

Research Article

Facile Synthesis of Porous NiO/rGO Hybrid Material: Perspectives for Electrochemical CO₂ Reduction

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Abstract

A porous nickel oxide/reduced graphene oxide (NiO/rGO) hybrid porous material was successfully synthesized via a simple wet-chemical approach followed by annealing at 400°C for 3 hours. XRD, FESEM, and Raman reveal the crystallinity and high purity of the prepared NiO/rGO. Linear Sweep Voltammetry (LSV) shows that in CO₂-saturated solution, the measured current density of NiO and NiO/rGO is 3.9 and 6.1 mA/cm² at -1.7 V vs. Ag/AgCl, respectively. The enhancement in cathodic current in CO₂ than in N₂ saturated solution is mainly originated from the CO₂ reduction over NiO/rGO electrode surface. After 20 min CO₂ER, ethanol (FE ~16%) was produced over NiO/rGO electrocatalyst at -0.9 V vs. Ag/AgCl. These results imply the capacity of NiO/rGO as an electrocatalyst for energy conversion application.

Keywords: Porous Material; NiO/rGO; Energy Conversion; CO₂ Reduction**Abbreviations**

NiO/rGO: Nickel oxide/reduced graphene oxide; XRD: X-ray Diffraction; FESEM: Field Emission Spectroscopy; LSV: Linear Sweep Voltammetry; Ag/AgCl: Silver/Silver Chloride; FE: Faradaic Efficiency

Introduction

Electrocatalysts have attracted enormous attention due to its potential application to solve energy and environmental crisis [1-2]. Catalytic CO₂ conversion to fuels represents a suitable solution as new energy source and protects our environment at the same time [3-4]. CO₂ electroreduction (CO₂ER) to valuable chemicals and liquid fuels (methanol, formic acid,...etc.) is considered as the most attractive approach to mitigate the CO₂ emission issue [5], besides it can be easily operated at room temperature and atmospheric pressure. Moreover, based on the applied potential and electrode material, variable products could be produced [6]. CO₂ER has been extensively studied over various surfaces such as metal and metal oxides [7-8]. Hydrogen Evolution Reaction (HER), high overpotential, and selectivity are the most common obstacles of CO₂ER [9]. Therefore, more research efforts are still in demand for an efficient, selective, and nonprecious electrocatalyst design. Transition Metal Oxides (TMOs) have been extensively studied for CO₂ electroreduction [2,5,10]. Among them, nickel oxide nanoparticles (NiO NPs) received much attention due to the low cost and its significant catalytic performance [11]. Because of the low specific surface area and active sites, NiO gives low hydrocarbon yield and low energy efficiency, which make its utilization for CO₂ER is limited.

Due to the synergistic effect and geometric structures, carbon-based electrode performs a superior catalytic activity for CO₂ER [12-13]. Reduced graphene oxide (rGO) as a new carbon form is a promising and exciting material for a variety of applications, owing to its extraordinary characteristics such as high surface area and excellent electron mobility. Recently, NiO/graphene hybrid found

potential applications in catalysis, batteries, and H₂ storage.

The electrochemical behavior of the synthesized NiO/rGO catalyst was evaluated using two-compartment electrochemical cell and 0.5 M NaHCO₃ as an aqueous electrolyte. The results displayed the role of rGO as catalyst support for CO₂ER. To the best of our knowledge, this is the first report for NiO/rGO evaluation as an electrocatalyst towards CO₂ reduction.

Experimental**Materials**

Nickel chloride hexahydrate (≥ 97%), hydroxylammonium chloride (NH₂OH.HCl), sodium hydroxide (≥ 99.5%), sodium dodecyl sulfate (SDS, ≥ 99%), and sodium bicarbonate (≥ 99.5%). All chemicals procured from Sigma-Aldrich and used as received.

Synthesis of NiO/rGO Hybrid Structure

Starting with graphite, we have synthesized Graphene Oxide (GO) using modified Hummers, methods [14]. GO stock solution (1 mg/mL) was prepared. After that, 0.3 mL of the prepared GO stock solution dissolved in 18.1 mL distilled water under sonication for 30 min. This was followed by, adding 0.3 mL 0.1 M NiCl₂·6H₂O and 0.01g SDS under vigorous stirring for 2h. Then, rapidly 0.54 mL 1 M NaOH and 1.2 mL 0.1 M NH₂OH.HCl are added and stirred for 30 min. After that, the formed solid was centrifuged, washed with H₂O and ethanol, and dried at 40°C for 18h. Finally, the collected powder was annealed at 400°C for 3h. Moreover, pure NiO powder was prepared via the same procedure without adding GO solution.

Characterization Tools

Powder X-ray diffraction (XRD, Rigaku MiniFlex) was used to identify the phase structure of the as-synthesized materials. The samples morphologies were investigated by a field emission scanning electron microscope (FESEM, Lyra 3, Tescan). EDX was used for elemental composition analysis. Raman spectra of the prepared NiO/rGO hybrid structure were collected in the range from 500 to 2000

cm⁻¹.

