

Formation of CoO-NiO Nanoparticles on Nitrogen Doped Porous Carbon as High Performance Supercapacitor Electrode

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Received: 25 August 2018 / Accepted: 18 October 2018 / Published: 30 November 2018

Doping porous carbon with transition metal oxides is highly desirable for high performance supercapacitors due to their synergistic effect. Herein, a highly dispersed CoO-NiO nanoparticle doped porous carbon (CoO-NiO@ZIF-C) was prepared by pyrolysis of Ni²⁺ and Co²⁺ ions impregnated ZIF-8. The metal nanoparticles catalyze the formation of graphitic carbon, while the N-doped carbon substrate confines the nanoparticles during the process. The resulted nanocomposite demonstrates excellent capacitive performance, which delivered a specific capacitance of 552.3 F g⁻¹ at current density of 1 A g⁻¹. Moreover, an asymmetric supercapacitor was successfully assembled using CoO-NiO@ZIF-C as positive electrode and reduced graphene oxide as the negative electrode. The two-electrode cell delivered a maximum energy density of 43.5 Wh kg⁻¹ at a power density of 1892.1 W kg⁻¹ with good stability.

Keywords: Supercapacitor; ZIF-8; CoO; NiO; graphitic; Nanocomposite

1. INTRODUCTION

With the day-to-day rising demand of energy globally, the energy storage and conversion technologies have drawn extensive attentions in recent year [1]. Among the diverse approaches of energy storage, storing the energy electrically is still the mainstream owing to its high efficiency, convenience, and reversibility [2]. Batteries and supercapacitors are the preference devices for electrical storage [3-5]. Compared with batteries, supercapacitors possess faster charge-discharge rate and higher power density, which are highly deserved to look into further [6, 7]. Generally, the charges can be stored in supercapacitor physically and chemically. In the physical process, the charges are separated and accumulated on the surface of the carbon-based electrode, which enables high power density and reliable

operation over 10000 of charge/discharge cycles. However, carbon-based materials only demonstrate limit capacitance in the range of 100-400 F/g, which restrains their wide application [8]. While in the chemical process, much higher capacitance can be obtained through storing the charges by reversible Faradic reactions at the electrode surface. Transition-metal oxides are excellent candidates as the electrode materials for supercapacitor owing to their multiple oxidation states [9-12]. However, poor conductivity and volume change in the charge-discharge process deteriorate the electrochemical performance in the long run [13]. Therefore, it is an urgent need to develop functionalized materials to overcome these obstacles.

One promising strategy to boost the capacitance of the materials is to combine of transition metal oxide with carbon materials [14-16]. For instance, Zhao and co-workers reported a 3D walnut-shaped TiO_2 and MoO_2 doped graphene electrode for high performance supercapacitor, which demonstrate an ultrahigh capacitance of 1636 F g^{-1} [17]. Bao et al. prepared 3D graphene frameworks/ Co_3O_4 composites for high performance supercapacitor [18]. However, intimate doping transition metal oxide with high dispersity on porous materials is still very challenging because the aggregation of the metal oxide nanoparticles is inevitable.

It is generally accepted that graphitic carbon demonstrates high conductivity than disordered carbon, which is more suitable for supercapacitor electrode materials [19]. However, the production of graphitic carbon is always done under high temperature ($>2200^\circ\text{C}$), which is energy-consuming and high cost. Furthermore, the products exhibit low specific surface areas [20]. Though graphitic carbon can be obtained at moderate temperatures using transition metals as catalyst [21], doping the metal nanoparticles in porous carbon is challenging.

In this study, inspired the catalytic graphitization of carbon by transition metal catalyst, a simple method was proposed to prepared transition metal oxide doped porous carbon. Ni and Co nanoparticle were reduced in the pore of metal organic framework (ZIF-8). The composite was then carbonized at 800°C . In this process, the metal nanoparticle doped graphitic carbon was formed. Followed the oxidation the metal nanoparticles, the transition metal oxide doped porous carbon was thus prepared. The CoO-NiO@ZIF-C nanocomposite displays excellent electrochemical performance, which is favorable for the preparation of the electrode for supercapacitor.

