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A strategy of using temporary space-holders to increase the capacity for Li-S batteries

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Abstract: The porous structure within the cathode material influences the capacity and operating performance of Li-S batteries. Here, we prepared special carbon material using sodium chloride as template/temporary space-holders to design mixture of micro-/meso-/macroporous structure with large surface area through a facile water bath and freeze-drying process. Such modification led to a high sulfur content of 73.2 % with remarkable initial capacity of 1378 mAh g⁻¹ at 0.1 A g⁻¹, and maintains 48.6% after 100 cycles. Moreover, the Li-S battery displayed superior rate capability of 807 mAh g⁻¹ at 1.0 A g⁻¹. This abundant micro-/meso-/macropores can improve the content of sulfur, relieve the loss of sulfur and exhibit superior cycling performance and rate capability.

Keywords: Micro-/meso-/macroporous; Carbon; rGO; Lithium-sulfur battery

1. Introduction

As energy-storage devices, Li-S batteries drawn more and more attention because of their high capacity, nature abundance and low cost [1-3]. However, some issues should to be solved to improve its applications, such as poor conductivity, shuttle effect and the slow redox reactions [4-6]. Furthermore, the severe volume change in the cycle process damage the structural integrity and limit cyclic stability [7,8].

To overcome these limitations, many carbonaceous materials can induce a better uniform distributed sulfur particle, such as meso/microporous carbon [9], reduced graphene oxide (rGO) [10], carbon nanotubes (CNTs) [11] have used as sulfur carrier. Especially, their superior specific surface area and tunable pore size [12], the micropores of porous carbon can accommodate volumetric change during the discharge process and inhibit the polysulfides dissolving in organic electrolytes [13]. For instance, Liang et al. prepared porous carbon nanotubes, which exhibited 511 mAh g⁻¹ at 1.675 A g⁻¹ over 500 cycles [14]. Wang et al. designed porous carbon using a hydrothermal method, it presented 908 mA h g⁻¹ at 0.167 A g⁻¹ over 100 cycles [15]. However, traditional carbonaceous materials usually prepared by hydrothermal method, have an open porous structure with a pore size of up to micrometers [16], which will lead to unsuccessful blocking of the porous surface and dissolution of the cathode as well as the shuttle effect of polysulfides.

Template method is generally quite simple method to synthesize porous carbon. Many templates such as carbonate [17], silica [18] and molecular sieves [19] have been acted in the preparation of the nanostructured porous carbon. Gao et al. reported a

porous hollow carbon aerogel by using nano-CaCO₃ as template. The composite cathode exhibits 252.5 mA h g⁻¹ at 1.675 A g⁻¹ over 500 cycles [20]. Gu and his co-workers synthesized a porous carbon bulk network by using SiO₂ nanospheres as templates, the composite as a sulfur host exhibits 760 mA h g⁻¹ over 150 cycles at 0.167 A g⁻¹ [21]. However, most introduced porous carbon hosts suffered from low content of sulfur due to their unsatisfactory surface structure such as low specific surface area.

Based on the above considerations, graphene/sulfur composite comes into sight for cathode materials. The rGO with a mass of functional groups, such as hydroxyl groups, carbonyl groups, and carboxyl groups [22-24], generate strong chemical interaction with sulfur, rGO/S cathode can effectively fix the sulfur particles and polysulfide intermediates, limit the dissolution of polysulfides [25]. For instance, Zhou and co-workers designed a porous graphene framework via a vacuum filtration method, which employed for Li-S batteries delivered 728 mA h g⁻¹ over 200 cycles at 0.335 A g⁻¹ [26]. Yang et al. synthesized graphene@sulfur composites by a microwave method, which delivered a capacity of 751 mAh g⁻¹ at 0.335 A g⁻¹ over 80 cycles [27]. Nevertheless, a serious problem is the oxygen containing functional coatings is up to the micrometer scale in thickness [28], it still remains a challenge to improving the conductivity of the graphene.

Starch is a high molecular carbohydrate, which is polymerized by glucose molecules. The starch is an abundant biopolymer in nature, which can be obtained from various plants, such as potato, corn, rice, and wheat. As a biomass carbon source, the starch is low-cost and friendly to the environment. The carbonization of starch releases water vapor, carbon dioxide and carbon monoxide, forming porous carbon with high

purity. Furthermore, sodium chloride (NaCl) nanoparticles can be used as temporary space holders and produce a large number of special macropores in the porous carbon material. In addition to the low price of NaCl, it is also easy to remove with water.

Herein, a facile and scalable strategy was designed to prepare a porous carbon-rGO with abundant micro-/meso- and macropores. The micro-/meso- and macroporous carbon-rGO (MMMPC-rGO) was obtained using starch as carbon source, using NaCl as the temporary space holders, via a facile water bath heating, freeze-drying process and a subsequent heat treatment. When applied in sulfur host, the MMMPC-rGO/S composite demonstrates a high reversible capacity and a superior rate performance. The outstanding electrochemical performance is mainly benefit from the effects of nano-size, conductive carbon networks and porosities.

2. Experimental

2.1 Preparation of MMMPC-rGO and MPC-rGO composites

Graphite oxide was obtained using the Hummers' method described supplementary information [29]. Then the graphite oxide (80 mg) was added into distilled water followed by sonicate for 2 h. Secondly, sodium chloride (NaCl, 0.6 g) and the starch (3.0 g) were sequentially added to the as-prepared rGO solution followed by sonicate for ten minutes. Then, the above solution was put into a water bath, maintained at 80 °C for 60 min. A gelatinous mixture was obtained and it was freeze-dried at -55 °C for 72 h. The mixture was heated at 750 °C for 120 min in N₂ atmosphere. Then, NaCl was leached using distilled water and dried at 110 °C for 120 min. Finally, the micro-/meso- and macropores carbon-rGO (MMMPC-rGO) sample was obtained. For comparison, microporous carbon doped with rGO (MPC-rGO) was synthesized through similar process without NaCl.

