



# Synthesis of Graphene Oxide by Modified Hummers Method and Hydrothermal Synthesis of Graphene-NiO Nano Composite for Supercapacitor Application

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## Abstract

Graphene oxide was synthesized by using modified Hummers method and also Graphene-NiO nanocomposite prepared by hydrothermal method with the use of graphene oxide solution,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and urea as raw materials. The synthesized nanocomposite was characterized by the XRD, Raman, SEM, TGA and energy dispersive spectrometer analysis. The results demonstrate that NiO nano particles uniformly covered on the surface of the graphene layer and Raman spectroscopy states that well formation of the Graphene-NiO Nano composite. CV curves of Graphene-NiO electrodes at different scan rates conveys that capacitance characteristic is very different from that of traditional electric double-layer capacitance in which the shape is normally an ideal rectangular shape. Therefore, cyclic voltammetry analysis is the evidence of these materials are having the ability of supercapacitor electrode material properties. TGA Analysis is used for the estimation of how much of graphene is exist in the Graphene-NiO nanocomposite.

**Keywords:** Graphene; Nanocomposite; Material; Capacitance; Pseudocapacitors

## Introduction

Graphene is a one-atom thick structure of  $\text{sp}^2$ -bonded carbon atoms. These carbon atoms are densely packed in a honeycomb crystal lattice structure. Since the detection in 2004, graphene has attracted fabulous research interest in energy-storage technologies due to its unusual properties, like great mechanical strength, large specific surface area and high electrical conductivity [1]. A lot of scientists said that graphene would be a competitive material for energy storage applications like batteries, solar cells and super capacitors etc. [2,3]. Now days, a lot of research has been launched into the development of graphene-based nanocomposites for supercapacitor applications, particularly for nano-composites that consist of graphene and transition-metal oxides such as  $\text{MnO}_2$ ,  $\text{ZnO}$ ,  $\text{NiO}$ ,  $\text{Co}_3\text{O}_4$  because they combine the advantages of both components and may offer special properties through the reinforcement or modification of each other [4]. Several graphene and transition-metal oxide nanocomposites such as graphene-NiO, graphene- $\text{MnO}_2$ , graphene- $\text{Mn}_3\text{O}_4$ , graphene- $\text{Bi}_2\text{O}_3$ , graphene- $\text{Co}_3\text{O}_4$  and graphene-  $\text{ZnO}$ , have been exploited and improved performance of pseudo supercapacitor has been found in these type of composite systems [5].

Electrochemical capacitors, which are also called as supercapacitors, are widely investigated due to their interesting properties in terms of fast recharge capability and high power density [6-8]. Depends upon the charge-storage mechanism, electrochemical supercapacitors can be divided into (a) Electrical Double-layer capacitors (EDLCs), in which capacitance arises from charge separation between electrode-electrolyte interface, and (b) pseudocapacitors concerns reversible redox reactions, in which the dominant process is of pseudo capacitive origin. Till now, carbon materials are widely used as electrode materials for EDLCs due to their good cycle life, large surface area, good processing ability and low cost [9-12]. However, carbon materials have some drawback like it suffers from low specific capacitance [13-16]. To improve energy and power densities, much effort has been dedicated to investigate pseudo capacitive transition-metal oxides which give higher capacitance due to multi electron transfer during fast faradaic reactions [17-21].

Transition-metal oxides can be separated into two groups: one is noble-metal oxides and another one is cheap-metal oxides. One example for the first one is  $\text{RuO}_2$ , whereas  $\text{Na}_x\text{MnO}_2$ ,  $\text{K}_x\text{MnO}_2$ ,  $\text{NiO}$ , and  $\text{Co}_3\text{O}_4$  are well-known as examples of the second one. Various forms of  $\text{RuO}_2$  exhibit superior electrochemical response [22-26]. Unluckily, the cost of  $\text{RuO}_2$  has limited its technological viability. So,  $\text{NiO}$  is considered to be a promising alternative for electrode materials in redox electrochemical capacitors because of its low cost, high capacitance, ease of synthesis [27-30].

