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Facile Synthesis of a NiCo₂O₄ Nanoparticles Mesoporous Carbon Composite as Electrode Materials for Supercapacitor

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Combination the materials together is a direct and forceful strategy to improve the electrochemical properties of each raw material. Herein, we present the method of hydrothermal process and treatment/calcination combination that is easy to synthesize a NiCo₂O₄ nanoparticles-mesoporous carbon composite (C/NiCo₂O₄). The result study electrochemical properties of materials revealed that the C/NiCo₂O₄ composite has excellent electrochemical properties compare with pristine NiCo₂O₄ or

carbon. In particular, maximum specific capacitance of C/NiCo₂O₄ material at a current density of 1 A.g⁻¹ is 204.28 F.g⁻¹, meanwhile the C_s of carbon and NiCo₂O₄ are 25.06 F.g⁻¹ and 178.78 F.g⁻¹, respectively. In addition, C/NiCo₂O₄ material also showed excellent capacitance retention, C_s maintained to 90.35% after 3000 charge-discharge continuous cycles. The results show that the C/NiCo₂O₄ is a promising material for application as supercapacitor electrode.

1. Introduction

Today, global fossil fuel reserves are running out, the world population is growing meanwhile, the demand of energy storage devices is increasing.^[1] This creates a great motivation to promote research and development of clean and friendly energy storage devices. In recent years, supercapacitor (SCs) is known as a promising energy storage device because it has many advantages, such as: high energy, superior energy density, excellent durability and high efficiency.^[2]

Based on to the charging mechanism, SCs are divided into two main categories: electrical double-layer capacitors (EDLCs) and Faradaic redox reaction pseudo-capacitors (PCs).^[2a,3] EDLCs accumulate electrical energy based solely on process absorption/desorption of electrolyte ions at the interface of electro-

lytes and electrodes. Therefore, carbon base materials with large specific surface area are commonly used for EDLCs, such as activated carbon,^[4] carbon foam,^[5] carbon nanotubes,^[6] graphene.^[7] PCs operate based on redox reactions between active material and ions of electrolyte on interface of their, so their working processes are limited by kinetics of redox reaction. Compared with EDLCs, PCs provide higher energy density, but lower power density. The well-known electrode materials for PCs are substances that have multiple oxidation states such as nano-structured metal oxides (MnO₂, NiCo₂O₄),^[8] metal sulfides,^[9] conductive polymers (PPy, PEDOT, PANI).^[10]

Recently, transition metal oxides have received intensive attention as electrode materials for energy storage applications because of their high specific capacitance (Cs), natural abundance, and easy fabrication to obtain nanostructures.^[11] Among them, NiCo₂O₄ oxide is a promising candidate for the applications because it consists of multiple oxidation state metals, has high electrical conductivity and superb capacity storage.^[8c] In addition, NiCo₂O₄ hybrid metal oxides possess higher conductivity and capacity than both NiO and Co₃O₄.^[8b,12] However, most transition metal oxides have certain limitations: low power density, poor rate capability and cycling stability.^[13] The number of studies has been investigated to resolve the problems and mainly focused on the direction of combining transition metal oxides with different conductive materials, especially carbon-based materials.^[14] Carbon is chosen because it has outstanding features such as superior electrical conductivity, high energy density, excellent capacitance retention and natural abundance.^[15] For example, Vedyappan Veeramani et al. successfully synthesized porous carbon nanosheets decorated NiCo₂O₄ with 3,4-ethylenedioxythiophene polymers (EDOT) in the form of carbon sources (C@NiCo₂O₄), the results show that when tested in the same conditions, Cs of C@NiCo₂O₄ was 162% higher than the C_s of NiCo₂O₄.^[16] Similarly,

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involving the combination of NiCo_2O_4 and carbon based materials: $\text{rGO@NiCo}_2\text{O}_4$,^[17] $\text{rGO@NiCo}_2\text{O}_4$ on nickel foam,^[18] $\text{rGO@MnFe}_2\text{O}_4\text{@PPy}$,^[19] core-shell of carbon nanosphere and NiCo_2O_4 ,^[20] these studies revealed that composite materials have C_s outperformed to its individual materials. However, the fabrication methods are complicated, high cost, not environment-friendly, and difficult to implement in large scale, which limit the practical applications as supercapacitor electrodes.

In this work, we provide a simply and eco-friendly method for synthesizing $\text{C/NiCo}_2\text{O}_4$ composite with high electrochemical efficiency. Where, carbon source is a popular commercial product and only one step calcination to obtain carbon without further processing. The results showed that, $\text{C/NiCo}_2\text{O}_4$ composite was successfully synthesized and the NiCo_2O_4 nanoparticles are evenly distributed on the carbon porous. The combination of carbon and NiCo_2O_4 creates a new material that operates under a hybrid capacitor mechanism. The material has higher electrochemical effective compare to the individual NiCo_2O_4 or carbon. In particular, the long-cycled test results indicated that $\text{C/NiCo}_2\text{O}_4$ material is capable of maintaining excellent capacitance.

