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Communication

“Soft” graphene oxide-organopolysulfide nanocomposites for superior pseudocapacitive lithium storage

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Graphical abstract



We report a "soft" graphene oxide-organopolysulfide nanocomposite with improved *pseudocapacitive* performance for high-potential (1-2.8 V vs. Li^0/Li^+), high-capacity (278 mA h g^{-1}) and stable (500 cycles) lithium storage.

ABSTRACT

We report a "soft" graphene oxide-polymeric organosulfide nanocomposite with improved pseudocapacitive performance for high-potential (1-2.8 V vs. Li^0/Li^+), high-capacity (278 mA h g^{-1}) and stable (500 cycles) lithium storage.

Keywords:

Lithium ion capacitor

Graphene oxide

Organic cathode

Polysulfide

Pseudocapacitor


Unlike the versatile electrochemical uses of graphene [1-4], the present electrochemical applications of graphene oxide (GO), a typical graphene derivative abundant with polar surface functionalities, are devoted to catalysis, luminescence and sensing [5]. Exploring the emerging potential of GO in electrochemical energy storage is thus of appreciable significance. Our group recently demonstrated the exceptional reversible lithium ion storage by both epoxide and carbonyl groups on GO cathodes in the potential range of 1.5~4.5 V vs. Li^0/Li^+ [6]. Graphene oxide stores lithium ions *via* a surface process which involves the opening and closing of C-O-C/C=O bonds upon lithium uptake and release. Fast reaction kinetics is permitted for lithium storage in this case compared to the slow bulk intercalation in between sp^2 carbon layers at low potentials (< 0.5 V). Another feature of this surface lithium ion storage is that as the discharge/charge capacity increases, the potential decreases/increases monotonously suggesting a pseudocapacitive lithiation of GO, which is distinguished from the plateau potential behaviour for lithium intercalation/de-intercalation.

Despite the high lithiation activity, the GO nanosheets are prone to restack; and aggregation often reduces the available surfaces for lithium storage which results in capacity loss. Similar problems were associated with graphene electrodes; and the nanopillaring concept was developed to solve them [7]. By mixing graphene with nanoparticles, the graphene nanosheets are physically separated. It is therefore feasible to adopt a similar concept to design GO-nanoparticle composites to cope with the aggregation issue. To reach this target, it is important to preserve the *pseudocapacitive* property for the composites. Therefore, the practical challenge is to find a nanoparticle material that 1) stores lithium ions at the medium-high potential ranges (1~4.5 V vs. Li^0/Li^+), and 2) exhibits *pseudocapacitive* behavior for lithiation and delithiation. A nanosized particulate organosulfide polymer that is from the vulcanization

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of polyacrylonitrile (hereby denoted as PANS) demonstrated a *pseudocapacitive* lithiation/de-lithiation behaviour within the appreciated potential range of 1~3 V vs. Li⁰/Li⁺ [8, 9]. The capacity of PANS is approachable to 400 mA h g⁻¹ depending on the synthesis conditions [9]. It is thus promising to develop a GO-PANS composite due to their well-matched lithiation potential windows and the similar *pseudocapacitive* properties. Another characteristic of this system is both components are "soft", *i.e.*, bearing polymeric scaffolds. The soft architecture is beneficial for buffering the structural expansion and shrinkage of the composite during the insertion and extraction of lithium ions. Herein, a simple physical blending method is used to fabricate this designer "soft" pseudocapacitive GO-PANS composite. We prepared GO by the modified Hummer's method (Experimental section in Supporting information) [10, 11]. The PANS was synthesized according to literature [8, 12, 13]. In the soft mixture, the weight of GO was controlled to get the best performance. We report the synergistic enhancement of the composite capacity and demonstrate the long-term stability for 500 cycles of discharge and recharge.

Fig. 1 depicts the X-ray photoelectron spectroscopy (XPS) C 1s spectrum of as-synthesized GO, the survey of which is shown in Fig. S1 in Supporting information. The state of oxidation of GO was confirmed by XPS and the survey spectrum shows the C/O atomic ratio of 2.54 (Fig. S1). The C 1s peak consists of three components locating at 284.8, 287, and 288.7 eV. These components are assigned to the carbon atoms in graphitic C-C, epoxide () group, >C=O species, respectively [14]. In addition, transmission electron microscopy was used to study the nanostructures of GO (Fig. 1b). The wrinkled morphology suggests the mechanical flexibility and softness of the material.

