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Chapter 3

Graphene-Paper Based Electrochemical Sensors

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Abstract

Graphene paper as a new form of graphene-supported nanomaterials has received worldwide attention since its first report in 2007. Due to their high flexibility, lightweight and good electrical conductivity, graphene papers have demonstrated the promising potential for crucial applications in electrochemical sensors and energy technologies among others. In this chapter, we present some examples to overview recent advances in the research and development of two-dimensional (2D) graphene papers as new materials for electrochemical sensors. The chapter covers the design, fabrication, functionalization and application evaluations of graphene papers. We *first* summarize the mainstream methods for fabrication of graphene papers/membranes, with the focus on chemical vapour deposition techniques and solution-processing assembly approaches. A large portion of this chapter is *then* devoted to the highlights of specific functionalization of graphene papers with polymer and nanoscale functional building blocks for electrochemical-sensing purposes. In terms of electrochemical-sensing applications, the emphasis is on enzyme-graphene and nanoparticle-graphene paper-based systems for the detection of glucose. We *finally* conclude this chapter with brief remarks and outlook.

Keywords: graphene paper, 2D-layered nanomaterials, electrochemical sensor, metal oxide, polymer, nanoparticle

1. Introduction

Precise monitoring of chemical or biological processes is of extreme importance for medical and biological applications. Electrochemical sensors can ideally fulfil that goal by converting a chemical or a biological response into a processable and quantifiable signal. In the past two decades, intensive research and development of electrochemical sensors have enabled to fabricate different types of devices. After the development of many successful commercial

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electrochemical sensors in the classic configurations, currently there is a notable transition and increasing demands for the development of flexible and wearable sensors. The development of flexible electrochemical sensors depends crucially on the discovery and preparation of free-standing and flexible new materials.

Flexible electronic devices, especially flexible electrochemical sensors, have become an advanced technology with the aim at solving some tremendous real-world challenges, such as in situ sensing for health and environmental problems. Compared with conventional devices, flexible electrode-based devices are versatile and highly adaptive. For example, such devices occupy less space and could be compatible with any shape-targeted systems such as human body and rough or irregular-shaped substrates. Ideal flexible electrodes should provide high conductivity for sensing electrons and thermal energy, high stability and excellent mechanical strength. In this regard, carbon nanotube (CNT)-based devices had dominated research and development attention before [1, 2], because of the unique one-dimensional nano-channel mechanical strength. However, one has come to realize that CNT-based flexible electrodes are largely limited to fundamental interests because of several serious technical challenges, such as high cost of producing CNTs, complex process of obtaining high-density vertically aligned CNTs, chemical and biocompatibility concerns and difficulties in achieving large-scale production, which can hardly overcome. On the other hand, the recent rise of synthesis and processing of two-dimensional (2D) graphene and its derivatives offer a new and promising opportunity for developing a novel class of flexible electrodes most likely with required physiochemical properties. Graphene paper, as one of the derivatives from graphene or graphene oxide (GO)-supported building blocks, was introduced by Ruoff and co-workers in 2007 [3]. Due to their remarkable mechanical property, tunable conductivity and versatile functionality, graphene papers could promote the research and development of new-generation flexible electrode-based sensors and other electronic devices. This chapter aims at highlighting some recent examples using graphene papers as electrode materials for developing flexible and ultrasensitive electrochemical sensors.

2. Synthesis of graphene paper-based electrodes

Thanks to the intrinsic planar structure of graphene sheets, it is feasible to effectively control the periodic alignment of graphene nanosheets into 2D graphene papers/films/membranes through ionic interaction, hydrophobic effect, hydrogen bonding and/or π-π stacking [4, 5]. The resulting 2D graphene materials not only retain some of the key properties of individual graphene sheets but also create new or collective properties resulting from their unique structure. Moreover, a wide range of functionalized materials, such as metal, polymer, metal oxide (MO) and other semiconductors, can be loaded into 2D-layered GO papers, endowing the graphene papers with multiple functionalities required by specific applications [4–8]. Given the excellent physicochemical properties of graphene paper and tunable functional groups, these 2D architectures have been widely studied for their applications in water purification, biomimetics, sensors, flexible electrodes, energy conversion and storage and optoelectronic

devices [7–11]. As outlined below, several crucial methods have been developed to assemble the layered structure of graphene papers.

2.1. Chemical vapour deposition

Chemical vapour deposition (CVD) is a chemical process used to produce high quality, high performance and solid materials. The CVD technique is a direct and promising method for the preparation of large-scale, near-perfect graphene films on various substrates. The graphene films obtained by CVD methods displayed high flexibility, transparency and electrical conductivity [12, 13], which is attractive for various electronic devices. Commonly, transition metals, such as Ge [14, 15], Ni [16, 17], Cu [18, 19], Rh [20–22] and Co [23, 24], are used as the substrates for the CVD growth of graphene films. Due to very low carbon solubility in Cu, ease of etching and feasibility of high-quality graphene transfer, Cu has emerged as a favoured substrate chosen mostly for the growth of large-area graphene films [25], which was first introduced by Ruoff's research group in 2009 [13]. Large-area and single-layer graphene films with a low percentage (less than 5%) of the areas having few layers can be deposited on copper substrates by CVD process using methane as a carbon source (**Figure 1a**). The graphene film was robust enough to be transferred onto Si/SiO_2 substrates for fabrication of dual-gated field-effect transistors. They also demonstrated that as-synthesized graphene films could be transferred to other substrates (**Figure 1b** and **c**). To meet some special requirements, non-metal materials, such as Si [14, 15], SiO_2 [26–28], BN [29, 30] and Si_3N_4 [31, 32], were also used as substrates. However, the non-metal substrates showed the drawback limitations including slow growth rate and discontinuous size. For the CVD growth of graphene films on a metal substrate, it is necessary to mention that a transfer step for the following integration of graphene film into any solid-state electronic devices is usually required. Given the polycrystalline nature of the film and roughness of metal foils, industrial roll-to-roll transfer technology could be employed. Moreover, free-standing and element-doped (e.g. N and S) [33] graphene films can also be prepared directly by the CVD technique. However, the conventional etching method could be satisfied at laboratory scales, but it is very challenging for the large-scale preparation of high-quality graphene films arising from high-handling skills and time-consuming setback.

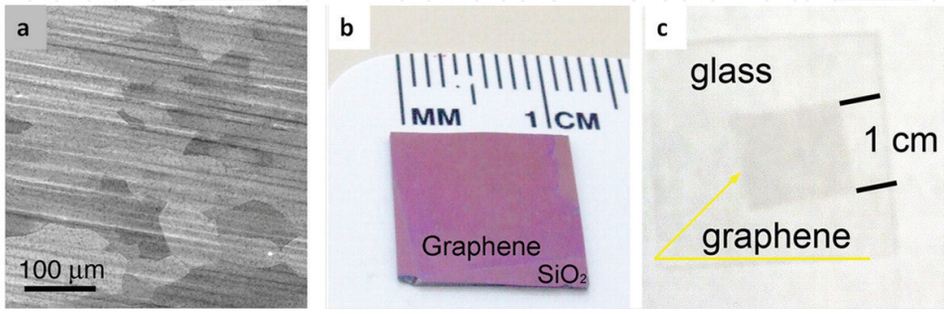


Figure 1. (**a**) SEM image of a graphene film on a copper foil after 30 min CVD growth. (**b** and **c**) Digital photographs of the CVD graphene film transferred onto a SiO_2/Si substrate and a glass plate, respectively [13].

2.2. Solution-processed assembly

Owing to oxygen containing polar functional groups existing on the surface and at the edges, GO is well dispersible in many polar solvents including water [34]. This structural feature and chemical capability facilitate GO as a favourite starting material for the assembly of various graphene architectures such as graphene papers and three-dimensional (3D) graphene sponges.

