



Graphene Oxide/Polyaniline Composites as Electrode Material for Supercapacitors

Sandeep Chauhan*

Department of Chemistry, Govt College Theog, Shimla, Himachal Pradesh, India

ABSTRACT

With increasing demand of energy, the need of efficient energy devices has increased faster than ever before. Moreover rapid consumption of fossil fuel as form of coal, oil, natural gas etc. has necessitated the use of cleaner and renewable sources of energy. At present, the devices based on renewable sources of energy such as solar and wind energies are extensively being developed. Supercapacitors have emerged as potential devices for the next generation of energy storage and are at the forefront of research on energy storage technology. They have great potential not only of fulfilling the portable energy requirements of the next generation but also can help to optimize energy consumption by complementing batteries in a variety of applications. To replace the conventional batteries, supercapacitors should be cost effective with high energy densities and must have long cycle life as compared to conventional batteries. Polyaniline (PANI) is one of the most important conducting polymers because of its unique electrical properties. Use of PANI as electrode materials for supercapacitors has attracted the attention of many researchers owing to their low cost, flexibility, high conductivity in doped states, ease of synthesis, tunable properties, good environmental and thermal stability and simple doping/dedoping chemistry. However, many limitations including poor cycling capability during charge/discharge processes, the large volumetric swelling and shrinking during doping and dedoping and poor life time have restricted the use of pristine PANI as electrode material for supercapacitors. These limitations can be overcome by forming composites between the carbon nanomaterials and PANI.

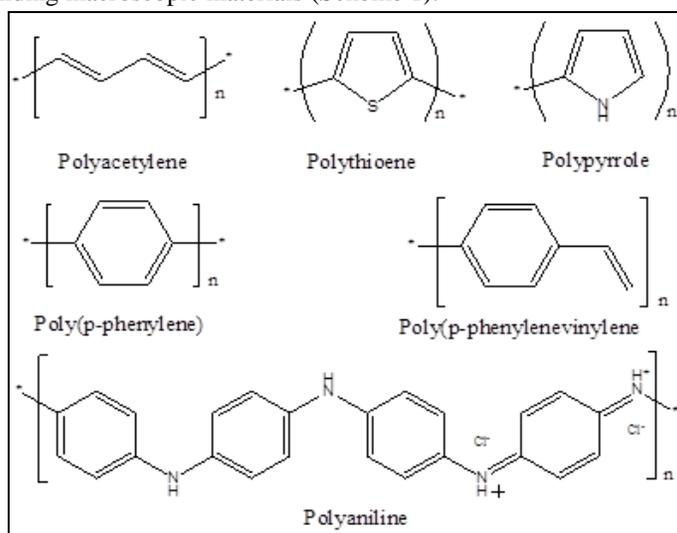
Keywords: Electrode material; Supercapacitors; Conventional batteries; Thermal stability; Carbon nanomaterials

INTRODUCTION

In the ever increasing scenario of environmental degradation, greenhouse gases emission and depletion of fossil fuels, cleaner and renewable sources of energy such as solar and wind energies are being explored extensively. In order to minimize environmental degradation, new technologies are being explored rapidly and require the elaboration of highly reliable energy storage devices. Supercapacitors or ultracapacitors seem to be the most suitable and potential candidates for the next generation of energy storage devices. As conventional batteries have many limitations, supercapacitors are at the forefront of research on energy storage technology. They not only can help to optimize energy consumption by complementing batteries in a variety of applications but are also regarded as possible replacements for batteries. To achieve these goals, the production costs of these supercapacitors should be competitive enough and their energy densities must surpass those of current batteries. Moreover, they must have long cycle life (>100, 000 cycles), superior rate capability, rapid charging/discharging rate, fast dynamics of charge propagation and low maintenance cost. In the present article, an attempt has been made to review some recent developments in the use of GO/PANI composites as electrode material for supercapacitors.

