

Article

Development of 3D-Printed MWCNTs/AC/BNNTs Ternary Composite Electrode Material with High-Capacitance Performance

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Abstract: Activated carbon (AC) and multiwalled carbon nanotubes (MWCNTs) have been extensively investigated in recent decades as electrical double-layer capacitor (EDLC) electrode materials for supercapacitors, owing to their superior capacitive properties and cycling stability performance. However, in the modern electronics industry, ternary electrode materials have been designed to develop high-performance and efficient energy storage devices. EDLC-based ternary materials are of great importance, where all the present components participate both individually and as a multicomponent electrode system to promote high-electrochemical performance electrode materials. In this study, we have incorporated an optimized content of boron nitride nanotube (BNNT) powder into a binary material composed of AC and MWCNTs to enhance their electrochemical performance using a pneumatic printer. The printed MWCNTs/AC/BNNTs ternary composite electrode material has shown a maximum specific capacitance of 262 F g^{-1} at a minimum current density of 1 A g^{-1} , with a capacitance retention of 49.61% at a maximum current density of 10 A g^{-1} . These results demonstrate that the printable MWCNTs/AC/BNNTs ternary composite electrode material is a potential candidate for the development of high-performance supercapacitors.

Keywords: 3D pneumatic printing; direct ink writing (DIW); boron nitride nanotube; activated carbon; multiwalled carbon nanotube; aqueous electrolyte



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1. Introduction

Over the past few decades, the depletion of fossil fuels and a significant increase in energy consumption have driven the development of efficient high-performance energy storage systems. Supercapacitors or electrochemical capacitors are the most promising and efficient energy storage devices owing to their long cycle life, high power density, fast charging/discharging and better safety tolerance compared to batteries [1–4]. Supercapacitors are classified broadly into two categories: pseudocapacitors and electrical double layer capacitors (EDLCs). The EDLCs possess a higher power density and excellent cycle stability. The charge storage mechanism in EDLCs follow the non-Faradaic reaction where the accumulation of electrostatic charge takes place at the interface of the porous electrode/electrolyte within a few angstroms. Carbon-structured materials, such as carbon nanotubes (CNTs), graphene and activated carbon (AC), are the most commonly used materials in the development of EDLC-based supercapacitors [5–9]. However, binary EDLC materials, such as CNT/graphene, AC/CNT and carbon black/graphene, are widely used, owing to their better electrochemical and cycling stability performance. Though, binary EDLC materials have shown improved electrochemical performance but still the reported performance of these materials remains insufficient for the development of high-performance supercapacitors. Qiang et al. fabricated an electrospun carbon nanofiber/graphene composite electrode material for a supercapacitor and reported a specific capacitance of 183 F g^{-1} [10]. Xue et al. reported a unique poly(3,4-ethylenedioxythiophene)/g-C₃N₄ binary electrode material with an electrochemical performance of 137 F g^{-1} [11]. A self-assembled graphene/CNTs

binary composite was prepared by Dingshan et al. [12] and the reported electrochemical performance of the respective binary material was 120 F g^{-1} . Bo et al. focused on the development of a three-dimensional nitrogen-doped graphene/CNT framework for supercapacitor applications [13]. The three-dimensional N-doped CNT/graphene framework delivered a specific capacitance of 180 F g^{-1} at a current density of 0.5 A g^{-1} . The poor electrochemical performance of binary EDLC electrode materials can degrade the energy density and power density performances of designed symmetric or asymmetric supercapacitor devices. To overcome the inferior electrochemical performance of binary EDLC materials, such as multiwalled carbon nanotubes/activated carbon (MWCNTs/AC), it is an ideal solution to develop ternary composite electrode materials. Boron nitride nanotubes (BNNTs) can be a suitable candidate to modify MWCNTs/AC EDLC-based materials. Recently, Abass et al. tested the electrochemical performance of a BNNT-modified, polymer-derived silicon oxycarbide composite electrode material with a maximum specific capacitance of 78.93 F g^{-1} [14]. Furthermore, Evgenia et al. designed and fabricated a SWCNTs/BNNT composite electrode material with an electrochemical performance of 82 F g^{-1} [15].

