Hierarchical Porous Graphene: CVD Growth on Metal Oxides for High-Rate Lithium-Sulfur battery and Superior Oxygen Evolution Electrocatalysis

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Abstract

Structural hierarchy plays an important role in the biological world and functional materials with optimized properties and high efficiency. With a growing concern and urgent development of sustainable energy systems and next-generation energy storage technologies, hierarchical porous graphene (HPG) materials have been intensively investigated over the past decades, which are demonstrated as promising electrode materials for various systems, such as lithium-sulfur (Li-S) batteries, supercapacitors, metal-air batteries, and fuel cells, with a remarkable capacity, high efficiency, long stability, and excellent rate capability. The promising applications of the hierarchical sp^2 carbon-based nanomaterials are highly dependent not only on their superior intrinsic physical properties, but also on their tunable structural characters. Despite of great progress, however, favorable regulation of their hierarchical porosity and multi-functionalities remains a challenge to extend their excellent properties from nanoscale to macroscale and thereby the practical applications.

Chemical Vapor Deposition (CVD) growth on the metal foil has been regarded as the most effective method to fabricate high-quality graphene films, while ineffective to modulate the structural hierarchy and criticized of its ultra-low production. Herein, we have creatively proposed a novel family of porous metal oxide templates for the catalytic CVD deposition of HPG materials, and scrupulously designed the process to modulate their properties towards satisfactory performances.

Firstly, a metal-embedded supported bifunctional catalyst was proposed for the in-situ growth of aligned carbon nanotube/graphene (ACNT/G) sandwiches via a two-step CVD growth, with the metal nanoparticles as catalysts for CNT formation and metal-oxide lamellar as hard template catalyst for graphene deposition.[1] NH3 was introduced during CVD to modify the chemical features (N-ACNT/G). Aligned CNTs and graphene layers were in situ anchored to each other, constructing a sandwich-like hierarchical architecture with efficient 3D electron transfer pathways and ion diffusion channels. The moderate chemical modulation induced by nitrogen doping introduced more defects and active sites to the carbon framework, thereby improving the interfacial adsorption and electrochemical behaviors. When the novel N-ACNT/G hybrids were used as cathode materials for Li-S batteries, greatly enhanced cyclic and rate performances were demonstrated. A high initial reversible capacity of 1152 mAh g^{-1} can be available at 1.0 C, maintaining ca. 880 mAh g^{-1} after 80 cycles, which was about 65 % higher than that of ACNTs. Even at a high current density of 5.0 C, a reversible capacity of ca. 770 mAh g^{-1} can be achieved. [2]

Furthermore, porous CaO with low cost, facile purification, and promising cyclic utilization was firstly adopted as oxide catalysts for the CVD growth of graphene.[3] On one hand, the CaO can serve as effective catalysts to stimulate the CVD growth of ultra-thin graphene with a self-limiting behavior due to vast surface defects and step-edges. On the other hand, the precise replication of their structural hierarchy result in an integrated HPG framework with abundant micro-sized in-plane vacancies, meso-

sized wrinkled pores, and macro-sized strutted cavities (CaO-G). The gas composition during CVD and nanostructure of catalysts significantly impact on the graphitization degree and hierarchical porosity of resultant materials. When applied in Li-S batteries, a high initial capacity of 434 mAh $g_{cathode}^{-1}$ can be achieved at 0.5 C, with an ultra-low cyclic fading rate of 0.11 % and high coulombic efficiency of 90 % without $LiNO_3$ addition for initial 150 cycles. A 74 % retention of the capacity at 0.1 C can be manifested at a very high current rate of 5.0 C.

Importantly, the HPG should not only be directly utilized as a hierarchical scaffold, but also can serve as effective regulators in composite fabrications, contributed from its tunable porosity, ultra-thin structure, hydrophobic surface and variable defects. A nitrogen-doped mesoporous graphene framework grown on mesoporous MgO templates was scrupulously designed to hybridize nanosized NiFe layered double hydroxides with an in-situ defect-anchored nucleation and spatially confined growth, leading to a uniformly decorated nano-sized active particles and strong coupled interface between active phase and conductive substrate.[4] The nNiFe LDH/NGF composite was demonstrated to overperform commercial Ir/C catalysts and compete favorably against reported alternatives for high-performance oxygen evolution reaction (OER) catalysis, with a remarkably low Tafel slope (~45 mV dec^{-1}), a substantially decreased overpotential (~337 mV required for 10 mA cm^{-2}), and enhanced durability.

These processes shed novel lights on the CVD fabrication of advanced graphene materials with porous metal oxide templates. It is instructive and expected to open up fresh perspectives and inspiring avenues on hierarchical graphene towards superior energy storage and oxygen electrocatalysis.

References

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Figure
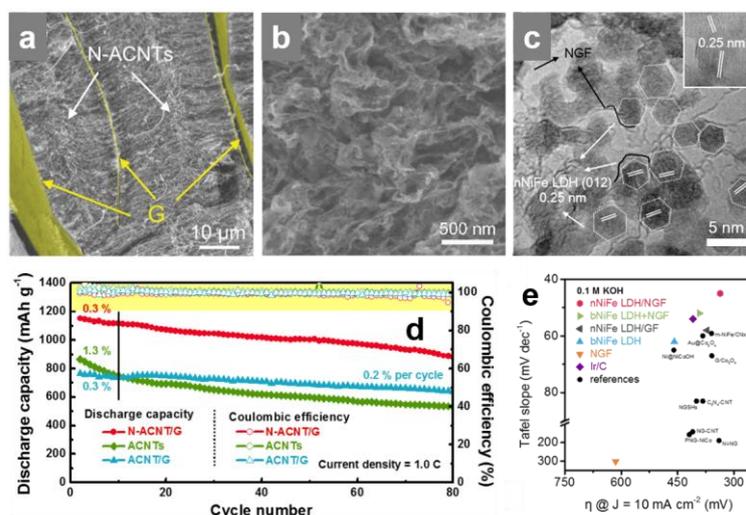
Figure 1. SEM image of a) N-ACNT/G and b) CaO-G, and c) TEM image of nNiFe LDH/NGF material. d) Li-S battery performances of N-ACNT/G and e) OER performances of nNiFe LDH/NGF.