CONDUCTING POLYMERS

In general polymers are insulators and most of their applications had relied on their insulating properties. But the polymers possessing ordered conjugation with extended π electrons and large carrier concentrations are known to exhibit electrical conductivity. Conjugated polymers are the organic compounds that have an extended π orbital system and conjugated carbon system along their polymer backbone, hence giving them unique optical and electrical properties [1,2]. Conductive polymers (CPs) combine the electrical properties of metals with the advantage of polymers such as light weight, greater workability, resistance to corrosion and cost effectiveness. In the last three decades, conducting polymers especially those with polyaromatic backbone including polypyrrole, polythiophene, polyaniline etc. have received a considerable attention and become an attractive subject of research because of their interesting properties and numerous application possibilities. Because of their unique electronic and physical properties and chemical stability, CPs are expected to find their potential applications in multidisciplinary areas such as electrical, electronics, electrochemical, sensors, batteries, electro-optic, supercapacitors, solar cells, semiconductor devices, etc. [3-5]. CPs synthesized in the form of one-dimensional nanostructures such as nanotubes, nanofibers, and nanowires are of particular interest, as their properties significantly differ from the properties of the corresponding macroscopic materials (Scheme 1).

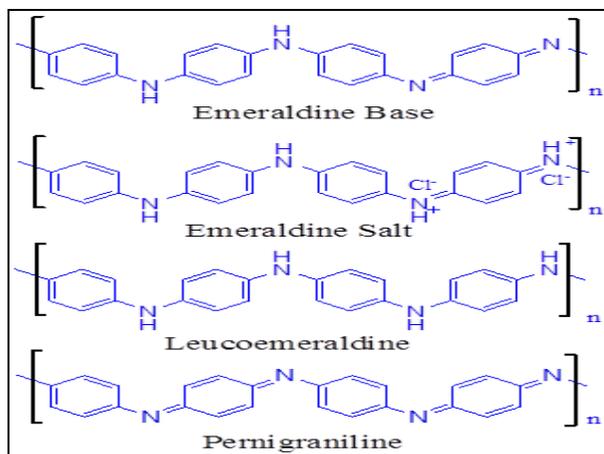


Scheme 1: Chemical structures of some of the organic CPs

Polyaniline as Potential Conducting Polymer

Among the available CPs, polyaniline (PANI) is found to be the most promising because of its unique electrical and optoelectronic properties due to extended π -conjugated electron systems, its ease of synthesis, low cost monomer, tunable properties, exceptional solution processability, good environmental and thermal stability, simple doping/dedoping chemistry and its fast switching rate (the ability to switch reversibly from its insulating to conducting state via either electrochemical or chemical doping). However, there are some drawbacks such as poor mechanical properties, lower effective surface area those restrict the use of PANI in many applications. Another major challenge is the control of size and morphology during the synthesis of nanostructured PANI. Therefore, there is ample scope for modifying the solubility, conductivity and processability of PANI through the selection of a suitable dopant and suitable level of doping during synthesis [6-11]. In order to overcome these limitations, aniline is often polymerized in the presence of variety of other organic and inorganic materials to enhance its properties.

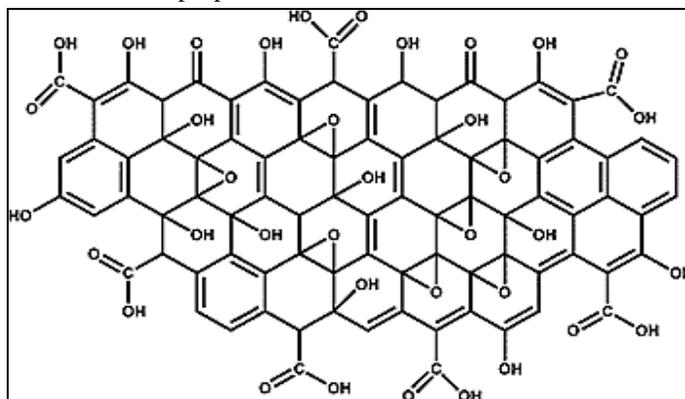
The conductivity of these conjugated polymers can be controlled and modified by the process of doping. Doping may be carried out by chemical methods [12-15], electrochemical methods [16] or photochemical methods. Doping increases in conductivity of these conjugated polymers to the extent that makes them highly conductive materials similar to metals. Therefore sometimes they are also called as Synthetic Metals. The enhancement of electric conductivity of a polymer via oxidative or reductive doping mainly depends on (a) the chemical reactivity of the dopant during polymerization, (b) the extent of doping and (c) the mobility of the dopant ions [17]. Stability of the conducting polymer is greatly affected by the nature of the dopant [18] (Scheme 2).



