

## Synthesis of LiCoO<sub>2</sub> Nanoparticles by a Sonochemical Method under the Multibubble Sonoluminescence Conditions

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Received August 18, 2009, Accepted December 14, 2009

LiCoO<sub>2</sub>, a cathode material for lithium rechargeable batteries, was prepared in a nanoscale through a simple sonochemistry. First, Co<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by reacting NaOH and CoCl<sub>2</sub> or CoSO<sub>4</sub> with a sonochemical method, operated at 20 kHz and 220 W for 20 min, very powerful multibubble sonoluminescence conditions for chemical reactions. Second, LiOH was coated onto the Co<sub>3</sub>O<sub>4</sub> nanoparticles by the same method as above. Finally, LiCoO<sub>2</sub> nanoparticles of about 10 ~ 30 nm size in diameter were obtained by the thermal treatment of the resulting LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles at 500 °C for 3 hr. This synthetic process is relatively quite mild and simple compared to the known method for the synthesis of LiCoO<sub>2</sub> nanoparticles. The materials synthesized were characterized by infrared spectroscopy, X-ray diffraction, inductively coupled plasma spectrometer, and high resolution-transmission electron microscopy analyses.

**Key Words:** Co<sub>3</sub>O<sub>4</sub> nanoparticles, LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles, LiCoO<sub>2</sub> nanoparticles

### Introduction

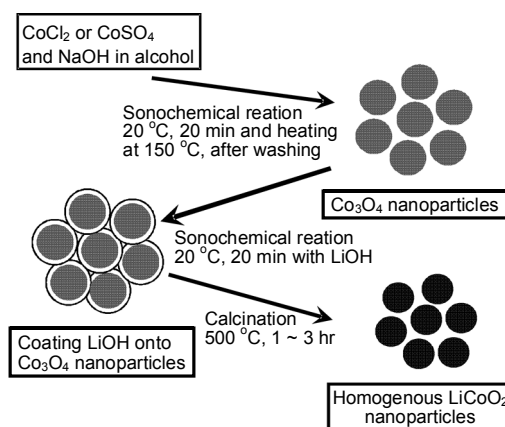
Lithium secondary batteries are being used worldwide as ubiquitous energy storage devices from mobile phones to electric vehicles.<sup>1</sup> Among the lithium battery electrode materials, LiCoO<sub>2</sub> has been the most attractive due to the best performance in terms of high specific energy density and excellent cycle life, so that it was already commercialized as a cathode material.<sup>1,2</sup> Numerous investigations on the syntheses and electrochemical properties of LiCoO<sub>2</sub> materials have been made to improve its performance,<sup>3-5</sup> and most of the works focused on the preparation of LiCoO<sub>2</sub> particles with various sizes and shapes through conventional solid-state reactions,<sup>6,7</sup> and solution-assisted methods such as sol-gel,<sup>8,9</sup> hydrothermal,<sup>10</sup> emulsion drying,<sup>11</sup> and other method.<sup>12</sup> In general, however, it was hard to make homogeneous LiCoO<sub>2</sub> nanoparticles; it typically required wearisome conditions, such as very high temperature, long producing time, and so on. To overcome such problems, many coating methods onto inorganic oxide nanoparticles, resulting into various core/shell type nanocrystals, were applied for its preparation.

The core/shell type materials were extensively studied through different methods, such as hydrothermal synthetic method, microwave, and sonochemistry.<sup>13-15</sup> Especially in the sonochemical method, it is relatively easy to control the coating depth of target materials by adjusting reaction conditions such as the amount of reactants and/or the sonication time.<sup>16,17</sup> In particular, the multi-component particles with core/shell structure, which can be prepared at the multibubble sonoluminescence condition, have recently drawn special attention due to their fascinating properties for various applications in catalysts,<sup>17</sup> luminescence<sup>18</sup> and lithium-ion batteries.<sup>19</sup>

The sonochemistry is an application of sonoluminescence which is a light emission phenomenon associated with the collapse of a gas bubble oscillating under an ultrasonic field. The intense local heating and high pressure inside the bubbles and liquid adjacent the bubble walls from such collapse can give

rise to unusual effects in chemical reactions<sup>20</sup> and the sonochemical process has been proven to be a useful technique to make novel materials with unusual properties. The estimated temperature and pressure in liquid zone around the collapsing bubble with equilibrium radius 5 μm, generated in a sonochemical reactor at a driving frequency of 20 kHz with an input power of 179 W were about 1000 °C and 500 atm, respectively.<sup>21</sup> The sonochemical reaction system in this study was operated at 20 kHz and 220 W, which produces very powerful multibubble sonoluminescence conditions compared to other typical ultrasound irradiation processes.<sup>21,22</sup>