Electrode Fabrication and Electrochemical Measurements

Cu metal pieces (fisher scientific company) were mechanically and chemically treated before used as substrate. For catalyst electrode fabrication, 1.0 mg of the prepared material was dispersed in 1.0 ml acetone and 60 μ l nafion (5 wt. %), then ultrasonicated until ink solution was formed. A 200 μ l from the ink solution was dropped on the Cu substrate and dried in air. To evaluate the catalyst/electrode behavior towards CO₂ER, LSV measurements and CO₂ reduction experiments were carried out under ambient conditions (see supplementary data).

Results and Discussion

Materials Characterization

The XRD patterns of the as-synthesized NiO and NiO/rGO are shown in Figure 1. XRD shows the diffraction peaks at 37.3°, 43.4°, 62.9°, 75.5°, and 79.5° which corresponding to the crystal orientations (111), (200), (220), (311), and (222), respectively. These peaks are indexed for NiO crystal planes which are in excellent agreement with JCPDS No. 04-0835. Moreover, the broadening peaks of NiO/rGO pattern than those of NiO associated with the contribution of graphene. No other peaks could be detected, revealing the purity and well crystallinity of the synthesized NiO powder. For more investigations, Raman scattering was employed to characterize carbon materials. As can be seen from Figure 2, the characteristic D and G bands of reduced graphene oxide appeared at 1345 cm⁻¹ and 1590 cm⁻¹, respectively. Furthermore, the intensity ratio of D:G bands for NiO/rGO sample is higher than that of GO (inset). This difference in intensity ratio reveals the removal of functional groups-containing oxygen during the reduction of graphene oxide [2].

The surface morphologies of the synthesized NiO and NiO/rGO samples were shown in Figure 3. As seen from Figure 3(a, b), NiO has a porous and belt-like structure consists of small particles. The porous structure of NiO nanoparticles is clearly revealed by SEM image Figure 3(b). Furthermore, the decoration of NiO with reduced graphene oxide layers is observed as shown in Figure 3(c, d). The porous NiO/rGO hybrid structure shows no big changes. Actually, it is clear from SEM images that some macropores up to ~250 nm and micropores are generated on the surfaces. EDX analysis confirmed the existence of Ni, O, and C (not shown here).

Electrochemical Behavior

To evaluate the catalytic activity of NiO/rGO electrocatalyst towards CO₂ reduction, Linear Sweep Voltammetry (LSV) measurements were carried out with and without CO₂-saturated 0.5 M NaHCO₃ aqueous solution at scan rate of 20 mV/s. Figure 4 shows the LSV of NiO and NiO/rGO electrodes under N₂ and CO₂ atmosphere. It is clear that NiO/rGO exhibited cathodic current density higher than that of NiO. Moreover, the measured current density in CO₂ saturated electrolyte is larger than that in N₂ saturated electrolyte over both NiO and NiO/rGO electrode surfaces. At -1.7 V vs. Ag/AgCl and in CO₂ saturated solution, the recorded current over NiO and NiO/rGO was 3.9 and 6.1 mA/cm², respectively. It is well known that the recorded current in N₂ saturated electrolyte is mainly conducted with hydrogen evolution reaction [12,15]. The enhanced current density in CO₂ saturated electrolyte is due to the

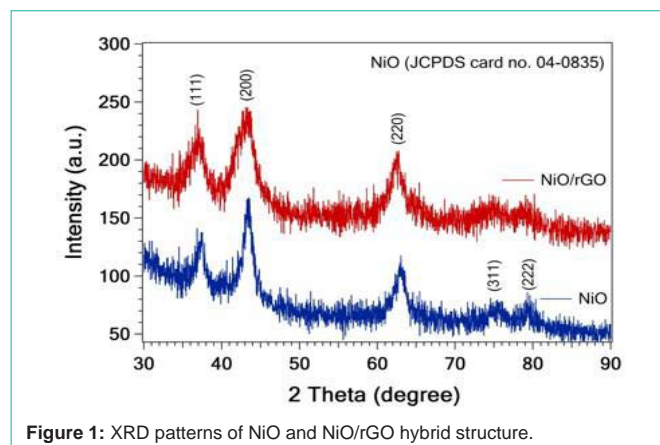


Figure 1: XRD patterns of NiO and NiO/rGO hybrid structure.

