Capacitance of MnO_2 Micro-flowers Decorated CNFsin Alkaline Electrolyte and Its Bi-functional Electrocatalytic Activity Toward Hydrazine Oxidation

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***Abstract*—Well dispersed MnO2 micro-flowers were grown directly on carbon nanofibers via a simple hydrothermal technique without any template. Structure and morphology were characterized by X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) equipped with rapid EDX (energy dispersive analysis of X-ray). The appealed characterization techniques specified that the obtained material is carbon nanofibers decorated by MnO2 micro-flowers. Super capacitive performance of the MnO2 micro-flowers decorated CNFs as active electrode material was evaluated by cyclic voltammetry (CV) in alkaline medium and yield a reasonable specific capacitance of 120 Fg−1 at 5 mV s−1. As a catalyst for hydrazine oxidation, the MnO2 micro-flowers decorated CNFs showed high current density. The impressive bi-functional electrochemical activity of MnO2 micro-flowers decorated CNFs is mainly attributed to its unique architectural structure.**

Keywords-supercapacitors; bi-functional; carbon nanofibers; hydrazine; direct liquid fuel cells

I. INTRODUCTION

Depletion of global fossil oil resources and environmental concerns has been the theme topics of the world economic and political circles over the past decades. It has been reported that, a significant portion of the total energy supply comes from fossil fuels, such as coal, oil and natural gas, causing a dramatic buildup of greenhouse gases in the atmosphere. In order to fulfil the growing demand of clean and high-efficient energy, alternative resource of energy independent of fossil fuels, must be developed[1-8].

Supercapacitors (also known as electrochemical capacitors) and direct liquid fuel cells are the most promising devices in the field of energy conversion and storage [9, 10]. Comparing with other types of direct liquid fuel cells, direct hydrazine fuel cell (DHFC) achieves a zero pollution emission; only nitrogen and water are produced during oxidation process. Moreover, there is no catalyst poisoning in direct hydrazine fuel cells. Similarly , supercapacitors are likely to show equal importance to batteries and fuel cells for future energy storage systemdue to their high power characteristics compared to batteries, high energy density compared to conventional capacitors, long cycling life and short charging time[11, 12].

The energy storage/conversion processes for supercapacitors define in two ways, and can be commonly classified as electrochemical double layer capacitors (EDLCs) and pseudocapacitors[13, 14]. In EDLCs energy store electrostatically while pseudocapacitors utilize fast and reversible Faradaic reactions between electrolyte and electroactive materials[5, 7].Electrode /catalyst materials are the key element to determine device performance, thus they have received great attention in recent years [9, 15-17].

In particular, cheap transition metal oxide based catalysts are desirable for both (supercapacitors & fuel cells), because they are electrochemically more active. Therefore, recent work has been focused on the synthesis and use of non-precious transition metal oxides. Among the auspicious substitute electrode material, MnO2 has been of specific attention for the past decade because of its abundance, low cost, high catalytic activity and non–toxicity[18]. But their poor electrical conductivity and low structural stability constrain their practical application.

To address these problems, a templet free design of 3D open architecture process has been developed [19-21].MnO2in the shape of micro-flower have been considered as one of the optimal nanostructure because of the fully exposed structure/high surface area which can facilitate the transportation of electrons and cations. But the synthesis of flower like architecture still faces a challenge owing to the fast and complex growing process.

Therefore, it is desirable to develop facile, environmentally friendly, low-cost, and template-free synthetic methods for the fabrication of MnO2micro-flowers with rich and proper porosity.

Herein, we present a facile self-assembled synthesis of MnO2 micro-flowers decorated carbon nanofibers. Self-assembled MnO2mocro-flowers decorated carbon nanofiber has extensively identified in terms of morphology and crystallinity. Moreover, the electrochemical property of the

materials has been investigated for supercapacitors and an electro-catalyst for hydrazine oxidation in an alkaline medium

II. EXPERIMENTAL

A. Materials

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B. Preparation of Carbon nanofibers

Polymeric aqueous solutions were firstly prepared by dissolving 15 wt % of Poly (Vinyl alcohol) (PVA) in 85 ml of distilled water and the mixture was stirred at 60° C for 24h to get see-through, clear and consistent mixture. The achieved sol-gel was electrospun at high voltage of 22 KV using DC power supply at room temperature. The ready nanofibers (NFs) mats were dried at room temperature for 24 h and then under vacuum for 12 h at 80° C and finally sintered at 1000°C for 6 h in nitrogen atmosphere with heating rate of 2.0°C/min.

C. Preparation of MnO_2micro-flowers Decorated CNFs

In a typical synthesis of *MnO_2micro-flowers decorated CNFs*, 0.1 mol/L manganese nitrate was added to into 120 mL deionized water under vigorous stirring. 0.5mol/L Co $(NH_2)_2$ (Urea) was then added into the solution and the solution was transferred into a 150 mL Teflon-lined stainless steel autoclave. A piece of carbon fiber mat was subsequently soaked in the solution, followed by heating the autoclave in an oven at 80 ℃ for 5h. The synthesized sample were then taken out, cleaned several times with DI water and ethanol, dried at 80 ℃ for about an hour, and annealed at 350 ℃ in air for 2 hours.

