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Enhancement of the electrochemical response of a V_2O_5 integrated biochar@poly(aniline–pyrrole) hybrid composite-coated graphite electrode

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The fabrication of sustainable electrode materials with high specific capacitance values is essential for designing energy-efficient supercapacitors. With this aim, herein, V_2O_5 -integrated biochar@poly(aniline–pyrrole), named the BC@CCp@ V_2O_5 hybrid composite, is evaluated as an electrode material. First, biochar (BC) is prepared *via* a simple hydrothermal treatment of sucrose solution. Then, conducting poly(aniline–pyrrole) (CCp) is incorporated *via* a seeded chemical oxidation method to yield BC@CCp composite particles. Finally, the BC@CCp composite is thoroughly blended with calcined V_2O_5 at a composite to V_2O_5 (w/w) ratio of 4:1. The morphology and surface composition of the BC@CCp@ V_2O_5 hybrid composite are analyzed and confirmed *via* electron microscopy and various spectral analyses. The electrochemical properties of BC@CCp, calcined V_2O_5 and the BC@CCp@ V_2O_5 -coated graphite electrode are measured and compared. According to galvanostatic charge discharge (GCD) measurements, the BC@CCp@ V_2O_5 -coated electrode shows an exceptionally high capacitance value of 4150.6 F g^{-1} at a current density of 1.0 A g^{-1} . The BC@CCp@ V_2O_5 -coated electrode also demonstrates excellent capacitance retention (134%) at 10.0 A g^{-1} after 1000 charge–discharge cycles. This significant enhancement in the capacitance and stability is achieved owing to the combination of the individual components' properties and the synergistic interplay between calcined V_2O_5 and the active centers of BC@CCp. These observations represent a significant advancement in the design of sustainable BC@CCp@ V_2O_5 electrode materials for application in energy-efficient supercapacitor devices.

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1. Introduction

Scientists and engineers are showing great concern towards energy and environmental problems, which has encouraged them to develop sustainable, eco-friendly energy future and energy-storage facilities. Among the energy storage facilities, electrochemical capacitors have attracted considerable attention because of their low ohmic equivalent series resistance, fast and reversible charge–discharge capability, high specific capacitance, high power density, high cycle stability, minimum maintenance costs and green technology.^{1–3} Supercapacitors are promising in developing a wide range of items, including

electronic devices, uninterruptible power supplies (UPSs), fuel cell vehicles, electric vehicles and large-scale smart electric grids. Supercapacitors are of two types based on their energy storage mechanisms. One type is electrical double-layer capacitors (EDLCs), which store energy *via* the adsorption–desorption of electrostatic ions at the electrode–electrolyte interface. The other is pseudocapacitors (PCs), which store energy through quick and reversible faradaic redox reactions occurring at the subsurface of electrode materials.^{4,5} Generally, PC electrode materials made from conducting polymers and metal oxides possess superior specific capacitances than EDLC electrode materials (*e.g.*, carbon-rich materials). Therefore, the combination of EDLC and PC materials will afford hybrid supercapacitor electrode materials with extraordinary charge storage capacities and high cycle stability and energy density.

Biochar (BC), a carbon-rich material, is a potential environment-friendly EDLC electrode material. Additionally, the regulation of the surface area, morphology and functionality of BC enables the design of numerous materials for applications in soil reclamation and energy storage and as adsorbents, catalysts, and supports for catalysts.^{6–12} However, the native BC electrode is not suitable for fabricating high energy storage

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devices because of its poor electrical conductivity, initial faradaic losses and swelling during cell reactions.¹³ Therefore, it has become mandatory to enhance the efficiency of BC-derived electrode materials through chemical modification. It has already been proven that conducting polymers, such as pyrrole (Py), aniline (Ani) and thiophene (PTh), containing π -conjugated double bonds can enhance redox reactions and charge-storage capacities.^{14–16} For example, BC combined with a conducting polymer and a metal oxide can generate electrode materials with a high energy storage capacity.^{12,16} The strong compatibility of carbon-rich BC with conducting polymers as well as the bonding of metal oxides with the electron-rich heteroatom of conducting polymers can introduce strong synergistic interactions among the individual components for stable composite formation. Hence, the designed materials will have a conducting backbone with improved electrical conductivity.¹⁷ Furthermore, the strong synergistic interaction will prevent the destruction of the conducting polymer backbone after repeated inclusion and exclusion of counter ions during the redox reactions. In return, the fabricated BC/conducting polymer/metal oxide hybrid composite will exhibit good cyclability, electrical conductivity, mechanical stability and distinct redox reactions when used as electrode materials in energy storage devices.

So far, different types of metal oxides, *e.g.*, Y_2O_3 , ZnO , CoO , SnO_2 , NiO , CeO_2 , WO_3 , Fe_3O_4 , TiO_2 , and V_2O_5 , have been employed for preparing conducting polymer composites, and some have been tested for supercapacitor applications.^{16,18–26} Among these metal oxides, vanadium pentoxide (V_2O_5) shows promising properties for supercapacitor applications, including high theoretical capacitance, different oxidation states (V^{2+} , V^{3+} , V^{4+} and V^{5+}), relatively low prices, multilayered structures and acceptable toxicity.^{27,28} Based on these advantages of V_2O_5 , a mechanical approach for its integration into BC-supported conducting polymers is developed in this study. In some research studies, the improvement in the performance of carbon/ V_2O_5 composites used as supercapacitor electrodes has already been discussed. For example, Saravanakumar *et al.* designed carbon-coated V_2O_5 ($\text{C@V}_2\text{O}_5$) and reported a higher capacitance, a superior rate capacity, lower charge transfer hindrance and better capacitance retention.²⁹ Li *et al.* created abundant oxygen vacancies in a V_2O_{5-x} @carbon cathode *via* the plasma-enhanced chemical vapor deposition method for applications in high-energy-density aqueous zinc-ion batteries.³⁰ Zhang *et al.* observed the enhancement in the specific capacitance of the 3D porous network structure of reduced graphene oxide/ V_2O_5 caused by better electron transfer between the electrode and electrolyte.³¹ Lee *et al.* also observed an improvement in the specific capacitance, energy density and cycle stability of a graphene/ V_2O_5 composite electrode.³² Identical observations were also reported for other carbon materials including carbon nanotubes and multiwalled carbon nanotubes.^{33–35} Very recently, Vishwakarma *et al.* observed a significant improvement in the specific capacitance (737 F g^{-1} at 1 A g^{-1}) of a 10% graphene-oxide-doped V_2O_5 nanocomposite electrode prepared under microwave irradiation.³⁶ Some researchers have studied the integration of V_2O_5 with

conducting polymers for energy storage applications. Shao *et al.* used the layer-by-layer technique to assemble hybrid electrodes comprising $\text{PAni-V}_2\text{O}_5$ and observed the electrochemical response from both components.³⁷ Wang and his group prepared a PPy-encapsulated V_2O_5 nanowire membrane and observed higher supercapacitive performance.³⁸ Tong *et al.* developed a core-shell-type $\text{V}_2\text{O}_5/\text{PAni}$ nanofiber and found a synergistic improvement in the electron transport and mechanical properties for energy storage.³⁹ Li *et al.* intercalated conductive poly(3,4-ethylenedioxythiophene) into V_2O_5 for enhancing the electron transport property and structural stability in zinc-ion batteries.⁴⁰ Bi *et al.* improved the electrochemical performance *via* the generation of oxygen vacancies in V_2O_5 coated with a conducting polymer.⁴¹ From this literature survey, it is evident that either carbon materials or conducting polymer in combination with V_2O_5 have been investigated for composite formation and applications in supercapacitor devices. However, to date, little attention has been given to the fabrication of supercapacitor electrodes that contain carbon-rich materials, conducting polymers and V_2O_5 . In only one research study, Tabrizi and his group designed PAni nanoarrays on a graphene oxide sheet using V_2O_5 and ammonium persulfate as dual oxidants.⁴² They observed a significant improvement in the specific capacitance (712 F g^{-1} at 0.5 A g^{-1} in $1 \text{ M H}_2\text{SO}_4$).

