

Synthesis of two-dimensional lamellar porous carbon from fluorene for supercapacitors

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Research

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Abstract

Lamellar porous carbons (LPCs) were prepared from fluorene with $\text{Mg}(\text{OH})_2$ as template precursors coupled with KOH activation. The as-prepared LPCs feature a large flaky structure containing a large number of micropores and mesopores. This unique structure have a big lateral size/thickness aspect ratio and a large specific surface area of $1879 \text{ m}^2 \text{ g}^{-1}$. As an electrode material, the LPC shows a high capacitance of 231 F g^{-1} at 0.05 A g^{-1} , excellent rate performance of 173 F g^{-1} at 100 A g^{-1} , and good cycle stability with 95.93% capacitance retention after 10,000 cycles in 6 M KOH electrolyte.

Introduction

Supercapacitor has aroused more and more attention because of the rapid charge-discharge rate, good stability and high power density(Kundu et al. 2019). And its performance is governed greatly by the electrode materials(Chen et al. 2019). At present, the electrode materials of supercapacitors are mainly divided into three types: carbon-based materials(Huang et al. 2019), metal oxide materials(Lee and Jang 2019), and conductive polymer materials(Xu et al. 2019). Among them, carbon-based materials as the promising commercial electrode materials attract great attention. As we all know, various carbon materials, such as activated carbons, carbon fibers, carbon nanotubes, carbon nanocages, and graphene have been investigated widely as electrode materials for supercapacitors (Borenstein et al. 2017). Graphene materials are ideal electrode materials due to their good electrical conductivity, stable electrochemical stability, and high theoretical specific surface area (Zhang and Samorì 2017). However, the stacking effect between the graphene sheets results in a partial loss of specific surface area. Therefore, many efforts have been devoted to increasing the surface area of the electrode material and improving the electrochemical performance of the supercapacitor without impairing the properties of the graphene material. Here, we use a template method coupled with *in-situ* activation of KOH to obtain graphene-like two-dimensional lamellar porous carbon materials (LPCs) from fluorene. The fluorene is uniformly mixed with KOH and $\text{Mg}(\text{OH})_2$. Then, the fluorene molecules are polymerized to form LPCs at high temperature. Finally, the template was removed by acid washing to obtain LPCs. This kind of thin LPCs contains abundant hierarchical pores in which most of them are small aspect ratio pores. The structure is favorable for the adsorption and desorption of electrolyte ions and rapid transmission, and ultimately enhances the ability of the supercapacitor to store charge ions (He et al. 2016).

Experimental

Fluorene was purchased from Aladdin Co. Ltd., KOH and $\text{Mg}(\text{OH})_2$ were obtained from Sinopharm Co. Ltd.. During the experiment, 12.0 g $\text{Mg}(\text{OH})_2$ and 12.0 g KOH were ground, respectively. Then it was mixed with 6.0 g fluorene and ground evenly to obtain a mixture. The resulting mixture was heated to $120 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C min}^{-1}$ for 30 min in flowing argon of 15 mL min^{-1} , followed by being heated to $400 \text{ }^\circ\text{C}$ for 30 min and the last heated to $900 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C min}^{-1}$ and kept for 60 min. After naturally cooling down to room temperature, the as-prepared sample was stirred in 2 M HCl aqueous solutions for 12 hours and then

repeatedly washed and filtered with hot deionized water. The as-prepared LPC is named as LPC₂, where the subscript 2 stands for the mass ratio of KOH to fluorene. Similarly, the LPC_{2.5} and LPC₃ represent the mass ratio of KOH to fluorene were 2.5 and 3 under the same conditions. The morphology of LPCs and Mg(OH)₂ were examined by transmission electron microscopy (TEM, JEOL-2100). The nitrogen adsorption-desorption isotherms of LPCs pore structure were obtained at 77 K. The X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250, USA) were used to analyze the chemical bonding states of the elements in LPCs. The electrochemical performance of the as-prepared LPCs was tested by a two-electrode cell. The electrodes were prepared by mixing LPCs and polytetrafluoroethylene (PTFE) in a mass ratio of 9:1, and made into a round sheet, then dried at 110 ° C for 2 hours in vacuum. Finally, the circular sheet was pressed onto the nickel foam to form a supercapacitor electrode. The electrode was immersed in a 6 M KOH aqueous electrolyte, and two similar electrodes were assembled into a button-type supercapacitor. The cyclic voltammetry (CV) and galvanostatic charge-discharge was performed on CHI760C electrochemical workstation (CH Instrument) and supercapacitance test system (SCTs, Arbin Instruments), respectively.

