



Direct Synthesis Carbon/Metal Oxide Composites for Electrochemical Capacitors Electrode

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ABSTRACT

This paper deals with the study of the carbon/metal oxide composites synthesis for electrochemical capacitor electrode material. Transition metal salts, such as FeCl₃ and TiCl₃ act as activator in the synthesis of activated carbon from gelam wood sawdust (*Melaleuca cajuputi* Powell) which also have the functions as substrates for the composites. The surface functionalities of activated carbons were modified using oxidative treatments. The changes on crystallography and surface functionalities were analyzed based on XRD and FTIR data. The electrical conductivities and electrochemical properties were determined using kelvin and cyclic voltammetry methods, respectively. FTIR analyses showed that the activation and oxidation treatments affected their surface functionalities. The XRD analyses showed that oxidative treatments also affected carbons crystallite. The electrical conductivities and electrochemical properties were influenced by their crystallite and surface functionalities. The shape of the cyclic voltammograms varied according to the changes on the surface functionalities and on the metals loading. TEM analyses indicated the existence of nanoparticles metal oxides in the carbon samples.

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1. Introduction

The chemistry of carbon in the past decade had been dominated by the finding of fullerenes and carbon nanostructures as new carbon allotropes (Harris 2005; Heller *et al.* 2006; Endo *et al.* 2008). It is well-known that carbonaceous materials like graphite, soot, coals, and chars have the characteristic in their structural appearances which vary from mostly random or amorphous to a perfectly ordered crystalline structure. Activated carbon materials are characterized by its high specific surface area and porosity. High surface area activated carbon has been extensively applied as electrode material in electrochemical capacitor (EC). Theoretically, activated carbon with higher surface area will have higher specific capacitance. However, in practice, it is more complicated to measure and usually the measured capacitance does not have a linear relationship with the specific area at the electrode material. The main reason for this phenomenon is that the pores may not be accessible by the electrolyte, especially the big organic ions and solvated ions. Ions which are too big to enter the pores will not contribute to the total double layer capacitance of the electrode material.

The use of carbon materials in electrochemistry has been related to their surface functional groups (Lpez-Garzn *et al.* 2003; Lim *et al.* 2004; Béguin *et al.* 2006). Surface chemical functional groups of carbons are derived from the activation process, the various processing routes, the used precursors, the activation conditions, and the post chemical treatment, such as oxidation (Shen *et al.* 2008; Wang *et al.* 2008). These factors also affect the crystallographic properties (Andrews *et al.* 2002; Mochida *et al.* 2006).

Meanwhile, many researchers have focused on the development of an alternative electrode material for EC. Many transition metal oxides showed to be suitable as electrode materials for ECs, such as ruthenium oxides. Ruthenium oxides are easy to prepare, stable in aqueous electrolytes and have very high capacitance (Wang *et al.* 2005), whilst the disadvantage of Ru₂O is the high cost of the raw material. Therefore, several metal oxides and hydroxides, for example Fe₂O₃, TiO₂, and NiO have been studied in order to obtain low cost materials, which were mixed with carbon electrode as composites. Instead of introducing high capacitance material to fabricated EC, it is also necessary to improve carbon the properties of carbon material. It was reported that the capacitance and electrical conductivity increased with the amount of surface oxygen functional groups (Bleda-Martinez *et al.* 2005) and the crystalline phase on the carbon.

In this work, gelam wood (paper-bark wood, *Melaleuca cajuputi* Powell) sawdust was used to prepare activated carbons using chemical activator i.e. transition metal salts which also act as composite precursors. A number of materials with different structures and surface functionalities have been obtained.

Surface functionalities of the activated carbon were modified by heating in concentrate nitric acid under reflux and by aging under hydrothermal condition. All carbons were applied as working electrode in the three electrodes system using acidic and basic aqueous medium, H₂SO₄ and KOH respectively. The materials were characterized in terms of crystallographic, surface chemistry and electrical conductivity. TEM was used to evaluate the size of carbon particles and metal loading in carbon samples.

