One step synthesis Pd/NiO@rGO/CNTs nanocomposite for energy storage as supercapacitor application

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Abstract. In this study, graphite oxide was reduced into reduced graphene oxide nanosheets (rGO NSs) by microwave with metal acetate of nickel and palladium to form the rGO-carbon nanotubes (CNTs) containing palladium (Pd) and nickel oxide (NiO) nanocomposite (Pd/NiO@rGO/CNTs nanocomposite). The synthesized nanocomposite presents remarkable performance for supercapacitor application especially in stability, exhibiting specific capacitance of 24 F/g at scan rate of 10 mV/s and excellent capacitance retention of 95% after 500 consecutive CV cycles at scan rate of 100 mV/s.

1. Introduction

Currently, with increasing demands for renewable and clean energy sources, extensive efforts have been made to improve energy storage devices, such as supercapacitors [1, 2]. Supercapacitors have fascinated incredible attention because of their high power delivery, long cycle life stability and fast charge-discharge performance. Usually, electrochemical supercapacitors are divided into two categories on the basis of their energy storage mechanism as (i) electrical double layer capacitor (EDLC) (porous carbon materials) and (ii) pseudocapacitor (conducting polymers/ metal oxides) [3]. The recent study is focused mostly on the progress of supercapacitors with combined electrodes containing redox active materials (conducting polymers/ metal oxides) and porous carbon materials for achieving both high energy density and power density [4-6].

Graphene have received tremendous attention because of its electrochemical properties [7, 8]. The derivatives of graphene as graphene oxide are characterized by a layered structure containing various oxygen functional groups [9] and very large specific surface area. To improve the performance of graphene oxide/rGO in energy storage applications, addition of metal oxides on its surfaces is an efficient method to tailor the electrochemical properties [10-12], since adding metal oxides with rGO shows the combined effect of pseudocapacitance and electric double capacitance [13-16].

In this study, Pd@rGO/CNTs nanocomposite materials were successfully synthesized via rapid microwave-assisted reduction of graphite oxide along with metal acetate (nickel (II) acetate (C₆H₅NiO₄) and palladium (II) acetate (C₂H₃O₂Pd)) using a simple microwave system. We found that in synthesized Pd/NiO@rGO/CNTs nanocomposite, rGO NSs was covered by CNTs, palladium nanoparticle (Pd NPs)
and nickel oxide nanoparticles (NiO NPs). The nanocomposites were used in electrode materials for supercapacitor performances of nanocomposite materials.

2. Experimental details

2.1. Synthesis of microwave-assisted Pd/NiO@rGO/CNTs nanocomposite

Graphite oxide was prepared by chemical oxidation of natural graphite powder using modified Staudenmaier’s method as reported previously [11, 17, 18]. GO powder and nickel (II) acetate (C₆H₅NiO₄) and palladium (II) acetate (C₆H₅Pd) were mixed in DI water and magnetic stirrer for 45 min. Next, the mixture solution was ultra-sonicated to achieve complete mixture solution. Finally, the solution was heated at 35 °C in oven for complete evaporation of water. The dried powder was irradiated by microwave by keeping the material in quartz cup at 700 W for 170 sec for the formation of Pd/NiO@rGO/CNTs nanocomposite.

2.2. Material characterizations and electrochemical measurements

The synthesized Pd/NiO@rGO/CNTs material was characterized by X-ray diffraction (XRD) (Rigaku Ultima IV), field emission scanning electron microscopy (SEM) (Dual Beam FIB/FEG model FEI Nova 200) and Raman spectroscopy (JASCO NRS-3100). The electrochemical measurements were performed by three-electrode cell system using a Solartron SI 1286 electrochemical workstation in 0.1 M KOH solution at room temperature. In three electrode system the Pd/NiO@rGO/CNTs nanocomposite material as working electrode, platinum (Pt) wire as a counter electrode and Ag/AgCl electrode as a reference electrode were used to determine the electrochemical applications.

