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A direct and sensitive electrochemical sensing platform based on ionic liquid functionalized graphene nanoplatelets for the detection of bisphenol A

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ABSTRACT

A simple electrochemical sensor for bisphenol A (BPA) was developed based on a composite of graphene nanoplatelets (GNPs) and 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate (ionic liquid, IL) as a modifier for glassy carbon paste electrodes (GCPEs). Scanning electron (SEM) and atomic force microscopy (AFM) were employed to characterize the morphology and surface modification. The electrochemical behavior of BPA on IL-GNP/GCPEs was investigated and the results showed that IL-GNP composites enhance the electrochemical signal toward BPA due to the synergetic effect of GNPs and IL. The experimental parameters including the amount of IL and GNPs, pH of solution, pulse potential, step potential, and scan rate were optimized. Under optimal conditions, the proposed sensor exhibited a linear relationship between signal and BPA concentrations ranging from 0.02-5.0 µM, with detection and quantification limits of 6.4 nM and 0.02 µM respectively. Moreover, the electrochemical sensor showed good repeatability (RSD = 3.3 %, n = 5 measurements), good reproducibility (RSD = 3.8 %, n = 5 sensors), high accuracy of 95.3-104.5% recovery, acceptable selectivity, and stability. The sensor was successfully applied to the determination of BPA in water samples in contact with plastic materials. The results were satisfactory and in agreement with reference values from a standard HPLC method.

Keywords: Bisphenol A, Electrochemical sensor, Graphene nanoplatelets, Ionic liquid

1. Introduction

Bisphenol A (BPA, 2,2-bis (4-hydroxyphenyl) propane) is a major monomer in the industrial production of polycarbonate polymers, epoxy resins, and numerous plastic articles. These have been widely used as containers for feed, water, food, inner surface coating of cans, dental sealants, and many other products [1-3]. However, BPA can easily migrate into the environment, food, and drinking water from the packaging products leading to negative health effects in humans upon exposure due to its endocrine-disrupting properties by mimicking estrogens [4-6]. In a recent report, the European Food Safety Authority suggested a tolerable daily intake level for BPA of 4 µg.kg^{-1} body weight per day [7]. Thus, it is desirable to develop a rapid, simple, sensitive and cost-effective method for the determination of BPA in daily life.

Several methods are available for the determination of BPA, such as gas chromatography [8], liquid chromatography [9], enzyme linked immunosorbent assays [10], chemiluminescence [11], and sensors based on quartz crystal microbalance [12], fluorescence [13], and electrochemistry [14-16]. Among these strategies, electrochemical detection is an attractive method because of fast response, low cost, easy preparation, instrument simplicity, high sensitivity, excellent selectivity, and real-time detection.

Recently, graphene nanoplatelets (GNPs) and their derivatives have attracted much interest for both fundamental investigations and applications because of their large surface area, high thermal and electrical conductivity, high mechanical strength, and fast electron transfer rate [17, 18]. They were used to develop electrochemical sensors to enhance the sensitivity for the detection of BPA. It is an electroactive molecule due to phenolic groups but its direct electrochemical oxidation is sluggish therefore using graphene nanoplatelets can improve the sensitivity [19].

However, GNPs have a high specific surface area and tend to irreversible aggregation through *Van der Waals* forces. This limits its practical applications [20]. Ionic liquids (ILs) have received great interest due to several recent reports which proved that they may facilitate the dispersion of GNPs by introducing a surface charge [21]. Moreover, ILs have been widely

used as electrode modifiers for the fabrication of electrochemical sensors because of their high ionic conductivity, wide electrochemical window, and good chemical stability [22]. The integration of ILs into functional graphene composites may not only increase their dispersibility but also improve their electrochemical performance.

