nitrogen co-doping and depicted it as an illustration (see Figure 4D). The nonessential oxygen-related surface functional groups (C—O and C—OH) in N-CQDs lower its electrical conductivity and obstruct Li^+ diffusion, limiting its energy storage performance. However, BN-CQD can offer high electrical conductivity and high Li^+ acceptability with boron and nitrogen co-doped CQD structure, which ascertains the enhanced C=O bonding ratio.

To examine the electrochemical kinetic performances of the fabricated anodes using N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD as active materials, EIS analyses were performed. Figure 5A shows the Nyquist plots of the N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD electrodes with an equivalent circuit model. The Nyquist plot can be divided into a semicircle region and an inclined line.³⁶ First, the semicircle in the high-frequencies region implies the charge transfer resistance, which corresponds to the interfacial resistance between the electrolyte and electrode. The 0.5BN-CQD electrode showed the smallest semicircle, indicating the enhanced electrical conductivity compared with the other electrodes. This result is mainly owing to the additional charge carriers from the boron and nitrogen dopants. Second, the inclined line is related to the Li^+ diffusivity, which is expressed by the Warburg

impedance. The 0.5BN-CQD electrode exhibits the lowest Warburg impedance, which is contributed by the enhanced Li^+ acceptability due to the tailored surface functional groups. Figure 5B shows the calculated Li^+ diffusion coefficients of the N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD electrodes using Equations (1) and (2)^{37,38}:

$$Z_R = \sigma_w \omega^{-1/2} + R_{ct} + R_e. \quad (1)$$

$$D = (RT)^2 / 2A(n^2 F^2 C \sigma_w)^2. \quad (2)$$

where, σ_w and R_e indicate the Warburg impedance coefficient corresponding to the Li^+ diffusion resistance of the electrode. D , R , T , and A represent the ion diffusion coefficient, ideal gas constant, temperature, and area, respectively. The 0.5BN-CQD electrode exhibited the superior Li^+ diffusion coefficient of $12.8 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ compared to other electrodes (7.2×10^{-14} , 8.8×10^{-14} , and $5.4 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ for N-CQD, 0.1BN-CQD, and 1.0BN-CQD, respectively). These results indicate that the 0.5BN-CQD electrode retains high electrical conductivity with high Li^+ diffusivity, which dominantly affects the electrochemical performance of the LIB anode.³⁹

Figure 6A shows the cycling stability of the electrodes up to 100 cycles. All electrodes showed high cycling stability up to the 100th cycle because all of them were prepared with carbon-based active materials. The specific capacity increased from the initial cycle to the 100th cycle for the N-CQD, 0.1BN-CQD, and 0.5BN-CQD electrodes. At the initial cycle, the N-CQD electrode showed a low specific capacity of $343.84 \text{ mAh g}^{-1}$ compared to the 0.1BN-CQD ($418.82 \text{ mAh g}^{-1}$) and 0.5BN-CQD ($485.13 \text{ mAh g}^{-1}$) electrodes. This result is owing to the doped boron atoms within the CQD, which provide extrinsic defects and additional active sites for Li^+ storage. However, 1.0BN-CQD showed the lowest specific capacity of 185.3 mAh g^{-1} despite a large amount of boron dopant. This is attributed to the excessive boron doping agent, which hinders the formation of C—C bonds in the CQD structure. Figure 6B shows the specific

