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Research Article

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Posted Date: September 30th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10644099/v1>

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Additional Declarations: No competing interests reported.

Chinese Ink Facilitated Synthesis of Nanostructured NiCo₂O₄ for Supercapacitors with Enhanced Performances

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Abstract

In this paper, it is demonstrated that Chinese ink can be used as an inert additive to improve the dispersion of transition metal oxides and thus enhance their electrochemical performance for supercapacitor applications, with nickel cobaltite (NiCo₂O₄) as the example, which was synthesis by using chemical co-precipitation method. The effect of Chinese ink on properties and performances of the NiCo₂O₄-ink hybrids, including phase composition, particle morphology, specific surface area and pore structure, as well as electrochemical behavior, was systematically studied. It can be concluded that the presence of Chinese ink can effectively and efficiently alleviate the agglomeration of NiCo₂O₄, thus increasing specific surface area and hence boosting electrochemical performance of the hybrids.

Keywords: Nickel cobaltite, Chinese ink, Nanostructured hybrids, Supercapacitor, Electrode, Specific capacitance

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1. Introduction

Among various transition metal oxides that are used as the electrode materials for pseudocapacitors, spinel binary metal oxide, NiCo_2O_4 (or NCO), stands out for its high theoretical capacitance and high electrical conductivity, as well as several other merits, such as cost-effectiveness, environmental friendliness and natural abundance [1]. According to the crystallographic structure of NiCo_2O_4 , nickel atoms occupy the octahedral sites and the cobalt atoms are located at the octahedral and tetrahedral interstices [2]. In terms of ion distribution, the structural formula of NiCo_2O_4 is expressed as $\text{Co}_{1-x}^{2+}\text{Co}_x^{3+}[\text{Co}^{3+}\text{Ni}_x^{2+}\text{Ni}_{1-x}^{3+}]\text{O}_4$ ($0 \leq x \leq 1$), in which there are two redox couples, i.e., $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ [3-5]. Benefiting from the crystal structure, NiCo_2O_4 shows an electrical conductivity that is two orders of magnitude higher than that of monometallic NiO or Co_3O_4 [6]. Besides, NiCo_2O_4 has richer oxidation states and thus exhibits higher capacitance than NiO and Co_3O_4 .

It has been widely accepted that nanostructured NiCo_2O_4 has excellent capacitive performance, because of the large surface area and the shortened ion and charge transportation paths [7]. Currently, various NiCo_2O_4 nanostructures, such as 0D nanoparticles [8, 9], 1D nanoneedles [10, 11], nanorods [12], nanowires [13, 14], 2D nanosheets [15, 16] and 3D porous network [17, 18], have been reported. Nanostructured NiCo_2O_4 can be synthesized by using various methods, such as low-temperature chemical co-precipitation and subsequent calcination [10, 12], hydrothermal reactions [13, 19, 20], electrodeposition [21, 22] and sol-gel processing [23]. Among these methods, low-temperature chemical co-precipitation, accompanied by subsequent calcination, is a simple and scalable approach to obtain nanostructured NiCo_2O_4 . However, self-assembled NiCo_2O_4 tends to agglomerate during the synthesis process, which badly impairs the electrochemical performance.

In some previous reports, surfactants, such as CTAB [24, 25] and PVP [26, 27], are used to tune the microstructure and the pore size of NiCo_2O_4 . As a ready-made colloidal suspension system, Chinese ink is assumed to possibly serve as an additive to facilitate the synthesis of highly dispersed nanostructured NiCo_2O_4 , by taking the advantages of the well-dispersed carbon black nanoparticles and the presence of glue. To prove the concept, Chinese ink was added the nickel and cobalt precursor solution during the

chemical co-precipitation process to prepare NiCo_2O_4 . At the same time, magnetic stirring was applied to ensure homogeneity of the mixture throughout the reaction process. The precipitated precursor powder was subjected to calcination at different temperatures. The formation of NiCo_2O_4 has confirmed by using XRD, XPS and Raman spectroscopy. Morphology evolution, surface information and electrochemical behavior of the NiCo_2O_4 -ink (or NCO-ink for short) hybrids were systematically studied, in order to clarify the effect of Chinese ink. The addition of Chinese ink can alleviate the aggregation of NiCo_2O_4 nanosheets, enlarge the specific surface area and ultimately boost the electrochemical performance of NiCo_2O_4 .

2. Experimental Methods

2.1. Synthesis of NCO-ink Hybrids

Synthesis process of the NCO-ink hybrids is schematically shown in Fig. S1, including two steps: (i) low-temperature chemical co-precipitation to form precursors and (ii) subsequent calcination to convert the precursors into cobalt–nickel bimetallic oxide. Chinese ink was mixed with the starting materials in the first step at different concentrations.

In a typical experimental procedure, three mixtures needed to be prepared in advance, including a diluted Chinese ink suspension (S_1), a solution containing Co^{2+} and Ni^{2+} (S_2) and a precipitant solution (S_3). A certain amount of Chinese ink was added into 20 mL deionized water. Under magnetic stirring, this surfactant-stabilized carbon black ink was quickly dispersed into water, forming a homogeneous suspension (S_1). 1 mmol nickel acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) and 2 mmol cobalt acetate tetrahydrate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) were dissolved in 30 mL deionized water to form the second solution (S_2). 12 mmol urea was dissolved in 10 mL deionized water to form the third solution (S_3). The S_1 and S_2 were first mixed and stirred for 5 min, and then the S_3 was added to the ($S_1 + S_2$) mixture. The resultant ($S_1 + S_2 + S_3$) mixture was transferred into a screw-cap reagent bottle, where the mixture was heated at 90°C in a water bath and stirred at 500 rpm for 4 h.

After the reaction was completed, the bottle was cooled down naturally. The precipitated products were collected through centrifugation, followed by washing with deionized water (three times) and ethanol (one time) to remove impurities. The purified products were dried in a vacuum oven at 60°C for 12 h. Then, the

dried grayish blue or black (when ink content was high) powder was calcined at different temperatures in air for 2 h, at a low heating rate of $2^{\circ}\text{C min}^{-1}$. The obtained black powder was ready for further characterization. The hybrids were labeled as NCO-ink_x, where NCO is NiCo₂O₄ and x denotes the addition amount of Chinese ink in grams.

2.2. Material Characterization

Morphology and microstructure of the hybrids were examined by using field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F, operated at 5 kV) and transmission electron microscopy (TEM, JEOL, JEM-2010 UHR). Crystallographic structures of the hybrids were characterized by using X-ray diffraction (XRD, Shimazu, XRD-6000) operated at 40 kV and 30 mA, with Cu K α radiation ($\lambda = 0.15406$ nm). Elemental composition and chemical states of the elements were studied by using X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALab 250Xi), equipped with a monochromatic Al K α (1486.7 eV) X-ray source. All spectra were calibrated by using C 1s peak (284.5 eV) as the reference. The peak fitting was done with the software XPSPEAK41. Raman spectra were recorded with Renishaw InVia Raman Microscope, equipped with Ar ion laser source (514 nm). The content of NiCo₂O₄ was determined by using thermogravimetric analysis (TGA), where the samples were heated at a ramping rate of $20^{\circ}\text{C min}^{-1}$ to 800°C in air. Specific surface area and pore structure were analyzed through physical adsorption of nitrogen at 77 K, performed with a TriStar II 3020 surface area analyzer from Micromeritics. The specific surface area was obtained by using the Brunauer–Emmett–Teller (BET) method, while the pore size and distribution were analyzed by using the Barrett-Joyner-Halenda (BJH) method.

2.3. Electrochemical Measurement

Electrochemical performance of the NCO-ink hybrids was characterized with a three-electrode cell, with a platinum plate as the counter electrode, an Hg/HgO electrode as the reference electrode and 2 M KOH aqueous solution as the electrolyte. To prepare the working electrode, the as-prepared sample was first mixed with acetylene black and polyvinylidene fluoride (PVDF) in a mass ratio of 80:10:10. For convenience, the PVDF was dissolved in 1-methyl-2-pyrrolidone (NMP) with a ratio of 5% in advance. The resultant mixture was kept stirring for 8 h to form a smooth slurry. If necessary, a certain amount of

ethanol was added to adjust viscosity of the slurry. The slurry was then spread onto a nickel foam current collector (about 1 cm²) by using a flat spatula and then dried in a vacuum oven at 60°C for 12 h. Loading density of the electrode materials was about 5.0 mg cm⁻². The resultant electrode was pressed with a hydraulic press at a pressure of 6 MPa for 10 s to ensure good contact between the active materials and the current collector and then immersed in the electrolyte for 15 min before the test to ensure a full wetting of the electrode.

Electrochemical behavior of the hybrids was measured in terms of cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS), which were conducted with an electrochemical workstation (BioLogic, VSP). The CV was measured within a potential window of -0.05 to 0.65 V (vs. Hg/HgO), at different scanning rates. The GCD was obtained in a potential window of 0.125 to 0.525 V (vs. Hg/HgO), at different current densities. Specific capacitance is calculated from the galvanostatic discharge curve, according to the following equation:

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

where I is the applied current, Δt is the discharging time and ΔV is the operating voltage window excluding IR drop.

EIS was tested at the open circuit potential over a frequency range from 100 kHz to 10 mHz, at an AC amplitude of 5 mV. The obtained data were fitted into equivalent circuits by the built-in function in the testing software. To test cycling stability, the electrode was continuously charged and discharged at a constant current density of 10 A g⁻¹ for 3000 cycles.