Carbon-based composite electrodes are widely used in electrochemical analysis due to the fact that they can be adapted to various electrode configurations with great flexibility in size and shape as well as their low cost, easy preparation, and renewal. Among these, glassy carbon paste electrodes (GCPEs) are a kind of carbon composite based electrode that combines the favorable electron transfer kinetics of glassy carbon with the advantages of composite paste electrodes [23, 24]. Therefore, GCPEs provide high electrochemical reactivity and a wide potential window with low background signal, and are suitable for various sensing and detection applications.

In this work, a sensitive electrochemical sensor based on an IL-GNP composite as a modifier for GCPEs was designed for the determination of BPA.

2. Experimental

2.1. Chemicals and reagents

Bisphenol A (BPA, $\geq$ 99%), glassy carbon powder (< 20 µm), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ($C_9H_{17}BF_4N_2$, $\geq$ 99%) and N,N dimethylformamide anhydrous (DMF, C_3H_7NO, 99.8%) were purchased from Sigma Aldrich. Graphene nanoplatelets (2-10 nm thickness) were purchased from Advanced Chemicals Supplier (ACS Material, Medford, USA). Anhydrous ethanol for preparing the BPA stock solution was obtained from CARLO ERBA. Phosphate buffer solutions (PBS, 0.1 M) with various pH values were used as supporting electrolyte prepared by mixing solutions of potassium dihydrogen phosphate (0.1 M) and disodium hydrogen phosphate (0.1 M). Water plastic bottles were purchased from a local market in Thailand. All other chemicals were of analytical reagent grade (Sigma Aldrich) and were used directly without further purification. Highly pure water (Milli-Q cartridge system, 18.2 MΩ.cm) was used throughout the experiments. Dilution of working solutions and samples was performed just before analysis with the proper phosphate buffer solution.

2.2. Apparatus and materials

The morphology of IL-GNP composites was recorded by a scanning electronic microscope (SEM, JSM-6010-LV, JEOL, USA). The glassy carbon paste was attached on the stub where non-porous carbon tapes had been placed before. The surface of the paste was polished with a Teflon sheet, and then the IL-GNP mixture was directly dropped onto the paste and allowed to dry completely in a desiccator. Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific, USA) was performed using the KBr pellet technique by mixing of 1 mg modifiers with 0.1 g KBr. The modified electrode surface was investigated by atomic force microscope (AFM, XE-100, Park systems, Korea). The smooth glassy carbon paste was placed on a microscope glass slide for AFM measurements analyzed in a (30 µm x 30 µm) area under ambient conditions. The experiments were performed using a silicon cantilever tip with the size of 125 µm length, 30 µm widths and 4 µm thicknesses. The tip had a radius of less than 10 nm and was operated with a frequency of 330 kHz and a constant force of 42 N/m. Imaging was carried out using taping mode at a scan rate of 0.3 Hz, 18.2 nm amplitude, 7.7 nm set point, and Z servo gain of 3.0. All electrochemical experiments were performed using a computer-controlled electrochemical workstation (Autolab, PGSTAT128N,

Metrohm, Switzerland) and evaluated with the corresponding software (NOVA software version 1.8). A conventional three-electrode system was carried out with a modified glassy carbon paste electrode (diameter 10 mm) as the working electrode, an Ag/AgCl (3 M KCl, Metrohm, Switzerland) as the reference electrode, and a platinum wire as the counter electrode (Metrohm, Switzerland). The pH was measured with a pH-meter (pH series 510, Eutech Instruments, The Netherlands). High performance liquid chromatography (HPLC, Ultimate 3000, Thermo Dionex, Archemica International, Germany) was used as a comparative method for the analysis of the samples.

2.3. Preparation of IL-GNP composite suspension and the electrochemical sensor

IL-GNPs were prepared according to previous studies [25] by dispersion of the GNPs in DMF (1.0 mg.mL^{-1}) using an ultrasonicator (CP1100T, CREST ultrasonics, Malaysia) for approximately 2 h to get a homogeneous suspension. Next, 20 µL of 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (IL) was added to the well-dispersed graphene suspension and sonicated for a further 30 min. Finally, the resulting mixture was centrifuged (D-37520, Sorvall Biofuge pico, Germany) at 10,000 rpm for 10 min. The supernatant was discarded and the solid residue was re-dispersed in 500 µL DMF and sonicated for a further 30 min before use.