2.2 Preparation of cathode materials

Briefly, the as-prepared products and sulfur powder (1:3) were mixed by manual mixing. The mixtures were heated at 165 °C for 30 h in Ar-filled atmosphere. Therefore, the MMMPC-rGO/S and MPC-rGO/S composites were obtained.

2.3 Li-S batteries assembly and material characterization (see SI).

3 Results and discussion

3.1 Characterization

The preparation process of MMMPC-rGO composite is presented in Fig. 1. First, the rGO solution was obtained via ultrasonic dispersion of the graphite oxide solution. Subsequently, sodium chloride and starch were put into the above rGO solution followed by ultrasonic mixing, water bath heating and freeze-drying, forming a gelatinous precursor with NaCl as the pore-forming agent. Second, the gelatinous precursor was carbonized at a high temperature of 750 °C for 2 h in N₂ atmosphere. Finally, the NaCl was leached via washing the sample with distilled water, resulting in porous carbon-rGO with abundant micropores, mesopores and macropores.

Scanning electron microscopy (SEM) images of the samples are shown in Fig. 2 and Fig. S1. Observing from Fig. S1, we can find that the products consist of some microplates with rough surface. Figs. 2a,b show the SEM images of MMMPC-rGO/NaCl sample, some of which look like cubic NaCl particles embedded in the composite. Energy dispersive X-ray spectroscopy (EDS) results shown in Fig. S2a confirms the existences of Na and Cl elements in the composite. The MMMPC-rGO with numerous macropores and the homogeneous pore sizes distribution with average size of 500 nm can be observed (Figs. 2c,d), indicating that cubic NaCl particles were successfully leached out after washing with distilled water, resulting in the porous

structure. It is well consistent with the EDS result of the MMMPC-rGO after washing with distilled water (Fig. S2b). Moreover, EDS was also performed to investigate the elements in the MMMPC-rGO/S composite shown in Fig. S2c, indicating the co-existence of carbon and sulfur elements. High-resolution transmission electron microscopy (HRTEM) images (Figs. 2e,f) also demonstrates the micro-/meso-/macroporous structure of the sample. The inset image presents the selected area electron diffraction (SAED) pattern of MMMPC-rGO, two rings presents (104) and (116) of the hexagonal structure [30].

As shown in Figs. 3a and b, MPC-rGO displayed a wrinkled laminar structure with stacks of some massive blocks. No macropores can be observed because no sodium chloride was added in the preparation process. TEM and HRTEM images (Figs. 3c and d) confirm the microporous structure and amorphous phase of the product.

Fig. 4a presents Brunner–Emmet–Teller (BET) results for MMMPC-rGO composite. The isotherm curves of MMMPC-rGO are a combination of Type I and Type IV isotherms [31]. Observing from the inset of Fig. 4a, MMMPC-rGO contains pores sizes ranging sizes from 0.308 to 28.4 nm, verifying the existence of micropores, mesopores and macropores. The specific surface area and total pore volume of MMMPC-rGO are ca. $438.6 \text{ m}^2 \text{ g}^{-1}$ and $0.269 \text{ cm}^3 \text{ g}^{-1}$, respectively. As for MPC-rGO, they are ca. $352.4 \text{ m}^2 \text{ g}^{-1}$ and $0.193 \text{ cm}^3 \text{ g}^{-1}$, respectively (Fig. S3). Therefore, large surface area and porous structure of the MMMPC-rGO could hold large sulfur loading and capture polysulfides, and the mesopores and macropores can facilitate charge transfer [32].

Fig. 4b shows the X-ray diffraction (XRD) patterns of samples. The diffraction peaks of the MMMPC-rGO/NaCl at 27.3°, 45.4°, 56.4°, and 75.2° are perfectly indexed to the (111), (220), (222) and (420) planes and can be assigned to NaCl (JCPDS no. 75-0306), indicating the presence of cubic phase NaCl [33]. However, after washing with distilled water, these peaks completely disappeared, suggesting complete removal of NaCl from the MMMPC-rGO. As for the XRD pattern of the MMMPC-rGO shown in Fig. 3b, a broad peak at ca. 26° can be observed, which attributes to the (002) plane of amorphous carbon [34]. As for the XRD pattern of the MMMPC-rGO/S composite, the characteristic peaks are similar with the peaks of sulfur powder, and the intensities of diffraction peaks are weaker than those of the pure sulfur powder, indicating the MMMPC-rGO material has been combined with sulfur powder. The peaks of sulfur powder are consistent with the characteristic peaks of orthorhombic sulfur (JCPDS no. 08-0247) [35]. Meanwhile, the broad peak of carbon at ca. 26° disappeared also suggests the MMMPC-rGO and sulfur have been combined successfully [36].

