

Hybrid graphene aerogel intermedium for bendable supercapacitor electrode

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Porous structure materials indicate brilliant distribution and great absorption ability, that suggesting the potential application of aerogel state graphene based materials. Aerogel intermedium assisted method was developed and optimised to prepare bendable electrode. Hydrothermal schedule was utilised suggesting potential application at low cost and large-scale factory print issues, rather than consuming high money cost and long labour time. Nickel sulphide has been anchored onto the graphene aerogels via one-pot hydrothermal method. The membrane electrode was made with the carbon ink and aerogel intermedium on the Poly(ethylene terephthalate) (PET) plate. The bendable electrode was fabricated with intermedium and commercial carbon ink, and indicates good performance and economic consumption. The complex membrane capacitor shows the much more brilliant performance than the pure carbon membrane capacitor, with specific capacitance (31.40 mF/cm^2 at 4 mV/s and 17.74 mF/cm^2 at 2 mA/cm^2).

1. Introduction: Stable and financial electrode material is significant, to obtain capacitor and battery with high energy density, under the background of economic and environmental crisis, where much research work has been done by pioneers [1, 2]. Some famous materials have been developed and investigated by researchers, such as the classical Li ions based battery electrode materials [3–7], in this sphere, some typical complex materials have been composed, for example the lithium-oxygen [8, 9], MoS_2 [10], hollow cobalt [11]. Na ions based battery, namely the famous NASICON matrix had been researched by pioneers [2]. The graphene [12–14], with unique properties [15, 16], has been prepared via multi-methods such as the Chemical Vapor Deposition (CVD) method [17] and hummers method [18] and used for batteries [19, 20] and supercapacitor [17, 21]. A kind of supercapacitor electrodes material intermedium has been prepared, for the unique advantages, via hydrothermal with low cost, which is widely used and comprehensively investigated by researchers [22]. Furthermore, energy storage enhance agency is anchored onto the aerogel matrix with the hydrothermal process.

Many kinds of materials have been prepared and investigated by researchers, to enhance the capacitor performance. The pseudo-substance, with redox reaction under the electrochemical reaction, has shown their power storage ability, such as Co_3O_4 [21], RuO_2 [23] and MnO_2 [17, 24], and then there are some sulphide active materials such as the Co_3S_4 [25], MnS [26] and NiS_2 [27]. Furthermore, some polymer-based materials have been researched as supercapacitor, such as PEDOT/PEDOS [28] and PPY [29]. On the one hand, the redox reaction provides the unique high performance to the capacitor, on the other hand, paste the mixture of active intermedium and carbon ink onto the PET matrix [30].

Nickel sulphide and relative compounds have been widely used to fabricate supercapacitor [27, 31]; hydrothermal method was utilised and optimised to prepare composite materials here. To make the benefits of advantages mentioned above, the hybrid aerogels were made into powder, and then mixed with carbon ink to prepare the high-performance bendable electrode. The aerogel intermedium is successfully composed via low-cost pathway, with the NiS_2 and NiS composite, showing electrochemical properties.

2. Experiment section: Intermedium was prepared via famous hydrothermal method [22, 32], as shown in Fig. 1a: dip 20 ml mixed solution (0.9 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1 mmol H_2NCSNH_2 and 20 ml deionised water) into the 10 ml 8 mg/ml GO water solution with mechanical stirring about 5 min. Then process the solution by 1 h ultrasonication modification. Next treat the glue-like liquid via hydrothermal process (180°C for 12 h) and freeze-drying process ($<20 \text{ Pa}$). Lastly, treat the dried aerogel thermally at 350°C for 180 min (120 min to increase the temperature and 60 min to keep the temperature) under N_2 protection atmosphere (0.04 MPa) in tubular furnace. Bendable electrode is made as shown in Fig. 1b: put aerogel intermedium into powder with die assistance. Then, mix the carbon ink and obtained aerogel powder (11 mg) into mixture. Then, plate the mixture into membrane (with scale of $8 \times 38 \text{ cm}^2$ and possible thickness of $9.3 \mu\text{m}$ according to thickness meter) on PET membrane with post-thermal treatment (80°C for 30 min).

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (99%), H_2NCSNH_2 (99%) and KOH (85%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Graphene oxide water dispersion (8 mg/ml) was purchased from SHANDONG OBG NEW MATERIAL Co., Ltd. Carbon ink (CH-8 MOD2) was purchased from JUJO CHEMICAL Co., Ltd. All the raw materials and chemical reagents were used without further purification.

