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Solvothermal Synthesis of Ni/Reduced Graphene Oxide Composites as Electrode Material for Supercapacitors

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ABSTRACT

A series of Ni/reduced graphene oxide (Ni/RGO) composites were synthesized through a simple solvothermal method. Detailed characterizations of the composite using transmission electron microscopy and field emission scanning electron microscopy indicated that Ni particles were uniformly dispersed on the RGO surfaces. The electrochemical performances of Ni/RGO composites were much higher than their counterparts of Ni and RGO, because of the Ni particles being firmly decorated with the RGO nanosheets and the synergistic effect between both components. Among the prepared composites, Ni/RGO–2 exhibits the best electrochemical performance; namely, a high specific capacitance of 547.3 F g^{-1} is obtained in 2 M KOH at 1 A g^{-1} and 81% of initial value is remained after a continuous cycling of 1000 times, which make it to be a promising electrode material for supercapacitors.

1. Introduction

Supercapacitors are widely used in consumer electronics, memory back–up systems, industrial power and energy management, and it is likely to show an equal importance to batteries for future energy storage systems [1,2]. Generally, the design and synthesis of electrode materials with high performance are key challenges for supercapacitors. Carbon–based materials are one of typical electrode materials used in supercapacitors and have been widely studied owing to their low cost, eco–friendliness, high stability and safety. Among numerous carbon materials, graphene has attracted extensive attention due to its special structure and unique electrical performance. It is demonstrated that graphene nanosheets possess high conductivity [3] and ultrahigh specific surface area [4], as well as excellent mechanical properties [5], which make it to be a promising electrode material for supercapacitors [6–8]. However, graphene nanosheets usually suffered from inevitable aggregation or restacking, and accordingly reduced its electrochemical properties. An effective solution is to load the redox–active electrode materials between the graphene nanosheets to keep them separated, and thus fully exploiting the advantages of pseudocapacitance and graphene–based electrical double–layer capacitance [9].

Up to now, various kinds of pseudocapacitive materials, including metal hydroxides [10,11], metal oxides [12–15], metal sulphides [16], and conductive polymers [17–19], have been widely investigated for supercapacitors. Among these pseudocapacitive materials, nickel oxide (NiO) material is of particular interest due to its features of high theoretical specific capacitance, low cost, environment friendly nature and good reversibility [20]. However, NiO usually suffers from low conductivity and poor stability, which seriously impedes its practical applications. Thus, it is necessary to seek other novel Ni–based electrode materials for supercapacitors.

Recently, some reports have demonstrated that Ni electrode with high conductivity has shown high electrochemical properties for supercapacitors. For examples, Ganesh *et al.* reported the template electrodeposition of Ni at room temperature from a nickel sulphamate bath, and the capacitance of Ni electrode was measured to be 50 F g^{-1} [21]. Xing *et al.* fabricated Ni nanoparticles by hydrazine hydrate ($N_2H_4{\cdot}H_2O$) reduction and its specific capacitance could reach up to 416.6 F g^{-1}, suggesting the possible application of Ni as high performance electrode materials for supercapacitors [22]. Furthermore, Lu *et al.* developed Ni–microfiber–supported carbon nanotube (CNT) aerogels through a catalytic chemical vapour deposition method, and a high specific capacitance of 359 F g^{-1} was achieved [23]. On the basis of these results, it is believed that Ni particles can be a promising pseudocapacitive material for supercapacitors. Although these achievements have been made, a number of challenges still need to be addressed, such as the complexity of synthesis method, expensive equipment,

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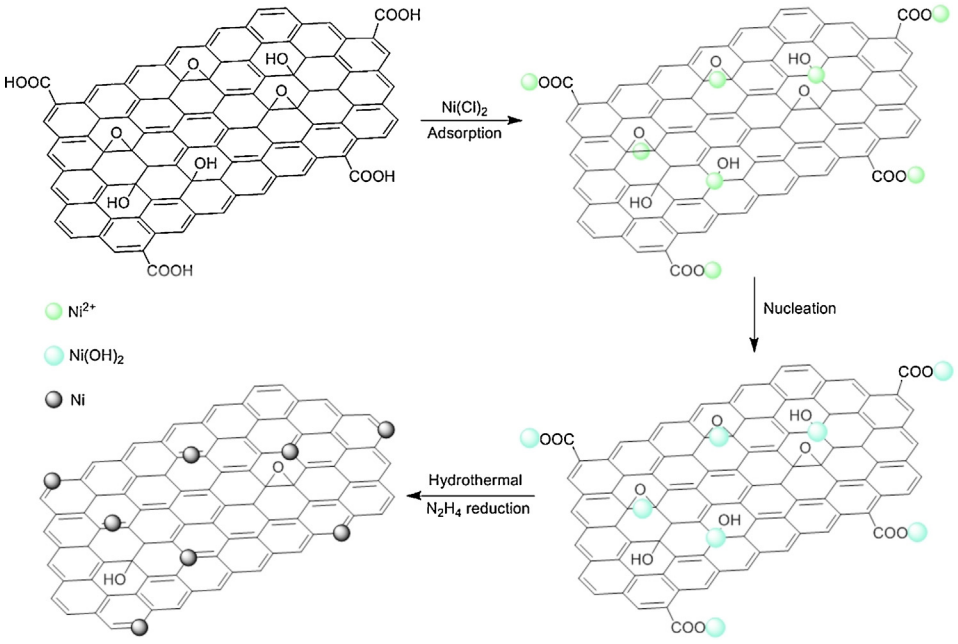