2. MATERIALS AND METHODS

2.1. Preparation of CoO-NiO@ZIF-C nanocomposite

ZIF-8 was prepared according the reference [22]. The produced ZIF-8 was washed with methanol five times and dried in a vacuum oven at 80°C . Then 1 g of ZIF-8, 0.1 g (2 mmol) of $\text{Ni}(\text{NO}_3)_2$, 0.354 g (2 mmol) of $\text{Co}(\text{NO}_3)_2$ were added in 50 mL of methanol and stirred vigorously for 12 h. After the solvent was evaporated at room temperature for about 24 h, the solid was collected and placed in a vessel. Then the vessel was transferred to a tube furnace and heated to 800°C with a heating rate of 5°C min^{-1} under nitrogen flow (15 mL min^{-1}). The temperature of the furnace was kept at 800°C for 2 h, and then allowed to cool down to room temperature. The resulting black powder was washed thoroughly with 6 M KOH solution to remove any residual Zn adducts. Next, the sample was thoroughly rinsed with deionized water and dried at 80°C for 12 h. The black product was then grounded into fine powder.

2.2. Characterization of CoO-NiO@ZIF-C nanocomposite

The instrumental information including scanning electron microscopy (SEM), transmission electron microscopic (TEM), selected-area electron diffraction (SEAD), Powder X-ray diffraction (XRD), Fourier transform infrared (FTIR), X-ray photoelectron spectroscopy (XPS), N₂ adsorption-desorption can be found in our previous paper [22].

2.3. Electrochemical tests

Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS) were recorded on an IM6e potentiostat (Zahner-Elektrik, Germany) using a conventional three-electrode system. The electrolyte is 6M KOH solution. The working electrode was prepared by mixing 20 wt% of polyvinylidene fluoride with sample (80 wt%). The nickel-foam (1 × 1 cm²) was used as current collectors. Platinum foil and saturated calomel electrode (SCE) and were used as the counter and reference electrodes, respectively. The specific capacitance was calculated based on equation (1), where I is the current intensity, $\int Vdt$ is the area under the experimental discharge curve, m is the mass of the active material and $V_f - V_i$ is the active potential window during discharge.

To assess the capability of the CoO-NiO@ZIF-C nanocomposite electrode for practical applications, an asymmetric two-electrode supercapacitor was fabricated by using CoO-NiO@ZIF-C as the positive electrode and reduced graphene oxide as the negative electrode. The mass loading on the positive electrode (m_+) and negative electrode (m_-) was calculated by equation (2). The power density and energy density of the two-electrode supercapacitors were calculated by equation (3, 4), respectively.

$$C_s = \frac{I \int (V) dt}{m(V_f - V_i)} \quad (1)$$

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (2)$$

$$E = (\frac{1}{2} C_s \Delta V^2) / 3.6 \quad (3)$$

$$P = \frac{3600 \times E}{\Delta t} \quad (4)$$

3. RESULTS AND DISCUSSION

3.1. Material synthesis

Owing to their exceptionally high specific surface area and controllable pore textures, metal-organic frameworks (MOFs) have been used templates or precursors to synthesize porous carbons [23]. Especially, ZIF-8 with imidazole group has been carbonized directly to prepare N-doped porous carbons [24]. The adsorption of the transition metal ions in the pore of ZIF-8 was supposed to improve electrochemical performance. For instance, the ZIF-8 derived porous carbon materials have been utilized in electrocatalysts [25], Li-ions batteries [26] and electrochemical capacitors [8, 27]. In this study, ZIF-8 was utilized as N-doped carbon precursor and support for transition metal oxides. At same time, the

in-situ formed metal nanoparticles catalyzed the production of graphitic carbon, which is promising to fabricate the electrochemical capacitor. The process of the preparation of CoO-NiO@ZIF-C is illustrated in Figure 1.



