



Cubane cluster interfaced carbon nanotube by ball milling for supercapacitors

Chinna Bathula^a, Aviraj Teli^a, Pranav Katkar^b, Aditya Narayan Singh^c, Soniya Naik^d, Hyun-Seok Kim^{a,*}

^a Division of Electronics and Electrical Engineering, Dongguk University–Seoul, Seoul, 04620, Republic of Korea

^b Department of Chemical and Biological Engineering, Gachon University, 1342 Seongnam-daero, Seongnam, 13120, Republic of Korea

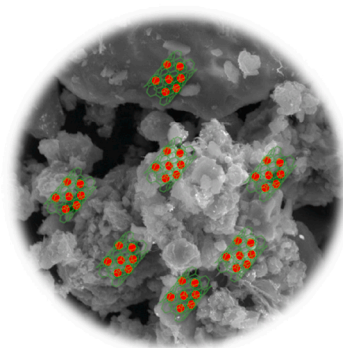
^c Department of Energy and Materials Engineering, Dongguk University–Seoul, Seoul, 04620, Republic of Korea

^d Chemical and Materials Engineering Department, University of Alberta, Edmonton, AB, T6G 2H5, Canada

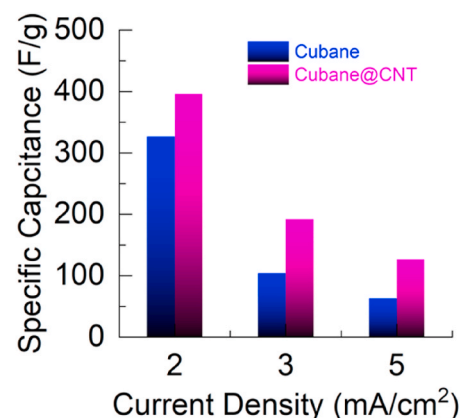
HIGHLIGHTS

- Cubane@CNT prepared by ball milling technique.
- TEM indicates well aligned cubane on CNT.
- Sp. Capacitance 396 F/g at a current intensity of 2 mA/cm².
- Power density of 123.75 W h kg^{−1} at an energy density of 1.5 W/kg
- Superior energy storage performance and commercial potential.

GRAPHICAL ABSTRACT



Cubane@CNT



ARTICLE INFO

Keywords:

CNT
Cubane cluster
Supercapacitors
Stability

ABSTRACT

Interest in the field of next generation energy storage devices using eco-friendly and economic pathways has grown dramatically by utilizing the nanocomposites. Nevertheless, their interim energy retainability and insignificant strength are interpreted as limitations to overcome. In the current work we integrated copper-based cubane cluster with carbon nanotube (cubane@CNT) by a facile green ball milling technique followed by crystallization with hot toluene. The structural integration of the cubane@CNT composite is resolved by the assistance of analytical tools. The Transmission electron microscopy (TEM) and Field emission scanning electron microscope (FESEM) analysis indicated the well-organized cubane on CNT. The specific capacitance shown by pristine cubane is 327 F/g. The cubane@CNT nanoarchitecture demonstrated an elevated capacitance of 396 F/g at current intensity of 2 mA/cm² and a cyclic retention of 96 % with 5000 charge/discharge cycles. In adding up, the cubane@CNT showed an excellent power density of 123.75 W h/kg and energy density of 1.5 W/kg. The

* Corresponding author.

E-mail address: hyunseokk@dongguk.edu (H.-S. Kim).

<https://doi.org/10.1016/j.jpowsour.2025.238952>

Received 18 April 2025; Received in revised form 1 October 2025; Accepted 24 November 2025

Available online 29 November 2025

0378-7753/© 2025 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

findings would flag a new approach of eco-friendly synthetic protocols for preparing ingredients concerning the enhanced-performing energy storing tools and commercial viability.

1. Introduction

The rapid development of energy storage technologies has triggered growing interest not only in innovative device design but also in the molecular-level engineering of new electrode materials suitable for industrial fabrication. With the increasing penetration of renewable energy [1] and the widespread use of portable electronics and electric vehicles, there is an urgent demand for devices that can deliver high power density, excellent cycle stability, and sustainable operation. Among various storage technologies [2–6], supercapacitors and batteries play complementary roles, with supercapacitors offering superior power characteristics and batteries delivering high energy density [7]. The consistency, stability, and long-term performance of such devices are crucial in enabling reliable integration into advanced energy systems.

Supercapacitors [8,9], also known as ultracapacitors, have emerged as highly promising energy storage devices owing to their fast charge–discharge capability, high power density, and long cycle life. They are increasingly employed in hybrid vehicles, grid-balancing systems, regenerative braking, and portable electronics where both power delivery and durability are essential. Supercapacitors can be broadly categorized into two classes: (i) pseudocapacitors [10], which rely on rapid Faradaic redox reactions occurring at or near the electrode surface, typically in transition-metal oxides [11], sulfides [12], and conducting polymers [13]; and (ii) electrical double-layer capacitors (EDLCs) [14], where charge is accumulated electrostatically at the electrode–electrolyte interface, as commonly observed in carbon-based materials. The electrochemical performance of supercapacitors is determined by a combination of material properties including conductivity, porosity, ion transport behavior, and structural stability [15].

In particular, carbon nanostructures such as activated carbon, graphene, and carbon nanotubes (CNTs) have been extensively investigated for EDLC applications due to their high electrical conductivity, mechanical strength, and chemical stability [16]. Among them, CNTs are especially attractive because of their one-dimensional structure, high aspect ratio, and ability to form conductive networks [17,18]. However, pristine CNTs typically exhibit modest specific capacitance due to their limited accessible surface area and the lack of redox-active sites [19]. To overcome these drawbacks, extensive efforts have been devoted to functionalization, doping, and hybridization strategies aimed at enhancing their electrochemical performance.

Hybrid materials that combine CNTs with transition-metal-based nanostructures or conducting polymers have shown particularly promising results [20,21]. For example, NiCo_2O_4 nanosheets grown on CNTs [22], NiSe nanoparticle-decorated CNT composites [23], and MOF-derived hybrids have demonstrated improved capacitance [24], rate capability, and stability. In such systems, the CNTs provide a conductive backbone that ensures fast electron transport [25], while the integrated transition-metal species introduce pseudocapacitive contributions and additional redox-active sites. Similarly, CNT–polymer hybrids have exhibited cooperative effects arising from molecular-level interactions, enhanced surface area, and shortened ion transport pathways. In addition, eco-friendly carbons derived from biowaste [26,27] have been successfully combined with CNTs to create low-cost electrode materials, underscoring the potential for sustainable approaches.

Despite these advances, challenges remain. Many existing CNT-based hybrids still suffer from issues such as poor cycling durability, agglomeration of nanoparticles, or complex synthetic routes that are difficult to scale. Therefore, there is a strong incentive to explore green, scalable, and cost-effective methods for producing high-performance CNT-based composites.

In recent years, synthetic methodology has been recognized as a key factor in determining both the electrochemical performance and the commercial viability of electrode materials. Conventional techniques such as hydrothermal synthesis, sol–gel methods, and electrospinning can provide excellent control over morphology but are often associated with toxic solvents, multi-step procedures, or limited scalability. By contrast, green synthesis routes [28] including microwave processing, sonochemical approaches, and mechanochemical methods are emerging as promising alternatives due to their reduced environmental impact, lower cost, and scalability.

Among these, high-energy ball milling [29] has gained particular attention as a mechanochemical synthesis method. It is a simple, solvent-free, and eco-friendly technique that uses mechanical forces such as fracture, shear, and cold welding to produce nanostructured materials with high reactivity and uniform mixing. Ball milling offers several advantages: it is cost-effective, reproducible, and versatile for producing a wide range of materials, including carbon-based composites, polymer–nanotube hybrids, and transition-metal oxides. Recent reports have demonstrated the successful application of ball milling in the preparation of doped carbons, polymer composites, and even organic semiconductors for light-emitting devices, highlighting its versatility beyond traditional materials [30]. For energy storage applications, ball milling provides an efficient route to create composites with nanoscale architectures, defect sites, and large accessible surface areas, which are beneficial for both ion and electron transport.

