Graphene oxide-assisted synthesis of LiMn$_2$O$_4$ nanopowder

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The article reports sol-gel synthesis of nanosized spinel-type lithium manganese oxide LiMn$_2$O$_4$ (LMO) carried out in the presence of graphene oxide (GO) and its electrochemical lithium insertion ability. The synthesis was performed in an aqueous environment with lithium acetate and manganese acetate used as precursors and citric acid as a chelating agent. The material was characterized by X-ray diffraction, SEM microscopy, Raman spectroscopy and cyclic voltammetry. The calcination step totally eliminated graphene from the final product, nevertheless its presence during the synthesis was found to affect the resulting LiMn$_2$O$_4$ morphology by markedly reducing the size of grains. Moreover, potentials of electrochemical lithium insertion/deinsertion reactions have been shifted, as observed in the cyclic voltammetry measurements. Along with the diminished grain size the voltammetric curves of the graphene oxide-modified material exhibit higher oxidation and lower reduction peak currents. The study demonstrates that GO mediation/assistance during the sol-gel synthesis fosters more nanostructured powder and changes the electrochemical characteristics of the product.

Keywords: LiMn$_2$O$_4$ spinel, graphene oxide, sol-gel synthesis, li-ion battery.

INTRODUCTION

Lithium-ion batteries (LIBs) are commonly used in portable electronic devices because of their high voltage and high energy density. They are also intensively investigated for applications in electric and hybrid vehicles, power backups and portable power tools. However, the fabrication of electrodes with a sufficient power density remains a challenge[1]. One way of enhancing the rate capability is to use nanostructural electrode materials. Nanomaterials offer a number of advantages, including: (1) a better accommodation of the strain of lithium insertion/extraction, and consequently, a prolonged cycle life; (2) new reactions that are not possible with bulk materials; (3) a larger electrode/electrolyte contact area; (4) short path lengths for the electronic and Li$^+$ transport, permitting operation with low electronic and Li$^+$ conductivity or high-power operation[2, 3]. Therefore, the use of well-dispersed nanoparticles along with suppression of their aggregation are of key importance in the production of highpower LIBs[4].

Spinel-type LiMn$_2$O$_4$ shows great promise as a LIB cathode material because of its low cost, low toxicity and abundant resources[5–8]. The electrochemical properties of this material strongly depend on its physicochemical characteristics, such as crystallinity, particle size, specific surface area[9] and character of chemical bonding[10]. These properties can be controlled by the conditions of the fabrication process. Various techniques of improving the rate capability have been developed recently, including the sol-gel[11], precipitation[12], hard template route[13], hydrothermal[14, 15], solid-state reaction[16] and flame-assisted spray[17] methods. Low capacity at high charge-discharge rates is believed to be caused by slow diffusion of the Li$^+$ ions[18] and low electrical conductivity[15] bringing about the necessity of searching new ways of material nanostructuring.

In this study we report on the preparation and characterization of spinel-structure LiMn$_2$O$_4$ (LMO) with nanometric particles, synthesized by the sol-gel method with graphene oxide (GO) used as a mediator/nanostructure promotor. Graphene hybrids are known to offer numerous advantages, such as: (1) good dispersion of the nanoparticles at the graphene template, preventing their agglomeration and in consequence maintaining their large surface area; (2) a high crystallinity of the nanoparticles; (3) a reduced resistivity of the hybrid through a high conductivity of the template[10]. In our work, high temperature calcinations follows the actual sol-gel reaction. Recently a similar but low temperature process of obtaining LMO/multiwalled carbon nanotubes (MWCNTs) hybrid structure has recently been described by Liu et al[19]. However, vast majority of scientific works indicate that much higher temperatures (typically 500–750°C) are needed to obtain spinel phase with satisfactory lithium insertion ability[9]. At these temperatures GO is known to burn-out[20].

A fundamental novelty of our work is that GO is only present in the reaction solution during the synthesis and is subsequently totally burnt out upon the calcination step. In spite of this, we have been able to demonstrate that the presence of GO significantly affected the morphology of the main product, clearly leading to obtaining LMO with grain size reduced to nano-scale. This effect of nanoparticle stabilization by GO in solution followed by its removal is referred to within this work as GO mediation in the process of LMO sol-gel synthesis.

