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Microwave-assisted in situ synthesis of cobalt nanoparticles decorated on reduced graphene oxide as promising electrodes for supercapacitors

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ABSTRACT

A series of cobalt nanoparticles/reduced graphene oxide (Co/RGO) composites have been successfully synthesized via a facile microwave-assisted synthetic route for the first time. The synthesized composites are comprised of Co particles that are uniformly anchored onto the surface of graphene sheets by in situ reducing. Powder X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR), Raman spectroscopy, Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), and Brunauer-Emmett-Teller (BET) analysis are performed for systematically characterizing the microstructure and composition of the as-prepared Co/RGO composites. Interestingly, the as-prepared composites show superior electrochemical performance to their counterparts of Co and RGO as electrodes for supercapacitors. As a result, Co/RGO-15 composite exhibits a high specific capacitance of 370.7 F g^{-1} at 5 mV s^{-1} in 2 M KOH aqueous solution as well as good rate capability. The excellent electrochemical performances are due to the 3D graphene conductive network and the synergetic effect of RGO and Co particles. Meanwhile, the capacitance retention keeps about 92.3% of the initial value after 2000 cycles at a current density of 2 A g^{-1}, suggesting that such hybrid electrode possesses a great potential application in energy-storage devices.

Introduction

For the past few years, considerable research efforts have been focused on alternative energy conversion and storage systems with high efficiency, low cost and environmental benignity [1–3], such as fuel cells, lithium ion battery and supercapacitors. Among all these candidates, supercapacitors (SCs), also known as electrochemical capacitors (ECs), have received a considerable amount of attention due to their attractive merits, such as higher power density, faster charge/discharge process, and longer cycle life compared with secondary batteries [4–6], which can be applied in the field of electric vehicles, electronic devices, and other power supply facilities. It is generally recognized that the performance of SCs strongly depends on the selection of electrode materials. Basically, there are two main categories of supercapacitors according to the energy storage mechanism: (i) electrical double-layer capacitors (EDLCs) and (ii) Faradaic pseudocapacitors [7,8]. Up to now, regarded as typical EDLCs, carbon-

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based materials are extensively investigated as electrodes owing to their attractive properties such as high surface area, lightweight, high electrical conductivity, low manufacturing cost and compatibility with other electrode materials [9,10]. Additionally, transition metal oxides such as RuO_2, NiO, MnO_2, SnO_2 and CoO with pseudocapacitive behavior can be used as promising electrode materials in pseudocapacitors [11–17]. Currently, EDLCs exhibit high power density, but suffer from low energy density; while pseudocapacitors possess a higher specific capacitance of 10–100 times than that of EDLCs, but also similarly encounter unstable cycle performance [7,18]. To solve these issues, efforts have been made to seek for excellent performance electrode materials. Though a great deal of progress has been made about the development of both two types of supercapacitors in recent years, the energy stored in supercapacitors is an order of magnitude lower than that of batteries, which greatly limits their applications that require high energy density and better overall performance. An efficient way for high energy density is to increase the capacitance and/or enlarge the operation voltage, because the energy density in a supercapacitor can be calculated using the formula of $E = 0.5CV^2$, where E is the energy density, C is the specific capacitance, and V is the cell voltage, respectively [19,20]. Therefore, the design and synthesis of new electrode materials with improved electrochemical and physical properties are the important factors in leading to high energy density for supercapacitors. In particular, considering their high power density and long cycling life, the efficient hybrid of EDLCs and pseudocapacitors can generate synergistic effect, subsequently improving the electrochemical performance [3].

As a rapidly rising star, graphene is newly found and has been the hot spot in energy storage fields owing to its unique features, such as extremely electrical conductivity, ultrahigh surface area, and strong mechanical stability [21]. These excellent merits make such novel material the most promising electrode material for EDLCs among carbon-based materials, such as carbon nanotubes [22], mesoporous carbon [23], carbon cloth [24], and active carbon [25]. An interest in the preparation of graphene based materials decorated with metal oxide and hydroxide has gradually arisen. Some reports, such as $Co(OH)_2$/graphene, MnO_2/graphene, Co_3O_4/graphene, $Ni(OH)_2$/graphene and NiO/graphene have shown that the addition of graphene can greatly help to improve the electrochemical performance of metal oxides and hydroxides [26–30]. Among these pseudocapacitive materials, Co-based materials are considered to be the most promising materials due to the features of high theoretical specific capacitance, low cost, low toxicity, and relatively small environmental impact [31,32]. However, Co-based materials usually suffer from poor cycling performance and low conductivity, which seriously impede their practical applications. Thus, it is necessary to hunt other novel Co-based electrode materials for supercapacitors.

Recently, some reports have demonstrated that Co electrode has outstanding electrochemical and catalytic characteristics. For example, Co/Carbon nanotubes (CNTs) (obtained by ball-milled), Co@C (synthesized by hydrothermal way) and Pt–Co/Graphene (prepared via electro-deposition) have endowed the composite materials with better electrochemical and electrocatalytic performance [33–35]. On the basis of these results, it is believed that Co particles can be a promising pseudocapacitive material for supercapacitors. Although these achievements have been obtained, a large number of challenges still need to be overcome, such as expensive equipment, complex synthesis method, difficult to scale up and time-consuming. More recently, microwave synthesis has been regarded as an indispensable technique for preparing nanomaterials [36]. Nevertheless, to the best of our knowledge, little literature is related to the application of Co/reduced graphene oxide (Co/RGO) composites as candidate electrode material for SCs, especially employing microwave technique for the synthesis of Co/RGO composites.

Based on the above results, an efficient microwave heating is proposed to synthesis highly-crystalline Co particles decorated on RGO in order to form Co/RGO composites as electrode materials for SCs. In these Co/RGO composites, Co can be converted into Co^{2+} by electrochemical oxidation [37–40], which possesses multiple oxidation states and enable rich Faradaic redox reactions for pseudocapacitance generation. When evaluated as an electrode material, the as-prepared Co/RGO composites show high specific capacitance, good rate capability and cycling stability. It is believed that the as-prepared Co/RGO composites could serve as a promising candidate for supercapacitor materials.

Experimental

Preparation of Co/RGO composites

All reagents used in our experiments were of analytical grade and were used directly without further purification. The Co/RGO composites were synthesized by a microwave method with different feeding ratios of graphite oxide (GO) and $CoCl_2 \cdot 6H_2O$. GO was obtained by the modified Hummers method as described anywhere [41]. The different feeding ratios were tuned by changing the amount of GO and keeping the constant amount of $CoCl_2 \cdot 6H_2O$. The product was named as Co/RGO-x, where x is the amount of GO. For example, the composite Co/RGO-15 was typically prepared as follows: 15 mL GO (2 mg mL^{-1}) suspension was dispersed in 10 mL ethylene glycol under ultrasonication for 1 h. 5 mL (2 mmol) solution of $CoCl_2 \cdot 6H_2O$ was added into the GO dispersion under magnetic stirring. After stirring for about 30 min, 3 mL $N_2H_4 \cdot H_2O$ (50%) was added to the mixture with vigorous stirring, followed by adding 0.3 g NaOH. Subsequently, the above suspension was placed in the center of a household microwave oven (750 W) and irradiated for 3 min, and then cooled to room temperature naturally. The product was collected by filtration, washed several times with deionized water and absolute ethanol respectively, and dried in a vacuum at 60 °C for 12 h. For comparison, RGO and Co particles were prepared by using the same microwave method without the adding of Co salt or GO.

Characterization of sample

Powder X-ray diffraction (XRD) analyses were carried out on D/max-γB diffractometer using Cu Kα radiation at a scanning