Flexible sodium-ion batteries using electrodes from *Samanea saman* tree leaf-derived carbon quantum dots decorated with SnO$_2$ and NaVO$_3$

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**Abstract**

Carbonaceous materials with large interlayer spacing and disordered structure are considered suitable as electrodes in sodium-ion batteries so as to overcome the problem encountered in conventional electrodes. In this study, carbon quantum dots (CQDs) decorated with SnO$_2$ and NaVO$_3$ are used as electrodes in the fabrication of flexible Na-ion batteries. CQDs are prepared from dead leaves of the *Samanea saman* tree through alkaline-peroxide treatment and hydrothermal carbonization. As-prepared CQDs exhibit a quantum yield of 21.03% at an excitation wavelength of 360 nm. Various separators such as indium-doped tin oxide/polyoxyethylene tridecyl ether (ITO/PTE), rice paper (RP), silicone with three big holes (SIL BH), silicone with many small holes (SIL SH) and cellulose paper (CP) have been tried in flexible Na-ion batteries. SIL SH achieved specific capacitance (881 F g$^{-1}$) than other separators due to the function of many small holes on the surface of the silicone. The SIL SH separator delivered higher discharge capacities of 141 and 114 mC g$^{-1}$ at 1.5 and 2.5 V than SIL BH. The RP separator delivered specific discharge capacities of 1087 and 347 mC g$^{-1}$ in the 1st and 50th cycles, respectively.
at 1 V. The RP separator delivered a high initial specific discharge capacity of 698 mC g⁻¹ at 2 V and maintained a good discharge capacity of 222 mC g⁻¹ in the 50th cycle. As compared to RP, SIL SH delivered high specific discharge capacity of 4246 in 1st cycle at 2 V but maintained a capacity of 71 mC g⁻¹ in the 50th cycle. This study reveals the scope of developing flexible Na-ion batteries with high capacity and cyclability using carbonaceous materials derived from the leaves of the S. saman tree.

**Graphical Abstract**

**Keywords:** biomass; carbon quantum dots; separators; gel-polymer electrolyte; flexible Na-ion battery

**Introduction**

Energy-storage technology has become a growing global concern over the past decade due to the practical application of renewable energy resources and environmental exigencies [1]. Alternate energy sources such as wind and photovoltaic technology are poised to complement the energy demand and are becoming increasingly prominent in several industrialized countries. The electricity thus produced is transferred into energy-storage devices of load-leveling transformers. Then, it is distributed to consumers through electrical grids [2]. Portable energy-storage devices may have their use in hybrid electric vehicles, plug-in hybrid electric vehicles and in sole electric vehicles (EVs). In addition, it plays an important role as an electronic component in supercapacitors, fuel cells and batteries. Among the many commercial storage provisions available on the market, Li-ion batteries (LIBs) have expanded their roles in EVs and power stations [3–5].

The LIB has immense electrochemical properties such as high voltage, high energy density and high specific power as well as a wide range of operating temperatures with good durability. As Li is a lightweight metallic element, it has a low redox potential (E⁰_{Li⁺/Li} = −3.04 V versus a standard hydrogen electrode (SHE)). In addition, it easily
Mn$_3$O$_4$ and Fe$_3$O$_4$ [24]. Among them, SnO$_2$ has been pre-
disposed of spent batteries may create soil pollution [6]. It
ment of EVs and hybrid EVs. Another concern is that the
as the demand increases due to the large-scale develop-
molten Li metal. However, LIBs have penetrated the portable elec-
for use in electrodes. Nanostructured carbon materials, espe-
cially carbon quantum dots (CQDs), have been considered
as one of the most promising electrodes for SIBs, due to
their ideal electrical conductivity, chemical stability, com-
patibility, abundance, low cost and sustainability [10]. In
anostructured carbon materials with micro or
mesopores create channels for ion diffusion so as to ac-
celerate the electrochemical reactions [11]. These pores
offer suitable channels for the permeation of anions and
cations that also endure the volume expansion of the
graphite layer in the nanostructured carbon materials [1].

The light-emitting quantum-sized carbon dots are
<10 nm in size and are known to be favourable as alter-
nate semiconducting materials to Si and Ge in various
applications due to their extra small size, hydrophilicity
and biocompatibility with excellent photoluminescence
[12]. Generally, CQDs are synthesized from chemical pre-
ursors. Recently, biomass wastes are being used as poten-
tial alternative feedstock for CQDs due to economic
and environmental considerations [13, 14]. Recently, many
works have reported on the synthesis of CQDs from waste
biomass such as the peels of oranges [15], watermelon [16]
and chestnut (Trapa bipinnata) [17], and various plant leaves
[18]. Biomass-based CQDs tend to avoid the growing con-
sumption of recalcitrant chemicals. In addition, biomass-
derived carbon electrodes have many advantages such as
a high specific surface area, large interlayer spacing, well
defined distribution of pore size, excellent electrical
conductivity and surface chemistry amenable for easy
modification [19]. Quantum-sized CQDs enhance reaction
kinetics, accommodate volume changes of active materi-
als and reduce the ionic diffusion path [20].

Several transition-metal oxides have been widely used
as anodes including SnO$_2$ [21], FeO$_2$ [22], CoO$_2$ [23], NiO, Co$_3$O$_4$,
Mn$_3$O$_4$ and Fe$_3$O$_4$ [24]. Among them, SnO$_2$ has been pre-
ferred as a promising anode material due to its relatively
high theoretical specific capacitance (~782 mAh g$^{-1}$), which
is higher than that of commercial graphite (~370 mAh g$^{-1}$). Besides, it is of low cost and is formed of a hierarchical
hollow structure. Pure SnO$_2$ is inhibited by its large initial
capacity loss and severe capacity fading, volume changes
due to the agglomeration of tin nanoparticles during al-
loying and de-alloying processes with metal ions affecting
the pulverization and loss of electrical contact in the elec-
rodos. In this context, it is found to be better to design
an SnO$_2$ composite typically combined with carbonaceous
materials especially CQDs to enhance the intrinsic prop-
ties. For instance, carbon-coated hierarchical SnO$_2$ hollow
spheres are reported to deliver as high as 1307.4 mAh g$^{-1}$
at 100 mA g$^{-1}$ [21].

