

## Reaction Mechanism and Kinetic of Graphene Supported $\text{Co}_3\text{O}_4$ Nanocubes with Lithium and Magnesium Studied by *in situ* TEM

Jinsong Wu<sup>1,2</sup>, Langli Luo<sup>1,2</sup>, Qianqian Li<sup>1,2</sup>, Vinayak P. Dravid<sup>1,2</sup>, Qunli Rao<sup>1,3</sup> and Junming Xu<sup>1,4</sup>

<sup>1</sup>. NUANCE Center, Northwestern University, Evanston, IL USA

<sup>2</sup>. Department of Materials Science and Engineering, Northwestern University, Evanston, IL USA

<sup>3</sup>. Department of Materials Science and Engineering, Shanghai Jiao-Tong University, Shanghai, China

<sup>4</sup>. College of Electronic Information, Hangzhou Dianzi University, Hangzhou, China

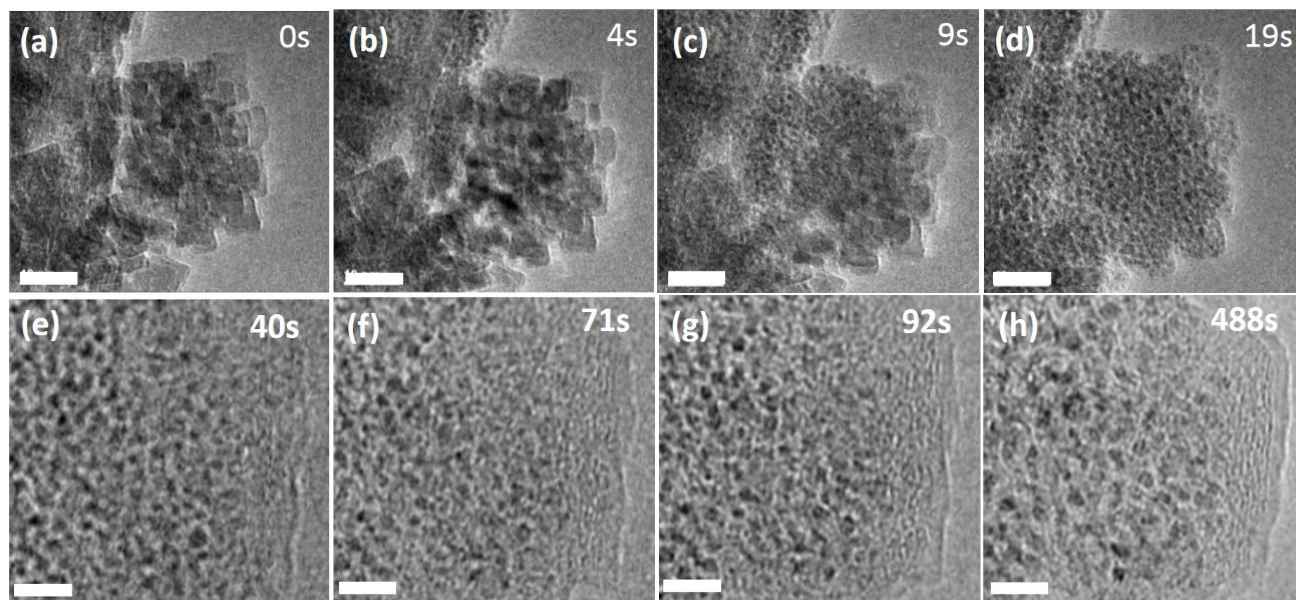
While most of current research on energy storage is focused on lithium-ion battery, the alternatives like magnesium and aluminum has many obvious advantages. For example, magnesium is a nature abundant element being the 5<sup>th</sup> most abundant element in the earth's crust. It is environmentally friendly, low price and has many safe characters, *i.e.* it is stable enough in ambient atmosphere to handle. However, currently there are many serious limitations in magnesium electrochemistry that prevents magnesium-ion battery being an efficient system for energy storage. In this work, by using high resolution *in-situ* transmission electron microscopy (TEM) the diffusion of multivalent ions and the solid-state reactions with  $\text{Co}_3\text{O}_4$  nanocubes and graphene have been studied, in order to explore the reaction mechanism for multivalent-ion batteries, in direct comparison to that of lithium-ion battery. Nano-composite materials, especially graphene-based nanostructure<sup>1-2</sup> have been developed for high-capacity anode materials showing enhanced high electron and lithium ion conductivity by graphene. Meanwhile, the emerging *in-situ* transmission electron microscopy (TEM) techniques with localized electrical measurement capabilities provide a practical platform to investigate electrochemical reactions in Li-ion battery materials by building a full or half "nano-cell" inside the TEM specimen chamber<sup>17</sup>. Such real-time observations of dynamic composition and microstructural evolution in the electrochemical reaction have provided many novel clues to understand the lithiation/de-lithiation mechanisms at nano or even atomic-scale for several novel anode materials<sup>18</sup>. Herein, we report a morphological and structural study of graphene sheets supported  $\text{Co}_3\text{O}_4$  nanocubes during the electrochemical reaction with lithium, and magnesium.

