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# Role of anions on structure and pseudocapacitive performance of metal double hydroxides decorated with nitrogen-doped graphene

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# Role of anions on structure and pseudocapacitive performance of metal double hydroxides decorated with nitrogen-doped graphene

## Abstract

Electrochemical capacitors (EC) bear faster charge-discharge; however, their real applications are still on a long way due to lower capacitance and energy densities which mainly arise from simple surface charge accumulation or/and reaction. Here, a novel synthesis strategy was designed to obtain the purposeful hybrids of nickel cobalt double hydroxide (NiCoDH) with genetic morphology to improve their electrochemical performance as electrode of EC. Nanostructures of metal hydroxides were grown on the nitrogen-doped graphene (NG) sheets by utilizing defects as nucleation sites and their composition was optimized both by tuning the ratio of Ni:Co as well as the counter halogen and carbonate anions to improve the porosity, stabilize the structure and mediate the redox reaction. The growth of the hybrids was guided by the Co ions through topochemical transformation supported by hopping charge transfer process and olation growth. NG overcoating successfully protects the nanostructure of NiCoDH during electrochemical test and enhances overall conductivity of the electrode, improving the mass and ionic transportations. As a result, the hybrid exhibits excellent capacitance of 2925 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, as well as long cyclic stability of 10,000 cycles with good capacity retention of 90% at 16 A g<sup>-1</sup>. Furthermore, the hybrid shows excellent energy and power densities of 52 Wh kg<sup>-1</sup> and 3191 W kg<sup>-1</sup>, respectively at discharge rate of 16 A g<sup>-1</sup>. It is expected that this strategy can be readily extended to other metal hydroxides, oxides and sulphides to improve their electrochemical performances.

## Keywords

structure, graphene, doped, nitrogen, decorated, hydroxides, double, anions, metal, role, performance, pseudocapacitive

## Disciplines

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# Role of anions on structure and pseudocapacitive performance of metal double hydroxides decorated with nitrogen-doped graphene

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Electrochemical capacitors (EC) bear faster charge-discharge; however, their real applications are still on a long way due to lower capacitance and energy densities which mainly arise from simple surface charge accumulation or/and reaction. Here, a novel synthesis strategy was designed to obtain the purposeful hybrids of nickel cobalt double hydroxide (NiCoDH) with genetic morphology to improve their electrochemical performance as electrode of EC. Nanostructures of metal hydroxides were grown on the nitrogen-doped graphene (NG) sheets by utilizing defects as nucleation sites and their composition was optimized both by tuning the ratio of Ni:Co as well as the counter halogen and carbonate anions to improve the porosity, stabilize the structure and mediate the redox reaction. The growth of the hybrids was guided by the Co ions through topochemical transformation supported by hoping charge transfer process and olation growth. NG overcoating successfully protects the nanostructure of NiCoDH during electrochemical test and enhances overall conductivity of the electrode, improving the mass and ionic transportations. As a result, the hybrid exhibits excellent capacitance of 2925 F g<sup>-1</sup> at 1 A g<sup>-1</sup>, as well as long cyclic stability of 10,000 cycles with good capacity retention of 90% at 16 A g<sup>-1</sup>. Furthermore, the hybrid shows excellent energy and power densities of 52 Wh kg<sup>-1</sup> and 3191 W kg<sup>-1</sup>, respectively at discharge rate of 16 A g<sup>-1</sup>. It is expected that this strategy can be readily extended to other metal hydroxides, oxides and sulphides to improve their electrochemical performances.

## INTRODUCTION

The depletion of natural energy sources (fossil fuels) and development of modern society demands clean, safe and efficient energy storage and delivery systems to meet the requirements of advanced life. In this regard, fuel cells, secondary batteries and capacitors have got key attention of researchers to realize the advanced electronics and electric vehicles (EVs) [1–5]. Among them, Electrochemical capac-

itors (EC) got tremendous attention because of their high capacitance, long cyclic life, fast charge-discharge, high power density, safety, simple electrical circuit, no memory effect and environmental benignity [6–8]. In general, traditional EC are classified as electrical double layer capacitor (EDLC) which stores energy by surface accumulation of charge and brings high power density, thus carbon-based materials are prominent as electrodes of EDLC [9–11]. But the simple charge accumulation limits the energy density of EDLC to very low value that hinders their wide applications in high energy devices [12,13]. The second class of EC is pseudocapacitors which utilize Faradaic redox reaction to store the energy and bring high energy density on minimal loss of power density [14–16]. However, the limited diffusion of the electrolyte in the electrode material hinders complete participation of all the possible reaction sites. It has been proved previously that the electrolyte cannot diffuse inside the crystalline materials beyond 30–40 nm in depth, which greatly limits the overall activity of the bulk material [14]. The complicated reaction kinetics of Faradaic redox process further limit the energy density, which can be improved by tuning the morphology, composition and structure of the electrode materials that will enable the bulk material to take part in a chemical reaction regardless of surface redox reaction [17]. Thus, large energy density of pseudocapacitors makes them very promising candidates for EVs and high energy density applications.

The state-of-the-art material for pseudocapacitors is RuO<sub>2</sub> because of its high conductivity, good capacitance and perfectly reversible chemical reaction, but its high cost and toxic nature impeded its application in real devices [18,19]. Thus, to make pseudocapacitors applicable alternative electrode materials are highly required with fascinating chemical reaction, better conductivity, high

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stability and capacitance as well as desired values of energy and power densities [20]. Keeping these merits in mind, researchers have developed alternative materials that include transition metal oxides, sulphides, hydroxides and their hybrids [7,21–23]. Among these, metal hydroxides become the focal point of research due to their high capacitance and great flexibility in morphology and structure [24–26]. However, their low rate capability limits the power density due to inadequate conductivity and failure of efficient transport of electron required for high power density [27,28]. To overcome this problem, several strategies were adopted likewise fabrication of their composite with carbon-based materials (graphene and activated carbon) to reduce the ion diffusion and electron transfer path resulting in the improved mass transport and rate capability [29–31]. But complicated fabrication methods which involve several tedious steps as well as collapse of synergism among the two components remain the key issues with aforementioned solution. Nanodesigning is another possible way to improve the rate capability but these structures fail to retain their high performance at higher current rates because of structural instability. However, the tuning of composition is also utilized to improve the rate capabilities and stability issues of EC electrodes e.g.,  $\text{NiCo}_2\text{O}_4$  with better conductivity than  $\text{NiO}$  and  $\text{Co}_x\text{O}_y$  [32]. Furthermore, introduction of carbonate and halogen ions as charge balancing counter anions can enhance the stability of the metal hydroxide. Therefore, recently there is a great focus on the metallic double hydroxides  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}[\text{A}_{x/n}^{n-} \cdot m\text{H}_2\text{O}]^{x-}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  are divalent and trivalent metal ions and  $\text{A}^{n-}$  is charge balancing counter anion to achieve the standard capacitance values for the applications of EC in EVs [33]. But still the limited access to redox sites, structural instability and poor conductivity limit their energy and power densities below the required critical values for their real applications in future devices [14,19]. Thus, a unique design of electrode material, which can improve the internal and external conductivities for efficient electron transfer from external circuit to redox site and *vice versa*, has good control over structural stability to retain its high performance at higher charge-discharge rates and an appropriate composition that facilitate faster and highly reversible Faradaic redox reaction, resulting in excellent performance both at capacitance and longevity.

