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# Microwave-assisted synthesis of Ru/mesoporous carbon composites for supercapacitors <sup>☆</sup>



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## ABSTRACT

Ruthenium/mesoporous carbon (Ru/MC) composites for supercapacitors were synthesized from RuCl<sub>3</sub> and peanut shell-derived MC by a microwave-assisted heating glycol reduction method. The specific capacitance of obtained Ru/MC composite increased with the increasing Ru mass loaded, maintaining 287 F g<sup>-1</sup> even after 1000 cycles at 20% loading of Ru for Ru<sub>20</sub>/MC. The contribution of Ru nanoparticles reached 48.7% of the total capacitance. The energy density of Ru<sub>20</sub>/MC capacitor in 6 M KOH electrolyte only dropped from 10.5 Wh kg<sup>-1</sup> to 9.8 Wh kg<sup>-1</sup> with the energy density retention of 93.3% after 1000 cycles, showing excellent cycle stability. The results indicate that the one-step microwave-assisted glycol reduction of RuCl<sub>3</sub> is a simple technique to the preparation of high performance Ru/MC composites for supercapacitors.

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## 1. Introduction

Supercapacitors including electric double layer capacitor (EDLC) and Faradic capacitor have attracted increasing interest in the power sources due to their high power density and long cycle life [1–3]. The charge storage in EDLC is based on the double layer while it is Faradic redox reaction for Faradic capacitor. Ruthenium (Ru) is known as the best electrode material for Faradic capacitor due to its outstanding specific capacitance and long cycle life. However, its practical utilization is limited because of the high cost of Ru element [4]. Due to the high thermal stability, reasonably high conductivity, relatively high surface area and cost effectiveness of carbon materials, it is a hot topic to develop a hybrid system that consists of an electrochemical double layer process and a Faradic redox reaction based on the Ru/carbon composites [5]. Carbon materials used as electrode materials include porous carbon and graphene, etc. [6–8]. Mesoporous carbons (MCs) with bigger pore size made at low cost are preferred as the carrier to make Ru/MC composites. Herein, one of the key issues is how to efficiently load Ru nanoparticles onto MCs. Here we report a facile technique to prepare Ru/MC composites from RuCl<sub>3</sub> and cheap

peanut shell-derived MC for supercapacitors by a microwave-assisted heating glycol reduction method.

## 2. Experimental

MC was prepared via a microwave-assisted heating method, as described elsewhere [9]. Briefly, the dried peanut shell with the particle size of 3 × 10 mm<sup>2</sup> was impregnated in ZnCl<sub>2</sub> solution at the ZnCl<sub>2</sub>/peanut shell mass ratio of 4 for 12 h while the total weight of ZnCl<sub>2</sub> and peanut shell was kept at 27 g. The ZnCl<sub>2</sub>-impregnated peanut shell was dried at 383 K for 24 h and then heated for 20 min by microwave to make MC in a LWMC-205 type microwave oven at 600 W of microwave power.

0.9 g MC powder was impregnated into the mixture of 20 mL of 0.05 M RuCl<sub>3</sub>·nH<sub>2</sub>O ethanol solution, 2 mL of 0.5 M sodium ethylate solution and 78 mL glycol. After 30 min ultrasonic treatment, the mixed solution was transferred to a 250 mL round flask equipped with mechanical agitation and reflux condenser, which was put into the above mentioned microwave reactor and then heated for 8 min to make Ru/MC composites at 400 W of microwave power. The resultant solution was filtered, and the Ru/MC composite was fully washed by acetone and distilled water, and finally dried at 50 °C for 24 h under vacuum before use. The Ru/MC composite was nominated as Ru<sub>x</sub>/MC, where the subscript x stands for the mass percentage of Ru in the composite.

