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Review

Two-dimensional polymer-based nanosheets for electrochemical energy storage and conversion

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ABSTRACT

Over the past decades, two-dimensional (2D) nanomaterials possessing planar layered architecture and unique electronic structures have been being quickly developed, due to their wide potential application in the fields of chemistry, physics, and materials science. As a new family of 2D nanomaterials, 2D polymer-based nanosheets, featuring excellent characters, such as tunable framework structures, light weight, flexibility, high specific surface, and good semiconducting properties, have been emerging as one kind of promising functional materials for optoelectronics, gas separation, catalysis and sensing, etc. In this review, the recent progress in synthetic approach and characterization of 2D polymer-based nanosheets were summarized, and their current advances in electrochemical energy storage and conversion including second batteries, supercapacitors, oxygen reduction and hydrogen evolution were discussed systematically.

Shuai Bi received his B.S. degree in applied chemistry from Shanghai Jiao Tong University in June 2014. He then joined the group of Professor Fan Zhang at Shanghai Jiao Tong University for Doctoral Training and began doctoral studies in September 2014 where his research interests focus on conjugated semiconducting polymers for energy conversion and storage.

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1. Introduction

With the overconsumption of natural resources (like oil and coal), energy shortages, as well as air pollution and global warming are emerging and threatening the development of modern society [1,2]. Thus, the demand for clean and renewable energy has attracted great attention in both academic and industrial fields in the past decades. Owing to the intrinsic existence of redox activity in chemical elements, electrochemical performance is considered as one of the most efficient methods for energy storage and conversion [3–5]. Together with the development of nanotechnology, various electronic devices, such as rechargeable batteries, supercapacitors and sensors, would become prospective products to improve the quality of life greatly [6–10]. Thus, design and construction of active electrode materials with rational microstructure and macrostructure to gain promising electrochemical behaviors are mandatory and urgent (Fig. 1).

To date, many materials have been investigated in search for the best performance for electrochemical energy storage. For example, noble metal materials (e.g. Pt, Au, etc.) typically are the most efficient electrocatalysts. Unfortunately, the scarcity and high cost of these catalysts severely restricted their practical applications [11,12]. Recently, two-dimensional (2D) nanomaterials, such as graphene [13,14], hexagonal boron-carbon-nitrogen [15–18], black phosphorus [19–22], metal oxide [23]/chloride [24]/sulfide [25,26]/selenide [27,28] and perovskite sheets [29], MXene [30] possess planar layered architecture, in which the lateral dimension is several orders of magnitude larger than that of thickness. 2D nanomaterials exhibit the rich chemical modification, anisotropic characters, excellent electrical properties as well as high specific surface areas, in comparison to that of zero-dimensional (0D), one dimensional (1D) nanomaterials [31]. Combined with their abundance sources, these 2D materials are reasonably suitable as the alternative key active components for applications in electrochemical devices [5,32].

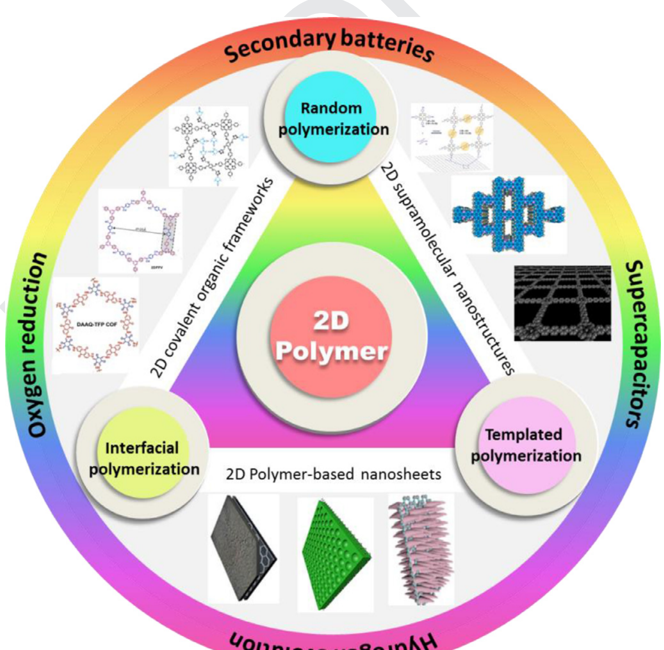

Fig. 1. Approach to two-dimensional polymer-based nanosheets for electrochemical energy storage and conversion.

Among the various 2D nanomaterials, graphene, a flat monolayer of carbon atoms arranged in a two dimensional (2D) honeycomb lattice, exhibits intriguing physical and chemical properties, including high charge mobility, superior thermal conductivity, large specific surface area, good chemical stability [33]. Moreover, the layer-by-layer self-assembly of graphene and other 2D nanomaterials with large overlapping areas into the graphene nanocomposites would bring them high mechanical properties as well as some superior electrochemical properties, originating from electrochemical activities in the 2D lattice plane [34,35]. These intriguing properties endow graphene-based nanosheets with great potential application in energy storage and conversion [36,37]. Unfortunately, the full-carbon of graphene with sp^2-hybridization gives the zero bandgap, limiting its applications, such as, low electrochemical capacity [31]. To overcome this obstacle, incorporating heteroatoms (e.g. B, N, S, P, halogens) into the carbon backbone of graphene represents an efficient strategy to finely tune the electrochemical performance for energy storage and conversion [38–45]. However, the quantitative preparation of these functionalized graphene is still the major challenge, which would limit the need for device fabrication in large scale. In this regard, searching for new 2D nanomaterials with high conductivity, controllable hierarchical porous structure, and good electrochemical activity is highly desirable in electrochemical energy storage research.

Alternatively, 2D polymer-based nanosheets, including 2D polymers [46–52], covalent organic frameworks (COFs) [53–59], 2D supramolecular organic nanostructures [60–65], etc, are the one of most fascinating fields, which open a novel avenue to the construction of 2D functionalized nanomaterials for various applications [66,67]. These nanosheets not only have similar planar, lightweight and flexible characteristics to graphene, but also hold the great advantages in structural control [68]. With the help of efficient chemical synthesis, heteroatoms can be incorporated into the frameworks of 2D polymeric nanosheets through the polymerization of heteroaromatic-based building blocks, like aniline [69,70], pyrrole [71,72], tricyanobenzene [73], dopamine [74], phthalocyanine [54], etc. Moreover, the thickness of nanosheets could be facile to be controlled by the combination of the molecular weight of polymers and precision macromolecular self-assembly approach [75]. In the past years, the remarkable achievements in synthesis, characterization, theoretical calculation and application of 2D polymer-based nanosheets have been witnessed. Even previous reviews have been concerned in the construction, properties and application of some branches of 2D polymeric nanomaterials, like COFs [53,76–78]. However, a systematic review on the synthesis of 2D polymer-based nanosheets for the application in electrochemical energy storage has not yet been documented as far as we know.

Typically, high electrochemically-active nanomaterials exhibit some attractive features as following: (i) interconnected porous structures with large specific surface areas; (ii) good conductivity; (iii) intrinsic electrochemical active sites [79,80]. To meet the critical needs above, 2D polymer-based nanosheets with well-defined hierarchical architectures comprising microporous and mesoporous structure have been extensively developed on the basis of versatile polymerization methods and highly designable functional building blocks. In this feature article, we particularly highlight the synthesis methodologies of 2D polymer-based nanosheets. Their applications in electrochemical energy storage and conversion including

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