Effective enhancement of electrochemical energy storage of cobalt-based nanocrystals by hybridization with nitrogen-doped carbon nanocages

Qingming Ma, Yuejian Yao, Minglei Yan, Jie Zhao, Chengxuan Ge, Qiang Wu^{*}, Lijun Yang, Xizhang Wang and Zheng Hu^{*}

ABSTRACT Cobalt-based oxygenic compounds $\text{Co}(\text{OH})_2$, CoO and Co_3O_4 are attractive for electrochemical energy storage owing to their high theoretical capacities and pseudocapacitive properties. Despite the great efforts to their compositional and morphological regulations, the performances to date are still quite limited owing to the low active surface area and sluggish charge transfer kinetics. Herein, different Co-based nanocrystals (Co-NCs) were conveniently anchored on the hierarchical nitrogen-doped carbon nanocages (hNCNCs) with high specific surface area and coexisting micro-meso-macropores to decrease the size and facilitate the charge transfer. Accordingly, a high specific capacity of 1170 F g^{-1} is achieved at 2 A g^{-1} for the $\text{Co}(\text{OH})_2/\text{hNCNCs}$ hybrid, in which the capacitance of $\text{Co}(\text{OH})_2$ ($2214 \text{ F g}_{\text{Co}(\text{OH})_2}^{-1}$) is approaching to its theoretical maximum (2595 F g^{-1}), demonstrating the high utilization of active materials by the hybridization with N-doped nanocarbons. This study also reveals that these Co-NCs store/release electrical energy *via* the same reversible redox reaction despite their different pristine compositions. This insight on the energy storage of Co-based nanomaterials suggests that the commonly-employed transformation of the Co-NCs from $\text{Co}(\text{OH})_2$ to CoO and Co_3O_4 on carbon supports is unnecessary and even could be harmful to the energy storage performance. The result is instructive to develop high-energy-density electrodes from transition metal compounds.

Keywords: Co-based nanocrystals, pseudocapacitance, hybridization, N-doped carbon nanocages, supercapacitors

INTRODUCTION

Batteries and supercapacitors have been widely used in portable electronics, electric vehicles and other electric

devices. Batteries usually exhibit high energy density but have to take hours to recharge, while supercapacitors enable rapid charge/discharge but have low energy density, which is determined by their respective electrochemical energy storage (EES) mechanisms [1–3]. Owing to the increasing demand on the combined high energy and high power densities, the performance improvement of EES devices is a hot yet challenging topic so far [4–6]. As the most important electrode materials for supercapacitors, carbon-based nanomaterials store charges *via* electrochemical double layer capacitive behavior and thus deliver high power density, but the energy density is restricted by the accessible surface area [7,8]. The second mechanism for capacitive energy storage, termed pseudocapacitance, was discovered by Conway [9], providing a promising means of achieving both high power and high energy densities. In the pseudocapacitive process, the reversible redox reactions occur at or near the surface of the electrode, leading to fast but much greater charge storage [10,11], which has attracted an increasing interest in recent years [11–15].

The cobalt-based oxygenic compounds, including $\text{Co}(\text{OH})_2$, CoO and Co_3O_4 , are attractive electrode materials for EES owing to their high theoretical capacities and pseudocapacitive properties [16–22]. Much effort has been dedicated to the compositional and morphological regulations of Co-based nanomaterials, but the available capacitances to date are still quite limited mainly because of the low active surface area and sluggish charge transfer kinetics (Table S1) [13–16,22–26]. To enhance the capacitive contribution, the Co-based nanomaterials were often grown on carbon supports or deposited on nickel foams for enhancing the conductivity and reducing the

Key Laboratory of Mesoscopic Chemistry of MOE and Jiangsu Provincial Lab for Nanotechnology, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

^{*} Corresponding authors (emails: wqchem@nju.edu.cn (Wu Q); zhenghu@nju.edu.cn (Hu Z))

size. But quite different performances were reported with unclear reason, usually without the systematic comparison of different Co-based nanomaterials (Table S2) [17–19,27–35]. Hence, there is still a large room in improving the pseudocapacitive performance of Co-based nanomaterials and unraveling the structure-performance relationship, which is of great significance for developing high-energy-density electrodes from transition metal compounds.

In recent years, we have developed the unique 3D hierarchical carbon-based nanocages featuring the large specific surface area, coexisting micro-meso-macropores, high conductivity and easy doping, which are very promising for electrochemical energy applications [36]. The hierarchical nitrogen-doped carbon nanocages (hNCNCs) are particularly suitable for anchoring metal-based species owing to the N doping, leading to the high dispersion, enhanced electric conductivity and good electrolyte wettability [36–39]. Herein, the Co(OH)_2 , CoO and Co_3O_4 nanocrystals were deliberately anchored on the hNCNCs by a facile microwave-assisted ethylene glycol (EG) method and post-heating. The optimized Co(OH)_2 /hNCNCs hybrid possesses small crystallites and improved charge transfer, achieving a high specific capacity of 1170 F g^{-1} at 2 A g^{-1} , with an ultrahigh capacitance of 2214 F g^{-1} for Co(OH)_2 , i.e., close to the theoretical maximum of Co(OH)_2 (2595 F g^{-1} in the potential window of 0–0.4 V) [13,40]. This study suggests an efficient way to exert the energy storage potential of transition metal compounds by hybridization with hNCNCs.

