

A Review on Doped and Defected Graphene-based materials for supercapacitor electrodes

Yogita Taluja, Devesh gupta, Deepak shankhla, Bhoopesh kumar Kumawat

Abstract— The graphene supercapacitor having brilliant surface area about $26.3 \times 10^6 \text{cm}^2/\text{g}$ [5], still it is unable to attain the essential energy density due to small quantum capacitance and poor accessibility to electrolyte. The functionalization of graphene can grow electrolyte wettability, electrical conductivity, electrode accessibility and capacitance [1,2]. Especially, Reasons for given preference to nitrogen doped graphene are it has favorable energy density, electrical conductivity, power density catalysis absorption and life cycle[3-4]. In this study, we see structural, the quantum capacitance, electronic properties of defected and nitrogen doped graphene sheet using Density Functional Theory (DFT) and non-equilibrium Green's function (NEGF) formalism for their practicable application as supercapacitor electrodes.

The 3N-Pyrrolic -type defect configuration having formalized high thermodynamic stability along with the electrical conductance in analogy to all the other configurations. The quantum capacitance of graphene surge with the pyrrolic concentration. A notable 486.32 uF/cm^2 quantum capacitance has been remarked at a pyrrolic concentration of 6.38%[4,5]. It suggests that the quantum capacitance of graphene grow with the pyrrolic concentration.

Index Terms—Graphene-based materials, Defect, DFT, Supercapacitors, Quantum Capacitance, pyrrolic, Functionalization.

1 INTRODUCTION

The demand for energy storage is on the bloom these days in view of growing energy consumption and declining fossil fuel resources. A previous surge in power generation through intermittent energy sources (wind, water and solar) stipulates the need[1] as we all knew that wind, water and solar is not stable with time. Solar energy can't be produce during night, the wind and tidal powers are dependent on the environment. That's why Growing the attention of the researcher on Supercapacitor. It is such a favorable device having fast charging and discharging represent by its high power density and extremely high life cycle greater than 1000 cycle[6-7]. Problem with the supercapacitor is its comparatively low energy density (5-10 Wh/kg) to conventional conventional storage devices lead-acid battery (20-35 Wh/kg), Li-ion battery (120-170 Wh/kg), LiMH battery (40-100 Wh/kg) [2,4,8,17,18] as, EDLCs Store energy through adsorption of ions at the electrode and electrolyte interface; high surface area by with good electrical conductivity are the necessary requirements to attain high energy densities.

Thus, besides developing the advanced electrolytes, the researchers have also focused on optimizing the electrode material. The graphene-based materials are prosperous for applications in supercapacitors electrode and other energy storage devices because of the intriguing properties, i.e., highly tunable surface area, outstanding electrical conductivity, excellent mechanical behavior and good chemical stability. It has been reported experimentally and theoretically, functionalization of graphene honeycombs can grow electrical conductivity, electrode, capacitance and electrolyte wettability, availability [11,12]. Mainly, Nitrogen doped graphene see as assuring material for electrical conductivity, ifetime, power density, catalysis adsorption and energy storage[13-17,1]. Substitution of nitrogen in pure graphene (pristine) commonly resultant donor states in the electronic structure. Beside that many survey state that the type of conductivity (p-type or n-type) depends on different factor and change by different ways[18-19]. In addition, surface properties of carbon just as surface polarity and electron donor affinity increase through the substitution of nitrogen.[16,1]

Similar nitrogen functionalization of defected carbon nanotubes (CNTs) by Rocha et al.[20] reported growing stability with nitrogen functionalization.[1]. As per the study, it is anticipated that for excel the adequate surface area reachability by electrolytic ion and quantum capacitance (CQ) of graphene bring up

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defect and doping modification onto graphene sheet[11-16]. The quantum capacitance is an intrinsic capacitance that exhibit by the material that having limited density of states at fermi level-Quantum capacitances and double-layer are the key factor for the total capacitance (C_T) that represent the energy density of super-capacitor. Therefore, electrode material having high quantum capacitance is must to use for obtain large energy densities. According to our quantum capacitance survey, pyrrolic rich graphenes are best option for raised quantum capacitances and improved surface area approachability. According to Dos profile study the pyrrolic defect are more preferable than pyridine defect[9]. Encourage, we examine the impact of growing pyrrolic concentration on the quantum capacitance of graphene sheet, and the impact of other defects such as Stone-Wales, pyridinic and graphitic on the quantum capacitance of pyrrolic graphene.

