Applied Surface Science xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Effects of CeO_2 nanoparticles on electrochemical properties of carbon/CeO_2 composites

Sumalin Phokha [a,*], Sitchai Hunpratub [a], Brian Usher [a], Adulphan Pimsawat [b], Narong Chanlek [c], Santi Maensiri [d]

[a] Department of Physics, Faculty of Science, Udon Thani Rajabhat University, Udon Thani 41000, Thailand
[b] Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[c] Synchrotron Light Research Institute (Public Organization), 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand
[d] School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

ARTICLE INFO

Article history:
Received 15 October 2017
Revised 16 February 2018
Accepted 21 February 2018
Available online xxxx

Keywords:
Carbon/CeO_2 composites
Coffee husks
Electrochemical
Capacity
Specific surface areas

ABSTRACT

The electrochemical properties of carbon were improved when composited with CeO_2 nanoparticles making this material a candidate for high performance energy storage devices. Carbon was obtained from coffee husks by calcining at a temperature of 600 °C for 1 h. Carbon/CeO_2 composite mixtures were prepared with 0, 10, 20 and 30 wt% CeO_2 nanoparticles referred to as carbon, carbon-10CeO_2, carbon-20CeO_2 and carbon-30CeO_2, respectively. The structure, morphology and valence states of the carbon/CeO_2 composites were characterized by X-ray diffraction (XRD), Raman spectroscopy (Raman), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Specific surface areas were measured using the Brunauer-Emmett-Teller method (BET) and the materials electrochemical properties were measured using a potentiostat/galvanostat cell system. The XRD and Raman results exhibited peaks corresponding to carbon and CeO_2, confirming the formation of a composite. XPS measurements confirmed the presence of Ce^{4+} and Ce^{3+}/oxygen vacancies in the CeO_2 nanoparticles. The specific surface areas measured were 216, 317, 340 and 270 m^2/g for carbon, carbon-10CeO_2, carbon-20CeO_2 and carbon-30CeO_2, respectively. Both the discharge capacity and specific capacitance were optimal for electrodes made from the carbon-30CeO_2 composite, being approximately 2 and 15 times better than that of carbon. These higher values are thought to be due to the contribution of the redox reaction $Ce^{3+} \leftrightarrow Ce^{4+}$ within the CeO_2 nanoparticles on the surface of the carbon.

1. Introduction

Novel energy storage systems (batteries and supercapacitors) with higher capacitances, higher power densities and long-term stability during charge-discharge cycling have attracted wide interest in recent years [1–3]. Carbon-based materials have commonly been used as electrodes over the past decade in electrochemical energy storage devices due to their large specific surface areas, high porosity and good mechanical and electrical properties [1–5]. Recently, carbon based nanomaterials such as activated carbon (AC), carbon nanotubes (CNTs), carbon nanofibers (CNFs), carbon nanowires (CNWs), graphene or reduced graphene oxides (rGO) have been investigated [4–8]. Composites of metal oxides (MO) or metals (M) with carbon have also been found to yield improved properties including better conductivity [3–8].

To date, various carbon-based nanomaterials composited with MO have been studied and found to show promise, including α-Fe_2O_3/carbon [3], Fe_2O_3/CNF [9], CeO_2/AC [5], SnO_2/carbon [10], MnO_2/CNW [6], MnO_2/AC [7], MnO/carbon [11], $MnFe_2O_4$/rGO [8], CNF/MnO_2 [12], CNF/$CuFe_2O_4$ [13], Co_3O_4/CNW [14], Mn_3O_4/CeO_2-rGO [15] and MnO_2-RuO_2/rGO [16]. CeO_2 is one of the most commonly employed rare earth metal oxides to have been synthesized in nanoparticle form due to its high chemical stability and low cost. CeO_2 is often used as a catalytic media due to its oxygen storage capacity via the Ce^{4+}/Ce^{3+} redox reaction [17–20]. Its unique redox properties originate from the fact that oxygen vacancies (V_O) are created in CeO_2 without changing its fluorite structure. Unfortunately, the specific capacitance (C_s) values of CeO_2 are still too low for CeO_2 nanoparticles prepared by the polymer pyrolysis method and calcined at 700 °C for 3 h (105 mA h/g) [21] or for CeO_2 nanoparticles prepared by the combustion method and calcined at 700 °C for 2 h (1.9 F/g) [22]. Recently, activated carbon prepared from different natural precursors such as rice husks

