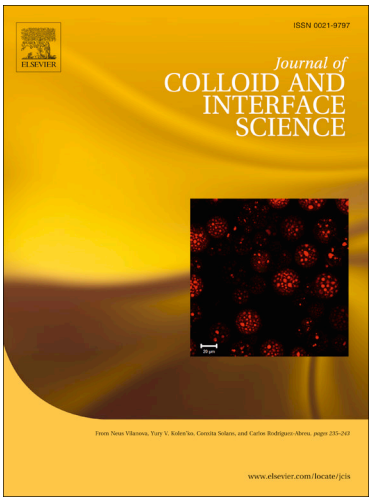

Regular Article

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The pristine graphene produced by liquid exfoliation of graphite in mixed solvent and its application to determination of dopamine

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Abstract:

The pristine graphene can be easily prepared in isopropanol-water mixture with salts as assistant via liquid-phase exfoliation method. The concentration of graphene dispersion reaches as high as 0.565 mg/mL. The graphene film prepared by drop-casting method shows an excellent electrical conductivity (7.095×10^4 S/m). Furthermore, an electrochemical biosensor based on the pristine graphene shows high selectivity and sensitivity for the determination of dopamine. The linear detection range for dopamine is 2.5-1500 μM with detection limit of 1.5 μM. This method provides a potential process for preparing high-quality graphene ready-to-use in low-boiling point solvent.

Key words: Graphene; Exfoliation; Mixed solvent; Salt; Electrochemical sensor

1. Introduction

Recent years, graphene has been received much attention due to its excellent physical and chemical properties such as high optical transparency (97.7%) [1], high mobility of charge carrier (1×10^5 $cm^2/V\cdot s$) [2], and superior electrical conductivity (1×10^6 S/m) [3]. So far, several routes for the production of graphene have been established such as mechanical exfoliation [4], epitaxial growth [5], chemical reduction of graphene oxide [6], and chemical vapor deposition (CVD) [7]. The above-mentioned methods have advantages and disadvantages [8]. For example, mechanical exfoliation method can prepare pristine graphene sheets but with low quantities. The epitaxial growth and CVD methods can generate large quantities and high quality graphene sheets but the conditions are complex and harsh. The chemical reduction of graphene oxide can produce graphene on a massive scale but with defects more or less. As a result, people are still committed to finding more efficient, low cost, and high yield methods for preparing high quality graphene nanosheets.

Liquid-phase exfoliation method is one of the alternative methods for facile production of graphene sheets. It is a way to exfoliate graphite to produce defect-free graphene in some well-chosen solvents with the help of ultrasonication [9]. However, the exfoliation efficacy in the pure solvents is usually very low and the process is time-consuming. Du et al. [10] found that some salts can greatly enhance the exfoliation efficacy in these organic solvents. The pristine graphene (PG) sheets obtained in these organic solvents have been applied to the electrochemical sensor successfully [11]. Because of the high surface energy of graphene, the best solvents

are likely to have high-boiling points and they are usually toxic and expensive [12]. Some cheap and volatile solvents with good biocompatibility have also been investigated for using as media for the liquid-phase exfoliation of graphite [13, 14]. They can be easily removed by simple vaporization, which is a desirable and important property in practical applications. However, usually much longer sonication times are needed in the case of these solvents with low-boiling point and the exfoliation efficiencies are commonly not very high [15].

Recently, some mixed solvent systems with low-boiling point have been studied for liquid exfoliation of graphite and its analogues such as boron nitride, molybdenum disulfide, and tungsten disulfide [16-18]. By choosing solvents with appropriate composition, highly stable graphene or graphene analogues suspensions can be obtained in mixtures of some low-boiling point solvents. The appropriate composition of mixed solvents can be partially predicted by the theory of Hansen solubility parameter (HSP) [19], which is a semi-empirical correlation developed to explain dissolution behavior of polymers [20]. The HSP distance R_a is often used to evaluate the compatibility between solvents and solutes (Eq. (1)).

$$R_a=\left[4\left(\delta_{D,solv}-\delta_{D,solu}\right)^2+\left(\delta_{P,solv}-\delta_{P,solu}\right)^2+\left(\delta_{H,solv}-\delta_{H,solu}\right)^2\right]^{0.5} \quad (1)$$

where δ_D, δ_P, and δ_H are the dispersive, polar, and hydrogen bonding solubility parameters of a solvent or solute, respectively. The smaller the R_a is, the more compatible the solute with the solvent becomes, and therefore the higher the solubility of the solute to be expected. For a solvent-mixed system, the δ_{blend} of the blend solvent can be calculated according to Eq. (2).

$$\delta_{\text{blend}} = \sum \Phi_{\text{n,comp}} \delta_{\text{n,comp}} \qquad (2)$$

where Φ is the volume percentage for each composition. Therefore the R_a of a blend can be reduced by adjusting its composition. For example, pure water and ethanol are both "poor" solvents for the exfoliation of graphite, while the mixture with an appropriate composition would become a "better" solvent, in which stable graphene dispersion can be obtained. Both Liu [17] and Chia [18] have reported the method of using water/ethanol mixture to prepare graphene nanosheets. However the reported exfoliation efficiencies are still low and more surprisingly the reported appropriate compositions are quite different, which may be related to the instability of graphene in this mixture system. The mixed solvent system of isopropanol (IPA) and water has been also investigated for the exfoliation of graphite [21]. Although the exfoliation efficacy in IPA-water mixture is better than that in pure IPA [22], pure ethanol [23], and ethanol-water mixture [18], it is still not very high. Herein we demonstrate the exfoliation efficacy can be further increased greatly by adding some salts to IPA/water mixtures. Our previous work has demonstrated that high quality defect-free PG can be obtained by the salt-assisted exfoliation in dimethyl sulfoxide (DMSO) and has been used to fabricate excellent electrochemical sensors [11]. However, DMSO has high-boiling point and is difficult to be removed, which makes it difficult to process PG into electrochemical sensor or other devices. Herein we demonstrate the PG obtained from the more volatile IPA/water system has the same high quality and this PG based electrochemical sensor also shows outstanding features for the determination of dopamine. This is the first time for the exfoliation of graphite via a

liquid-phase method in low-boiling point mixed solvent with addition of salts. The as-prepared PG could be directly and more easily applied to the electrochemical sensor.

