

Size Engineering of Graphene Shells by Template CVD Method

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Introduction

Carbon nano-shell structure material has unique spatial structure of nanomaterials and has been widely used in catalysis, energy storage batteries, photoelectric conversion and water treatment. The last project confirmed that graphene shell (50nm) has great electrochemical performance (high specific capacity, stability, etc.) as anode materials in lithium-ion batteries. This project used the hard template method to synthesize graphene shell material of different size in constant hours and characterizes the morphology properties. A lithium-ion battery with multi-layer graphene shell as anode materials was constructed and electrochemical tests were carried out to explore the synergy effects of graphene shells' size on its morphology properties and electrochemical performance.

Experimental Section

4.0 g nanostructured MgO of three different size (10nm, 50nm, 200nm) is evenly put on the quartz boat, followed by heating treatment in atmosphere of Ar at a flow rate of 200 mL/min for 1h, 3h and 6h respectively. The reactions are constructed at a temperature of 800 °C, followed by cooling down to room temperature under the Ar flow. The graphene shell (GS) samples of nine different conditions are finally obtained by acid treatment in 1 M/L HCl.

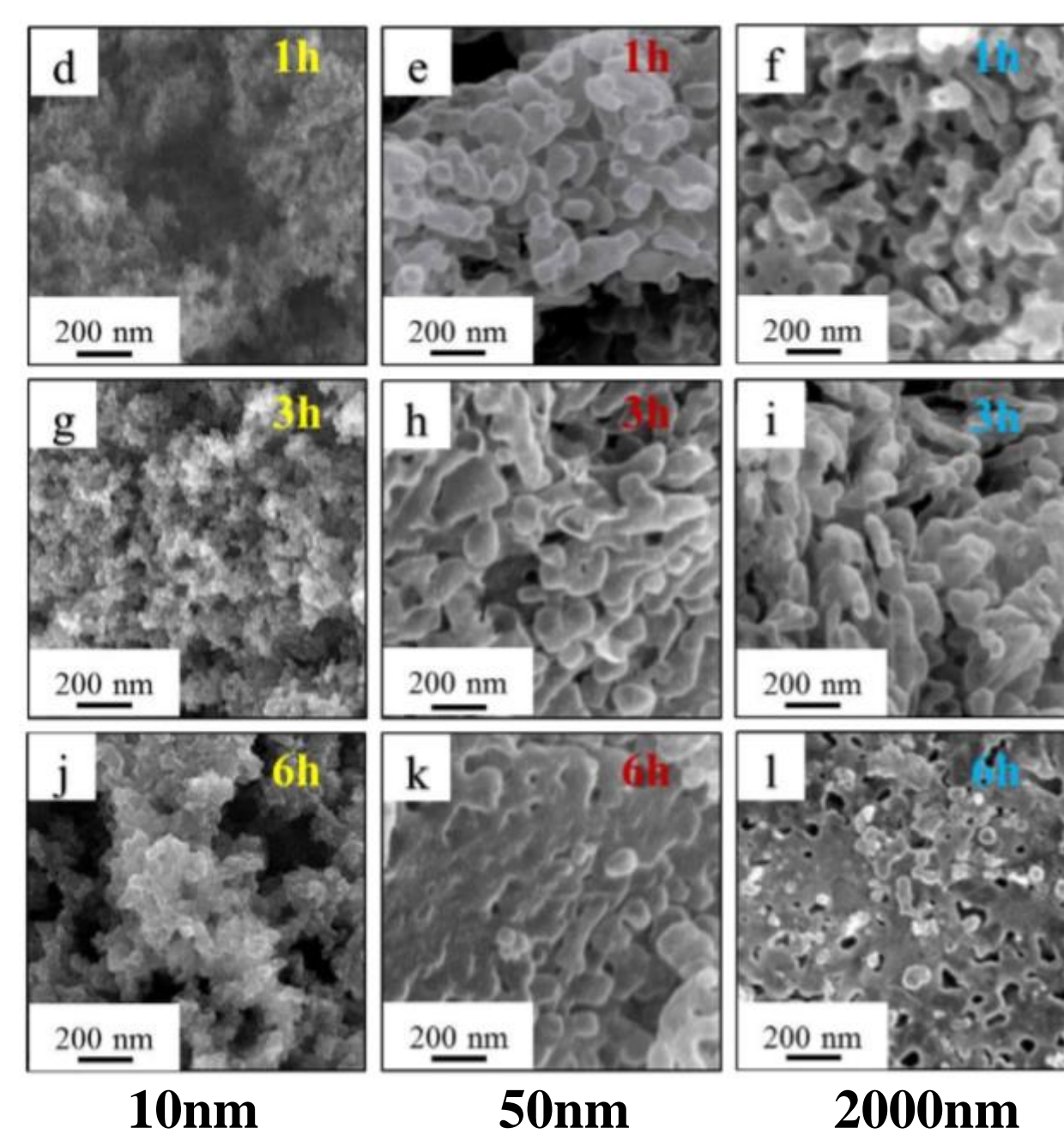


Figure 1. SEM images of (a-c) MgO and GS obtained at (d-f) 1h, (g-i) 3h, and (j-l) 6h, respectively, sizes from left to right are 10nm, 50nm, 200nm.

Results and Discussions

Morphology Characterization

By the reaction time increasing, samples of three sizes all show a decrease in graininess and share a joint-growth trend. Single particles still can be observed faintly in GS of 3 hour, while the boundaries between grains starts to merge. By 6 hour, three samples are all flaky, which means particles have been organized into layers and start to form bulks. TEM images clearly show that as the growth time increases, all size particles appear a similar channel-structure and tend to start fusion growth and less time will be taken to achieve this trend with size of GS increase.