3. Characterisation: Intermedium materials were characterised by powder X-ray diffraction (XRD, PANalytical B.V. XPert Pro MPD) and scanning electron microscopy (FEI-Sirion 200). Electrode properties were characterised under half-cell and full-cell configuration by Electrochemistry Workstation (BioLogic Science Instruments, VMP3) with KOH (3 mol/l). The electrochemical impedance spectroscopy measurements were characterised from 100 kHz to 0.01 Hz. The average active electrode materials mass is 3.7 mg. Membrane thickness is tested by thickness meter of SHANGHAI D&G MEASTRUMENT Co., Ltd. Activation action is processed before test.

4. Results and discussion: XRD pattern of hybrid aerogel materials is shown in Fig. 2, where the approximate concentration ratio (NiS_2 versus NiS) is about 1.47, calculated and obtained

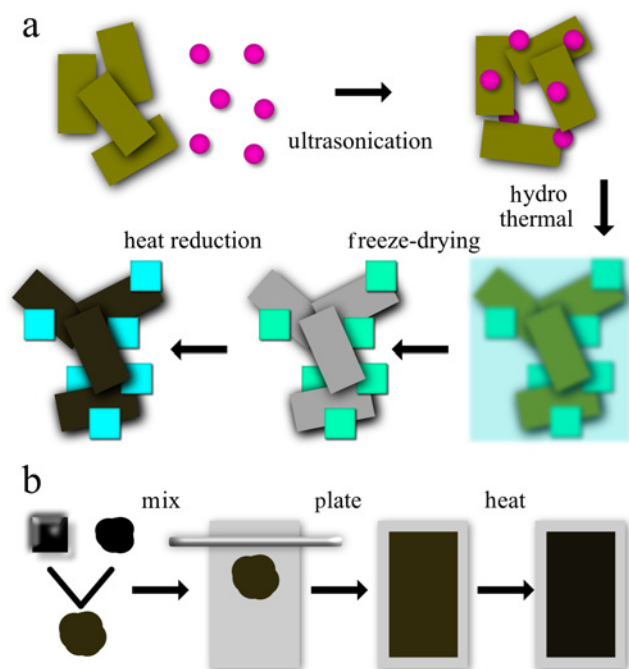


Fig. 1 Schematic illustration to prepare bendable supercapacitor electrode
a Preparation schedule of aerogel intermedium
b Preparation illustration for membrane electrode

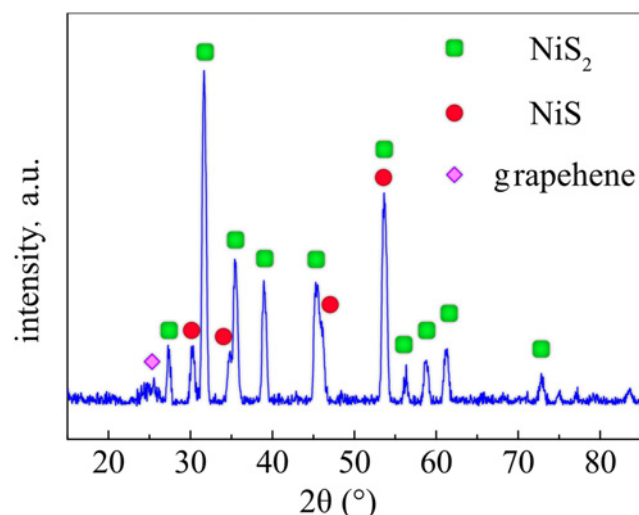


Fig. 2 XRD pattern of nickel sulphide anchored graphene aerogel

according to the reference theory and the Software Toolkit of Lucent Technologies Inc. [33].

Figs. 3*a* and *b* display the morphology of the hybrid aerogel. The cubes (NiS_2 and NiS) with diameters about $2\text{ }\mu\text{m}$ (shown in Fig. 3*b*) are distributed in the aerogel matrix homogeneously, because of the interaction between the metal ions with positive charge and the graphene oxide with negative charge, as reported Fe^{3+} ions by pioneers [34], which can facilitate the dispersion and the distribution of the graphene oxide layers and ions, for which the great structure and morphology would like to build as a result.

Fig. 4*a* presents the preparation of the membrane electrode via the easy-handling surface plating method. The thickness of the membrane is $<20\text{ }\mu\text{m}$ defined by the coating tool with the thickness of $20\text{ }\mu\text{m}$. Fig. 4*b* presents the bendable property, for which the membrane can be recovered after bended into a cycle ring

