Graphene nanosheets for enhanced lithium storage in lithium ion batteries

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ABSTRACT

Graphene nanosheets were synthesized in large quantities using a chemical approach. Field emission electron microscope observation revealed that loose graphene nanosheets agglomerated and crumpled naturally into shapes resembling flower-petals. High resolution transmission electron microscope analysis, Raman spectroscopy and ultraviolet-visible spectroscopy measurements confirmed the graphitic crystalline structure of the graphene nanosheets. The nanosheets exhibited an enhanced lithium storage capacity as anodes in lithium-ion cells and good cyclic performance.

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1. Introduction

Lithium-ion batteries currently are ubiquitous power sources for portable electronics, using the chemistry of lithium cobalt oxide (LiCoO₂) cathode and graphite anode [1–3]. The energy density and performance of lithium-ion batteries largely depend on the physical and chemical properties of the cathode and anode materials. The possibilities for the improvement of cathode materials are quite limited due to the stringent requirements such as high potential, structural stability, and inclusion of lithium in the structure [4,5]. Nevertheless, there is considerable room for exploring new anode materials, owing to many materials having reversible lithium storage capability.

Recently, graphene, a single layer of carbon (carbon atoms in a two-dimensional (2D) honeycomb lattice), was found to exist as a free-standing form and exhibits many unusual and intriguing physical, chemical and mechanical properties [6,7]. Due to the high quality of the sp² carbon lattice, electrons were found to move ballistically in graphene layer even at ambient temperature [8,9]. Graphene powders have been successfully applied in polymers to produce highly conductive plastics [10]. Despite the optimistic expectation on graphene-based electronics, it is unlikely that this will appear in next two decades. Current research mainly focuses on fundamental research. In the meantime, one of exciting possibility is the use of bulk graphene powders as anode materials for reversible lithium storage in lithium-ion batteries [11].

The maximum specific lithium insertion capacity for graphite (3D network of graphene) is 372 mAh/g, corresponding to the formation of LiC₆ – a first stage graphite intercalation compounds (GIC). During the intercalation process, lithium transfers its 2s electrons to the carbon host and is situated between the carbon sheets. High capacity carbon materials have also been reported. This could be mainly ascribed to (i) lithium insertion within the “cavities” in the material [12], (ii) lithium absorbed on each side of the carbon sheet [13], (iii) lithium binding on the so called “covalent” site [14], and (iv) lithium binding on hydrogen terminated edges of graphene fragments in carbon materials [15]. Owing to its large surface-to-volume ratio and highly conductive nature, graphene may have properties that make it suitable for reversible lithium storage in lithium-ion batteries. This is because lithium ions could be bound not only on both sides of graphene sheets, but also on the edges and covalent sites of the graphene nanoplatelets. Therefore, it is expected that graphene
could overtake its 3D counterpart (graphite) for enhanced lithium storage in lithium-ion batteries. Herein, we report the chemical synthesis of graphene nanosheets and their electrochemical performance as anodes in lithium-ion cells.

2. Experimental

2.1. Chemical synthesis of graphene nanosheets

In a typical synthesis process, natural graphite powders (SP-1, Bay Carbon, MI, USA) were oxidized to graphite oxide using a modified Hummers method [16]. One gram graphite powder and 0.5 g sodium nitrate were poured into 70 ml concentrated H2SO4 (under ice bath). Then 3 g K2MnO4 was gradually added. The mixture was stirred for 2 h and then diluted with de-ionised (DI) water. After that, 5% H2O2 was added into the solution until the colour of the mixture changed to brilliant yellow. The as-obtained graphite oxide was re-dispersed in DI water and then exfoliated to generate graphene oxide nanosheets by ultrasonication using a Brandson Digital Sonifier (S450D, 40% amplitude). The brown graphene oxide nanosheet dispersion was poured into a round-bottomed flask, to which hydrazine monohydrate (as reducing agent) was added. The mixed solution was then refluxed at 100 °C for 2 h, over which the colour of the solution gradually changed to dark black as the graphene nanosheet dispersion was formed. The dispersion was further centrifuged for 15 min at 3000 rpm to remove a small amount of precipitate. The supernatant of the graphene nanosheet dispersion was directly dried in a vacuum oven to obtain the bulk of graphene nanosheet powders.

