



## A facile method for preparation of graphene film electrodes with tailor-made dimensions with Vaseline as the insulating binder

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### ABSTRACT

This communication describes a facile but effective method to prepare graphene film electrodes with tunable dimensions with Vaseline as the insulating binder. Cyclic voltammetry (CV) studies reveal that the as-prepared graphene film electrodes have tunable dimensions ranging from a conventional electrode to a nanoelectrode ensemble, depending on the amount of graphene dispersed into the insulating Vaseline matrix. A large amount of graphene (typically, 10.0  $\mu\text{g/mL}$ ) leads to the formation of the film electrodes with a conventional dimension, while a small amount of graphene (typically, 1.0  $\mu\text{g/mL}$ ) essentially yields the graphene film electrodes like a nanoelectrode ensemble. As one new kind of carbon-based film electrodes with tailor-made dimensions and a good electrochemical activity as well as a high stability, the graphene film electrodes are believed to be potentially useful for fundamental electrochemical studies and for practical applications.

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### 1. Introduction

The recent discovery of graphene has triggered enormous interests both from the fundamental studies and practical aspects due to its distinctive geometries and novel physicochemical properties [1,2]. To date, most studies on graphene have been focused on its preparation, theoretical calculation, physical properties, chemical functionalization and so forth [3–7]. Recent concerns have also been made on the electrochemical properties of graphene and such investigations have demonstrated that, as a new kind of carbon nanostructures, graphene exhibits good electrochemical activities and is thus potentially useful both in the fundamental electrochemical studies and in the practical applications [8–12]. For instance, graphene is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. Since this kind of carbon nanostructure can be considered as a basic building block for other kinds of graphitic materials including 0D fullerenes, 1D nanotubes and 3D graphite [1,14], the study of its electrochemical activity is of fundamental importance in understanding the carbon-based electrochemistry [15–17]. Moreover, graphene has recently been demonstrated to show excellent electrochemical catalytic activities towards physiologically important species, such as neurotransmitters, and the species involved in the oxidase/dehy-

drogenase enzymatic reactions [9–13]. This property essentially enables this kind of carbon nanostructure to be potentially used as a new kind of electrode materials with potential applications in electrochemical sensing and biosensing.

On the other hand, the enhanced mass transport, the reduced  $iR$  drop and the increased faradaic-to-charging current ratio at the microelectrodes and their ensembles have substantially made these kinds of electrodes advantageous over the electrodes with a conventional dimension both in the fundamental and practical aspects [18]. For example, the enhanced mass transport at the microelectrodes essentially enables the fast heterogeneous electron-transfer kinetic measurements to be readily and reliably carried out under a steady-state condition, rather than a transient one. Additionally, the small size of this kind of electrodes has made it possible for the voltammetric measurements in the microenvironmental and biological systems [19–21].

Motivated by the striking properties of graphene and the wide uses of microelectrodes in the fundamental and practical electrochemical studies, this communication describes a facile but effective method to prepare graphene film electrodes with tailor-made dimensions ranging from a conventional electrode to a nanoelectrode ensemble by using Vaseline as the insulating binder. To the best of our knowledge, this is the first demonstration on the method to prepare the graphene film electrodes with tunable dimensions and the prepared electrodes are reasonably envisaged to be useful for electrochemical studies and applications.

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## 2. Experimental

### 2.1. Reagents and materials

Benzene, hexane, anhydrous sodium sulfate, N,N-dimethylformamide (DMF) and colloidal white Vaseline were purchased from Beijing Chemical Co. (Beijing, China) and used without further purification. Aqueous dispersion of pristine graphene oxide (0.05 wt.%) was prepared according to the modified Hummers method [22] and aqueous dispersion of graphene (0.01 wt.%) was prepared by the chemical reduction of graphene oxide with hydrazine, as reported previously [3]. Doubly distilled water was used throughout the experiments.