Many cathode materials including layered transition-
metal oxides, transition-metal fluorides, phosphates,
fluorophosphates, pyrophosphates, sulphides, sulphates,
Prussian blue and organic polymers have been explored
for use in SIBs. Among these, vanadium(V)-based cathode
materials, especially sodium-layered oxides (Na$_x$VO$_3$),
have been considered as efficient electrodes due to their
high operating voltages, theoretical capacities and energy
densities as well as their rich electrochemical reaction
[25]. Na$_3$V$_2$O$_8$ shows high performance in LIBs whereas its
cyclability and rate capability are poor in SIBs. Therefore,
carbon is coated on the surface of the electrode to increase
the electrical conductivity and facilitate electron transpor-
tation in the electrode as well as to improve the cyclability
during long-term charge and discharge processes [26].

Song et al. reported that the hierarchical architecture of
carbon-coated Na$_3$V$_2$O$_8$ nanotubes delivered an initial
capacity of 168 mA g$^{-1}$ and reached a maximum capacity rate
of 209 mA g$^{-1}$ at 0.1°C [27].

Gel-polymer electrolytes (GPEs) play an important role
in flexible batteries. GPEs overcome the issues of liquid
electrolytes especially in flexible batteries by replacing li-
quid electrolytes so as to prevent any leakage. GPEs with
an inherent flexibility offer a wide potential electrochem-
ical window with low toxicity and high safety. GPEs have
been widely used in flexible batteries due to their good
ionic conductivity, non-flammability, high thermal sta-
bility, resistance to leakage and mechanical stability [28].
Poly(acrylonitrile) (PAN)-based gel electrolytes have high
ionic conductivity ($\sim 10^{-3}$ S cm$^{-1}$) at 25°C [29]. For instance,
high-performance GPEs comprising polyacrylonitrile/
thermoplastic polyurethane/polystyrene (PAN/TPU/PS) ex-
hibit a maximum ionic conductivity of $3.9 \times 10^{-3}$ S cm$^{-1}$ at
room temperature with an electrochemical stability of 5.8
V [30]. In addition to the above, the role of separators needs
to be studied, as they are an integral part of the battery.

In the present study, CQDs are synthesized from dead
leaves of the tree Samanea saman by an alkaline-peroxide-
assisted hydrothermal carbonization (HTC) method.
Synthesized CQDs decorated with SnO$_2$ (CQDs@SnO$_2$)
and NaVO$_3$ (CQDs@NaVO$_3$) are used as anode and cathode
materials in the fabrication of flexible SIBs. PVA-based
poly(3-hexylthiophene) (P3HT) is used as the gel-polymer
electrolyte in SIBs. The synthesized CQDs, forming the anode and cathode materials, are characterized through ultraviolet-visible (UV-vis) spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) study, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM). Various separators such as indium tin oxide coated polyoxyethylene tridecyl ether (ITO/PTE), rice paper (RP), silicone with three big holes (SIL BH), silicone with many small holes (SIL SH) and cellulose paper (CP) are tested in flexible batteries. The electrochemical performances of fabricated batteries are investigated by cyclic voltammetry. The charge-discharge profile is studied using chronoamperometry and the cyclability at 1 and 2 V is investigated using the chrono charge-discharge technique.

1 Materials and methods

1.1 Materials

The sodium metavanadate (NaVO₃), tin (II) chloride dehydrate (SnCl₂·2H₂O), polyvinyl alcohol (PVA), poly(3-hexylthiophene) (P3HT), indium-doped tin oxide/polyoxyethylene tridecyl ether (ITO/PTE) sheet (surface resistivity of 60 Ω/sq, 1 ft.L × 1 ft.W × 5 mil. thickness), 1-methyl-2-pyrrolidone anhydrous, polytetrafluoroethylene (Sigma-Aldrich), sodium hydroxide (NaOH), sulforic acid (95–97%) (Merck), carbon black Vulcan XC-72 R (Fuel Cell Earth), hydrogen peroxide (40% m/v in water) (H₂O₂) (Carlo Erba reagents) and CP (CAT No:3001–845) are required shortly before the commencement of the project. Dead leaves of the tree S. saman were collected from King Mongkut’s University of Technology Thonburi, Bangkhuntien campus, Bangkok, Thailand. All other chemicals were used as received without any purification.

1.2 Preparation of CQDs from dead leaves of the tree S. saman

The dead leaves of the tree S. saman were separated from miscellaneous plant matter, cleaned with tap water, dried under sunlight, further dried in a hot-air oven at 80°C and powdered. The alkaline-peroxide-assisted hydrothermal carbonization method was followed in the synthesis of the CQDs. Initially, 3 g of leaf powder was mixed with 0.2 M sodium hydroxide solution (70 mL). Then, 10 mL of hydrogen peroxide solution was added into the above mixture. The mixture was stirred at room temperature for 2 h and dried in a muffle furnace at 195 ± 5°C for 12 h. After completion of the reaction, the mixture was centrifuged at 10 000 r.p.m. at 25°C for 15 minutes. The solid was washed first with distilled water and then with ethanol. The purified material was dried in a hot-air oven at 75°C and calcined at 500°C for 2 h in a muffle furnace to obtain pure SnO₂ nanoparticles.

1.3 Purification of CQDs

The solution obtained after centrifugation was washed using dichloromethane to remove any unreacted organic moieties. It was then transferred to a rotary evaporator (70°C, 600–200 mbar) to remove the water. The viscous form of the remnant was further dried in a hot-air oven at 60°C until the moisture was removed to the maximum. It (CQDs) was subsequently stored in a refrigerator at –30°C overnight and then freeze dried at –50°C, 1 mbar for 7 h to completely remove the moisture content. The solid form of CQDs were treated with absolute ethanol (99.9%) by shaking in a centrifuge tube [31]. The content was centrifuged to obtain solid CQDs. The solid CQDs were calcined in a tubular furnace at 700°C for 2 h under an N₂ atmosphere. The calcined CQDs (purified) showed solubility in distilled water and emitted a blue colour at 360 nm (Scheme 1).