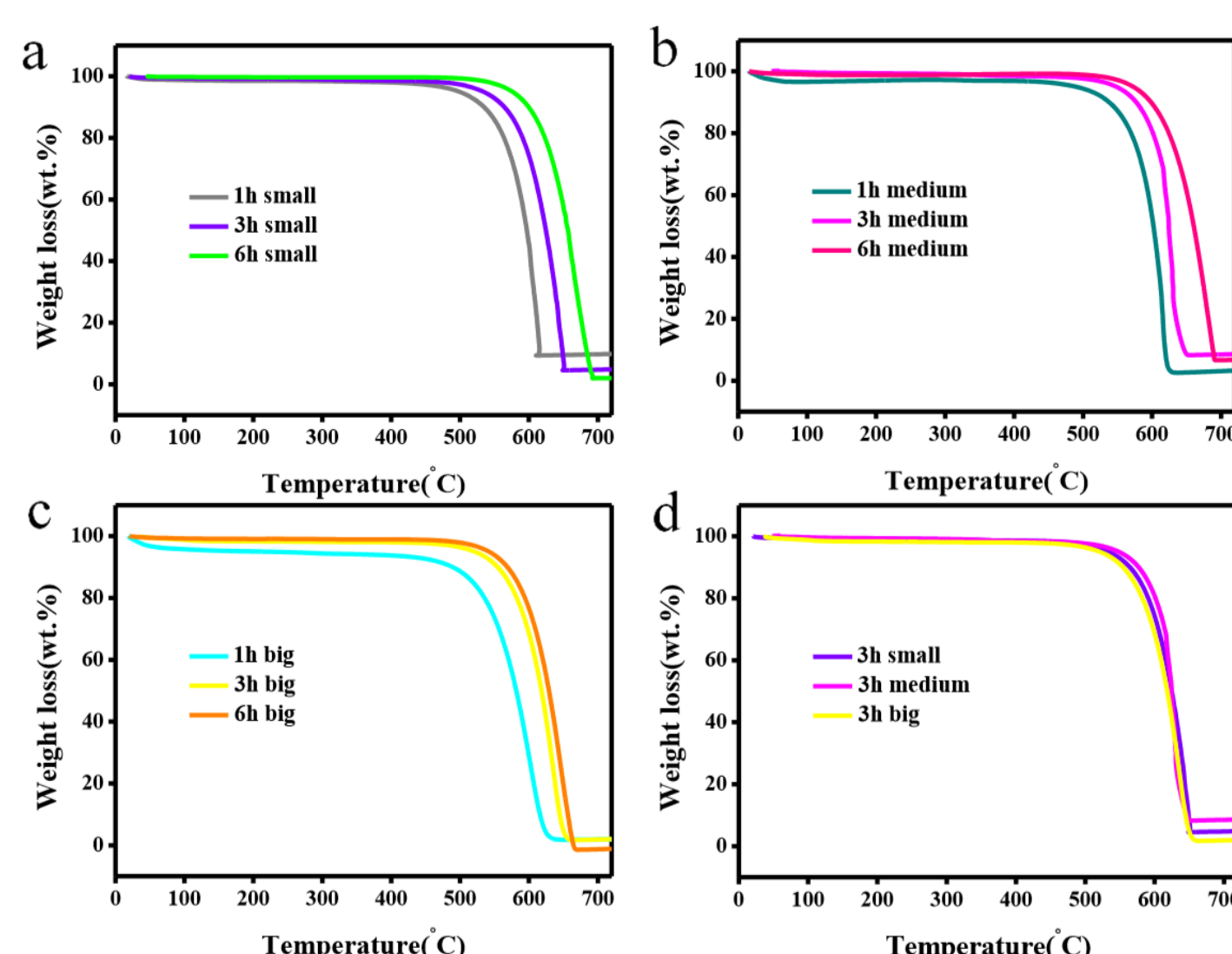


Figure 3. Thermogravimetric curves of graphene shells at three hours (1,3,6h) of (a) 10nm; (b) 50nm; (c) 200nm. (d) Thermogravimetric curves of three sizes at 3h.

Figure 3 shows thermogravimetric characterization of graphene shells. With the increase of the reaction time, the weight loss curve of graphene shells of same size sample shifts backward, indicating an increase of the degree of defects and graphitization, which is consistent with the results of morphological characterization.

Figure 4 is the Raman analysis of graphene shells. As the growth time increases, each particles tends to connect with each other and forms large secondary particles, resulting in an increasing overall size, a smaller energy gap, and a red-shifted spectral line.