There are various binary and ternary EDLC composite electrode materials reported for supercapacitor applications; however, according to our literature survey, the printed EDLC materials based on the unique combination of MWCNTs/AC/BNNTs with excellent electrochemical properties have not yet been reported. The printing process, which is cost effective, rapid prototyping, easy customization and environmentally friendly due to the simplified processes, has shown great potential to design and fabricate high-performance energy storage devices, with the following enlisted advantages: First, it provides outstanding printing flexibility and precise geometry controllability with a wide range of bulk and nanomaterial materials in any form (powders, liquids and metals) [16]. In addition, hierarchically porous structures and composite materials can be printed, which have the advantage to enhance the electrochemical performance of energy storage devices [17]. Finally, electrodes films can be printed with both thin and thick configurations, especially with high aspect ratios. Additive manufacturing technology, such as inkjet printing, direct ink writing (DIW) and fused deposition modeling, have been extensively explored for printing technology. DIW technology offer various advantages, such as easy to operate inks with varied viscosities, highly accurate printability, excellent repeatability and able to design complex microstructures. We have adopted DIW technology for the development of electrodes for the supercapacitor application. In this study, for the first time, the MWCNTs/AC/BNNTs composite was patterned using a pneumatic printing process, and its electrochemical performance was tested in detail in a 6 M KOH electrolyte solution. The printed MWCNTs/AC/BNNTs composite electrode has shown a high specific capacitance value of 262 F g^{-1} at a minimum current density of 1 A g^{-1} . Furthermore, the novel fabricated ternary electrode material also showed an improved capacitance retention of 49.61% at a maximum current density of 10 A g^{-1} .

2. Experimental

2.1. Fabrication of Printed MWCNTs/AC/BNNTs Ternary Composite Material

The materials used to fabricate the MWCNTs/AC/BNNTs composite electrode material were purchased and used directly to prepare the electrode material without any further treatment. The MWCNTs were purchased from Korea Co, AC was purchased from Korea Co. and the BNNTs were synthesized according to the following given procedure at the Plasma Center, Department of Physics, Jeonbuk National University, Republic of Korea. The BNNTs were synthesized using a 60 kW radio-frequency (RF) plasma torch system. The BNNT synthesis method using a plasma torch process was introduced by K. S. Kim [18]; it involves forming a high-temperature plasma of *h*-BN powder and then synthesizing BNNTs during the process of collecting in the collector. It is characteristic of this synthesis method that improved the BNNT manufacturing reaction by adding hydrogen during the synthesis process. However, while it is possible to synthesize BNNTs with very small diam-

eters and excellent crystallization, this method inevitably produces h-BN residual powder and amorphous products during synthesis. The amorphous products are removed through a refining process. The printed MWCNTs/AC/BNNTs composite electrode material was synthesized according to the following listed steps. Initially, certain amounts of MWCNTs and AC (by equal weight ratio as 50 mg each) were taken to mix with certain selected different weight percentages of (BNNTs) (e.g., 0, 0.25, 0.50, 0.75 and 1 wt.%), i.e., 0, 0.25, 0.50, 0.75 and 1 mg. The ternary mixture of the MWCNTs/AC/BNNTs composite material was then mixed uniformly by grinding it for 1 h with a mortar and pestle. To prepare the ternary MWCNTs/AC/BNNTs composite electrode material, a mixture consisting of MWCNTs/AC/BNNTs, carbon black and poly(vinylidene fluoride) at a mass ratio of 8:1:1 (80, 10 and 10 mg) was well grounded for another 1 h with a mortar and pestle. Then the slurry of the latterly prepared mixture was prepared by adding N-methyl-2-pyrrolidinone into it. To make a uniform slurry of the MWCNTs/AC/BNNTs/N-methyl-2-pyrrolidinone solution, it was stirred for 120 min. As the uniform ink was prepared (as shown in the inset of Figure 1), the as-obtained MWCNTs/AC/BNNTs composite suspension was poured into a syringe framework and placed on a pneumatic dispensing system (Musashi Engineering Shot-Mini 200Sx, Japan) to apply a controlled pressure for the printing process. The syringe was mounted on a robotic head controlled by commercial software that enabled deposition of the ink composed of MWCNTs/AC/BNNTs through a movable stage. The film of the profile to be printed was transmitted to the robotic arm by the software as a series of coordinates. Air pressure of 72 KPa was applied from the dispenser, which forced the material (MWCNTs/AC/BNNTs) out of the syringe through the attached stainless-steel nozzle (model SNA-21G-B) of 21 Gauge, with a 0.52 mm internal diameter. The MWCNTs/AC/BNNTs composite solution was deposited layer-by-layer on a stainless-steel sheet skeleton. Finally, it was dried at 60 °C for 24 h before testing of its electrochemical properties.

