Synthesis of MnO_2/Carbon Dots Nanocomposite Derived From Rice Husk for Supercapacitor Electrodes

Akhiruddin Maddu*‡, Angga Saputra*, Noor Intan Ayuningtiyas*, Annisa Tsalsabila*, Andes Ismayana**, Nurhalim***, Sugianto Arjo****

*Department of Physics, Faculty of Mathematics and Natural Sciences, Bogor Agricultural University, Bogor, Indonesia

**Department of Agroindustrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University, Bogor, Indonesia

***Department of Agronomy and Holticulture, Faculty of Agriculture, Bogor Agricultural University, Bogor, Indonesia

***Department of Physics Education, Universitas Muhammadiyah Prof. Dr. HAMKA, Jakarta, Indonesia

(akhiruddin@apps.ipb.ac.id, angga_saputra@apps.ipb.ac.id, ayuningtyas298@gamail.com, annisatsalsabila@gmail.com, andesismayana@ipb.ac.id, nurhalimh98@gmail.com, s.arjo@uhamka.ac.id)

‡ Corresponding Author; Akhiruddin Maddu, Department of Physics FMIPA IPB, Dramaga, Bogor 16680, Indonesia
Tel: +62 251 862 5728,

Fax: +62 251 862 5728, akhiruddin@apps.ipb.ac.id

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Abstract- This article reports the use of carbon dots (CDs) derived from rice husk that was composited with MnO_2 to be applied as supercapacitor electrodes. CDs were synthesized by acid hydrolysis method with the addition of urea as nitrogen doping source. CDs produced were well dispersed in water and show a blue-green emission under UV light exposure. Photoluminescence test was carried out by excitation using a violet laser (405 nm) that showed a broad spectrum with the peak wavelength at 497 nm. The average particle size of CDs was found about 11 nm taken using particle size analyzer (PSA). MnO_2/CDs nanocomposites were made by mixing MnO_2 and CDs solution. X-ray Diffraction (XRD) analysis confirmed that the MnO_2/CDs nanocomposites have been formed. Energy Dispersive X-ray Spectroscopy (EDXS) analysis confirmed the presence of any element that forming the nanocomposites. The electrodes were fabricated by coating the MnO_2/CDs nanocomposites onto the glassy graphite electrode, then measured their electrochemical characteristics to determine the specific capacitance of the electrodes. The high specific capacitance value was found up to 300 F/g based on the cyclic voltammetry data.

Keywords- Carbon dots; rice husk; specific capacitance; supercapacitor.

1. Introduction

A supercapacitor is a new device for energy storage system that is different from a battery or traditional capacitor that have a low capacity for energy storage. As an electrochemical capacitor, supercapacitor is excellent as energy storage devices because they have high power density, high energy density, excellent reversibility, and long life cycles compared to batteries or conventional capacitors [1, 2]. Supercapacitors have a capacity of thousands times higher in energy storage than conventional capacitors [3], so that the supercapacitors offer broad and efficient application opportunities in energy storage system [4].

Currently, supercapacitors and ultracapacitors have been applied in much energy storage and control systems, such as hybrid power storage and control systems generated from several energy conversion systems including photovoltaic/fuel cell hybrid [5], wind/photovoltaic hybrid [6], photovoltaic/ microturbine hybrid [7], and wind/photovoltaic/diesel hybrid [8]. In addition, supercapacitors have also been applied in various energy storage systems such as in electrical vehicles [9,10] and power electronic transformer [11].

Generally, the supercapacitor electrodes utilize a porous carbon or also called activated carbon [12, 13]. The porous carbon has an advantage as electrodes in supercapacitors because of its ability to trap much more ions as well as have a high conductivity to facilitate the electron transfer in the supercapacitor electrodes [14]. One of the carbon material which intensively developed nowadays is carbon dots (CDs). Since the discovery of CDs as a new material of carbon, CDs has been studied intensively and continues to grow rapidly to date. CDs have been widely applied in many areas such as electronics, medicine, environment, and energy fields. In the energy field, CDs are widely developed as electrodes for energy conversion and storage devices such as solar cells, batteries, and supercapacitors.