In this study, $\text{BC@CCp@V}_2\text{O}_5$ (CCp stands for 'conducting Ani-Py copolymer') hybrid composite particles are prepared and evaluated for potential use as a sustainable electrode material in supercapacitors. The objective of incorporating the Ani-Py copolymer, instead of a homopolymer, is to increase the structural uniformity of copolymer chains, π -conjugation and final conductivity.^{12,43} According to this investigation, it is also possible to accommodate the distinct advantages of PAni and PPy in one matrix.⁴⁴ It is important to mention that BC, a low-cost biomass, has not been studied for hosting CCp and V_2O_5 . More precisely, no such three-component hybrid system, *i.e.*, V_2O_5 -integrated BC@CCp , has been evaluated as an electrode material for applications in batteries. First, BC was prepared by the hydrothermal heat treatment of a sucrose solution, a comparatively safe natural material. Then, BC@CCp was obtained by the redox-initiator-activated chemical oxidation of aniline and pyrrole using BC as core particles. Finally, the final $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite was obtained by only mechanically blending the washed and dried BC@CCp powder with the calcined V_2O_5 powder in a w/w ratio of 4:1. The preparation scheme is presented in Fig. 1. The composite formation was examined using electron microscopy, Fourier transform IR (FTIR) spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The overall spectral and image analyses confirmed the generation of (Ani-Py) copolymer realms and the integration of V_2O_5 on the BC surface. A graphite rod was coated with the $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite, and its electrochemical performance was compared with the respective BC@CCp composite and calcined V_2O_5 -coated graphite rod. The coating of the $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite resulted in a remarkable improvement in the specific capacitance, cycle stability and rate capacity along with



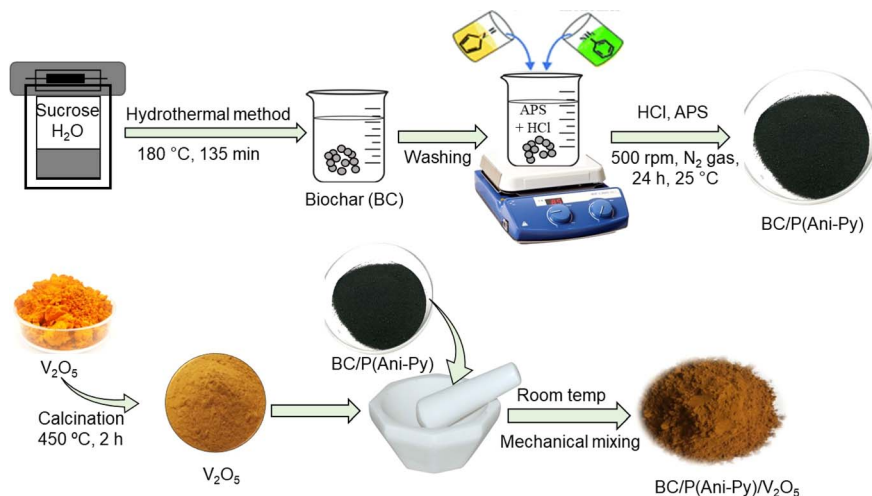


Fig. 1 Synthesis scheme for the BC@CCp@V₂O₅ hybrid composite.

a reduction in the charge transfer resistance. Specifically, the BC@CCp@V₂O₅-coated graphite electrode displayed fast charging and comparatively slow discharging, a prerequisite for energy-efficient storage devices.

2. Materials and method

2.1. Materials

Monomer-grade aniline and pyrrole and reagent-grade sucrose, procured from Sigma-Aldrich Chemie GmbH, USA, were used as received. Analytical-grade V₂O₅ was purchased from Merck, India, for preparing the hybrid composite. Ammonium persulfate ((NH₄)₂S₂O₈) and HCl from Merck, India, were utilized as the oxidant and dopant, respectively. The non-ionic Triton X-405 surfactant, purchased from Sigma-Aldrich Chemie GmbH, USA, was used to stabilize the composite suspension. KCl (Merck, India) was used as the electrolyte during electrochemical analysis. The polyvinylidene fluoride (PVDF) binder and *N*-methyl-2-pyrrolidone (NMP), procured from Sigma-Aldrich Chemie GmbH, USA, were employed to coat the graphite working electrode. Distilled deionized (DD) water was collected from a water purification unit (Puricom, Taiwan) installed in the department.

2.2. Preparation of BC core particles

A suspension of BC core particles was obtained *via* the hydrothermal treatment of a sucrose solution, according to our previous study.¹² In detail, 100 mL of a sucrose solution (0.8 M) in DD water was taken in a Teflon-lined stainless-steel reactor. The reactor was heated to 180 °C in an oven for 135 min. The black BC particles were isolated by centrifugation (6000 rpm) and repeatedly cleaned using DD water until the supernatant became clear.

2.3. Preparation of BC@CCp composite particles

The electroactive BC@CCp composite particles were prepared *via* the *in situ* chemical oxidation method. According to our

previous study, a weight ratio of 1:1 for BC to the mixed monomer was selected for the composite preparation.¹² Aniline and pyrrole contents in the monomer mixture were identical on a weight basis. BC core particles (1.0 g), requisite amounts of each monomer (total 1.0 g) and Triton X-405 were taken in a glass reactor containing 50 mL of 0.1 M HCl. The reactant mixture was thoroughly stirred on a magnetic stirrer at 500 rpm to form a homogeneous dispersion. After temperature equalization at 25 °C, an aqueous (NH₄)₂S₂O₈ (2.0 g) solution was slowly added under continuous stirring. The oxidative copolymerization started immediately. The reaction was continued for 24 h in a N₂ atmosphere, and the pH was controlled near 1.0. The black BC@CCp composite particles were cleaned *via* repeated washing with DD water till the remaining dispersion medium became transparent.

2.4. Preparation of the BC@CCp@V₂O₅ hybrid composite

Commercial V₂O₅, taken in a platinum crucible, was transferred to a muffle furnace (Gallenkamp, Germany) connected to an external thermocouple and heated to 450 °C at a heating rate of 6 °C min⁻¹. The calcination was continued for 2 h in an air-tight condition in order to achieve higher crystallinity and capacitance values.³² The calcined V₂O₅ powder and previously washed BC@CCp composite powder were mechanically blended in a glass mortar equipped with a hand pestle for approximately 20 min at 25 °C to obtain an almost-homogeneous powdered mixture. The weight ratio of BC@CCp to V₂O₅ was maintained at 4:1 during blending. The as-synthesized BC@CCp@V₂O₅ hybrid composite was characterized, and electrochemical measurements were performed without washing it.

2.5. Material characterization

The surface topography, morphology and size distribution of prepared particles were assessed by scanning electron microscopy (SEM; JSM-6510, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM; JEM-1230, JEOL, Japan). FTIR spectroscopy (PerkinElmer, FTIR-100, USA) was used to examine the



changes in the surface composition during the step-wise preparation of hybrid composites. XPS (PHI X-tool, ULVAC-PHI, Inc., Japan) was employed for investigating the surface elemental composition and valence states of vanadium. During the acquisition of XPS spectra, a monochromatic Al K α radiation (1486.6 eV) at 15 kV, 50 W and an X-ray current of 20 mA were applied. The acquisition area was 20 μm , the take-off angle was fixed at 45°, and the pressure in the measurement chamber was 8.0×10^{-7} Pa. The pass energy was fixed at 280 eV, and the step size was set at 1.0 eV. The XRD patterns of the dried samples were measured at 25 °C using an X-ray diffractometer (Bruker D8 Advance, Germany). A Cu K α radiation (λ) of 1.5406 Å, a tube voltage of 33 kV, and a tube current of 45 mA were used for measuring diffraction intensities in 2θ values from 5° to 90° at a scanning rate of 10° min $^{-1}$.

2.6. Electrochemical measurements

The cyclic voltammetry (CV), galvanostatic charging–discharging (GCD), and potential electrochemical impedance spectroscopy (PEIS) measurements were carried out using a Corrtest electrochemical workstation, CS350, China. A three-electrode system was used for this purpose. The graphite rod coated with the relevant sample was used as the working electrode. At the same time, a platinum wire was used as the counter electrode, and Ag/AgCl was used as the reference electrode. All electrochemical measurements were conducted in a 1.0 M KCl electrolyte solution at 25 °C. The active segment of the graphite rod was coated/modified with a homogeneous mash of the electroactive sample and PVDF binder in a 90 : 10 weight ratio mixed in the NMP solvent. The electroactive materials used for electrode fabrication were the BC@CCp composite, calcined V $_2$ O $_5$ and BC@CCp@V $_2$ O $_5$ hybrid composite, respectively. The fabricated working electrode was heated to dryness at 60 °C for 12 h before electrochemical measurements. The loading of the electroactive sample was maintained in the range from 1.5 to 2.0 mg, and the electrode area was 6.15 cm 2 .

In order to ensure an inert atmosphere, N $_2$ gas was first passed through the electrolyte for 10 min. The active part of the graphite electrode was immersed in the electrolyte solution. CV experiments were performed within the potential range from –0.2 to +0.6 V, and the scan rate was fixed at 50 mV s $^{-1}$. The effects of different scan rates (10–100 mV s $^{-1}$) and potential windows (–0.2 to + 1.0 V) were also studied for the BC@CCp@V $_2$ O $_5$ hybrid composite-modified electrode to understand the optimal operating voltage and the effectiveness of the hybrid composite as an electrode material.

