



Short communication

Recycled waste paper—A new source of raw material for electric double-layer capacitors

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ARTICLE INFO

Article history:

Received 17 November 2008

Received in revised form 12 December 2008

Accepted 4 January 2009

Available online 30 January 2009

Keywords:

Activated carbon

Newspaper

Supercapacitor

Potassium hydroxide activation

Surface area

ABSTRACT

For the first time, a new carbon–carbon composite electrode material for supercapacitors is prepared by simple KOH activation of waste newspaper. The amorphous nature and surface morphology of the carbon composite are investigated by X-ray diffraction (XRD), N₂ adsorption/desorption and scanning electron microscopy. The surface area and pore diameter are 416 m² g⁻¹ and 5.9 nm, respectively. Electrochemical characteristics are evaluated by cyclic voltammetry (CV) and charge–discharge tests in 6.0 M KOH at a 1 mA cm⁻² current density. The CV results reveal a maximum specific capacitance of 180 F g⁻¹ at a 2 mV s⁻¹ scan rate and the data explore a development of new use for waste paper into a valuable energy storage material.

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1. Introduction

According to a recent report, approximately one-fifth of the contents of household dustbins consist of paper, of which half is newspaper and magazines. This is equivalent to over 4 kg of wastepaper per household each week. Present approximations suggest that 80% of the waste stream is disposed as landfill, 10% is incinerated, and the other 10% is recycled. Recycling or reuse is the best current solution for reducing the disposal problem [1]. The magnitude of energy production from solid waste provides a small percentage of today's soaring power demands. There is therefore an urgent need to supply alternate energy from other resources as some forms of fuels are approaching depletion.

At present, activated carbon has been used as an electrode material in electrochemical double-layer capacitors (EDLCs) due to its high surface area and high capacitance. Activated carbon can be produced either by physical or chemical activation. In physical activation, the raw material is carbonized under an inert atmosphere and then activated at high temperature using either steam or carbon dioxide as the activating reagent. In chemical activation, the precursor is treated with chemicals to help the initial hydration. Generally, chemical activation is the preferred route as it achieves higher yields, larger surface areas, low operating temperatures, and is cost-

effective [2,3]. The mesopores (diameter of 2–50 nm) of activated carbon can be produced with specific characteristics depending on the raw materials and the activation technique. The higher the content of micropore, the better in order to obtain high capacitance values and a contribution of mesopores helps the mobility of ions through the porosity of the material. The micropores participate in the charge-storage processes and the mesopores are necessary for a fast accessibility of ions. We have chosen KOH as the oxidizing agent for the activation process as it can differentially improve the porosity of the materials.

Two types of energy-storage mechanism have been studied in supercapacitors: electrochemical double-layer capacitors (EDLC) and pseudo-capacitors. In an EDLC, energy storage is accumulated from the electronic and ionic charges between an electrode and electrolyte interface. Porous carbons are attractive for EDLCs due to their large surface area, high pore accessibility, good thermal and chemical stability, and low cost. The energy storage in carbon-based supercapacitors involves charge separation at the high surface area carbon|electrolyte solution interface [4–6]. Various forms of carbonaceous materials, such as bamboo, wood, cotton, banana fibre and camphor, have been employed as electrode precursors for EDLCs [7–11]. The high adsorption capacities of activated carbons are usually related to their specific surface area, pore volume and porosity [12].

In the present work, waste newspapers have been selected as the raw material for producing activated carbon. Waste newspaper is a cheap raw material that can be used for supercapacitors

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Table 1
Porous surface parameters of RF gel and WP carbon.

| Sample | BET surface area (m ² g ⁻¹) | Langmuir surface area (m ² g ⁻¹) | t-plot micropore area (m ² g ⁻¹) | Micropore volume (cm ³ g ⁻¹) | Average pore diameter (desorption) (nm) |
|-----------|--|---|---|---|---|
| RF gel | 525.80 | 696.87 | 439.53 | 0.259 | 3.9 |
| WP carbon | 416.59 | 553.45 | 324.52 | 0.225 | 5.9 |

with special focus on upgrading waste to valuable energy. The authors are interested in adding value to these waste newspapers by preparing activated carbons, as they are great in quantity and low-cost. Shimada et al. [13] have prepared activated carbon from waste newsprint paper by activation using 8% phenol resin and have studied its absorption capacities. Though activated carbon has been prepared from waste newsprint paper, for the first time, we have used this activated carbon as electrode material for supercapacitors and studied its physicochemical properties by means of various techniques. Hence, the purpose of this study is to examine the feasibility of obtaining activated carbon from waste newspapers and evaluate the applicability of the obtained carbon as an electrode material for EDLCs. For comparison, a carbon gel has been prepared from phenol and its electrochemical properties investigated.