* Corresponding author.
E-mail address: sumalinphokha@gmail.com (S. Phokha).

https://doi.org/10.1016/j.apsusc.2018.02.209
0169-4332/

[23], banana peel [24], bamboo [25] and pomelo peel [26], and using various activating agents such as KOH, $KHCO_3$, $ZnCl_2$, H_3PO_4 have exhibited high surface areas and high specific capacities. For example, Gu et al. prepared carbon by KOH activation of bamboo resulting in a surface area of 776.07 m^2/g and a specific capacity of 605.7 mA h/g at 1C [25]. In another study, a large surface area of 1533 m^2/g was reported for carbon prepared from a pomelo peel precursor following KOH activation and this material exhibited a specific capacity of 750 mA h/g after 220 cycles at 0.2 C [26]. Other work used rice husks as a precursor to fabricate carbon by the hydrothermal carbonization method, but showed a lower surface area of 243 m^2/g and a lower specific capacity of 396 mA h/g at 0.2 C [23]. All of these studies measured relatively large surface areas and consequently high porosities, with their relatively large specific capacities due to the higher ion storage capacity of electrochemical energy systems. The differences in the measured surface areas of carbon materials is not only due to the different natural precursors used but is also due to differences in the activation conditions employed, such as the chemical reagents and process temperatures used, which can influence the pore formation process in carbon [25–28]. Furthermore, activated carbon can be used as a matrix to composite with other materials such as MO to increase surface areas and deliver excellent electrochemical performance [13,29]. For example, CNF/$CuFe_2O_4$ composites were reported by Nilmoung et al. [13] to exhibit a surface area of 191 m^2/g which was significantly higher than that of CNF of 30 m^2/g. Similarly, Aravinda et al. have used activated carbon (sourced from ACS Materials) with mixed phases of CeO_2 nanoparticles prepared using a mixer mill. The CeO_2/AC composite containing 10 wt% CeO_2 exhibited a specific capacitance of 162 F/g with about 99% retention of the initial capacitance even up to 1000 cycles [5]. This specific capacitance was higher than the value for activated carbon of 105 F/g [5]. To date, no studies have reported the electrochemical properties of carbon prepared from a coffee husk precursor mixed with CeO_2 nanoparticles. Therefore, it is of interest to study the enhancement of surface area and its effect on specific capacity in carbon/CeO_2 composites prepared from coffee husks for the purpose of energy storage applications.

In this work, we have studied the effect of CeO_2 concentration in carbon/CeO_2 composites (0, 10, 20 and 30 wt% of CeO_2 nanoparticles) prepared by the wet–ball milling method on their electrochemical properties. Carbon/CeO_2 composites employed as electrode materials were found to exhibit excellent electrical conductivity compared to either carbon or CeO_2 alone. The structure, morphology and $Ce^{4+}/Ce^{3+}/V_O$ states of the samples were characterized using X-ray diffraction (XRD), Raman spectroscopy (Raman), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) and X-ray photoelectron spectroscopy (XPS). The specific surface areas were measured using the Brunauer-Emmett-Teller method (BET) and the specific capacitances were measured on all samples using a potentiostat/-galvanostat electrochemical cell system.

