High-performance Hybrid Supercapacitors Based on Self-supported 3D Ultrathin Porous Quaternary Zn-Ni-Al-Co Oxide Nanosheets

Qiaobao Zhang ^{a, b}, Bote Zhao ^b, Jiexi Wang ^c, Chong Qu ^b, Haibin Sun ^b, Kaili Zhang ^{a, *}, Meilin Liu ^{b, *}

^a Department of Mechanical and Biomedical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong

^b School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta 30332-0245, GA, United States

^c School of Metallurgy and Environment, Central South University, 932, South Lushan Road, Changsha, P.R. China, 410083

*Corresponding authors:

Kaili Zhang, E-mail address: kaizhang@cityu.edu.hk

Meilin Liu, E-mail address: meilin.liu@mse.gatech.edu

Abstract

Mixed transition metal oxides with hierarchical, porous structures, constructed from interconnected nano-building blocks, are considered promising positive electrodes for high-performance hybrid supercapacitors. Here we report our findings in design, fabrication, and characterization of 3D hierarchical, porous quaternary zinc-nickel-aluminum-cobalt oxide (ZNACO) architectures assembled from well-aligned nanosheets grown directly on nickel foam using a facile and scalable chemical bath deposition process followed by calcination. When tested as a binder-free electrode in a 3-electrode configuration, the ZNACO display high specific capacity (839.2 Cg^{-1} at 1 Ag^{-1}) and outstanding rate capability ($\sim 82\%$ capacity retention from 1 Ag^{-1} to 20 Ag^{-1}), superior to those of binary-component NiCo_2O_4 and ZnCo_2O_4 as well as single-component Co_3O_4 electrode. More remarkably, a hybrid supercapacitor consisting of an as-fabricated ZNACO positive electrode and an activated carbon negative electrode exhibits a high energy density of 72.4 Wh kg^{-1} at a power density of 533 W kg^{-1} while maintaining excellent cycling stability ($\sim 90\%$ capacitance retention after 10,000 cycles at 10 Ag^{-1}), demonstrating a promising potential for development of high-performance hybrid supercapacitors. Further, the unique electrode architecture is also applicable to other electrochemical systems such as batteries, fuel cells, and membrane reactors.

Keywords: Oxide nanosheet; Porous electrode ; Hybrid supercapacitors; Transition metal oxides; Three-dimensional structures

Introduction

With the increasing concern about environmental issues and the rapid depletion of

fossil fuels, considerable efforts have been devoted to the use of clean and sustainable energy. Because of the intermittent nature of the alternative energy, however, the viability of broad commercialization of renewable energy hinges on novel technologies for electrochemical energy storage [1–6]. Among all types of electrical energy storage devices, supercapacitors (also known as electrochemical capacitors), are considered the most promising one because of their superior performance characteristics, including high power density, short charging time, long operational life, and excellent safety[7–10]. They are potential candidates for a wide range of applications, from electric vehicles to smart grids[1,9,11–14]. Hybrid supercapacitors combine an carbon-based negative electrode, which stores energy using fast ion adsorption[2,9], with a battery-type positive electrode (typically transition metal oxides and hydroxides) based on fast redox reactions[3,15–17]. Hybrid supercapacitors have received particular attention as they offer much higher specific capacitance and energy densities, often more than one order of magnitude higher than those of electrochemical double layer capacitors (EDLCs)[15,17]. It is well known that the performance of a hybrid supercapacitor is determined mainly by the battery-type positive electrode[16]. Accordingly, nanostructured transition metal oxides (NTMOs) are being widely explored as positive electrode for hybrid supercapacitors to increase the specific capacitance and energy density[18–23]. NTMOs also have the advantages of easy large-scale fabrication and excellent flexibility in structures and morphology. In particular, mixed NTMOs involving different metal ions are emerging as high-performance electrode materials for hybrid supercapacitors because of several advantages over a simple NTMO, including high electrochemical activities, improved electronic conductivity (due to their multiple oxidation states for interfacial reversible faradaic reactions), and relatively low

activation energy for electron transfer between cations[19,24]. However, the poor intrinsic conductivity of these mixed NTMOs still limits their electrochemical performance[7].

Development of well-defined hierarchical porous structures of mixed NTMOs arrays that are directly bonded to conductive substrates as integrated electrodes (without addition of binders and conductive additives) are proven to be an effective strategy to achieving high-performance hybrid supercapacitors[25]. Specifically, the direct attachment of each mixed NTMOs array nano-building block to the current collector can build up an expressway for rapid charge transfer[26,27]. Moreover, the hierarchical porous feature of the mixed NTMOs not only enables the full exposure and good accessibility of electroactive sites to liquid electrolyte, resulting in increased electrode/electrolyte contact area, but also offers short electron and ion diffusion paths, allowing fast rate capability, both of which are prerequisite for the construction of high-performance hybrid supercapacitors[28]. Recently, various hierarchical, self-supported, porous nanostructured electrodes have been reported to exhibit enhanced electrochemical performance [6,29–32]. In spite of these advances, rational design and synthesis of hierarchical, porous, multi-component (more than 3 metal components) mixed NTMOs with a homogeneous structure directly grown on a current collector by a simple and easy scale-up process remains a significant challenge. Moreover, the commonly used solution-based method for the synthesis of self-supported NTMOs is a hydrothermal process in a pressurized container (autoclave) at relatively high temperatures (normally higher than 100 °C) for a long period of time. This process is less likely to be scaled up at low cost and may not be suitable for practical applications[33]. Therefore, it is highly desirable to develop a simple process for fabrication of mixed NTMOs with desired properties that can be

easily scaled up at low cost.

It has been demonstrated that the incorporation of aluminum and zinc elements in nickel and cobalt hydroxides or aluminum and cobalt co-doped nickel hydroxides is able to significantly enhance their electrochemical performance when used as electrodes for supercapacitors[34,35]. Moreover, improved electrochemical performance in comparison with Co_3O_4 has been obtained when much cheaper and more eco-friendly alternative zinc and nickel elements are incorporated in Co_3O_4 to form cobalt-based mixed NTMOs, which offer an effective way for constructing high-performance electrode for hybrid supercapacitors[5,32]. The enhancement is originated from their complex chemical compositions involving different mixed valence states at these multi-metal centers and synergetic effects among them [24]. Furthermore, it has also been found that the electrode based on mixed oxides of Mn-Ni-Co (ternary-component) exhibits higher electrochemical performance than that based on the oxides of binary-component Ni-Co, due mainly to the enhanced oxidation states and synergistic effects of the multi-metal components in the electrodes[36].

