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Hollow C nanobox: An efficient Ge anode supporting structure applied to high-performance Li ion batteries

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ABSTRACT

Diverse strategies have been used to address the irreversible structural collapse issues of Ge-based anodes associated with lithium insertion/extraction. In this research, the hollow C-Ge and C-Si core-shell (Ge@C and Si@C) anode materials are successfully synthesized through a facile chemical vapor deposition (CVD) method onto hollow carbon nanoboxes. Compared with the Si@C nanoboxes anode, the Ge@C nanoboxes display better cycling performance, which is attributed to the Ge intrinsic favorable electronic/ionic conductivities and the distinctive Ge anode configurations. In addition, the conductive carbon nanobox supporting structure not only effectively accommodates the volume change of the amorphous Ge nanoparticles during the repeated cycling, but also significantly enhances the reaction kinetics of the Ge active material due to the enlarged surface area. More importantly, the nanoarchitecture of this un-protective Ge shell layer anode can be well maintained even after long-term cycling and the $LiCoO_2$||Separator($LiPF_6$+EC + DEC)||Ge@C full battery also display superior cyclability.

1. Introduction

Germanium, owing to its high theoretical Li^+ storage ability ($Li_{3.75}Ge$; 1384 mAh/g) and favorable electronic/ionic conductivities than the same IVA group Si, has drawn significant attention in the field of lithium-ion battery(LIB) anode materials [1–5]. However, similar to Si, the volume expansion problem during repeated Li^+ alloying/de-alloying processes hinders further practical applications [6–10]. Previously, Ge nanowires and Ge/C nanocomposites have been the two major approaches to circumventing the pulverization effect and improving the cycling performance [11–14]. For example, Chan et al. first synthesized Ge nanowire electrodes using the vapor-liquid-solid (VLS) method and displayed an improved rate of performance for Li^+ storage [15]. The Kennedy group also prepared Ge nanowire anodes using the metal-catalyst (Sn) chemical vapor deposition (CVD) technique and formed three-dimensional (3D) interconnect porous nanostructures after only a few cycles, which exhibited a high cycling stability [16]. Additionally, Ngo et al. synthesized 3D porous Ge/C nanocomposite particles using a thermal decomposition process and obtained a superior cyclability and rate capability [17,18]. Wang et al. recently reported the hierarchical porous germanium/reduced graphene oxide (Ge/rGO) microspheres LIB anode which were fabricated by a scalable spray drying technique and distinctively delivered excellent high reversible capacity and cycling life. Both the 3D conductive rGO network and the porous structure are together favorable to effectively alleviate the Ge anode volume changes and improve the electrochemical performance [19]. Moreover, it is found that the Ge can be successfully evaporated on the seamless graphene carbon nanotube current collector surface and exhibits promising rate capability [20]. Another kind of mesoporous germanium (Ge) particles were prepared by reduction of GeO_2 under a mild temperature for high performance LIBs due to the obtained large surface area and enough void spaces which can improve reactivity and accessibility of Li ions during cycling [21,22]. However, the electrochemical properties of most reported Ge anodes, especially those based on the CVD methodology, still have some room to be further investigated and optimized. In addition, the existence of extra noble metal catalyst nanoparticles in Ge electrodes should result in a reduced Li storage capability and increased cost.

Most recently, carbon nanoboxes, due to their hollow nanostructure and good conductivity properties, have attracted researchers to design and construct high-performance electrochemical energy storage systems [23–26]. Notably, in our

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previous work, a novel etching-in-a-box approach was employed to successfully fabricate Fe_3O_4/C yolk-shelled nanocubes from Fe_2O_3/PDA (polydopamine) nanocubes, exhibiting excellent cycling stability [23]. Meanwhile, the FeS_2/C york-shell nanobox sodium-ion battery (SIB) anodes were facilely synthesized and achieved remarkable electrochemical properties [24]. Similarly, He et al. also used the highly conductive Fe_3O_4/C nanobox framework as a highly efficient S host to design Li-S batteries [25]. Based on the Fe_2O_3/PDA nanocube, Dong and co-workers prepared porous Fe_2N/C nanoboxes using facile confined anion conversion under an NH_3 gas flow and delivered ultra-stable cycling performance [26]. Therefore, an efficient way to improve the electrochemical properties of batteries is by configuring and designing rational C nanobox-based micro/nano electrodes.