2.2.1. Vacuum filtration

To build a well-organized 2D macroscopic structure using single-layer GO sheets as a start material, Ruoff's group introduced a facile method for the fabrication of graphene paper. That is, GO sheets could be assembled into a paper-like material under a directional flow. Vacuum filtration of colloidal dispersions of GO sheets through an anodic membrane filter yielded free-standing GO papers with tunable thickness and mechanical property in a dried state. The fracture edges of a GO paper sample were imaged by scanning electron microscopy (SEM) to reveal its well-ordered layers over almost the entire cross section of the paper sample. The sandwiched structure between less densely packed 'wavy' skin layers was approximately 100–200 nm thick. In a typical GO paper specimen, the layer-to-layer distance (d-spacing) was measured as approximately 0.83 nm by the X-ray diffraction (XRD) spectrum [3]. As a result of its facile processability, vacuum filtration has been popularly used to prepare free-standing graphene papers. For example, cellular graphene paper was prepared by the following three steps [35]. *Firstly*, direct filtration of partially reduced GO with ascorbic acid mixture solution was performed. *Then*, the vacuum was disconnected immediately once no free dispersion was left on the filter paper and both the filter membrane and partially reduced GO (rGO) paper were vertically immersed into a liquid nitrogen bath for a rapid freezing about 30 min. *Finally*, graphene paper was further reduced by thermal reduction to enhance its electrical conductivity. From low-magnification SEM image of the as-prepared porous graphene paper (**Figure 2a**), the paper has a thickness of about 12.6 μm with continuous open networks. Thanks to ice-crystal templating, graphene paper also displayed honeycomb-like structures with the pore sizes varying in the range of hundreds of nanometres to several micrometres, as shown by the high-magnification SEM images (**Figure 2c** and **d**). The porous walls consisting of thin layers of graphene sheets were also clearly imaged by both SEM and transmission electron microscopy (TEM) (**Figure 2a**, **e** and **f**). High-resolution TEM (HRTEM) images further revealed that there are many crumpled 5–10 nm graphene sheets stacked on the surface of the graphene walls that are several tens of nanometres thick [35]. Our group has used GO as a starting material and further functionalized it with *Prussian Blue* (PB) nanoparticles (PBNPs) [36] or PB-shelled Au nanoparticles, Au@PBNPs [37] to develop a new kind of free-standing and flexible graphene papers. These PB-functionalized rGO papers are highly flexible and electroactive, and they were tested for use as disposable non-enzymatic electrochemical sensors.

2.2.2. Layer-by-layer assembly

Self-assembly is a popular approach towards cost-effective preparation of thin films, which has also been applied for fabricating multilayer graphene papers with tunable composition

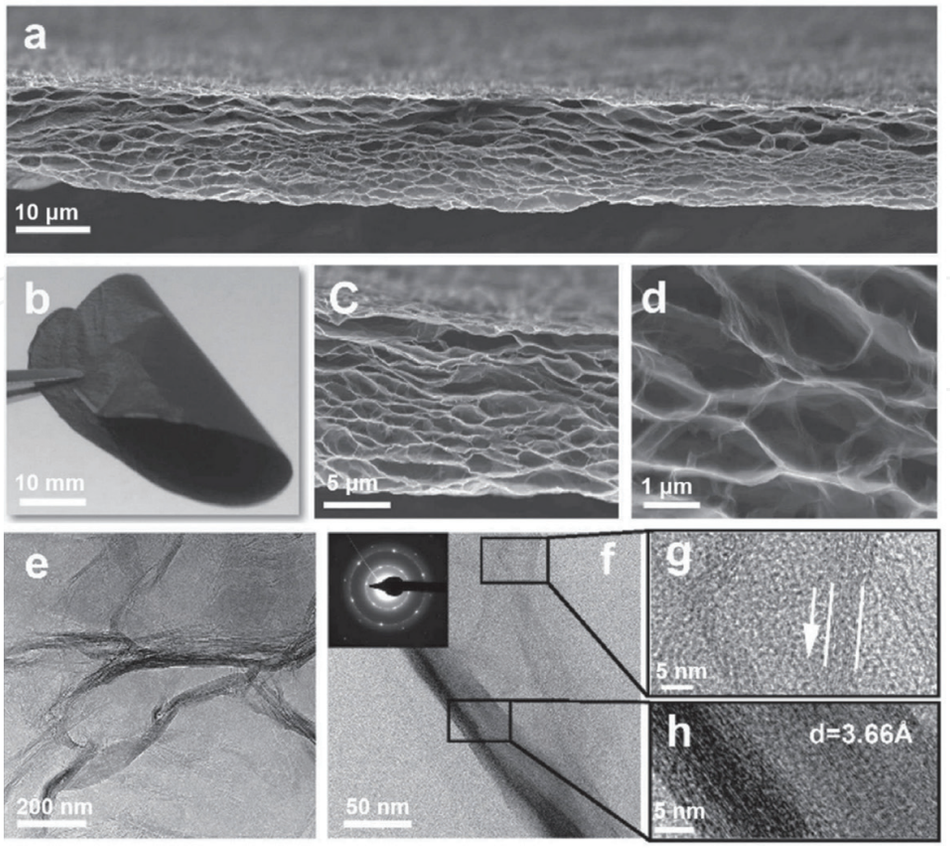


Figure 2. Structural features of rGO paper: (**a**) Cross-sectional SEM image of rGO paper after complete reduction. (**b**) Digital photograph of as-prepared rGO paper. (**c** and **d**) High-resolution cross-sectional SEM images of rGO paper. (**e**) TEM image of a part of graphene paper. (**f–h**) HRTEM images of the porous walls in the graphene paper. The inset image in (**f**) is the selected area diffraction pattern of the porous wall [35].

and architecture [8, 10, 38]. The driving forces involved in layer-by-layer (LBL) assembly generally include hydrogen bonding, electrostatic interaction and covalent bonding [8, 39, 40]. Zou and Kim reported a diffusion-driven LBL assembly process to prepare graphene-based architecture and demonstrated its application for the construction of GO sheets into various 3D macrostructures [41]. This assembly process is driven by the complexation of the negatively charged GO sheets and positively charged branched polyethylenimine (b-PEI) at a defined interface. The key step for assembling GO sheets to GO paper is that the diffusion of b-PEI molecules allows the complex to continuously grow into foam-like frameworks with tunable porosity. In a typical experimental process as shown in **Figure 3**, a small amount of the b-PEI solution was *first* dropped on certain substrates, for example, a glass plate (**Figure 3a**) or a filter paper (**Figure 3e**). *Then*, the b-PEI containing substrate was immersed in a GO suspension and left on a shaker for 24 h. After the formation of films, the samples were purified by dialysis in distilled (DI) water for 2–3 days. In the *final* step, the GO film was dried by normal heating or by freeze-drying. To their surprise, the GO film obtained by heating dry is a dense, tightly packed multilayer film (**Figure 3d**), which can be explained by the surface tension of water pulling the GO sheets together during evaporation. By contrast, freeze-drying the sample minimized such effects and helped preserve the porous structure (**Figure 3c**). Furthermore, the pore size could be adjusted by using different solvents [41].

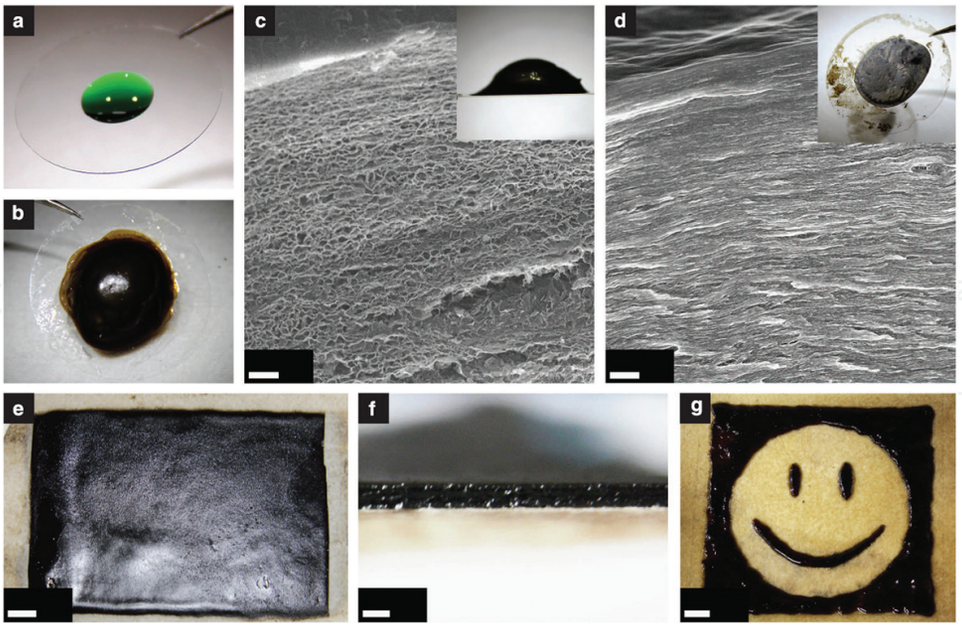


Figure 3. (**a**) A drop of b-PEI solution was *first* deposited onto the substrate. (**b**) When the glass slide was immersed in a GO suspension, a thick film developed over the b-PEI covered area. (**c**) Foam-like structured 3D graphene paper sample obtained by freeze-drying is revealed by the SEM image. (**d**) Compact structured graphene paper was prepared by oven drying. (**e**) A large-area (8 cm × 10 cm) film prepared on a filter paper is photographed. (**f** and **g**) This shows the graphene film formed only on the area to which b-PEI was dropped, allowing to pattern the film into a pre-designed shape such as a simplified face shown in **(g)** [41].