Inspired by the previous promising findings, here we present a facile chemical bath deposition (CBD) process followed by calcination for the synthesis of 3D hierarchical, porous architectures of homogeneous quaternary Zn-Ni-Al-Co oxide (ZNACO) nanosheets, considered as Zn, Ni and Al ions doped into Co_3O_4 supported on Ni foam of large area. Compared to the commonly used hydrothermal method, this low-temperature synthesis method is simple, low-cost, easy for scaling up without the need for high-pressure apparatus. The as-fabricated ZNACO is assembled from ultrathin porous nanosheets with homogenous distributions of metal elements throughout the structure. The nanosheets are composed of numerous highly crystalline

nanoparticles, offering a large number of mesopores for fast ion transport and enabling full exposure of active materials (ZNACO nanocrystals) to the electrolyte. The formation of mixed valence states at these multi-metal centers in ZNACO is expected to offer a synergistic effect on redox reactions and render the desirable electronic conductivity for efficient energy storage. The self-supported ZNACO nanosheets can be directly used as binder-free electrodes for supercapacitors, demonstrating high specific capacity and outstanding rate capability, superior to those of binary-component NiCo_2O_4 (NCO) and ZnCo_2O_4 (ZCO) and single-component of Co_3O_4 (CO) electrodes. More importantly, a hybrid supercapacitor composed of a ZNACO positive electrode and AC negative electrode demonstrated high energy density and excellent cycling stability (~90% capacity retention after 10,000 cycles at 10 Ag^{-1}), holding great promise for practical application in high-performance energy storage systems.

2. Experimental Section

2.1 Preparation of ZNACO nanosheets on Ni foam

In a typical procedure, the as-cleaned substrates (3D macroporous Ni foam) with the backsides coated with polyimide tape were fixed onto a polytetrafluoroethylene holder and immersed in a closed 600 mL Pyrex beaker with 400 mL aqueous solution, containing 27.89 g of urea, 1.19 g (0.01 M) of zinc nitrate hexahydrate, 3.49 g (0.04 M) of nickel(II) nitrate hexahydrate, 1.5 g (0.01 M) of aluminum nitrate nonahydrate, and 10.48 g (0.09 M) of cobalt(II) nitrate hexahydrate. The beaker containing the growth solution and substrates was then covered with an aluminum foil and placed in an oven maintained at 90°C for 4 h. After the beaker naturally cooled down to room temperature, the substrates were then taken out of the solution and rinsed with

distilled water and cleaned in distilled water by ultrasonic for several times. Finally, the as-fabricated samples were annealed at 350 °C under normal argon gas for 2 h to obtain hierarchical porous architectures of quaternary ZNACO nanosheets.

2.2 Sample characterization

The morphology, crystalline structure, and composition of the as-grown ZNACO nanosheets were characterized using field emission scanning electron microscopy (Hitachi S4800 FESEM), transmission electron microscopy (FEI Tecnai G2 20 TEM), and X-ray diffraction (RigakuSmartLab XRD). A thermogravimetric analysis (TGA) instrument (SDT Q600 thermo gravimetric / differential thermal analyzer) was employed to examine the thermal behaviors. The specific surface areas and pore diameter distributions of the oxides powders were measured using a Quantachrome NOVA 2000e analyzer with a method of Brunauer-Emmet-Teller (BET) and BJH (Barrett–Joyner–Halenda). Before gas-sorption measurement, each sample was degassed in vacuum at 300 °C for 3 h

2.3 Electrochemical performance evaluation

For supercapacitors test, the as-synthesized quaternary ZNACO nanosheets on Ni foam were dried at 80 °C overnight under vacuum and then used as the working electrodes in a three-electrode cell with a platinum counter electrode and a Hg/HgO reference electrode. The electrochemical tests were performed using a Solartron system (SI 1286 electrochemical workstation and SI 1255 HF frequency response analyzer). Cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) were performed on cells in 2 M KOH aqueous solution at room temperature in the frequency range from 0.01 Hz to 100 kHz with amplitude of 5 mV under the open-circuit conditions. The methodological details

for determining the mass loading of active electrode materials are as follows: the mass difference of the Ni foam substrate before and after the ZNACO nanosheets deposition was used as the mass of ZNACO nanosheets. Typically, the weight of a 1cm² Ni foam was recorded as m_1 (in mg). After the deposition of ZNCO nanosheets, the weight of the as-obtained sample was carefully recorded as m_2 using a microbalance (METTLER TOLEDO XS3DU) with an accuracy of 1 ug. The mass of ZNACO nanosheets is equal to $m_2 - m_1$ and is determined to be around 1.95 mg. As suggested by Brousse et al.[15], it is inappropriate to describe cobalt or mixed cobalt-based oxides as pseudocapacitive electrode materials because they undergo faradaic reactions, in which their electrochemical signature (e.g., cyclic voltammogram and charge/discharge curve) is analogous to that of a “battery” material. Accordingly, the specific galvanostatic capacity (C) instead of capacitance of the electrodes should be calculated according to the following equations:

$$C = i_m \cdot \Delta t \quad (1)$$

where $i_m = I/m$ (A·g⁻¹) is the current density, I is the current, m is the mass of the active electrode material and Δt is the discharge time.

A hybrid supercapacitor containing ZNACO nanosheets on 3D Ni foam as the positive electrode, active carbon (AC) casted on 3D Ni foam as the negative electrode and one piece of NKK film (MPF30AC-100, Nippon Kodoshi Corporation, Kochi, Japan) as the separator in a 2 M KOH solution was assembled into a split test cell (MTI Corporation) and measured using a two electrode configuration at room temperature. The AC on Ni foam electrode was prepared according to the following steps: First, 95 wt% AC was homogeneously mixed with 5 wt% polyvinylidene fluoride. Second, appropriate N-methyl pyrrolidone (NMP) was added into the mixture as a solvent to make slurry, which was then pressed onto Ni foam. Finally,

the as-prepared electrode was dried at 100 °C under vacuum for 12 h to remove the solvent. The electrochemical tests were performed using the Solartron system whereas the long-term cycling performance was evaluated using an Arbin testing system (MSTAT, BT-2143). As suggested by Mai et al.[37], for the hybrid supercapacitor with its non-symmetric GCD curve resulted from the quasi-reversible faradic reactions, the faradic reaction charge/voltage ratio in the cell no longer remains constant and varies with time, the specific galvanostatic capacity (C) of the hybrid supercapacitor should be calculated according to the following equation:

$$C = \frac{2i_m \int V dt}{V^2|_{V_i}^{V_f}} \quad (2)$$

where $i_m = I/m$ ($A \cdot g^{-1}$) is the current density, I is the current, m is the total mass of the positive and negative electrode materials, V is the potential with an initial and final value of V_i and V_f , respectively. Considering that the GCD curve of our ZNACO//AC hybrid supercapacitor is non-symmetric, its specific galvanostatic capacity (C) is thus calculated based on equation (2).