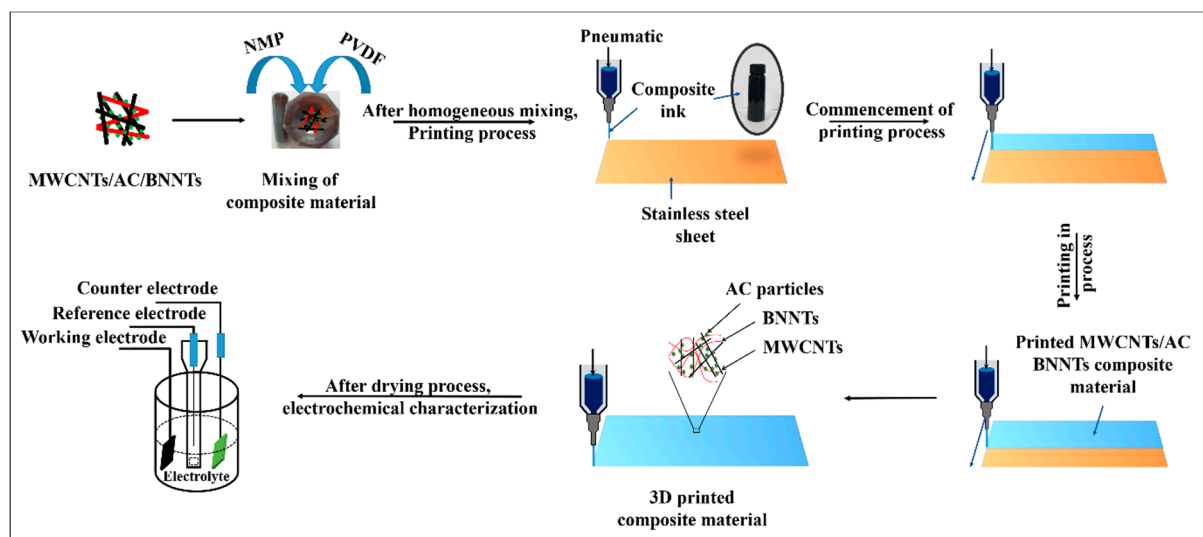


Figure 1. Schematic diagram illustrating the synthesis steps involved in the fabrication of the printed multiwalled carbon nanotubes/activated carbon/boron nitride nanotubes (MWCNTs/AC/BNNTs) ternary composite electrode material.

2.2. Material Characterizations

The morphological and other phase analyses of the as-synthesized MWCNTs/AC/BNNTs@SS sheet ternary electrode material were characterized through available various physical characterization methods, e.g., field emission scanning microscopy (FE-SEM), X-ray diffraction (XRD) and Raman spectroscopy. The micro-structural characteristics of the ternary MWCNTs/AC/BNNTs composite electrode material was examined by using the FE-SEM installed at Center-wide Research Facilities, Jeonbuk National University, Republic of Korea. The elemental composition of the as-prepared samples was investigated

by an energy dispersive X-ray spectroscopy coupled with the FE-SEM. A phase analysis of the ternary MWCNTs/AC/BNNTs composite electrode material was examined by (XRD) spectroscopy, Rigaku diffractometry, Japan. The X-Ray diffraction (XRD) patterns of samples were recorded within the 2θ range of 10° – 80° , at the lowest scan rate of 1° min^{-1} . Furthermore, Raman analysis was performed to assess the quality index of the as-prepared ternary MWCNTs/AC/BNNTs composite electrode material. The room temperature Raman analysis of the samples were recorded in the spectral range of 800 – 3000 cm^{-1} , using Raman imaging microscopy (Nanofinder 30; Tokyo Instruments Co., Osaka, Japan).

2.3. Electrochemical Testing

To test the electrochemical performance of the printed MWCNTs/AC/BNNTs composite electrode material in a three-electrode system, a stainless-steel sheet (printed with MWCNTs/AC/BNNTs) with dimensions of $1 \times 1 \text{ cm}^2$ was used directly as a working electrode, with Pt foil as a counter electrode and Hg/HgO as a reference electrode. The electrochemical performance of the printed MWCNTs/AC/BNNTs composite electrode material was tested at an electrochemical work station (SP-150 model, Bio-Logic, France, driven by EC-lab 11.25 software) in a 6 M KOH electrolyte solution. Furthermore, the kinetics of the electrical conductivity of the MWCNTs/AC/BNNTs composite electrode material were studied by electrochemical impedance spectroscopy (EIS) in the frequency range of 100 kHz to 0.01 Hz at the same electrochemical station.

The specific capacitance of the working electrode was computed by Equation (1) [19,20].

$$C_m = \frac{2ISVdt}{m\Delta V^2} \quad (1)$$

where, ΔV , I , m and $\int Vdt$ represent the working potential window (V) of the MWCNTs/AC/BNNTs composite electrode material, electron flow of the charging-discharging cycle (A), mass of the deposited MWCNTs/AC/BNNTs composite material (g) and integral area under the discharge curve of the galvanostatic charge/discharge (GCD) cycle, respectively.

3. Results and Discussion

The scheme adopted to design and develop the printed MWCNTs/AC/BNNTs ternary composite material is well described in the experimental section and also is shown in Figure 1. An optical image of the printed MWCNTs/AC/BNNTs ternary composite material is illustrated in Figure 2. The film was printed on the 316-SS sheet with the aid of 3D DIW technique by applying the suitable printing conditions (discussed in detail in experimental section). Furthermore, the FE-SEM microstructural characterizations of the MWCNTs/AC/BNNTs ternary composite material at various magnifications are illustrated in Figure 3.