To investigate the chemical states of the elements in the MMMPC-rGO/S, X-ray photoelectron spectroscopy (XPS) measurement was performed. Fig. 5a shows the survey spectrum of MMMPC-rGO/S composites, demonstrating the existence of C, O and S elements. C1s spectrum (Fig. 5b) exhibits three peaks located at 284.7, 286.3 and 289.6 eV, assigning to C-C, C-O and O-C=O bonds, respectively [37]. Part of GO was reduced during the calcination process, resulting a lower peak of oxygen-containing functional groups [17,38]. O 1s spectrum (Fig. 5c) is fitted into two bonds including S-O (532.5 eV) and C-O-C (533.8 eV), respectively [39]. As shown in Fig. 5d, S 2p_{3/2}

(164.2 eV) and S $2p_{1/2}$ (164.9 eV) peaks can be obtained [40]. These chemical bonds within the MMMPC-rGO/S composite can effectively trap the sulfur particles and relieve the diffusion of polysulfide in the redox process [38,41].

Raman spectrum was generally performed to describe the structural characteristic of the carbonaceous materials. As shown in Fig. 6a, the three small peaks below 510 cm^{-1} are corresponding to the peak of sulfur [42], indicating the sulfur was combined to MMMPC-rGO. In addition, two peaks at 1337 and 1594 cm^{-1} come from the D and G bands of carbon [43,44]. D band presents the defect of the carbon, while G band is assigned to graphitic carbon atoms. The value of I_D/I_G for MMMPC-rGO is 0.90, indicating its graphite structure, facilitating the charge transfer in the redox process [45,46]. The defects can enhance the sulfur loading in MMMPC-rGO [39,42,47]. Moreover, the I_D/I_G value of MMMPC-rGO is lower than that of MMMPC-rGO/S (0.91), confirming that the MMMPC-rGO/S composite possesses more lattice defects. Observing from the Raman spectra of MPC-rGO/S, MPC-rGO (Fig. S4), similar results can be obtained. To further investigate the content of sulfur in the MMMPC-rGO/S composite, thermogravimetric analysis (TGA) was conducted at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from room temperature to $800\text{ }^\circ\text{C}$ in the air. Fig. 6b shown the sulfur load among the MMMPC-rGO/S is approximately 73.2%. While the sulfur load among the MPC-rGO/S is ca. 69.7%. Furthermore, sulfur loss at $200\text{--}400\text{ }^\circ\text{C}$, and the additional loss from $400\text{ }^\circ\text{C}$ can be ascribed to the oxidation of the MMMPC-rGO and MPC-rGO in air [48].

3.2 Electrochemical properties

Fig. 7a exhibited the cyclic voltammetry (CV) curves of MMMPC-rGO/S composite at 0.1 mV s^{-1} . For the 1st cycle, one peak at ca. 2.42 V corresponds to the transforms of S_8 to Li_2S_n . Another peak at ca. 1.98 V is ascribed to the reduction of Li_2S_n to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$. In addition, one peak (2.24 V) is attributed to the oxidation of Li_2S to polysulfides. From the second cycle, the peak shifts to 2.41 V, which is due to the anode reaction [49]. Two peaks presented at approximately 2.24 and 2.01 V are corresponding to the reduction of S_8 to Li_2S_n and $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$, respectively [50-52]. Compared with the first reduction reaction process at approximately 2.24 V, the second reaction process at approximately 2.01 V involves more lithium ions. Therefore, the area of the reduction peak at 2.01 V is larger than that of the reduction peak at 2.24 V. For the comparison, Fig. S5 exhibited the CV curves of the MPC-rGO/S composite. Similar reduction and oxidation peaks can be observed from Fig. S5.

Fig. 7b illustrated the discharge/charge profiles of the MMMPC-rGO/S. The capacities are 1378, 1331, 1303, 822 and 668 mAh g^{-1} for the 1st, 2nd, 3rd, 50th and 100th cycles. The discharge platforms and charge platform are approximately consistent with the CV peaks. Moreover, the MPC-rGO/S cathode also delivered good rate capacities as shown in Fig. S6. Fig. 7c shows the rate capabilities of MMMPC-rGO/S and MPC-rGO/S. The initial capacities of MMMPC-rGO/S cathode are 1367 mAh g^{-1} at 0.1 A g^{-1} , 1078 mAh g^{-1} at 0.2 A g^{-1} , 920 mAh g^{-1} at 0.5 A g^{-1} and 807 mAh g^{-1} at 1.0 A g^{-1} , and backing to 1054 mAh g^{-1} at 0.1 A g^{-1} . For comparison, the MPC-rGO/S cathode delivered capacities of 792, 513, 433 and 339 mAh g^{-1} from 0.1 to 1.0 A g^{-1} .

Fig. 7d exhibits the performances of the MMMPC-rGO/S and MPC-rGO/S

electrodes at 0.1 A g^{-1} . The MMMPC-rGO/S delivers an initial capacity of 1378 mAh g^{-1} . In contrast, MPC-rGO/S composite exhibits only 837 mAh g^{-1} . Fig. 7e shows the cycling performances of the MMMPC-rGO/S and MPC-rGO/S electrodes at 0.5 A g^{-1} . The first discharge capacity of the MMMPC-rGO/S is 1043 mAh g^{-1} , and the MPC-rGO/S composite exhibits only 640 mAh g^{-1} . The capacity of MMMPC-rGO/S composite maintains 673 mAh g^{-1} over 200 cycles. Moreover, the discharge/charge profiles of the MMMPC-rGO/S composite at 0.5 A g^{-1} are shown in Fig. S7a. As shown in Fig. 7f, MMMPC-rGO/S composite possessed an initial capacity of 852 mAh g^{-1} and retained 597 mAh g^{-1} after 500 cycles. The discharge/charge profiles of the MMMPC-rGO/S composite at 1.0 A g^{-1} are shown in Fig. S7b. The capacity of MMMPC-rGO/S cathode is high, indicating that the sodium chloride as temporary space-holders can anchor polysulfides [53]. Furthermore, the cyclic performance of MMMPC-rGO/S is compared with PC aerogel/GO [54], N-doped GO/PC [55] N-doped GO/metal oxide [56], and other materials etc. [57-60], the comparison of the cycling performance of just mentioned carbonaceous materials served as sulfur carriers are listed in Table S1. Although significant progress has been reported in the corresponding literature, the excellent electrochemical capabilities of MMMPC-rGO/S electrode mainly due to the following aspects. First, the large surface area of MMMPC-rGO may enhance sulfur load and capture polysulfides during charge/discharge process. Second, the micropores can provide containers for immobilizing sulfur and polysulfides. Finally, the coexistences of micro-/meso-/macroporous structure can relieve the shuttle effect via effectively capture polysulfides.