GCD experiments in the potential range from –0.2 to +0.6 V were carried out at a fixed current density of 1.0 A g $^{-1}$ using the identical electrode after subsequent CV measurements. The effects of different current densities (1.0 to 5.0 A g $^{-1}$) on GCD curves were also studied for calcined V $_2$ O $_5$ and BC@CCp@V $_2$ O $_5$ hybrid composite-coated graphite electrodes. PEIS experiments for all three fabricated electrodes were performed in the frequency range from 5×10^{-2} to 5×10^{-5} Hz, and the scan rate was maintained at 50 mV s $^{-1}$. ZSimpWin software was used to process experimental PEIS data. Cycle stability tests from the GCD measurements of each fabricated graphite electrode were also performed at a current density of 10.0 A g $^{-1}$. The error range was calculated from three successive measurements, observed maximum of up to 2% at different points. The specific capacitance (C_s) of the respective electroactive sample was calculated from the GCD curve according to eqn (1):

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

where ΔV is the discharge potential, barring the IR drop, m is the mass (g) of the sample coated on the electrode, and I and Δt are the discharge current (A) and time (s), respectively. The energy density (E ; Wh kg $^{-1}$) and power density (P ; W kg $^{-1}$) of each fabricated electrode were calculated from GCD experiments using eqn (2) and (3), respectively:

$$E = \frac{C_s \times (\Delta V)^2}{2 \times 3.6} \quad (2)$$

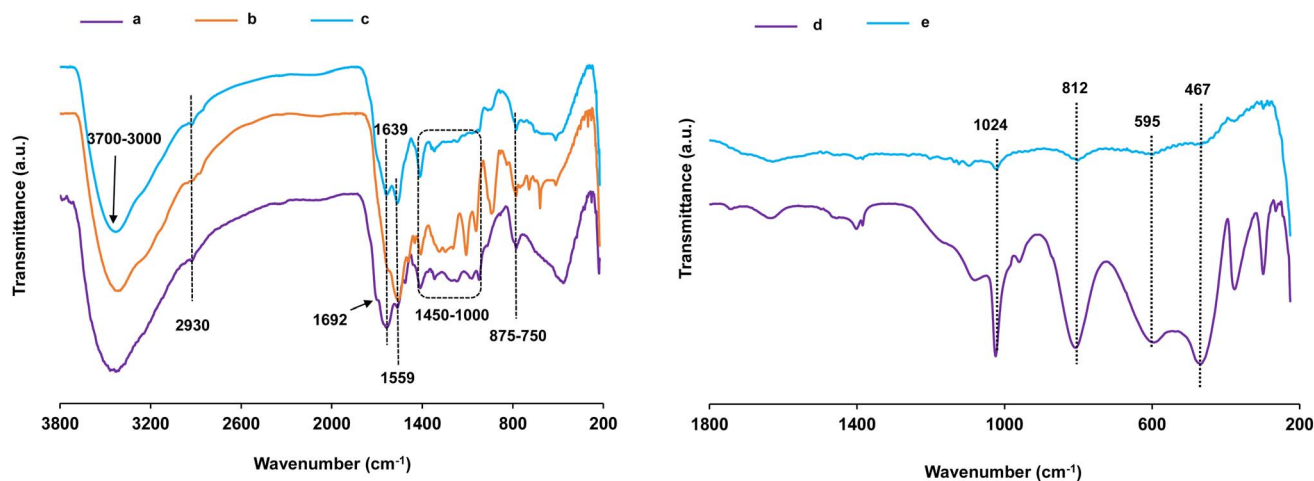


Fig. 2 FT-IR spectra of the BC core (a), CCp (b), BC@CCp composite (c), calcined V $_2$ O $_5$ (d) and BC@CCp@V $_2$ O $_5$ hybrid composite (e) particles recorded in KBr pellets.

$$P = \frac{E \times 3600}{\Delta t} \quad (3)$$

The capacitance retention stability (%), V_{cm} was calculated using eqn (4):

$$V_{cm} = \frac{C_s^1}{C_s^2} \times 100 \quad (4)$$

where C_s^1 and C_s^2 are the specific capacitances in the first and specific cycles, respectively.

3. Results and discussion

3.1. Characterization

The spectral analysis obtained from FTIR spectroscopy gives information about the surface functionality of the reaction product. A comparative plot of the FTIR spectra of the BC core, CCp, BC@CCp, calcined V_2O_5 , and BC@CCp@ V_2O_5 is given in Fig. 2. The spectrum of the BC core (Fig. 2a) illustrates the stretching signals at approximately 2930 and 3000–3700 cm^{-1} , attributed to aliphatic C–H and O–H (moisture) vibrations, respectively. The vibrations of the C=O group derived from carbonyl, quinone, and ester/carboxyl functionalities and the aromatic C=C functional group can be verified from the bands at 1692, 1639 and 1559 cm^{-1} , respectively.^{45,46} The stretching and bending signals of C=C, C–O (ester or ether) and phenolic O–H are recognizable in the 1000–1450 cm^{-1} range.^{47,48} The out-of-plane bending vibrations of the aromatic C–H group are represented by the bands in the 875–750 cm^{-1} region.⁴⁷ It is important to add that during batch-wise preparation, no significant structural change in BC was observed, as indicated by the FTIR spectra from different batches. In the spectrum of CCp (Fig. 2b), the wide bands at 1559 and 1639 cm^{-1} correspond to the quinonoid C–C stretching of the PANi block and

C=C/C–C stretching of the PPy block, respectively.^{44,48} They are a sign of the reaction between aniline and pyrrole during oxidative copolymerization. The absorption at 1112 cm^{-1} perhaps corresponds to the in-plane C–H bending vibration originated from substituted benzene in PANi.⁴⁸ The absorption signals averaged at 1390 and 1480 cm^{-1} can be assigned to the semiquinonoid ring (–N–ring) and benzenoid ring (C=C) stretching vibrations of PANi, respectively.⁴⁹ The intense peak for the C–C out-of-ring deformation of the PPy segment is found at 960 cm^{-1} .⁵⁰ Comparatively, the spectrum of BC@CCp composite particles (Fig. 2c) is dominated by peaks resembling the absorption signals of CCp. These comparative spectral analyses suggest that BC surface modification occurs, and the BC@CCp composite is obtained. The spectrum of the native calcined V_2O_5 powder (Fig. 2d) shows an absorption peak at 467 cm^{-1} , corresponding to the stretching of shared oxygen among three vanadium atoms, and the signal at 812 cm^{-1} corresponds to V–O–V vibrations.⁵¹ The other highly intense absorption band at 1024 cm^{-1} signifies crystalline orthorhombic V_2O_5 and the stretching absorption modes of V=O.^{38,51} The suppression of the absorption signals derived from CCp in the BC@CCp@ V_2O_5 hybrid composite (Fig. 2e) indicates the possible coverage of the BC@CCp composite by V_2O_5 particles. The solid–solid interaction does not produce any noticeable red/blue shift of the characteristic absorption signals of V_2O_5 .

The surface topographies and size distributions of the BC core, BC/CCp, calcined V_2O_5 and BC@CCp@ V_2O_5 are confirmed from the SEM images given in Fig. 3. The almost-sphere-shaped BC core particles (Fig. 3a) are fairly polydispersed with respect to the size distribution. The average diameter and coefficient of variation (CV) estimated using ImageJ software are 2.56 μm and 11.66%, respectively. The surface of the BC core appears smooth with clear boundaries and is almost free from aggregation. The surface of the BC core became heterogeneous after the formation of the BC@CCp composite (Fig. 3b) *via* the seeded chemical

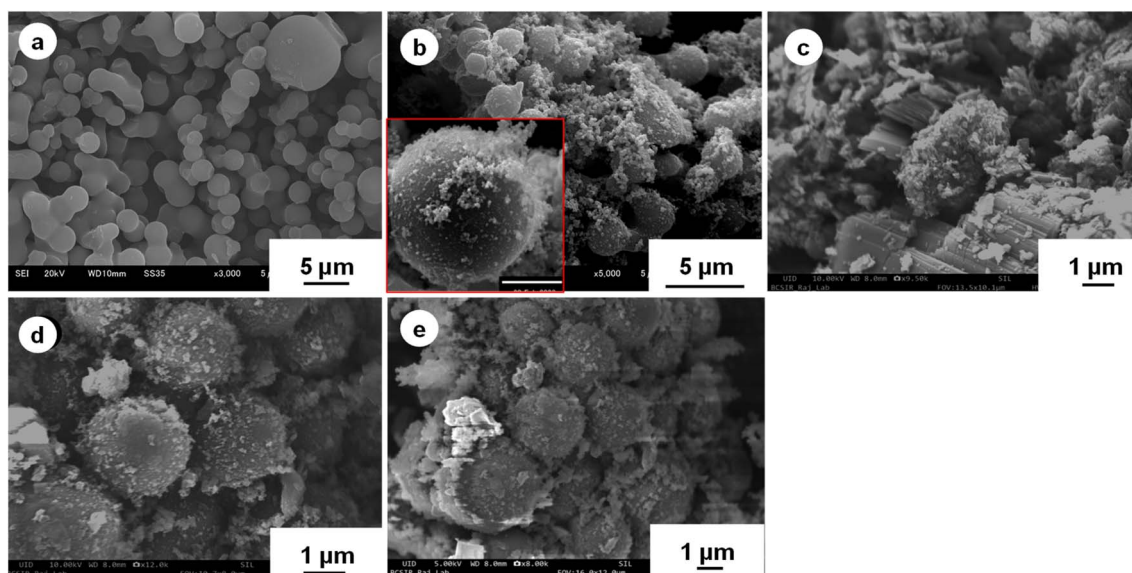


Fig. 3 SEM images of the BC core (a), BC@CCp composite (b), calcined V_2O_5 (c) and BC@CCp@ V_2O_5 hybrid composite (d and e) particles.



