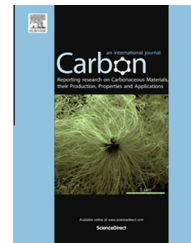


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# In situ co-deposition of nickel hexacyanoferrate nanocubes on the reduced graphene oxides for supercapacitors

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## ABSTRACT

A facile co-precipitation strategy is developed to prepare nickel hexacyanoferrate nanocubes (NiHCF NBs) supported on the reduced graphene oxide (rGO) in the presence of poly(diallyldimethylammonium chloride) (PDDA). The NiHCF NBs are uniformly deposited on the rGO by electrostatic interaction. Their size can be tuned from 10 nm to 85 nm by changing their content from 32.6% to 68.2%. Under the optimal condition, NiHCF/PDDA/rGO hybrids are composed of 51.4% NiHCF NBs with an average size of 38 nm. The specific capacitance of NiHCF/PDDA/rGO hybrids reaches up to 1320 F g<sup>-1</sup> at a discharge density of 0.2 A g<sup>-1</sup>, more than twice that of the pure NiHCF, as well as slight capacitance decay by 15% at 0.2 A g<sup>-1</sup> and excellent cycling stability with 87.2% of its initial capacitance after 10,000 discharge/charge cycles. More importantly, NiHCF/PDDA/rGO hybrids exhibit an ultrahigh energy density of 58.7 Wh kg<sup>-1</sup> at the power density of 80 W kg<sup>-1</sup>. The superior storage energy performance of NiHCF/PDDA/rGO hybrids, such as high specific capacitance, good rate capacity and long cycling stability, positions them as a promising candidate for supercapacitor materials.

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## 1. Introduction

Ever increasing demand for sustainable and environmentally-friendly energy has speed up the pursuit of alternative energy conversion/storage systems, including fuel cells, solar cells, secondary lithium-ion batteries and supercapacitors [1]. Among them, supercapacitors are superior in term of ultralong cycling stability, high power density and fast

charge/discharge rate [2,3], demonstrating feasibility in potential application, such as portable electronics, back-up power storage and hybrid electric vehicles [4,5]. However, their typical energy density, <10 Wh kg<sup>-1</sup>, is the lowest, e.g., in comparison with ca. 200 Wh kg<sup>-1</sup> of a lithium secondary battery, limiting their practical use as primary power sources for quick start of a hybrid vehicle in conjunction with a battery [1].

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Supercapacitors can be divided into the electrical double layer capacitors (EDLCs) and pseudocapacitors on the basis of the energy storage mechanism. The EDLCs performance depends on the available surface area of the electrodes and the finite charge separation between the electrode materials and the electrolyte. But for pseudocapacitor, the energy storage capability was determined by the fast and reversible faradic reaction near the surface [6]. Pseudocapacitor can provide with a huge specific capacitance, which far exceeds that of an EDLC. Most of pseudocapacitors are based on redoxable transition metal oxides/hydroxides [7–9] and conducting polymers [10,11]. They are poor in conductivity, and usually suffer from cycling stability due to swelling and shrinkage of the electroactive species during charge/dedoping process [12]. On the other hand, EDLCs are made of carbonaceous materials [2,13], they are highly conductive and maintain particularly stable during the long running process. Therefore, supercapacitors can be commercialized in hope of a perfect combination of these pseudocapacitive materials with the high-surface-area carbonaceous materials [14].

Recently, transition metal hexacyanoferrates (MHCF, M represents as Fe, Co, Ni, et al.), a zeolite-like Prussian blue coordination compound, attract increasing interest in application as supercapacitors due to their unique structure, low cost, reversible redox ability and superior environmental benignancy [15–17]. Lisowaka-Oleksiak et al. [15] prepared MHCF network inside poly(3,4-ethylenedioxythiophene) (PEDOT) films for electrochemical capacitors by the electrochemical deposition process. Specific capacitance of hybrid materials is equal to 70, 70 and 50 F cm<sup>-3</sup> for PEDOT/CoHCF, PEDOT/NiHCF and PEDOT/FeHCF, respectively. Chen et al. synthesized nanosized NiHCF by co-precipitation method. The specific capacitance of NiHCF was 574.7 F g<sup>-1</sup> obtained at the current density of 0.2 A g<sup>-1</sup> with 91% capacitance retention over 1000 charge/recharge cycles [16].

