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学位論文題目	Preparation of Biocarbon Derived from Sugarcane Bagasse and Its Composites for Application in Supercapacitors （サトウキビバガス由来のバイオカーボンとその複合材料の創製およびスーパーキャパシタへの応用）
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論 文 内 容 要 旨

Supercapacitors are one of the most promising energy storage devices due to their good energy density, superior power density, fast charge/discharge rate, and long cycle life, and hence they exhibit promising applications in portable devices, renewable energy and transportation. Based on the different charge storage mechanisms, supercapacitors can generally be divided into two types, i.e., the electrical double-layer capacitors (EDLC) and the pseudocapacitors. Carbon materials, such as active carbon, graphene and carbon nanotube, are usually used in EDLC electrode. However, their further application are normally limited by their low energy density, complicated preparation conditions or special facilities and thus high cost. In the present work, a low cost and convenient method was first used to prepare allium-giganteum-like biocarbon (KWB) from sugarcane bagasse, and then different kinds of carbon-based composite materials including manganese dioxide (MnO_2)/KWB, polyaniline (PANI)/KWB, and iron oxide (Fe_3O_4)/KWB were obtained. All of the above materials were used as electrode materials of supercapacitors, and morphology, chemical

composition and electrochemical performance of the obtained supercapacitors were investigated. Besides, due to the unique structure of KWB, all the composites show superior performance in supercapacitors.

In Chapter 1, the research backgrounds, research significance, research purpose and the construction of this thesis are particularly described.

In Chapter 2, the properties of experimental materials used in this thesis are presented. The experimental methods and characterizations are also particularly described in this chapter.

In Chapter 3, KWB were derived from sugarcane bagasse via one-step carbonization and activation method. The results showed that both the mass ratio of potassium hydroxide (KOH) to sugarcane bagasse and the temperature of carbonization could influence the morphology and chemical composition of KWB, thereby further affect the electrochemical performance of the KWB. Under the optimum conditions, the SEM images of KWB showed the excellent 3D hierarchical porous network structure with allium-giganteum-like, which also has the best specific surface area. It promises the excellent electrochemical performance when used as electrode materials for supercapacitors. What's more, KWB also could be used as carbon-base to prepare other composites in the further research.

In Chapter 4, MnO_2/KWB (KWBM) composites have been prepared by a simple method. The MnO_2 nanosheets anchored on the surface of biocarbon and obtained the KWBM, and KWB was used as both scaffolds and reducing agents for MnO_2 growth. The analysis results demonstrated that chemical composition and microstructure of KWBM were closely related to the mass ratio of $KMnO_4$/KWB, which further impacted the electrochemical performance of KWBM profoundly. Especially, the KWBM-4 exhibited a higher specific capacitance of 402 F g^{-1} at a current density of 1 A g^{-1} in three-electrode system. The asymmetric two-electrode system with outstanding energy density was assembled by employing the KWBM-4 as the positive electrode and the KWB as the negative electrode. The two-electrode system displays a high energy density of 25.9 Wh kg^{-1} at a power density of 750 W kg^{-1} within a potential range of 0-1.5 V. Furthermore, the system exhibited high cycle stability with only 5.8 % loss of its initial capacitance after 2000 cycles.

In Chapter 5, a coral-like polyaniline/KWB (PANI/KWB) composites was prepared via in-site

polymerization method. The PANI/KWB composites were obtained using KWB as the scaffolds for PANI growth and [CMMIm]Cl ionic liquid as dopant. The different mass ratio of aniline monomer (An) and KWB were investigated. The results indicated that chemical composition and microstructure of PANI/KWB were closely related to the mass ratio of aniline monomer (An) and KWB, which further impacted electrochemical performance of PANI/KWB profoundly. Especially, the PANI/KWB-4 exhibited the highest specific capacitance of 447 F g^{-1} at a current density of 0.5 A g^{-1}. Furthermore, the asymmetric two-electrode system based on PANI/KWB-4 as positive electrode and KWB as negative electrode was successfully assembled with a voltage window of 0~1.6 V, exhibiting high energy density (27.3 Wh kg^{-1}) and power density (800 W kg^{-1}), and excellent cycling stability (87% capacitance retention after 2000 cycles).

