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Polydopamine-assisted carbon nanotubes/Co_3O_4 composites for rechargeable Li-air batteries

Taek Han Yoon, Yong Joon Park*

Department of Advanced Materials Engineering, Kyonggi University, Gyeonggi-do 443-760, Republic of Korea

HIGHLIGHTS

► Polydopamine layer was introduced as reacting assistant between the CNTs and the oxide catalyst (Co_3O_4).
► The polydopamine layer was found to be very effective for the adhesion of nanosized Co_3O_4 particles on the surface of CNTs.
► The air electrode containing polydopamine-assisted CNTs/Co_3O_4 composites showed superior catalytic activities in Li-air cells.

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ABSTRACT

We synthesize a carbon nanotubes (CNTs)/Co_3O_4 nanocomposite and demonstrate its electrochemical properties as an effective catalyst in Li-air cells. In particular, we introduce polydopamine as a binding agent (or reaction assistant) for CNTs and a catalyst with redox properties (Co_3O_4). Polydopamine coated on the surface of CNTs is expected to offer hydrophilicity and reactivity with oxide-sources. The CNTs/Co_3O_4 composite prepared using polydopamine layers shows homogeneously dispersed Co_3O_4 nanoparticles on the surface of the CNTs, thereby confirming that our new facile approach allows effective interaction between the carbon support and the oxide component. The air electrode containing polydopamine-assisted CNTs/Co_3O_4 composites shows superior catalytic activities in Li-air cells. This can be attributed to the wide catalytic-active area that provides well-dispersed nanosized Co_3O_4 particles as well as to the reduced contact resistance as a result of the close contact between CNTs and oxide (Co_3O_4).

1. Introduction

Li-air batteries are one of the most promising new technologies among the various energy storage systems owing to their extremely high theoretical energy density [1–7]. However, the maximum theoretical energy density of Li-air batteries cannot be fully achieved in practice. In the case of Li-air battery systems using non-aqueous (organic) electrolytes, the practically available capacity of the system is highly attributed to the air electrode composed of a catalyst and a carbon material [8–13]. The air electrode significantly affects the rechargeability and over-potential properties of the Li-air cell. Among the components of the air electrode, the catalyst is important in that it can enhance the charge reaction by reducing the voltage required to dissociate the reaction products (such as Li_2O_2) into lithium metal and oxygen [14]. However, the oxide catalysts, which are generally used for air electrodes, are poor electric conductors and they are typically used mixed with porous carbon materials for reaction and as storage sites for reaction products. Although some types of carbons show catalytic activity this is not typically sufficient to dissociate the reaction products and produce oxygen evolution [9–12]. Considering separated roles of the catalyst and the carbon material, a composite electrode would be more effective in enhancing the catalytic activity of air electrodes. In particular, if the nanosized catalysts could be homogeneously dispersed on the surface of the porous carbon material, the number of catalytic active sites would be increased, thereby improving the electrochemical activity of the air electrodes.

Herein, a nanosized oxide-catalyst was composited with CNTs to enhance the catalytic activity of the air electrode in Li/air batteries. The methods for preparing these composite electrodes have been reported considerably [15–17]. In this study, a new and facile approach based on the introduction of a polydopamine coating layer as a special adhesive between the carbon and the oxide is described. The polydopamine coating has discovered in the process of analyzing the mussel's special ability. Thus, mussels can be

* Corresponding author.
E-mail addresses: yjpark2006@kyonggi.ac.kr, yjparketri@yahoo.co.kr (Y.J. Park).

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strongly attached to all types of organic/inorganic surfaces. The Messersmith group attributed this strong adhesion ability to the presence 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine amino acids [18,19]. Based on this finding, polydopamine containing both DOPA and lysine side chain functionalities was suggested as a strong binding agent. Remarkably, the polydopamine coating layers were found to be a versatile platform for secondary surface-mediated reactions [19]. For example, a polydopamine layer significantly promoted the reaction of various source materials such as metals, ceramics, and polymers with the coated substrates [19–23]. Based on the understanding of this special ability of polydopamine, we used it as a binding agent between carbon and the oxide catalyst. This process is very simple and facile, and is a green technology. Moreover, this method can be applied not only to CNTs but also to any type and shape of carbon materials.

We report herein a new process to fabricate CNTs/Co_3O_4 composites using a polydopamine layer, and their electrochemical property, as air electrodes for Li/air cells were determined. To the best of our knowledge, this is the first study reporting a polydopamine coating approach in carbon and oxide-containing electrodes. Co_3O_4 has generated an extensive interest as a promising catalyst in various application fields [24–27]. The CNTs serve to support the catalyst, thereby providing a surface for the redox reaction to occur. It is expected that the CNTs/Co_3O_4 composite shows excellent catalytic activities because of the nanoscale catalytic size, large surface area for reaction, and enhanced electronic conductivity.

