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Synthesis of $Li_4Ti_5O_{12}$/Graphene Nano-Material by Microwave-Assisted Hydrothermal Method

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$Li_4Ti_5O_{12}$ (LTO) has been widely researched as an anode material of lithium ion battery for its high lithium intercalation-deintercalation potential, fast charge–discharge rate, excellent reversibility, structural stability and high safety [1]. But the low inherent electronic conductivity of LTO ($<10^{-13}$S cm^{-1}) at room temperature largely prevents its applications, especially its high-rate performance.

We report an approach to synthesize a new LTO/graphene nanostructure, where LTO nanoparticles were grown up on the surface of graphene sheets through a microwave-assisted hydrothermal reaction.

1. Experimental Method

The overall synthetic procedure of LTO/graphene nanostructure mainly includes four steps.

Firstly, graphene oxide (GO) was fabricated by Hummers method [2]. Then the vacuum-dried GO (0.1 g) was thoroughly dispersed in ethyleneglycol (EG, 40 mL) by the ultrasonification for 3 h. Subsequently, 8 ml of EG/GO solution, 0.5 g of 1-octyl-3-methylimidazolium chloride ($C_{12}H_{23}ClN_2$, ionic liquid (IL)), 0.39 g of $LiOH \cdot H_2O$, 2 mL of H_2O_2, and 1.5 g of $Ti(OBu)_4$ were added into 40 mL of H_2O under stirring at room temperature. After stirring for 2 h, the solution was transferred into a Teflon-lined heat-resistant plastic autoclave and treated by microwave-assisted hydrothermal reaction at 180℃ for 20 min,and then annealed at 550℃ for 6 h under N_2 atmosphere. The final product was denoted as LTO/graphene-IL and the intermediate graphene exfoliated by IL was denoted as grapheme-IL. For comparison, the microwave-assisted hydrothermal reaction was carried out without adding GO and IL, or with GO but without IL, where the products were denoted as LTO and LTO/graphene, respectively.

The microstructure of the samples was investigated by TEM (“JEM-1400”), HR-TEM (“JEM-2100”), AFM (“Nanoscope IIIA”) and XRD (“Rigaku D/Max II”), and the composition by TG analytical equipment (“NETZSCHSTA 499F3”) and the specific surface area and pore size distribution by N_2 adsorption–desorption measurements (“ASAP－2020”).

2. Outcome and Explanation

The XRD patterns of LTO, LTO/graphene and LTO/graphene－IL samples are compared in Fig. 1.

After annealing, all the products show the spinel LTO structure detected as JCPDS: 49-0207.

In the case of LTO/graphene-IL sample, the precursors were completely transferred into $Li_4Ti_5O_{12}$, while some crystalline anatase TiO_2(JCPDS:21-1272) was detected in the LTO/graphene sample due to the existence of carboxyl groups in GO restricting the interaction between Li ion and the precursor of Ti.

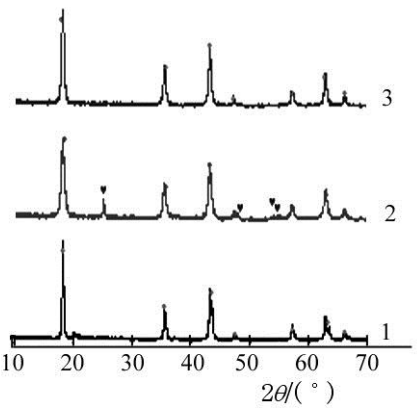

Fig. 1. XRD patterns of the synthesized LTO(1), LTO/graphene(2) and LTO/graphene-IL (3) samples

As shown in Fig. 2, LTO crystals grow on the surface of the exfoliated graphene, and LTO nanoparticles are uniform with diameter of about 18～20 nm. The crystal lattice of the LTO nanoparticle can be clearly observed (in the insert HRTEM, Fig. 2), consistent with the calculation by Debye–Scherrer equation (D=0.89λ/βcos(θ)). The graphene was marked with an open circle in Fig. 2 and LTO nanoparticles were finely dispersed over the surface of the graphene. It can be seen from AFM image of LTO/graphene-IL that there has been no any free-graphene and LTO nanoparticles uniformly grow on the surface of the graphene.

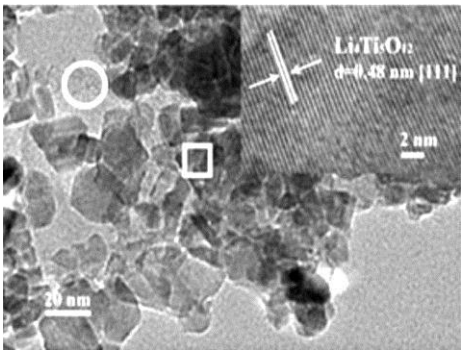

Fig. 2. TEM image of LTO/grapheme-IL sample
The insert corresponds to the HRTEM image taken from the square.