EXPERIMENTAL

Preparation of GO

Graphene oxide (GO) was obtained from natural graphite by a modified Hummers method[21]. Expandable graphite flakes (Asbury Carbons, grade 1721) were

thermally treated at 1050°C for 1 minute. Next, 4 g of the resulting powder and 2 g of sodium nitrite were dispersed into 92 ml of 96% sulfuric acid. The mixture was placed in an ice bath and cooled to 0°C. The solution was stirred mechanically and 12 g of $KMnO_4$ was slowly added when stirring. The temperature was kept below 20°C. The ice bath was removed and the mixture was left for 24 h at room temperature.

The temperature was brought to 35°C where it was maintained for 30 min while the solution was stirred mechanically. The stirring continued and 184 ml of distilled water was carefully added to the paste stirred. The temperature was subsequently increased to 98°C and maintained for 15 minutes. Next, the suspension was diluted with 225 ml of water and the same amount of 3% hydrogen peroxide.

To remove the residual manganese ions the suspension was precipitated by repeated dilution with 3% hydrochloric acid and centrifuging at 5000 rpm for about 20 minutes. The presence of sulphate ions was checked with barium chloride. When the test result was negative, the suspension was diluted with distilled water and centrifuged several times until pH became neutral. The product was diluted by deionized water to obtain a concentration of 1 mg of carbon used for reaction in 1 ml of water. Finally, the suspension was sonicated in ultrasonic bath.

GO-assisted preparation of LMO

Spinel LMO was obtained by the sol-gel process carried out in the presence of graphene oxide (GO). The synthesis scheme of nanostructural, GOmediated $LiMn_2O_4$ spinel is shown in Fig. 1. In a typical reaction 4 mmol (408.1 mg) of 97% lithium acetate dihydrate (Sigma-Aldrich) was dissolved in 25 ml of deionized water and, separately, 8 mmol (1.9607 g) of 99% manganese acetate tetrahydrate (CHEMPUR) was dissolved in 50 ml of deionized water. The solutions were mixed and added slowly to a solution of 1.9212 g of citric acid

monohydrate (CHEMPUR), used as a chelating agent, in 30 ml of deionized water. The mixture was stirred for 1 h before the addition of 20 ml of a previously obtained GO suspension. The mixture was stirred for another 30 minutes, then evaporated at 60°C, dried at 150°C, and calcined at 800°C for 6 h in air. The obtained material is designated as LMO(GO).

As a reference, base line LMO material (designated as LMO) was synthesized in an analogous way but without GO participation.

Material characterization

The structure of the synthesized LMO and LMO(GO) samples was characterized by X-ray powder diffraction (XRD) with a Siemens D500 diffractometer with a CuK_α radiation ($\lambda = 1.542$ Å) source. The morphology of the materials and their particle size were examined by scanning electron microscopy (SEM) (Cross Bean Auriga, Carl Zeiss setup).

The Raman spectra were taken using inVia Raman spectrometer (Renishaw) with a 514.5 nm laser excitation and an LWDx50 lens. All the measurements were accumulated 10 times.

The electrochemical properties were investigated with a two-electrode Swagelok type electrochemical cell with a lithium foil as a counter and reference electrode, and an LP30 electrolyte (1M $LiPF_6$ in EC/DEC 1:1, Merck). The working electrode was prepared by mixing 85%wt. of the active material, LMO or LMO(GO), 10%wt. of acetylene black (Timcal C-NERGY™ Super C65) and 5% wt of polyvinylidene fluoride (Kynar Flex 2851 PVdF, Arkema Inc.) as a binder dissolved in N-methylpyrrolidone (NMP). The slurry was mixed, dispersed onto a 12 mm Al foil discs and dried in vacuum at 120°C for at least 8 h. Each electrode contained 1–2 mg of dried slurry. The assembly process was carried out in argon atmosphere in a glove box. The cyclic voltammetry measurements were carried out at 0.5 mV s^{-1} in a voltage range of 3.0–4.3 V with the application of VMP3 modular 16 channel potentiostat/galvanostat (Bio-Logic).