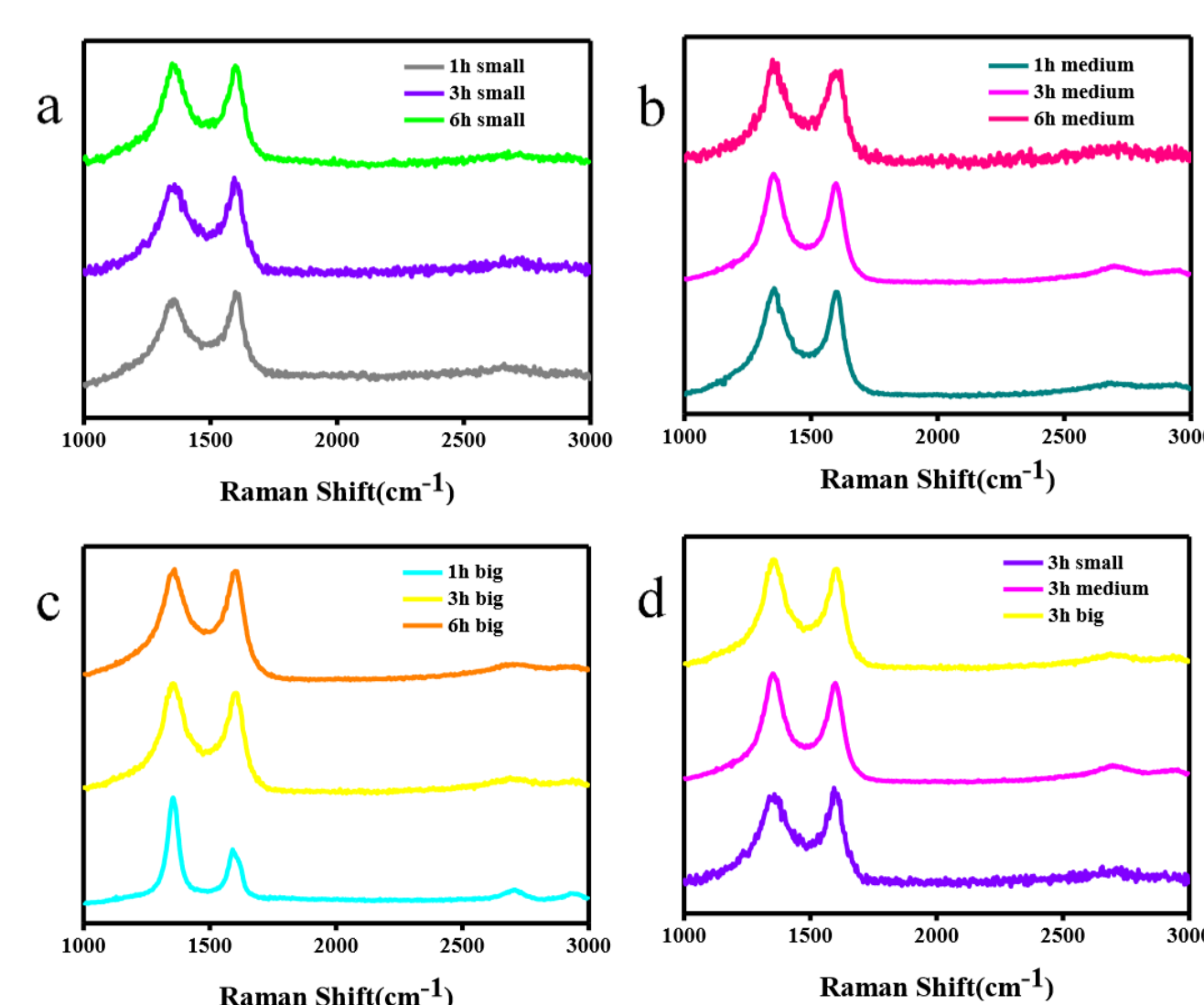


Figure 4. Raman spectra graphene shells at three hours (1,3,6h) of (a) 10nm; (b) 50nm; (c) 200nm. (d) Raman spectra of three size at 3h.

Conclusions

This project has realized the controllable preparation of graphene shells by adjusting reaction time and templates' size: anode materials with different layer numbers and sizes can be synthesized as required. The growth mechanism of graphite shells is explored: material particles increase their layer numbers rapidly and focus on connecting with each other into layers within three hours, while after that, layers overlap to form bulks. Within a same growing hour, layer number of a single graphene shell increase with size, resulting in the specific capacity of graphene shells show a bell-curve mode at a high current density.

Electrochemical Performance

* Electrochemical performance of GS of different hours in three size respectively

