

Preparation and characterization of Polyacrylonitrile/Manganese Dioxides- based Carbon Nanofibers via electrospinning process

F E Che Othman^{1,2}, N Yusof^{1,2}, J Jaafar^{1,2}, A F Ismail^{1,2}, H Hasbullah^{1,2}, N Abdullah^{1,2}, M S Ismail^{1,2}

¹Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia.

²Faculty of Petroleum and Renewable Energy Engineering (FPREE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Bahru, Malaysia.

E-mail: ^{1,2}norhaniza@petroleum.utm.my

Abstract. This research reports the production of precursor polyacrylonitrile (PAN)/manganese dioxide (MnO₂) nanofibers (NFs) via electrospinning method followed by stabilization and carbonization processes. Nowadays, electrospinning has become a suitable method in manufacturing continuous NFs, thus it is employed to fabricate NFs in this study. The microstructural properties and adsorption competencies of the produced NFs were also studied. The NFs were prepared by electrospinning the polymer solution of Polyacrylonitrile (PAN) and Manganese Dioxide (MnO₂) in N, N-Dimethylformamide (DMF) solvent. The factors considered in this study were various polymer PAN/MnO₂ concentrations which will significantly affect the specific surface area, fiber morphology and the diameter of the NFs prepared. Subsequently, heat treatment is applied by setting up the stabilization temperature at 275 °C and carbonization temperature at 800 °C with constant dwelling time (30 min). Nitrogen gas at constant rate 0.2 L/min was used for stabilization and carbonization with the stabilization rate (2 °C/min) and carbonization rate (5 °C/min). The carbon nanofibers (CNFs) produced were characterized using Scanning Electron Microscopy (SEM), Brunauer Emmett and Teller (BET) surface area and Fourier Transmission Infrared Spectroscopy (FTIR). It was found that the PAN/MnO₂ CNFs were successfully produced with the carbonization temperature of 800 °C. The prepared PAN/MnO₂ CNFs prepared showed an enhanced in specific surface area about two times compared to it precursor NFs.

1. Introduction

The environmental effect of continuously relying on using fossil fuel is already felt by the whole world in the form of greenhouse effects from the combustion of fossil fuels such as diesel, gasoline (petrol) and kerosene [1].

^{1,2}To whom any correspondence should be addressed.



Due to this environmental crisis, researchers have proposed the use of less harmful fuels such as the natural gas in order to reduce dependable on other heavy fossil fuels. Natural gas (NG) has shown a growing interest because of its wide availability as it supplies 20 % of the world's commercial energy needs [2]. This is due to the fact that natural gas is still available in abundance and is the cleanest fossil fuels as it produces a cleaner combustion and a better consumption [1,3], with incredibly less non- carbon emissions [4,5,6,7].

In the case of natural gas, their uses as an automotive fuel present the advantage of their lower emissions relative to gasoline. However, the main limitation is the problem of their storage on a limited on-board tank volume. Advanced storage units with sufficiently high (volumetric and gravimetric) energy storage capacity need to be developed. Among the possible alternatives for storing NG such as liquefied natural gas (LNG) and compressed natural gas (CNG), adsorbed natural gas (ANG) happened to be the most suitable way as this technique can store NG at very low pressure (4 MPa)[8] by utilizing microporous solid as their adsorbents. Nevertheless, for on-board storage applications, additional constraints are still placed on developing further the carbon adsorbents to increase the storage capacity. Currently, the use of carbon adsorbents especially ACFs [9], has allowed the storage of considerable amounts of natural gas at room temperature and at pressures lower than 4 MPa, thus making it more attractive for practical use [10].

In order to implement the ANG method, the biggest drawbacks that need to be overcome by the researchers is the development and evaluation of adsorbents [11]. However, the fabrications of fibers also play a vital role in physical microstructure of the fibers itself. Based on valuable developments in the nano-era, wide potential applications for carbon fibers were expected and huge efforts were concentrated on their synthesis. This issue has caused an increasing in the quantity of correlated study articles published in the last two decades. It has been generally accepted that the quality of the high performance electrospun NFs greatly depend on the processing condition and composition of the precursor as well as the heat treatment. Therefore, electrospinning which is a simple and interesting method to make very fine carbon nanofibers (CNFs) in the diameter range about 10 μm to 10 nm with polyacrylonitrile (PAN) has been greatly developed. The development of the nanofibers contributed to significant improvement of the production of nanofibers offering high porosity and high surface area to volume ratio. To date, many researchers have developed CNFs embedded with metal and metal oxides to increase the gas adsorption activity. This is because metal oxides itself has large specific surface area that enhance the surface reactivity and consequently improved adsorptivity.