RESULTS AND DISCUSSION

Structure and morphology

Figure 2 presents the XRD patterns of the obtained LMO(GO) and base line LMO. The diffraction lines are indexed and indicate clearly for the cubic spinel system (space group: Fd3m, spinel), ICDD: 35–782, which provides evidence of successful synthesis of spinel $LiMn_2O_4$ by the sol gel process. The diffractograms feature six characteristic peaks at 2θ angles of 18.6°, 30.6°, 36.1°, 37.8°, 44.0°, 48.0°, 58.2° for CuK_α radiation ($\lambda = 1.542$ Å), corresponding to the crystal planes (111), (220), (311), (222), (400), (331) and (511), respectively. The average size of the crystallites is ca. 43 nm (as calculated by the Scherrer formula, allowing for the instrumental line broadening). The LMO(GO) unit cell parameter and volume calculated from the XRD data are 8.230 Å and 557.4 Å^3, respectively. A small amount of the Mn_3O_4 phase is observed in the LMO sample. The results of these studies provide evidence that the spinel-structure lithium manganese oxide is obtained in
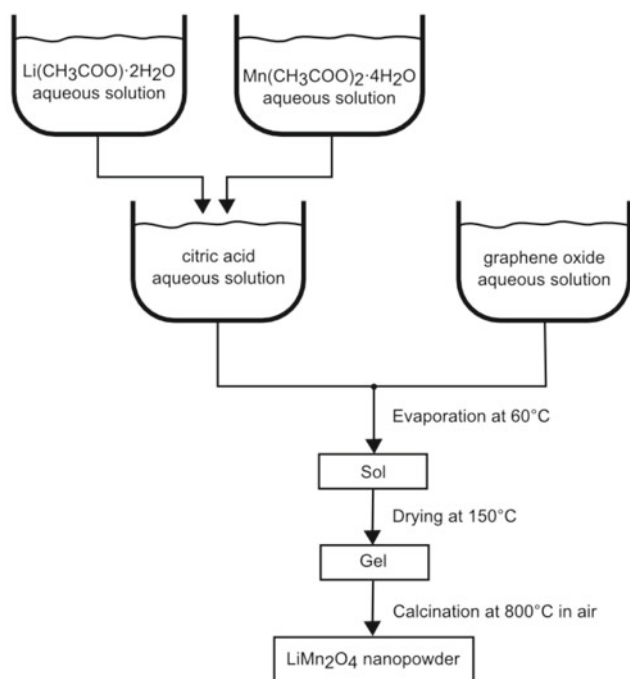

Figure 1. Flowchart of synthesis of LMO(GO) nanopowder
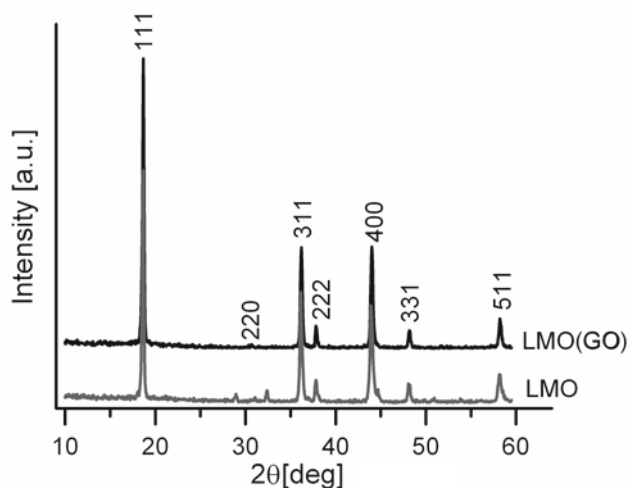
Figure 2. X-ray diffraction patterns recorded for LMO and LMO(GO) samples

the sol-gel process, both with the addition of GO and for the reference sample.

Figure 3 shows scanning electron microscopy images of LMO (a,b) and LMO(GO) (c,d), each at two levels of magnification. Both samples consist of well developed, agglomerated octahedral LMO crystals habit characteristic for the spinel crystallographic group. There is a dramatic difference in the individual particle size and morphology. LMO sample consists of relatively large (of the order of 1 μm), well developed crystals with terrace arrangement. Contrary to this, the LMO(GO) sample is composed of ca. 100 nm size particles, loosely interconnected to form a sponge-like structure.