Fig. 1. Schematic illustration for the synthesis of Ni/RGO composites.

difficult to fabricate bulk–materials, poor connection between carbon substrate and the active materials, etc.

Based on the above statements, Ni/reduced graphene oxide (Ni/RGO) composites prepared by a facile method are expected to be a very promising electrode material for supercapacitors. Since metallic Ni nanoparticles serve as a spacer, it will greatly reduce the aggregation of RGO nanosheets. On the other hand, the existence of RGO will increase the conductivity and cycling stability of the composite electrode. At present, Ni/RGO composites have presented great potentials in the applications of heterogeneous catalysts [24], spintronics [25], direct ethanol fuel cells [26], Li–ion rechargeable batteries [27], etc. However, to the best of our knowledge, no literature is related to the application of Ni/RGO composites as electrode material for supercapacitors until now. Therefore, in the present work, we employed $NiCl_2$ and negatively charged GO nanosheets as the starting materials, where GO was decorated with Ni^{2+} driven by electrostatic interactions. Subsequent solvothermal treatment and in situ reduction resulted in the formation of the Ni/RGO composites. In these Ni/RGO composites, Ni can be converted into Ni(II) by electrochemical oxidation [28,29], which possess multiple oxidation states and enable rich redox reactions for pseudocapacitance generation. As a consequence, the as–prepared Ni/RGO composites show high specific capacitance and good rate capability, which make it a promising candidate as electrode material for supercapacitors.

2. Experimental

2.1. Synthesis of Ni/RGO composites

Graphite powder (<20 μm, synthetic) was purchased from Sigma–Aldrich. GO was synthesized from graphite powder using a modified Hummers method [30,31]. After being purified by dialysis, the GO was diluted to a 6 mg mL^{-1} colloidal suspension with ultrapure water (>18 MΩ cm) for the following experiment. Ni/RGO composites were synthesized according to a simple solvothermal method [32]. Typically, 2.0 mL GO suspension was dispersed in 30 mL ethylene glycol by sonication for 1 h, then 0.12 g $NiCl_2{\cdot}6H_2O$ was added to the above solution and followed by stirring at room temperature for 10 min. Afterwards, 2.0 mL $N_2H_4{\cdot}H_2O$ and 0.2 g NaOH were added to the mixture with vigorous stirring. Finally, the above suspension was transferred and sealed into a 50 mL autoclave, and subjected to the solvothermal treatment at 100 °C for 12 h. After cooling to room temperature naturally, the resultant black precipitate was separated by vacuum filtration, washed with large amounts of ethanol and water. A series of Ni/RGO composites with different amount of GO used in the first step were obtained after being freeze–dried overnight and denoted as Ni/RGO–x (x = 1.0, 2.0, 4.0 and 8.0 mL, respectively). For comparison, RGO and Ni particles were also respectively synthesized through the same method without adding Ni salt or GO. Oxidation of Ni was carried out by annealing the Ni/RGO–2 in air at 350 °C for 5 h, and denoted as NiO/RGO–2.

2.2. Material characterizations

X–ray diffraction patterns (XRD, Rigaku D/MAX 2400 diffractometer) were recorded using Cu–Kα radiation (λ=1.5406 Å) operating at 40 kV and 60 mA. Raman spectra were performed with a micro–Raman system (Renishaw, In Via) with 633 nm line of Ar ion laser as an excitation source. Thermogravimetric and differential thermal analysis (TG–DTA, STA 449 C TG–DSC thermal analyzer) were carried out from room temperature to 800 °C with a heating rate of 10 °C min^{-1} in air. The morphology and microstructure of the samples were characterized by field emission scanning electron microscopy (FESEM, JSM–6701F, JEOL) and transmission electron microscopy (TEM, FEI Tecnai G2 F30). The atomic concentrations of carbon, oxygen, and nickel were determined by X–ray photoelectron spectrometer (XPS, PHI–5702, Physical Electronics, USA) using monochromated Al–Kα radiation under a pressure of 3×10^{-8} Torr.

2.3. Electrochemical measurements

The electrochemical measurements were carried out on an electrochemical working station (CHI660 C, Shanghai, China) in a half–cell setup configuration at room temperature with 2 M KOH