Fig. 8a exhibits the CV curves of the MMMPC-rGO/S cathode at serials scanning rates. The relationship of several mechanisms can be analyzed according to:

$$i = aV^b \quad (1)$$

$$\log i = b \log v + \log a \quad (2)$$

where i is the current, and v represent scan rate, a and b are constant. The process of charge-storage controlled by the diffusion when $b=0.5$, and if $b=1.0$ presents the capacitive-controlled behavior [61-63]. Fig. 8b shows the anodic and cathodic peaks, the values of the slopes are 0.609 and 0.863, respectively, indicating the MMMPC-rGO electrode process is capacitive-controlled behavior. The contribution ratio at each scan rate is demonstrated in Fig. 8c. Moreover, when scan rate at 1 mV s^{-1} , capacitive contribution ratio reaches up to 82.8%, demonstrating micro-/meso-/microporous structure can facilitate the transfer of Li^+ and increase the discharge capacity. The Li^+ diffusion coefficient (D_{Li^+}) was calculated from the CV curves using the Randles-Sevcik equation (3). As shown in Fig. 8d, the peak currents (I_p) of the anodic peak (peak1) and cathodic peak (peak 2) change linearly with the square root of scanning rate ($v^{1/2}$):

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (3)$$

here n represents number of electrons in per reaction ($n=2$), A represents contact area ($A=1.13 \text{ cm}^2$), and C_{Li^+} is the Li^+ concentration in the electrode ($C_{\text{Li}^+} = 1.0 \times 10 \text{ mol cm}^{-3}$) [64,65]. The MMMPC-rGO cathode exhibits the D_{Li^+} values of peak 1 and peak 2 were 2.24×10^{-10} and $1.98 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$, respectively [25,66].

The impedance measurements were carried out by applying an AC amplitude of 5 mVrms on an equilibrium potential of 2.3 V (vs. Li/Li⁺) over the frequency range of 10 mHz to 100 kHz. Electrochemical impedance spectroscopy (EIS) curves before and after 500 cycles are shown in Fig. 9, the insets correspond to the equivalent circuit models for MMMPC-rGO/S and MPC-rGO/S electrodes. The Nyquist plots (Fig. 9a) are consisted of a semicircle and a slanted line. The semicircle is attributed to the charge-transfer resistance (R_{ct}) between cathode materials and electrolyte, and the slanted line is corresponded to Li⁺ diffusion [67]. The MMMPC-rGO/S and MPC-rGO/S electrodes exhibit two semicircles (Fig. 9b) after cycling test. The new semicircle corresponds to SEI film resistance (R_2) [68,69]. Table S2 exhibited the fitting results of MMMPC-rGO/S and MPC-rGO/S electrodes. The value of R_{ct} for the MMMPC-rGO/S cathode is 67.16 Ω before cycling test. After cycles, the R_{ct} values are 1.42 Ω and 14.96 Ω for MMMPC-rGO/S, MPC-rGO/S electrodes, respectively. After 500 cycles, the R_{ct} value is smaller than that of fresh electrode which means that the micro-/meso-/microporous structure with high specific surface area resulting in a promoted transmission of Li ion [70]. For the MMMPC-rGO cathode, the micropores can enhance content sulfur, capture the polysulfides. Moreover, meso-macropores can charge transfer and facilitate electrolyte infiltration [4,38,71]. Therefore, the MMMPC-rGO with micro-/meso-/macropores exhibit superior electrochemical performances.

4. Conclusions

Herein, an MMMPC-rGO composite consisting of the micro-/meso-/macroporous carbon doped with reduced graphene oxide is synthesized via a simple water bath,

freeze-drying and heat treatment. With using sodium chloride as the pore-forming agents, the electrochemical performance has been greatly improved. The MMMPC-rGO/S composite with 73.2 wt% sulfur delivers an initial capacity of 1043 mAh g⁻¹ at 0.2 A g⁻¹, and it retains 750 mAh g⁻¹ over 100 cycles. The outstanding performances are ascribed to the micro-/meso-/macroporous structure in the internal of MMMPC-rGO. Porous carbon exhibits an excellent mechanical flexibility. Moreover, the porous structure can increase S load and relieve the shuttle effect. The introduced graphene-based material can form conductive networks and improve rate performance.

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Appendix A Supplementary data

Supplementary data to this article can be found online at

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Figure captions

Fig. 1 Schematic illustration of synthesis procedure of MMMPC-rGO composite.

Fig. 2 (a, b) SEM images of MMMPC-rGO/NaCl. (c, d) SEM, (e) TEM and (f) HRTEM images of MMMPC-rGO. Inset shows SAED pattern of MMMPC-rGO.