2. Experimental

2.1 Materials

Natural graphite powder (particle size ≈ 10.4 μm), IPA, sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$), ethylenediaminetetraacetic acid disodium salt (EDTA-2Na), trisodium citrate dihydrate ($C_6H_7Na_3O_7 \cdot 10H_2O$), ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$), potassium chloride (KCl), and glucose (Glu) were purchased from Shanghai Chemical Reagent Co. Ltd. Dopamine (DA) and uric acid (UA) were bought from Aladdin. All the reagents are analytical grade except graphite. Phosphate buffer solution (PBS, pH = 7.0, 0.1 mol/L (M)) was prepared by sodium hydroxide and potassium dihydrogen phosphate. Deionized water (resistivity is 18.25 MΩ·cm) were used throughout the whole experimental process.

2.2 Methods

2.2.1 Preparation of pristine graphene sheets

PG dispersions were prepared by liquid-phase exfoliation of graphite in solvent under sonication. Briefly, 30 mg graphite powder and 60 mg salt were dispersed in 5.0 mL IPA-water mixture (volume percentage (vol%) of IPA is from 0% to 100%). The various mixtures were then placed in an ultrasonic cleaner with a frequency of 40 KHz (DTC-15, DingTai biochemical technology equipment manufacturing Co., Ltd.)

for 2 h at room temperature. After sonication, the as-prepared dispersions were then centrifuged for 30 min at 3000 rpm (relative centrifugal force is 850 g) using a UNIVERSAL 320 centrifuge (Hettich Co., Ltd., Germany). Finally, the supernatants were collected carefully using a pipette. The concentration of graphene dispersions were calculated based on the Lambert-Beer law ($A=\alpha \cdot C \cdot l$, where A is absorbance, α is absorption coefficient of 3620 mL/mg·m [12], C (mg/mL) is concentration, and l (m) is length of path. The PG dispersion (1 mg/mL) was prepared typically as follow: the as prepared PG dispersion was aggregated by adding few drops of saturated KCl solution, washed several times with water. Then the precipitate were dried in oven at 60 ºC for 5 h and re-dispersed in 80 vol% IPA-water mixture.

2.2.2 Preparation of sensors

A glassy carbon electrode (GCE, diameter: 3 mm) was polished with 1.0, 0.3, and 0.05 μm Al_2O_3 powder and then rinsed with 50 vol% ethanol/water mixture and ultrapure water successively. Then 20 μL 1 mg/mL PG was loaded on the GCE surface and dried at ambient temperature.

2.3 Characterization

UV-Vis absorption spectra were measured on a Shimadzu UV3600 spectrophotometer. Transmission electron microscopy (TEM) was performed on a Hitachi-7650 electron microscope operating at an accelerating voltage of 80 kV. The samples were prepared by dropping a diluted PG dispersion on holey amorphous carbon TEM grids (400 meshes). Atomic force microscope (AFM) measurement was taken on a Molecular Imaging PicoPlus AFM in an AC mode and sample was

deposited onto a fresh mica substrate by drop-casting. The electrical conductivity of sample film was measured by a four-point probe method using a resistivity meter (Loresta GP MCP-T610, Mitsubishi Chemical Corp.).

2.4 Electrochemical measurements

Cyclic voltammograms (CV), amperometric responses (i-t curve), and electrochemical impedances spectroscopy (EIS) were performed on a CHI 660c electrochemical workstation (Shanghai CH Instruments Co.). In a three-electrode system, a bare or modified GCE (PG/GCE) was used as the working electrode, a platinum ring as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. CV curves were measured in the potential range of -0.2 to 0.6 V at different scan rates. Amperometric responses were employed at an applied potential of 0.18 V. EIS were performed in the frequency range from 0.01 to 100 KHz.

3. Results and discussion

3.1 Optimize the condition of exfoliation

According to the HSP users' handbook [20], the HSP of water, IPA, and graphene are shown in Table 1. The R_a of a blend with different vol% of IPA is calculated according to the Eq. (1) and the δ_{blend} used in Eq. (1) is calculated according to Eq. (2). As shown in Figure 1a, for the IPA-water mixtures, the curve of the relationship between the R_a and vol% of IPA exhibits a parabola-like trend. The minimum of R_a is obtained at ~30 vol% of IPA. Figure 1b shows the photograph of several graphene

suspensions in different IPA-water mixtures. Pure IPA and pure water are "poor" solvents to disperse graphite just as shown by the highly transparent, almost colorless supernatants in Figure 1b. However, the IPA-water mixtures with different compositions exhibit significantly different dispersing ability toward graphene. At appropriate IPA-water ratios, dark dispersions of graphene were obtained. A maximum concentration (0.050 mg/mL, estimated by UV–Vis absorbance) of the centrifuged dispersion was obtained at the ~30 vol% of IPA, highly consistent with the calculated result by HSP theory. However, it should be noted, both the maximum concentration, best IPA-water ratio or the minimum R_a for IPA-water system are quite different from the data reported in the literature [21]. The maximum concentration in this work (0.050 mg/mL) is much higher than that in literature (0.021 mg/mL) [21] and it is obtained in an IPA-water system with ~30 vol% of IPA (or ~25% mass fraction of IPA) together with the minimum R_a, quite different from the most appropriate ratio which has been reported (~55% mass fraction of IPA) [21]. The different calculated result of R_a should be due to the different HSP value (δ_D, δ_P, and δ_H) of water selected. Actually, four sets of HSP value for water have been reported in literature [20]. The selection of HSP value of water is important and should be done carefully. The experimental date obtained in this work prefer to support the set of HSP value of water with δ_D, δ_P, and δ_H as 18.1, 12.9, and 15.5, respectively, as shown in Table 1. With this set of HSP value, the calculated minimum R_a matches the appropriate composition perfectly, as shown in Figure 1. However, the maximum concentration in IPA-water mixture (0.050 mg/mL) is still lower than those obtained

in the mixtures of high-boiling point solvents [24]. In order to further increase the exfoliation efficacy, some salts were added into this IPA-water system to investigate their possible assistant effect.