2. Materials and Methods

The sawdust particles were screened through 100 mesh wire sieved and treated with 20% HCl for 1 day, filtered, washed with demin-water then dried over night at 110°C. Sawdust particles were impregnated with solution of transition metal, i.e TiCl₃ or FeCl₃ and then were heat-treated under N₂ atmosphere at 700°C for 8-10 hours. The obtained carbon samples were considered as the composite of carbon and metal oxide. Carbon/metal composite were oxidized in concentrated nitric acid under reflux or under pressurized water vapor in the hydrothermal reactor. The nitric acid oxidation was carried out at 60°C for 3 hours as described by Mahalakshmy *et al.* (2009) and the hydrothermal process was conducted at 200°C for 16 hours (Titirici *et al.* 2007). The products were separated by centrifuge and washed with abundant demin-water.

Structural change was detected chemically with FTIR and XRD patterns. X-ray diffraction (XRD) patterns of the carbons were obtained on a Shimadzu X-ray diffractometer XRD 7000 operating at 40 kV and 30 mA, using Cu-K_α radiation. All XRD spectra were analyzed with X-Powder software (ICDD) to obtained quantitative value for crystallographic parameter (Martin-Islan *et al.* 2006). Plane spacing (d_{002}) was calculated by applying Bragg's equation to the [002] diffraction peak, while the crystallite sizes along the c-axis, L_c , and a-axis, L_a , were deduced by Scherrer's equation applied to the [002] and the [100], [110]

diffraction peaks, respectively (Awitdrus *et al.* 2010). FTIR spectra were obtained on Shimadzu IR Prestige 21. The dispersion of metal loading in carbon and the size of the carbon particles were evaluated by the TEM micrographs. TEM micrographs were obtained on JEM-1200EX.

The EC electrodes were fabricated by mixing the composite powder with PTFE binder (Merck, 99%) in isopropanol (Merck, 99%). 20 drops of triethanolamine (TEA) were added into the mixture. Circular electrodes were obtained from 1.5 g of mixture paste in a 20 mm diameter mold, and pressed under 3 tons load and the molded pastes were heated at 300°C on a hot plate for an hour and removed from mold after being cooled.

Electrochemical test for the electrodes were conducted using cyclic voltammetry technique in three electrodes configuration potentiostat. Ag/AgCl electrode was used as reference electrode and Platinum rod was used as the counter electrode. Considering that the anodic voltammetric charges and cathodic voltammetric charges are not the same in the shape of voltammogram curve, the average specific capacitance of the electrode was calculated using integral area approximation (Kuo *et al.* 2007)

$$C_{avg} = \frac{\Delta Q}{(w \times \Delta V)} = \frac{\left(\int IdV \right)}{(s \times \Delta V \times w)} \quad [1]$$

Where ΔQ is the total amount of the charge accumulated over a potential window, ΔV , w is the mass of active material in one electrode, I is the current, and s is the potential scan rate. Hence $\left(\int IdV \right)$ is integral area of voltammogram curve.

3. Results and Discussion

Sawdust particles impregnated with metallic salt were treated by heating in nitrogen atmosphere, metal salt decomposed into the corresponding metallic oxides, which were subsequently reduced the mass of composites (Encinar *et al.* 1997; Antal *et al.* 2003). As the temperature rise, the carbon came close to metal particles.

These particles have diameters in the range of 10-50 nm and built some clusters. This features were revealed by the TEM image obtained for the carbon/Fe₂O₃ composite (Figure

1A). Carbons with nanoporous were formed around the metal oxide particles through a catalytic mechanism that involved the dissolution of amorphous carbon into the catalyst particles followed by the precipitation of graphitic carbon. Figure 1a shows the metal oxide particles, which were surrounded by graphitic carbon shells. The thickness of the carbon layer for these nanostructures was in the range of 10-17 nm, which was in good agreement with the L_c values estimated from the analysis of the XRD patterns. The distinction between carbons and metal oxide particles were clearly shown. In the background, carbon structures were mixed with cluster of metal oxide particles. During the thermal treatment at 700 °C, only the carbon in contact with the metal oxide particles was converted into carbon nanostructures, the rest of the material remained as amorphous carbon. Consequently, the carbonized material contains organized carbon mixed with non-organized carbon. This is clearly shown in Figure 1B where both structures were displayed.