3. Results and Discussion

3.1. Formation Mechanism

NCO-ink hybrids were prepared in two steps, including a simple chemical co-precipitation process and a subsequent calcination process. In the chemical co-precipitation process, urea was used as the precipitating agents. Once the reaction temperature went to 85°C, HMT will first decompose to release NH₃ and CO₂, which will further hydrolyze to produce OH⁻ and CO₃²⁻, as described in the following equations [28, 29]:



The OH^- and CO_3^{2-} anions would react with the metal cations (Ni^{2+} and Co^{2+}) to produce the cobalt-nickel bimetallic carbonate hydroxide salt through the following reaction:



The resultant cobalt-nickel bimetallic carbonate hydroxide hydrate will convert into cobalt–nickel bimetallic oxide (NiCo_2O_4) during calcination, accompanied by the release of CO_2 and H_2O , as described below:

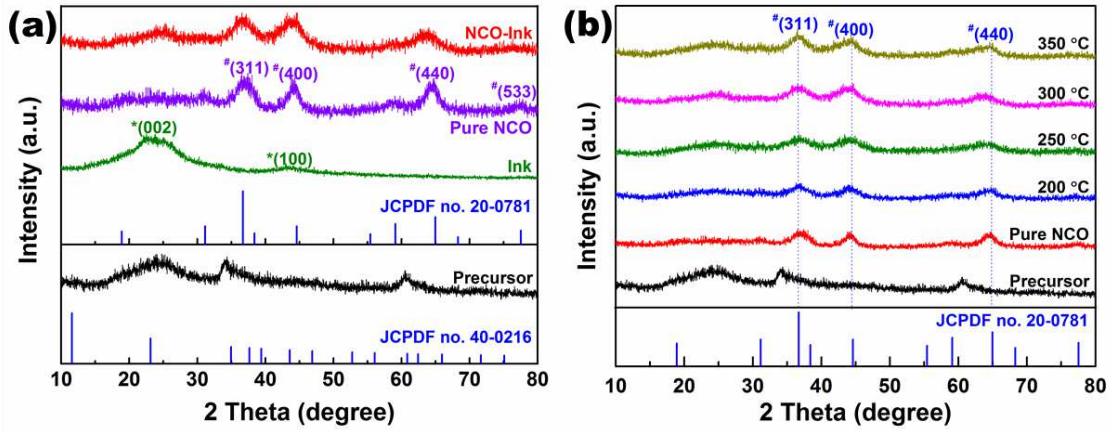
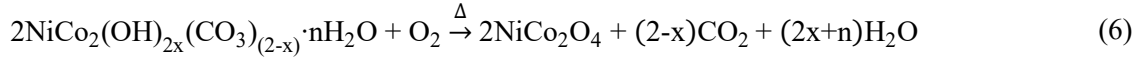


Fig. 1. XRD patterns: (a) the NCO precursor, dried ink, pure NCO (calcined at 300 °C), and the NCO-ink_{3.6} hybrid (calcined at 300 °C) and (b) pure NCO and the NCO-ink_{3.6} hybrids calcined at different temperatures.

XRD was conducted to investigate the phase change during the heat treatment and to confirm the formation of NCO. Fig. 1 (a) shows XRD patterns of the hybrid calcined at 300 °C and its precursor. For comparison, patterns of the pristine dried ink and pure NCO are also included in the figure. The precursor can be indexed to the cobalt-nickel bimetallic carbonate hydroxide hydrate, while the calcined hybrid is indexed to the

cubic spinel NiCo_2O_4 (JCPDS, No. 20-0781). In the calcined hybrid, the peaks at $2\theta = 31.3^\circ$, 36.7° , 64.9° and 77.3° are respectively indexed as (311), (400) (440) and (533) crystalline planes of spinel NCO, in line with those in the pattern of pure NCO. It is noteworthy that the peaks in these patterns are broad and dispersive, indicating low crystallinity of the NCO. Moreover, the presence of amorphous carbon black (from Chinese ink) would also attenuate the diffraction peak or even overshadow some weak peaks. However, no peak from the precursor is present, implying that the precursor has completely decomposed after calcination. XRD patterns of the hybrid NCO-ink_{3.6} calcined at different temperatures are depicted in Fig. 1 (b). The characteristic diffraction peaks at $2\theta = 31.3^\circ$, 36.7° , 64.9° began to show up, after the hybrid was calcined at 200°C , suggesting that the precursor was successfully converted to NCO at 200°C for 2 h. According to the XRD results, it seems that high calcination temperature does not have pronounced effect on the crystallinity of NCO. However, high calcination temperature would cause oxidation of the carbon black, which will be discussed later.

As observed in Fig. 2 (a), the spectra of pure NCO and calcined hybrids have two evident bands centered at about 654 cm^{-1} and 182 cm^{-1} , corresponding to the A_{1g} and the E_{2g} modes of NiCo_2O_4 , respectively, while the other two weak bands centered at about 458 cm^{-1} and 506 cm^{-1} correspond to the E_g and the F_{2g} mode of NCO, respectively [30, 31]. Generally, five bands are expected to be present in the Raman spectra of spinel oxides. For, Co_3O_4 , it shows three intensive bands at 693 cm^{-1} , 526 cm^{-1} and 485 cm^{-1} [32]. The band at 693 cm^{-1} is assigned to the vibration of Co^{3+} , which is a highly symmetric mode and largely decided by the octahedral oxygen ions. However, it is very sensitive to the substitution of Ni^{2+} ions, because the Ni^{2+} substitution can not only lower the concentration of $\text{Co}^{3+}/\text{octahedral O}^{2-}$, but also induce disordering in the lattice and disturb the symmetric mode. Therefore, this band turns weak and shifts to lower frequency upon being substituted by Ni^{2+} ions. As for the bands at 526 cm^{-1} and 485 cm^{-1} , they are ascribed to the combined vibration of octahedral and tetrahedral oxygen atoms in the lattice. Similar to the band at 693 cm^{-1} , these two bands broaden with the Ni^{2+} substitution as the $\text{Co}^{3+}/\text{tetrahedral O}^{2-}$ decreases, and $\text{Ni}^{2+}/\text{octahedral O}^{2-}$ forms that is predicted to have a Raman feature in lower frequency than $\text{Co}^{3+}/\text{octahedral O}^{2-}$ [33]. Compared with pure Co_3O_4 , the hybrids exhibit weaker bands at lower frequency, corresponding to Co-O and Ni-O

vibrations. However, such bands are not remarkable in the spectrum of the precursor. This implies that the cobalt-nickel bimetallic carbonate hydroxide hydrate has been successfully converted into NCO after calcination at $\geq 200^\circ\text{C}$ for 2 h, which is in agreement with the XRD results. Nevertheless, the Raman results also suggest that high calcination temperature does not necessarily improve crystallinity of the resultant NCO.

As demonstrated in Fig. 2 (b), the spectra of the precursor and the hybrids calcined at temperatures of $\leq 300^\circ\text{C}$ have two broad evident bands centered at about 1360 cm^{-1} and 1590 cm^{-1} , corresponding to the D and the G band of carbon, respectively. The G band, the E_{2g} mode of graphite, represents the bond-stretching motion of sp^2 -carbon atoms in the 2-D hexagonal lattice, while the D band, the breathing mode of rings of κ -point phonons of A_{1g} symmetry, represents the defects and disorders in the graphitic carbon layers [31, 34]. These two characteristic bands can be considered as the evidence for the presence of carbon black. The D and G bands turn weak in intensity with the increasing calcination temperature and eventually become discernible, when the calcination temperature is higher than 300°C . This indicates that high calcination temperature caused the loss of carbon black in the hybrids, which is attributed to the intensified oxidation of carbon black in air, as evidenced by the TGA analysis results.

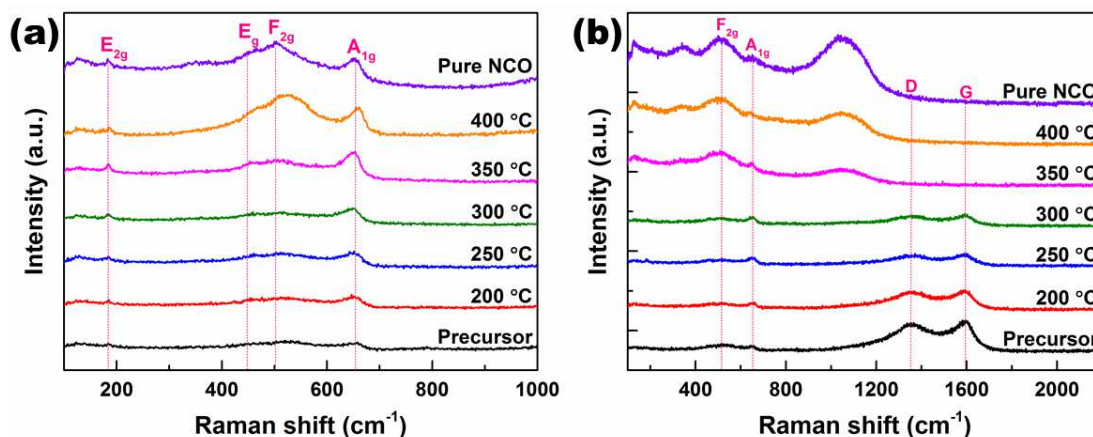


Fig. 2. Raman spectra of the NiCo_2O_4 , precursor, pure NiCo_2O_4 and $\text{NCO-ink}_{3,6}$ calcinated at different temperatures: (a) $100\text{--}1000\text{ cm}^{-1}$ and (b) $100\text{--}2200\text{ cm}^{-1}$.