Figure 1. Synthetic scheme of CoO-NiO@ZIF-C

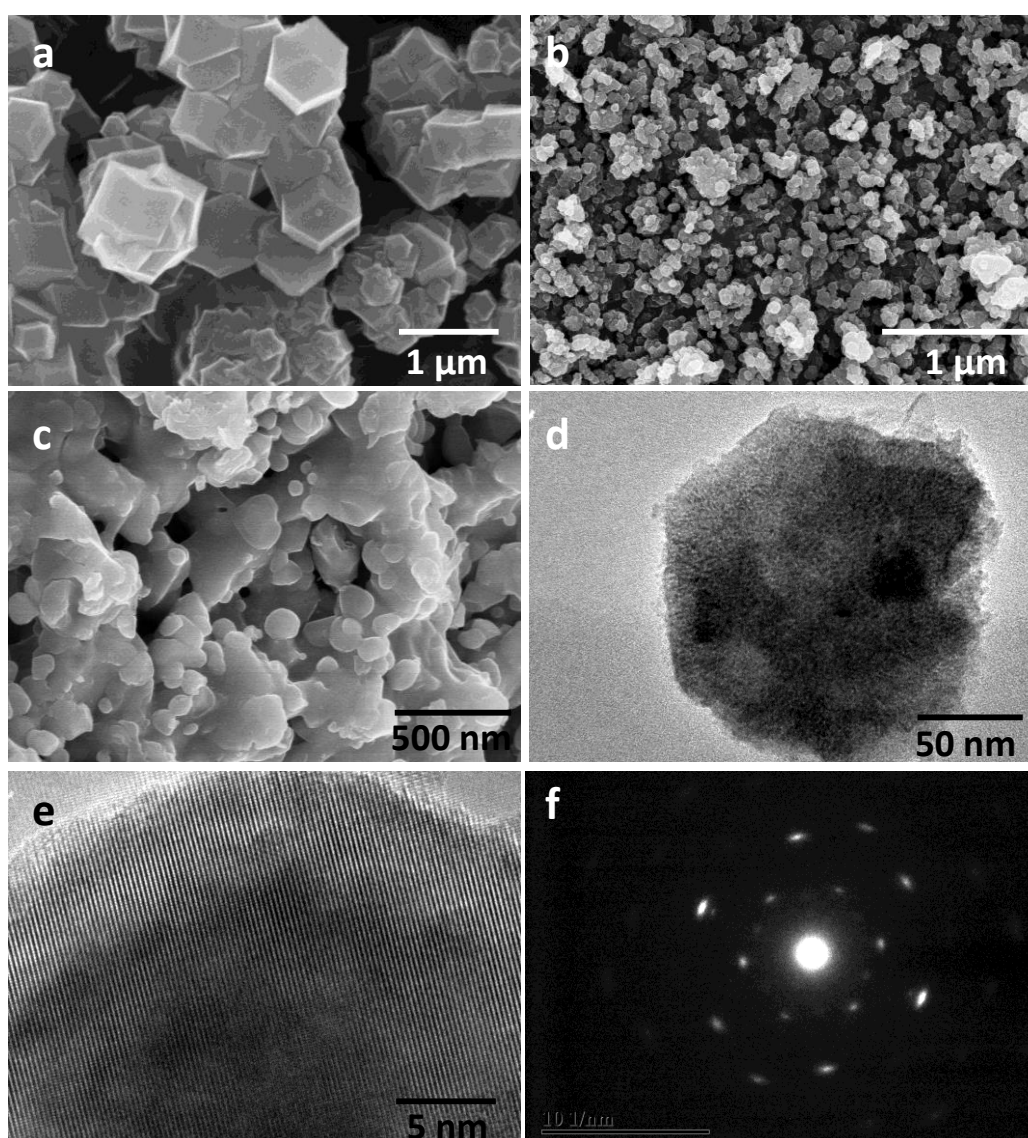


Figure 2. SEM images of ZIF-C (a) and CoO-NiO@ZIF-C (b,c); TEM images (d), HRTEM (e) and SEAD of CoO-NiO@ZIF-C.

The morphological information of the samples was characterized by SEM and TEM (Figure 2). The obtained porous carbon can retain the morphology of the ZIF-8 precursors (Figure 2a), which is identical to the previous report [28]. However, while the adsorption of Ni^{2+} and Co^{2+} ions in the pore of ZIF-8, the carbonized product demonstrate irregular granule (Figure 2b,c). Presumably, during the carbonization, the decomposition of the metal salts release gases and broken the skeleton of ZIF-8. TEM image further confirmed that the CoO-NiO nanoparticles were doped on the porous carbon (Figure 2d). The lattice fringe is identified to be 0.23 nm from the high resolution TEM (HRTEM) (Figure 2e), which is indexed to the (101) plane of a hexagonal crystal structure for the NiO [29]. The corresponding SAED pattern of CoO-NiO@ZIF-C can be indexed to the (111), (002), (220), and (311) planes of NiO or CoO (Figure 2f).

Figure 3 shows the EDX elemental maps of CoO-NiO@ZIF-C. It is clear to see that N, originated from the ZIF-8, is well doped on the surface of carbon. O has similar distribution with Co and Ni, indicating that Co and Ni are in the form of oxides. The Ni and Co oxides were surrounded by the carbon, which could potentially improve the electron transfer of the metal oxides [9]. Ni and Co has almost the same shape of map, indicating Co and Ni are well mixed together.

Figure 4 shows the powder XRD patterns of the samples. Two broad peaks centered at $2\theta = 24.8^\circ$ and 43.4° are observed in the sample of ZIF-C, which are assigned to the (001) and (100) planes of graphitic carbon [30]. The (001) plane shifts to higher angle of 30.7° in the XRD pattern of CoO-NiO@ZIF-C, indicating an improved graphitization degree [31]. The peaks appearing at 36.8° , 42.7° , 61.9° and 74.4° are indexed to the (111), (200), (220) and (311) reflections of CoO oxide, respectively, which is consistent with SEAD results. It should be noted that CoO and NiO phases are very similar. It is hard to distinguish them. The particle size of CoO was calculated to be 38.4 nm from Scherrer equation [32], which is identical to the results of TEM images. In addition, no diffraction peak corresponding to zinc component was detected, which suggests that it was removed by KOH solution in both samples completely.