The XRD diffraction patterns of the carbon/metal oxide composite (figure 2) confirm that the carbon materials contained a few amorphous phase. In fact, the non-composite carbon samples prepared from the same precursor exhibit intense XRD peaks at $2\theta = 15^\circ$, 28° and 45° which respectively correspond to the [100], [011] and [002] diffractions of the graphitic framework.

The crystallographic parameters of the carbons were deduced from the analysis of the XRD spectra. Thus, the plane spacing (d_{002}) was calculated by applying Bragg's equation to the [002] diffraction peak, while the crystallite sizes along the c-axis, L_c , and a-axis, L_a , are deduced by Scherrer's equation applied to the [002] and the [100], [110] diffraction peaks, respectively. Values of these parameters are presented in Table 1 and Table 2.

The d-spacing values are presented for [002] reflections indicate the distance between layer planes. Samples synthesized with catalyst have lower values for crystallite size and d-spacing. Carbon in Carbon/ Fe_2O_3 composite was smaller (5 Å) than non-composite carbon (5.3 Å). Nevertheless all d-spacing values of carbon samples which were 5-6 Å, indicated the layer planes were not registered but simply parallel without three-dimensional order also known as turbostratic stacking. L_a and L_c confirmed that carbons and carbon/metal oxide composite were composed of many quasi-graphitic crystallites.