2. Experimental

2.1. Synthesis of carbon from waste paper

For the preparation of activated carbon, the waste newspaper was cut into small pieces and soaked in hot water to make a pulp. 1.0 g of pulp was added to 10 mL of 50 wt.% KOH and stirred well until forming a thick paste. The colour of the solution changed from clear yellow to deep red after addition of the KOH. The precursor was dried in a vacuum oven at 90 °C for 12 h and pyrolyzed at 500 °C under flowing argon and a heating ramp of 10 °C min⁻¹ with a hold period of 1 h. After reaching room temperature, the resulting sample was washed with de-ionized water and 0.1 M HCl until the pH of the solution was approximately 7. The sample was then dried at 150 °C for 24 h and the final activated carbon synthesized from the waste newspaper, hereafter denoted as WP carbon. Resorcinol (0.29 M) and formaldehyde (0.57 M) were mixed thoroughly and after forming a homogeneous solution, sodium carbonate (4.0 mM) was added as a catalyst (5% in total) [14]. The carbon aerogel was prepared in the above-described method and is denoted as RF gel. The specific capacitance of the electrodes in cells was calculated by using the following equation:

$$C = It/Vm \quad (1)$$

where I is the discharge current, t is the discharge time, V is the voltage difference in discharge, m is the mass of the material.

2.2. Electrode preparation

The electrodes for the electrochemical studies were fabricated as follows: 10.0 mg of synthesized activated carbon was mixed with 3.0 mg of Teflonized acetylene black (TAB). The slurry was pressed on a stainless-steel mesh with a 1 cm² geometrical area. The electrochemical measurements (cyclic voltammetry and electrochemical impedance analysis) were carried out in a three-electrode cell using carbon coated on stainless steel as the working electrode with a platinum wire and a saturated calomel electrode (SCE) as the counter and the reference electrode, respectively. A two-electrode cell was assembled for galvanostatic charge–discharge tests in the 6.0 M KOH electrolyte.

2.3. Physical characterization and electrochemical tests

Powder X-ray diffraction (XRD) patterns were recorded between 10° and 80° on a X-ray diffractometer (Rint 1000, Rigaku, Japan), with a Cu K α radiation source. The morphology of the waste paper carbon was examined by field emission scanning electron microscopy (S-4700, Hitachi, Japan). BET (Brunauer, Emmett, and Teller) surface area measurements were made by a micromeritics ASAP 2010 surface analyzer (Micromeritics, USA). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out with a Zhaner electrochemical measurement unit (IM6e, Zahner, Germany). The CV was recorded from –0.6 to –0.1 V vs. a reference electrode at various scan rates, 2, 5, 10, and 25 mV s⁻¹. The EIS measurement was analyzed within a frequency range of 20 kHz to 0.01 Hz at an open-circuit potential with an a.c. amplitude of 10 mV. A charge–discharge test was carried out between a cell voltage of 0 and 1 V at a current density of 1 mA cm⁻² by using a Nagano system (BTS-2004 W, Nagano, Japan).

3. Results and discussion

3.1. XRD analysis and surface morphology

Fig. 1 shows XRD spectra of activated carbon prepared from WP carbon and RF gel using KOH activation. The broad peaks that appear at 2 θ values of 22° and 41° in both XRD patterns correspond to the (100) and (111) planes, respectively. Although there are no discernible peaks, the decrease in peak intensity indicates the amorphous state of the material.