Therefore, in this study, the writers aim to fabricate CNFs by electrospinning method using a composite solution containing polyacrylonitrile (PAN) and different concentration of Manganese Dioxide (0, 1 and 2 wt.% MnO_2) in N,N-dimethylformamide (DMF). Then, PAN/ MnO_2 -based NFs are prepared by undergoing the heat treatment processes which are stabilization (275 $^{\circ}\text{C}$) and carbonization (800 $^{\circ}\text{C}$). The CNFs were characterized using Scanning Electron Microscopy (SEM), Fourier Transmission Infrared Spectroscopy (FTIR), and Brunauer Emmett and Teller (BET) surface area.

2. Experimental

2.1 Materials

Polyacrylonitrile (PAN, $M_w = 150,000$), which contained 91.4 wt.% acrylonitrile monomer ($\text{CH}_2=\text{CHCN}$) and 8.6 wt.% methylacrylate comonomer ($\text{CH}_2=\text{CHCOOHCH}_3$) was purchased from Sigma-Aldrich (USA). The average molecular weight of polymer was about 55,500 Da. Dimethylformamide (DMF; ~ 99.98 % purity) and manganese dioxides were also purchased from Sigma-Aldrich (USA).

2.2 Preparation of PAN nanofibers with N,N-dimethylformamide and metal oxides

The dope solution was prepared by adding 0, 1, and 2 wt.% of MnO₂ into 90, 89, and 88 wt.% of DMF, respectively. The mixture was stirred for at least 5 hours to ensure the MnO₂ dispersed well in the solution before adding up the PAN 10 wt.%. The dope was left to stir for 24 hours. The electrospinning process was carried out at optimum parameters as extracted from literature review; the voltage used is 12 kV, the infusion rate was 1 ml/min and the distance of the tip of needle to the collector was 20 cm, where aluminium foils were used as the collectors.

2.3 Carbonization of PAN-based nanofibers

All PAN nanofibers were stabilized at 275 °C under nitrogen gas flow at a heating rate of 2 °C/min with 30 minutes dwelling time. Then, the stabilized PAN nanofibers were carbonized by using nitrogen gas at 800 °C at the heating rate of 5 °C/min with 30 minutes dwelling time. The gas flow rate for both stabilization and carbonization were maintained at 0.2 L/min.

2.4 Characterization

The physical morphological features of both NFs and CNFs were observed using Scanning Electron Microscopy (SEM), whereas Brunauer Emmett and Teller (BET) method have been used to determine the specific surface area of the precursor NFs and CNFs, and Fourier Transmission Infrared Spectroscopy (FTIR) analysis depicts the presence of a variety of functional groups of both NFs and CNFs.

3. Results and Discussions

3.1 Scanning Electron Microscopy (SEM)

The SEM micrographs in Figure 3.1 (a, c and e) showed the electrospun nanofibers of various MnO₂ loading before carbonization. There was a variety of fibers' thread were produced such as straight line and bent fibers. Moreover, a few beads can be detected from the micrograph and this is due to the inconsistent or uncontrolled electrospinning condition such as surrounding environment temperature. Predictably, in Figure 3.1(e) 2 wt.% MnO₂ composition revealed more presence of white spot compared to 1 wt.% MnO₂ (Figure 3.1(c)). The electrospun precursor (0 wt.% of MnO₂) shows the average diameter ranging from 488 nm to 612 nm as can be seen in Figure 3.1 (a). From physical observations of SEM micrographs, the PAN nanofibers generated without MnO₂ loading (Figure 3.1(a)) have the most straight line fibers as compared to other precursors with 1 and 2 wt. % of MnO₂.