2.2.3. Other solution processing methods

Besides the methods mentioned above, solution casting, spin coating, spray coating and dip coating [42–45] have also been explored for the preparation of graphene papers or films. For example, GO or rGO solution was deposited on poly(ethylene terephthalate) (PET), SiO_2/P++Si and Au via various techniques to prepare thin films [46–49], although it is still a challenge to obtain graphene films with uniform thickness and few wrinkles by such type of approaches.

2.3. Electrophoretic deposition

Common synthetic approaches for the fabrication of graphene papers often use harsh chemicals and require complex pathways. Furthermore, the subsequent transfer process of the graphene paper onto a specific substrate even makes the overall process more complicated and time-consuming. In contrast to these concerns, electrophoretic deposition (EPD) process is useful for applying materials to any electrically conductive surface. With the advantages of low cost, easy handling and suitability for industry-scale production, EPD has been an effective technique to deposit graphene on conductive substrates for a wide range of applications [50]. A number of reports have demonstrated the deposition of GO on various substrates for the fabrication of suitable electrodes via EPD process, such as Cu and Ni foams, ITO, stainless steel and Pt [50, 51]. As a representative example, Liu et al. developed a two-step procedure,

which involved EPD of GO and its subsequent transformation of GO to rGO by in situ electrochemical reduction. More recently, a single-step preparation procedure of metal-supported rGO film was reported. A schematic of the electrochemical setup used for the preparation of stainless steel-supported rGO is shown in **Figure 4** [52]. The wireless graphite was oxidized into a colloidal dispersion of GO due to the effect of an electric field, and GO nanosheets migrated electrophoretically towards the anodic side of the electrochemical cell where they were deposited by van der Waals forces in the form of rGO film ($d_{(002)}$ = 0.395 nm). This method introduced a new low-cost, straightforward, up-scalable and green approach for high-yield production of large-area rGO thin films [52].

2.4. Other methods

In addition, a number of other approaches have also been reported for constructing graphene papers/films with hierarchical structures and high electrochemical or physical performances. For instance, Cao et al. constructed graphene films with high conductivity and mechanical stability via reduction-oxidation reactions between GO and active-metal substrates [53]. Honeycomb-structured graphene films were prepared by the template method [54, 55]. Bubble-like structured graphene film was also fabricated using monodispersed poly(methyl methacrylate) (PMAA) latex spheres as the sacrificial templates [56].

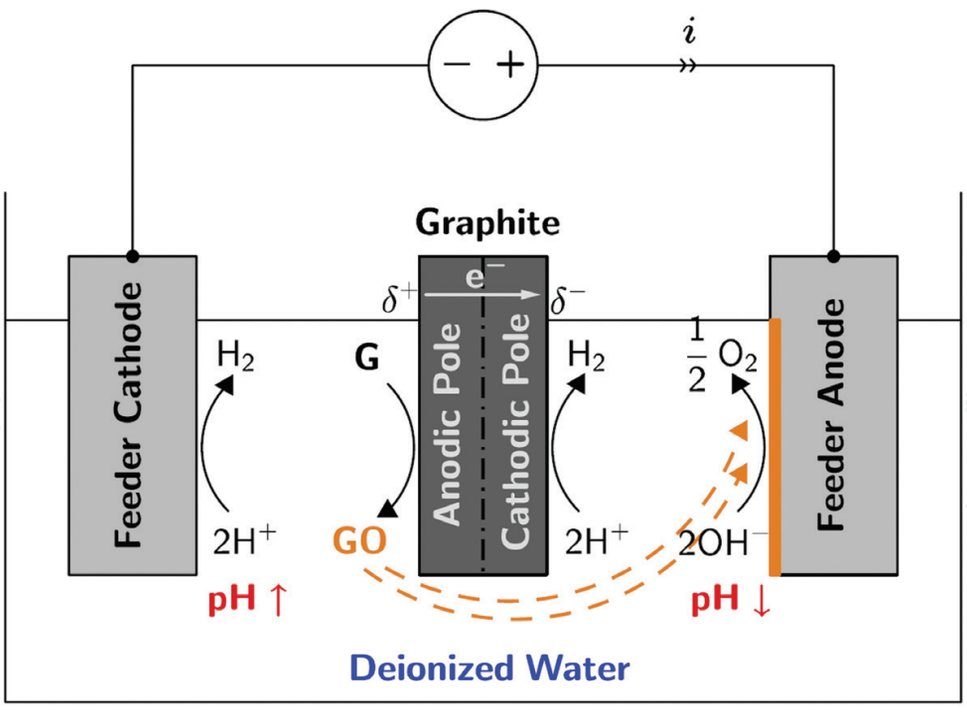


Figure 4. In a typical synthesis process, a voltage bias is applied between two stainless steel-feeding electrodes inducing a polarization of the wireless graphite. On the cathodic pole, water reduction reaction takes place, whereas GO, resulting from the oxidation of the anodic side of the graphite rod, migrates electrophoretically towards the positive stainless steel to be deposited in the form of a uniform light yellow thin film consisting of rGO nanosheets [52].

3. Structural and morphologic characterization

As-synthesized graphene papers are a very promising candidate for energy device and sensor applications. Structural characterization is of paramount importance for understanding the correlation between their nanostructures and performances. Therefore, some advanced techniques are intensively used to characterize graphene paper-based materials, such as atomic force microscopy (AFM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). In particular, electronic microscopies (SEM and TEM) are among the most powerful techniques to reveal the structural details of nanostructured graphene papers. For example, a combination of TEM and SEM was used to systematically characterize Au@PBNPs hybrid graphene papers. It is shown that Au@PB NPs were well distributed on graphene sheet surface (**Figure 5**), and cross-sectional SEM images indicated that the Au@PB NPs were successfully doped into the interlayers of the graphene paper to form a layer-by-layer sandwiched structure (**Figure 6**) [37].

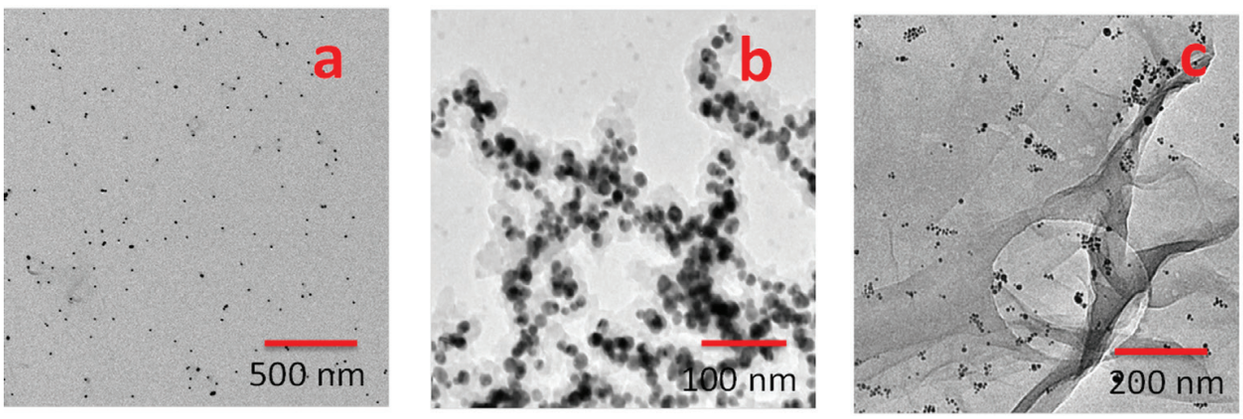


Figure 5. TEM images of different types of nanoparticles in the free form and in the immobilized form on GO sheets: (**a**) AuNPs; (**b**) core/shell Au@PBNPs and (**c**) core/shell Au@PBNPs on GO sheets [37].

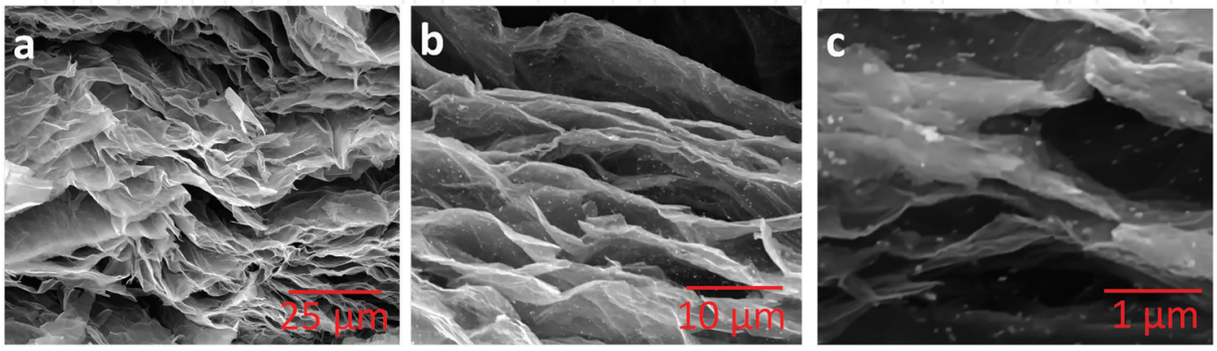


Figure 6. Cross-sectional SEM images of Au@PBNP-functionalized rGO papers with various magnifications [37].