2.2. Nanostructural and physical characterisation of graphene nanosheets

The structure of the pristine graphene nanosheets were analysed by X-ray diffraction (XRD, Philips 1730 X-ray diffractometer), field emission electron microscope (FESEM, JEOL 7001F), and transmission electron microscopy (TEM) using a JEOL 2011 TEM facility. Graphene nanosheets were also characterised by Raman spectroscopy using a Jobin Yvon HR800 confocal Raman spectrometer with 632.8 nm diode laser excitation on 1800-line grating. UV–Vis spectroscopy measurements were performed on a graphene nanosheet aqueous dispersion, using a Shimadzu UV1700 UV–Vis spectrometer.

2.3. Electrochemical testing of graphene nanosheets as anodes in lithium-ion cells

Graphene nanosheets obtained from chemical reduction contains —H and —OH groups. Therefore, we heat treated the as-prepared graphene nanosheets at 500 °C in argon atmosphere to remove —H and —OH groups. Then, graphene nanosheet powders were mixed with a binder poly(vinylidene fluoride) (PVdF) at weight ratios of 90:10 in N-methyl-2-pyrrolidone (NMP) solvent to form a slurry. Then, the resultant slurries were uniformly pasted on Cu foil with a blade. These prepared electrode sheets were dried at 120 °C in a vacuum oven for 12 h and pressed under a pressure of approximately 200 kg/cm². CR2032-type coin cells were assembled in a glove box for electrochemical characterisation. The electrolyte was 1 M LiPF6 in a 1:1 mixture of ethylene carbonate and dimethyl carbonate. Li metal foil was used as the counter and reference electrode. The cells were galvanostatically charged and discharged at a current density of 1C within the range of 0.01–3.0 V. Cyclic voltammetry (CV) curves were measured at 0.1 mV/s within the range of 0.01–3.0 V using an electrochemistry working station (CHI660C).

3. Results and discussion

Fig. 1a shows a FEG-SEM image of bulk graphene nanosheets at low magnification. The loose graphene nanosheets tend to stick together to form fluffy agglomerates with a flower-like appearance. A magnified view of one such agglomerate is shown in Fig. 1b, from which we can clearly see the nanosheets forming flower petal-like shape. Multilayer graphene nanosheets stick together if there is no perturbation by an external force. Graphene nanosheet petals are naturally crumpled and curved, which is visible in the micrometer domain.

TEM and HRTEM analysis were performed on the as-prepared graphene nanosheets to determine their features in Fig. 1 – (a) Low magnification FEG-SEM image of loose graphene nanosheet powders. (b) High magnification FEG-SEM view of graphene nanosheet petals.
nanometer domain. Fig. 2a shows a low magnification TEM image of the bulk of graphene nanosheets. Giant graphene nanosheets (a few tens of square micrometers in area) were observed to form a covering on the top of the copper grid, like transparent silk. Graphene nanosheets are scrolled and entangled with each other. Corrugation and scrolling are part of the intrinsic nature of graphene nanosheets, which result from the fact that the 2D membrane structure becomes thermodynamically stable via bending [17,18]. Through FEG-SEM and TEM analysis, we found that both multilayer graphene nanosheet petals and individual single graphene nanosheets tend to scroll. Therefore, nanovoids and nanocavities would exist in the scrolled graphene nanosheets. Fig. 2b shows a high magnification TEM image of the basal planes of graphene nanosheets, which are featureless. Due to scrolling and folding of graphene nanosheets, we would be able to observe the cross section view of stacked graphene nanosheets. Fig. 2c shows a HRTEM image of stacked graphene layers, in which it is clearly visible that graphene nanosheets are scrolled to a tubular structure. In general, only 2–3 layers of graphene sheets were observed, indicating excellent dispersing of graphene nanosheets. Fig. 2d exhibits another HRTEM image of the cross section view of stacked graphene layers. The interplanar distance was measured to be 0.37 nm corresponding to the spacing of the (0 0 2) planes, which is larger than that of graphite (d_{002} = 0.34 nm). A selected area electron diffraction pattern (SAED) of the featureless region was recorded along the [0 0 1] zone axis (perpendicular to the basal plane) and is shown as the inset in Fig. 2d. The diffraction dots were fully indexed to the hexagonal graphite crystal structure, unambiguously confirming the graphitic crystalline nature of the graphene nanosheets.