Figure 3.1 (c) showed the SEM image of fibers with 1 wt.% of MnO₂ composition which mostly has straight line fibers and a few bent fibers. In addition, the physical sign of white spot on the fibers indicated the presence of 1 wt.% of MnO₂ on the fibers. The fibrous nature of precursor nanofibers reveals a range of fiber diameters which from 792 nm to 1.45 µm. Figure 3.1 (e) shows SEM images of the precursor nanofibers with additives concentration of 2 wt.% MnO₂ revealed more presence of MnO₂ (white spot). The physical morphology of 2 wt.% MnO₂ precursor show mostly bent fibers and contain few beads and its average diameter ranging from 642 nm to 761 nm. Nevertheless, future study on solution and process parameters may give better understanding on how it affects the diameter of nanofibers. In theory, smaller diameter gives high specific surface area might due to the interaction of metal oxides with PAN precursor [12,13].

Figure 3.1 (b,d and f) demonstrated the SEM images of PAN/MnO₂- based NFs with each composition (0, 1 and 2 %) after carbonization. The rougher and wrinkled fibers portrayed the shrinkage of the diameter of nanofibers during stabilization and carbonization process. From the SEM observation of 800 °C carbonization temperature, it can be seen that 2 wt.% of MnO₂ composition produced smallest fibers diameter if compare to others composition and its average diameter around 335nm to 722nm.

This is due to the catalytic effects of MnO_2 with the PAN precursor such as graphitization of carbon as it helps bind the carbon element together which resulting nanofibers with smaller diameter that gives high specific surface area [12].