Fig. 2 shows the differences between the SEM images on the external surfaces of the activated carbon prepared from RF gel and WP carbon. It is evident from the SEM that the pores are more compact in WP carbon, uniformly distributed, and that there is a good network of interconnected pores in the mesoporous range. Porous structures with many cavities are observed in both materials with the size of the pores of the WP carbon higher than that of RF gel. The cavities on the surface of the carbon may be due to the evaporation

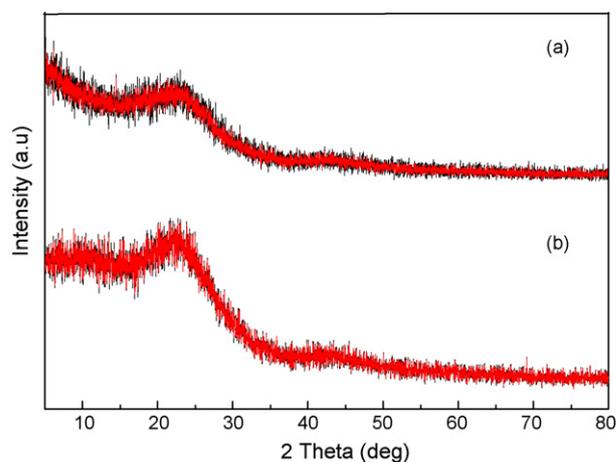


Fig. 1. XRD spectra of activated carbon prepared from (a) RF gel and (b) WP carbon.

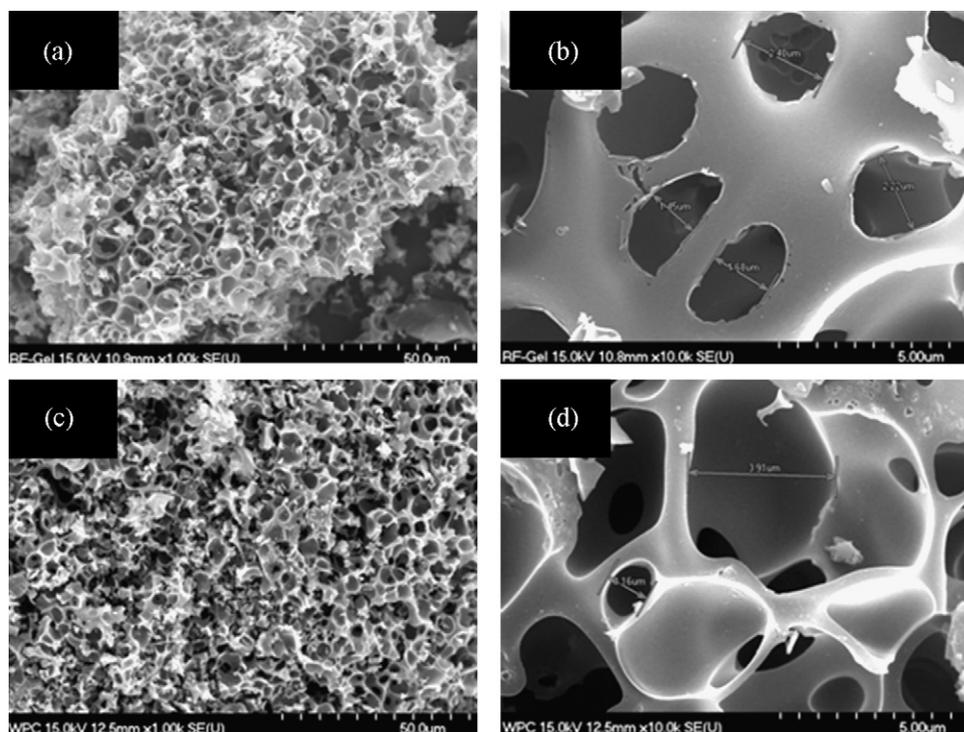


Fig. 2. SEM images of (a, b) RF gel and (c, d) WP paper.

of the activating agent (KOH), which leaves space during carbonization. The pore diameter of the RF gel is smaller than that of WP carbon. Table 1 depicts the porous textural parameters, such as BET surface area, Langmuir surface area and micropore volume calculated by the t -method at $p/p^0 = 0.97$, and the average pore diameter obtained by the BJH (Barrett–Joiner–Halenda) method from the desorption branch of the isotherm. The RF gel has a high surface area ($525 \text{ m}^2 \text{ g}^{-1}$) and a low average pore diameter ($3.9 \mu\text{m}$) compared with the higher pore diameter ($5.9 \mu\text{m}$) of the WP carbon. This is the highest pore diameter of activated carbon obtained from waste newspaper and, moreover, from natural sources (banana, coconut, bamboo) reported in previous literature [2,7]. It is well known that micropores with high pore diameter play an important role in promoting fast ion adsorption into the bulk of the material. In KOH activation, the pore generation in the carbon material is due to the presence of oxygen in the KOH, which results in elimination of cross-linking and stabilization of carbon atoms in the crystallites [15]. In addition, during carbonization, metallic potassium intercalates into the carbon structure and breaks the lamellae arrangement of the crystallite.