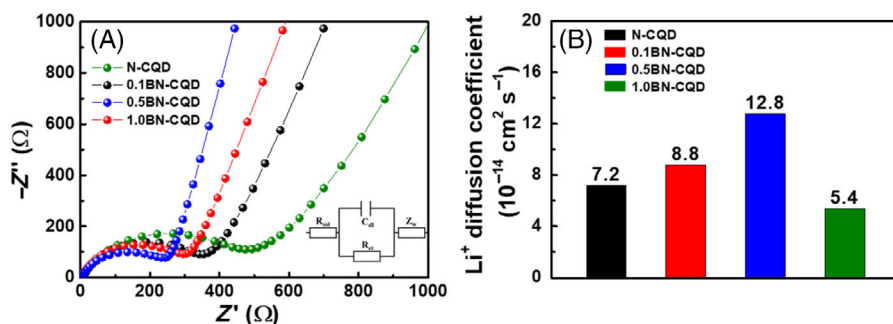
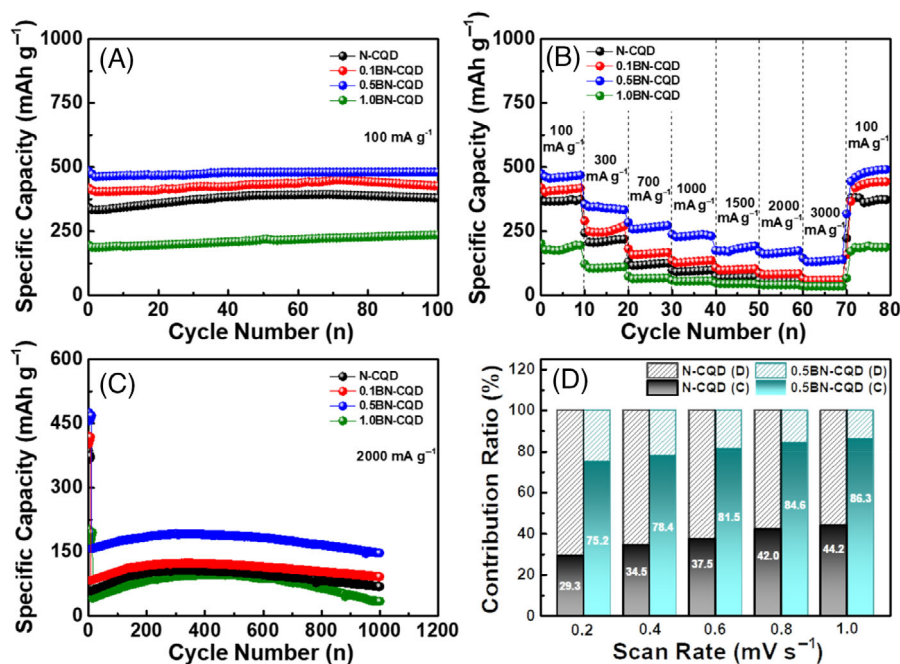


FIGURE 5 (A) Nyquist plots with applied circuit model and (B) calculated Li -ion diffusion coefficient of N-CQD, 0.1BN-CQD, 0.5BN-CQD, and 1.0BN-CQD electrodes, respectively. BN-CQD, boron and nitrogen co-doped carbon quantum dots; N-CQD, nitrogen co-doped carbon quantum dots

FIGURE 6 (A) Cycling stability up to 100 cycles at a current density of 100 mA g^{-1} , (B) specific capacities at varied current densities of 100, 300, 700, 1000, 1500, 2000, and 3000 mA g^{-1} , and (C) cycling stability at a high current density of 2000 mA g^{-1} up to 1000 cycles of all the fabricated electrodes with (D) summarized diffusion (D) and capacitive (C) reaction ratio for N-CQD and 0.5BN-CQD electrodes. BN-CQD, boron and nitrogen co-doped carbon quantum dots; N-CQD, nitrogen co-doped carbon quantum dots