EXPERIMENTAL SECTION

Synthesis

The hNCNCs support was prepared by *in situ* MgO template method [36], with a large specific surface area ($834 \text{ m}^2 \text{ g}^{-1}$), high conductivity (131.1 S m^{-1}) and high nitrogen content of 9.4 at.% (Fig. S1). The Co-based nanocrystals (Co-NCs) were immobilized onto the hNCNCs by a microwave-assisted EG process [41,42]. Briefly, hNCNCs (50 mg) were dispersed in EG (50 mL) under ultrasonic treatment and stirring, and then an appropriate amount of cobalt acetate tetrahydrate ($\text{Co(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O}$) was added into the suspension. After stirring for 3 h, the pH of the suspension was adjusted to ~8 by adding NaOH/EG solution (0.2 mol L^{-1}) dropwise, followed by the irradiation in a microwave oven (700 W) for 90 s for the deposition of cobalt hydroxide on hNCNCs. The obtained hybrids were heat-

treated at different temperatures (150, 200 and 250°C) in Ar or air for 2 h, and the products were simply denoted as Ar-*T* and O_2 -*T* ($T=150, 200, 250$), respectively. For comparison, two control samples were prepared with the undoped hierarchical carbon nanocages (hCNCs) as support or without support by the EG process and post-heating at 150°C in Ar for 2 h, denoted as Co(OH)_2 /hCNCs and pure Co(OH)_2 , respectively.

Electrochemical measurements

Electrochemical performances were evaluated on Biologic VMP3 workstation using a three-electrode system. The working electrode was prepared by spreading a slurry of Co-NCs/hNCNCs, acetylene black and polyvinylidene fluoride (with a weight ratio of 8:1:1) on a nickel mesh and drying in vacuum at 110°C for 15 h. The areal loading of Co-NCs/hNCNCs on Ni mesh was $\sim 1.5 \text{ mg cm}^{-2}$ in each. A platinum wire was used as the counter electrode, Ag/AgCl as the reference electrode, and 6 mol L^{-1} KOH solution as electrolyte. Cyclic voltammetry (CV) measurements were conducted in the range of 0–0.5 V, and galvanostatic charging/discharging (GCD) tests were conducted in the range of 0–0.4 V. The electrochemical impedance spectroscopies (EIS) spectra were recorded in the frequency range of 10^5 – 10^{-2} Hz . When calculating the specific capacitances (C_m , F g^{-1}) based on the GCD curves, the contribution of bare Ni mesh electrode was subtracted. The aqueous asymmetric supercapacitors were fabricated with the optimized hybrid electrode and the activated carbon (AC) electrode. The mass ratio of the positive to negative materials was set to be ~0.35 according to the charge balance theory [24,35]. The coin cell (2032) was constructed using a cellulose membrane as the separator and 6 mol L^{-1} KOH as the electrolyte. The energy density (*E*) and power density (*P*) of the supercapacitors were calculated as the following equations:

$$E = \int_0^t \frac{IV}{m} dt, P = \frac{1}{t} \int_0^t \frac{IV}{m} dt, \quad (1)$$

where *I*, *V*, *m*, and *t* are the current, discharge voltage range, total mass of the positive and negative electrode materials, and discharge time, respectively.

RESULTS AND DISCUSSION

Promotion effect of hNCNCs support

Usually the hybridization of electrode materials with carbon-based supports can effectively improve the EES performance [3,7]. Three Co-NCs samples with hNCNCs

or hCNCs supports or without support, which were similarly-prepared by heat-treatment at 150°C in Ar for 2 h, were compared to illuminate the promotion effect of the hCNCs support, as shown in Fig. 1 and Figs S2–S4. X-ray diffraction (XRD) analysis indicates that all the three samples are $\text{Co}(\text{OH})_2$. The $\text{Co}(\text{OH})_2/\text{hCNCs}$ (i.e., Ar-150) and $\text{Co}(\text{OH})_2/\text{hCNCs}$ have the mass fraction of $\text{Co}(\text{OH})_2$ of 51.9 and 55.2 wt.%, respectively (Fig. S3). High-resolution transmission electron microscopy (HRTEM) observations show that abundant $\text{Co}(\text{OH})_2$ nanocrystals of 2–5 nm in size are highly dispersed on hCNCs (Fig. 1a, b, Fig. S2), while those on hCNCs have

a broad size distribution in the range of 5–20 nm with a little aggregation (Fig. 1c, d). The lattice fringes of the nanocrystals with the distance of 0.234 and 0.133 nm can be assigned to (002) and (201) planes of $\text{Co}(\text{OH})_2$, respectively, which confirm the species of $\text{Co}(\text{OH})_2$ in these two hybrids (Fig. 1b, d). The $\text{Co}(\text{OH})_2$ nanocrystals on hCNCs and hCNCs are different, with the smaller sizes and higher dispersion for the former as expected due to the strong interaction between the nitrogen dopants and the Co-based species [36,41]. Without carbon-based supports, the pure $\text{Co}(\text{OH})_2$ nanocrystals are sheetlike with the width of several tens of nanometers (Fig. S3).

Figure 1 Characterizations of $\text{Co}(\text{OH})_2/\text{hCNCs}$, $\text{Co}(\text{OH})_2/\text{hCNCs}$ and pure $\text{Co}(\text{OH})_2$. (a–d) Typical HRTEM images of $\text{Co}(\text{OH})_2/\text{hCNCs}$ (a, b) and $\text{Co}(\text{OH})_2/\text{hCNCs}$ (c, d). Inset of (b) is the particle size distribution by counting more than 300 $\text{Co}(\text{OH})_2$ nanocrystals. (e) EIS spectra. (f) Capacitance of the active $\text{Co}(\text{OH})_2$ as a function of current density (Fig. S5). Note: In (b, d), the fringes with the distance of 0.234 and 0.133 nm can be assigned to (002) and (201) planes of $\text{Co}(\text{OH})_2$ (PDF#45-0031), respectively.