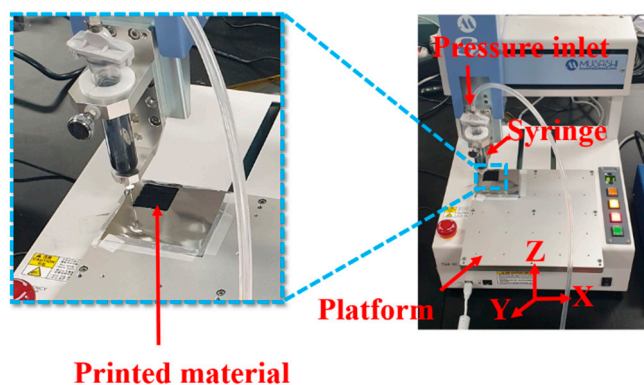


Figure 2. Optical image of the printed MWCNTs/AC/BNNTs ternary composite material.

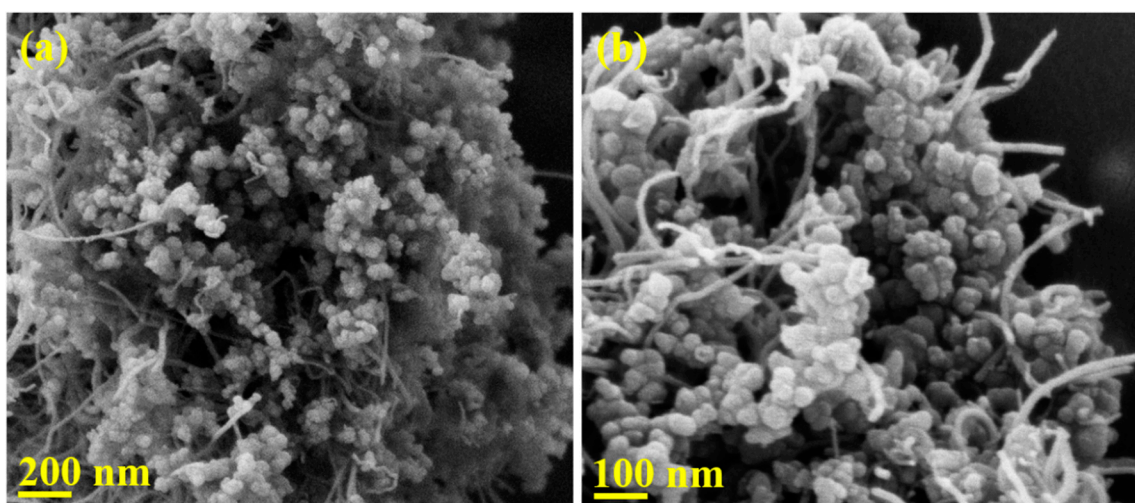


Figure 3. (a,b) FE-SEM images of the MWCNTs/AC/BNNTs ternary composite material at different magnifications.

We can observe spherical and tubular-like structures of the claimed MWCNTs/AC/BNNTs ternary composite material. The tubular-like structures are associated with MWCNTs and BNNTs, while the spherical morphology in the FESEM images indicates the presence of AC. The multicomponent design was beneficial to develop the high-performance MWCNTs/AC/BNNTs composite electrode material, where each component contributed individually as well as working as a multicomponent system with enhanced synergistic interaction during the electrochemical reaction. The presence of the tubular-like structures of MWCNTs and BNNTs were beneficial enough to reduce the agglomeration phenomena of the AC spherical particles and to achieve high electrochemical performance of the MWCNTs/AC/BNNTs composite electrode material. The crystallinity level of the possible phases of MWCNTs/AC/BNNTs composite material was investigated through an XRD analysis (Figure 4a). The peaks appearing at the 2θ position of 25.48° and 42.49° represent crystal planes (002) and (100) of the typical graphitic carbon structure [21,22]. In addition, the BNNT crystal planes (002) and (101) also appear at the same 2θ positions of 25.48° and 42.49° , respectively [23,24]. Thus, the highly crystalline structure of the as-synthesized MWCNTs/AC/BNNTs ternary composite material is verified by the XRD analysis. Raman spectroscopy is an important tool to analyze the crystalline quality index of carbon-based materials such as MWCNTs. The two typical bands, i.e., the “D” and “G” bands, have appeared in the typical Raman spectra (Figure 4b) of the MWCNTs/AC/BNNTs ternary composite material. The respective bands have appeared at the Raman shift (cm^{-1}) positions of 1334 and 1563.84, respectively, and indicate the presence of incompletely graphitized carbon atoms. The high intensity of the G-band peak in comparison to the D-band peak clearly indicates a high crystallinity level of the as-synthesized MWCNTs-based composite electrode material. The ratio between I_D/I_G was estimated to be 0.85. Furthermore, the BET surface area and pore size of AC, MWCNT and BNNT was analyzed by the nitrogen adsorption-desorption isotherm method with the help of Brunauer–Emmett–Teller (BET) technique and detailed results are presented in (Figure 4c–e) and Table 1.