Figure 2a shows the concentrations of various graphene dispersions prepared in IPA-water mixtures with addition of different kinds of salts: EDTA-2Na (△), $C_6H_7Na_3O_7 \cdot 10H_2O$ (●), $(NH_4)_2C_2O_4 \cdot H_2O$ (○), and $Na_4P_2O_7 \cdot 10H_2O$ (▼), respectively. For comparison, the concentrations of graphene dispersions prepared in various IPA-water mixtures (▲) without any salt are also shown in Figure 2a. The concentrations of PG dispersions obtained in various systems are summarized in Table 2. In pure IPA, all the four salts can enhance the exfoliation efficacy and $C_6H_7Na_3O_7 \cdot 10H_2O$ shows the best effect, with which the PG concentration is 20 times enhanced. However, in IPA-water mixtures, $C_6H_7Na_3O_7 \cdot 10H_2O$ shows the worst effect, instead, $Na_4P_2O_7 \cdot 10H_2O$ shows the best effect. With the addition of $Na_4P_2O_7 \cdot 10H_2O$, the PG concentration arrives 0.565 mg/mL, which is 280 times enhanced compared to that in pure IPA (0.002 mg/mL), over 10 times higher than the highest concentration can be obtained in IPA-water mixture without salts (0.050 mg/mL), and even close to or higher than those obtained in mixtures of high-boiling point solvents [25]. This may be due to the strong complexation ability of the pyrophosphate ion, which can easily adsorb on the surface of graphene. The graphene sheets with the same charge would repel each other and form a stable solution [26]. The photographs of various dispersions obtained in IPA-water-$Na_4P_2O_7$ system are shown in Figure 2b. The supernatants prepared in 50 vol% to 90 vol% of IPA are dark black, while other

supernatants are almost transparent. The best proportion of IPA in IPA-water-$Na_4P_2O_7$ system is around 80 vol%, different from that in IPA-water without salt (30 vol%). The addition of other three salts also cause the variation of the best proportion of IPA, all change from 30 vol% to 90 vol%, as shown in Table 2. It might indicate that HSP theory is no longer suitable in a mixed-solvent system with addition of salts. The concentrations of graphene dispersions in literature [27-29] are shown in Table 3 for comparison.

3.2 Characterization of pristine graphene

The UV-Vis absorption spectrum of graphene dispersion obtained from different exfoliation solvent-mixed system: 90 vol% IPA with $C_6H_7Na_3O_7 \cdot 10H_2O$ (a), 90 vol% IPA with EDTA-2Na (b), 30 vol% IPA without any salts (c), 90 vol% IPA with $(NH_4)_2C_2O_4 \cdot H_2O$ (d), and 80 vol% IPA with $Na_4P_2O_7 \cdot 10H_2O$ (e) are shown in Figure 3. The strong absorption peaks appear at 268 nm in all those systems, indicating the obtained graphene has a completely π-conjugated structure [30].

Figure 4a and 4b shows the TEM images of graphene sheets prepared in IPA-water and IPA-water-$Na_4P_2O_7$. The sizes of graphene sheets are about hundreds nanometer. Figure 4c shows the AFM image of graphene sheet obtained in IPA-water-$Na_4P_2O_7$ system containing 80 vol% IPA. The thickness of graphene sheet is about 0.4 nm as shown in Figure 4d, which indicates the obtained graphene sheet is single-layered. The results show that graphite can be successfully exfoliated in IPA (80 vol%)-water-$Na_4P_2O_7$ system. The graphene dispersion obtained in this system is therefore used for the further electrochemical application.

3.3 Electrochemical detection of dopamine

The electrochemical detection of DA was investigated by CV. Figure 5 depicts the CV behavior of 1 mM DA detected on bare GCE and PG/GCE in PBS solution. There are no redox peaks shown on GCE and PG/GCE in blank solutions. A pair of well-defined redox peaks is observed on PG/GCE when the solution containing 1 mM DA and its peak current is much higher than that on the bare GCE. This may be due to the fact that PG has a good electroactive and a large surface area, which offers many active sites to improve the transfer of electrons between the DA and electrode.

The possible reaction mechanism of detecting DA on PG/GCE can be discussed as follows: at the anodic scan, DA molecular is transformed into dopamine-o-quinone (DOQ) under electrochemical oxidization with releasing two protons and two electrons. At the cathodic scan, the DOQ molecular is returned into DA molecular under electrochemical reduction [31,32]. The process is shown in Figure 6.

Figure 7 shows the EIS results of GCE and PG/GCE in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{4-/3-}$. A small semicircle appears at the high frequency on GCE, the diameter of the semicircle is usually regarded as the charge transfer resistance (R_{ct}). In comparison, there is almost no semicircle at the high frequency on GCE/PG, indicating a negligible R_{ct} and a fast transfer of electrons on the surface of PG/GCE [2].

The reaction kinetic of DA on the PG/GCE was illustrated by investigating the relationship between peak currents and scan rates. Figure 8a shows the CV behavior of 1 mM DA detected on PG/GCE in PBS solution at various scan rates from 10 to

400 mV/s. As shown in Figure 8b, the oxidation peak currents are proportional to the square root of the corresponding scan rates, indicating the electrochemical reaction of DA on the PG/GCE can be considered as a diffusion-controlled process.

Figure 9 depicts the amperometric response of DA on PG/GCE by successively adding DA into a continuous stirring PBS solution at the working potential of 0.18 V. The inset in Figure 9a shows the linear relationship between the concentration of DA and the corresponding I_{pa}. The linear equation is described as I_{pa} (μA) = (0.1044 ± 0.0022) C (μM) + (0.1431 ± 0.0748), with a correlation coefficient (R^2) of 0.9909. The response range is 2.5-1500 μM and the detection limit is 1.5 μM at a signal to noise ratio of 3. Figure 9b is the magnified portion of the amperometric responses curves with low concentrations of DA. The different modified electrodes in the detection of DA are given in Table 4 for comparison [11, 33-36]. The sensor based on PG in this work shows lower detection limit compared to the other modified electrodes.

Selectivity is an important parameter for a sensor. Figure 10 shows the amperometric responses of 30 μM DA in the presence of 30 μM UA and 30 μM Glu. The DA shows a clear amperometric response, while UA and Glu have not exhibit any obvious amperometric signals. In addition, the addition of UA and Glu do not disturb the continued determination of DA. These results suggest that the fabricated sensor exhibited an excellent selectivity towards DA.

