INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 19609–19620

Available online at www.sciencedirect.com

ScienceDirect

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

A copper based metal-organic framework as single source for the synthesis of electrode materials for high-performance supercapacitors and glucose sensing applications

Inayat Ali Khan [a], *Amin Badshah* [a,**], *Muhammad Amtiaz Nadeem* [a,c], *Naghma Haider* [b], *Muhammad Arif Nadeem* [a,*]

[a] *Catalysis and Nanomaterials Lab 27, Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan*
[b] *Geoscience Advanced Research Laboratories, Geological Survey of Pakistan, Chakshahzad Town, Islamabad, Pakistan*
[c] *Department of Environmental Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan*

ARTICLE INFO

Article history:
Received 11 July 2014
Received in revised form
26 August 2014
Accepted 19 September 2014
Available online 16 October 2014

Keywords:
Pyrolysis
X-ray photoelectron spectroscopy
Supercapacitance
Glucose sensing

ABSTRACT

The article describes the conversion of MOF-199 to Cu–Cu_2O–CuO/C 700 (**1**) and Cu–Cu_2O–CuO/C 800 (**2**) nanostructures by simple pyrolysis at 700 and 800 °C under inert atmosphere. The X-ray photoelectron spectroscopy analysis reveals that the nanostructures Cu–Cu_2O–CuO/C consist of graphitic carbon functionalized with carboxylic, carbonyl and hydroxyl functional groups with copper/copper oxide particles on surfaces. The electrochemical properties of **1** and **2** are evaluated as electrode material for supercapacitors using cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy. The results for the capacitive performance from cyclic voltammetry and galvanostatic charge/discharge reveal that both the samples have gravimetric capacitance greater than 750 F g^{-1} at a scan rate of 2 mV s^{-1} and current density of 2 mA cm^{-2}. The samples retain about 43% of their initial capacitance even at high scan rate of 75 mV s^{-1}. The cycling performance of the nanostructures illustrate that there is 5.5% capacitance loss after 3000 cycles. The sample **1** and **2** are washed with 1 mol L^{-1} HCl solution to obtain copper oxide free materials Cu/C 700 (**3**) and Cu/C 800 (**4**). Samples **3** and **4** are tested as electrocatalysts for glucose sensing and the cyclic voltammetry measurement shows enhanced current densities compared to the literature values.

* *Corresponding author*. Tel.: +92 51 9064 2062.
** *Corresponding author*. Tel.: +92 51 9064 21321.
E-mail addresses: aminbadshah@yahoo.com (A. Badshah), arifchemist@hotmail.com, manadeem@qau.edu.pk (M.A. Nadeem).
http://dx.doi.org/10.1016/j.ijhydene.2014.09.106

Introduction

Metal-organic frameworks (MOFs) present a new class of porous crystalline materials that can have exceptionally high specific surface area and chemically tunable structures [1]. MOFs can be constructed from variety of metal oxide clusters and organic linkers [2]. MOFs have been used for a range of applications like gas storage [3], separation [4], chemical sensing [5], nonlinear optics [6], biomedical imaging [7], drug delivery [8], heterogeneous catalysis [9] and solar energy harvesting [10] etc. MOFs and their derived materials are fundamentally interesting and practically useful from electrochemical point of view. MOFs derived inorganic functional materials have been paid very little attention for the electrochemical detection of organic compounds, even though the excellent structural properties could potentially make them interesting for electrochemical application.

MOF-199 (HKUST-1) was originally synthesized by Chui et al. in 1999 [11]. It has a high specific surface area (1925 $m^2\ g^{-1}$) [12] and an interconnected 3D pore system with pore size of 9 Å × 9 Å. MOF-199 consists of repeated $Cu_2(COO)_4$ paddle wheel units with copper dimers as four connectors and benzene-1,3,5-tricarboxylate as three connectors, forming a cubic, wide-open framework [11–15]. Mao et al. [16] for the first time applied MOF-199 directly as electrocatalyst for oxygen reduction reaction (ORR). Similarly, Kumar et al. [17] have demonstrated the uniform film of MOF-199 on glassy carbon electrode as an efficient electrocatalyst for the selective reduction of carbon dioxide into oxalic acid. MOFs derived functional inorganic material like carbon, metal oxide decorated carbon materials and metal oxide under controlled synthetic condition for various potential application have been demonstrated by numerous researchers [18,19]. Liu and coworkers [20] for the first time reported the synthesis of porous carbon from Zn-based MOF for supercapacitor application. Recently, we have reported MOF-5 derived carbon as electrode materials in direct ethanol fuel cells (DEFCs) [21].Ogale and coworkers [22] utilized Fe-based MOF (MOF-53, 88B) for the synthesis of Fe_2O_4-porous carbon nanocomposite for water treatment. Jung et al. [23] also obtained ZnO hollow nanostructures from Zn-based MOF by control thermal treatment. Lin and coworkers [24] have published MOF derived Fe_2O_3–TiO_2 based composite for photocatalytic water splitting. Recently MOF-199 [25] was used for the synthesis of CuO nanostructures as anode materials for Li-ion batteries (LIB).