Within this context, the design of hybrid electrodes that integrate carbon nanotubes with redox-active molecular architectures has emerged as an exciting direction. One such architecture is the cubane cluster [31], a copper-based cluster with unique electronic properties and abundant active sites. By combining cubane clusters with CNTs, it is possible to combinely enhance electrochemical performance: CNTs act as conductive pathways that facilitate rapid electron transfer, while cubane introduces additional Faradaic activity and structural diversity [32].

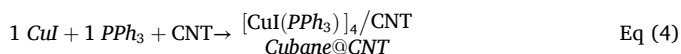
In the present work, we report the fabrication of a novel cubane@CNT composite prepared via a facile green ball milling approach followed by crystallization in hot toluene. This eco-friendly synthetic route ensures reproducibility, scalability, and minimal environmental impact, while yielding a hybrid material with well-dispersed cubane clusters anchored onto CNT frameworks. The structure and composition of the composite were systematically characterized by XRD, TEM, SEM, and XPS, which confirmed the successful integration of cubane onto the CNT surface and uniform distribution of constituent elements.

Electrochemical evaluation revealed that the cubane@CNT composite delivered an enhanced specific capacitance of 396 F/g at a current density of 2 mA/cm², superior to pristine cubane electrodes. The material also exhibited remarkable cycling stability, retaining 96 % of its capacitance after 5000 charge–discharge cycles, as well as a high-power density of 123.75 W h/kg at an energy density of 1.5 W/kg. These results demonstrate the synergistic effect between cubane and CNTs, where cubane provides abundant surface redox sites while CNTs enable fast ion/electron transport and prevent structural collapse during cycling.

This study thus establishes a promising strategy for designing next-generation electrode materials for supercapacitors by combining redox-active molecular clusters with conductive carbon nanostructures using green, scalable methods. Beyond advancing the fundamental understanding of cubane–CNT interactions, this work underscores the broader importance of eco-friendly mechanochemical synthesis in the development of sustainable, high-performance energy storage devices.

2. Results and discussion

The preparation of Cubane@CNT is accomplished by utilizing the highly efficient and environmentally friendly ball milling wherein strong mechanical forces plays significant role using the copper iodide, triphenyl phosphene and carbon nanotube precursors. The crude product obtained further purified by crystallization with hot toluene. The schematic presentation for the preparation of Cubane@CNT is presented in Fig. 1 (a). The pristine cubane is also prepared by the same procedure without using carbon nanotubes. Mechanism for cubane formation is as previously reported in the literature. The synthesis with a CuI: PPh₃ ratio of 1 : 3 yielded upon crystallization the monomer [CuI(PPh₃)₃] [33], but also a new polymorph [CuI(PPh₃)₃] which is a metastable form. A CuI: PPh₃ ratio of 1 : 2 yielded the dimer [CuI(PPh₃)_{1.5}]₂ [34] and, finally, a CuI: PPh₃ ratio of 1 : 1 yielded the crystallization of the cubane-like compounds [CuI(PPh₃)₄] [35]. The photographic images of synthesized cubane and cubane@CNT are shown in Fig. 1 (c) and (d) respectively.



In order to understand the phase purity the XRD measurements were carried out and the XRD patterns of cubane and cubane@CNT are illustrated in Fig. 1b manifesting the crystalline nature of cubane on CNT architecture. The signals for I-Cu are observed at 8 and 9 °A, whereas Cu-Cu signals appeared at 10 and 11 °A. The peaks at 16, 17 and 18 °A are ascribed to Cu-P. The weak signals emerge at 3 °A for I-Cu-I. The signals for the cubane are well agreeing with our earlier report [36]. Nevertheless, in case of cubane@CNT additional minor peaks observed for 002

plane of CNT at 25.2° as the 2θ value [37]. All the characteristic signals strongly support the formation of cubane@CNT. The results are well agreed with the theoretical studies [38] and also with literature report [39].

The surface morphology studies for the cubane@CNT are carried out by using TEM and SEM analysis the results are displayed in Figs. 2 and 3, respectively. The TEM images of various magnification are shown in Fig. 2a–c. The TEM micrographs (Fig. 2a–c) clearly demonstrate the successful integration of cubane clusters onto the CNT framework. At low magnification, the CNTs exhibit a uniform tubular morphology with well-defined walls, while higher magnification reveals cubane nanoparticles anchored along the nanotube surfaces. The intimate contact between cubane and CNT suggests efficient interfacial interactions, which are crucial for charge transfer during electrochemical processes. The high-resolution TEM (Fig. 2d) shows lattice fringes corresponding to the (002) plane of CNTs, with an interplanar spacing of ~0.34 nm, confirming the preservation of graphitic order. Additional fringes observed at ~0.21 nm can be attributed to cubane domains, validating their crystalline nature after ball milling and crystallization. The selected area electron diffraction (SAED) pattern (Fig. 2e) further indicates a semi-crystalline nature with concentric rings, consistent with the coexistence of ordered CNTs and polycrystalline cubane particles. The lattice parameters are calculated and presented in Fig. 2(f and g).

SEM analysis provides complementary evidence of the morphological features of the cubane@CNT composite. Pristine CNTs (Fig. 3a–c) display a typical entangled fibrous network, whereas after hybridization with cubane (Fig. 3d–f), a distinct surface roughness and granular decoration along the CNTs can be observed. The map sum spectrum (Fig. 3g) and elemental mapping (Fig. 3(h–l)) demonstrates homogeneous distribution of Cu, P, I, and C throughout the composite, confirming the uniform dispersion of cubane clusters across the CNT network. This uniformity is essential to avoid localized aggregation, thereby enhancing electrochemically active surface area and ensuring reproducibility of performance. The cubane nanoparticles appear as bright, uniformly dispersed islands on the nanotube scaffold, signifying

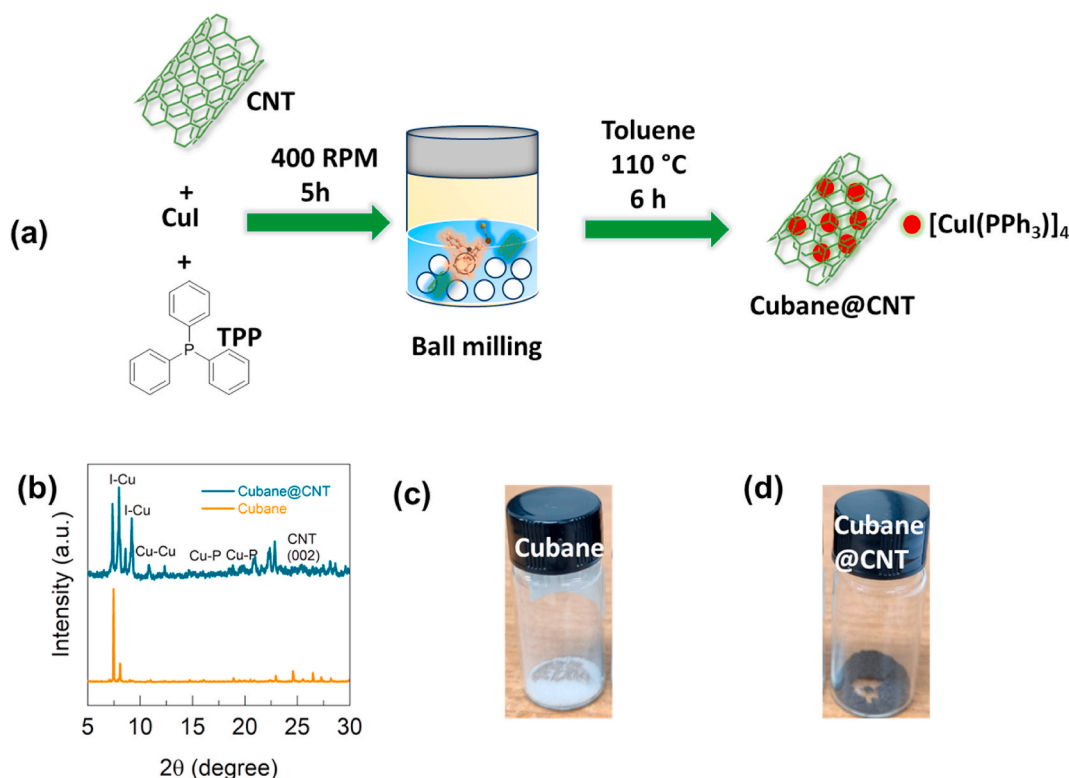


Fig. 1. (a) Scheme for the preparation of cubane@CNT by ball milling (b) XRD for cubane@CNT, photographic images of (c) cubane and (d) cubane@CNT