4. Functionalization of graphene papers

The preparation and applications of graphene paper-based materials are attracting huge interests due to their unique electronic, optical, magnetic, thermal and mechanical properties. Compared to pure graphene papers, functionalized graphene papers or membranes can offer notable advantages ascribed to their hybrid structure, specific functionality and improved physicochemical properties. In general, graphene papers could be functionalized with a variety of chemical components such as metallic materials, metal oxides, polymers and supramolecular units, via various methods. Here, we only focus on three types of functional derivation, that is, metallic nanostructures, metal compounds and polymers, which are in favour of electrochemical-sensing applications.

4.1. Metallic nanostructures

Nanostructured metals are attracting intensive interests from the scientific community, owing to their fabulous properties and diversity of applications [57, 58]. A number of studies have explored the cooperation and synergistic effects between nanostructured metals and graphene paper, such as Pt nanoparticles (PtNPs) [59], Pt nanowires (PtNWs) [60], Au@Pt core-shell NPs [61], Au nanoparticles (AuNPs) [62] and Ag nanoparticles (NPs) [63]. As we mentioned in Section 2.1, CVD has made a great contribution to the preparation of graphene films. Hydrocarbon gases, through CVD consolidating on metal surfaces, enable the formation of a uniform and large-size graphene film, which can then be transferred onto solid substrates decorated with metallic NPs [64]. For example, Du and co-workers fabricated an AuNP-modified graphene film by a CVD-thermal release tape method, which has been used as an active substrate for the surface-enhanced Raman scattering (SERS) detection of analytes [65]. Furthermore, to enhance the electrical properties and surface plasmon signal of the graphene film, Ag nanowire was deposited further on the graphene film by a two-step procedure. In general, graphene films were *first* prepared by a CVD method, and then Ag nanowire was deposited on the graphene film by either physical loading [66], physical vapour deposition (PVD) [67], spin coating [68] or electrochemical pulse deposition [63].

Self-assembly provides a simple and time-saving way to prepare large-scale nanostructure-modified graphene paper by precisely controlling the experimental parameters. For example, AgNP-graphene hybrid paper was assembled through electrostatic self-assembly. *Firstly*, polycation-modified AgNPs were synthesized and *then* conjugated to a GO sheet. The reduction of GO and absorption of AgNPs occurred simultaneously, resulting in the formation of AgNP-graphene hybrid paper [69]. With the similar strategy, a homogeneous mixture of a GO suspension with AuNPs allowed self-assembly at the air/liquid interface to form a multi-layered GO-AuNP composite film [70]. As shown in **Figure 7a**, UV-vis absorption spectra of GO, AuNP, GO-AuNP and GO-SWCNT solutions indicate that AuNPs did not influence the π-electronic transitions in the aromatic carbon-carbon of GO, but the electrostatic repulsion between the deprotonated carboxylic groups at the edge of GO nanosheet and negatively charged AuNPs modulated the electronic environment of AuNPs, causing the blue shift of the absorption of

AuNPs by 4 nm. The resulting rGO-AuNP film (**Figure 7b**) showed an enhanced electrode kinetics and a cyclic voltammetric response in proportion to the amount of AuNPs incorporated. An enhancement of anodic peak current was clearly observed compared with that of the pure rGO films [70]. Zhang et al. developed a one-step strategy to synthesize self-assembled AuNP-graphene hybrid paper [71]. A mixture solution containing both GO and $HAuCl_4$ was directly used as a starting material. The two precursors were reduced into rGO and AuNPs, respectively, by glucose under heat treatment, and rGO and AuNPs *then* self-assembled into a multi-layered paper structure upon solvent evaporation. *Finally*, a PET film was used to harvest the formed AuNP-graphene hybrid paper [71]. Moreover, rGO/$Ni(OH)_2$ paper was prepared by the EPD process, which offered a facile, rapid, scalable and environmentally friendly method for making graphene paper [72]. $NiCo_2O_4$ was grown on the surfaces of porous N-doped graphene sheets through hydrogen bonding, van der Waals forces or covalent bonding with the functional groups of graphene such as –COOH groups. The as-prepared hierarchically porous graphene paper with $NiCo_2O_4$ displayed a remarkable catalytic activity towards oxygen evolution reaction (OER) [73].

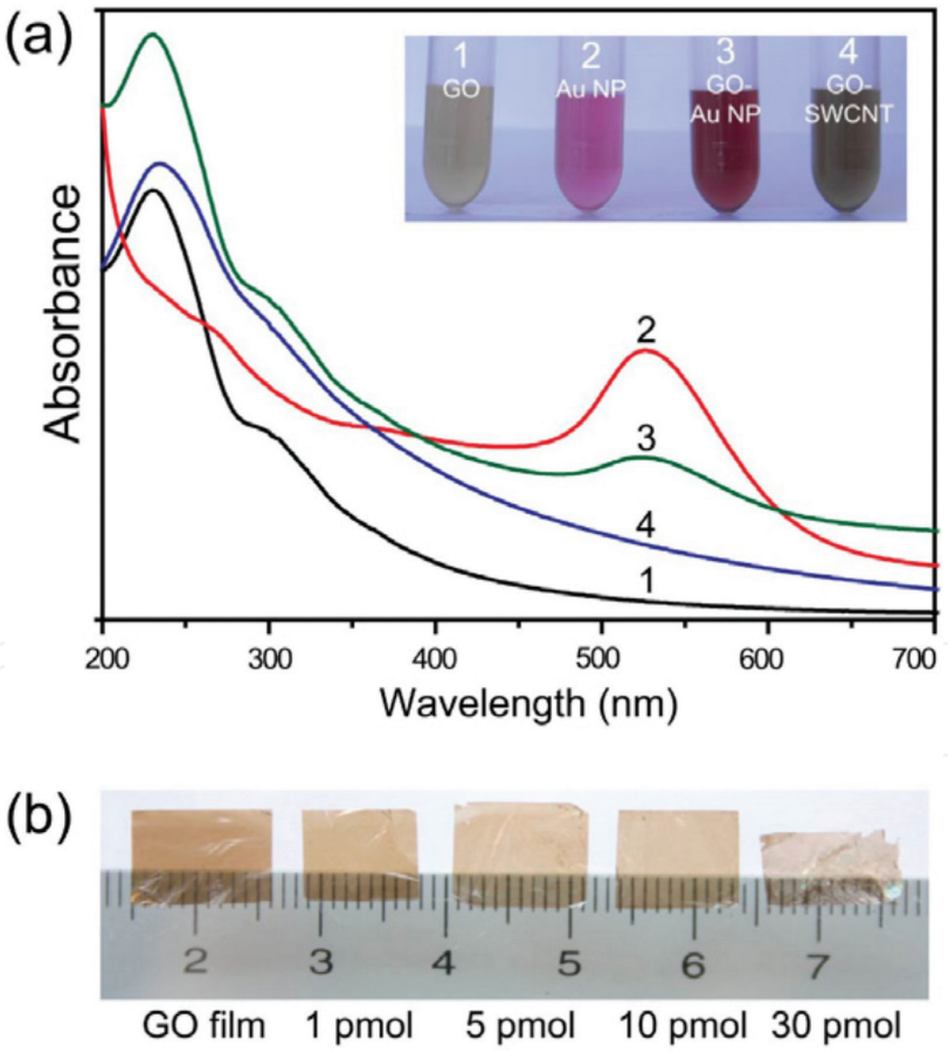


Figure 7. (**a**) UV-vis absorption spectra and digital images (inset) of 1: GO, 2: AuNP, 3: GO-AuNP and 4: GO–SWCNT solution. (**b**) Top-layered GO-AuNP composite films with a variation of the AuNP concentration from 1 to 30 p mol [70].

N-doped graphene-SnO_2 papers were prepared by inducing the 7,7,8,8-tetracyanoquinodimethane anion as both the nitrogen source and a complexing agent to formulate a sandwich structure, which exhibited a large capacity, high-rate capability and excellent cycling stability for electrochemical energy storage, such as lithium-ion batteries [74]. As noted, metallic nanostructure-modified graphene papers could also be prepared by the EPD process or vacuum filtration method [8, 75].