There are many researchers around the world have developed supercapacitors that use the carbon materials as an electrode, usually in composite form with other materials such as MnO_2. It is well known that MnO_2 has pseudocapacitive properties so that often utilized as an electrode in supercapacitors. Generally, a supercapacitor with an electrode utilizing MnO_2 or carbon alone results in a smaller specific capacitance than those using composite of both materials. The research conducted by Song et al [15] showed a specific capacitance of 245 F/g that used electrode from MnO2 alone. While the research conducted by Li et al [16] using MnO_2/CNTs nanocomposite electrode showed a specific capacitance of 201 F/g. The better result was performed by Huang et al [17] using MnO_2/graphene nanocomposite electrode with a specific capacitance of 350 F/g.

In this work, we developed a supercapacitor electrode based on MnO_2/CDs nanocomposite. There is the previous study that is similar to our work, as which is done by Xu et al [18] which resulted in a specific capacitance of 210 F/g. The difference with this work is in the carbon source used, Xu et al [18] taken the CDs from sucrose while in our work the CDs were derived from rice husks. The use of CDs as an electrode for supercapacitors is very promising because it can produce a super electrochemical performance when combined with pseudocapacitive materials such as MnO_2 [18]. Other studies that use CDs nanocomposite as an electrode for supercapacitor were performed by Chen et al [19] that showed in an areal specific capacitance of 0.88 F/cm^2 and Genc et al [20] with an areal specific capacitance of 17.3 μF/cm^2.

Carbon sources can be obtained everywhere, including those based on natural resources such as plant parts, either agricultural yield or waste [21]. The activity of agricultural processing usually generates a lot of waste, for example, rice processing waste that includes straw and husk. The husk waste is about 20 % of the whole rice plant, where every one ton of grain will produce 0.24 tons of rice husk [22]. The main contents of rice husk include 38% cellulose, 18% hemicellulose, 22% lignin, and silica. Overall carbon content in rice husks is about 67% of total weight [23]. High carbon contents in rice husks can be utilized as CDs source [24].

The aim of this work is to enhance the supercapacity performance of the MnO_2 electrode with addition of CDs derived from rice husk. The use of CDs from rice husk as electrode component in supercapacitor can give the added value for agricultural waste.

2. Experimental Works

2.1 Preparation of rice husk

A total of 50 g of rice husk waste was washed using clean water twice to remove macro impurities from the rice husk waste. After washing, rice husk is boiled in 600 ml of 2M HCl solution to remove metal oxide. Furthermore, acidic rice husk waste is neutralized with distilled water and dried at temperature of 105 ^oC for 4 hours.

2.2 Synthesis and characterization of carbon dots (CDs)

Synthesis of CDs was carried out by acidic hydrolysis method by mixing rice husks that had been washed with H_2SO_4 and added urea as a source of nitrogen doping. This synthesis method adopted the work done by Wee et al [25], but different in the carbon source used, in this study used rice husk as a source of CDs while Wee et al [25] took CDs from bovine serum albumin. A total of 12.5 g of rice husk that has been washed was fed into a beaker and then 100 mL of H_2SO_4 (12 mol/L) and 4 g urea was added. Beaker was wrapped with aluminum foil and heated in a furnace at 120 ^oC for 30 minutes. The solution was diluted with 100 ml of distilled water and filtered using filter paper to obtain a yellowish brown supernatant. The supernatant is poured into a dark bottle and stored in refrigerated and dark place to be characterized its properties later. The optical property was characterized by measuring photoluminescence emission using spectrofluorometer, while particle size distribution was measured using particle size analyzer (PSA).

2.3 Synthesis of MnO_2/CDs nanocomposite

MnO_2/CDs nanocomposites were synthesized in aqueous solution by dropping MnO_2 powder into CDs solution to form a paste. This nanocomposite electrode system is similar to that developed by Xu et al [18], just different in the source of CDs used, that is, from sucrose. In this work, two samples of MnO_2/CDs nanocomposites were made with volume variations of carbon dots solution. One of the samples was prepared by mixing 10 g of MnO_2 powder and 75 ml CDs solution, while the other sample was prepared by mixing 10 g of MnO_2 powder with 125 ml CDs solution. Both samples were stirred using a hotplate magnetic stirrer at 300 rpm while heated at 100 °C for 3 hours. The final product was filtered and neutralized with distilled water and then dried over hotplate stirrer at a temperature of 80 ^oC to dry.