Results And Discussion

Figure 1 shows the TEM images of Mg(OH)₂ templates precursor and LPCs. The TEM image of Mg(OH)₂ precursor exhibits a sheet-like structure with the size ranging from 500 to 1000 nm as shown in Fig. 1(a). Figure 1(b-d) shows the TEM of LPC₂, LPC_{2.5} and LPC₃, respectively. It can be seen clearly that the as-prepared LPCs exhibits a large lamellar structure with a small portion of wrinkles. This structure can help to increase the specific surface area and electrical conductivity of LPCs. The pores in the lamellar structure of LPCs are short pores, which is important for improving the rate performance of the supercapacitor (He et al. 2016).

The nitrogen adsorption was used to characterize the pore structure. As shown in Fig. 2(a), all the samples show I type and IV type curves with a steep uptakes ($P/P_0 < 0.01$) and has a small hysteresis loop ($0.4 < P/P_0 < 1.0$), indicating the presence of micropores and mesopores in the LPCs (Tang et al. 2017). Figure 2(b) shows the pore size distribution curve of the LPCs, which contains a large number of micropores with diameter of 1–2 nm and a small amount of mesopores with diameter of 2–5 nm. The detailed pore structure parameters of LPCs are listed in Table 1. The average pore size of LPCs is between 2.22 and 2.45 nm. And LPC_{2.5} exhibits the largest surface area, which is due to the appropriate amount of KOH. The specific surface area of LPC_{2.5} reaches 1879 m² g⁻¹, which is higher than that of LPC₂ and LPC₃. The specific surface area of the LPCs increases at first and then decreases with the increase of the alkali dosage. When KOH is excessive, it will cause large etching of the carbon material and collapse of the cell walls, which will result in less specific surface area of the material. These results indicate that the pore structure of LPCs can be adjusted by changing the mass ratio of carbon source to active agent appropriately.

Figure 2(c) shows the XPS survey spectrum of three LPCs. It can be seen clearly that the two peaks are Cls and Ols, respectively. Figure 2(d) shows the Ols orbital analysis of the sample of LPC_{2.5}, which mainly contain C = O (531.9 eV) and C-O (533.4 eV) functional groups. The oxygen-containing functional groups are expected to increase the wettability of the materials (Wang et al. 2017).

The electrochemical performance of LPCs as electrode materials for supercapacitor were tested in 6 M KOH electrolyte. Figure 3(a) shows the galvanostatic charge-discharge curves of the LPC electrodes at 1 A g⁻¹ current density. All the GCD curves show equicrural triangle shape, which shows that LPC as the electrode material has the ideal capacitance behavior and no obvious pseudocapacitance behavior. In addition, the IR drop of LPC_{2.5} is only 0.0032 V, indicating that the internal impedance of LPC_{2.5} is small (Zhang et al. 2017). Figure 3(b) shows the variation of the specific capacitance of LPC electrodes vs. the discharge current density. It can be found that the specific capacitance decreases slowly with the increase of current density from 0.05 A g⁻¹ to 100 A g⁻¹. Obviously, the LPC_{2.5} electrode shows the biggest specific capacitance among the LPC electrodes, which is reached 231 F g⁻¹ at 0.05 A g⁻¹. When the discharge current density is increased to 100 A g⁻¹, the capacitance of the LPC_{2.5} remains 173 F g⁻¹, indicating an outstanding rate capability. The excellent performance of LPC_{2.5} is ascribed to its high surface area, well-balanced micropores and mesopores for ion fast transport and storage, and as well as thin layered structures in LPC materials help to achieve good electron conduction. Figure 3(c) shows the Ragone plots of LPC electrodes in 6 M KOH aqueous electrolyte. The energy density of LPC_{2.5} capacitor reaches 8.03 Wh kg⁻¹ at 0.05 A g⁻¹ and 5.35 Wh kg⁻¹ at 100 A g⁻¹, with the energy density retention of 66.63%. The high energy retention of LPC_{2.5} capacitor is attributed to the highest electrical conductivity and the lamellar structure (Choudhary et al. 2017). In addition, LPC_{2.5}-based device also exhibit excellent cycling stability as demonstrated in Fig. 3(d). The capacitance retention of LPC_{2.5} is up to 95.93% after 10,000 cycles.