XPS was applied to confirm the formation of NCO. Three samples were selected as examples, including (i) NCO-ink_{3.6} without calcination, (ii) NCO-ink_{3.6} calcined at 200°C and (iii) NCO-ink_{3.6} calcined at 300°C. The obtained XPS spectra are shown in Fig. 3. The survey spectra (Fig. (a)) reveal the presence of Ni, Co, O and C, and the absence of other impurity elements. As such, it can be claimed that the addition of Chinese ink into the co-precipitation solution did not introduce a considerable amount of impurities, but might result in unexpected reactions. The high-resolution (core-level) spectra of Ni 2p and Co 2p are deconvoluted by using the Gaussian fitting method, with the software XPSPEAK 4.1. The Ni 2p spectrum of the precursor shows two major peaks at 857.4 eV and 874.8 eV, with a spin-energy separation of 17.4 eV, accompanied by two satellite peaks at 863.0 eV and 880.4 eV. They correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, which are the characteristic peaks of Ni²⁺. Similarly, the Co 2p spectrum also shows two characteristic peaks at 782.5 eV (Co 2p_{3/2}) and 798.1 eV (Co 2p_{1/2}), with a spin-energy separation of 15.6 eV, indicating the presence of Co²⁺[35].

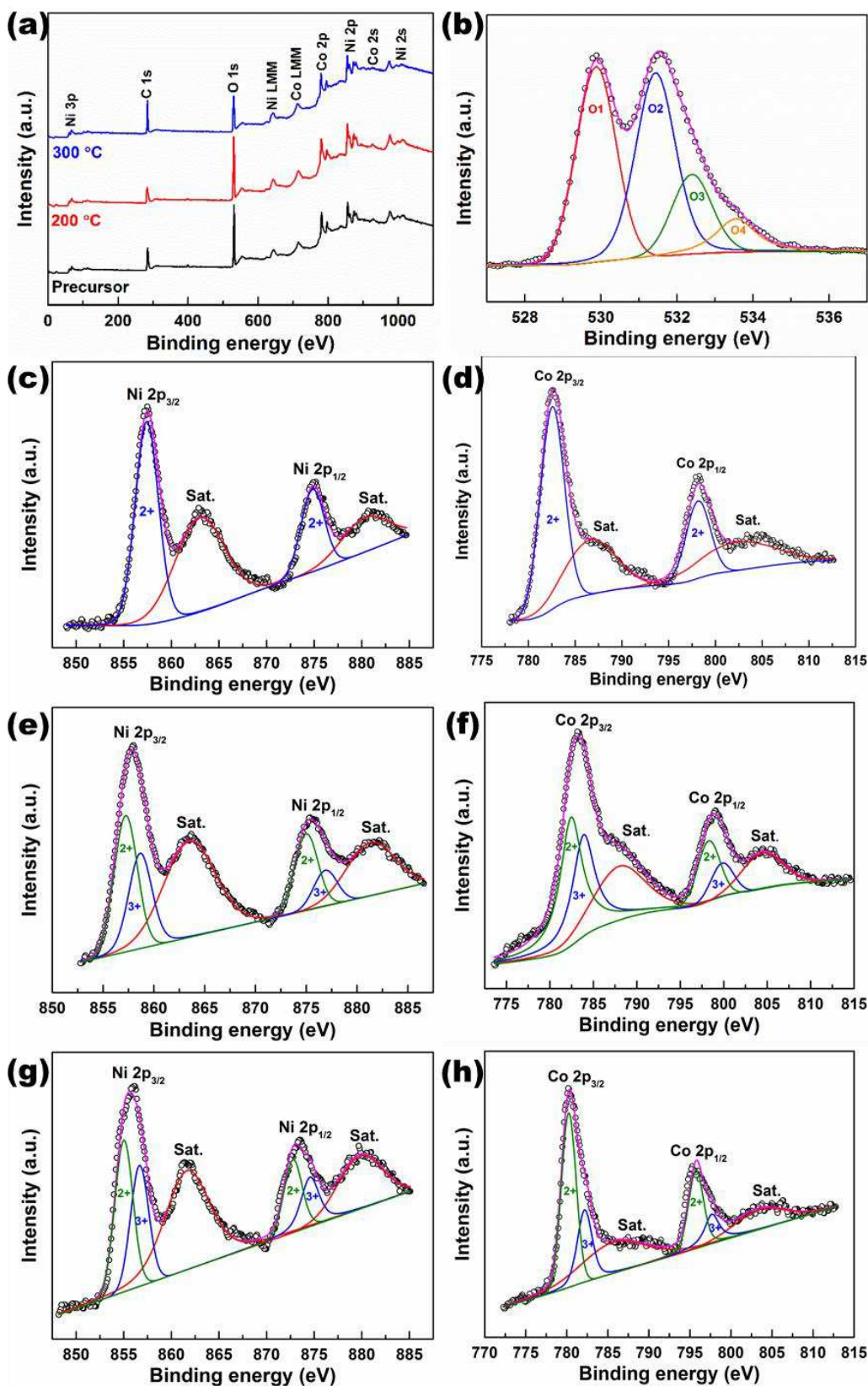


Fig. 3. (a) XPS survey spectra of the hybrid NCO-ink_{3.6} before calcination and after calcination at 200 °C

and 300°C. (b) O 1s core-level XPS spectrum of the hybrid calcined at 200°C, (c, e, g) Ni 2p core-level XPS spectra. (d, f, h) Co core-level XPS spectra. (c, d) the NCO precursor, (e, f) NCO-ink_{3.6} calcined 200°C, and (g, h) NCO-ink_{3.6} calcined 300°C.

It is thus can be concluded that no redox reaction occurred during the chemical co-precipitation process and both Ni and Co exist in the precursor with only one valence state. In contrast, in the calcind hybrids, both Ni 2p and Co 2p core-level spectra can be well fitted with two spin-orbit doublets and two shakeup satellites at the high binding energy sides (labelled at “Sat.”), meaning that both Ni and Co are present in two valence states. For example, in the Ni 2p spectrum of the 200°C-calcined hybrid, the fitted peaks at 857.2 eV and 875.0 eV are ascribed to Ni²⁺, while the two at 858.7 eV and 876.7 eV are attributed to Ni³⁺ [36]. In addition, Co in this hybrid demonstrates similar XPS spectrum, with the only difference in the binding energy. Curve fitting results of these three samples are listed in Table 1, which are in agreement with the literature data [31, 36-42].

Table 1 XPS spectral fitting parameters for Ni 2p_{1/2}, Ni 2p_{3/2}, Co 2p_{1/2} and Co 2p_{3/2}: binding energy (eV) and spectral component separation (eV)

Samples		2p _{3/2} Peak position (eV)			2p _{1/2} Peak position (eV)			Δ_{BE} (eV)
		2 ⁺	3 ⁺	Sat.	2 ⁺	3 ⁺	Sat.	
Ni	Precursor	857.4	—	863.0	874.8	—	880.4	17.4
	200 °C	857.2	858.7	863.5	875.0	876.9	881.3	17.5
	300 °C	855.0	856.7	861.7	872.8	874.6	879.8	17.4
Co	Precursor	782.5	—	786.7	798.2	—	802.3	15.6
	200 °C	782.4	783.9	788.0	798.3	799.8	804.4	15.6
	300 °C	780.2	782.2	785.7	795.7	797.7	803.5	15.5

Besides, as illustrated in Fig. 3 (b), the O 1s core-level XPS spectrum of the hybrid calcined at 200°C can

be deconvoluted into four components, denoted as O1, O2, O3 and O4. The well-defined component O1 at 529.8 eV is attributed to the typical metal-oxygen bonds [37]. The component O2 at 531.4 eV is related to oxygen in OH⁻ groups, whose presence indicates that some oxygen atoms are replaced by OH⁻ groups or the NCO is somewhat hydroxylated [43]. The component O3 is attributed to the defect sites with low oxygen coordination or contaminants [37, 43]. The component O4 is ascribed to the combination of physically/chemically absorbed water at or near surface [37]. With these XPS analysis results, it is confirmed that the calcination process not only facilitated the conversion of the cobalt-nickel bimetallic carbonate hydroxide into cobalt-nickel bimetallic oxides, but also triggered partial oxidation of the cobalt and nickel to higher valence state. The coexistence of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ is beneficial to the electrochemical performance of hybrids.

As presented in Fig. 4, the pristine ink (dried at the same temperature as the precursor before TGA) undergoes two remarkable steps of weight loss at about 320°C and 480°C, which can be respectively attributed to the thermal decomposition of the matters used in the Chinese ink (i.e., glue and other additives) and the oxidation of carbon black into CO₂ or CO. As a result, the precursors also experienced similar weight loss at these two temperature ranges. Besides, for the precursors, the evident weight loss at 280°C, which is indicated by a sharp peak in the derivative TGA curve, is related to the decomposition of the precursor to form NCO, while releasing H₂O and CO₂.