2.4 Characterization of MnO_2/CDs nanocomposites

Characterization using X-ray diffractometer (XRD) was performed to analyze the crystal phase in the MnO_2/CDs nanocomposite sample. X-ray diffraction patterns were recorded in the angle range (2θ) from 10-50^o by using X-ray diffractometer (XRD) with a CuKα radiation source (λ = 1.54Å) at 40kV and 30mA. The analysis using scanning electron microscopy (SEM) is intended to determine the surface morphology of the nanocomposite. In addition, also determined its chemical composition by using energy dispersive X-ray spectroscopy (EDXS). Characterization

using FTIR (Fourier transform infrared) spectrometer was performed to determine the molecular groups of the samples.

2.5 Cyclic voltametry measurement

The MnO_2/CDs nanocomposite was coated on the tip of glassy graphite electrode to explore the electrochemical performance of electrode by measuring cyclic voltammetry using a Potentiostat/Galvanostat equipment. A cyclic voltammogram (CV) is galvanic charge/discharge curve from where the specific capacitance of supercapacitor electrodes can be determined.

3. Results and Discussion

3.1 Characteristics of CDs

CDs derived from rice husks by acidic hydrolysis method were characterized by measuring the photoluminescence emission and particle size distribution. The photoluminescence test was performed by irradiating the CDs solution in the cuvette using a UV lamp with wavelength 365 nm then taken the image. The resulting luminescence is blue-green when exposed to UV light (365 nm), while in ambient light conditions (white light) the CDs are yellowish brown, as shown in the insert image in Figure 1. To obtain the photoluminescence emission spectrum, the CDs solution was excited with a Violet Laser (405 nm) then measured its emission spectrum using a spectrofluorometer (USB400 Spectrofluorometer, Ocean Optics).

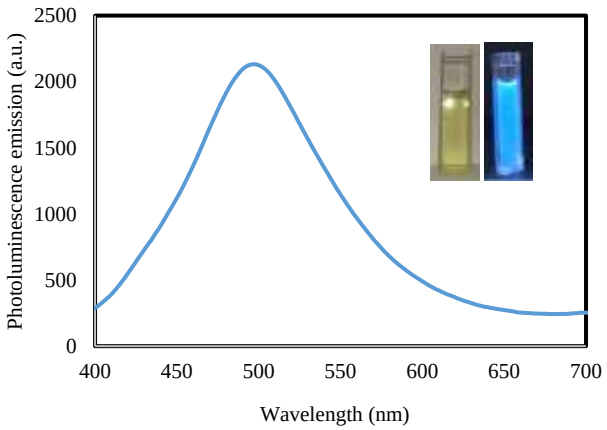

Fig. 1. Photoluminescence emission spectra of CDs derived from rice husks.

Figure 1 shows the photoluminescence spectrum of the CDs solution. The resulting spectrum is wider enough that indicate a diverse particle size distribution of CDs with a peak emission at 497 nm corresponding to the blue-green emissions. Photoluminescence emission that tends to shift towards the longer wavelength is because the excitation source used has a fairly large wavelength (405 nm), similar with that was resulted in the previous study by Jhonsi and Thulasi [26]. As another previous study has known, the greater the excitation wavelength will result in emissions being shifted to larger wavelengths as well [27].

Particle size distribution of CDs was measured by using particle size analyzer (PSA). The measurement of the particle size distribution is done three times for the same CDs sample. Figure 2 shows the particle size distribution of CDs solution derived from rice husks by acidic oxidation using concentrated H_2SO_4 solution. From the three times of measurements, the distributions are not much different, either the shape, the range, the width or the height of the curves, means that the data deviation is not too large. Each measurement resulted in an average particle size of the CDs sample, then all the three particle size was averaged again and founded an average particle size of 11 nm. With the small size, these carbon nanoparticles are suitable to be combined with MnO_2 to form nanocomposite to enhance the electrochemical performance of supercapacitors.