Scheme 2: Different forms of polyaniline

Graphene Oxide

Graphene oxide (GO) has a structure of an oxidized graphene having hydroxy, carboxy and epoxy groups. Although graphene consists of only sp^2 carbons, GO consists of some sp^3 carbons and structural defects. The structure, properties and applications of graphene oxide depend on particular synthesis method and degree of oxidation. It typically preserves the layer structure of the parent graphite, but the layers are buckled and the interlayer spacing is about two times larger (~ 0.7 nm) than that of graphite. There are various synthetic methods to synthesize GO. Several functional groups can be introduced on GO because of the presence of oxygen-based groups [19]. Graphene oxides prepared using sulphuric acid (e.g. Hummers method) contains some impurity, for example in a form of organosulfate groups [20-22]. There is evidence of "buckling" (deviation from planarity), folding and cracking [23] of graphene oxide sheets upon deposition of the layers on a choice of substrate. The detailed structure of GO is still not understood due to the strong disorders and irregular packing of the layers, but following structure (Scheme 3) is the most probable structure proposed on the basis of available evidences.



Scheme 3: Structure of GO

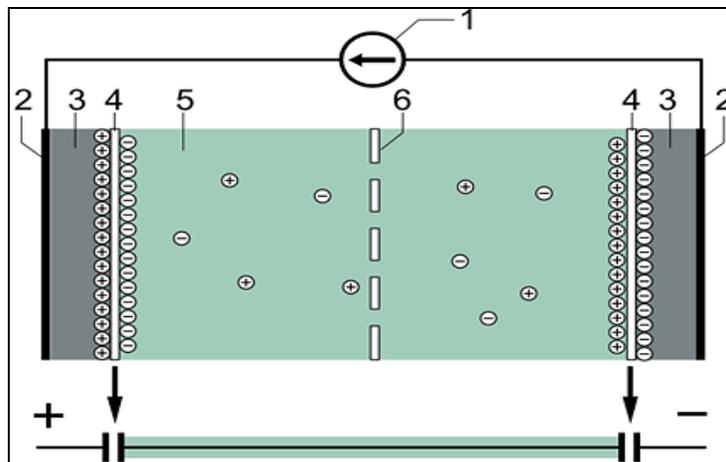
Supercapacitors: An Overview

A supercapacitor, also known as ultracapacitor or electric double-layer capacitor is a high-capacity electrochemical capacitor with much higher capacitance values than conventional capacitors. These devices have capacity to store 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, marvelous ability to charge and discharge within seconds without damage and impacting service life, remarkable ability to accept and deliver charge and ability to perform in harsh environments (Scheme 4).

Basic Architecture of Supercapacitors

Like an ordinary capacitor, a supercapacitor has two electrodes separated by a dielectric. Electrodes must have good conductivity, high temperature stability, long-term chemical stability, high corrosion resistance, high surface areas per unit volume and mass and environmental friendliness. In most of the supercapacitors, the electrodes are coated with activated carbon which is a very porous substance with an extraordinarily high specific surface area. Other

materials used in electrodes include activated carbon fibres, carbon aerogel, carbide-derived carbon, graphene, carbon nanotubes, metal oxides, conductive polymers etc. Electrolytes used in supercapacitors consist of a solvent and dissolved chemicals that dissociate into cations and anions. In supercapacitors, electrolytes are the electrically conductive connection between the two electrodes. The electrolyte must be chemically inert and should not chemically react with the other materials in the capacitor to ensure long time stable behavior of the capacitor's electrical parameters. The viscosity of the electrolyte must be low enough to wet the porous, sponge-like structure of the electrodes. Separators, separate the two electrodes to prevent a short circuit by direct contact. Separator is generally very thin (a few hundredths of a millimeter) and must be very porous to the conducting ions to minimize equivalent series resistance. Moreover, separators must be chemically inert to protect the electrolyte's stability and conductivity. Materials used in separator include nonwoven porous polymeric films like polyacrylonitrile or Kapton, woven glass fibers or porous woven ceramic fibres.



