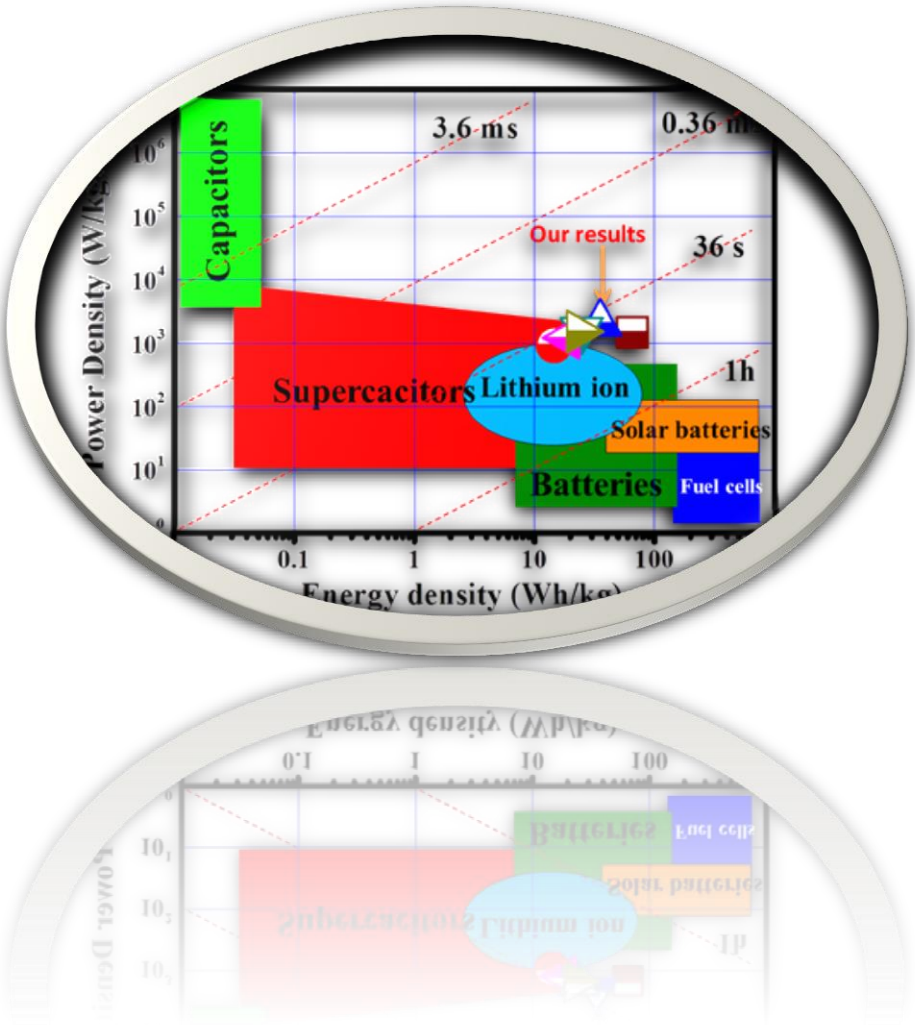
Chapter 9

Conclusions and future works



9.1 Conclusions of the thesis

The research work done in this thesis focused on the synthesis of 2-D nanomaterials and their nanocomposites for supercapacitor energy storage applications. For the development of supercapacitor, correct choice of electrode materials and electrolyte solutions are played very significant role. The following points emerged as conclusions from the detail works done described in the chapters 4-8 of the thesis:

1. A systematic study was done to prepare the 2-D nanosheets of TMOs from their bulks by mixed solvent exfoliation using ethanol and water. The results concludes two poor solvents ethanol and water can be a good solvent for exfoliating TMOs when they combined in a particular volume fraction. The versatile mixed solvent method is scalable and gives high concentration (0.42 mg/ml, 0.47 mg/ml and 0.40 mg/ml for MoO_3, MnO_2 and RuO_2 respectively) dispersion of TMOs nanosheets, higher than that reported previously. We have quantitatively analyzed the absorption spectra for all dispersions to optimize the volume fractions of water and ethanol to disperse TMOs. The results showed concentrations of TMOs dispersions are directly dependent on the volume fraction of ethanol in water with maximum concentration at 65% ethanol in water for MoO_3.Whereas for both MnO_2 and RuO_2 maximum concentration was obtained at 50% mixed solvent. This mixed-solvent strategy gives great freedom to the researches to design ideal solvent system from unlimited number of possible solvent mixture for various layered materials to exfoliate. Exfoliation of TMOs in mixture of two low boiling point solvents offers obvious advantages, including low cost, less toxicity compare to previously used organic solvents, no additive required, and easy removal. AFM and HRTEM and FESEM study shows that mostly bi-layer nanosheets are with average lateral size of 300 nm for MoO_3, 200 nm for MnO_2 and 100 nm for RuO_2 were obtained. The exfoliated nanosheets obtained specific surface area of 55.7 m^2 /g, 48.6 m^2 /g, 53.5 m^2/ g for MoO_3, MnO_2 and RuO_2 nanosheets respectively. Whereas, the total specific surface area of 151.4 m^2 /g, 122.8 m^2 /g, 142.6 m^2 /g were obtained for the MoO_3/SWCNT, MnO_2/SWCNT and RuO_2/SWCNT nanocomposites respectively. The large specific surface area and mesoporous structure provides more active sites and shortening ion diffusion paths between electrode and electrolyte for electrochemical reactions, which reflected in the electrochemical result obtained for SWCNT/TMOs thin films supercapacitor.