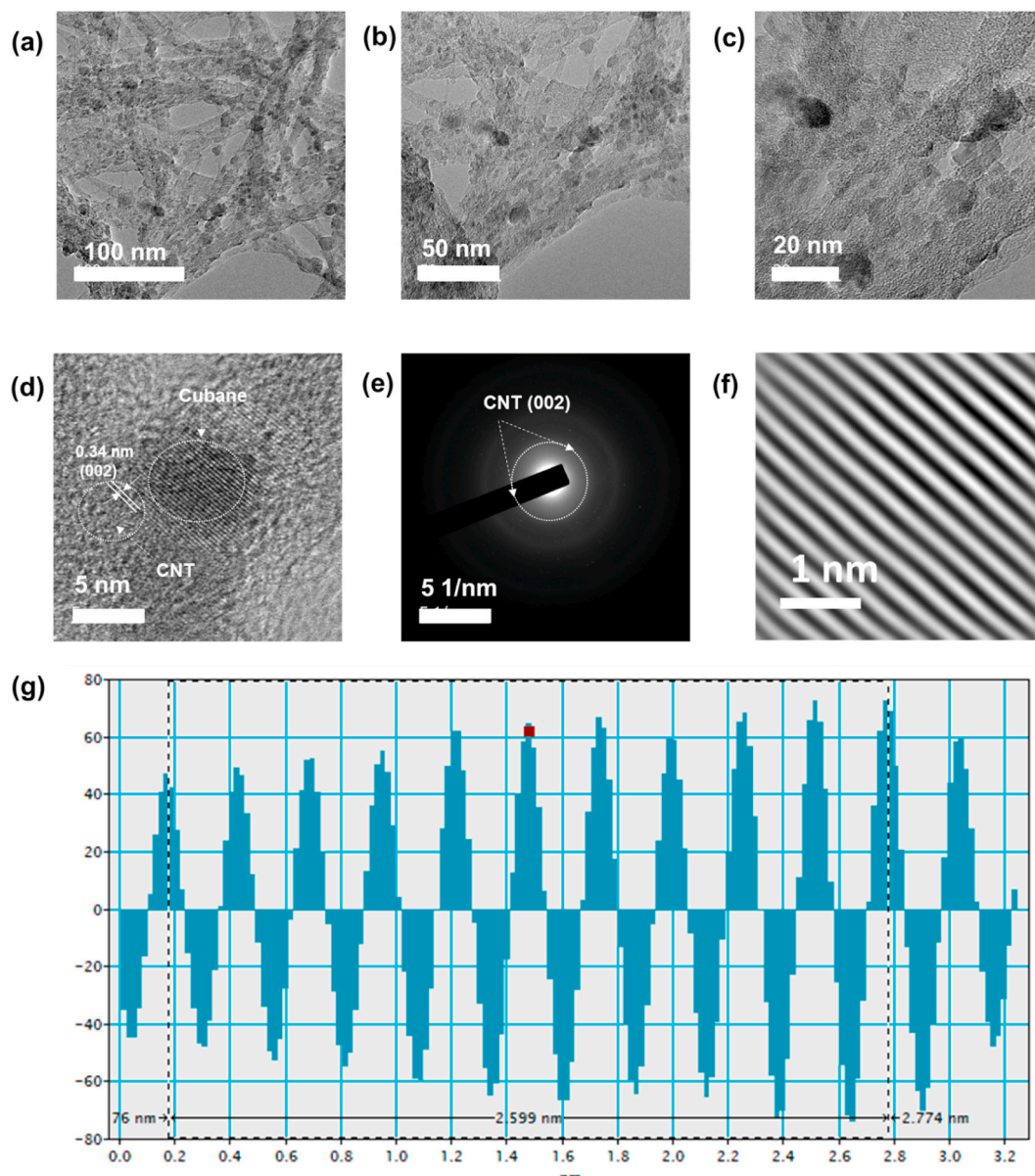


Fig. 2. (a–c) TEM images cubane@CNT with different magnifications, (d) HRTEM of cubane@CNT, (e) SAED pattern of cubane@CNT, (f–g) lattice parameters.

effective attachment without noticeable agglomeration. This architecture promotes enhanced electrolyte accessibility and short ion-diffusion paths. Moreover, the interlaced CNT framework serves as a mechanically robust skeleton that prevents cubane detachment during repeated charge–discharge cycles. The observed morphology thus supports the superior cycling stability of cubane@CNT, as the CNT backbone mitigates structural collapse while cubane provides abundant redox-active sites. The synergistic morphology, verified by SEM, underpins the high capacitance and long-term retention reported in the electrochemical measurements. The bulk nano islands of cubane are clearly seen on CNT as determined by the SEM and TEM analysis. SEM images for pristine cubane is displayed in Fig. S1.

The surface analysis of the cubane@CNT composite is determined by XPS analysis and presented in Fig. 4(a–d). The Cu 2p XPS spectrum is presented in Fig. 4 a show that there are two peaks at 953.5 and 932.4 eV corresponding to the Cu 2p_{1/2} and Cu 2p_{3/2}, respectively, confirming the existence of Cu in the sample [40]. The I 3 d spectrum is presented in Fig. 4 b demonstrated two peaks at binding energies 632.0 and 620.2 eV were assigned to I 3d_{3/2} and I 3d_{5/2} manifesting presence of I atom in the composite [41] As shown in Fig. 4 c the peak at binding energy 129.94

eV is allocated to P 2p of the composite [36]. The C1s XPS spectra is presented in Fig. 4 d shows two distinguishing peaks at 283.53 eV for sp² carbon particularly for materials like amorphous carbon of CNT and 284.7 for C–C carbon of triphenyl ring [42]. The shift in the Cu 2p peaks from 952.0 to 932.1 eV corresponding to the Cu 2p_{1/2} and Cu 2p_{3/2} to a higher binding energy of 953.5 and 932.4 eV followed by shift of P 2p from 130.2 eV to 129.94 eV indicates the formation of P–Cu bond. Thus, the surface analysis manifested the presence of Cu 2p, I 3 d, C 1s, and P 2p in the cubane@CNT which is well supported by SEM EDS analysis. BET estimation was utilized to examine the surface qualities of cubane and Cubane@CNT and presented in Fig. S2 indicating the enlarged surface area (438.6 cm³/g), which is greater than that of the of pristine Cubane NPs (102.3 cm³/g). Pure Cubane and Cubane@CNT fusion presented category of typical IV isotherms, which were attributed mesoporous material existed in both samples [43,44].