The EIS spectra give the charge transfer resistances (R_{ct}) of 0.09, 0.08 and $0.24\ \Omega$ for $\text{Co(OH)}_2/\text{hNCNCs}$, $\text{Co(OH)}_2/\text{hCNCs}$ and Co(OH)_2 , respectively (Fig. 1e, Table S3). Hence, the hybridization of Co(OH)_2 with the carbon-based nanocages much decreases the R_{ct} , thereby beneficial to the charge transfer. The $\text{Co(OH)}_2/\text{hNCNCs}$ hybrid presents the best EES performance with high capacitance and superior rate capability (Fig. 1f), due to the smaller particle size and better electrolyte wettability (Fig. S4). Specifically, at the current density of $2\ \text{A g}^{-1}$, the capacitance of the active Co(OH)_2 is $2214\ \text{F g}^{-1}$ for $\text{Co(OH)}_2/\text{hNCNCs}$ (Fig. S5), much higher than $1431\ \text{F g}^{-1}$ for $\text{Co(OH)}_2/\text{hCNCs}$ and $850\ \text{F g}^{-1}$ for Co(OH)_2 . The $\text{Co(OH)}_2/\text{hNCNCs}$ delivers a capacitance of $1127\ \text{F g}_{\text{Co(OH)}_2}^{-1}$ as the current density increases to $100\ \text{A g}^{-1}$, with a high retention of 51.0%, obviously higher than the $\text{Co(OH)}_2/\text{hCNCs}$ (44.2%) and pure Co(OH)_2 (36.5%) (Fig. 1f). This result indicates that the hybridization of Co(OH)_2 with hNCNCs promotes the EES performance, superior to the case with hCNCs.

Optimizing mass fraction of active materials on hNCNCs

As known, the mass fraction of active material on the support strongly influences the electrochemical performance. A series of $\text{Co(OH)}_2/\text{hNCNCs}$ hybrids were synthesized by changing the feedstock of cobalt acetate during the microwave-assisted deposition, followed by the calcination at 150°C in Ar atmosphere for 2 h. The mass fraction of Co(OH)_2 is tuned to be 37.0, 51.9, 67.7 and 83.3 wt.%, with the size and aggregation of Co(OH)_2 nanocrystals increasing, which leads to the decrease of conductivity and specific surface area as well as the increase of R_{ct} (Figs S6–S9). The electrochemical tests indicate that the $\text{Co(OH)}_2/\text{hNCNCs}$ with the mass fraction of 51.9 wt.% shows the best EES performance in terms of specific capacitance and rate capability, which is a tradeoff between active material amount and charge transfer kinetics (Fig. S9).

EES performance comparison of different Co-NCs/hNCNCs hybrids

To compare the EES performance of Co(OH)_2 , CoO and Co_3O_4 , a series of Co-NCs/hNCNCs hybrids were prepared by heat-treating the same precursor of $\text{Co(OH)}_2/\text{hNCNCs}$ (51.9 wt.% in Ar or air at 150, 200 or 250°C for 2 h. The obtained samples, i.e., Ar-150, Ar-200, Ar-250, O_2 -150, O_2 -200, and O_2 -250, respectively, were characterized by HRTEM, XRD and X-ray photoelectron spectroscopy (XPS) as shown in Fig. 2. The Ar-150 sample contains abundant Co(OH)_2 nanocrystals of

2–5 nm (Fig. 1a, b). Increasing the heating temperature under Ar leads to the transformation of Co(OH)_2 into CoO for the Ar-200 and Ar-250 (Fig. 2a, d), accompanied by a slight increase of the nanocrystal size owing to the sintering (Fig. 1a and Fig. S10). The lattice fringes of the nanocrystals with the distance of 0.227 nm in Fig. 2a and 0.262 nm in Fig. S10b can be assigned to the (200) and (111) planes of CoO, which confirm the species of CoO in Ar-250. The mass fraction of CoO is 44.0 and 43.9 wt.% for the Ar-200 and Ar-250, respectively (Fig. S11). The decreased mass fraction relative to Ar-150 mainly results from the decomposition of Co(OH)_2 to CoO.

The heat treatment in air leads to different situations. The O_2 -150 is similar to the Ar-150, containing the highly dispersive Co(OH)_2 nanocrystals of 2–5 nm in size (Fig. 2b, d). The mass fraction of the O_2 -150 is 51.5 wt.%, similar to that of Ar-150 (Fig. S11). The treatment at higher temperature results in the conversion of Co(OH)_2 into Co_3O_4 for the O_2 -200 and O_2 -250 (Fig. 2c, d), with the particle sizes increased to ca. 5–20 nm for the O_2 -250 (Fig. S10). The lattice fringes with the distance of 0.234 nm in Fig. 2b can be assigned to the (002) planes of Co(OH)_2 , confirming the species of Co(OH)_2 in O_2 -150. The lattice fringes with the distance of 0.467 nm in Fig. 2c and 0.156 and 0.286 nm in Fig. S10d are assigned to the (111), (511) and (220) planes of Co_3O_4 , confirming the species of Co_3O_4 in O_2 -250. The mass fraction of Co_3O_4 in the O_2 -200 and O_2 -250 is 50.9 and 60.3 wt.%, respectively (Fig. S11). The obviously higher mass fractions of Co_3O_4 in the O_2 -200 and O_2 -250 (relative to 47.8 wt.% in theory according to 51.5 wt.% of Co(OH)_2 in O_2 -150) result from the partial oxidation of hNCNCs in the presence of Co species [43] with the more severe situation for the O_2 -250.

