Electrochemical and Textural Characterization of RuO_2-SnO_2-Graphene under Co-precipitation / Hydrothermal Conditions

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ABSTRACT

RuO_2-SnO_2-graphene (RSG) nanocomposites were synthesized under co-precipitation/hydrothermal conditions. During the co-precipitation, RuO_2 and SnO_2 nanoparticles were anchored to partially reduced graphene oxide, which acted as a dispersant for achieving more electrochemical active sites. The morphology and structure change were characterized through scanning electron microscopy, transmission electron microscopy and X-ray diffraction. The electrochemical performance was evaluated through chronopotentiometry, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results showed that the corporation of SnO_2 and partially reduced graphene oxide to RuO_2 significantly influenced the morphology and crystalline process, and thus enhanced the comprehensive electrochemical performance. Samples with hydrothermal treatment exhibited higher crystallinity and specific capacitance of 154 F/g ~ 200F/g at 1 A/g. Samples without hydrothermal treatment showed relative higher specific capacitance of 250 F/g ~ 436 F/g at 1 A/g.

Keywords: graphene, supercapacitor, precipitation

1. INTRODUCTION

Supercapacitors with superior power density, reversibility, stability and long cycle life have attracted worldwide attention as power supply for commercial electronic devices and as a supplementary component of batteries or fuel cells for hybrid electric vehicle use[1].

RuO_2 is a kind of best known electrode materials with remarkable pseudocapacitance, while its commercialization is limited by high cost and ineffective utilization. Thus, other components were added to reduce the cost and effectively disperse RuO_2 particles[2, 3]. Graphene, as the newly emerging material, has a vast application in various area, such as electronics and energy storage and conversion system[4]. Moreover, graphene derivatives with unique 2D structure and huge surface area can serve as an excellent electrode in supercapacitors storing energy mainly by electrochemical double layer capacitance. To reduce the cost and intrigue synergistic effects, another component of SnO_2 was also introduced by adding $SnCl_2$ solution, which would in-situ reduce graphene oxides that helps to form a conducting network for charge storage. Thus, the aim of integrating electrochemical active components and graphene is to better utilize the advantages of each component and explore broader applications of graphene-based composites.

In this report, ternary composites of RSG derived from different input ratio of $RuCl_3$, $SnCl_2$ and graphene oxides were prepared by using co-precipitation / hydrothermal approaches followed by thermal treatment.

2. MATERIALS and EXPERIMENTS

2.1 Preparation of RSG Nanocomposites

Firstly, graphene oxide (GO) was synthesized according to previous reports by our group[5]. To prepare RSG nanocomposites, different precursors were mixed in a certain ratio by weight, then co-precipitation/hydrothermal process and annealing treatment were conducted, as specifically depicted in Tab. 1. $RuCl_3 \cdot xH_2O$ and $SnCl_2 \cdot 2H_2O$ were purchased from Beijing Chemicals (China). More experiments with varied reactant ratios were done and only four samples were chosen to be discussed.

Sample	$RuCl_3 \cdot xH_2O$:$SnCl_2 \cdot 2H_2O$:GO	pH	Hydrothermal process		Annealing treatment	
			T (℃)	t (h)	T (℃)	t (h)
RSG1	30:6:0.5	7~9	200	15	200	2.5
RSG2	30:6:1					
RSG3	30:6:1		none			2
RSG4	30:6:1.5					

Tab. 1 Preparation condition of RSG nanocomposites

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2.2 Materials Characterization

SEM (FEI NOVA Nano230, Japan), EDS, TEM (JEOL 2010Ⅱ, Japan), SAED and XRD (Rigaku Ltd., Japan) were used to characterize the morphology and microstructure change of as-prepared RuO_2-SnO_2-graphene composites.

2.3 Electrochemical Measurements

The electrochemical performance was carried out on a CHI 660B workstation (Chenhua Corp. China) via chronopotentiometry, cyclic voltammetry and AC impedance methods using a three--electrode configuration[5].

3 RESULTS and DISCUSSION

3.1 Textural Characterization

Hydrothermal process would not significantly change the morphology of RSG composites as shown in Fig. 1a and Fig. 1b. Both of RSG1 and RSG3 show loosely packed agglomerates made of RuO_2 and SnO_2 nanodots decorated on wavy reduced graphene oxide sheets. The coarse surface would supply more accessible surface for charge storage. The elemental mapping results (Fig. 1e-g) reveal that all elements are homogeneously distributed, thus co-precipitation of RuO_2 and SnO_2 nanoparticles are uniformly anchored TEM image of RSG3 (Fig. 1h) shows that the magnitude of nanodots with clear crystal lattice is less than 5 nm and corresponding SAED reveals faint diffraction rings as shown in Fig. 1i.

As shown in Tab. 2, the EDS results show element content in each RSG nanocomposite.