Fig. 3 (a, b) SEM, (c) TEM and (d) HRTEM images of MPC-rGO. Inset shows SAED pattern of MPC-rGO.

Fig. 4 (a) Nitrogen adsorption/desorption isotherms of MMMPC-rGO, inset shows the pore size distribution of MMMPC-rGO. (b) XRD patterns of MMMPC-rGO/NaCl, MMMPC-rGO, MMMPC-rGO/S and sulfur.

Fig. 5 XPS spectra of MMMPC-rGO/S: (a) survey spectrum, (b) C 1s spectrum, (c) O 1s spectrum, and (d) S 2p spectrum.

Fig. 6 (a) Raman spectra of MMMPC-rGO, MMMPC-rGO/S and (b) TGA curves of MMMPC-rGO, MMMPC-rGO/S, MPC-rGO/S and commercial sulfur powder.

Fig. 7 (a) CV curves of MMMPC-rGO/S composites in potential range of 1.6-2.8 V at a scanning rate of 0.1 mV s^{-1} . (b) Charge/discharge profiles of MMMPC-rGO/S composites at 0.1 A g^{-1} . (c) Rate performance of MMMPC-rGO/S and MPC-rGO/S cathodes. Cycling capacity of MMMPC-rGO/S and MPC-rGO/S cathodes at (d) 0.1 A g^{-1} over 100 cycles, (e) 0.5 A g^{-1} over 200 cycles and (f) 1.0 A g^{-1} over 500 cycles.

Fig. 8 (a) CV curves of MMMPC-rGO/S composites at different scan rates ranging from 0.1 to 1 mV S^{-1} . (b) Plots of $\log i$ versus $\log v$. (c) Percentages of capacitive contribution at different scan rates for MMMPC-rGO/S cathode. (d) Plots of CV peak currents versus the square root of scan rate for anodic reaction of $\text{Li}_2\text{S}/\text{S}_8$ (Peak1) and cathodic reaction of $\text{S}_8/\text{Li}_2\text{S}_4$ (Peak2).

Fig. 9 Nyquist plots of MMMPC-rGO/S and MPC-rGO/S cathodes (a) before cycling test and (b) after 500 cycles. Insets are the corresponding simulation circuit models.

Figures

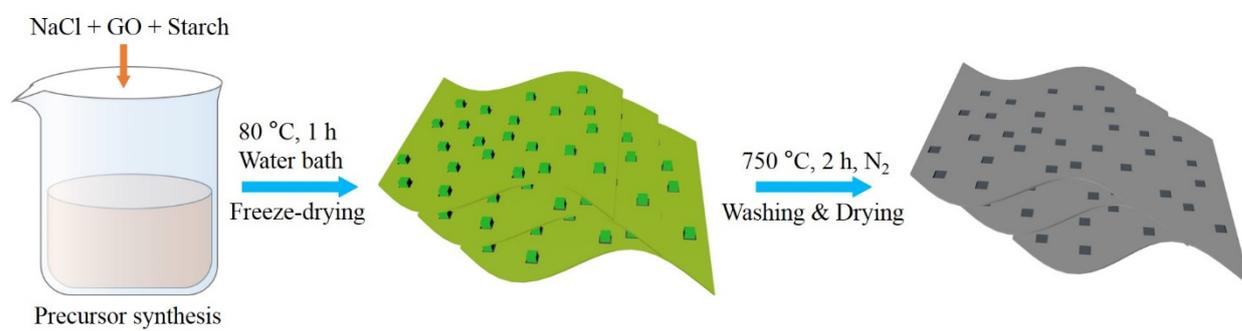


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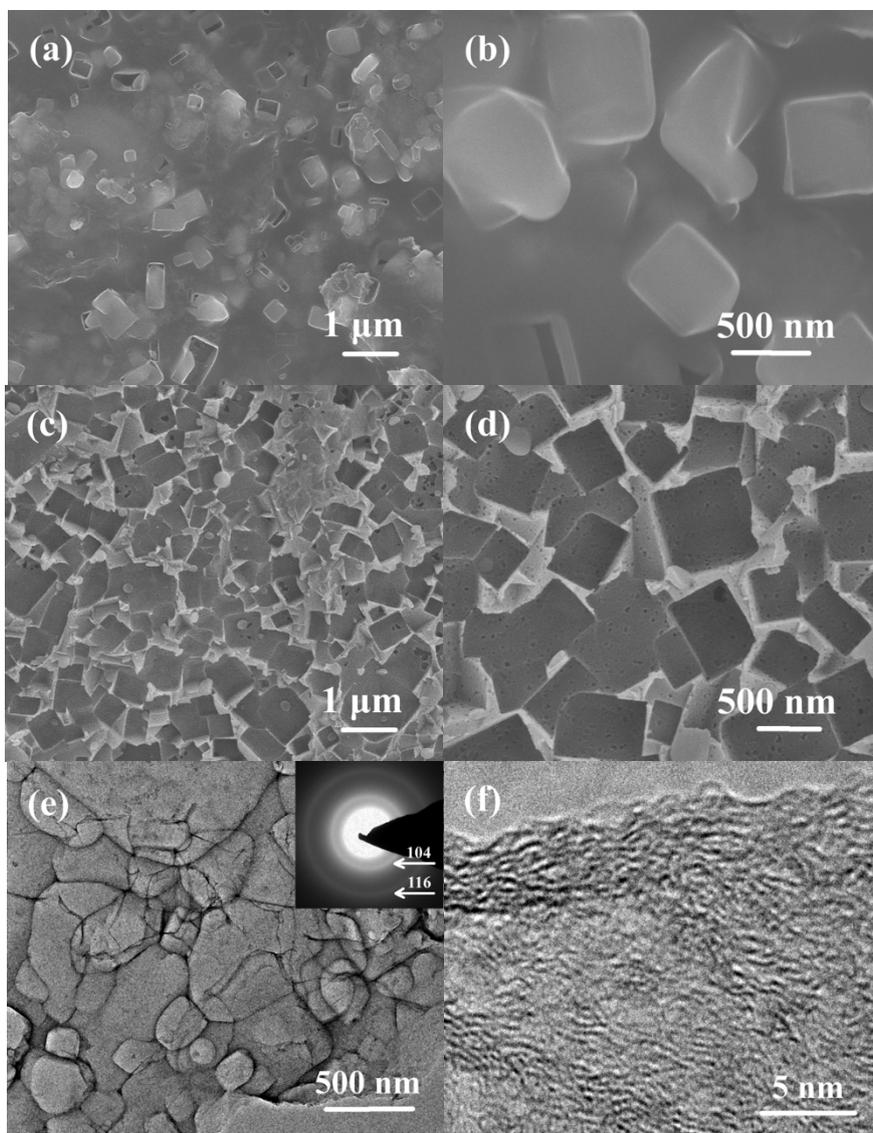