2 RESULTS AND DISCUSSION

2.1 Structural and stability analysis

The stability, electrical conducting and electronic nature ability of different Graphene congurations have been examined for pristine, pyrrolic and pyridine defect with varying nitrogen substitutional doping concentrations depicted in Figs. 1 and 2. The defect vacancy is genrated in a $5*5*1$ repeated graphene basis and the under-coordinated atoms at the vacuum are substitutionally doped with nitrogens (N) to receive functionalized defects pyridine-type and pyrrolic-type. Nitrogen as a dopant has been preferred as it was reported earlier by some researchers to arises the energy storage capacity of graphene supercapacitors [11,12,14-16]. The measured bond lengths at the defect edges are tabulated in Table 1. The fluctuations in the bond length are largely witnessed at the dopant positions. The C-N bond length is discovered to be relatively smaller than the C-C bond length despite the fact that all atoms have undergone sp^2 hybridization; this power be due to the high electronegativity of dopant Nitrogen. 1N-pyridine configuration has demonstrated the strongest C-N bond of all the functional doping configurations owing to its smaller C-N bond length. In pyrrolic defect, the carbon atoms fencing the vacancy come closer giving a pentagoneoctagon-pentagon like formation and fence C-C bond lengths growd by a small amount of 0.05 \AA when compared with the pristine graphene bond length of 1.420 \AA . Thermodynamic stability, a critical factor in opting the defected and functionalized graphene sheets for super- capacitor electrode applications, has been evaluated through formation energy calculations. The stability of defect edges in each conguration has been evaluated by calculating the formation energy per unit length of the edge (E_f) using eq.

$$E_f = \frac{(E_{Dop} - xE_C - y\frac{E_{N_2}}{2})}{L}$$

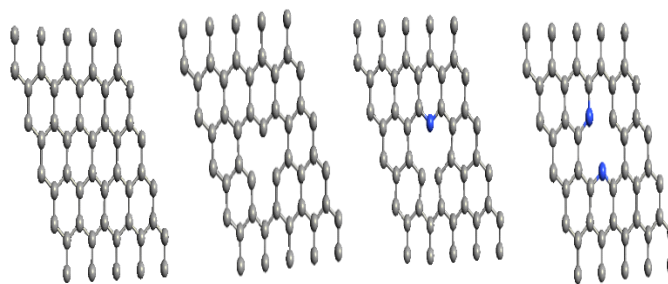


Fig. 1 Optimized sheets of (a) Pristine Graphene (b) Pyridine Defect (c) 1N-Pyridine Defect (d) 2N-Pyridine Defect and (e) 3N-Pyridine Defect defects.

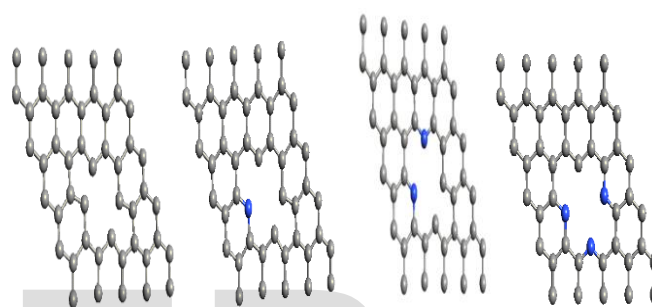


Fig. 2 Optimized sheet of (a) pyrrolic defect, (b) 1N-Pyrrolic Defect, (c) 2N-Pyrrolic Defect, (d) 3N-Pyrrolic Defect.