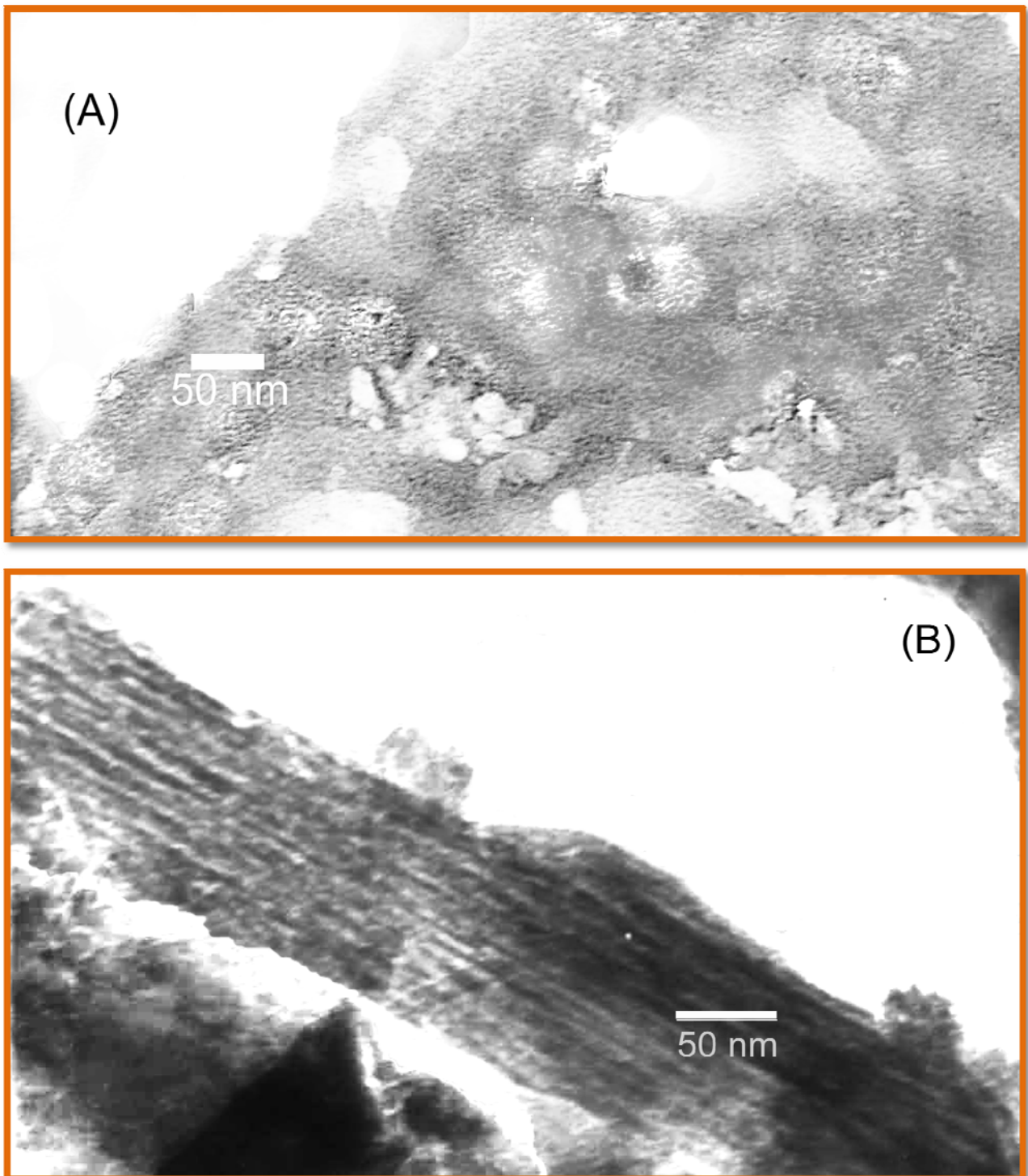


Figure 1: TEM images of carbon/Fe₂O₃ composite, iron oxide cluster exist in carbon matrix (A) and amorphous carbon mixed with crystallite carbon in the activated carbon (B).

The FTIR spectra in Figure 3 and 4 show for the carbon/metal composites, composite carbons and oxidative treated for carbon surface. By means of the FTIR spectroscopy, it is possible to analyze the chemical functionalities of these samples. Generally, the hydrothermal

oxidation would result more surface functionalities than the HNO₃ oxidation. In Figure 3 surface functionalities of carbon/metal composite changed significantly in the C/TiO₂ composite.

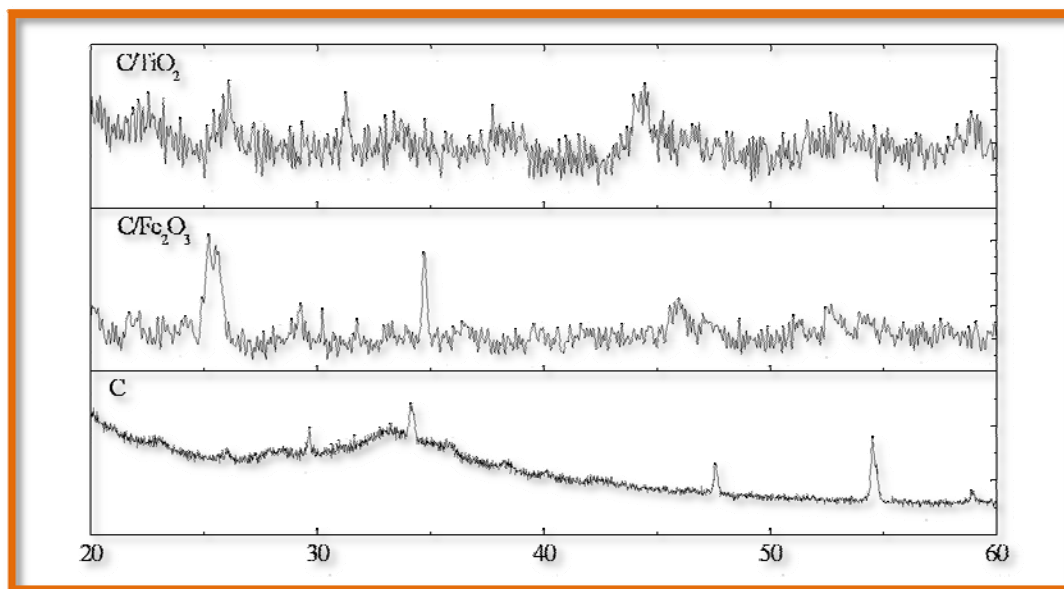


Figure 2: XRD patterns of carbon/metal oxide composites and non-composite carbon. The crystallographic parameters of the carbons were deduced from the analysis of these plots.

