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Printing graphene-carbon nanotube-ionic liquid gel on graphene paper: Towards flexible electrodes with efficient loading of PtAu alloy nanoparticles for electrochemical sensing of blood glucose

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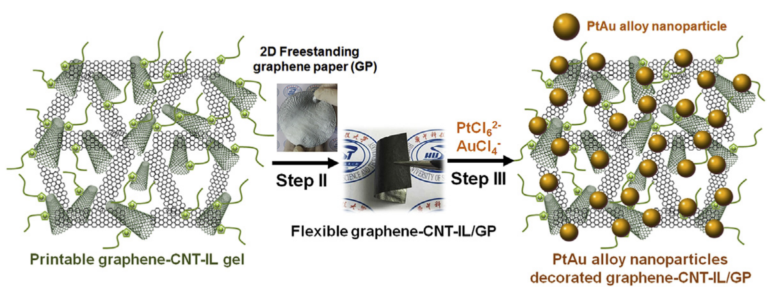
HIGHLIGHTS

- Self-assembly of graphene nanosheets and carbon nanotubes into three-dimensional porous nanohybrid material.
- Printing of graphene–carbon nanotube nanohybrid material on free-standing graphene paper using ionic liquids as the binder.
- Ultrasonic-electrodeposition of PtAu alloy nanoparticles on flexible graphene-based nanohybrid paper electrode.
- Nonenzymatic electrochemical sensing of glucose in human blood samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing demands for portable, wearable, and implantable sensing devices have stimulated growing interest in innovative electrode materials. In this work, we have demonstrated that printing a conductive ink formulated by blending three-dimensional (3D) porous graphene–carbon nanotube (CNT) assembly with ionic liquid (IL) on two-dimensional (2D) graphene paper (GP), leads to a free-standing GP supported graphene–CNT–IL nanocomposite (graphene–CNT–IL/GP). The incorporation of highly conductive CNTs into graphene assembly effectively increases its surface area and improves its electrical and mechanical properties. The graphene–CNT–IL/GP, as freestanding and flexible substrates, allows for efficient loading of PtAu alloy nanoparticles by means of ultrasonic-electrochemical deposition. Owing to the synergistic effect of PtAu alloy nanoparticles, 3D porous graphene–CNT scaffold, IL binder and 2D flexible GP substrate, the resultant lightweight nanohybrid paper electrode exhibits excellent sensing performances in nonenzymatic electrochemical detection of glucose in terms of sensitivity, selectivity, reproducibility and mechanical properties.

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1. Introduction

The emergence of a myriad of recently launched portable, wearable and even implantable sensing devices based on bendable and/or stretchable, robust and biocompatible electrodes has received significant attention owing to their great potential in point-of-care medical diagnostics, skin-like electronics, human-machine interfacing, wearable health monitoring and subcutaneously implanted applications [1–7]. In particular, considerable research efforts have been dedicated to developing flexible electrodes for sensor systems that can sustain significant mechanical stress. Integrating metal thin film with flexible substrates, such as polydimethyl siloxane, polyethylene terephthalate, polyimide by vacuum depositions, etchings and etc., represents a popular approach towards flexible printed electrodes [8]. However, these methods involve multiple complicated processing steps and the thin metal patterns are vulnerable to mechanical stress and harsh chemical environments, limiting their broad applications in sensor developments [9,10].

Here we report the development of a new type of flexible graphene-based nanohybrid paper by taking advantage of a facile printing method. Graphene nanomaterials have recently been vigorously investigated because of their unique chemical, electrical, optical and mechanical properties [11,12], and therefore hold great promise for a broad spectrum of applications in electronics, biomedicine, functional coatings, thermal management, catalysis, energy storage/conversion devices, and chemical sensors [13–16]. Graphene features unique collection properties such as high surface-to-volume ratio, abundant available active site for adsorption of target chemicals, high electrical conductivity and carrier mobility, that are of particular importance for developing electrochemical sensors. More interestingly, graphene nanosheets can be self-assembled into macroscopic architectures, *e.g.*, two-dimensional (2D) freestanding paper-like film and three-dimensional (3D) porous network [17–20]. Depending on how the individual nanosheets are assembled, the graphene-based bulk materials can show a combination of intriguing characteristics among large surface area, light weight, excellent mechanical strength, superior electrical conductivity, chemical inertness, good biocompatibility, making them promising candidates as tissue engineering scaffold and flexible conductive electrode substrates for electrochemical biosensors.