III. RESULT AND DISCUSSIONS

The phase composition and phase structure of as obtained nanostructure were examined by X-ray powder diffraction (XRD). Figure I displays the X-ray diffraction spectrogram of MnO_2 micro-flowers decorated CNFs. Comparing XRD spectrogram of the synthesized materials with the standard diffraction spectra, the synthesized product is crystalline MnO_2. As shown in the obtained XRD pattern, the diffraction peaks at 2θ values of 28.84°, 37.52°, 56.92°, 60.27° and 72.71° indexing as the (310), (211), (431), (521) and (312) crystal planes, respectively indicate formation of MnO_2; the most prominent peak being at 28.84°. This peak can be correlated to (310) *hkl* indices of pure tetragonal structure [space group: I4/m (87)] according to the JCPDS no.: 00-044-0141 with lattice constants $a=b=9.7847$ Å, $c=2.8630$ Å; $\alpha=\beta=\gamma=90$, suggesting MnO_2structure mainly grows along the (310) face. The main challenge in developing MnO_2 micro-flowers decorated carbon nanofibers is to uniformly incorporate MnO_2micro-flowers attach onto carbon nanofibers, and this attachment is mainly dependent on the synthesis route.In order to crop MnO_2 outgrown on the carbon nanofiber, the nanofibers produced after calcination was allowed to go through a hydrothermal treatment as mentioned in the experimental section.

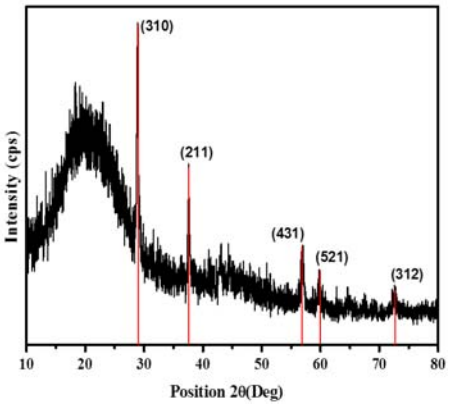

FIGURE I. XRD SPECTRA FOR THE OBTAINED MNO_2 MICRO-FLOWERS DECORATED CNFS

Figure II represents FE-SEM images for the product obtained by the hydrothermal treatment process.As revealed, the uniform micro-flowers with an average size about 75 μm,outgrow on the surface of nanofibers due to hydrothermal treatment (Figure II (a)). At a higher magnification (inset of Figure I (a)), these micro-flowers show hierarchical structures consisting of nanorods with a diameter of about 15~20 nm and a length of about 1 μm.It is also noticed that the micro-flowers are evenly distributed in the network of carbon nanofibers. The diameter of the carbon nanofibers varies from 400 to 700 nm (Figure II (b)). From the EDX spectra, the presence of Manganese (Mn), oxygen (O) and carbon (C) can be detected are shown in Figure II(c); the atomic and weight percentage of carbon, manganese and oxygen are summarized in the inset in Figure II(c).It is hypothesized that the uniformly embedded electronic conducting network of carbon nanofibers can improve the high-rate capability as well as the specific capacitance of the materials. Moreover, carbon nanofibers network with hierarchical MnO_2 micro-flowers can shorten the diffusion path for charge-carrier ions, whereas the large liquid–solid interface simplifies ion exchange between the electrode and electrolyte[22]. Raman spectroscopy was executed to examine the local structure of MnO_2 micro-flowers decorated CNFs. As shown in Figure III, two broad overlapping peaks centered on 1321 and 1590 cm^{-1} that correspond to the disordered (D band) and graphite (G band), arising from the disordered structure of carbon [23]. Concerning MnO_2, the Raman peaks observed at 368(marked by red circles & arrow along with high magnification)and 646 cm^{-1} demonstrate MnO_2 microstructures.

An electrochemical performance analysis of MnO_2 micro-flowers decorated CNFswas performed using CV. The specific capacitance of the composite can be calculated with CV results according to the following equation[24]:

Here, C_{sp} is the specific capacitance, m is the mass of the grafted composite, *v is* the potential scan rate, ΔV is the sweep potential window and I (V) is the voltammetric current on CV curves, A is the geometric area of the electrodes respectively. Figure III shows the rate-dependent cyclic voltammetry (CV) curves of MnO_2 micro-flowers decorated CNFs at various scan

rates (5,10, 25, 50 and 75 mVs^{-1}) between -0.2 V and 1.0 V (vs. Ag/AgCl) in 1 M KOH electrolyte. The CV curves have fairly rectangular in shape, which is a typical capacitive behavior of carbon materials. In addition, the current densities increase along with increasing scan rates, suggesting good rate performance.