### 2.2. Preparation of graphene film electrodes

Glassy carbon electrodes (GC, 3 mm diameter) were used as the substrate to prepare the graphene film electrodes. GC electrodes were first polished with emery paper and then with aqueous slurries of fine alumina powders (0.3 and 0.05  $\mu\text{m}$ ) on a polishing cloth. After that, the electrodes were then rinsed with doubly distilled water and acetone in an ultrasonic bath, each for 5 min, and were finally rinsed with doubly distilled water. In a typical experiment, Vaseline (50 mg) was dissolved into 5 mL of hexane or benzene and the mixture was vigorously stirred for 10 min to obtain a homogeneous solution. Aqueous dispersion of graphene was first diluted with isopyknic DMF, then dehydrated with excess anhydrous sodium sulfate, and finally stored at room temperature overnight. Then, different amounts of the resulting graphene was added to the Vaseline solution and the as-prepared dispersions were sonicated for 10 min to give homogeneous dispersions containing different contents of graphene, i.e., 10.0 and 1.0  $\mu\text{g}/\text{mL}$  in this study. An aliquot of 0.5  $\mu\text{L}$  of the dispersion was dip-coated on GC electrodes and the electrodes were allowed for solvent evaporation at ambient temperature for 30 min. Alternatively, the graphene film electrodes could also be prepared by first mixing 50  $\mu\text{L}$  or 5.0  $\mu\text{L}$  of the aqueous dispersion of graphene into 50 mg colloidal Vaseline, and then grinding the mixtures in an agate mortar for ca. 30 min to form a homogeneous gel. The film electrodes were prepared by rubbing GC electrodes on the gels placed on a smooth glass plate.

### 2.3. Electrochemical measurements

Electrochemical measurements were carried out with a computer-controlled electrochemical analyzer (CHI 660A, Chenhua, China) in a two-compartment electrochemical cell with graphene film electrodes as working electrode, a platinum spiral wire as counter electrode, and an Ag/AgCl electrode (KCl-saturated) as reference electrode. A 0.10 M KCl solution was used as supporting electrolyte. All electrochemical measurements were conducted at room temperature.

## 3. Results and discussion

Fig. 1 depicts typical cyclic voltammograms (CVs) obtained at the graphene film electrodes prepared with different contents of graphene in Vaseline in 0.10 M KCl solution containing  $\text{Fe}(\text{CN})_6^{3-}$ . A large difference in the CV shape was clearly observed at the film electrodes. Typically, a pair of well-defined and peak-shaped redox wave was recorded at the electrodes when the content of graphene in the Vaseline solution was as high as 10.0  $\mu\text{g}/\text{mL}$  (Fig. 1A), indicating that the process of the redox couple at such electrodes was semi-infinite linear diffusion-controlled and that the film electrodes essentially act as a conventional electrode. In addition, the

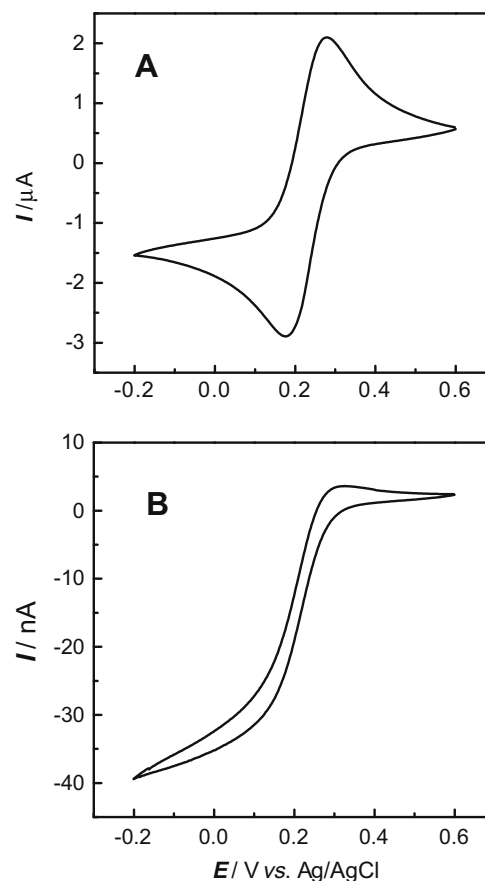
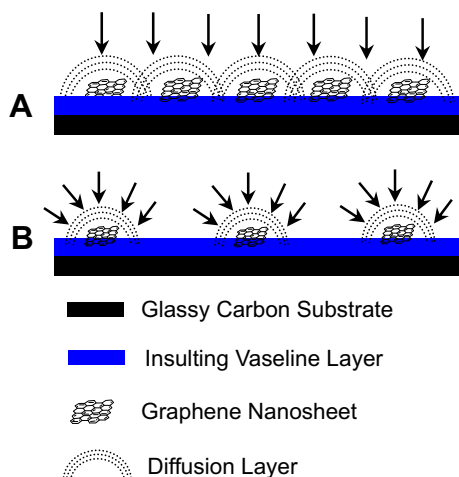


