Functionalized Composite based on Graphene & its application in Energy Storage

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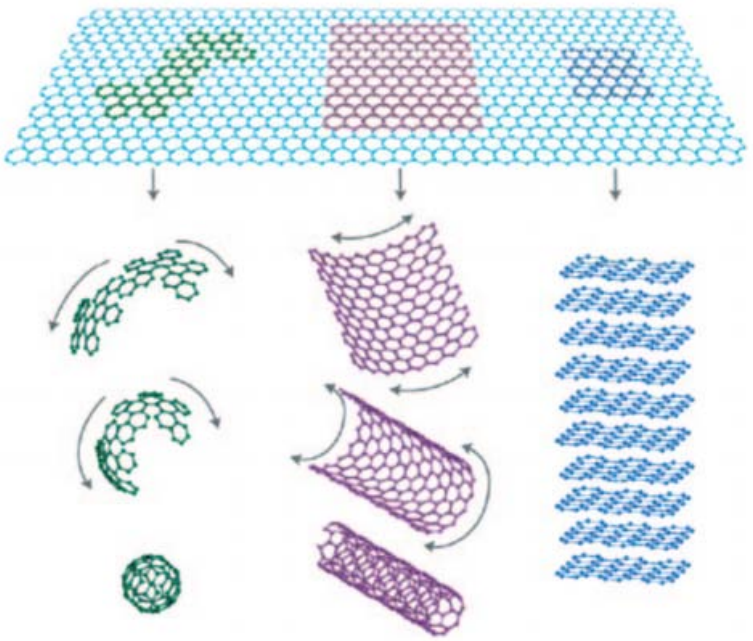
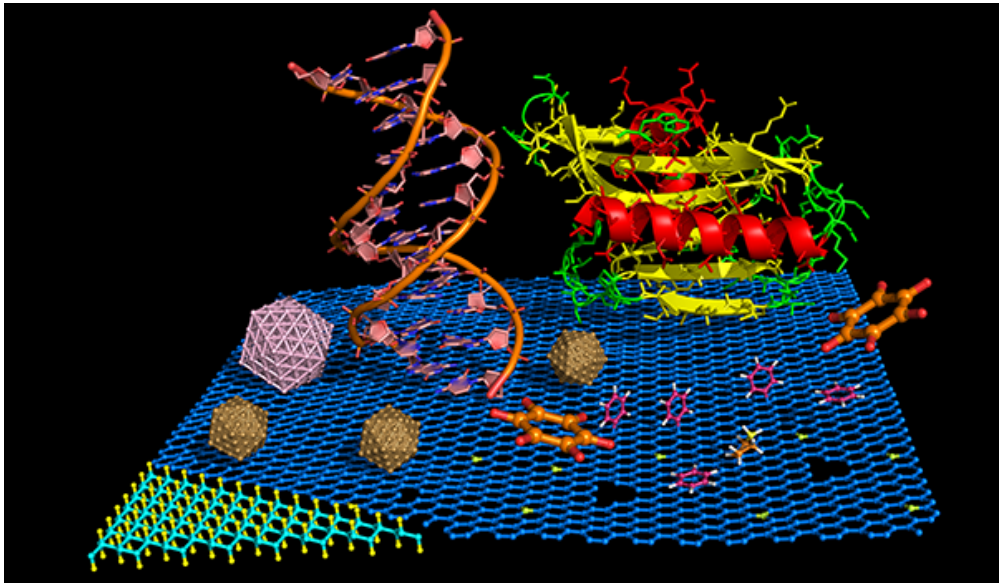
Outline

- Background introduction
- The roles of graphene in energy storage system
- The recent work in our lab.

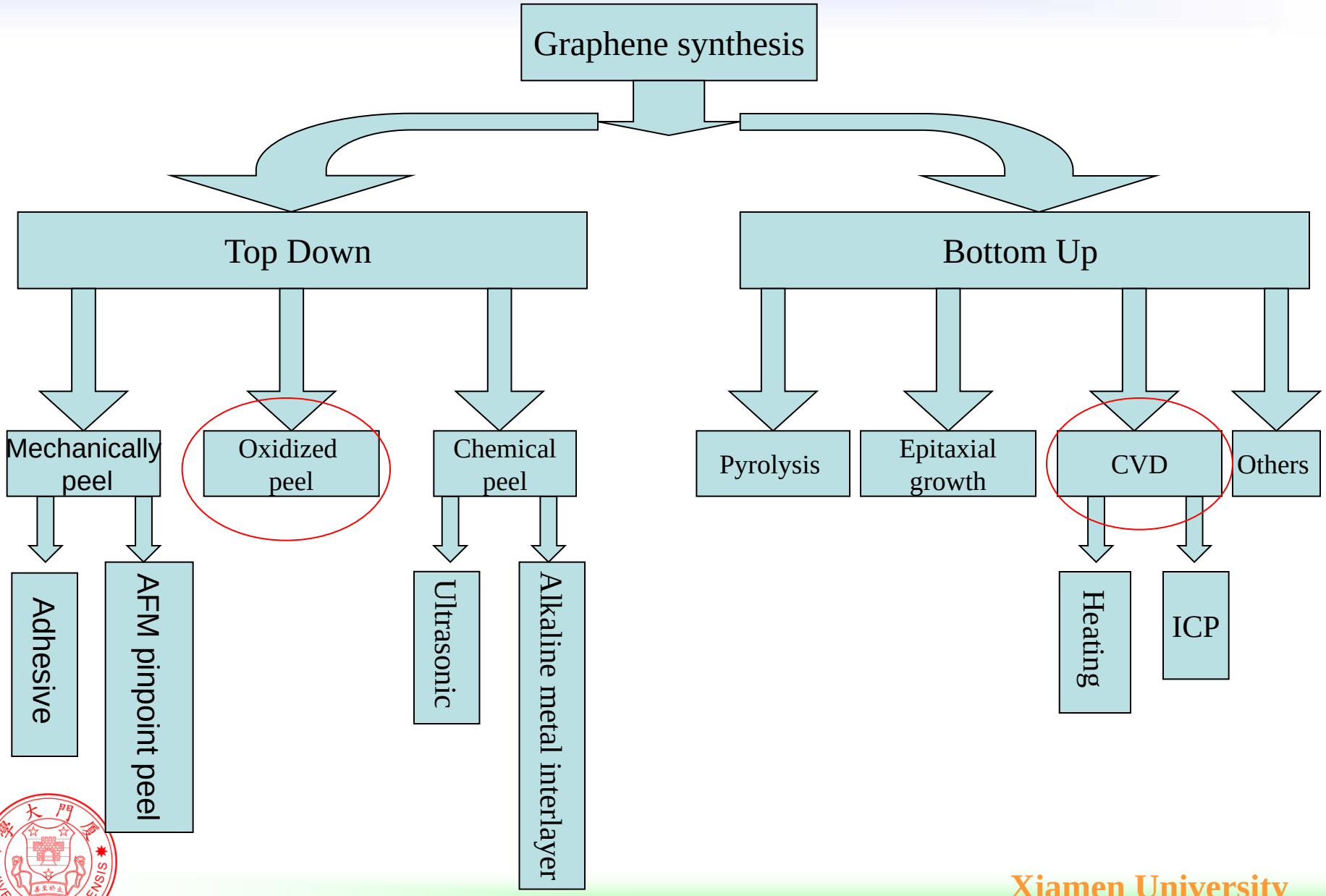
Graphene, the two-dimensional *sp*^{2}-hybridized carbon, is currently, without any doubt, the most intensively studied material.



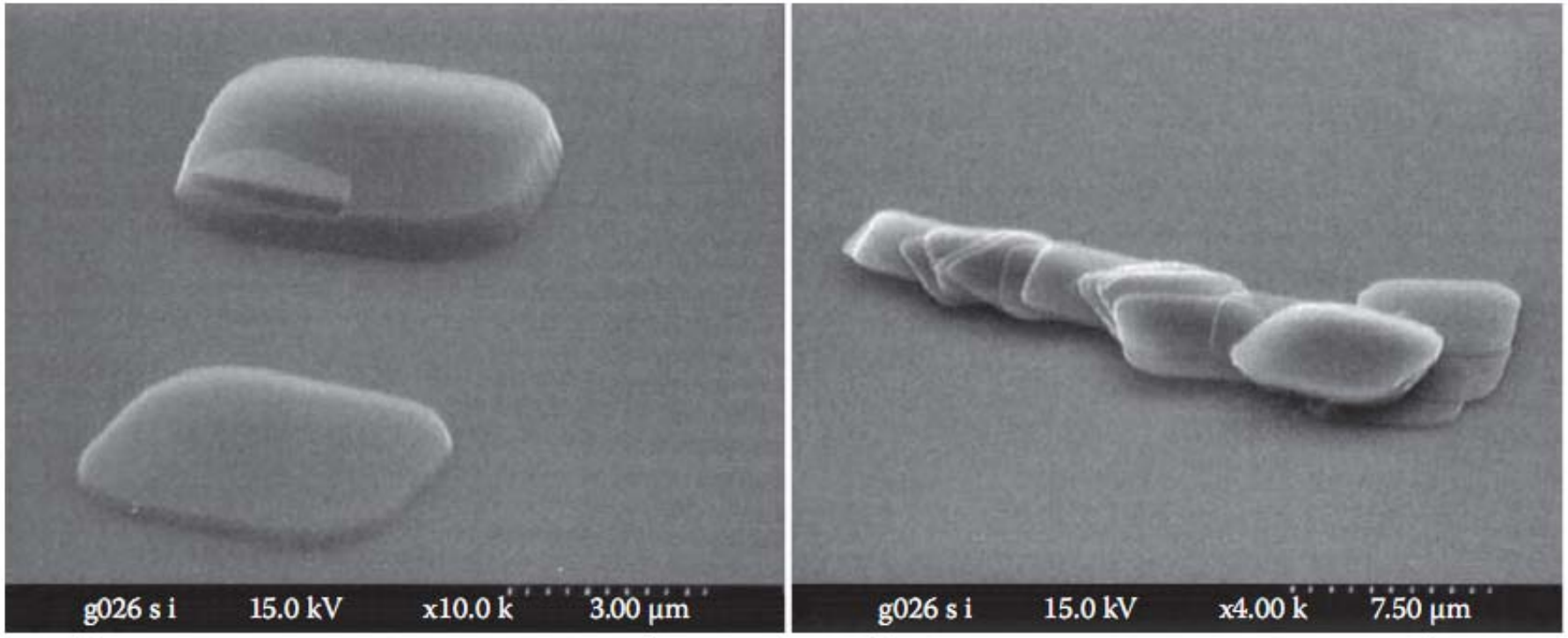


Graphene has potential applications in many fields, such as energy storage systems, nano-based electronic devices, conductive thin film, chemical sensors, catalyst etc.

Synthesis for graphene



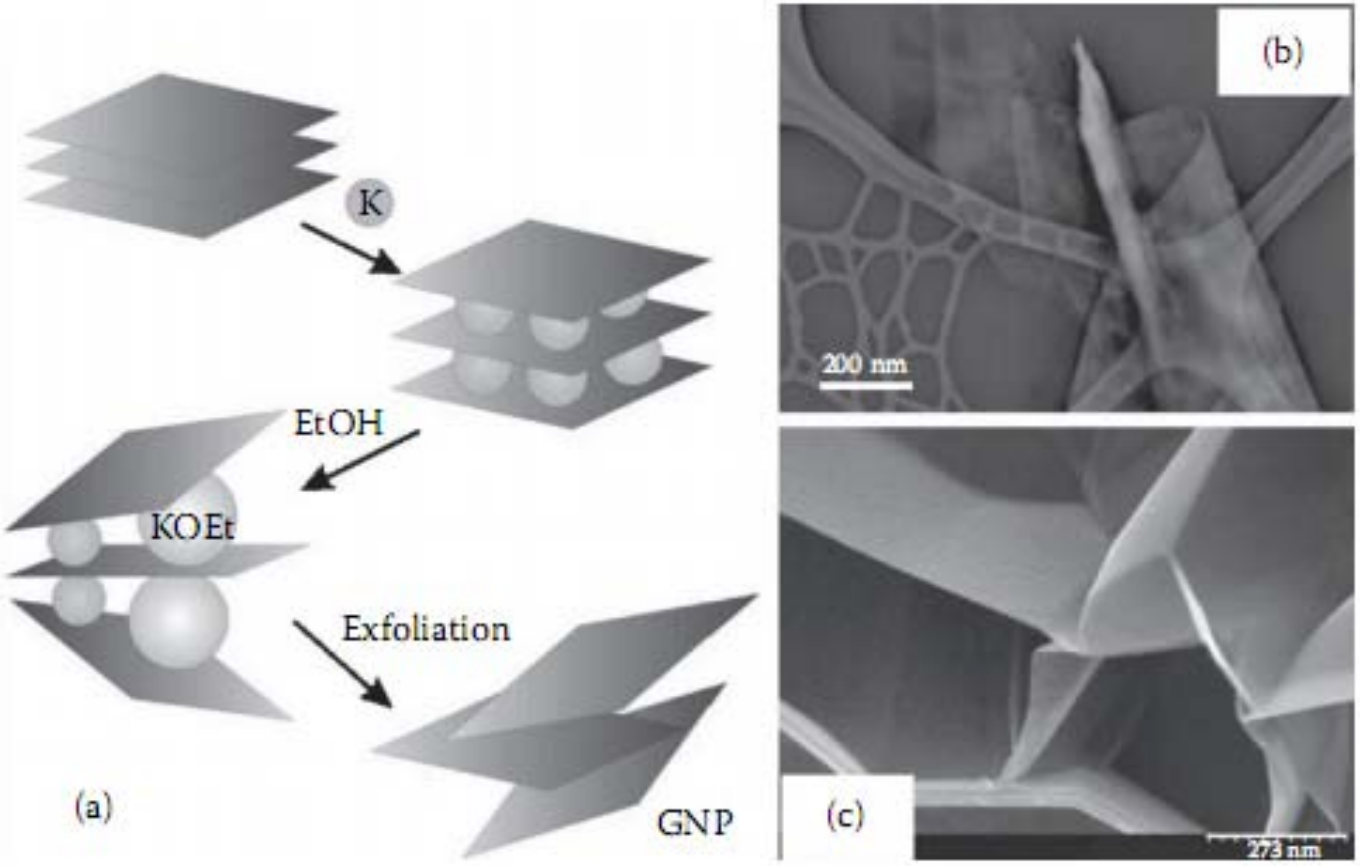
For example, mechanically peel



(a) (b)

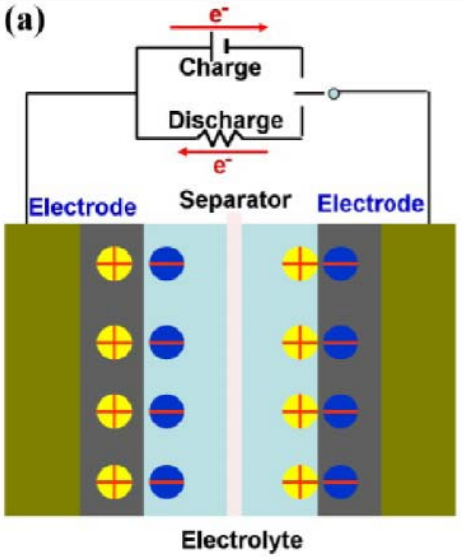
SEM of thin graphite layer peeled by AFM pinpoint on HOPG surface