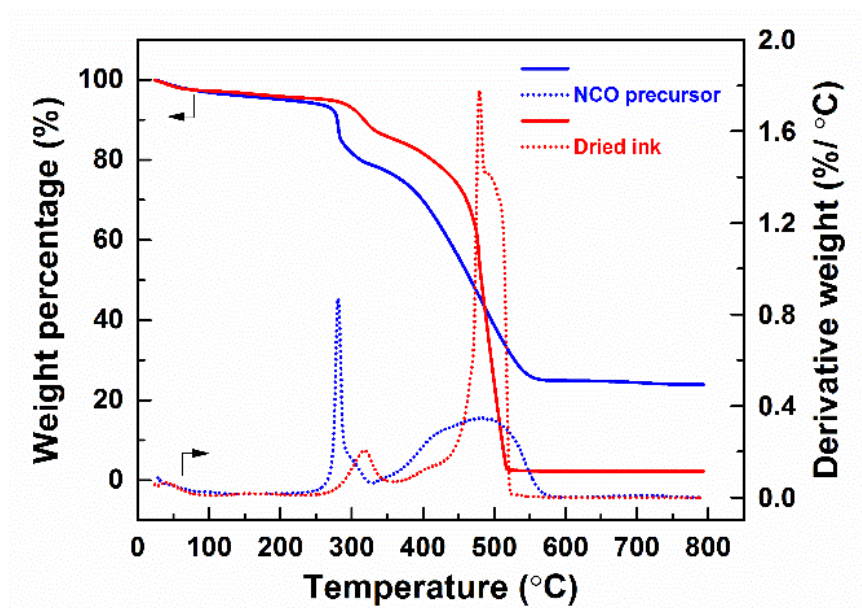


Fig. 4. TG and DTG curves of the NCO precursor and air-dried pristine ink, which were heated to 800°C in air at a ramping rate of 20°C min⁻¹.

3.2. Morphologies of the hybrids

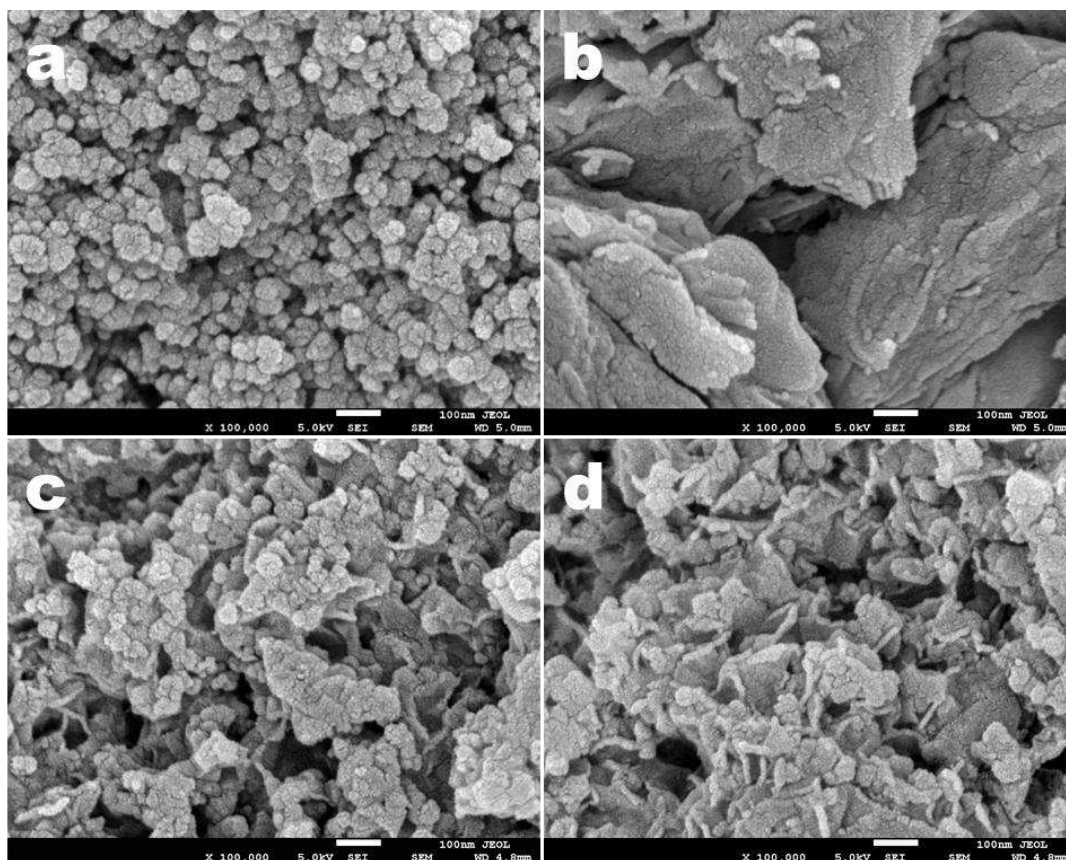


Fig. 5. SEM images of different samples: (a) pristine Chinese ink calcined at 300°C, (b) pure NCO calcined at 300°C, (c) precursor of the NCO-ink_{3.6} hybrid and (d) the NCO-ink_{3.6} hybrid calcined at 300°C.

3.2.1. Effect of Chinese ink

Fig. 5 shows representative SEM images of different samples. According to the Chinese ink supplier, the carbon used as the black pigment is commercial carbon black (Fig. 5 (a)). Different from soot or lampblack, which is widely used in traditional Chinese ink, commercial carbon black is produced under controlled conditions, in order to obtain desired properties to fulfill the requirements of different applications. Therefore, carbon black has smaller particle sizes and a narrower particle size distribution than soot and lampblack [44]. The carbon black particles are present in an aciniform shape, similar to a bunch of grapes, rather than an independently dispersed spherical shape as might be expected. The particle size of these constituent primary particles ranges over 50–100 nm, estimated from the SEM image. In addition, according

to the TEM image (Fig. 6 (c)), the constituent primary particles are actually composed of numerous imperfect graphite layers oriented around the center. The graphite layers endow carbon black with quasi-crystal features, as confirmed by the XRD or Raman results.

As shown in Fig. (c, d), for the hybrid NCO-ink_{3.6} before and after calcination at 300°C for 2 h, NCO is present in the shape of nanoflakes, while the carbon black particles are inserted into the space in between the NCO nanoflakes. Obviously, these two samples share similar morphology, indicating that no remarkable change occurred during the calcination process at 300°C. The presence of carbon black particles dramatically alleviates the aggregation of NCO and create numerous voids that can benefit the penetration of ions. By contrast, the sample prepared under the same conditions without the addition of Chinese ink (Fig. 5 (b)) displays an agglomerated structure. These thick layers will become barriers to the ion diffusion during charging/discharging.

Representative TEM images of the NCO-ink_{3.6} hybrid calcined at 300°C are depicted in Fig. 6 (a, b). The carbon black particles can be readily distinguished from the NCO nanoflakes, because the carbon black particles are composed of multiple graphite layers surrounding a center, rather than regular lattice fringes as the NCO nanoflakes. In the HRTEM image of the NCO nanoflakes, there are two distinct lattice fringes, with lattice spacings of 0.25 nm and 0.21 nm, corresponding to the (311) and (400) lattice planes of the spinel NCO, respectively. As observed in these TEM images, the NCO nanoflakes are in close contact with carbon black particles, which is conducive to fast charge transportation.