Here, we report our findings in synthesis and design of unique hybrids of nickel and nickel cobalt double hydroxide nanostructures wrapped in nitrogen-doped graphene ( $\text{NiH@NG}$  &  $\text{NiCoDH@NG}$ ) sheets. These developed unique hybrids showed high performance, excellent rate capability, as well as long cyclic life. The hybrids simply prepared by the hydrothermal method at moderate condi-

tion without the involvement of any tedious step confirmed its scalability and resulted in well-defined network of nanostructures confined in NG sheets. Furthermore, as-synthesized  $\text{NiCoDH@NG}$  hybrid had specific composition comprised of highly active positive host ions, charge balancing counter anions ( $\text{Cl}^-$  and  $\text{CO}_3^{2-}$ ) to stabilize the structure and solvation molecules that can promote the deep diffusion of electrolyte ions and enable the utilization of maximum redox sites. Further as-obtained  $\text{NiCoDH@NG}$  hybrid possesses single crystalline nature along the entire nanostructure, and thus highly orientated structure promoted the efficient electron transport from redox site to electron collector and *vice versa* which allows nickel and cobalt to contribute towards their double pseudocapacitance proficiently. Moreover, perfect confinement of  $\text{NiCoDH}$  nanostructures in NG sheets improved their overall conductivity and structural stability. NG sheets efficiently enhanced the electronic and mass transport by providing highly conductive backbone network. As a result, the electrode based on the hybrid showed remarkably enhanced performance compared with most of the previously reported nickel cobalt double hydroxide/oxide. The developed hybrid is highly electroactive for reversible charge storage not only at lower discharge rates but also at higher rates. Thus, the hybrid exhibited a very high capacitance of  $2925 \text{ F g}^{-1}$  at discharge rate of  $1 \text{ A g}^{-1}$  which proved the contribution from almost all the available redox active sites. In contrast to most reported materials which are prone to capacitance loss upon increase in discharge rate, the hybrid showed minimal capacitance loss (retaining  $2336 \text{ F g}^{-1}$ ) when the discharge rate was as high as  $16 \text{ A g}^{-1}$ . We believe that our synthesis method to develop unique hybrid electrode nanostructures with specific composition will bring the realization of EC in practical applications as prominent energy storage device.

## EXPERIMENTAL SECTION

### Preparation of nitrogen-doped graphene (NG)

The NG was prepared from graphite oxide (GO) through a solvothermal process. In a typical synthesis, 80 mg of GO was sonicated in 10 mL of water for 20 min, and then 70 mL of ammonia solution (25%) was added. After that, 600 mg of NaOH was added and stirred adequately for 30 min to homogenize the mixture well. This mixture was transferred to an 100 mL Teflon-lined autoclave and the reaction occurred in an oven at  $200^\circ\text{C}$  for 12 h. After the reaction completed, the NG was collected by centrifugation and washed with HCl solution to remove residual  $\text{NH}_3$ , followed by washing with water and ethanol repeatedly for six times. The final product was dried in a vacuum oven at  $70^\circ\text{C}$  for 3 h.

### Synthesis of NiH@NG hybrid

NiH@NG hybrid was synthesized using hydrothermal method by treating  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  with urea ( $\text{CO}(\text{NH}_2)_2$ ). In a typical reaction, 714 mg of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and 180 mg  $\text{CO}(\text{NH}_2)_2$  were dissolved in 15 mL of water by stirring for 10 min. Afterward the already sonicated (30 min) NG was added to the reaction mixture under continuous stirring for further 20 min and the mixture was then transferred to a 25 mL Teflon-lined autoclave. Then the autoclave was placed into an oven at  $100^\circ\text{C}$  and the reaction was carried out for 12 h. After the completion of reaction, product was collected by centrifugation, washed six times with excess amount of water and ethanol, repeatedly. Finally, the solid product was dried at  $60^\circ\text{C}$  for 6 h in a vacuum oven. Similar method was adopted to prepare NiH nanostructures for comparative study by excluding NG from the reactants.

### Synthesis of NiCoDH@NG hybrid

The NiCoDH@NG hybrid was synthesized via hydrothermal process, by mixing 357 mg of each  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  along with 180 mg  $\text{CO}(\text{NH}_2)_2$  in 15 mL of water, and the reaction mixture was stirred for 10 min. Afterward the already sonicated NG (for 30 min) was added to the reaction mixture, stirred for further 20 min and then transferred to a 25 mL Teflon-lined stainless steel autoclave. Finally, the reaction was performed at  $100^\circ\text{C}$  for 12 h (to observe the effect of Co concentration on the growth of NiCoDH nanostructures, reaction was carried out with different molar ratio of Co:Ni). At last, centrifugation was adopted to obtain the final product, and it was rinsed six times with excess amount of water and ethanol repeatedly and dried at  $70^\circ\text{C}$  for 6 h under vacuum. Similar method was adopted to prepare NiCoDH nanostructures for comparative study by excluding NG from the reactants.

### Characterizations

X-ray diffraction (XRD) studies were done using a Philips X' Pert Pro X-ray diffractometer equipped with  $\text{Cu K}\alpha$  radiation. The accelerating voltage and current were 40 kV and 200 mA, respectively. The XRD patterns were performed in the  $2\theta$  range of  $5\text{--}70^\circ$ . The morphological characterization of the product was carried out by using FEI Tecnai T20 and F30 transmission electron microscope (TEM). Scanning electron microscope (SEM) characterization was done using Hitachi S-4800. Elemental composition of the hybrids was analyzed by X-ray photoelectron spectroscopy (XPS), Kartos Axis Ultra with monochromatized  $\text{Al K}\alpha$  radiation (1486.6 eV). Fourier transform infrared (FTIR) spectrum was recorded using Nicolet EC-TOR22. The Brunauer-Emmett-Teller (BET) analysis was done using ASAP 2010.