For the Ar-150 and O_2 -150, the Co 2p core level spectra are quite similar with each other as expected since the Co species exist as Co(OH)_2 for both samples (Fig. 2e). The two major peaks around 781.3 and 797.2 eV correspond to Co $2p_{3/2}$ and Co $2p_{1/2}$, accompanied by two satellite peaks at 785.3 and 802.7 eV, consistent with that for Co(OH)_2 [25]. For the Ar-250, the Co 2p signals locate at 780.6 and 796.3 eV for Co $2p_{3/2}$ and Co $2p_{1/2}$, with a little shift to the lower binding energy (BE) side, which can be assigned to CoO [26], consistent with the XRD pattern (Fig. 2d). For the O_2 -250, the Co 2p signals show asymmetric shapes, which can be deconvoluted into two kinds of Co species, i.e., Co^{2+} with BE at 781.3 and 796.9 eV and Co^{3+} with BE at 779.8 and 795.0 eV, respectively, in agreement with the Co_3O_4 species [20]. These results indicate the successful preparation of different Co-NCs/hNCNCs hybrids.

Figure 2 Characterizations on a series of Co-NCs/hNCNCs hybrids. (a–c) TEM images of Ar-250 (a), O₂-150 (b) and O₂-250 (c). Insets are the corresponding HRTEM images. (d) XRD patterns. (e) XPS fine spectra of Co 2p. Note: The lattice distances of 0.227, 0.234 and 0.467 nm in (a–c) can be assigned to the (200) planes of CoO (PDF#42-1300), (002) of Co(OH)₂ (PDF#45-0031) and (111) of Co₃O₄ (PDF# 43-1003), respectively.

The electrochemical performances of the series of Co-NCs/hNCNCs are depicted in Fig. 3 by using three-electrode system in 6 mol L⁻¹ KOH solution. A pair of stable peaks appear in the CV curves after the electrode activation (Fig. 3a). The redox peaks are quite similar for these hybrids despite their different pristine compositions of Co(OH)₂, CoO and Co₃O₄, which implies the same redox reaction during charging/discharging. The GCD curves show a discharge plateau at ~0.2 V (vs. Ag/AgCl) and a charge plateau at ~0.28 V, also supporting the energy storage mechanism *via* redox reaction for the different Co-NCs (Fig. 3b) [11]. The specific capacitances based on the total hybrid mass decrease with increasing heating temperature, in the order of Ar-150 > Ar-200 > Ar-250 and O₂-150 > O₂-200 > O₂-250 (Fig. 3c). With the same heating temperature, the Ar-*T* samples have higher capacitances than the O₂-*T*, which results from the increased *R*_{ct} due to the partial oxidation of hNCNCs support for the latter (Fig. 3c, Tables S3, S4). All samples show the Coulombic efficiency of >95% (Table S5). Among them, the Ar-150 exhibits the best EES performance in terms of specific capacitance and rate capability, with the highest specific capacitances of 1170, 1095, 1030,

920, 840, 730, 670 and 593 F g⁻¹ at the current density of 2, 5, 10, 20, 30, 50, 70 and 100 A g⁻¹, respectively. When increasing the current density from 2 to 100 A g⁻¹, its capacitance retention of 51.0% is higher than that of 31.0% for Ar-200, 32.0% for Ar-250, 45.0% for O₂-150, 27.0% for O₂-200 and 3.0% for O₂-250 (Fig. 3c). After subtracting the contribution of hNCNCs (Fig. S5), the Co(OH)₂ in Ar-150 exhibits a high specific capacitance of 2214 F g⁻¹ at 2 A g⁻¹, close to the theoretical maximum of 2595 F g⁻¹ for Co(OH)₂ (Fig. S12). The cycling stability of the Ar-150 was tested by continuous CV scans at 100 mV s⁻¹. The result indicates the electrode shows an activation process in the first ~500 scans and ~92% of capacitance (relative to the highest point) is retained after 4000 cycles, showing excellent long-term stability (Fig. 3d). These results indicate that the hybridization of Co(OH)₂ with hNCNCs effectively increases the utilization of active material, leading to the top-rank EES performance for the Co-based nanomaterials (Table S1, S2).

