

Cite this: *J. Mater. Chem. A*, 2018, 6, 58Received 1st November 2017  
Accepted 24th November 2017

DOI: 10.1039/c7ta09616j

rsc.li/materials-a

## Polyampholyte-doped aligned polymer hydrogels as anisotropic electrolytes for ultrahigh-capacity supercapacitors†

Junjie Wei,<sup>a</sup> Chengyao Yin,<sup>a</sup> Huanlei Wang<sup>b</sup> and Qigang Wang<sup>id</sup>\*<sup>a</sup>

Pressure-resistant polymer gel electrolytes with convenient ion channels are a key challenge for wearable energy devices to improve their safety and reliability. Our biomimetic aligned hierarchical design and facile polyampholyte doping of the polymer hydrogels are utilized to simultaneously achieve high strength and large ionic mobility, despite the fact that these two factors of traditional polymer gels are mutually restricted by the Flory–Rehner equation. The viscosity-dependent hot-ice templates endow the polymer hydrogels with large aligned pores that are adjustable from 19 to 68  $\mu\text{m}$ , which can benefit their ion mobility and capacity due to the shortened ion migration distance within the electrolytes. The further copolymerization of the polyampholyte component within the hydrogel network can further enhance the capacity due to the increased adhesion between the hydrogel electrolytes and the charged carbon electrode materials. The optimized supercapacitor capacity of the aligned gel electrolytes was  $201.5 \text{ F g}^{-1}$  at a  $0.1 \text{ A g}^{-1}$  current density in the vertical direction, larger than that of a liquid electrolyte of  $159.0 \text{ F g}^{-1}$ . Our hybrid polymer hydrogel has demonstrated high electrochemical performance due to the aligned structure and charging-adjusted adhesion by the polyampholyte.

As our daily wearable electronics demands have continued to grow, solid state energy storage devices have emerged as a mainstream direction in modern electronics and related multidisciplinary fields.<sup>1–6</sup> Ionic conducting gels are arising as promising electrolyte materials for supercapacitors and other energy devices due to the ignorable leakage of liquid and their large flexibility in the semi-solid state.<sup>7–11</sup> As an example, Watanabe's group prepared a supercapacitor with good electrochemical performance using ion gel electrolytes and inverse opal carbon electrodes.<sup>12</sup> Peng's group developed a fiber-shaped

stretchable supercapacitor based on the use of a PVA/ $\text{H}_3\text{PO}_4$  gel electrolyte and a winding structure design.<sup>13</sup> The development of completely flexible and stretchable energy devices without a separator has resulted in further mechanical requirements for gel electrolytes beyond high ionic conductivity.<sup>14–16</sup> Our group have designed self-recoverable gel electrolytes with high mechanical strength, the electrochemical performances of which can be adjusted by pressure deformation and altering the water content.<sup>17</sup> Zhi and Xie have collaborated to fabricate a stretchable supercapacitor based on  $\text{SiO}_2$  nanoparticle-crosslinked polyacrylamide hydrogel electrolytes with a high tensile strength and elongation.<sup>18,19</sup>

To date, compromising between the strength modulus and ionic diffusion of polymer gel electrolytes has been challenging for researchers due to the theoretical restriction imposed by the Flory–Rehner equation.<sup>20</sup> Many natural materials, such as bone, shells, wood and plant stems, exhibit an excellent combination of contradictory strength and diffusion due to their large-scale aligned porous structure.<sup>21</sup> Therefore, biomimetic materials with aligned micrometer-sized hierarchical pores have been shown to be of significant importance in the electronics and biological fields.<sup>22–27</sup> The ice-crystal templating method is commonly used to design aligned micrometer-sized porous structures in soft materials *via* a directional freezing process.<sup>28–30</sup> Cooper's group introduced a directional freezing approach employing various polymer chains, inorganic nanoparticles or their mixtures to form aligned porous materials.<sup>30</sup> Bai's group have continually developed a series of ice-templating methods and bidirectional freezing techniques to prepare aligned biomedical materials with the required mechanical properties and desired hierarchical pores simultaneously.<sup>31–33</sup> Utilizing directional freezing and further copolymerization, our group prepared aligned gel electrolytes with anisotropic ionic mobility and optimized electrochemical performances.<sup>34</sup>