The thermogravimetric analysis (TGA) for MC and Ru/MC composites was carried out in a thermal analysis instrument (TG-60, Japan) in 30 mL min<sup>-1</sup> air at 5 °C min<sup>-1</sup> to 800 °C. The

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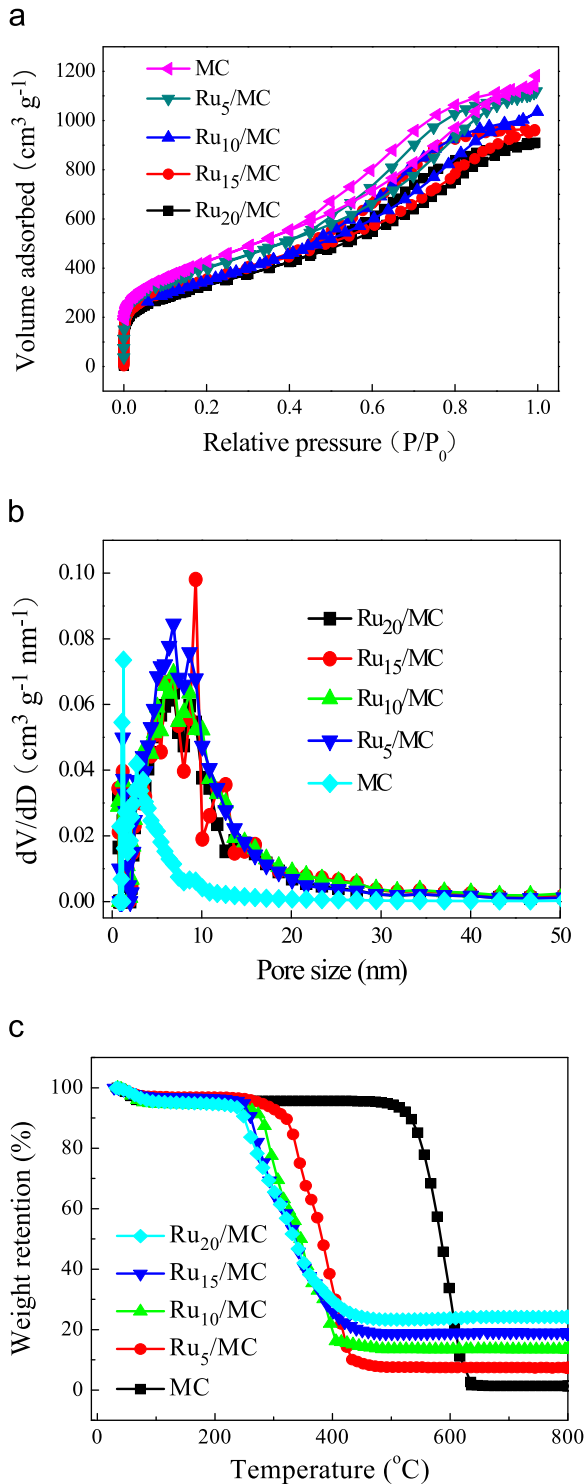
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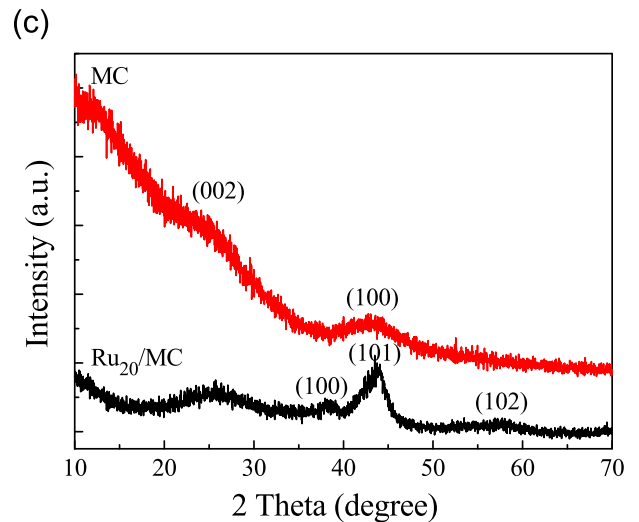
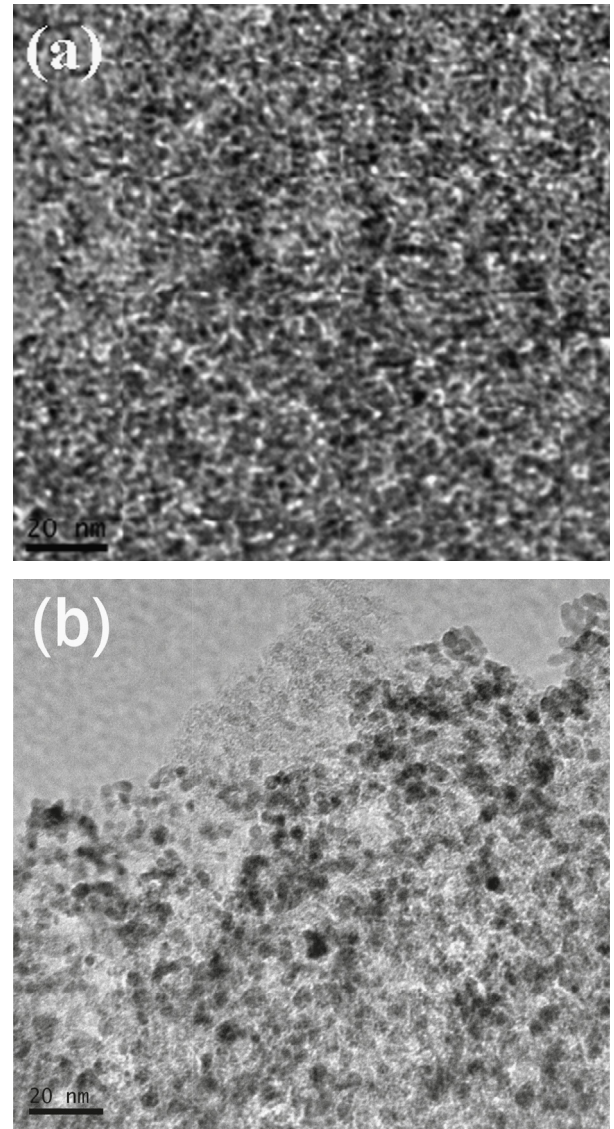
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pristine MC and Ru/MC composites were characterized by transmission electron microscope (TEM, JEOL-2100), X-ray diffraction (XRD, Philips X'pert Prosuper, CuK $\alpha$  Radiation) and N<sub>2</sub> adsorption (ASAP2010). The electrode of symmetrical supercapacitor was fabricated by mixing the composite, carbon black and poly(tetrafluoroethylene) in a weight ratio of 87:5:8. More details can be found elsewhere [10]. The supercapacitors made from the composites were evaluated in 6 M KOH aqueous electrolyte by cyclic