3. Results and Discussion

The preparation process of hierarchical porous structures of quaternary ZNACO nanosheets grown directly on Ni foam is schematically illustrated in Figure 1(a-c). The whole process involves two simple steps. First, hierarchically structured ZNACO-precursor nanosheet arrays were *in situ* grown on Ni foam via a facile CBD method. The XRD pattern of the as-synthesized ZNACO-precursor nanosheets confirms that they are **cobalt-based layered double hydroxides** (Figure S1, supporting information). Second, the as-obtained hierarchically structured ZNACO **layered double hydroxides** nanosheet arrays were thermally transformed to hierarchically porous structures of ZNACO nanosheet arrays supported on Ni foam via a simple

calcination process in argon accompanied by the release of CO₂ and H₂O gases as indicated in reaction (3) with the color of the samples changed from light pink to black (Figure S2, supporting information) [1,38].

Figure 1. (a) Schematic illustration of the synthetic process of ultrathin ZNACO nanosheets grown directly on Ni foam and SEM images of (b) ZNACO-precursor nanosheets on Ni foam, inset is an image with lower magnification, (c-e) ZNACO nanosheets on Ni foam, (f) XRD pattern of ZNACO nanosheets powder sample and (g) the N₂ absorption-desorption isotherm of the as-prepared ZNACO nanosheets, the inset is the pore distribution.

Figure 1(b) shows the typical SEM images of ZNACO-precursor nanosheet arrays on Ni foam. As can be seen, the nanosheets are uniformly grown on the 3D skeleton of Ni foam to form a conformal coating on its surface over a large area and these nanosheets are in fact interconnected with each other forming a flower-like structure, which might possess better mechanical strength [8]. After annealing, it can be found that the as-obtained sample still retains the 3D skeleton structure of the Ni foam, and the surface of the Ni foam is uniformly covered with ZNACO as seen in Figure 1(c). From the enlarged views (Figure 1(d-e)), it is observed that the as-obtained ZNACO nanosheets sample perfectly inherits the flower-like network structure and morphology of its corresponding ZNACO-precursor without calcination-induced significant alterations. These as-formed nanosheets with a lateral size of several hundred nanometers are intercrossed with each other, creating loose porous nanostructures with abundant open space and electroactive surface sites. It is interesting to observe that the simultaneous incorporation of multi-component of Zn, Ni and Al element into Co_3O_4 results in a remarkable morphological transformation from nanowires to ultrathin nanosheets (Figure S3, supporting information). The ultrathin nanosheet morphology has proven to be advantageous for efficient ion and electron transport since the thickness of the nanosheets is much smaller than the diameter of the nanowires, and for better accommodating the volume variation, which is more favorable for the performance enhancement of supercapacitors[8,39].

The thermal behavior of ZNACO-precursor nanosheets is investigated by DTA-TG measurements and the result is shown Figure S4(a). Two weight loss regions at below 200 °C and in the range of 200 °C to 300°C can be observed, which might be respectively attributed to the dehydration of physically adsorbed water and the decomposition of ZNACO-precursor nanosheets to ZNACO nanosheets. The

temperature of 350 °C is thus selected so as to complete thermal decomposition of ZNACO-precursor nanosheets to ZNACO nanosheets. The crystallographic structure and phase purity of as-synthesized ZNACO nanosheets are determined by powder X-ray diffraction (XRD) and the results are shown in Figure 1(f). It can be clearly seen that almost all identified peaks can be indexed as a spinel structure (space group $Fd\bar{3}m$), which is isostructural to well-crystallized cubic spinel Co_3O_4 (PDF #43-1003), indicating that the partial replacement of cobalt ions by nickel, aluminum, and zinc ions does not change the crystal structure of spinel Co_3O_4 [27], similar to the XRD patterns of the as-prepared ZNCO, NCO, ZCO and CO samples shown in Figure S5 in supporting information. The elemental composition of the ZNACO nanosheets grown directly on Si substrate is examined by energy dispersive X-ray (EDX) measurements (Figure S4(b), supporting information), which confirms the existence of the elements Ni, Co, Zn, Al, O, Si and C, while the Si and C signals originate from the silicon substrate and carbon paste, respectively. The mesoporous features of ZNACO nanosheets are examined by nitrogen isothermal adsorption-desorption measurements as depicted in Figure 1(g). The N_2 adsorption–desorption isotherm is characteristic of type IV with a type H2 hysteresis loop observed in the range 0.8-1.0 P/P_0 , an indication of its mesoporous structures[40]. The inset in the Figure 1(g) shows the corresponding pore size distribution derived from desorption data and calculated from the isotherm using the BJH model, demonstrating a relatively narrow pore size distribution (3–27 nm) centered at approximately 5.7 nm, which further confirms the mesoporous feature of ZNACO nanosheets. The BET specific surface area of ZNACO nanosheets is estimated to be $83.5 \text{ m}^2\text{g}^{-1}$, which is higher than those of ZNCO ($67.2 \text{ m}^2\text{g}^{-1}$), ZCO ($58.6 \text{ m}^2\text{g}^{-1}$), NCO ($63.2 \text{ m}^2\text{g}^{-1}$) and CO ($41.6 \text{ m}^2\text{g}^{-1}$) samples (Figure S6, supporting information), indicating an increase in surface area

due to morphology change, i.e., smaller nanosheets formation caused by Al doping.