Through the occasional observation of an interesting high-school experiment, we noticed that transparent  $\text{NaAc}\cdot 3\text{H}_2\text{O}$  needle-like crystals with an aligned arrangement and

<sup>a</sup>School of Chemical Science and Engineering, Tongji University, Shanghai 200092, P. R. China. E-mail: wangqg66@tongji.edu.cn

<sup>b</sup>Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, P. R. China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ta09616j

# Water-Deactivated Polyelectrolyte Hydrogel Electrolytes for Flexible High-Voltage Supercapacitors

Junjie Wei,<sup>[a]</sup> Jie Zhou,<sup>[a]</sup> Shasha Su,<sup>[b]</sup> Jinhua Jiang,<sup>[b]</sup> Jing Feng,<sup>[b]</sup> and Qigang Wang<sup>\*[a]</sup>

With the boom of flexible electronic products and wearable devices, flexible energy storage devices, for example, supercapacitors with high performance, are attracting increasing interest. A flexible water-deactivated polyelectrolyte hydrogel electrolyte with good mechanical properties and high ionic conductivity was prepared by using an anionic polymer, carboxy methyl cellulose, and a cationic monomer, methacrylamidopropyltrimethyl ammonium chloride. It was then applied in a supercapacitor with flexible activated carbon electrodes. This flexible supercapacitor possesses a high operating voltage of 2.1 V owing to the low electrochemical activity for water within the hydrogel as a result of the 'molecular cages' effect and hydrophilic interactions between functional groups and surrounding water molecules. Furthermore, this supercapacitor exhibits good flexibility and tailorability. As the first example of water-deactivated polyelectrolyte hydrogel electrolytes in applications involving flexible high-voltage supercapacitors, this work provides a platform for the design of energy storage devices with high energy density for flexible and wearable electronic devices.

Supercapacitors, important electrochemical energy storage devices, have attracted a great deal of attention owing to their unique advantages of fast charging/discharging ability, long cycle life, and high power density.<sup>[1]</sup> They are complement to or can even replace batteries in energy storage areas, especially in which high power delivery is needed.<sup>[2]</sup> However, current supercapacitors using liquid-state electrolytes face an enormous challenge as a result of leakage and instability.<sup>[3]</sup> Similarly, all-solid-state electrolytes (such as ceramic electrolytes) based supercapacitors fail to meet the growing demands of emerging flexible and wearable electronics because of their rigidity.<sup>[4]</sup> Therefore, more effort has been devoted to developing flexible supercapacitors by using quasi-solid-state electrolytes, such as gel electrolytes.<sup>[5]</sup>

Recently, gel electrolyte based flexible supercapacitors with specific functions have made great progress, including stretchable supercapacitors,<sup>[6]</sup> self-healable supercapacitors,<sup>[7]</sup> cold-re-

sistant,<sup>[8]</sup> and heat-resistant<sup>[9]</sup> supercapacitors. For example, Yu and co-workers<sup>[6c]</sup> developed an all-gel-state fiber-shaped supercapacitor by using polyaniline (PANI)/graphene oxide (GO) hybrid hydrogel electrodes and a polyvinyl alcohol (PVA)-based gel electrolyte. This supercapacitor achieved about 40% strain based on the application of the spring-like structure. Highly stretchable supercapacitors based on SiO<sub>2</sub> nanoparticle cross-linked hydrogel electrolytes were reported by the group of Zhi and Xie.<sup>[7a,10]</sup> This supercapacitor benefited from the intrinsic stretchability, self-healing capability of the gel electrolytes, and can retain full capacitance during 600% stretching and 20 cycles of breaking/healing. However, this self-healing capability is limited to the gel electrolyte; the electrodes and the electrolyte/electrodes interfaces were not taken into consideration. Pan and co-workers<sup>[7b]</sup> reported a full-scale healable supercapacitor, which can recover its electrolyte, electrodes, and even its interfaces based on dynamic diol-borate ester bonding both in a PVA gel based electrolyte and electrodes. Widening the range of working temperature is also important for supercapacitors. A cold-resistant supercapacitor employing a hydrogel electrolyte with high content of salts was reported by Tao et al.,<sup>[8a]</sup> the capacitance of which can maintain at least 80% at -10 °C. As for heat resistance, we<sup>[9a]</sup> prepared a high-temperature supercapacitor by using a tough ionic liquid based gel electrolyte, which can operate well at 200 °C. Although there is much research on multifunctioning flexible supercapacitors, little focus has been on simultaneously improving their safety and electrochemical performance. This may involve, for electrolytes, enhancing their mechanical strength, ionic conductivity, and broadening the operating voltage for devices, especially for hydrogel electrolyte based supercapacitors.

