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Review

Graphene and graphene oxide: Functionalization and nano-bio-catalytic system for enzyme immobilization and biotechnological perspective

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ABSTRACT

Graphene-based nanomaterials have gained high research interest in different fields related to proteins and thus are rapidly becoming the most widely investigated carbon-based materials. Their exceptional physiochemical properties such as electrical, optical, thermal and mechanical strength enable graphene to render graphene-based nanostructured materials suitable for applications in different fields such as electroanalytical chemistry, electrochemical sensors and immobilization of biomolecules and enzymes. The structural feature of oxygenated graphene, i.e., graphene oxide (GO) covered with different functionalities such as epoxy, hydroxyl, and carboxylic group, open a new direction of chemical modification of GO with desired properties. This review describes the recent progress related to the structural geometry, physiochemical characteristics, and functionalization of GO, and the development of graphene-based novel carriers as host for enzyme immobilization. Graphene derivatives-based applications are progressively increasing, in recent years. Therefore, from the bio-catalysis and biotransformation viewpoint, the biotechnological perspective of graphene-immobilized nano-bio-catalysts is of supreme interest. The structural geometry, unique properties, and functionalization of graphene derivatives and graphene-based nanomaterials as host for enzyme immobilization are highlighted in this review. Also, the role of GO-based catalytic systems such as microfluidic bio-catalysis, enzyme-based biofuel cells, and biosensors are also discussed with potential future perspectives of these multifaceted materials.

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1. Introduction

Graphene oxide (GO) is an excellent derivative of one atom thick layer graphene with exceptional physicochemical properties including high intrinsic mobility (200,000 $cm^2 V^{-1} S^{-1}$), good optical transmittance (~97.7%), large specific area (2630 $m^2 g^{-1}$), high Young's modulus (~1.0 TPa), good electrical and thermal conductivity (~5000 $W m^{-1} K^{-1}$) and unmatched pliability and impermeability [1–3]. These interesting properties of sp2 bonded graphene give significant attention to some applications, and it appears as a rising star in material science [4]. It is not surprising that worldwide electrochemical circle has already paid a lot of attention to its numerous properties. GO is a specific type of graphene, which provides the route to synthesize graphene chemically or thermally. The chemical treatment of graphite produced a single layer of GO, which includes oxidation and exfoliation in water or suitable organic solvent [5]. The preparation of GO includes the first separation of graphite layers followed by oxidation which increases the distance between layers. This distance greatly depends on the extent of oxidation to produce oxygenated functional group on GO sheets [6].

Several structural models have been proposed in accordance with GO structure [7,8]. These models assume many oxygen-containing functional groups such as hydroxyl, carboxyl, epoxy, carbonyl, phenol, lactone and quinone present on its single layered 2-D sheets. Among these functional groups, epoxy and hydroxyl groups are present on the basal plane, and a small amount of carboxyl, lactone, phenol, carbonyl, and quinone groups are present at the edges of the 2-D sheet [9–11]. The electronic, electrochemical and mechanical properties of GO depend on these oxygenated groups. These oxygenated functional group in GO enhanced some features, such as they give hydrophilic nature to GO which makes it readily dispersible in water and many other solvents [12]. The adoption of high dispersibility renders it unique material for electrode coating in electrically conductive materials [11]. The extent of these oxygenated groups greatly depends on the synthesis route and the stoichiometric conversion rate. On the other hand, in comparison with graphene, the oxygenated group in GO may significantly reduce its electronic properties, and thus limit its applications in electrochemistry [13]. These oxygenated groups can be further employed for chemical modification to generate different functionalities on GO sheets [14]. These functionalities, covalently or non-covalently, turn on many directions for GO, such as immobilization of different electroactive species to design active electrochemical systems, preparation of stable dispersion in organic solvents, and stabilization of GO sheets from agglomeration in organic solvents by nanoparticles coating [15–17]. Among them, enzyme immobilization is a fascinating technology which facilitates the separation, modulation of catalytic properties and reuses of the immobilized enzymes [18–20]. Over the past years, numerous types of support carriers have been developed using different materials with different functionalities for enzyme immobilization purposes [21–40]. However, the layered structure of GO-based carbon nanomaterial with the large surface area, ease of functionalization, fascinating electronic properties, and excellent thermal and mechanical stability make it appealing for enzyme immobilization. Moreover, due to these distinct properties, GO has appeared as an efficient candidate in biotechnology, bioelectronics, bio-imaging, tissue engineering and bio-sensing [41–46].