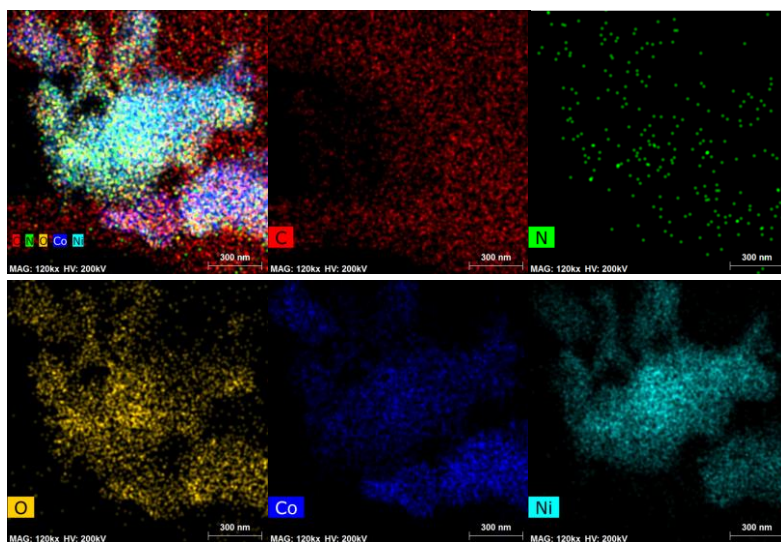


Figure 3. EDX elemental maps of C, N, O, Co and Ni in CoO-NiO@ZIF-C.

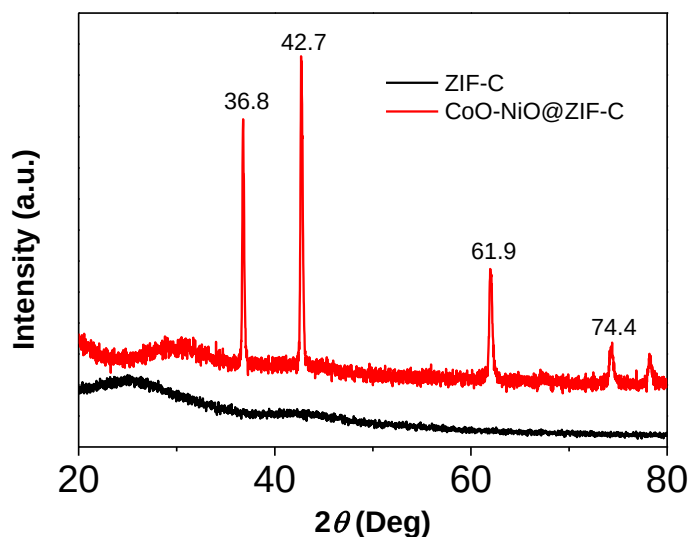


Figure 4. XRD patterns of the ZIF-C and CoO-NiO@ZIF-C.

The chemical state of the elements in CoO-NiO@ZIF-C was analyzed by XPS. As shown in Figure 6, the peaks of C 1s, N 1s, O 1s, Co 2p, and Ni 2p can be clearly seen in the full spectrum of CoO-NiO@ZIF-C. The high-resolution peaks were further fitted with a Gaussian–Lorentzian line shape, and a linear background was subtracted from the spectrum. In the Co 2p spectrum in Figure 6b, a Co 2p_{3/2} peak located at 781.1 eV accompanies the prominent shake-up satellite peak at 786.2 eV and a Co 2p_{1/2} peak located at 797.1 eV accompanies the shake-up satellite peak at 803.1 eV; these peaks all verify the presence of the CoO phase [33]. Similarly, the peaks located at 855.3 and 872.8 eV are indexed to the characteristic Ni 2p_{3/2} and Ni 2p_{1/2} states of Ni²⁺. Two obvious shake-up satellites are located at 878.8 and 861.2 eV (Figure 6c), indicating the presence of NiO. The C 1s signal in Figure 6d can be divided into three peaks, which correspond to the C=C (284.7 eV), C–N/C–O (285.5 eV), and C=O (286.7 eV) bonds [34]. The signal of N 1s is deconvoluted into three peaks (Figure 6e), indicating successful N-doping of the material [35]. Finally, the O 1s spectrum is also shown in Figure 5f, and the three peaks at 531.6, 532.3, and 533.9 eV are attributed to M-oxide (M=Co, Ni), C=O groups or C–O–C groups, and C–OH groups, respectively.

