Solid State Sciences 71 (2017) 51–60

Contents lists available at ScienceDirect

Solid State Sciences

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

Self-assembled dopamine nanolayers wrapped carbon nanotubes as carbon-carbon bi-functional nanocatalyst for highly efficient oxygen reduction reaction and antiviral drug monitoring

Diab Khalafallah [a], Naeem Akhtar [b], Othman Y. Alothman [c, d], H. Fouad [e, f, *], Khalil Abdelrazek khalil [a, g, **]

[a] Mechanical Design and Materials Department, Faculty of Energy Engineering, Aswan University, P.O. Box 81521, Aswan, Egypt
[b] Institute of Chemical Sciences, Bhauddin Zakriya University, Multan Pakistan
[c] Chemical Engineering Department, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia
[d] Deanship of Graduate Studies, Saudi Electronic University, Riyadh 11673, Saudi Arabia
[e] Department of Applied Medical Science, Riyadh Community College, King Saud University, Riyadh, 11437, Saudi Arabia
[f] Biomedical Engineering Department, Faculty of Engineering, Helwan University, P. O. Box 11792, Helwan, Egypt
[g] Department of Mechanical Engineering, College of Engineering, University of Sharjah, P.O. Box 27272, Sharjah, United Arab Emirates

ARTICLE INFO

Article history:
Received 15 May 2017
Received in revised form
29 June 2017
Accepted 1 July 2017
Available online 5 July 2017

Keywords:
Dopamine
Carbon nanotubes
Oxygen reduction reaction
Antiviral drug
Nanohybrid

ABSTRACT

Oxygen reduction reaction (ORR) catalysts are the heart of eco-friendly energy resources particularly low temperature fuel cells. Although valuable efforts have been devoted to synthesize high performance catalysts for ORR, considerable challenges are extremely desirable in the development of energy technologies. Herein, we report a simple self-polymerization method to build a thin film of dopamine along the tubular nanostructures of multi-walled carbon nanotubes (CNT) in a weak alkaline solution. The dopamine@CNT hybrid (denoted as DA@CNT) reveals an enhanced electrocatalytic activity towards ORR with highly positive onset potential and cathodic current as a result of their outstanding features of longitudinal mesoporous structure, high surface area, and ornamentation of DA layers with nitrogen moieties, which enable fast electron transport and fully exposed electroactive sites. Impressively, the as-obtained hybrid afford remarkable electrochemical durability for prolonged test time of 60,000 s compared to benchmark Pt/C (20 wt%) catalyst. Furthermore, the developed DA@CNT electrode was successfully applied to access the quality of antiviral drug named Valacyclovir (VCR). The DA@CNT electrode shows enhanced sensing performance in terms of large linear range (3–75 nM), low limit of detection (2.55 nM) than CNT based electrode, indicating the effectiveness of the DA coating. Interestingly, the synergetic effect of nanostructured DA and CNT can significantly boost the electronic configuration and exposure level of active species for ORR and biomolecule recognition. Therefore, the existing carbon-based porous electrocatalyst may find numerous translational applications as attractive alternative to noble metals in polymer electrolyte membrane fuel cells and quality control assessment of pharmaceutical and therapeutic drugs.

1. Introduction

The sustainable generation of green fuels represents one of the major challenges in the next decades due to the increasing depletion of convential fossil fuels and continuous progress in environmental pollution [1–3]. Thus, the development of attractive alternative energy conversion and storage systems with high energy densities is of great significance [1–4]. Similarly, accurate determination of pharmaceuticals is of practical interest to control its quality, formulation and stability. VCR is a pro-drug of the antiviral drug acyclovir majorly used as a therapeutic agent against viral infection and also for the suppression of genital herpes in HIV infected patients [5,6]. It has great advantages over the other

* Corresponding author. Department of Applied Medical Science, Riyadh Community College, King Saud University, Riyadh, 11437, Saudi Arabia.
** Corresponding author. Mechanical Design and Materials Department, Faculty of Energy Engineering, Aswan University, P.O. Box 81521, Aswan, Egypt.
E-mail addresses: menhfef@ksu.edu.sa (H. Fouad), kabdelmawgoud@sharjah.ac.ae (K. Abdelrazek khalil).

http://dx.doi.org/10.1016/j.solidstatesciences.2017.07.002
1293-2558/

therapeutic and antiviral drugs because of its low side effects and cheap price [7]. Thus, quantitative analysis of VCR is highly demanded to control the quality of antiviral drugs.

It is noteworthy to mention that efficacy of ORR and sensitivity of the electrode is highly dependent upon the cathode kinetics [8]. However, the sluggish kinetics can largely reduce the reaction rates. Several precious metal electrocatalysts (i.e. RuO_2, Pt, and IrO_2) and non-noble metal catalysts have been widely used to enhance the kinetics of ORR and sensitivity of the designed electrode [9]. But, their high cost, poor stability, and weak durability hamper their commercialization applications [10]. Therefore, it is highly desirable to explore inexpensive and efficient electrocatalysts with superior ORR performance and improved biomolecule sensing ability. Previous studies demonstrated that the carbon based materials possess a facile electron movement which is indispensible issue to attain high performance ORR activity [11]. Moreover, doping other metals with carbonaceous species can significantly boost the electronic features and provide better electrocatalytic performance [1–3].