The MoO_3/SWCNT flexible symmetric solid state supercapacitor delivered maximum specific capacitance of 717 F/g at 5 mV/s, whereas MnO_2-SWCNT and RuO_2-SWCNT symmetric supercapacitor exhibited a specific capacitance of 540 F/g and 676 F/g respectively. The symmetric supercapacitors exhibit excellent flexibility and long cycle life, leading to an extremely high energy density (24.89 Wh/Kg at 1.61 kW/kg, 18.73 Wh/Kg at 1.21 kW/Kg and 23.48 Wh/Kg at 1.52 kW/Kg), whereas, in-plane micro supercapacitors based on few layered MnO_2 and SWCNT hybrid displayed excellent specific capacitance of 560.22 F/g with significant energy density of 77.80 Wh/kg.

2. A systematic study was conducted for the synthesis of $BiVO_4$ nanoparticle by varying the hydrothermal reaction conditions. The well crystalline $BiVO_4$ nanoparticles having almost same in shape and size with an average dimension of ~20–30 nm are obtained at the optimum growth duration of 90 min. The growth mechanism of the morphology was investigated by SEM analysis. We have also synthesized $BiVO_4$ embedded rGO hybrid nanostructure with three different GO concentrations by a simple cost effective hydrothermal method. Structure, surface morphology and capacitive behaviours of $BiVO_4$/rGO hybrid were well investigated. We have studied the electrochemical properties of as prepared hybrid to know its performance as symmetric supercapacitor electrodes with both PVA/H_2SO_4 solid and Na_2SO_4 aqueous electrolytes. The obtained maximum specific capacitance is 400 F/g at 5 mV/s scan rate in solid electrolyte and 245 F/g in aqueous Na_2SO_4 at same scan rate. High energy density (35.37 Wh/Kg) and excellent cycle stability makes this hybrid suitable for application in supercapacitor.
3. Well crystalline BiOCl nanoplates were prepared by simple hydrothermal route. BiOCl /MWCNT based nanocomposites with different weight percentage of BiOCl as electrodes were designed for light-weight flexible high performance thin film supercapacitor. As prepared nanoplates was characterized by XRD, Raman, FESEM, TEM and XPS. The N_2 adsorption–desorption measurement result shows among different compositions, composite with 60 wt% BiOCl exhibits maximum specific surface area of 22.750m^2/g . The 60 wt% BiOCl composite flexible supercapacitor delivered highest specific capacitance of 421F/g and energy density 14.62 Wh/Kg. Excellent cycle stability with only 6% reduction in specific capacitance after 2000 cycles and good stability under

bending, making the fabricated supercapacitor extremely promising as a flexible energy storage device.

4. MoS_2 nano sheets and MoS_2/rGO hybrid also synthesized by hydrothermal route. The thin film of hybrid electrodes on an Au coated PET obtained specific capacitance of of 14.09mF/cm^2 at 5mV/s, much higher than that of only MoS_2 electrodes 0.79mF/cm^2 at the same scan rate. Hybrid electrode exhibits high energy density of 5.71mWh/cm^2 and a power density of 54.1mW/cm^2. The composite electrode exhibits an excellent stability after 1000 cycles.
5. Vanadyl phosphate nano sheets/MWCNT free standing thin films were prepared by vacuum filtering. The nanocomposite electrode yielded a specific capacitance of 236 F/g at the scan rate 5 mV/s much higher than that of MWCNT electrodes (49 F/g) at the same scan rate. The nanocomposite electrode exhibited energy density of 65.6 Wh/Kg at a power density 1476 W/Kg. could be a good candidate for electrode of supercapacitor with superior energy efficiency.Fig. 9.1 represents the Ragone plot of our 2-D material based supercapacitor compare with reported literature. Overall, the work based on the 2-D nanomaterials presented in this thesis mostly enhanced the energy storage performance of the supercapacitors towards light weight flexible energy storage device applications.