If GO had passed into the final LMO sample it should also be detectable by means of Raman spectrometry as graphene (or, more precisely, thermally reduced graphene oxide). To verify this, Raman spectra of LMO and LMO-(GO) samples in the spectral range of 100–3600 cm^{-1}, obtained with 514.5 nm excitation, are shown in Fig. 4a, compared with spectrum of thermally reduced graphene oxide (rGO) in the Fig. 4 b. Both LMO spectra consist of a strong band at ca. 625 cm^{-1}, a shoulder at ca. 570 cm^{-1}, and two weak bands at ca. 470 cm^{-1} and 360 cm^{-1}. The band at 625 cm^{-1} can be ascribed to symmetric stretching vibrations of the MnO$_6$ octahedrons. The band at 570 cm^{-1} seems to be associated with vibrations of Mn^{IV}-O bonds. The low-intensity bands at ca. 470 cm^{-1} and 360 cm^{-1} can be attributed to Mn-O and Li-O bonds, respectively[22]. Raman spectrum of rGO obtained with 514.5 nm excitation features the so-called G-band associated with sp^2 carbon bond stretching at ca. 1590 cm^{-1} and so-called D-band at ca. 1350 cm^{-1} activated by defects[23].

The comparison of the Raman spectra of the LMO-(GO) sample and rGO does not show the presence of the later in the synthesized material. This confirms the hypothesis of decomposition of GO upon calcination.

To sum up, neither XRD and Raman spectra nor SEM micrographs do reveal any presence of graphene structures. Apparently GO mediator has been totally burnt out during the calcination step. In spite of this, however, it is evident that the spinel morphology has been modified towards nanodispersion. A possible explanation for this phenomenon is that during the sol gel synthesis GO nanoparticles act as nanoparticle stabilizers, not allowing
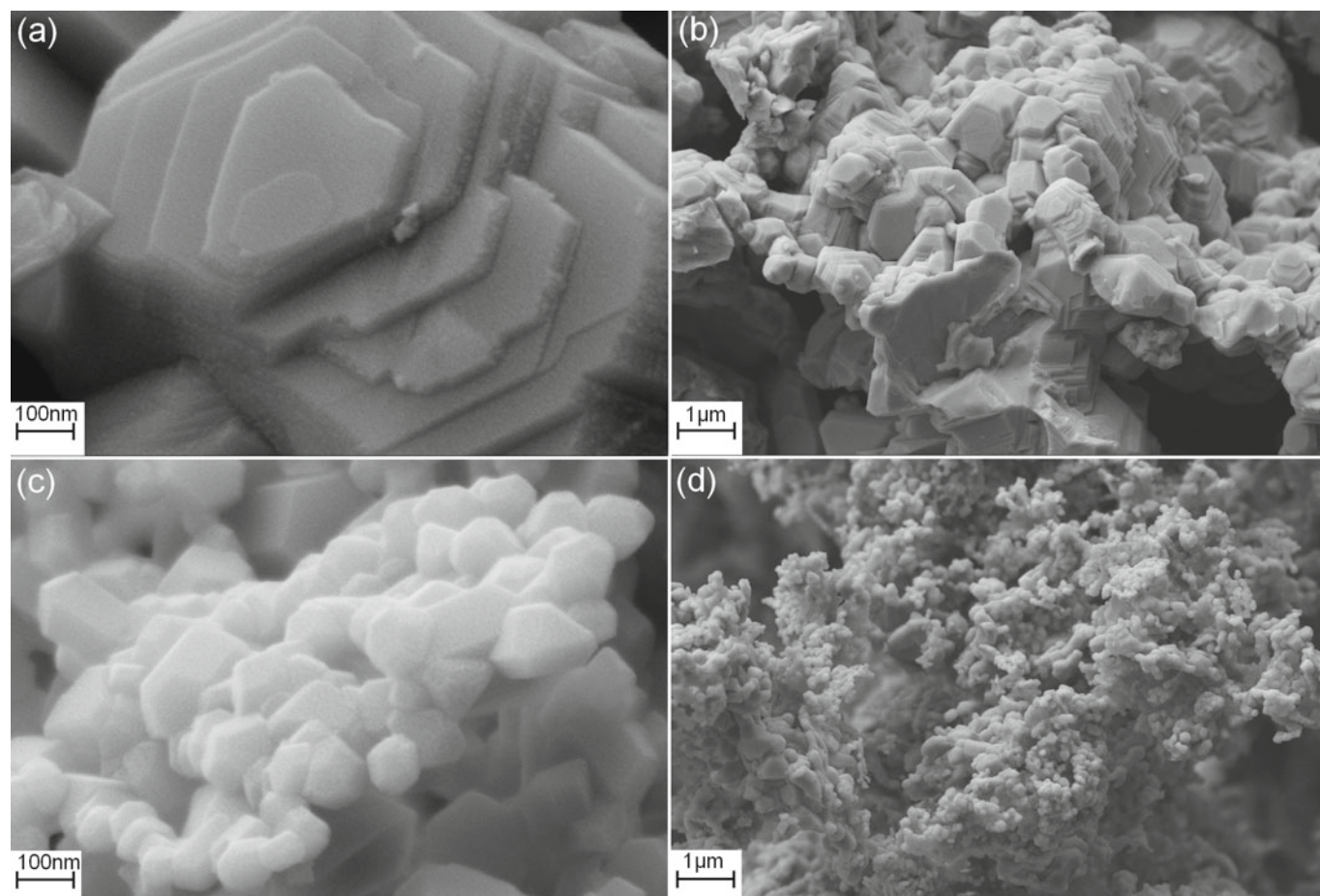