The addition of graphene in electrochemical supercapacitors requires a graphene film synthesized on a large-scale with decent uniformity. There are numerous deposition techniques available for the synthesis of graphene like chemical reduction of graphite oxide, chemical vapour deposition, epitaxial growth and vacuum filtration [31-36]. Up to now, the graphene is prepared by the GO film reduction. These are still of great value due to its low-cost, ease of process and low-temperature [37]. Hence nickel oxide ( $\text{NiO}$ ) among many transition metal oxides, shows outstanding cycle-life stability and high specific capacitance resulting from fast electron and ion transport, excellent structural stability and large Electro active surface area [2]. But these superior properties vary tremendously depending upon preparation methods [38,39].

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## Experimental Procedure

### Required chemicals

Graphite Flakes (acid treated 99%, Asbury Carbons), Potassium permanganate (99%, RFCL), Sodium nitrate (98%, Nice chemicals), Hydrogen peroxide (40% wt, Emplura), Sulphuric acid (98%, ACS), Hydrochloric acid (35%, RANKEM),  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and Urea.

### Graphene oxide preparation by using modified Hummer's method

Graphene oxide (GO) was prepared from graphite flakes by using modified Hummer's method. The step by step synthesis is as follows :

1.2 g of Graphite flakes and 2 g of  $\text{NaNO}_3$  and 50 ml of  $\text{H}_2\text{SO}_4$  (98%) were mixed in a 1000 ml volumetric flask kept under at ice bath (0-6°C) with stirring continuously.

2. The sample mixture was stirred for 2 hrs at the same temperature and 6 g of potassium permanganate ( $\text{KMnO}_4$ ) was added to the suspension very slowly. The addition rate was controlled carefully to preserve the reaction temperature lower than 14°C.

3. Then the ice bath was removed, and the sample mixture was stirred at 30°C til it became pasty brownish and kept under stirring for 2 hrs. For every half an hour, increase the temperature.

4. Then it was weakened with the slow addition of 100 ml of water. The reaction temperature was increased quickly to 96°C with effervescence, and the color changes to brown type of color.

5. Further, this solution mixture was weakened by the addition of 200 ml of water stirred continuously.

6. The solution mixture was finally treated with 8 ml  $\text{H}_2\text{O}_2$  to terminate the reaction by the form of yellow colour.

7. For purification, the mixture was washed by centrifugation and rinsing with 8% HCL and then deionized (DI) water for various times.

8. After filtration and then it dried in hot air oven, the graphene Oxide (GO) was obtained as a powder.

### Preparation of graphene-NiO nano composite by hydrothermal method

1. Firstly, 2.98 g nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was dissolved in 8 ml of deionized water and added into 20 ml graphene oxide with stirring for 60 min.

2. The pH of the solution was maintained to around 8.0 by the addition of 20 ml urea drop by drop.

3. The solution mixture was stirred forcefully for 60 min to mix equally and transferred into a 100 ml steel autoclave. Then the autoclave was sealed, moved into muffle furnace and kept at 150°C for 5 h.

4. After that the autoclave cools down to room temperature, the solution mixture was vacuum-filtered to get the precursor then washed with ethanol and DI water 2 or 3 times to remove the probable absorbed ions, metal salts and remained raw material, then dried at 80°C for 12 hrs.

5. At last, the obtained precursor was calcinated at 400°C for 4 h in a muffle furnace. Then the Graphene-NiO nanocomposite was obtained after calcination and collected for characterization.

6. For comparison, pure NiO was also prepared by the same process without GO.

7. The graphene was synthesized by pyrolyzing dried GO in  $\text{N}_2$  atmosphere at the same temperature with hybrid material (400°C for 4 h).

### Characterization

The obtained precursors were characterized by X-ray powder diffraction (XRD), Field-emission scanning electron microscopy (SEM), EDS and Raman spectroscopy.