To get insight into the EES mechanism of Co-NCs/hNCNCs hybrids, four samples of Ar-150, Ar-250, O₂-150 and O₂-250 containing different active species of Co(OH)₂, CoO and Co₃O₄ are grouped with detailed XPS

Figure 3 Electrochemical results of the series of Co-NCs/hNCNCs hybrids. (a) CV curves at a sweep rate of 50 mV s⁻¹. (b) GCD curves at 2 A g⁻¹. (c) Rate performances based on the total electrode mass (the data come from Fig. S13). (d) Cycling performance of Ar-150 at 100 mV s⁻¹.

and electrochemical characterizations as presented in Fig. 4. After the electrochemical tests, the Co 2p fine spectra of the four samples are quite similar with each other (Fig. 4a), which is different from the case for the original samples (Fig. 2e). The two major peaks show asymmetric shapes arising from two kinds of Co species, i.e., the Co(OH)₂ with BE at 781.4 and 796.7 eV and the Co³⁺-OOH with BE at 780.2 and 795.3 eV [44] (Fig. 4a). This result indicates that the reversible redox reaction occurs between Co(OH)₂ and CoOOH *via*: $\text{Co(OH)}_2 + \text{OH}^- \leftrightarrow \text{CoOOH} + \text{H}_2\text{O} + \text{e}^-$, in agreement with the result of the CV curves (Fig. 3a). In other words, the CoO and Co₃O₄ nanocrystals in the Ar-250 and O₂-250 are converted into Co(OH)₂ during the electrochemical activation, and then the redox reactions occur between Co(OH)₂ and CoOOH. As known, the CV measurements at different sweep rates can provide the information about the electrochemical behavior of electrode materials during charging/discharging. The current response (*i*) to an applied sweep rate (*v*, mV s⁻¹) depends on whether the redox reaction is diffusion-limited (battery-type) or sur-

face-controlled (pseudocapacitive), presenting the linear $i-v^{1/2}$ and $i-v$ response, respectively [11]. The $i-v$ plots for the four samples present a linear relationship, indicating their pseudocapacitive behaviors (Fig. 4b). This result indicates that the pseudocapacitive performance of the Co-NCs/hNCNCs is independent of the pristine composition of Co-NCs, which is a new understanding on the EES of Co-based nanomaterials.

Though having the same active materials, the size and charge transfer kinetics are different for the series of Co-NCs/hNCNCs hybrids, leading to the different EES performances. The preceding results have indicated that, with increasing heating temperature, the size of the Co-NCs increases (Figs 1, 2), accompanied by the partial oxidation of hNCNCs in the air case (Fig. S11). Such a structural evolution leads to the impeded charge transfer as reflected by the EIS spectra shown in Fig. 5. The R_{ct} increases from 0.09 to 0.14 and 0.16 Ω for Ar-*T*, and from 0.12 to 0.15 and 0.17 Ω for O₂-*T* with increasing heating temperature (Fig. 5, Table S3). Usually, the smaller size and enhanced charge transfer kinetics enable the higher

Figure 4 Comparison of the characterizations on Ar-150, Ar-250, O₂-150 and O₂-250. (a) Co 2p XPS spectra of the electrode materials after electrochemical testing. (b) The plots of anodic peak current *versus* sweep rate in CV measurements.

Figure 5 EIS spectra of the series of Co-NCs/hNCNCs hybrids. (a) Nyquist plots at the high frequency region. Inset is the simulated equivalent serial circuit. (b) R_{ct} of the Ar- T and O₂- T hybrids.

utilization of active materials for EES, as shown in Fig. 4. The larger-sized Co-NCs in the Ar-250 and O₂-250 can only be partially converted into Co(OH)₂ and CoOOH species as reflected by their larger XPS peak widths than those for Ar-150 and O₂-150 (Fig. 4a). Such situations, together with the larger R_{ct} , lead to lower utilization of Co-based nanomaterials in the Ar-250 and O₂-250, as reflected by the smaller slopes in the i - v plots (Fig. 4b). Hence, the EES performance of the Co-NCs/hNCNCs shows the evolutions of Ar-150 > Ar-200 > Ar-250 and O₂-150 > O₂-200 > O₂-250 (Fig. 3c). The Ar-150 hybrid possesses the smallest particle size and the lowest R_{ct} , which ensures large active surface area as well as short solid-state diffusion length for OH⁻ ions. Additionally, the hierarchical N-doped carbon mesostructure enables

good electrolyte wettability (Fig. S4) [39], and the 3D interconnected yet porous framework benefits fast electron conduction and electrolyte reservation. The synergism of these features endow the Ar-150 with the best EES performance. This study demonstrates that the hybridization with N-doped nanocarbons is an efficient way to improve the EES performance of transition metal compounds. Furthermore, this study reveals that the Co-NCs store/release electrical energy *via* the same reversible redox reaction in alkaline media despite the different pristine compositions. It is suggested that the commonly-employed transformation of the Co-NCs from Co(OH)₂ to CoO and Co₃O₄ on carbon supports in literatures [27,45,46] is unnecessary and even may be harmful to their EES performance taking into account the sintering

of particles and the damage to the carbon support during the transformation.

Device performances

The aqueous asymmetric supercapacitors (ASCs) were assembled with the optimal $\text{Co}(\text{OH})_2/\text{hNCNCs}$ (Ar-150) and AC in 6 mol L^{-1} KOH, with the performance demonstrated in Fig. 6. The strong redox peaks in the CV curves arise from the Faradaic reaction of Co-based active materials (Fig. 6a). The $\text{Co}(\text{OH})_2/\text{hNCNCs}/\text{AC}$ ASCs can work within a large voltage window of 1.6 V, and a wide current density range of $0\text{--}20 \text{ A g}^{-1}$ (Fig. 6b). The ASC delivers a high energy density of 33.0 Wh kg^{-1} at a power density of 0.8 kW kg^{-1} and remains 14.0 Wh kg^{-1} even at a high power density of 16.3 kW kg^{-1} , much higher than the AC//AC symmetric supercapacitor (Fig. 6c). Particularly, the $\text{Co}(\text{OH})_2/\text{hNCNCs}/\text{AC}$ ASC presents the combined high power density with large energy density, locating at the top-rank level to date (Fig. S14) [4,14,15,19,22,24,35]. The demo experiment shows that two tandem ASCs can light up two LED lights

and drive a timer for 5 h (Fig. S15). The $\text{Co}(\text{OH})_2/\text{hNCNCs}/\text{AC}$ ASC also shows outstanding cycling stability with $\sim 90.5\%$ capacitance retention (relative to the highest point) after 8000 cycles scanning at 100 mV s^{-1} (Fig. 6d). All these performances indicate the potential of the $\text{Co}(\text{OH})_2/\text{hNCNCs}$ hybrids for practical applications in EES.

