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A new route of magnetic biochar based polyaniline composites for supercapacitor electrode materials

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ABSTRACT

In this paper, abundantly available durian's rind was opted as raw material to synthesize magnetic biochar in the presence of three different metallic salts by employing a novel vacuum condition in an electrical muffle furnace. Magnetic biochar was successfully produced with a maximum BET surface area value of 835 m^2/g at the pyrolysis temperature and time of 800 °C and 25 min. This magnetic biochar was successfully employed to support and disperse polyaniline (PANI) particles for the application as supercapacitor electrode materials. The produced magnetic biochar – PANI composite exhibited an enhanced specific capacitance compared to the pure PANI and magnetic biochar. The highest specific capacitance of 615 F/g at 10 mV/s and energy density of 76.88 Wh/kg were demonstrated by the MBCA composite, which is considered favorably high compared to the existing PANI coated carbon composites. This magnetic biochar – PANI composites exhibits a good potential for future supercapacitor applications.

1. Introduction

A well-known futurist, Ray Kurzweil stated that "We won't experience 100 years of progress in the 21st century, it will be more like 20,000 years of progress at today's rate", back in the year 2001 [1]. This statement acknowledges the growth of technology we are going through in this modernization era. The introduction of the wireless internet, smartphones, Facebook, and Twitter proves how much things have changed in the past 10 years. Hence, these examples can predict on how vastly different things will be in the upcoming 10 or 100 years. The development of a smartphone from a telephone booth shows that the idea of technology is getting bigger while the silicon transistors being used in the gadgets are getting smaller. This transformation shows that innovative ideas can be generated and achieved for the development of the nation. As for the nanotechnology sectors, robots can get smaller and smaller till they will be able to insert it into bodies to repair damaged tissues. On the other hand, energy generation issue can be solved by increasing the generation of solar power due to the growth in the nanotechnology sector. The famous quote by Neil Armstrong, "That's one small step for man, one giant leap for mankind" is proven day by day through new discovery throughout the world.

One of the important elements in the electronic industry would be the microelectronics field in which it utilizes tiny or micro components to manufacture electronics. The first integrated circuit was fabricated back in the year 1960s during the electronics revolution [2] and the industry has grown intensely, resulting in a faster, smaller and cheaper integrated circuit [3–5]. The integrated circuit is generally comprised of conductors, semiconductors, capacitors, supercapacitors, and insulators attached to it in which the semiconductors act as the active device component [6–8]. On the other hand, conductors are commonly used on the integrated circuit to provide interconnection applications, for electrostatic discharge and for the electromagnetic interference of the electronic equipment. Insulators, on the other hand, are common polymers which are extensively used as encapsulants, materials for the packaging and housing of electronic equipment [7,8]. On the contrary, supercapacitors are generally used as an energy storage device which is receiving much attention due to its wide application in portable electronics, telecommunications, and intermittent electrical energy [9–11]. Thus, the material which being used in the electrode which enhances the energy storage capability is gaining much attention and research interest from energy storage and

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materials science fields [12–15]. On par with this application of these devices, conducting polymers provides a unique combination of properties that can be used as a replacement in microelectronics.

Among various conductive polymer, polyaniline (PANI) exhibited a good performance as the supercapacitor electrode material due its influential properties such as high charge density, good electrical conductivity in various doped states, ease of fabrication for large-scale devices and low cost [16,17]. Generally, PANI exists in a form of green protonated emeraldine which is produced by the oxidative polymerization of aniline process in aqueous acids such hydrochloric acid, HCl, and this form was able to provide an electrical conductivity ranging from 10^{-2} to 10^{0} S/cm [18]. However, the application of PANI as the electrode in supercapacitor faced a downfall due to its large volumetric swelling and shrinking during the charge – discharge process due to ion doping and de – doping process. This downfall led to a structural breakdown and flaking off PANI [19,20]. One of the efficient ways to improve the electrochemical stability of PANI was by incorporating earth-abundant capacitive carbon materials such as graphene [21], ordered mesoporous carbon [22] and carbon nanotubes (CNT) [23]. The significant combination of essential mechanical strength of carbon material and high pseudocapacitance of the PANI stands out to be the contributing factor towards the high output energy of the produced electrode composite [16,20]. This effective combination of carbon material with PANI faced difficulty in terms of high cost, limited resource of raw material, and complicated preparation process [24–26]. Hence, low-cost carbon materials which were prepared from the abundantly available biomass resources were employed to produce carbon-PANI composites with significant capacitive performance as an electrode for supercapacitor materials.