### Electrochemical tests

Electrochemical tests were investigated by Electrochemical Work station. The three-electrode cell consists of Ag/AgCl as reference electrode and Platinum (Pt) foil as counter electrode. The working electrode was prepared by mixing the Active material (1 mg), Ethanol (1 ml) and Nafion solution (1 ml) and sonicated it for 30 min to form gel. And this Gel was dropped onto the Working electrode and dried it overnight. The electrolyte was 1 M  $\text{H}_2\text{SO}_4$  aqueous solution.

### Results and Discussions

X-ray diffraction analysis was done to know the crystal size and crystal phase and structure of the synthesized samples (Figure 1). The diffraction peaks related to pure Cubic NiO occurs at  $2\theta=37.1^\circ, 43.1^\circ, 62.7^\circ, 75.3^\circ, 79.2^\circ$  can be readily written as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystal planes, and the widening of the diffraction peaks advises a very small size of NiO nanoparticles. The average grain size of pure NiO and G-NiO are 80 nm and 12 nm calculated by using Scherer's formula ( $D = 0.89\lambda/B \cos\theta$ ). It is clearly show that the particle size of pure NiO is larger than that of G-NiO and it is mostly due to the presence of graphene. In the G-NiO sample, there is no distinctive peak of Graphene oxide ( $2\theta=10.9^\circ$ ) or graphite Flakes ( $2\theta=24.6^\circ$ ), advising that the graphene oxide was well condensed.

Figure 2 shows the Raman spectrum of Graphene-NiO and NiO. Four Raman peaks positioned at about 383, 521, 710 and 1092  $\text{cm}^{-1}$  are detected in both spectra, equivalent to the shaking peaks of NiO. The first two peaks could be recognized to the 1<sup>st</sup> order transverse optical and longitudinal optical phonon types of NiO, respectively. The peaks at 710 and 1092  $\text{cm}^{-1}$  could be allotted to 2<sup>nd</sup> order transverse optical and longitudinal optical phonon modes of NiO. For graphene-NiO Nanocomposite, the Raman peaks of D line and G line is allotted to the  $E_{2g}$  phonon of Carbon  $\text{sp}^2$  atoms, and the D line is a living mode of k-point phonons of  $A_{1g}$  symmetry. The remaining peaks are in agreement with the pure nickel oxide. Such a result further confirms that the crystalline structure of graphene-NiO nanocomposite has been obtained.

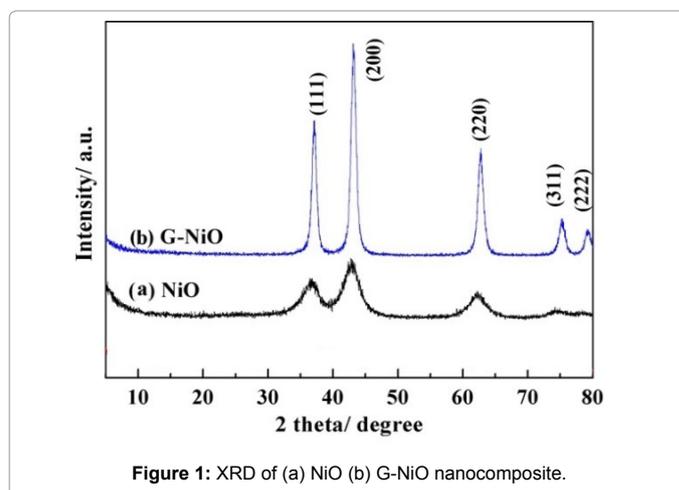


Figure 1: XRD of (a) NiO (b) G-NiO nanocomposite.

The microstructure, morphology and particle size of as-synthesized pure nickel oxide and Graphene-NiO Nanocomposites were understood by SEM and TEM analysis. The SEM image of pure nickel oxide (Figure 3a) shows that the particle size is around 80 nm and these nanoparticles combined with each other. Figure 3b shows a SEM image of the Graphene-NiO nanocomposite consists of thin, randomly aggregated and wrinkled graphene sheets closely related with each other and forming a chaotic solid with particle size of 1-10 nm. The higher magnification SEM image of Figure 3b further tells that tiny NiO nanoparticles are spread on the curly graphene nanosheets. Unusually, the particle size of the NiO grown on graphene is much lesser than pure NiO synthesized by the same process, because of the confining effect of disordered graphene nanosheets. More likely, the anchoring NiO nanoparticles could act as an inserter to prevent the re-stacking of separate graphene nanosheets.