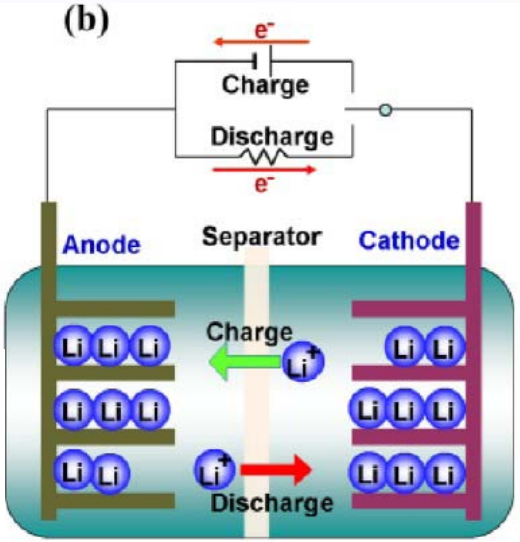
For example, chemical peel

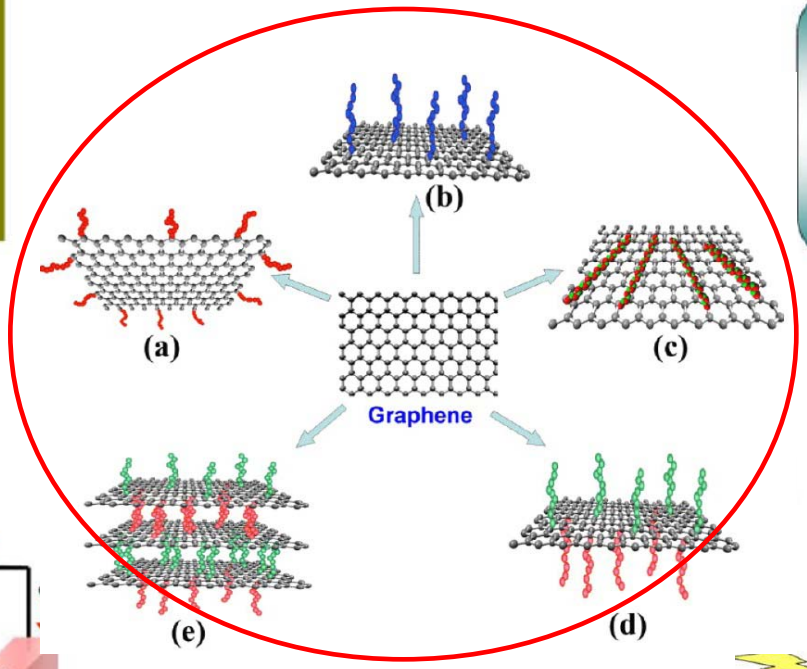


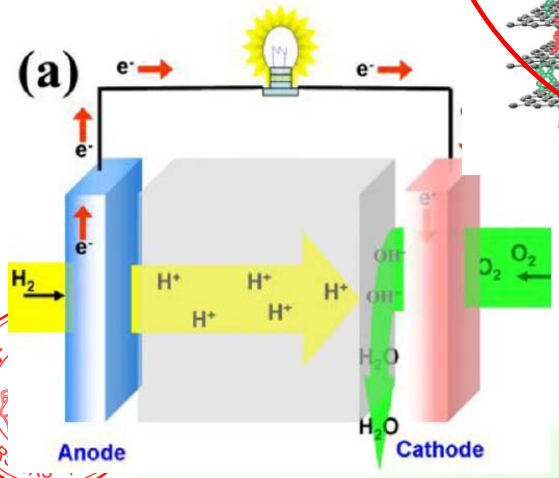
Schematic of chemical peel by alkaline metal and the TEM and SEM of final productions

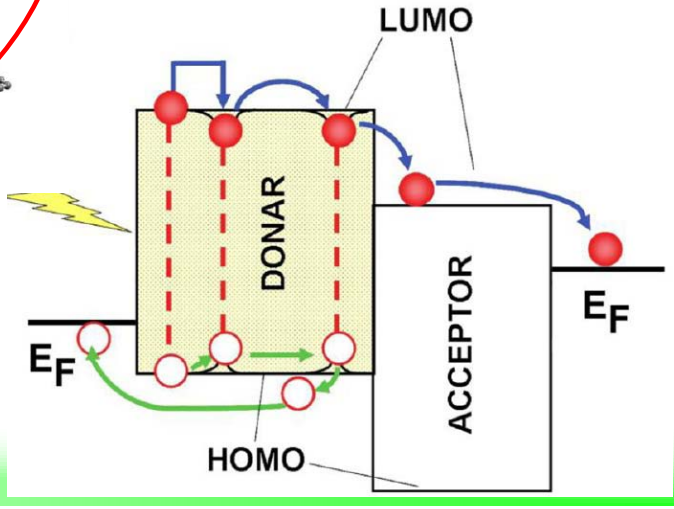
The main applications of graphene-based in energy storage/conversion







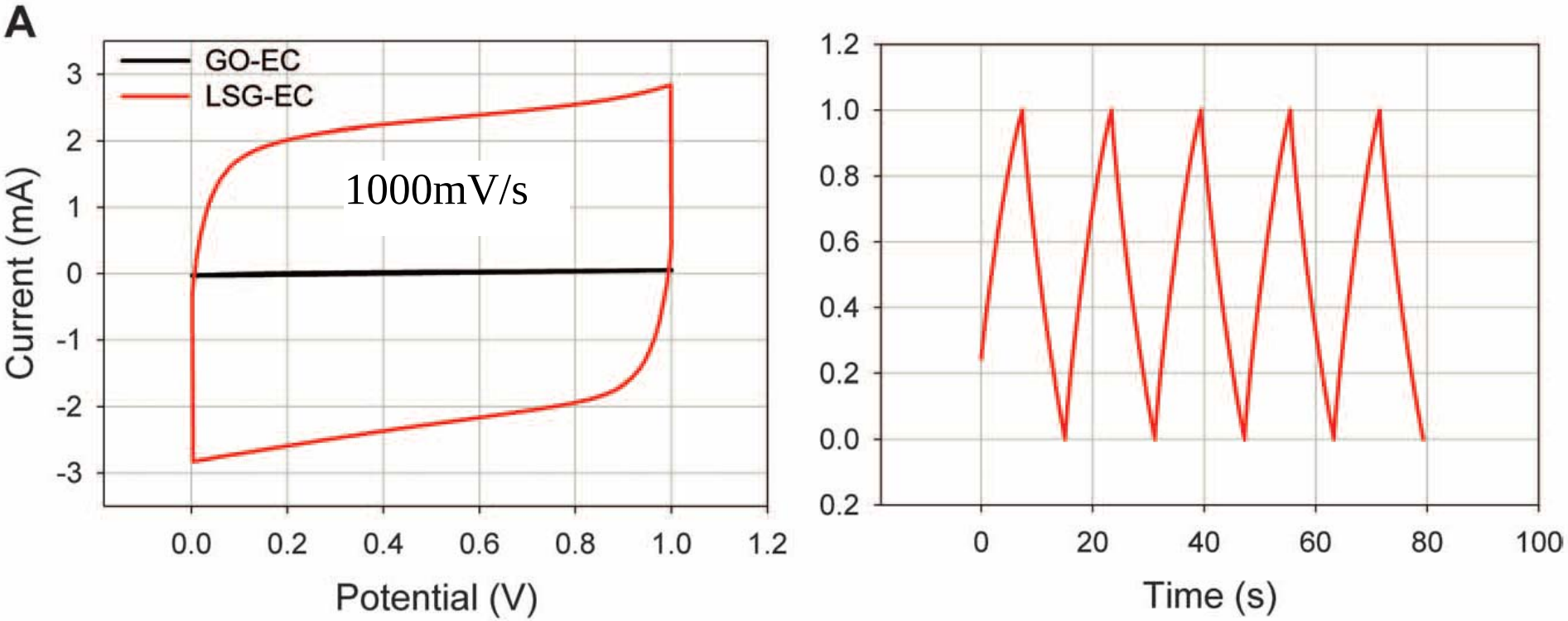




The roles in electrochemical storage & conversion system

- As active materials
- To construct electron conductive matrix
- The control & design of the reaction states for active materials

As active materials, supercapacitor



Evaluation of the performance of an LSG electrochemical capacitor in aqueous 1.0 M H3PO4 solution. (A) Cyclic voltammetry of LSG- and GO-ECs at a scan rate of 1000 mV/s. A rectangular CV shape is observed for the LSG-EC, indicating an efficient double-layer formation. (B) Galvanostatic charge/discharge (CC) curves of an LSG-EC measured at a high current density of 10 A/gLSG/electrode

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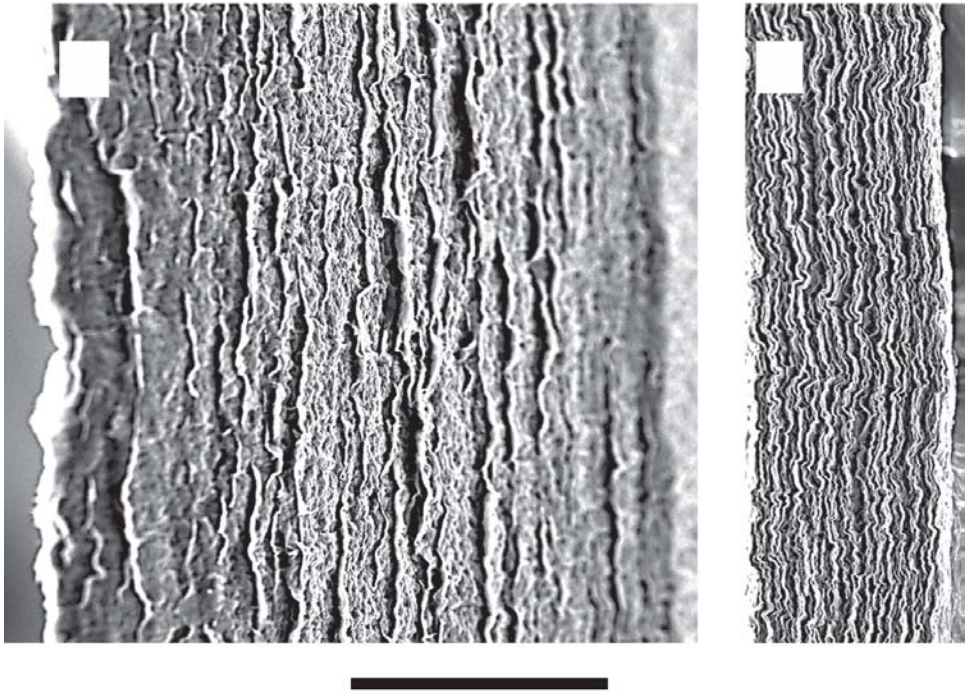
As active materials, supercapacitor---compact capacitive energy storage based on graphene



Liquid-Mediated Dense Integration of Graphene Materials for Compact Capacitive Energy Storage

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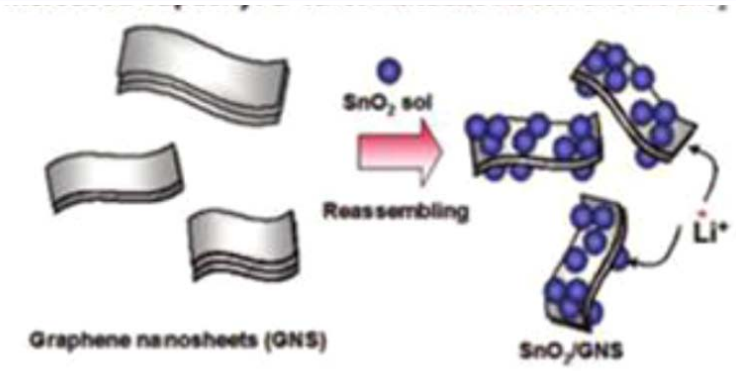
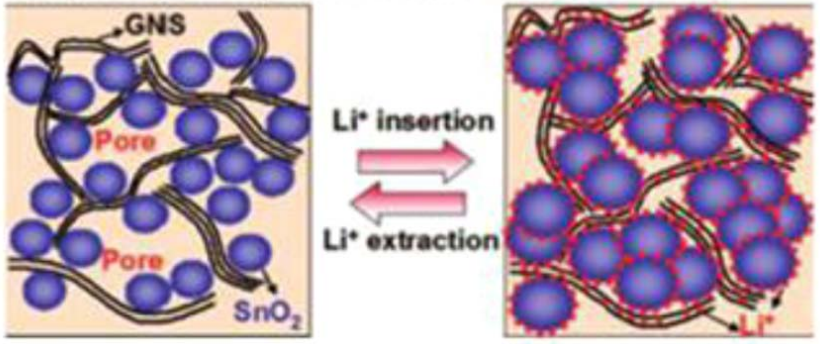
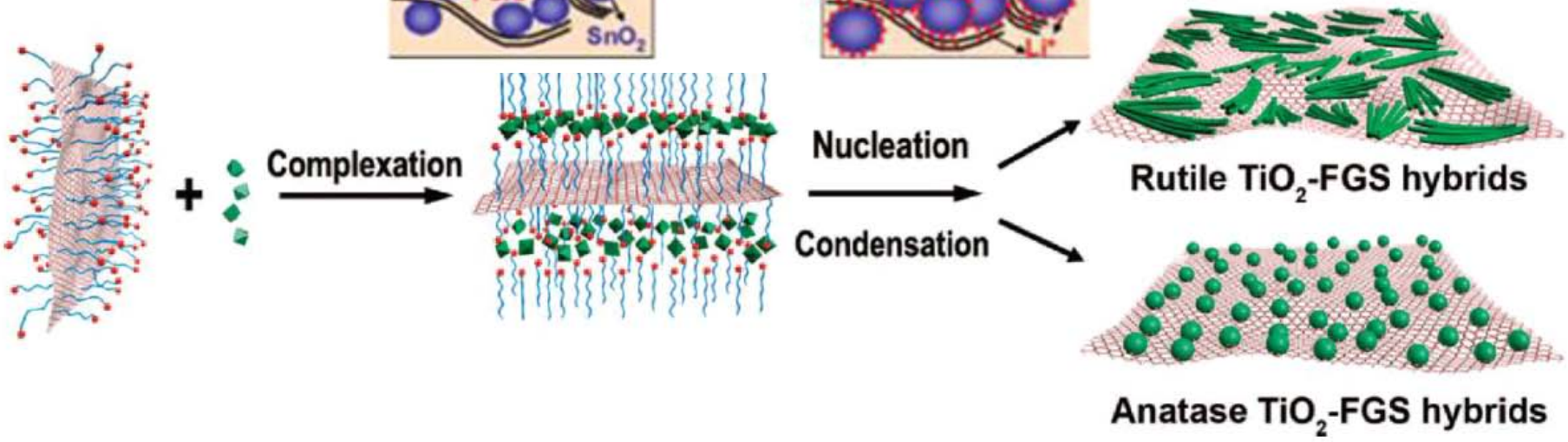
To build an electronic conductive matrix & control the reactive states of activ materials