Table 1: Crystallographic parameters values for selected carbon/metal oxide composite

Sample	L _a (nm)	L _c (nm)	d-sp. (Å)
Ref. Carbon	2	4	5.6
Non-composite Carbon	2	6	5,3
Carbon/Fe ₂ O ₃ composite	2	2	5,0
Carbon/TiO ₂ composite	3	4	5.0

Table 2: Calculated carbon atom distribution for selected carbon/metal composite

Sample	Layer Percentage		
	Random	Parallel Layer	Single Layer
Reference Carbon	8	31	61
Non-composite carbon	0	39	61
Carbon/Fe ₂ O ₃ composite	1	42	57
Carbon/TiO ₂ composite	3	46	51

It is clearly shown that all carbons spectra have double small peaks in around 2300 – 2400 cm⁻¹ which is the sum of some double bond stretching vibration of C=N, C=O and N=O.

The transmission value at $2300\text{-}2400\text{ cm}^{-1}$, approximately will be in line with the value of transmission in the region $1350\text{-}1700\text{ cm}^{-1}$ which is also appears as double medium peaks.

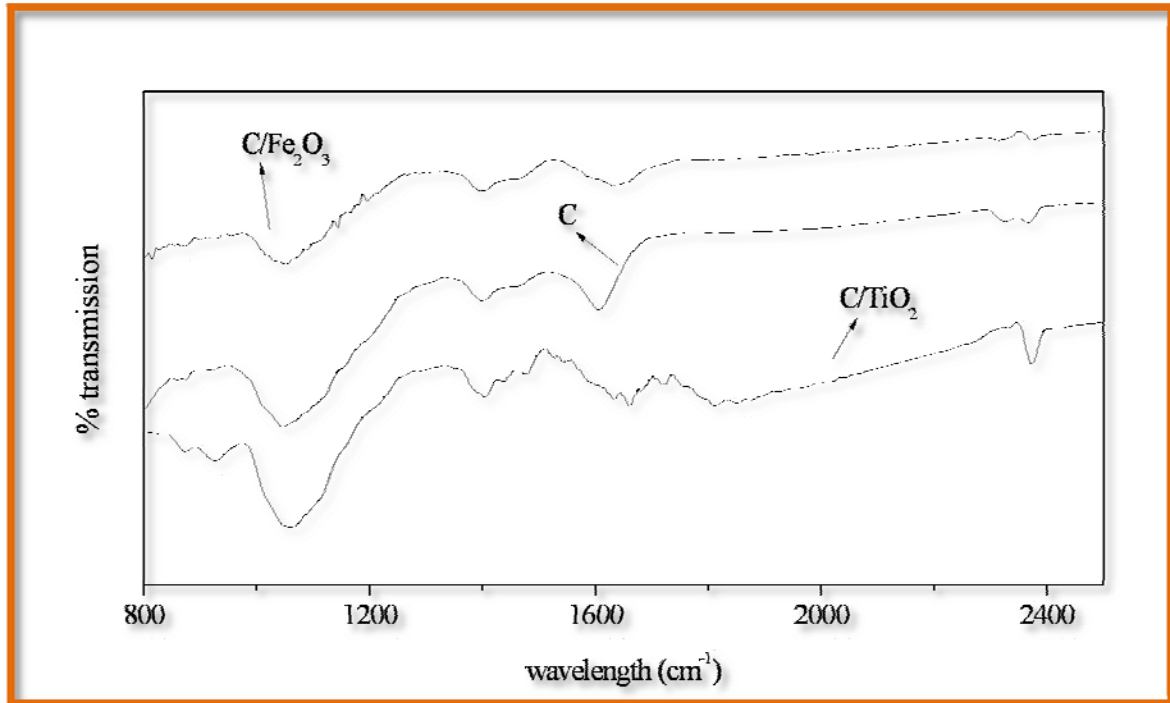


Figure 3: FTIR spectra of carbon/metal oxide composite: C/TiO₂ C/Fe₂O₃ and non-composite carbon: C.