voltammetry (CV) on an electrochemical workstation (CHI-760C) while the charge–discharge performance of supercapacitors was tested on a land cell tester (CT-2001A) [10].



**Fig. 1.** (a) N<sub>2</sub> adsorption–desorption isotherms and (b) pore size distribution of MC and Ru/MC composites. (c) Weight retention of MC and Ru/MC composites vs. temperature.



**Fig. 2.** TEM images of: (a) MC and (b) Ru<sub>20</sub>/MC. (c) XRD patterns of MC and Ru<sub>20</sub>/MC.

### 3. Results and discussion

Fig. 1(a and b) gives the  $N_2$  adsorption–desorption isotherms and pore size distribution of MC and Ru/MC composites, respectively showing that the macropores in MC are ignorable. The specific surface area ( $S_{BET}$ ) of MC is  $1552 \text{ m}^2 \text{ g}^{-1}$  with  $1467 \text{ m}^2 \text{ g}^{-1}$  of mesopore surface area and  $85 \text{ m}^2 \text{ g}^{-1}$  of micropore surface area. The mesopore percentage of MC reaches 97.8%, and the average pore size of MC is 4.52 nm, mainly centering at 2–15 nm. The  $S_{BET}$  of Ru<sub>5</sub>/MC, Ru<sub>10</sub>/MC, Ru<sub>15</sub>/MC and Ru<sub>20</sub>/MC composites is 1436, 1318, 1257 and  $1176 \text{ m}^2 \text{ g}^{-1}$ , respectively while the total pore volume is 1.71, 1.54, 1.47 and  $1.40 \text{ cm}^3 \text{ g}^{-1}$ , showing an obvious

