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Extended abstract

EXTENDED ABSTRACT

Supercapacitors based on graphene/pseudocapacitive materials•

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Abstract: Composites of graphene and SnO_2 were successfully prepared by a single step simultaneous synthesis of SnO_2 and reduction of graphene oxide (GO). Three different compositions of precursor solution resulted in different composite materials containing graphene and SnO_2. The reaction was realized by microwave-assisted hydrothermal synthesis. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) gave insight into the morphology and composition of the obtained materials. Good capacitive/ /pseudocapacitive properties of the obtained material suitable for supercapacitor application were registered by cyclic voltammetry, from where specific capacitance values up to 93 F g^{-1} were determined.

Keywords: graphene oxide, graphene, SnO_2, supercapacitor, morphology, cyclic voltammetry.

Materials having pseudocapacitive redox reactions are promising candidates for applications demanding high energy/high power. Their specific capacitance value, C_s, goes up to 750 F g^{-1}, while for double layer charging/discharging, it goes up to 150 F g^{-1}. The most important metal oxides with pseudocapacitive redox reactions are RuO_2, MnO_2, IrO_2, MoO_2, V_2O_5 and SnO_2.[1–3] In order to improve their properties and increase their specific capacitance, a great deal of research effort has been directed at the optimization of electron and ion conductivities.[1] This can be accomplished by application of 2D graphene sheets structures as supports for pseudocapacitive materials. Due to its properties, such as

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high electrical conductivity, high surface area and flexibility, graphene fulfils the basic requirements for improving the properties of pseudocapacitive materials.[4]

SnO_2 has unique electrical and optical properties that enable its application in catalysis, gas sensors, solar cells and transparent electrode materials. Among the various metal oxides, tin-based materials have attracted considerable attention as an electrode material for energy storage due to its low cost, abundance and environmental aspects.[5–9] It has been used as the anode material for Li secondary batteries,[5,6] whereby its pseudocapacitive properties were studied.[7,8]

In this work, a simple simultaneous synthesis of SnO_2 and reduction of graphene oxide (GO) was realised using microwave-assisted hydrothermal synthesis. This method was selected due to its effects, such as rapid volumetric heating, increased reaction rates and shortened reaction time. Hydrothermal synthesis and microwave assisted hydrothermal synthesis are useful for accelerating the de-protonation reaction of $Sn(H_2O)_x(OH^-)_y{}^{(4-y)+}$ to $SnO_2 \cdot nH_2O$ offering good control of both particle size and particle size distribution.[10] A hydrothermal reaction was mostly used for the preparation graphene/SnO_2 composite materials,[5,6,11,12] while Lim *et al.*[11] successfully prepared a graphene/SnO_2 composite in a microwave process. Lim *et al.* also suggested electrostatic interaction between the negatively charged GO functional groups and Sn^{2+}, thereby providing nucleation centres for growth of SnO_2 nanoparticles on the graphene sheets.

In this work, three different approaches for the synthesis of the composite materials were studied. Good interaction of Sn^{2+} and GO molecule could be achieved by retarding the hydrolysis rate of Sn^{2+} and for this reason, $SnCl_2$ dissolved in HCl solution or an ethanol/water mixture was used during the synthesis. In the first procedure, $SnCl_2$ was dissolved directly in a GO solution (1.85 g dm^{-3}) containing water and ethanol, to obtain a 15 or 25 mmol dm^{-3} solution of Sn^{2+}. The mixture was heated in a microwave assisted hydrothermal reactor at temperatures ranging from 60–70 °C for 5 min (composite **1**). In the second procedure, the same amount of $SnCl_2$ was dissolved in ethanol and subsequently mixed with a GO water solution and heated to the same temperatures as in the first approach (composite **2**). In the third procedure, $SnCl_2$ was dissolved in 25 % HCl (5 mL) with addition of ethanol (4 mL) to obtain 0.24 mol dm^{-3} solution[12] and subsequently, it was mixed with the GO water solution and heated to the same temperatures as previously reported (composite **3**). The GO used in this work was obtained by the Hummers method.[13] In all experiments after the heat treatment, the brown colour of GO had become black, indicating successful reduction of GO. The temperature used in this work was limited to 60–70 °C due to the large pressure increase that was obtained during the heating process. Usually, higher temperatures were used for both graphene reduction[14] and SnO_2 synthesis, approaching 90 °C for graphene oxide reduction and approaching 160–180 °C for SnO_2 synthesis.[5,6,11,12] It is believed that the pressure increase is the result of the GO reduction process during which oxygen functionalities are removed and CO_2 released.