In conjugation to that, durian's rind is found to be abundantly available in Malaysia with a significant advantage of environmentally friendly and low-cost. Although durian is largely consumed by Malaysians due to its prolific implementations, its demand hindered by the generation of huge amount of durian residues consisting of its shell, seeds, peels and rinds [27]. In order to avoid any environmental related issues due to the poor management of durian's rind, these rind were converted into biochar by heating at high temperatures under an inert or zero oxygen atmospheres to synthesize a low-cost biochar consisting of an impressive porous structure which favors better ion diffusion and electrolyte access, leading to a good electrochemical activity [28]. In recent years, durian's rind have been employed as an electrode's material for supercapacitors application which exhibited a good electrochemical performance [29]. However, there is only a few number of studies which focuses the application of metal derived biochar, or also known as magnetic biochar along with PANI as the electrode material for supercapacitors [30]. The magnetic biochar's properties such as high surface area and its ability of conducting electricity were found to enhance the capacitance value of the composite produced and ease the abundant loading of pseudocapacitive materials via serving as nucleation and anchoring sites [31].

Hence, motivated by these numerous interesting work, we successfully converted durian's rind into hematite and magnetite-loaded magnetic biochar by employing a novel vacuum condition in an electrical muffle furnace. This magnetic biochar was characterized to study its morphology and to detect the presence of hematite and magnetite. It was then used to synthesize the novel PANI coated hematite and magnetite doped biochar composite through an in-situ polymerization process in the presence of aniline monomer, magnetic biochar, and oxidant. These composites were fabricated as an electrode for supercapacitor and its electrical conductivity, capacitance and morphology were studied as well.

2. Materials and methods

2.1. Collection and grinding of raw material

Durian's rind was collected from a durian stall located in Kuala Lumpur. These durian's rinds were made sure not to be contaminated with fungus and in a dry condition when it was collected. The collected durian's rind was then were chopped into a smaller piece to ease the cleaning process. These durian's rind were then washed thoroughly to remove all the dirt from the rind and leftover durian on the inner part of rind while any durian's rind spotted with fungus were discarded. The washed durian rind was then dried in vacuum oven for 5 days continuously at 105 °C.

The grinding process was carried out at Forest Research Institute of Malaysia (FRIM) by employing a two-stage grinding process. The initial grinding process was done to obtain a particle with a size of less than 1 mm and the second grinding process was carried out to obtain particles with size less than 20 μm by employing the ball mill grinder through a continuous grinding and sieving process. The ground durian's rind particles were sieved to obtain a particle size of less than 20 μm and the grinding process is repeated until the required particle size is obtained. High yield of durian rind's particles was obtained by employing this two-stage grinding process due to the less lost in mass during the grinding. The ground durian's rind particles were then stored tightly in a sealed bag which was then placed in a desiccator.

2.2. Preparation of metal ion – durian's rind biomass

Analytical grade metal salt of iron (III) oxide, Fe_2O_3, iron (II) sulphate heptahydrate, $FeSO_4{\cdot}7H_2O$ and iron (III) chloride hexahydrate, $FeCl_3{\cdot}6H_2O$ along with ground durian's rind particles were used for the oxidization process to achieve a better porous structure at the surface of durian particles together with the attachment of carboxylic and carbonyl group on the surface of durian particles prior the pyrolysis process [32].

Initially, 200 mL of 1.0 M respective metal's ion salt solution were transferred into a 1L Pyrex laboratory bottle, followed by the addition of 150 mL of nitric acid, HNO_3 and 50 mL of potassium permanganate, $KMnO_4$ in the ratio of 3:1 as suggested by [33] for an optimum functionalization process. This solution was mixed uniformly prior the addition of 200 g of ground durian's rind particles into 400 mL mixture in 1 L Pyrex laboratory bottle. The mixture in the bottle was sonicated for 5 h at 40 °C with 50% vibration energy. The mixture was then dried in vacuum oven for 5 days continuously at a temperature of 70 °C to obtain the metal ion – durian rind biomass. The mixture was uniformly mixed every 6–10 h during the drying process to ensure a uniform drying throughout the particles. The dried biomass was then crushed using a mortar and pestle which were sieved later on to obtain particles with size less than 20 μm.

2.3. Synthesis of magnetic biochar

The prepared biomass was then used to produce magnetic biochar in a programmable muffle furnace model WiseTherm, FP-03, 1000 °C, 3 L with a vacuum condition. As can be seen from Fig. 1, a closed crucible containing the 50 g of dried biomass was kept in the middle of the furnace and the furnace door was closed tightly. The syngas effluent's tip at the top of the furnace was connected to a vacuum pump in which the air in the furnace will be sucked out to ensure a vacuum condition present in the furnace during the pyrolysis process. The control valve then will be closed tightly upon ensuring the pressure inside the muffle furnace reduces until a constant value in the pressure gauge is attained. The pyrolysis process was then carried out at 800 °C for 25 min. The muffle