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STEM-HAADF Imaging Study of Spinel Cubic $Li_4Ti_5O_{12}$ Nanocrystals

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Spinel cubic $Li_4Ti_5O_{12}$ (LTO) has attracted great attention as a novel anode material for high performance Li-ion battery [1]. The LTO anode can provide a theoretical capacity of 175 mAh/g with negligible volume change during charging and discharging [1]. However, the high-current rate performance of pure LTO anode is seriously hindered by its low electrical conductivity [2]. Carbon-coating has been approved to be an effective method to improve the electrical conductivity of LTO anode material, carbon-coated LTO nanocrystals (C-LTO) have been investigated [3, 4]. It is critically important to understand the influence of the carbon-coating effects on high-rate performance [5]. In this study, the C-LTO anode nanocrystal with optimized thin coating layers were successfully synthesized.

In the present work, crystalline phase and coating structure were characterized by TEM imaging and high resolution TEM imaging using a JEOL 2010F FEG transmission electron microscopy. Atomic resolution structure of high-angle-annular dark-field (HAADF)-STEM images were obtained with collection semi-angles from 50 to 180 mrad in spherical aberration-corrected (Cs-corrected) scanning transmission electron microscopy of JEOL 2100F STEM/TEM operated at 200 kV.

TEM images and HRTEM images in Figure 1 (a) confirmed that the C-LTO nanocrystal have a well-defined spinel nanocrystal structure, and exhibited the spherical particle shape with amorphous carbon-coating and uniform thickness of less than 5 nm. Figure 1 (b) revealed that the well-resolved lattice fringes have an interplanar distance of 0.48 nm, corresponding to the d-spacing of the facets of the spinel LTO structure.

Cs-corrected STEM technique allows us to obtain atomic-resolution HAADF images and count the number of atoms in an atomic column of a crystal [6]. The typical high-resolution STEM-HAADF images at the atomic scale are showed in Figure 2 (a). The titanium atom sites (16d), lithium atom sites (16d) and oxygen atom site (32e) can be clearly visualized in the enlarge atomic resolution HAADF image in Figure 2 (b), which is consistent with the atomic occupancies in schematic lattice view of spinel LTO along the [110] direction, as showed in LTO [110] projection model in Figure 4 (c). Bscially, such like the [110] projection of spinel LTO is most suitable for observing Li, O, and Ti atoms directly, because separate columns of these atoms are aligned in this [110] direction. It is worth noting that the pure spinel LTO phase was synthesized and further confirmed. The improved high-current rate performance can be ascribed to high phase purity and the enhanced intrinsic electronic conductivity resulting from the synergistic effect of nanocrystals, carbon-coating and uniform thin thickness.

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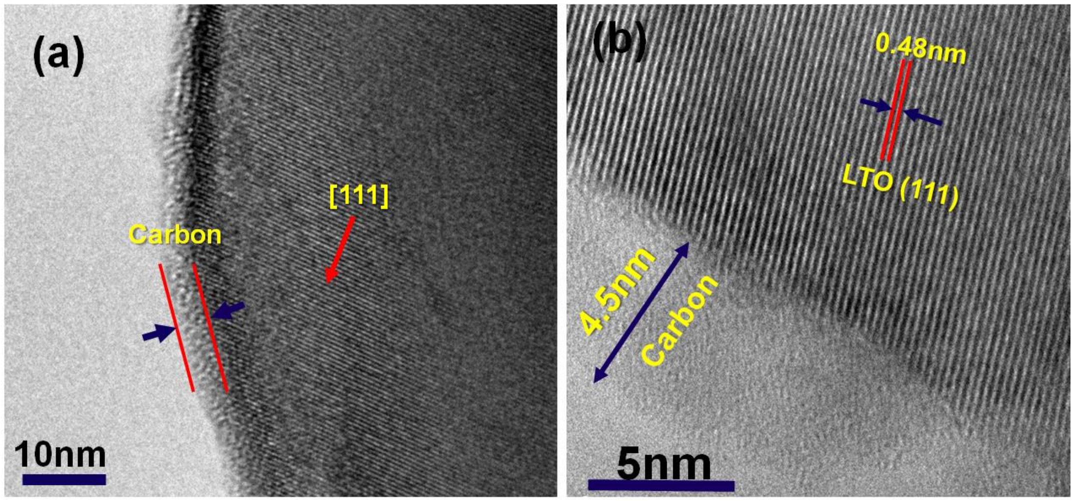

Figure 1. TEM images (a) and HRTEM images (b) of the C-LTO nanocrystal. The well-crystallized structure and an amorphous carbon layer covering (~4.5 nm) is clearly observed.

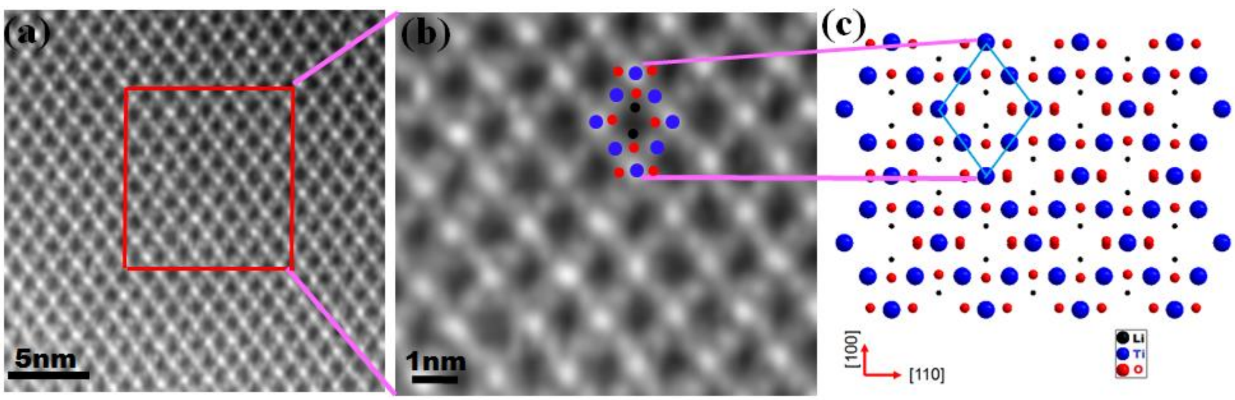

Figure 2. (a) High-resolution STEM-HAADF images at atomic scale, (b) The enlarged HAADF panel showed atomic structure of LTO crystal plane, (c) Schematic lattice view of spinel LTO along the [110] direction, corresponding to the 16d, 32e, and 8a sites in the LTO atomic lattice.

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