Upon charging with lithium-ions, the  $\text{Co}_3\text{O}_4$  nanocubes decompose to small Co metal nanoparticles (2-3 nm) and embedded in as-formed  $\text{Li}_2\text{O}$  matrix; reversely, the CoO nanoparticles formed on the site of Co accompanying the decomposition of  $\text{Li}_2\text{O}$  in the discharging process. The lithiation process is dominated by surface diffusion of  $\text{Li}^+$  and graphene sheets enhance the  $\text{Li}^+$  diffusion leading to a fast charging process. However, upon charge with magnesium, the  $\text{Mg}^{2+}$  diffusion is sluggish and there is no sign of conversion reaction between Mg and  $\text{Co}_3\text{O}_4$  at room temperature. Instead, a thin film consisting of metal Mg nanoparticles is formed on the surface of graphene due to a process similar to metal plating. The  $\text{Al}^{3+}$  diffusion is even more sluggish and there is no electrochemical reaction between Al and  $\text{Co}_3\text{O}_4$  can be observed at room temperature. The finding may shed light on the development of batteries with high energy density based on multivalent ions other than lithium.

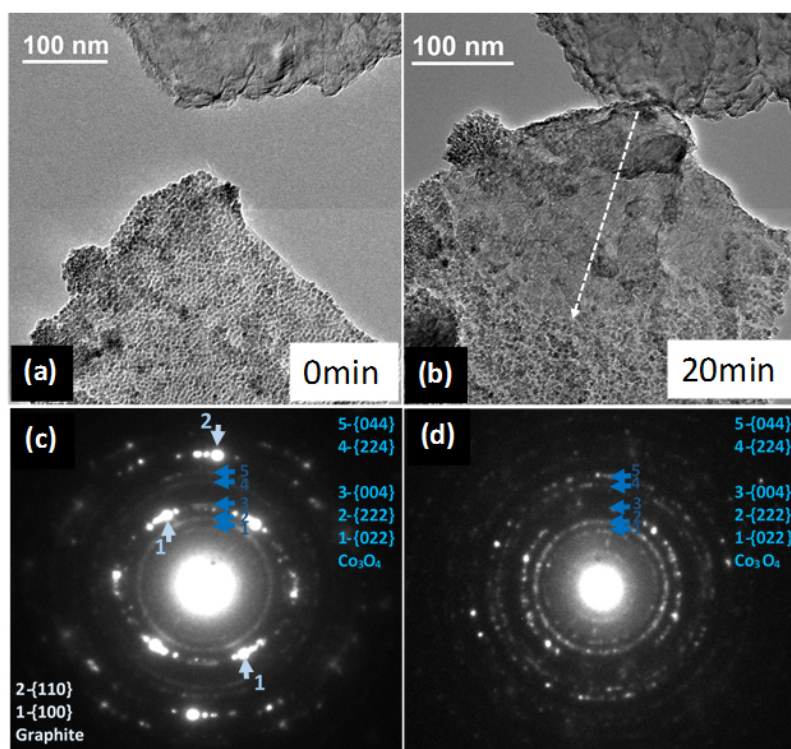
### References:

- [1] H. Wang, *et al.* Journal of the American Chemical Society **132**, (2010), p.13978.
- [2] X. Zhu, *et al.* ACS Nano **5**, (2011), p.3333.
- [3] J.Y. Huang, *et al.* Science **330**, (2010), p.1515.
- [4] L. Luo, *et al.* Scientific Reports **4**, (2014), article number 3863.
- [5] L. Luo, *et al.* ACS Nano **8**, (2014), p. 11560.

[6] This work was supported as part of the Center for Electrochemical Energy Science, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DEAC02-06CH11357. This work was also supported by the NUANCE Center new initiatives, and made use of the EPIC facility (NUANCE Center-Northwestern University), which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center, The Nanoscale Science and Engineering Center (EEC-0118025/003), both programs of the National Science Foundation; the State of Illinois; and Northwestern University.



**Figure 1.** Time-resolved TEM images of electrochemical lithiation process (a) to (d); and delithiation process (e) to (h) of  $\text{Co}_3\text{O}_4$  nanocubes on graphene. The scale bar is 10nm.



**Figure 2.** Microstructural evolutions in the magnesiation process. (a) The MgO/Mg probe and the  $\text{Co}_3\text{O}_4$ /Graphene nanocomposites loaded on a Au tip, prior to the electrochemical magnesiation. (b) TEM image of the reaction front of magnesiation after the electric bias of -5 V has been applied. The front moves forward about 240 nm in 20 minutes. (c) SAED pattern of  $\text{Co}_3\text{O}_4$ /Graphene nanocomposites before the magnesiation reaction. (d) SAED pattern of  $\text{Co}_3\text{O}_4$ /Graphene nanocomposites after the magnesiation reaction.