4. Conclusions

In this work, few-layered graphene sheets were easily obtained in low-boiling point mixtures of isopropanol and water with addition of $Na_4P_2O_7 \cdot 10H_2O$ as assistant. The concentration of graphene dispersion is as high as 0.565 mg/mL. This is the first time for the exfoliation of graphite in a salt-assisted low-boiling point mixed-solvent system. The exfoliating efficiency is increased up to 10 times compared with the best in IPA-water mixtures without salts, and close to or even higher than those in mixtures of high-boiling point solvents. The graphene obtained in this low-boiling point solvent with salts as assistant can also be used for electrochemical sensor. The sensor exhibits a wide detection range, low detection limit, and a high selectivity toward DA.

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Figure captions

Figure 1 (a) The value of C_{PG} (the concentration of PG, black filled square) and R_a (the HSP distance, red filled circle) in mixed-solvent system with different volume percentage of IPA from 0% to 100%. (b) Photographs of graphene suspensions in different IPA-water mixtures.

Figure 2 (a) The corresponding concentrations of various graphene dispersions prepared in 5 mL IPA-water mixed-solvent system without salts (▲) or with addition of EDTA-2Na (△), $C_6H_7Na_3O_7 \cdot 10H_2O$ (●), $(NH_4)_2C_2O_4 \cdot H_2O$ (○), and $Na_4P_2O_7 \cdot 10H_2O$ (▼). (b) Photographs of the graphene dispersions prepared in 5 mL IPA-water mixture with $Na_4P_2O_7 \cdot 10H_2O$.

Figure 3 Typical UV-Vis absorption spectrum of graphene dispersion prepared in different exfoliation solvent-mixed system: 90 vol% IPA with $C_6H_7Na_3O_7 \cdot 10H_2O$ (a), 90 vol% IPA with EDTA-2Na (b), 30 vol% IPA without any salts (c), 90 vol% IPA with $(NH_4)_2C_2O_4 \cdot H_2O$ (d), and 80 vol% IPA with $Na_4P_2O_7 \cdot 10H_2O$ (e).

Figure 4 TEM images of graphene sheets produced by different exfoliation solvent-mixed system: 30 vol% IPA without any salts (a) and 80 vol% IPA with $Na_4P_2O_7 \cdot 10H_2O$ (b). AFM image of graphene sheet obtained in IPA-water-$Na_4P_2O_7$ system containing 80 vol% IPA (c) and the corresponding line profile taken along the green line (d).

Figure 5 CV curves on GCE and PG/GCE in blank PBS (pH = 7.0, 0.1 M) solution or containing 1 mM DA. Scan rate: 50 mV/s.

Figure 6 Schematic illustration of reaction mechanism for detecting DA .

Figure 7 EIS of GCE and PG/GCE in 0.1 M KCl solution containing 5 mM $[Fe(CN)_6]^{4-/3-}$.

Figure 8 (a) CV curves on PG/GCE in PBS (0.1 M, pH = 7.0) containing 1 mM DA at various scan rates from 10 to 400 mV/s. (b) The relationship between oxidation peak currents and various scan rates.

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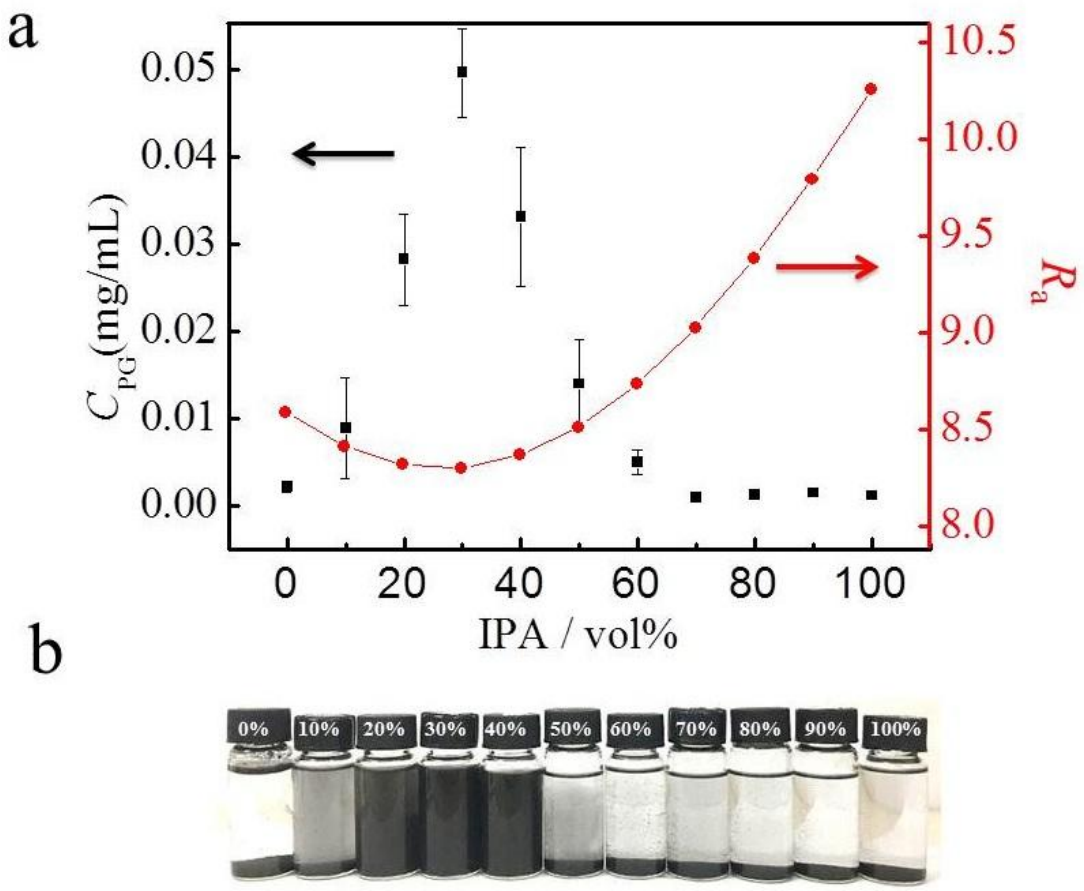
Table 3 The concentration of graphene dispersion prepared via other liquid-phase system for comparison.

Table 4 Liner range and detection limit from literatures for comparison.