Fig. 5a–c presents the CV profiles of cubane and cubane@CNT electrodes, recorded in a three-electrode configuration at scan rates ranging from 10 to 100 mV/s within the potential window of –1 to 0.5 V vs. Ag/AgCl. The mass loading of active material was maintained at 1 mg/cm². CV curve demonstrates cubane and cubane@CNT electrode having

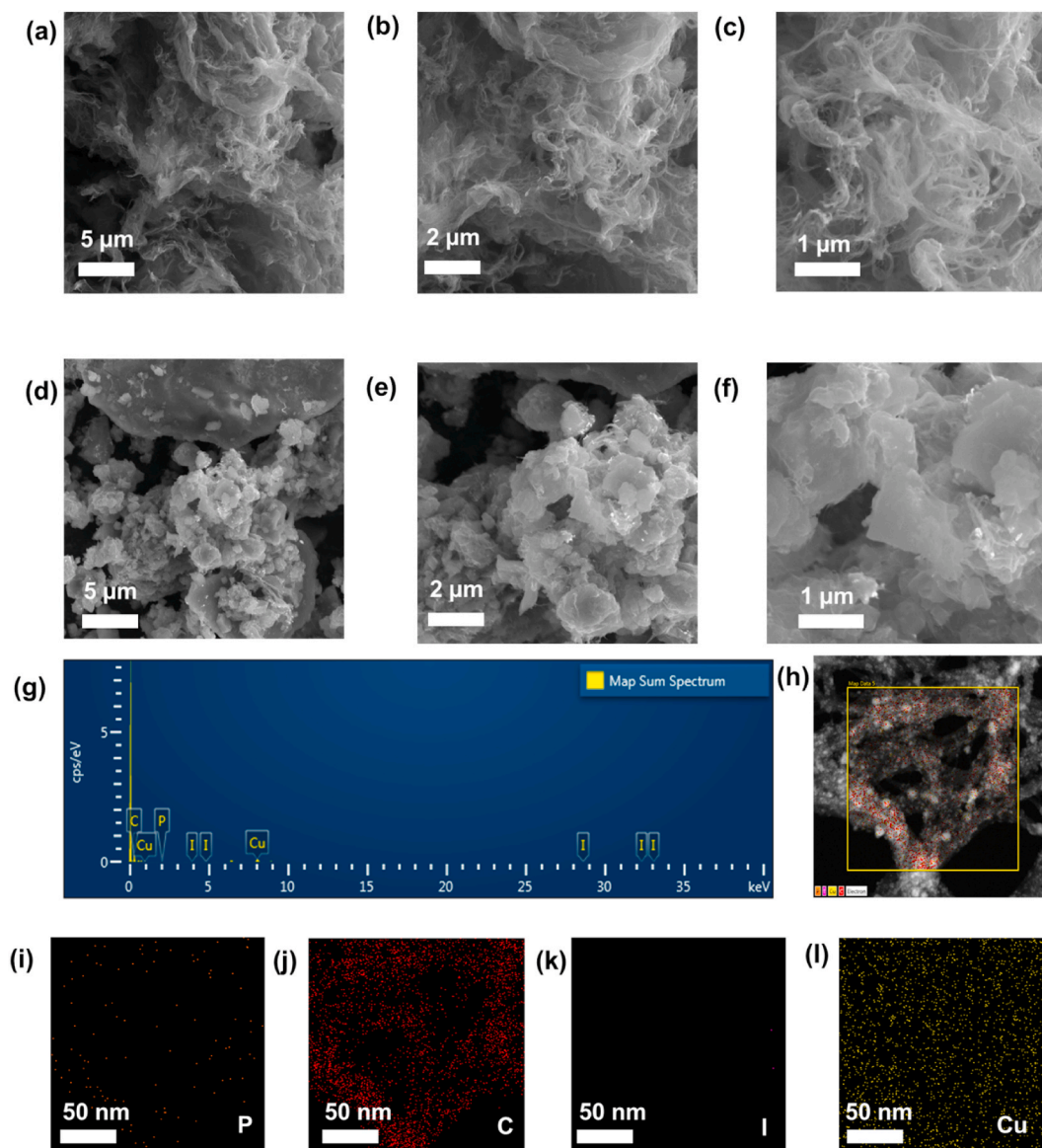


Fig. 3. SEM images for (a–c) CNT, (d–f) cubane@CNT, (g) sum map spectrum for cubane@CNT, (h–l) Mapping showing P, C, I, Cu.

potential sweeps from -1 to 0.5 V as unique appearance amongst compelling pair of redox peaks about the anodic and cathodic sites. The area enclosed by CV curve of cubane@CNT electrode is significantly larger compared to that of bare cubane electrode at 10 mV/s (Fig. 5a). This is due to CNTs provide a highly conductive network that improves electron transport, lowering internal resistance and enabling more efficient redox activity of cubane. Also, CNTs offer a porous, high-surface-area framework that exposes more active sites of cubane for electrochemical reactions. [45,46]

Fig. 5b and (c) show the CV curves of cubane and cubane@CNT electrodes respectively, investigated at various scan rates ranging from 10 to 100 mV/s within a -1 to 0.5 V vs Ag/AgCl potential window. It is observed that, with increasing scan rate up to 100 mV/s, the CV curves of electrodes exhibit a more rectangular shape. The absence of distinct redox peaks indicates charge storage mechanism is predominantly governed by an electric double-layer process. There is no change in CV shape for varying scan rates shows good rate capability of Cubane and Cubine@CNT electrode materials [47].

During the charge storage process, a large number of K^+ ions accumulate at the electrode–electrolyte interface, forming an electric double layer. In the case of the cubane@CNT electrode, the observed features

indicate that an interconnected architecture provides abundant and well-defined surface redox-active sites. These active sites are generated through the synergistic interaction between cubane and CNT, which not only enhances ion accessibility but also promotes efficient surface redox reactions. Moreover, the presence of defect-rich sites further contributes to improved charge storage by facilitating reversible faradaic processes [39].

From CV analysis the specific capacity of as fabricated electrodes has been investigated using equation below,

$$C_{sp} = \frac{\int I dV}{m \times dV \times \theta} \quad (5)$$

Where, $\int I dV$: area under the CV curve at specific scan rate, m: deposited mass of electrode material, dV: potential window, θ : scan rate.

The specific capacities of cubane calculated at different scan rates, 10 , 20 , 40 , 60 and 100 mV/s were found to be 103.5 F/g, 74.7 F/g, 54.6 F/g, 45.4 F/g, 39.9 F/g and 32.2 F/g respectively. In the case of cubane@CNT electrodes, the capacities determined were 139.1 F/g, 113.7 F/g, 89.1 F/g, 75.8 F/g, 68.4 F/g and 63.9 F/g respectively. It is observed that the specific capacity of cubane@CNT electrode (139.1 F/g) is higher than that of bare cubane electrode (103.5 F/g) at a scan rate of