Currently, carbon free-metal based materials have been shown to be potential candidates for energy conversion, storage devices and biomolecule recognition [12]. In addition, these materials are drawing considerable attentions due to their higher electric conductivity and electrochemical stability even in alkaline solution with low fabrication cost. Interestingly, their metal free architectures can perfectly frustrate the release of metallic species, leading to diminish the resulting environmental pollution. Thus, these unique features make these materials promising electrocatalyst for the development of highly stable, sensitive and efficient electrode system for ORR and electrochemical sensing system [13–16].

Carbon free metals based electrocatalysts are normally prepared through pyrolysis of polymers or organic compounds [17–19], template methods [20,21], chemical vapor deposition [22,23], and treatment of carbon precursors [24,25]. Despite the fruitful success has been made, there are still various inseparable issues related to the synthesis including (i) high cost and low yield of the production processes, (ii) toxicity of some carbon precursors, (iii) low specific surface area, (iv) aggregation of nanoparticles with each other due to strong van der Waals forces [26], which might inhibit the full utilization of exposed electroactive species for electrochemical reactions. Recently, Dai and co-workers have successfully synthesized grapheme sheets on the surface of CNTs to enhance the electrocatalytic activity via exfoliating the external wall of carbon nanotubes [27]. Lv et al. reported an appealing hybrid of N-graphene and CNT through a water assisted chemical vapour deposition (CVD) approach in which the graphitic layers were dispersed inside the cavities of CNT [28]. However, the convential CVD reaction was achieved after a long time with low yield.

Thus, it is extremely imperative to develop a simple and cost-effective synthesis strategy to fabricating carbon metal free materials on a large scale which can markedly guarantee excellent electrical connection with sustained electron pathways and facile ion transport. Nanostructured hybrids with highly conductive and active counterparts can provide abundance surface redox active sites with improved conductivity [14,15]. Alongside, pinning active nanoparticles at the external surfaces of CNT tubular structure can significantly enhance the active surfaces accessible to electrochemical reactions, leading to mass and electron transfer due to short diffusion pathways and higher conductivity [29]. The synergetic effect of both components can notably increase the current density and decrease over potential.

Herein, dopamine supported CNT (DA@CNT) nanoarchitectures successfully prepared via one-step synthesis strategy based on self-polymerization of dopamine layers on the outer surfaces of CNTs. Embedding the DA nano-layers on the tubular structure of the CNT can help to improve the electric conductivity of CNT and subsequently short the electron transport pathways. We intensively explore the ORR activity in 1 M KOH solution, the resulting DA@CNT catalyst exhibits a low peroxide yield and a positive half-wave potential, loosely approaching those of the commercially available Pt/C (20 wt%). In addition, our ORR electrocatalyst displays large current density under prolonged operation stability. Furthermore, developed electrode was successfully employed to monitor the quantity of VCR in PBS electrolyte with high sensitivity even in the presence of coexisting electro active species including ascorbic acid (AA), dopamine (DA), uric acid (UA) and glucose (GLU). The elevated electrocatalytic activity of the as-obtained DA@CNT hybrid can be attributed to, (i) unique structural features with fast shuttling of electrons, (ii) large surface area with enhanced active sites, and (iii) mesoporous morphology with low diffusion resistance. Thus, our present report may offer a potential strategy toward the development of effective electro-catalysts.

2. Materials

Dopamine hydrochloride (99%), multiwalled carbon nanotubes (MWCNTs), ascorbic acid (AA), dopamine (DA), uric acid (UA) and glucose (GLU) were purchased from Sigma–Aldrich Company Ltd., USA.VALTREX (valacyclovir) tablets were purchased from local medical store in Pakistan. Phosphate buffer and sulfuric acid were obtained from Nacalai Tesque Co. (Japan) purchased from Nacalai Tesque Co., Japan. All of the supplied chemicals and reagents were of analytical grade and used as received.

2.1. Modification of CNT

The as-received commercially available MWCNTs were first oxidized to obtain oxygen containing group using strong acidic solutions as described elsewhere [30]. In a typical synthesis route, 700 mg of MWCNT were ultra-sonicated in 250 mL concentrated sulfuric acid (H_2SO_4) for 1 h at 45 °C. Then, the resulting mixture was magnetically stirred for 4 h at 75 °C using water bath system. The harvested precipitate was carefully rinsed with deionized water several times, lyophilized, and finally annealed at 500 °C for 1 h under argon flux.

2.2. Synthesis of DA@CNTs nanocomposite

The pre-oxidized CNT were employed as scaffolds to grow a thin film of dopamine on their outer tubular architecture. Subsequently, 100 mg of chemically treated CNT was suspended into 100 mL phosphate buffer solution (pH 8) under sonication treatment for 30 min. After that 400 mg of dopamine hydrochloride was added and then the whole reaction mixture was continuously stirred at room temperature for 4 h. The obtained sold product was collected, washed thoroughly with deionized water, and finally lyophilized for 8 h at 50 °C.

2.3. Characterization of catalyst

The field emission scanning electron microscopy (FE-SEM) observations were conducted on a JEOL model 6500 operated at 12 kV. Transition electron microscope images were measured by a JEM-2100F at 200 kV. The phase purity of the samples was inspected using via wide angle powder X-ray diffraction (WA-XRD) using a Bruker D8 Advance diffractometer with monochromated $Cu_{K\alpha}$-radiation ($\lambda = 1.54178$ Å) at a voltage of 40 kV. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method using BELSORP36 analyzer (JP. BEL Co., Ltd.) at −196 °C. X-ray photoelectron spectroscopy (XPS) investigations were conducted