Electrochemical properties of SnO_2/rGO nanocomposites

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Abstract

SnO_2 nanoparticles were deposited on reduced graphene oxide (rGO) to obtain SnO_2/rGO composites with high energy storage capacitance. For this purpose, graphite oxide (GtO) was synthesized and hydrothermally treated in presence of Sn precursor. The quantity of GtO was varied to tune the heterostructures' composition and the particles size of the SnO_2.

The XRD and SEM analyses revealed that the GtO was exfoliated, reduced and decorated with SnO_2 nano-particles during the hydrothermal treatment. With the increase of GtO quantity the SnO_2 particle size decreased from ~30 nm to ~14 nm. The Cyclic Voltammetry analysis showed that the pure rGO exhibited typical supercapacitor behavior. All the SnO_2/rGO composites exhibited significantly increased specific capacitance in comparison to the pure SnO_2. The SnO_2/rGO with the highest GtO content showed capacitance ~ 200 $F.g^{-1}$ that was comparable to that of the pure rGO. The result was related to the small particles size of SnO_2 and their distribution between the rGO sheets.

Keywords: graphene, SnO_2, composites, supercapacitor

1. Introduction

Efficient energy storage in the form of batteries and supercapacitors is believed to solve urgent environmental issues. The n-type semiconductor SnO_2 is traditionally used as electrode material for Li^+ batteries (Zhao 2019). Also, the decoration of graphene oxide with small amounts of various metal oxides like RuO_2, NiO, MnO etc. has been reported to improve its specific capacitance due to the high conductivity, specific surface area and stability against restacking (Liu 2012).

In this study, the SnO_2 was coupled with rGO via one-step hydrothermal route aiming at increased capacitance of SnO_2 and the rGO.

2. Experimental

GtO was prepared by oxidation of natural graphite via Hummers method. Water suspensions (35 mL) with 3, 12 and 120 mg/mL GtO were sonicated for 5 min. Then, 3.6 mmol $SnCl_4.H_2O$ and adequate quantity for 1M NaOH were added under stirring. The suspensions was transferred to an autoclave and treated for 16 h at 200 °C. The collected powders were washed and dried in air. The prepared pure SnO_2, rGO and composite materials nominated as xGS, where x=4, 12 and 120, were characterized using XRD and SEM analyses. TG measurements were carried out in O_2 atmosphere. Cyclic Voltammetry (CV) and Impedance measurements were performed in 0.5M KCl employing three-electrode cell with glassy carbon, Pt and Ag/AgCl as working, counting and reference electrodes, respectively.

3. Results and Discussion

The XRD diagrams (Figure 1) revealed the successful synthesis of SnO_2 as well as reduction of GtO to rGO. The intensity of the SnO_2 diffraction peaks decreased with increase of the GO content and for the 120G/S composite SnO_2 was not detected.

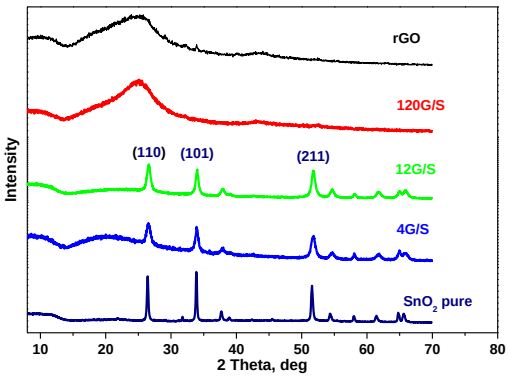

Figure 1. XRD patterns of the synthesized materials

The size of its crystallites calculated using Scherrer's equation decreased from ~35 nm to ~14 nm (Table 1).The mass fraction of SnO_2 decreased gradually as well. The presence of small amount of SnO_2 in sample 120G/S not detected by XRD, was revealed by the TG analysis.

Table 1. SnO_2 crystallite size (CS) and mass fraction (MF) and the specific capacitance values calculated from CV (C_{CV}) and Impedance (C_Z) data

Sample	SnO_2	4G/S	12G/S	120G/S	rGO
CS, nm	34.7	16.1	13.5	-	-
NF, %	100	83.67	66.86	4.94	-
C_{CV}, $F.g^{-1}$	1.5	12.6	162.2	185.9	166.5
C_Z, $F.g^{-1}$	0.31	7.5	170.8	217.9	147.4

The SEM images of the pure and composite SnO_2/rGO materials (Figure 2) revealed typical SnO_2 crystals and detached rGO layers. The morphology of the composites decreasing is in accordance with the XRD results with quantity and particle size of the SnO_2 component. For the 120G/S composite SnO_2 particles were not observed.