Fig. 1. Typical CVs for 1.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  at the graphene film electrodes in 0.10 M KCl solution. The electrodes were prepared by mixing 10.0  $\mu\text{g}/\text{mL}$  (A) and 1.0  $\mu\text{g}/\text{mL}$  (B) graphene into the Vaseline solution. Scan rate, 10  $\text{mV s}^{-1}$ .

near unity of the ratio of the cathodic-to-anodic peak current (0.99 at 10  $\text{mV s}^{-1}$ ) and the small peak-to-peak separation (73  $\text{mV}$  at 10  $\text{mV s}^{-1}$ ) essentially suggest a fast electron-transfer process of  $\text{Fe}(\text{CN})_6^{3-/4-}$  at the graphene film electrodes prepared here with Vaseline as the binder. Interestingly, when the content of the graphene dispersed in the Vaseline solution was decreased to 1.0  $\mu\text{g}/\text{mL}$ , the CV obtained at the as-prepared graphene film electrodes for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple changed dramatically as shown in Fig. 1B. A typical sigmoidal-shaped voltammetric response was obtained at the film electrodes, demonstrating that a nonlinear diffusion process was involved in the redox process of  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple and that the film electrodes behave as a nanoelectrode ensemble. The dependency of the CV shape of the graphene film electrodes on the graphene content in the Vaseline matrix could be understood by the different exposure of graphene from the insulating Vaseline layer and thereby the possibility of overlapping of the diffusion layer of the exposed graphene nanoelectrodes, as schematically shown in Scheme 1. For instance, the peak-shaped CV result obtained with the graphene film electrodes with a large amount of graphene in the Vaseline matrix was attributed to the close spacing of the graphene nanoelectrodes exposed from the insulating Vaseline matrix and thus the overlap of diffusion layer of each graphene nanoelectrode (Scheme 1A). Meanwhile, the sigmoidal-shaped voltammetric response obtained with the graphene film electrodes with a small amount of graphene in the Vaseline matrix was ascribed to the low surface density of graphene nanoelectrodes exposed from the Vaseline matrix [18,23]. In such a case, the diffusion layer of each exposed graphene nanoelectrode was well separated, resulting in a radial diffusion process at the as-prepared nanoelectrode ensemble (Scheme 1B).

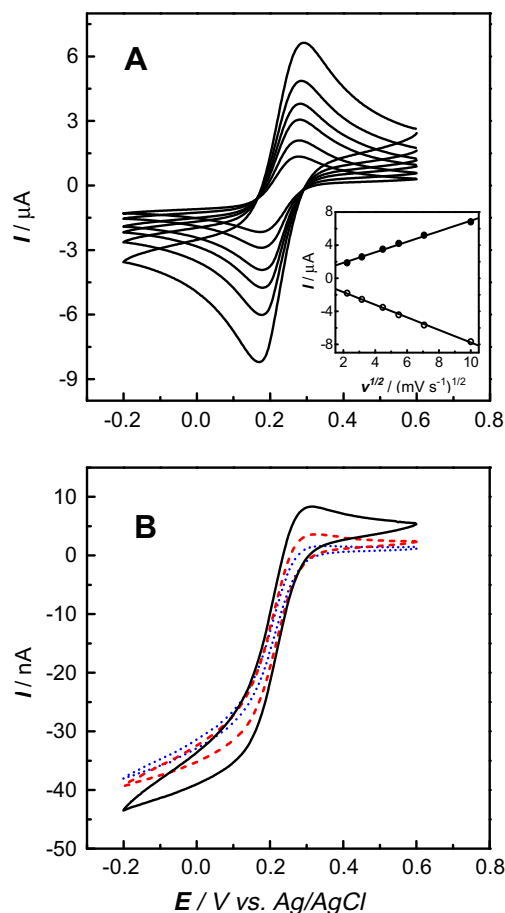


**Scheme 1.** Schematic illustration of the strategy for preparation of graphene film electrodes with tailor-made dimensions ranging from a conventional electrode (A) to a nano-electrode ensemble (B) by using Vaseline as the insulating binder.