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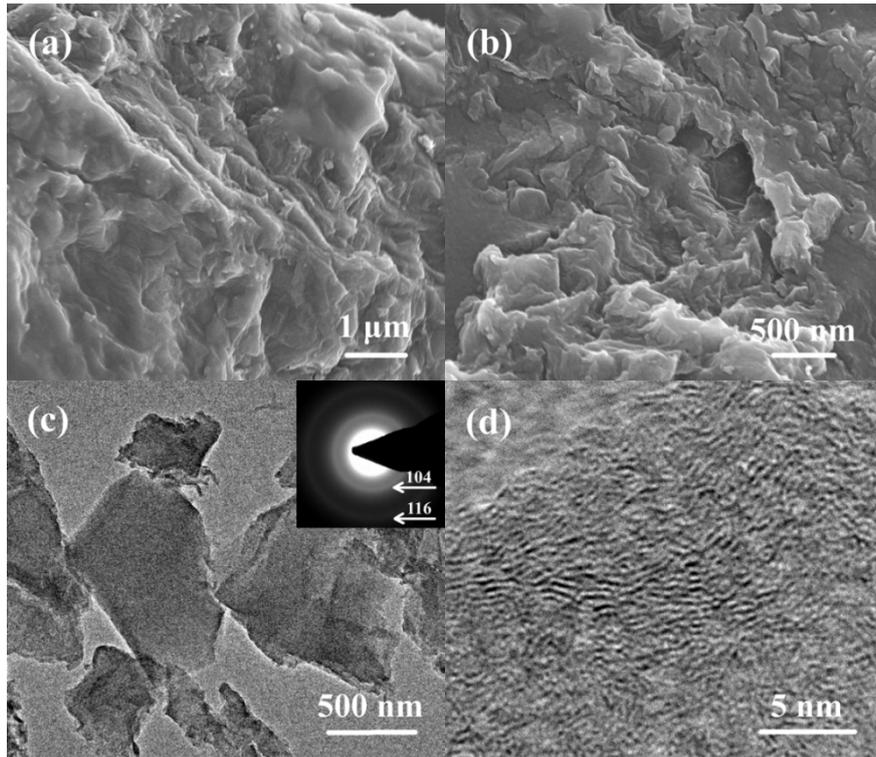


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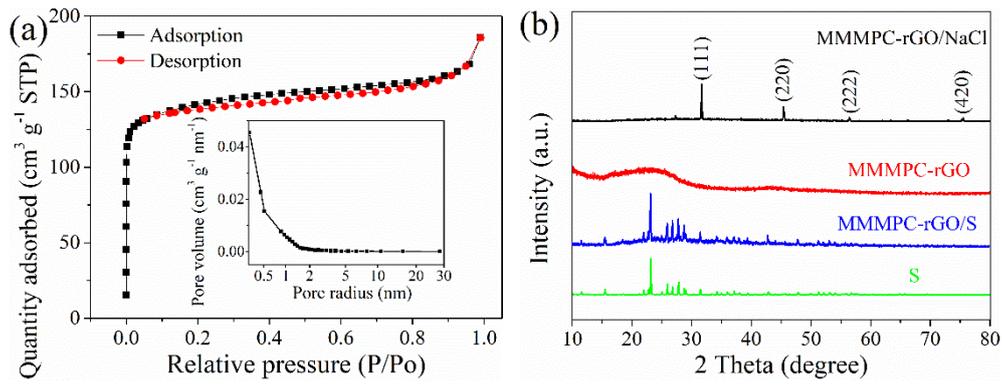