drop due to the loading of Ru nanoparticles on MC. Fig. 1(c) is the TGA curves of MC and Ru/MC composites in air. There is no weight loss for all Ru/MC composites at more than  $450 \text{ }^\circ\text{C}$ , and the remains are  $\text{RuO}_x$  according to our previous work [11]. The mass percentage of  $\text{RuO}_x$  is 7.2%, 13.3%, 18.7% and 24.1%, respectively in Ru<sub>5</sub>/MC, Ru<sub>10</sub>/MC, Ru<sub>15</sub>/MC and Ru<sub>20</sub>/MC composites. For MC, it begins to combust at ca.  $473 \text{ }^\circ\text{C}$ , and almost burns up at  $636 \text{ }^\circ\text{C}$ . For Ru/MC composites, the initial and end combusting temperatures shift to lower temperature due to the catalysis effect of Ru. Moreover, the more the Ru mass loaded, the lower the initial combusting temperature, which is 237, 240, 252 and  $264 \text{ }^\circ\text{C}$ , respectively for Ru<sub>20</sub>/MC, Ru<sub>15</sub>/MC, Ru<sub>10</sub>/MC and Ru<sub>5</sub>/MC.

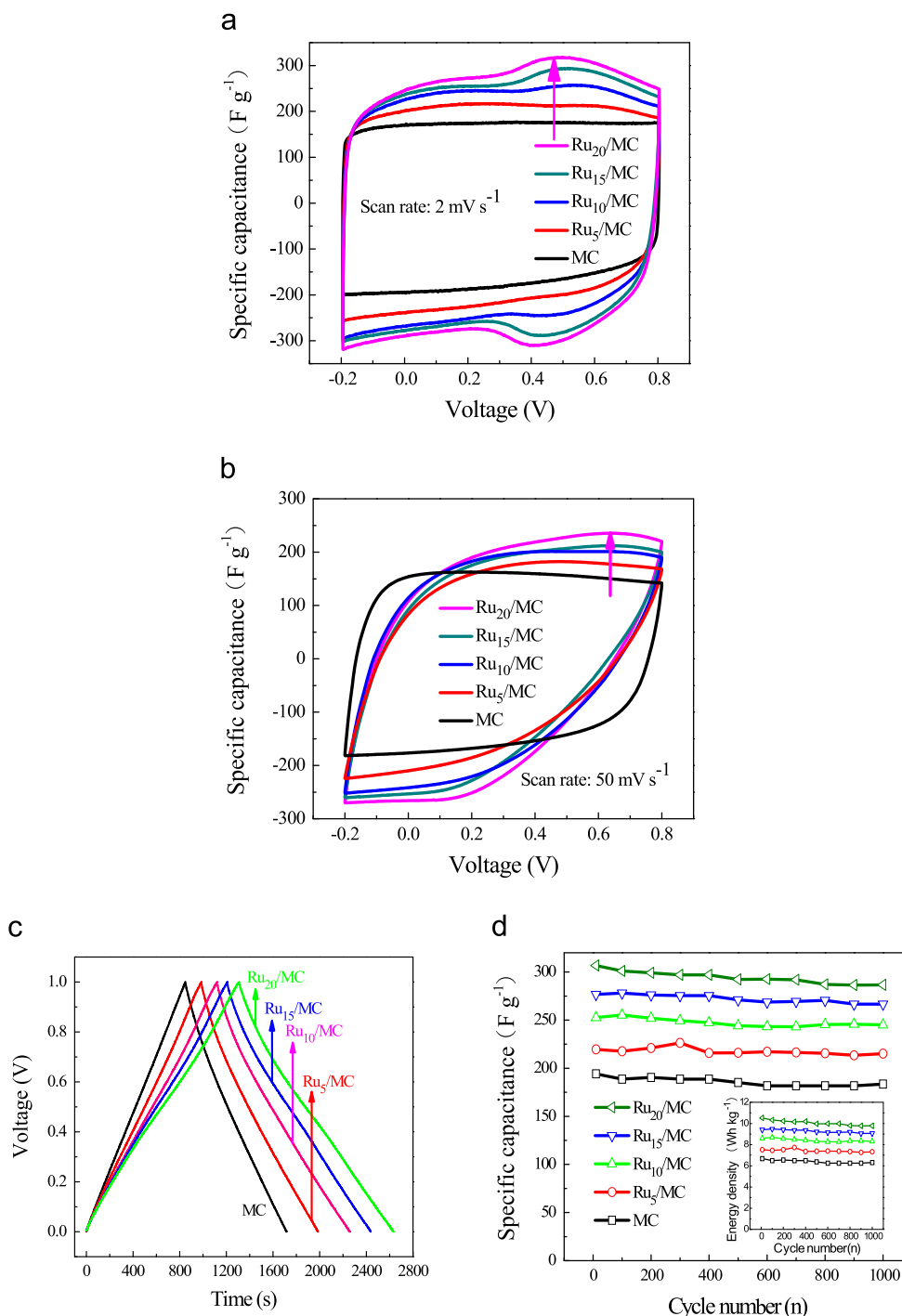


Fig. 3. CV curves of MC and Ru/MC electrodes at different scan rates: (a)  $2 \text{ mV s}^{-1}$  and (b)  $50 \text{ mV s}^{-1}$ . (c) Charge/discharge curves of MC and Ru/MC composite electrodes. (d) Specific capacitance of MC and Ru/MC composite electrodes vs. cycle number.

Fig. 2(a and b) is the TEM image of MC and Ru<sub>20</sub>/MC, respectively. The abundant mesopores in Fig. 2(a) are formed due to ZnCl<sub>2</sub> activation and the removal of volatile matters in peanut shell. The mesopores at ca. 2–15 nm are consistent with the results shown