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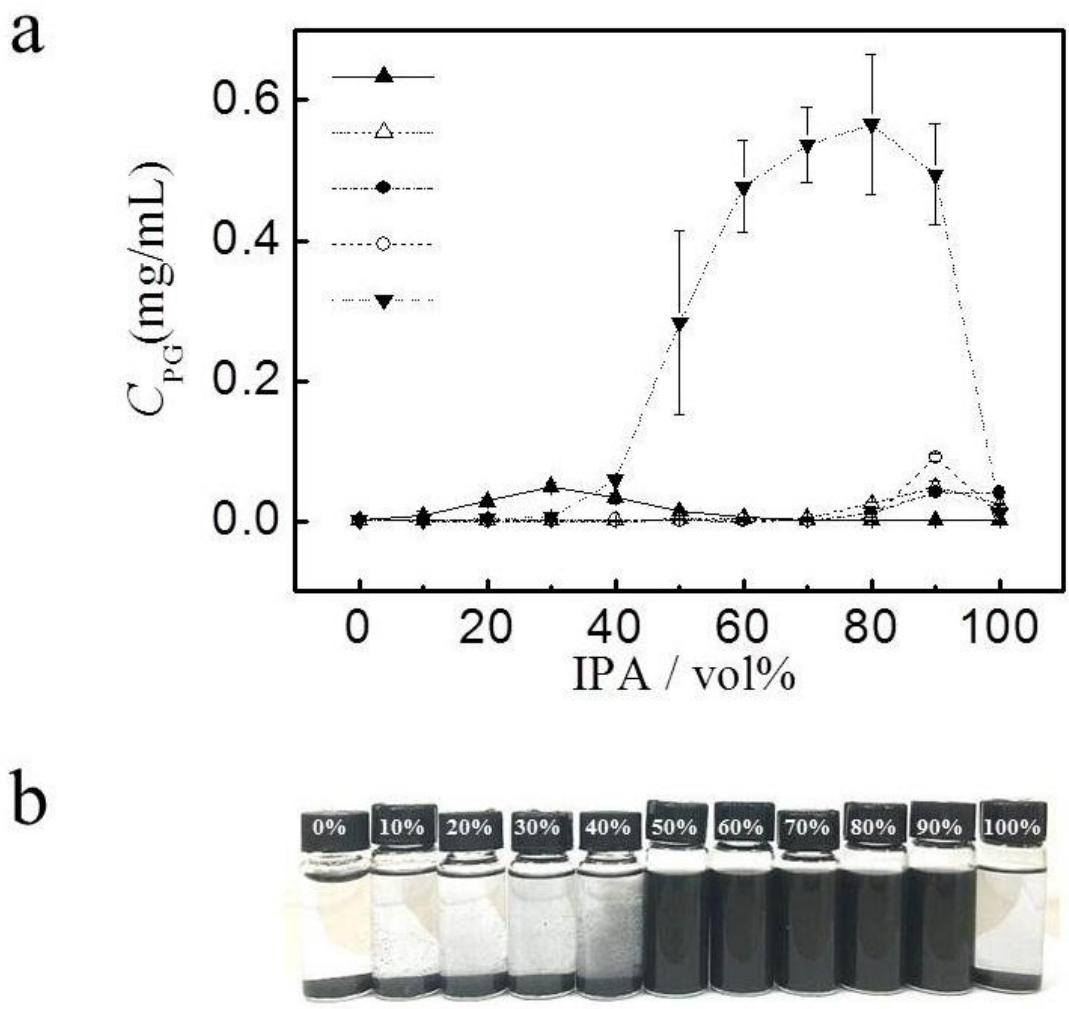

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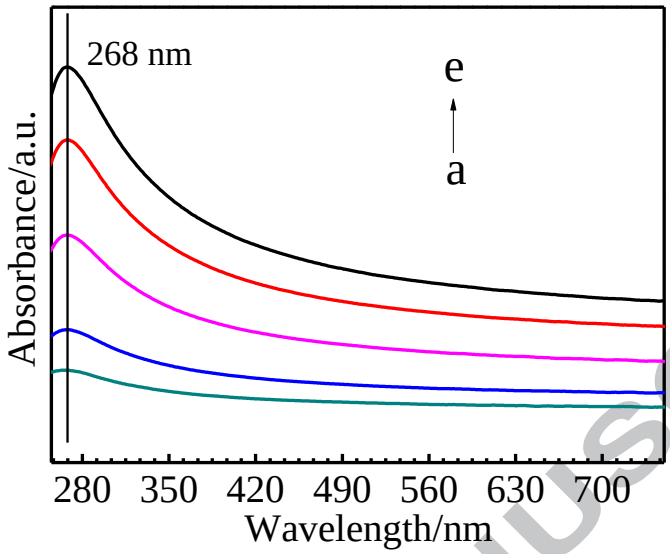

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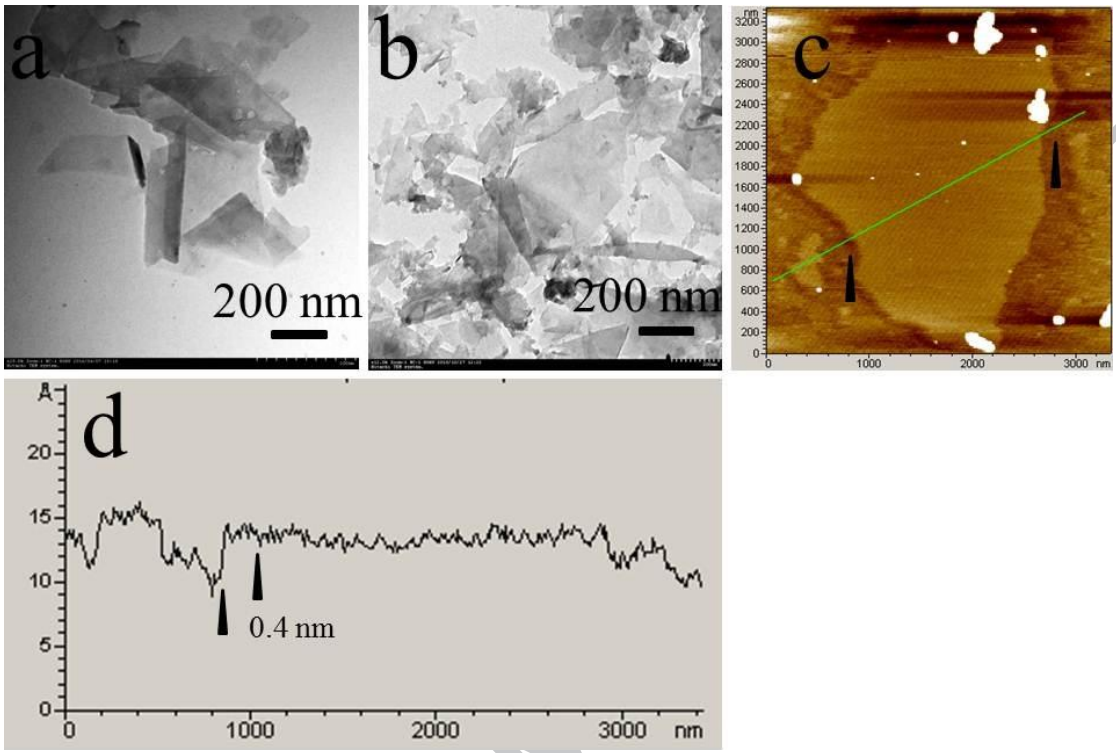