where E_{Dop} is the energy of the defected/functionalized sheet, E_C is the energy per carbon atom of pristine graphene, E_{N_2} is energy of nitrogen gas, L is the length the sheet deliberated (9.8 \AA), x and y are the total number of carbon and nitrogen atoms in the sheet, severally. The calculated formation energies per unit length of edge for various defected and functionalized sheets are listed in Table 1, where the configuration possessing lower formation energy is dared to be most stable. The sign against the formation energy conveys the 'endothermic' or 'exothermic' nature of the alteration and/or adulteration process of pristine graphene sheet. Positive formation energy refers the defect/functionalization formation to endothermic process, where the energy gets engaged. Whereas, negative E_f refers to an energy releasing process, exothermic. The calculated E_f for all the configurations is positive indicating the endothermic nature of the defect creation and functionalization. Formation of pyrrolic defect is engaged to be more static and energetically favorable than Pyridine defect. Growing the nitrogen functionalization on defect site is observed to grow the stability of the defect. cause being the dangling bond of the under-coordinated carbon is replaced by the lone pair of nitrogen at every substitutional doping site. Hence, formation of 3N-pyrrolic is observed to be more static and energetically favorable than other configurations considered.

2.2. Electronic nature

High Conductivity is a essential requirement for any supercapacitor electrode and therefore metallic sheets are largely preferred over semiconducting sheets for design of electrodes. To realise the band nature of defected and Functionalized graphene sheets, the band structures are evoked and plotted in Fig. 3; where the Fermi level is located at energy zero. The long-familiar zero band gap feature of pristine graphene sheet is confirmed from the plotted band gap in Fig. 3(a). as all other defected and functionalized structures show metallicity as seen from Fig. 3. On intimately examining the band structure plots, functionalized sheets and the defected are observed to offer acceptor-type energy levels close to the Fermi level. Because of being the p-type conducting nature of defected and functionalized sheets, referable to the deficiency of electrons in comparison to pristine sheet.

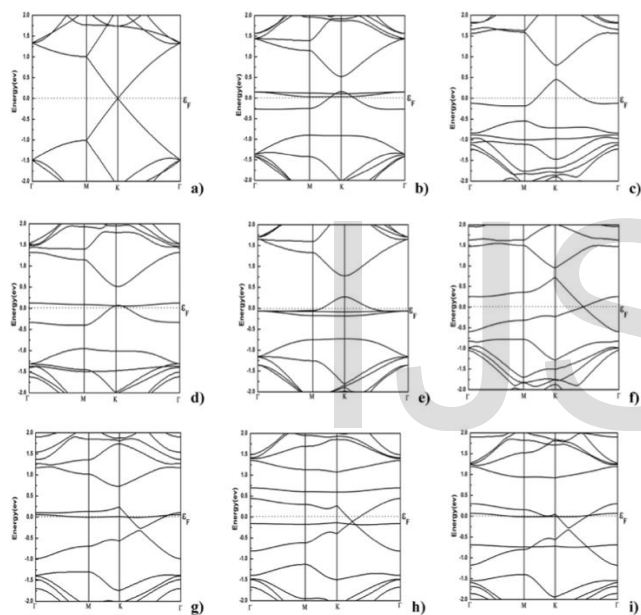


Fig. 3 Band structure of (a) Pristine graphene sheet, (b) Pyridine Defect, (c) 1N-Pyridine Defect (d) 2N-Pyridine Defect (e) 3N-Pyridine Defect (f) pyrrolic defect, (g) 1N-Pyrrolic Defect, (h) 2N-Pyrrolic Defect and (i) 3N-Pyrrolic Defect[]

Table-1: Measured Bond lengths, Formation energies and observed band nature over pristine graphene sheet, defected (Pyridine, 1N-Pyridine, 2N-Pyridine, 3N-Pyridine, pyrrolic, 1N-Pyrrolic, 2N-Pyrrolic and 3N-Pyrrolic Defect) graphene sheets.