CONCLUSIONS

The $\text{Co}(\text{OH})_2$, CoO and Co_3O_4 nanocrystals anchored on hNCNCs were deliberately prepared, and the systematic comparison revealed that all the Co-NCs/hNCNCs hybrids showed pseudocapacitive behaviors *via* the same reversible redox reactions between $\text{Co}(\text{OH})_2$ and CoOOH , regardless of their different pristine compositions. Taking advantage of the large specific surface area, coexisting micro-meso-macropores, high conductivity and nitrogen-doping of hNCNCs, the $\text{Co}(\text{OH})_2/\text{hNCNCs}$ (Ar-150) hybrid possesses small size of active component and enhanced charge transfer kinetics, thus presenting the best EES performance including an ultrahigh capa-

Figure 6 Electrochemical performances of the $\text{Co}(\text{OH})_2/\text{hNCNCs}/\text{AC}$ asymmetric supercapacitors. (a) CV curves. (b) GCD curves. (c) Ragone plots. (d) Stability for 8000 cycles at a scan rate of 100 mV s^{-1} . In (c), the data for meso- $\text{NiO}/\text{Ni}/\text{hNCNCs}$ [4], $\text{Co}(\text{OH})_2/\text{VN}$ [14], $\text{Co}_3\text{O}_4/\text{porous carbon}$ [15], $\text{Co}_3\text{O}_4/\text{Co}(\text{OH})_2/\text{AC}$ [19], $\text{Co}(\text{OH})_2/\text{AC}$ [22], $\text{Co}(\text{OH})_2/\text{Co}_3\text{O}_4/\text{AC}$ [24], $\text{Co}(\text{OH})_2/\text{CoS}_2/\text{AC}$ [35] and AC//AC (symmetric supercapacitor) are also listed for comparison.

citance of $2214 \text{ F g}_{\text{Co(OH)}_2}^{-1}$ approaching the theoretical maximum of active Co(OH)_2 . The aqueous asymmetric $\text{Co(OH)}_2/\text{hNCNCs}/\text{AC}$ supercapacitor delivers both high energy and high power densities superior to the AC/AC symmetric supercapacitor, showing great potential of $\text{Co(OH)}_2/\text{hNCNCs}$ as electrodes for high-performance supercapacitors. This study demonstrates that the hybridization with N-doped nanocarbons is efficient to facilitate the energy storage potential of Co-NCs, and the commonly-employed transformation of the Co-NCs from Co(OH)_2 to CoO and Co_3O_4 on carbon supports is unnecessary and even may be harmful to the EES performance. This study is instructive to develop high-energy-density electrodes from transition metal compounds.