1.4 Synthesis of tin oxide (SnO₂) nanoparticles

To synthesize the SnO₂ nanoparticles, 3 g of tin(II) chloride dihydrate (SnCl₂·2H₂O) was added with 0.2 M of NaOH (0.56 g of NaOH dissolved in 70 mL of distilled water) and 10 mL of H₂O₂. The content was stirred at room temperature (25°C) for 2 h. Then, it was transferred to a Teflon-lined autoclave and placed in a muffle furnace at 195 ± 5°C for 12 h. After completion of the reaction, the mixture was centrifuged at 10 000 r.p.m. at 25°C for 15 minutes. The solid was washed first with distilled water and then with ethanol. The purified material was dried in a hot-air oven at 75°C and calcined at 500°C for 2 h in a muffle furnace to obtain pure SnO₂ nanoparticles.

1.5 Synthesis of CQD-decorated SnO₂ nanoparticles (anode)

The supernatant liquid of CQDs (20 mL) (Section 1.2) was added with ethanol (10 mL). It was mixed with 0.5 g of synthesized SnO₂ nanoparticles. The suspension was stirred at room temperature for 2 h and dried in a hot-air oven at 60°C to evaporate the moisture. The CQD-decorated SnO₂ nanoparticles thus obtained were calcined at 700°C for 2 h under an N₂ atmosphere. The calcined material was used in the fabrication of the anode.

1.6 Synthesis of CQD-decorated NaVO₃ nanoparticles (cathode)

CQD-decorated NaVO₃ nanoparticles were prepared as per the procedure contained in Section 1.5. The synthesized material was used in the fabrication of the cathode.

1.7 Synthesis of gel-polymer electrolyte PVA/P3HT

PVA (1 g) was dissolved in 10 mL distilled water to which 1 g of concentrated H₂SO₄ was added. The mixture was heated (85°C) and stirred for 2 h to form a gel [32]. A solution containing 50 mg poly(3-hexylthiophene) (P3HT) dissolved in...
3 mL of chloroform was added to the above PVA gel. Then, it was stirred at 40°C for 30 minutes to get a black-coloured gel.

1.8 Materials characterizations
A UV-vis spectrometer (Biotek), FTIR spectrometer (Thermo Nicolet Corporation), XRD using Ni-filtered Cu Kα radiation (\(\lambda = 1.54 \text{ Å}\)) at 40 kV and 40 mA (Rigaku RINT 2100), SEM (JEOL, JSM-6610LV), TEM (JEOL JEM 2100-Plus 200 kV) and EDS (INCA-xart) were employed to characterize the optical properties, morphology, size, structure and composition of the synthesized materials.

1.9 Fabrication of flexible SIBs
A schematic diagram of the design details of a flexible battery are presented in Fig. 1a and b. The active material (CQDs@SnO\(_2\) or CQDs@NaVO\(_3\)) in powder form was mixed well with conductive carbon black Vulcan XC-72R and polytetrafluoroethylene (weight ratios of 70:25:5) in 1-methyl-2-pyrrolidone using a vortex. The mixture was kept for 48 h at room temperature to form a homogeneous slurry. The slurry was coated on the ITO/PTE (2 cm × 1 cm, 5 mil. thickness) using the doctor blade technique. The coated substrate was dried at 50°C for 2 h. The current collector copper sheet (0.1 mm thickness) was...
tightly pressed onto the surface of anode and cathode up to a distance of 1 cm from the edge of the substrate to get a good electrical contact. PVA/P3HT was used as a gel-polymer electrolyte. Various separators: ITO/PTE (0.1-mm thickness, area: 2 cm²), RP (0.1-mm thickness, area: 2 cm²), SIL BH (1-mm thickness with three holes of 4-mm dia. each, area: 2 cm²), SIL SH (1-mm thickness with many holes of 1-mm dia. each, area: 2 cm²) and CP (0.1-mm thickness, area: 2 cm²) were investigated. The separator was dipped well into the gel-polymer electrolyte with the anode surface rested in it for a few minutes. The cathode was then placed on the top side of the separator. The edges were sealed using sticky tape so as to prevent leakage of the electrolyte. Further, the battery was shielded well with three layers of white paper masking tape to avoid air contact. The fabricated batteries were preserved in a closed container.

1.10 Electrochemical studies

The electrochemical storage properties of cyclic voltammograms (0–3.5 V vs Na/Na⁺, 0.5 mV s⁻¹), charge–discharge performances by chronoamperometry (1–2.5 V) and chrono charge–discharge (50 cycles) in different potentials at room temperature using an Autolab (AUT 86930) were studied in a frequency ranging from 0.1 Hz to 0.1 MHz at an open-circuit potential of 0.02 V.

2 Results and discussion

2.1 Synthesis of CQDs by alkaline-peroxide-assisted HTC

The alkaline-peroxide-assisted hydrothermal carbonization method is used to synthesize CQDs from cleaned and dried leaves of the tree S. saman. Major chemical compositions of the leaves under study are crude protein 22.6%, neutral detergent fibre 47.5% and acid detergent fibre 36.9% [33]. The dead-leaves powder was pre-treated with alkaline-peroxide solution. The above was processed in HTC to get CQDs. The procedure for synthesizing CQDs from dead leaves and its morphology and fluorescence are presented in Scheme 2. The dead leaves were passed through hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization followed by a hydrothermal carbonization process so as to obtain smaller monomers [34–36].

Alkaline-hydrogen-peroxide treatment is a simple procedure to enhance the properties of CQDs. This method is widely used in delignification and bleaching in the pulping industry through the oxidation of hydrogen peroxide. Hydrogen peroxide dissociates with sodium hydroxide to form hydroperoxyl (HOO⁻) ions (H₂O₂ + OH⁻ → H₂O + HOO⁻). The hydroperoxyl ions act as a strong oxidant that enhances the yield of quantum dots with abundant functional groups on the surface. On increasing the concentration of NaOH–H₂O₂ within the optimum level, the particle size tends to decrease. Beyond the optimum concentration, the particle size increases dramatically by aggregation [36, 37]. NaOH (70 mL of 0.2 M solution) and 10 mL of H₂O₂ were used in this study. Alkaline-peroxide-assisted hydrothermal carbonization offers Na-doped CQDs to enhance sodiation/desodiation during the charging and discharging processes in SIBs.