Conclusions

LPCs were successfully synthesized from small fluorene by layered Mg(OH)₂ template coupling with *in-situ* KOH activation. The LPCs exhibit high capacitance (231 F g⁻¹ at 0.05 A g⁻¹), good rate performance (173 F g⁻¹ at 100 A g⁻¹), and excellent cycle stability (95.93% capacitance retention after 10,000 cycles at 5 A g⁻¹). This new approach has great research potential for large-scale industrial production of promising LPCs from solid polycyclic hydrocarbon molecules for supercapacitors.

Declarations

Acknowledgments

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Table

Table 1. The pore structure parameters of LPCs.

Samples	D_{ap} (nm)	S_{BET} ($m^2 g^{-1}$)	V_t ($cm^3 g^{-1}$)	V_{mic} ($cm^3 g^{-1}$)
LPC ₂	2.45	1640	1.00	0.106
LPC _{2.5}	2.22	1879	1.04	0.144
LPC ₃	2.39	1394	0.83	0.077

Figures

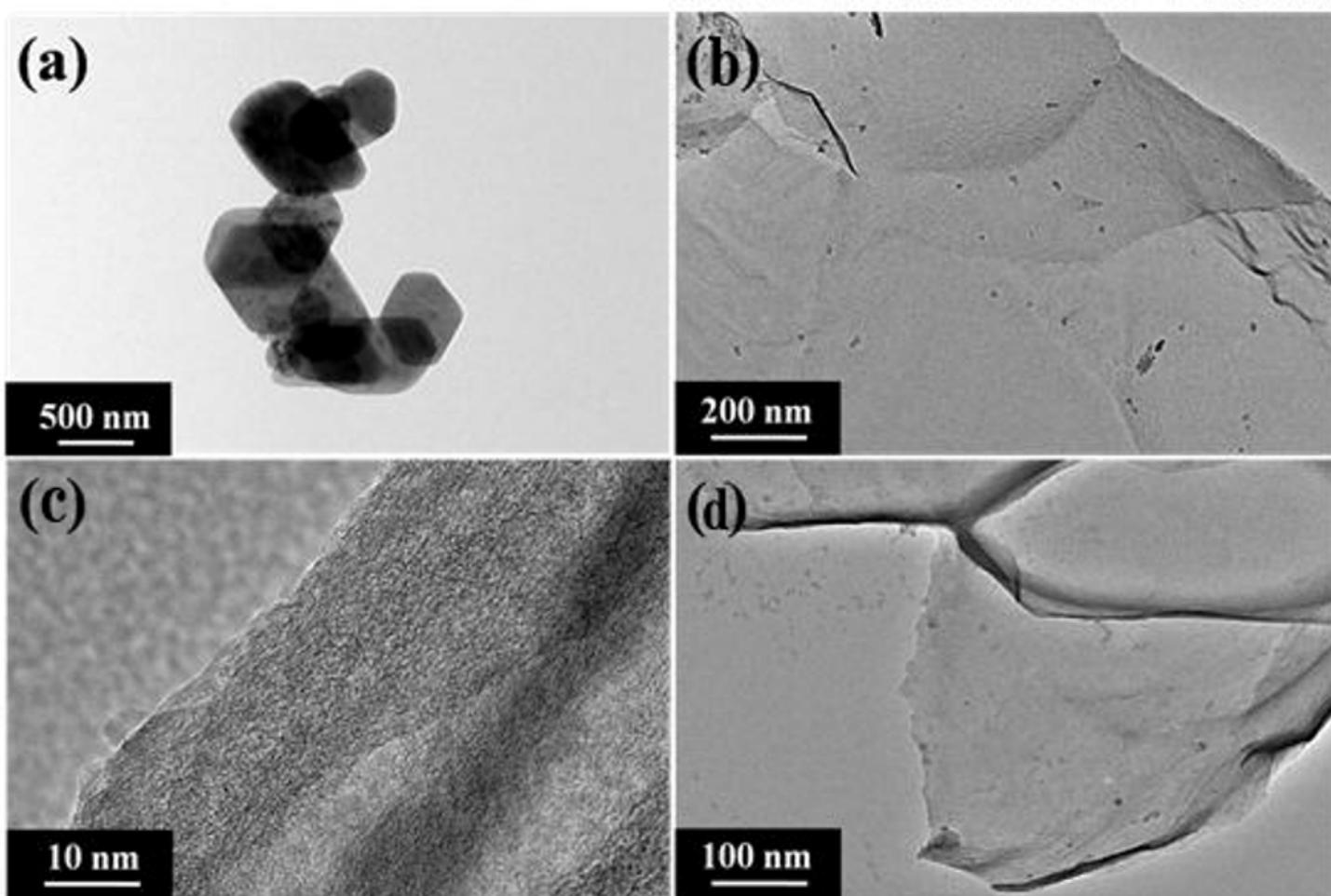


Figure 1

(a) TEM image of Mg(OH)₂; (b) TEM image of LPC₂; (c) TEM image of LPC_{2.5}; (d) TEM image of LPC₃.