capacities at current densities of 100, 300, 700, 1000, 1500, 2000, and 3000 mA g^{-1} , to demonstrate the Li^+ storage performance at high current density and rate capability for all the electrodes. The specific capacity of the electrodes decreased as the current density was varied from 100 to 3000 mA g^{-1} owing to the insufficient ion diffusion and electron transfer kinetics by comparison to the applied current. The 0.5BN-CQD electrode showed the highest specific capacity of 130.4 mAh g^{-1} at a current density of 3000 mA g^{-1} with a superior retention rate of 27.9% compared to the N-CQD (37.6 mAh g^{-1}), 0.1BN-CQD (58.6 mAh g^{-1}), and 1.0BN-CQD (32.6 mAh g^{-1}) electrodes. This excellent rate capability of the 0.5BN-CQD electrode is attributed to the improved electrical conductivity from boron and nitrogen dopants and enhanced Li^+ acceptability from the enriched C=O surface functional group. Figure 6C shows the cycling stability at a high current density of 2000 mA g^{-1} to evaluate the ultrafast charge/discharge capability. The long-term cycling performance was investigated for all the fabricated electrodes for up to 1000 cycles. The 0.5BN-CQD electrode showed an excellent specific capacity of 147.1 mAh g^{-1} with a capacity retention of 88% after 1000 cycles at a current density of 2000 mA g^{-1} compared to the other electrodes. As mentioned in the Figure 5, the excellent ultrafast energy storage capability of 0.5BN-CQD electrode is predominantly contributed by the enhanced Li^+ diffusion coefficient. Further, to identify the kinetic behaviors, cyclic voltammetry (CV) curves of N-CQD and 0.5BN-CQD electrodes were measured at varying scan rates from 0.2 to 1.0 mV s^{-1} . The capacitive

proportion of the charge/discharge reaction was estimated using below equation (Equation 3).⁴⁰

$$I(V) = k_1 v + k_2 v^{1/2}. \quad (3)$$

where, $k_1 v$ correspond to the capacitive behavior and $k_2 v^{1/2}$ correspond to the diffusive behavior region. Thus, the CV data of N-CQD electrode and 0.5N-CQD electrode can be sorted into two parts, which was summarized in Figure 6D. Because the capacitive-dominant CV curve signifies fast charge transfer with high Li^+ diffusivity, Figure 6D represents the ultrafast energy storage capability of the electrodes.⁴¹ Compared with the N-CQD electrode, the 0.5NB-CQD electrode showed the largest capacitive behavior ratio (86.3%) at a scan rate of 1.0 mV s^{-1} , supporting its superior rate capability, as shown in Figure 6C.

This study investigates an oxygen-related surface functional group-tailored, boron and nitrogen co-doped CQDs for self-reliant LIB anode applications. The 0.5BN-CQD electrode showed a high specific capacity and ultrafast energy storage capability; therefore, it circumvents its limitations as an independent anode material. This significant performance improvement is attributed to the following factors: First, boron and nitrogen co-doped structures with sufficient charge carriers enable high conductivity with fast electron transfer, which contributes to the enhanced ultrafast energy storage capability. Second, the boron dopant generates additional charge storage sites and facilitates the formation of C=O bonds in CQDs

with high Li^+ acceptability, which contributes to the high specific capacity.

4 | CONCLUSION

In this study, we successfully synthesized surface functional group-tailored boron and nitrogen co-doped CQDs using a simple hydrothermal process for self-reliant LIB anode applications. Through the development of the BN-CQD structure, superior electrical conductivity and fast kinetic properties can be achieved. Further, during the hydrothermal process, the added boron dopant forms the C—B bonds and facilitates the generation of C=O bonding functional groups. The 0.5BN-CQD electrode showed superior electrochemical performance compared with conventional carbon-based electrodes: a high specific capacity of $485.13 \text{ mAh g}^{-1}$ at 100 mA g^{-1} , superior ultrafast energy storage performance of 130.4 mAh g^{-1} at 3000 mA g^{-1} with high retention rate of 27.9% and capacity retention of 88% after 1000 cycles. The improvement in the electrochemical performance of the 0.5BN-CQD electrode was attributed to the (a) high electrical conductivity with boron and nitrogen co-doped structure, providing sufficient charge carriers for the ultrafast energy storage capability, and (b) application of boron dopant, generating additional active sites and facilitating the formation of C=O bonding functional groups with high specific capacity and high Li^+ acceptability. Therefore, the proposed BN-CQD is a promising self-reliant anode material for next-generation LIB applications.

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ORCID

Kue-Ho Kim  <https://orcid.org/0000-0002-9067-2446>

Hyo-Jin Ahn  <https://orcid.org/0000-0002-5786-3937>

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