oxidative copolymerization of aniline with pyrrole. The tiny particles attached to the surface are perhaps the electroactive (Ani-Py) copolymer, *i.e.*, CCp. It is apparent from the image that due to the limited surface area, some independent copolymer particles are formed. In some instances, the tiny independent particles are perhaps organized into hairy structures on the BC surface. For clear identification, an inset image of one comparatively larger BC@CCp composite particle is shown in Fig. 3b. The mean diameter and CV of BC@CCp composite particles are 2.90 μm and 9.6%, respectively. The calcined V_2O_5 particles shown in Fig. 3c have different shaped morphologies, *e.g.*, corpuscular (spherical and ellipsoid), linear (rod), flake and sheet types. The size distribution of V_2O_5 particles is broad, and the smaller particles have dimensions less than 100 nm. The surface morphology of the BC@CCp@ V_2O_5 hybrid composite (Fig. 3d and e) is considerably different from that of the reference BC@CCp composite particles. The surface heterogeneity increases, and tiny particles similar to V_2O_5 can be seen adhered to the surface of the hybrid composite. The increase in the density of adhered tiny particles on the surface of the BC@CCp composite is another indication of hybrid composite formation with V_2O_5 . Under the preparation conditions, there should be some free V_2O_5 particles, but their presence could not be confirmed from the image (Fig. 3d and e). The mean diameter of BC@CCp@ V_2O_5 hybrid particles increases to 3.86 μm . Overall, results confirm the formation of conductive hybrid composite particles with V_2O_5 attached to the surface *via* some solid-phase interactions created *via* rubbing, polymer layer deformation, entanglement within the hairy network, and solid bridge formation, which can take place even at room temperature.^{52,53}

The morphologies of BC@CCp, calcined V_2O_5 and BC@CCp@ V_2O_5 were further analyzed by TEM observation. The TEM image of BC@CCp composite particles (Fig. 4a) confirms the hairy growth of CCp on the surface of BC particles. As such, the surface of composite particles becomes non-smooth and heterogeneous after seeded oxidative copolymerization. An identical observation is also made in the SEM image of BC@CCp composite particles (Fig. 3b). Comparatively, the surface of the BC@CCp@ V_2O_5 hybrid composite particle (Fig. 4c) is slightly different, containing a network of smaller particles. In the network, around the dark-colored spherical BC particles, we can see various-shaped V_2O_5 particles, including a rod-shaped particle, as indicated by an arrow in Fig. 4c.

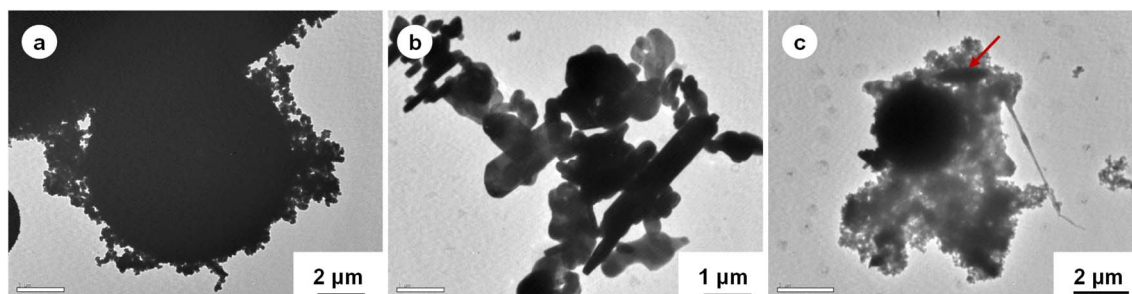


Fig. 4 TEM images of the BC@CCp composite (a), calcined V_2O_5 (b) and BC@CCp@ V_2O_5 hybrid composite (c) particles.

XPS, a surface-sensitive analytical tool, was used to understand the basic elemental constituents and valence states of vanadium in V_2O_5 . In addition to the carbon and oxygen signals, the XPS survey spectrum of the BC@CCp composite (Fig. 5a) shows the presence of N1s, which is derived from the CCp layer. Furthermore, the spectrum of the BC@CCp@ V_2O_5 hybrid composite (Fig. 5c) shows the existence of the $\text{V}2\text{p}^3$ signal at ~ 525 eV. The signal intensity of $\text{V}2\text{p}^3$ in the BC@CCp@ V_2O_5 hybrid composite is obviously lower than that in native V_2O_5 . The atom percentages of carbon, oxygen and nitrogen elements in the BC@CCp@ V_2O_5 hybrid composite are not worth mentioning because it is prepared by simple mechanical blending.

The valence states of vanadium were further evaluated in the calcined V_2O_5 and BC@CCp@ V_2O_5 hybrid composite *via* the deconvolution of the core-line spectrum of vanadium. As can be seen in Fig. 6a, the core-line signal of $\text{V}2\text{p}^3$ in calcined V_2O_5 can be differentiated into two signals corresponding to $\text{V}2\text{p}_{3/2}$ and $\text{V}2\text{p}_{1/2}$ at 516.6 eV and 524.0 eV, respectively. The separation of the spin-orbit component by 7.4 eV confirms V^{5+} as the dominant fraction.^{38,54} The deconvoluted $\text{V}2\text{p}_{3/2}$ core-level spectrum exhibits two peaks at 515.4 and 516.6 eV, representing the oxidation states of vanadium (V^{4+} and V^{5+}), respectively.⁵⁵ V^{5+} accounts for 66.9% of the peak area, while V^{4+} constitutes only 2.8%. The other peak at 518.1 eV is assignable to the X-ray satellite of the O1s core-level.⁵⁵ Similar findings are observed from the deconvolution of the $\text{V}2\text{p}^3$ core-line signal for the BC@CCp@ V_2O_5 hybrid composite (Fig. 6b). However, the

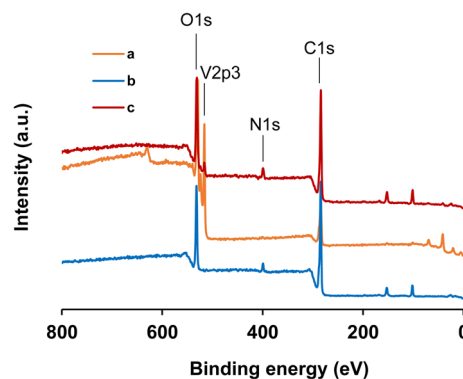


Fig. 5 XPS survey spectra of the BC@CCp composite (a), calcined V_2O_5 (b) and BC@CCp@ V_2O_5 hybrid composite (c) particles.

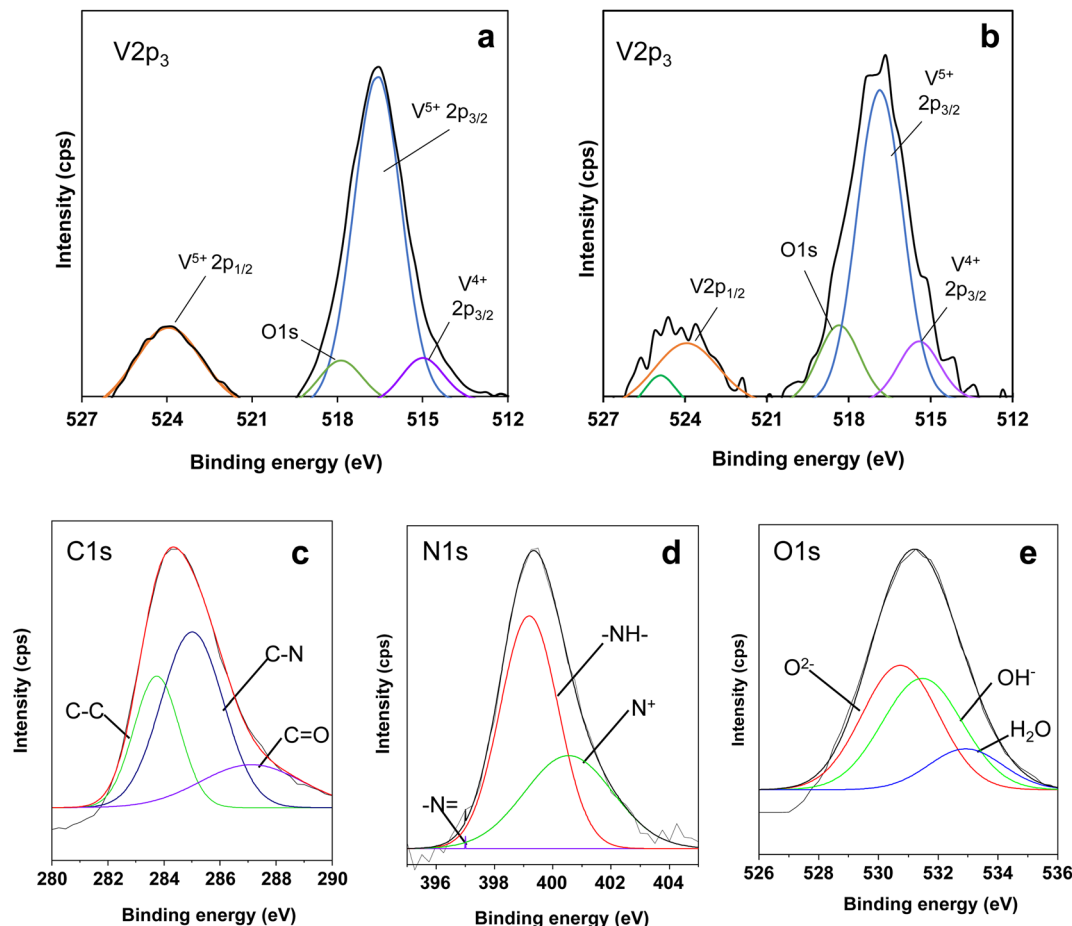


Fig. 6 XPS deconvoluted core-line spectra of $V2p^3$ (a and b), $C1s$ (c), $N1s$ (d) and $O1s$ (e) in the calcined V_2O_5 (a) and $BC@CCp@V_2O_5$ hybrid composite (b–e) particles.