Received 4 April 2019; accepted 2 June 2019;
published online 13 June 2019

- Winter M, Brodd RJ. What are batteries, fuel cells, and supercapacitors? *Chem Rev*, 2004, 104: 4245–4270
- Goodenough JB. Evolution of strategies for modern rechargeable batteries. *Acc Chem Res*, 2013, 46: 1053–1061
- Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev*, 2012, 41: 797–828
- Lai H, Wu Q, Zhao J, *et al.* Mesoporous NiO/Ni composites for high-performance electrochemical energy storage. *Energy Environ Sci*, 2016, 9: 2053–2060
- Cheng F, Liang J, Tao Z, *et al.* Functional materials for rechargeable batteries. *Adv Mater*, 2011, 23: 1695–1715
- Wang J, Dong S, Ding B, *et al.* Pseudocapacitive materials for electrochemical capacitors: from rational synthesis to capacitance optimization. *Nat Sci Rev*, 2017, 4: 71–90
- Chen X, Paul R, Dai L. Carbon-based supercapacitors for efficient energy storage. *Nat Sci Rev*, 2017, 4: 453–489
- Jiang H, Lee PS, Li C. 3D carbon based nanostructures for advanced supercapacitors. *Energy Environ Sci*, 2013, 6: 41–53
- Conway BE. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*. New York: Kluwer Academic/Plenum Publishers, 1999
- Simon P, Gogotsi Y, Dunn B. Where do batteries end and supercapacitors begin? *Science*, 2014, 343: 1210–1211
- Augustyn V, Simon P, Dunn B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ Sci*, 2014, 7: 1597–1614
- Zhu YG, Wang Y, Shi Y, *et al.* CoO nanoflowers woven by CNT network for high energy density flexible micro-supercapacitor. *Nano Energy*, 2014, 3: 46–54
- Jagade AD, Jamadade VS, Pusawale SN, *et al.* Effect of scan rate on the morphology of potentiodynamically deposited $\beta\text{-Co(OH)}_2$ and corresponding supercapacitive performance. *Electrochim Acta*, 2012, 78: 92–97
- Wang R, Yan X, Lang J, *et al.* A hybrid supercapacitor based on flower-like Co(OH)_2 and urchin-like VN electrode materials. *J Mater Chem A*, 2014, 2: 12724–12732
- Salunkhe RR, Tang J, Kamachi Y, *et al.* Asymmetric supercapacitors using 3D nanoporous carbon and cobalt oxide electrodes synthesized from a single metal–organic framework. *ACS Nano*, 2015, 9: 6288–6296
- Zhao T, Jiang H, Ma J. Surfactant-assisted electrochemical deposition of α -cobalt hydroxide for supercapacitors. *J Power Sources*, 2011, 196: 860–864
- Yang S, Liu Y, Hao Y, *et al.* Oxygen-vacancy abundant ultrafine Co_3O_4 /graphene composites for high-rate supercapacitor electrodes. *Adv Sci*, 2018, 5: 1700659
- Xia X, Tu J, Zhang Y, *et al.* Freestanding Co_3O_4 nanowire array for high performance supercapacitors. *RSC Adv*, 2012, 2: 1835–1841
- Mei J, Fu W, Zhang Z, *et al.* Vertically-aligned Co_3O_4 nanowires interconnected with Co(OH)_2 nanosheets as supercapacitor electrode. *Energy*, 2017, 139: 1153–1158
- Xiang K, Xu Z, Qu T, *et al.* Two dimensional oxygen-vacancy-rich Co_3O_4 nanosheets with excellent supercapacitor performances. *Chem Commun*, 2017, 53: 12410–12413
- Zhou C, Zhang Y, Li Y, *et al.* Construction of high-capacitance 3D CoO@polypyrrole nanowire array electrode for aqueous asymmetric supercapacitor. *Nano Lett*, 2013, 13: 2078–2085
- Wang Z, Liu Y, Gao C, *et al.* A porous Co(OH)_2 material derived from a MOF template and its superior energy storage performance for supercapacitors. *J Mater Chem A*, 2015, 3: 20658–20663
- Pang H, Li X, Zhao Q, *et al.* One-pot synthesis of heterogeneous Co_3O_4 -nanocube/ Co(OH)_2 -nanosheet hybrids for high-performance flexible asymmetric all-solid-state supercapacitors. *Nano Energy*, 2017, 35: 138–145
- Jing M, Yang Y, Zhu Y, *et al.* An asymmetric ultracapacitors utilizing $\alpha\text{-Co(OH)}_2/\text{Co}_3\text{O}_4$ flakes assisted by electrochemically alternating voltage. *Electrochim Acta*, 2014, 141: 234–240
- Xue T, Wang X, Lee JM. Dual-template synthesis of Co(OH)_2 with mesoporous nanowire structure and its application in supercapacitor. *J Power Sources*, 2012, 201: 382–386
- Zheng C, Cao C, Ali Z, *et al.* Enhanced electrochemical performance of ball milled CoO for supercapacitor applications. *J Mater Chem A*, 2014, 2: 16467–16473
- Zhou Y, Zou X, Zhao Z, *et al.* CoO/rGO composite prepared by a facile direct-flame approach for high-power supercapacitors. *Ceramics Int*, 2018, 44: 16900–16907
- Patil UM, Nam MS, Sohn JS, *et al.* Controlled electrochemical growth of Co(OH)_2 flakes on 3D multilayered graphene foam for high performance supercapacitors. *J Mater Chem A*, 2014, 2: 19075–19083
- Jiang J, Liu J, Ding R, *et al.* Large-scale uniform $\alpha\text{-Co(OH)}_2$ long nanowire arrays grown on graphite as pseudocapacitor electrodes. *ACS Appl Mater Interfaces*, 2011, 3: 99–103
- Zhang F, Yuan C, Zhu J, *et al.* Flexible films derived from electrospun carbon nanofibers incorporated with Co_3O_4 hollow nanoparticles as self-supported electrodes for electrochemical capacitors. *Adv Funct Mater*, 2013, 23: 3909–3915
- Wang H, Qing C, Guo J, *et al.* Highly conductive carbon–CoO hybrid nanostructure arrays with enhanced electrochemical performance for asymmetric supercapacitors. *J Mater Chem A*, 2014, 2: 11776–11783
- Zhang F, Yuan C, Lu X, *et al.* Facile growth of mesoporous Co_3O_4 nanowire arrays on Ni foam for high performance electrochemical capacitors. *J Power Sources*, 2012, 203: 250–256
- Gao Y, Chen S, Cao D, *et al.* Electrochemical capacitance of Co_3O_4 nanowire arrays supported on nickel foam. *J Power Sources*, 2010, 195: 1757–1760
- Patil UM, Lee SC, Sohn JS, *et al.* Enhanced symmetric super-

capacitive performance of $\text{Co}(\text{OH})_2$ nanorods decorated conducting porous graphene foam electrodes. *Electrochim Acta*, 2014, 129: 334–342