2. Results and Discussion

2.1. Structural and morphological characterization

The XRD profile observed for NiCo_2O_4 and $\text{C/NiCo}_2\text{O}_4$ are shown in Figure 1a. The main diffraction peaks in XRD pattern of NiCo_2O_4 material located at 19.01° , 31.22° , 36.73° , 38.35° , 44.67° , 55.52° , 59.14° and 65.02° are indexed to the (111), (220), (311), (222), (400), (422), (511) and (440) planes, respectively and can be assigned to NiCo_2O_4 phase (JCPDS #73-1702), which has cubic spinel structure and space group $\text{Fd-}3\text{m}$ (227). The XRD pattern of $\text{C/NiCo}_2\text{O}_4$ material also shown all diffraction peaks of NiCo_2O_4 phase but with weaker diffraction intensity. It has been known that the XRD peak intensity is related to both the crystal structure and composition. Therefore, the reduction in the intensity of XRD pattern of $\text{C/NiCo}_2\text{O}_4$ as compared to NiCo_2O_4 material is thought to be due to their difference in composition. In addition, there are no diffraction peaks of carbon in XRD pattern of the $\text{C/NiCo}_2\text{O}_4$ composite indicating that carbon in the composite is amorphous. In all XRD profile unable to detect other peaks indicates that the $\text{C/NiCo}_2\text{O}_4$ composite has a high purity.

Figure 1 b TG curves of carbon, NiCo_2O_4 and $\text{C/NiCo}_2\text{O}_4$. It can be seen in all TGA curves, there is a small mass loss due to evaporation of moisture. For TGA curve of carbon, the mass loss in the temperature range from 400 to 600°C is

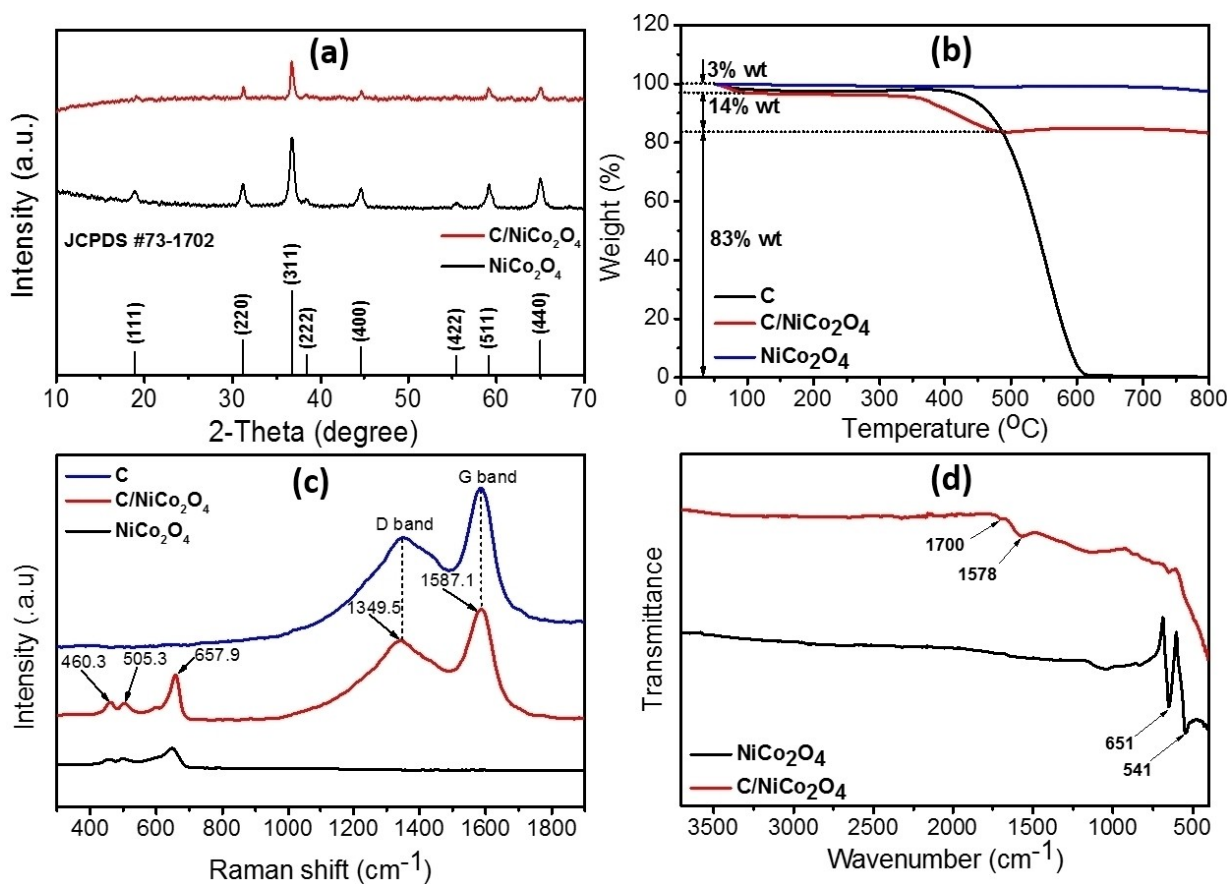


Figure 1. (a) XRD patterns of the NiCo_2O_4 and $\text{C/NiCo}_2\text{O}_4$; (b) TG analysis of Carbon, NiCo_2O_4 and $\text{C/NiCo}_2\text{O}_4$; (c) Raman spectra of Carbon, NiCo_2O_4 and $\text{C/NiCo}_2\text{O}_4$; (d) FT-IR of NiCo_2O_4 and $\text{C/NiCo}_2\text{O}_4$.

attributed to the combustion of amorphous carbon; when the temperature is higher than 600 °C, the weight of analytical sample is approximately of zero, this result indicates that there are no inorganic impurities. Meanwhile, the burning of amorphous carbon in C/NiCo₂O₄ sample at temperature range from 350 to 500 °C shows the mass of analysed sample decreased by 12.4%, which indicates that the ratio of carbon in the C/NiCo₂O₄ composite is ~ 12.4%. It also reveals that the presence of NiCo₂O₄ in C/NiCo₂O₄ lead to carbon burned at lower temperature, which has been reported in other hybrid materials such as rGO@MnFe₂O₄@PPy,^[19] carbon fiber/Ni-Co composites.^[21]