3. Result and discussions

Figure 1 (a-d) shows the SEM image of Pd/NiO@rGO/CNTs nanocomposite at different magnifications. The surfaces morphology of the nanocomposite clearly shows that CNTs are grown on the surfaces of rGO NSs. These CNTs are grown on rGO NSs with help of Ni NPs and then attached with Pd and NiO NPs. The formation of NiO NPs was possible due to high temperature during reduction and exfoliation of graphite oxide (including metal salts) under microwave irradiation. The length of as grown CNTs was of micron length (Figure 1d). The nearly uniform distribution of CNTs with Pd/NiO NPs on rGO NSs enhances the electrochemical performance of the material.

![Figure 1. SEM images Pd/NiO@rGO/CNTs nanocomposite.](image-url)
Figure 2a shows an XRD pattern of the as-synthesized Pd/NiO@rGO/CNTs nanocomposite. The strongest peak at 2θ = 26.3 corresponds to (002) diffraction peak for rGO/CNTs. The diffraction peaks at 2θ = 40.0, 46.5 and 68.7 correspond to (111), (200) and (220) for Pd NPs [19]. The peak position at 2θ = 44.6 reveals the signature of Ni NPs which acts as catalyst to form the CNTs. The other diffraction peaks at 2θ = 75.5 and 43.1 show that there is also formation of NiO NPs under microwave irradiation for in-situ growth of CNTs on rGO surfaces. The well-resolved diffraction peaks in Figure 2a reveal the good crystalline nature of rGO/CNTs, Pd and NiO which form the Pd/NiO@rGO/CNTs nanocomposite. Figure 2b shows the Raman spectrum of the nanocomposite with two characteristic peaks of the D and G bands at ~1365 and ~1585 cm⁻¹, respectively [20]. The peak intensity ratio of D-band to G-band (I_D/I_G) is associated with defect formation in rGO NSs. The calculated ratio of I_D/I_G was 1.0 and can be ascribed to the presence of defects in the obtained rGO and CNTs.

Figure 3a shows the CV curves of Pd/NiO@rGO/CNTs nanocomposite electrode at different scan rates (10 to 100 mV/s).

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Figure 3. (a) CV curves of Pd/NiO@rGO/CNTs nanocomposite electrode at various scan rates, (b) dependence of specific capacitance of Pd/NiO@rGO/CNTs nanocomposite electrode at various scan rates. (c) Cycling stability of Pd/NiO@rGO/CNTs nanocomposite electrodes using consecutive CV cycles (Inset: CV test for 500 cycles at 100 mV/s).
By increasing the scan rate, current increases and the oxidation peak shifts to a more positive position, whereas the reduction peak shifts to a more negative position (Figure 3a). The shifts may be caused by the expected increase in internal diffusion resistance within the pseudocapacitive substance with increasing scan rate. The calculated specific capacitance \((C_s)\) values obtained from the CV curve are shown in Figure 3b varying from 24.23 to 15.10 F/g at scan rates of 10 to 100 mV/s, respectively. Cycle stability Pd/NiO@rGO/CNTs nanocomposite electrode was tested via continuous CV cycling as shown in Figure 3c. Very symmetric and repetitive curves were observed except initial few cycles. The specific capacitance slightly decreases (~5%) in the initial 10 cycles due to the activation process [21, 22]. After over 10 cycles, the ~95% capacitance retention of Pd/NiO@rGO/CNTs nanocomposite electrode was still retained, indicating its excellent stability.

4. Conclusions

The applied rapid microwave-assisted synthesis method for Pd/NiO@rGO/CNTs nanocomposite is simple and facile, allowing for large scale synthesis in few tens of seconds. The small size Pd/NiO NPs were found to be nearly uniformly distributed of the rGO NSs with CNTs. The electrode of Pd/NiO@rGO/CNTs nanocomposite exhibits specific capacitance of 24 F/g and excellent stability over a consecutive CV testing with capacitance retention of ~95% over 500 cycles. With an optimized growth of CNTs and Pd/NiO NPs on the surfaces of rGO NSs, the as-synthesized Pd/NiO@rGO/CNTs nanocomposite exhibited excellent performance and long-term cycling stability.

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