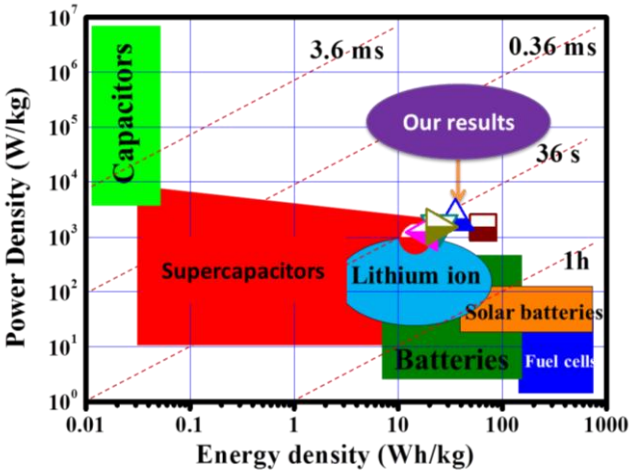


Figure 9.1. Ragone plot of our 2-D material based supercapacitor compare with reported literature.

9.2 Future Works

In recent years due to the fast development of electronic devices including flexible smart window, flexible transparent touch screens, electronic books etc., investigation on flexible transparent electrodes has attracted huge attention.[1–5] commercially available transparent ITO (Indium tin oxide) electrode may be replaced by carbon nanotubes (CNTs)[6], graphene[7], metal nanowires[8], Conductive polymers based transparent electrode to improve the performance of supercapacitor. Energy density is directly proportional to the square of the voltage window as well as the capacitance value, so enhancement of the energy density can be done by increasing both voltage window and capacitance value. Adding redox-active materials such as copper chloride, potassium iodide, hydroquinone etc. into the electrolytes is an easy process to improve the electrochemical performances because of extra pseudo capacitance contribution from the redox active electrolyte at the electrode-electrolyte interface.

Some of the future prospects of these present research works can be explored as follows

1. BiOCl/SWCNT based flexible transparent high performance supercapacitors.
2. Fe_2O_3/SWCNT based flexible transparent thin film supercapacitor with AgNWs as current collector.
3. Improve electrochemical performance of BiOCl/rGO supercapacitors after adding redox-active materials to the electrolyte.

9.3 References

1. S. De, P.E. Lyons, S. Sorel, E.M. Doherty, P.J. King, W.J. Blau, P.N. Nirmalraj, J.J. Boland, V. Scardaci, J. Joimel, J.N. Coleman, *ACS Nano* ,2009, **3**,714–720.
2. H.Z. Geng, K.K. Kim, K.P. So, Y.S. Lee, Y. Chang, Y.H. Lee, *J. Am. Chem. Soc.*,2007,**129**,7758–7759.
3. Y. Zhou, F. Zhang, K. Tvingstedt, S. Barrau, F. Li, W. Tian, O. Inganäs, *Appl. Phys. Lett.*,2008,**92**, 2006–2009.
4. G. Eda, Y.Y. Lin, S. Miller, C.W. Chen, W.F. Su, M. Chhowalla, *Appl. Phys. Lett.,* 2008, **92**,10–13.

5. W. Hong, Y. Xu, G. Lu, C. Li, G. Shi, *Electrochem. Commun.* ,2008, 101555–1558.
6. X. Wang, L. Zhi, K. Müllen, *Nano Lett.*, 2008, **8**,323–327.
7. S. Bae, H. Kim, Y. Lee, X. Xu, J.S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. Il Song, Y.J. Kim, K.S. Kim, B. Özyilmaz, J.H. Ahn, B.H. Hong, S. Iijima, *Nat. Nanotechnol.*,2010,**5**,574–578.
8. J. Lee, P. Lee, H.B. Lee, S. Hong, I. Lee, J. Yeo, S.S. Lee, T.S. Kim, D. Lee, S.H. Ko, *Adv. Funct. Mater.*,2013,**23,**4171–4176
9. N. Kim, S. Kee, S.H. Lee, B.H. Lee, Y.H. Kahng, Y.R. Jo, B.J. Kim, K. Lee, *Adv. Mater.*, 2014, **26**,2268–2272.