Binder-free graphene film via solvent exchange process as anode in Li-ion battery

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Abstract

Graphene showcases several key properties that can address emerging technological needs, in particular for the conversion and storage of energy in the ever-growing market of portable and wearable electronic devices [1]. The challenge lying ahead is to develop high-quality graphene in large volumes to ultimately suit the needs of an industrial-scale production [2]. Liquid-phase exfoliation (LPE) of graphite [3] is a promising tool for mass production of single and multi-layer graphene flakes, which can be prepared in the form of inks [4], thin films [3], and composites [5]. In particular, LPE graphene has been considered an ideal yet not fully explored material for anode in Li-ion battery [6] thanks to its chemical stability, large surface area and excellent electrical conductivity [7,8].

Here we report the fabrication of graphene-based anodes by LPE of graphite in N-Methyl-2-pyrrolidone (NMP). By using a combination of sono-chemical exfoliation and ultracentrifugation we were able to obtain graphene flakes with controlled morphological properties (single and few-layer graphene flakes with lateral size of ~100nm (Fig.a)) [6,9]. A solvent exchange process is used to remove the NMP and re-disperse the flakes in ethanol [10], which has a lower boiling point. This procedure promotes the sedimentation of the graphene flakes in solution (concentration ~10mg/ml) due to the low surface tension of ethanol (~22 mN/m)[3]. By drop-casting the sediment flakes at ambient conditions (pressure and temperature) on a copper foil we are able to form a graphene film (Fig. b), avoiding high temperature deposition that can cause a partial oxidation of the flakes. Our electrodes have a significant advantage with respect to traditional Li-ion battery anodes requiring a binder (*e.g.*, polyvinylidene fluoride) to draw the material together [2]. In fact, a binder-free anode film can avoid numerous drawbacks*, such as* time-consuming treatments to dissolve and dry the binders, additional mass loading, and possible performance degradation during charge-discharge cycles [11].

We tested our graphene film as anode against Li foil and the battery provided a specific capacity of 443 mAh/g after 50 cycles at a current density of 100 mA/g (higher than the specific capacity -185 mAh/g- of NMP-based graphene electrode tested in the same experimental conditions), with a Coloumbic efficiency approaching 100% (Fig.c). This in turn opens the way to the optimization of energy/power densities, lifetime, safety, while minimizing the cost and the environmental impact of this energy-storage technology.

References

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Figures

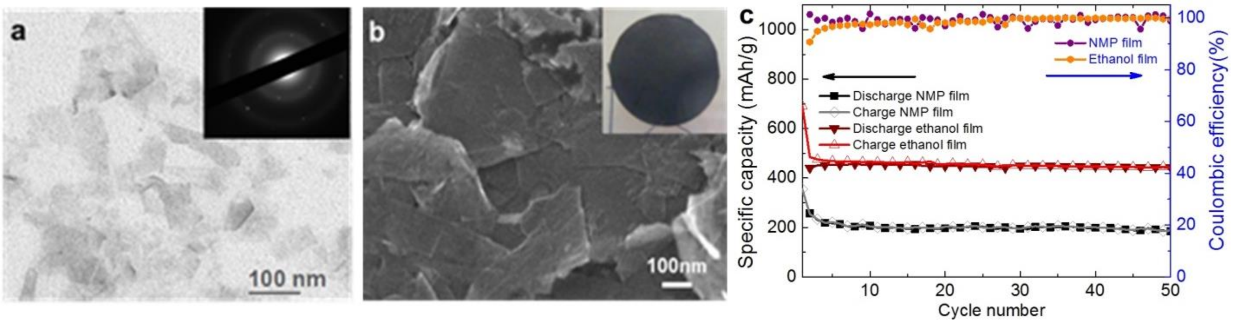

Figure: a) Bright-field TEM image of graphene flakes at high magnification. Inset: Electron diffraction pattern collected on an area of 2 µm in diameter. The $10\bar{1}0$ and $11\bar{2}0$ polycrystalline diffraction rings of graphene are clearly visible. **b)** SEM image of graphene film on Cu foil. Inset: optical image of the graphene-Cu supported electrode. **c)** Prolonged cycling (black NMP film; red ethanol film) and corresponding Coulombic efficiency (purple dots NMP film; orange dots ethanol film). Rate: 100 mAg^{-1}.