2.2 Characterizations of synthesized materials

The absorption and emission spectra of the purified CQDs are presented in Fig. 2a–g. The absorbance at 285 nm is due to π-π transitions by the aromatic C=C bond in the core.
A broad shoulder at 335 nm reveals that the n–π* transition occurs by C=O from the surface of CQDs (Fig. 2a). Variations do occur in the absorbance spectrum of CQDs decorated with SnO$_2$ and NaVO$_3$ (Fig. 1b and c). CQDs exhibit a maximum emission wavelength of 457 nm at the excitation wavelength of 360 nm. However, on increasing the absorbance spectrum of CQDs decorated with SnO$_2$ and NaVO$_3$. CQDs exhibit a maximum emission wavelength of 457 nm at the excitation wavelength of 360 nm. However, on increasing the
excitation wavelength from 380 to 460 nm with an increment rate of 20 nm, the intensity of the emission decreases gradually, as shown in Fig. 2d. The synthesized CQDs emit strong blue-coloured radiation while CQD-decorated SnO$_2$ and CQD-decorated NaVO$_3$ emit a weak blue colour at 360 nm (Fig. 2a–c). The emission is known to be influenced by various defects such as the size and functional groups on the surface of the CQDs. The quantum yield of CQDs is calculated to be 21.03% by quinine sulphate as the reference, which is in line with earlier works (Table 1).

The quantum yield is in accordance with the concentration of HOO–, which in turn relies on the concentrations of various functional groups. Table 1 provides a comparison of quantum yield (QY) and size of CQDs from various biomass sources.

![Fig. 3: FTIR spectra of (a) unpurified CQDs, (b) purified CQDs, (c) calcined CQDs, (d) CQDs@SnO$_2$, (e) CQDs@NaVO$_3$, and (f) functional groups on the surface of CQDs](image-url)

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Table 1: Comparison of quantum yield (QY) and size of CQDs from various biomass sources

| Biomass                      | Method                                | Reaction conditions                                      | Size (nm) | QY       | Reference          |
|------------------------------|---------------------------------------|---------------------------------------------------------|-----------|----------|--------------------|
| Azadirachta indica leaves    | Hydrothermal carbonization (HTC)      | Temp. 150°C for 4 h                                      | 3.2       | 27.2     | [39]               |
| Oriental plane leaves        | Pyrolysis                             | NA                                                      | 3.7       | 16.4 (oriental plane) | 15.3 (lotus) | 11.8 (pine) | [40] |
| Mint leaves                  | HTC                                   | Temp. 200°C for 4 h                                      | 4–9       | 7.64     | [41]               |
| Bamboo leaves                | HTC                                   | Temp. 200°C for 6 h                                      | NA        | 7.1      | [42]               |
| Glucose                     | Pyrolysis                             | Temp. 200°C for 6 h                                      | NA        | 4.03     | [37]               |
| Glucose                     | HTC and alkaline-peroxide treatment   | Temp. 200°C for 6 h (HTC) and 0.3 M/2.4 wt% of NaOH and H$_2$O$_2$ (alkaline-peroxide treatment) | NA        | 14.9     |                    |
| Purple perilla               | HTC                                   | Temp. 260°C for 5 h                                      | 2.8       | 9.01     | [43]               |
| Samanea saman (Rain tree)    | Alkaline-peroxide-treatment-assisted HTC | Temp. 260°C for 5 h with alkaline-peroxide treatment (0.2 M/10 mL) for 2 h at RT and HTC (195 ± 5°C for 16 h) | 4.00 ± 0.964 | 21.03 | This study |

*Temp., temperature; NA, not available.*
SnO₂ and NaVO₃ have absorbance and stretching vibrational mode of C=O is identified at the peaks and C=C stretching vibration. The absorbance bands of C=O and C–H (Fig. 3d and e). CQDs, CQD-decorated SnO₂ and CQD-decorated NaVO₃ are presented in Fig. 3a–e. The functional groups of CQDs have ketonic, carbonyl and hydroxyl functional groups as indicated by the FTIR spectra (Fig. 3a and b). In addition, the excitation-dependent emission is related to the anti-stokes emission and surface-energy trap of CQDs that give forth blue-coloured radiation under UV light [37, 44]. The different excitation wavelengths may cause consecutive excited energy distributions, charge separation, electron confinement and holes on the surface of CQDs [45, 46].

The FTIR spectra of unpurified CQDs, purified CQDs and calcined CQDs along with those of CQD-decorated SnO₂ and CQD-decorated NaVO₃ are presented in Fig. 3a–e. The bands at 630–660 cm⁻¹ are attributed to the stretching vibration of C–H. The band at ~1060 cm⁻¹ reveals the asymmetric stretching mode of C–NH–C. Peaks associated with the stretching vibration modes of carboxyl (–COOH) and hydroxyl (–OH) are at ~1753 and ~3437 cm⁻¹, respectively. The characteristic peaks at ~2854 and ~2925 cm⁻¹ are assigned to the stretching vibration modes of sp² and sp³ C–H, respectively [47]. The peaks at 1400 to 1450 cm⁻¹ correspond to the C=C stretching vibration. The absorbance vibrational mode of C=O is identified at the peaks at ~1630–1640 cm⁻¹ [48]. The functional groups of CQDs are eliminated by purification (Fig. 3b) as confirmed by that of the unpurified CQDs (Fig. 3a). The calcined CQDs have limited functional groups (Fig. 3c) as compared to those of purified and unpurified CQDs due to calcination at high temperature that eliminates several functional groups. The solubility of CQDs in water is in the order of unpurified CQDs > purified CQDs > calcined CQDs due to the number of functional groups present on the surface of CQDs. The peaks at 424 and 833 cm⁻¹ reveal the presence of absorbance and stretching bands of Sn–O (Fig. 3d). The stretching vibration bands of V–O–V and V–O occur at 738 and 930 cm⁻¹, respectively (Fig. 3d). CQD-decorated SnO₂ and NaVO₃ have absorbance and stretching vibration bands of C=O and C–H (Fig. 3d and e).