The surface electronic state and the composition of the ZNACOs nanosheets are analyzed by X-ray photoelectron spectroscopy (XPS) and the corresponding results are presented in Figure 2. The survey spectrum shown in Figure 2(a) indicates the presence of Ni, Co, Al, Zn and O as well as C and the absence of other impurities in the ZNACOs nanosheet sample. By using a Gaussian fitting method, the high-resolution Co2p emission spectrum (Figure 2b) is best fitted with two spin-orbit doublets, which are characteristic of Co^{2+} and Co^{3+} , and two couple of shakeup satellites (identified as “Sat.”)[4]. For the high-resolution Ni 2p spectrum, it consists of two spin-orbit doublets at 855.4 eV and 872.5 eV, suggesting the coexistence of Ni^{2+} and Ni^{3+} and two shakeup satellites[4]. For high-resolution Zn 2p spectrum, two major peaks at 1020.7 and 1043.8 eV are ascribed to Zn $2p_{3/2}$ and Zn $2p_{1/2}$ of Zn(II), respectively[41]. The high-resolution Al 2p spectrum shows one peak with binding energy values of 73.1 eV, indicating the presence of Al^{3+} . The O 1s peaks at 529.4 and 531.3 eV correspond to the oxygen species in ZNACO[41]. The atomic percentage of Ni, Co, Al, Zn, and O elements as well as C element from reference in the ZNACO is estimated to be 8.42, 13.51, 3.51, 9.43, 41.75 and 23.38, respectively, which is largely coincident with the EDX analyses. It is noted that the atomic ratio of metal elements in the ZNACO sample is different from the intended composition, due likely to many factors, including different coordination and precipitation ability of Zn, Ni, Al and Co in the precursor solution and the conditions for preparation of the samples[42]. This has been widely observed by others.[42–44]

Figure 2. XPS of (a) survey, (b) high-resolution Co2p, (c) Ni2p, (d) Zn2p, (e) Al2p and (f) O1s spectra of ZNACO nanosheets.

Transmission electron microscopy (TEM) is used to further investigate the detailed microstructures and morphologies of as-obtained ZNACO nanosheets. As seen in Figure 3(a), the as-obtained ZNACO nanosheets feature a transparent, folded, silk-like morphology, indicating the ultrathin nature and the highly porous feature of the nanosheets. It should be noted that the dark strips are generally the folded edges or wrinkles of the nanosheets[8]. It is evident from a closer view that these ultrathin nanosheets are highly porous but structurally continuous, composed of numerous nanoparticles. It reveals that the ZNACO nanosheets are only 4 nm in thickness. The HRTEM image (Figure 3(b)) shows clear fringes with a measured interplanar spacing of 0.46 nm that corresponds to the interplanar distance of the (111) plane of spinel ZNACO phase[8]. The corresponding selected area electron diffraction (SAED) pattern shown in Figure 3(c) contains well-defined diffraction rings, suggesting their polycrystalline characteristics, and the diffraction rings can be readily indexed to the (200), (311), (400), (511) and (440) planes of the ZNACO phase[8], in accordance

with the XRD results. To further confirm the successful formation of quaternary ZNACO nanosheets, TEM elemental mapping analysis on a representative nanosheet, as shown in Figure 3(d), unambiguously reveals that the elements of Zn, Co, Ni, Al and O are distributed homogeneously in the whole nanosheet.

Figure 3. (a) Low-magnification TEM image of individual ZNACO nanosheets, (b) HRTEM image, (c) the corresponding SAED pattern of ZNACO nanosheets and (d) TEM-EDX mapping images of individual ZNACO nanosheets.

Enlightened by the advantageously structural features and compositional advantages,

the electrochemical performance of ZNACO nanosheets grown directly on Ni foam as electrode for supercapacitors is evaluated in a three-electrode configuration in 2M KOH aqueous electrolyte by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) tests. For comparison, the electrochemical performances of Co_3O_4 (CO) nanowires (Figure S7a-c and SEM image in Figure S3a, supporting information), NiCo_2O_4 (NCO) nanowires (Figure S7d-f and SEM image in Figure S3b, supporting information), ZnCo_2O_4 (ZCO) nanosheets (Figure S7g-i and SEM image in Figure S3c, supporting information) and zinc–nickel–cobalt oxide (ZNCO) nanosheets (Figure S7j-m and SEM image in Figure S3f, supporting information) grown on Ni foam as electrodes for supercapacitors are also measured under the same conditions. The comparative CV curves of self-supported CO nanowires, NCO nanowires, ZCO nanosheets, ZNCO nanosheets, and ZNACO nanosheets electrodes in the potential range between -0.1 and 0.5 V (versus Hg/HgO) at a scan rate of 5 mVs^{-1} are shown in Figure 4(a). Evidently, the ZNACO nanosheets electrode exhibits the highest current density and the largest increment in the CV integrated area than any other electrode, indicating the significantly enhanced electrochemical reaction activity and charge storage. Their corresponding GCD curves at a current density of 5 A g^{-1} in the potential range between 0 and 0.5 V (versus Hg/HgO) is depicted in Figure 4(b). It is clearly seen that ZNACO nanosheets electrode delivers the longest discharge time, corresponding to the highest specific capacity. To gain more insight into the electrochemical behavior of the cells based on different electrode materials, we performed EIS on test cells, as shown in Figure 4(c). Each of the impedance spectrum consists of two segments, a small loop at the high-frequency region (corresponding mainly to the charge transfer resistance of the electrode, an indication of the electron transfer kinetics of the redox reaction at the electrode interface) and a straight line at

the low-frequency region (originated largely from Warburg impedance or the diffusive resistance of the electrolyte into the interior part of the electrode) [45,46]. All cells with four types of different electrodes exhibited relatively low Warburg impedance, an indication of facile electrolyte diffusion to the surface of the electrodes in all cases [47]. However, in the high frequency region, the impedances of ZNACO, ZNCO, and NCO electrodes are much smaller than that of the CO electrode, suggesting enhanced charge transfer kinetics of the redox reaction [48]. In particular, ZNACO electrode showed the lowest polarization impedance (i.e., the smallest size of the impedance loop) among all electrode materials studied. Also, the intersection value of the impedance loop with the real axis at high frequencies for ZNACO, ZNCO, and NCO are 0.31 Ω , 0.39 Ω , and 0.43 Ω , respectively, whereas that of the CO electrode is 1.03 Ω , indicating that ZNACO is a promising electrode with enhanced electrical conductivity (small sheet resistance) and fast charge transfer kinetics.