binding energies for V^{4+} and V^{5+} oxidation states and $O1s$ are slightly shifted to 516.4, 516.9, and 518.3 eV in the hybrid composite, respectively. The enrichment of the higher-valence V^{5+} state to 72.4% in the hybrid composite may account for this positive deviation in the binding energy.⁵⁶ The positive deviation in the binding energy may also occur from a variation in the chemical environment.⁵⁶ In the present case, the change in the chemical environment around the vanadium nucleus due to the presence of an electron-rich CCp chain is less likely because the hybrid composite is prepared by the simple mechanical blending of two solid powders.⁵⁶ However, it is not yet known whether the solid-phase interaction during mechanical blending produces a positive shift in the binding energy.

The $C1s$ core-line spectrum of the ultimate $BC@CCp@V_2O_5$ hybrid composite (Fig. 6c) can be deconvoluted into three bonding groups attributed to C–C, C–N and carbonyl/quinone at approximately 284.2, 285.5 and 287.9 eV, respectively.¹² The deconvolution of the $N1s$ core-line spectrum (Fig. 6d) results in three signals at approximately 398.6, 400.0 and 401.2 eV, corresponding to $-N=$ (imine), $-NH-$ (amine) and N^+ (oxidized amine) groups, respectively. Furthermore, the $O1s$ core-line peak (Fig. 6e) can be deconvoluted into three peaks at

approximately 530.7, 531.5, and 533.0 eV. The peaks at 530.7 and 531.5 eV are assigned to V–O and V–OH bonds, respectively.⁵⁷ The other peak at 533.0 eV is related to the adsorbed H_2O –OH, where $-OH$ groups are hydrogen-bonded to H_2O . Regardless of the interactions, all these structural and chemical component analyses confirm the incorporation of V_2O_5 in the hybrid composite.

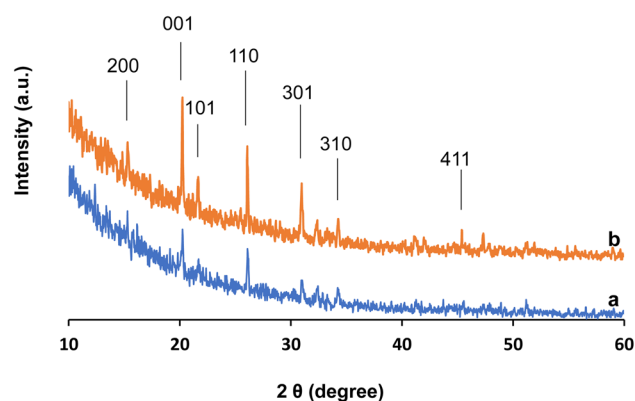


Fig. 7 XRD patterns of calcined V_2O_5 (a) and $BC@CCp@V_2O_5$ hybrid composite (b) particles.



The XRD pattern of calcined V_2O_5 (Fig. 7a) shows the characteristic peaks of the orthorhombic crystal structure of V_2O_5 at 2θ values of 15.28° , 20.22° , 21.66° , 26.11° , 30.99° , 34.21° and 45.52° , corresponding to the (200), (001), (101), (110), (301), (310) and (411) lattice planes (JCPDS 41-1426), respectively.⁵⁸ These characteristic peaks are also present in the $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite, sometimes with slight deviations. In calcined V_2O_5 , the (001) lattice plane at 20.22° has the highest intensity, with a d -spacing of 4.388 \AA , while in the hybrid composite, the same peak has an almost identical d -spacing of 4.386° . However, the peak intensity of the respective (001) and (110) lattice planes considerably increases in the hybrid composite. The shift of the (110) lattice plane at 26.11° in calcined V_2O_5 to a lower angle of 26.05° in the hybrid composite indicates the expansion of the interlayer distance.⁵⁹ This enlarged interlayer distance will favorably enhance the accessible contact area for the electrolyte and hence the electrochemical performance of the cell.⁶⁰ The mean crystallite sizes of V_2O_5 in the calcined V_2O_5 and $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite, estimated from the Debye-Scherrer equation using the diffraction signal, are 48.2 and 40.1 nm , respectively. The decrease in the crystallite size in the hybrid composite is possibly induced by the blending operation and solid-phase interaction.

3.2. Electrochemical performance

CV measurements were carried out for BC@CCp -, calcined V_2O_5 - and $\text{BC@CCp@V}_2\text{O}_5$ -coated graphite electrodes in a 1.0 M KCl solution at 25°C . Independent of the electrode nature,

rectangular-shaped CV curves (Fig. 8(A)a) are obtained in the -0.2 V to $+0.6 \text{ V}$ potential range at a fixed scan rate (50 mV s^{-1}). It is also apparent that the doping-dedoping reaction progresses almost reversibly. This behavior suggests that the fabricated graphite electrodes possess good capacitive performance. Moreover, the $\text{BC@CCp@V}_2\text{O}_5$ -coated graphite electrode demonstrates better current response than the two other coated graphite electrodes (Fig. 8(A)b and c). Alternatively, it can be seen from Fig. 8(A)a that the CV curve of the $\text{BC@CCp@V}_2\text{O}_5$ -coated graphite electrode has the highest integral area and hence the highest capacitance value among all three fabricated electrodes.⁶¹ Obviously, the incorporation of CCp, calcined V_2O_5 and BC in the hybrid composite increases the number of electro-conductive sites and thus contributes to the faradaic redox process more aggressively at the electrode-electrolyte junction.

To obtain information about the rate capability, the electrochemical performance of the best-performing $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite-coated electrode was further tested by recording CV curves at different scan rates ranging from 10 to 100 mV s^{-1} . The findings shown in Fig. 8B display that the peak current improves with an increase in the scan rate while almost preserving the shape of CV curves. The retention of the reversible charging-discharging process and favorable rate capability over a broad range of scan rates prove the potential of the fabricated $\text{BC@CCp@V}_2\text{O}_5$ electrode as an electroactive material.⁶² To explore the optimal potential window, the CV curves were also recorded in different potential windows from -0.2 V to $+1.0 \text{ V}$ at a constant scan rate of 50 mV s^{-1} .

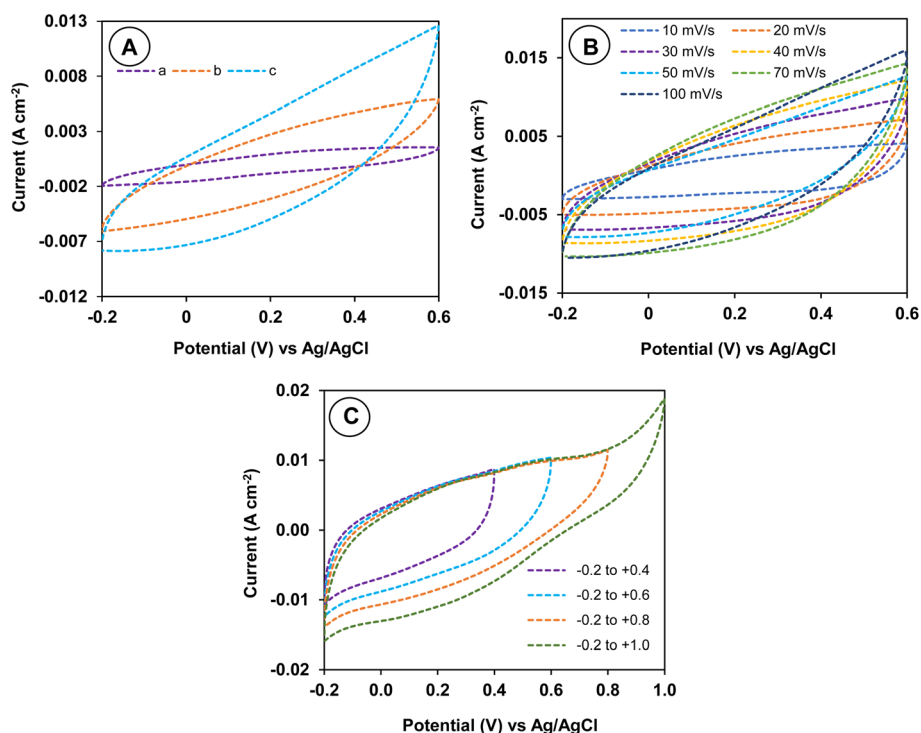


Fig. 8 (A) CV curves of the BC@CCp composite- (a), calcined V_2O_5 - (b) and $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite-coated (c) graphite electrodes at a scan rate of 50 mV s^{-1} . (B and C) CV curves of the $\text{BC@CCp@V}_2\text{O}_5$ hybrid composite-coated graphite electrode at different (B) scan rates and (C) potential ranges.