In the present work, we developed a high-performance flexible electrode for electrochemical biosensor by printing 3D graphene–carbon nanotube (CNT) assembly on 2D graphene paper (GP), using ionic liquid (IL) as a binder, which enables the good adhesion of 3D graphene–CNT nanohybrid to the 2D graphene substrate. As shown in Fig. 1, the graphene nanosheets and CNT were co-assembled into 3D porous graphene–CNT cylinder aerogel. The incorporation of CNTs into graphene assembly not only effectively avoids the restacking of graphene nanosheets into densely packed layered structures, but also increases its electronic conductivity and mechanical robustness. The resultant graphene–CNT nanohybrid material was blended with IL (*i.e.*, 1-butyl-3-methylimidazolium tetrafluoroborate, $BMIMBF_4$) binder, which is known to interact with graphene and CNT by means of the cation–π interaction between the imidazolium ring of IL and the π-bonded surface [21]. IL has also aroused great interest because of its fascinating characteristics such as insignificant vapour pressure, high ionic conductivity, high chemical and thermal stabilities, wide solubility of various organic and inorganic compounds, low toxicity, and tunability of properties [22–24]. Our findings demonstrate that the 3D porous graphene–CNT aerogel and IL can be blended to form viscous fluid (functional graphene–CNT–IL gel), which can be used as a conductive ink for printing on GP to form freestanding GP-supported 3D graphene–CNT–IL nanocomposite (graphene–CNT–IL/GP). We have demonstrated that the flexible conductive graphene–CNT–IL/GP substrate with large surface area led to efficient ultrasonic-electrochemical deposition of PtAu alloy nanoparticles with favorable size and uniform size distribution.

The rapid, convenient, sensitive and reliable detection of blood glucose levels is of great importance in fundamental biological and physiological research as well as the medical diagnosis/management and physiological monitoring [25]. Previous studies have demonstrated that the non-enzymatic electrochemical sensors based on metal oxides, noble metals and their alloys such as AgO [26], CuO [27,28], Co_3O_4 [29], Ag [30], Au [31], PtRu [32], PtNi [33], PtPd [24], PdNi [34] and PdFe [35], possess high electrocatalytic activity toward the direct oxidation of glucose, which give rise to an improved overall performance of the electrochemical glucose sensor. For the electrodeposition of metal nanoparticles, the graphene–CNT–IL/GP processes several advantages including large surface area derived from the 3D porous network structure of graphene–CNT scaffold and abundant nucleation sites originated from the functional groups on IL molecules, which effectively improve the dispersion and adhesion of metal nanoparticles on graphene–CNT–IL/GP electrode. Benefit from the synergistic effect of PtAu alloy nanoparticles, 3D porous graphene–CNT–IL support and flexible and robust GP substrate, the resultant PtAu alloy nanoparticles decorated graphene–CNT–IL/GP (PtAu/graphene–CNT–IL/GP) electrode show excellent sensing performances of high sensitivity, reproducibility stability, anti-interference ability as well as unique mechanical flexibility, stability and tailorable shape, and can be used for the highly reliable measurement of glucose in real human blood samples.

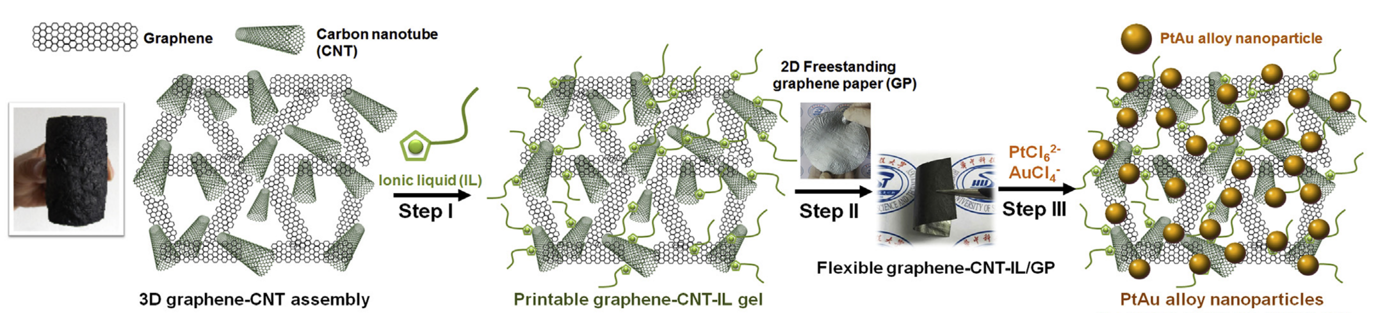

Fig. 1. Preparation process of PtAu alloy nanoparticles decorated graphene–CNT–IL/GP. Step I: Grinding 3D graphene–CNT assembly with IL to form printable graphene–CNT–IL gel; Step II: Printing graphene–CNT–IL gel on GP; Step III: Ultrasonic-electrodepositing PtAu alloy nanoparticles on graphene–CNT–IL–GP electrode.