Table 1. Physical properties of activated carbon, multiwalled carbon nanotubes and boron nitride nanotubes.

Sample	BET Surface Area ($\text{m}^2 \text{g}^{-1}$)	Size of Pore ($\text{\AA}$)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)
Multiwalled carbon nanotubes	62.0763	201.7726	0.313132
Activated carbon	271.7288	365.4881	2.482841
Boron nitride nanotubes	54.6504	202.8095	0.277091

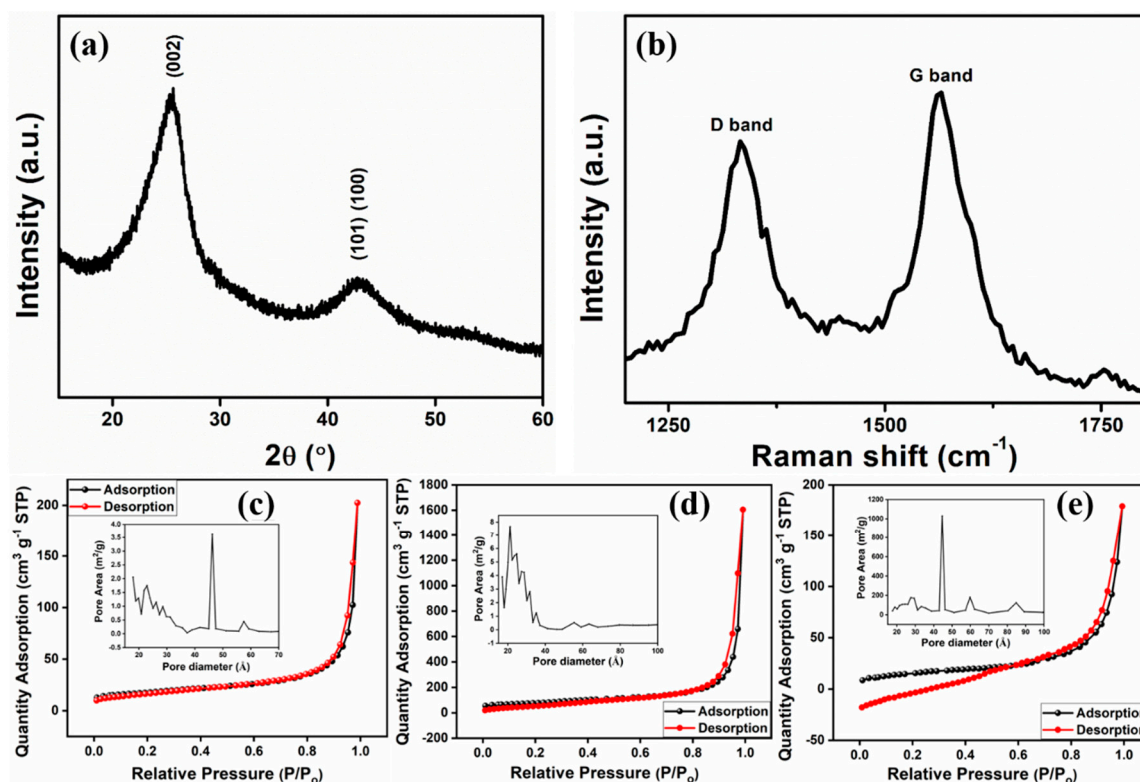


Figure 4. (a,b) The typical XRD and Raman analyses of the MWCNTs/AC/BNNTs ternary composite material, respectively. (c–e) N_2 adsorption–desorption isotherms (inset show pore size distribution) of the MWCNTs, activated carbon and BNNTs, respectively.