The height of peaks indicate the presence of stretching vibrational of C and N single bond for some bonding configurations such as isocyanate ($-\text{C}-\text{N}=\text{O}$), nitrile and isonitrile (Escobar-Alarcón et al. 2005). The value of absorption around $2300\text{-}2400\text{ cm}^{-1}$ will be lower than that occurs in the region $1350\text{-}1700\text{ cm}^{-1}$ due to the destruction of symmetry bond $\text{C}=\text{C}$.

Single bond vibration band of C and O appears in $1000 - 1100\text{ cm}^{-1}$ as broad peak. The height of the peaks indicated the presence of bending vibrations for same bonding configurations, such as C-O-C, C-O-O, and C-C-O (Matson *et al.* 1970). These features are possessed on non-composite carbon and C/TiO₂ composite. The absorption intensity increase significantly in below 1000 cm^{-1} for C/TiO₂ composite considered as the opposite effect of increasing absorption intensity in the rest of wave number range. Wave numbers below 1000 cm^{-1} are referred as C-C single bond.

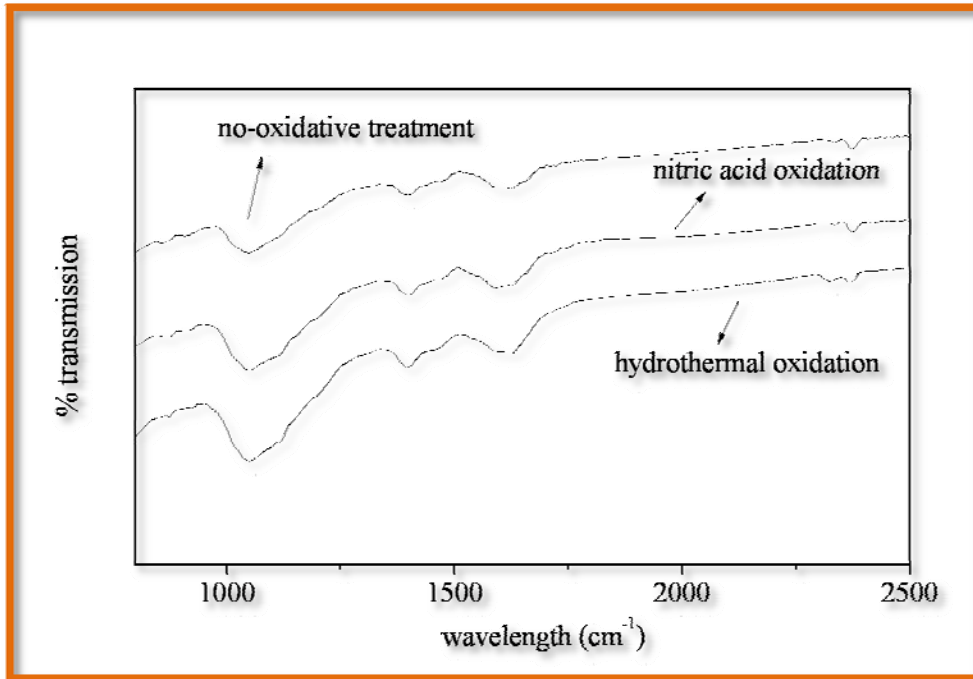


Figure 4: FTIR spectra of carbon/metal composite without oxidation treatment, with hydrothermal oxidation and nitric acid oxidation.

Due to this very broad band it is difficult to determine the transmission bands related to those C-O bending vibrations. Furthermore, in the FTIR spectra of composite C/TiO₂ around 1350-1700 cm⁻¹ where the absorption intensity decreased, is accompanied by increased intensity of absorption at wave numbers around 1900-2000 cm⁻¹ shows the changes in functional groups carbon surface. While the surface of the carbon non-composite and C/TiO₂ composite have much more C = O, C = N, and C = C bond; the majority of the double bonds on the surface of C/Fe₂O₃ composite change to a triple bond or two adjacent double bonds of C, N and O atoms. These features are formed due to the reactivity of Fe atoms.