The SEM of PANS material exhibits the uniform nanosized particles with an average diameter of approximate 200 nm (Fig. 2a). The composite was also characterized by XPS, FTIR and Raman spectroscopies. Fig. 2b illustrates the FTIR of the PANS material. The characteristic peaks at 1427 cm⁻¹ and 803 cm⁻¹ are assigned to the cyclic structures [15]. The peak in the region of 600-800 cm⁻¹ is attributed to the C-S stretching [15, 16]. This is also suggested by the XPS S 2p profile with a main peak at 163.7 eV corresponding to the S in C-S bonds or S chemically attached to C [15]. However the peak at 161.5 eV is unknown. The elemental composition of PANS is listed in Table S1 (Supporting information). The Raman spectrum showed the typical pattern of partially graphitized carbon in the PANS material. The D peak (1350 cm⁻¹) and G peak (1535 cm⁻¹) are the main peaks in the spectrum. The former is due to the disordered structure and the latter corresponds to the graphitic structure. A weak peak at 804 cm⁻¹ might be related to the C-S bonds [15].

A simple physical blending method was used to prepare the GO-PANS composite. A fixed amount of PANS powder (35 mg) was ground with different amounts of layer-structure GO (GO1-PANS: 1 mg GO, GO2-PANS: 2 mg GO, GO5-PANS: 5 mg GO, GO10-PANS: 10 mg GO). For comparison, the individual electrochemical performance of GO and PANS was also evaluated separately. The specific capacity was evaluated based on the weight of the GO-PANS composite, GO, or PANS, respectively. Fig. 3a shows that the discharge-recharge profiles of different cathode materials. It is obvious that all samples show the quasi-linear dependence of voltage on specific capacity, which is characteristic of the pseudocapacitive behavior. The comparison on the specific capacity of the GO-PANS composites is shown in Fig. 3b. The GO-PANS cathode discharge capacity increases from the initial 57.7 mA h g⁻¹ of pure GO or 189.1 mA h g⁻¹ for pure PANS to the 217.8, 278.0, 253.6, 215.4 mA h g⁻¹ for the composites GO1-PANS, GO2-PANS, GO5-PANS, and GO10-PANS, respectively. It is noticed that the actual capacity of our GO is less than the theoretical capacity reported previously [6]. One rational reason is the GO synthesized in this work was dried directly in oven rather than freeze dried. It is accepted that direct oven drying induced aggregation of GO thus reasonably lowered capacity. The actual capacity for GO-PANS nanocomposites can be calculated according to: GO specific capacity (57.7 mA h g⁻¹) × GO weight ratio + PANS specific capacity (189.1 mA h g⁻¹) × PANS weight ratio. Accordingly, the calculated specific capacity is 185.4, 182.0, 172.7, and 159.9 mA h g⁻¹ for the composites GO1-PANS, GO2-PANS, GO5-PANS, and GO10-PANS, respectively. The maximum capacity of 278.0 mA h g⁻¹ is reached for the GO2-PANS composite.

It is speculated that the extra increment of the actual capacity of the GO-PANS composites compared with the calculated capacity is related to the synergistic effects. As already known in graphene-metal oxide composites [7], the synergistic capacity enhancement is attributed to the nanopillaring effect. In our case, it is that the 0D PANS nanoparticles successfully separated the 2D GO nanosheets while GO also prevents the agglomeration of PANS nanoparticles. This spatial separation generates more nanoscale voids in the composites that allow more accessible interfaces for lithium storage. In the meantime, the highest capacity is only achievable when the concentration of PANS is at 94.6 wt%, which is likely corresponding to the optimum spatial separation. This is due to the very large lateral dimension of GO nanosheets (micron scale, Fig. 1b). When the amount of PANS is relatively lower, the huge GO nanosheets, which are also very soft and flexible, can not be thoroughly pillared because of the low surface coverage by PANS. However, as the PANS amount further increases to 97.2 wt%, the intrinsic aggregation of PANS nanoparticles become more significant, which in turn degrades the capacity. It is necessary to stress that the optimum content of PANS for the highest capacity can be possibly reduced by advanced mixing/homogenizing technology, such as ultrasonication. Even though, our results demonstrated the promising lithiation activity of the GO-PANS nanocomposites. According to Fig. 3c, the new composites have 100% coulombic efficiency. The cycle stability of GO-PANS is compared with GO and PANS as shown in Fig. 3d. Although the capacity of GO is relatively lower, its stability is much better than that of PANS. As increasing the GO content, the stability of the GO-PANS composites is also improved. The weak stability of pure PANS cathode is related to the volume expansion upon lithiation and the formation of soluble polysulfides [12]. Among all the cathode materials tested, the best one of GO2-PANS have the advantages of the better conductivity with small

amount of GO added compared with GO5-PANS and GO10-PANS due to the addition of low conductivity of high oxygen content of GO. But compared with original PANS composite, the addition of GO limited the transition of sulfur species and reduce the loss of active materials cause the unique layer structure of GO with high oxygen content function as dikes. GO1-PANS with low content of GO could not reach the coverage rate of GO2-PANS, which may result in the loss of active material during charge and discharge, same with original PANS composite. Our results display that the GO functions both mechanically and chemically to buffer the volume change and trap the polysulfides, and hence lead to the improved stability of the GO□PANS composites.