The improved electrochemical performance is likely attributed to the homogenous structure of the ZNACO with uniform distribution of Zn, Ni, Co and Al elements, the increased number of oxidation states, and the synergies between different metallic elements of the ZNACO electrode. This could be explained as follows: First, the incorporation of foreign Zn^{2+} into the Co_3O_4 lattice could lead to a change in the chemical environment of Co ions, which could facilitate the formation of Co^{4+} species ($\text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^-$) and thus contribute to the enhanced electrochemical activity[49,50]. Moreover, Zn doping is believed capable of increasing the number of active sites (Co^{3+}) on the surfaces of nanosheets, thus facilitating easy access of reaction species to the active sites.[49–51]Second, the incorporation of Ni element could produce more polarons, thus resulting in a

significant increase in electrical conductivity. Moreover, it offers rich redox reactions that enables multiple oxidation states (involving Ni^{2+} , Ni^{3+} , and Ni^{4+}), leading to high electrochemical activity (more active redox states)[5,49,52] Third, the incorporation of the smaller and more highly charged Al^{3+} ion could distort the octahedral symmetry of Co ligands, promoting the supposedly inert Co(III) to be further oxidized to Co(IV) and thus resulting in enhanced electrochemical activity[53–56]. Furthermore, despite playing little role as an active site, the redox-inactive Al^{3+} ions in ZNACO might still play some roles by assisting the reacting species in accessing the highly oxidized Co ions in the material, thereby allowing to undergo the redox reactions more efficient. Such improvements are due likely to the increase in surface area originated from the morphology change, i.e., smaller nanosheets formation caused by Al doping [57], as confirmed by BET results (Figure 1(g)). Finally, the synergistic effects between different metal cations (enhanced electrical conductivity and reduced charge transfer resistance or fast reaction kinetics as confirmed by EIS) should also be beneficial for the enhanced electrochemical performance of the ZNACO electrode. All in all, the enhanced performance of the ZNACO electrodes is attributed to the marked morphology change (i.e., smaller nanosheets formation caused by Al doping, which increases electrochemical surface area), the complementarities and synergetic effect of Al^{3+} and Zn^{2+} -doping-induced $\text{Co}^{3+}/\text{Co}^{4+}$ oxidation combined with Ni^{2+} -doping-induced $\text{Ni}^{3+}/\text{Ni}^{4+}$ oxidation.

Figure 4(d) shows some representative CV curves of ZNACO nanosheets electrode within the potential range of -0.1 and 0.5 V versus Hg/HgO at scan rates ranging from 1 to 30 mVs^{-1} . A pair of intense redox peaks within 0.1 to 0.5 V (versus Hg/HgO) can be clearly seen in all CV curves, indicating the strong battery-type behaviors of the as-obtained electrode[8,15]. The redox peaks were explicitly defined, which could

relate to the combined contributions from the redox reactions derived from cobalt-nickel oxide as shown in following reactions [5,58]:

In contrast to previous studies that observed separated redox peaks from CO[27], the electrodes fabricated herein exhibited only one pair of redox peaks, which has also been widely observed by others [5][58]. The absence of peak separation might be due to the well mixing of Zn, Ni, Al, and Co composites as revealed by the XRD and EDS analyses as well as the potential synergetic effects between Zn, Ni, Al and Co ions. It is also evident that the peak current increases with increasing the scan rate, suggesting a rapid diffusion-controlled electrolyte ion transport kinetic at the interface[4]. More interestingly, with the 30-fold increase in the sweep rate from 1 to 30 mV s^{-1} , the shape of the CV curves is not obviously changed and a pair of redox peaks is still visible with the cathodic peak shifts slightly from 0.31 to 0.25 V, suggesting this electrode configuration is beneficial to fast redox reactions because of the good contact between the electroactive ZNACO nanosheets and the conductive Ni foam substrate[8]. Figure 4(e) shows the typical GCD measurement of self-supported ZNACO nanosheets electrode at various current densities ranged from 1 to 20 Ag^{-1} with the voltage between 0 and 0.5 V (versus Hg/HgO). From Figure 4(d), it is evident that all these charging and discharging curves show a distinct plateau region between 0.3 and 0.2 V, which is consistent with the CV curves, confirming battery-type characteristics of the electrode[15]. The specific capacity of the self-supported ZNACO nanosheets electrode can be calculated based on the charge-discharge curves in Figure 4(d) according to equation (1) and the results are plotted in Figure 4(f), while the areal capacitances of the ZNACO

electrode as well as the ZNCO, NCO, ZCO and CO electrodes are presented in Figure S8 in supporting information. Encouragingly, the self-supported ZNACOnanosheets electrode exhibits high specific capacity of 839 (3.27 Fcm⁻²), 794 (3.1 Fcm⁻²), 791 (3.08 Fcm⁻²), 741 (2.89 Fcm⁻²), and 688 (2.68 Fcm⁻²) C g⁻¹ (here, C is the amount of charge in Coulomb) at the discharge current densities of 1, 2, 5, 10, and 20 A g⁻¹, respectively. This performance is better than that of CO nanowires (Figure S7(c), supporting information), NCO nanowires (Figure S7(f), supporting information), ZCO nanosheets (Figure S7(i), supporting information) and ZNCO nanosheets (Figure S7(m), supporting information) electrodes and other nanostructured MTMOs electrodes reported previously (Table S1, supporting information). More remarkably, the high capacity of 839 Cg⁻¹ at 1 Ag⁻¹ of self-supported ZNACO nanosheets electrode is maintained remarkably up to 82 % (688 Cg⁻¹) of that measured at 20 Ag⁻¹, higher than that of NCO nanowires (75%) (Figure S7(f), supporting information), ZCO nanosheets (63%) (Figure S7(i), supporting information) and ZNCO nanosheets (78%) electrodes (Figure S7(m), supporting information), indicating its outstanding rate capability. Figure 4(e) shows the long-term cycling performance of self-supported ZNACO nanosheets electrode at a high current density of 20 Ag⁻¹ over 5,000 cycles. It can be observed that the specific capacity of the ZNACO nanosheets electrode increases slightly for the initial 1,000 cycles, which may due to the gradual activation of the electrode [26,28,29,59]and fades very slowly after that, illustrating the excellent long-term electrochemical stability of the ZNACO nanosheets electrode. Even after 5,000 cycles, the specific capacity is still slightly larger than the value of the first cycle. Additoanlly, the long-term electrochemical stability can be further verified by the very stable charge/discharge curve for last ten cycles (inset of Figure 4(f)). After

long-term cycling, the porous nanosheets morphology of ZNACO (Figure S9, supporting information) is well maintained and these nanosheets are still attached on the surface of Ni foam, demonstrating excellent cycling stability. It is noted that the Al content in ZNACO is found to influence the electrochemical performance of ZNACO electrode (Figure S10, supporting information). The specific capacity is observed to decrease significantly when too much Al was incorporated in ZNACO, indicating that proper incorporation of Al into ZNACO is an effective approach to enhance performance.