Defected configuration	C-C bond length(Å)	C-N bond length	Formation energy E_f (eV/Å)	Band Nature
Pristine Graphene	1.420	-	--	Zero-bandgap
Pyrolic	1.400-1.414	-	0.82	Metallic
1N- Pyrrolic	1.408 - 1.530	1.327	0.51	Metallic
2N- Pyrrolic	1.419-1.443	1.332-1.365	0.42	Metallic
3N- Pyrrolic	1.453	1.355	0.24	Metallic
Pyridine	1.472	-	5.45	Metallic
1N- Pyridine	1.377-1.480	1.343-1.354	0.78	Metallic
2N- Pyridine	1.391 - 1.443	1.353-1.355	0.71	Metallic
3N- Pyridine	1.391-1.478	1.329-1.347	0.48	Metallic

The quantity of the acceptor-type energy levels near the Fermi level deviated between 1 and 4 calculating upon the type of defect and functionalization. The pyrrolic configuration has 3 acceptor-type energy levels near the Fermi level, might be due to the presence of 3 under-coordinated atoms at the defect edge. The 1N-pyrrolic, 2N-pyrrolic and 3N-pyrrolic configurations are detected to have 1, 2, and 3 acceptor-type energy levels, severally, which is in coincidence with the number of Nitrogens doped into graphene sheet. The number of acceptor-type energy levels in Pyridine and its functionalized configurations varied between 2 and 4, where the 2N-pyridine and 3N-pyridine type functionalized sheets have 4 levels. Fig. 4 shows the Density of States (DOS) for the pristine, defected and functionalized sheets, where the Fermi level is adjusted to 0 eV. The SV defect DOS in Fig. 4(a) is highly different from that of pristine graphene DOS with remarkable peaks near the Fermi level. These peaks are a result of unbonded electrons from under-coordinated carbon atoms at the vacancy site.

Assemble from the pristine case, the peaks in DOS are mainly imputable to the delocalized p-cloud and are majorly located in the conduction band. Comparable to the every "at looking band observed in the band structure, a sharp peak in the DOS is witnessed. We have also executed the analysis of projected DOS calculations, which revealed the negligible influence of s- orbitals on the DOS owing to their engagement in the formation of strong σ -bonds. As, the p-orbitals are observed to have great contribution to DOS due to their devotion in the formation of weak as well as delocalized π -bonds. 3N-pyrrolic configuration

has the highest blooms over all the functionalized configurations, which was earlier observed as the most stable configuration in the prior section.

blue balls indicate carbon and nitrogen atoms, respectively [4]. The quantum capacitance is calculated from the Dos profile given in fig. 4 to understand the application of defected configuration for electrode of supercapacitor. Mathematical formula for the calculation of the quantum capacitance is stated as $C_Q = \frac{dQ}{d\phi}$. Where ϕ is external potential. Chemical potential of electrons is effected by, the charge on graphene is [7].