The surface area of the CoO-NiO@ZIF-C was also examined by N₂ adsorption/desorption method (Figure 6). The isotherm of CoO-NiO@ZIF-C shows a typical IV type curve (Figure 6a), which indicates the existence of mesopores [6]. The calculated Brunauer–Emmett–Teller (BET) surface area for CoO-NiO@ZIF-C is 784.8 m² g^{−1}. CoO-NiO@ZIF-C shows much higher surface area than reported transition metal doped carbon nanocomposite, which could be due to the unique structure of the sample. The pore-size distribution plot in Figure 6b exhibits a sharp peak at approximately 4.0 nm, confirming the existence of mesopores in CoO-NiO@ZIF-C. It is well known that mesoporous structure of the materials is beneficial to the access of electrolyte ions, which can improve the electrochemical performance of the materials [36].

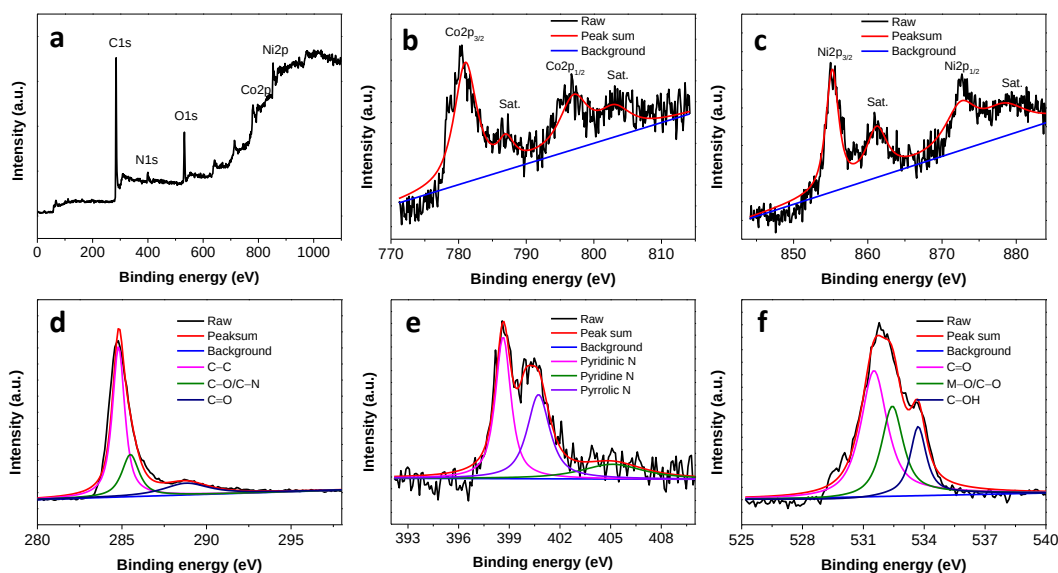


Figure 5. (a) Full XP spectrum of CoO-NiO@ZIF-C and high-resolution spectra of the (b) Co 2p, (c) Ni 2p, (d) C 1s, (e) N 1s, and (f) O 1s states.

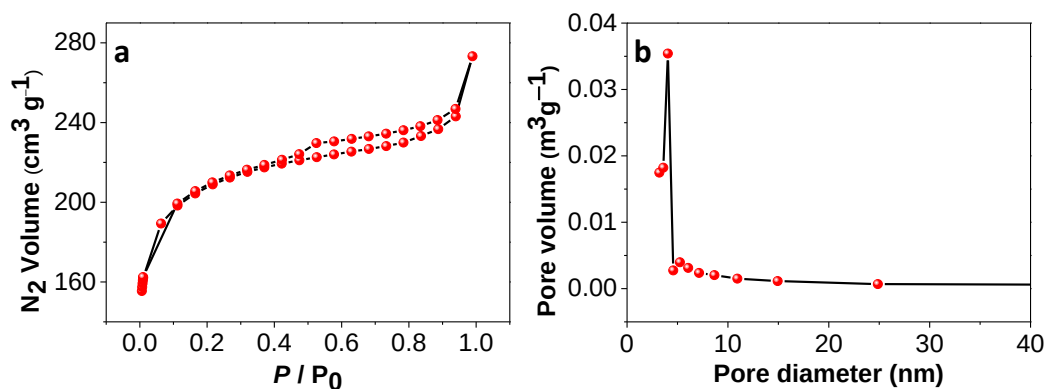


Figure 6. (a) N₂ adsorption/desorption isotherms of CoO-NiO@ZIF-C, and (b) pore-size distribution curves for CoO-NiO@ZIF-C.