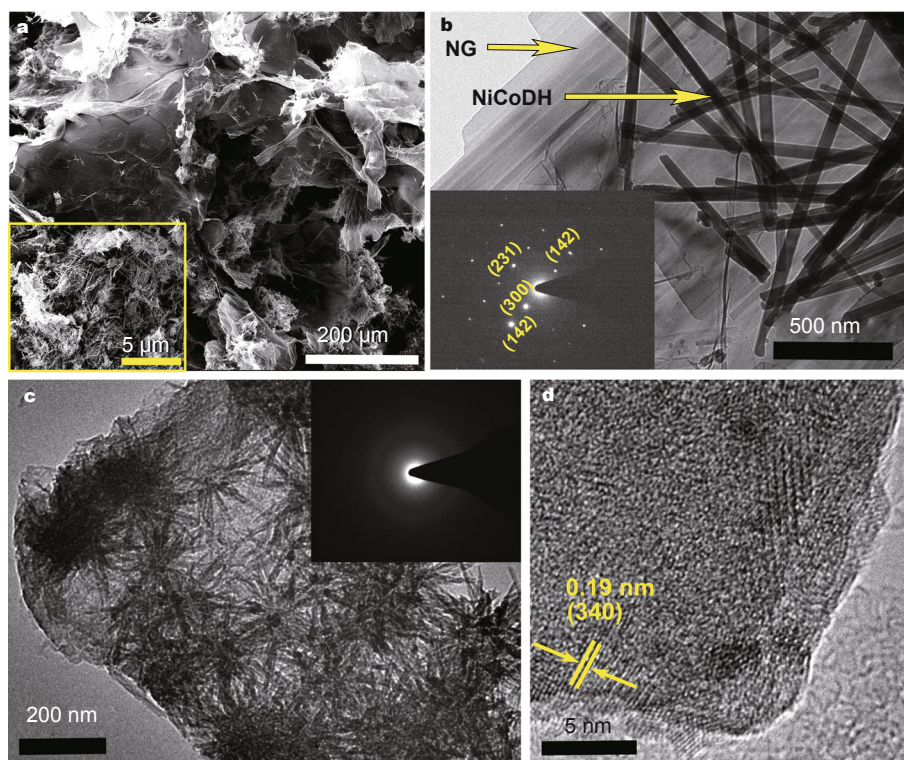
### Electrochemical measurements

Electrochemical measurements of the hybrids were performed on a LAND CT 2001A analyzer at different current densities with a potential window of  $-0.1$  to  $0.3$  V vs. standard calomel electrode (SCE) in three-electrode cell. The working electrode was made of active material (with mass loading of  $0.8\text{--}1.5$  mg), conductive agent (acetylene black) and polymer binder (polytetrafluoroethylene, PTFE) in a weight ratio of 80:10:10, and this mixture was prepared and loaded on nickel foam ( $1\text{ cm} \times 1\text{ cm}$ ) with various mass loadings to assure the repeatability of the electrochemical results and minimize the uncertainties due to small mass loadings. To remove the moisture or solvent contents, the electrode was dried at  $60^\circ\text{C}$  for 12 h under vacuum. A SCE electrode saturated with KCl solution and nickel foam was used as the reference and counter electrodes, respectively. The 1 M KOH was used as electrolyte. The cyclic voltammetry (CV) curves of materials were carried out at different scanning rates ( $5\text{--}100\text{ mV s}^{-1}$ ) between  $-0.1$  to  $0.3$  V vs. SCE and electrochemical impedance spectroscopy (EIS) in the range of 10 to 100 mHz on CHI 760C (Shanghai Chenhua). All the performances were tested at room temperature. The capacitance, energy and power densities presented in this work are calculated using equations  $C = (I \times t)/(m \times V)$ ,  $E = 1/2CV^2$  and  $P = E/t$ , respectively, where  $C$  is the capacitance,  $t$  is the discharge time of capacitor,  $I$  is the current,  $m$  is the mass of the working electrode and  $V$  is the potential window. In addition,  $E$  and  $P$  denote energy density and power density, respectively.

### RESULTS AND DISCUSSION

The morphological aspects, structural characteristics, compositional analysis and porosity of the hybrids were carried out by means of SEM, TEM, high resolution TEM (HRTEM), scattered area electron diffraction (SAED), XRD, XPS, FTIR, thermal gravimetric analyzer (TGA), BET surface area analysis and Barrett-Joyner-Halenda (BJH) pore size measurements. Fig. 1a presents the typical SEM image of the as-synthesized NiCoDH@NG hybrid. The nanostructured NiCoDH are firmly attached to and well-dispersed on the graphene sheets, and the graphene sheets retain their sheet-like morphology well and strongly interconnected with each other. The morphology and mesopores of such nanostructures can efficiently facilitate the electronic and mass transport, which could be evidenced in their electrochemical characterization [34]. Fig. 1b shows the TEM image of the NiCoDH@NG hybrid, which further confirms that the nanostructured NiCoDH are well-dispersed on graphene sheets with strong adhesion between them. The inset of Fig. 1b represents the SAED pattern of the NiCoDH@NG hybrid which confirms the quasi-single-crystalline growth of nanostructures that is directed by Co