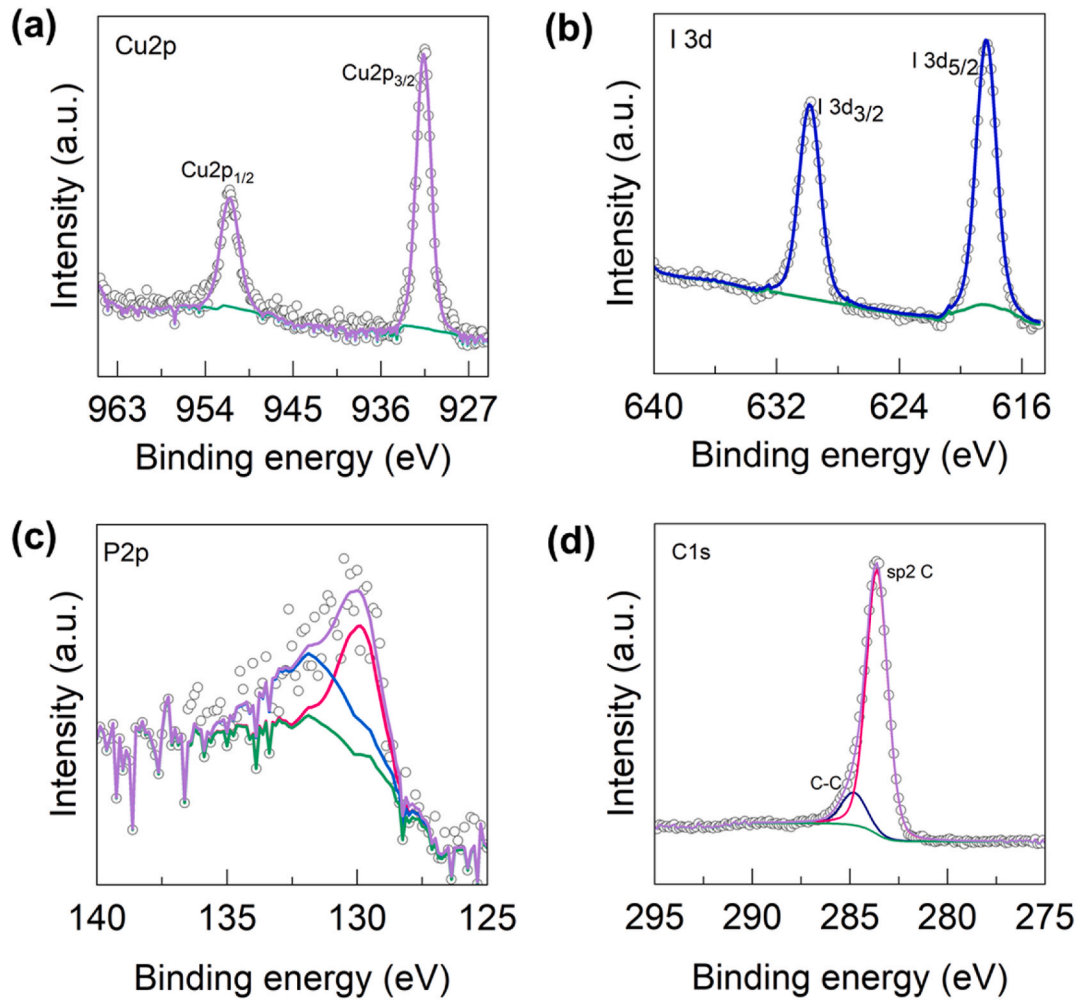


Fig. 4. XPS spectra for cubane@CNT, (a) Cu 2p, (b) I 3 d, (c) P 2p, (4) C1s.

10 mV/s. This corresponds to an increase in charge storage capacity of approximately 25 % upon compositing cubane with CNT.

The cubane@CNT composite exhibits a significantly enhanced capacitance compared to the individual components. This improvement arises from the synergistic interaction between cubane nanostructures and CNTs, which prevents aggregation of active materials, reduces CNT stacking, and provides a larger accessible electrochemical surface area. As a result, both the pseudocapacitance of cubane and the electric double-layer capacitance of CNTs are effectively utilized, leading to superior overall charge storage performance.

2.1. Charge storage kinetics

The charge storage kinetics of cubane and cubane@CNT electrodes were systematically evaluated from CV curves recorded at different scan rates, as shown in Fig. 5b and (c), using Dunn's method. The relationship between the scan rate (θ) and the corresponding current at a fixed potential was employed to distinguish the capacitive-controlled ($k_1\theta$) and diffusion-controlled ($k_2\theta^{1/2}$) contributions according to the following equation:

$$i = k_1 \theta + k_2 \theta^{1/2} \quad (6)$$

Fig. 5(h–i) presents the column graph illustrating the relative contributions of capacitive (EDLC) and diffusion-controlled (redox) processes within the total current at scan rates ranging from 10 mV/s to 100 mV/s. It is observed that the cubane electrode exhibits a dominant diffusion-controlled contribution of ~73.2 %. Upon compositing with

CNT, this contribution decreases to 59.1 %, which is consistent with the well-known EDLC characteristics of CNT-based materials. Furthermore, Fig. 5(h and i) highlights the increase in capacitive contribution for both cubane and cubane@CNT electrodes with increasing scan rates. Specifically, the capacitive fraction progressively enhances from 10 mV/s to 100 mV/s, confirming the faster charge transfer kinetics and improved surface-driven storage at higher scan rates.

Moreover, the energy storage and power delivery performance of electrode was investigated by measuring galvanostatic charge-discharge tests at different applied current density for electrode materials. Fig. 5d shows, GCD of cubane and cubane@CNT compared at 2 mA/cm² within a –1 to 0.5 V vs Ag/AgCl potential window. The shape of GCD curve seems to be nearly triangular confirms pseudocapacitive behavior of fabricated electrode material. The energy storage capacity of electrode in term of specific capacity (C_{sp}), energy density (ED), power density (PD) and etc. have been calculated based on GCD data using equations mentioned below [48–50].

$$C_{sp} = \frac{I \times dT}{m \times dV} \quad (7)$$

$$ED = \frac{1}{2 \times 3.6} C_{sp} \times dV^2 \quad (8)$$

$$PD = \frac{ED}{dT} \times 3600 \quad (9)$$

where, I: applied current density, dT: discharge time, m: deposited mass,

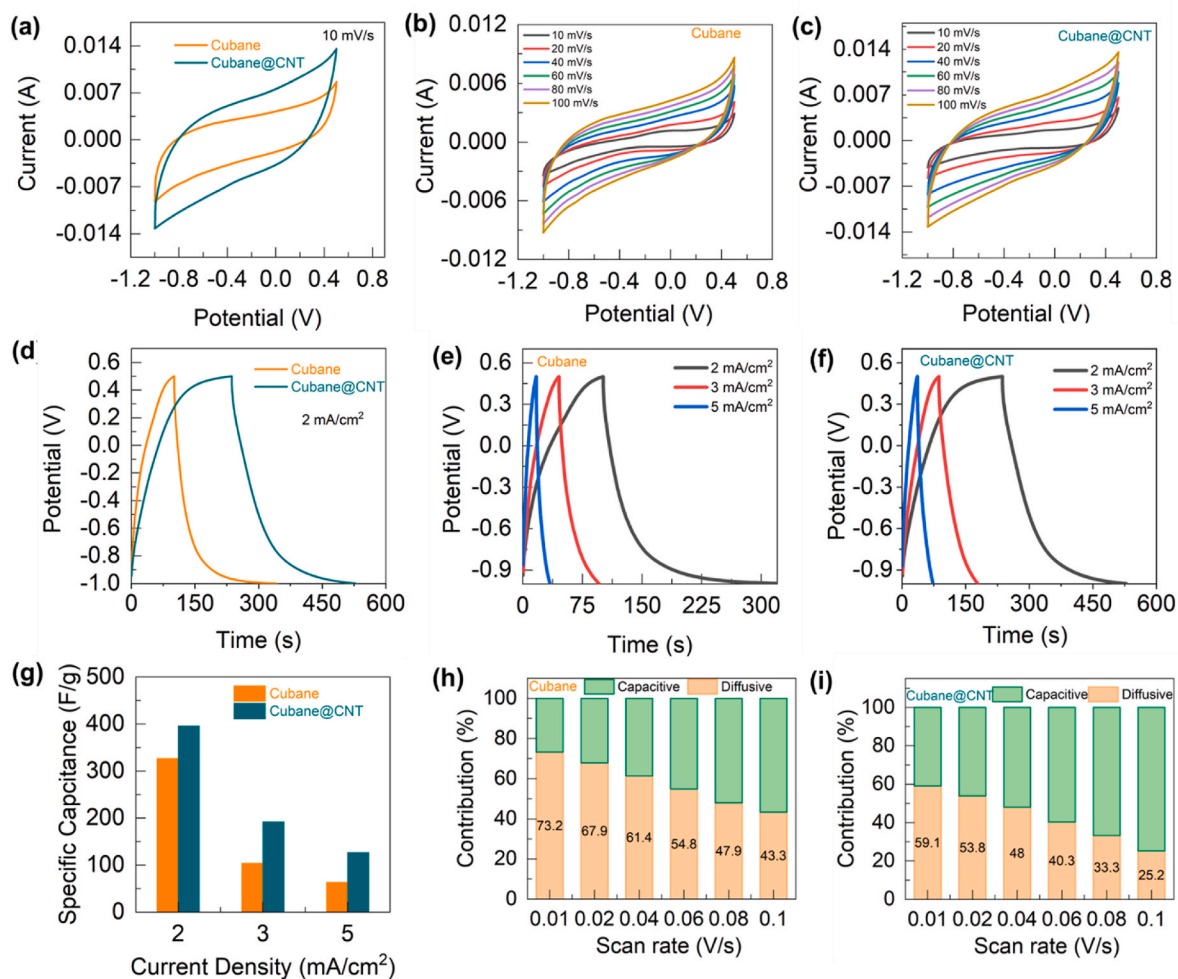


Fig. 5. (a) CV for cubane and cubane@CNT at 10 mV/s, (b) CV for cubane at 10 - 100 mV/s, (c) CV for cubane@CNT at 10 - 100 mV/s, (d) GCD for cubane and cubane@CNT at 2 mA/cm², (e) GCD for cubane at different current range, (f) GCD for cubane@CNT at different current range, (g) Specific capacitance of cubane and cubane@CNT, (h & i) charge storage kinetics of cubane and cubane@CNT electrodes at 10 - 100 mV/s.

and dV: potential window.