In Chapter 6, Fe_3O_4/KWB nanocomposites (KBFe) were prepared via a chemical coprecipitation method under different mass ratio of Fe_3O_4 to KWB. As a result, the chemical composition and microstructure of the KBFe were intimately related to the mass ratio of Fe_3O_4 and KWB, which impacted the electrochemical performance of the KBFe profoundly. Especially, the KBFe-4 displayed the highest specific capacitance of 342 F g^{-1} at a current density of 1 A g^{-1}. Furthermore, the asymmetric two-electrode system based on KWBM composite as positive electrode and KBFe-4 as negative electrode was successfully assembled with a voltage window of 0~1.6 V, and exhibited high energy density (29.1 Wh kg^{-1}) and power density (800 W kg^{-1}), along with excellent cycling stability (89.5% capacitance retention after 1000 cycles).

In Chapter 7, general conclusions of the study are made. All biocarbon-based composites prepared in this research showed the excellent electrochemical performance. The novel carbon and its composites can be expected to use for application in supercapacitors.

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論文審査結果要旨

本論文は、低コストかつ優れた電気化学性能を有する新規スーパーキャパシタ用電極材料の開発を目的として、サトウキビバガスからバイオカーボンおよびその複合材料を創製し、その電気特性に及ぼす作製条件とモルフォロジーの影響を検討したものである。本論文は全 7 章で構成されている。

第 1 章では緒論として、電極材料に関する既存の研究から本研究の背景を述べ、本研究の目的を示している。第 2 章では材料および試験方法として、カーボン材料とその複合材料の作製方法およびそれらの電気化学性能の測定方法、モルフォロジー、分子構造と化学成分などの分析方法について説明している。第 3 章では、三次元網目構造を有するバイオカーボンの創製を狙いとして、水酸化カリウム賦活法と高温炭化法によりバガスからバイオマス（KWB）活性炭材料を作製し、材料の特性に及ぼすそれらの添加量の影響を検討している。それより、賦活性化の程度と炭化温度は材料の構造と特性に大きく影響し、特に、水酸化カリウムとバガス材料の質量比が 0.6:1 で、炭化温度が 800℃の作製条件のとき、最大比容量 196 F g^{-1} のバイオカーボン材料が得られることを明らかにしている。第 4 章では、作製したバイカーボンを母材として、直接合成法により二酸化マンガン/バイオカーボン複合材料（KWBM）を作製し、KWBM の特性に及ぼす原材料質量比の影響を検討した。それより、過マンガン酸カリウムと KWB の質量比が 1:1 で、KWBM は最大比容量 402 F g^{-1} を示すことを明らかにしている。第 5 章では、*in-situ* 化学酸化重合法によりポリアニリン/バイオカーボン複合材料（PANI/KWB）を作製し、PANI/KWB の特性に及ぼすアニリンモノマー (An) と KWB の質量比の影響を検討した。それより An と KWB が 40:1 で、PANI/KWB は最大比容量 447 F g^{-1} を示すことを明らかにしている。第 6 章では、化学共沈法により四酸化三鉄（Fe_3O_4）/バイオカーボン複合材料（KBFe）を作製し、KBFe の特性に及ぼす Fe_3O_4 と KWB の質量比の影響を検討した。Fe_3O_4 と KWB が 1:1 で、KBFe は最大比容量 342 F g^{-1} を示すことを明らかにしている。第 7 章は結論であり、研究結果をまとめている。

以上、本論文は学術的、工学的価値が高く、その研究成果は、優れた新規カーボン材料とカーボンベース複合材料としてスーパーキャパシタへの応用に期待できる。また、研究業績として、査読付国際学術論文 3 編、国際会議 1 件、国内会議 2 件を公表している。

よって、本論文は博士（工学）の学位論文として合格と認める。