The unmodified GCPE was prepared by weighing 1.4 g of glassy carbon powder and 0.6 g of mineral oil (70:30 m:m) and manually mixing in a mortar and grinding homogeneously. The glassy carbon paste was filled in the drilling hole of an electrode holder with a diameter of 1 cm and a depth of 0.5 cm. Contact to the paste was made with a copper wire through the electrode holder. The surface of the paste was polished with a Teflon sheet to a smooth and shiny appearance. For modification 7 µL of the IL-GNP mixture was directly dropped onto the sensing area of the GCPE surface and allowed to dry completely at room temperature to give a uniformly coated electrode (IL-GNP/GCPE). The procedure for the preparation of the modified electrode is illustrated in Fig. 1A.

2.4. Electrochemical measurements

Cyclic voltammetry (CV) was carried out by sweeping the potential from -0.5 to +1.0 V at a scan rate of 0.1 V.s^{-1} in a 10 mL electrochemical cell containing 0.1 M KCl and 5 mM Fe(CN)$_6^{3-/4-}$. The EIS curves were recorded in 0.1 M KCl containing the mixed solution of 5 mM K$_3$[Fe(CN)$_6$] and 5 mM K$_4$[Fe(CN)$_6$] within a frequency range of 10,000-0.1 Hz and an amplitude of 0.01 V.

Differential pulse voltammetric (DPV) measurements were recorded with 10 mL of PBS solution (pH 8.0) containing BPA with different concentrations in the potential range from +0.2 to +1.0 V with a pulse amplitude of 75 mV, a step potential of 30 mV, and a scan rate of 50 mV.s^{-1}. All experiments were carried out at room temperature.

2.5. Chromatographic conditions

The HPLC system consisted of a chromatographic pump, an autosampler injector with a 100 µL sample loop, a C18 column (4.6 x 250 mm, Acclaim^{TM}120), and a diode array detector (Ultimate 3000, DIONEX, Germany). The HPLC measurement was adapted from previous studies [26-28] and the conditions for HPLC analyses were optimized isocratically using a mixture of acetonitrile and water (60:40, v:v) as a mobile phase which was sonicated and degassed before use. The flow rate was 1.0 mL.min^{-1} and the detection wavelength 228 nm. Analysis of each sample was performed in triplicate.

2.6. Sample preparation

The extraction of BPA from plastic bottles and water samples were conducted following the procedure reported elsewhere [29, 30] but with a minor modification. Plastic bottles (drinking water bottles) produced from poly ethylene terephthalate and polyethylene were purchased from a local supermarket (Ubon Ratchathani, Thailand). They were cut into small pieces and cleaned thoroughly with highly pure water, then powdered using a grinder (A11 basic Analytical Mill, Industries Kaiser Argentina, Germany). After sieving (300 Mic., ASTM E11, Endecotts Ltd., England), about 1.00 g of each plastic powder was added to 20 mL of acetonitrile, which was sealed and extracted by ultrasonication for 2 h. After filtration the liquid phase was concentrated by a rotary evaporator (Hei-VAP Precision, Heidolph Instruments, Germany). Then, BPA standard solution (1 mg/mL of final concentration) was spiked into the obtained samples for recovery tests.

Drinking water sample (100 mL) from the plastic bottle was placed into a 250 mL separatory funnel. BPA in the drinking water sample was extracted with 45 mL of dichloromethane for three times. The extracts were washed with brine, dried with anhydrous sodium sulfate, and then removed solvent by a rotary evaporator (temperature of 50°C) till dryness. The sample residue was re-dissolved with 40 mL hexane and 30 mL acetonitrile. After that, the acetonitrile phase was concentrated by a rotary evaporator (temperature of 50°C) and made a final volume of 2 mL. In case of spiked samples, the extracts were 20 fold dilutions before measurement.