After the reduction process, the obtained solid product suspended in the reaction mixture was washed intensively with water and finally it was left with an appropriate amount of water in order to obtain a paste or a suspension. In addition, some of it was dried in order to perform characterisation by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) (Fig. 1). The typical microstructure of the graphene and graphene oxide surface shows wrinkled sheets interconnecting with each other in a continuous structure.[15] The SEM images of the composite materials revealed that the obtained morphology was different from those of graphene or graphene oxide and from the EDX analysis it was evident that the resulting composite materials contained tin and carbon. Therefore, it could be concluded that the hydrothermal synthesis of graphene/SnO_2 was successfully performed. The most significant impact of SnO_2 on the GO microstructure was registered for **2**, where the microstructural characteristic of GO had almost disappeared. It is also evident from EDX analysis that **2** contained the highest amount of SnO_2. On the other hand, **1** showed the presence of SnO_2 but a GO-like microstructure was also evident. Since the amount of SnO_2 was similar to that in **2**, this indicates that the layer was less homogenous with respect to that of **2**. In the case of **3**, Cl was included within the structure of the material, GO microstructural properties were present and the lowest amount of SnO_2 was obtained. From the reported results, it follows that SnO_2 particles *in situ* decorated the surface of the graphene nanosheets. However, it is important to stress that the composites had different microstructures and contained different amounts of SnO_2 (Fig. 1).

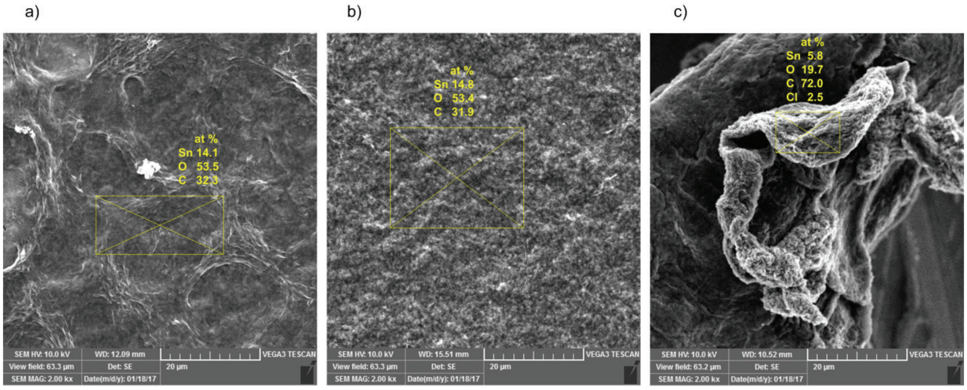

Fig. 1. SEM–EDX analysis of composites **1**(a), **2** (b) and **3**(c).

The pseudocapacitive properties of the obtained SnO_2/graphene composite materials were examined in a three-electrode cell. The working electrode was prepared by applying a water suspension or paste of the composite material on a carbon support (aluminium coated with carbon, Gelon Lib Group, China, A = = 0.48 cm^2). The amount of active material varied from 0.03–0.30 mg. The counter electrode was a Pt-foil and the reference electrode was a saturated calomel electrode. Cyclic voltammetry was performed using a potentiostat/galvanostat Princeton Applied Research 236A in the potential range from –0.8 to 0.8 V at a scan rate of 50 mV s^{-1}. High currents and high reversibility were achieved over a wide potential range during electrode polarisation in 0.5 mol dm^{-3} Na_2SO_4 solution (Fig 2a). It is well known that during polarisation graphene shows a constant current over a wide potential range,[14] while SnO_2 shows non-ideal pseudocapacitive behaviour with continuously increasing current at potentials more negative than 0 V. In this potential range, the Sn^{4+} to Sn^{2+} transition occurs (Fig 2b).