2. Experimental

2.1. Synthesis of polydopamine-assisted CNTs/Co_3O_4 composite

All the chemicals used herein were of analytical purity and used as received. The polydopamine-coated CNTs material was prepared by simple immersion of the CNTs into a dopamine solution containing a tris-buffer solution (10 mM, pH 8.5) and methanol as co-solvents (CH_3OH:buffer = 1:1 v/v). The mixture solution was mechanical stirred for 4 h at room temperatures until a good suspension was formed. After that, the suspension was centrifuged and the solid was subsequently washed with distilled water and ethanol. The polydopamine-coated CNTs were dispersed in 50 ml of a 4 mM $Co(NO_3)_2 \cdot 6H_2O$ (cobalt nitrate hexahydrate) aqueous solution for 30 min. Subsequently, a 0.2 M NH_4OH aqueous solution was slowly dropped into the above solution to adjust the pH value to 10, and then stirred for 8 h. After that, the mixture solution was centrifuged, the resulting solid washed for several times with ethanol and distilled water, and then dried at 90 °C for 24 h. Finally, the dried product was annealed under air at 450 °C for 4 h, after which the final product was obtained. Fig. 1 illustrates the overall fabrication process of polydopamine-assisted CNTs/Co_3O_4 composites.

The X-ray diffraction (XRD) patterns of the samples were obtained with a Rigaku X-ray diffractometer equipped with monochromatized Cu-Kα radiation (λ = 1.5406 Å). X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe (Ulvac-PHI)) analysis was

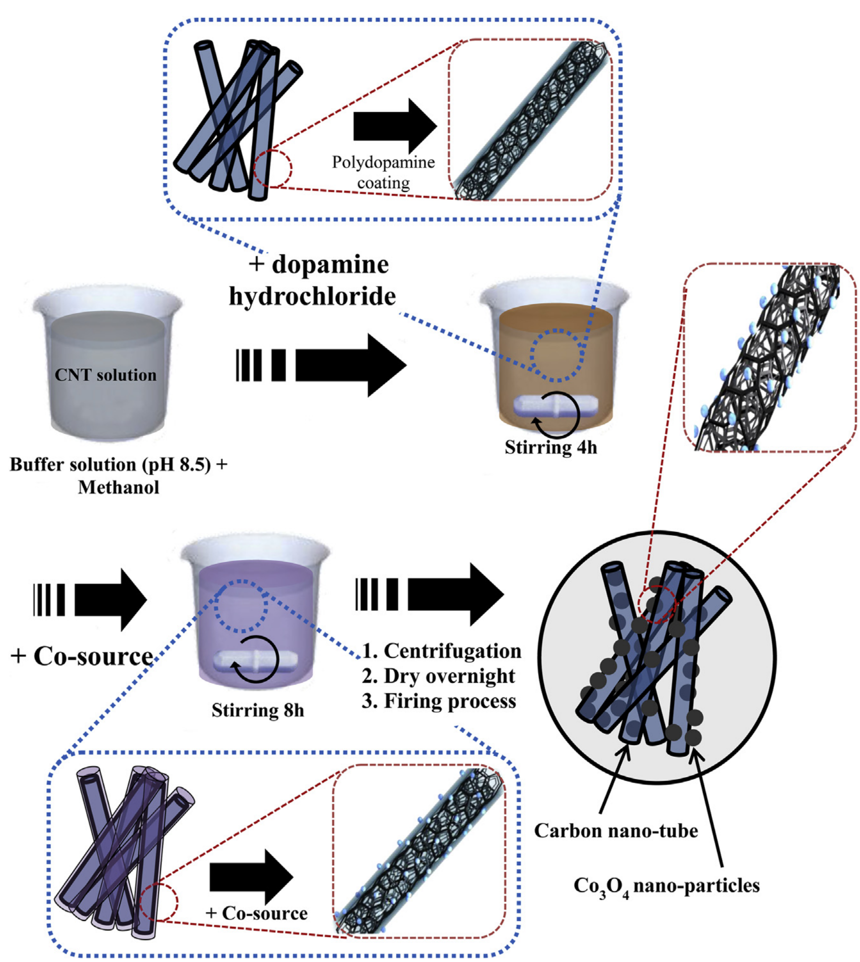

Fig. 1. Scheme of the synthetic procedure for obtaining polydopamine-assisted CNTs/Co_3O_4 composites.