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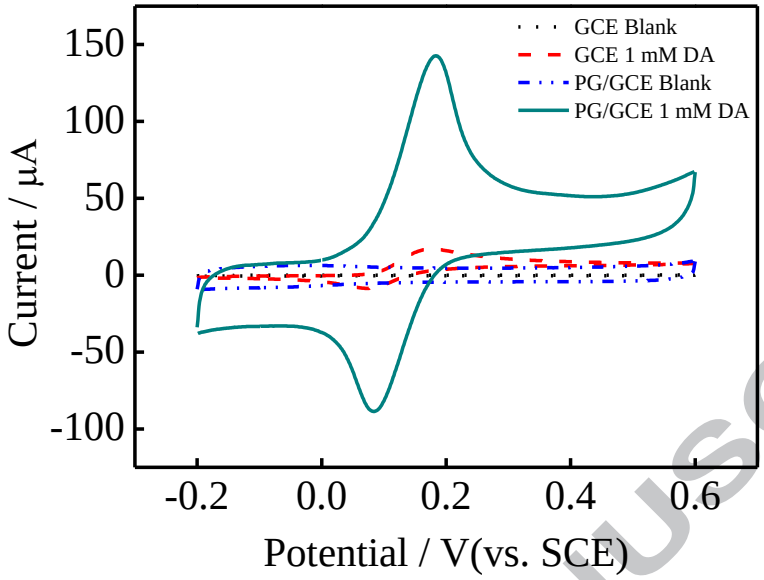

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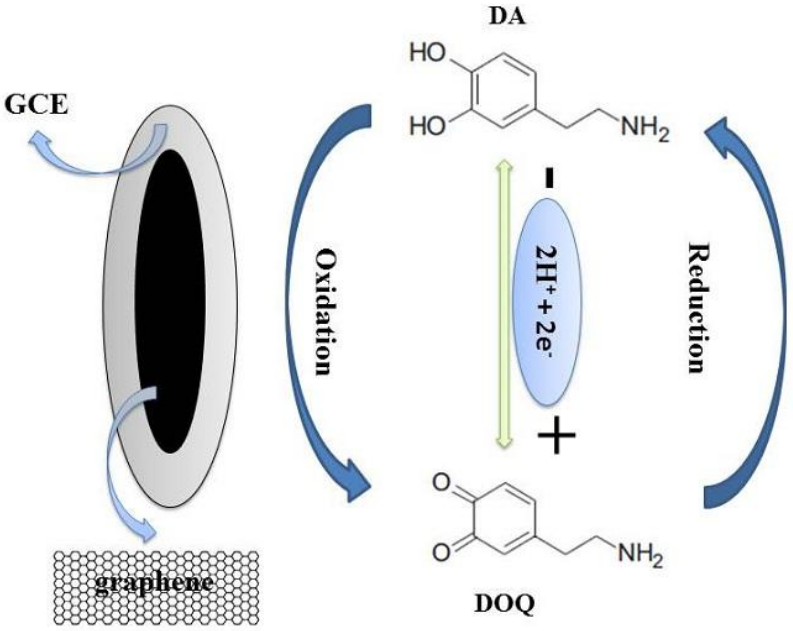

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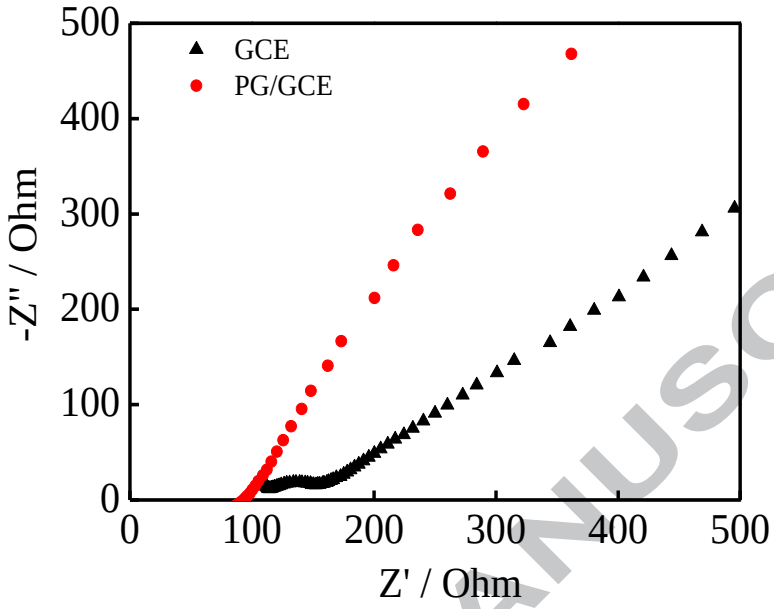