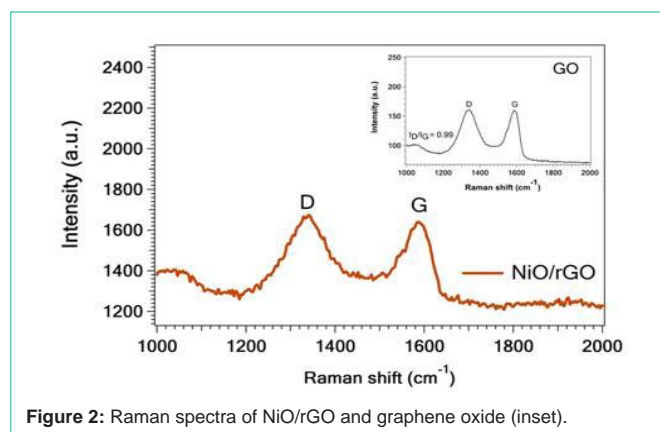


Figure 2: Raman spectra of NiO/rGO and graphene oxide (inset).

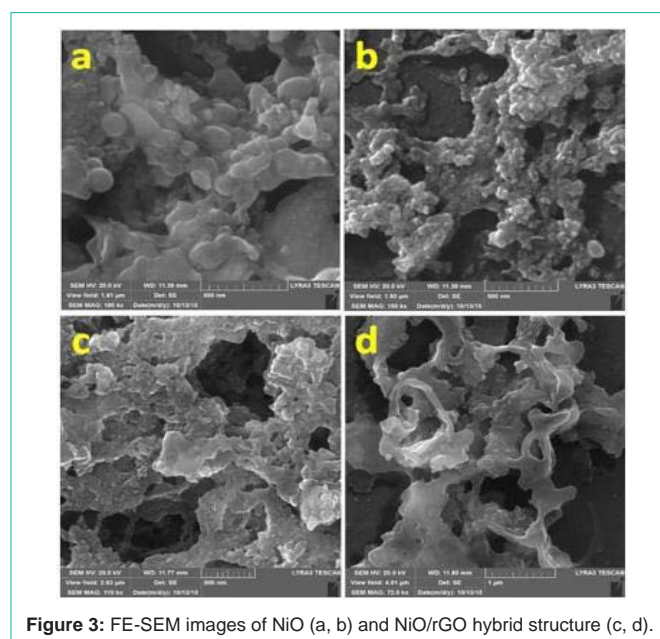


Figure 3: FE-SEM images of NiO (a, b) and NiO/rGO hybrid structure (c, d).

CO₂ reduction reaction over electrode surface. LSV curves show a cathodic peak at -1.2 V. This may be attributed to the reduction of Ni²⁺ to Ni⁰. The results confirmed the catalytic activity of NiO/rGO as an electrocatalyst and implying the role of rGO as supporting catalyst towards CO₂ER. The reduction experiment was carried out

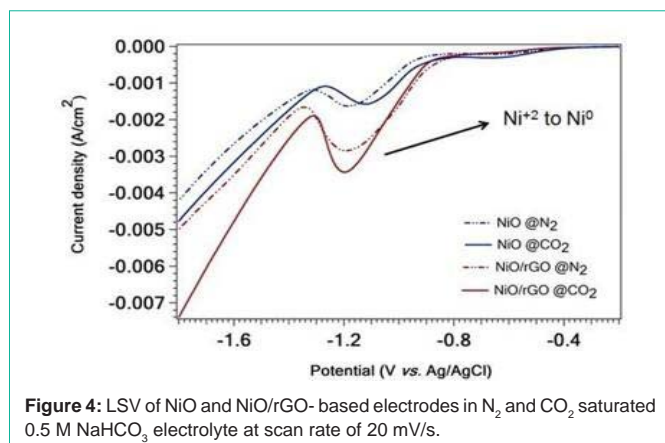


Figure 4: LSV of NiO and NiO/rGO-based electrodes in N_2 and CO_2 saturated 0.5 M $NaHCO_3$ electrolyte at scan rate of 20 mV/s.

using chronoamperometry method. After 20 min reduction process, liquid sample was withdrawn and injected into GC-MS. Actually, ethanol was found to be produced over NiO/rGO electrode surface at -0.9 V (see supplementary data Figure S1). It is well known that applied potential, material loading, electrolyte, pH, and temperature are significant key factors in CO_2 electroreduction. Although the Faradaic efficiency of ethanol formation calculated over NiO/rGO is ~16%, these results are promising indeed and future work is needed for better performance and understanding the reaction mechanism.

Conclusions

Here in, the successful synthesis of NiO nanoparticles decorated with rGO layers has been done via simple wet-chemical approach followed by annealing at $400^\circ C$ for 3h. By using very low catalyst loading, Cu-modified NiO/rGO displayed the highest cathodic current density (6.1 mA/cm^2) compared to Cu-modified NiO electrode (3.9 mA/cm^2) in CO_2 -saturated 0.5 M $NaHCO_3$ at -1.7 V vs. Ag/AgCl. This current enhancement attributed to the role of rGO contribution. LSV results indicate the initiation of CO_2 reduction reaction over NiO/rGO electrode surface. The electrocatalytic performance of NiO/rGO is mainly attributed to the porous structure and the synergistic effect of NiO and rGO.

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