



## Communication

# An in-plane heterostructure of graphene and titanium carbide for efficient polysulfide confinement



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## ABSTRACT

Lithium polysulfide (LiPS) shuttling is one of the main obstacles hindering the practical use of lithium-sulfur (Li-S) batteries. Constructing an interlayer composed of carbon or noncarbon materials on separator is a promising way to restrain the LiPS shuttling, but such a layer always hinders the Li ion diffusion and is hard to realize the reuse of the captured LiPSs. In this study, an in-plane heterostructure constructed by graphene and titanium carbide (TiC) was prepared by directly using graphene as a template and the carbon source to react with TiCl<sub>4</sub> under thermal treatment. In this process, graphene was partially transformed into TiC forming such a heterostructure, which is benefit to reducing the Li ion and electron diffusion barrier. Moreover, the TiC has strong affinity towards LiPSs and high conductivity. Thus, the in-plane heterostructures filtered on a separator as a coating layer effectively blocks the shuttle of LiPSs and greatly improves the sulfur utilization and cycling performance, indicating a promising way to promote the practical applications of high performance Li-S batteries.

## 1. Introduction

The shuttling of soluble lithium polysulfides (LiPSs) from cathode to anode is one of the main obstacles hindering the practical use of the lithium-sulfur (Li-S) battery, a representative next-generation energy storage system with a high theoretical energy density (2600 Wh kg<sup>-1</sup>) [1,2]. Tremendous efforts have been made to address this problem by compositing sulfur with carbons, conductive polymers or metal-based compounds [3–10]. These materials restrain the shuttling by the physical or chemical bindings towards the LiPSs, but they normally occupy large volume and weight in the electrode, resulting in the decrease of the energy density of battery. Alternatively, a LiPS blocking interlayer placed between the separator and cathode can restrain the shuttling more efficiently [11,12]. The free-standing interlayer or the coating on separator composed of above materials has been proposed to serve as such layer. The key for such layer is that it should not only block and trap the LiPSs, but also be conductive to realize the reuse of the trapped LiPSs. Although carbon materials always have high

conductivity that is favour to the conversion of LiPSs, their nonpolar nature results in poor affinity towards polar LiPSs [13–16]. In contrast, the polar metal compounds show strong chemical binding towards LiPSs, but they are normally semiconductors with low conductivity [17–20]. Both cases result in the slow LiPS conversion kinetics, and thus, the shuttling of LiPSs cannot be effectively blocked.

A conductive and polar material is crucial to improve the blocking efficiency by realizing the fast conversion of soluble LiPSs into insoluble products [21–23]. The heteroatom doping of carbon, such as N and S doping, can improve the affinity of LiPSs with carbon surface. As a typical example, graphene helps realize the highest heteroatom utilization due to its two-dimensional structure [7,24]. However, the content of doped heteroatoms is normally lower than 10% in carbon [24,25]. Another critical point for the fast LiPS conversion is the fast Li ion diffusion to realize the couple of electrons and Li ions, but the Li ion diffusion barrier on graphene is much larger than that on metal compounds demonstrated by previous studies [26,27]. Although the hybridization of carbon with noncarbon compo-

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nents can help overcome the above problems to some extent, the weakly bound interface between them does not facilitate the fast electron transfer and the LiPS migration from noncarbon surface to carbon for conversion [18].

Herein, we proposed an in-plane heterostructure composed of graphene and conductive titanium carbide (TiC) to realize the strong LiPS binding and fast LiPS conversion. Such heterostructures are prepared by using graphene as the two-dimensional (2D) reactive template for the TiC synthesis, and as a result, a part of graphene was transformed into TiC zones forming a bound interface between them, which greatly decreases the LiPS and electron diffusion barrier. The TiC not only has strong interfacial interaction towards LiPSs, but also creates Li ion diffusion channels on graphene surface [27,28]. The relative high TiC content in the formed heterostructure ensures the strong binding ability towards LiPSs, at the same time, graphene acts as a physical blocking barrier hindering the pass through of LiPSs and constructs a long range conductive network, guaranteeing their fast conversion. Moreover, the TiC content can be easily controlled by tuning the titanium-based precursors. Thus, the coating layer constructed by the graphene-TiC in-plane heterostructure (denoted G-TiC) on separator greatly restrains the shuttling of LiPSs, which is superior to the coating layers composed of the heteroatom-doped graphene and the most of carbon-noncarbon hybrids those are hard to balance the ion and electron transfer for LiPS confinement and fast conversion.

## 2. Experimental section

### 2.1. Preparation of in-plane graphene/titanium carbide heterostructures

The graphene was used as the carbon source and placed near the gas inlet. The Ar protective gas was with a flow rate of 100 sccm. The other (Ar+5% H<sub>2</sub>)/TiCl<sub>4</sub> gaseous mixture was introduced into the furnace tube with a flow rate equal to 300 sccm when the furnace temperature rose to 1200 °C, and the reaction lasted for 2.5 h. After that, the Ar protective gas was turned to 300 sccm. The final black G-TiC heterostructures were obtained, and the TiC contents are 25 wt% (denoted as G-25%TiC). When setting the reaction time at 1.5 h and 4 h, the heterostructures with 18 wt% and 40 wt% TiC (denoted as G-18%TiC and G-40%TiC) were prepared. For comparison, graphene (denoted as G) was synthesized by a thermal exfoliation method and a continuous thermal treatment at 1200 °C.