Here, we report a flexible supercapacitor that possesses not only a high operating voltage and energy density, but also good mechanical and electrochemical performance. These features are achieved by employing a water-deactivated polyelectrolyte hydrogel electrolyte containing 1 M Li<sub>2</sub>SO<sub>4</sub> as the electrolyte salt. Polyelectrolyte is a class of charged polymers with abundant positive and negative groups.<sup>[11]</sup> These functional groups can build special ion migration channels under the application of an external electric field to accelerate ionic migration and improve ionic conductivity.<sup>[12]</sup> Further, neutral Li<sub>2</sub>SO<sub>4</sub> is a common electrolyte salt used to widen the operating voltage for aqueous electrolytes.<sup>[13]</sup> As shown in Figure 1 a, the water-deactivated polyelectrolyte hydrogel electrolyte was synthesized by using a simple UV photoinduced radical polymerization method using a cationic monomer and an anionic polymer. First, the precursor solution, comprising 1 M Li<sub>2</sub>SO<sub>4</sub> aqueous solution, 0.0–6.0 wt% anionic polymer (carboxy methyl cellulose, CMC), 15 wt% cationic monomer (methacrylamidopro-

[a] Dr. J. Wei, J. Zhou, Prof. Dr. Q. Wang  
School of Chemical Science and Engineering, Tongji University  
Shanghai 200092 (P. R. China)  
E-mail: wangqg66@tongji.edu.cn

[b] S. Su, J. Jiang, J. Feng  
Evonik (Shanghai) Investment Management Co., Ltd.  
68 Chundong Road, Shanghai 201108 (P. R. China)

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/cssc.201801277>.

# Dissolution–Crystallization Transition within a Polymer Hydrogel for a Processable Ultratough Electrolyte

Junjie Wei, Gumi Wei, Yinghui Shang, Jie Zhou, Chu Wu, and Qigang Wang\*

Although nonliquid electrolytes have been developed rapidly under the condition of safe demand of energy storage devices, the inherent weaknesses in ionic conductivity, mechanical properties, or interfacial compatibility severely hinder their application under a harsh environment. Inspired by the hybridized characteristics of composite materials and the potential advantages of hydrated crystals, a processable crystal-type gel electrolyte with good comprehensive performance via the dissolution–crystallization transition of NaAc within hydrogel is creatively prepared. The use of NaAc crystal within a hydrogel leads to nearly 26 000 times greater modulus (474.24 MPa) and higher operating voltage (2.0 V) than the hydrogel without the crystal. The reliable supercapacitor using this electrolyte can work in extreme environment (−40 to 80 °C, even in the fire or in liquid nitrogen within a short time) benefiting from its phase-transition capacity. This investigation offers a facile and versatile way to construct an ideal gel electrolyte for next-generation energy storage devices.

With the proliferation of energy storage devices and the improvement of its electrochemical performance, more and more researchers are beginning to shift their attention to non-liquid electrolyte materials due to the urgent demand for the safety issue.<sup>[1–4]</sup> Through several decades, there are extensive advances in various classes of nonliquid electrolytes, including ceramic electrolyte, polymer electrolyte, and hydrogel electrolyte. However, these existing nonliquid electrolytes still have some inherent disadvantages. The hydrogel electrolytes suffer from the narrow operating voltage and weak mechanical strength in practical applications. Current efforts to solve the problem can be divided into two categories: selecting appropriate solvent and electrolyte salt to broaden its operating voltage and temperature,<sup>[5–7]</sup> and designing polymer network with noncovalent crosslink to enhance its mechanical properties.<sup>[8–10]</sup> However, the successful noncovalent design in hydrogel will suffer from disturbance in the selected polar solvent; only few work can achieve good electrochemical and mechanical performance by complicated solvent exchanges.<sup>[11]</sup> Besides, the bad interfacial compatibility of ceramic electrolyte<sup>[12,13]</sup> and the low ionic conductivity of polymer electrolyte<sup>[14,15]</sup> are also great challenges

to be faced. Therefore, it's necessary to develop a new nonliquid electrolyte with comprehensive performance for fulfilling various energy devices.