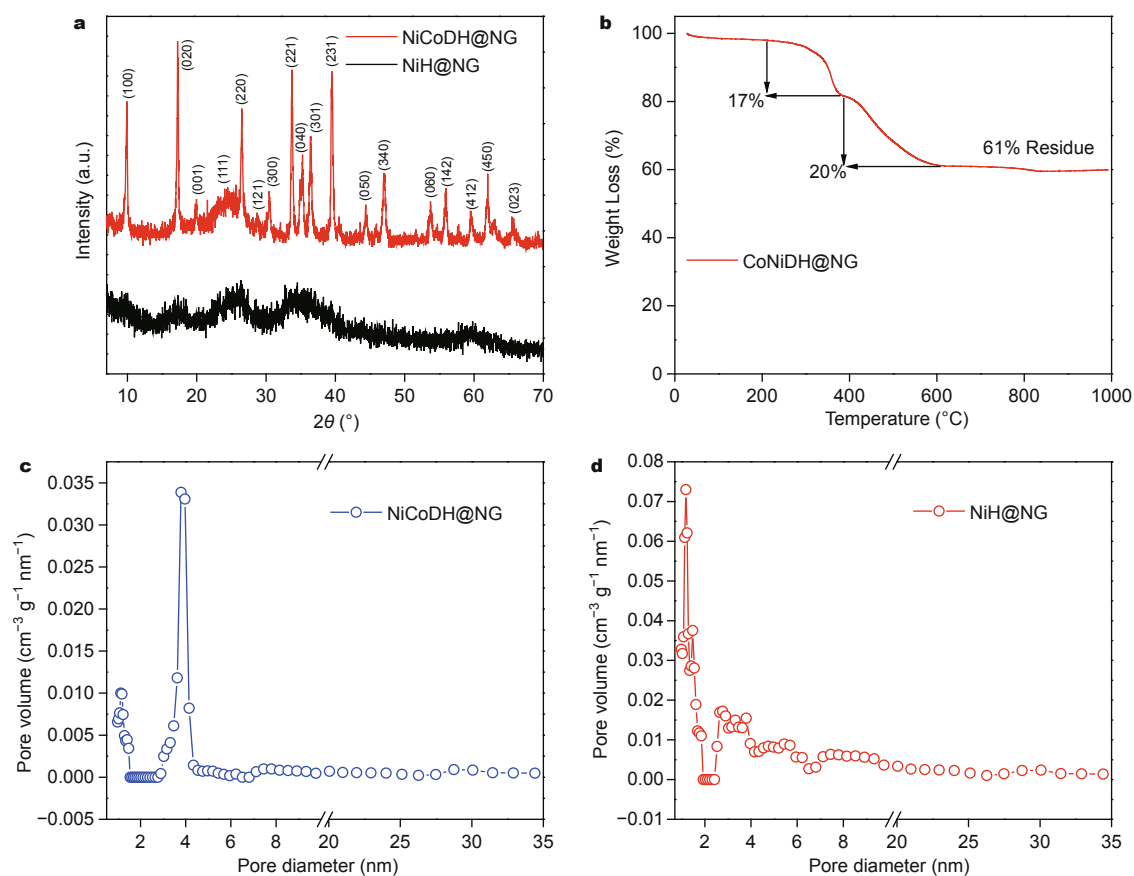


**Figure 1** (a) SEM image of NiCoDH@NG hybrid (the inset shows its high magnification SEM image). (b) TEM image of NiCoDH@NG hybrid (the inset is its SAED pattern). (c) TEM image of NiH@NG hybrid (the inset is its SAED pattern). (d) HRTEM image of NiCoDH@NG hybrid.

ions, since very weak circular diffraction signals observed in the case of NiH@NG proves the polycrystalline nature of NiCoDH (the inset of Fig. 1c). Amorphous nanostructures of NiH are highly intermingled on the graphene sheets due to their non-directional growth as depicted in the TEM image of NiH@NG hybrid, as shown in Fig. 1c. To further confirm the structure of NiCoDH@NG hybrid, HRTEM study was carried out (Fig. 1d). According to the standard card No. JPDFS 48-0083, the inter planer spacing of 0.19 nm corresponding to the diffraction plane of (340) is evidenced and it is in agreement with the XRD results.

Since no obvious peak is presented in the XRD pattern of NiH@NG hybrid (Fig. 2a), the as-synthesized NiH@NG hybrid is in amorphous form in nature. But the addition of Co leads to well-defined diffraction peaks, which confirms the well-crystalline growth of NiCoDH nanostructures on the NG sheets and all the peaks are well-matched with their respective plans according to the standard card No. JPDFS 48-0083. It is interesting to observe that with the addition of Co precursor, NiCoDH@NG hybrid becomes highly crystalline. Thus, to verify it we have performed series of experiments (with different molar ratios of Co and Ni) and found that the reflection of X-ray became enhanced as the concentration of Co ions in the hybrid increased, as shown in Fig. S1. This shift in crystallinity of hybrid after the

addition of Co proves that the growth of NiCoDH nanostructures is mainly defined by Co ions. It is commonly observed in the mixed Ni and Co systems that  $\text{Co}^{2+}$  can easily be oxidized to  $\text{Co}^{3+}$  in the solution and it defines the growth directions and phase of the NiCoDH nanostructures [35]. More importantly, the introduction of Co improves the size uniformity and the porosity of NiCoDH nanostructures [33]. It can be attributed to the highly oriented growth through the incorporation of Co and control over self-aggregation of nanostructures. Furthermore as XRD results indicated (Figs 2a and S1), the addition of Co can induce active material crystal transition from amorphous NiH to highly crystalline NiCoDH and bring well-defined oriented growth [36]. Moreover, excessive positive electric charge is induced to the nanostructures in double hydroxide by isomorphically replacement of bivalent cations with trivalent ones and inhibits the excessive self-aggregation of NiCoDH nanostructures by electrostatic repulsion [37]. However, the addition of Co further provides good adhesion to the NG sheets by better nucleation on the defect sites and improves the particle size of NiCoDH. Furthermore, a broad peak observed at  $2\theta$  value of  $26^\circ$  indicates the existence of graphene in the hybrid structure but the NiCoDH peak presented at the same diffraction angle confirms that the NG sheets are majorly covered by the NiCoDH nano-



**Figure 2** (a) XRD patterns of NiH@NG and NiCoDH@NG hybrids. (b) TGA curve of NiCoDH@NG hybrid. Pore size distribution curves of (c) NiCoDH@NG and (d) NiH@NG hybrids.

structures (as further confirmed by the SEM image, the inset of Fig. 1a) [20,38]. The preferential growth mechanism of NiCoDH nanostructures can be simply explained by the topochemical transformation which involves a rapid oxidation of outermost bivalent ions at the edge sites with inward advance oxidation front and charge proliferation within the nanostructure. This kind of charge proliferation might be supported by valence interchange or charge transfer among neighboring donor and acceptor sites which are called electron or hole hopping. In general, hopping model can be applicable if the valence variable ions (cobalt) are located at the same crystallographic position [37]. Thus, a bivalent ion can be oxidized to trivalent and a valence interchange reaction occurs among the adjacent bivalent and trivalent ions, which is possible if the trivalent ion is attached to hydroxyl (oxygen) bonds. However, any outermost bivalent ion oxidized to trivalent by donating electron to halogen can be reduced back by accepting electron and releases a hole in the lattice particularly away from the reducing site. This kind of transformation provides the stability and halogen ions for continuous reaction. Furthermore, the as-

formed randomly dispersed primary particles undergo the ololation reaction with each other and this kind of aggregation results in the growth of NiCoDH nanostructures that are mainly guided by the Co ions, as observed by the TEM studies of different samples with various Co ratios (Fig. S2), and it confirms that increasing Co concentration results in the well-defined nanostructures of NiCoDH in contrast to amorphous NiH. Further, lower temperature synthesis allows fast and well-crystalline growth by increasing the generation time of primary particles and provides sufficient time for the ololation reaction among the primary particles.

To further confirm the amount of graphene in the hybrid structure, TGA studies under air were carried out (Figs 2b and S3) from room temperature to 1000°C at the rate of 10°C min<sup>-1</sup>. Two stages of weight loss are observed. The first stage is from ~200 to 350°C which corresponds to the loss of absorbed water, hydroxyl and carboxyl groups and counter anions from the hybrid. The second stage is the removal of graphene by oxidation process, and takes place between ~400 and 600°C [39]. The TGA studies confirm that NiCoDH@NG hybrids contain almost 20% NG