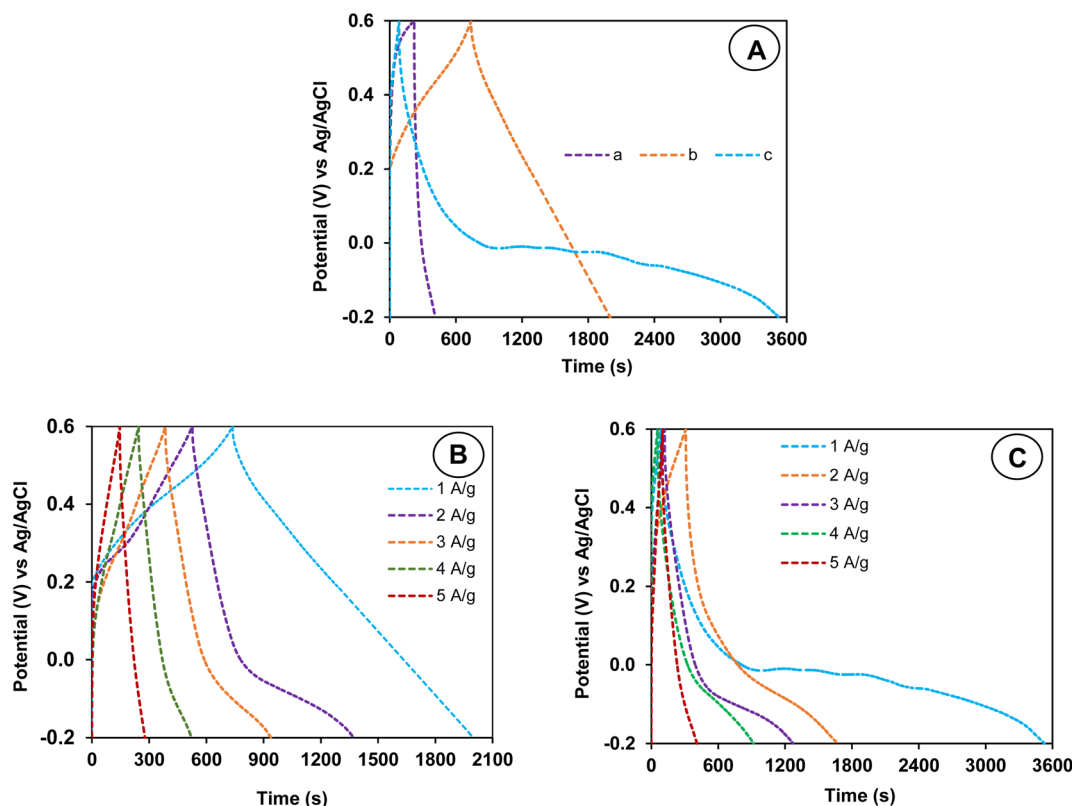


Fig. 9 (A) GCD curves of BC@CCp- (a), calcined V_2O_5 - (b) and BC@CCp@ V_2O_5 -coated (c) graphite electrodes at a constant current density of 1.0 A g^{-1} . (B and C) GCD curves of calcined V_2O_5 - (B) and BC@CCp@ V_2O_5 -coated (C) graphite electrodes at different current densities.

s^{-1} . The almost-rectangular-shaped CV curves (Fig. 8C) demonstrate that the electrode coated with the hybrid composite possesses good capacitive behavior in the potential range up to 1.0 V. Therefore, the overall comparative analysis of CV results indicates that the improved compatibility among carbon-rich BC, conducting copolymer and V_2O_5 considerably enhances the electrochemical performance and rate capability.

After CV experiments, the same modified graphite electrodes were utilized for GCD measurements (Fig. 9(A)a) in the identical potential region from -0.2 V to $+0.6 \text{ V}$, and the current density was fixed at 1.0 A g^{-1} . This shows that the fabricated graphite electrode is stable because the color of the electrolyte does not noticeably change owing to the diffusion or solubilization of coated conducting materials. All GCD curves show an insignificant IR drop. This finding is an indication of good capacitive behavior in reversible electrochemical processes.⁶³ Interestingly, the BC@CCp@ V_2O_5 composite-coated graphite electrode has a longer discharge time compared to its charging time after the inclusion of three components, *i.e.*, BC, CCp and V_2O_5 in the same electrode. This charging–discharging behavior is desirable for high-performance energy storage materials.⁶³ Comparatively, such behavior is not observed for the two other fabricated graphite electrodes (Fig. 9(A)b and c). The specific capacitances obtained from the respective GCD curves of BC@CCp, calcined V_2O_5 - and BC@CCp@ V_2O_5 -coated electrodes are 243.2, 2498.2 and 4150.6 F g^{-1} , respectively. The enhancement and superiority of the capacitance value of the

BC@CCp@ V_2O_5 -coated electrode indicate the comparable synergistic interaction and compatibility among the carbon-rich BC, electroconductive copolymer, calcined V_2O_5 and graphite rod.^{64,65} Relatively, the higher energy storage efficiency of the BC@CCp@ V_2O_5 -coated graphite electrode is thus facilitated by good contact among different electroactive phases and the better transport of electrons or ions through conducting channels. After the GCD experiment, the influence of different current densities (1.0 to 5.0 A g^{-1}) on the GCD potential was examined for calcined V_2O_5 - (Fig. 9B) and BC@CCp@ V_2O_5 -coated graphite electrodes (Fig. 9C). The retention of charge–discharge behavior independent of the current density implies good rate capability. Fig. 9B and C also indicates that a decrease in the current density prolongs the charge–discharge time. The

Table 1 Specific capacitance calculated from GCD curves at different current densities

Current density (A g^{-1})	Specific capacitance (F g^{-1})		
	BC@CCp	Calcined V_2O_5	BC@CCp@ V_2O_5
1	243.25	2498.2	4150.6
2	291.25	2147.2	2936.5
3	314.625	2038.1	2628.4
4	218.5	1389.5	1903.5
5	135.25	840.6	1814.4



values of the specific capacitance of different fabricated electrodes calculated from GCD plots are shown in Table 1. The gradual decrease in the specific capacitance at higher current densities apparently originates from slower charge diffusion, limited faradaic reactions and impassable electrochemically active surface areas.⁶² The slower charging–discharging kinetics at higher current densities thus decreases the electrode efficiency.⁶⁶ Despite the decrease in the specific capacitance with increasing current density, the BC@CCp@V₂O₅-coated electrode still displays high capacitance, which decreases from 4150.6 F g^{−1} at 1.0 A g^{−1} to 1814.4 F g^{−1} at 5.0 A g^{−1}. It is apparent from Table 1 that the BC@CCp@V₂O₅-coated graphite electrode retains ~44.0% of the original capacitance value at a higher current density of 5 A g^{−1}, which confirms the substantial sustainability and rate capability. Previously, we observed that high current density does not have a significant influence on the specific capacitance for the BC@CCp-coated electrode. It was predicted that BC, containing active binding sites (*e.g.*, −OH/ester/ether/carboxyl), and electroactive nitrogen-rich CCp comprising P(Ani-Py) would produce a stable and compact network that would partially inhibit the volume change during charging–discharging operation.¹² This same phenomenon also plays a role in the improved sustainability and excellent rate performance of the BC@CCp@V₂O₅-coated graphite electrode. Therefore, in agreement with CV results, GCD measurements also show a remarkable improvement in the specific capacitance, sustainability and rate performance after the integration of V₂O₅ into BC@CCp. However, more efforts can be made to enhance sustainability at higher current densities *via* the *in situ* nucleation and growth of V₂O₅ nanoparticles in the presence of BC@CCp because such methods should produce a more stable compact network.

When BC, CCp, and V₂O₅ are combined into a single hybrid composite, the electrochemical performance is boosted. BC provides a conductive backbone that supports the movement of electrons across the composite. The conductive copolymer, CCp, acts as an additional electron transfer medium, enhancing the electron conductivity *via* its redox property. V₂O₅ adds

a high-capacitance mechanism *via* its ability to undergo redox reactions, further boosting the electrochemical performance. During the charging process, ions from the electrolyte intercalate into the nanocomposite structure, and V₂O₅ and CCp undergo redox reactions. BC assists the electron flow between CCp and V₂O₅, maximizing charge storage. V₂O₅ exhibits pseudocapacitance *via* faradaic reactions, where V₂O₅ undergoes a reversible change in oxidation states during charge–discharge cycles. During charging, V₂O₅ undergoes reduction because it accepts an electron (*e.g.*, from V⁵⁺ to V⁴⁺), and during discharge, V₂O₅ is oxidized (*e.g.*, from V⁴⁺ to V⁵⁺). BC and CCp, *via* solid-phase interactions, help prevent the loss and agglomeration of V₂O₅ particles, keeping them distributed and accessible for redox reactions. This leads to the better mechanical stability and improved charge–discharge performance of the supercapacitor.