Figure 3c we can tell only elements C, O and Ni are present. The percentage weight of NiO is calculated to be approaching the theoretical value, advising that all the Ni<sup>2+</sup> are completely dropped as the hydrolysis of urea.

Figure 4 shows the CV curves of the Graphene-NiO electrode at

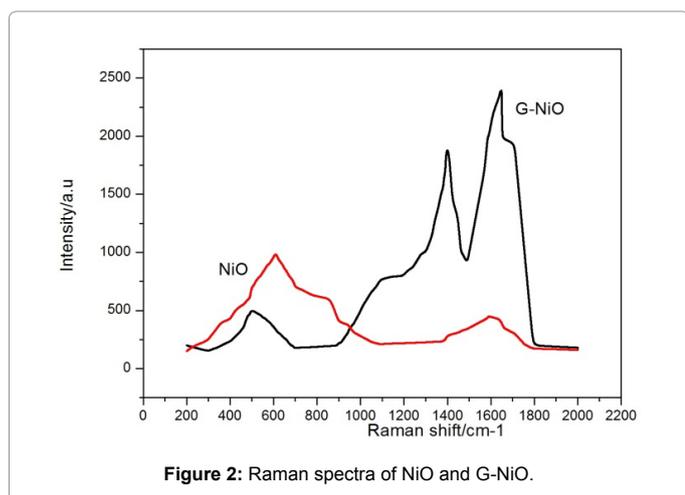


Figure 2: Raman spectra of NiO and G-NiO.

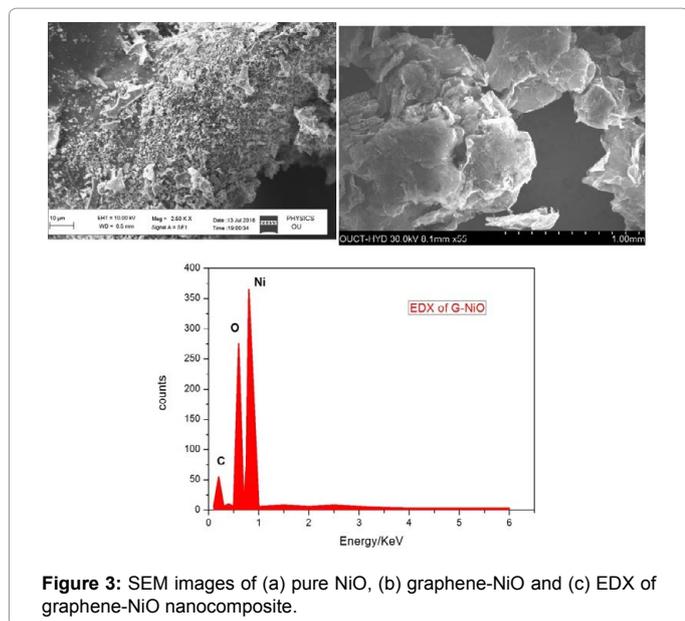


Figure 3: SEM images of (a) pure NiO, (b) graphene-NiO and (c) EDX of graphene-NiO nanocomposite.

different scan rates. The shapes of the CV disclose that the capacitance characteristic is very different from that of traditional electric double-layer capacitance in which the shape is generally an ideal rectangular shape. A NiO supercapacitor in an alkaline solution depend on charge storage in the electric double layer at the electrode/electrolyte boundary and charge storage in the host product through redox reactions on the surfaces and hydroxyl ion diffusion in the host product. As scan rate increases from 10 mv/sec to 200 mv/sec the current subsequently increases while the shape of CV curves changes little and much rapid current responses on voltage reversal at each end potential, which indicates good electrochemical capacitive nature for graphene-NiO porous structures. Figure 5 shows the Tga analysis of the G-NiO nanocomposite. By the help of Tga, we can estimate how much of graphene is present in the G-NiO nano composite.