Figure 4. (a) Typical CV curves of self-supported CO nanowires, NCO nanowires, ZCO nanosheets, ZNCO nanosheets and ZNACO nanosheets electrodes at a scan rate

of 5 mVs^{-1} , (b) their corresponding GCD curves at a current density of 5 Ag^{-1} , (c) Nyquist plots of cells with ZNACO, ZNCO, NCO, and CO electrodes, inset is the impedances at the high frequency region (d) typical CV curves of the self-supported ZNACO nanosheets electrode at various scan rates ranging from 1 to 30 mVs^{-1} , (e) its corresponding GCD curves at various current densities ranging from 1 Ag^{-1} to 20 Ag^{-1} , (f) its corresponding specific capacity as a function of current density and (g) long-term cyclic performance of ZNACO nanosheets electrode at a current density of 20 Ag^{-1} (corresponding charge/discharge curves of the last 10 cycles for the 5000 cycles is shown in inset).

To further evaluate the self-supported ZNACO nanosheets electrode for practical supercapacitors application, we fabricate a hybrid supercapacitor with self-supported ZNACO nanosheets electrode as the positive electrode and active carbon (AC) (Figure S11, supporting information) as the negative electrode (identified as ZNACOs//AC hybrid supercapacitor). According to the CV studies for the individual ZNACO and AC electrodes (Figure S12, supporting Information), the mass ratio of the positive electrode to the negative electrode is optimized to 0.312 to balance the charge between positive and negative electrodes. With the as-made ZNACO nanosheets as the positive electrode, an aqueous hybrid supercapacitor is assembled, whereby the negative electrode is made of AC as shown in Figure 5(a). Figure 5(b) shows the typical CV curves of an as-fabricated ZNACOs//AC hybrid supercapacitor at different scan rates in the potential range of 0–1.5 V in 2 M KOH aqueous electrolyte. A pair of well-defined redox peaks between 0.8V~1.5 V are visible in all CV curves, indicating battery-type behavior of the as-fabricated ZNACOs//AC hybrid supercapacitor. Its corresponding galvanostatic charge/discharge curves at various current densities are present in Figure 5(c), showing that these discharge curves are

slightly nonlinear with the potential, which is in congruent with CV results. The specific capacitance of ZNACOs//AC hybrid supercapacitor is calculated to be 232, 215, 192, 166, 134, and 73 F g^{-1} at current densities of 0.5, 1, 2.5, 5, 10, and 25 A g^{-1} (based on the total mass of active materials from both positive and negative electrodes), respectively, as seen in Figure 5(d), from its galvanostatic charge-discharge curves (Figure 5(b)) according to the equation (2). Figure 5(e) reveals the cycling performance of ZNACO//AC hybrid supercapacitor measured at a current density of 10 A g^{-1} up to 10,000 cycles. Impressively, ~90% of its initial specific capacitance can be maintained after 10,000 cycles, illustrating the excellent long-term electrochemical stability of the hybrid supercapacitor device.

Energy and power density are the two most important performance parameters of supercapacitors, which can be calculated from the GCD curves of the hybrid supercapacitors using the following equations: [4].

$$E = \frac{I \int V dt}{m} \quad (6)$$

$$P = \frac{E}{\Delta t} \quad (7)$$

where E is energy density (Wh kg^{-1}), P is power density (W kg^{-1}), I is the charge-discharge current, V(t) is the cell voltage, dt is the time differential, m is the total mass of the positive and negative electrode materials, and Δt is the discharging time. Figure 5(f) presents a Ragone plot (energy density vs. power density) for the ZNACO//AC hybrid supercapacitor, demonstrating an energy density of 72.4 Wh kg^{-1} at a power density of 533 W kg^{-1} and energy density of 22.7 Wh kg^{-1} even at a power density of 24.77 kW kg^{-1} , superior to many systems reported previously, such as hollow NiCo_2O_4 spheres//AC[60], flower-like NiCo_2O_4 microspheres//AC[61], NiWO_4 //AC[62], CoMoO_4 //AC[63], Co_3O_4 //AC[64], CuCo_2O_4 //AC[65], urchin-like NiCo_2O_4 microspheres//AC[66] and ZnCo_2O_4 nanowires//AC[67]. Furthermore, a

simple application to power a commercial light-emitting diode (LED) is demonstrated. After being charged to 3V, two hybrid supercapacitors connected in series can easily light a 5 mm diameter green round LED indicator with a working voltage of 2.1 V as shown in inset of Figure 5(e) (see corresponding video file in supporting Information)

Figure 5. (a) Schematic illustration of the ZNACO//AC hybrid supercapacitor configuration, electrochemical performance of the ZNACO//AC hybrid supercapacitor of (b) cyclic voltammetry curves, (c) galvanostatic charge/discharge curves, (d) cell capacitance vs current density, (e) cycling stability performance at a

current density of 10 Ag^{-1} , inset is its corresponding charge/discharge curves of the last 5 cycles and **photograph of a green round LED indicator powered by two hybrid supercapacitors**, and (f) Ragone plot (energy density vs power density).

The improved electrochemical performance of the self-supported ZNACO nanosheets is attributed largely to their unique architecture and compositional advantages. First, the mesoporous feature of the ZNACO nanosheets and large open spaces among neighboring interconnected nanosheets enable the full exposure of active materials to electrolyte, thus greatly enhancing ion and electron transport, which is vital to high rate capability and large capacity. It also alleviates the volume change during the repeated cycling and prevents the agglomeration of active materials, leading to superior cycling stability[8,26]. Second, the formation of mixed valence states at these multi-metal centers in the spinel ZNACO and their synergetic effects between different ions render the desirable electronic conductivity for efficient energy storage and provide rich redox reactions involving different ions for high specific capacity[24,36]. Moreover, the direct attachment and close contact of ZNACO nanosheets on a highly conductive Ni foam substrate could ensure good mechanical adhesion and more importantly build up an express path for fast electron transport, important to outstanding rate capability[27]. Furthermore, the integrated 3D porous electrode architectures could ensure every ZNACO nanosheet to participate in the ultrafast electrochemical reaction and allow facile electrolyte ion access for fast redox reactions, which would contribute to the specific capacity and lead to enhanced rate performance[26]. Finally, the complex chemical compositions and their synergetic effects among different metallic elements in ZNACO nanosheets may favor for achieving high electrochemical activities, leading to enhanced electrochemical

performance.