The Raman spectra of NiCo₂O₄, Carbon and C/NiCo₂O₄ samples shown in Figure 1c. In the Raman spectrum of carbon showed the presence of double peaks at 1349.5 and 1587.1 cm⁻¹, which can be assigned to the D band and G band of carbon amorphous, respectively.^[22] These observations are also evident in the Raman spectrum of C/NiCo₂O₄ and indicated the presence of carbon amorphous in the C/NiCo₂O₄ material. In addition, the appearance of peaks at 460.3, 505.3 and 657.9 cm⁻¹ in the Raman spectrum of C/NiCo₂O₄ attributed to the E_g, F_{2g}, and A_{1g} vibration modes of the NiCo₂O₄ spinel

structure, respectively.^[23] This the result match well with the Raman spectrum of NiCo₂O₄ and confirm the formation of NiCo₂O₄ in the synthesized materials.

Figure 1d presents the FT-IR spectra of all synthesized materials. In the spectrum of NiCo₂O₄ material, there are two sharp peaks at low frequencies (541 cm⁻¹ and 651 cm⁻¹), which correspond to the stretching vibrations of Ni–O and Co–O bonds in NiCo₂O₄.^[24] Meanwhile, two peaks corresponding to Ni–O and Co–O bonds in the FT-IR of C/NiCo₂O₄ composite appearance with weak intensity, this due to the existence of carbon in its. In addition, the presence of two peaks at roughly 1578 and 1700 cm⁻¹ can be assigned to the stretching vibrations of the C–C and C=O bonds, respectively.^[24–25] The results proved the presence of carbon in the C/NiCo₂O₄ material.

The morphology of carbon, NiCo₂O₄ and C/NiCo₂O₄ were investigated using SEM, TEM measurements and the result showed in Figure 2. As shown in SEM and TEM images, NiCo₂O₄ particle has a polyhedral shape with some degrees of aggregation and its average size is typically about 50 nm. Meanwhile, SEM and TEM images of C/NiCo₂O₄ show that the NiCo₂O₄ particles are uniformly distributed into amorphous

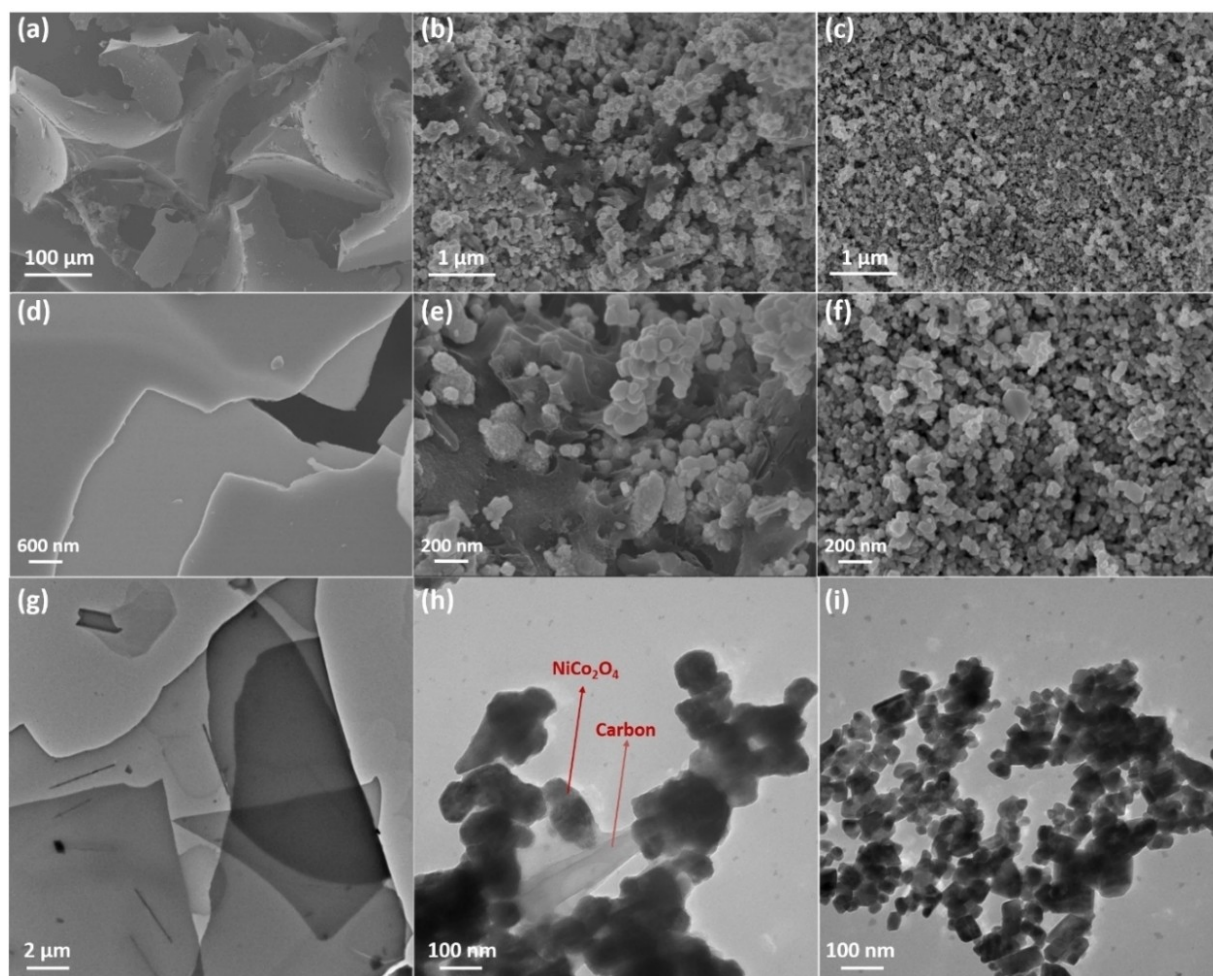


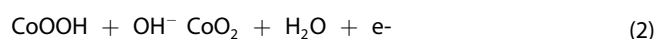
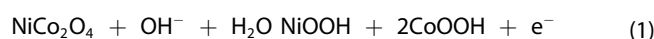
Figure 2. SEM and TEM images of Carbon (a, d, g); C/NiCo₂O₄ (b, e, h) and NiCo₂O₄ (c, f, i)