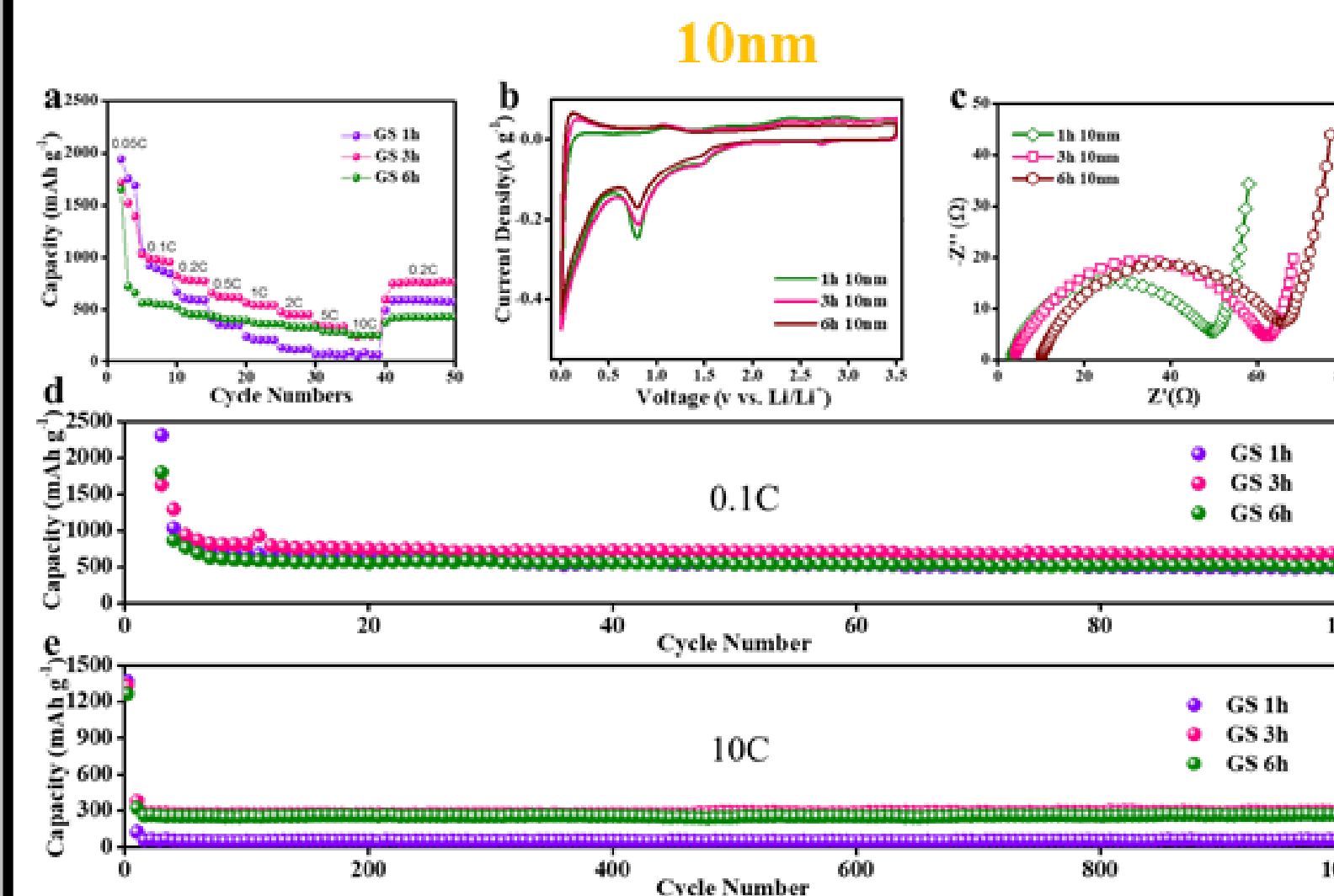


Figure 5. Electrochemical performance of GS (10nm) of different hours (a) Rate. (b) CV curves. (c) EIS. Long-term cycling at a current density of (d) 0.1C; (e) 10C.

The electrochemical properties of GSs, which prepared by templates in three size (10nm, 50nm, 200nm) and each heated by different hours separately, as anode material in Lithium-ion batteries have been evaluated by charge-discharge cycling, cyclic voltammetry and electrochemical impedance.

Electrochemical tests show no matter the size of the template material, graphene shells heated at 800 °C with 3 hours always have a best electrochemical performance compared with GS of other hours, including an outstanding large specific capacity (both at current density of 0.1C and 10C), better rate performance and lower impedance values.