Hydrogel electrolyte with hydrated salt crystal may be a new candidate to solve the above requirements by the introduction of new phase. The hydrated salt crystals, as one kind of industrial liquid–solid phase change materials, can be immobilized into hydrogel by the facile dissolution–crystallization transition. The demonstrated polymer gel electrolyte with NaAc·3H<sub>2</sub>O crystal as aligned porous template was designed by the in situ supersaturated crystallization of NaAc.<sup>[16,17]</sup> The introduction of inorganic crystal into polymer hydrogel can form the inorganic–organic composite with enhanced mechanical strength due to hydrogen bond or other synergistic effects.<sup>[18,19]</sup> The bound hydrated salt can suppress the electrochemical activity of water and broaden operating voltage of aqueous electrolyte<sup>[20]</sup> due to the strong interaction with water molecules, similar to the solvation sheath in “water-in-salt” electrolyte.<sup>[21–23]</sup> The high-concentrated salts within crystal-type gel can also efficiently reduce the freezing point and increase the boiling point of aqueous solutions.<sup>[24]</sup> At last, the hydrated salt crystal can endow gel electrolytes with thermal-resistant performance through liquid–solid phase transition accompanied by endothermic and exothermic phenomena.<sup>[25,26]</sup> All in all, the crystal-type composite gel electrolyte can realize the comprehensive performance, including ultrahigh toughness, high operating voltage, extreme temperature tolerance, and good interfacial compatibility by a facile dissolution–crystallization transition approach.

In this work, the pioneering crystal-type composite gel with excellent performance was prepared using a facile method that employed the crystallization of NaAc. There are only three main components in the precursor solution (Figure 1a,b): distilled water, abundant soluble salt, and a certain amount of monomer (or macromolecule). First, a high concentration of the salt solution was prepared by dissolving excessive soluble salt in the distilled water at high temperature. Then, the hydrogel was formed by UV irradiation for monomer solution (Figure 1c). Finally, the supersaturated salt within hydrogel was initiated to crystallize by placing a small crystal particle as seed on the surface of the hydrogel, and soon the crystal-type composite gel with extensive soluble salt crystals was obtained (Figure 1d). Typically, the crystal-type composite gel containing 15 wt% acrylamide (AAm) monomer and a certain quality of

J. Wei, G. Wei, Y. Shang, J. Zhou, C. Wu, Prof. Q. Wang  
School of Chemical Science and Engineering  
Tongji University  
Shanghai 200092, P. R. China  
E-mail: wangqg66@tongji.edu.cn



The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201900248>.

DOI: 10.1002/adma.201900248

# Hofmeister Effect-Aided Assembly of Enhanced Hydrogel Supercapacitor with Excellent Interfacial Contact and Reliability

Junjie Wei and Qigang Wang\*

The hydrogel electrolyte has been researched extensively to meet the multifunctional demands for energy storage devices. However, due to the weak mechanical strength of hydrogel electrolytes, the poor interfacial contact between electrolyte and electrode, and the conflict between mechanical strength and interface, the reliability and interfacial needed are needed to be further improved. Herein, an extremely tough poly(vinyl alcohol) (PVA) hydrogel electrolyte and a novel “two-step” in situ assembly method for supercapacitors are developed utilizing the Hofmeister effect on PVA molecules. The supercapacitor assembled by this method exhibits excellent performance, especially in reliability and interfacial properties, attributed to the ultrahigh mechanical properties and the unique interface binding phase. The investigation offers a simple and versatile way to construct next generation multifunctional solid-state energy storage devices with superior safety, stability, and environmental adaptability.

