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Nickel Oxide/Carbon Nanotubes as Active Hybrid Material for Oxygen Evolution Reaction

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Abstract

Carbon nanotubes are of great interest due to their high surface area and rich edge sites, which are favorable for wide applications. Here, a simple and efficient routine is presented by decoration of multi-wall carbon nanotube (MWCNT) with nickel oxide (NiO) nanoparticles.The morphologies of NiO-MWCNT were investigated by using scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). In alkaline media, the carbon paste electrode (CPE) modified with NiO-MWCNT catalyses oxygen evolution reaction (OER) with an onset potential of 0.61 V (vs. Ag|AgCl|KCl_{3M}), showing a synergistic effect between MWCNT and NiO nanoparticles.After the long-term *I-t*measurement, high electrochemical stability confirms the improved electrocatalytic performance of NiO-MWCNT. This study affords us a NiO-MWCNT based electrocatalyst with high performance and strong durability under alkaline conditions, which can be applied to energy conversion and storage.

Keywords: Multi-wall carbon nanotubes,Nickel oxide nanoparticles, Oxygen evolution reaction, Electrocatalyst.

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Introduction

The oxygen evolution reaction (OER) plays an important role in the devices of energy conversion and storage, such as fuel cells and metal-air batteries [1-6]. Electrochemical water splitting has been basically mature for production of oxygen promoted by electrolysis derived from variableand intermittent renewables [7,8]. The anodic oxygen evolution reaction (OER) has a slow reaction rate owing to the multi-steps transfer of four electrons with high activation energy and large overpotentials [9,10]. Therefore, we need a stable and high performance electrocatalyst so as to lower the large overpotential and accelerate the OER.

It is well known that transition-metal chalcogenides have prominent electronic structures and physical appearance, for instance, excellent conductivity, magnetic property and half-metallicity [11–13]. First-row transition metals have been proved to be efficient OER catalysts [14,15]. Among these, nickel- and cobalt- based catalysts have been demonstrated to be efficient electro-catalysts [14]. However, these candidates have been proved to process inferior electrocatalytic performances in nature [16-31]. It is worth noting that designing different nanostructure and crystal phase of electrocatalysts may increase the number of active sites and the electrocatalytic activity.

Recent efforts to meet these challenges have focused on enhancing the catalytic activity of these noble metal catalysts by using a suitable carbon-based support, such as carbon black [32-34], carbon nanotubes (CNTs) [35], carbon nanofibers [36], and graphene [37,38]. Of these, the CNTs are attractive as support materials owing to their low costs, good electrical conductivity, huge surface area, and high thermal stability originating from their well-developed graphitic structures [39].The CNTs might be modified by surface functionalization to introduce hydrophilic groups such as –COOH and –OH groups onto CNT surfaces. These polar groups could enhance the solubility of CNTs and also create anchor points for the effective loading of metal nanoparticles [40].

Here, we present a low cost method to synthesize NiO nanoparticles deposited onto the surface of MWCNTs as the catalysts for the OER. The electrochemical measurments of NiO-MWCNT indicate prominent improvements of OER activity and electrical conductivity compared to NiO and MWCNT, and also revealing a long-term stability in basic media. The enhanced mechanism of OER activity has been discussed.

Experimental

Materials

Multi-wall carbon nanotubes (MWCNTs) (outer diameter: 20-40 nm, length: 5-15 µm, purity>97) were purchased from Shenzhen Nano-Technologies Port Co., Ltd. (China). Nickel nitrate and sodium hydroxide were from Aldrich and used as received. The solvent used for the electrochemical studies was twice distilled water.

Apparatus

The pH was measured using a pH meter model 250Ion Analyzer using a combined electrode. Electrochemical measurements were performed with potentiostat/galvanostat (Sama 500-c Electrochemical Analysis system, Sama, Iran). A conventional three-electrode system consisting of Ag|AgCl|KCl_{3M} as the reference electrode, a NiO–MWCNT/CPE as a working electrode and a platinum wire as auxiliary electrode were used.