Conclusion

In summary, 3D hierarchical, porous quaternary ZNACO nanosheets grown directly on Ni foam as binder-free electrodes for hybrid supercapacitors have been successfully prepared through a facile and easy scale up CBD process combined with a simple post-annealing treatment. The resultant electrodes exhibit high specific capacity (839 Cg^{-1} at 1 Ag^{-1}) and outstanding rate capability (688 Cg^{-1} at 20 Ag^{-1}), owing to their structural and compositional advantages. A hybrid supercapacitor using self-supported ZNACO nanosheets as the positive electrode and AC as the negative electrode has also been successfully fabricated, which delivers high energy of 72.4 Wh kg^{-1} at a power density of 533 W kg^{-1} while maintaining outstanding cycle life (a capacitance loss of only around 10 % even after 10,000 cycles). Such a protocol to construct 3D hierarchical mesoporous mixed TMOs nanosheets may hold great potential for construction of other nanostructured electrode materials for high-performance hybrid supercapacitors; it may also find applications in a wide range devices for chemical and energy transformation.

Acknowledgments

This work was supported by Hong Kong Research Grants Council (grant no. CityU 11216815), NSAF (grant no. U1330132) and the US National Science Foundation (DMR-1410320)

References

- [1] G. Zhang, X. Lou, *Adv. Mater.* 25 (2012) 976.
- [2] G. Wang, L. Zhang, J. Zhang, *Chem. Soc. Rev.* 41 (2012) 797.
- [3] V. Augustyn, P. Simon, B. Dunn, *Energy Environ. Sci.* 7 (2014) 1597.
- [4] X. Xiong, G. Waller, D. Ding, D. Chen, B. Rainwater, B. Zhao, Z. Wang, M. Liu, *Nano Energy* 16 (2015) 71.
- [5] D.P. Dubal, P. Gomez-Romero, B.R. Sankapal, R. Holze, *Nano Energy* 11 (2015) 377.
- [6] J. Wang, X. Zhang, Q. Wei, H. Lv, Y. Tian, Z. Tong, X. Liu, J. Hao, H. Qu, J. Zhao, Y. Li, L. Mai, *Nano Energy* 19 (2016) 222.
- [7] G. Zhang, H. Wu, H. Hoster, M. Chan-Park, X. Lou, *Energy Environ. Sci.* 5 (2012) 9453.
- [8] C. Yuan, J. Li, L. Hou, X. Zhang, L. Shen, X. Lou, *Adv. Funct. Mater.* 22 (2012) 4592.
- [9] Z. Yu, L. Tetard, L. Zhai, J. Thomas, *Energy Environ. Sci.* 00 (2015) 1.
- [10] Z. Chen, J. Wen, C. Yan, L. Rice, H. Sohn, M. Shen, M. Cai, B. Dunn, Y. Lu, *Adv. Energy Mater.* 1 (2011) 551.
- [11] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X.W. Lou, *Adv. Mater.* 24 (2012) 5166.
- [12] L. Qu, Y. Zhao, A.M. Khan, C. Han, K.M. Hercule, M. Yan, X. Liu, W. Chen, D. Wang, Z. Cai, W. Xu, K. Zhao, X. Zheng, L. Mai, *Nano Lett.* 15 (2015) 2037.
- [13] Y. Peng, Z. Chen, J. Wen, Q. Xiao, D. Weng, S. He, H. Geng, Y. Lu, *Nano*

- Res. 4 (2011) 216.
- [14] C. Guan, J. Liu, Y. Wang, L. Mao, Z. Fan, Z. Shen, H. Zhang, J. Wang, ACS Nano (2015) 5198.
- [15] T. Brousse, D. Belanger, J.W. Long, J. Electrochem. Soc. 162 (2015) A5185.
- [16] G.X. Pan, X.H. Xia, F. Cao, J. Chen, Y.J. Zhang, Electrochim. Acta 173 (2015) 385.
- [17] T.-W. Lin, M.-C. Hsiao, S.-W. Chou, H.-H. Shen, J.-Y. Lin, J. Electrochem. Soc. 162 (2015) 1493.
- [18] L. Huang, D. Chen, Y. Ding, S. Feng, Z.L. Wang, M. Liu, ACS Appl. Mater. Interfaces 5 (2013) 11159.
- [19] T. Wang, Y. Guo, B. Zhao, S. Yu, H.P. Yang, D. Lu, X.Z. Fu, R. Sun, C.P. Wong, J. Power Sources 286 (2015) 371.
- [20] P. Hao, Z. Zhao, L. Li, C.-C. Tuan, H. Li, Y. Sang, H. Jiang, C.P. Wong, H. Liu, Nanoscale 7 (2015) 14401.
- [21] T. Brezesinski, J. Wang, S.H. Tolbert, B. Dunn, Nat. Mater. 9 (2010) 146.
- [22] C.. Guan, Y.. Wang, Y.. Hu, J.. Liu, K.H.. Ho, W.. Zhao, Z.. Fan, Z.. Shen, H.. Zhang, J.. Wang, J. Mater. Chem. A 3 (2015) 23283.
- [23] C. Guan, Y. Wang, M. Zacharias, J. Wang, H.J. Fan, Nanotechnology 26 (2015) 014001.
- [24] C. Yuan, H. Bin Wu, Y. Xie, X.W.D. Lou, Angew. Chem. Int. Ed. Engl. 53 (2014) 1488.
- [25] S. Peng, L. Li, H. Bin Wu, S. Madhavi, X.W.D. Lou, Adv. Energy Mater. 5