Graphene has been considered as an ideal electrode materials for supercapacitors because of its extremely high theoretical surface area (2630 m<sup>2</sup> g<sup>-1</sup>) and a superior theoretical capacitance (550 F g<sup>-1</sup>) [18,19]. Herein, we demonstrate an in situ co-precipitation strategy to prepare NiHCF nanocubes (NBs) supported on the reduced graphene oxide (rGO) in the presence of poly(diallyldimethylammonium chloride) (PDDA). In this composite, PDDA serves as a stabilizer for rGO in the process of chemical reduction; it also acts as a linker to anchor NiHCF nanocubes onto the surface of rGO. The rGOs function as the substrate upon which to deposit the NiHCF NBs. Besides, the rGOs improve the electrical conductivity of the hybrids, and increase the effective utilization of NiHCF. As a result, the NiHCF/PDDA/rGO hybrids possess a huge specific capacitance, excellent rate capacity and superior cycling stability, providing with a promising candidate for supercapacitors in commercial utility.

## 2. Experimental

### 2.1. Chemicals and materials

Graphite powders (320 meshes) and PDDA (20%, Mw ca. 65,000) were purchased from Acros. NaNO<sub>3</sub>, KMnO<sub>4</sub>,

K<sub>3</sub>[Fe(CN)<sub>6</sub>], Ni(NO<sub>3</sub>)<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> (98%) and H<sub>2</sub>O<sub>2</sub> (30%) were obtained from Shanghai reagent Co. Inc. Water was purified by a Milli-Q system.

### 2.2. Preparation of graphene oxide (GO)

GO was synthesized by slight modification to Hummer's method [20]. Graphite powder (0.4 g), NaNO<sub>3</sub> (0.4 g) and H<sub>2</sub>SO<sub>4</sub> (20 mL) were cooled and sonicated in an ice bath for 20 min. Then 2.4 g of KMnO<sub>4</sub> was added slowly into the graphite powder solution at 20 °C, and the mixture was vigorously stirred at 35 °C for 4 h. The oxidation step was stopped by dropwise addition of 20 mL de-ionized water and 12 mL H<sub>2</sub>O<sub>2</sub> (30%) solution, and the GO solution was washed and filtrated with 200 mL HCl (1 M). In order to remove ion and excess acid, this GO solution was dispersed in de-ionized water and dialyzed for 1 week until its pH value increased from 4 to 6.

### 2.3. Preparation of PDDA/rGO hybrids

PDDA/rGO hybrids were prepared according to the reference in the presence of PDDA [21]. In brief, 20% PDDA (0.5 mL) solution was added to 0.05% GO solution (100 mL) and stirred for 30 min. The pH value of the mixture were adjusted to 10 by 30% NH<sub>3</sub>·H<sub>2</sub>O. Then 80% hydrazine hydrate (0.5 mL) was introduced. GO were reduced in the presence of PDDA under stirring for 24 h at 90 °C. Finally, the PDDA/rGO hybrids were recovered by centrifugation, and the precipitates washed with distilled water, and then re-dispersed readily in water to form a black suspension.

The preparation of pure rGO was similar to that of PDDA/rGO, except that no PDDA was added.

### 2.4. Preparation of NiHCF/PDDA/rGO hybrids

NiHCF/PDDA/rGO hybrids were prepared by co-precipitation of K<sub>3</sub>[Fe(CN)<sub>6</sub>] and Ni(NO<sub>3</sub>)<sub>2</sub> on the surface of PDDA/rGO hybrids in acid aqueous solution. A certain amount of K<sub>3</sub>[Fe(CN)<sub>6</sub>] (20 mM) were added into 50 mL PDDA/rGO dispersion (0.2 mg mL<sup>-1</sup>) in batches. The Fe(CN)<sub>6</sub><sup>3-</sup> will be adsorbed on to the surface of PDDA/rGO hybrids due to electrostatic interaction. This process will proceed under ultrasonic wave for 4 h. The mixture were adjusted to pH 1.0 by HCl, then a certain amount of NiNO<sub>3</sub> (20 mM) equal to K<sub>3</sub>[Fe(CN)<sub>6</sub>] were added and stirred for 4 h. The resulting NiHCF/PDDA/rGO hybrids were collected by centrifugation and washed with de-ionized water and ethanol.

For comparison, the hybrids, K<sub>3</sub>[Fe(CN)<sub>6</sub>] adsorbed on to the rGo is prepared according to the synthesis of the NiHCF/PDDA/rGO hybrids without addition of Ni<sup>2+</sup> ion (Fe(CN)<sub>6</sub><sup>3-</sup>/PDDA/rGO). The pure NiHCF was also prepared in the strategy similar to that of NiHCF/PDDA/rGO hybrids without PDDA/rGO hybrids.

### 2.5. Characterization

Thermogravimetric analysis (TGA) was recorded on Netzsch STA 449 C analyzer at a heating rate of 10 °C/min under nitrogen.

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