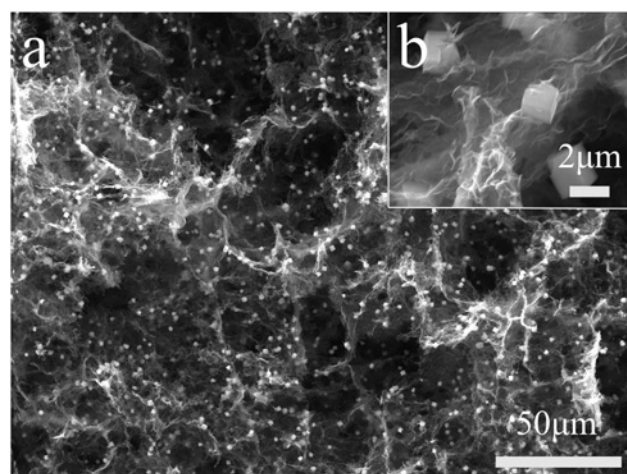


Fig. 3 Hybrid aerogel morphology with
a 500× magnification
b 10,000× magnification

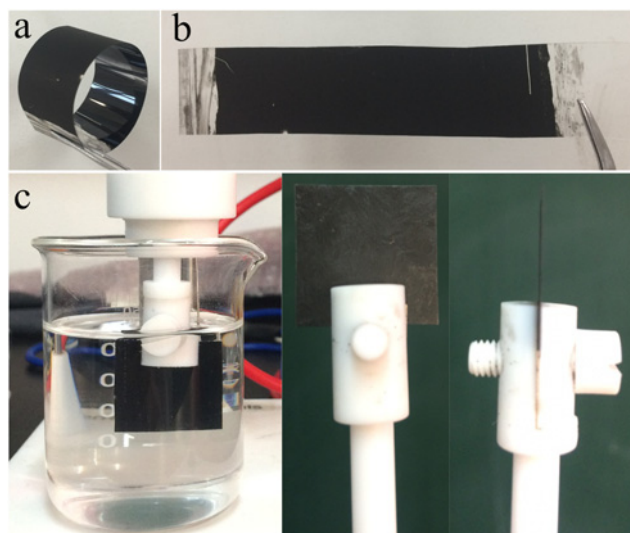


Fig. 4 Bendable electrode as prepared and the system for electrochemical testing
a, b Profile of membrane electrode
c Electrochemical test system and electrode spotlight

without the visible active substance loss. Fig. 4*c* presents the shape and state of the as-coated membrane electrode and shows the electrochemical test configuration and the electrode membrane state, for which the electrochemical performance can be characterised via the half-cell matrix under three-electrode system (with membrane electrode the scale of $2\times 2\text{ cm}^2$).

Valid performance enhancing ability was demonstrated by the different performance with and without aerogel intermedium as shown in Fig. 5. The results suggest the low-cost performance enhance pathway, while there still is the much space to increase the equipment energy storage compared to the pioneer work with nickel foam template (82.5 Wh/kg at 930 W/kg) [35]. For the possible attempt the layer electrode with porous structure could be researched if possible in the furthermore research work.

Half-cell electrochemical performance is shown in Fig. 6. cyclic voltammetry (CV) curves (from 4 to 200 mV/s) of the electrode are shown in Fig. 6*a*. The electrode shows brilliant CV properties. Fig. 6 shows the charge and discharge property, where the reliable performance of the membrane capacitor electrode is demonstrated, the composite material presents the obviously enlarged discharge