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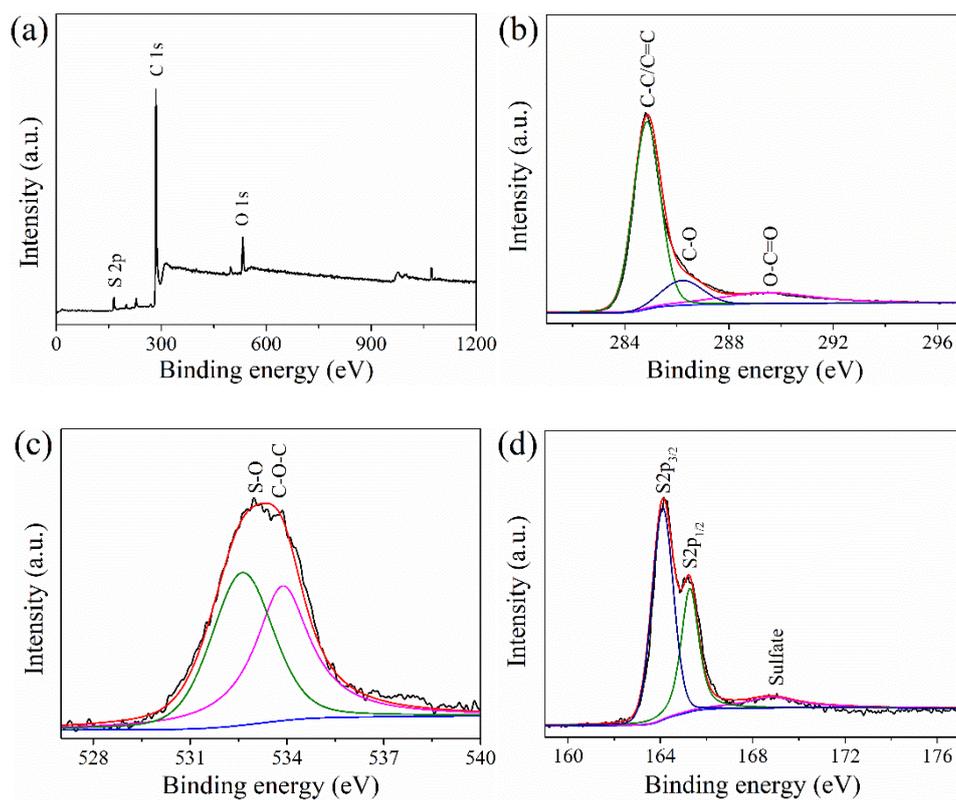


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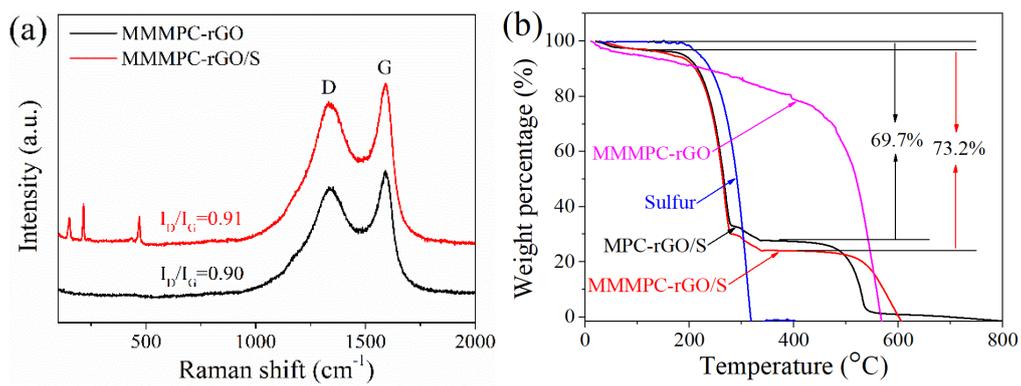


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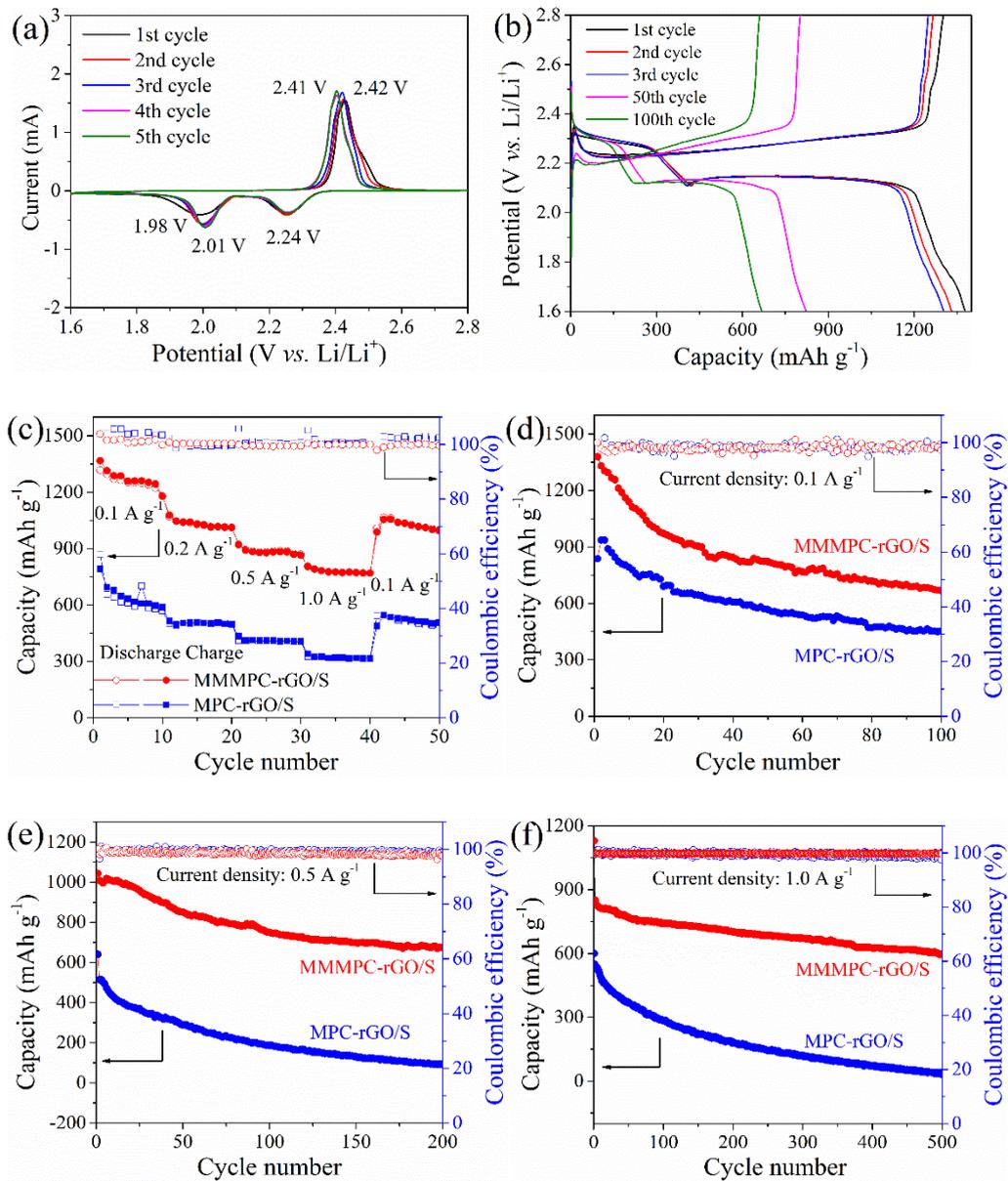


