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RAPID COMMUNICATION

# Interconnected carbon nanotube/graphene nanosphere scaffolds as free-standing paper electrode for high-rate and ultra-stable lithium-sulfur batteries

Lin Zhu[a,b,1], Hong-Jie Peng[b,1], Jiyuan Liang[c], Jia-Qi Huang[b,*], Cheng-Meng Chen[d], Xuefeng Guo[c], Wancheng Zhu[a,*], Peng Li[e], Qiang Zhang[b,*]

[a]*Department of Chemical Engineering, Qufu Normal University, Shandong 273165, China*
[b]*Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*
[c]*Key Laboratory of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*
[d]*Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 Taoyuan South Road, Taiyuan 030001, China*
[e]*Beijing Tsingna Technology Co., Ltd, Beijing 100084, China*

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**Abstract**
The rational design and fabrication of flexible electrodes with high capacity, high rate capability, and high cycling stability is of urgent need for bendable, wearable, and implantable electronic devices. The integration of conductive nanocarbon as flexible scaffolds is an efficient and effective route toward flexible high-energy-density lithium-sulfur batteries. Herein, a free-standing paper electrode was constructed by rational integration of high conductive super-long carbon nanotubes (CNTs) and nano-sized hollow graphene spheres (GSs) through a room-temperature solution-processable method for lithium-sulfur batteries. The hollow GSs afforded close space to accommodate sulfur species, sustain the volume fluctuation during cycling, and retard the dissolution of polysulfides and parasitic shuttle. The graphene walls of GSs and super-long CNTs synergistically constructed hierarchical short-/long-range electron/ion pathways.

*Corresponding authors.
*E-mail addresses:* jqhuang@tsinghua.edu.cn (J.-Q. Huang), zhuwancheng@tsinghua.org.cn (W. Zhu), zhang-qiang@mails.tsinghua.edu.cn (Q. Zhang).
[1]Both authors contributed equally to this work.

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Consequently, the as-obtained flexible paper electrode was with a high sulfur utilization of 81% (corresponding to 1346 mA h $g^{-1}$) at a current density of 0.17 A $g^{-1}$ (0.19 mA $cm^{-2}$), a high-rate capacity retention of 40% when the current density increased to supreme 16.7 A $g^{-1}$ (18.4 mA $cm^{-2}$), and a superior capacity retention of 89.0% over 500 cycles. This proof-of-concept research indicated the well hybridization of graphene and CNTs holds promise in the efficient use as flexible electrodes for future flexible electronics.


## Introduction

The commercial success of flat-panel displays starts an era of flexible electronics, leading to their new applications in rollable displays [1]. Other promising applications, including thin film solar cells, touch screens, wearable sensors, implantable medical devices, artificial skins, conformable active radio-frequency identification tags, and sensors, have attracted intensive interest in building electronic devices directly on flexible substrates. Driven by the growing demand for electronics permitting lightweight design, portability, and low manufacturing cost, the flexible electronics have been highly concerned by scientific communities as well as material and electronic industries [1-4]. However, these flexible electronics cannot be realized unless corresponding power sources are developed.

Lithium-ion batteries dominate the current portable device market due to their high energy density, high output voltage, long life, and environmentally friendly operation. However, currently the most commonly used rechargeable batteries are still too heavy, thick, rigid, and bulky to match practical requirements of flexible devices [3]. Advanced flexible electrochemical energy storage systems with various sizes, shapes, and mechanical properties are urgently required for the development of bendable, wearable, and implantable electronic devices. The key challenge to realize flexible batteries is to design and fabricate energy materials with high capacity, high rate capability, cycling stability, good conductivity, and robust flexibility, coupled with high performance electrolytes and separators in a rational assembly [3,5].

Lithium-sulfur batteries with a theoretical energy density of 2600 W h $kg^{-1}$ have attracted great attentions as a promising candidate for flexible power sources [6,7]. The sulfur electrode possesses valuable characteristics of low equivalent weight, high capacity, low cost (around 150 \$ $t^{-1}$), and nontoxicity. However, the insulating nature of sulfur and lithium sulfide, the volume fluctuation during cycling, and the shuttle mechanism induced by the dissolution and diffusion of polysulfide intermediates hinder the full utilization of sulfur in a cell. The introduction of nanocarbon and/or conductive polymer scaffolds into sulfur cathodes exhibited a remarkable improvement in the electrochemical performance [8-10]. For instance, carbon nanotubes (CNTs) with extraordinary electrical conductivity and robust mechanical properties rendered outstanding performance when serving as conducting agents [11-16]. Wrinkled graphene materials were effective scaffolds for lithium-sulfur batteries because of their high accommodation capability of sulfur and tunable surface properties [17-21]. According to the demand for a high-performance flexible sulfur cathode towards ultimate flexible devices, a desirable scaffolds should be rationally designed with following "3H" characteristics: (1) high three-dimensional (3D) electrical conductivity of the whole cathode scaffolds; (2) high accommodation capability for the sulfur-containing compounds; and (3) high mechanical strength to withstand the volume fluctuation during repeated cycling. As a successful paradigm for "3H" feature, super-long CNTs were served as both adhesive binders and conductive agents for flexible paper cathode in a lithium-sulfur batteries with high areal capacity for their advances in long-range electron transport, electrolyte accommodation, and mechanical robustness [12-14]. However, the entrapment of the polysulfides in the flexible CNT paper, which is the key for high cycling stability, should be further improved. The incorporation of porous carbon into CNT framework is consequently considered to confine polysulfides and retard the shuttle effect. For instance, free-standing carbide-derived carbon/CNT/sulfur cathode with high in-plane conductivity and enhanced cycling stability have been firstly proposed and realized by Kaskel's group [22]. The microporous carbon nanofiber/CNT/sulfur paper reported by Yu and co-workers exhibited much better cycle performance and rate performance compared to CNT-free cathode [23]. The microsized spherical porous carbon/CNT/sulfur composites with a high tap density and high sulfur content were successfully fabricated by Wang and co-workers to reduce the resistance of the composite and to improve the performance of lithium-sulfur batteries at high areal current densities [24]. Free-standing electrodes with rational pore structures and conducting networks by the *in-situ* assembly of CNTs and mesoporous carbon nanocages have been explored by our group [25]. Except for super-long CNTs, carbon fibers [26] and 3D graphene foam [27] also successfully served as current collectors with both 3D macropores to support huge amounts of sulfur and long-range electron paths. The rational design of the flexible cathode materials for "3H" high-capacity, high-rate, and high-stability lithium-sulfur batteries is still in extensive demand. Briefly, "3H" electrode and material design leads to "3H" energy-storage devices. The wise choice of $sp^2$ carbon building blocks and rational design of flexible electrodes based on CNT and graphene is the first step to fully demonstrate the "3H to 3H" idea and allow mechanistic insight on the energy chemistry based on nanomaterials.

To prove the "3H to 3H" concept, we employed super-long CNTs as the highly conductive network for long-range electron transfer and hollow graphene nanospheres (GS) as bifunctional building blocks to accommodate active sulfur and conduct the electron locally. The reason we selected hollow GS was aroused from its strong confinement of sulfur-containing compounds by the well-defined cavities