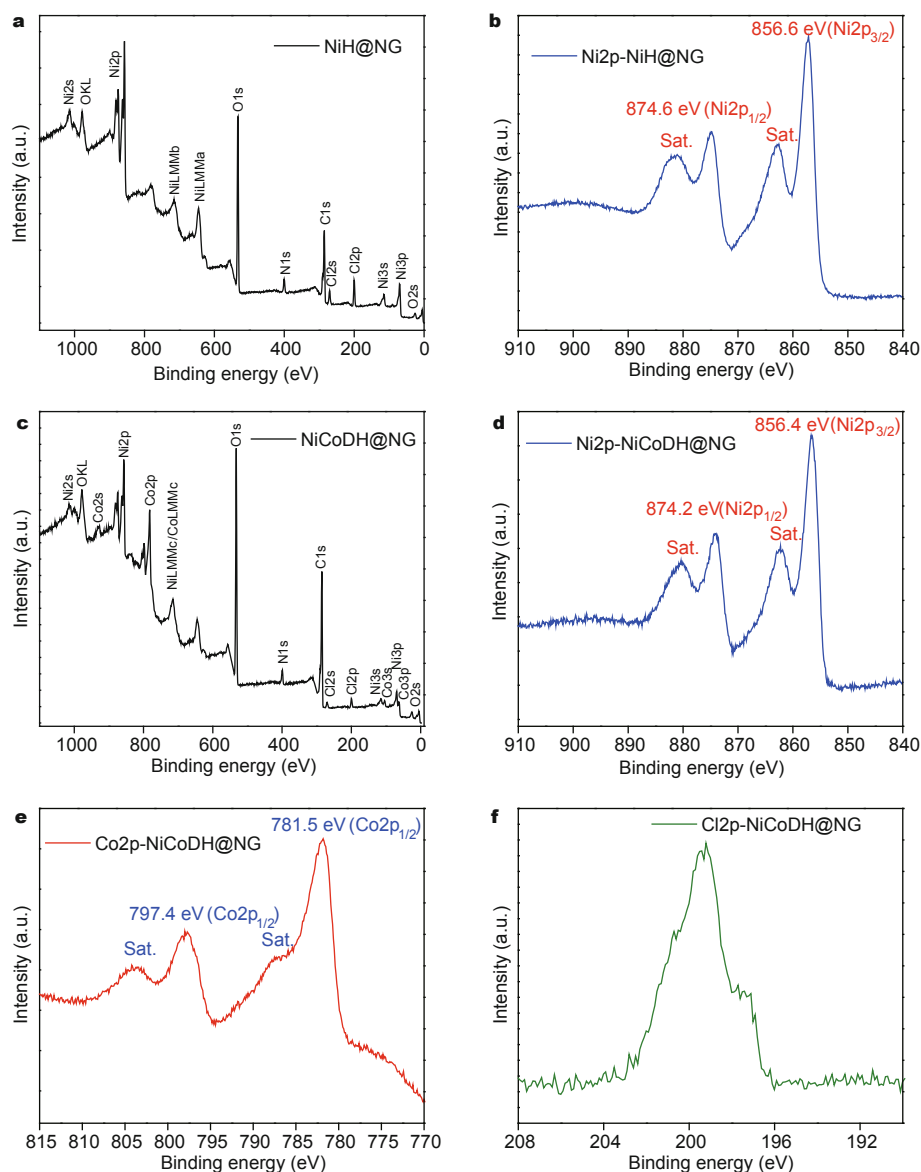
and 61% metallic contents. Here it should be noted that to obtain the best synergistic effect for improving the performance, the optimal mass concentration of graphene in the hybrids is 20%, in order to maintain high conductivity from NG and redox activity from NiCoDH. The porosity is another important factor in determining the electrochemical properties of electrode materials, thus BET and BJH measurements were performed to determine the specific surface area and pore size distribution. From BJH measurements, it is found that incorporation of Co further tune the pore size distribution and increase the pore sizes. Figs S4 and 5 show that NiH@NG ( $128.2 \text{ m}^2 \text{ g}^{-1}$ ) displays higher specific surface area than NiCoDH@NG because of its highly amorphous nature. The specific surface area of NiCoDH nanostructure with highly crystalline growth is reduced by the existence of halogen ions in the hybrids, resulting in the increase of inter-particle spacing, which is also confirmed by the sharp diffraction peaks at lower angle in XRD spectrum (Fig. 2a) [33]. Interestingly, NiCoDH@NG hybrid shows the pore size distribution is mainly around 3.8 nm which enable the charge storage at faster charge-discharge rates without loss of capacity (Fig. 2c). However, the pore size distribution of NiH@NG is about 1.5 nm (Fig. 2d), which proves that the incorporation of Co effectively increases the pore size [36]. Furthermore, it is well known that mesopores play a critical role in electrochemical process by facilitating the mass diffusion and transport through efficient and deep penetration of electrolyte, resulting in faster movement of ions and higher electroactive surface area [40].

To explore the chemical composition and valance state of the elements, XPS studies were carried out as shown in Fig. 3. From XPS studies of NiH@NG and NiCoDH@NG hybrids (Figs 3a and c), it is found that the spectra of both samples contain the core level of Ni, C, Cl, N, and O, and furthermore in the XPS spectrum of NiCoDH@NG a core level of Co is also presented. XPS spectrum of NiCoDH@NG hybrid confirms the equimolar ratio of Ni:Co (7.99:8.52), where a small variation might be due to the surface characterization ability of XPS. In Ni2p spectrum (Figs 3b and d) of both hybrids two shakeup satellite peaks (sat.) along with two spin orbit doublets can be assigned to Ni2p<sub>1/2</sub> (874 eV) and Ni2p<sub>3/2</sub> (856 eV) signals of Ni<sup>2+</sup> [23,35]. Similarly, in Co2p spectrum of NiCoDH@NG hybrid spin orbit splitting energy value is almost 15.9 eV (Co2p<sub>1/2</sub>: 797.4 eV and Co2p<sub>3/2</sub>: 781.5 eV) and sat. peak intensity of Co2p<sub>3/2</sub> is pretty low confirming the co-existence of Co<sup>2+</sup> and Co<sup>3+</sup> in the hybrid (Fig. 3e) [33,36]. The existence of the core level of Cl<sup>-</sup> in both hybrids (Figs 3f and S6) confirms that the growth of the nanostructures is mediated by topochemical transformation, and Cl<sup>-</sup> ions can effectively oxidize the metallic cations and create the porosity in the nanostructures

to support efficient mass transfer during electrochemical performance [41]. In fact, halogen atoms induce positive charge to the host nanostructure and reduce itself to halide anion, and the electrostatic attraction remains them inside the host structure, which is arranged in well-defined wire-like morphology as observed by TEM. Furthermore, Fig. S7 presents the XPS C1s spectrum of NiCoDH@NG hybrid, which confirms the existence of three different kinds of carbon bonding with nitrogen (285.8 eV), adjacent carbon (284.4 eV) and carboxyl/hydroxyl groups (289.0 eV), proving the successful doping of nitrogen and graphitic nature of the grapheme [42]. Further existence of hydroxyl groups also confirms the high wettability of the electrode with electrolyte. The existence of the hydroxyl groups was further confirmed by using FTIR (Fig. S8), which illustrates that NiCoDH@NG has abundant amount of hydroxyl groups that assures its wettability with electrolyte and helps in the deep penetration of electrolyte in electrode. as shown in Fig. S9, it is obvious that NiCoDH@NG contains different kind of nitrogen species, as N1s fitted spectrum confirms the existence of pyridinic, graphitic and amino nitrogen. The percentage of each nitrogen center is determined and it is found that the hybrid contains larger concentration of pyridinic (55.03%) in comparison with that of graphitic (24.42%) and amino (20.55%). It is well-known that electrochemical properties of graphene are more improved by the presence of pyridinic nitrogen, thus existence of larger contents of pyridinic nitrogen is favorable to improve the electrochemical properties of hybrid [38]. Furthermore, the XPS spectrum of the bare NiCoDH nanostructures also shows core level of carbon that confirms the existence of carbonate ions in the NiCoDH nanostructures as structure stabilizer counter anions (Fig. S10). To confirm the doping of nitrogen in the basal plans of graphene, XPS studies of NG was done (Fig. S11) that confirm that graphene contains abundant amount of nitrogen as well as core level of oxygen, which also confirms the existence of carboxyl and hydroxyl groups [43].