We report a new method for the preparation of homogeneous LiCoO<sub>2</sub> nanoparticles under relatively mild conditions. As shown in Scheme 1, first, NaOH and CoCl<sub>2</sub> or CoSO<sub>4</sub> were reacted to prepare Co<sub>3</sub>O<sub>4</sub> nanoparticles by sonochemistry. Second, LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles was prepared using Co<sub>3</sub>O<sub>4</sub> and LiOH by the same sonochemical method as above. Finally, they were transformed into LiCoO<sub>2</sub> nanoparticles by thermal heating at 500 °C for 3 hr.



**Scheme 1.** Three step method for LiCoO<sub>2</sub> nanoparticles preparation through sonochemistry.

### Experimental Details

All solvents were refluxed over molecular sieves 3 Å (pellets, 3.2 mm) to remove water molecules and then distilled before using them. An experimental apparatus described in our previous papers<sup>16</sup> for sonochemistry system was used. It consists of a cylindrical quartz cell into, which a 5 mm diameter titanium horn (Misonix XL2020, USA) is inserted. The solvent in the cell was kept at 1.4 atm with argon gas and the temperature of the solution inside the cell was kept to around 20 °C by a circulating water, which was found to be optimal condition for the coating process.<sup>13</sup>

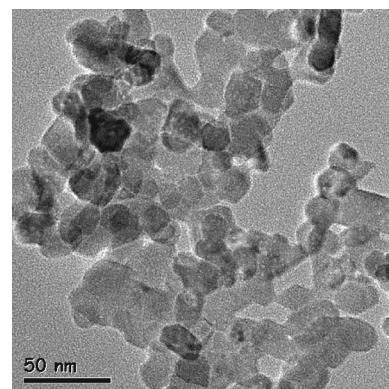
**Preparing the Co<sub>3</sub>O<sub>4</sub> nanoparticles.** Co<sub>3</sub>O<sub>4</sub> nanoparticles were prepared by reacting NaOH (2 mmol) and CoCl<sub>2</sub> or CoSO<sub>4</sub> (1 mmol) with a 2:1 ratio in methanol or ethanol (13 mL) through a one pot reaction under the described sonochemical conditions for 20 min. The resulting products were washed 3 times using methanol or ethanol, and then they were heated at 150 °C for 1 hour.

**LiOH coating onto Co<sub>3</sub>O<sub>4</sub> nanoparticles.** Co<sub>3</sub>O<sub>4</sub> nanoparticles were coated with LiOH through a one pot reaction under the same sonochemical conditions as above since the LiOH-coated Co<sub>3</sub>O<sub>4</sub> particles are very likely to be a useful precursor for the preparation of LiCoO<sub>2</sub> nanoparticles. In order to find best coating depth for the preparation of LiCoO<sub>2</sub> nanoparticles, several different reaction ratios between LiOH and Co<sub>3</sub>O<sub>4</sub> such as 1:1, 1.5:1, and 2:1 were tried. Each LiOH·H<sub>2</sub>O and Co<sub>3</sub>O<sub>4</sub> in methyl alcohol (13 mL) solution was sonicated at the aforementioned conditions for 20 min. The color of LiOH-coated nanoparticles was gray and the resulting particles were washed by DI-water, alcohol, acetone in order and dried at vacuum oven at 60 °C for 12 hr.

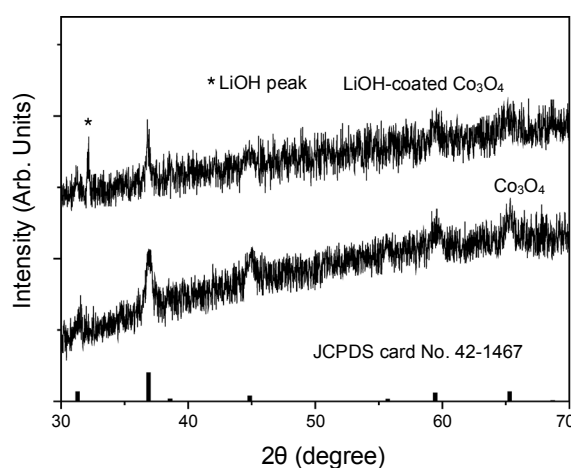
**Preparation of LiCoO<sub>2</sub> nanoparticles.** LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles as a precursor were heated at 500 °C for 1 ~ 3 hr for the formation of LiCoO<sub>2</sub> nanoparticles. Only the coated precursor from the reaction ratio 2:1 between LiOH and Co<sub>3</sub>O<sub>4</sub> was transformed into the LiCoO<sub>2</sub> nanoparticles with proper stoichiometry. The resulting materials were characterized by various instruments, such as X-ray diffractometer (Scintag XDS-2000), infrared spectroscopy (varian FTS 1000), field emission-transmission electron microscope (Techani G2 F30), energy dispersive X-ray spectroscopy, and inductively coupled plasma spectrometer (JY-Ultima-2).

