Author: Ouyang, Bo
Title: Plasma assisted carbon-based nano-composite architectures for energy storage devices
Institute: Thesis (Ph.D.) National Institute of Education, Nanyang Technological University
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Supervisor(s): Rawat, Rajdeep Singh
Abstract

Carbonaceous materials exhibit many preferable characteristics that include structural polymorphism, excellent chemical inertness, cost-efficiency, broad potential range, comparatively inert electrochemistry, rich surface chemistry as well as electrocatalytic performance towards various redox reactions. Therefore, numerous carbonaceous materials have been exploited and been extensively investigated for a variety of electrochemical applications such as electrocatalysis, energy storage and conversion, light-emitting devices, and biotechnologies.

Among different types of carbonaceous materials, graphene has received considerable attention because of its outstanding features. The reliable and scaled-up fabrication towards different types of graphene including graphene oxide (GO) as well as reduced graphene oxide (rGO), provides a broad range of possibilities for synthesizing graphene-based materials for a variety of applications. Currently, they are mostly synthesized by chemical methods. However, these chemically-derived graphene architectures always suffer from major issues including relatively lower conductivity and aggregation. Therefore, vertical graphene nanosheets (VGNSs) deliver the tremendous potential for high-performance energy storage devices including lithium ion batteries (LIBs) and supercapacitors (SCs) because of their extraordinary electrical transport features, enhanced specific surface area and particularly, an intrinsic three dimensional (3D) reactive framework.

Nonetheless, one of the most essential challenges is to materialize the VGNS-based energy storage devices owing to the lower specific capacitance, relatively higher processing temperature, depressed bonding towards other active materials, uncontrolled architecture, and non-cost-efficient method for synthesis. Moreover, the exact mechanism of VGNS still remains controversial, which also limit the development of VGNS-based devices.
Abstract

Moreover, environmentally-friendly and highly flexible energy storage devices have received remarkable research interests because of the increasing requirement for sustainable energy in the modern electronic industry and due to increasing concern about environmental degradation. Therefore, commercial carbon cloth (CC), which is composed of numerous uniform carbon microfibers, holds great promise as the 3D support substrate and current collector during the preparation towards flexible electrode due to the cost-efficiency, considerable conductivity as well as outstanding mechanical strength and flexibility. Numerous electroactive materials, including MnO$_2$, Co$_3$O$_4$, TiO$_2$ and ZnO have been anchored onto CC surface for enhanced electrochemical properties along with the considerably flexible feature. Nonetheless, because of the incompatibility issue between the 3D conductive substrate and loaded active materials, direct anchoring of active materials along with the optimized porous architecture onto such 3D porous substrate still pose the considerable challenge.

Furthermore, the coating technique based on carbon-based materials has been described to remain efficient to enhance the charging-discharging capacity of LIBs for decreasing the irreversible capacity during the first charging/discharging cycle as well as enhancing the cycling stability. It has been reported that graphitic carbon coating can boost the electronic/ion conductivity and therefore enhance the electrochemical property of active materials. Additionally, homogeneous graphene quantum dot (GQD) covering can release the generation of solid electrolyte interphase (SEI) films onto the electrode surface and meanwhile effectively separate the nano-structures from each other, protecting active materials from capacity fading and agglomeration as well as minimize the dissolution of active materials.
Abstract

In our first research, we have presented a fast, simple, one-step and cost-effective approach for directly fabricating graphene nanomesh (GNM) architecture on 3D porous nickel foam at a relatively low temperature (<950 °C). Such approach not only delivers 3D-GNM with low energy expenses and little environmental contamination but also contribute to further investigation on the growth mechanism of VGNS. Moreover, such 3D-GNM also exhibits the promising supercapacitive performance, indicating the possibility of achieving highly stable electrodes in SC applications.

Secondly, the as-prepared VGNS on porous nickel foam is used as an extraordinary substrate of energy storage devices including LIBs and SCs. We have demonstrated that the as-synthesized 3D vertical graphene (3DVG) foam exhibits much higher electrochemical performance than the 3D graphene (3DG) foam comprising of mostly horizontal graphene. This is because of the exposed edges and inherent vertical structure in 3DVG, giving rise to a novel substrate for energy storage devices. Furthermore, the as-obtained MoS$_2$ anchored 3DVG (MoS$_2$@3DVG) composites synergistically combine the advantages of MoS$_2$ and 3DVG, largely enhancing the overall performance not only in Li-ion storage capacity but in cyclic stability because of faster ion transfer and closer contact between active material and the conductive substrate. Moreover, we also control the amount of VGNS grown on the substrate surface through different deposition duration. Such architecture serves as a promising material as the binder-free electrode towards SC applications. The decoration of the 3DVG foam with MnO$_2$ demonstrates that the nano-composite not only improve the specific capacitance but also retain the cyclability. Our 3DVG structure, therefore, supply a series of expected features as a platform for next-generation SCs. All results apparently indicate that 3DVG holds great potential for broad applications including catalysis, sensors, and energy storage devices.
Afterward, we have applied one-step plasma activation strategy to simultaneously achieve the hierarchical 3D nanostructured network along with the introduction of nitrogen-containing functional groups onto the commercial CC surface, resulting in distinctly enhanced electrochemical performance due to the enhancement of electronic conductivity and surface wettability towards electron-donor tendency. The hierarchical nitrogen doped carbon cloth (hNCC) with excellent electrochemical property has readily been achieved by simple nitrification of CC within nitrogen plasma environment. Moreover importantly, the optical emission spectroscopy was applied to further demonstrate a plausible mechanism for the achievement of hNCC, which will not only confirm the achievement of excellent performance in energy storage devices but also contribute to a generalized approach for controllable activation of hierarchical 3D nano-architecture.

Finally, we have presented two different types of carbon coatings on the surface of transition metal nitride and oxides for achieving better LIB performances. In terms of GQDs coated onto highly hierarchical nickel nitride (hNi₃N), we have firstly fabricated the highly purified hNi₃N via a facile and environmentally-friendly plasma activation. Subsequently, electrophoresis process has been applied for deposition of homogeneous layer of GQDs. The homogeneous GQDs have been applied to serve as an effective sensitizer and stabilizer on the hNi₃N surface for enhanced Li-ion storage performance. Moreover, the plausible mechanism of growing hNi₃N via plasma activation has been proposed for extending such approach to other metal nitrides. On the other hand, amorphous carbon shell with different thickness has been covered onto layered double oxide (LDO) nanosheets via plasma-based strategy. Via controlling plasma parameters, the thickness of carbon layer can be well controlled. Additionally, carbon doping has also been achieved into active materials for enhanced overall conductivity of the nano-composites. Such plasma-based approach
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has paved a novel pathway to achieve controllable carbon introduction into LDOs for enhancing the LIB performances.