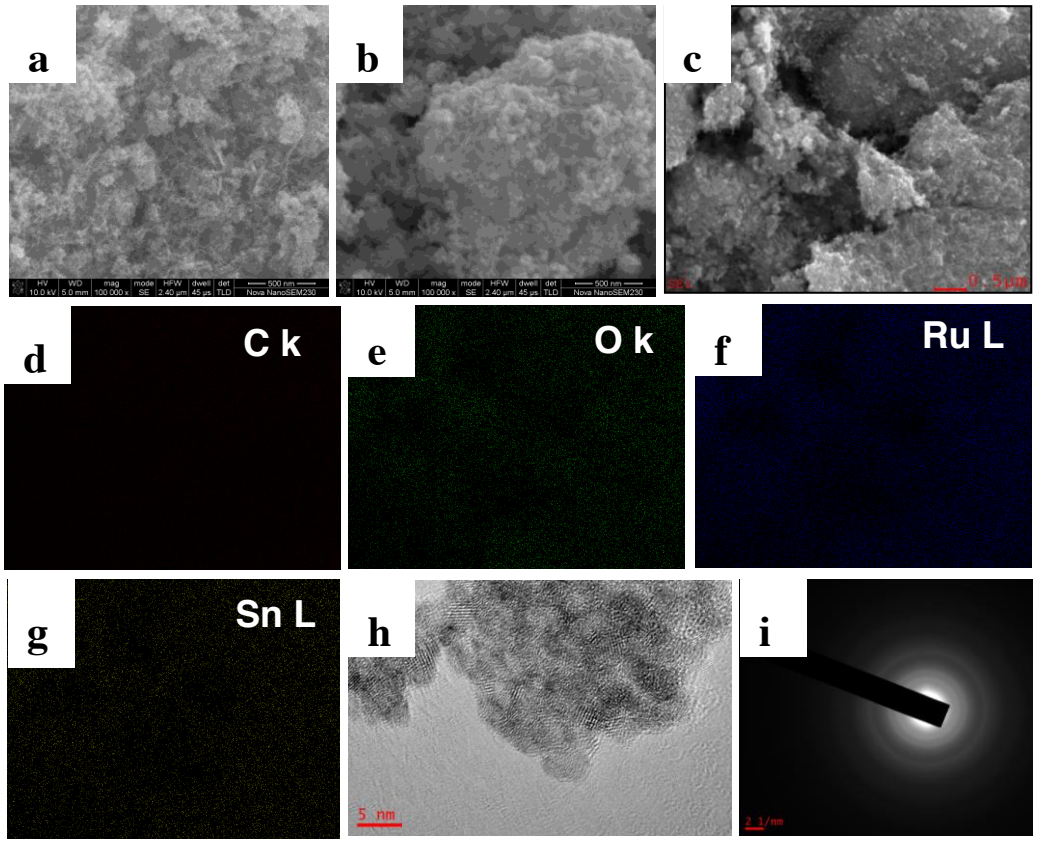

Fig. 1 SEM images of (a) RSG1, (b,c) RSG3 and (d-g) elemental mapping based on (c), TEM image of (h) RSG 3 and (i) its SAED

Element (at. %)	RSG1	RSG2	RSG3	RSG4
C	42.44	24.69	13.99	17.22
O	37.77	44.38	51.59	48.07
Ru	17.90	25.36	27.74	26.47
Sn	1.89	5.58	6.69	8.24

Tab. 2 Element content in RSG nanocomposites

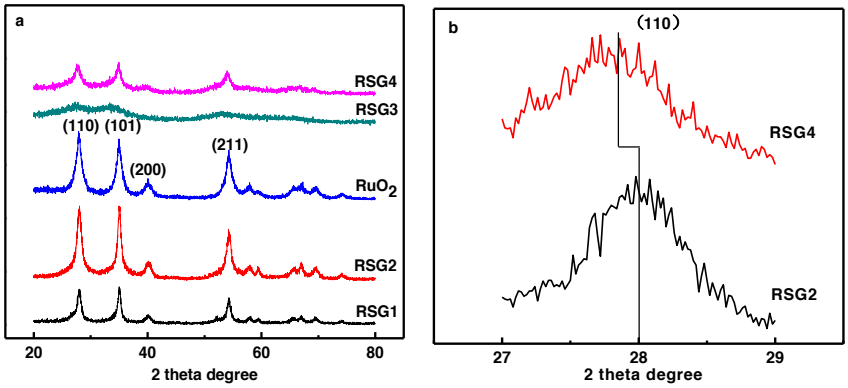

Fig. 2 XRD patterns of (a) RSGs and RuO_2, and (b) (110) peaks of RSG2 and RSG4

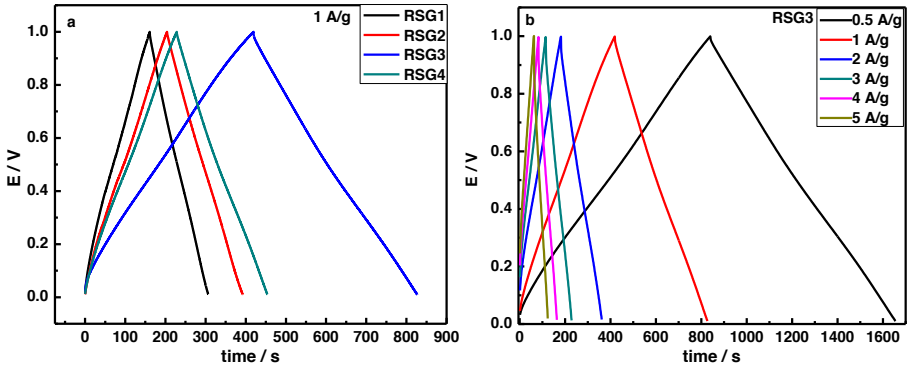

Fig. 3 Galvanostatic charging-discharging curves of (a) RSGs at 1 A/g, and (b) RSG3 at different current densities