The calculated specific capacity from GCD curves of cubane and cubane@CNT is about 326 F/g and 396 F/g respectively, at 2 mA/cm² applied current density. The CNT network improves electrical conductivity and ion diffusion, reducing internal resistance. This enables more complete utilization of cubane's redox-active sites during

charge-discharge, which is reflected as extended discharge curves. The hybrid electrode benefits from the pseudocapacitance of cubane (surface redox reactions) and the EDLC from CNT (fast ion adsorption). Together, these effects broaden the discharge profile and increase the effective capacity.

In addition, the GCD curves of cubane and cubane@CNT electrodes

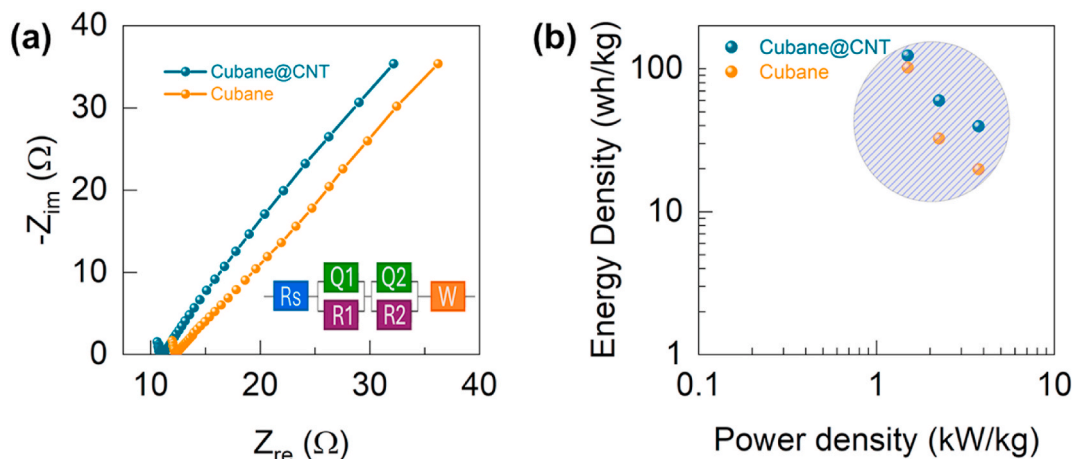


Fig. 6. (a) EIS for cubane and cubane@CNT, (b) Energy density vs. Power density for cubane and cubane@CNT.

were recorded at different current densities (2, 3, and 5 mA/cm²), as shown in Fig. 5(e and f). In case of cubane the specific capacitance observed were 326, 104 and 63 F/g whereas the corresponding cubane@CNT delivered 396, 192 and 126 F/g at 2, 3, and 5 mA/cm² respectively. It is observed that the specific capacity decreases with increasing current density, which is a typical behavior of electrode materials. The variation in specific capacity with current density is further illustrated in Fig. 5g through a column graph.

Electrochemical impedance spectroscopy (EIS) was also performed for both electrodes in the frequency range of 10⁵ Hz–0.1 Hz at open-circuit potential using a three-electrode system. The Nyquist plots are displayed in Fig. 6a, and the fitted data were analyzed using an equivalent circuit model. The bare cubane electrode shows an equivalent series resistance (ESR) of approximately 12.3 Ω, which is reduced to 11.0 Ω for the cubane@CNT composite. This reduction in resistance is attributed to the incorporation of CNTs, which provide efficient electron transport pathways within the composite matrix, thereby facilitating faster charge transfer. Furthermore, Fig. 6b presents the Ragone plots of the synthesized electrode materials, highlighting the relationship between energy density and power density at different current densities. The results confirm that the cubane@CNT composite exhibits enhanced energy and power density compared to bare cubane. Finally, the cycling durability of the electrodes during repeated redox processes was evaluated. Fig. S3 (a and b) presents the cyclic stability data of cubane and cubane@CNT electrodes, measured over 5000 cycles. Both electrodes exhibit excellent stability, with the cubane electrode retaining about 93 % of its initial capacitance, while the cubane@CNT composite demonstrates improved retention of 96.2 %. The enhanced stability of cubane@CNT is attributed to the CNTs, which act as a robust conductive scaffold, buffering the volume changes of cubane during charge–discharge cycling and maintaining structural integrity. The minor capacity loss (~3.8 %) observed in the composite is likely due to gradual surface degradation, side reactions, and slight resistance build-up caused by repeated ion insertion/extraction processes. Nonetheless, the cubane@CNT electrode clearly demonstrates superior long-term electrochemical stability compared to bare cubane.

3. Conclusion

In summary we adopted an eco-friendly green ball milling synthetic protocol to produce cubane@CNT for application in energy storage. The structural analysis revealed nanocluster architecture on CNT. The elevated supercapacitive performance of Cubane@CNT (396 F/g at 2 mA/cm²) is owing to its enlarged surface area which is greater than that of pristine cubane NPs determined by BET analysis. The high surface area and pores provides significant active sites, extremely permeable organization enabled ionic distribution in three electrode systems. The capacitances of bare cubane and cubane@CNT combination were almost 327 and 396 F/g, respectively at 2 mA/cm². The cubane and cubane@CNT also exhibited the capacitance retention of 93 % and 96.2 % after 5000 cycles at a current density of 2 mA/cm² respectively. This report establishes a technique for fabricating materials for energy storage applications. Ultimately, the present investigation confirms that cubane and cubane@CNT electrode materials are a viable choice for the fabrication of energy storage devices such as supercapacitors. Further extension of work such as structure modification and supercapacitor engineering are in progress to achieve even better results is in progress in our laboratory.

CRediT authorship contribution statement

Chinna Bathula: Writing – original draft, Data curation, Conceptualization. **Aviraj Teli:** Formal analysis. **Pranav Katkar:** Formal analysis. **Aditya Narayan Singh:** Formal analysis. **Soniya Naik:** Formal analysis. **Hyun-Seok Kim:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. RS-2024-00405691).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2025.238952>.

Data availability

Data will be made available on request.