carbon and its average size is about 100 nm, suggesting that NiCo₂O₄ precursors added into molten sucrose result in a larger NiCo₂O₄ agglomeration but keep its polyhedron shape not changed. The SEM, TEM images of carbon show that the morphology of amorphous carbon is like muddy clays and the surface of the carbon is clean. The additional SEM images of the materials can be seen in the Supporting Information [Supporting Figure S1, S2, and S3].

To evaluate chemical composition of materials, we were using energy dispersive X-ray spectroscopy (EDS) analysis and the result showed in Figure 3. The EDS results confirm the presence of C and O in carbon; Ni, Co, and O in NiCo₂O₄; C, Ni, Co, and O in C/NiCo₂O₄. The present of oxygen atomic in the carbon sample with atomic percentage about 13.51%, which indicates that 1 hour carbonization is not long enough, therefore need to consider more the effect of carbonization time or temperature to properties of carbon obtained. Figure 3f shows the EDS result of NiCo₂O₄ material, where the atomic ratio of Ni/Co/O is 1: 2.1: 4.1 indicating that the component of the NiCo₂O₄ product is closed to the desired NiCo₂O₄ phase. Meanwhile, atomic ratio of Ni/Co/O in the C/NiCo₂O₄ composite (Figure 3e) is 1:2.18:5.39 [Supporting Table S1]. The ratio of Ni/Co in the NiCo₂O₄ and C/NiCo₂O₄ is equivalent but atomic ratio of Ni/O change from 1:4.1 up to 1:5.39. As shown in the EDS results for carbon materials (Figure 3d), O atom appear in carbon materials with a percentage of about 13.5%. Due to the total of O atoms in the C/NiCo₂O₄ material include of O in carbon and O in NiCo₂O₄, the percentage of O atoms in C/NiCo₂O₄ is evidently higher than that of NiCo₂O₄.

2.2. Electrochemical characteristics CV analysis

To estimate electrochemical performance of synthesized materials, CV test was performed at a scan rate of 20 mV.s⁻¹ for all materials and the result showed in Figure 4a. The CV curve of carbon looks like a rectangle, which shows the working process of carbon complying with the EDLC mechanism.^[7] Meanwhile, in CV curves of C/NiCo₂O₄ and NiCo₂O₄, a pair of redox peaks is clearly observed, which were attributed to redox reactions relating to conversions of A-O/A-O-OH (A=Ni or Co).^[26] In a potential window of 0 to 0.5 V in an alkaline solution, redox reaction between NiCo₂O₄ and OH⁻ ion of KOH electrolyte can be described by the following equations:



The results confirming that, C/NiCo₂O₄ and NiCo₂O₄ exhibit pseudocapacitor behaviour based on electron transfer process, and their main mechanism for energy storage is based on redox reactions. Figure 4a also shows that the CV curve of C/NiCo₂O₄ has internal area higher than carbon and NiCo₂O₄, indicating that C/NiCo₂O₄ has the largest C_s. The C_s improvement of the C/NiCo₂O₄ material compared pristine carbon or NiCo₂O₄ is ascribed to a synergistic effect of carbon and NiCo₂O₄ components in its.^[17,19, 21]

CV measurements of C/NiCo₂O₄ material conducted at different scan rates from 10–100 mV.s⁻¹ within the potential range of -0.45 - 0.45 V is displayed in Figure 4b. The increasing of current densities at redox peak when increasing scan rate indicate that the redox reactions on surface of C/NiCo₂O₄ electrode occur rapidly,^[27] which is essential for being super-