Enhanced cyclability via 3-D flexible structure



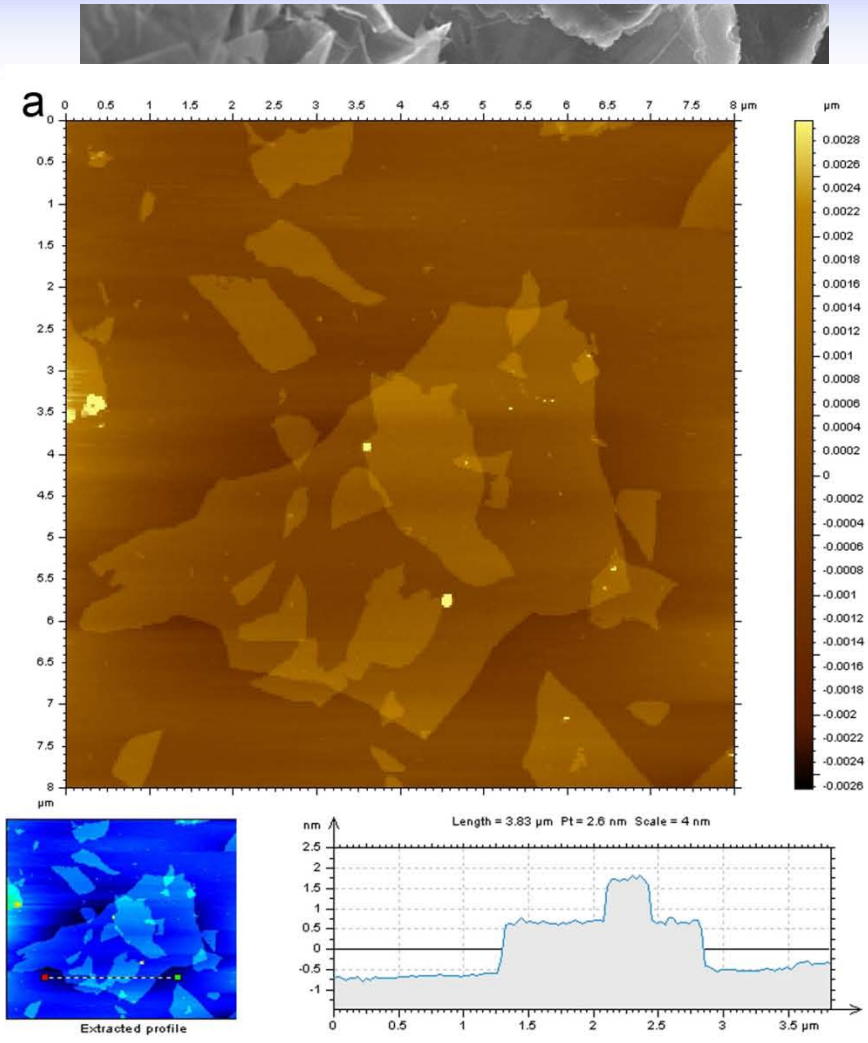


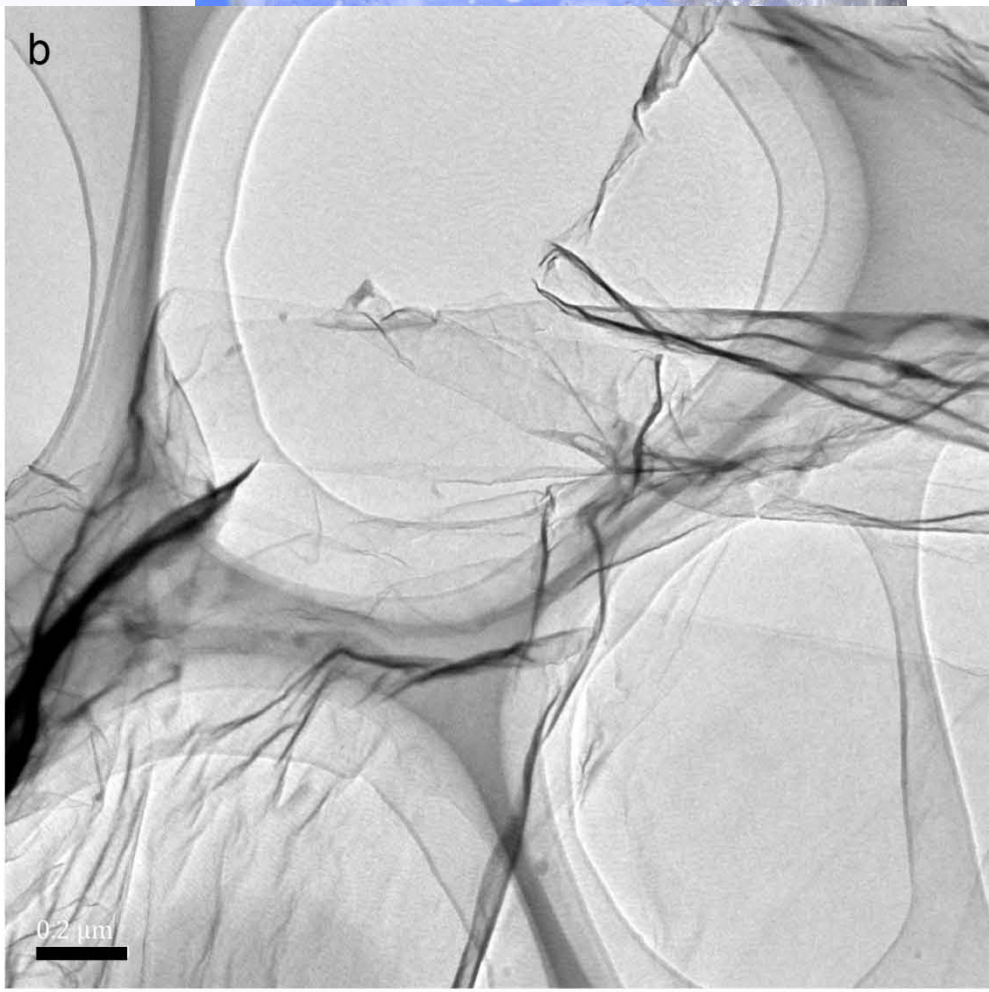
Recent work in our lab

- Preparation in lab
- Two kinds of graphene
- Graphene-sulfur composites
- Graphene-transition metal oxide composites
- Graphene-based catalyst for Li/air battery
- Nitrogen doped grapene and its composites

The preparations and two types of grephene

Preparations





500 1000 1500 2000 2500

Raman shift cm^{-1}

10 20 30 40 50 60

2θ

Two kinds of reduced graphene

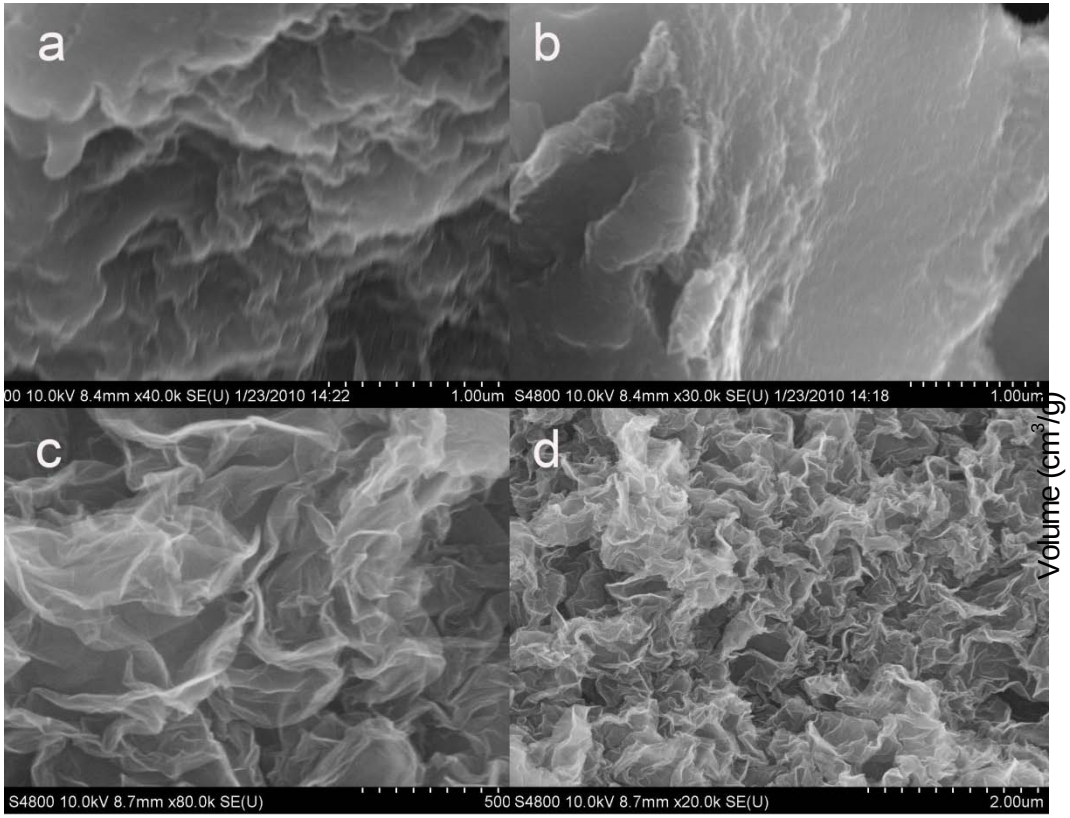
Chemical reduced by hydrothermal --- RGO

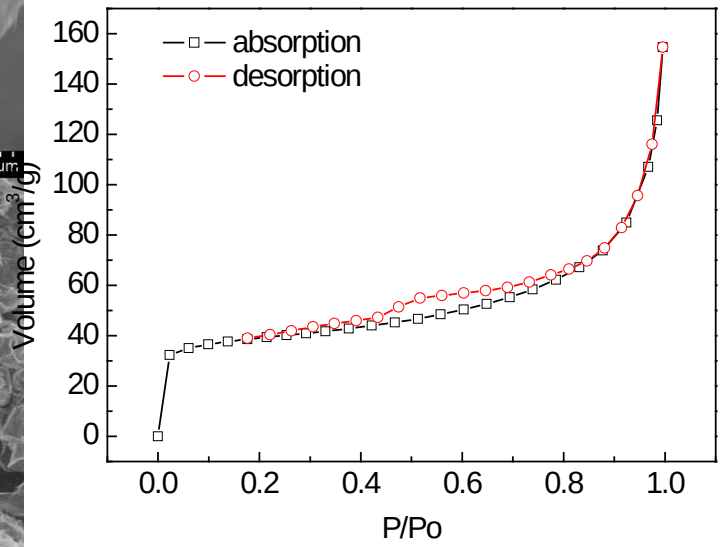
Reduced at high temperature --- MG

RGO	Low conductivity	More functional groups	Agglomeration easy	More defects
MG	High conductivity	Less functional groups	Agglomeration uneasy	Less defects

The composites with sulfur & the comparisons between RGO-based and MG-based

Reduced graphene oxides by hydrothermal method（RGO）

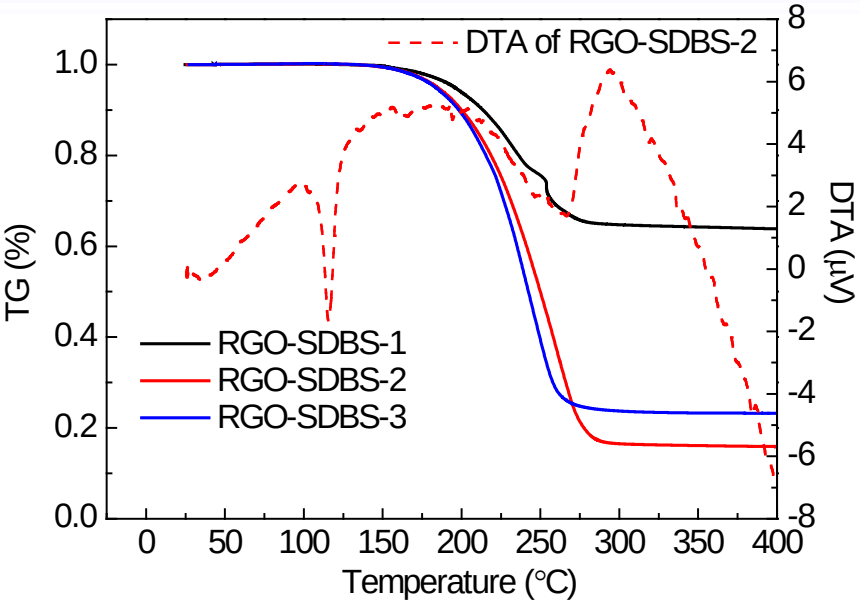




SEM of RGO with Different surfactant SDBS(a,b) and P123(c,d)

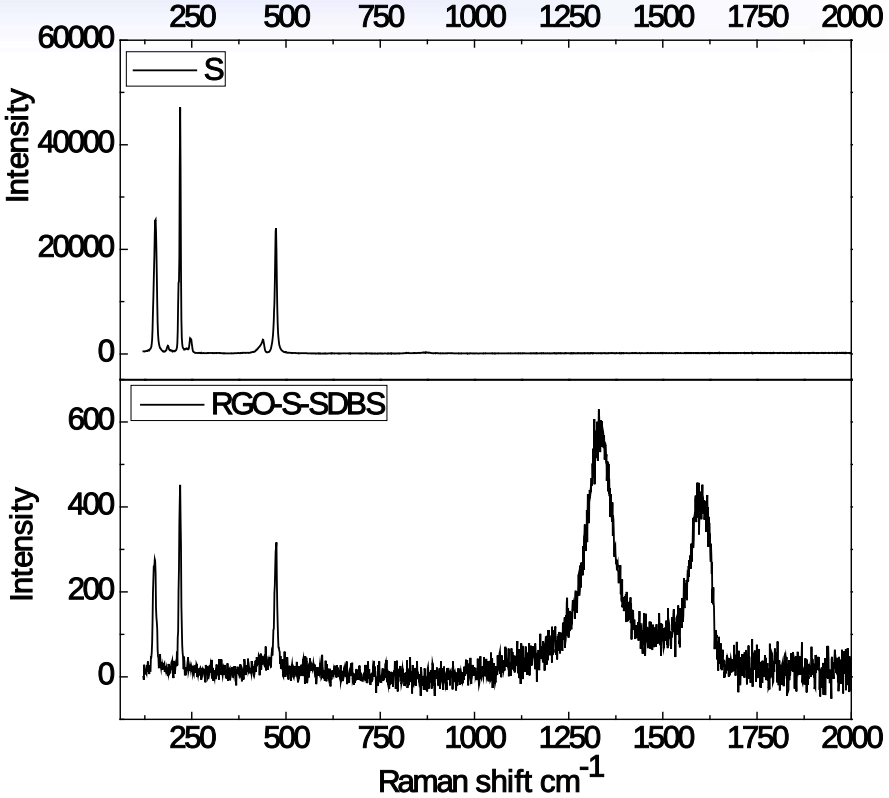
The isothermal absorption/deabsorption Curves of RGO hydrothermal reduced with P123 exist

RGO-S-SDBS composites

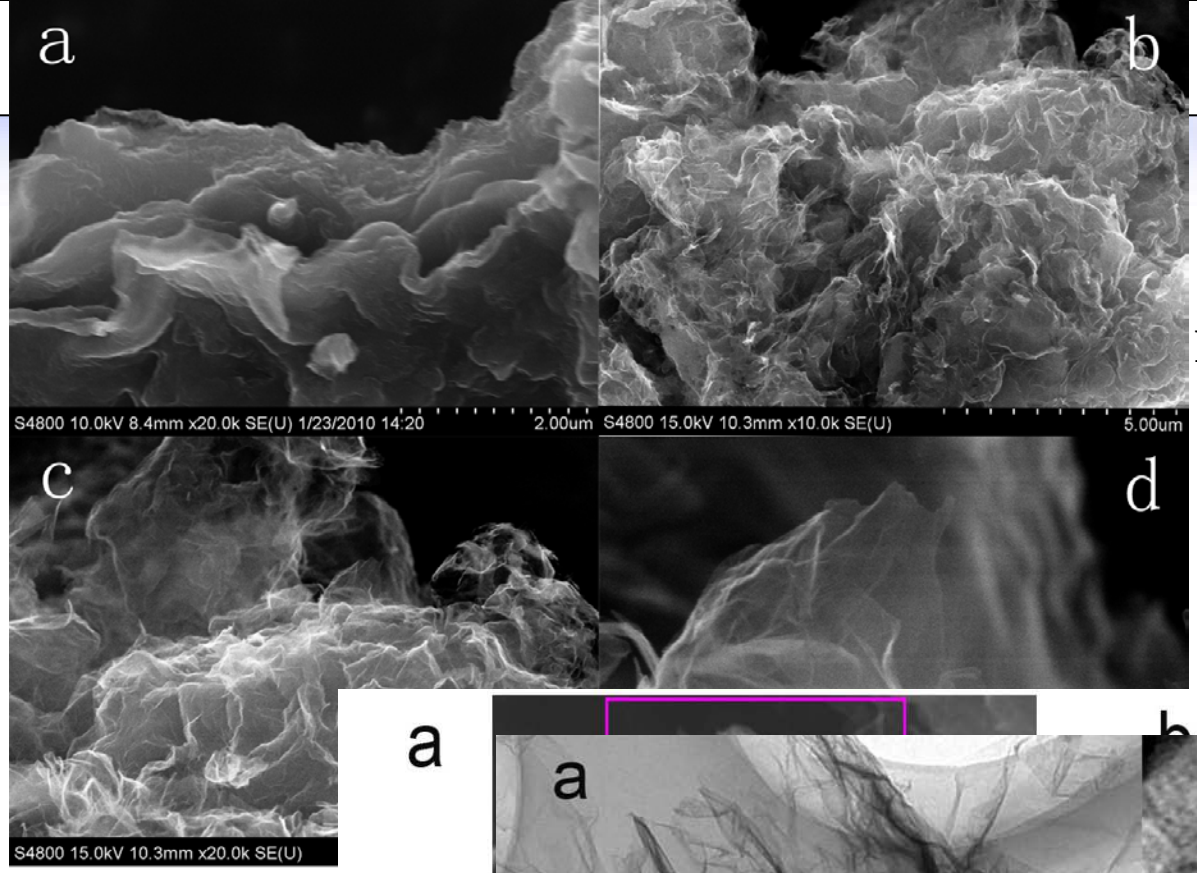


The TG and DTA curves of RGO-S-SDBS samples with different sulfur contents

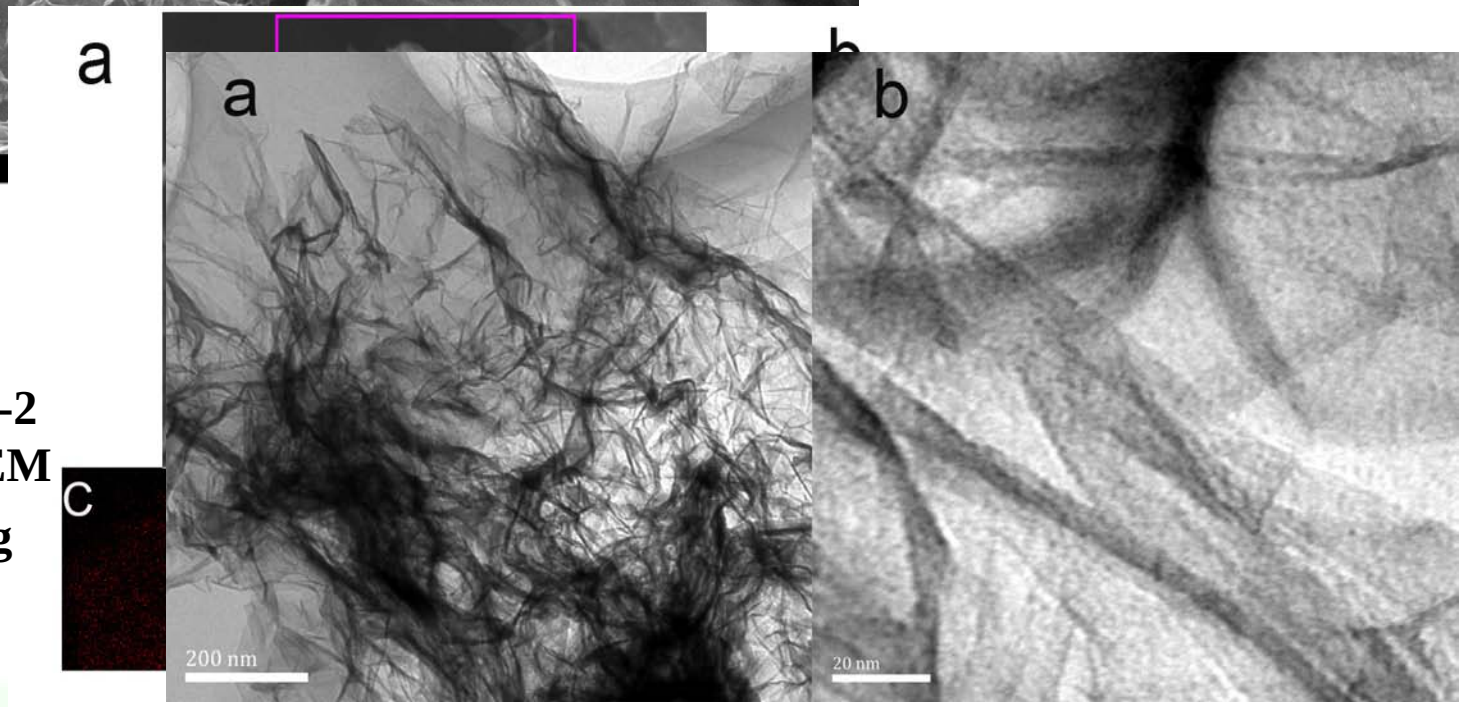
RGO-S-SDBS-1： 34.6%wt
RGO-S-SDBS-2： 75.2%wt
RGO-S-SDBS-3： 79.3%wt