3.2 Electrochemical performance of CoO-NiO@ZIF-C

Figure 7 shows the galvanostatic charge-discharge (GCD) curves of the ZIF-C and CoO-NiO@ZIF-C electrodes. The curve of CoO-NiO@ZIF-C electrode shows typical feature of pseudocapacitor. The charges can be stored and released quickly at equivalent time, indicating a good reversibility. The discharging time of ZIF-C was much shorter than that of CoO-NiO@ZIF-C, indicating a lower charge storage capability under same conditions. The capacitances calculated from the GCD curve were 552.3 and 104.4 F/g for CoO-NiO@ZIF-C and ZIF-C, respectively. The capacitance of CoO-NiO@ZIF-C electrode is more than 5 times higher than that of ZIF-C, which indicates that the doping of CoO-NiO dramatically improve the electrochemical performance of ZIF-C. As listed in Table 1, the capacitance of CoO-NiO@ZIF-C electrode is comparable with the Co-based transition metal oxide materials.

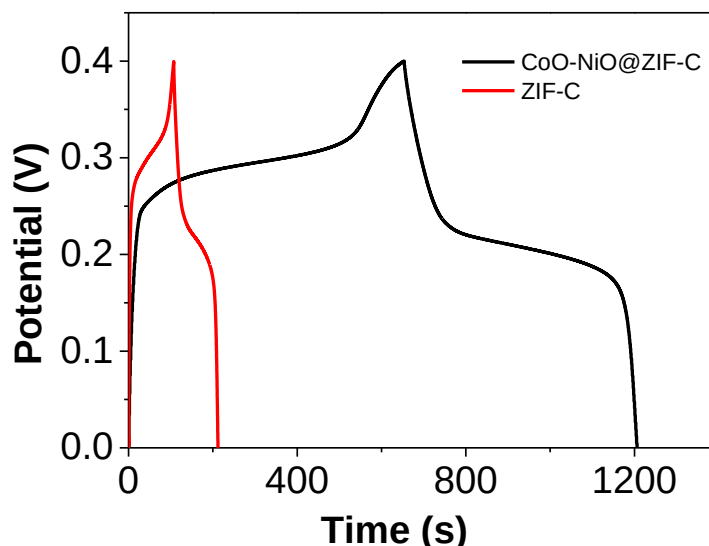


Figure 7. GCD curves of the CoO-NiO@ZIF-C and ZIF-C electrodes at a current density of 1 A g^{-1} .

Table 1. Comparison of the electrochemical performance of the CoO-NiO@ZIF-C electrode with reported electrodes

Sample	Current density (A g^{-1})	Specific capacitance (F g^{-1})	Reference
Co_3O_4 @CNTs/PIn	1	442.5	[37]
porous Co_3O_4	1	150	[38]
Co/RGO	1	295	[39]
CF/VAGN/ Mn_3O_4	1	670	[40]
Co_3O_4 @PPy/ MnO_2	0.5	782	[41]
CoO	1	594	[42]
3D Ni-Co LDH/NiNw	0.125	466.6	[43]
N-C@GC/CNTs	2	252.1	[35]
CoAl-LDH	1	616.9	[44]
CoO-NiO@ZIF-C	1	552.3	This work

Figure 8 shows the CoO-NiO@ZIF-C electrode GCD curve of CoO-NiO@ZIF-C at different current density. It can be observed that the discharging time of the electrode gradually decreased as the current density increased. The capacitances of CoO-NiO@ZIF-C were calculated to be 552.3, 549.2, 525, 501, and 484.5 F g^{-1} at current densities of 1, 2, 5, 10, and 15 A g^{-1} , respectively. The electrode can retain 87.7% of the initial capacitance when the current density was increased to 15 A g^{-1} .