Hydrogel electrolyte has attracted intensive research attention due to the booming development of various flexible electrochemical energy storage devices and electronics.<sup>[1,2]</sup> Compared with other solid electrolytes, hydrogel electrolyte exhibits better performances in ionic conductivity and additional functions, such as flexibility,<sup>[3,4]</sup> stretchability,<sup>[5,6]</sup> self-healability,<sup>[7,8]</sup> and self-protection,<sup>[9–11]</sup> owing to the highly abundant and tunable chemistries of hydrogel materials. However, there is a severe conflict between high mechanical strength and good interfacial property for hydrogel electrolyte, just like other solid electrolytes. Interfacial property between electrolyte and electrodes is a crucial problem for nonliquid electrolyte, especially for solid electrolyte with high mechanical strength.<sup>[12–14]</sup> Obviously, unlike the liquid electrolyte that has good wettability with electrodes, the rigid contact between solid electrolytes and electrode result in a large interfacial resistance. In most cases, the cells were assembled by inserting the stand-alone gel electrolyte, which has been premade *ex situ* in the form of film, between two electrodes. Compared with these cases, the hydrogel

electrolytes prepared in situ within cells have more advantages in interfacial resistance and utilization of electrodes.<sup>[15–17]</sup> For example, Wang et al. prepared a tetraethylene glycol dimethyl ether gel electrolyte for Li-air battery through in situ cross-linking reaction on the surface of Li anode. This battery exhibited long cycle life and robust flexibility owing to the tight adhesion between in situ gel electrolyte and electrodes.<sup>[18]</sup> Nevertheless, there are some defects to be solved for this method of in situ preparation, such as tough operation conditions, potentially unwanted side reactions and poor controllability.<sup>[15,19–21]</sup> What's worse, the in situ hydrogel electrolyte limits the reliability of devices in case of physical damage due to the inherently poor mechanical properties,<sup>[22,23]</sup> which severely hinders its further application.

The solubility of hydrophilic polymers (including synthetic and natural polymers) in aqueous systems is affected by salt ions, an effect known as the Hofmeister effect.<sup>[24–26]</sup> Since it was first proposed in 1888 to describe protein precipitation, Hofmeister effect have been studied in many fields, such as analytical extraction, gel-coagel transitions, colloid stability, and so on.<sup>[24,27]</sup> Recently, Hofmeister effect was also proved that it is an efficient method to adjust the mechanical properties of hydrophilic polymer hydrogel. Wang et al. reported a tough and ductile gelatin hydrogel by immersing the prepared gelatin gel into an ammonium sulfate solution, this treated hydrogel has an extraordinary ultimate strength of 12 MPa based on Hofmeister effect.<sup>[28]</sup> Similarly, Kouwer et al. tuned both the thermoresponsive behavior and mechanical properties of polyisocyanides hydrogel by utilizing the Hofmeister series.<sup>[29]</sup> While these studies have nothing to do with electrochemical energy storage devices, they provide us abundant experience to design tough hydrogel electrolyte for reliable devices. Furthermore, the above enhanced method based on premade weak hydrogel points a new possibility to solve the presented issue of in situ gelation. Therefore, we designed a supercapacitor with high mechanical safety and interfacial compatibility employing enhanced tough poly(vinyl alcohol) (PVA) gel electrolyte via the simple two-step in situ assembled approach of soaking sandwiched electrode/premade PVA gel/electrode in  $(\text{NH}_4)_2\text{SO}_4$  solution based on Hofmeister effect.

Herein, the enhanced tough PVA hydrogel electrolyte with excellent mechanical performance was prepared through

J. Wei, Prof. Q. Wang  
School of Chemical Science and Engineering  
Tongji University  
Shanghai 200092, P. R. China  
E-mail: wangqg66@tongji.edu.cn

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/smt.201900558>.

DOI: 10.1002/smt.201900558



## (12)发明专利申请

(10)申请公布号 CN 109810225 A

(43)申请公布日 2019.05.28

(21)申请号 201910190477.3

(22)申请日 2019.03.13

(71)申请人 同济大学

地址 200092 上海市杨浦区四平路1239号

(72)发明人 魏俊杰 王启刚

(74)专利代理机构 上海科盛知识产权代理有限公司 31225

代理人 林君如

H01G 11/56(2013.01)

H01M 10/0565(2010.01)

H01G 9/20(2006.01)

C08L 89/00(2006.01)

C08L 1/28(2006.01)

C08L 33/26(2006.01)

C08L 33/14(2006.01)

(51)Int.Cl.