Raman spectrum of RGO-S-SDBS composites and sulfur



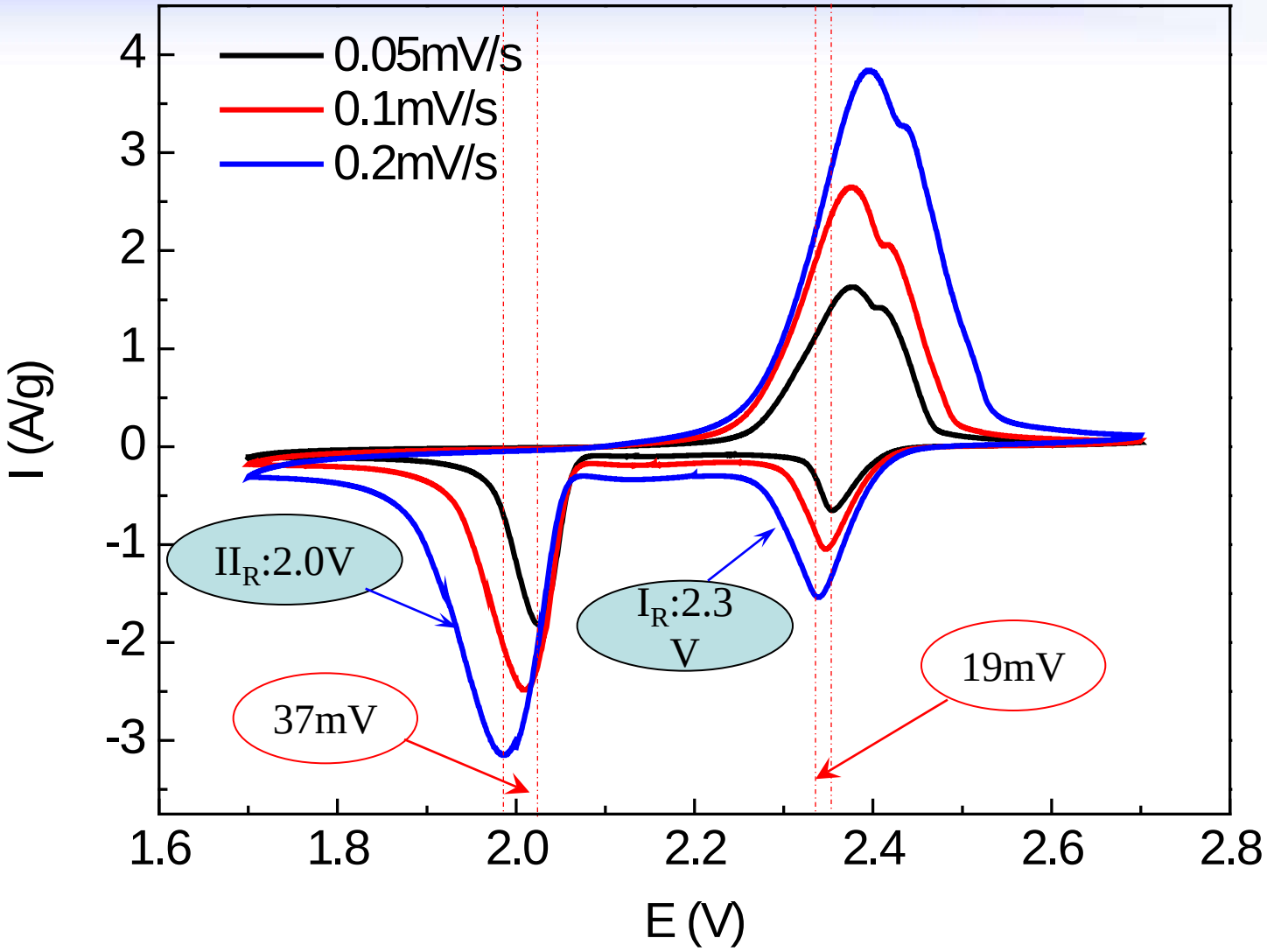
Comparation between RGO（a）and RGO-S-SDBS-2（b, c, d）SEM



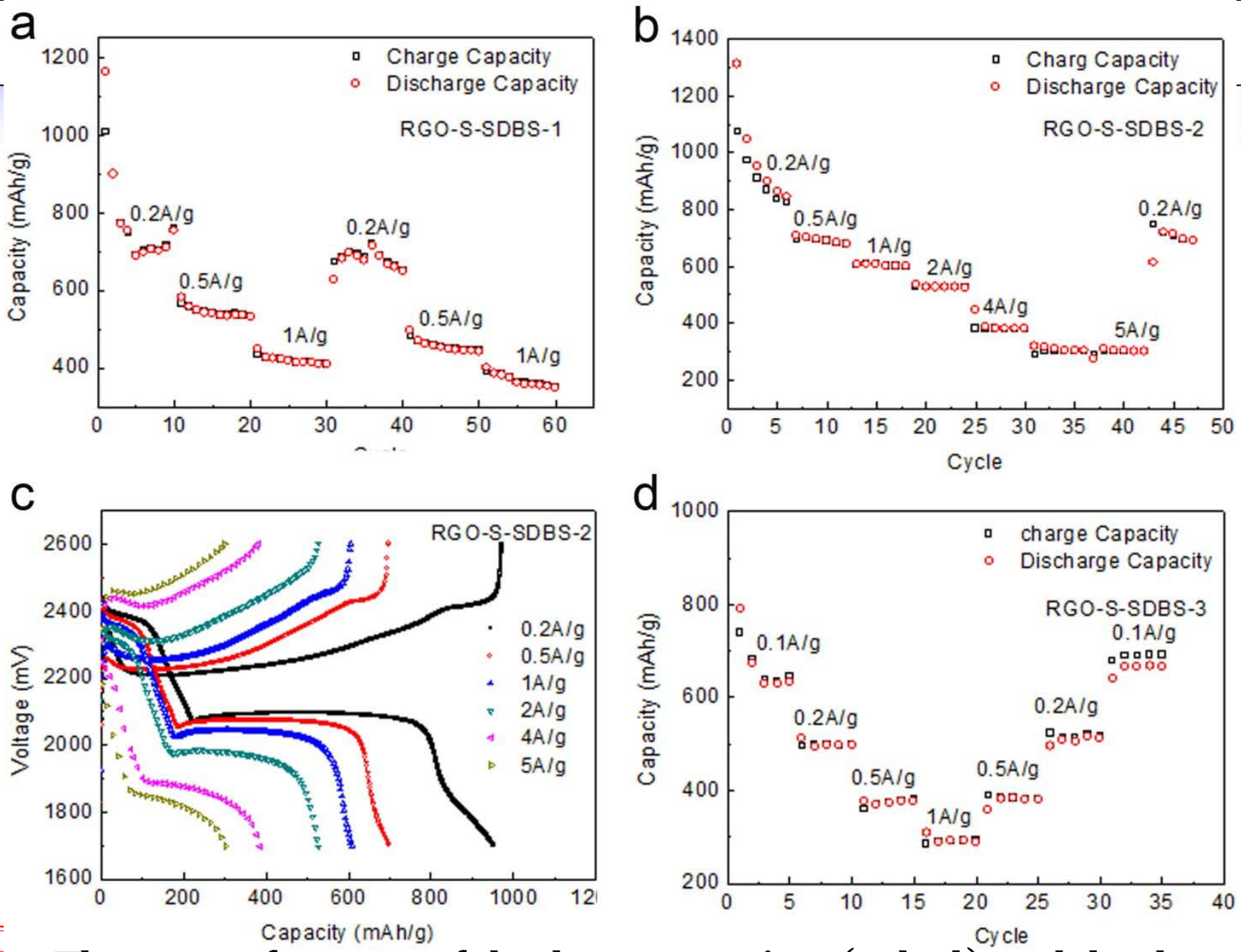
RGO-S-SDBS-2 composites TEM

C, S, O distributions on RGO-S-SDBS-2 by SEM mapping

The electrochemical performance of RGO-S-SDBS composites

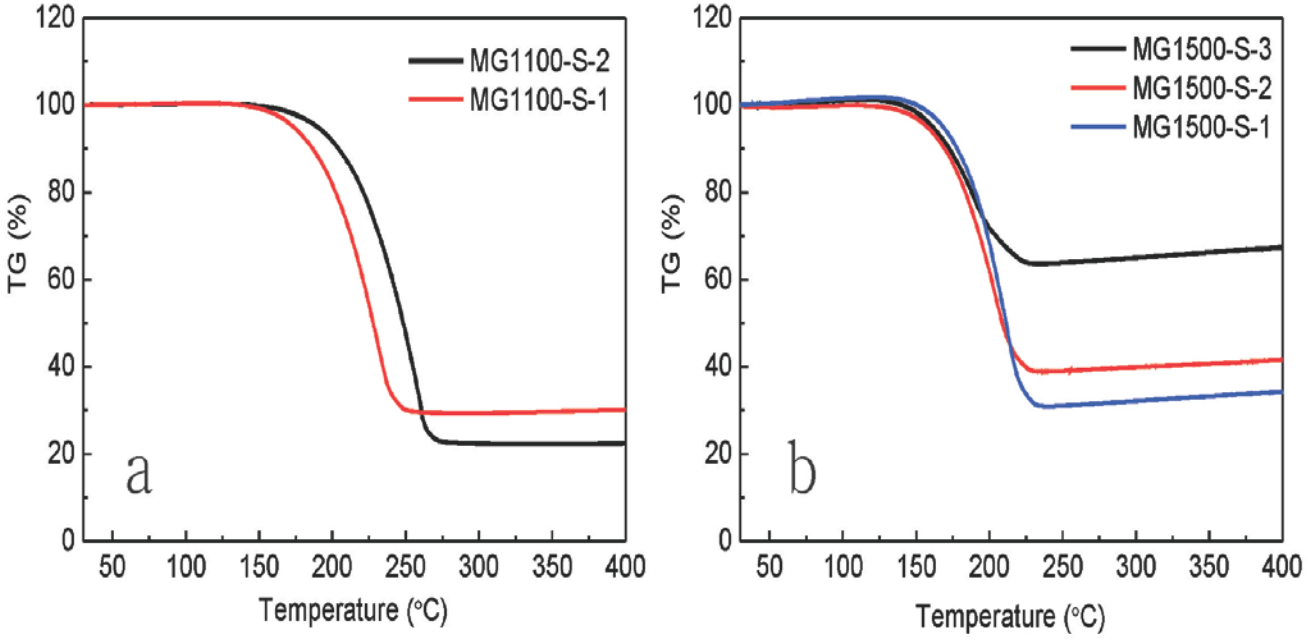


The CV curves, RGO-S-SDBS-2 composite at different scan rate



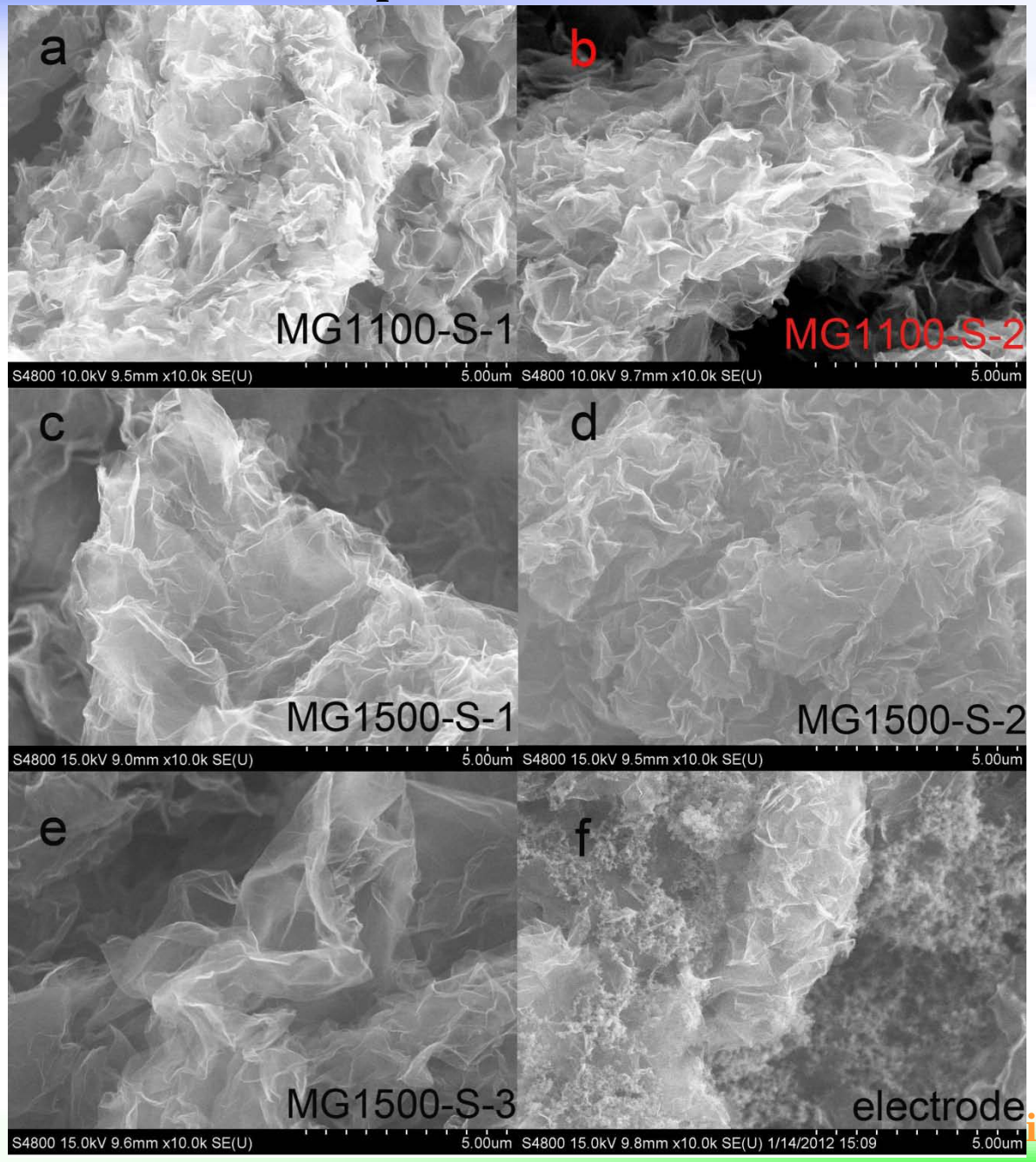
The rate performance of the three composites（a, b, d）and the charge-discharge curves of RGO-S-SDBS-2 at different current densities(c).