The XRD patterns of the uncalcined CQDs, calcined CQDs, CQD-decorated SnO₂ and CQD-decorated NaVO₃ are presented in Fig. 4a–d. A dominant peak at 26° and a small peak at 23° appear in all the materials that correspond to the crystalline planes of (0 0 2) and (1 2 0) diffraction of disordered carbonate structure with interlayer spacing of 0.33 and 0.37 nm. Uncalcined CQDs express small peaks at 18°, 29°, 34°, 46° and 54° corresponding to (1 0 3), (3 0 0), (1 2 3), (1 0 0) and (0 1 3) diffraction planes, which indicates that carbon remains at random (Fig. 4a). CQDs are known to contain many oxygen-holding groups on the surface, which is consistent with EDS data [44]. Two small peaks (18° and 46°) are absent in calcined CQDs as high-temperature calcination eliminates the peaks (Joint Committee on Powder Diffraction Standards (JCPDS) number: 75–1621, 50–1082, 50–0926, 75–0444, 48–1206, 22–1069) (Fig. 4b). The diffraction planes (2 0 0), (1 0 3), (1 2 0), (4 0 0), (2 0 1), (5 0 1) and (0 1 2) identified in CQDs@NaVO₃ are attributed to NaVO₃ (JCPDS number: 32–1197, 89–9051) (Fig. 4d). The CQDs of d-spacing are found (0.37 nm) using the JCPDS database, which is consistent with TEM data. In addition, CQDs have a hexagonal structure that is consistent with the SEM image (Fig. 5b). The peaks at 34°, 38°, 52° and 55° correspond to the (1 1 0), (1 1 1), (2 0 1) and (2 2 0) diffraction planes of SnO₂ (JCPDS number: 41–1445, 85–0712, 72–2324). It suggests the purity of SnO₂ (Fig. 4c). The average crystalline size of uncalcined CQDs, calcined CQDs, CQD@SnO₂ and CQDs@NaVO₃ are calculated to be 12.8, 11.5, 11.9 and 14.4 nm, respectively, through Scherer’s equation.

Morphological studies of uncalcined CQDs, calcined CQDs, CQD@SnO₂ and CQDs@NaVO₃ were investigated using SEM (Fig. 5a–d). The morphological structure of CQDs obtained from the dead leaves of S. saman is shown in Fig. 5a. Protein is known to be in the form of crystalline nanorods in synthesized calcined CQDs. Neutral detergent fibre and acid detergent fibre form flakes when agglomerated. Calcined CQDs are crystalline (Fig. 5b) when compared to uncalcined CQDs (Fig. 5a) due to the effect of high temperature (700°C).
under an N₂ atmosphere. In addition, a porous consistency is formed in the detergent fibre of the calcined CQDs (Fig. 5b). A hexagonal structure appears on calcined CQDs (Fig. 5b), which is in relation to the XRD pattern (Fig. 4b) and also with the TEM images of CQDs@SnO₂ (Fig. 7a and b). CQD-decorated SnO₂ appears as nanorods due to agglomeration (Fig. 5c). CQD-decorated NaVO₃ appears like a tree with roots and branches. Nanosized crystalline particles of CQDs are seen on the rod-shaped roots, which may be a vanadium compound of NaVO₃. CQDs from fibre materials are flake-shaped with differently sized pores (Fig. 5d).

The elemental composition of synthesized materials was analysed using the EDS technique (Fig. 6). Uncalcined as well as calcined CQDs mainly consist of C, O and Na, which reveals that the CQDs are made up of an oxygenous carbon structure. Both the materials contain higher oxygen than carbon due to NaOH and H₂O₂, which offer relatively high specific capacitance and rate capability (Fig. 6a and b). Na is present in these synthesized materials, since the alkaline-peroxide (NaOH–H₂O₂)-assisted hydrothermal carbonization is being used in the preparation. CQD-decorated SnO₂ has high amounts of Sn (60.14%) and...
O (31.03%) (Fig. 6c). The cathodic material (CQDs@NaVO₃) mainly consists of V (35.99%) and O (38.61%) (Fig. 6d).

The morphology and structure of calcined CQDs, CQDs@SnO₂ and CQDs@NaVO₃ were investigated using TEM (Fig. 7a–c). The mean diameter of the calcined CQDs is 4.0 ± 0.96 nm (n = 20) (Fig. S1a in the online Supplementary Data). Selected area (electron) diffraction (SAED) of calcined CQDs exhibits a hexagonal lattice structure with different crystallographic planes (1 0 3) and (1 2 3) that are in agreement with the XRD pattern and SEM of calcined CQDs. In addition, the distance between the two lattice points is 3.82 nm. Calcined CQDs are <10 nm in size and have many crystalline planes (2 0 1), (1 0 0), (0 0 2) and (3 0 0) with interlayer spacing of 0.371, 0.301, 0.340 and 0.306 nm. In addition, CQDs have the regular arrangement of carbon atoms (Fig. 7a). The yellow-coloured figures are the magnification of the Digital Micrograph software for calculating the values of d-spacing of the crystalline planes (Fig. 7b and c). CQDs derived from dead leaves have an interlayer spacing of 0.371 nm, with a high surface area, large interior voids and shortened mass or charge transportation lengths that effectively improve the specific capacity, rate capability and cycling stability of the SIBs [19, 48, 49].

The diameter of CQDs@SnO₂ ranges from 2.11 to 10.75 nm with an average of 6.37 ± 2.15 nm (n = 43) (Fig. S1b in the online Supplementary Data). The particles are seen agglomerated with many crystalline lattice planes. The lattice fringes of these particles are distinct with interlayer spacing of 0.390 and 0.335 nm corresponding to the planes of (1 2 0) and (1 1 0) representing the CQDs and SnO₂, respectively. SAED reveals that the planes of SnO₂ (0 0 2) and (1 1 0) and CQDs (1 2 3) and (0 0 2) agree with the pattern of