From the result shown in the above graph, the weight loss of water is approximately equal to 7.6% when the temperature varies from the room temperature to 160°C. Next the weight loss regarding functional group decomposition is equal to 1.6% and its temperature rises from the 160°C to 250°C. And 12% of weight loss is due to the reaction of carbon and oxides and its temperature changes from 250°C to 620°C. Last but not least the weight loss of graphene is 13%.

## Conclusion

In summary, synthesis of Graphene oxide was done by using modified hummers method and Graphene-NiO nanocomposites have been effectively prepared by a hydrothermal method. SEM analysis tells that graphene sheets were well ornamented by the NiO nanoparticles to form a complex ordered nanostructures with rich pore size distribution and large specific surface area. XRD analysis specified that

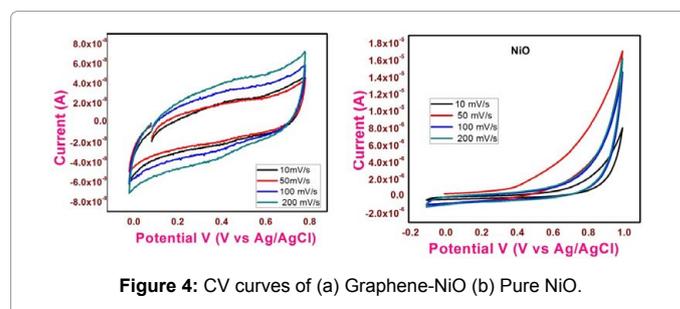


Figure 4: CV curves of (a) Graphene-NiO (b) Pure NiO.

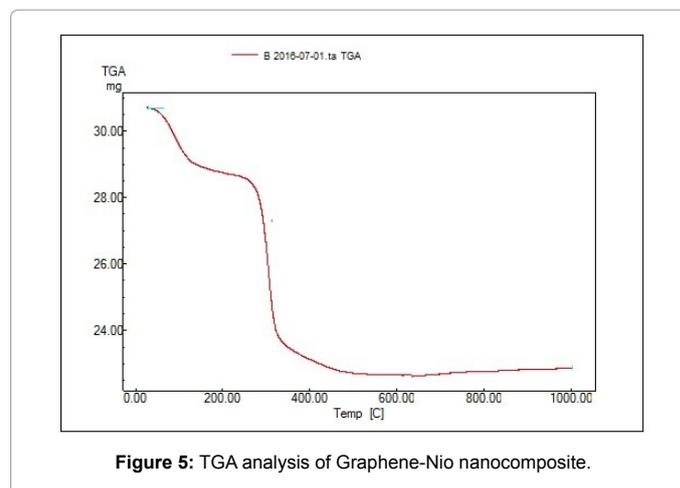


Figure 5: TGA analysis of Graphene-NiO nanocomposite.

GO and G-NiO composite phases and the average grain size of pure NiO and porous G-NiO are 82 nm and 12 nm. Raman spectrum of GO and Graphene-NiO displays that well formation of GO and composite. Cyclic voltammetry analysis is the evidence of these materials are having the ability of supercapacitor electrode materials. And also TGA Analysis gives the information about how much of graphene is present in the Graphene-NiO) nanocomposite.