The formation of the graphene film electrodes with tailor-made dimensions were further verified with the CVs obtained with the electrodes for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox couple at various potential scan rates, as shown in Fig. 2. At the film electrodes prepared with a large amount of graphene dispersed into the Vaseline matrix (i.e., 10.0  $\mu\text{g}/\text{mL}$ ), both anodic and cathodic peak currents clearly increase with increasing potential scan rate and are linear with the square root of the potential scan rate within a range from 5 to 100  $\text{mV s}^{-1}$  (Fig. 2A). These again demonstrate a semi-infinite linear diffusion-controlled feature of the redox process of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  couple at the electrodes, which is characteristic of the electrodes of a conventional dimension. While, at the film electrodes prepared with a low content of graphene in the Vaseline matrix (i.e., 1.0  $\mu\text{g}/\text{mL}$ ), the limiting currents are almost independent of potential scan rate up to 50  $\text{mV s}^{-1}$  (Fig. 2B), suggesting that the electrodes behave as a nano-electrode ensemble.

The results described above substantially demonstrate that the simply varying the content of graphene in the insulating Vaseline matrix could efficiently tune the dimensions of the as-prepared graphene film electrodes from a conventional electrode to a nano-electrode ensemble. Although some methods, such as sol-gel [24] and self-assembly monolayer [25], have been previously reported to prepare the electrodes with different dimensions, the method demonstrated here is still remarkable in terms of the method simplicity by simply adjusting the content of graphene into the Vaseline matrix and the use of low-cost Vaseline as the insulating binder as well as the biocompatibility of the Vaseline binder that could eventually enable the entrapments of biocatalysts, such as enzymes and proteins into the matrix to fabricate graphene-based biosensors.

In addition to the tailor-made dimensions, the graphene film electrodes with Vaseline as the insulating binder also possess a good electrochemical activity, which was evident from the small peak-to-peak separation obtained at the conventional electrodes (Fig. 1A) and the very slight hysteresis between the forward and backward sweeps obtained at the nano-electrode ensemble (Fig. 1B). Moreover, both the conventional electrode and the nano-electrode ensemble prepared in this study were durable for consecutive potential cycling and almost no decrease in the currents was observed after continuously scanning the electrodes in 0.10 M KCl solution containing 1.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  for at least 50 cycles. All these properties of the graphene film electrodes are envisaged to substantially enable them very useful not only for



**Fig. 2.** Typical CVs for 1.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  at the graphene film electrodes in 0.10 M KCl solution with various potential scan rates. The electrodes were prepared by mixing 10.0  $\mu\text{g}/\text{mL}$  (A) and 1.0  $\mu\text{g}/\text{mL}$  (B) graphene into the Vaseline solution. Scan rates in A were 5, 10, 20, 30, 50 and 100  $\text{mV s}^{-1}$  (from inner to outer). Inset, plots of anodic and cathodic peak currents against the square root of scan rates. Scan rates in B were 5  $\text{mV s}^{-1}$  (short-dotted blue curve), 10  $\text{mV s}^{-1}$  (short-dashed red curve) and 50  $\text{mV s}^{-1}$  (solid black curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fundamental electrochemical studies but also for electroanalytical applications.

#### 4. Conclusions

We have demonstrated a facile and effective method for the preparation of graphene film electrodes by simply using Vaseline as the insulating matrix to confine graphene onto electrode surface. The dimensions of the as-prepared film electrodes could be readily tailored from a conventional electrode to a nano-electrode ensemble by adjusting the content of graphene into the Vaseline matrix. The electrodes prepared here process a good electrochemical activity and stability and are thus envisaged to be useful for fundamental studies on carbon-based electrochemistry and for practical electrochemical applications.

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