4.2. Metallic compound nanostructures

Metallic compounds, especially transition metal oxides (TMOs) or transition metal hydroxides (TMHs), are a key family of materials in a variety of current demanding needs for sensor, catalysis, energy storage and conversion, optical electronics and piezoelectric mechanics, attributed to their nature of versatile functionality [76]. Given such a fact, metallic compound-functionalized graphene papers have been a hot topic in recent years. Commonly, metal oxide and GO were synthesized separately, and then MO-graphene paper was fabricated through mixing the two (or more) components and applying a typical vacuum filtration process. For example, our group has reported the fabrication of free-standing graphene–*Prussian* blue (PB) composite paper through the filtration of chemically compatible graphene–PB nanohybrids, with the overall procedure shown in **Figure 8**. PB nanoparticles were *first* attached into rGO by the electrostatic attraction, and the hybrid material was *then* directly assembled into 2D flexible graphene paper sensor [36]. SnO_2 nanosphere hybrid graphene paper was prepared by direct vacuum filtration method. Using the similar strategy, Fe_2O_3 NPs [77], $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ NPs [78] and MnO_2 NPs [79] were successfully combined with graphene paper. In addition, graphene/MnO_2 paper could be fabricated by filtration of the mixture of GO with $Mn(NO_3)_2$ and $KMnO_4$ solution and was then subjected to the reduction of GO to rGO [80]. In some cases, nanostructured metallic compounds only functionalized the graphene-paper surface rather than the interlayers. Such metallic compound-functionalized graphene hybrid materials were obtained mainly by the growth of nanostructured metallic compounds on the surface of graphene films by various techniques. For example, pulse laser deposition was applied to deposit V_2O_5 film on the graphene paper surface to yield flexible energy storage devices [81]. NiO [82], TiO_2 [83–85], indium-gallium-zinc oxide [86] and PtNPs/MnO_2 nanowires [61] were all successfully deposited onto graphene paper surfaces for specific functionalization.

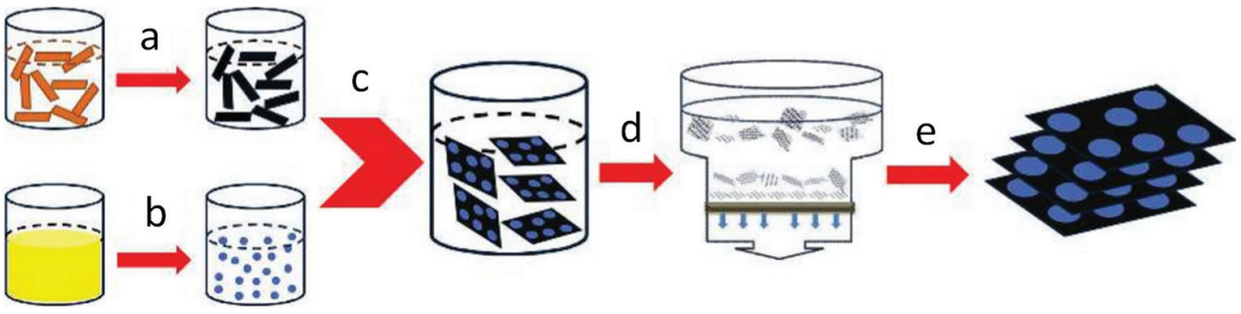


Figure 8. Schematic illustration of the preparation procedure for PBNP-functionalized graphene papers: (**a**) chemical reduction of GO to rGO, (b) synthesis procedure of PNBPs, (**c**) preparation of PBNPs–rGO hybrid nanosheets, (**d**) vacuum filtration to produce graphene paper and (e) annealing process to enhance the paper conductivity [36].

In addition, non-metallic nanostructures such as those carbon-containing building blocks (e.g. CNTs, fullerenes, carbon black, carbon fibre and carbon spheres), Si, SiO_2, Si_3N_4 and others [7, 10, 51] were also widely used to functionalize graphene papers.

4.3. Polymers

Besides inorganic nanocomposites, polymer-functionalized graphene papers also have widely been used for sensor and energy conversion and storage applications. In general, the polymer could be stabilized with graphene paper through the two approaches: (1) covalent bonding. Because GO contains a notable number of oxygen-containing groups, it provides remarkable opportunities for further modification with polymer either by 'grafting to' or by 'grafting from' techniques. (2) Non-covalent attachment such as electrostatic attraction, hydrogen bonding or π–π stacking; a variety of polymers have been incorporated into graphene-based films with a uniform multilayer structure and novel functionality, such as polyaniline [87–91], poly(sodium 4-styrenesulfonate) [92] and poly(p-phenylene vinylene) [48]. Recently, Mu et al. developed a series of PVDF-modified graphene monolayer papers with a gradient rGO/GO structure. In the gradient graphene paper, the GO region could respond to the environment stimuli including changes in humidity, temperature or light, leading to shrinking or swelling of the GO sheets [93]. In another example, poly-dopamine was used to functionalize graphene paper, the as-prepared graphene paper displayed high performance of responses to moisture, heat and light. The response of this water-driven

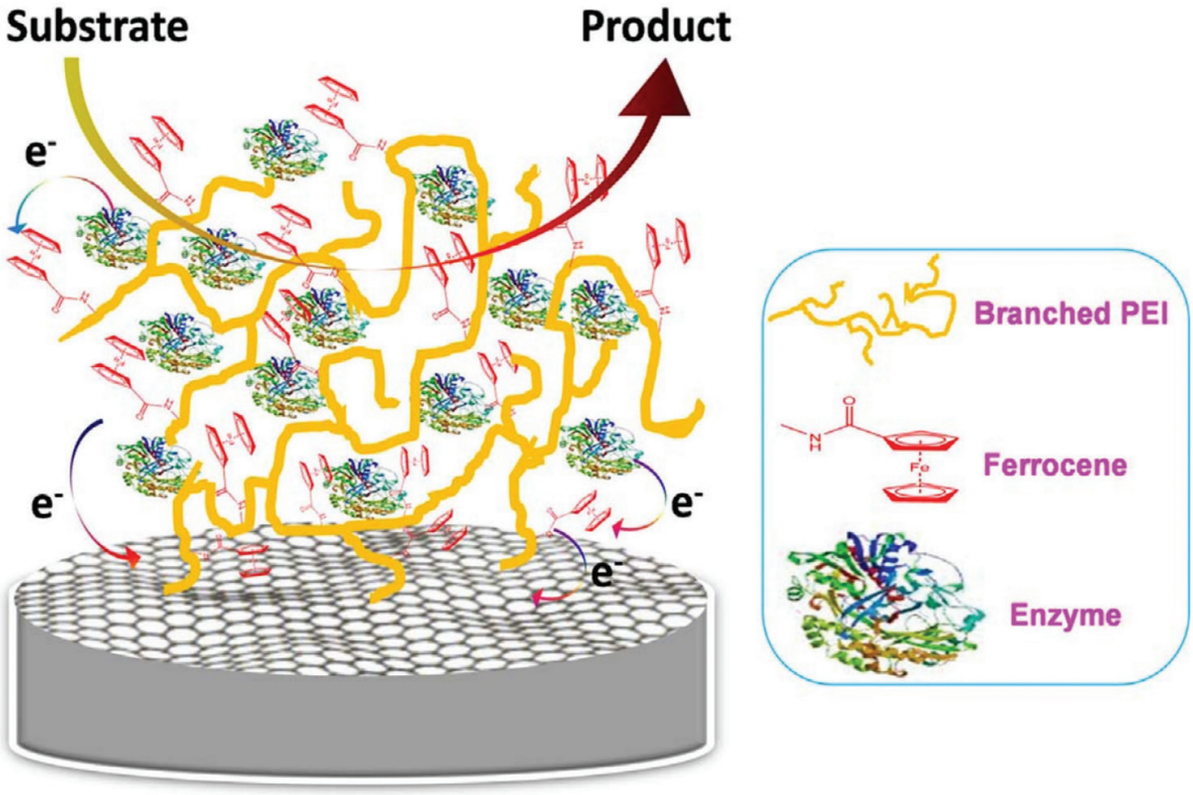


Figure 9. Schematic illustration of structure, electron transfer and bioelectrocatalysis of Fc-rGOP-enzyme hybrid systems [95].

actuator to multiple stimuli allows the artificial muscles and electric generators to be fabricated [94]. In our recent work, as shown in **Figure 9**, a highly branched PEI (b-PEI) was used for reduction and simultaneous derivation of GO to form a biocompatible polymeric matrix on rGO nanosheet. Ferrocene redox moieties were then grafted onto rGO nanosheets through the polymer matrix. The as-prepared functional composite is electrochemically active and enabled to accommodate enzymes stably. For proof-of-the concept studies, two crucial redox enzymes for biosensors (i.e. cholesterol oxidase and glucose oxidase (GOx)) were used to test the platform with good outcomes [95].