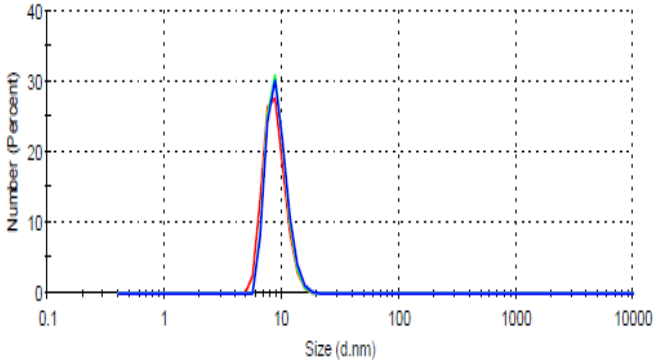

Fig. 2. Particle size distribution of CDs derived from rice husk

3.2 Characteristics of MnO_2/CDs nanocomposite

Characteristics of MnO_2/CDs nanocomposite that tested including crystal structure, surface morphology, and chemical composition. The crystal structure was characterized by using X-ray diffractometer (XRD) which aims to determine the crystal phase of the nanocomposite samples. The surface morphology of nanocomposites was observed by using Scanning Electron Microscope (SEM) to determine the shape and distribution of grain in the sample, while the atomic composition of the nanocomposite was determined from EDXS analysis results that taken simultaneously with SEM image retrieval.

Figure 3 shows the XRD pattern for two MnO_2/CDs nanocomposite samples that have been synthesized from rice husks. Both samples exhibit similar diffraction pattern, where the β-MnO_2 phase appeared dominating compared to the other phases as predicted. The diffraction peaks of β-MnO_2 with the strong intensities is associated with the crystal planes of (110), (101), (111) and (211), respectively. The XRD pattern for β-MnO_2 is matching with the Joint Committee on Powder Diffraction Standards (JCPDS) No. 24-0735 [28, 29]. On the XRD pattern also appeared the carbon peak despite the weak intensity at an angle (2θ) around 26° associated with the crystal plane of (002) [30]. This diffraction pattern confirmed that the MnO_2/CDs nanocomposites have been formed. A broad peak at an angle (2θ) around 22° was identified as residual SiO_2 from rice husk [30].

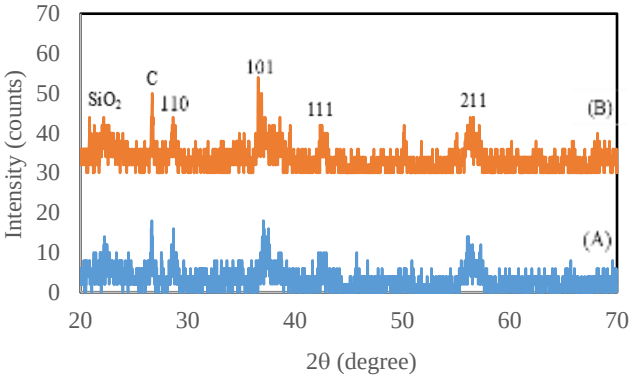

Fig. 3. XRD pattern of MnO_2/CDs nanocomposites with the addition of (A) 75 mL and (B) 125 mL of CDs solution.

Figure 4 shows the SEM images of two MnO_2/CDs nanocomposite samples with different amount of CDs addition, each is 75 and 125 mL. The SEM images show a slight difference between the two samples tested, where the sample with higher CDs fractions looks to be more agglomerated than the sample with lower CDs fractions that looks to be dispersed. In general, the surface morphology of the nanocomposite samples looked porous, making them suitable to be applied as electrodes for supercapacitors. Nanocomposite sample with the addition of 125 mL of CDs solution is more compact and more porous than other sample making it more effective as a supercapacitor electrode.