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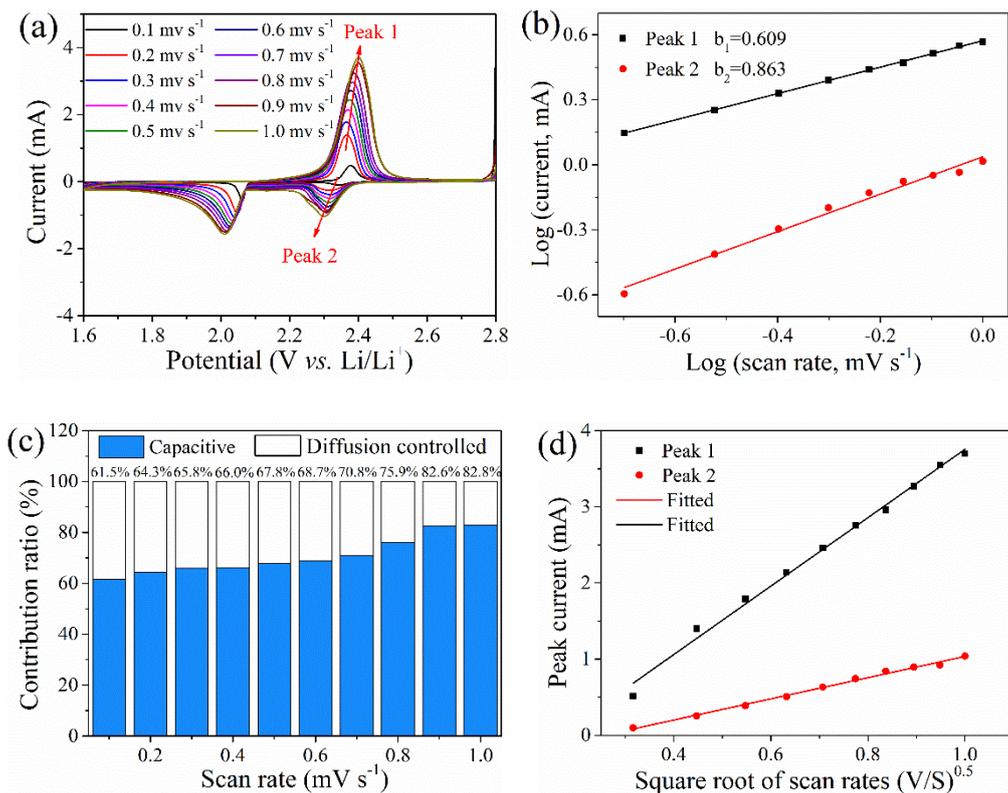


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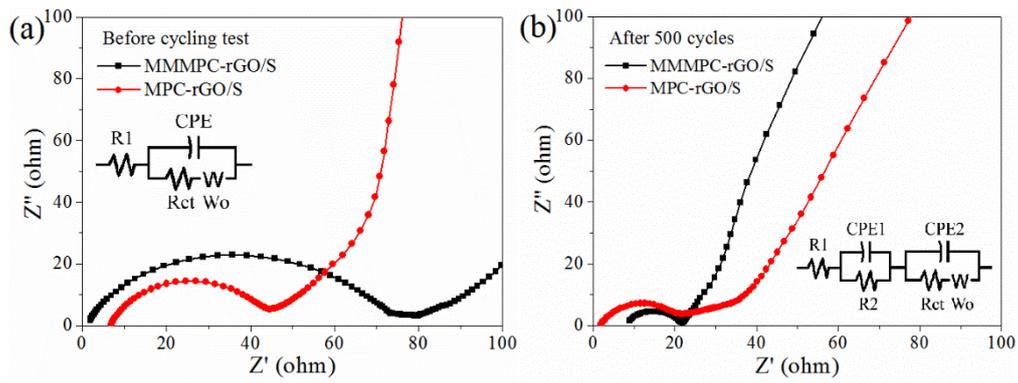


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