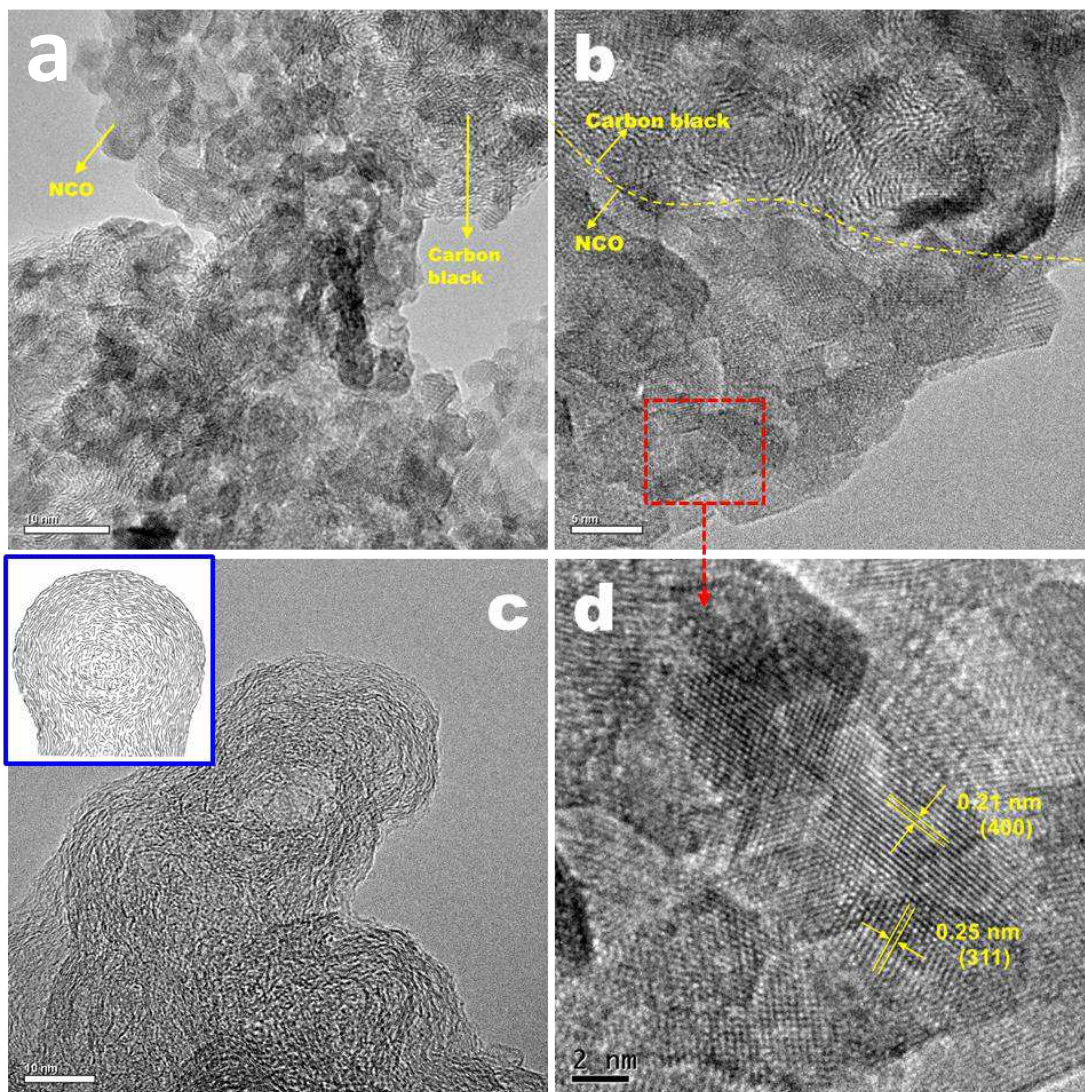


Fig. 6. (a, b) TEM images of the NCO-ink_{3.6} hybrid calcined at 300°C. (c) TEM image of the pristine carbon black used in the Chinese ink, with the inset showing a schematic drawing of the structure of carbon black. (d) HRTEM of representative NCO nanoflakes.

Based on the FESEM and TEM results, the formation mechanism of NCO can be proposed. In the first step, when the temperature reaches a certain level, urea would gradually hydrolyze to produce OH^- and CO_3^{2-} anions, as described by Eqs. (2-4). These cations caused the co-precipitation of Ni^{2+} and Co^{2+} cations, producing precipitate of cobalt-nickel bimetallic carbonate hydroxide hydrate, as given by Eq. (5). The precipitated precursor can cover or wrap the carbon black particles from the Chinese ink. The high

dispersity of the carbon black particles, along with the action of vigorous magnetic stirring, ensured a uniform precipitation of the precursor onto surface of the carbon black particles. Otherwise, obvious phase separation would occur at the end of the reaction without the magnetic stirring, where a lower part containing more carbon black particles and an upper part containing more pale blue precipitate were observed. This is because the carbon black particles covered (or wrapped) by the precipitate first settled down due to the gravity, but the subsequently resultant precipitate could only cover the top carbon black layer. At the end of the co-precipitation reaction, the homogeneous carbon black-NCO precursors were obtained. In the second step, the precursor gradually converted into the NCO as the temperature rises at relatively low heating rates. Such structures combining carbon as the substrate and epitaxially grown NCO in our NCO-ink hybrids are not reported in other carbon nanomaterials [45-47].

3.2.2. Effect of calcination temperature

Fig. 7 demonstrates SEM images of the hybrids NCO-ink_{3,6} calcined at different temperatures. In the hybrids calcined at 200°C, 250°C and 300°C, morphology of the precursor was well preserved, in which the carbon black particles are inserted into the NCO nanoflakes, creating numerous voids. However, as the calcination temperature is further increased, the content of carbon black particles reduced obviously, because of oxidation of the carbon black in air.

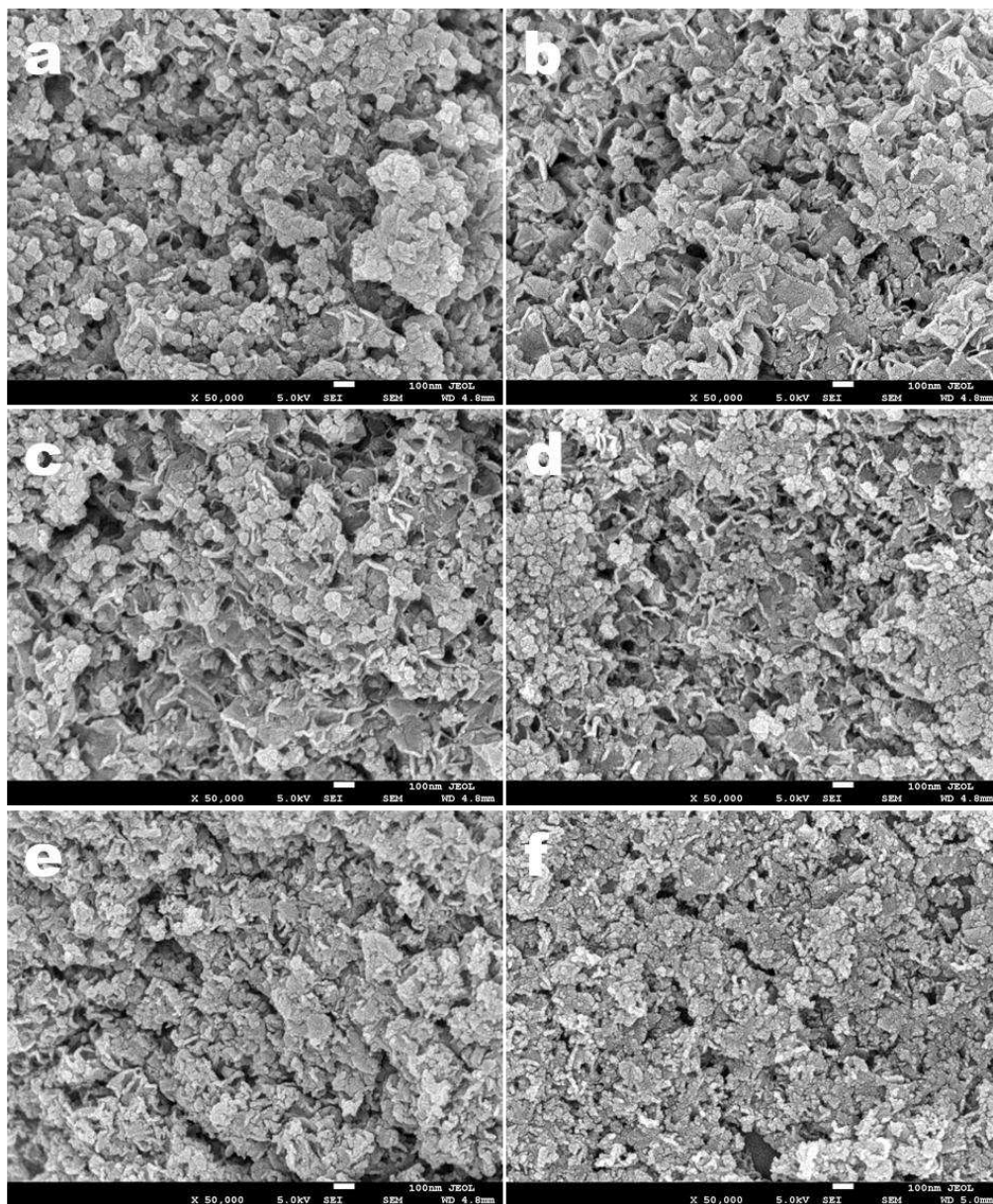


Fig. 7. SEM images of the hybrids NCO-ink_{3.6} calcined at different temperatures: (a) precursor, (b) 200°C, (c) 250°C, (d) 300°C, (e) 350°C and (f) 400°C.

Evidence of this can be found from the Raman (Fig. 2) and the TGA (Fig. 4) analysis results. In the TGA curves, the low-temperature-calcined samples (200°C, 250°C and 300°C), which preserve more carbon black during calcination, underwent a sharp weight loss in the temperature range of 300-500°C. In contrast, the high-temperature-calcined samples (350°C and 400°C) only show a small weight loss in this

temperature range. Higher calcination temperature led to a smaller retained amount carbon black in the hybrid, which is indicated by the higher weight retention at 600°C. It is noteworthy that metal oxides can function as catalyst to lower the oxidation temperature for carbon black [48]. Hence, by comparing the DTG curves in Figure 6.10b and Figure 6.6, it can be seen that the center of the peak that reveals the intensive oxidation of carbon black shifts from around 480°C to 400°C. Consequently, the calcination temperature should be well controlled in order to achieve the optimum condition for the growth of NCO nanoflakes without sacrificing carbon black. Otherwise, in the absence of sufficient carbon black, contiguous NCO nanoflakes tend to fuse together into clusters. This will reduce the overall surface area and the pore size. Evidence can be found from the analysis on the BET surface area (discussed below).