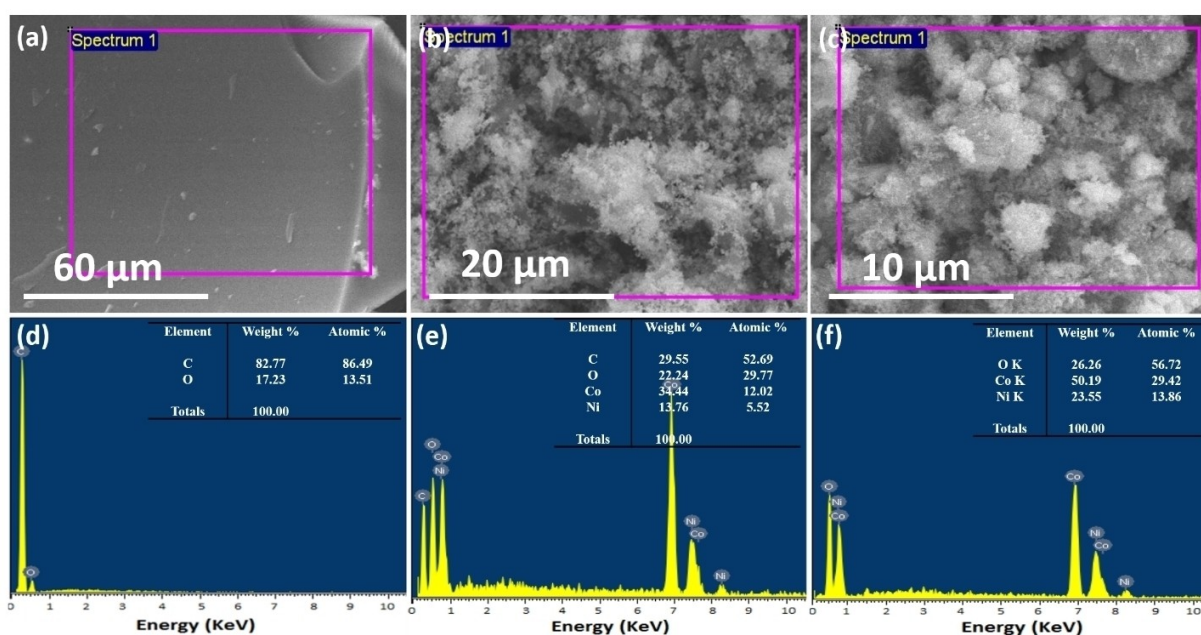


Figure 3. SEM images and corresponding EDS profiles of Carbon (a, d); C/NiCo₂O₄ (b, e) and NiCo₂O₄ (c, f).

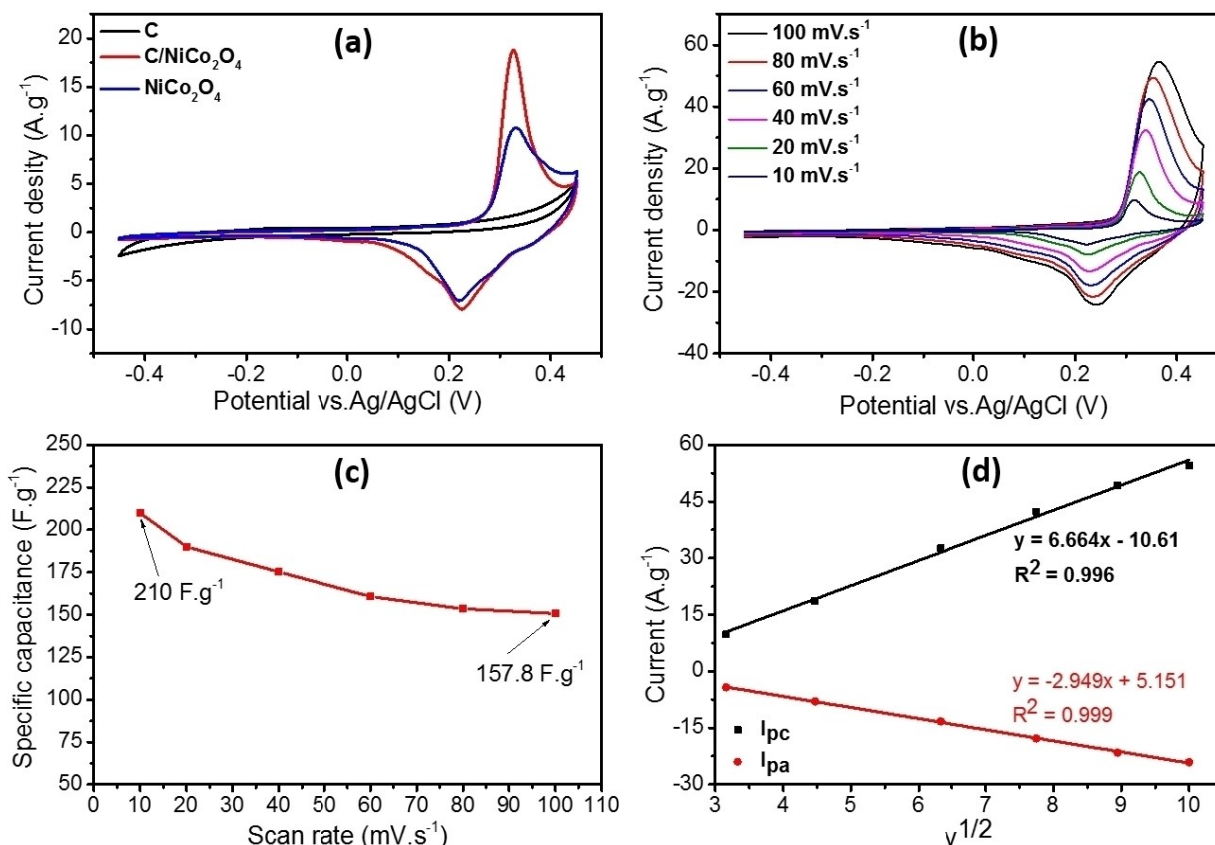


Figure 4. (a) CV curves of all materials at a scan rate of 20 mV.s^{-1} ; (b) CV curves of C/NiCo₂O₄ at different scan rates; (c) C_s of C/NiCo₂O₄ at different scan rates; (d) Randles-Sevcik plots for C/NiCo₂O₄.

capacitor electrode materials. Figure 4c displays the C_s of C/NiCo₂O₄ materials at different scan rate. As shown in Figure 4c, the C_s of the C/NiCo₂O₄ increases as scanning rate decreases: when increases scan rates from 10–100 mV.s^{-1} , C_s of C/NiCo₂O₄ decreases from 210–157.8 F.g^{-1} . The small decreases of C_s when increases scan rate suggest C/NiCo₂O₄ has high rate capacity, which reflects its charging performance at a high charging rate. In scan rate range, rate capacity is the ratio between the C_s at maximum scan rate and the C_s at minimum scan rate. The rate capacity of the C/NiCo₂O₄ is 0.75, this value is superior proving that C/NiCo₂O₄ material not only capably delivers high energy density but also high power density. More specifically, both the anodic peak current (I_{pa}) and the cathodic peak current (I_{pc}) increase linearly with the square root of the scan rate ($v^{1/2}$) (Figure 4d), which consisted well with the Randles-Sevcik equation.^[28] These observations suggest that redox reactions occurred at the electrode/electrolyte interface are apparently reversible and only limited by electrolyte diffusion.