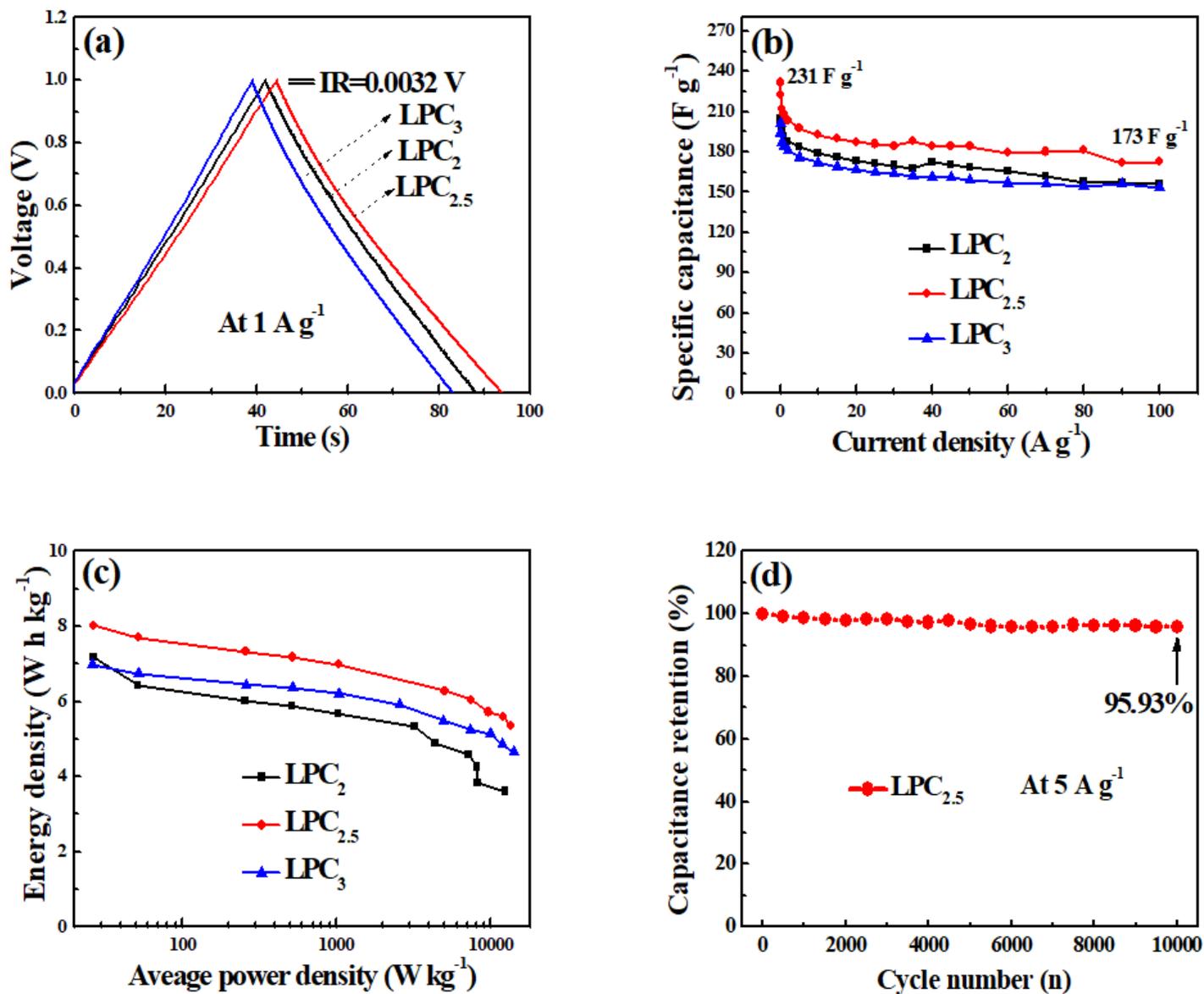


Figure 2

(a) N₂ absorption/desorption isotherms of LPCs; (b) pore size distribution curves of LPCs; (c) XPS spectra of LPCs; (d) O1s spectrum of LPC_{2.5}.