MG-S composites

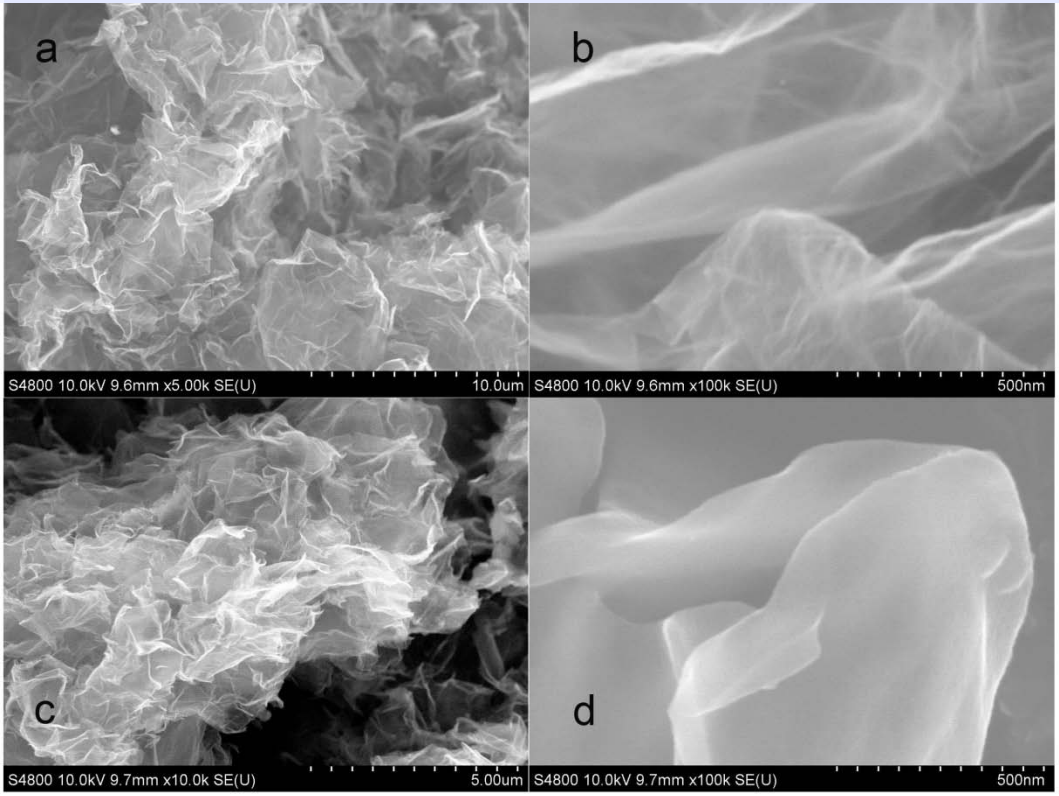


Samples	MG1100-S-1	MG1100-S-2	MG1500-S-1	MG1500-S-2	MG1500-S-3
Sulfur contents（%）	75.0	69.8	69.5	60.7	36.7

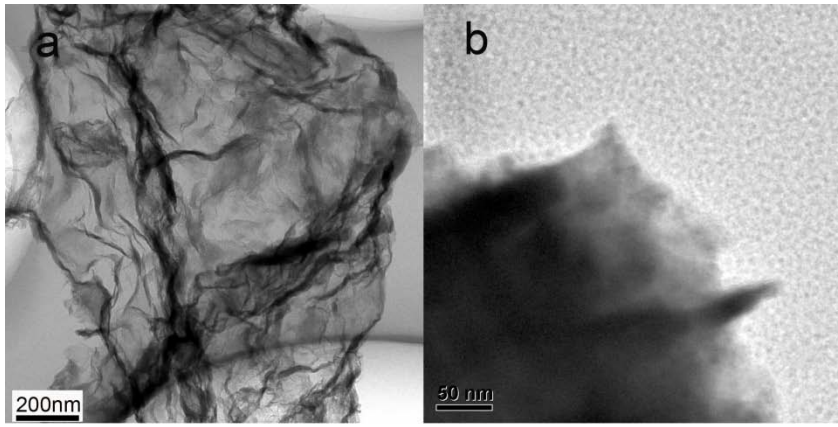
SEM for different composites

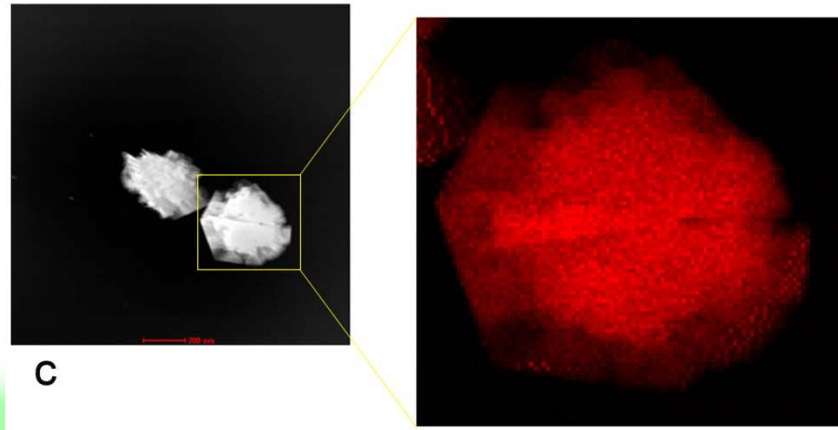


MG-S composites



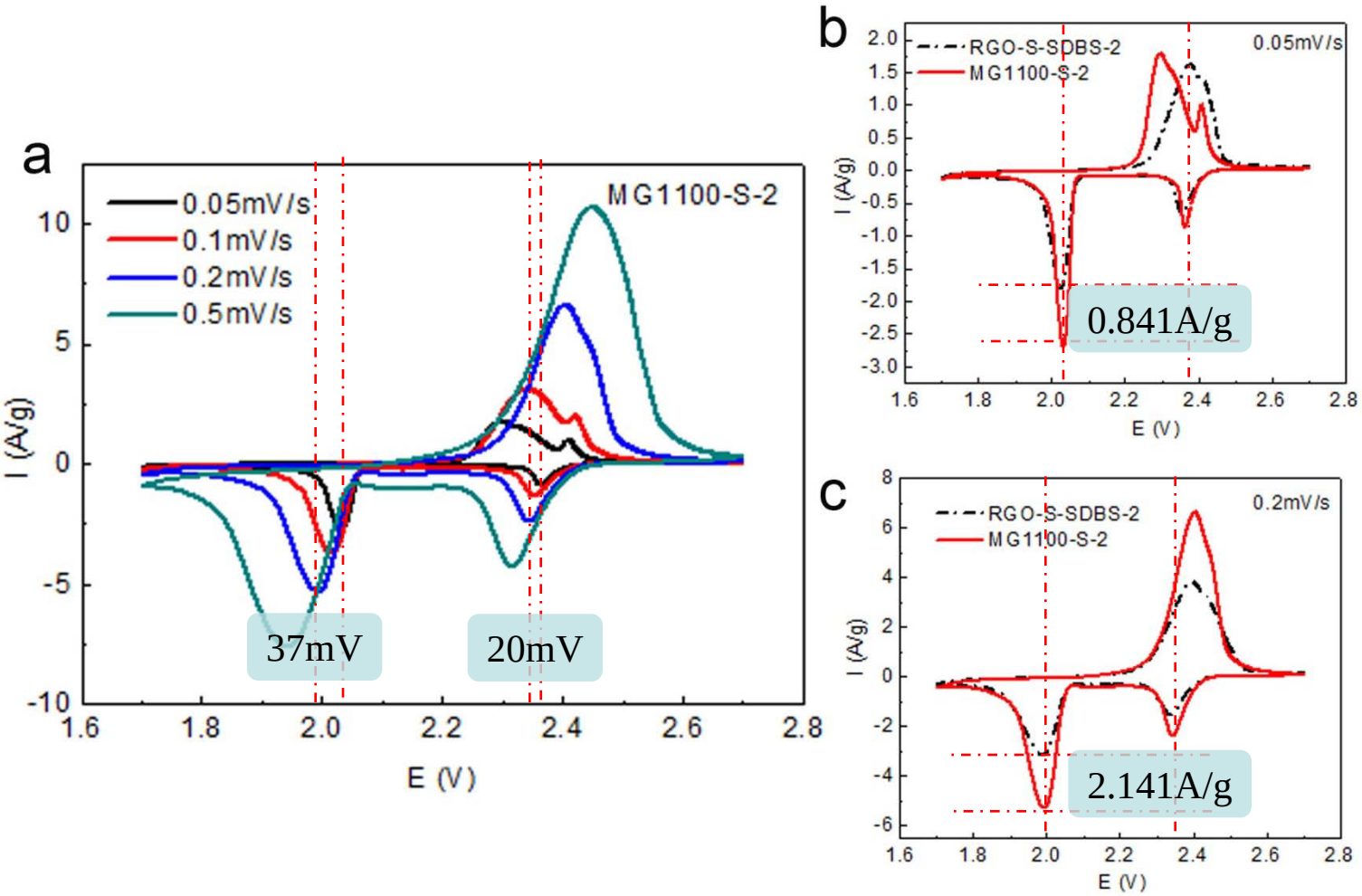
SEM before and after sulfur coating，（a）MG1100，（b）MG1100-S-2





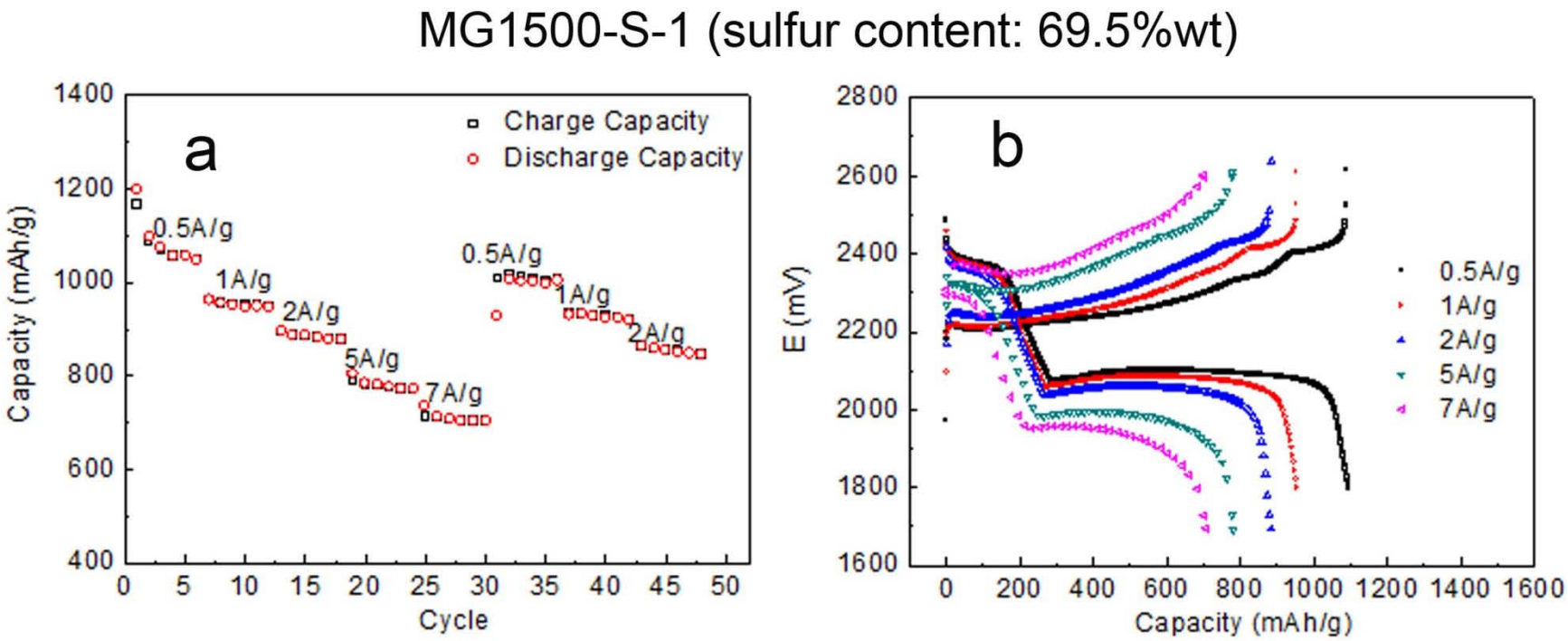
TEM of MG1100-S-2（a，b）and S mapping（c）

MG-S composites



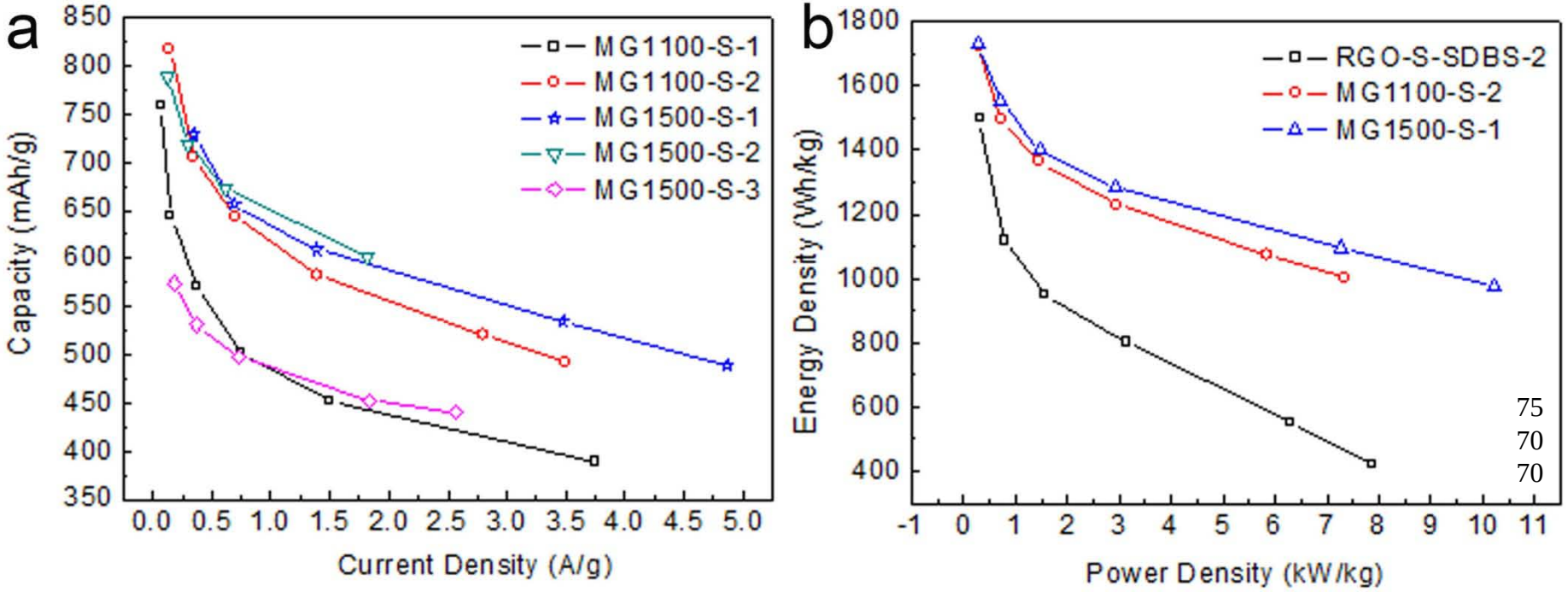
The CV curves of MG1100-S-2 composite at different scan rates (a) and the comparisons of RGO-S-SDBS-2 and MG1100-S-2 at 0.05 mV/s（b）and 0.2 mV/s（c）

The electrochemical performance of MG1500-S-1



MG1500-S-1 composite, rate performance (a) and charge-discharge curves at different current density (b)