Preparation of modified electrode

Carbon paste electrode (CPE) was prepared by hand-mixing of graphite powder plus paraffin until a uniformly wetted paste was obtained. The paste was then packed into a glass tube (internal radius 2.5 mm). Electrical contact was made by pushing a copper wire down the glass tube. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. Finally, 5 µL of the MWCNTdispersed solution (1 mg of MWCNTs in 5 mL of DMF) was dropped onto the surface of the CPE and it was dried in an oven air at 50 °C to remove the solvent. The MWCNTs on CPE was decorated with NiO nanoparticles by the cyclic voltammetry for 15 cycles with a scan rate 100 mV s^{-1} in phosphate buffer solution (pH=7.00) containing 1 mM nickel nitrate.

Results and discussion

Characterization of NiO–MWCNT/CPE

The feature of NiO–MWCNT/CPEsurface was observed by SEM and the elemental analysis was performed by EDS (Figure1). The changes in surface morphology due to decorating of NiO on to the MWCNT (Figures1a and 1b). Figure1c shows the EDS analysis of the NiO–MWCNT/CPEfilm. It becomes clear that NiO decorated onto the MWCNTs.

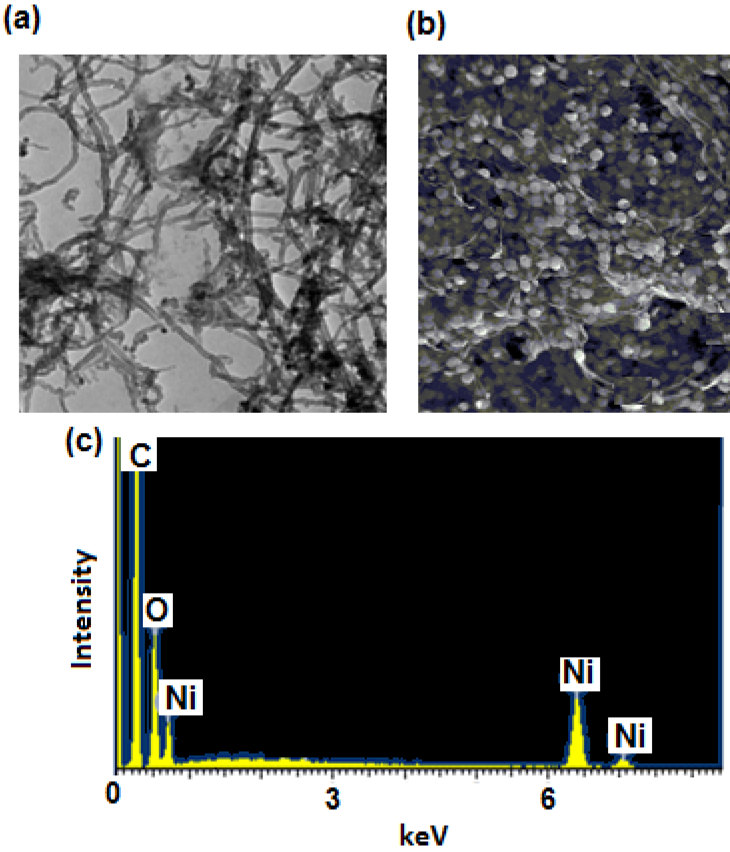

Figure 1. SEM images of (a) MWCNT/CPE and (b) NiO–MWCNT/CPE and (c) EDS spectra of NiO-MWCNT/CPE.