The electrochemical performance of the printed MWCNTs/AC/BNNTs composite was studied in detailed in a three-electrode system and the relevant results are illustrated in Figure 5. The added different contents (0, 0.25, 0.50, 0.75 and 1 wt.%) of the BNNTs in MWCNTs/AC are marked by the given series of MWCNTs/AC-1, MWCNTs/AC/BNNTs-2, MWCNTs/AC/BNNTs-3, MWCNTs/AC/BNNTs-4 and MWCNTs/AC/BNNTs-5 composite materials, respectively. We can observe that the printed MWCNTs/AC/BNNTs-3 composite electrode material has shown high electrochemical performance in terms of both the cyclic-voltammetry (CV) and GCD outputs. A possible reason for the improved electrochemical performance of MWCNTs/AC/BNNTs-3 is that the addition of the optimal BNNTs content weakened the agglomeration phenomena of the AC particles and MWCNTs in the composite electrode material. In addition, BNNTs are very stable in acidic as well as in basic aqueous electrolytes and also the presence of BNNTs increase the electrolyte uptake. The reduced agglomeration phenomena of the MWCNTs/AC/BNNTs-3 composite electrode material may have resulted possibly in the improved surface area and maximum access to the electrolyte solution in the electroactive multicomponent system [14]. Another possible reason for the improved electrochemical properties of the MWCNTs/AC/BNNTs-3 composite electrode material is that the printed multicomponent system allows each component to participate with a synergistic effect to boost its electrochemical performance. However, MWCNTs/AC-1, MWCNTs/AC/BNNTs-2, MWCNTs/AC/BNNTs-4 and MWCNTs/AC/BNNTs-5 have shown inferior electrochemical performance in comparison to the MWCNTs/AC/BNNTs-3 composite material, owing to insufficient and overdoses of the BNNT contents in the composite electrode material, respectively. Once the optimization stage was fully investigated, the electrochemical performance of the optimized printed MWCNTs/AC/BNNTs-3 composite electrode material was studied in detail (Figure 5).

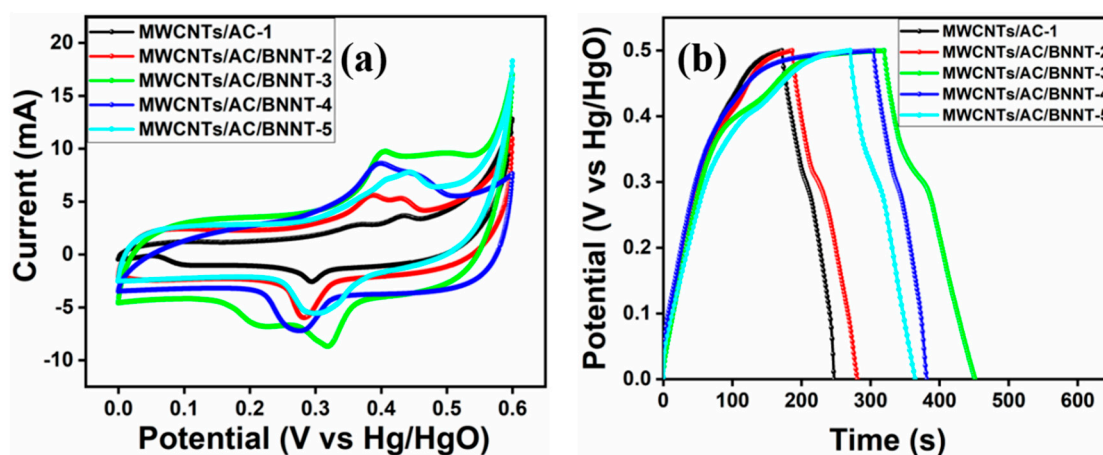


Figure 5. Electrochemical characterizations of printed the MWCNTs/AC/BNNTs ternary composite material with different contents of BNNT material: (a) cyclic-voltammetry (CV) response measured at a scan rate of 30 mV s^{-1} ; and (b) galvanostatic charging–discharging (GCD) curves measured at a current density of 1 A g^{-1} .

The CV response of the printed MWCNTs/AC/BNNTs-3 composite electrode material was investigated thoroughly at various scan rates (Figure 6a). The current density of the composite electrode material increased with an increasing scan rate, ranging from lower to maximum values of 5 to 100 mV s^{-1} . Similarly, the electrochemical performance of the printed MWCNTs/AC/BNNTs-3 composite electrode material in terms of the GCD was also measured, and the recorded results are depicted in Figure 6b. The MWCNTs/AC/BNNTs-3 composite has shown a lengthy charging–discharging cycle at a minimum current density of 1 A g^{-1} , while the charging–discharging cycle lengths were decreased as the current density was increased from 1 to 10 A g^{-1} . The specific capacitance of the MWCNTs/AC/BNNTs-3 composite electrode material was calculated from the measured GCD plots according to Equation (1). The MWCNTs/AC/BNNTs-3 composite has shown a maximum specific capacitance of 262 F g^{-1} at 1 A g^{-1} with 49.61% capacitance retention at a maximum current density of 10 A g^{-1} . In addition, the charge transfer and solution resistance kinetics were studied by EIS and the measured results are displayed in Figure 6d. The as-fabricated MWCNTs/AC/BNNTs-3 composite has shown a minimum charge transfer resistance (R_{ct}) of 0.15Ω due to the presence of multiple carbon-based elements, such as AC and MWCNTs. Moreover, the stability testing of the printed MWCNTs/AC/BNNTs-3 composite film was also evaluated (Figure 6e) and it demonstrated a specific capacitance retention of 95% after the maximum number of cycles (1000).