in Fig. 1(a and b). Fig. 2(b) shows that Ru nanoparticles are well-dispersed on MC, which is expected to increase the capacitance of Ru/MC composites compared to the pristine MC. Fig. 2(c) is the XRD patterns of MC and Ru<sub>20</sub>/MC. The weak diffraction peaks at ca. 25° and 44° are 002 and 100 peaks of MC, respectively. The diffraction peaks at 38°, 42°, 44° and 58° are belonged to pure Ru (JCPDS No. 65-1863). The weak peak of Ru at 42° shows that Ru nanoparticles in Ru<sub>20</sub>/MC composite are amorphous. As mentioned above, the remains at more than 450 °C in Fig. 1(c) are RuO<sub>2</sub>. Hence, the mass percentage of Ru loaded on MC in Ru<sub>5</sub>/MC, Ru<sub>10</sub>/MC, Ru<sub>15</sub>/MC and Ru<sub>20</sub>/MC is 5%, 10%, 14% and 18%, respectively. That is to say, Ru can be completely loaded onto MC in lower concentration of Ru-containing solution.

Fig. 3(a and b) gives the CV curves of MC and Ru/MC electrodes at the scan rate of 2 and 50 mV s<sup>-1</sup>, respectively. According to the formula introduced in literature [7], the capacitance of MC at the scan rate of 2 mV s<sup>-1</sup> reaches 171 F g<sup>-1</sup> while it remains 146 F g<sup>-1</sup> at the scan rate of 50 mV s<sup>-1</sup> with capacitance retention of 85.4%, showing good rate performance. The capacitances of Ru<sub>5</sub>/MC, Ru<sub>10</sub>/MC, Ru<sub>15</sub>/MC and Ru<sub>20</sub>/MC at the scan rate of 2 mV s<sup>-1</sup> reach 204, 234, 253 and 269 F g<sup>-1</sup>, respectively, showing an obvious increase with increasing Ru mass loaded.