Properties of modified electrode

The cyclic voltammogram of the NiO–MWCNT/CPE in 0.1 M NaOH solutionis shown in Figure2. A pair of well-defined redox peaks was obtained in the cyclic voltammogram of the NiO–MWCNT modified CPE in 0.1 M NaOH. The anodic peak potential observed at about 500 mV, and the cathodic peak potential at about 320 mV are ascribed to the Ni(III)/(II) redox couple in 0.1 M NaOH. NiO–MWCNT/CPE exhibited a more remarkable current response, indicating an excellent electrocatalytic property of OER.The surface concentration of the electroactive NiO on NiO–MWCNT/CPE, Γ (in molcm^{-2}), can be estimated using the equation [41]:

$$\Gamma = Q/nFA \quad (1)$$

Where Q is the charge consumed in coulombs, obtained from integrating the anodic (or cathodic) peak area in cyclic voltammogram under the background correction. The average Γ value of $(9.21 \pm 0.78) \times 10^{-10}$ mol cm^{-2} was obtained.

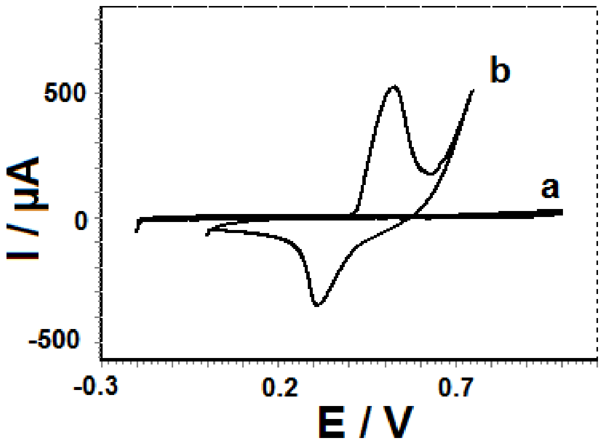

Figure 2. Cyclic voltammogram of (a) CPE and (b) NiO–MWCNT/CPE in 0.1 M NaOH solution at scan rate of 100 mV s^{-1}.

Figure 3A depicts the CV curves of NiO–MWCNT/CPE in 0.1 M NaOH at various scan rates. As the scan rate increases, the anodic peak potentials shift to more positive and the cathodic peak potentials convert to negative direction and the peak currents are enhanced with the increasing of the scan rate. According to the plot of the anodic and the cathodic peak currents against the scan rate shown Figure3B, it is found that the anodic and the cathodic peak currents are linearly proportional to potential sweep rate, indicating that electrode process is surface-controlled in this range of potential scan rate [29].

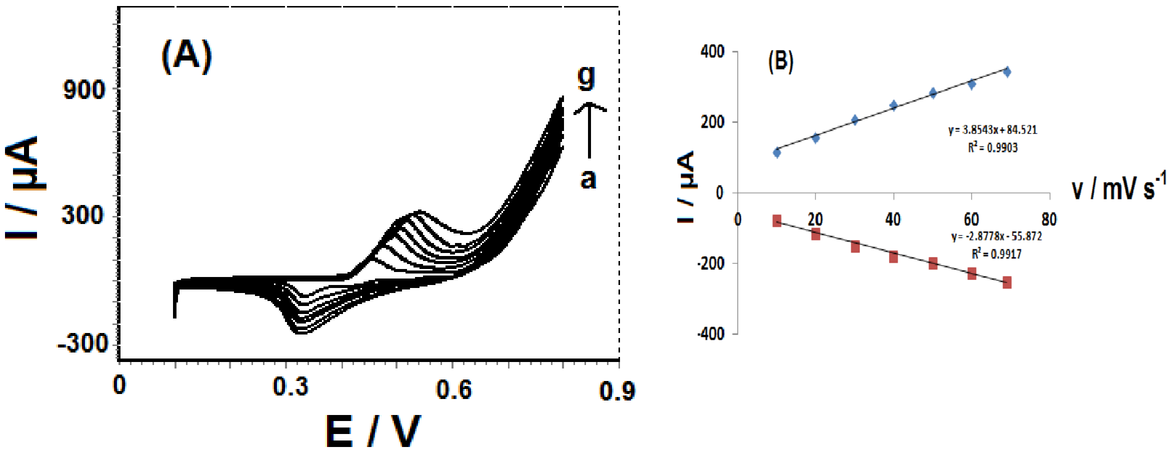

Figure 3. (A) Cyclic voltammogram of NiO–MWCNT/CPE in 0.1 M NaOH solution at scan rate of (a) 10, (b) 20, (c) 30, (d) 40, (e) 50, (f) 60 and (g) 70 mV s^{-1}. (B) The plots of peak current versus scan rate.