3.3. Specific surface area

Figure 6.11a depicts Nitrogen adsorption-desorption isotherms (77 K) of different samples calcined at 300°C are depicted in Fig. 8 (a). These isotherms can all be categorized as the Type IV isotherms, characterized by a hysteresis loop, indicating the presence of mesoporous structure in the samples [31, 37]. For pure NCO, the hysteresis loop is observed in the range from 0.4 to 1.0 P/P_0 , whereas that of the dried ink is in the range from 0.8 to 1.0 P/P_0 . For the NCO-ink hybrids, with increasing loading mass of ink, the shape of the isothermal gradually changes from “NCO-dominated” to “ink-dominated”. A similar trend is also observed in the BJH pore size distribution plots, where the pure NCO demonstrates a narrow pore size distribution centered at about 4 nm, while the dried ink shows a broad pore size distribution ranging from 4 nm to 50 nm. For low-ink-content hybrids (NCO-ink_{0.9} and NCO-ink_{1.8}), the presence of Chinese ink shifts the center of the peak to 15 nm. However, for high-ink-content hybrids (NCO-ink_{3.6} and NCO-ink_{7.2}), the presence of Chinese ink not only shifts the center of the peak, but also broadens the pore size distribution. It can be thus concluded that the carbon black particles function well as spacers to create large voids in the hybrids. As a result, the NCO-ink hybrids show higher BET specific surface area (Fig. 8 (c)) and larger BJH adsorption average pore size than pure NCO. The hybrid with 1.8 g Chinese ink has the largest BET specific surface area of 217 m²·g⁻¹. Nonetheless, due to the low specific surface area nature of ink (calcined at this temperature), excessive addition of Chinese ink led to decrease in specific surface area.

In addition, the effect of calcination temperature on surface area and pore structure was also examined. As observed in Fig. 8 (a), the hybrids calcined at different temperatures share similar Type IV isothermals, indicating that the mesoporous structure was still preserved at higher calcination temperatures. The increasing calcination temperature tends to increase the specific surface area and the average pore size, but meanwhile, it also broadens the pore size distribution. This is possibly because the removal of glue on the carbon black surface at high temperatures broke the carbon black clusters and hence improved the dispersion of the carbon black particles in the hybrids. However, too high calcination temperature caused counterproductive result, majority of the carbon black was burned. The enlarged average pore size can be ascribed to the voids created due to the removal of carbon black particles.

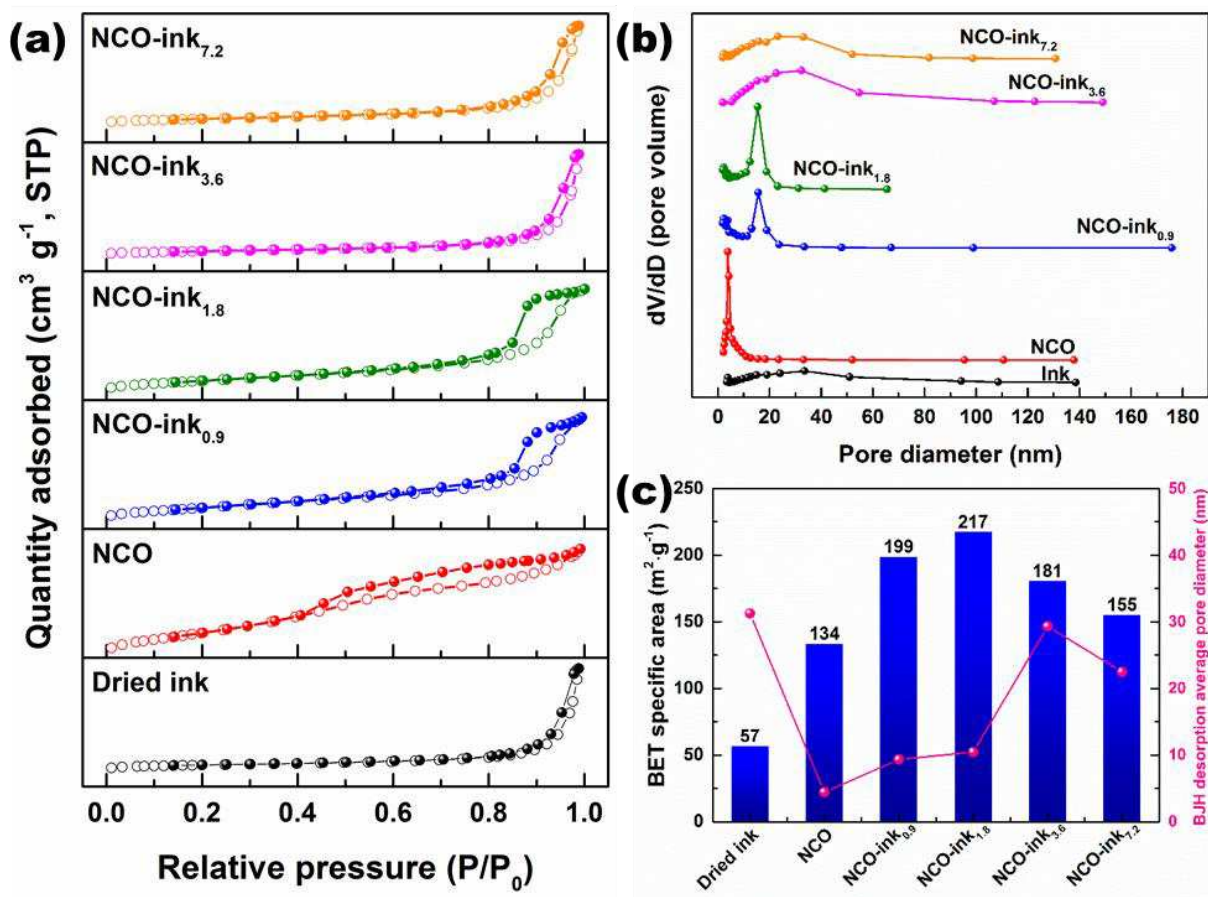


Fig. 8. (a) Nitrogen adsorption-desorption isotherms of ink, pure NCO and NCO-ink hybrids with different content of ink, were all the samples were calcined at 300°C. (b) BJH pore size distribution plots, determined

from the adsorption branch of the N₂ isothermals. (c) Calculated BET specific surface area and BJH desorption average pore diameter.

In summary, with an appropriate content of Chinese ink and a proper calcination temperature, the hybrid can be tuned to have optimal large specific surface area and decent mesoporous structure, which are the desired features for electrodes of SCs.

3.4. Electrochemical performances

Pseudocapacitive behaviors of the NCO-ink hybrids were characterized with the data of CV, GCD and EIS, which were performed in a three-electrode cell with a platinum plate as the counter electrode, a Hg/HgO electrode as the reference electrode and a 2 M KOH aqueous solution as the electrolyte.

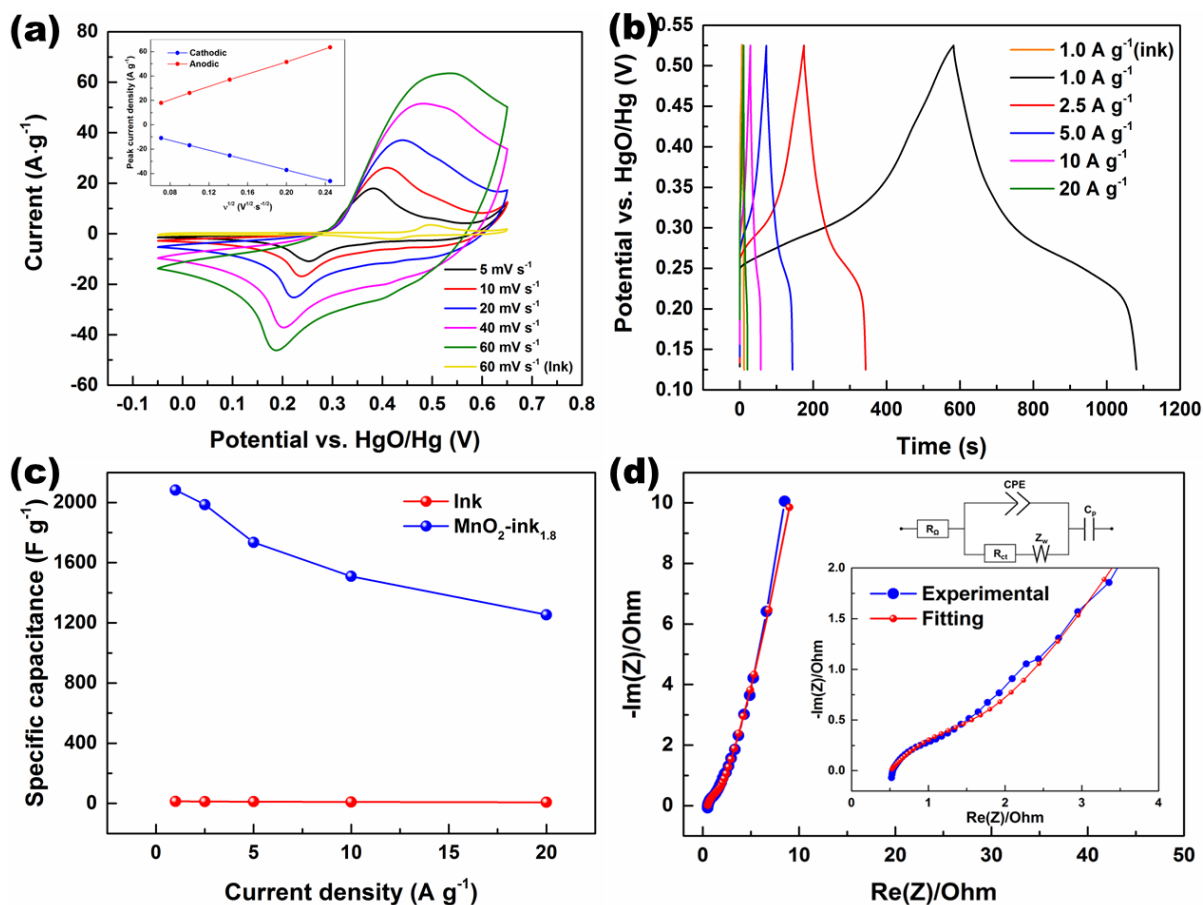
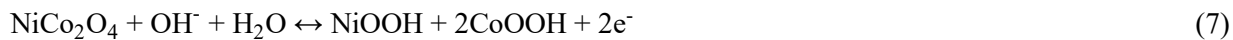