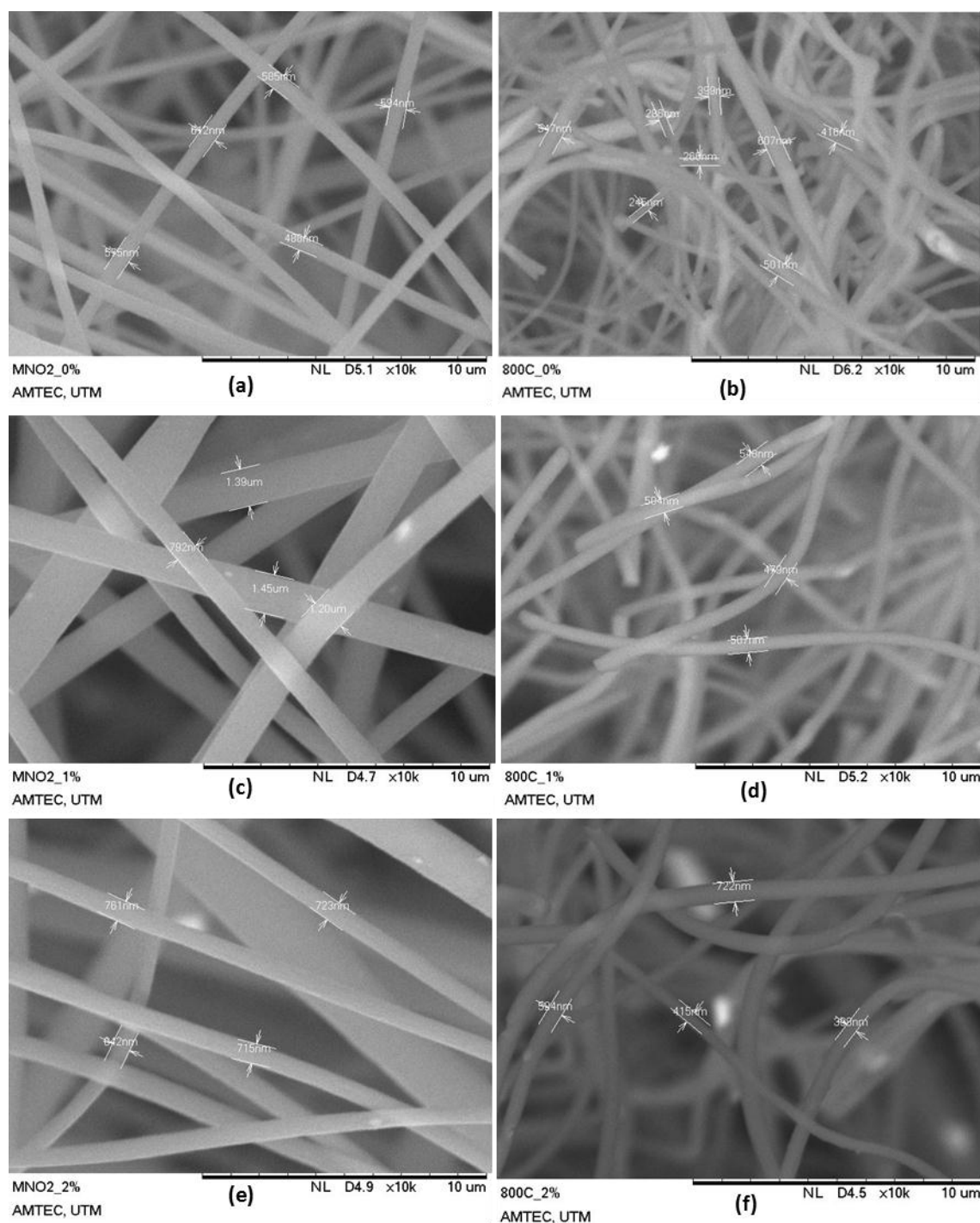


Figure 1 SEM images of 0 wt.% (a and b), 1 wt.% (c and d), and 2 wt.% (e and f) of MnO_2 before and after carbonization at 800 °C

3.2 Fourier Transmission Infrared Spectroscopy (FTIR)

PAN-based nanofibers (NFs) typically will show the existence of CH_2 , $\text{C}\equiv\text{N}$, $\text{C}=\text{O}$, $\text{C}-\text{O}$ and $\text{C}-\text{H}$ bonds but after complete pyrolysis process most of these transition compounds were expected to evolve as volatilities and only carbon and hydrogen atoms remain. Figure 3.2 (a) shows the FTIR spectra of PAN NFs precursor of 0, 1, and 2 wt.% MnO_2 before carbonization. As can be seen, there are seven peaks at the wavenumber of 2914.44, 2241.28, 2160.27, 1618.28, 1450.47, 1350.17 and 1063.78 cm^{-1} that representing several functional groups appeared in both sole and modified PAN NFs.