Fig. 5: Continued.
the XRD. The interlayer spacing of CQDs with a hexagonal structure is 0.33 nm, which corresponds to a lattice plane of (0 0 2) (Fig. 7b) [50]. The SAED pattern of CQDs@NaVO3 shows a spherical structure with an interlayer spacing of 0.259 and 0.155 nm corresponding to the planes of (3 1 0) and (1 0 3) representing NaVO3 and CQD at 35°C and 59°C (Fig. 7c). The surface of the CQDs@NaVO3 has many crystalline planes with different interlayer spacing of 0.292,
0.239, 0.378 and 0.296 nm corresponding to the planes of (3 0 1), (2 1 3), (0 0 2) and (3 0 1), respectively, which remains consistent with the XRD pattern of CQDs (Fig. 4a and b) and CQDs@NaVO₃ (Fig. 4d). The Na-ion is larger (1.02 Å) than the Li-ion (0.76 Å), causing difficulty in intercalating them into graphite due to the short interlayer distance of graphite (~0.34 nm) [20, 51, 52]. Biomass-derived CQDs with a porous structure are chosen in this study so as to...
Fig. 8: Cyclic voltagrams of various separators in SIBs at various scan rates (0.5–25 mV s⁻¹) and the redox performance behaviour at 0.5 mV s⁻¹ (three cycles) (I) ITO/PTE (a₁, a₂), (II) RP (b₁, b₂), (III) SIL BH (c₁, c₂), (IV) SIL SH (d₁, d₂) and (V) CP (e₁, e₂)
overcome the problems caused by graphite due to its large interlayer distance coupled with a disordered structure. Synthesized CQDs@SnO₂ and CQDs@NaVO₃ facilitate the intercalation of Na-ions efficiently during the charging and discharging processes due to the large interlayer distances of 0.39 and 0.378 nm.

### 2.3 Electrochemical performances of flexible Na-ion batteries

The cyclic voltammetry (CV) of the fabricated batteries using different separators was studied at various scan rates (25, 10, 5, 3, 1 and 0.5 mV s⁻¹) and in three initial cyclic CVs at 0.5 mV s⁻¹ within the potential range of 0–3.5 V in order to characterize the performance of the batteries (Fig. 8I–V). The capacitance values are high at low scan rates. The CVs of batteries show peaks arising from reversible oxidation and reduction reactions at various scan rates. Peaks are formed by the Na-ion insertion and extraction in the CQDs together with the gel-polymer electrolyte [53]. In the ITO/PTE separator, the oxidation peaks at 0.1 and 0.53 V, corresponding to the reduction peak at 0.03 V, appear in the first cycle whereas the oxidation peak at 0.53 V disappears in the subsequent cycles. In addition, the height of the oxidation and reduction peaks is seen as reduced in the second and third cycles, even when the current is reduced. The CV curves of the second and third cycles overlap indicating a good cycling performance of CQDs with porous structured anode and cathode materials during sodiation and desodiation processes [10]. The anodic peak at 0.1 V originates from the reversible sodiation/desodiation process [54] (Fig. 8I a2). In addition, there is no distinct peak indicating the decomposition of the electrolyte and it may be seen that the second and third cycles are superimposed. It reveals that there is no solid electrolyte interface (SEI) formed on the electrode surface and most of the Na-ions are reversibly drawn into the CQDs [55].

In the case of RP as the separator in SIBs, there are two oxidation peaks at 0.26 and 0.87 V and reduction peaks at 0.52 and 0.64 V, respectively. This battery releases a higher current by oxidation peaks than the ITO/PTE separator whereas the reduction peaks have low current values (Fig. 8II b2). The area of the reduction peaks is lower than that of the oxidation peaks. The two irreversible reduction peaks at 0.52 and 0.64 V in all the cycles reveal that there is no formation of SEI. The reversible reduction peaks at 0.52 and 0.64 V are attributed to Na-ion insertion–extraction in the interlayers of the CQDs [56]. The SIL BH separator in SIBs has oxidation (0.11 V) and reduction (0.08 V) peaks (Fig. 8II c2) whose response is similar to that of the ITO/PTE separator. But, the reduction peak of SIL BH releases a current lower than that of ITO/PTE. In the case of SIL SH, the CV of the separator shows three oxidation peaks at 0.16, 0.86 and 1.31 V (Fig. 8I V d2) when compared to SIL BH. The irreversible reduction peaks occur at 0.3, 0.18 and 0.06 V in the consecutive three cycles. The study reveals that the holes on the surface of silicone influence the performance of the batteries. Silicone with many small holes (SIL SH) has a higher amount of gel loading than that of silicone with larger holes (SIL BH). In SIBs with CP as the separator, two anodic peaks are formed at 0.05 and 0.12 V in all the cycles. But, the cathodic peak of the first cycle at 0.1 V and the second and third cycles of the cathodic peak formed at 0.06 V are superimposed (Fig. 8V e2).

The specific capacitance value of fabricated batteries is calculated from the following formula using a mathematical area (Equation 1) for the CV curve at a scan rate of 0.5 mV s⁻¹:

\[
\text{Specific capacitance (F g}^{-1}) = \frac{\int i \, dv}{m \times v \times (v_f - v_i)} \tag{1}
\]

where \( \int i \, dv \) denotes the integral area under the CV curve, \( m \) is the mass of the active material on the surface of the working electrode (g), \( v \) is the scan rate (0.5 mV s⁻¹) and \( (v_f - v_i) \) is the functional potential window (V).

The specific capacitance value of the batteries ITO/PTE, RP, SIL BH, SIL SH and CP are 13, 266, 116, 881 and 183 F g⁻¹, respectively. SIL SH has achieved a higher specific capacitance (881 F g⁻¹) than SIL BH (116 F g⁻¹) due to the number and size of the holes on the surface of the flexible silicone sheet. SIL BH may have higher amount of gel-polymer electrolyte than SIL BH. The capacitance values of SIL SH are higher at low scan rates than at higher scan rates and are near to the ideal shape. While charging all batteries at 0.5 mV s⁻¹ from zero potential, the current initially increases and then decreases as the electric potential is increased expressing a hump in the CV curve [57, 58].

Charge–discharge studies made using chronopotentiometry for fabricated batteries at 1, 1.5, 2 and 2.5 V for 1 h are presented in Fig. 9I–V and the data of its origin are shown in Fig. S2I–IV in the online Supplementary Data. The specific capacitance of fabricated batteries is calculated from the charge and discharge profile as shown in Equation 2:

\[
\text{Specific charge or discharge capacity (mC g}^{-1}) = \frac{0.5 \times (i_f - i_i) \times (t_f + t_i)}{m} \times 10^3 \tag{2}
\]

where \((t_f - t_i)\) denotes the time duration (s), \((i_f + i_i)\) denotes is the charge (C) and \(m\) refers to the mass of the active material on the surface of working electrode (g).