3.2. Electrochemical impedance analysis

Electrochemical impedance spectroscopy is a powerful technique for investigating the capacitive behaviour of electrochemical cells used to check the ability of the novel carbon materials. Typical Nyquist impedance spectra recorded at a potential of 10 mV within a frequency range of 20 kHz to 0.01 Hz for RF gel and WP carbon are shown in Fig. 3. Both plots show a single semicircle in the high-frequency region and a straight line in the low-frequency region. In the high-frequency range, there is a small internal resistance (R_s) at the point intersecting the real axis that may be the ionic resistance of electrolyte, the intrinsic resistance of the active material and current-collector in its interface. The semicircle observed in the middle frequency range reveals the charge-transfer resistance (R_{ct}), which is 0.6Ω for WP carbon and 1.5Ω for RF gel. In the low-

frequency region, both impedance plots exhibit a vertical line due to diffusion processes.

The straight line in both plots reveals the capacitive nature of the activated carbons. The semicircle is correlated with the porous structure of the carbons and the diameter of the semicircle refers to the polarization resistance. In the figure, it is explicit that the polarization resistance is high for RF gel compared with WP carbon. This indicates that WP carbon is more amorphous than RF gel, which is in agreement with the XRD data. From the Nyquist plot, the specific capacitance of the activated carbon electrodes can be calculated by using: $C = -1/(2\pi f Z'' m)$, where f , Z'' , and m are the frequency (0.01 Hz), the imaginary impedance and the mass of the active material, respectively. The capacitance values of 159 and 176 F g^{-1} obtained for RF gel and WP carbon are slightly lower than the capacitance values obtained from CV and charge–discharge tests.

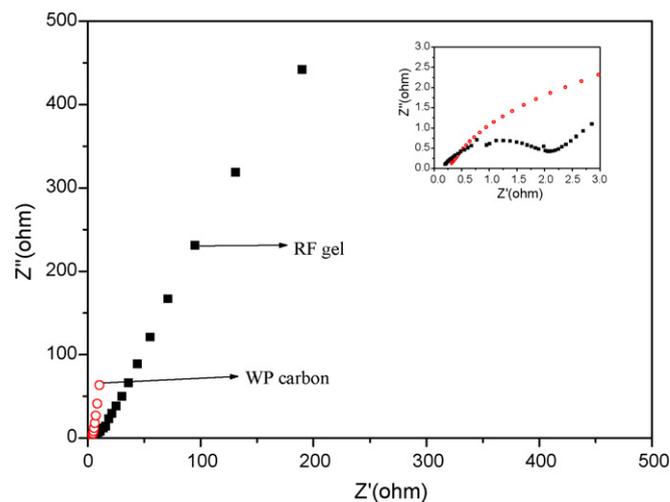


Fig. 3. Nyquist plot of activated carbons prepared from RF gel and WP carbon.

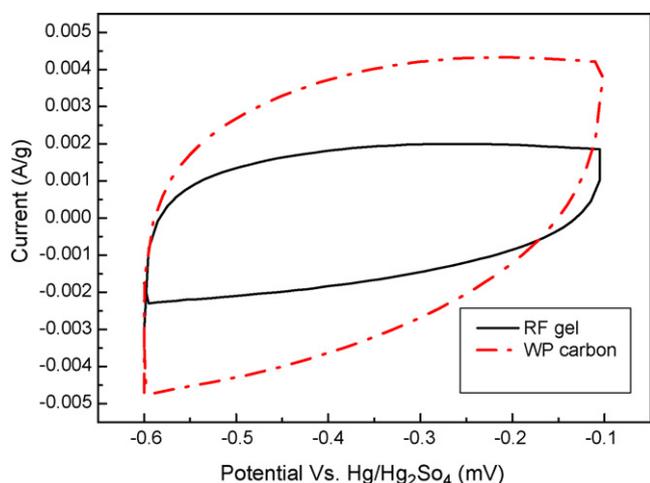


Fig. 4. Cyclic voltammograms of activated carbon obtained at 10 mV s^{-1} .