References

- [1] J. Tian, S.A. Culley, H.R. Maier, A.C. Zecchin, Is renewable energy sustainable? Potential relationships between renewable energy production and the sustainable development goals, *npj Climate Action* 3 (2024) 35, <https://doi.org/10.1038/s44168-024-00120-6>.
- [2] J.B. Goodenough, How we made the Li-ion rechargeable battery, *Nat. Electron.* 1 (2018), <https://doi.org/10.1038/s41928-018-0048-6>, 204–204.
- [3] A.N. Singh, M. Islam, A. Meena, M. Faizan, D. Han, C. Bathula, A. Hajibabaei, R. Anand, K.W. Nam, Unleashing the potential of sodium-ion batteries: current state and future directions for sustainable energy storage, *Adv. Funct. Mater.* 33 (2023) 2304617, <https://doi.org/10.1002/adfm.202304617>.
- [4] A.N. Singh, M.H. Kim, A. Meena, T.U. Wi, H.W. Lee, K.S. Kim, Na/Al codoped layered cathode with defects as bifunctional electrocatalyst for high-performance Li-ion battery and oxygen evolution reaction, *Small* 17 (2021) 2005605, <https://doi.org/10.1002/smll.202005605>.
- [5] Z. Liang, J. He, C. Hu, X. Pu, H. Khani, L. Dai, D. Fan, A. Manthiram, Z.-L. Wang, Next-generation energy harvesting and storage technologies for robots across all scales, *Advanced Intelligent Systems* 5 (2023) 2200045, <https://doi.org/10.1002/aisy.202200045>.
- [6] P. Wei, M. Abid, H. Adun, D. Kemena Awoh, D. Cai, J.H. Zaini, O. Bamisile, Progress in energy storage technologies and methods for renewable energy systems application, *Appl. Sci.* 13 (2023) 5626.
- [7] A.N. Singh, K. Hassan, C. Bathula, K.W. Nam, Decoding the puzzle: recent breakthroughs in understanding degradation mechanisms of Li-ion batteries, *Dalton Trans.* 52 (2023) 17061–17083, <https://doi.org/10.1039/d3dt02957c>.
- [8] K. Dissanayake, D. Kularatna-Abeywardana, A review of supercapacitors: materials, technology, challenges, and renewable energy applications, *J. Energy Storage* 96 (2024) 112563, <https://doi.org/10.1016/j.est.2024.112563>.
- [9] D.P. Chatterjee, A.K. Nandi, A review on the recent advances in hybrid supercapacitors, *J. Mater. Chem. A* 9 (2021) 15880–15918, <https://doi.org/10.1039/D1TA02505H>.
- [10] H.W. Park, K.C. Roh, Recent advances in and perspectives on pseudocapacitive materials for Supercapacitors—A review, *J. Power Sources* 557 (2023) 232558, <https://doi.org/10.1016/j.jpowsour.2022.232558>.
- [11] F. Ahmad, A. Shahzad, M. Danish, M. Fatima, M. Adnan, S. Atiq, M. Asim, M. A. Khan, Q.U. Ain, R. Perveen, Recent developments in transition metal oxide-based electrode composites for supercapacitor applications, *J. Energy Storage* 81 (2024) 110430, <https://doi.org/10.1016/j.est.2024.110430>.
- [12] O. Öztürk, E. Gür, Layered transition metal sulfides for supercapacitor applications, *Chemelectrochem* 11 (2024) e202300575, <https://doi.org/10.1002/celec.202300575>.
- [13] S. Sardana, A. Gupta, K. Singh, A.S. Maan, A. Ohlan, Conducting polymer hydrogel based electrode materials for supercapacitor applications, *J. Energy Storage* 45 (2022) 103510, <https://doi.org/10.1016/j.est.2021.103510>.
- [14] J. Liu, J. Wang, C. Xu, H. Jiang, C. Li, L. Zhang, J. Lin, Z.X. Shen, Advanced energy storage devices: basic principles, analytical methods, and rational materials design, *Adv. Sci.* 5 (2018) 1700322.
- [15] R.R. Palem, S. Ramesh, I. Rabani, G. Shimoga, C. Bathula, H.S. Kim, Y.-S. Seo, H.-S. Kim, S.-H. Lee, Microstructurally assembled transition metal oxides with cellulose nanocrystals for high-performance supercapacitors, *J. Energy Storage* 50 (2022) 104712.
- [16] S. Hussain, I. Rabani, D. Vikraman, A. Feroze, K. Karuppasamy, Z.u. Haq, Y.-S. Seo, S.-H. Chun, H.-S. Kim, J. Jung, Hybrid design using carbon nanotubes decorated with Mo₂C and W₂C nanoparticles for supercapacitors and hydrogen evolution reactions, *ACS Sustain. Chem. Eng.* 8 (2020) 12248–12259.