Scheme 4: A typical supercapacitor: 1) power source, 2) collector, 3) polarized electrode, 4) helmholtz double layer, 5) electrolyte having positive and negative ions, 6) separator

Classification of Supercapacitors

In supercapacitor storage of electrical energy takes place via two storage principles: static double-layer capacitance and electrochemical pseudocapacitance. On the basis of storage principles, supercapacitors are classified into three classes (Scheme 5):

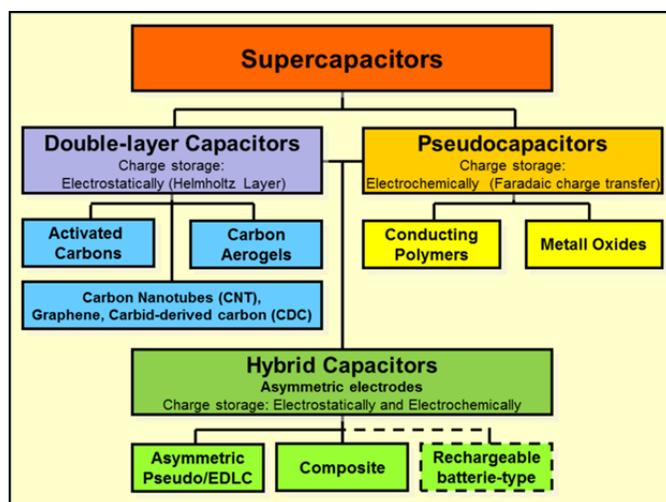
- (i) **Double-layer capacitors:** They have activated carbon electrodes or derivatives with much higher electrostatic double-layer capacitance than electrochemical pseudocapacitance.
- (ii) **Pseudocapacitors:** They involve transition metal oxide or conducting polymer electrodes with a high electrochemical pseudocapacitance.
- (iii) **Hybrid capacitors:** They exhibit mostly electrostatic and the other mostly electrochemical capacitance, such as lithium-ion capacitors.

Working Principle of Supercapacitors

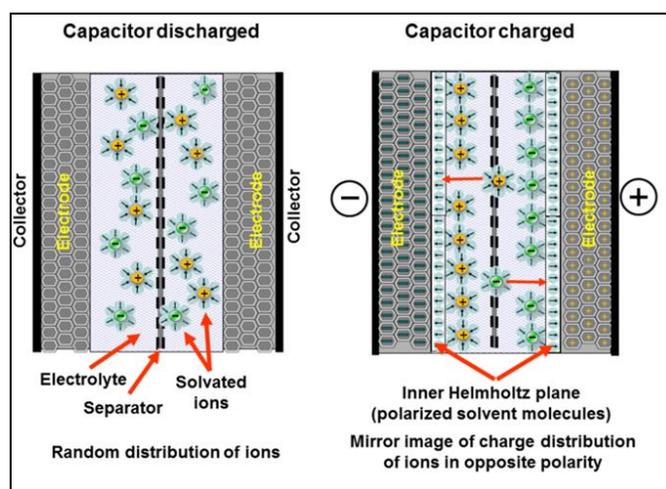
In Supercapacitor, the electrolyte is polarized by the charged plates. Positive ions of the electrolyte are attracted by the negative charge of one plate; conversely, the negative ions by the positive charge of the other plate. This movement of the ions form a second charge, the double layer allows the supercapacitor to store much more electrical energy providing a higher power performance (Scheme 6).

GO-PANI Composites as Electrode Material for Supercapacitors

Uses of CPs have attracted the attention of researchers worldwide as possible electrode materials for supercapacitors owing to their low cost [24], flexibility, [25] and high conductivity in doped states [26,27]. However, the poor cycling capability of these CP based supercapacitors arising mainly due to structural instability during charge/discharge processes is a major challenge. Moreover, the large volumetric swelling and shrinking during doping and dedoping leads to poor lifetime [28]. Many reports are available in literature aiming to overcome these limitations by forming composites between the carbon nanomaterials and conducting polymers [29].