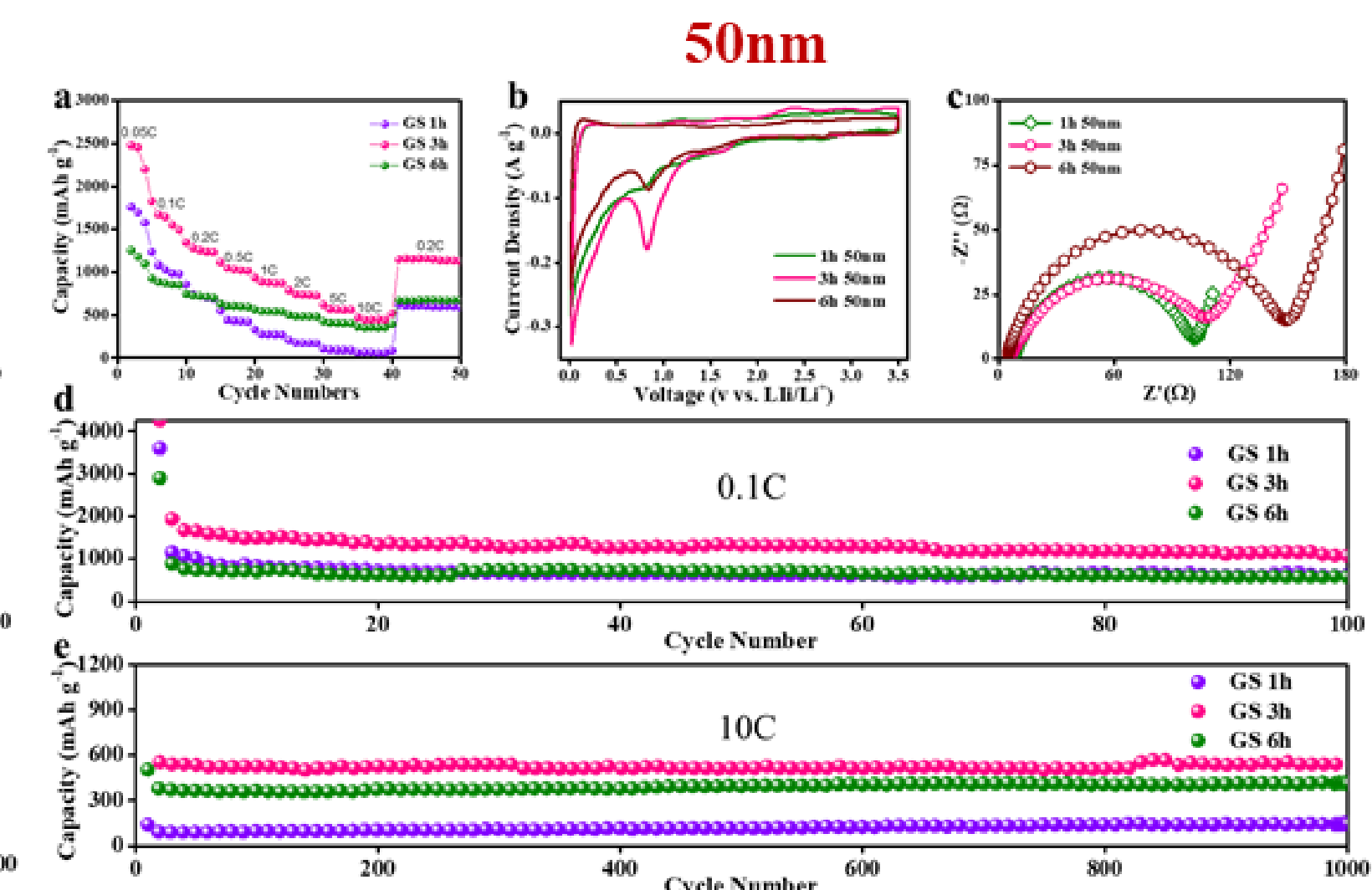


Figure 6. Electrochemical performance of GS (50nm) of different hours (a) Rate. (b) CV curves. (c) EIS. Long-term cycling at a current density of (d) 0.1C; (e) 10C.