Overall, the existence of micropores and hydroxyl groups shorten the electrolyte diffusion time and increase the electrode wettability. The mesopores are helpful for the efficient mass transport to improve the rate capability, while the presence of NG enhances the conductivity and fasters the electron movements in the electrode and the structure is stabilized by the counter anions as well. Thus, these factors emphasize that the above designed hybrid is highly favourable for use as electrode in EC. Therefore, electrochemical response of the NiCoDH@NG hybrid electrode was first recorded by using cyclic voltammetry (CV) as shown in Fig. 4a. The CV curves clearly depict that energy storage is mainly occurred by the Faradaic redox reaction because of the presence of strong redox peaks.

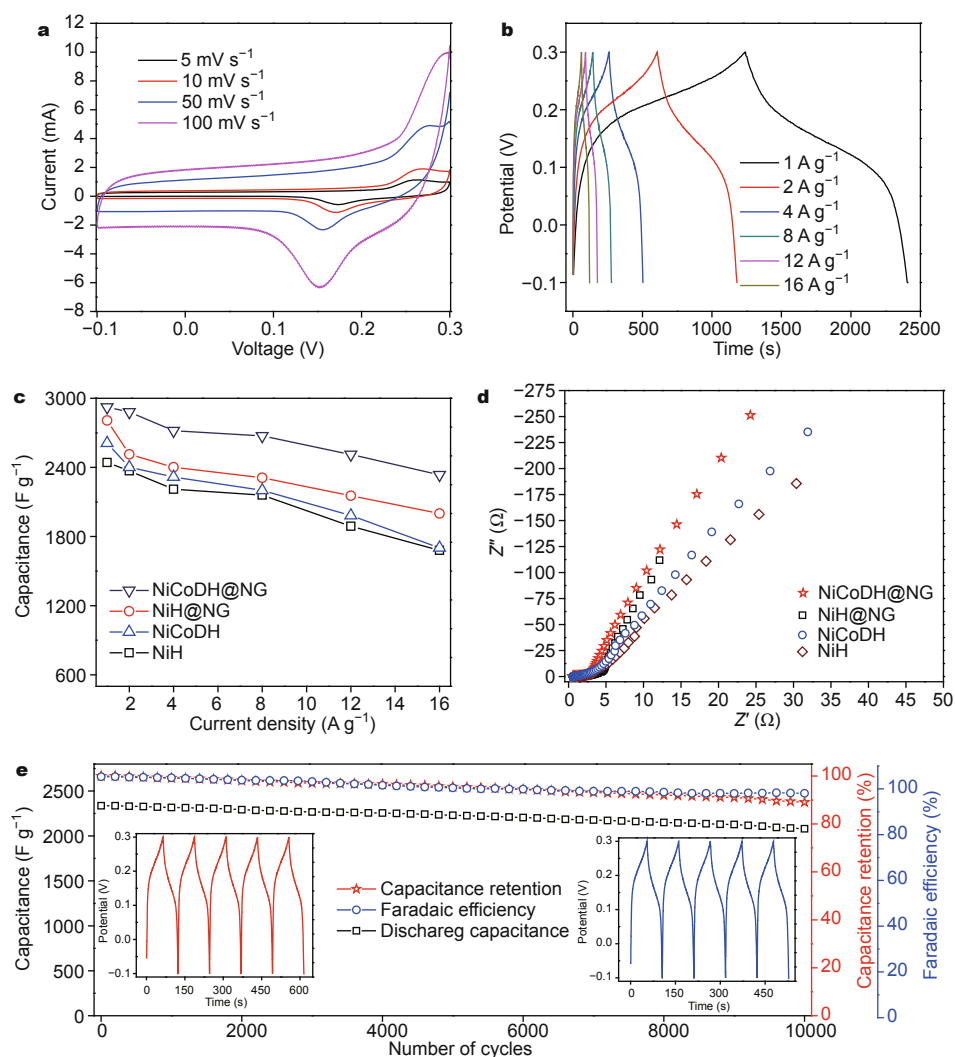




**Figure 3** (a) XPS survey spectrum of NiH@NG hybrid. (b) High resolution Ni2p spectrum of NiH@NG hybrid. (c) XPS survey spectrum of NiCoDH@NG hybrid. High resolution spectra of (d) Ni2p, (e) Co2p and (f) Cl2p of NiCoDH@NG hybrid, respectively.

Therefore, the existence of redox peaks in the voltage range of  $-0.1$  to  $0.3$  V approves the pseudocapacitive nature of the NiCoDH@NG hybrid. In fact, the electrochemical reaction of the NiCoDH@NG hybrid is basically governed by the quasi-reversible-electron transfer process that principally involves the  $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$  redox couple which is mediated by the hydroxyl ions in the alkaline electrolyte [41]. The peaks at  $0.15$  V (anodic sweep) and  $0.25$  V (cathodic sweep) under the scan rate of  $10 \text{ mV s}^{-1}$  correspond to the reduction and oxidation process, respectively. A linear increase in peak current was observed with the increasing scan rate, signifying that the electronic and

mass transfer is fast enough with respect to the scan rates. As scan rate increases from  $5$  to  $100 \text{ mV s}^{-1}$ , a small shift in the redox peak position confirms that the hybrid still keeps its structure and high conductivity, and a pair of redox peak still exists in the CV curves, suggesting that the NiCoDH@NG hybrid electrode is capable for fast redox reactions while most of the other reported materials show large shift because of the increasing diffusion barrier to ions [22,27]. Furthermore, linear voltage plateaus are observed in constant charge-discharge curves of NiCoDH@NG (Fig. 4b) regardless of the static plateaus, confirming the extrinsic pseudocapacitive nature of the hybrid, which