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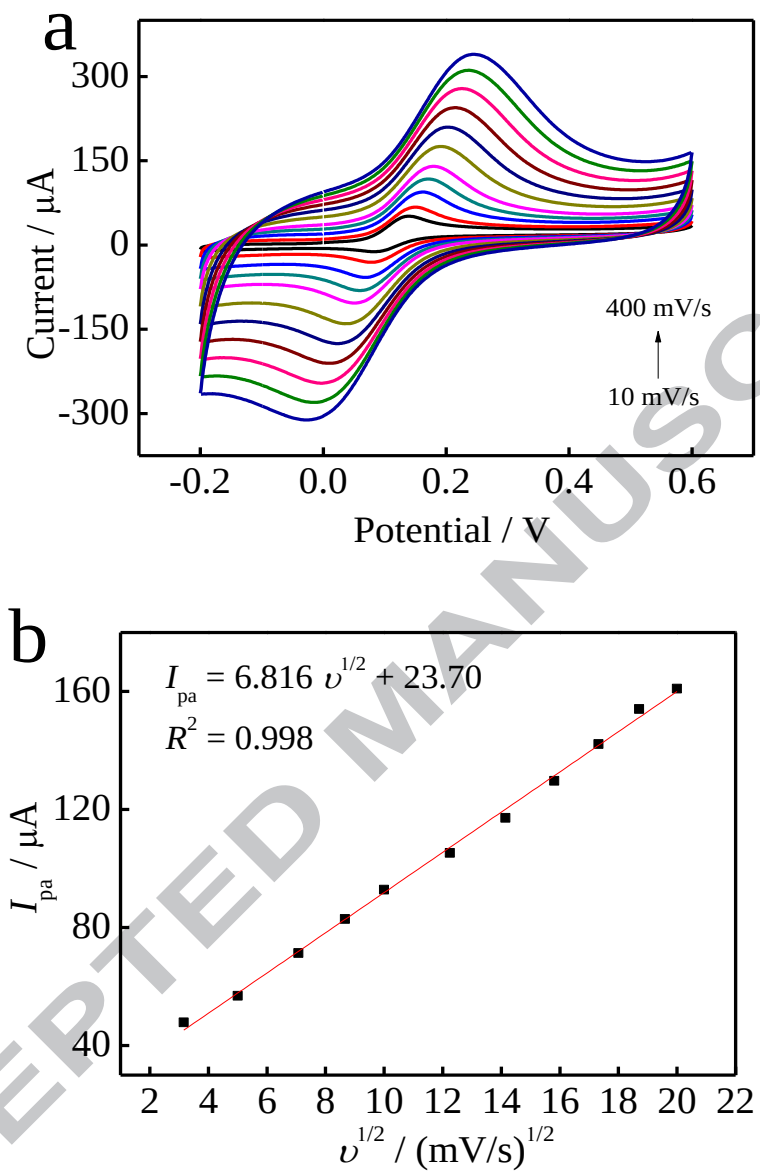

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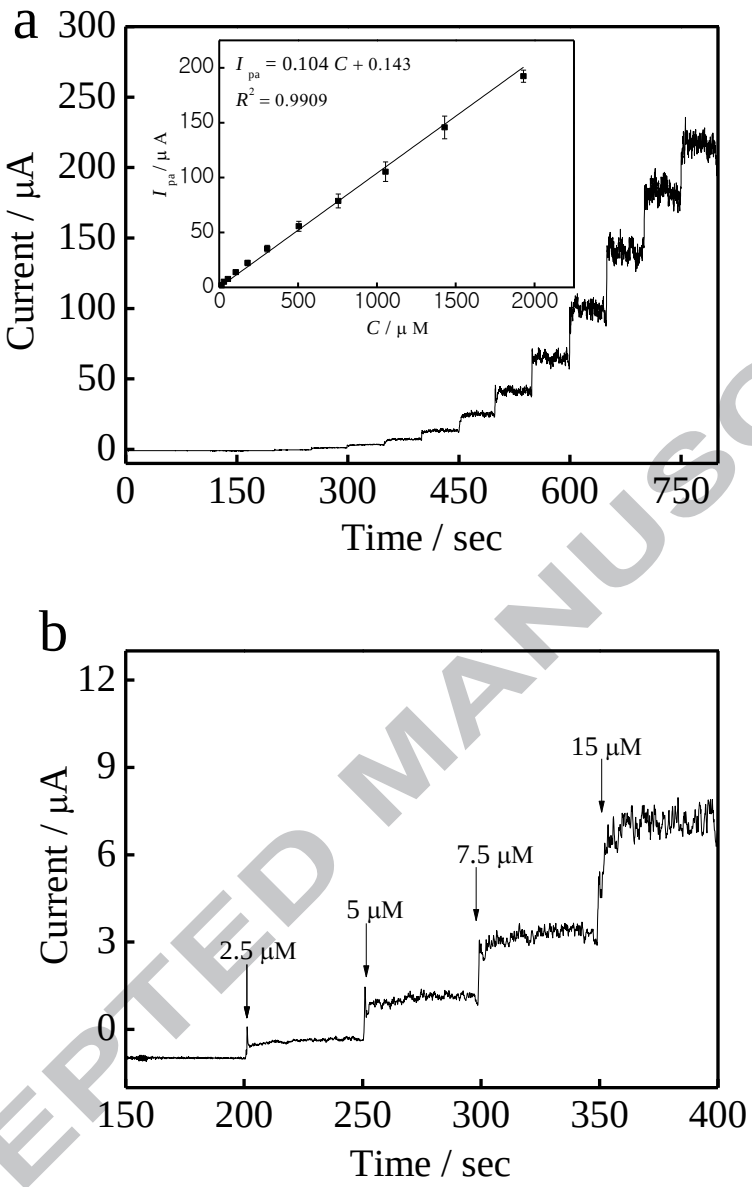

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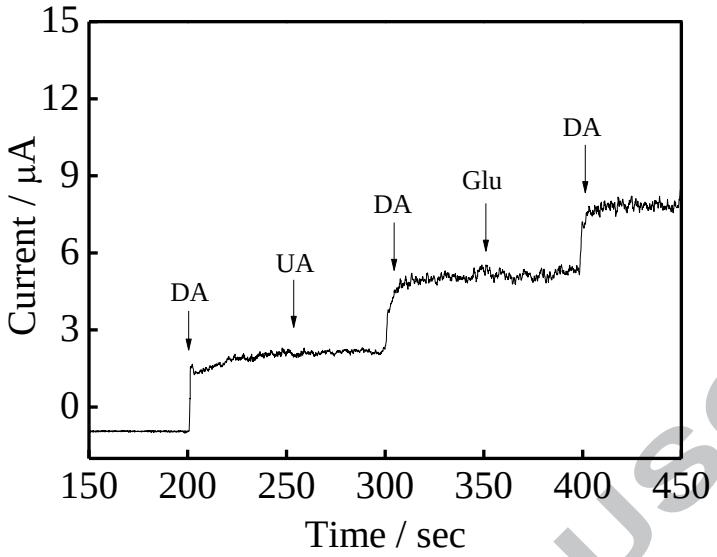

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Table 1 HSP of the substances.

substances	δ_D	δ_P	δ_H
IPA	15.8	6.1	16.4
Water	18.1	12.9	15.5
Graphene	18.0	9.3	7.7

Table 2 The concentrations (mg/mL) of PG dispersion obtained in pure IPA, IPA-Water, and IPA-Water-salt.