C08F 220/56(2006.01)

C08F 222/38(2006.01)

C08F 220/38(2006.01)

C08F 220/58(2006.01)

C08F 2/48(2006.01)

C08J 3/075(2006.01)

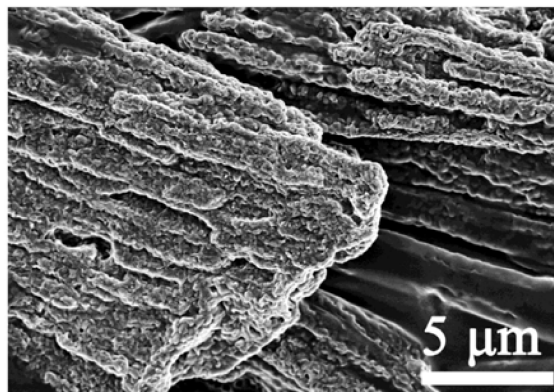
权利要求书1页 说明书8页 附图5页

### (54)发明名称

一种结晶型复合凝胶电解质及其制备方法和应用

### (57)摘要

本发明涉及一种结晶型复合凝胶电解质的制备方法和应用,其特征在于,包括以下步骤:  
(1)将成胶组分和可溶性盐加入水中,搅拌至完全溶解成为透明均一的溶液,得到凝胶前驱液;  
(2)将步骤(1)得到的凝胶前驱液进行成胶,制备得到含有饱和和可溶性盐的水凝胶;(3)在步骤(2)制备得到的水凝胶上方放置晶种,即得到结晶型的复合凝胶电解质。与现有技术相比,本发明制备过程简单高效,材料廉价易得,制备得到的复合凝胶电解质具有更高的机械强度和离子电导率,可应用于超级电容器等储能器件,对于不同环境温度可自主调节材料温度,即使是在极端环境中,也能维持体系在短时间内保持温度稳定,在应对火灾等灾害时具有重要意义。





# 学术先锋

同济大学2019年研究生

同济大学党委研究生工作部 共青团同济大学委员会  
同济大学研究生会



# 荣誉证书

魏俊杰同学：

被评为2017-2018学年同济大学

## 优秀学生

证书编号：同团奖2019150202

共青团同济大学委员会

二〇一九年一月

同济大学委员会

T201901015



同济大学  
TONGJI UNIVERSITY

# 获奖证书

魏俊杰 魏谷米 尚英辉 周杰 同学：

你（们）的作品 基于醋酸钠结晶的高性能防灾型凝胶电解质的研发  
在2019同济大学“挑战杯”比赛中荣获：

## 一等奖

指导老师：王启刚

特颁此证，以资鼓励。

同济大学第四届“卓越杯”大学生科技创新竞赛  
暨第十六届“挑战杯”全国大学生课外学术科技作品同济校内赛组委会  
共青团同济大学委员会（代）  
同济大学女贝云  
二〇一九年五月



NO.201810161



同濟大學  
TONGJI UNIVERSITY

# 奖学金证书

## Scholarship Certification

魏俊杰

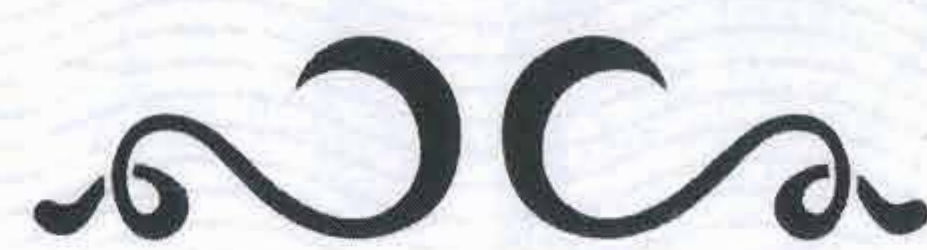
学号：1510584

荣获 2017-2018 学年同济大学亨斯  
迈聚氨酯奖学金（特等奖）。特颁此  
证，以资鼓励。

This is to certify that Mr. Wei Junjie has  
been awarded The Grand Prize of Huntsman  
Polyurethanes Scholarship of Tongji  
University in the 2017-2018 academic year.



# 获奖证书



高亚伟 刘新华 魏俊杰 徐景妍 武尚卿 仇钦棋 邵强 同学

你(们)的作品《柔性储能器件的研制》

在2016年创青春全国大学生创业大赛同济大学选拔赛中荣获

## 银奖

共青团同济大学委员会

二〇一六年四月

同济大学委员会