5. Applications of graphene paper as electrochemical-sensing platforms

Graphene papers with the advantages of low price, high quality and simple synthesis process have a potential to apply in electronic and optoelectronic devices, electrochemical energy devices, water treatment and sensors [7, 8, 10, 50, 51]. Especially the self-assembled 2D graphene papers/films/membranes functionalized with nanostructured metals, polymers and biomolecules are promising candidates for sensing applications, as summarized in **Table 1**, which is an overview of enzyme-based and non-enzymatic graphene papers/films sensors for the detection of glucose. In particular, in the field of electrochemical biosensors with high sensitivity, these candidates have found widespread uses in clinic diagnosis, environment monitoring and for

Composite material	Electrocatalyst	Linear range	LOD	Sensitivity ($\mu A\ cm^{-2}\ mM^{-1}$)	References
PBNPs/GP/GOD	GOD	6-8 mM	10 μM	25	[36]
MnO_2/PtNPs/GP	PtNPs	10-46000 μM	20 μM	52.36	[60]
AuNPs/GP	AuNPs	100-30000 μM	5 μ M	58.54	[61]
AuNPs/PANI/GP/GOD	GOD	200-11200 μM	100 μM		[88]
Fc/GP/GOD	GOD	100-15500 μM	5 μM	3.45	[95]
CuO NC/GP	CuO	2-4000 μM	0.7 μM	1360	[100]
CuO/S-GP	CuO	100-10500 μM	0.08 μM	1298	[101]
CS/N-GP/GOD	GOD	200-1800 μM	64 μM	10.5	[111]
AuNPs/GP/GOD	GOD	20-2260 μM	4.1 μM	3.855	[112]
ZrO_2/GP/GOD	GOD	200-1600 μM	45.6 μM	7.6	[113]
AuNPs/PBNPs/CS/GP/GOD	GOD	25-3200 μM	10 μM	58.7	[114]
GOD/CS/Fc/GO	GOD	20-6780 μM	7.6 μM	10	[115]
TEOS/APTES/Fc/CS/GP/GOD	GOD	20-5390 μM	6.5 μM	19.5	[116]
NiNPs/GP	NiNPs	1-110 μM	-	813	[117]
NiO/GP	NiO	20-2100 μM	0.1 μM	1020	[118]
PtNPs/GP	PtNPs	2-2100 μM	1 μM	1508	[119]
CuO/GP	CuO	1-8000 μM	1 μM	1065	[120]
Co_3O_4/gP	Co_3O_4	up to 80 μM	25 nM	669.78	[121]

PANi, polyaniline; GP, graphene paper or graphene film; GOD, glucose oxidase; CS, chitosan; Fc, ferrocene.

Table 1. Overview of enzyme-contained and non-enzymatic graphene paper/film sensors for detection of glucose.

quality control in industrial, food and agricultural products [9, 34, 59, 61, 96]. In Section 5, we mainly address the applications of graphene papers as different types of electrochemical sensor.

5.1. Enzyme-graphene paper sensors

Graphene paper displayed outstanding physical and electrochemical properties, such as high conductivity, large surface area, abundant defect sites, superior electrocatalytic activity and fast electron transfer rate, hence various enzyme biosensors based on this attractive material have been fabricated recently [11, 95]. We have successfully fabricated graphene paper doped with chemically compatible PBNPs as a nanohybrid electrocatalyst [36]. *Prussian* blue was loaded on the graphene nanosheet by electrostatic attraction. The as-prepared PBNPs–rGO papers are further capable of biocompatible accommodation of enzymes for the development of free-standing enzyme-based biosensors.

The correlation between the electrocatalytic current and glucose concentration shows a linear relation up to about 6–8 mM with a sensitivity of 25 μA mM^{-1} cm^{-2} and the detection limit down to about 10 μM. Furthermore, our group had recently explored a facile way for the successful synthesis of redox active and bioengineering of rGO for the development of versatile biosensing platform [95]. We developed a simple way for the synthesis of ferrocene (Fc) functionalization of highly b-PEI-linked rGO as well as the development of biocompatible matrix for accommodation of different bio-recognition elements. Ferrocene redox moieties were attached to rGO nanosheets through PEI. The polymer acts as both a reducing agent and a molecular spacer for rGO. Fc-PEI-rGO is electrochemically active and can offer a biocompatible microenvironment for immobilization of cholesterol oxidase and glucose oxidase. The as-constructed electroactive matrix was further used for the development of integrated biosensing platforms for cholesterol and glucose sensing. As measured, the current-time (*I-t*) and calibration curves are shown in **Figure 10**, the detection limit of the biosensors for glucose and cholesterol is 5 and 0.5 μM ($S/N = 3$), respectively. The linear response range of the biosensor is from 0.1 to 15.5 mM for glucose. Furthermore, this biosensing platform shows good anti-interference ability and reasonable stability. The nanohybrid biosensing materials can be further combined with screen-printed electrodes, which were successfully used for measuring the glucose level of real human serum samples. In addition to these two enzymes, other enzymes can also be immobilized onto graphene-based electrodes for the construction of various enzyme biosensors, including horseradish peroxidase (HRP), alcohol dehydrogenase (ADH), catalase and urease [87, 97–99].

5.2. Non-enzymatic sensors for detection of small biomolecules

Glucose oxidase-modified electrode is the most common class of amperometric biosensors for glucose detection because GOx enables catalytic oxidation of glucose with high sensitivity and selectivity. However, enzyme-modified electrodes have some disadvantages such as the instability of the electrode and unsatisfactory reproducibility, complicated enzyme immobilization procedure and high cost of enzymes. For addressing such challenging issues, non-enzymatic glucose biosensors based on graphene papers have been explored. As mentioned above, nanostructured MO displayed high performance for the fabrication of electrochemical

sensors. The working principles of using MO as an electrochemical catalyst for the detection of glucose can be described by Eqs. (1) and (2). A couple of redox peaks are obtained in a basic solution, and MO(OH) can then oxidize glucose to glucolactone, leading to a remarkable increase in the anodic peak current. Graphene paper plays a key role as supporting electrode and speeding up electron transfer reaction. Several studies have reported that MO-functionalized graphene papers can sensitively detect glucose without any biological materials involved in the fabrication of sensors. For example, CuO, a p-type semiconductor with a narrow band gap of 1.2 eV, is very promising for the development of glucose sensors because of high specific surface area, good electrochemical activity and the possibility of promoting electron transfer reactions at a lower overpotential. For example, CuO nanocubes were deposited on a graphene film by the EPD process, under the optimized conditions, a linear