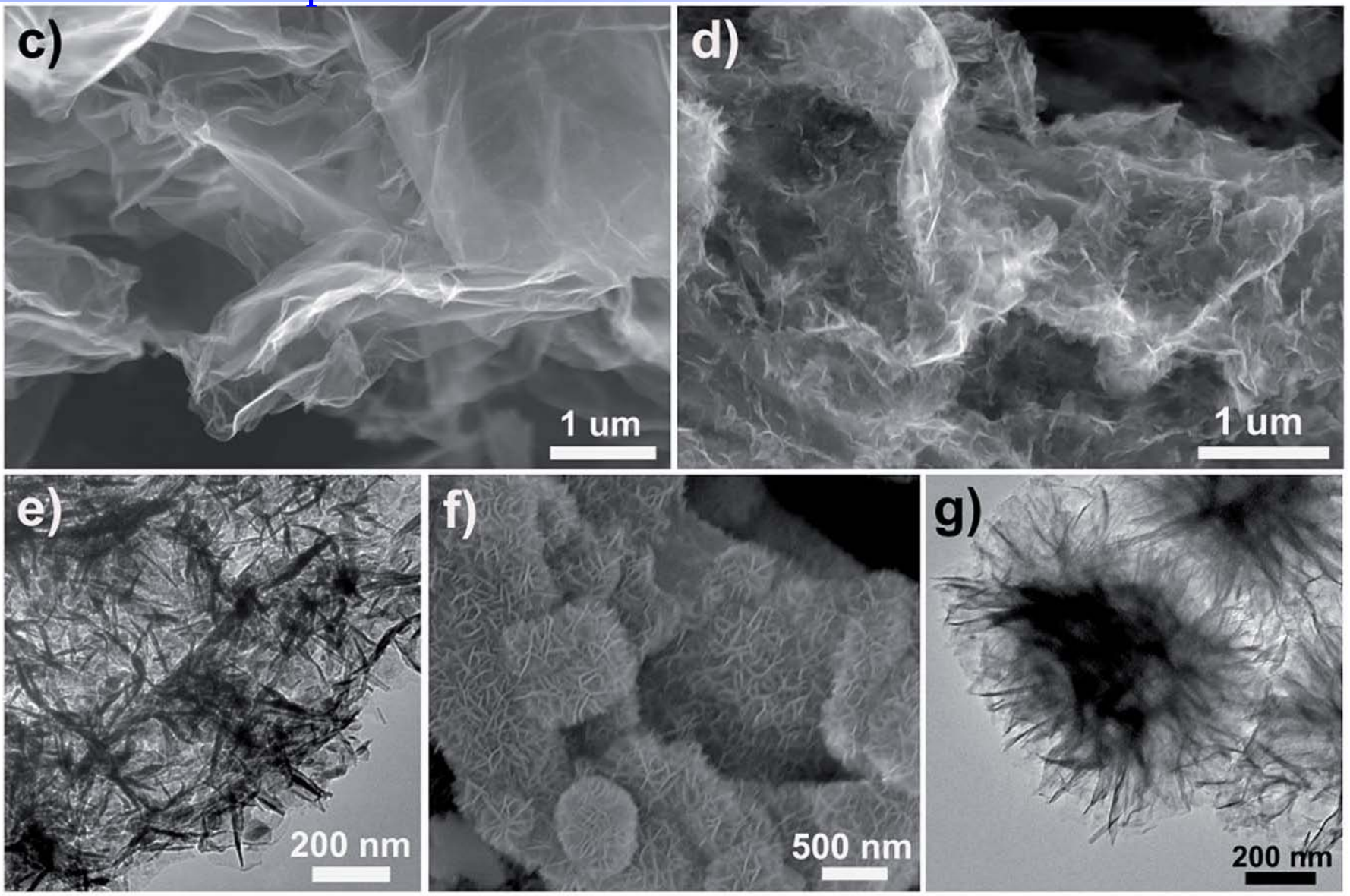
The rate properties of MG-S series & Comparisons between MG-based and RGO-based composites in terms of rate performance



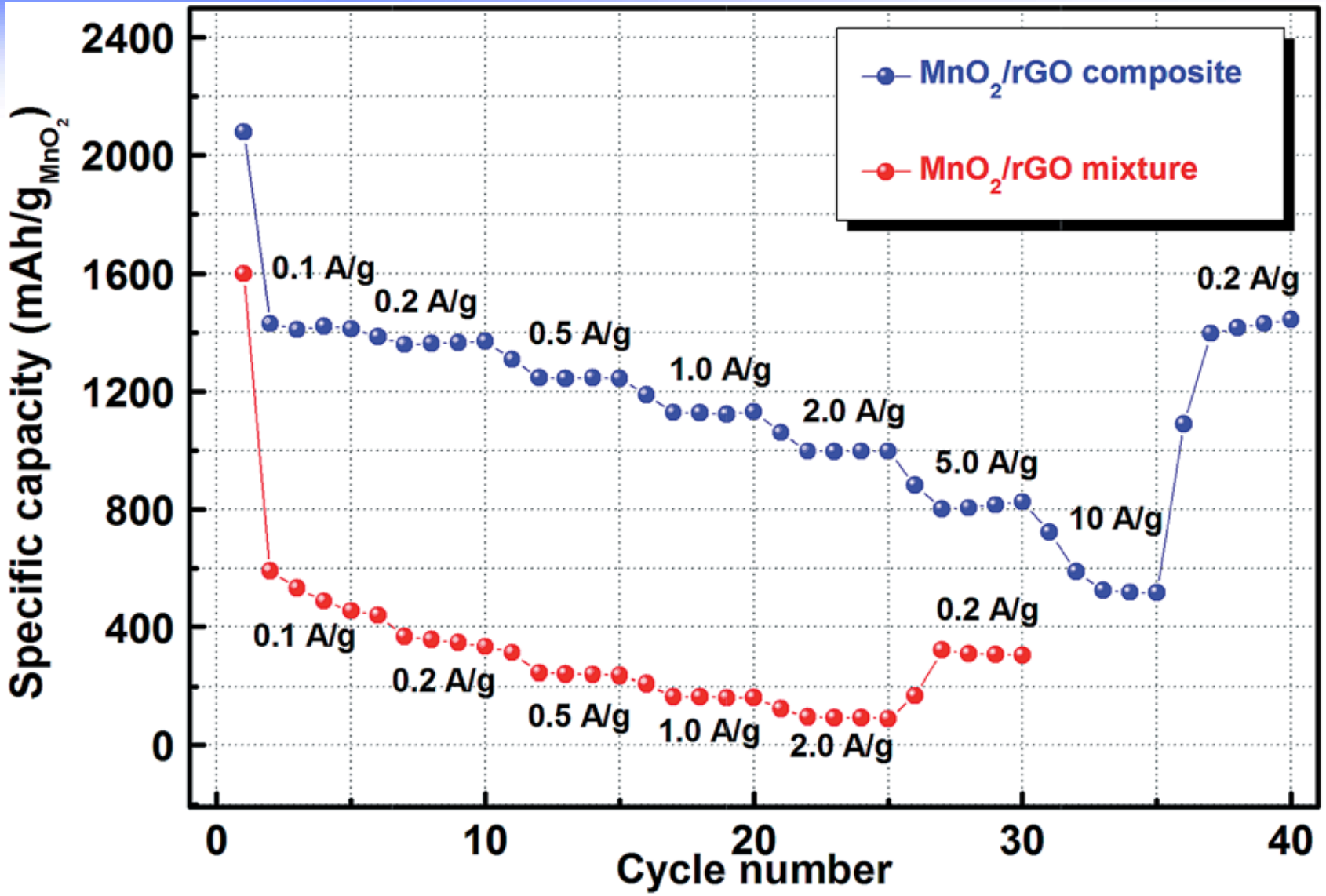
The rate performance of five MG-based composites (a) and the comparisons of RGO-S-SDBS-2, MG1100-S-2 and MG1500-S-1 in terms of power density and energy density (b), all the specific capacity is based on composite mass.

The composites with MnO_2 & the MnO_2 mechanism changed

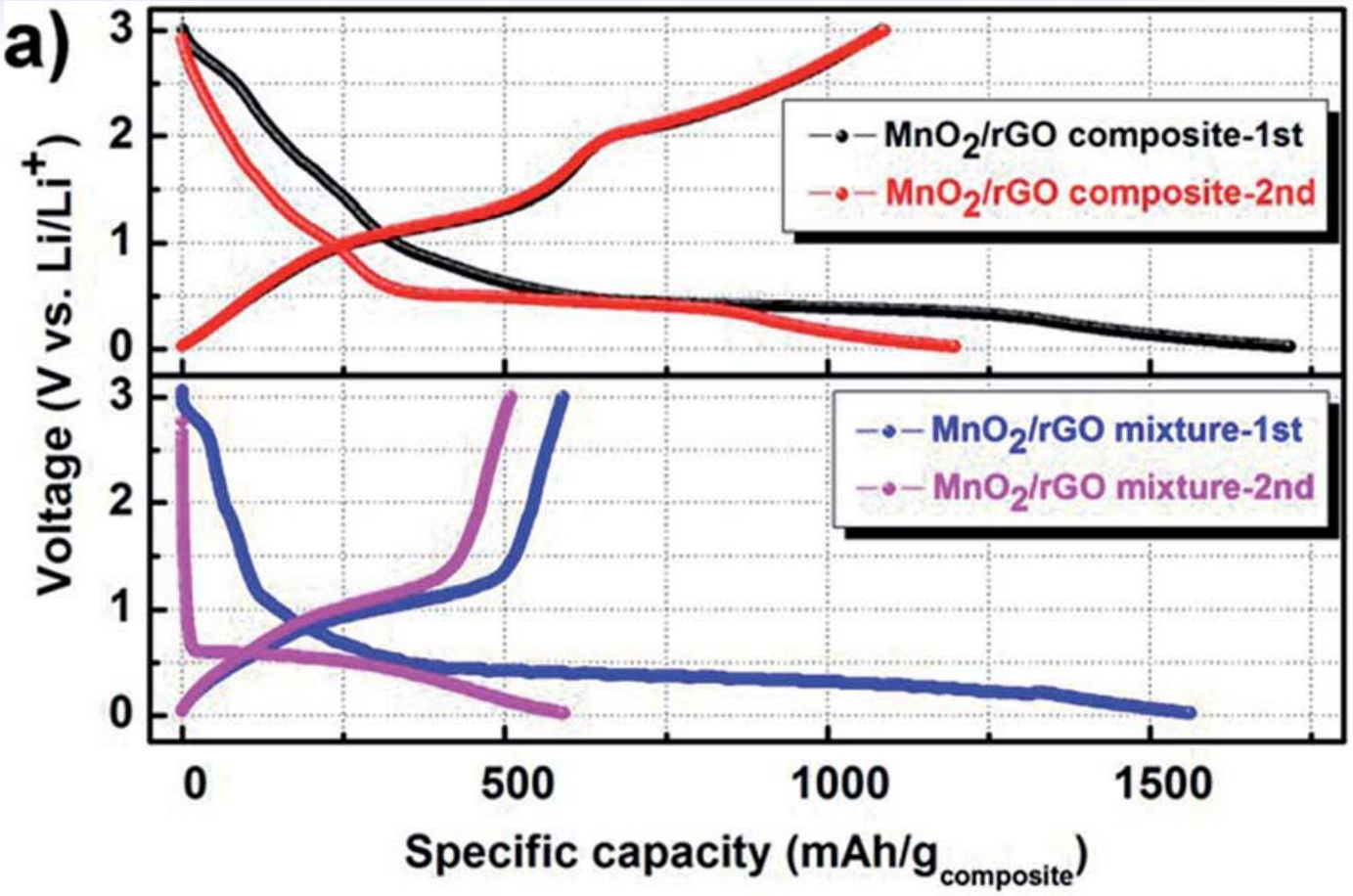
RGO-MnO2 composites



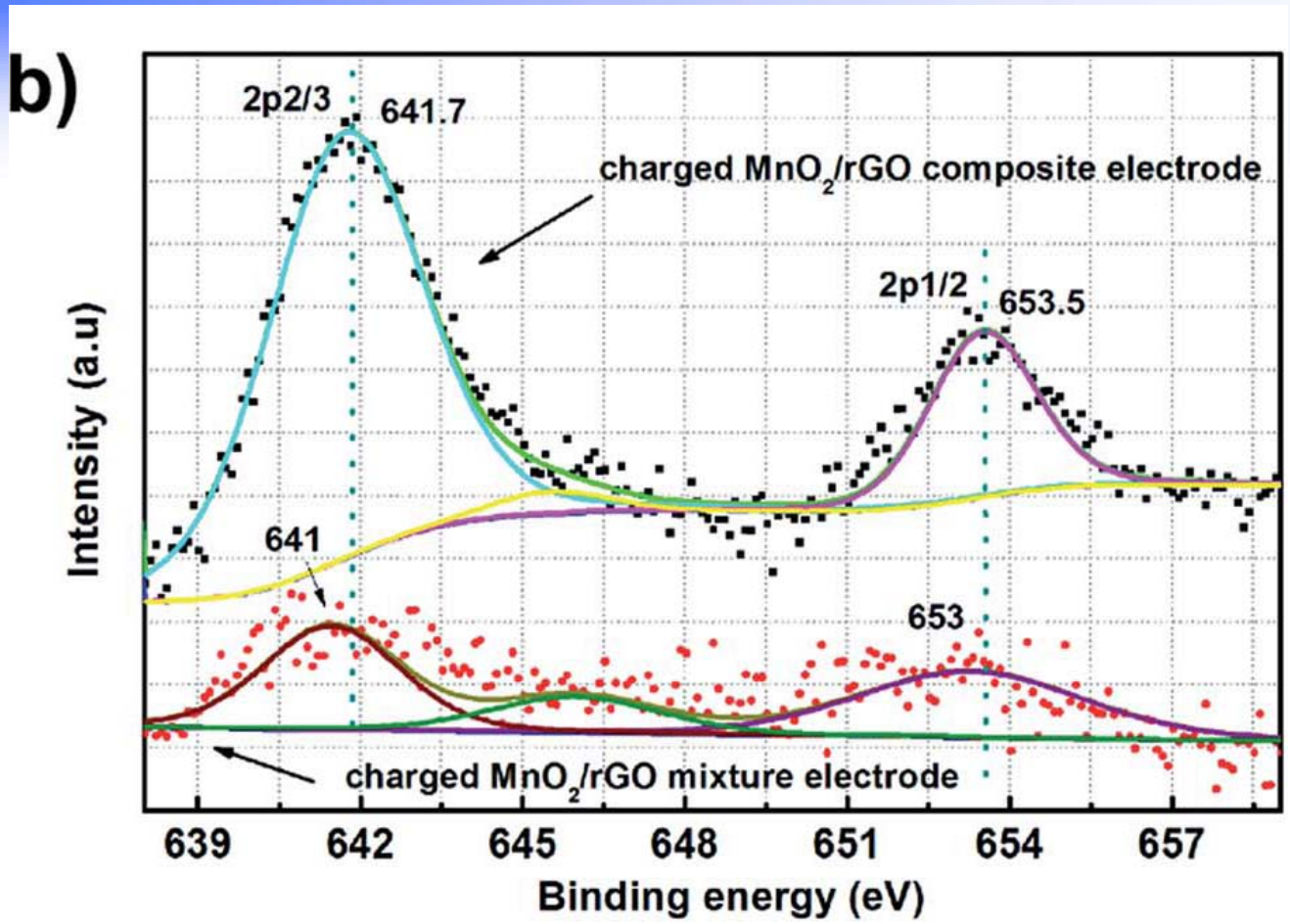
(c) The SEM image of the rGO nanosheets. (d) The SEM and (e) TEM images of the MnO2–rGO composite. (f) The SEM and (g) TEM images of the pure MnO2.



Rate performances of the MnO2–rGO composite and the MnO2–rGO mixture electrodes at different current densities with the voltage window between 0.02 V and 3 V.



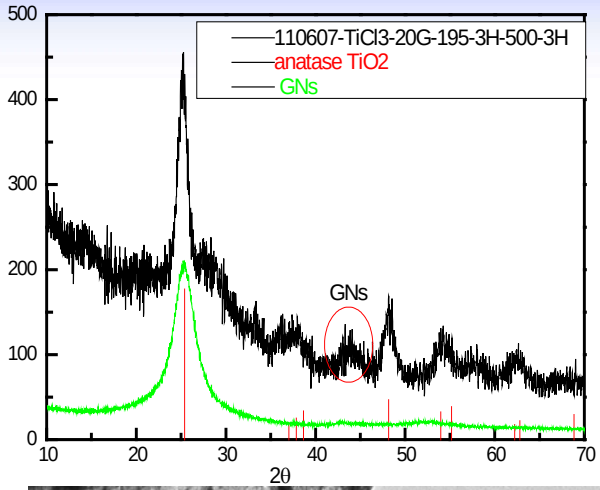
The reduction process of MnO2–rGO composite may also possess two steps: MnO2 + 2Li+ + 2e/Li2O + MnO, and MnO+ 2Li+ + 2e/Li2O + Mn. However, only step occurred for MnO2-rGO mixture.