2. Experimental

Firstly, carbon was prepared using coffee husks obtained from farms in the north-east of Thailand as the starting material. Briefly, 40 g of coffee husks were washed with distilled water, dried at 100 °C for 24 h and ground for 24 h to obtain a homogeneous particle size. This precursor was activated with $ZnCl_2$ solution (1.3628 g of $ZnCl_2$ in 120 ml of DI water), dried in an oven at 100 °C for 24 h and then calcined at 600 °C for 1 h in a sealed crucible. The activated carbon was removed with a 5 mol L^{-1} HCl solution at 80 °C, washed with distilled water until it showed a constant pH of 5.0 and then dried at 80 °C for 24 h. Secondly, nanoparticles of CeO_2 were synthesized using a polymer pyrolysis method followed by calcination in air for 3 h at 600 °C as described in previous work [30]. Finally, 2.7 g of carbon and 0.3 g of CeO_2 nanoparticles were combined and wet–ball milled in ethanol for 24 h and then dried at 80 °C for 24 h to remove the ethanol. These quantities were used for the preparation of the 10 wt% CeO_2 nanoparticles in carbon, subsequently described as carbon-10CeO_2. To make the carbon-20CeO_2 and carbon-30CeO_2 composites, the same procedure was

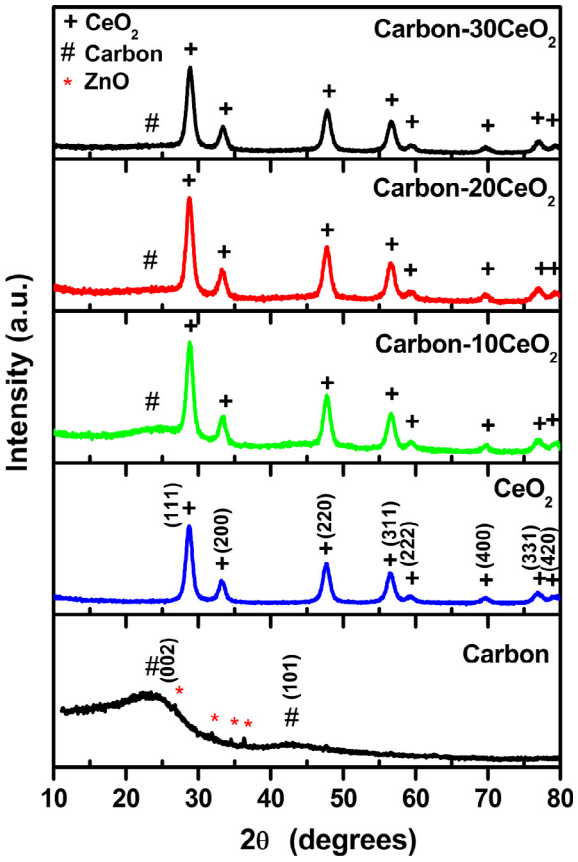

Fig. 1. XRD patterns obtained from carbon, CeO_2 nanoparticles and carbon/CeO_2 composites.

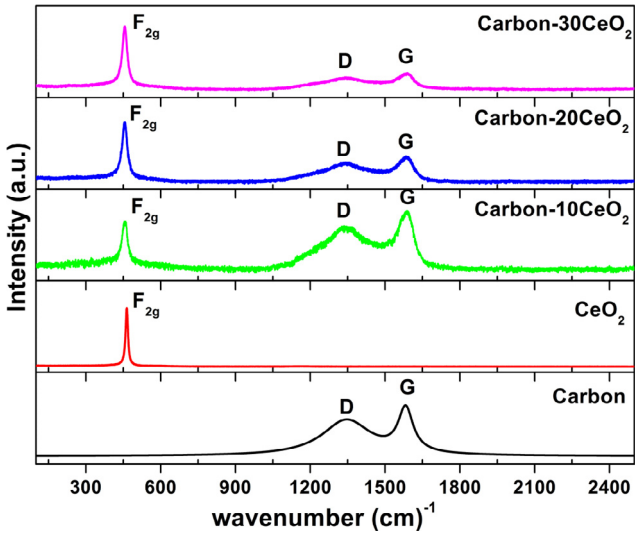

Fig. 2. Raman spectra obtained from carbon, CeO_2 nanoparticles and carbon/CeO_2 composites.

Please cite this article in press as: S. Phokha et al., Effects of CeO_2 nanoparticles on electrochemical properties of carbon/CeO_2 composites, Appl. Surf. Sci. (2018), https://doi.org/10.1016/j.apsusc.2018.02.209