Figure 4 showed vibrations around 1350-1700 cm⁻¹ which indicated the defacement of the sp² bonding symmetry between carbon layers. This feature caused the vibrations of C-C single bond becomes active (Lazar *et al.* 2005) and could be characterized by the appearance of two absorption bands centered in pairs ± 1395 and ± 1610 cm⁻¹. The absorption bands in this region will appear synchronous with the absorption band at 1350-1700 cm⁻¹.

The change in crystallography and surface functional groups will affect the electrical resistivity of carbon. Electrical resistivity is proportional to the magnitude of electrical

conductivity (Mochidzuki *et al.* 2003). Therefore, conductivity can be explained by the results of resistivity measurement. Resistivity measurements were carried out to produce some value, namely 0.08, 0.09 and 0.23 respectively to the electrodes of activated carbon without oxidation treatment, oxidation with nitric acid and with water vapour in hydrothermal condition. Electrical conductivity values of carbon are influenced by the presence of sp^2 carbon in the activated carbon. Their existence in activated carbon is influenced by the temperature applied to produce activated carbon. The information about electrical conductivity is needed to study electrochemical behavior of carbon electrode as well as the presence of surface functional groups in carbons

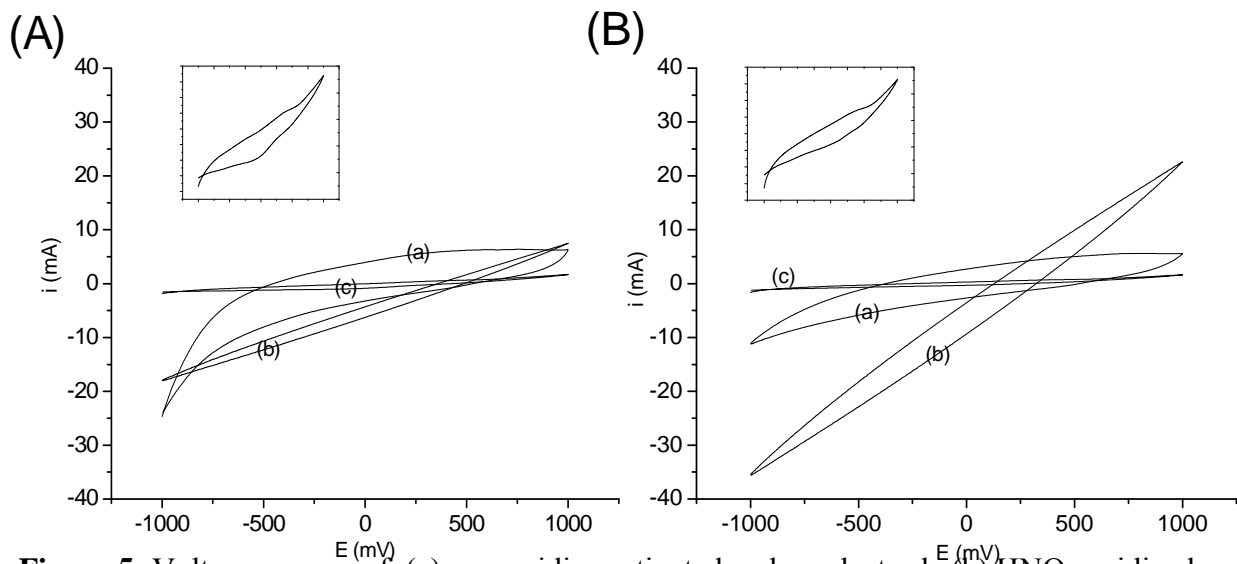


Figure 5: Voltammogram of (a) non oxidize activated carbon electrode (b) HNO_3 oxidized-activated carbon and (c) vapour oxidized activated carbon in 1M H_2SO_4 (A) and 2M H_2SO_4 (B) potential scan rate was 20 mV/s. Inset pictures are used to clarify voltammogram (c).