To obtain the surface electrochemical information, the PEIS of the respective fabricated graphite electrode was investigated, and the related Nyquist plots are shown in Fig. 10A. The Nyquist plot generally has two segments: one is a higher-frequency semicircle zone and the other is a straight-line region at lower frequencies. Here, the absence of the semicircle segment at higher frequencies indicates that neither of the fabricated electrodes hinders the electron flow from the electrolyte to the inner part of the electrode.⁶⁷ Additionally, the maximum slope of the low-frequency straight-line region in the plot of the BC@CCp@V₂O₅-coated graphite electrode (Fig. 10(A)c) suggests that the electrode possesses excellent capacitance performance with the least diffusion resistance.^{44,68,69} The equivalent circuit of the BC@CCp@V₂O₅ hybrid composite-coated electrode is shown in Fig. 10B, where *R*₁ is the resistance of the coating layer, *R*₂ is the resistance to charge transfer, and Warburg impedance *W*₀ corresponds to the faradaic impedance. The parallel connection between the constant phase element (CPE) and *R*₂ is referred to as the charge-transfer-limiting process.

The long-time cycling performance of BC@CCp-, calcined V₂O₅- and BC@CCp@V₂O₅-coated graphite electrodes was evaluated *via* GCD cycle experiments. The experiment was

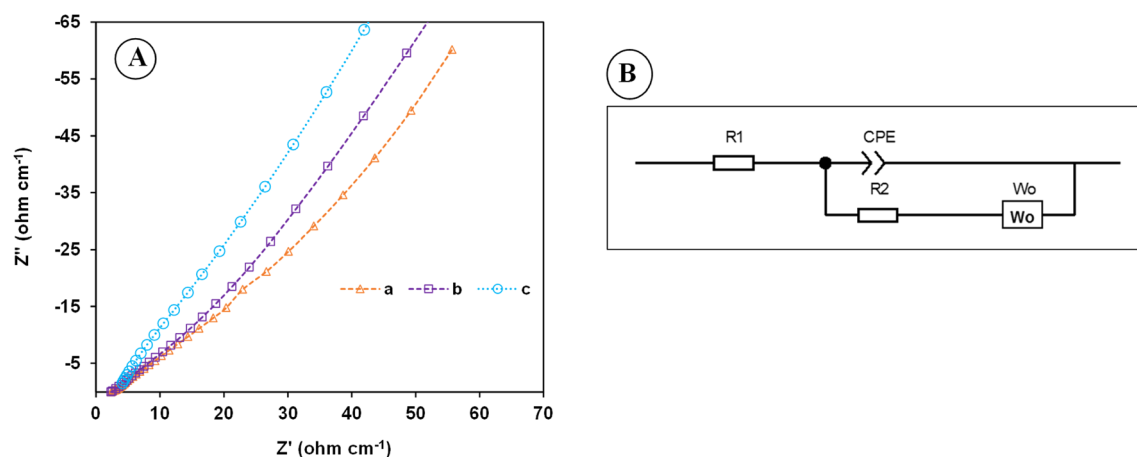


Fig. 10 (A) The Nyquist plots of the PEIS of BC@CCp- (a), calcined V₂O₅- (b) and BC@CCp@V₂O₅-coated (c) graphite electrodes in a 1.0 M KCl solution over in frequency range from 5×10^{-2} to 5×10^{-5} Hz measured at a 50 mV s^{-1} scan rate. (B) A sample equivalent circuit fitted with the Nyquist plot.

performed up to 1000 cycles at a current density of 10.0 A g^{-1} , and the potential range was identical from -0.2 V to $+0.6 \text{ V}$. During the experiment, no visible change in the electrolyte color due to the peeling off of electroactive materials from the graphite electrode was observed. As illustrated in Fig. 11A, the reference BC@CCp- and calcined V_2O_5 -coated electrodes demonstrate a slightly downward trend in capacitance values, expressed as retention stability in percentage, which decreases to 96.6% and 83.3%, respectively, after 1000 cycles. The incorporation of BC and formation of a stable network *via* hydrogen bonding between the BC functional groups and electroactive copolymer reduces the extent of degradation during repeated charging–discharging operations. BC@CCp mostly follows a combination of type I and type II cycle stabilities, and the charge storage is accompanied by reversible processes of the adsorption–desorption of ions and electrochemical redox reactions at the electrode–electrolyte junction.⁷⁰ Importantly, when calcined V_2O_5 is only mechanically blended with BC@CCp, the capacitance of the resultant BC@CCp/ V_2O_5 -coated graphite electrode first slightly decreases, then gradually increases to

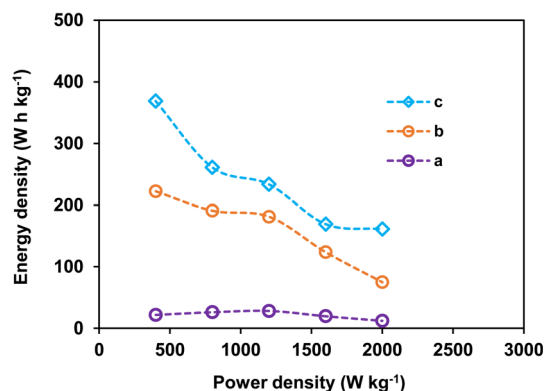


Fig. 12 Ragone plot of the BC@CCp/ V_2O_5 hybrid composite-coated graphite electrode studied at current densities of 1.0 – 5.0 A g^{-1} .

134% up to 800 cycles, and finally remains almost steady. The initial decrease in the specific capacitance up to the 26th cycles is perhaps due to the insufficient wetting of the BC@CCp/ V_2O_5 -coated electrode surface by the aqueous KCl electrolyte