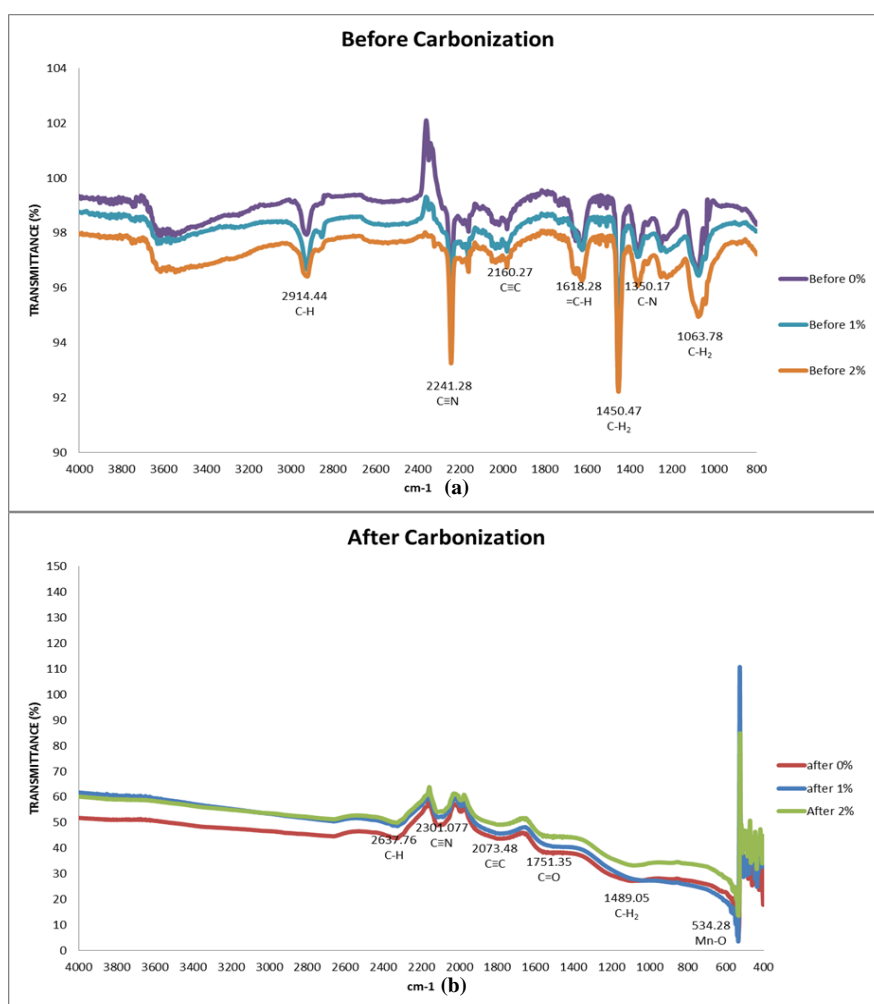


Figure 2 (a) FTIR spectrum of PAN nanofibers before carbonization (b) FTIR spectrum of PAN nanofibers after carbonization

Figure 3.2(b) show the spectrum of both carbonized sole and modified PAN NFs. After carbonization, most of the high peaks observed in Figure 3.2(a) either diminished or replaced with other peaks. This is because during oxidation, numerous new transition structures were formed such as ketones, aldehydes and carboxylic acid and all of these bonds were expected to be removed during pyrolysis process. However, carbonization conducted cannot completely converted the polymer into carbon as the existence of other groups ($\text{C}\equiv\text{N}$, $\text{C}=\text{O}$) as shown in the Figure 3.2(b). The presence of MnO_2 also can be observed in the FTIR spectrum of PAN. The wavenumbers of MnO_2 is approximately at 534.28 cm^{-1} corresponds to the $\text{Mn}-\text{O}$ bond [14,15]. From the above result, it can be confirmed that the synthesized nanomaterial manganese oxide is added into the NFs. There is not

much change of the FTIR spectrum between the NFs with the varied of MnO_2 loading because the compounds are still the same but only varies in quantity. It can be concluded that carbonization process seems not enough to remove all non-carbons atom (N, O) in all PAN NF samples and another pyrolysis steps (activation) are believed to convert almost 99% polymer into carbon can be done in future study.

3.3 Brunauer, Emmett and Teller (BET) surface area

In this study, the single point BET method have been used in order to determine the specific surface area of nanofibers with and without manganese dioxide (MnO_2) loading before and after carbonization as summarized in Figure 3.3. The specific surface area of 0, 1, and 2 wt.% MnO_2 before carbonization were 9.13 m^2/g , 10.26 m^2/g , and 12.45 m^2/g , respectively.

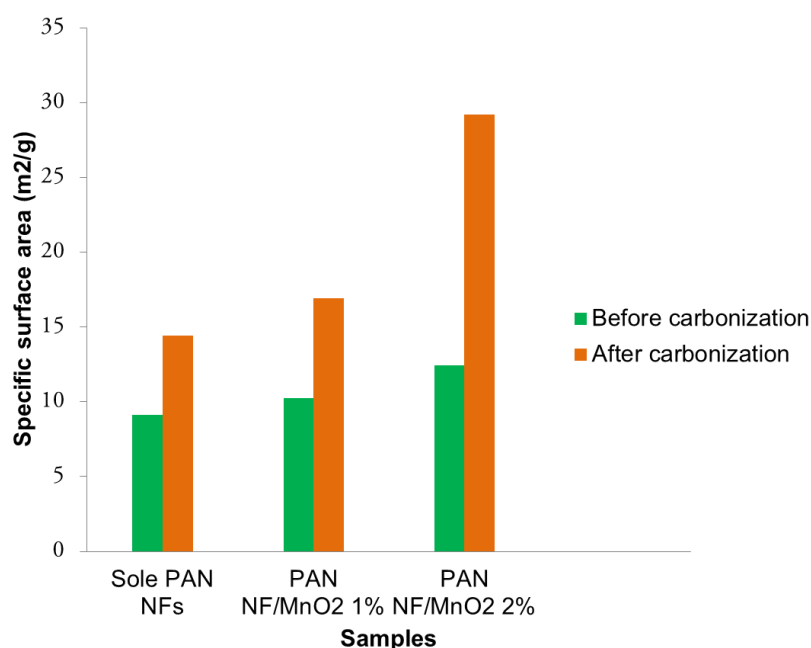


Figure 3. Specific surface area of nanofibers with different concentration of manganese dioxide loading before and after carbonization

As tabulated in Figure 3.3, the pure PAN NFs show the lowest specific surface area of 9.13 m^2/g and when the compositions of MnO_2 are increased from 1 wt.% to 2 wt.%, the surface area increased from 10.26 m^2/g to 12.45 m^2/g . Overall, the specific surface area values show $0 < 1 < 2$ % MnO_2 while the diameter of the fibers show a reverse trend.