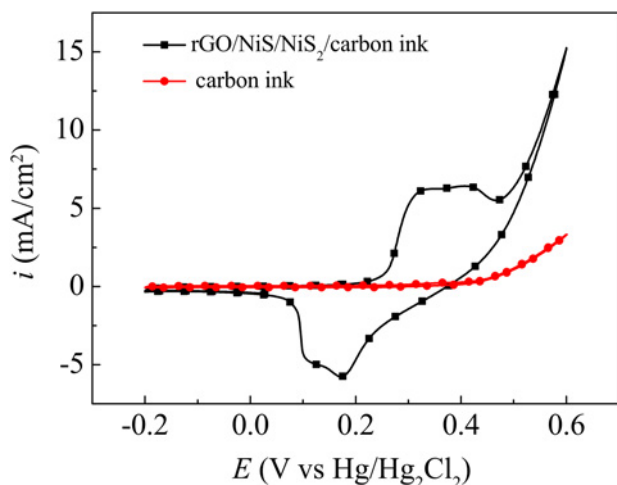


Fig. 5 CV performance (20 mV/s) with and without performance booster agency

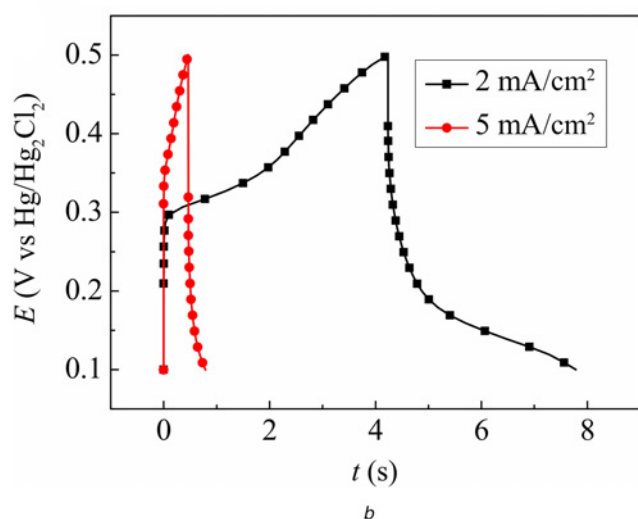
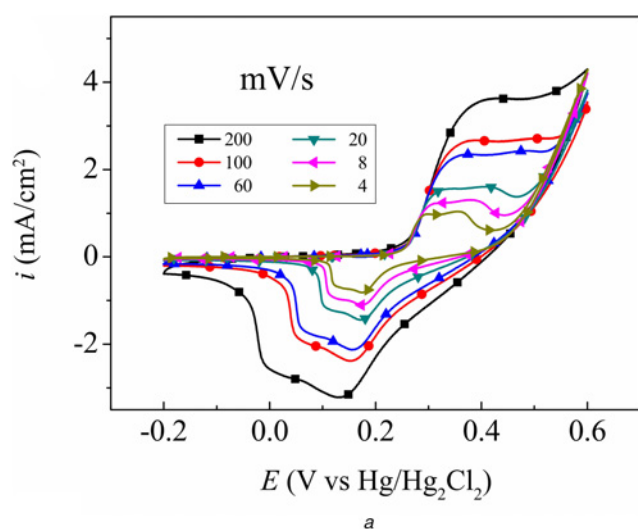


Fig. 6 Half-cell electrochemical performances
a CV curves under scan rate variation
b Charge and discharge curves

time, suggesting the enhanced energy storage ability than carbon ink printed electrode.

Fig. 7 indicates the full-cell symmetric capacitor performance. CV properties (from 4 to 200 mV/s) are shown in Fig. 7a.

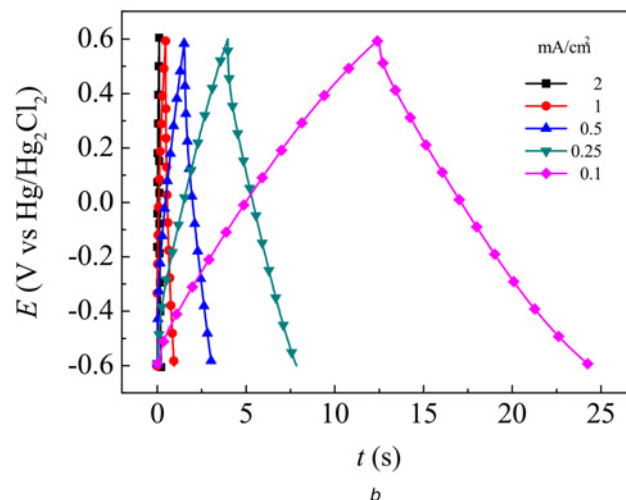
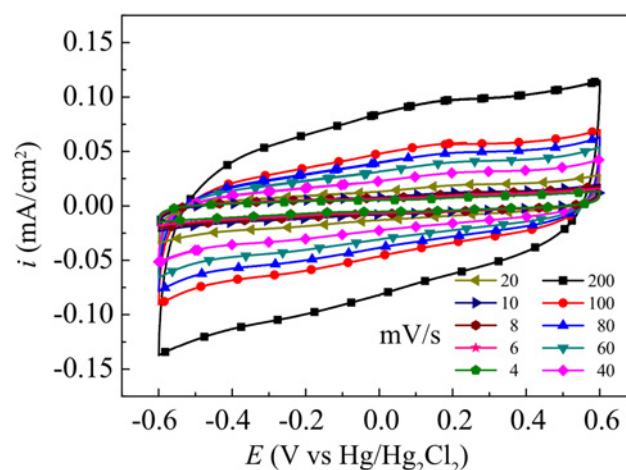


Fig. 7 Full-cell electrochemical performances
a CV curves under scan rate variation
b Charge and discharge curves for electrodes

Charge and discharge performance (from 0.1 to 2 mA/cm²) is clear and same as the common carbon-based capacitor as shown in Fig. 7b.

5. Conclusion: The graphene aerogel intermedium was prepared via hydrothermal method with one step. The membrane-based plant supercapacitor electrode has been fabricated via easy-handling pathway. Half-cell test shows good specific capacitance (31.40 mF/cm² at 4 mV/s and 17.74 mF/cm² at 2 mA/cm²) and low resistance (3.491 Ω). The work completed here would provide a positive reference for other researchers.

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7 References

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