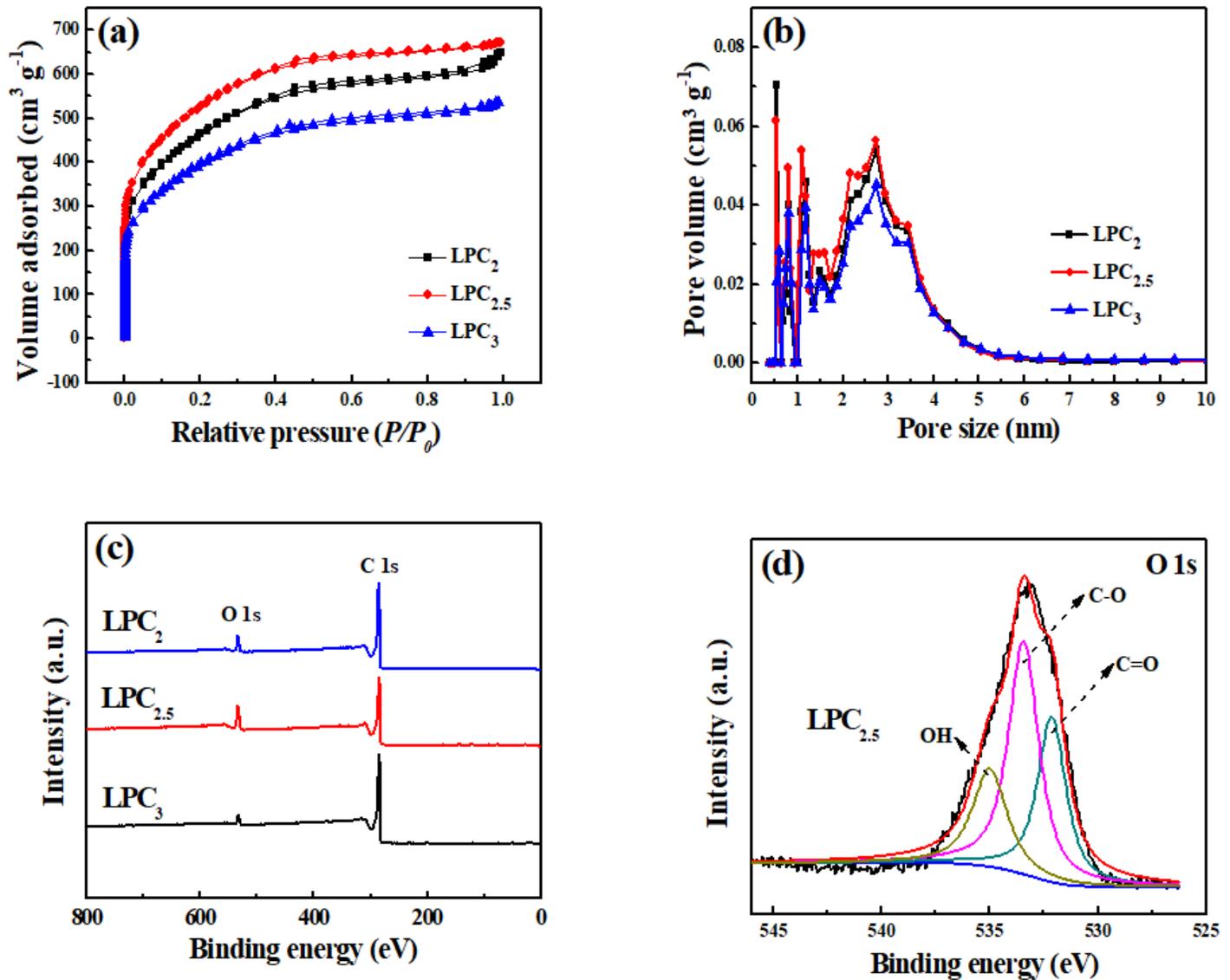


Figure 3

(a) Charge/discharge curves of LPCs; (b) specific capacitance of LPCs at different current densities; (c) ragone plot of LPCs; (d) capacitance retention of LPC2.5 after 10000 cycles.

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