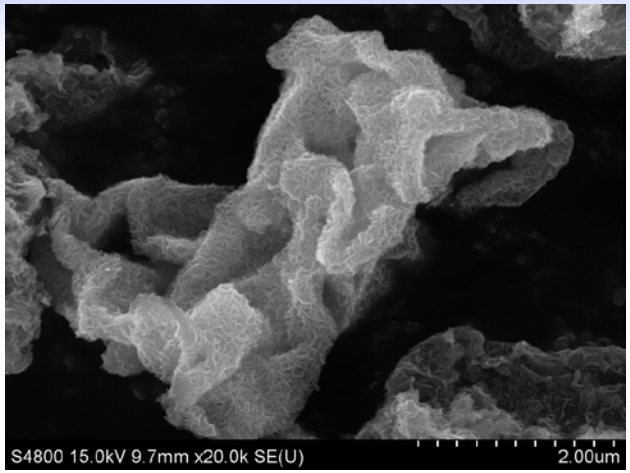


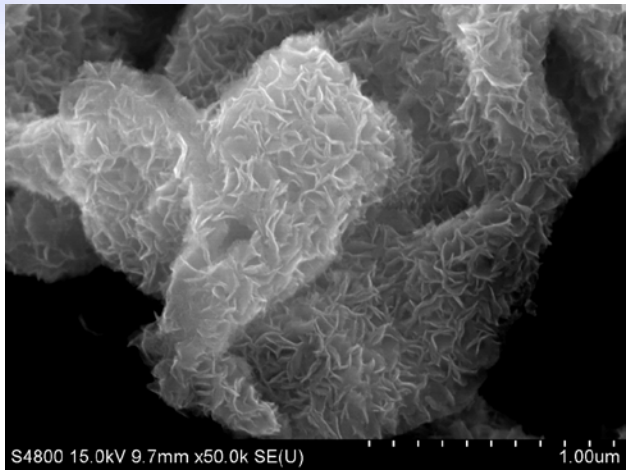
The spin energy of Mn 2p3/2 and Mn 2p1/2 of the charged MnO2–rGO composite electrode are centered at 641.7 and 653.5 eV, respectively. The energy separation is calculated to be 11.8 eV, which is in a good agreement with that of MnO2. As comparison, the peaks of Mn 2p3/2 and Mn 2p1/2 in the charged MnO2–rGO mixture electrode are very weak and centered at 641 and 653 eV, which well agree with those reported characteristic binding energies in MnO.

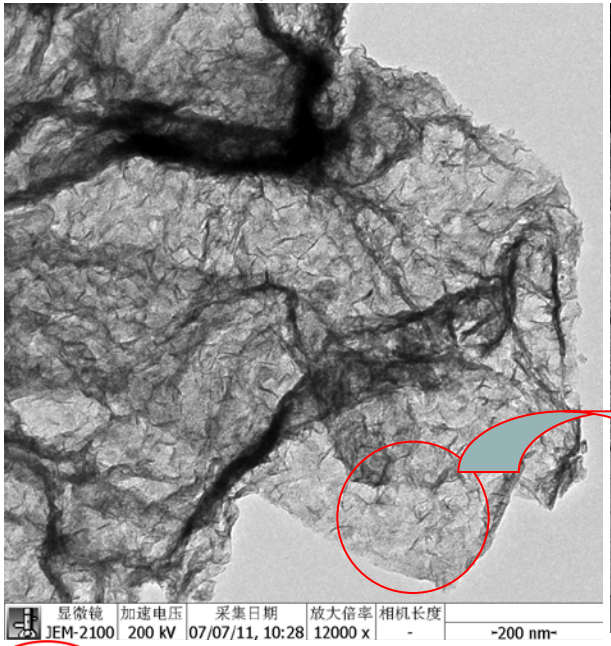
The Composites with TiO2 & the very high rate performance

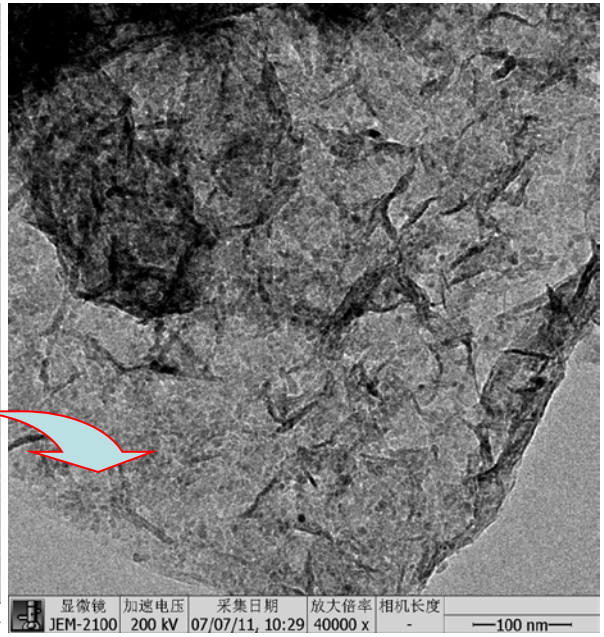
RGO-TiO2 composites

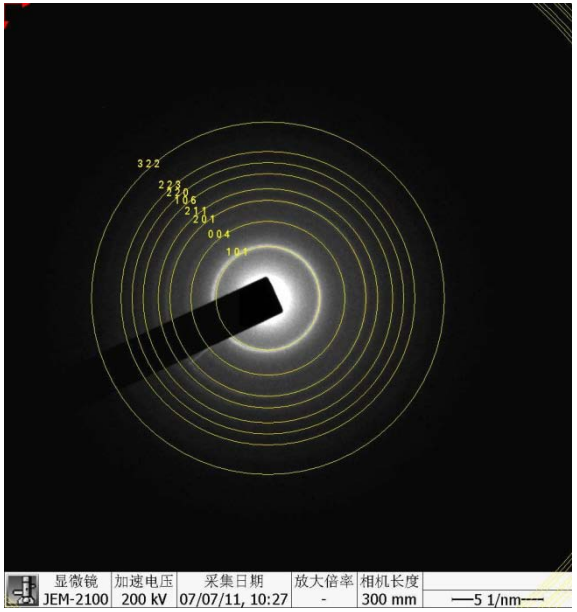






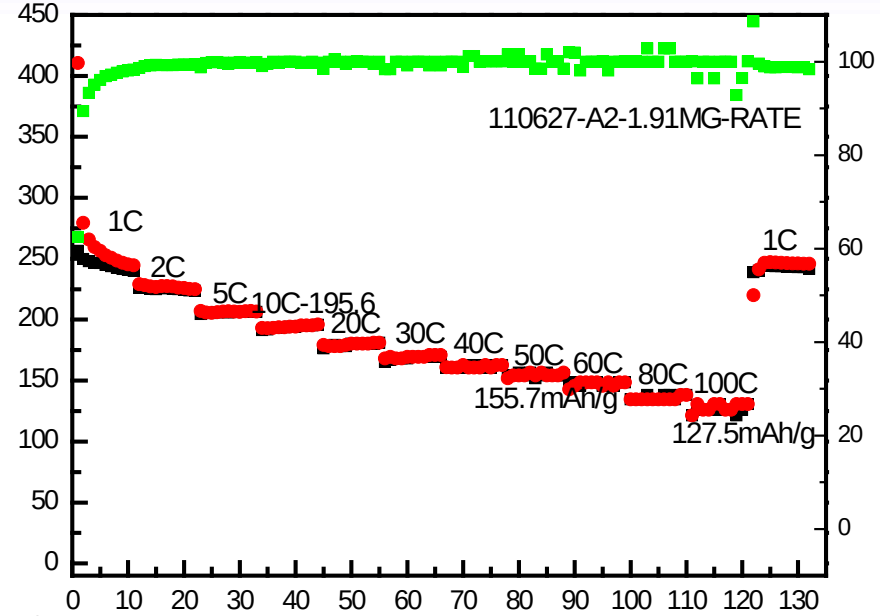


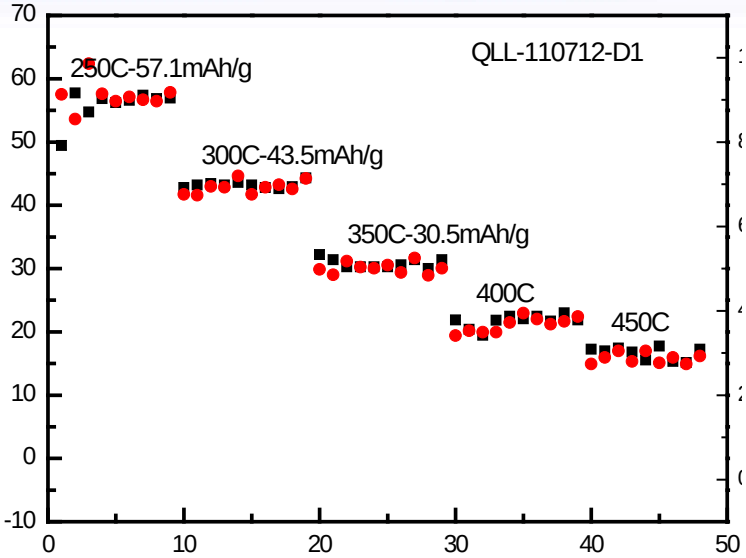


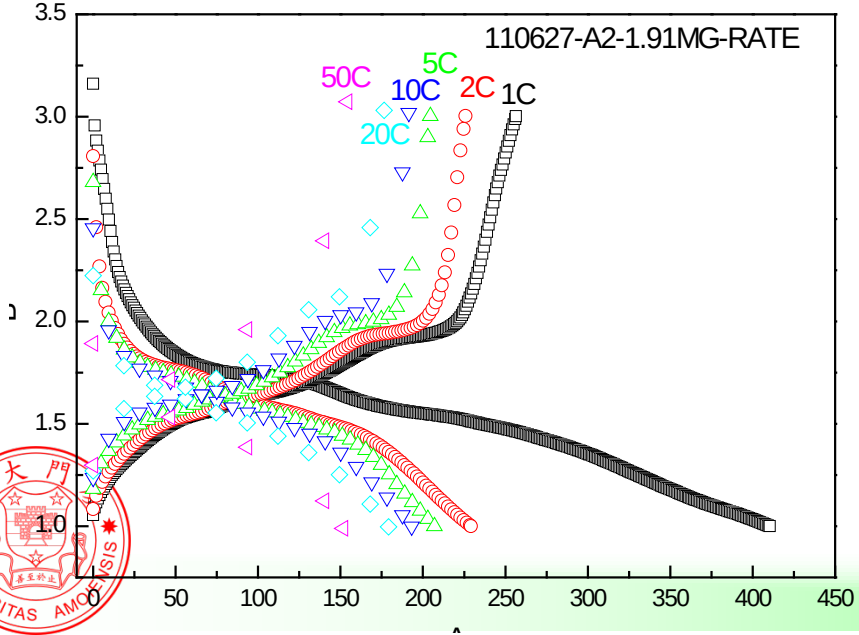


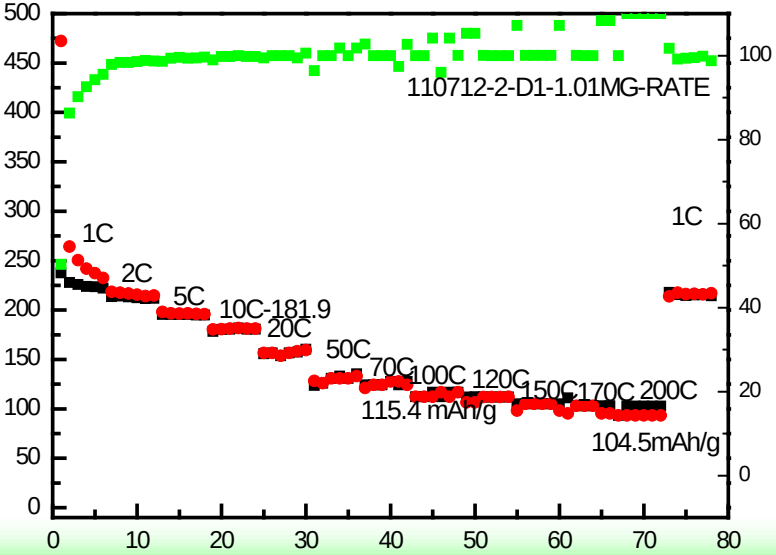
TEM & SAED of RGO-TiO2 composites. The TiO2 particles were distributed evenly, also resulting in avoiding graphene agglomeration.