Electrocatalytic properties of the NiO–MWCNT/CPE

The electrocatalysis of OER was studied at surface of CPE, MWCNT/CPE, NiO/CPE and NiO–MWCNT/CPE in 0.1 M NaOH solution by linear sweep voltammetry (LSV), and results were shown in Figure4. As expected, the electrocatalytic activity improves after deposition of NiO–MWCNT on CPE. The carbon nanotubes decorated by NiO nanoparticles makes a significant increase in catalytic ability as though the onset potential of OER occurs at about 0.6 V and is indicated by an abrupt increase of the anodic current density.

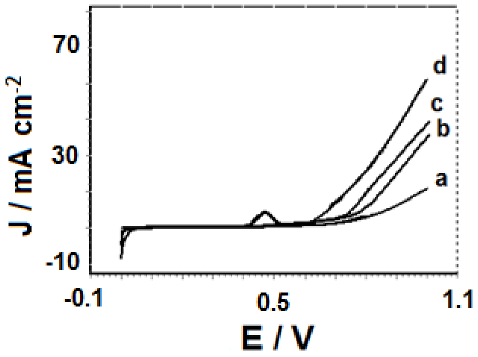

Figure 4. LSVs for the OER on (a) CPE, (b) MWCNT/CPE, NiO/CPE and NiO–MWCNT/CPE in 0.1 M NaOH solution at scan rate of 10 mV s^{-1}.

It is generally accepted that under open circuit potential, nickel in alkaline media forms a thin layer of $Ni(OH)_2$ which can be oxidized to β-NiOOH. It is supported by the reversible transformation between $Ni(OH)_2$ and NiOOH, which is feasible under the prevailing conditions of potential and pH. Thus, it is presumed that the β-NiOOH phase is involved according to [42,43]:

$$2\beta\text{-NiOOH} + (O^-)_{ads} \rightarrow 2NiO_2 + H_2O + e^- \quad (2)$$

$$NiO_2 + (OH)_{ads} \rightarrow \beta\text{-NiOOH} + (O)_{ads} \quad (3)$$

The Study of effective parameters on electrocatalytic activity of NiO–MWCNT/CPE toward OER

The NiO nanoparticles content decorated onto MWCNTs was controlled by different cycles of cyclic voltammetry during the preparation of NiO–MWCNT/CPE. Figure5 shows the linear sweep voltammograms of OER for NiO–MWCNT/CPE in a 0.1 M NaOH solution at different cycles. As can be seen, 15 cycle was chosen as optimum ratio for electrocatalytic activity of OER and further studies were performed at this cycle.

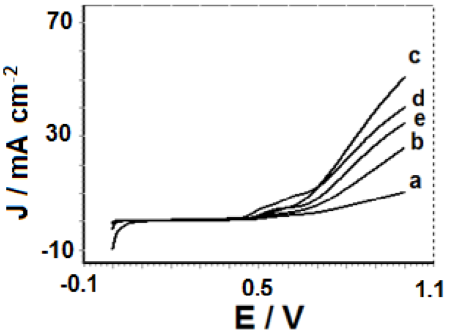

Figure 5. LSVs of NiO–MWCNT/CPE by (a) 5, (b) 10, (c) 15, (d) 20 and (e) 30 cycles of cyclic voltammetry during the preparation in 0.1 M NaOH solution at scan rate of 10 mV s^{-1}.

LSVs of NiO–MWCNT/CPE in various pH of NaOH solutions were recorded (Figure6). As can be expected, the OER current density increases with increasing of pH.