On increasing the potential from 1.0 to 2.5 V, the specific discharge capacities increase in the ITO/PTE separator. But the specific charge capacity is low at high voltages (Fig. 9I). RP as a separator has a high specific discharge capacity at high voltages of 2.0 and 2.5 V but it has poor charge and discharge capacities at 1–1.5 V (Fig. 9II). CP has high specific charge capacities at high voltages (1 and 1.5 V) whereas the discharge capacity gradually increases on increasing the voltage (Fig. 9V). Both the silicone separators delivered higher specific charge and discharge capacities at 1 and 2 V than those of other separators (Fig. 9III and IV). However, the specific discharge capacities
are lower than the specific charge capacities due to poor desodiation at 1 V. At 1.5 V, SIL SH delivered a higher specific discharge capacity (141 mC g\(^{-1}\)) than SIL BH (32 mC g\(^{-1}\)). RP delivered a specific charge capacity of 23 mC g\(^{-1}\) and a discharge capacity of 22 mC g\(^{-1}\) at 1.5 V. CP has a specific discharge capacity of 39 mC g\(^{-1}\) at 1.5 V. SIL SH delivered a specific charge capacity of 600 mC g\(^{-1}\) and a discharge capacity of 141 mC g\(^{-1}\) at 1.5 V and 2.5 V. However, both the separators (SIL BH and SIL SH) in SIBs performed well compared to other separators, as silicone has excellent thermal and electrical insulating properties and the holes on the surface of silicone bear a high loading of gel-polymer electrolyte. In addition, silicone rubber has a high pore size (5.27 ± 1.44 to 218.03 ± 17.95 µm) [59, 60] that enhances the electrolyte-uptake property and allows the movement of Na-ions from cathode to anode and anode to cathode during charge and discharge processes.

The cyclic performances of CQDs@SnO\(_2\) and CQDs@NaVO\(_3\) in different separators were also evaluated at 1 and
2 V and are shown in Fig. 10I–V. The raw data from Autolab are shown in Fig. S3I–V in the online Supplementary Data. RP had a specific charge capacity of 1298 mC g\(^{-1}\) in the first cycle at 1 V and subsequently the charge capacity reduced to 466, 398 and 365 in the 10th, 25th and 50th cycles. It delivered good specific discharge capacities at 1087, 412, 368 and 347 mC g\(^{-1}\) in the 1st, 10th, 25th and 50th cycles at 1 V. In the ITO/PTE separator, there is poor performance in charge and discharge behaviour, as ITO has a low porosity that may affect the sodiation/desodiation process during charge and discharge processes. SIL BH delivered a specific charge and discharge capacity of 455 and 131 mC g\(^{-1}\) in the first cycle at 1 V (Fig. 10III), which are higher than SIL SH (88 and 45 mC g\(^{-1}\)) (Fig. 4). In the 50th cycle, SIL SH delivered higher specific charge and discharge capacities (420 and 225 mC g\(^{-1}\)) than SIL BH (110 and 30 mC g\(^{-1}\)). CP has a good charge and discharge cyclability compared to that of ITO/PTE at 1 and 2 V, as ITO/PTE has low surface resistivity (60 \(\Omega\) sq\(^{-1}\)). At 2 V, RP delivered a lower specific charge capacity (477 mC g\(^{-1}\)) than at 1 V (1298 mC g\(^{-1}\)) in the first cycle, whereas it delivered a lower specific charge capacity (222 mC g\(^{-1}\)) than 1 V (347 mC g\(^{-1}\)) in the 50th cycle (Fig. 10II). The charge- and discharge-specific capacities are low at a high voltage (2 V) in RP, SIL BH and CP. However, SIL SH delivered high initial specific charge capacities in the 1st and 10th cycles (2938 and 3621 mC...
Discharging at 1 V

- At 1 V, the specific discharge capacities of RP were 4246 mC g⁻¹ and 347 mC g⁻¹ in the 1st and 50th cycles, respectively.
- SIL SH delivered a specific discharge capacity of 223 mC g⁻¹ in the 1st cycle and 171 mC g⁻¹ in the 25th cycle.

Table 2: Specific power and energy of all fabricated batteries in various cyclic abilities at 1 and 2 V