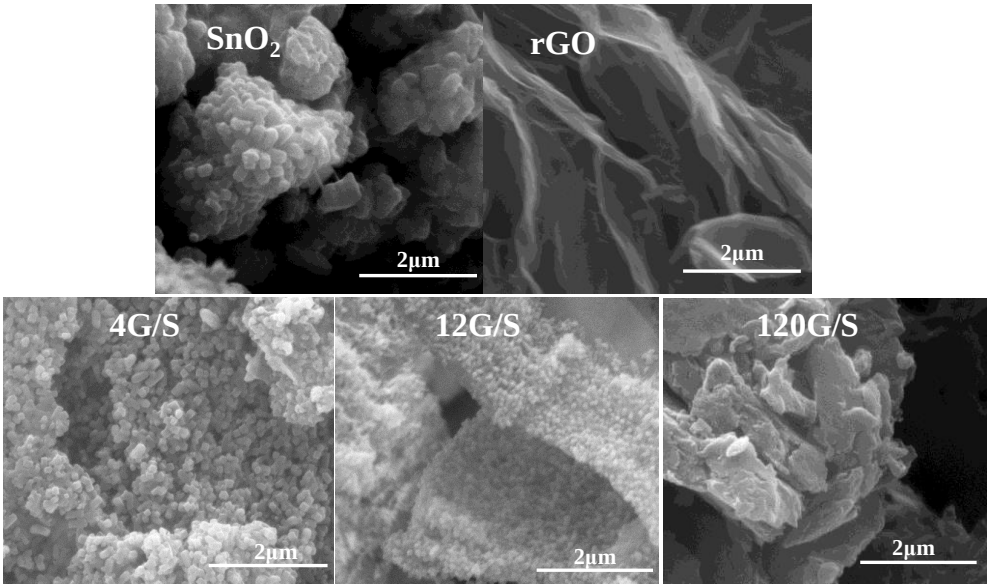

Figure 2. SEM images of the pure SnO_2 and rGO as well as the composites with different SnO_2/rGO ratios

The electrochemical analysis showed that the capacitance of SnO_2 significantly increased after coupling with rGO. The specific capacitance was calculated on the base of the CV and Impedance (Figure 3) measurements.

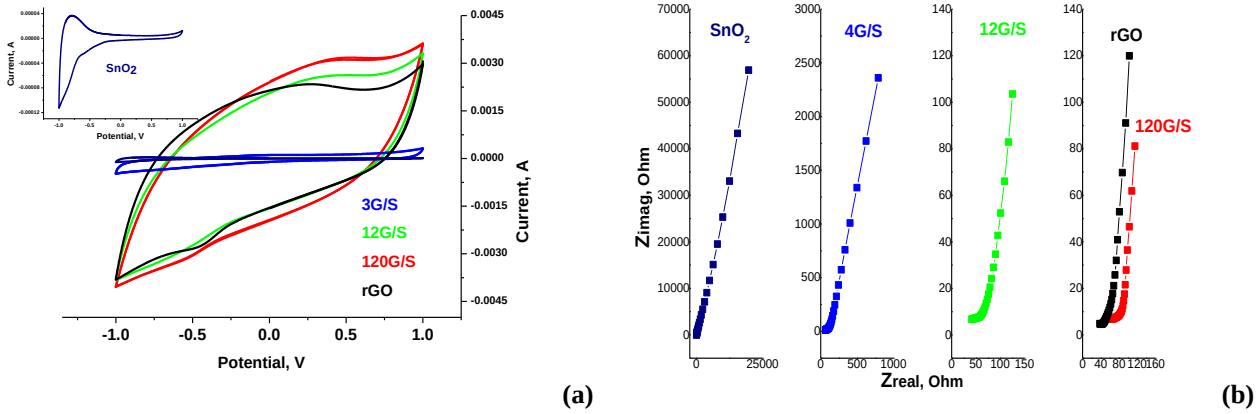

Figure 3. CV curves measured at scan rate 0.1 $V.s^{-1}$ (a) and Nyquist plots in frequency range 0.1 Hz – 100 kHz (b)

Best results were obtained for the composite with the highest rGO content. The C_{CV} and C_Z capacitance values of the 120G/SnO_2 were comparable and slightly higher than those of the pure rGO.

4. Conclusions

SnO_2, rGO and their composites were prepared by simultaneous synthesis of SnO_2 and GtO reduction via one-step hydrothermal process. The increase of the GtO amount led not only to decrease of the of the SnO_2 mass fraction in the composites from ~84 to ~5%, but also to decrease of the crystallite size from ~35 to ~14 nm. The electrochemical analysis revealed that the capacitance of the SnO_2 was significantly increased when coupled with reduced graphene oxide. The composite with the highest rGO content exhibited specific capacitance ~ 200 $F.g^{-1}$ comparable with the capacitance of the pure rGO. The outcome was related to the small particle size of the SnO_2 and its distribution on the rGO sheets.

References

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