**Figure 4** (a) CV curves of NiCoDH@NG hybrid at different scan rates in the voltage range of  $-0.1$  to  $0.3$  V vs. SCE. (b) Galvanostatic discharge curves of NiCoDH@NG hybrid at different current densities. (c) Specific capacitance of NiH, NiCoDH, NiH@NG hybrid and NiCoDH@NG hybrid electrodes at different current densities. (d) Nyquist spectra of NiH, NiCoDH, NiH@NG hybrid and NiCoDH@NG hybrid electrodes over the frequency range from  $100$  to  $10$  mHz. (e) Long cyclic performance, Faradaic efficiency and capacitance retention of NiCoDH@NG hybrid at current densities of  $16$  A  $g^{-1}$  in the voltage range of  $-0.1$  to  $0.3$  vs. SCE (the inset shows its first and last five charge-discharge curves at current densities of  $16$  A  $g^{-1}$  in the voltage range of  $-0.1$  to  $0.3$  vs. SCE).

provides all redox sites easily accessible to electrolyte as investigated by Simon *et al.* [44]. Similar charge-discharge curves are also observed for NiH, NiCoDH and NiH@NG hybrid (Fig. S12), but show lower capacitive performance of  $2442.5$ ,  $2611$ ,  $2807$  F  $g^{-1}$ , respectively in comparison to the NiCoDH@NG hybrid ( $2924$  F  $g^{-1}$ ) because of their low conductivity which affects the reaction kinetics. Additionally, with increasing charge-discharge rates, no change in shapes of charge-discharge curves confirms that the energy storage is not controlled by the diffusion of ions, which means that hybrid facilitates the faster mass transportation even at higher rates, showing no sluggish reaction kinet-

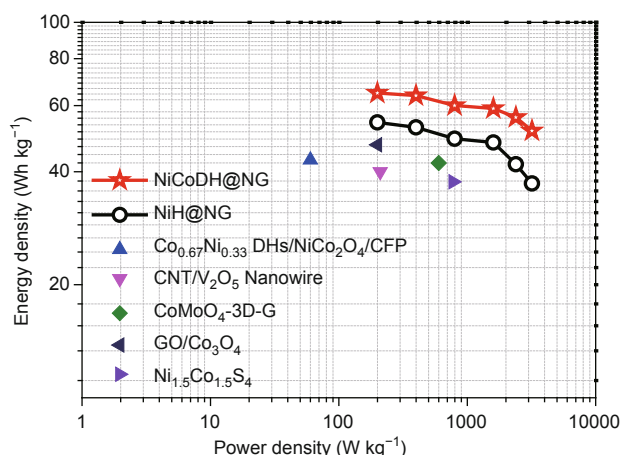
ics involved [44]. Therefore, to explore the rate capability, the hybrid was tested at different current densities, and the results exhibit very stable and improved performances of  $2924$ ,  $2881$ ,  $2718$ ,  $2673$ ,  $2512$  and  $2336$  F  $g^{-1}$  at  $1.0$ ,  $2.0$ ,  $4.0$ ,  $8.0$ ,  $12$  and  $16$  A  $g^{-1}$ , respectively (Fig. 4c). Interestingly, it is found that the hybrid shows minimal loss of capacitance with increasing rate and exhibits extremely high capacitance retention of up to  $80\%$  when the discharge rate is increased from  $1$  to  $16$  A  $g^{-1}$ , which is much enhanced in comparison to NiH ( $68\%$ ), NiCoDH ( $65\%$ ) and NiH@NG ( $71\%$ ), as shown in Fig. S13. Thus, high capacitance retention with varying current rates confirms the capability of

the hybrid to keep efficient transportation of electrons and ions because of its unique composition and structure. Furthermore, capacitive performance of NG is also noted and it is found that NG contribution is negligible in capacitance ( $100 \text{ F g}^{-1}$  at  $1 \text{ A g}^{-1}$ ) as shown in Fig. S14, and the capacitance mainly comes from NiCoDH nanostructures. In fact, the existence of NG improves the electronic movement across the electrode, and fine pore size and its distribution improve the mass transportation while the existence of chloride and carbonate anions stabilizes the structure and improves quasi-reversible-electron transfer process during the reduction and oxidation of metal in the redox reaction ( $\text{Ni}^{2+}/\text{Ni}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$ ) with hydroxyl ions of electrolyte. To explore the role of NG and structural features on the electronic conductivity and mass transportation, EIS was utilized as shown in Fig. 4d. The Nyquist profiles show the semicircle in the high frequency region and a straight vertical inclined line in the lower frequency region. The charge transfer resistance ( $R_{\text{ct}}$ ) measured using appropriate Randles equivalent circuit is shown in Fig. S15a, the calculated  $R_{\text{ct}}$  values for NiH, NiCoDH, NiH@NG and NiCoDH@NG are 4.29, 3.25, 2.23 and  $1.60 \Omega$ , respectively, which prove that the introduction of NG significantly improves the electronic properties and provides faster highway for electron transfer. Furthermore, the vertical spikes confirm the capacitive behaviour of all samples, suggesting that the incorporation of both Co and NG efficiently improves the ionic diffusion and lowers the Warburg resistance ( $W$ ). The improved mass transportation is actually due to the improved structural features of the NiCoDH@NG hybrid as confirmed by the BJH and XRD studies.

Cyclic stability is a critical parameter for the practical application of electrode materials. Thus, in order to investigate the cyclic life of the electrode, galvanostatic charge-discharge analysis was carried out for 10,000 cycles at  $16 \text{ A g}^{-1}$  in the voltage range of  $-1.0$  to  $0.3 \text{ V}$  in  $1 \text{ M KOH}$  solution, as shown in Fig. 4e. It is worth noting that the hybrid shows highly stable performance of  $2336 \text{ F g}^{-1}$  and keeps up to 90% of it after 10,000 cycles, which demonstrates very high capacitance retention capability of the hybrid electrode (Fig. 4e). Furthermore, Coulombic/Faradaic efficiency is the indication of reversibility of the pseudocapacitive performance of electrode which is prone to structural changes, increasing barrier to ionic diffusion or lowering conductivity at higher discharge rates [27,45]. So, the Faradaic efficiency of NiCoDH@NG hybrid is calculated from galvanostatic charge-discharge profile and interestingly the hybrid keeps almost 98.1% of its reversibility after 10,000 cycles, delineating that the composition and structure of the electrode material remain the same after such a long cyclic life and emphasizing its ability to be potentially used in real devices. Furthermore, the hybrid shows simi-