In summary, we report the first example of the use of graphene oxide-organosulfide nanocomposites as lithiation active electrode materials. The *pseudocapacitive* lithiation capacity of the nanocomposites was synergistically enhanced, which is ascribed to the nanopillaring effects. We also noticed that the flexible and chemically active graphene oxide nanosheets play critically in improving cycle stability.

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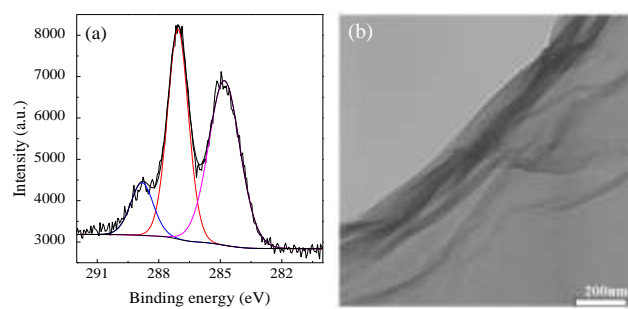


Fig. 1. (a) High resolution XPS C 1s spectrum and (b) Low magnification TEM image of GO.

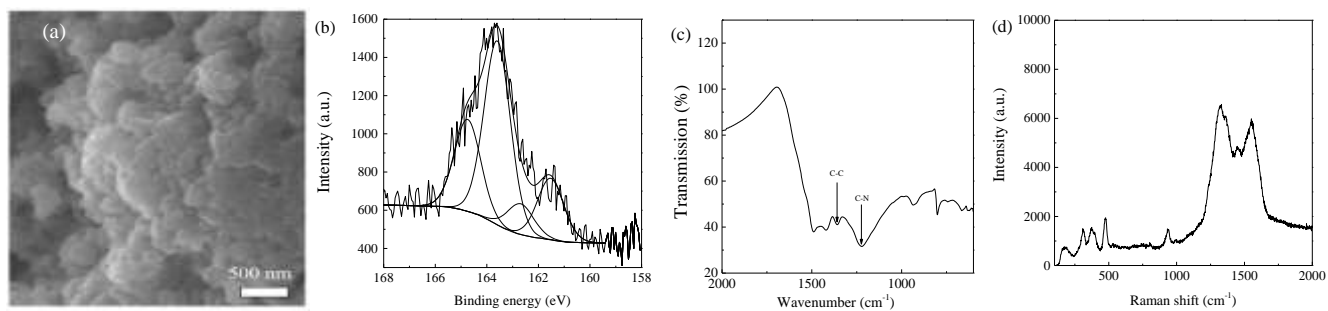


Fig. 2. SEM image (a), high resolution XPS S 2p spectrum (b), (c) FTIR and Raman spectra (d) of PANS.

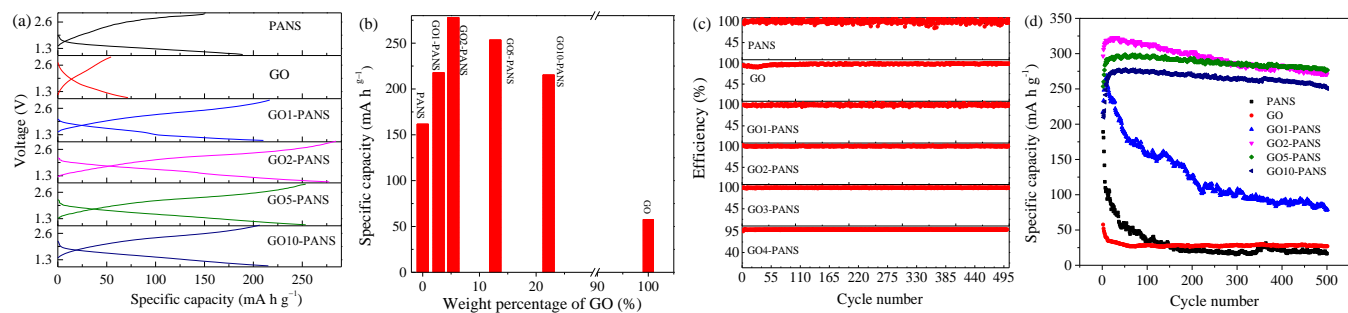


Fig. 3. Electrochemical performance of the GO-PANS composites with different contents of GO and PANS: (a) the 2nd cycle discharge and charge curves, (b) the dependence of specific capacity on the weight content of GO, (c) the coulombic efficiency, and (d) the cycle stability. All data were collected at 1500 mA/gGO.