- 35 Yang W, Qu G, Chen M, *et al.* Effective NaBH_4 -exfoliated ultrathin multilayer $\text{Co}(\text{OH})_2$ nanosheets arrays and sulfidation for energy storage. *Nanotechnology*, 2018, 29: 295403
- 36 Wu Q, Yang L, Wang X, *et al.* From carbon-based nanotubes to nanocages for advanced energy conversion and storage. *Acc Chem Res*, 2017, 50: 435–444
- 37 Feng H, Ma J, Hu Z. Nitrogen-doped carbon nanotubes functionalized by transition metal atoms: A density functional study. *J Mater Chem*, 2010, 20: 1702–1708
- 38 Zhang Z, Chen Y, Zhou L, *et al.* The simplest construction of single-site catalysts by the synergism of micropore trapping and nitrogen anchoring. *Nat Commun*, 2019, 10: 1657
- 39 Zhao J, Lai H, Lyu Z, *et al.* Hydrophilic hierarchical nitrogen-doped carbon nanocages for ultrahigh supercapacitive performance. *Adv Mater*, 2015, 27: 3541–3545
- 40 Pralong V, Delahaye-Vidal A, Beaudoin B, *et al.* Oxidation mechanism of cobalt hydroxide to cobalt oxyhydroxide. *J Mater Chem*, 1999, 9: 955–960
- 41 Chen S, Wang L, Wu Q, *et al.* Advanced non-precious electrocatalyst of the mixed valence CoO_x nanocrystals supported on N-doped carbon nanocages for oxygen reduction. *Sci China Chem*, 2015, 58: 180–186
- 42 Zhang Z, Wu Q, Mao K, *et al.* Efficient ternary synergism of platinum/tin oxide/nitrogen-doped carbon leading to high-performance ethanol oxidation. *ACS Catal*, 2018, 8: 8477–8483
- 43 Oktaviano HS, Yamada K, Waki K. Nano-drilled multiwalled carbon nanotubes: Characterizations and application for LIB anode materials. *J Mater Chem*, 2012, 22: 25167–25173
- 44 Li Z, Duan H, Shao M, *et al.* Ordered-vacancy-induced cation intercalation into layered double hydroxides: A general approach for high-performance supercapacitors. *Chem*, 2018, 4: 2168–2179
- 45 Zou Y, Kinloch IA, Dryfe RAW. Mesoporous vertical Co_3O_4 nanosheet arrays on nitrogen-doped graphene foam with enhanced charge-storage performance. *ACS Appl Mater Interfaces*, 2015, 7: 22831–22838
- 46 Lee KK, Chin WS, Sow CH. Cobalt-based compounds and composites as electrode materials for high-performance electrochemical capacitors. *J Mater Chem A*, 2014, 2: 17212–17248

Acknowledgements This work was jointly supported by the National Key Research and Development Program of China (2017YFA0206500 and 2018YFA0209103), the National Natural Science Foundation of China (21832003, 21773111, 51571110 and 21573107), and the Fundamental Research Funds for the Central Universities (020514380126).

Author contributions Wu Q and Hu Z conceived and supervised the project; Ma Q performed the experiments; Yao Y, Yan M, Zhao J, Ge C and Wang X helped to characterize the samples; Ma Q, Wu Q and Hu Z analyzed the data and wrote the paper with support from Yang L and Wang X. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information Supplementary data are available in the online version of the paper.

Qingming Ma received his Bachelor degree from the School of Chemistry and Chemical Engineering, Inner Mongolia University in 2016. He is currently a Master candidate in the School of Chemistry and Chemical Engineering, Nanjing University. His current research interest is the design of high-performance electrode nanomaterials for energy storage.

Qiang Wu obtained his BSc (1999) and PhD (2004) degrees in chemistry from Nanjing University. He was appointed an associate professor in 2006, and a professor at Nanjing University in 2015. As a Hua-Ying Scholar, he worked at Stanford University for one year. His scientific interest focuses on the rational design of nano-/mesostructured materials and their applications in energy storage and conversion.

Zheng Hu received his BSc (1985) and PhD (1991) degrees in physics from Nanjing University. He became an associate professor of chemistry in 1993, and acquired the professor position in 1999, and Cheung Kong Scholar professor in 2007. He was awarded the National Natural Science Foundation of China for Outstanding Young Scientists (2005). He is engaged in the research of physical chemistry and materials chemistry addressing the growth mechanism, materials design and energy applications of a range of nano-/mesostructured materials, especially carbon-based materials, group III nitrides and transition metal oxides.

钴基纳米晶-氮掺杂碳纳米笼复合材料的构建与电化学储能性能研究

麻青明, 姚月坚, 闫明磊, 赵杰, 葛承宣, 吴强*, 杨立军, 王喜章, 胡征

摘要 $\text{Co}(\text{OH})_2$ 、 CoO 和 Co_3O_4 等钴基化合物因具有高理论容量和赝电容性质而备受关注。但受限于活性表面积小、电荷传输缓慢等原因, 钴基纳米材料的实际储能性能却有限。本文以我们前期开发的具有大比表面积、高导电性和微孔-介孔-大孔共存的分级结构氮掺杂碳纳米笼(hNCNCs)为载体, 成功构建了晶粒尺寸小、电荷转移快的系列钴基纳米晶-hNCNCs复合材料, 有效地提高了活性材料的利用率。其中, $\text{Co}(\text{OH})_2/\text{hNCNCs}$ 在 2 A g^{-1} 下表现出 1170 F g^{-1} 的高比容量, 基于活性物种 $\text{Co}(\text{OH})_2$ 的比电容高达 2214 F g^{-1} , 接近其理论值(2595 F g^{-1})。研究发现, 具有不同组成的 $\text{Co}(\text{OH})_2$ 、 CoO 和 Co_3O_4 纳米晶通过相同的可逆氧化还原反应存储/释放电能。这种新的储能机理表明将碳基载体上的活性物种 $\text{Co}(\text{OH})_2$ 转化为 CoO 或 Co_3O_4 的操作是非必要的, 甚至可能损害其储能性能。本研究可为开发过渡金属化合物基高能量密度电极材料提供借鉴。