- (2015) n/a.
- [26] L. Shen, Q. Che, H. Li, X. Zhang, *Adv. Funct. Mater.* (2013) DOI: 10.1002/adfm.201303138.
- [27] F. Zhang, C. Yuan, X. Lu, L. Zhang, Q. Che, X. Zhang, *J. Power Sources* 203 (2012) 250.
- [28] X. Xia, J. Tu, Y. Zhang, X. Wang, C. Gu, X.-B. Zhao, H.J. Fan, *ACS Nano* 6 (2012) 5531.
- [29] K. Xiao, L. Xia, G. Liu, S. Wang, L.-X. Ding, H. Wang, *J. Mater. Chem. A* 3 (2015) 6128.
- [30] B. Liu, B. Liu, Q. Wang, X. Wang, Q. Xiang, D. Chen, G. Shen, *ACS Appl. Mater. Interfaces* 5 (2013) 10011.
- [31] K. Xu, R. Zou, W. Li, Q. Liu, X. Liu, L. An, J. Hu, *J. Mater. Chem. A* (2014) 10090.
- [32] S. Wang, J. Pu, Y. Tong, Y. Cheng, Y. Gao, Z. Wang, *J. Mater. Chem. A* 2 (2014) 5434.
- [33] Q. Yang, Z. Lu, J. Liu, X. Lei, Z. Chang, L. Luo, X. Sun, *Prog. Nat. Sci. Mater. Int.* 23 (2013) 351.
- [34] J. Huang, T. Lei, X. Wei, X. Liu, T. Liu, D. Cao, J. Yin, G. Wang, *J. Power Sources* 232 (2013) 370.
- [35] J. Tang, D. Liu, Y. Zheng, X. Li, X. Wang, D. He, *J. Mater. Chem. A* 2 (2014) 2585.
- [36] G. Xiong, P. He, L. Liu, T. Chen, Fisher Timothy S, 3 (2015) 1.

- [37] L.-Q. Mai, A. Minhas-Khan, X. Tian, K.M. Hercule, Y.-L. Zhao, X. Lin, X. Xu, *Nat. Commun.* 4 (2013) 2923.
- [38] L. Zhu, Z. Wen, W. Mei, Y. Li, Z. Ye, *J. Phys. Chem. C* 117 (2013) 20465.
- [39] G. Zhang, X. Lou, *Sci. Rep.* 3 (2013) 1470.
- [40] J. Li, S. Xiong, Y. Liu, Z. Ju, Y. Qian, *ACS Appl. Mater. Interfaces* 5 (2013) 981.
- [41] W. Luo, X. Hu, Y. Sun, Y. Huang, *J. Mater. Chem.* 22 (2012) 8916.
- [42] L. Batteries, R. Wu, X. Qian, K. Zhou, J. Wei, J. Lou, P.M. Ajayan, *ACS Nano* (2014) 6297.
- [43] L. Yu, L. Zhang, H. Bin Wu, G. Zhang, X.W. (David) Lou, *Energy Environ. Sci.* 6 (2013) 2664.
- [44] G.. b Xiong, P.. b c He, L.. Liu, T.. Chen, T.S.. b Fisher, *J. Mater. Chem. A* 3 (2015) 22940.
- [45] C. Shang, S. Dong, S. Wang, D. Xiao, P. Han, X. Wang, L. Gu, G. Cui, *ACS Nano* (2013).
- [46] J. Xu, S. Gai, F. He, N. Niu, P. Gao, Y. Chen, P. Yang, *Dalt. Trans.* 43 (2014) 11667.
- [47] Q. Yang, Z. Lu, X. Sun, J. Liu, *Sci. Rep.* 3 (2013) 3537.
- [48] H. Xia, D. Zhu, Z. Luo, Y. Yu, X. Shi, G. Yuan, J. Xie, *Sci. Rep.* 3 (2013) 2978.
- [49] X. Zhang, J. Zhang, K. Wang, *ACS Appl. Mater. Interfaces* 7 (2015) 21745.
- [50] X. Liu, Z. Chang, L. Luo, T. Xu, X. Lei, J. Liu, X. Sun, *Chem. Mater.* 26

- (2014) 1889.
- [51] X. Zou, A. Goswami, T. Asefa, J. Am. Chem. Soc. 135 (2013) 17242.
  - [52] Y. Li, P. Hasin, Y. Wu, Adv. Mater. 22 (2010) 1926.
  - [53] P. Yee, K. Keat, Y. Ng, C. Haur, W. Shong, Electrochem. Commun. 43 (2014) 9.
  - [54] V. Gupta, S. Gupta, N. Miura, J. Power Sources 177 (2008) 685.
  - [55] D.H. Buss, J. Bauer, W. Diembeck, O. Glemser, J. Chem. Soc. Chem. Commun. (1985) 81.
  - [56] J. Melorose, R. Perroy, S. Careas, Statew. Agric. L. Use Baseline 2015 1 (2015).
  - [57] M. Gong, Y. Li, H. Zhang, B. Zhang, W. Zhou, J. Feng, H. Wang, Y. Liang, Z. Fan, J. Liu, H. Dai, Energy Environ. Sci. 7 (2014) 2025.
  - [58] Y. Zhang, L. Li, H. Su, W. Huang, X. Dong, J. Mater. Chem. A 3 (2015) 43.
  - [59] X. Liu, S. Shi, Q. Xiong, L. Li, ACS Appl. Mater. Interfaces 5 (2013) 8790.
  - [60] X. Li, L. Jiang, C. Zhou, J. Liu, H. Zeng, NPG Asia Mater. 7 (2015) e165.
  - [61] J. Zhang, F. Liu, J.P. Cheng, X.B. Zhang, ACS Appl. Mater. Interfaces 7 (2015) 17630.
  - [62] L. Niu, Z. Li, Y. Xu, J. Sun, W. Hong, X. Liu, J. Wang, S. Yang, ACS Appl. Mater. Interfaces 5 (2013) 8044.
  - [63] X. Yu, B. Lu, Z. Xu, Adv. Mater. 26 (2014) 1044.
  - [64] X. Zhang, Y. Zhao, C. Xu, Nanoscale 6 (2014) 3638.
  - [65] A. Pendashteh, S.E. Moosavifard, M.S. Rahmanifar, Y. Wang, M.F. El-Kady,

- R.B. Kaner, M.F. Mousavi, Chem. Mater. (2015) 150420104203005.
- [66] Y. Lei, Y. Wang, W. Yang, H. Yuan, D. Xiao, RSC Adv. 5 (2014) 7575.
- [67] B. Guan, D. Guo, L. Hu, G. Zhang, T. Fu, W. Ren, J. Li, Q. Li, J. Mater. Chem. A 2 (2014) 16116.