Capillary induced Ge Uniformly Distributed in N-doped Carbon Nanotubes with Enhanced Li-Storage Performance

Haipeng Guo[a], Boyang Ruan[a], Lili Liu[a], Lei Zhang[a], Zhanliang Tao[a], Shulei Chou[a], Jiazhao Wang*[a], Huakun Liu*[a]

[a] Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522 Australia

E-mail: hg476@uowmail.edu.au

Germanium has attracted much attention as a promising anode material for lithium ion batteries due to its outstanding lithium-ion diffusivity, high electrical conductivity, and large theoretical capacity. Unfortunately, germanium suffers from huge volume expansion (over 300%). The using of nanostructure has been proven to be the most effective way to accommodate the volume changes. Hence, the fabrication of germanium within hollow carbon nanotube structure would be highly desirable for improved electrochemical performance.

In general, PPy nanotubes were first added into deionized water, followed by ultrasonic. Meanwhile, GeO_2 were dissolved in NaOH solution. After stirring, the two solutions were mixed together. The pH of the solution was slowly adjusted to 7 with dilute HCl. Then, poly(vinylpyrrolidone) was added into the solution. After drying out, the sample was annealed to 650 °C at a rate of 5 °C min^{-1} in H_2 atmosphere. Finally, the sample was washed with ethanol and deionized water several times.

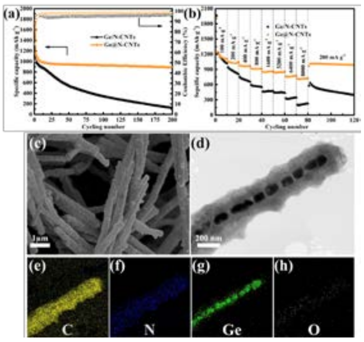

Figure 1. (a) Cycling stability and (b) Rate capabilities of Ge/N-CNTs and Ge@N-CNTs. (c) SEM and (d) TEM images of Ge@N-CNTs. Elemental mapping images of an individual Ge@N-CNTs nanotubes.

The SEM and TEM images show the details of the unique Ge@N-CNTs (Figure 1). The dark inner Ge cores are homogeneously encapsulated by the N-CNTs shells, and there are some void spaces not only between the individual Ge nanoparticles, but also between the Ge core and the N-CNTs shells. These uniformly distributed Ge nanoparticles could facilitate Li^+ ion transport through reducing the diffusion distance. Furthermore, the void spaces and the N-CNTs could effectively suppress the huge volume expansion. In addition, the interconnected network of the N-CNTs could afford good electrical conductivity of the electrode. Therefore, when investigated as anode material, the Ge@N-CNTs manifests high specific capacity, outstanding cycling stability, and excellent rate capacity.

In conclusion, we have presented a facile and novel strategy to fabricate Ge@N-CNTs composite with Ge nanoparticles uniformly encapsulated in robust N-CNTs shells by using capillary action. The unique Ge@N-CNTs composite with Ge nanoparticles uniformly distributed in the robust N-CNTs could be obtained. The Ge@N-CNTs demonstrates outstanding cycling stability and excellent rate capability in comparison with Ge/N-CNTs, which could be attributed to the efficiently utilization of the void spaces provided by the uniformly distributed Ge nanoparticles.