3.3. Cyclic voltammetry

Cyclic voltammetric measurements were performed over a potential range of -0.6 to -0.1 V vs. the reference electrode to examine the electrochemical characteristics of the resulting electrodes in 6.0 M KOH . The rectangular-like behaviour of the CV curves in Fig. 4 shows that the activated carbons are capacitive and highly reversible. The cyclic voltammograms reveal that both electrodes are stable in the alkaline KOH solution within the selected potential window. In CV curves, WP carbon displays a higher current during the potential sweep, which is expected from the contribution of a high pore diameter. The difference between the ohmic resistance of the electrolyte at the top and bottom of the micropores influences the charge–discharge rates [16]. As shown in Table 2, the maximum specific capacitance is 180 and 150 F g^{-1} for WP carbon and RF gel, respectively. The specific capacitance decreases to 43 F g^{-1} at 25 mV s^{-1} for the RF gel, whereas that for WP carbon decreases gradually to 95 F g^{-1} , even at higher sweep rates. Higher sweep rates increase the potential difference and thus enhance the charge–discharge delay at the bottom of the micropores. The porous structure with a high pore diameter in WP carbon can accommodate more electrolyte and increases electrochemical activation. Generally, for activated carbons, there is a linear relationship between specific surface area and capacitance. In the case of WP carbon, the specific surface area is moderate, i.e., $416 \text{ m}^2 \text{ g}^{-1}$, but with a high pore diameter. Hence, the ability of charge accumulation at the electrode|electrolyte interface strongly depends on ion accessibility to the high pore diameter and the total number of defects. The pore size is believed to have an effect on the resistance due to the change in the amount of electrolyte retained. It is believed that a standard amount of vacuum would retain more electrolyte.

3.4. Galvanostatic charge–discharge analysis

In order to confirm the cycling stability of the carbon materials synthesized from WP carbon and RF gel, galvanostatic

Table 2
Specific capacitance of RF gel and WP carbon from cyclic voltammogram.

| Scan rate (mV s^{-1}) | Specific capacitance (F g^{-1}) | |
|----------------------------------|--|-----------|
| | RF gel | WP carbon |
| 2 | 150 | 180 |
| 5 | 124 | 170 |
| 10 | 85 | 97 |
| 25 | 43 | 95 |

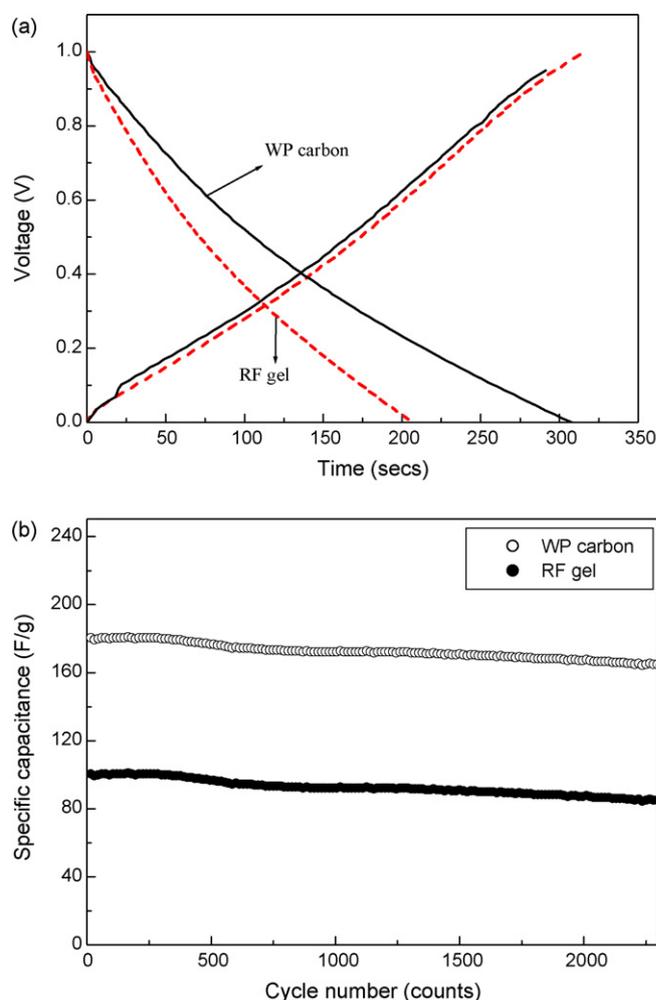


Fig. 5. (a) Typical charge–discharge profiles of RF gel and WP carbon; (b) discharge profiles of RF gel and WP carbon.