Scheme 5: Types of supercapacitors: double-layer capacitors and pseudocapacitors as well as hybrid capacitors are defined over their electrode designs



Scheme 6: Working of an ideal double-layer capacitor. Applying a voltage to the capacitor at both electrodes a Helmholtz double-layer will be formed separating the ions in the electrolyte in a mirror charge distribution of opposite polarity

On one hand, carbon nanomaterials, such as carbon nanotubes, graphene, graphene oxide and reduced graphene oxide increase the mechanical strength [30] and cycle-life whereas, conducting polymers enhance the capacitance and cycling capability. One major advantage of using GO to form composites is the availability of various functional groups, such as hydroxyl, epoxide, carbonyl and carboxyl on its basal planes and edges, those can be utilized for chemical functionalization [31]. Kim et al. [32] reported the synthesis of polyaniline/reduced grapheme nanosheet composites by polymerization through chemical oxidation and study of the capacitance behavior of the materials using a three-electrode system. Nguyen et al. [33] reported a facile and efficient two-step method to synthesize polyaniline grafted reduced graphene oxide (RGO-g-PANI) composites for promising material for capacitors. RGO was first surface-modified with 1,3-diaminopropane, which provided reactive NH_2 groups that was polymerized with aniline, and grafted with polymer chains. The specific capacitance of the composite was found to be 1337 F g^{-1} at a very high current density of 15 A g^{-1} , highlighting its promising applications as an efficient electrode material for supercapacitors with excellent cyclic stability with only 18.75% decrease in capacitance after 5000 cycles. Zhang et al. [34] reported that PANI and polypyrrole deposited on RGO substrate reach capacitance degradation of ~18-19% after 1000 cycles. A novel phase separated polyaniline/graphene hydrogel (PANI/GHG) composite was synthesized as the electrode materials for high-rate supercapacitors. In the composite, the PANI mainly distributed outside and near the surface of the porous GHG matrix. Such a phase-separated structure provided unblocked channels for electrolyte diffusion; the composites exhibited a high specific capacitance of 783 F g^{-1} at the current density of 27.3 A g^{-1} [35]. It was reported that in PANI/sulphonated multi-walled carbon nanotubes composite, there

was a loss of only 10% of its initial capacitance after 1000 cycles [36]. PANI/graphene composites of different compositions were prepared by in situ polymerization of aniline to PANI in the presence of graphene powder. PANI/graphene composites exhibited higher current in cyclic voltammetry study compared to either neat PANI or neat graphene. The value of capacitance achieved for PANI/graphene composites was found to depend on the size of graphene sheet [37]. GO nanosheets homogeneously coated by PANI nanofibers with diameter of 45 nm were synthesized by in situ polymerization of aniline monomer in the GO suspension for use in supercapacitors. Cyclic voltammetry studies exhibited high specific capacitance (676 F g^{-1}) at a discharge current density of 1.0 A g^{-1} in $1 \text{ M H}_2\text{SO}_4$ solution, much higher than PANI electrode (230 F g^{-1}). The excellent performance was attributed to the synergetic effect of GO and PANI nanofibers, which would shorten ion diffusion length and made higher materials utilization [38]. Polyaniline deposited on coral-like monolithic carbon based supercapacitor electrode achieved capacitance degradation of about 22% after 1000 cycles at a scan rate of 100 mV s^{-1} [39]. A hierarchical nanocomposite of PANI nanowire arrays covalently bonded on RGO was synthesized via a novel route for high-performance supercapacitors. The first step involved the grafting of nitrophenyl groups on RGO via C-C bond and the second step involved reduction of nitrophenyl groups to aminophenyl which act as anchor sites for the growth of PANI arrays on RGO. The nanocomposites showed high capacitance of 590 F g^{-1} at 0.1 A g^{-1} , and had no loss of capacitance after 200 cycles at 2 A g^{-1} [40]. Carbon nanotube embedded in polypyrrole nanowire electrode showed a loss of 15% of capacitance after 1000 cycles at 1 A g^{-1} current density [41]. PANI nano fibres were incorporated into GO layers by interfacial polymerization pathway in order to improve the supercapacitor performance of PANI. PANI-GO hybrid composite obtained in semi-crystalline form showed good conductivity (1.7 S cm^{-1}) and specific capacitance (365 F g^{-1}) higher than PANI (280 F g^{-1}) [42]. Synthesis of highly crystalline and conductive GO-PANI composite without using conventional oxidants by *in situ* polymerization of aniline in the presence of GO as oxidant was reported. The higher conductivity of doped GO-PANI composite as compared to that of GO-PANI obtained by ammonium persulfate assisted polymerization was attributed to higher crystallinity and/or chemical grafting of PANI to GO, which created common conjugated paths between GO and PANI [43]. A potential electrode material for supercapacitor based on Nitrogen-doped graphene prepared by pyrolysis of the PANI/GO composite exhibited a high electrochemical performance with specific capacitance up to 206 F g^{-1} at a current density of 1 A g^{-1} . The composite also showed an excellent cyclic stability of about 92.5% of the initial value after 1000 cycles at a scan rate of 50 mV s^{-1} [44]. Carbonaceous shell-coated PANI and polypyrrole electrodes showed capacitance degradations of ~5 and ~15%, respectively after 10000 cycles at a scan rate of 100 mV s^{-1} [45].