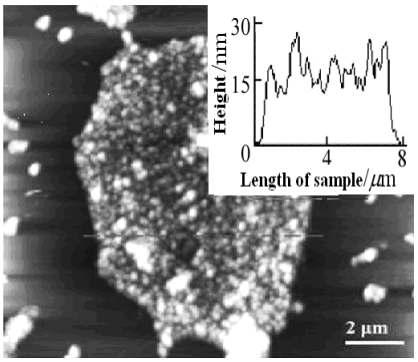

Fig. 3. AFM image of LTO/grapheme-IL sample
The insert corresponds to the thickness analysis.

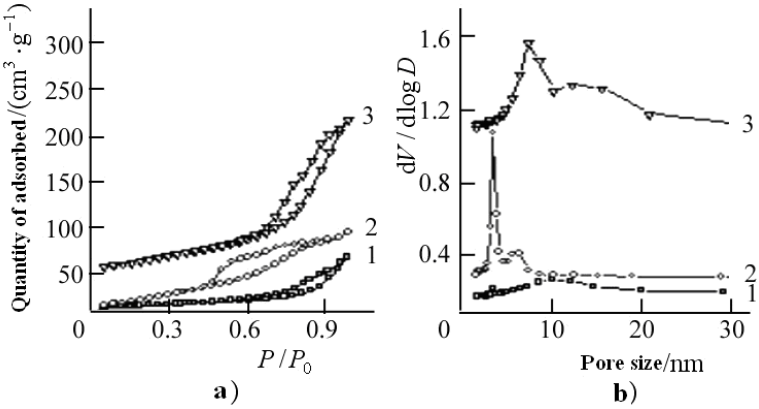

Fig. 4. N_2 absorption/desorption isotherms (a) and the pore size distribution (b) of different samples
1－LTO, 2－LTO/graphene, 3－LTO/graphene－IL

As you can see from Fig.3,the composite has two-dimensional microstructure with average 20 nm. Considering that the size of LTO nanoparticle in TEM image is 18 nm, LTO nanoparticles were uniformly anchored on graphene with a layer.

Fig. 4 shows N_2 absorption/desorption isotherms and the pore size distribution of

LTO, LTO/graphene and LTO/grapheme-IL samples.

The specific surface areas of LTO, LTO/graphene and LTO/grapheme-IL samples are 18.6, 33.4 and 75.6 m^2g^{-1}, respectively. The small surface area of LTO can be attributed to the aggregation of nanoparticles. The pore size distributions further indicate that the average mesoporous size of LTO/graphene-IL (7.1nm) is larger than that of LTO/graphene (3.7nm). The surface area also increases, attributed to LTO nanoparticles intercalated into the space between graphene layers, forming well-dispersed nanoparticles.

Fig. 5 shows XPS spectra of LTO/graphene, LTO/graphene-IL. For LTO/graphene, two experimental peaks could be fitted into three peaks with bonding energy of 284.8, 286.5 and 289.9 eV corresponding to C－C, C－O and O=C－O. It shows the presence of non-reduced carboxyl groups in graphenes after microwave-assisted hydrothermal method.

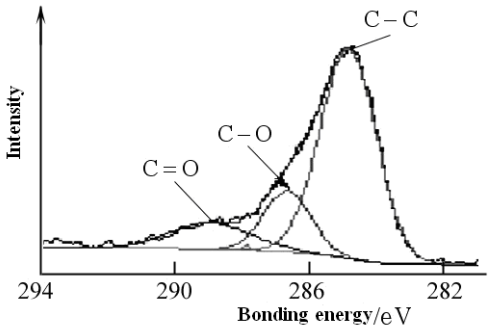

Fig. 5. XPS spectra of LTO/grapheme-IL sample

After adding IL, the bonding energy of C 1s/2 increases. For example, LTO/graphene－IL exhibits three bonding energy peaks at 248.8, 286.6 and 288.9 eV corresponding to C－C, C－O and C=O. This indicates that adding IL is beneficial to remove the oxygen of GO.

After annealing at 550℃, 1p/2 peak corresponding to N of IL in sample is eliminated. This indicates that IL is removed from reduced GO [3]. According to the TG curves, LTO/graphene－IL contains 2.5% of carbon which improves the conductibility. The contents of graphene and IL in the final LTO/grapheme-IL product are 2.10 and 0.49% respectively.

Conclusion

The LTO/graphene－IL synthesized by a microwave－assisted hydrothermal method using graphene exfoliated by ionic liquid has two-dimensional structure with a total thickness of about 20 nm and LTO nanoparticles uniformly grow on the surface of thin graphene sheets. The microstructure of LTO/graphene－IL helps to improve the electric conductibility by enlarging electrode/electrolyte contact area.

References

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