### 2.2. The coating layer fabrication

G-TiC and G products were dispersed in ethanol (50 mL) and sonicated for 1.5 h, then were filtered on a commercial separator (microporous polypropylene (PP), Celgard 2500) to gain the coating layer (0.46 mg cm<sup>-2</sup>), respectively, which are denoted G-TiC-S and G-S. For comparison, the 25 wt%-commercial TiC nanoparticles mixed with graphene (denoted as p-G-TiC) were controlled to have the same mass loading on the commercial separator.

### 2.3. Materials characterization

X-ray diffraction (XRD) patterns were performed on a Rigaku D/MAX 2500/PC diffractometer with Cu K $\alpha$  radiation (40 kV, 100 mA,  $\lambda$  = 0.154 nm) between 10 and 140°. Raman spectra was obtained with a Lab RAM HR800 (Horiba) using 532 nm incident radiation. Scanning electron microscopy (SEM) was characterized by a field emission scanning electron microscope (FE-SEM, ZEISS SUPRA 55) at 5 kV and transmission electron microscopy (TEM) was operated on JEM 3100 F (JEOL, Japan) at 200 kV. G-TiC heterostructures product and graphene were respectively soaked in the vials of Li<sub>2</sub>S<sub>6</sub> solution (0.2 mol L<sup>-1</sup>) diluted in 1, 3-dioxolane (DOL)/1, 2-dimethoxyethane (DME) (1:1 by volume) for 24 h. The Li<sub>2</sub>S<sub>6</sub> solution was prepared by

dissolving an appropriate amount of S<sub>8</sub> and Li<sub>2</sub>S in DOL mixed with DME in a volumetric ratio of 1:1, the solution was then stirred at 70 °C in an Ar-filled glove box overnight. The equal solution without adding anything was used as a control. X-ray photoelectron spectroscopy (XPS) was measured by an ESCALAB 250Xi (Thermo Fisher) with a monochromatic Al K $\alpha$  source. Thermogravimetric (TG) analysis (NETZSCH, SFA449) of the heterostructures product was carried out in an air atmosphere at a heating rate of 10 °C/min to 900 °C so as to remove the graphene. The electronic conductivity of G-25% TiC-S and G-S were measured by a standard four-point-probe resistivity measurement system (MCP-T610, Japan), and three different positions are measured to obtain the average value.

### 2.4. Li-S cell assembly and electrochemical measurements

The cathode electrode was fabricated by mixing 80 wt% graphene-sulfur hybrid with 10 wt% multi-walled carbon nanotubes (MWCNT) and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP). Thus, a long range and continuous conductive network in material and electrode can be constructed by combining the two-dimensional graphene and one-dimensional carbon nanotube together, ensuring the high utilization of sulfur. Graphene and sulfur were uniformly mixed with 1.5:8.5 mass ratio and then were heated at 155 °C for 12 h in a sealed vessel filled with Ar protection to gain the graphene-sulfur hybrid. The loading of sulfur in each electrode is about 1.1–1.4 mg cm<sup>-2</sup>. The electrolyte solution was 1 mol L<sup>-1</sup> lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in DOL and DME (1:1 by volume) with a 0.2 mol L<sup>-1</sup> LiNO<sub>3</sub> additive. The cell with a lithium metal foil as the anode was assembled in an argon-filled glove box and its electrochemical performance was measured by CR2032 coin cells. Galvanostatically test was performed on a Land 2001A battery testing system between 1.7 and 2.8 V (vs. Li<sup>+</sup>/Li). Cyclic voltammetry (CV) measurements were carried out over the potential range of 1.7–2.8 V (vs. Li<sup>+</sup>/Li) at a scan rate of 0.1 mV s<sup>-1</sup> on a VMP3 electrochemical workstation (Bio Logic) and electrochemical impedance spectroscopy (EIS) was conducted using an amplitude of 5 mV with scanning frequency range from 10 mHz to 100 kHz on the same workstation.

## 3. Results and discussion

The G-TiC was prepared by the direct reaction of graphene with TiCl<sub>4</sub> vapour in the Ar/H<sub>2</sub> atmosphere under the thermal treatment, and the schematic preparation process is presented in Fig. 1a. The SEM image in Fig. 1b shows the graphene (denoted G) is thin and flat but with some wrinkles. After the reaction, it can be seen the obvious contrast change on some parts of graphene that some white regions appear due to the existence of heavy element of Ti in the TiC, indicating these regions of graphene has been transformed into TiC (Fig. 1c). The TEM image in Fig. 1d shows similar result that is in accordance with the SEM image. High resolution TEM image in Fig. 1e further confirms the transformation of graphene into TiC and the formation in-plane heterostructure. A boundary of graphene and TiC is obscure and shows a smooth transition, suggesting an intergradation of them. The exposed lattice fringes of TiC are 0.25 and 0.218 nm, corresponding to the (111) and (200) planes [29,30].

The crystal structure of the prepared G-TiC and graphene was further characterized by X-ray diffraction (XRD) (Fig. S1) and Raman spectroscopy (Fig. S2). The typical peaks located at 35.91°, 41.71°, 60.49°, 72.37° and 76.14° in the XRD patterns can be indexed to the (111), (200), (220), (311) and (222) planes of TiC (JCPDS No. 32-1383) [31]. At the same time, the Raman scattering peaks at 262, 425 and 605 cm<sup>-1</sup> are ascribed to TiC, while the peaks at 1350 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> are the D-band and G-band of graphene, respectively [32]. These clear demonstrate the existence of graphene and TiC in the formed heterostructure. To further determine the TiC content, thermogravimetric (TG) analysis in air atmosphere was conducted with a

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