CONCLUSION

To sustain the economic and industrial growth of the world, energy is the most important factor. Need of clean and green energy devices have been realized for long time. Along with solar and wind energies, supercapacitors also have great potential to fulfill the energy requirements of next generations. From the foregone discussion, it is evident that a lot of reports on supercapacitors especially based on conducting polymers are available in literature. A considerable amount of work has been carried out to design supercapacitors with high energy densities, long cycle life, superior rate capability and rapid charging/discharging rate.

REFERENCES

- [1] PJ Kaveeta; RG Prasad; SJ Venkata; RS Aparna; AR Phani. *Nano Biomed Eng.* **2012**, 4, 144-149.
- [2] GB Shumaila; VS Lakshmi; M Alam; AM Siddiqui; M Zulfequar; M Husain. *Curr Applied Phys.* **2010**, 11, 217-222.
- [3] D Majumdar; M Baskey; SK Saha. *Macromol Rapid Commun.* **2011**, 32, 12, 77-1283.
- [4] H Yu; T Wang; B Wen; M Lu; Z Xu; C Zhu; Y Chen; X Xue; C Sun; M Cao. *J Mater Chem.* **2012**, 22, 21679-21685.
- [5] KC Huang; JH Huang; CH Wu; CY Liu; HW Chen; CW Chu; CL Lin; KC Ho. *J Mater Chem.* **2011**, 21, 10384-10389.
- [6] M Wan. *Macromol Rapid Commun.* **2009**, 30, 963-975.
- [7] C Laslau; Z Zucovic; J Travas-Sejdic. *Prog Polym Sci.* **2010**, 35, 1403-1419.
- [8] HD Tran; JM D'Arcy; Y Wang; PJ Beltramo; VA Stron; RB Kaner. *J Mater Chem.* **2011**, 21, 3534-3550.
- [9] J Wang; D Zhang. *Adv Polym Technol.* **2013**, 32, 323-330.
- [10] D Li; J Huang; RB Kaner. *Acc Chem Res.* **2009**, 42, 135-145.
- [11] JM Kinyanjui; NR Wijeratne; J Hanks; DW Hatchett. *Electrochimica Acta.* **2006**, 51, 2825-2835.
- [12] U Rana; K Chakrabartib; S Malik. *J Mater Chem.* **2012**, 22, 15665-15671.