As the printed MWCNTs/AC/BNNTs composite film has shown a high electrochemical-performance in terms of specific capacitance, so the possible working electrochemical mechanism of the ternary composite is illustrated in Figure 7 and explained as follows: Firstly, it is a ternary composite material, where each of the present material has participated individually during the electrochemical testing. Secondly, the presence of spherical-shaped AC particles has provided highly conducting channels for the ultra-fast movement of electrons and ions. Thirdly, the presence of optimized BNNT contents have resulted in an MWCNTs/AC/BNNTs system with better dispersion, extra electrolyte uptake and less agglomeration. Therefore, the electrolyte ions have better and improved access to the electroactive materials to respond with highly specific capacitance. Finally, the printed process has helped to obtain maximum areal density of the electroactive MWCNTs/AC/BNNTs material to display its suitable electrochemical-performance.

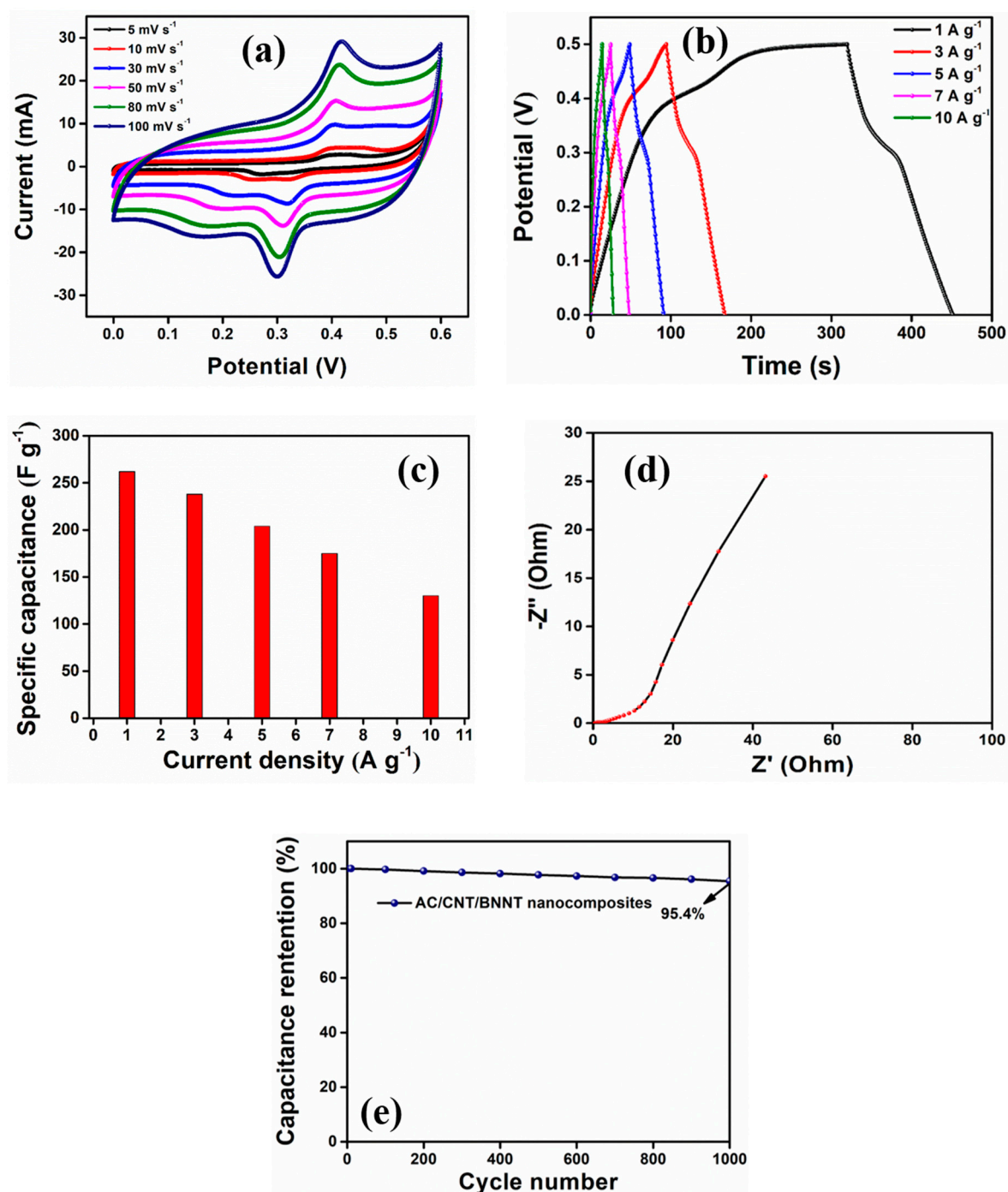


Figure 6. Electrochemical characterizations of the printed MWCNTs/AC/BNNTs ternary composite material with an optimized BNNT content: (a) cyclic-voltammetry (CV) response measured at various scan rates; (b) galvanostatic charging-discharging (GCD) curves measured at various current densities; (c) measured specific capacitance at various current densities; (d) electrochemical impedance spectroscopy (EIS) measurements; and (e) cycling stability performance of the MWCNTs/AC/BNNTs ternary composite material.