Electrochemical behavior of the carbons depended on the presence of oxygen-containing surface functional groups. Voltammogram in Figure 5A shows that both oxidation treatments and acid concentration give the distinctive features in electrochemical behavior. This feature are arise due to avialibility of charge carrier i.e. ion. Non-faradaic process in carbon electrode was detected in voltammogram. Capacitance value for non treated carbon electrode was 0.35 F/g. Oxidative treatment tends to construct faradaic process in voltammetry system and tends to demonstrate non-faradaic process while acid oxidize with HNO_3 tends to reduce the double layer facet in electrode. Capacitance values for treated carbon electrode were 1.258 F/g and 0.053 F/g.

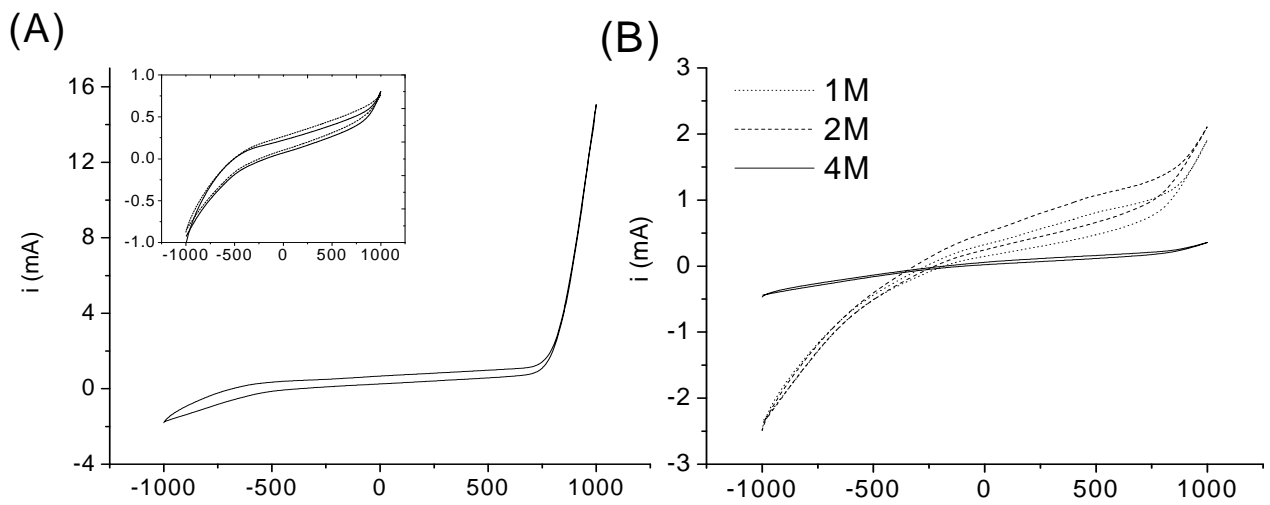


Figure 6: Voltammogram of carbon/metal oxide composite electrode (A) Carbon/TiO₂ composite in 2M H₂SO₄ electrolyte, (B) Carbon/Fe₂O₃ composite in KOH electrolyte, scan rate was 20 mV/s.

Both carbon/TiO₂ and carbon/Fe₂O₃ composites exhibited faradaic process in the end of anodic process marked by sharp peak in the both plots. Specific capacitances were calculated and derived from 2M KOH voltammogram were 0,102 F/g and 0.077F/g for C/TiO₂ and C/Fe₂O₃, respectively.

4. Conclusion

Direct synthesis metal oxide/carbon composites produced amorphous and crystallite carbon and metal oxide clusters in their structures. XRD patterns and TEM images indicated that some particles of metal loaded on carbon were nanometer-scale. The shapes of cyclic voltammograms varied in relation with the changes in the surface functional groups of the carbon. Non-faradaic process of carbon composite was detected over voltammogram on all samples, which indicated the capability to carry capacitive process. Both carbon/TiO₂ and carbon/Fe₂O₃ composites exhibited faradaic process in the end of anodic process. Owing to this unique characteristic, simple preparation and the abundance availability of material, gelam wood sawdust should become a potential candidate as cheap and environment friendly electrode material for electrochemical capacitor.

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