GCD analysis

To evaluate the C_s of all synthesized materials, GCD measurements were conducted within the potential range of -0.45 to 0.45 V at different current densities from 1 to 6 A.g^{-1} and the

GCD voltage profile of all materials showed in Figure 5(a–c). The GCD curve of carbon is almost triangular, indicating that the electrical storage mechanism is EDLC. The result is completely consistent with the CV curve of the carbon in Figure 4a. The GCD voltage profiles of C/NiCo₂O₄ and NiCo₂O₄ (Figure 5b and 5c) show one voltage plateau, which match well with the I_{pc} and I_{pa} peaks occurred in CV curves (Figure 4a), indicating that the NiCo₂O₄ and C/NiCo₂O₄ exhibit pseudocapacitor behaviour based on electron transfer process and their primary energy storage mechanism is based on redox reactions. The small difference between discharge and charge potential plateau in GCD profiles indicates a high electrochemical reversibility and small series resistances of the electrode.^[26,28]

As analyzed in the part result of CV measurement, rate capability is an important parameter for materials use as supercapacitor electrode. To estimate rate capability, the C_s of all materials at different current densities were calculated from GCD profiles and plotted in Figure 5d, the C_s of all materials were listed in the Supporting Information [Supporting Table S2]. It can be seen that, the small decreases of C_s for all materials when discharge current density increases showing the fast Faradaic redox reaction kinetics and the remarkable rate capability of the electrode materials. At the same current density, C_s of C/NiCo₂O₄ composite material is always higher

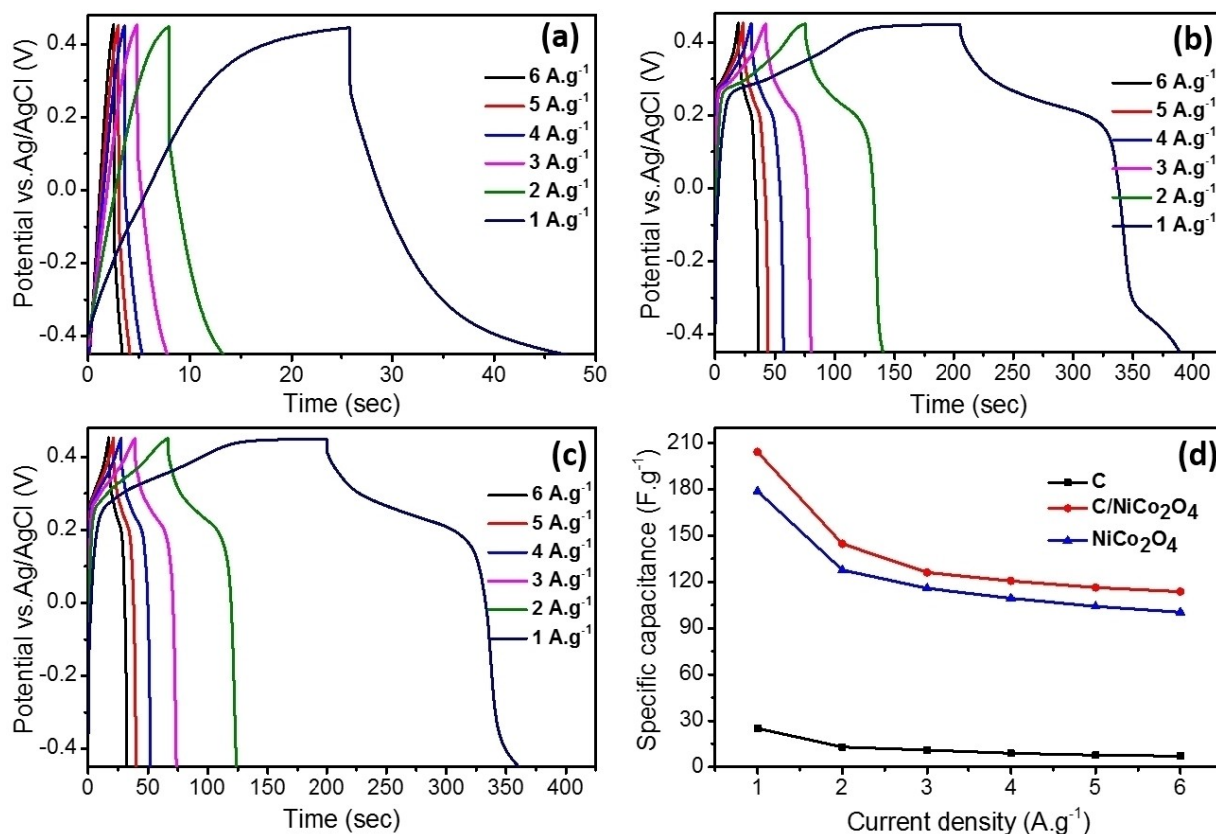


Figure 5. (a - c) GCD curves, (d) Specific capacitance of the carbon, C/NiCo₂O₄ and NiCo₂O₄ at different current densities.

than those of pristine carbon and NiCo₂O₄: at a current density of 1 A.g⁻¹, C_s of C/NiCo₂O₄ is 204.28 F.g⁻¹, which is higher than C_s of NiCo₂O₄ (178.78 F.g⁻¹) and carbon (25.06 F.g⁻¹). These results agree well with the results of the CV analysis and show strong evidence of the synergistic effect between carbon and NiCo₂O₄ in C/NiCo₂O₄ material. This synergistic effect actually is the combination of both two charging mechanism in EDCL and PCs, which also appeared in composite materials based carbon and oxide metals such as: rGO@NiCo₂O₄,^[17] rGO@NiCo₂O₄ on nickel foam,^[18] 3D-Graphen@NiCo₂O₄,^[29] NiCo₂O₄ on ultra-thin foam carbon 3D.^[30] The C_s of C/NiCo₂O₄ composite is superior or equivalent to that of carbon, NiCo₂O₄ and their hybrid composites, as listed in Table 1.