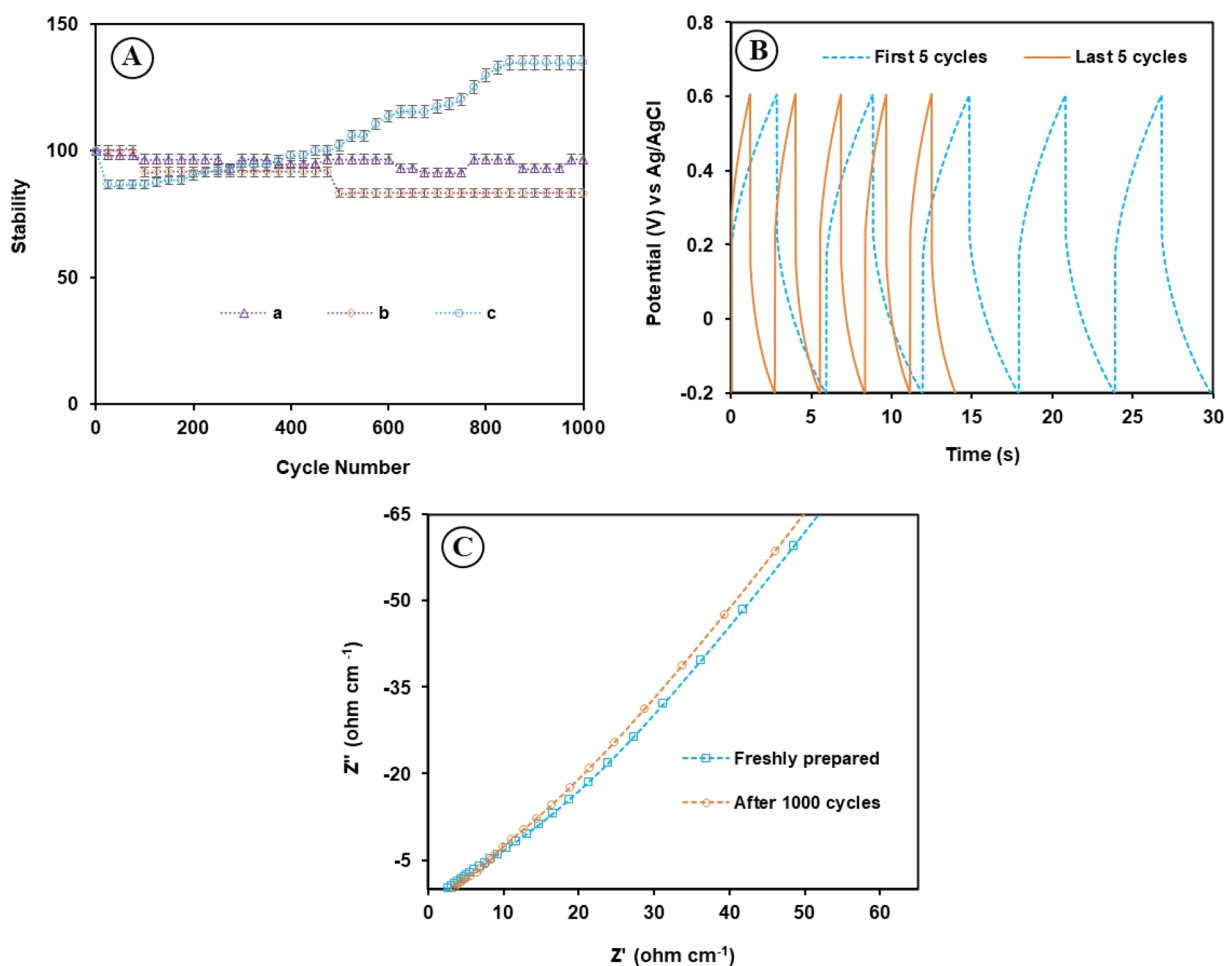


Fig. 11 (A) Cycling stability of the BC@CCp- (a), calcined V_2O_5 - (b) and BC@CCp/ V_2O_5 -coated (c) graphite electrodes estimated from GCD curves in a 1.0 M KCl solution at a current density of 10.0 A g^{-1} . (B) Charging–discharging behavior of the BC@CCp/ V_2O_5 -coated graphite electrode *versus* time during the first and last five cycles. (C) Nyquist plots recorded for the fresh BC@CCp/ V_2O_5 -coated graphite electrode and the same electrode after 1000 charge–discharge cycles.



Table 2 Electrochemical properties of V₂O₅-based nanocomposite supercapacitors

Composite	Electrolyte	Current density (A g ⁻¹)	Capacitance (F g ⁻¹)	Power density (W Kg ⁻¹)	Energy density (Wh Kg ⁻¹)	Ref.
C@V ₂ O ₅ nanorods	0.5 M K ₂ SO ₄	0.5	417	170	9.4	29
V ₂ O _{5-x} @C composite	1 M KCl	1	277.6 mA h g ⁻¹	—	—	30
RGO/V ₂ O ₅	—	1	320	—	—	31
Graphene/V ₂ O ₅	—	1	189	—	—	32
V ₂ O ₅ /CNTs-SAC	2 M NaNO ₃	10	357.5	—	—	33
V ₂ O ₅ /f-MWCNT	—	0.5	410	121	8.9	35
V ₂ O ₅ @PPy	—	0.2	344	—	—	38
PEDOT-VO	—	0.5	370.5 mA h g ⁻¹	—	—	40
Vo-V ₂ O ₅ /CP	1 M Na ₂ SO ₄	0.5	614	—	—	41
PANI/GO-V-APS	1 M H ₂ SO ₄	0.5	712	—	—	42
V ₂ O ₅ /MWCNTs	LiClO ₄	1.0	160.15	2300	27.07	73
V ₂ O ₅ -pBOA-graphene	—	1.0	986	—	49	74
rGO/V ₂ O ₅	Organic electrolyte	0.1	384	275	80.4	75
Graphene/VO _x	—	1.0	1110	72	54	76
V ₂ O ₅ /rGO	KCl	1.0	635	900	79.5	77
V ₂ O ₅ -PANI	LiCl	0.5 (mA cm ⁻²)	443	720	69.2	78
V ₂ O ₅ -PANI	LiClO ₄	1.0 (mA cm ⁻²)	1115	—	—	79
V ₂ O ₅ /rGO	Aqueous	1.0	537	500	74.58	80
V ₂ O ₅ @PPy	—	1.0	307	161	37	65
BC@CCp@V ₂ O ₅	KCl	1.0	4150.6	400	368.9	This work

solution at the threshold of the electrochemical process because this is a compact hybrid structure of three components.^{71,72} Subsequently, the gradual increase in the specific capacitance may have come from the wetting and electro-activation of the electrode surface by the electrolyte solution during the cycling experiment. It is also probable that under the applied electric field, more V⁵⁺ becomes available at the electrode surface for redox reactions. Furthermore, stable composite formation *via* solid-phase interactions between the BC@CCp and calcined V₂O₅ powder inhibits the structural collapse of V₂O₅, which occurred in the case of the V₂O₅-coated electrode. As a direct proof, the GCD curves of the first five cycles are compared with the last five cycles in Fig. 11B. This figure shows that the charge-discharge time is lower in the first five cycles than in the last five cycles. The enhancement in the cycle stability of the BC@CCp@V₂O₅-coated graphite electrode is further confirmed using PEIS study and the corresponding Nyquist plots of the as-coated graphite electrode before and after 1000 charge-discharge cycles, as shown in Fig. 11C. The slight increase in the slope of the low-frequency straight-line region from the electrode after 1000 cycles indicates an increase in the capacitive performance and a decrease in the diffusion resistance. The porous and interconnected network of BC enables better mechanical interlocking and stress distribution and minimizes cracking or detachment of the active material during electrochemical operation. This synergistic effect ensures long-term cycling stability while maintaining low interfacial resistance.

In order to justify the application potential of the fabricated graphite electrodes in energy storage devices, comparative Ragone plots, showing the relationship between the energy density and power density, are given in Fig. 12. The fabricated graphite electrode made from the BC@CCp@V₂O₅ hybrid composite possesses the highest energy density of 368.9 Wh

kg⁻¹ when the power density is 400 W kg⁻¹. Results suggest that the prepared hybrid composite possesses very high capacity, reasonably good for efficient use in supercapacitor electrodes.

To understand the application viability, the specific capacitance, energy, and power density values of the BC@CCp@V₂O₅ hybrid composite-coated graphite electrode are compared with literature values of some V₂O₅-based composite electrode materials (Table 2). It is evident that our fabricated hybrid composite-coated graphite electrode is better, at least in terms of the specific capacitance and energy density.

The findings suggest that the integration of three components (*i.e.*, carbon-rich BC, conducting copolymer and V₂O₅) into a hybrid composite and subsequent coating on a graphite electrode produces a stable network *via* hydrogen bonding and solid-phase interactions. Such a strong and stable network remarkably improves the capacitance value, capacitance retention, cycle stability, and rate capability, which have rarely been observed for other hybrid electrode materials, as stated in the literature.

4. Conclusions

In this study, BC, a carbon-rich biomass, is utilized for hosting a conducting copolymer and a metal oxide, *i.e.*, CCp and calcined V₂O₅. The objective is to determine the utility of BC as a low-cost, easily accessible green material for developing sustainable electrode materials for supercapacitor applications. First, the 2.56 μm sphere-shaped BC core particles are prepared by the simple hydrothermal treatment of a 0.8 M sucrose solution at 180 °C. Then, BC@CCp composite particles are synthesized by the *in situ* chemical oxidative copolymerization of aniline and pyrrole while maintaining the w/w ratio of BC to CCp at 1:1. Finally, the ultimate BC@CCp@V₂O₅ hybrid



composite is produced by mechanically blending a mixture of BC@CCp and calcined V_2O_5 in a w/w ratio of 4:1. The size distribution and surface morphology analyses indicated the formation of the hybrid composite *via* the solid-phase synergy between the BC@CCp composite and V_2O_5 . XPS analysis revealed the domination of vanadium in the V^{5+} oxidation state. The electrochemical performance of BC@CCp-, calcined V_2O_5 - and BC@CCp@ V_2O_5 -coated graphite electrodes is measured and compared using CV, GCD, and PEIS curves. The specific capacitances of BC@CCp-, calcined V_2O_5 -, and BC@CCp@ V_2O_5 -coated electrodes are 243.2, 2498.2, and 4150.6 F g⁻¹ at a current density of 1.0 A g⁻¹, respectively. In addition to the maximum specific capacitance, the BC@CCp@ V_2O_5 -coated graphite electrode displays an enhanced rate capacity, low charge transfer resistance, and good cycle stability. Importantly, the BC@CCp@ V_2O_5 -coated electrode exhibits quick charging and relatively long discharging times during GCD cycle experiments. The fabricated electrode also shows a high energy density of 368.9 Wh kg⁻¹ at a power density of 400.0 W kg⁻¹. Thus, the V_2O_5 -integrated BC@CCp hybrid composite has good potential for use as a sustainable electrode material, and BC is a good platform for hosting CCp and V_2O_5 for designing highly efficient supercapacitor electrodes. There is also a good prospect of further enhancing the electrochemical performance by reducing the size distribution of anchored V_2O_5 to the nanorange.

Data availability

The data supporting this article have been included as part of the manuscript.

Author contributions

Md. Mahabur Rahman: methodology, investigation, formal analysis, data curation, validation, and writing – original draft. Abdulla Al Mamun: methodology, investigation, formal analysis, and data curation, validation. Hideto Minami: investigation and data curation. Md. Kawsar Hossain: investigation and data curation. S. Manjura Hoque: investigation and data curation. Mostafa K. Sharafat: resources. Hasan Ahmad: supervision, conceptualization, data curation, resources, project administration, and writing – review and editing.

Conflicts of interest

The authors have no competing interests to declare that are relevant to the content of this article.

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