Salts	Pure IPA	IPA-Water
Without salts	0.002	0.050 (30 vol% IPA)
EDTA-2Na	0.023	0.049 (90 vol% IPA)
$C_6H_7Na_3O_7 \cdot 10H_2O$	0.041	0.042 (90 vo% IPA)
$(NH_4)_2C_2O_4 \cdot H_2O$	0.011	0.091 (90 vol% IPA)
$Na_4P_2O_7 \cdot 10H_2O$	0.024	0.565 (80 vol% IPA)

Table 3 The concentration of graphene dispersion prepared via other liquid-phase system for comparison.

Solvents	Exfoliation conditions	*C* (mg/mL)	Ref.
Acetone/THF[a]/water	Horn-probe sonication, 1 h	0.26	27
1,2-DCB[b]/isobutanol (9:1)	Bath sonication, 1 h	0.10	28
NMP/NaOH	Bath sonication, 1.5 h	0.07	29
IPA/H_2O (4:1)	Sonication, 2 h	0.565	This work

[a] THF: tetrahydrofuran;

[b] 1,2-DCB: 1, 2-Dichlorobenzene.

Table 4 Liner range and detection limit from literatures for comparison.

Electrode	Linear range (μM)	Detection limit (μM)	Ref.
PG/GCE	5-710	2.00 ± 0.25	[11]
CRGO[a]/GCE	4-100	2.64	[33]
SDS[b]/CPE[c]	8-134	3.70 ± 0.01	[34]
PEDOT[d]/MPE[e]	12-48	1.5	[35]
TiO_2/graphene/GCE	5-200	2	[36]
Pristine graphene/GCE	2.5-1500	1.5	This work

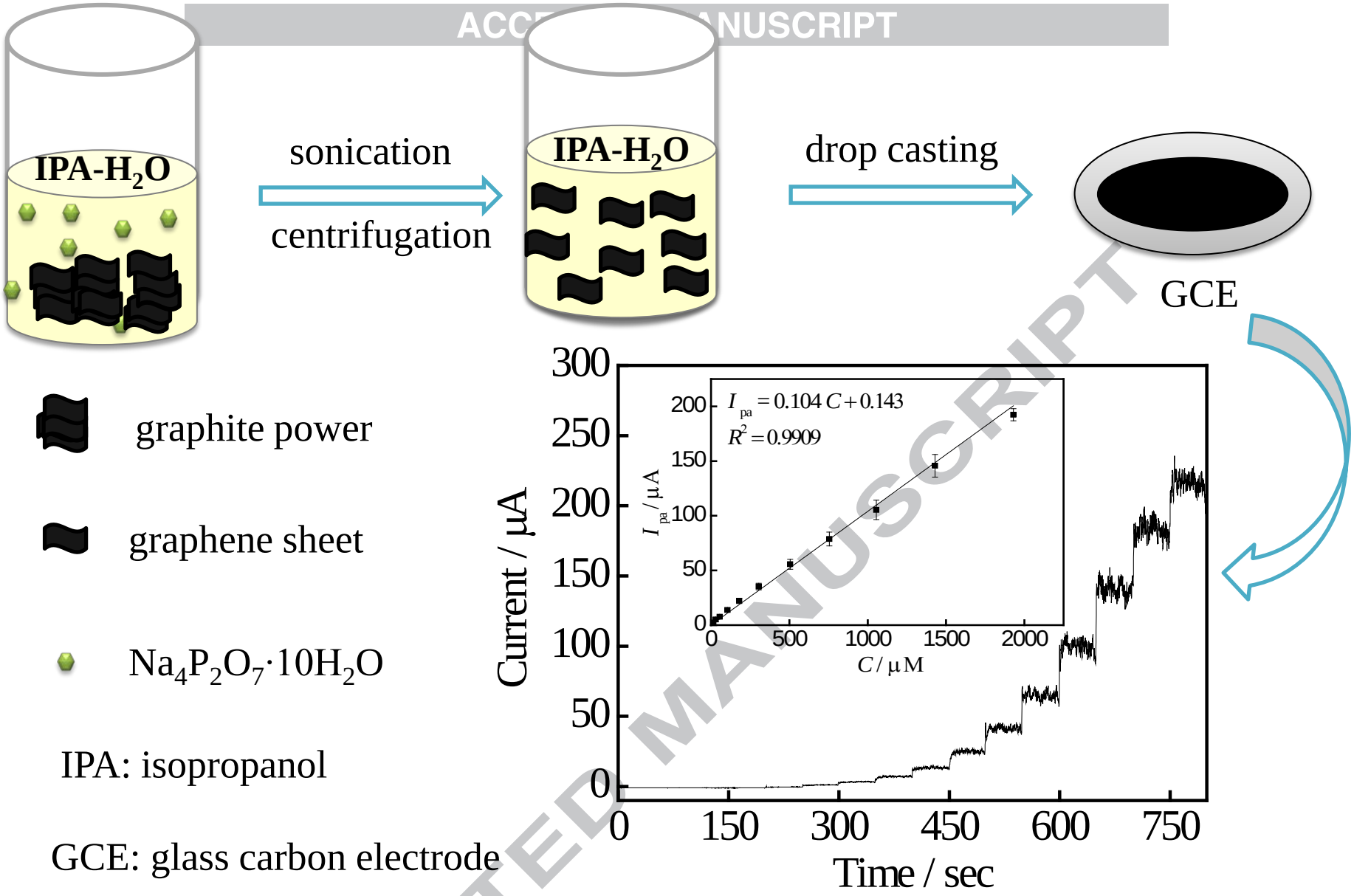
[a] CRGO: chemical reduction of graphene oxide;

[b] SDS: sodium dodecyl sulfate micelles;

[c] CPE: carbon paste electrode;

[d] PEDOT: 3,4-ethylenedioxythiophene;

[e] MPE: Ni/silicon microchannel plate electrode.



Preparation of pristine graphene in IPA-water-$Na_4P_2O_7$ and its application to determination of dopamine