Fig. 9. (a) CV curves of the hybrid NCO-ink_{1.8} at scanning rates of 5-60 mV s⁻¹, with the inset depicting the plot of anodic and cathodic peak current density versus scanning rate $v^{1/2}$. (b) GCD curves of the hybrid NCO-ink_{1.8} at current densities of 1-20 A g⁻¹ within a potential window of 0.125-0.525 V (vs. Hg/HgO). (c) Specific capacitances of the dried ink and the hybrid NCO-ink_{1.8} at different current densities. (d) Nyquist plots of the hybrid NCO-ink_{1.8} with the corresponding fitting curve and equivalent circuit.

The hybrid NCO-ink_{1.8} calcined at 200°C was representatively selected for the characterization. Fig. 9 (a) displays CV curves within a potential window of -0.05 to 0.65 V (vs. Hg/HgO) at sweeping rates of - 60 mV·s⁻¹. In each CV curve, there is a pair of well-defined peaks, which is the pseudocapacitive feature of the electrode. The pair of peaks is mainly ascribed to the Faradaic redox reactions between OH⁻ anions and the Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ transitions. Since the redox potentials of Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ are very close,

the two peaks overlap and integrates into a pair of peaks. The redox reactions can be expressed as below [40, 49]:



As the scanning rate is increased, the anodic and cathodic currents increase, with slight positive/negative shifts in the anodic/cathodic peaks, due to the strengthened electric polarization. This indicates that the electrochemical process is governed by the diffusion of ions, since the ions can diffuse faster and give rise to a more rapid current response at higher scanning rates. Besides, noting the inset in Fig. 9 (a), there is a linear relationship between the anodic/cathodic peak currents and the square root of the scanning rate, which also reveals that the redox reaction is diffusion-controlled [37]. In comparison, the CV curve of the pristine dried Chinese ink (at 60 mV s^{-1}) encloses a very small area, indicating its low capacitance. The pair of weak peaks in the CV curve of the dried ink is attributed to some redox reactions between the nickel foam and the electrolyte. In view of this, the capacitance contribution from the ink and the current collector was ignored.

To quantify specific capacitance of the hybrids, GCD measurement was carried out within a potential window of 0.125 to 0.525 V vs HgO/Hg, at different current densities. As illustrated in Fig. 9 (b), the charging and discharging curves are non-linear, with a plateau in the range of 0.25–0.32 V and 0.30–0.23 V (at 1 A g^{-1}), corresponding to the redox reactions. Only a very small IR drop is observed, suggesting the low equivalent series resistance of the electrode. The calculated specific capacitance is displayed in Fig. 9 (c). In this case, only 60% of the initial specific capacitance (at 1 A g^{-1}) is retained, when the current density is increased by 20 times.

Electrochemical impedance spectroscopy (EIS) analysis was performed to probe the detailed electrochemical behaviors of the working electrode. Fig. 9 (d) shows the experimental data and the fitted Nyquist plots, together with the corresponding equivalent circuit. As observed, the curve has an intercept of 0.5Ω at the real axis, which is known as the equivalent series resistance (ESR), which a combination of (i) the intrinsic electrical resistance of the electrode and the current collector, (ii) the ionic resistance of the

electrolyte and (iii) the contact resistance between the electrode and the current collector [50]. Besides, the curve exhibits distinct deviation from the vertical line in the low-frequency range, which means that the electrochemical process is limited by ion diffusion at low frequencies.

In addition, the semicircle that represents the Faradaic resistance (charge transfer resistance) is not evident in this case. More information can be extracted from the equivalent circuit, which is composed of five components, i.e., R_Ω , R_{ct} , CPE , Z_w and C_p . R_Ω can be simply equated with the ESR. R_{ct} reflects the charge transfer resistance, i.e., the kinetic resistance in the ion transfer at the electrode-electrolyte interface, and/or the intrinsic charge transfer resistance of the electrode [50]. CPE , a constant phase element, represents the electrical double-layer capacitor (imperfect capacitor) [37]. Z_w is a diffusion-controlled element, denoting the Warburg impedance that is attributed to the diffusion resistance of the electrolyte ions within the porous electrode [37]. C_p is a Faradaic pseudocapacitor, denoting the reversible redox reactions between the electrode and electrolyte.

3.4.1. Effect of Chinese ink on electrochemical performance of NCO

It has been illustrated that the addition of Chinese ink prevents the agglomeration of NCO, which improves the pore structure and enlarges the surface area for NCO. Thus, it is foreseeable that the addition of Chinese ink will have a positive effect on the electrochemical performance of NCO. Fig. 10 (a) depicts CV curves of the NCO-ink hybrids with different loading mass of Chinese ink. Obviously, the enclosed area of the CV curves increases with increasing loading mass of Chinese ink, suggesting an improvement in specific capacitance. Meanwhile, with increasing loading mass of Chinese ink, the anodic peak shifts to a lower potential, while the cathodic peak shifts to a higher potential.

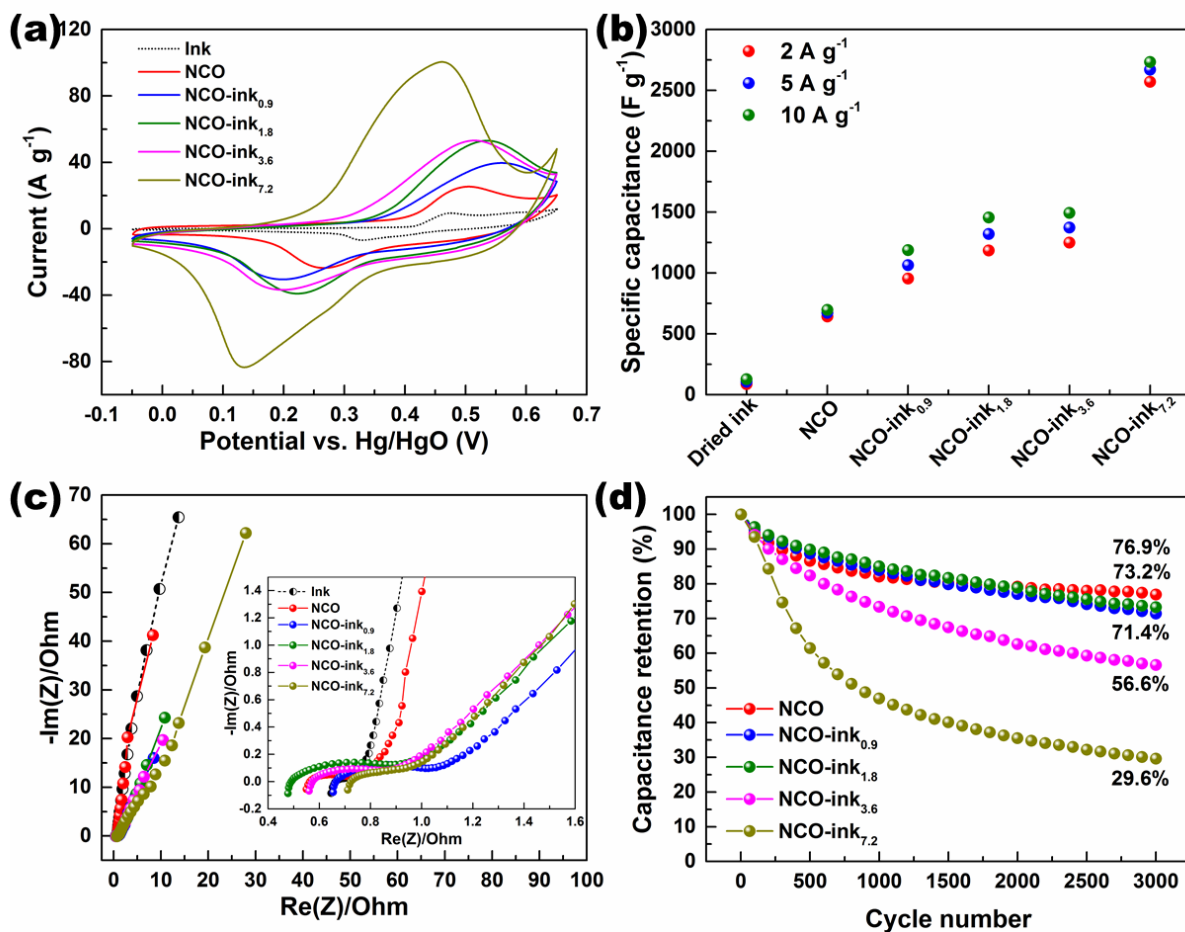


Fig. 10. (a) CV curves of dried ink and the NCO-ink hybrids with different contents (0, 0.9, 1.8, 3.6 and 7.2 g) of Chinese ink. (b) Specific capacitance of dried ink and the NCO-ink hybrids with different content of Chinese ink at 2 10 $A\ g^{-1}$, 5 10 $A\ g^{-1}$ and 10 $A\ g^{-1}$. (c) Nyquist plots of dried ink and the NCO-ink hybrids with different contents of Chinese ink. (d) Cycling stability of the NCO-ink hybrids with different contents of Chinese ink.