## References

- Lee JK, Smith KB, Hayner CM, Kung HH (2010) Silicon nanoparticles-graphene paper composites for Li ion battery anodes. *Chem Commun* 46: 2025-2027.
- Zhao B, Song J, Liu P, Xu W, Fang T, et al. (2011) Monolayer graphene/NiO nanosheets with two-dimension structure for supercapacitors. *J Mater Chem* 21: 18792-18798.
- Lee JW, Ahn T, Soundararajan D, Ko JM, Kim JD (2011) Non-aqueous approach to the preparation of reduced graphene oxide/a-Ni(OH)<sub>2</sub> hybrid composites and their high capacitance behaviour. *Chem Commun* 47: 6305-6307.
- Zhang Y, Zhu J, Song X, Zhong X (2008) Controlling the synthesis of CoO nanocrystals with various morphologies. *J Phys Chem C* 112: 5322-5327.
- Wei W, Yang S, Zhou H, Lieberwirth I, Feng X, et al. (2013) 3D graphene foams cross-linked with pre-encapsulated Fe<sub>3</sub>O<sub>4</sub> nanospheres for enhanced lithium storage. *Adv Mater* 25: 2909-2914.
- Futaba DN, Hata K, Yamada T, Hiraoka T, Hayamizu Y, et al. (2006) Shape-engineerable and highly densely packed single-walled carbon nanotubes and their application as super-capacitor electrodes. *Nat Mater* 5: 987-994.
- Zhu Y, Murali S, Stoller MD, Ganesh KJ, Cai W, et al. (2011) Carbon-based supercapacitors produced by activation of grapheme. *Science* 332: 1537-1541.
- Jiang C, Zhan B, Li C, Huang W, Dong X (2014) Synthesis of three-dimensional selfstanding graphene/Ni(OH)<sub>2</sub> composites for high-performance supercapacitors. *RSC Adv* 4: 18080.
- Chen S, Duan J, Tang Y, Zhang Qiao S (2013) Hybrid hydrogels of porous grapheme and nickel hydroxide as advanced supercapacitor materials. *Chem Eur J* 19: 7118-7124.
- Chen K, Chen L, Chen Y, Bai H, Li L (2012) Three-dimensional porous graphene based composite materials: electrochemical synthesis and application. *J Mater Chem* 22: 20968-20976.
- Xu MW, Bao SJ, Li HL (2007) Synthesis and characterization of mesoporous nickel oxide for electrochemical capacitor. *J Solid State Electrochem* 11: 372-377.
- Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, et al. (2006) Graphene-based composite materials. *Nature* 442: 282-286.
- Kim E, Son D, Kim TG, Cho J, Park B, et al. (2004) A mesoporous/crystalline composite material containing tin phosphate for use as the anode in lithium-ion batteries. *Angewandte Chemie International Edition* 43: 5987-5990.
- Lou XW, Deng D, Lee JY, Feng J, Archer LA (2008) Self-supported formation of needlelike co<sub>3</sub>o<sub>4</sub> nanotubes and their application as lithium-ion battery electrodes. *Advanced Materials* 20: 258-262.
- Hou Y, Cheng Y, Hobson T, Liu J (2010) Design and synthesis of hierarchical MnO<sub>2</sub> nanospheres-carbon nanotubes-conducting polymer ternary composite for high performance electrochemical electrodes. *Nano Letters* 10: 2727-2733.
- Zhu X, Zhu Y, Murali S, Stoller MD, Ruoff RS (2011) Nanostructured reduced graphene oxide-Fe<sub>2</sub>O<sub>3</sub> composite as a high-performance anode material for lithium ion batteries. *ACS Nano* 5: 3333-3338.
- Hosogai S, Tsutsumi H (2009) Electrospun nickel oxide-polymer fibrous electrodes for electrochemical capacitors and effect of heat treatment process on their performance. *J Power Sources* 194: 1213-1217.
- Wu NL (2002) Nanocrystalline oxide supercapacitors. *Mater Chem Phys* 75: 6-11.
- Brezesinski T, Wang J, Tolbert SH, Dunn B (2010) Ordered mesoporous a-MoO<sub>3</sub> with iso-oriented nanocrystalline walls for thin-film pseudocapacitors. *Nat Mater* 9: 146-151.
