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In situ Transmission Electron Microscopy of Lithiation Dynamics in a SnO_2 Hollow Nanosphere

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Hollow-nanostructured materials are promising anodes for Li ion batteries (LIBs) due to their advantage of low density, large surface area and short diffusion length for mass and charge transports [1]. In order to design efficient hollow-nanostructured electrodes, understanding their lithiation process is highly demanded. Since *in situ* transmission electron microscopy (TEM) is a powerful and versatile tool to reveal both structural and chemical reactions in real-time, alloying reaction with Li of hollow nanospheres has been demonstrated using the *in situ* TEM [2]. However, their conversion reaction for lithiation is still ambiguous.

Thus, in this work, we report lithiation dynamics of SnO_2 hollow nanospheres, a representative conversion-type anode for LIBs. SnO_2 hollow nanospheres are synthesized with hydrothermal method [3]. The synthesized nanospheres are placed on the W tip and they are mounted on one side of biasing TEM holder. For counter electrode, Li metal is placed on the other side of the holder. With short exposure in air, the surface of Li metal is oxidized to Li_2O, which works as a solid electrolyte. Operation voltage is applied by 5 V to the system after making a contact between the Li/Li_2O and the nanosphere.

In Figure 1(a), TEM image shows that synthesized SnO_2 nanospheres have uniform hollow shape and size (~100 nm). Figure 1(b) shows their selected-area electron diffraction (SAED) pattern, indicating tetragonal SnO_2 polycrystals. We monitor lithiation process of a single sphere, as shown in Figure 2 (a). Upon electric field, Li ions move toward to the nanosphere from the Li/Li_2O and sphere's volume expands due to the lithiation. It is noticeable that very small Sn particles (~ 2 nm) are formed (Figure 2 (b) and 2 (c)) and no agglomeration of Sn is observed, which is commonly found during lithiation of SnO_2 electrode in previous studies in nanoparticles and nanowires [4, 5]. As shown in Figure 2 (b) and 2(c), very small Sn particles (~ 2 nm) are formed after lithiation. It is assumed that agglomeration of Sn is prevented by the hollow structure, as large volume of inner void can accommodate the nucleated Sn produced from conversion reaction.

In summary, we synthesized SnO_2 hollow nanosphere and visualized its lithiation dynamics using *in situ* TEM. This work provides rich information showing no agglomeration was found during lithiation unlike in nanoparticles or nanowires and will contribute to design of advanced batteries using hollow structured conversion-type anode materials for LIBs [6].

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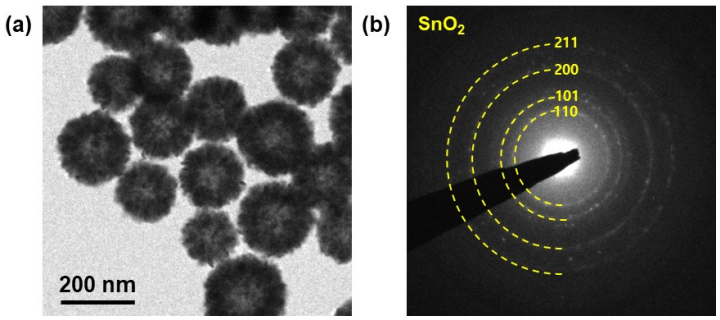

Figure 1. (a) TEM images of SnO_2 hollow nanospheres and (b) the corresponding SAED pattern. The nanospheres are dispersed uniformly.

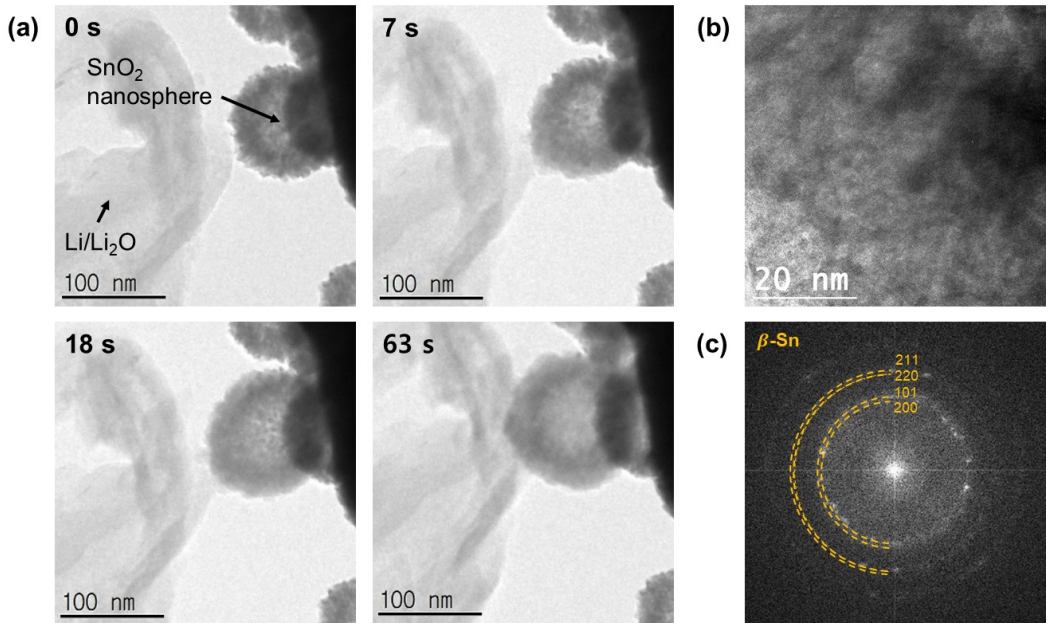

Figure 2. (a) Time-series TEM images showing lithiation process of SnO_2 hollow nanosphere, (b) HRTEM image of lithiated SnO_2 hollow nanosphere and (c) corresponding FFT pattern.

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