The energy density (E) and power density (P) of the materials were calculated from the C_s values at different current densities, and the results are plotted in Figure 6a. The energy density and power density of the C/NiCo₂O₄ are superior to pristine NiCo₂O₄ and carbon. The C/NiCo₂O₄ material delivers an energy density of 5.75 Wh.kg⁻¹ at a power density of 112.5 W.kg⁻¹. Even at high power density of 675 W.kg⁻¹, C/NiCo₂O₄ still delivers an energy density of 3.2 Wh.kg⁻¹. Meanwhile, energy density of carbon and NiCo₂O₄ is lower than that of C/NiCo₂O₄ at the same power density.

Table 1. Comparison of capacitance performance of previously reported carbon, NiCo₂O₄ and hybrid composite materials.

Electrode materials	Method of synthesis	Electrolyte	Window potential	C _s	Reference
NiCo ₂ O ₄ -decorated porous carbon	Hydrothermal/ Calcination	6 M KOH	0 – 0.5 V	596.8 F.g ⁻¹ at 2 A.g ⁻¹	[16]
NiCo ₂ O ₄ -decorated carbon fiber	Solvothermal/ Calcination	2 M KOH	0 – 0.45 V	456 F.g ⁻¹ at 2 A.g ⁻¹	[31]
NiCo ₂ O ₄ /Carbon active composite	Hydrothermal	6 M KOH	0 – 0.5 V	96.6 F.g ⁻¹ at 1 A.g ⁻¹	[32]
Carbon-Based Spinel NiCo ₂ O ₄	Hydrothermal	6 M KOH	0 – 0.6 V	201 F.g ⁻¹ at 2 A.g ⁻¹	[33]
C/NiCo ₂ O ₄	Hydrothermal/ Calcination	3 M KOH	-0.45 – 0.45	204.3 F.g ⁻¹ at 1 A.g ⁻¹	This study

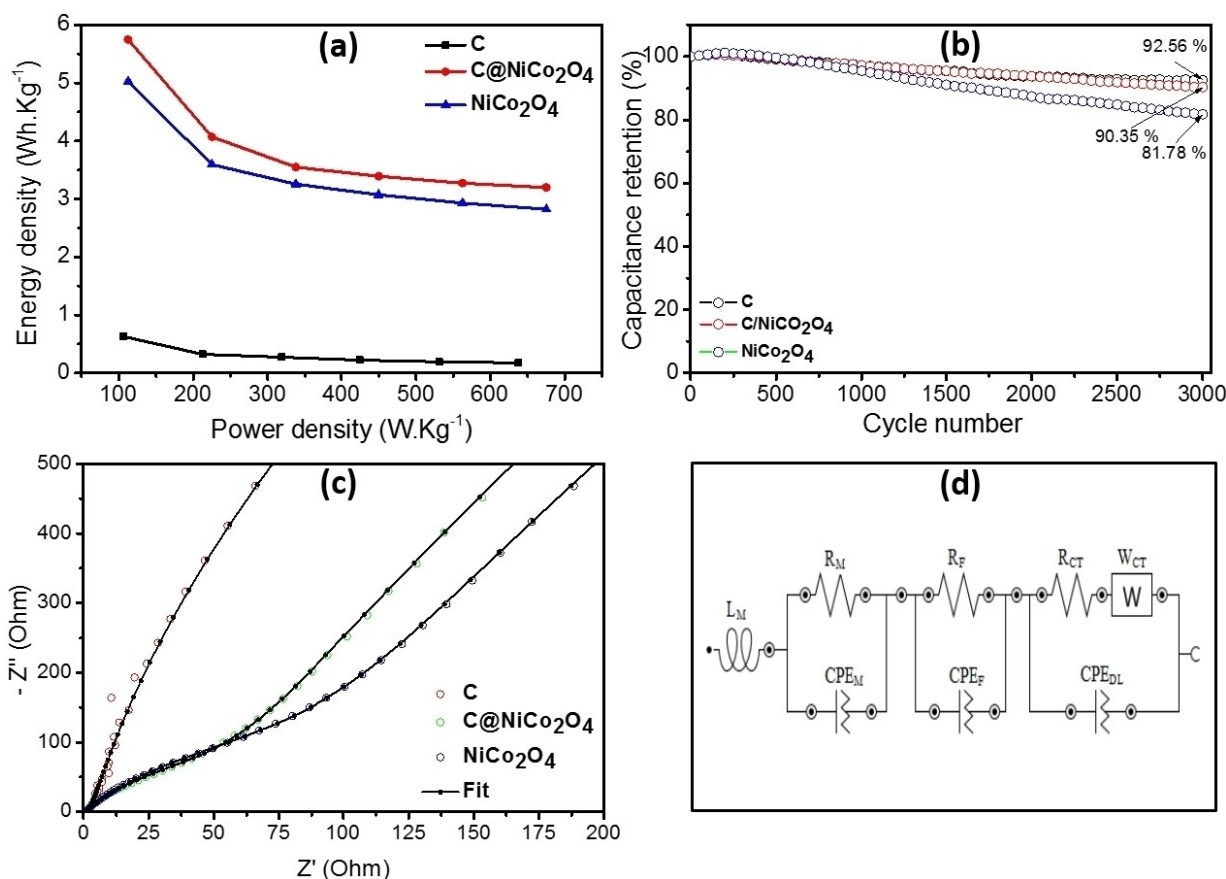


Figure 6. (a) Ragone plot of Carbon, NiCo₂O₄ and C/NiCo₂O₄; (b) Cycling performance of carbon, NiCo₂O₄ and C/NiCo₂O₄ for 3000 cycles at a current density of 2 A.g⁻¹; (c) Nyquist plots of carbon, NiCo₂O₄ and C/NiCo₂O₄ at full frequency range; (d) Equivalent circuit diagram used for fitting EIS data