Figure 3. SEM images of LMO (a, b) and LMO(GO) (c, d) powders
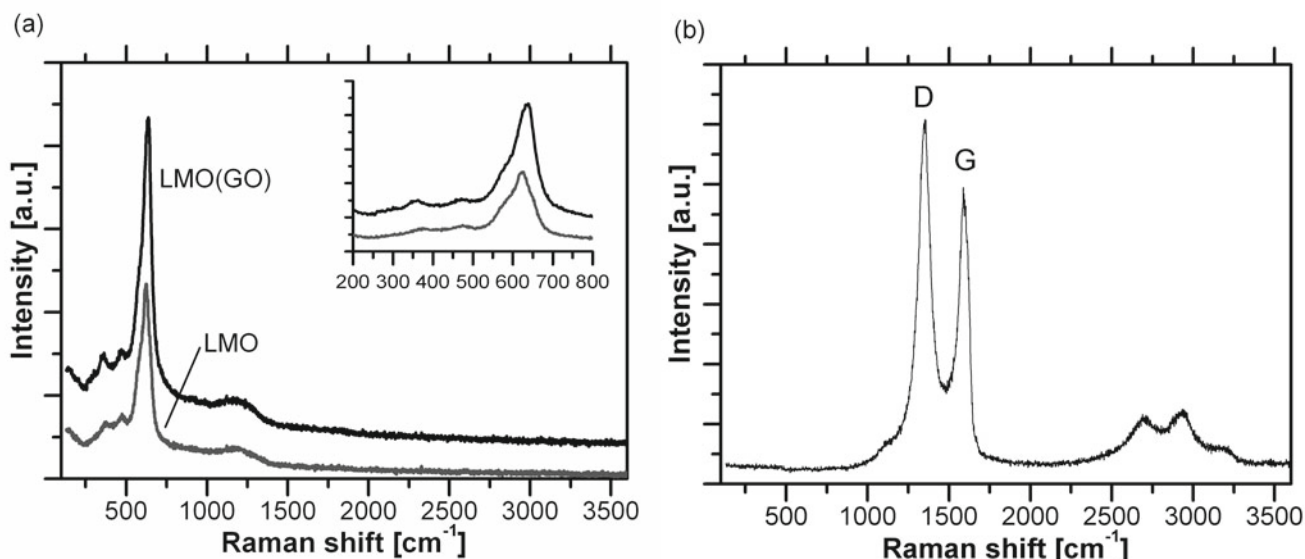
Figure 4. Raman spectra of LMO and LMO(GO) samples (a) and of thermally treated graphene oxide (b)

the LMO grains to grow above the diameter of ca. 100 nm. It is possible because of an excellent solubility of GO in water solutions. A similar behavior is well known for the so-called polyol syntheses of nanopowders, where glycols are applied as nanoparticle stabilizing agents.