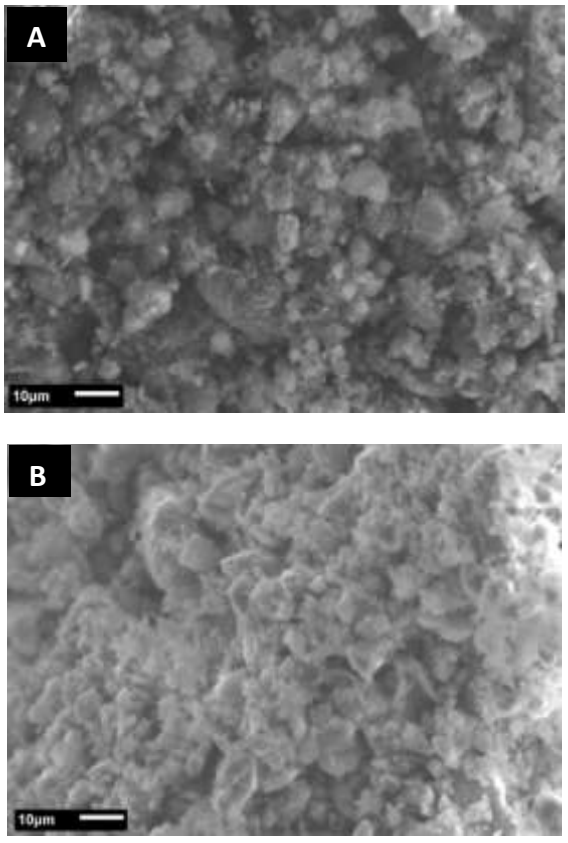

Fig. 4. SEM images of MnO_2/CDs nanocomposite with the addition of (A) 75 mL and (B) 125 mL of CDs solution

The energy dispersive X-ray spectroscopy (EDXS) analysis was conducted to study the chemical composition of the nanocomposite samples. Figure 5 shows an EDXS spectrum of the MnO_2/CDs nanocomposite, where the C, Mn, and O elements can be detected and identified easily. It is certain that the C element is coming from the CDs, while Mn and O elements are coming from the manganese oxide (MnO_2). Therefore, EDXS data confirmed that the MnO_2/CDs nanocomposite has been formed by the presence of the composite forming elements. In the spectrum, there are also elements of Al, Si, and K which are estimated to come from the raw material of rice husks.

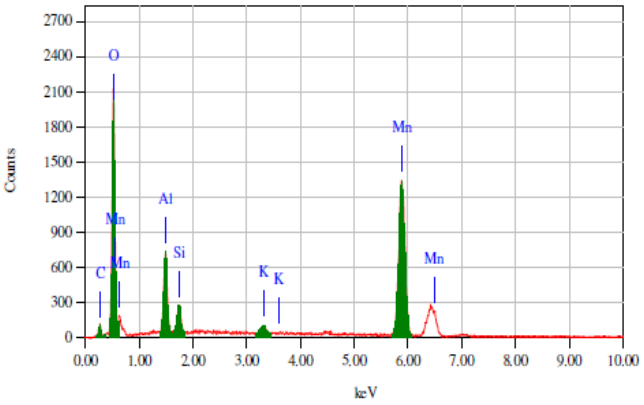

Fig. 5. EDXS spectrum of MnO_2/CDs nanocomposite

The presence of functional groups in the infrared absorption range of the MnO_2/CDs nanocomposite samples was identified by using FTIR spectrometer. The FTIR characterization results of two samples of the MnO_2/CDs nanocomposite are shown in Figure 6. Each absorption band of given spectra indicates a specific functional group in the sample due to its interaction between infrared waves, the interaction being the absorption of infrared energy by molecules to vibrate.

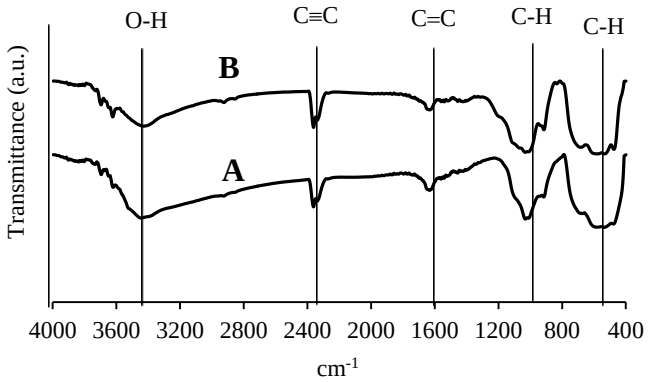

Fig. 6. FTIR spectra of MnO_2/CDs nanocomposite

The functional groups identified in the infrared transmittance spectra respectively are the O-H, C = C, C≡C, and C-H groups [31, 32]. The hydroxyl group extends to an area of about 3400 cm^{-1} indicating a hygroscopic sample by