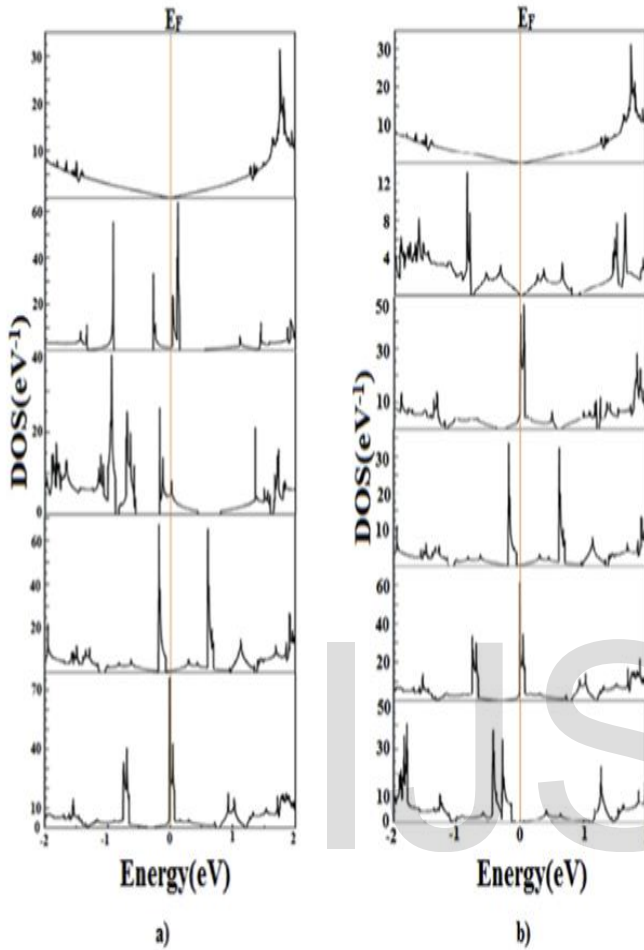


Fig. 4. Density of State (DOS) for a) Pristine graphene sheet, pyrrolic 1N-Pyrrolic, 2N-Pyrrolic and 3N-Pyrrolic and b) Pristine Graphene Sheet, Pyridine, 1N-Pyridine, 2N-Pyridine, 3N-Pyridine type defected sheet (from top to bottom) Fermi level (E_F) is located at energy zero. [4]

2.3 Quantum capacitance

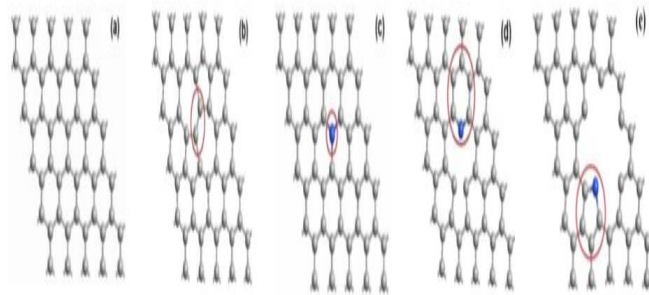


Fig.5. Different graphene defect configurations studied, (a) Pristine Graphene, (b) Stone-Wales, (c) Graphitic, (d) Pyridinic, and (e) Pyrrolic (The defect sites are circled red. The grey and