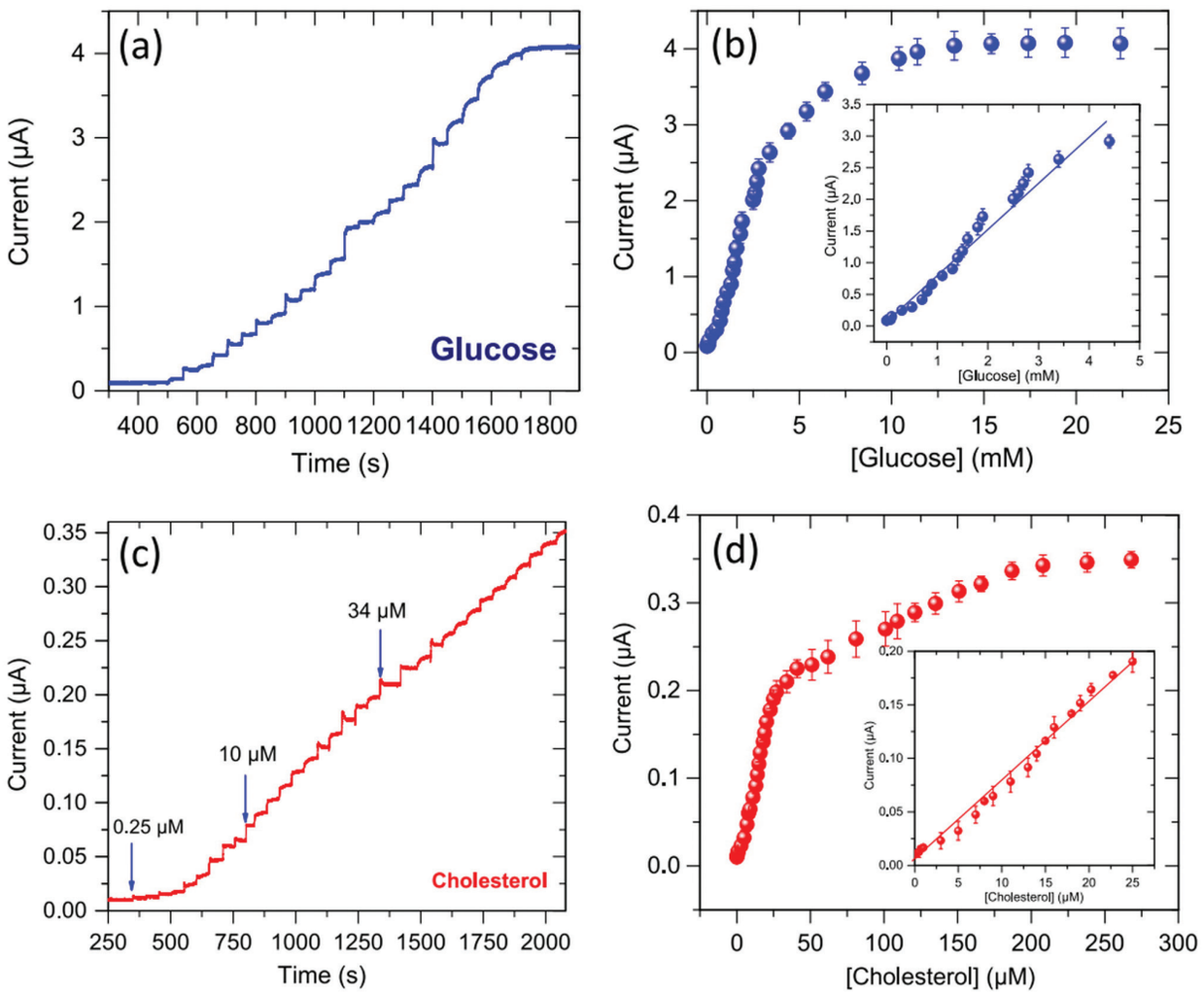


Figure 10. (**a**) Current-time (*I-t*) curve obtained at Fc-rGOP-GOx/GCE electrode upon successive injection of glucose, (**b**) dependence of electrocatalytic currents on the glucose concentration, (**c**) amperometric responses to cholesterol with Fc-rGOP-ChOx/GCE electrode and (**d**) calibration curve for cholesterol. The insets in (**b**) and (**d**) are the linear part of current responses to the substrates. Electrolyte: 10 mM PBS (pH 7.0); the working electrode potential fixed at 0.4 V (vs SCE); substrate (either glucose or cholesterol) solution was injected at a regular time interval to the supporting electrolyte which was under stirring [95].

range up to 4 mM with a sensitivity of 1360 μA mM^{-1} cm^{-2} at a positive potential (i.e. 0.55 V) was achieved [100]. In order to improve the performance of CuO-modified graphene paper as non-enzymatic sensor, CuO-functionalized S-doped graphene was successfully synthesized through a facile microwave-assisted approach. The CuO/S-doped graphene-based sensor exhibited a rapid response of 2s (**Figure 11**), a wide linear range of 0.1–10.5 mM, a high sensitivity of 1298.6 μA mM^{-1} cm^{-2} and a low detection limit of 80 nM. Moreover, this biosensing platform showed good anti-interference ability and reasonable stability (**Figure 11**) [101]. In another case, PtNPs/MnO_2 nanowires/graphene paper used as a free-standing paper electrode for non-enzymatic detection of glucose, the sensor response is linear to the glucose concentrations in the range from 0.1 to 30.0 mM with a detection limit of 0.02 mM (S/N = 3) and detection sensitivity of 58.54 μA cm^{-2} mM^{-1} [61]. Moreover, nanostructured NiO [102] and CoO [103] were loaded on graphene paper through various advanced techniques for the fabrication of ultrasensitive non-enzymatic sensors

$$MO + OH^- \rightarrow MO(OH) + e- \quad (1)$$

$$MO(OH) + glucose \rightarrow MO + gluconolactone \quad (2)$$

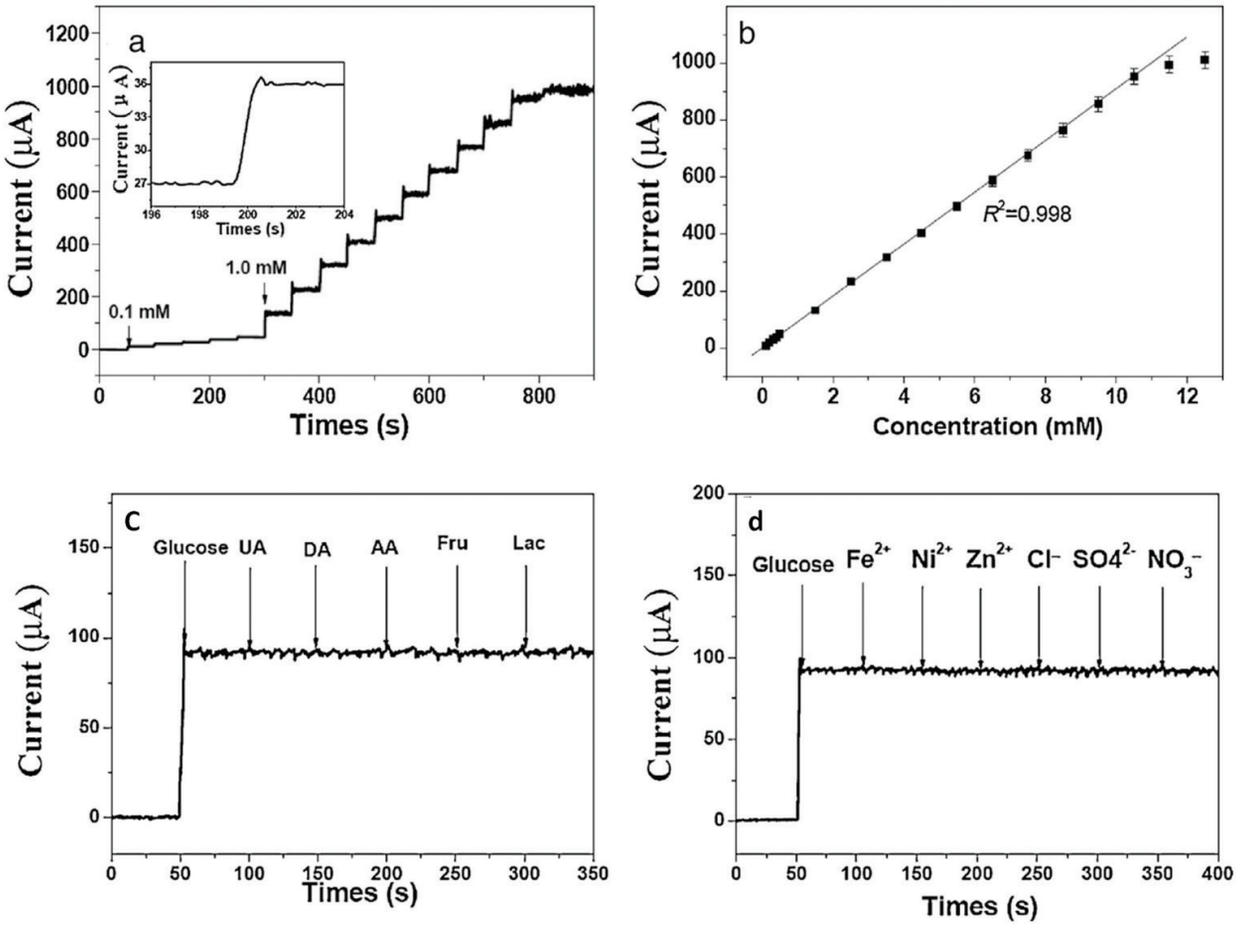


Figure 11. (**a**) Amperometric responses to the successive addition of glucose in 0.1 M NaOH at 0.50 V (the inset showing the response time upon the addition of 0.1 mM glucose). (**b**) The calibration curve of the current response to glucose. (**c**) Interference test with continuous injections of glucose (1.0 mM) and UA, DA, AA, fructose and lactose (with the same concentration of 0.1 mM). (**d**) Interference tests with continuous injections of 1.0 mM glucose and 0.10 mM of other ions [101].

Ascorbic acid (AA), dopamine (DA), uric acid (UA) and other small biomolecules are among the key small biomolecules that affect human health. Therefore, electrochemical sensing of those small biomolecules has played a vital role in monitoring the health. Recently, building electrochemical-sensing platforms based on graphene-supported nanomaterials for the detection of those small biomolecules has been a hot topic, due to the fast electron transfer kinetics and superior electrocatalytic activity of graphene-based materials. Dopamine is one of the mostly studied small biomolecules using graphene-based biosensors. Determination of dopamine, ascorbic acid and uric acid concentration is crucial, because the concentration level of these molecules in human body is closely linked to the health status. Graphene film-based electrodes as electrochemical sensors have shown high performance towards the analysis of dopamine, ascorbic acid and uric acid [104–110]. For example, Xia and co-workers developed a multifunctional electrochemical sensor based on N-doped graphene (NG), which can be used to simultaneously determine AA, DA and UA [105].