The increased concentration of glucose in the blood of human being could cause diabetes mellitus, one of the major health afflictions worldwide [26]. Therefore, the quantitative determination of glucose is a focused research area that receives extensive attention because of its importance in the field of biotechnology, clinical diagnostics and food industry application [27]. One of the methods is nonenzymatic glucose sensing by metal or metal oxide nanostructures (NSs) modified electrode [28]. Monometallic (Au, Cu, Cu_2O, Co etc.) [29,30], bimetallic (Au–Ag, Pt–Ni, Cu–Co, Ag–Ni etc.) [31,32] and trimetallic (Pt–Pd–Co, Pt–Ni–Co, Cu–Co–Ni etc.) [33,34] nanomaterials deposited on various carbon sources like graphene, carbon nanotubes etc. have been used for glucose sensing. The electrochemical supercapacitors are attracting greater interest owing to their high power density and longer life cycle compared with batteries and higher energy density than conventional capacitors. Supercapacitors have potential applications in electric vehicles, portable electronics [35], wearable displays, and artificial electronic skin and distributed sensors [36,37]. Carbon based materials like carbon nanotubes (CNTs) [38–40], activated carbon [41], carbon onions [42], carbon fibers [43] and graphene [44,45] have been used to fabricate supercapacitors. Decorating the surface of carbon materials with metal/metal oxide [46,47] and conducting polymer [48,49] can further improve their electrochemical performance which would result in enhanced capacitance. Wang and coworkers [50] have fabricated a flexible solid-state supercapacitor based on carbon nanoparticles and MnO_2 nanorods. Similarly, Li et al. [51] have reported mesoporous MnO_2/carbon aerogel composites for high performance supercapacitor. Song and coworkers [52] have reported anthill-like Cu@carbonnanocomposites obtained by simple thermolysis of a Cu-based metal organic framework (MOF-199) for nonenzymatic glucose sensing. In the present work, we report the synthesis of Cu–Cu_2O–CuO/C nanostructures by thermal treatment of HKUST-1 (MOF-199) at 700 °C and 800 °C in argon atmosphere. The obtained samples were evaluated as electrode materials for supercapacitor applications. The samples were treated with acid (1 mol L^{-1}HCl) solution to produce Cu/C 700 and Cu/C 800 nanostructures which were checked as electrocatalysts for glucose sensing.

Experimental section

Synthesis of MOF-199

For the synthesis of MOF-199, copper nitrate trihydrate [$Cu(NO_3)_2.3H_2O$ (0.72 g i.e. 3 mmol)] was dissolved in dimethylformamide (DMF, 20 mL). A suspension of 1,3,5-benzene tricarboxylic acid [$C_9H_6O_6$ (0.21 g i.e. 1 mmol)] in DMF (10 mL) was prepared and then triethylamine (Et_3N) was added to make a clear solution. The acid solution was stirred at room temperature and the salt solution was added drop wise. Finally blue precipitate of MOF-199 was obtained by filtration, washed with DMF and dried at 70 °C. PXRD spectrum of synthesized material (Figure S1) closely matched with the data simulated from single crystal reported in the literature [11].

Carbonization process

MOF-199 was vacuum dried at 200 °C and 250 mbar pressure (using Fistreem furnace with Vacuubrand 2008/05 vacuum pump) for 3 h to remove the solvent present in the pores. The dried product was transferred to a ceramic boat which is placed in a quartz tube fixed in a tube furnace (Nabertherm B 180). Initially the air was excluded by continuous flow of argon for 30 min and then the MOF-199 was heated up to 700 °C and 800 °C for 4 h to obtain **1** and **2**. These samples were washed with aqueous HCl solution (1 mol L^{-1}) to remove copper oxides. The oxides free samples were designated as Cu/C 700 (**3**) and Cu/C 800 (**4**).