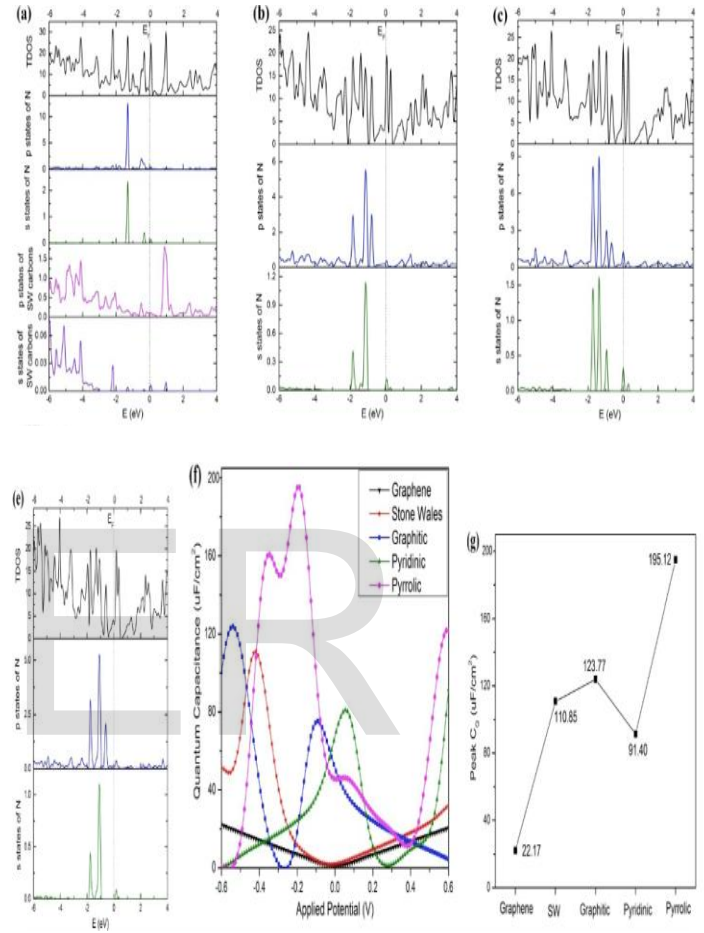


Fig.6 Total density of states (TDOS) and Projected DOS (PDOS) for (a) Pristine-graphene, (b) Stone-Wales (SW), (c) graphitic, (d) pyridinic, and (e) pyrrolic defected graphenes (Fermi level (E_F) is located at energy zero, DOS are in the units of eV^{-1}). (f) Quantum Capacitance plotted as a function of applied potential for different primary defects, (g) peak value of quantum capacitance for different primary defects. [5]

$$Q = e \int_{-\infty}^{\infty} D(E) [f(E) - f(E - \phi)] dE$$

Here, $D(E)$ is the DOS, $f(E)$ is Fermi-Dirac distribution function, E use to represent Energy with reference to Fermi level, and e is elementary charge (1.6×10^{-19} C). By differentiating Q with respect to ϕ , one can find the expression for quantum capacitance as, [5]

$$C_Q = \frac{dQ}{d\phi} = e^2 \int_{-\infty}^{\infty} D(E) [F_T(E - \phi)] dE$$

Here, F_T is the thermal broadening function, given by,

$$F_T(E) = \frac{1}{4KT} \operatorname{sech} 2 \left(\frac{E}{2KT} \right)$$

After finishing the required correction inside the hyperbolic secant function for sustain the charging / discharge synchronization among quantum capacitance and DOS profile, the final expression for C_Q is given as [9].

$$C_Q = \frac{e^2}{4KT} \int_{-\infty}^{\infty} D(E) \operatorname{sech} \operatorname{sech} 2 \left(\frac{E+\phi}{2KT} \right) dE$$

Quantum capacitance analysis of is done by track fixed band estimate that is basically the DOS profile of the graphene system is supposed to be not affected by charging/ discharging. In Figure 6(f) we plotted calculated quantum capacitance for pristine graphene and other functionalized graphene sheet over the applied potential range -0.6 V to 0.6 V (electrochemical range for aqueous electrolytes) and it show that injecting defect onto graphene sheet have resulted increase in the quantum capacitance over most of the applied potential. Our computed quantum capacitance for pristine graphene is in an excellent agreement with the previous reports results [9-10,20].

The pinnacle value of C_Q for pristine graphene is calculated as 22.17 uF/cm² at -0.6 V. While for Stone-Wales defect peak value is 110.85 uF/cm² at -0.41 V, for graphitic defect it is 123.77uF/cm² at -0.54V, for pyridinic defect it is 91.39 uF/cm² at 0.6V, and for pyrrolic defect, it is 195.12 uF/cm² at -0.18V. In excellent agreement with the previous report is the C_Q of the graphitic defect (doping concentration of 2%). Table 1 list the peak C_Q observed for pristine graphene and its primary defects and picturized in Fig.6(b), where the bloom C_Q follows the drift pyrrolic > graphitic > Stone Wales > Pyridine > pristine graphene. Thus, the pyrrolic defect has lead its counterparts with noteworthy 195.12 uF/cm² of C_Q , which is a result of an enormous peak located at 0.18 eV of TDOS profile. The Stone-Wales, pyrrolic and graphitic defected graphenes recommend high quantum capacitances at the negative side of the electrochemical window, and therefore it may be the best fit for cathode electrode of asymmetric supercapacitors. Those elements shows peak in the positive of electrochemical window is best fit for anode electrode pyridinic graphene do the same.

Conceiving the notable C_Q of pyrrolic graphene, we have progressed further to analyze the impact of growing pyrrolic concentration by with combinational pyrrolic conceiving on the graphene sheet.

3 CONCLUSION

In this paper we survey different ways affecting the energy density of graphene supercapacitors which are the affect of defects and nitrogen doping concentration on the structural, capacitive and electronic properties. Formation energy calculations validate the growing stability of defects with nitrogen functional doping, where pyrrolic-type configurations are detected to be most stable. The electronic nature of the considered graphene systems has been analyzed in terms of band structure and DOS profile.