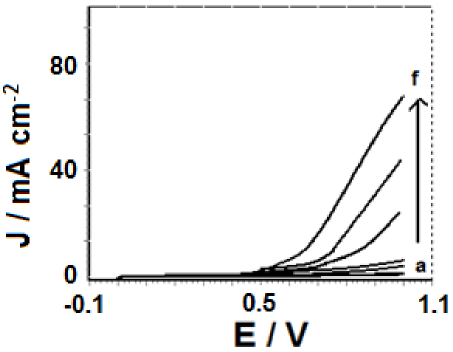

Figure 6.LSVs of NiO–MWCNT/CPE at pH: (a) 8, (b) 9, (c) 10, (d) 11, (e) 12 and (f) 13 of 0.1 M NaOH solution at scan rate of 10 mV s^{-1}.

Energy savings

In order to express potential in term of the oxygen over-potential, η (when the reference electrode is Ag/AgCl electrode) can be estimated using the following equation [43]:

$$\eta = E_{meas} - E_{rev} \quad (4)$$

Where E_{meas} is the measured electrode potential and E_{rev} is the reversible electrode potential. When the reference electrode is Ag/AgCl in the same solution as the working anode E_{rev}=0,0.463−0.222=0.241V.Clearly, in this case, η is related to the voltage, E_{meas}, measured on the Ag/AgCl scale as follows:

$$\eta = E_{meas} - 0.241V (5)$$

The average η values for current density of 5, 10, 20 and 30 mA cm^{-2} were obtained 98, 147, 185 and 240 mV, respectively.

The significant decrease in the potential obtained after the modification with NiO-MWNT corresponds to a reduction in the rate of energy consumption at the anode and consequently decreases the energy consumption in the overall process. The energy saving at the anode is given by [43]:

$$P_{(a)}=\Delta E_{(a)}F/3600 \qquad (6)$$

Where $\Delta E_{(a)}$ is the anodic potential shift at a current density and $P_{(a)}$ is the kilowatt-hours per kilogram of oxygen gas. The value of $P_{(a)}$ was calculated 21.2, 21.5, 21.8 and 22.4 kW h kg^{-1}at current densities of 5, 10, 20 and 30 mA cm^{-2}, respectively. The observed power saving of oxygen gas for our designed sensor was compared with those already reported in papers [29–31,43–46]. As can be seen, the power saving of oxygen gas is comparable. Also, the trapping effect of the profusely generated O_2 gas bubbles at the modified electrodes with the increase in current density is low and the values of $P_{(a)}$ increase with the increase in current density.

In addition, the long-term stability of NiO–MWCNT modified CPE for OER was investigated with chronoamperometric curve recorded at 0.63 Vin 0.1 M NaOH. The result is shown in Figure 7, indicating that the current does not drop significantly even after 3000 s. These might be attributed to the NiO–MWNT electrocatalyst for the OER at the surface CPE shows greater stability and higher activity.

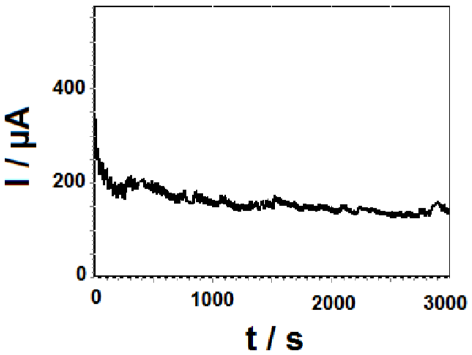

Figure 7. The long-term stability plot of NiO–MWCNTfor OER versus time.

Conclusions

We have successfully developed NiO–MWCNT as an efficient and durable catalyst by the cyclic voltammetry for 15 cycles. The NiO–MWCNT exhibits good properties towards oxygen evolution reaction in alkaline solution.

Further, the present modified electrodes were highly stable, and notorious procedure was involved in electrode modification.

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