- [13] U Rana; S Malik. *Chem Commun.* **2012**, 48, 10862-10864.
- [14] S Mondal; U Rana; S. Malik. *Chem Commun.* **2015**, 51, 12365-12368.
- [15] SM Reda; SMA Ghannam. *Adv Mat Phy Chem.* **2012**, 2, 75-81.
- [16] CTP da Silva; VL Kupfer; GR da Silva; MP Moisés; MAG Trindade; NLC Domingues; AW Rinaldi. *Thin Film Int J Electrochem Sci.* **2016**, 11, 5380-5394.
- [17] U Rana; S Mondal; J Sannigrahi; PK Sukul; MA Amin; S Majumdar; S Malik. *J Mater Chem.* **2014**, 2, 3382-3389.
- [18] HD Tran; JM D'Arcy; Y Wang; PJ Beltramo; VA Strong; RB Kaner. *J Mater Chem.* **2011**, 21, 3534-3550.
- [19] H Kinoshita; Y Nishina; AA Alias; M Fujii. *Carbon.* **2014**, 66, 720-728.
- [20] HC Schniepp; JL Li; MJ McAllister; H Sai; M Herrera-Alonso; DH Adamson; RK Prud'Homme; R Car; DA Saville; IA Aksay. *J Phy Chem.* **2006**, 110, 8535-8539.
- [21] D Pandey; R Reifengerger; R Piner. *Surface Science.* **2008**, 602, 1607-1613.
- [22] S Eigler; C Dotzer; F Hof; W Bauer; A Hirsch. *Chem-Eur J.* **2013**, 19, 9490-9499.
- [23] DK Pandey; TF Chung; G Prakash; R Piner; YP Chen; R. Reifengerger. *Surf Sci.* **2011**, 17, 605-611.
- [24] X Peng; K Huo; J Fu; X Zhang; B Gao; PK Chu. *Chem Commun.* **2013**, 49, 10172-10174.
- [25] HP Cong; XC Ren; P Wang; SH Yu. *Energ Environ Sci.* **2013**, 6, 1185-1191.
- [26] Y Hou; Y Cheng, T Hobson; J Liu. *Nano Lett.* **2010**, 10, 2727-2733.
- [27] C Zhou; Y Zhang; Y Li; J Liu. *Nano Lett.* **2013**, 13, 2078-2085.
- [28] Y Zhao; B Liu; L Pan; G Yu. *Energ Environ Sci.* **2013**, 6, 2856-2870.
- [29] Q Zhang; Y Li; Y Feng; W Feng. *Electrochem Acta.* **2013**, 90, 95-100.
- [30] J Du; HM Cheng. *Macromol Chem Phys.* **2012**, 213, 1060-1077.
- [31] A Lerf; H He; M Forster; J Klinowski. *J Phy Chem.* **1998**, 102, 4477-4482.
- [32] J Kim; SJ Park; S Kim. *Carbon Lett.* **2013**, 14, 51-57.
- [33] VH Nguyen; C Lamiel; D Kharismadewi; VC Tran; JJ Shim. *J Electroanal Chem.* **2015**, 758, 148-155.
- [34] J Zhang; X S Zhao. *J Phys Chem.* **2012**, 116, 5420-5426.
- [35] J Wu; Q Zhang; A Zhou; Z Huang; H Bai; L Li. *Adv Mater.* **2016**, 28, 10211-10216.
- [36] ZZ Zhu; GC Wang; MQ Sun; XW Li; CZ Li. *Electrochim Acta.* **2011**, 56, 1366-1372.
- [37] DK Mahla; S Bhandari; M Rahaman; D Khastgir. *J Electrochem Sci Eng.* **2013**, 3, 157-166.
- [38] J Li; H Xie; Y Li. *J Nanosci Nanotechnol.* **2015**, 15, 3280-3283.
- [39] Y Wang; S Tao; Y An; S Wu; C Meng. *J Mater Chem.* **2013**, 1, 8876-8887.
- [40] L Wang; Y Ye; X Lu; Z Wen; Z Li; H Hou; Y Song. *Sci Rep.* **2013**, 3, 3568-3572.
- [41] H Fu; Z J Du; W Zou; HQ Lia; C Zhang. *J Mater Chem.* **2013**, 1, 14943-14950.
- [42] U Male; P Srinivasan; BS Singu. *Int Nano Lett.* **2015**, 5, 231-240.
- [43] MHM Moghadam; S Sabury; MM Gudarzi; F Sharif. *J Polym Sc Polym Chem.* **2014**, 52, 1545-1554.
- [44] WD Wang; XQ Lin; HB Zhao; QF Lü. *J Anal Appl Pyrol.* **2016**, 120, 27-36.
- [45] T Liu; L Finn; M Yu; H Wang; T Zhai; X Lu; Y Tong; Y Li. *Nano Lett.* **2014**, 14, 2522-2527.