The p-type conductivity of graphene sheet is identified by Significant acceptor-type energy levels stated near the fermi level after bringing in defects and functionalization. Particularly, the 3N-pyrrolic configuration has exhibited superior thermodynamic stability as well as electrical conductance, and therefore may be a suitable choice for supercapacitor electrode applications. Indeed as per our conclusion pyrrolic defect as more advantageous than pyridinic and Pristine.

REFERENCES

- [1] Conway, Brian E. *Electrochemical supercapacitors: scientific fundamentals and technological applications*. Springer Science & Business Media, 2013.
- [2] Simon, Patrice, and Yury Gogotsi. "Materials for electrochemical capacitors." *Nanoscience and technology: a collection of reviews from Nature journals*. 2010. 320-329.
- [3] Fujimoto, Yoshitaka, and Susumu Saito. "Energetics and electronic structures of pyridine-type defects in nitrogen-doped carbon nanotubes." *Physica E: Low-dimensional Systems and Nanostructures* 43.3 (2011): 677-680.
- [4] Taluja, Yogita, et al. "Defect and functionalized graphene for supercapacitor electrodes." *Superlattices and Microstructures* 98 (2016): 306-315.
- [5] SanthiBhushan, Boddepalli, et al. "Quantum Capacitance Estimations of Pyrrolic-Rich Graphene for Supercapacitor Electrodes." *IEEE Transactions on Nanotechnology* 17.2 (2017): 205-211.(2)
- [6] Zhan, Cheng, et al. "Enhancing graphene capacitance by nitrogen: effects of doping configuration and concentration." *Physical Chemistry Chemical Physics* 18.6 (2016): 4668-4674.
- [7] Michele, and Giovanni Sandrone. "Ab initio study of corundum-like Me₂O₃ oxides (Me= Ti, V, Cr, Fe, Co, Ni)." *Faraday Discussions* 106 (1997): 189-203.
- [8] Ke, Qingqing, and John Wang. "Graphene-based materials for supercapacitor electrodes—A review." *Journal of Materiomics* 2.1 (2016): 37-54.(graphene)
- [9] Liu, Xianbin, Yuying Zheng, and Xiaoli Wang. "Controllable preparation of polyaniline-graphene nanocomposites using functionalized graphene for supercapacitor electrodes." *Chemistry—A European Journal* 21.29 (2015): 10408-10415.(intro)
- [10] Fan, Xiaofeng, W. T. Zheng, and Jer-Lai Kuo. "Adsorption and diffusion of Li on pristine and defective graphene." *ACS applied materials & interfaces* 4.5 (2012): 2432-2438.(prins)
- [11] Wang, Yongguang, et al. "High-performance flexible solid-state carbon cloth supercapacitors based on highly processible N-graphene doped polyacrylic acid/polyaniline composites." *Scientific reports* 6 (2016): 12883.(result)
- [12] Yang, Junghoon, et al. "Rapid and controllable synthesis of nitrogen doped reduced graphene oxide using microwave-assisted hydrothermal reaction for high power-density supercapacitors." *Carbon* 73 (2014): 106-113.(yang)
- [13] Qiu, Yongcai, Xinfeng Zhang, and Shihe Yang. "High performance supercapacitors based on highly conductive nitrogen-doped graphene sheets." *Physical Chemistry Chemical Physics* 13.27 (2011): 12554-12558.(3)
- [14] Jeong, Hyung Mo, et al. "Nitrogen-doped graphene for high-performance ultracapacitors and the importance of nitrogen-doped sites at basal planes." *Nano letters* 11.6 (2011): 2472-2477.(4)
- [15] Luo, Gaixia, et al. "Hole defects and nitrogen doping in graphene: implication for supercapacitor applications." *ACS applied materials & interfaces* 5.21 (2013): 11184-11193.(5)
- [16] Shen, Hao, et al. "N-substituted defective graphene sheets: promising electrode materials for Na-ion batteries." *RSC advances* 5.22 (2015): 17042-17048.(6)