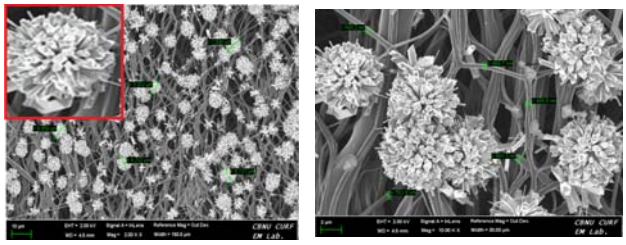

FIGURE II. FESEM IMAGE OF MNO_2 MICRO-FLOWERS DECORATED CNFS(A AND B) AND EDX SPECTRUM (C) OF MNO_2 MICRO-FLOWERS DECORATED CNFS

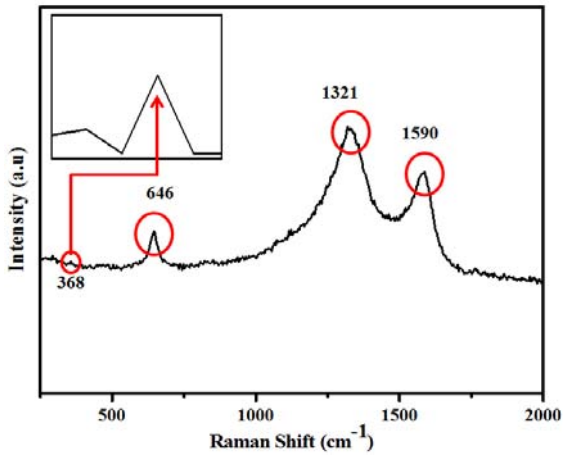

FIGURE III. RAMAN SPECTRA FOR THE OBTAINED MNO_2 MICRO-FLOWERS DECORATED CNFS

The specific capacitances of nanostructure at different scan rates are shown in Figure IV. The specific capacitance decreases with the increase of scan rates from 5 to 75 mVs^{-1}. At low scan rates ($5mVs^{-1}$), both active areas (internal and external) of the surfaces of electrodes could take part in reaction while at high scan rate ($75mVs^{-1}$) the diffusion of the electrolyte ions was limited thus only the external surface area of electrodes could participatein ion transfer reaction. As shown in Figure IV the maximum specific capacitance obtained at a scan rate of 5 mVs^{-1} of was 120 Fg^{-1}.Typical catalytic response of MnO_2 micro-flowers decorated CNFsin 1 M KOH + 0.5 M hydrazine is shown in Figure V. The CV curve in Figure V. indicates an excellent electrocatalytic activity of nanostructure by showing effective hydrazine oxidation with high current density in presence of hydrazine (Red). At the potential of 1 V, the current density of the nanostructure reached 38 mA cm^{-2}, which was about double than that in 1 M KOH . Therefore, the MnO_2 micro-flowers decorated CNFselectrode possessed the superior electrocatalytic activity toward hydrazine electro-oxidation.

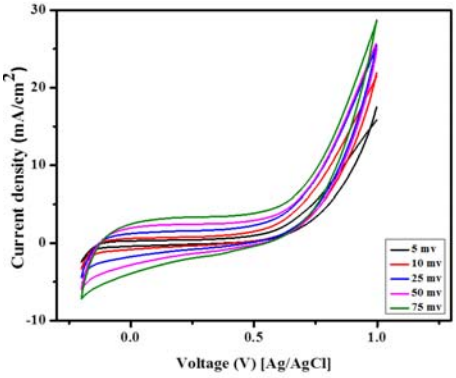

FIGURE IV. CYCLIC VOLTAMMOGRAMS OF THE MNO_2 MICRO-FLOWERS DECORATED CNFS IN 1 M KOH SOLUTION AT DIFFERENT SCAN RATES.

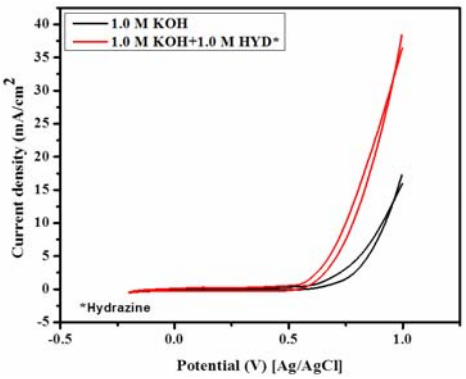

FIGURE V. TYPICAL CYCLIC VOLTAMMOGRAM OF THE MNO_2 MICRO-FLOWERS DECORATED CNFS MEASURED IN 1 M KOH AND 1 M KOH+0.5 M HYDRAZINE AT 50 MV/S..

IV. CONCLUSION

MnO_2 micro-flowers decorated carbons nanofibers hierarchical structure can be prepared by calcination of electrospun nanofiber mats composed of poly vinyl acetate followed by hydrothermal treatment and were demonstrated to be superior bi-functional electrode material for energy conversion and storage devices. MnO_2 micro-flowers decorated carbon nanofibers electrode exhibited reasonable capacitance of 120 Fg^{-1} at low scan rate. Interestingly, the MnO_2 micro-flowers decorated carbon nanofibers showed hydrazine electrooxidation with high current density (38 mA/cm^2). The MnO_2 micro-flowers decorated carbon nanofibers electrode can be a hopeful catalyst for energy conversion and storage devices

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