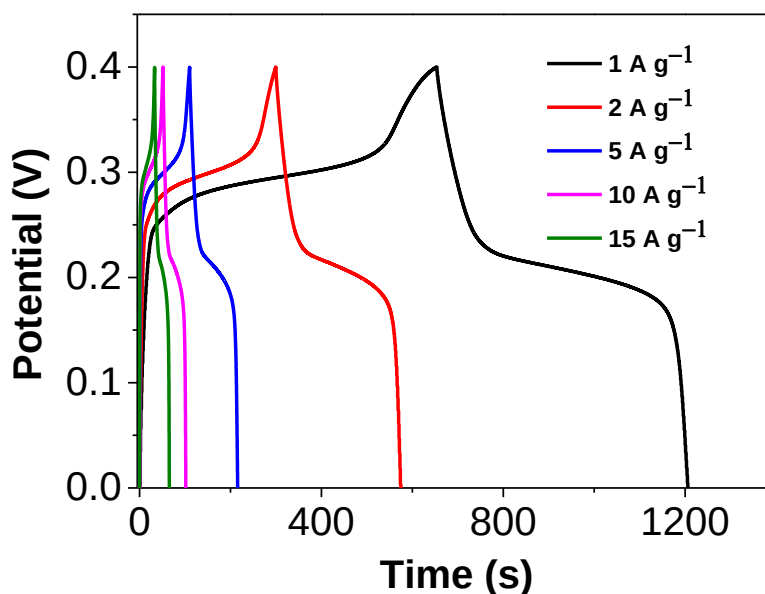


Figure 8. GCD curves of the CoO-NiO@ZIF-C at the different density of 1, 2, 5, 10 and 15 A/g.

The CVs of CoO-NiO@ZIF-C at various scan rates are shown in Figure 9. One couple of redox peaks located at around 0.3 V in the CV curves, indicating a faradaic redox reaction behavior [45-48]. When the scan rate is increased from 5 to 100 mV s⁻¹ in a 6.0 M KOH solution, the peak current densities increase with the scan rates. The shape of the CV curves well retained. The possible charge storage mechanism for CoO-NiO can be expressed by the following equation [49]:

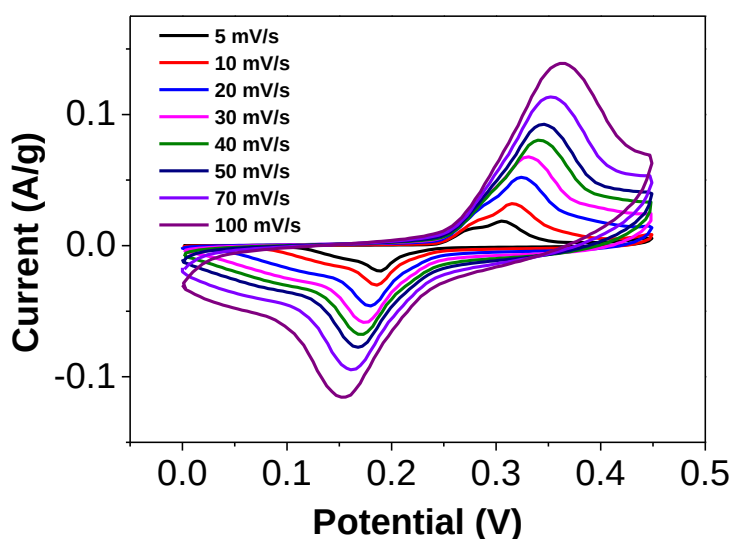


Figure 9. CV curves of the CoO-NiO@ZIF-C at scan rates.

To access the possible application of CoO-NiO@ZIF-C, a two-electrode asymmetric cell was set

up by using CoO-NiO@ZIF-C as positive electrode and reduced graphene as negative electrode. Figure 10 shows the CV curves of the CoO-NiO@ZIF-C//rGO asymmetric cell in different potential windows from 1.1 to 1.5 V. The asymmetric supercapacitor had a stable potential window up to 1.5 V. Therefore, 1.5 V was selected to investigate the electrochemical performance of the asymmetric cell.

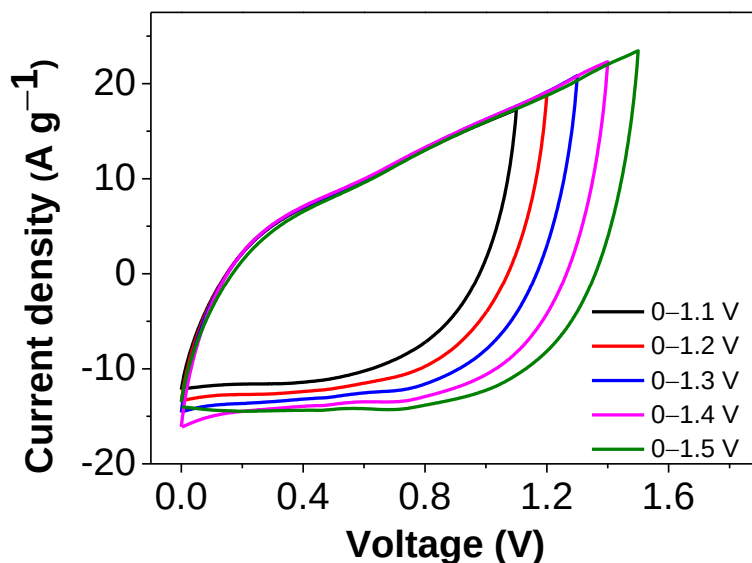


Figure 10. CV curves of the CoO-NiO@ZIF-C//rGO at scan rates.