Electrochemical performance

The materials have been subjected to preliminary assessment in terms of the ability of reversible electrochemical lithium cation insertion. Figure 5 presents cyclic voltammetry curves of the LMO and LMO(GO) as cathode materials versus lithium metal counter/reference electrodes. Base line LMO sample exhibits typical voltametric response with two-step electrochemical reaction. The oxidative and reductive peaks of the LMO(GO) curves are shifted towards higher and lower voltages, respectively, as compared with the LMO peaks. The oxidative peak maxima in the 1st cycle occur at 4.04 V and 4.18 V for LMO, against 4.14 V and 4.28 V for LMO(GO). The reductive peak maxima occur at 3.95 V and 4.08 V for LMO against 3.85 V and 3.99 V for LMO(GO). Peak maxima shifts suggest lower reaction reversibility of LMO(GO) which does not exactly what

one could expect in light of markedly smaller particle size of this sample. LMO(GO) particles, being smaller than the LMO particles, should have a shorter ion path, which should improve the reaction reversibility[24]. What is more, the two characteristic peaks are merged. For this preliminary study one must assume that sample LMO(GO), although more nanostructural, is more difficult to make homogenous mixture with the conducting agent, thus giving rise to additional internal resistance. This drawback is however purely technological in nature and can relatively easily be overcome by appropriate electrode optimization. A promising feature resulting from cyclic voltammetry curves is visibly better cycle stability of LMO(GO) sample in comparison to LMO.

CONCLUSIONS

We have successfully synthesized spinel-structure $LiMn_2O_4$ by the conventional sol-gel process modified by the usage of graphene oxide as a mediator. The main finding and fundamental novelty of this work is that graphene oxide present in the reaction solution significantly reduces the average grain size of the resulting $LiMn_2O_4$ powder by ca. one order of magnitude, down
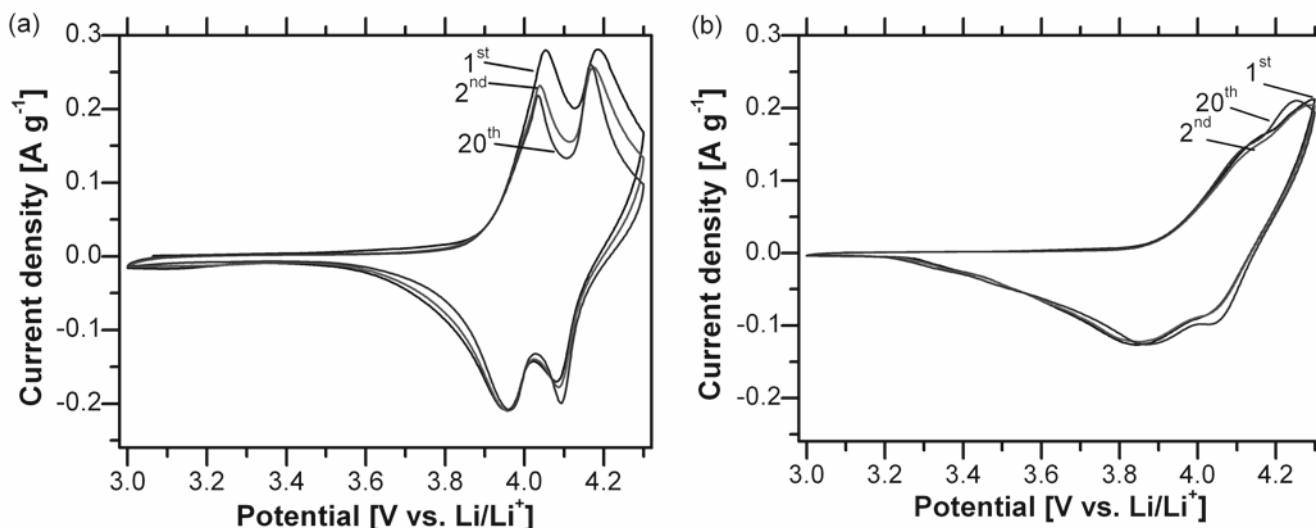

Figure 5. Cyclic voltammetric curves of LMO (a) and LMO(GO) (b) electrode obtained at a scan rate of 0.5 mV s^{-1}

to about 100 nm. GO is subsequently totally removed in the calcinations process so the observed effect has been referred to as mediation or assistance. To our knowledge, such an action of GO, analogous to well known glycol action in polyol nanoparticle syntheses, has never been reported so far in literature. The material exhibit satisfactory lithium insertion ability, as evidenced by cyclic voltammetry, however further optimization is necessary to attain the expected electrochemical performance of the cathodes.

Acknowledgements

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