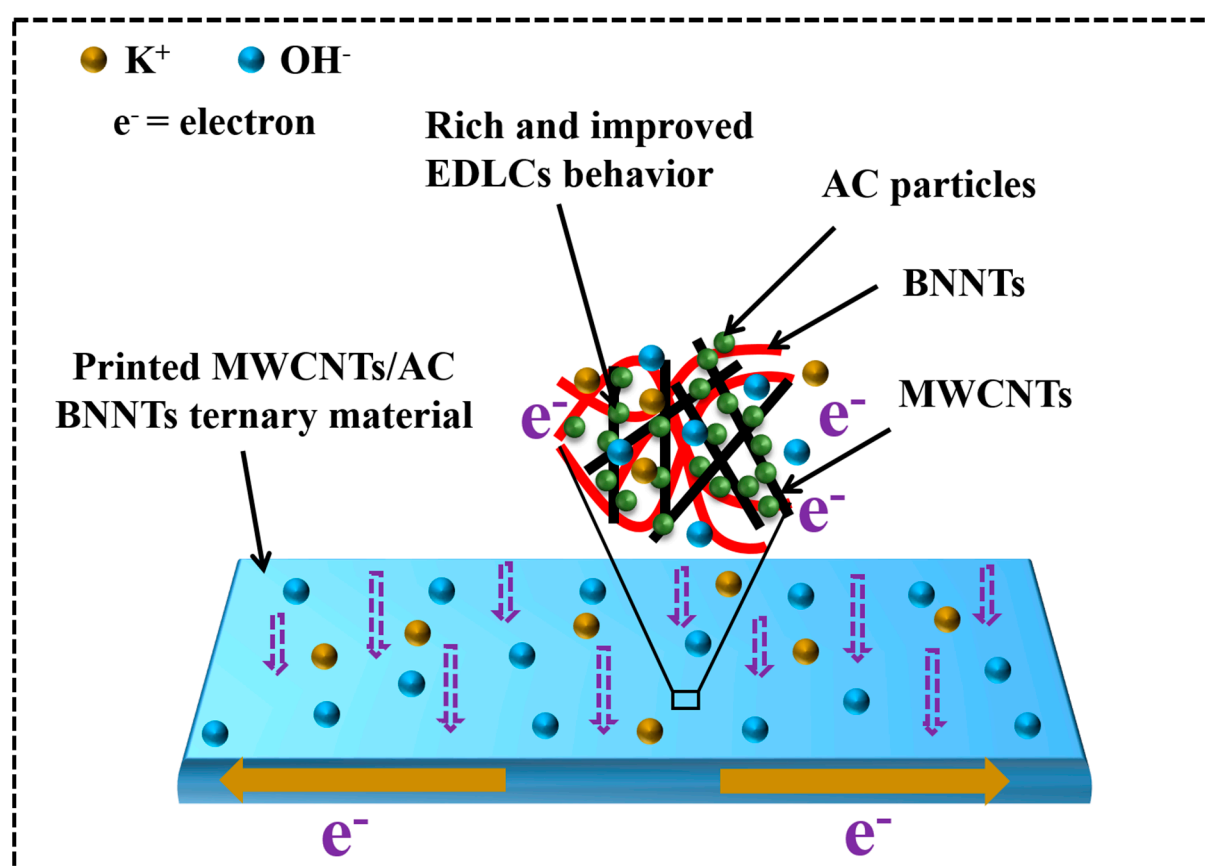


Figure 7. Schematic diagram showing the improved and rich electrical double layer capacitor (EDLC) behavior of the printed MWCNTs/AC/BNNTs ternary composite material.

4. Conclusions

In summary, for the first time, a high-performance 3D-printed MWCNTs/AC/BNNTs ternary composite electrode material for supercapacitor applications was successfully developed in this study. The formation of the MWCNTs/AC/BNNTs ternary composite electrode material was well-established with the aid of various available physical characterization methods. The as-printed MWCNTs/AC/BNNTs ternary composite electrode material exhibited a high specific capacitance of 262 F g^{-1} at a low current density of 1 A g^{-1} in a three-electrode configuration. Furthermore, the MWCNTs/AC/BNNTs ternary composite electrode material displayed a highly specific capacitance retention of 49.61% at a maximum current density of 10 A g^{-1} . The new findings of this research work will provide opportunities to design and fabricate printable EDLC-based ternary composite electrode materials for high-performance supercapacitors.

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