Plasma Synthesis of 3-Dimensional Graphene-Based Materials

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Three-dimensional (3D) graphene is composed of interconnected graphene layers that form 3D porous structures. Because of self-assembly of two-dimensional (2D) graphene sheets into 3D structures, 3D graphene can largely retain the unique properties of individual graphene sheets such as high electrical conductivity and large specific surface area. Ideally, 3D graphene-based porous framework can be applied as both structural backbone and current collector in free-standing electrode of electrochemical energy storage and conversion systems such as supercapacitors, batteries, and fuel cells.

Typical 3D graphene structures reported in the literature include graphene foams and graphene sponges. Chen's group pioneered the synthesis of graphene foams using nickel nanoporous substrate as the template by chemical vapor deposition (CVD).[1] In this method, however, the nickel templates need to be removed by chemical etching after graphene CVD. Distinguished from these kinds of 3D graphenes, vertical graphene array (VGA), also called as carbon nanowalls (CNWs), is self-supported network of few-layer graphene sheets standing almost vertically on the substrate to form 3D graphenes with wall-like structure. The VGAs have been fabricated by plasma-enhanced CVD employing methane and hydrogen mixtures on heated substrates.[2] VGAs possess intimate contact with substrate at their bottom, exposed edges at their top, and easily accessible open surfaces of the graphene nanosheets. Moreover, 3D graphenes with sponge-like structure can be obtained by changing the plasma condition. Both 3D graphenes with wall and sponge structures possess large specific surface area and spaces surrounded by nanographene sheets. The high porosity, large specific surface area, and excellent electrical conductivity render these 3D graphene-based materials having potential applications in many fields.

Plasma synthesis of 3D graphenes with different morphologies has been carried out with changing plasma conditions including pressure, mixing ratio of CH_4/H_2 mixture, additives such as Ar and N_2, temperature of substrate, and frequency of plasma source. Figures 1(a) and 1(b) show top view and cross-sectional SEM images of 3D graphene films with wall-like and sponge-like structures grown on Si substrates, respectively.

3D graphene-based materials are useful as electrodes of electrochemical sensor and fuel cell/battery. This idea is based on the large surface area of chemically stable graphene combined with surface modification/decoration with metal nanoparticles (NPs) and biomolecules. Figure 2 shows schematic illustration of fuel cell (left) and secondary battery (right), where 3D graphene-based materials are used as electrodes. For these applications, graphene surface was decorated with metals and biomolecules to be used as electrodes of fuel cell/battery and sensor. For example, platinum (Pt) NPs were prepared on graphene surface of VGAs by the reduction of Pt salt precursors. Pt NPs-loaded VGAs were applied to the electrodes of proton-exchange membrane fuel cell (PEMFC) and hydrogen peroxide (H_2O_2) sensor.[3,4] Moreover, glucose oxidase (GOD) was selected as an oxidoreductase enzyme and the GOD was immobilized on the hydrophilized surface of VGA to be used as electrode materials for glucose fuel cell (GFC). In addition, we propose applying 3D graphenes as conductive backbone of sulfur electrode of Li-S battery.

Electrochemical experiments demonstrate that 3D graphene-based materials can be promising materials for electrochemical sensing and energy conversion applications.

References

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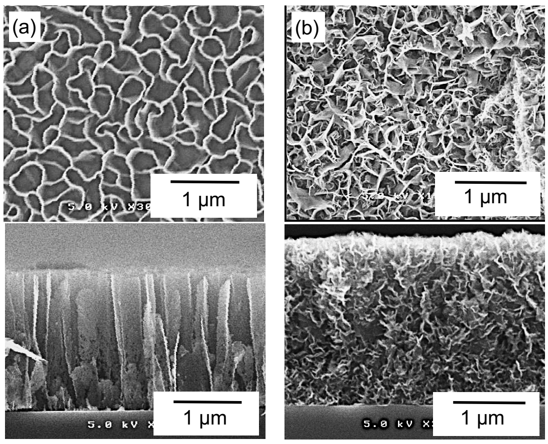

Figure 1. Top view and cross-sectional SEM images of 3D graphene films with (a) wall-like and (b) sponge-like structures grown on Si.

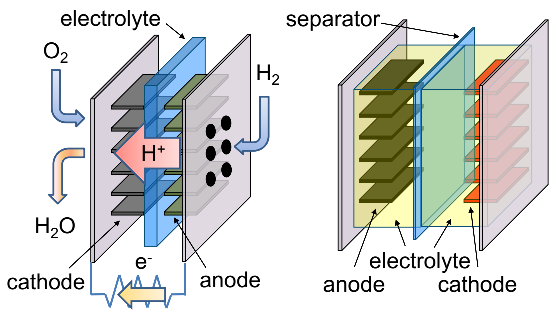

Figure 2. Schematic illustration of fuel cell (left) and secondary battery (right), where 3D graphene-based materials are used as electrodes.