### Result and Discussion

Figure 1 and 2 show the transmission electron microscopic image and XRD pattern of Co<sub>3</sub>O<sub>4</sub> nanoparticles prepared through the aforementioned sonochemical reaction. The yield is 97%. It is interesting to note that there were no other compounds such as CoO or Co<sub>2</sub>O<sub>3</sub>. On the other hand, there was a mixture of various cobalt oxides at the lower sonochemical conditions. The size of the bare Co<sub>3</sub>O<sub>4</sub> nanoparticles was about 10 to 40 nm with quite narrow size distribution. In Figure 2, the XRD pattern of Co<sub>3</sub>O<sub>4</sub> nanoparticles indicates a cubic phase<sup>23</sup> and the XRD pattern of the LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles indicates that the LiOH is in a tetragonal phase<sup>24</sup> with most intense picks at  $2\theta = 32.9^\circ$  corresponding to (101) planes. The relatively low intensities of



**Figure 1.** TEM image of Co<sub>3</sub>O<sub>4</sub> nanoparticles prepared under the described sonochemical conditions.

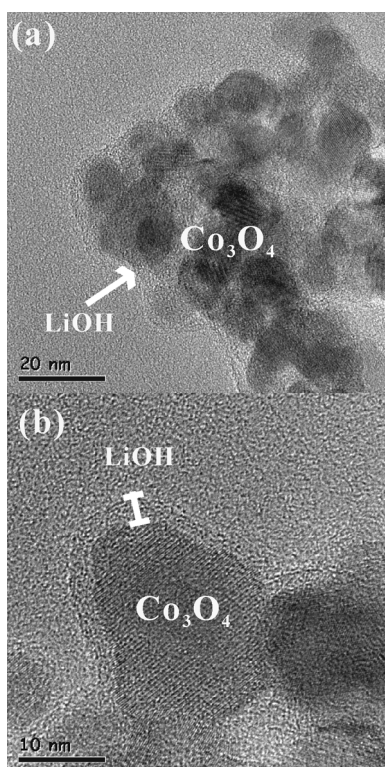


**Figure 2.** XRD data of Co<sub>3</sub>O<sub>4</sub> and LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles. The perpendicular bars at the bottom of the graph are from the reference of Powder Diffraction File of Co<sub>3</sub>O<sub>4</sub>.

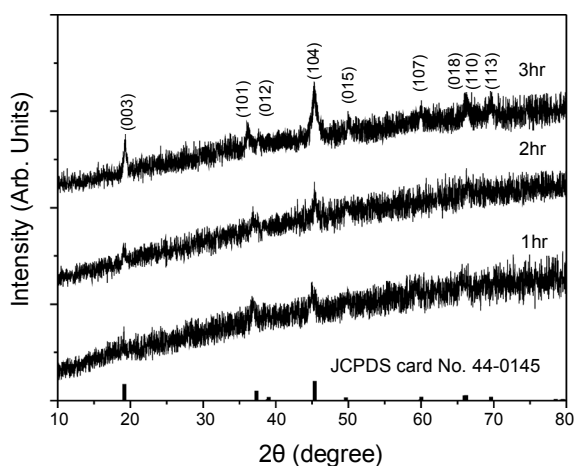
picks are assumed to arise from the fact that the particles are nano-sized and the LiOH is thinly coated on Co<sub>3</sub>O<sub>4</sub>. In addition, its IR spectra showed various characteristic peaks due to LiOH at 3438, 2585, 2365, 1806, 1637, 1512, 1436, 1085, 866, 733, and 633 cm<sup>-1</sup>.<sup>25</sup>