Raman spectroscopy is a non-destructive approach to characterise graphitic materials, in particular to determine ordered and disordered crystal structures of graphene nanosheets. Fig. 3 shows Raman spectrum of as-prepared graphene nanosheets. As a comparison, Raman spectrum of high crystalline graphite powders is also presented as the inset in Fig. 3. Raman peaks D line and G line can be well distinguished. Graphene nanosheets exhibit a strong D line at 1350 cm$^{-1}$, corresponding to a breathing mode or k-point photons of A\textsubscript{1g} symmetry, and a relatively weak G line at 1580 cm$^{-1}$, which should be assigned to the in-plane bond-stretching motion of pairs of C sp\(^2\) atoms (the first order scattering of the E\textsubscript{2g} photons). The D mode is forbidden in perfect graphite (therefore, very weak as shown in the inset in Fig. 3 for graphite powders) and only becomes active in the presence of disorder [19]. The significant increase of D/G intensity ratio, comparing to the well crystalline graphite, indicated the decrease of the size of the in-plane sp\(^2\) domains and partially disordered crystal structure of graphene nanosheets [20,21]. The optical properties of graphene nanosheet dispersion was measured by ultraviolet–visible (UV–Vis) spectroscopy (as shown in Fig. 4). The spectra show an absorption peak at 265 nm, indicating that graphene nanosheets have a graphite structure. The absorption at 265 nm (4.675 eV) is generally regarded as the excitation of $\pi$-plasmon of graphitic structure [22].

The electrochemical properties of graphene nanosheets as anodes in lithium-ion cells were evaluated via constant current charge/discharge cycling in the potential range from
0.02 to 3.0 V at 1 C rate. The charge/discharge profiles of graphene anode in the first cycle and the 100th cycle are shown in Fig. 5. Graphene anode delivered a specific capacity of 945 mAh/g in the initial discharging and a reversible capacity of 650 mAh/g in the first charging. The irreversible capacity could be associated with the formation of the SEI layer in the first cycle. The shape of the discharge and charge curves is typical of nanosize carbonaceous materials. In the discharge process (lithium insertion), the slope of the curve starts from 3.0 V, and the largest part of the specific capacity (>70%) falls in the region below 0.5 V. During the charge process (lithium extraction), an appreciable potential hysteresis exists, in which the inserted lithium ions were removed in a wide voltage range of 0.05–3.0 V. This observed unique electrochemical behaviour matches well with the micro- and nano-structure of graphene nanosheets. As indicated by FEG-SEM and HRTEM analysis, graphene agglomerates consists of interlocked multilayer graphene nanosheets. The capacity below 0.5 V could correspond to the lithium binding on the basal plane of graphene nanosheets. While, the capacity above 0.5 V could be ascribed to the faradic capacitance on the surface or on the edge sites of graphene nanosheets [23]. It has been proposed that lithium ions can be adsorbed on both sides of the graphene sheet that arranged like a “house of cards” in hard carbons, leading to two layers of lithium for each graphene sheet, with a theoretical capacity of 744 mAh/g through the formation of Li2C6 [13,15]. On the other hand, nano-cavities between graphene nanosheets due to scrolling and crumpling could also contribute to the lithium storage. According to the micropore mechanism, the extraction of lithium from the nano-cavities has to go through the ‘way’ of graphene crystallites. The interaction between lithium atoms and nanopores results in an appreciable voltage hysteresis during the charging process [24]. Therefore, graphene nanosheet electrode exhibited lithium storage behaviour that was typical of both soft graphitized carbon and hard carbon. The cyclic voltammograms (CV) of graphene anode are shown as the inset in Fig. 5. The shape of the CV...
curves matches well with the charge/discharge profiles (Fig. 5).

The cyclability of graphene nanosheet electrode was examined under long-term cycling over 100 cycles, which demonstrated a good cyclic performance and reversibility (as shown in Fig. 6). After 100 cycles, the graphene anode still maintained a specific capacity of 460 mAh/g, which represents a much enhanced performance than that of graphite anodes. Further improvements are expected by tuning the size of individual graphene nanosheets and graphitic structure of graphene nanosheets through synthesis process and heat treatment.

4. Conclusions

In summary, we have prepared graphene nanosheets in large quantity by a soft-chemistry approach. FEG-SEM observation revealed that loose graphene nanosheets agglomerated and crumpled naturally into shapes resembling flower-petals. HRTEM analysis, Raman spectroscopy and UV–Vis spectroscopy confirmed the graphitic crystalline structure of graphene nanosheets. We applied graphene nanosheets as anodes for lithium storage in lithium-ion cells. Graphene nanosheet anodes exhibited an enhanced reversible lithium storage capacity as anode in lithium-ion cells and good cyclic performance.

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