The electrochemical performance of RGO-TiO2 composites



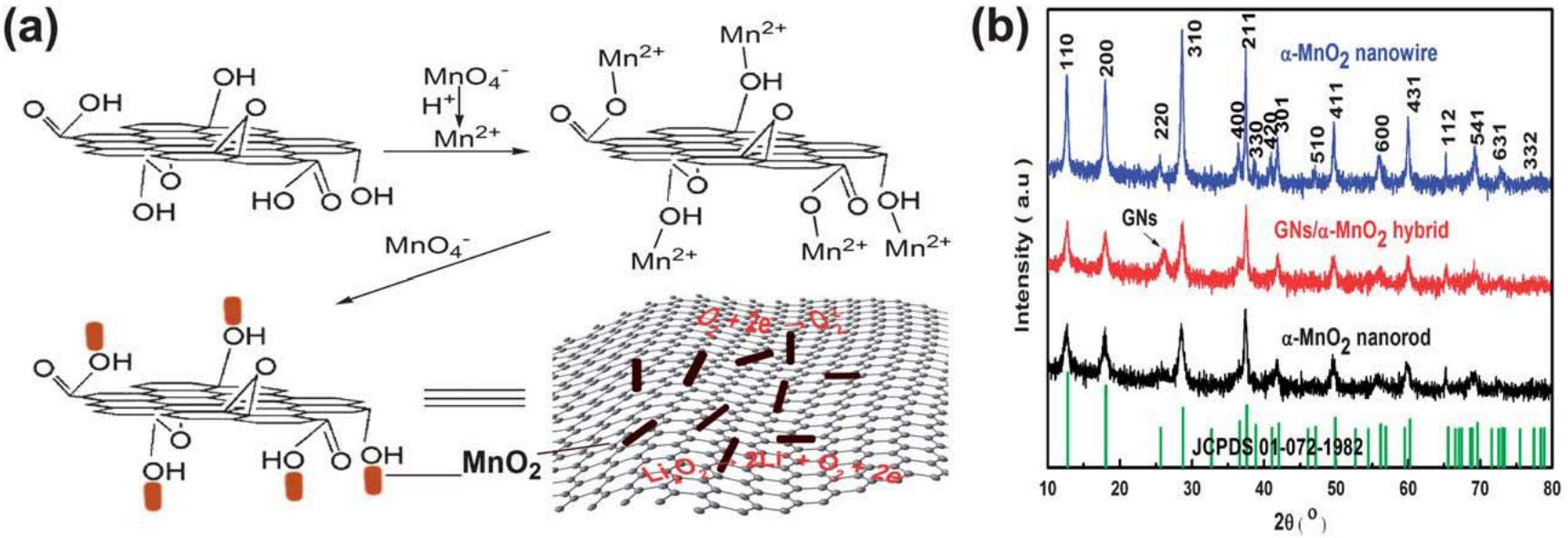




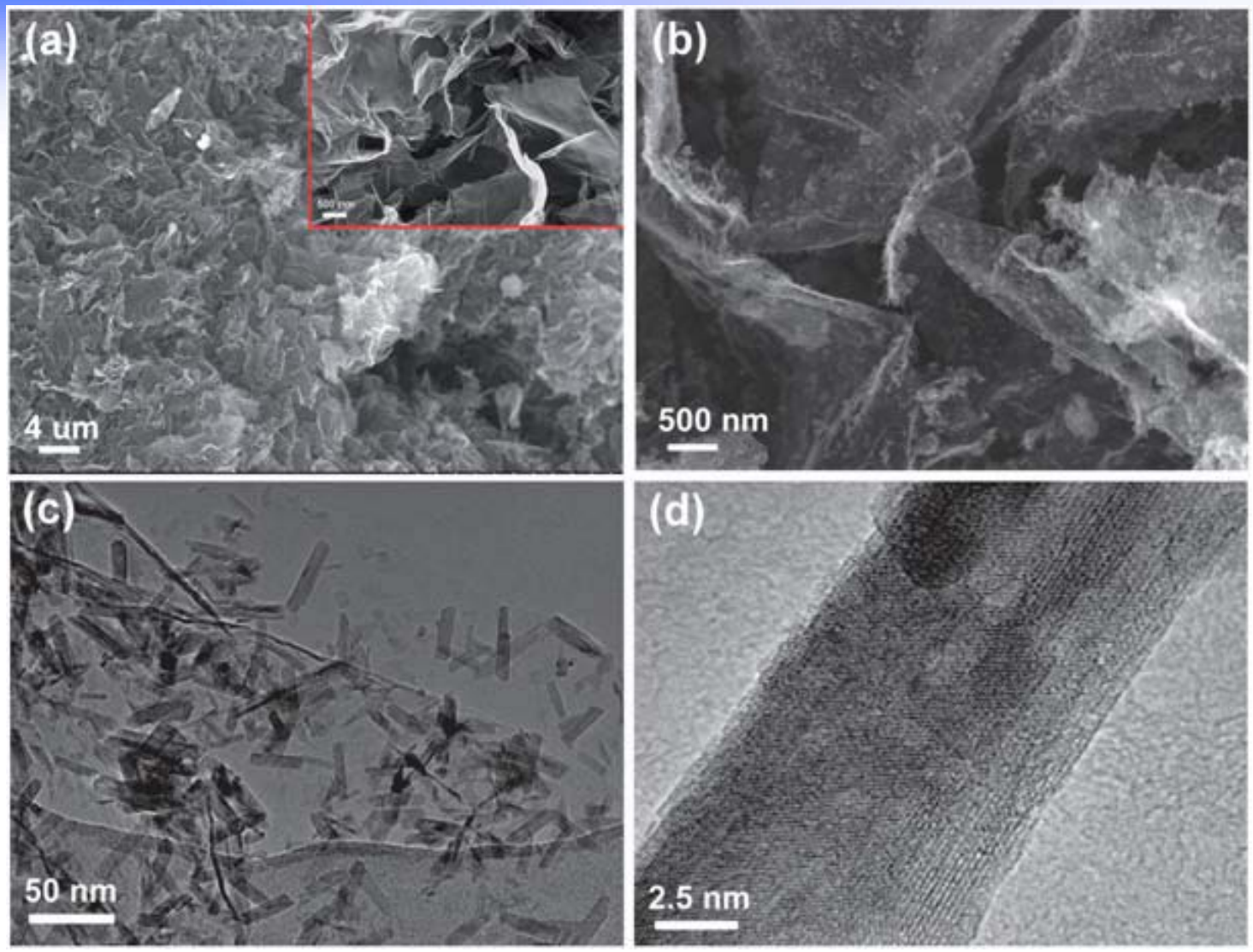


The composites with MnO2 used in Li/Air batteries

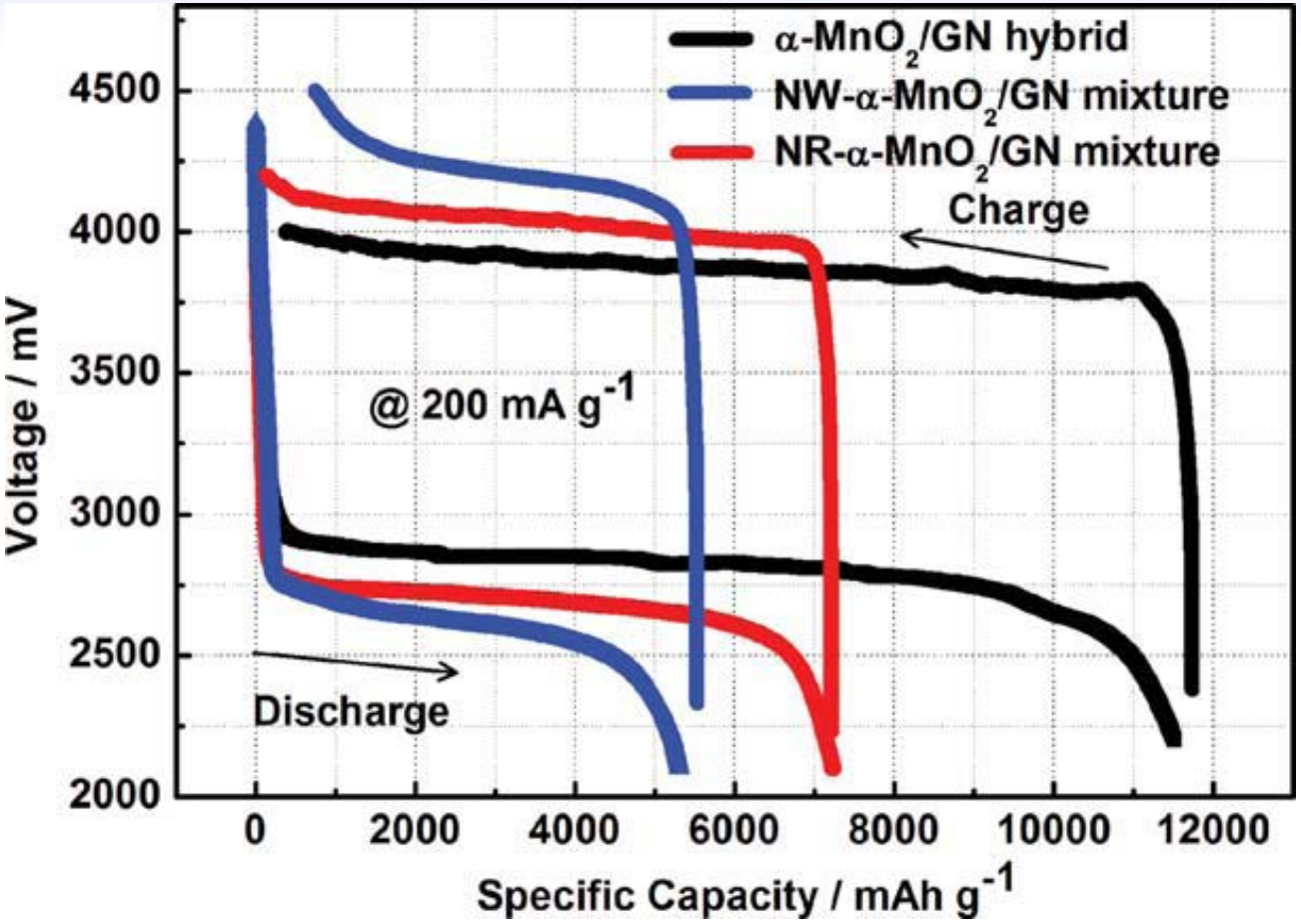
MG-based transition metal oxides as catalyst in Li/air battery



(a) Schematic drawing of the growth of a-MnO2 nanorods on GNs and the schematic structure of the a-MnO2/GN hybrid. (b) X-ray diffraction patterns of a-MnO2/GN hybrid, a-MnO2 nanowires and a-MnO2 nanorods.



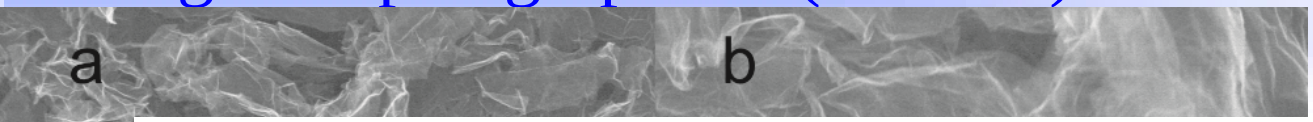
(a) SEM image of the as prepared graphene nanosheets with a porous and intertwined structure. (b) SEM image of the a-MnO2/GN hybrid with a-MnO2 uniformly dispersed on the GNs surface. (c) A low magnification TEM image of the GN/a-MnO2 hybrid. (d) A high magnification TEM image of a-MnO2 nanorods indicates well-crystallized a-MnO2.

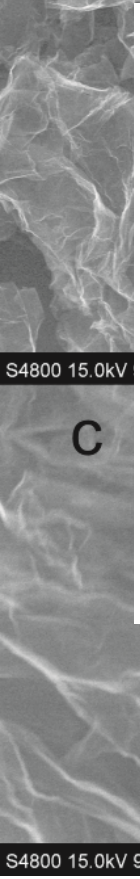


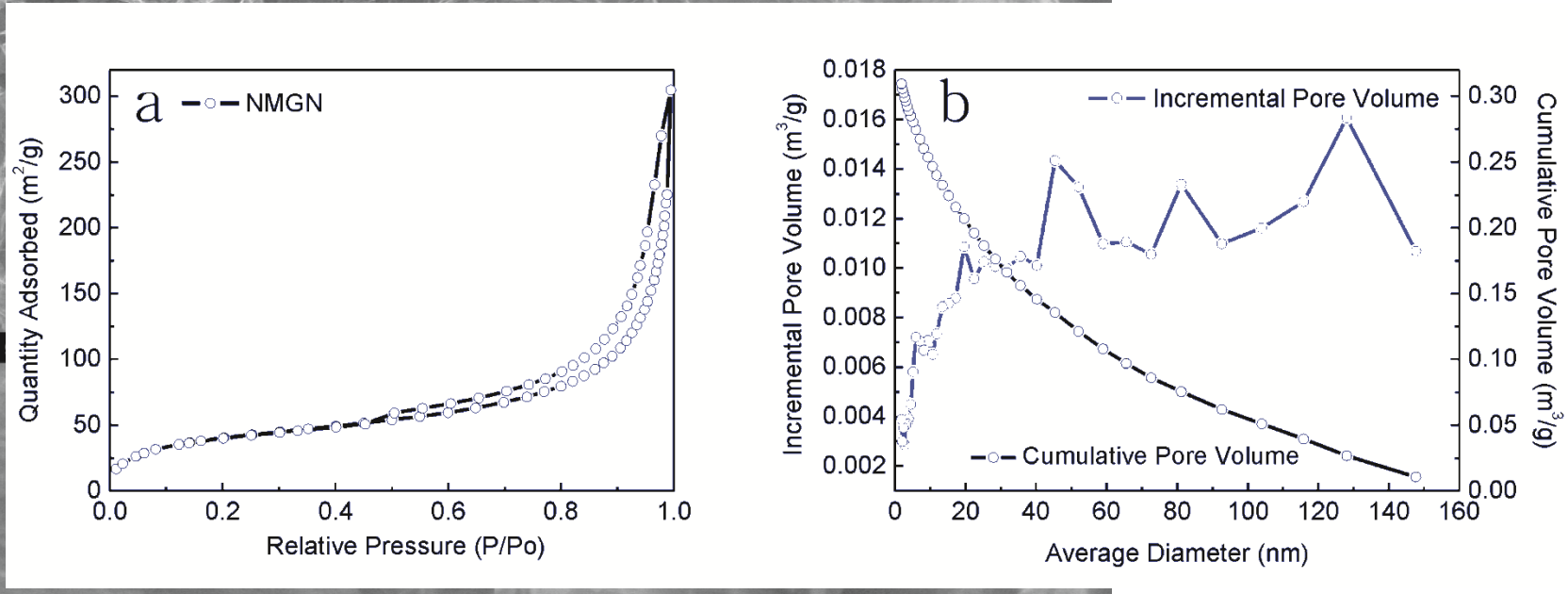
Discharging and charging profiles of Li–O2 batteries based on three different catalysts, a-MnO2/GN hybrid, NW-a-MnO2/GNmixture and NR-a-MnO2/GN mixture. The current density and capacities were based on the mass of GNs.

The nitrogen doped grephene

Nitrogen doped graphene (NMGN)

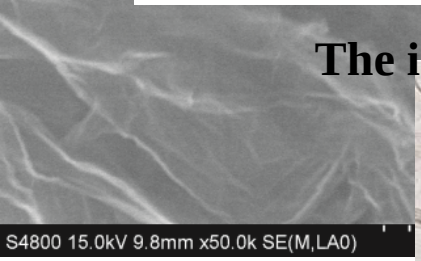




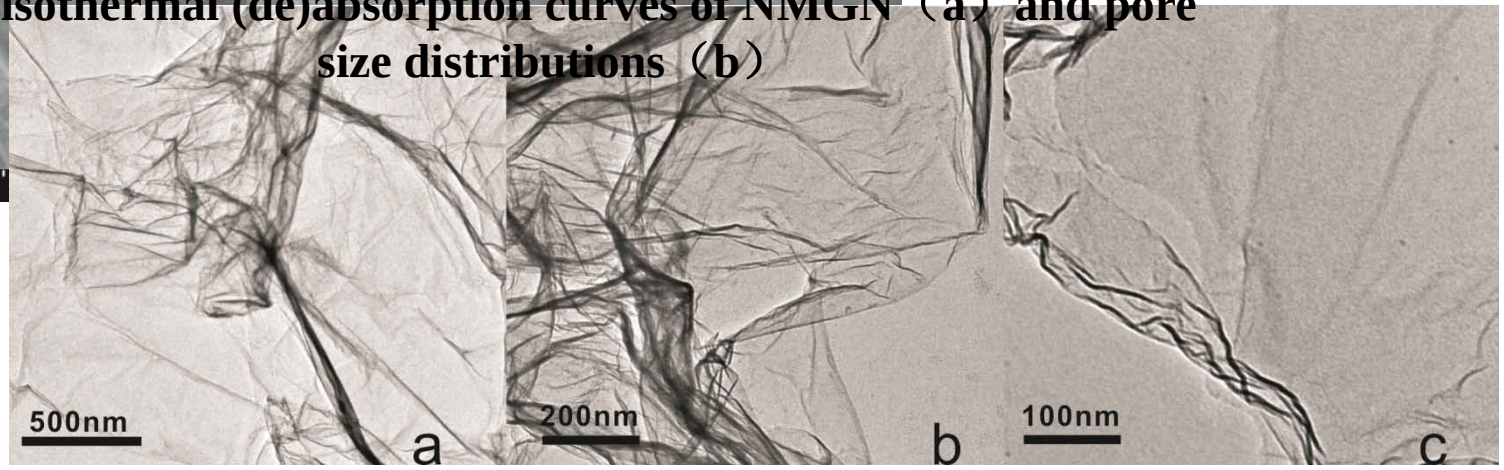


The isothermal (de)absorption curves of NMGN（a）and pore size distributions（b）

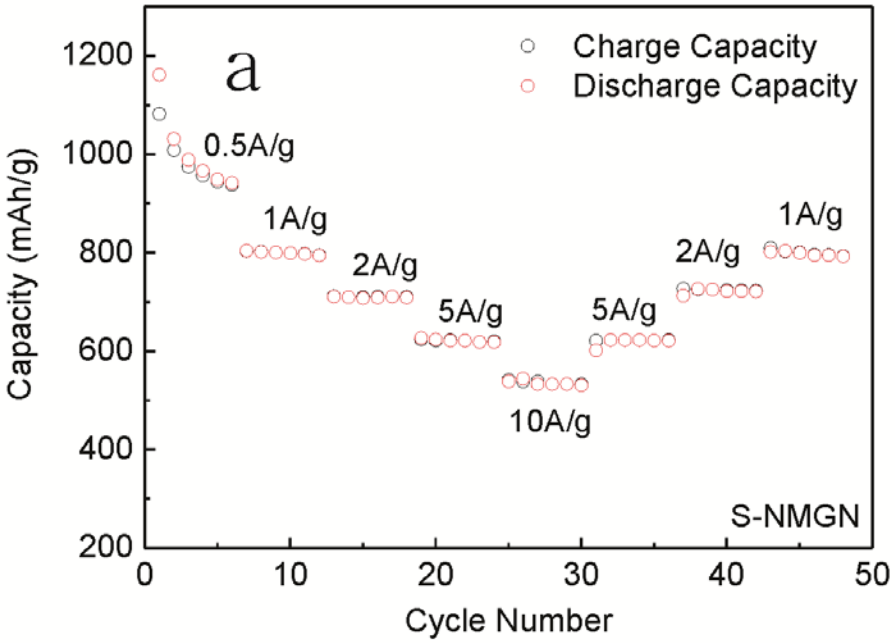
（a, sor

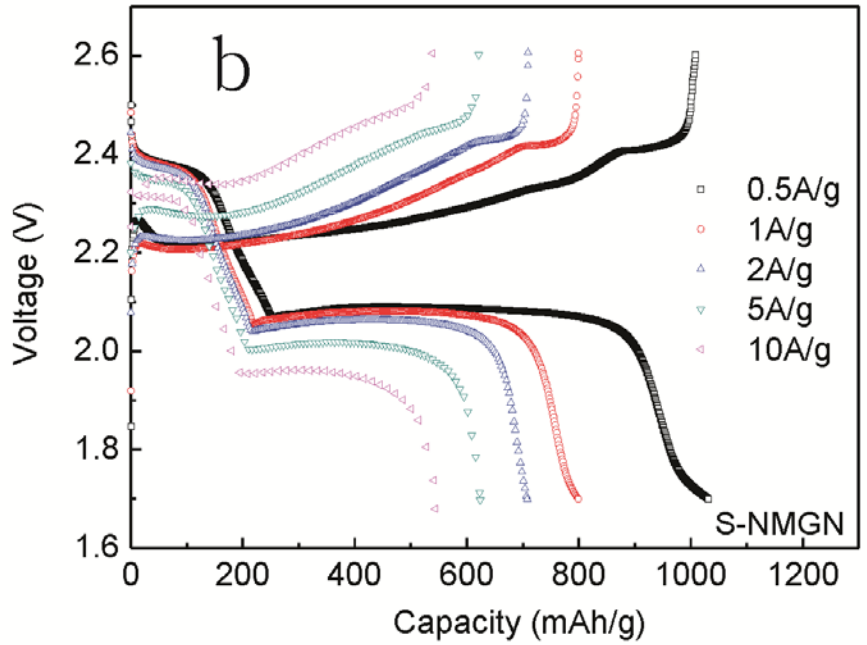


TEM of NMGN



The electrochemical performance of NMGN-sulfur composites





Current (A/g)	0.5	1	2	5	10
Capacity(mAh/g)	1161~941	804~794	711~710	624~618	541~530

Summary

Energy issue will be a severe challenge for humankinds in the future. As a typic 2-D stucture material, graphene can not only build a reactive spot for active species but also alter, sometimes, the reactive mechanism, thus could be used to design and control a desired state of active materials. So, it is of great significance for electrochemical energy storage system.

Thanks for your attention
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