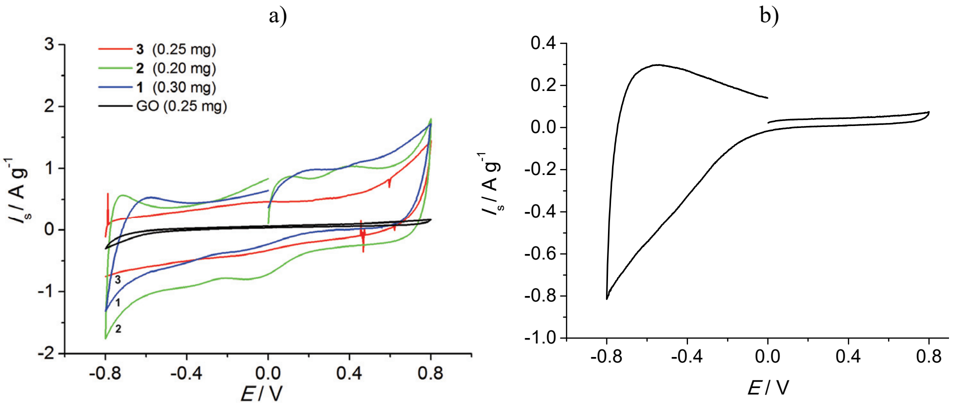

Fig. 2. Cyclic voltammograms of: a) GO and different composite materials and b) SnO_2 deposited at a glassy carbon support.

For the composite materials investigated in this work, almost constant currents, originating from charging/discharging of the graphene layer, were registered within the potential window of investigation. The good capacitive response is evidence that the GO was reduced to the more conductive graphene form. Moreover, in the potential range from –0.4 to –0.8 V, a current response characteristic for SnO_2 is also evident, indicating that SnO_2 contributes to the overall capacitive/pseudocapacitive response. The continuous increase in the cathodic current and the anodic current peak representing the SnO_2 redox reaction did not develop the same for each layer. They were the most prominent in the case of **2** and the least prominent in the case of **3**. These observations are in accordance with SEM results that revealed almost complete coverage of graphene with SnO_2 for **2** and a GO-like microstructure for **1** and **3**.

It is possible to determine the C_s values of the obtained layers by integration of the cyclic voltammogram curves (Fig. 2) and such calculations were reported previously.[15] It was found that the C_s values of the prepared composites depend significantly on the amount of material deposited on the carbon support. Thus, in the case when 0.25 or 0.03 mg of **2** was applied to the carbon support, C_s values of 26 and 91 F g^{-1} were obtained, respectively. In the case of **3** for 0.25 or 0.03 mg, the C_s values were 14 and 93 F g^{-1}, respectively. These observations are a consequence of the better utilization of the composite material in the case of thinner layers. Furthermore, it was found out that electrodes containing from 0.10 to 0.30 mg of active material showed specific capacitance values, in F g^{-1}, ranging from 5–17, 4–26 and 3–14 for **1**, **2** and **3**, respectively. The obtained results indicated that the capacitive properties depended on the method of preparations and the highest C_s values were registered for **2**, when the $SnCl_2$ was dissolved in absolute ethanol and afterwards mixed with the GO solution. The lowest C_s value was registered for **3**. Evidently, although the acid environment used during the synthesis of **3** retarded the hydrolysis process and although the reduction was realised at increased Sn^{2+} concentration, these experimental conditions did not improve the degree of GO reduction and, consequently, in this case lower C_s values were registered. Such behaviour could be explained by the fact that GO is more easily reduced at increased pH values.[16] The amount of SnO_2 was also lower, compared to the amount in the other composites, which additionally influenced the C_s value.

From the results obtained in this work, it can be concluded that composite **2** exhibited the best capacitive properties with a C_s value up to 91 F g^{-1}, which is comparable or even higher compared to the values obtained previously for graphene or SnO_2.[2,6,17] It is obvious that the synergistic effect of these two constituents resulted in enhanced capacitive properties suitable for supercapacitor application.

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ИЗВОД

СУПЕРКОНДЕНЗАТОРИ ЗАСНОВАНИ НА ГРАФЕН/ПСЕУДОКАПАЦИТИВНИМ МАТЕРИЈАЛИМА

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Коришћењем микроталасног реактора у поступку хидротермалне синтезе успешно су припремљени композити графена и SnO_2. Током реакције извршена је симултана синтеза SnO_2 и редукција графен-оксида. Три различита састава раствора прекурсора резултирала су ситнтезом три различита композитна материјала гафена и SnO_2. Скенирајућа електронска микроскопија (SEM) и спектроскопија дифракције X-зрака (EDX) омогућили су увид у морфологију и састав добијених композитних материјала. Добра капацитивна/псеудокапацитивна својства композита, погодна за примену у суперкондензаторима, регистрована су цикличном волтаметијом. Вредности специфичне капацитивности испитаних материјала износиле су до 93 F g^{-1} .

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