- [17] N. Hillier, S. Yong, S. Beeby, The good, the bad and the porous: a review of carbonaceous materials for flexible supercapacitor applications, *Energy Rep.* 6 (2020) 148–156.
- [18] E. Lim, C. Jo, J. Lee, A mini review of designed mesoporous materials for energy-storage applications: from electric double-layer capacitors to hybrid supercapacitors, *Nanoscale* 8 (2016) 7827–7833.
- [19] X. Ma, Y. Dong, C. He, N. Jiang, Y. Yang, Integration of carbon nanotubes and azo-coupled redox-active polymers into core-shell structured cathodes with favorable lithium storage, *Mater. Adv.* 3 (2022) 5818–5825.
- [20] J. Zhang, F. Liu, J. Cheng, X. Zhang, Binary nickel-cobalt oxides electrode materials for high-performance supercapacitors: influence of its composition and porous nature, *ACS Appl. Mater. Interfaces* 7 (2015) 17630–17640.
- [21] Q. Meng, K. Cai, Y. Chen, L. Chen, Research progress on conducting polymer based supercapacitor electrode materials, *Nano Energy* 36 (2017) 268–285.
- [22] H. Cheng, Y.-Z. Su, P.-Y. Kuang, G.-F. Chen, Z.-Q. Liu, Hierarchical NiCo₂O₄ nanosheet-decorated carbon nanotubes towards highly efficient electrocatalyst for water oxidation, *J. Mater. Chem. A* 3 (2015) 19314–19321, <https://doi.org/10.1039/C5TA03985A>.
- [23] L. Wang, C. Lin, T. Liang, N. Wang, J. Feng, W. Yan, NiSe₂ encapsulated in N-doped TiN/carbon nanoparticles intertwined with CNTs for enhanced Na-ion storage by pseudocapacitance, *Ceram. Int.* 48 (2022) 14098–14106, <https://doi.org/10.1016/j.ceramint.2022.01.295>.
- [24] S. Li, J. Luo, J. Wang, Y. Zhu, J. Feng, N. Fu, H. Wang, Y. Guo, D. Tian, Y. Zheng, et al., Hybrid supercapacitors using metal-organic framework derived nickel-sulfur compounds, *J. Colloid Interface Sci.* 669 (2024) 265–274, <https://doi.org/10.1016/j.jcis.2024.04.205>.
- [25] N. Muralidharan, E. Teblum, A.S. Westover, D. Schauben, A. Itzhak, M. Muallem, G.D. Nessim, C.L. Pint, Carbon nanotube reinforced structural composite supercapacitor, *Sci. Rep.* 8 (2018) 17662, <https://doi.org/10.1038/s41598-018-34963-x>.
- [26] A.T.A. Ahmed, R. Soni, A.S. Ansari, C.Y. Lee, H.-S. Kim, H. Im, C. Bathula, Biowaste-derived graphitic carbon interfaced TiO₂ as anode for lithium-ion battery, *Surf. Interfaces* 35 (2022) 102404.
- [27] S.S.Y. Law, G. Liou, Y. Nagai, J. Giménez-Dejor, A. Tateishi, K. Tsuchiya, Y. Kodama, T. Fujigaya, K. Numata, Polymer-coated carbon nanotube hybrids with functional peptides for gene delivery into plant mitochondria, *Nat. Commun.* 13 (2022) 2417, <https://doi.org/10.1038/s41467-022-30185-y>.
- [28] J. Meena, S.S. Sivasubramaniam, E. David, S. K. Green supercapacitors: review and perspectives on sustainable template-free synthesis of metal and metal oxide nanoparticles, *RSC Sustain.* 2 (2024) 1224–1245, <https://doi.org/10.1039/d4su00009a>.
- [29] Y. Wang, X. Bai, W. Wang, Y. Lu, F. Zhang, B. Zhai, X. Wang, Y. Song, Ball milling-assisted synthesis and electrochemical performance of porous carbon with controlled morphology and graphitization degree for supercapacitors, *J. Energy Storage* 38 (2021) 102496, <https://doi.org/10.1016/j.est.2021.102496>.
- [30] K. Naseem, Z. Ali, P. Chen, A. Tahir, F. Qin, A. Fayyaz, M.D. Albaqami, S. Mohammad, B. Akkinepally, S. Ali, M.S. Javed, Supercapacitive behavior and energy storage properties of molybdenum carbide ceramics synthesized via ball milling technique, *Ceram. Int.* 50 (2024) 9572–9580, <https://doi.org/10.1016/j.ceramint.2023.12.276>.
- [31] S. Khan, S. Chand, C. Chakraborty, Ultramicroporous Co(II)-Squarate framework with Co₄(μ₃-OH)₄ cubane structures: a pseudocapacitor electrode for advanced energy storage devices, *Chem. Eng. J.* 516 (2025) 164232, <https://doi.org/10.1016/j.cej.2025.164232>.
- [32] B. Chinna, R. Iqra, K. Abhijit, O. Henry, P. Supriya, K.S. Nabeen, H. Jung-Hoon, S. Young-Soo, K. Hyun-Seok, Sonochemically exfoliated polymer-carbon nanotube interface for high performance supercapacitors, *J. Colloid Interface Sci.* 606 (2022) 1792–1799, <https://doi.org/10.1016/j.jcis.2021.08.136>.
- [33] P.F. Barron, J.C. Dyason, P.C. Healy, L.M. Engelhardt, C. Pakawatchai, V. A. Patrick, A.H. White, Lewis-base adducts of Group 11 metal(I) compounds. Part 28. Solid-state phosphorus-31 cross-polarization magic-angle spinning nuclear magnetic resonance and structural studies on the mononuclear 3: 1 adducts of triphenylphosphine with copper(I) halides, *J. Chem. Soc., Dalton Trans.* (1987) 1099–1106, <https://doi.org/10.1039/DT9870001099>.
- [34] P.G. Eller, G.J. Kubas, R.R. Ryan, Synthesis and properties of sulfur dioxide adducts of organophosphinecopper(I) iodides. Structures of the dinuclear compounds tetrakis(methyldiphenylphosphine)di-μ₂-iodo-dicopper(I)-sulfur dioxide and tris(triphenylphosphine)di-μ₂-iodo-dicopper(I), *Inorg. Chem.* 16 (1977) 2454–2462, <https://pubs.acs.org/doi/10.1021/ic50176a006>.
- [35] J.C. Dyason, P.C. Healy, L.M. Engelhardt, C. Pakawatchai, V.A. Patrick, C. L. Raston, A.H. White, Lewis-base adducts of Group 1B metal(I) compounds. Part 16. Synthesis, structure, and solid-state phosphorus-31 nuclear magnetic resonance spectra of some novel [Cu₄X₄L₄](X = halogen, L = N, P base)‘cubane’ clusters, *J. Chem. Soc., Dalton Trans.* (1985) 831–838, <https://doi.org/10.1039/DT9850000831>.
- [36] G.S. Vijaya, N. Soniya, J. Atanu, K. Abhijit, S. Sankar, I. Hyunsik, K. Hyun-Seok, S. Jung Inn, B. Chinna, Mechanochemically interlocked cubane copper complex interface for WOLED, *J. Colloid Interface Sci.* 633 (2023) 589–597, <https://doi.org/10.1016/j.jcis.2022.11.125>.
- [37] C. Bathula, I. Rabani, S. Ramesh, S.-H. Lee, R.R. Palem, A.T.A. Ahmed, H.S. Kim, Y.-S. Seo, H.-S. Kim, Highly efficient solid-state synthesis of Co₃O₄ on multiwalled carbon nanotubes for supercapacitors, *J. Alloys Compd.* 887 (2021) 161307, <https://doi.org/10.1016/j.jcis.2022.11.125>.
- [38] H. Kitagawa, Y. Ozawa, K. Toriumi, Flexibility of cubane-like Cu₄L₄ framework: temperature dependence of molecular structure and luminescence thermochromism of [Cu₄L₄(PPh₃)₄] in two polymorphic crystalline states, *Chem. Commun.* 46 (2010) 6302–6304, <https://doi.org/10.1039/C0CC01434F>.
- [39] L. Zhang, F. Lin, M. Ye, D. Tian, J. Jin, Y. Huang, Y. Jiang, Y. Wang, X. Chen, Luminescence sensing of oxygen using copper iodide hybrid material, *Sens. Actuators, B* 346 (2021) 130566, <https://doi.org/10.1016/j.snb.2021.130566>.
- [40] P. Wei, L. Lingxia, Y. Shihui, Z. Haoran, Y. Pan, Structure, binding energy and optoelectrical properties of p-type CuI thinfilms: the effects of thickness, *Appl. Surf. Sci.* 502 (2020) 144424, <https://doi.org/10.1016/j.apsusc.2019.144424>.
- [41] X.C. Adriele, R.B. Devina Krystel, W. Yue, L. He-Kuan, Y. Yi Yan, L. Ning, Fast-acting and skin-compatible antimicrobial coating on CottonFabrics via in situ self-assembly of phosphine-coordinated copper iodide clusters, *ACS Appl. Eng. Mater.* 2 (2024) 2864–2874, <https://doi.org/10.1021/acsaenm.4c00548>.
- [42] V. Sydorochuk, O.I. Poddubnaya, M.M. Tsyba, O. Zakutnevskyy, O. Khyzhun, S. Khalameida, A.M. Puziy, Photocatalytic degradation of dyes using phosphorus-containing activated carbons, *Appl. Surf. Sci.* 535 (2021) 147667, <https://doi.org/10.1016/j.apsusc.2020.147667>.
- [43] J. Yu, G. Wang, B. Cheng, M. Zhou, Effects of hydrothermal temperature and time on the photocatalytic activity and microstructures of bimodal mesoporous TiO₂ powders, *Appl. Catal. B Environ.* 69 (2007) 171–180, <https://doi.org/10.1016/j.apcatb.2006.06.022>.
- [44] J. Yan, Y. Huang, Y. Yan, X. Zhao, P. Liu, The composition design of MOF-derived Co-Fe bimetallic autocatalysis carbon nanotubes with controllable electromagnetic properties, composite part A, *Appl. Sci. and Manufacturing* 139 (2020) 106107, <https://doi.org/10.1016/j.compositesa.2020.106107>.
- [45] V. Kakani, S. Ramesh, H.M. Yadav, A. Kumar, S. Shinde, S. Sandhu, L.N.D. Quang, H.S. Kim, H.-S. Kim, H. Kim, Facile synthesis of CuO/NiO/nitrogen doped rGO by ultrasonication for high performance supercapacitors, *J. Alloys Compd.* 847 (2020) 156411, <https://doi.org/10.1016/j.jallcom.2020.156411>.
- [46] A. De Adhikari, A. Morag, J. Seo, J.M. Kim, R. Jelinek, Polydiacetylene-perylenediimide supercapacitors, *ChemSusChem* 13 (2020) 3230–3236, <https://doi.org/10.1002/cssc.202000440>.
- [47] Y. Liu, J. Zhou, J. Tang, W. Tang, Three-dimensional, chemically bonded polypyrrole/bacterial cellulose/graphene composites for high-performance supercapacitors, *Chem. Mater.* 27 (2015) 7034–7041, <https://doi.org/10.1021/acs.chemmater.5b03060>.
- [48] I. Rabani, S. Hussain, D. Vikraman, Y.-S. Seo, J. Jung, A. Jana, N.K. Shrestha, M. Jalalah, Y.-Y. Noh, S.A. Patil, 1D-CoSe₂ nanoarray: a designed structure for efficient hydrogen evolution and symmetric supercapacitor characteristics, *Dalton Trans.* 49 (2020) 14191–14200, <https://doi.org/10.1039/D0DT02548H>.
- [49] I. Rabani, J. Yoo, C. Bathula, S. Hussain, Y.-S. Seo, The role of uniformly distributed ZnO nanoparticles on cellulose nanofibers in flexible solid state symmetric supercapacitors, *J. Mater. Chem. A* 9 (2021) 11580–11594, <https://doi.org/10.1039/D1TA01644J>.
- [50] A.W. Lang, J.F. Ponder, A.M. Österholm, N.J. Kennard, R.H. Bulloch, J. R. Reynolds, Flexible, aqueous-electrolyte supercapacitors based on water-processable dioxathiophene polymer/carbon nanotube textile electrodes, *J. Mater. Chem. A* 5 (2017) 23887–23897, <https://doi.org/10.1039/C7TA07932J>.