Fig. 3(c) is the charge/discharge curves of MC and Ru/MC electrodes in 6 M KOH electrolyte at the current density of 0.05 A g<sup>-1</sup>. The variation of specific capacitance with cycle number at the current density of 0.05 A g<sup>-1</sup> is shown in Fig. 3(d). After 1000 cycles, the specific capacitance of MC electrode reaches 184 F g<sup>-1</sup>. Compared to the capacitance of the pristine MC, the capacitances of Ru<sub>5</sub>/MC, Ru<sub>10</sub>/MC, Ru<sub>15</sub>/MC and Ru<sub>20</sub>/MC reach 215, 245, 267 and 287 F g<sup>-1</sup>, showing an obvious rise of 16.8%, 33.2%, 45.1% and 56.0%, respectively, which is ascribed to the capacitance contributed by the well-dispersed Ru nanoparticles. The inset in Fig. 3(d) is the energy density of MC and Ru/MC capacitors with the cycle number. After 1000 cycles, the energy density of Ru<sub>20</sub>/MC capacitor only drops from 10.5 Wh kg<sup>-1</sup> to 9.8 Wh kg<sup>-1</sup> with energy retention of 93.3%. With the dropping of Ru mass loaded, the energy density retentions of Ru<sub>15</sub>/MC, Ru<sub>10</sub>/MC and Ru<sub>5</sub>/MC capacitors rise from 96.4% to 97.5%, showing excellent cycle stability.

The contributed capacitance by Ru in Ru/MC composite is calculated according to the formula reported in our previous work [11]. It is found that the contributed capacitances by Ru in Ru<sub>5</sub>/MC, Ru<sub>10</sub>/MC, Ru<sub>15</sub>/MC and Ru<sub>20</sub>/MC are 804, 799, 738 and 699 F g<sup>-1</sup>,

respectively, while the contribution of Ru nanoparticles rises from 18.7% to 48.7% of the total capacitance of the composites. Pusawale et al. [12] reported that the specific capacitance of SnO<sub>2</sub>/RuO<sub>2</sub> composite made by a chemical bath deposition containing 15% RuCl<sub>3</sub> reached 150 F g<sup>-1</sup> and the energy density of SnO<sub>2</sub>/RuO<sub>2</sub> capacitor reached 4.9 Wh kg<sup>-1</sup>. It was reported that the specific capacitance of RuO<sub>2</sub>·xH<sub>2</sub>O reached 342 F g<sup>-1</sup> [13]. In our case, both the capacitance contributed by loaded Ru and the energy density of Ru/MC capacitor are obviously higher than those reported in literature [12,13]. The above results show that the well-dispersed Ru nanoparticles on MC contribute greatly to the high performance of Ru/MC for supercapacitors.

#### 4. Conclusions

Ru/MC composites for supercapacitors were synthesized from RuCl<sub>3</sub> by a microwave-assisted glycol reduction method. The specific capacitance of Ru<sub>20</sub>/MC composites remained 287 F g<sup>-1</sup> after 1000 cycles. The contribution of Ru nanoparticles reached 48.7% of the total capacitance due to the well-dispersed Ru nanoparticles. The energy density of Ru<sub>20</sub>/MC capacitor only dropped from 10.5 Wh kg<sup>-1</sup> to 9.8 Wh kg<sup>-1</sup> with energy retention of 93.3% after 1000 cycles, showing excellent cycle stability. The results indicate that the one-step microwave-assisted heating glycol reduction is a simple technique to the preparation of high performance Ru/MC composites for supercapacitors.

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