Figure 3 shows the high resolution transmission electron microscopic image of the LiOH-coated Co<sub>3</sub>O<sub>4</sub> nanoparticles, indicating that LiOH is evenly coated on the surface of Co<sub>3</sub>O<sub>4</sub>. The coating depth of LiOH on Co<sub>3</sub>O<sub>4</sub> from the reaction ratio of 2:1 between LiOH and CoCl<sub>2</sub> was found to be about 3 ~ 5 nm range. It should be noted that rapid syntheses with very homogeneous size of LiOH and subsequent coating of the particles onto Co<sub>3</sub>O<sub>4</sub> nanoparticles under the described sonochemical conditions might be attributed to the existence of transient supercritical state in the liquid layer adjacent to the bubble wall around the collapse point.<sup>26</sup>

Only the precursor with the reactant ratio of 2:1 for LiOH and Co<sub>3</sub>O<sub>4</sub> was transformed into LiCoO<sub>2</sub> nanoparticles by thermal treatments at 300 ~ 500 °C for 1 ~ 3 hr. In the cases of other precursors with the reactant ratio of 1:1 or 1.5:1 for LiOH and Co<sub>3</sub>O<sub>4</sub>, there was unreacted Co<sub>3</sub>O<sub>4</sub> in their XRD patterns. Figure 4 shows XRD data of LiCoO<sub>2</sub> nanoparticles. According to in-



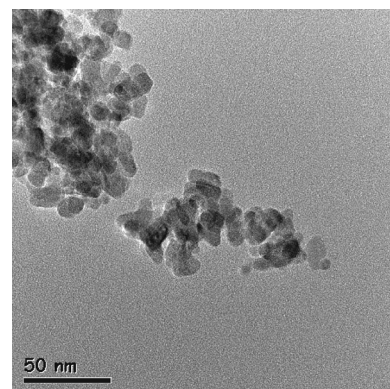
**Figure 3.** TEM images of LiOH-coated  $\text{Co}_3\text{O}_4$  nanoparticles prepared under the described sonochemical conditions.



**Figure 4.** XRD data of  $\text{LiCoO}_2$  nanoparticles prepared at  $500\text{ }^\circ\text{C}$  for 1 ~ 3 hr. The perpendicular bars at the bottom of the graph are from the reference of Powder Diffraction File of  $\text{LiCoO}_2$ .

creasing temperature, the peak intensity becomes stronger. The XRD pattern of the  $\text{LiCoO}_2$  nanoparticles indicates a cubic phase<sup>27</sup> with most intense peaks at  $2\theta = 19.2^\circ, 37.3^\circ, 39.0^\circ, 45.4^\circ, 49.7^\circ, 60.0^\circ, 66.0^\circ, 66.2^\circ, \text{ and } 69.6^\circ$ , corresponding to (003), (101), (012), (104), (015), (107), (018), (110), and (113) planes.

Figure 5 shows the high resolution transmission electron microscopic image of  $\text{LiCoO}_2$  nanoparticles. Their size was about 10 to 30 nm in diameter, which was a little bit smaller to that of  $\text{Co}_3\text{O}_4$  nanoparticles. These nanoparticles are very pure in phase and quite homogeneous in their sizes and their shapes. In addition,



**Figure 5.** TEM image of  $\text{LiCoO}_2$  nanoparticles prepared at  $500\text{ }^\circ\text{C}$  for 3 hr.

EDX analyses show that the atomic percents of Co and O are 33.50 and 66.49% and ICP analyses also show Li : Co ratio of 1.002 : 1.000. These results indicate the exact stoichiometric elemental ratio of  $\text{LiCoO}_2$  nanoparticles.

## Conclusions

In conclusion,  $\text{Co}_3\text{O}_4$  nanoparticles were prepared by a one pot sonochemical reaction at room temperature using NaOH and  $\text{CoCl}_2$  or  $\text{CoSO}_4$  in water. Subsequently, LiOH-coated  $\text{Co}_3\text{O}_4$  nanoparticles were prepared by the same methods using LiOH and prepared  $\text{Co}_3\text{O}_4$  nanoparticles. The crystalline phase of the coated LiOH on  $\text{Co}_3\text{O}_4$  was tetragonal and the depth of coated LiOH onto  $\text{Co}_3\text{O}_4$  nanoparticles was found to be about 3 - 5 nm. As a precursor, the LiOH-coated  $\text{Co}_3\text{O}_4$  nanoparticles from the reaction ratio of 2:1 between LiOH and  $\text{Co}_3\text{O}_4$  were used for the synthesis  $\text{LiCoO}_2$  nanoparticles by heating at  $500\text{ }^\circ\text{C}$  for 3 h. These are the mildest conditions for  $\text{LiCoO}_2$  nanoparticle preparations.<sup>1-7</sup>

**Acknowledgments.** This research was supported by the Chung-Ang University Research Scholarship Grant for J.Y. Park and C. H. Hwang in 2009.

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