| Various separators in SIBs | Charging at 1 V | Discharging at 1 V | Charging at 2 V | Discharging at 2 V |
|---------------------------|----------------|-------------------|----------------|-------------------|
|                           | 1st cycle      | 10th cycle        | 25th cycle     | 50th cycle        |
|                           | Specific power | Specific energy   | Specific power | Specific energy   |
|                           | (mW g⁻¹)       | (Wh g⁻¹)          | (mW g⁻¹)       | (Wh g⁻¹)          |
| ITO/PTE                   | 42.67          | 12.45             | 18.55          | 5.11              |
| RP                        | 1307.83        | 389.09            | 467.51         | 139.75            |
| SIL BH                    | 461.84         | 136.24            | 223.87         | 66.65             |
| SIL SH                    | 92.00          | 26.33             | 63.56          | 18.58             |
| CP                        | 153.08         | 44.83             | 74.87          | 21.97             |
|                           | 28.24          | 8.37              | 14.28          | 4.23              |
|                           | 399.68         | 119.41            | 157.97         | 46.89             |
|                           | 54.59          | 15.89             | 42.14          | 125.90            |
|                           | 56.62          | 16.50             | 33.18          | 9.94              |
|                           | 23.33          | 6.69              | 104.63         | 32.57             |
|                           | 1098.85        | 325.97            | 413.63         | 123.59            |
|                           | 135.81         | 39.07             | 57.94          | 16.90             |
|                           | 64.61          | 13.41             | 33.89          | 9.68              |
|                           | 107.68         | 31.82             | 42.71          | 12.33             |
|                           | 37.36          | 10.27             | 1393.99        | 418.77            |
|                           | 1393.99        | 418.77            | 633.92         | 189.18            |
|                           | 216.97         | 62.00             | 177.88         | 52.37             |
|                           | 8600.71        | 2546.99           | 6126.51        | 1800.92           |
|                           | 123.47         | 35.31             | 79.56          | 22.90             |
|                           | 28.24          | 8.37              | 14.28          | 4.23              |
|                           | 1043           | 30.89             | 413.63         | 123.59            |
|                           | 135.81         | 39.07             | 57.94          | 16.90             |
|                           | 64.61          | 13.41             | 33.89          | 9.68              |
|                           | 107.68         | 31.82             | 42.71          | 12.33             |
|                           | 37.36          | 10.27             | 1393.99        | 418.77            |
|                           | 1393.99        | 418.77            | 633.92         | 189.18            |
|                           | 216.97         | 62.00             | 177.88         | 52.37             |
|                           | 8600.71        | 2546.99           | 6126.51        | 1800.92           |
|                           | 123.47         | 35.31             | 79.56          | 22.90             |
EIS was performed to study the resistance of charge transfer ($R_q$) and Na-ion diffusion. The ion-diffusion behaviour between the electrodes and the gel-polymer electrolyte was examined from the slope at the low-frequency region of the Nyquist plot. In the high-frequency region of the Nyquist plot, the $R_q$ is acquired from the diameter of the semicircle of the charge-transfer resistance occurring at the interface of the electrode and the electrolyte [63, 64]. ITO/PTE shows a larger semicircle with the $R_q$ value (≈280 kΩ) than the other separators (Fig. S4 in the online Supplementary Data). The large semicircle indicates that PVA/P3HT has high interfacial resistance in ITO/PTE with poor charge propagation [65]. The diameter of the above semicircle is small when compared to those of RP, SIL BH, SIL SH and CP. In this study, PVA with a P3HT gel-polymer electrolyte was used. PVA has a low electrical conductivity ($1.63 \times 10^{-12} \text{ S cm}^{-1}$ at RT) whereas P3HT has high electrical conductivity ($12.7 \text{ S cm}^{-1}$). PVA and P3HT were used at a weight ratio of 1:0.05. P3HT is used as a solution in chloroform. It is reported that the P3HT-g-PVA prepared in hexane has higher electrical conductivity ($6.9 \times 10^{-7} \text{ S cm}^{-1}$) than P3HT-g-PVA prepared in chloroform ($3.3 \times 10^{-8} \text{ S cm}^{-1}$) or in acetonitrile ($2.9 \times 10^{-8} \text{ S cm}^{-1}$) [66]. High interfacial resistance is reported to occur in the presence of a large amount of PVA with P3HT. An equivalent circuit for the EIS data is shown in the inset of Fig. S4 in the online Supplementary Data. $R_q$, $C$, $R_t$, and $W$ are the internal resistance, capacitance, charge-transfer resistance and Warburg resistance (mass-transfer resistance) of the SEI layers. $R_q$ represents the bulk resistance of the cell, which includes the resistance due to the electrodes, separator and electrolyte [67]. The straight line at low frequencies is the Warburg impedance, which is directly associated with the diffusion of the Na-ion at the electrode–electrolyte interface [68]. SIL SH and SIL BH have low interfacial resistance compared to the other separators. In addition, they have high charge-transfer resistances compared to the other separators of RP, CP (moderate) and ITO/PTE (low). They have a low range of interfacial resistance (~400 Ω), as the silicone rubber has a high electrical insulating property (1–100 TΩ). CP starts from an interfacial resistance of ~560 Ω, which is slightly higher than that of SIL BH and SIL SH. CP, a universal material, is known to function as a good insulator. On account of its capacitance, ITO/PTE shows a higher performance than CP, SIL BH and SIL SH. CP has higher initial resistance than ITO/PTE, SIL BH and SIL SH. ITO/PTE expresses higher mass-transfer resistance than RP, SIL BH and SIL SH than that of CP due to the large pore size with more distribution on the surface area. This study reveals that the high ratio (≈1:0.05) between PVA and P3HT and an effective insulating material (silicone) as the separator can effectively enhance the performance of SIBs.

3 Conclusion

CQDs were prepared using the alkaline-peroxide-assisted hydrothermal carbonization method from the dead leaves of the tree S. saman with a quantum yield of 21.03% at an excitation wavelength of 360 nm. These CQDs were decorated with SnO$_2$ and NaVO$_3$, and used as anode and cathode materials in flexible Na-ion batteries. CQD showed $sp^3$ and $sp^1$ stretching vibration modes of hybridized carbon atoms at the surface. CQDs, CQDs@SnO$_2$ and CQDs@NaVO$_3$ showed excitation-dependent wavelengths. The average crystalline sizes of the uncalcined CQDs, calcined CQDs, CQDs@SnO$_2$ and CQDs@NaVO$_3$ were 12.8, 11.5, 11.9 and 14.4 nm. Calcined CQDs exhibited a hexagonal structure with an interlayer spacing of 0.37 nm as known from XRD and TEM studies and occurred as nanorods with a porous structure. CQDs@SnO$_2$ was of crystalline nature with several lattice planes whereas CQDs@NaVO$_3$ was of nanorods with tiny porous crystals on the surface. The performance of five separators (ITO/PTE, RP, SIL BH, SIL SH and CP) in flexible Na-ion batteries was evaluated. CV studies showed that the silicone-based separator SIL SH showed higher specific capacitance (881 F g$^{-1}$) than SIL BH (116 F g$^{-1}$). The specific discharge capacities of RP during the 1st, 10th, 25th and 50th cycles at 1 V were 1087, 412, 368 and 347 mC g$^{-1}$. The charge- and discharge-specific capacities were observed to reduce at 2 V in RP, SIL BH and CP. SIL BH displayed a high initial specific discharge capacity in the 1st and 10th cycles (4246 and 3003 mC g$^{-1}$) at 2 V whereas, in the 25th and 50th cycles, there were lower specific discharge capacities (130 and 71 mC g$^{-1}$) than those of CP and SIL BH. SIL SH and SIL BH have higher specific capacitance than the other separators whereas RP has better cyclic stability than the other separators. RP is edible and therefore it is not encouraged to be used as a separator due to the expected conflict. In the context of using PVA/P3HT gel as a polymer electrolyte, there is a need to optimize the concentration of P3HT for use in SIBs. Once the gel-polymer electrolyte is optimized, silicone-sheet separators of different thicknesses and dimensions are to be studied so as to enhance the performance level of batteries. Besides, different binary metal oxides having nanostructured porous carbon and polyanion sodium hosts are to be tried as anodes and cathodes to improve the performance of flexible SIBs.

Supplementary data

Supplementary data is available at Clean Energy online.

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Conflict of Interest

None declared.
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