2. Structural geometry and properties of graphene derivatives

The oxygen decorated honeycomb lattice of graphene sheet which bonded together through pi bonds is considered as GO. All these oxygen-containing functional groups are present at the basal plane and edges of graphene sheets. But the precise structure of GO is still unknown as the content of oxygen-containing functional groups depends on the degree of oxidation and reaction time which significantly affect the structure of GO. As graphite has hygroscopic nature and nonstoichiometric composition, so its structure is still under discussion. After long theoretical and experimental efforts, several models have been proposed for a considerable understanding of graphite structure. In this context, Ruess [47], Scholz and Boehm [48], Nakajima et al. [49], Nakajima and Matsuo [50] and Lerf et al. [51] devoted massive research efforts to elucidate the presence of epoxy, hydroxyl, ether linkage between 1,2 carbon and 1,3 carbon, carbonyl, enol and keto type of functional group, perpendicular sp3 linkage of carbon layers and alicyclic rings, respectively. In accordance with these proposed model, Szabó et al. [7] recently reported that propound trans linked cyclohexane and phenol, tertiary hydroxyl, quinone, 1, 3 ether, ketone and C═C containing hexagons are present in graphite oxide. Similarly, Dreyer et al. [5] rationalized the difference between all these proposed models and interpreted the structure analogies corresponding to these models.

Though many fundamental features of the GO structure have been delineated, it still lacks a clear picture of GO structure. It is evident from a proposed model that GO contains both sp2 bonded hexagonal carbons and sp3 bonded carbon atom having oxygen-containing functionalities (Fig. 1). It means that GO contains two types of regions, i.e., (1) an sp3 hybridized oxidized region, and (2) the un-oxidized sp2 region [9,52]. The structure of GO can be further explored using different spectroscopic and microscopic techniques, for example, the thickness and defects in GO layers can be investigated by atomic force microscopy (AFM) [53]. The structural features such as the extent of oxidation are measured by scanning tunneling microscopy (STM) to distinguish it from the pristine graphene [54]. High-resolution transmission electron microscopy (HRTEM) is utilized to achieve imaging of layered atom and defects at the topography of GO lattice [55]. Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) explained how sp2 carbon atoms in graphene are converted into sp3 hybridized bonds after the attachment of oxygenated functional groups. The structure of electronic excitations which occurred with low-loss in GO can also be manipulated by using STEM and EELS techniques [13]. Transmission electron microscopy (TEM) operates as an aberration-correction technique to achieve atomic resolution imaging and in-situ measurement of pentagons/heptagons defects, point defects, and Stone-Wales defects [56]. Similarly, solid-state nuclear magnetic resonance (SSNMR) [57], Raman spectroscopy [58], Fourier transform infrared spectroscopy (FT-IR) [59], X-ray photoelectron spectroscopy (XPS) [60] and X-ray absorption near edge spectroscopy (XANES) [61] are widely used to scrutinize the chemical composition of GO and existence of different functional groups. Each functional group present in GO gives a characteristic peak in a specific area, which is very helpful to nominate each functional group separately.

The theoretical studies based on first-principle calculations also provided considerable information about the structure of GO in the presence of different oxygen-containing functional groups. Density functional theory (DFT) proved very helpful to evaluate the oxygenated functional group by providing possible kinetics and thermodynamic mechanism. Simply, these calculation permits to identify basic oxygen-containing functional groups such as epoxide and hydroxide which are in close for the measurements of the band gap [62,63]. These band gap value greatly depend on the functionalities present on GO which can be tunable by changing the content of these functional groups [64]. Furthermore, these first-principle based theoretical simulation calculations provide the information to manipulate the spectroscopic data and acquire precise spectroscopic results [65].

The presence of oxygenated functional groups in GO and its 2-D nature make it readily available as insulator, conductor and semiconductor material. It exhibits excellent electrical, mechanical, optical, electrochemical and thermal properties. There are many factors which greatly affect the electronic properties of GO such as structural disorder and degree of oxidations. However, it can be converted into semiconductor reduced graphene oxide (rGO) and semimetal graphene by the reducing