Figure 11 shows the CoO-NiO@ZIF-C//rGO asymmetric cell was galvanostatically charged and discharged over the voltage range of 0–1.5 V. A high specific capacitance of 170.3 F g^{-1} can be obtained at a current density of 1 A g^{-1} . The CoO-NiO@ZIF-C//rGO asymmetric supercapacitor delivered an energy density of 43.5 Wh kg^{-1} at a power density of 1892.1 W kg^{-1} and a high power density of 14890 W kg^{-1} at the energy density of 19.7 Wh kg^{-1} .

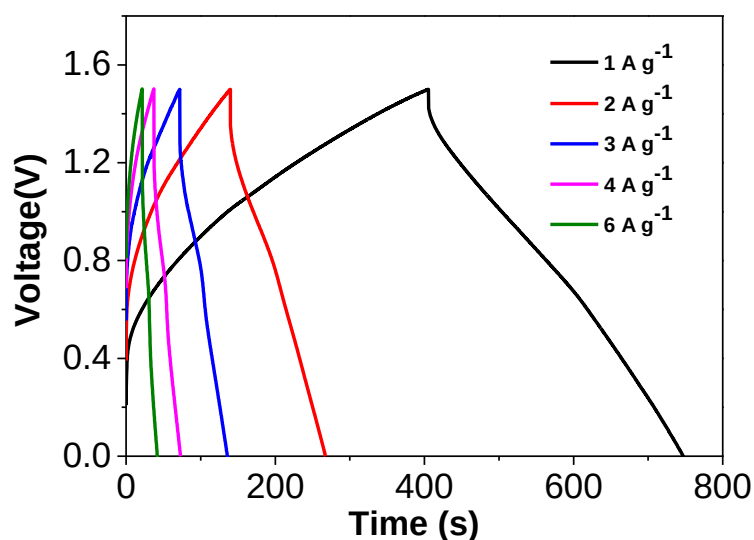


Figure 11. CV curves of the CoO-NiO@ZIF-C//rGO at scan rates.

The cycling stability of the asymmetric supercapacitor was studied by charging-discharging the cell for 3000 cycles at the current density of 1 A/g. As shown in Figure 12, the asymmetric supercapacitor can retain 87% of its initial capacitance at the current density of 1 A/g, demonstrating high electrochemical stability.

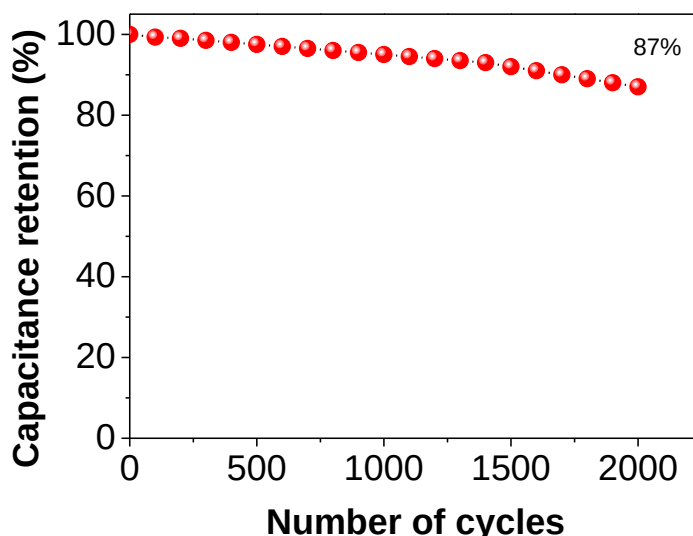


Figure 12. Cycling stability of the CoO-NiO@ZIF-C//rGO asymmetric supercapacitor.

4. CONCLUSIONS

In summary, CoO-NiO was doped on ZIF-8 derived carbon by carbonization of Ni^{2+} and Co^{2+} ions impregnated ZIF-8. The resultant product CoO-NiO@ZIF-C demonstrates excellent electrochemical supercapacitive performance. By paring CoO-NiO@ZIF-C with reduced graphene, the two-electrode cell delivered an energy density of 43.5 Wh kg^{-1} at a power density of 1892.1 W kg^{-1} . Furthermore, the two-electrode asymmetric supercapacitor shows high stability, demonstrating potential application in energy storage devices.

ACKNOWLEDGEMENTS

The authors appreciate financial support from GUET excellent graduate thesis program (16YJPYSS30), NSFC (51861004, 51561006 and U1501242), and the GXNSF (2016GXNSFFA380012, AD17195073, and 2017GXNSFDA198018,).

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