- Rudge A, Davey J, Raistrick I, Gottesfeld S, Ferraris JP (1994) Conducting polymers as active materials in electrochemical capacitors. *J Power Sources* 47: 89-107.
- Snook GA, Kao P, Best AS (2011) Conducting-polymer-based supercapacitor devices and electrodes. *J Power Sources* 196: 1-12.
- Yuan C, Zhang X, Su L, Gao B, Shen L (2009) Facile synthesis and self-assembly of hierarchical porous NiO nano/micro spherical superstructures for high performance supercapacitors. *J Mater Chem* 19: 5772-5777.
- Ding S, Zhu T, Chen JS, Wang Z, Yuan C, et al. (2011) Controlled synthesis of hierarchical NiO nanosheet hollow spheres with enhanced supercapacitive performance. *J Mater Chem* 21: 6602-6606.
- Li X, Zhu Y, Cai W, Borysiak M, Han B, et al. (2009) Transfer of large-area graphene films for high-performance transparent conductive electrodes. *Nano Lett* 9: 4359-4363.
- Lin CC, Yen CC (2008) Manganese oxide precipitated into activated carbon electrodes for electrochemical capacitors. *J Appl Electrochem* 38: 1677-1681.
- Cheng MY, Hwang BJ (2010) Mesoporous carbon-encapsulated NiO nanocomposite negative electrode materials for high-rate Li-ion battery. *J Power Sources* 195: 4977-4983.
- Wang YG, Xia YY (2006) Electrochemical capacitance characterization of NiO with ordered mesoporous structure synthesized by template SBA-15. *Electrochim Acta* 51: 3223-3227.
- Yang S, Wu X, Chen C, Dong H, Hu W, et al. (2012) Spherical a-Ni(OH)<sub>2</sub> nanoarchitecture grown on graphene as advanced electrochemical pseudocapacitor materials. *Chem Commun* 48: 2773-2775.
- Gao F, Wei Q, Yang J, Bi H, Wang M (2013) Synthesis of graphene/nickel oxide composite with improved electrochemical performance in capacitors. *Ionics* 19: 1883-1889.
- Rolison DR, Long JW, Lytle JC, Fischer AE, Rhodes CP, et al. (2009) Multifunctional 3D nanoarchitectures for energy storage and conversion. *Chem Soc Rev* 38: 226-252.
- Xu Y, Huang X, Lin Z, Zhong X, Huang Y, et al. (2013) One-step strategy to graphene/Ni(OH)<sub>2</sub> composite hydrogels as advanced three-dimensional supercapacitor electrode materials. *Nano Res* 6: 65-76.
- Zhang F, Zhu D, Chen XA, Xu X, Yang Z, et al. (2014) A nickel hydroxide-coated 3D porous graphene hollow sphere framework as a high performance electrode material for supercapacitors. *Phys Chem Chem Phys* 16: 4186-4192.
- Hummers WS, Offeman RE (1958) Preparation of graphitic oxide. *J Am Chem Soc* 80: 1339.
- Pham VH, Dang TT, Hur SH, Kim EJ, Chung JS (2012) Highly conductive poly(methyl methacrylate) (PMMA)-reduced graphene oxide composite prepared by self-assembly of PMMA latex and graphene oxide through electrostatic interaction. *ACS Appl Mater Interfaces* 4: 2630-2636.
- Pei S, Cheng HM (2012) The reduction of graphene oxide. *Carbon* 50: 210-3228.
- Lee JW, Ahn T, Soundararajan D, Ko JM, Kim JD (2011) Non-aqueous approach to the preparation of reduced graphene oxide/a-Ni(OH)<sub>2</sub> hybrid composites and their high capacitance behaviour. *Chem Commun* 47: 6305-6307.
- Ferrari AC, Robertson J (2000) Interpretation of raman spectra of disordered and amorphous carbon. *Phys Rev B* 61: 14095-14107.
- Wang B, Park J, Wang C, Ahn H, Wang G (2010) Mn<sub>3</sub>O<sub>4</sub> nanoparticles embedded into graphene nanosheets: preparation, characterization, and electrochemical properties for supercapacitors. *Electrochim Acta* 55: 6812-6817.
- Tuinstra F, Koenig JL (1970) Raman spectrum of graphite. *J Chem Phys* 53: 1126-1130.