absorbing water vapor from the air. C-H bending vibrations are identified at wavenumbers in the range of 500-900 cm^{-1} and 950-1225 cm^{-1}. The presence of C-H groups comes from the typical aromatic compounds of the sample. The C≡C and C=C functional groups also appeared indicating the carbon content of the sample, the C≡C functional group strengthened as the CDs solution increased in the composite sample. This can be interpreted that the carbon content in the nanocomposite sample increased with the addition of CDs solution in the precursor used. Strengthened carbon functional groups at the infrared spectra are correlated with XRD data, where the carbon diffraction peaks strengthen as carbon in the sample increased.

Table 1 presents the infrared absorption wavenumbers for two samples of MnO_2/CDs nanocomposites with variations in the volume of CDs solution added to MnO_2 precursors, each was 75 and 125 mL. Groups emerging from infrared absorption are similar to those reported in existing references [31, 32].

Table 1. The functional groups of MnO_2/CDs nanocomposites with a variation content of CDs solution.

Functional groups	Samples with CDs addition		
	Ref.[31,32]	75 mL	125 mL
C-H (*Bending*)	500-900	535.47	534.32
C-H (*Bending*)	950-1225	1031.36	1032.12
C=C (*Stretching*)	1627-1680	1631.40	1631.05
C=C (*Stretching*)	2100-2260	2361.19	2360.94
O-H (*Stretching*)	2950-3570	3444.37	3429.03

3.3 Cyclic voltammogram and specific capacitance

The cyclic voltammetric test was performed to know the specific capacitance of electrochemical capacitors that utilized MnO_2/CDs nanocomposite as the electrodes. The shape and area of the cyclic voltammogram (CV) indicate qualitatively the specific capacitance value of the electrochemical capacitor. Quantitatively, the specific capacitance can be obtained by performing calculations based on the cyclic voltammogram curve using the following equation (1) [33],

$$C_s\,(F/g) = \frac{2I}{m(\frac{dV}{dt})} \qquad [1]$$

where C_s is specific capacitance (F/g), I is constant discharge current (A), m is mass of active material (g), and dV/dt is scan rate (V/s).

Figure 7 shows cyclic voltammogram (CV) curves of the supercapacitors that utilized MnO_2/CDs nanocomposite electrodes with an addition of 75 mL and 125 mL of CDs solutions, respectively. The mass of active material of the electrodes is 0.1 g. The two curves were taken at the scan rate (k) of 0.1V/second.

Based on the CV curve, the electrode with an addition of 125 mL of CDs solution has a constant discharge current is larger than the electrode with an addition of 75 mL of CDs solution. The constant discharge current for the electrode with an addition of 75 mL of CDs solution has a constant discharge current of 0.9A, so that was obtained a specific capacitance of 180 F/g. While the constant discharge current for the electrode with an addition of 125 mL of CDs solution is 1.5A so that the specific capacitance was obtained about of 300 F/g, larger than electrode with an addition of 75 mL of CDs solution. This means that the addition of more CDs into the MnO_2/CDs nanocomposite electrode significantly enhanced the specific capacitance value.This result is larger than those obtained by Song et al [15] which used only pure MnO_2 materials as electrode with a specific capacitance of 201 F/g. Thus it is evident that the addition of CDs into MnO_2 will result in a larger specific capacitance than with MnO_2 alone. This is because CDs has super electrochemical performance when combined with pseudocapacitive materials [18], such as MnO_2 so that it can significantly increase the specific capacitance of an electrochemical supercapacitor.

The results obtained in this study were also better than those obtained by Li et al [16] which used nanocomposite MnO_2/CNTs electrode. Thus, the incorporation of CDs with MnO_2 is more effective in improving the electrochemical performance of a supercapacitor compared to a combination of MnO_2 with CNTs. This is because of as zero-dimensional (0-D) nanocarbon material, CDs can facilitate the transfer of electrons more efficient and effective than CNTs in combining with MnO_2 to enhance specific capacitance of supercapacitors.