N-doped graphene exhibited high performance for electrochemical sensing of AA, DA and UA due to its unique structure and physiochemical property. The electrochemical sensor had a wide linear response to AA, DA and UA [105]. Moreover, some important small molecules for food safety control also could be detected by using graphene paper-based electrodes. As an example, an Orange II sensor was fabricated based on PtNP-functionalized rGO film. This sensor was evaluated for the detection of Orange II in an acetate buffer. The results showed a wide linear range (1×10^{-8}–6×10^{-7} M) and the detection limit could be down to 3.4×10^{-10} M (at $S/N = 3$). The as-prepared electrochemical sensor also showed high selectivity, impressive stability and promising responses to real samples with an excellent recovery [59].

5.3. Electrochemiluminescence sensors

Electrochemiluminescence (ECL) is a kind of luminescence induced by electrochemical reactions normally at liquid/solid interfaces. ECL has proven to be a highly sensitive and selective method and is a very useful tool in analytical science. The ECL method combines the advantages of chemiluminescent analysis with the ease of reaction control by applying an electrode potential. Therefore, ECL-based sensors have recently been developed using graphene papers. For example, based on $Ru(bpy)_3^{2+}$ and alcohol dehydrogenase-modified graphene/bovine serum albumin composite film, ethanol biosensor was developed [122]. In another case, Li et al. developed an ultrasensitive ECL sensor for the detection of DA. In this study, cationic polythiophene derivative, poly[3-(1,10-dimethyl-4-piperidinemethylene)thiophene-2,5-diyl chloride] (PTh-D), was used to improve stability, and NH_2–graphene acted as electron transfer accelerator. Under the optimal experimental conditions, the ECL signal linearly decreased with the increase of DA concentration in the range of 0.1–50.0 mM with a detection limit of 0.04 mM (**Figure 12**). This simple prepared ECL sensor also exhibited high selectivity, good reproducibility and long-term stability. The proposed ECL sensor was also evaluated by detecting DA in real samples [123]. Xu et al. obtained a paper-based solid-state ECL sensor based on poly(sodium 4-styrenesulfonate)-functionalized graphene/Nafion composite film. Very impressively, the detection limit could be down to ($S/N = 3$) 5.0 nM. The sensor exhibited excellent reproducibility and long-term stability. Moreover, highly porous Fe_3O_4 nanocrystal clusters were added to poly(sodium 4-styrenesulphonate) hybrid graphene paper for further

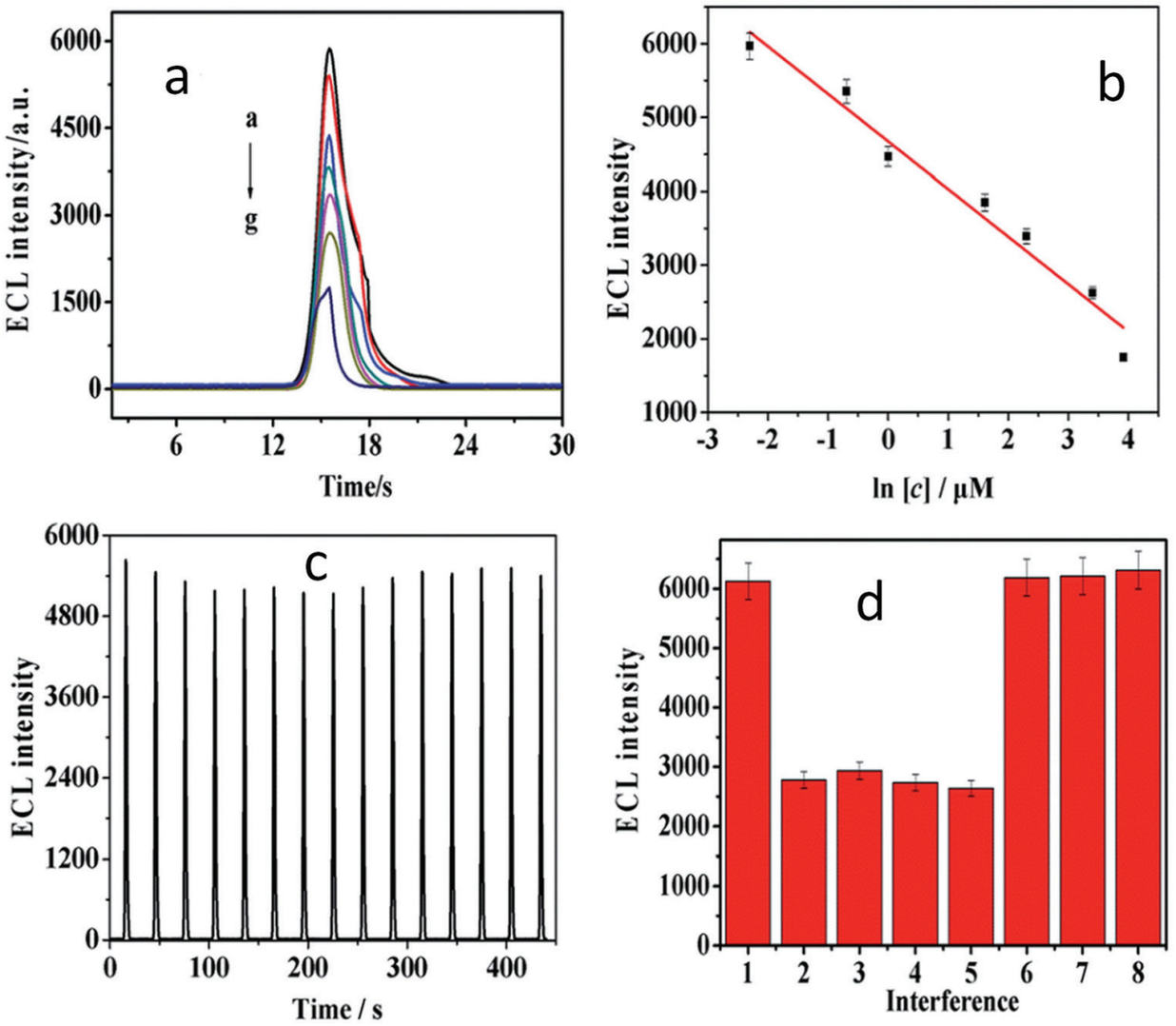


Figure 12. (**a**) The response of ECL to DA, from (a) to (g): 0.1 to 50 mM. (**b**) Corresponding calibration curve of response ECL versus DA concentrations. (**c**) The ECL intensity of the sensor in a solution containing 0.1 M KCl and 0.5 mM DA under continuous scanning for 15 cycles. (**d**) The interference tests of the ECL sensor [123].

enhancing the specific ability of graphene paper. This type of graphene paper-based sensors showed a high performance to detect those specific compounds containing tertiary amino groups and DNA with guanine and adenine [92, 124].

5.4. Others

Immunosensors are among the most important sensors for biomedical applications. Due to high flexibility and conductivity, the development of graphene paper-based electrochemical immunosensors is highly desirable [125]. Indeed, there are some striking examples in this regard. For example, a simple and label-free electrochemical impedimetric immunosensor for immunoglobulin G (IgG) based on chemically modified graphene was prepared by the Martin group [126]. In another example, an efficient, low cost and robust impedimetric immunosensor for the rapid and sensitive detection of *Escherichia coli* O157:H7 (*E. coli* O157:H7) was developed by using AuNP-functionalized free-standing graphene paper electrodes.

Electrochemical impedance spectroscopy (EIS) was used to detect *E. coli* O157:H7 captured on the paper electrode, and a broad linear range (1.5×10^2–1.5×10^7 cfu mL^{-1}) and a low detection limit (1.5×10^2 cfu mL^{-1}) were achieved [127].

6. Concluding remarks and outlook

In summary, worldwide researchers have explored graphene paper-based sensors by exploiting their unique advantages including high sensitivity, conductivity and in situ sensing. The recent research advances suggest that graphene paper-based materials could play a significant role in developing flexible sensors and electronic devices due to their intriguing structural and functional features. However, the progresses are accompanied by new challenges. Among the possibly critical challenges, the biocompatibility, electronic conductivity and stretchable capability are likely mostly concerned. In this regard, the further development of graphene papers by incorporation of biocompatible and conducting polymers is particularly encouraged. Although there are these challenges to be overcome in order to meet practically capable applications in real world, we would like to believe that flexible and free-standing graphene papers should continue emerging as a widely useful material platform for developing electrochemical-sensing technologies in the near future.

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