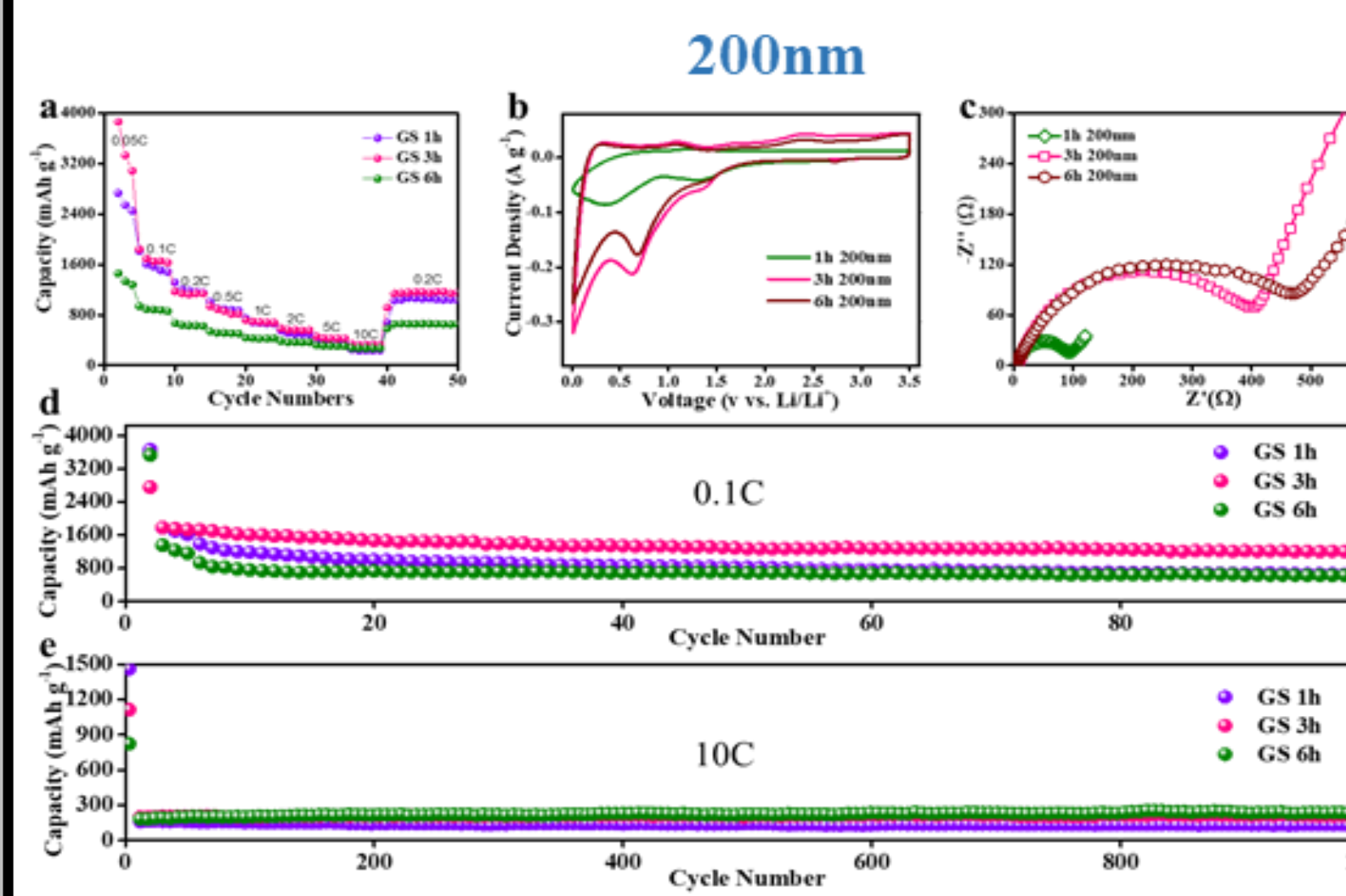


Figure 7. Electrochemical performance of GS (200nm) of different hours (a) Rate. (b) CV curves. (c) EIS. Long-term cycling at a current density of (d) 0.1C; (e) 10C.

As shown in Figures 5, 6, and 7, graphene shells of one hour in different size all have a great specific capacity when charging-discharging at a current density of 0.1C, while keep the worst capacity at a current density of 10C. This is because one-hour heating time is quite short for particles to grow enough layers in their surface or connect with each other to form pieces. Thus shell structure is relatively fragile at that time and not resistant to the rapid desorption and insertion of lithium-ions.