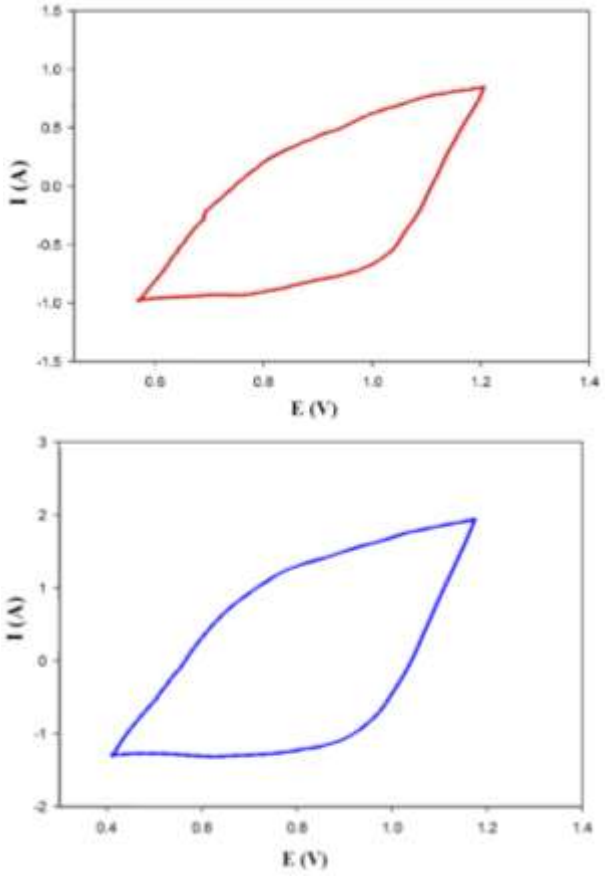

Fig. 7. Cyclic voltammogram of MnO_2/CDs nanocomposite electrodes with addition of (above) 75 mL and (below) 125 mL of CDs solution

However, the results obtained in this study were smaller than those obtained by Huang et al [17] which used the MnO_2/graphene nanocomposite with a specific capacitance of 350 F/g. This is due to the excellent electrochemical properties of the graphene in its application as an electrochemical capacitor. As a two-dimensional (2-D) nanocarbon material, graphene has the advantage of applying to an electrochemical supercapacitor because of its large specific surface area and an efficient electron transfer channel [17]. Thus the MnO_2/graphene composite is more effective than the MnO_2/CDs composite in improving the electrochemical performance of a supercapacitor.

Based on the above results it is known that the increase in the fraction of CDs in the MnO_2/CDs nanocomposite electrode enhanced the specific capacitance value of electrochemical supercapacitor. That is because CDs have an important role to facilitate the polarization of the charge at the electrode-electrolyte interface and facilitate the transfer of electrons in the electrode thereby increasing the specific capacitance of the electrochemical supercapacitor. Overall, these results suggest that CDs derived from rice husks suitable to be combined with MnO_2 to be applied as electrodes in an electrochemical supercapacitors.

4. Conclusions

Carbon dots (CDs) have been successfully synthesized from rice husks via a simple route by acid hydrolysis method using H_2SO_4 acid solution. The average particle size of CDs was found about of 11 nm with blue-green emission when exposure with UV light source at a wavelength of 365 nm. The peak of photoluminescence emission was found at 497 nm when excited by violet laser with a wavelength of 405 nm. MnO_2/CDs nanocomposites that synthesized by mixing the MnO_2 powder with CDs solution shows a porous morphology and suitable to be applied as a supercapacitor electrode. Supercapacitors have been successively fabricated utilizing MnO_2/CDs nanocomposite as an electrode and succeeded in demonstrating a good electrochemical performance based on the results of a cyclic voltammetry measurement. The resulting specific capacitance that determined from a cyclic voltammogram curve confirmed that more content of CDs solution in the MnO_2/CDs nanocomposite electrode resulted in a higher specific capacitance up to 300 F/g. This research suggests that MnO_2/CDs nanocomposite derived from rice husks can be a potential candidate as an electrode in an electrochemical supercapacitor.

Acknowledgements

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