Bas and co-workers [16] showed that the BET surface areas measured before carbonization were in the range of 64-75 m^2/g . This study is slightly lower when comparing to the specific surface area of PAN NFs obtained which is from 9.13-12.45 m^2/g compared to Bas and co-workers. Carbonization of the nanofibers increased the surface areas of the fibers up to 29.20 m^2/g . The low SSA obtained in this study was due to the incomplete pyrolysis process as the temperature of the tube furnace does not increase regularly as set up in first hour and because of this problem, the burn-off of nanofibers was incomplete. This data indicates that the addition of MnO_2 in precursor solution resulting an increase in specific surface area of fiber materials, however the pyrolysis process also contribute great effects to the completeness combustion of the fibers.

The results concurred with theoretical ideas which stated that the amount of metal oxides will increase the specific surface area up to its optimum loading. Most of the journals revealed the results obtained are from CNFs. Thus, the experimental precursor might enhance the surface area once it's

been carbonized. These results somehow provide an avenue for the enhancement of adsorption properties of CNFs by improving the surface area of its precursor NFs.

4. Conclusions

As a result, all precursors of PAN/ MnO₂-based CNFs were successfully fabricated by using electrospinning method. It clearly demonstrates that, the PAN/ MnO₂ CNFs diameter and specific surface area were found to be affected by concentration of metal oxides. The average diameter of all precursors was approximately ranging from 980 to 287 nm. Moreover, the FTIR peaks at 534.28 cm⁻¹ indicated the presence of MnO₂ inside the composite CNFs. The increment of the amount of metal oxide nanoparticles up to 2 wt. % embedded in precursor also increased its specific surface area about two times compared to its precursor NF. It can be concluded that CNFs embedded with higher MnO₂ (up to its maximum loading) possessed better characteristics in terms of fiber diameter or specific surface area.

5. References

- [1] Vasiliev L L, Kanonchik L E, Kulakov A G and Babenko V A 2007 *Int. J. Therm. Sci.* **46** 914-25
- [2] Azeman M 2009 Gas Processing & Liquefaction. SKG 5113.
- [3] Zakaria Z, Mustafa A and Lim T P 2009 *International Journal of Oil, Gas and Coal Technology* **2** 4 365-78
- [4] Broom D P and Thomas K M 2013 *Materials Research Society Bulletin* **38** 412-21
- [5] Yusof N and Ismail A F 2012 *J. Anal. Appl. Pyrolysis* **93** 1-13
- [6] Yusof N and Ismail A F 2012 *Polym. Eng. & Sci. J.* **52** 360-66
- [7] Yusof N, Ismail A F, Rana D and Matsuura T 2012 *Mater. Lett.* **82** 16-18
- [8] Zubizarreta L, Arenillas A and Pis J J 2009 *Int. J. Hydrogen Energy* **34** 4575-78
- [9] Lozano C D, Alcaniz M J, de la Casa L M A, Cazorla A D and Linares S A 2002 *Fuel* **81** **14** 1777-1803
- [10] Linares S A and Cazorla A D 2013 Activated Carbon Fibers *Handbook Advanced Ceramics* (Amsterdam: Elsevier Inc.) Chapter 2.9
- [11] Im J S, Park S J, Kim T and Lee Y S 2009 *International Journal of Hydrogen Energy* **34** 3382
- [12] Cuenya B R 2010 *Thin Solid Films* **518** 3127
- [13] Nowak J D and Ca C B 2009 *Journal of Materials Science* **44** 2408
- [14] Kang L, Zhang M, Liu Z H and Ooi K 2007 *Spectrochim. Acta. A* **67** 864
- [15] Li L, Pan Y, Chen L and Li G. 2007 *Solid State Chem.* **180** 2896
- [16] Bas S, Hakil O, Dumanli A G and Yurum 2008 *Hacettepe J. Biol. & Chem.* **36** **3** 247-53

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