It is understandable that the sample with high content of Chinese ink will have a relatively low content of NCO, since all the electrodes contain almost the same weight of NCO-ink hybrids. The sample with lower content of NCO would less polarized, so the anodic peak locates at less positive potential [51]. The specific capacitance of these NCO-ink hybrids was estimated from GCD at current densities of 2 10 $A\ g^{-1}$, 5 10 $A\ g^{-1}$ and 10 $A\ g^{-1}$, within a potential window of 0.125 to 0.525 V (vs. Hg/HgO). In accordance with the CV, the

gravimetric specific capacitance of NCO is evidently boosted by the addition of Chinese ink. The sample NCO-ink_{7.2} shows a specific capacitance of 2733 F g⁻¹ at a current density 2 A g⁻¹, which is higher than literature data [43, 52, 53].

Fig. 10 (c) shows Nyquist plots of the hybrids. As expected, the introduction of Chinese ink reduced the diffusion resistance of NCO, because the carbon black particles efficiently mitigated the aggregation of NCO and created voids in between the NCO particles, which is favorable for ion transportation. Meanwhile, Chinese ink also increased the charge transfer resistance, due to the resistive nature of the glue. It is worth mentioning that the EIS measurement is susceptible to various factors, especially the surface conditions of the electrode. Accordingly, different testing results could be obtained for the same sample. In this case, gas emission resulting from the decomposition of water tends to occur when the potential is risen up. The gas emission gas would cause divorce of the active materials from the nickel foam, while the presence of gas in the electrode also altered surface condition of the electrode. Although special measures had been taken to ensure similar testing condition, there are uncertain factors leading to differences in the results. Therefore, the EIS results are not reliable to correlate with the content of Chinese ink.

The cycling stability of these NCO-ink hybrids was evaluated by continuous charging and discharging at a high current density of 10 A g⁻¹ for 3000 cycles. Fig. 10 (d) shows evolution behaviors of capacitance retention with cycle numbers. The NCO-ink hybrids have a shorter cycling life than the pure NCO, with the cycling life to be worsened with increasing content of Chinese ink, which can be possibly attributed to the dropping in active materials caused by gas emission, when the potential is raised up. It is observed that the sample with more Chinese ink has a more intensive gas emission when charged to high potentials.

3.4.2. Effect of calcination temperature

Fig. 11 (a) shows CV curves measured at 20 mV s⁻¹ of the NCO-ink_{3.6} hybrids calcined at different temperatures, while Fig. 11 (b) depicts specific capacitances of the samples calculated from GCD at 5 A g⁻¹ within a potential from 0.125 to 0.525 V. The CV curves of all the samples have a similar shape but different enclosing areas, indicating that the calcination temperature does not change the electrochemical behavior, but reduces the specific capacitance. The sample calcined at 250°C has the highest specific

capacitance. Nonetheless, the specific capacitance tends to decrease with increasing calcination temperature above 250°C.

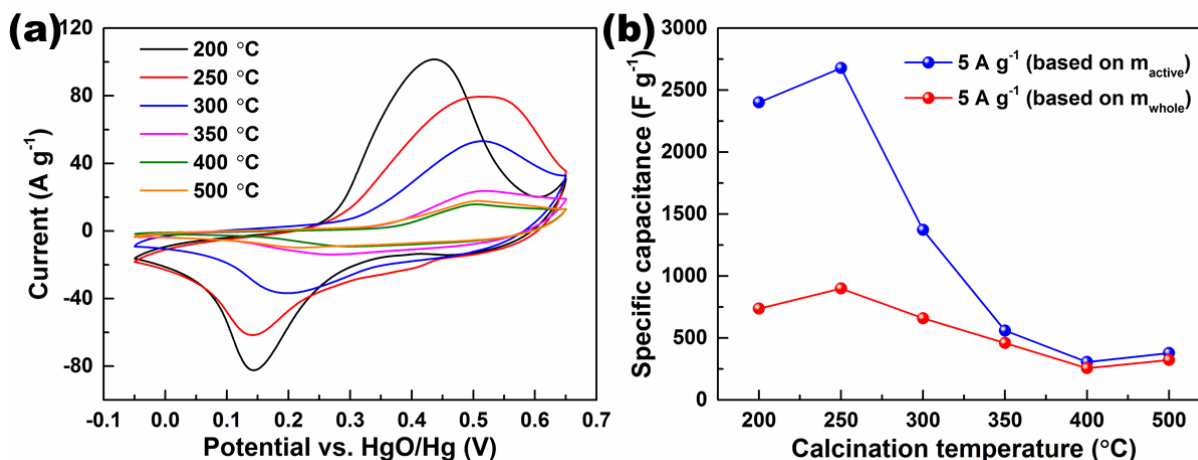


Fig. 11. (a) CV curves of the NCO-ink hybrids calcined at different temperatures. (b) Specific capacitance of the NCO-ink hybrids at 5 A g⁻¹ versus calcination temperature, based on the mass of the active material and the whole electrode.

During calcination, the cobalt-nickel bimetallic carbonate hydroxide hydrate gradually converted into NCO, while the from the from Chinese ink decomposed and the carbon black was oxidized and gasified in air. Meanwhile, the crystallization of NCO of is increased with increasing calcination temperature. As demonstrated by the XRD results, the NCO precursor converted into NCO when the calcination temperature is $\geq 200^\circ\text{C}$. Above 300°C , the carbon black is almost completely removed due to the oxidation, as confirmed by the results of Raman spectroscopy and TGA. According to the BET surface analysis, a high calcination temperature is apparently beneficial to a high specific surface area, since the removal of glue and carbon black created large voids in NCO. The inconsistency between the specific capacitance and specific surface area can be explained in this way. Based on the BJH pore size, the pore size distribution was broadened after high temperature calcination, which is unfavorable for electrochemical performance. In addition, the oxidation of the carbon black at high calcination temperatures led to reduction in electrical conductivity.

Accordingly, the specific capacitance is decreased with increasing calcination temperature.

Table 2. Calculated values of the components in the equivalent circuit.

	200°C	300°C	400°C	500°C
R_{Ω} (Ω)	0.466	0.564	0.51	0.45
CPE ($mF.s^{\alpha-1}$)	15.7	4.28	3.52	3.463
α	0.608	0.738	0.761	0.785
R_{ct} (Ω)	2.102	0.643	0.919	0.523
Z_w ($\Omega.s^{-0.5}$)	2.468	2.056	2.471	2.596
C_p (F)	10.09	8.17	4.658	1.236

EIS gives an insight into the electrochemical behavior. The obtained data are fitted into the equivalent electric circuits which are identical to those in Fig. 9 (d). The derived values of the components are listed in Table 2. It is noticeable that the Warburg diffusion resistance is reduced, as the calcination temperature is increased from 200°C to 300°C, which can be attributed to the removal of glue. However, above 300°C, the Warburg diffusion resistance is increased with increasing calcination temperature. This is because of the removal of carbon black at 400°C (or 500°C), resulting in stacking of the NCO nanoflakes and hence blocking of ion transportation, in agreement with the FESEM results. Therefore, the pseudocapacitance is decreased with increasing calcination temperature. It is necessary to address this issue in terms of practical application, where one possible strategy is to use low-temperature calcination in air, combined with high-temperature annealing in reducing environment.

4. Conclusions

High-surface-area $NiCo_2O_4$ nanoflakes have been synthesized through chemical co-precipitation and subsequent calcination. Commercial Chinese ink was added in the precursor solution to provide well-dispersed carbon black particles. The presence of the carbon black particles effectively alleviated the stacking of the precipitated $NiCo_2O_4$ precursor, while contributing additional electrical conductivity. Accordingly, the BET specific surface area was increased from $134 \text{ m}^2 \text{ g}^{-1}$ for the pure $NiCo_2O_4$ to the maximum $217 \text{ m}^2 \text{ g}^{-1}$ for the sample with 1.8 g Chinese ink. The addition of Chinese ink had a positive effect on the specific capacitance, but a negative effect on the cycling stability of the $NiCo_2O_4$ -ink hybrids.

The hybrid with 7.2 g Chinese ink showed the maximum specific capacitance of 2733 F g⁻¹ at 2 A g⁻¹, but only retained 29.6% of the initial capacitance after 3000 cycles of charging/discharging, which should be addressed for practical applications. Besides, specific capacitance tended to decline with increasing calcination temperature, especially above 300°C. Nevertheless, it is proven that commercial Chinese ink can be directly used to offer well-dispersed carbon black particles as the spacer and electrical reinforcers for NiCo₂O₄. Admittedly, electrochemical performance, especially the cycling stability still remains to be improved. One possible solution is a combination of low temperature calcination in air and high temperature annealing in reducing environment.

Acknowledgement

One of authors (Zhuohao Xiao) acknowledges the financial support by the National Natural Science Foundation of China (U25A20247).

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