charge–discharge tests were conducted at a current density of 1 mA cm^{-2} , between 0 and 1.0 V in a 6.0 M KOH electrolyte. Fig. 5(a) presents the typical charge–discharge cycle performances of RF gel and WP carbon. The charge–discharge profiles of the two carbon materials clearly indicate capacitive behaviour with minimum internal resistance. The values of specific capacitance obtained from tests for 2300 cycles are given in Fig. 5(b). In the case of RF gel prepared by the simple pyrolysis method, the capacity decreases slowly over time with considerable capacity obtained in the voltage range of 0 – 1 V , whereas the capacity of the WP based carbon is constant from the first cycle up to 2000 cycles, as can be seen clearly in Fig. 5(b). The porous nature of the carbon is generally governed by the removal of interior carbon atoms during pyrolysis and the removal of potassium salts during washing. This is more facile with WP carbon than with RF gel, leading to a high pore diameter. Comparing the electrochemical performance of the carbon derived from RF gel and WP carbon in 6.0 M KOH , the RF gel has a higher surface area, though the electrochemical performance of the WP carbon is better. This may be due to the high pore diameter and low internal resistance. The morphology of the carbon after 2300 cycles is shown in Fig. 6. The WP carbon particles [Fig. 6(b)] are smaller and interconnect more densely than the RF gel particles [Fig. 6(a)]. This suggests that cross-linked morphology influences the porous properties of WP carbon. The initial discharge capacity is 100 F g^{-1} for RF gel. A maximum specific capacitance of 180 F g^{-1} is obtained for WP carbon based on the single electrode

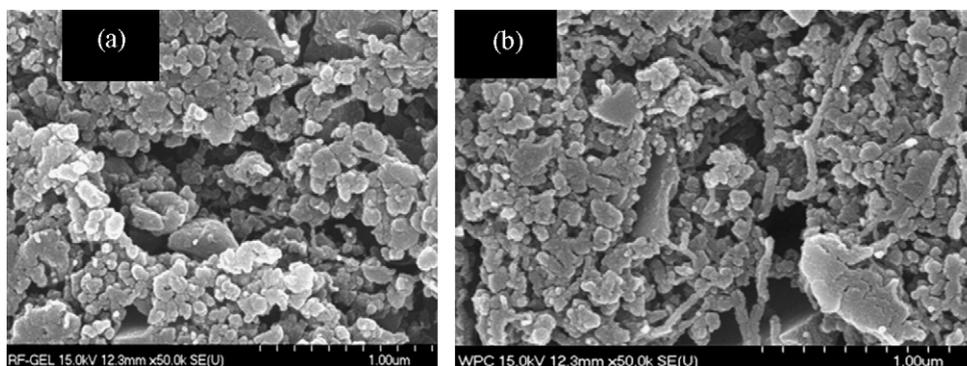


Fig. 6. SEM images of (a) RF gel and (b) WP carbon after 2300 cycles.

weight of the material, which is higher than bamboo- (60 F g^{-1}) and firewood- (120 F g^{-1}) based activated carbons [4,17]. This demonstrates that the activated carbon prepared from WP carbon has high conductivity.

4. Conclusions

Carbon from waste newspapers has been successfully prepared by a simple pyrolysis technique treatment with KOH. The long cycle stability of WP carbon is due to its structure, good surface morphology, high pore diameter and high surface area. From the charge–discharge profiles, a maximum specific capacitance of 160 F g^{-1} is obtained for WP carbon with 99% columbic efficiency at a current density of 1 mA cm^{-2} . It is noteworthy to mention that the source of the raw material is cost effective for making green technology.

Acknowledgements

This work was supported by the Korean Research Foundation Grant funded by the Korean government (MOEHRD)-(KRF-2007-412-J02003). One of the authors D. Kalpana, is grateful to Prof. A.K. Shukla, Director, CECRI and CSIR for granting leave to undertake a post-doctoral fellowship at Chonnam National University, South

Korea. This author thanks Dr. K. Vijayamohan and his group for their fruitful discussions.

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