As depicted in Scheme 1, the as-fabricated Fe_2O_3 nanocubes were first coated by a polydopamine (PDA) thin layer via a facile solution procedure. Then, hollow C nanoboxes were successfully obtained after PDA shell carbonization and the Fe_3O_4 nanocubes etching processes. Subsequently, an amorphous Ge nanoparticles and Si thin film electrodes were directly and separately deposited on the hollow C nanobox surfaces without using any metal catalyst during the CVD process. These newly reported Ge@C anodes exhibit superior electrochemical performance; this is attributed to the hollow nanostructures of the C supporting material, which enable increased surface area which promotes electrochemical reactions as well as facile relaxation of the mechanical stress caused by the Ge nanoparticles volume changes associated with Li ions. Moreover, the enough space between the Ge nanoparticles anode can also well alleviate the Ge electrode volume expansion and thus finally bring the improved electrochemical performance. Notably, the full battery Ge@C||$LiCoO_2$ was also configured and displayed good cyclability. Finally, the postmortem morphologies of the cycled Ge@C and Si@C nanobox anodes were characterized, further confirming the structural stability of these hollow architecture electrodes and the Ge electrode configuration merits.

2. Experiment section

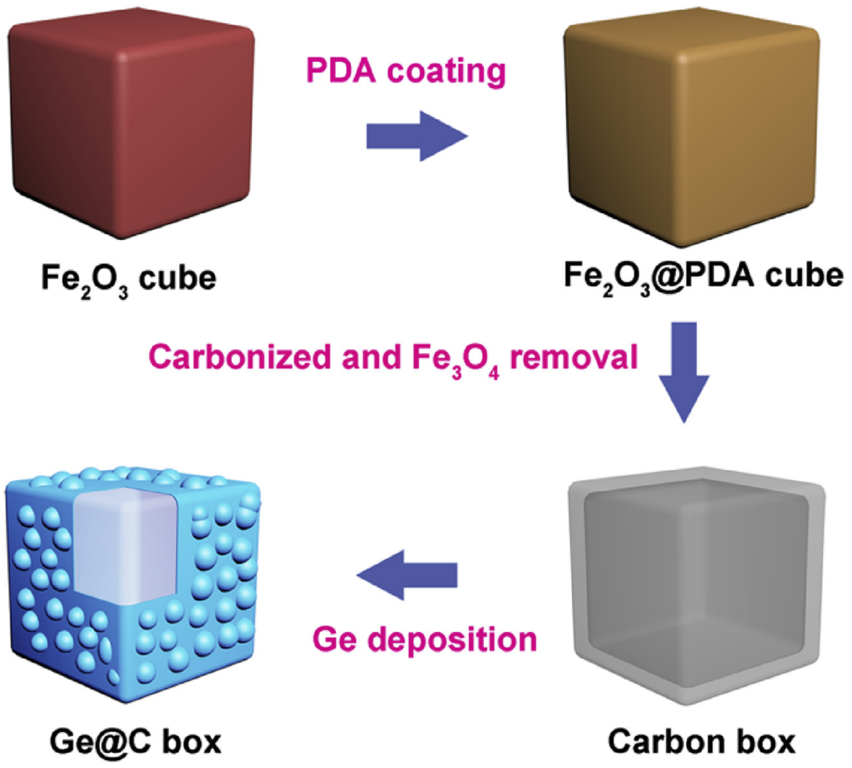
2.1. Fabrication of carbon nanobox and Ge@C nanocomposites

2.1.1. Fe_2O_3 nanocube templates preparation

Typically, the $Fe(OH)_3$ gel was firstly obtained by adding 5.4 M NaOH (50 mL) solution to the 2.0 M $FeCl_3$ (50 mL) solution within 5 min and stirred continuously at 75 °C. Then, after stirred for another 5 min, the resultant $Fe(OH)_3$ gel was put into in a preheated oven (100 °C) for 4 days. Finally, after the oven decreased to room temperature naturally, the red colour Fe_2O_3 nanocubes were centrifuged for several times using the deionized water (DI) and ethanol solution before drying at 70 °C overnight (final product weight: ~6 g).

2.1.2. Hollow C nanobox, Si@C and Ge@C nanobox anodes preparation

Firstly, the as-fabricated Fe_2O_3 nanocubes (320 mg) and dopamine (PDA, 120 mg) hydrochloride were dispersed together into the Tris-buffer solution (100 mL, 10 mM). After stirring for 4 h, the above sample was again collected after the same centrifugation and drying process. Secondly, the Fe_2O_3@PDA core-shelled nanocubes were transformed into Fe_3O_4@C core-shelled nanocubes after the annealing procedure in Ar atmosphere for 3 h at 500 °C. After that, the hollow carbon nanoboxes were then obtained via the Fe_3O_4 cube core removal in HCl (4 M) solution and the following centrifugation&drying process. Eventually, the as-prepared carbon nanoboxes (100 mg) were loaded in a ceramic boat and transferred into the chemical vapor deposition (CVD) chamber for 20 min Ge(Si) shell growth and the final Ge@C(Si@C)mass was around 200 mg(160 mg). The temperature of the Ge and Si deposition was set at 330 °C and 520 °C respectively. The GeH_4/H_2(SiH_4/H_2) gas



Scheme. 1. Illustration of the Ge@C nanobox anodes fabrication process.