SC (F/g)	0.1 A/g	0.5 A/g	1 A/g	2 A/g	3 A/g	4 A/g	5 A/g
RSG1	160.00	160.00	154.36	150.00	146.67	138.67	131.25
RSG2	205.00	200.00	200.00	189.47	187.50	184.62	184.20
RSG3	455.17	445.43	436.36	397.67	391.5	391.05	388.75
RSG4	255.00	250.00	250.00	232.00	227.28	218.20	215.00

Tab. 3 Specific capacitance of RSGs based on discharging curves

Comparison of RSG1 with RSG2 or RSG3 with RSG4 in Fig. 2a, it can be deducted that the increase of Sn precursor resulted in sharper diffraction peaks indicating higher cristallinity. The quite broad diffraction peaks of RSG3 is consistent with faint rings shown in SAED pattern (Fig. 1i). Owing to close lattice parameters of SnO_2 and RuO_2[6], at a certain condition, the (110) diffraction peaks in XRD patterns showed negative shift (Fig. 2b), denoting that the nucleation and/or growth rate of hydrous RuO_2 from the precursor solutions was changed by introducing Sn ions, presumably due to different solvating rates of Ru and Sn precursors and the probable deposition of RuO_2–enriched $(Ru_\theta Sn_{1-\theta})O_2$ onto SnO_2 seeds[7].

3.2 Electrochemical Performance

Due to the semiconductive property of SnO_2 and the lack of a redox couple in the investigated potential region, the surface electrochemical properties of RSGs are dominated by the redox properties of the Ru^{4+} cations. As shown in Fig. 3a, all RSG electrodes exhibit symmetric curves and ideal capacitance characteristics. The specific capacitance (SC) at different current densities was calculated based on discharging curves[6] and shown in Tab. 3.

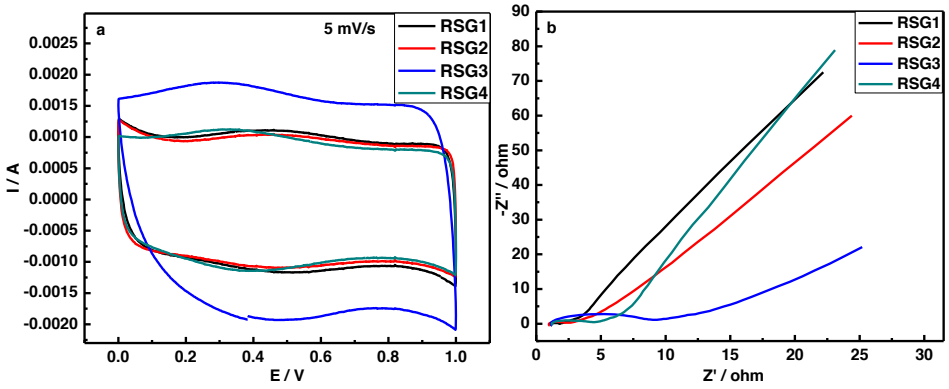

Fig. 4 (a) Cyclic voltammograms and (b) Nyquist plots of RSGs

As shown in Fig. 4a, all CV curves are symmetric, indicating potential ideal use for supercapacitors. It can also be seen that RSG3 with amorphous structure and atomic-scale mixing of Ru and Sn atoms, which may intrigue an enhancement in the electrochemical active surface and promote the average electron-transfer number per Ru atom, shows maxium enveloped area. In fact, an increase in defects due to minor difference in the lattice structure between RuO_2 and SnO_2 will enhance the utilization of oxyruthenium species[7, 8]. And a higher degree of atomic-scale mixing means more obvious synergism since inter-diffusion of Ru and Sn atoms can occur only at the contact interface between RuO_2 and SnO_2 nanoparticles. The reason why samples with higher crystallinity show lower capacitance is the gradual movement of defect atoms from metastable sites to the energy-favorable positions during growth of crystallites, which would cause a loss in the active sites (loss of defects and water, and increase of diffusion barrier of proton) while promote the electron conductivity[9]. As shown in Fig 4b, the RSG3 with more defects has relative large high frequency arc, which relates larger electronic resistance within the electrode material[10] and is consistant with the lower crystallinity as shown in Fig. 2a.

In summary, samples with hydrothermal treatment exhibit higher crystallinity, lower resistance and specific capacitance of 154 F/g ~ 200 F/g at 1 A/g. Samples without hydrothermal treatment show negative shift in RuO_2 (110) diffraction peak and relative higher specific capacitance of 250 F/g ~ 436 F/g at 1 A/g.

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