lar charge-discharge profile in its first and last cycles that verifies similar energy storage mechanism with on-going charge-discharge cycles (the inset of Fig. 4e). However, Fig. S15b presents the Nyquist plot of NiCoDH@NG electrode before and after 10,000 cycles, and quite similar profile confirms that there is only a slight change in the electronic and mass transportation after 10,000 cycles. The existence of vertical spike in lower frequency region after 10,000 cycles confirms that hybrid still bears high capacitive performance and shows no diffusion barrier to electrolyte. Similarly, the cyclic lives of the NiH, NiCoDH and NiH@NG are explored for 10,000 cycles that show capacitance of 1600, 1702 and  $2000 \text{ F g}^{-1}$  at current density of  $16 \text{ A g}^{-1}$  and keep their capacitance up to 76.8%, 83.7% and 82.3%, respectively, as shown in Fig. S16. Lower capacitance retentions of all these electrodes compared with NiCoDH@NG electrode confirms that NiCoDH@NG hybrid takes advantages of the co-existence of NG and Co in the structure, which improves the structure of electrode and creates better mesoporosity enhancing overall conductivity of the electrode. Furthermore, the incorporation of nitrogen in the graphene significantly improves its conductivity and electrochemical performance by disturbing its electronic cloud and density of state, hence it is beneficial to improve the overall performance of the hybrid [46]. Thus, electrode based on the above designed hybrid takes benefits from efficient electronic flow, deep penetration of electrolyte species enhancing the Faradaic redox reactions, while  $\text{Cl}^-$  ions provide the structural stability necessary for reversibility of the electrode to mediate the redox reaction along with hydroxyl ions by electron transfer in quasi-reversible oxidation and reduction process of nickel and cobalt ions. Therefore, such a design of electrode structure can efficiently transport charge not only under lower discharge rates but also at higher rates without loss of capacitance. This can be extended to other metal hydroxide, oxides and sulphides to improve their capacitive performances.

Energy density is an important factor to develop EC electrode to overcome its limitation in real application for EVs since it is very important for ECs to come up with high capacitance and energy density. Fig. 5 presents the Ragone plot, showing high energy density values of the NiCoDH@NG hybrid along with excellent energy density retention upon increasing charge-discharge rates. The NiCoDH@NG hybrid shows energy density of  $65 \text{ Wh kg}^{-1}$  at current density of  $1 \text{ A g}^{-1}$  and keeps high value up to  $52 \text{ Wh kg}^{-1}$  at current density of  $16 \text{ A g}^{-1}$ , as well as brings the high power density ( $3191 \text{ W kg}^{-1}$ ). The Ragone plot also displays the comparison of the present results with the recently published values (values are taken for three-electrode cell) and it is obvious that our results show prominently high energy densities without much compromise on power densi-



**Figure 5** Ragone plot related to the power and energy densities of NiH@NG and NiCoDH@NG hybrids at different current densities in comparison with recently published literature corresponding to high energy density values for three-electrode cell (reported data is adopted from Refs. [22,30,35,47–49]).

ties [22,30,35,47–49]. It is also worth noting that electrode composed of NiH@NG hybrid also shows much improved results than previous data but lower than the NiCoDH@NG hybrid. Thus, higher values of capacitance and energy densities highlight the advantages of unique structure and composition of the NiCoDH@NG hybrid as explained above. Keeping in mind, the environment benign aqueous electrolyte and facile synthesis method of the NiCoDH@NG hybrid with high capacitive and energy density is successfully developed, and our NiCoDH@NG hybrid is favorable for applications in high energy storage devices.

## CONCLUSIONS

In summary, NiCoDH@NG hybrid was synthesized through a facile hydrothermal process under industrially acceptable conditions. The defects in NG sheets acted as nucleation sites and the growth was controlled by the Co ions via topochemical transformation supported by hopping charge transfer process among halogen and neighbouring metal ions as well as olation growth. A specific composition of hybrid nanostructures was tuned both for metallic components and counter anions to improve the structural features. The deep penetration of electrolyte was achieved through fine porosity and existence of hydroxyl groups in the nanostructures of the hybrid. The redox reaction was enhanced by the halogen ions through charge transfer to neighbouring metallic ions along with hydroxyl ions of electrolyte. Thus, the resulted nanostructured hybrid exhibited excellent capacitance of  $2925 \text{ F g}^{-1}$  and energy density of  $65 \text{ Wh kg}^{-1}$  at current density of  $1 \text{ A g}^{-1}$ . Further the hybrid showed good capacity retention of 90% at  $16 \text{ A g}^{-1}$  after 10,000 cycles. Furthermore, the hybrid displayed ex-

cellent energy density retention and kept up to  $52 \text{ Wh kg}^{-1}$  at  $3191 \text{ W kg}^{-1}$  as current density was increased from  $1.0$  to  $16 \text{ A g}^{-1}$ . Using this approach to tune the nanostructures in the electrode materials proves to be a revolution since the approach provides simultaneous control over the structure and composition, and improved performance compared with most of the reported materials, thus providing a real opportunity to realize future electronic devices.

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**Author contributions** Mahmood N and Hou Y designed the experiments after discussion with Cao C and carried out the synthesis of all the samples; Mahmood N and Tahir M performed the electrochemical characterization of the developed electrodes; Yang W and Gu X performed the XPS analysis; Cao C, Mahmood A and Zhang Y analysed the electrochemical results; all the authors contributed in the discussion part; paper was written by Mahmood N and all the authors have revised it.

**Conflict of interest** The authors declare that they have no conflict of interest.

**Supplementary information** Electronic Supplementary Information (ESI) is available in the online version of the paper, including part of experimental section, TEM images, XRD, XPS, XPS fitted spectra, FTIR, Nyquist curve, equivalent circuit, charge-discharge curve and cyclic performance of Hybrids.



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**中文摘要** 超级电容器因为具有充放电时间短的特点引起了人们的广泛关注. 然而, 由于电极表面的电荷积聚和化学反应, 电容器的比电容及能量密度大大降低, 限制了超级电容器的实际应用. 本文提出了一种新颖的合成方法用以制备基于镍钴双氢氧化物的复合材料, 该复合材料作为超级电容器的电极具有优异的电化学性能. 利用氮掺杂石墨烯的缺陷, 金属氢氧化物纳米结构在氮掺杂石墨烯表面生长, 形成复合结构. 通过调节并优化镍钴的元素比以及卤素离子、碳酸根离子的含量, 能够改善材料的孔隙度、提高材料结构的稳定性以及促进电化学反应. 金属氢氧化物的形成由钴离子的氧化反应引导, 并通过定向生长方式形成一维结构. 氮掺杂石墨烯有效保护镍钴双氢氧化物的纳米结构, 使其在电化学测试中不被破坏, 同时, 氮掺杂石墨烯还能够提高电极的导电性, 利于物质及离子传输. 电化学测试表明, 该复合材料在电流密度为  $1 \text{ A g}^{-1}$  时, 比电容高达  $2925 \text{ F g}^{-1}$ , 并且在高电流密度下 ( $16 \text{ A g}^{-1}$ ) 展现出了优异的循环稳定性, 在 10,000 次循环后比电容仍然保持在 90%. 在  $16 \text{ A g}^{-1}$  的电流密度下, 材料的能量密度和功率密度分别达到了  $52 \text{ Wh kg}^{-1}$  和  $3191 \text{ W kg}^{-1}$ . 该合成方法为制备基于金属氢氧化物、氧化物、硫化物等高性能超级电容器电极提供了新的途径.