Cycling stability

The cycling performance of synthesized materials was evaluated by repeating GCD measurement for 3000 cycles at a current density of 2 A.g⁻¹. For NiCo₂O₄ and C/NiCo₂O₄ materials, it can be seen that the C_s increases upon cycling and reaches the maximum at ca. 150th cycle (Figure 6b), meanwhile, C_s of carbon reaches maximum value on the first cycle. The maximum C_s of NiCo₂O₄ and C/NiCo₂O₄ corresponds to full activation of the NiCo₂O₄. As shown in Figure 6b, after 3000 cycles the C_s of carbon, C/NiCo₂O₄ and NiCo₂O₄ retained 92.56, 90.35 and 81.78%, respectively. The higher capacitance retention of C/NiCo₂O₄ compared to NiCo₂O₄ indicates the presence of carbon indeed contributed an important role. The carbon not only increases the electric storage capacity but also increases the stability of NiCo₂O₄ structure during faradaic charging/discharging reaction. The electrochemical performance of C/NiCo₂O₄ material clearly demonstrates that it is an attractive material for supercapacitor applications.

EIS analysis

To evaluate parameters related to the electrochemical reaction kinetics, EIS analysis was conducted in frequency range of

0.1 - 10⁵ Hz and the Nyquist plots presented in Figure 6c. In order to understand the electrochemical behavior of the supercapacitors, an equivalent circuit was used to fit the Nyquist plots. As seen in Figure 6d, three components in the equivalent circuit can be respectively assigned to electrochemical responses of the electrode materials - including grain and interior grain boundary ((L_M-(R_M//CPE_M), electrode/electrolyte interphase ((R_{CT}-W_{CT})/CPE_{DL}), and pseudocapacitance contribution (R_F//CPE_F).^[34] The fitted results were summarized in Table 2.

Generally, the impedance behaviors of the electrode/electrolyte interphases are quite similar, with the conductivity mostly depend on the Warburg diffusion processes. The characteristics of high conductivity and poor crystal structure of the synthetic carbon was respectively proved by a low value of R_M and a high value of CPE_M for the case of the carbon electrode. The fitted results were also pointed out the good pseudocapacitance behaviour of NiCo₂O₄ in comparison with the synthetic carbon material. As seen in the table, the Faradaic resistance (R_F) of the NiCo₂O₄ electrode (37.66 Ω) was much lower than that of the carbon electrode (2124.3 Ω). In summary, it can be concluded that the complementary contributions of the high conductivity of the hard carbon and

Table 2. Fitted parameters of equivalent circuit for EIS data of the Carbon, C/NiCo₂O₄ and NiCo₂O₄ electrodes.

Contributors /Activities	Parameters	Samples		
		C	C/NiCo ₂ O ₄	NiCo ₂ O ₄
Electrode material	L_M (H)	7.147E-16	4.6173E-6	1.5477E-7
	R_M (Ω)	38.869	39.515	89.37
	CPE_M (F)	0.032963	0.00889	0.003643
Faradaic capacitance	R_F (Ω)	2124.3	31.813	37.66
	CPE_F (F)	0.002683	0.00237	0.002963
	R_{CT} (Ω)	3.6587E-13	1.0924E-14	2.5993E-16
Electrode /electrolyte interphase	ZW_{CT} (Ω)	1871.6	1797.9	1312.1
	CPE_{dl} (F)	0.001049	0.00199	0.001887

the good pseudocapacitance behaviour of NiCo₂O₄ resulted in a superior performance of the C/NiCo₂O₄ supercapacitor.

3. Conclusions

The C/NiCo₂O₄ composite material has successfully prepared by facile combined hydrothermal treatment/calcination route. The XRD, TGA, FT-IR, Raman, SEM, TEM, EDS results confirmed the amorphous structure of carbon and the spinel structure of the as-prepared NiCo₂O₄ nanoparticles. The measurements of CV, GCD, and EIS revealed that the combination of carbon and NiCo₂O₄ created a synergistic effect, leading to higher C_s of C/NiCo₂O₄ than that of pristine NiCo₂O₄ or carbon. The C/NiCo₂O₄ composite exhibited an excellent C_s of 204.28 F.g⁻¹ at a current density of 1 A.g⁻¹, meanwhile the C_s of carbon and NiCo₂O₄ are 25.06 F.g⁻¹ and 178.78 F.g⁻¹, respectively. The C/NiCo₂O₄ possessed high capacitance retention of 90.35% after 3000 cycles charge/discharge at a current density of 2 A.g⁻¹. In addition, the synthesized method was simple and low cost, which provided a feasible route for the mass-production of the porous metal oxides and amorphous carbon composite as supercapacitor materials.

Supporting Information Summary

Details of chemicals, material synthesis method, method of analyzing characterization and electrochemical for all synthesized materials are provided in supporting information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: C/NiCo₂O₄ composite · Energy conversion · Hydrothermal synthesis · Supercapacitor · Synergistic effect.

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