* Electrochemical performance of GS (3h) in different size

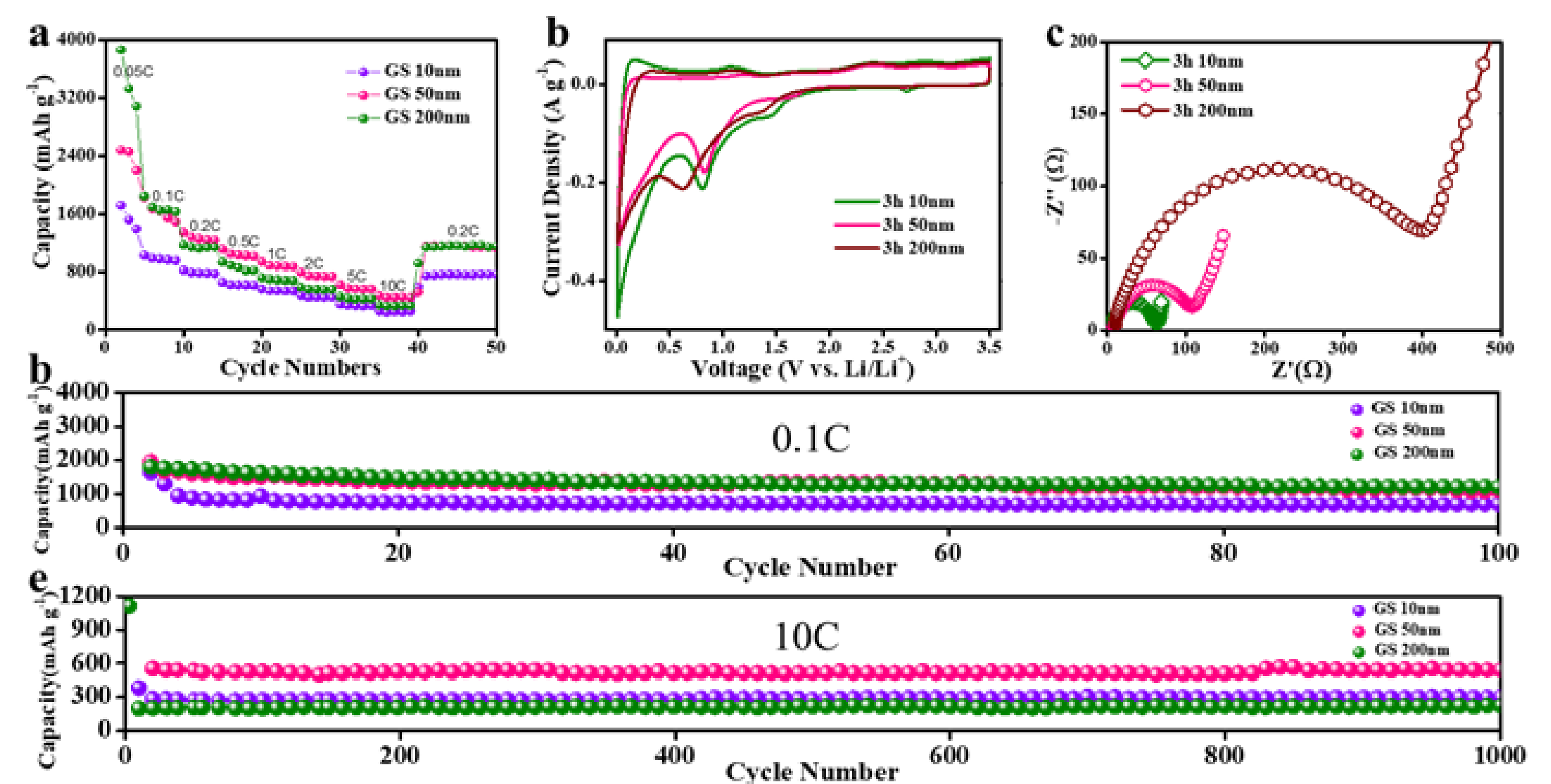


Figure 8. Electrochemical performance of GS (3h) of different sizes (a) Rate. (b) CV curves. (c) EIS. Long-term cycling at a current density of (d) 0.1C; (e) 10C.

Graphene shells of 50nm of three hours have an optimal electrochemical performance in three sizes, including the most outstanding large specific capacity (both at current density of 0.1C and 10C), better rate performance and lower impedance values. This is because graphene shells in small size have high degree of granulation and lack channels between particles, thus the propagation speed of lithium-ions is relatively slow; while graphene particles with large size are almost completely stacked into a sheet, which result in a reduced squeeze between layers and a weakened lithium storage space.