A known amount of the obtained sample solution was injected into a 5 mL electrochemical cell containing PBS solution (pH 8.0) and detected by the IL-GNP/GCPE sensor with DPV under optimum conditions. In parallel, the sample solution was filtered with a 0.45 µm nylon syringe filter and analyzed by HPLC.
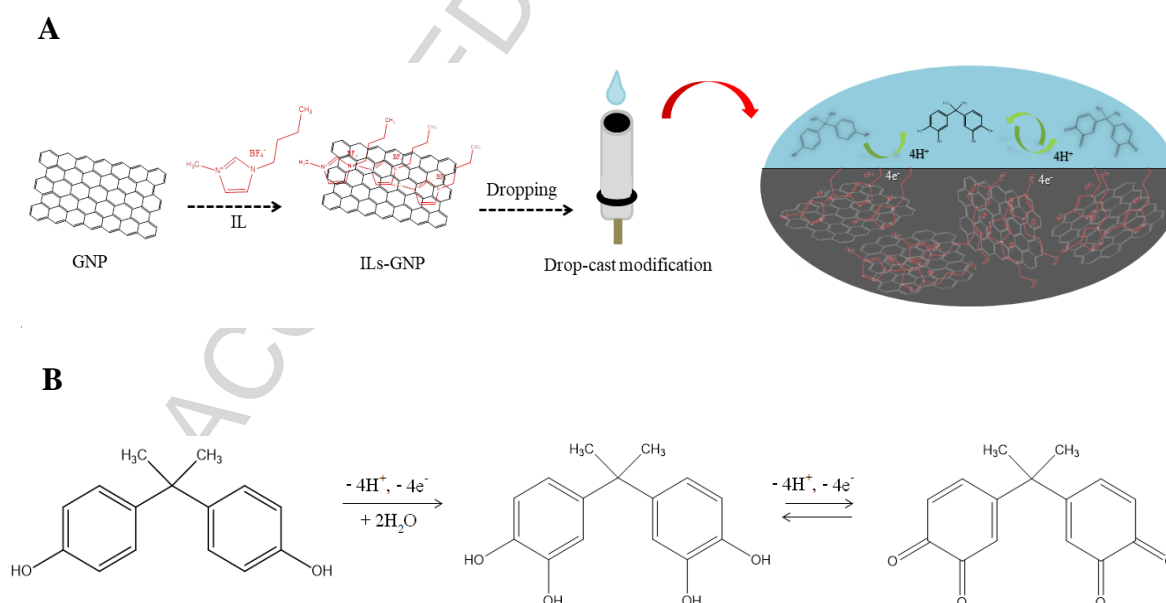
A

B

Fig. 1. (A) Schematic diagram of the electrochemical sensor preparation and (B) the BPA sensing mechanism.

3. Results and discussion

3.1. Characterization of IL-GNP

The morphology of the IL-GNP composite dispersed on a GCPE surface was characterized by SEM (Fig. 2A). In contrast to the unmodified glassy carbon paste (left image) which exhibits well spherical structures with an average diameter of about 4-10 µm, which is consistent with the size provided by the supplier (particle size < 20 µm). The morphology of the modified surface shows thin wrinkling sheet-like stacked layers. This is somehow also reflected by AFM (Fig. 2B). The roughness root meant square (R_q) of the bare GCPE was found to be 1.15 µm with a depth of 4.76 µm. When the IL-GNP composite was deposited on the GCPE surface, the rough surface became smoother than the bare electrode with a R_q roughness of 0.87 µm.

The FTIR pattern of GNP, IL, and IL-GNP are shown in Fig. 2C. The characteristic absorption peaks at 1083, 1635, and 3440 cm^{-1} were attributed to the vibration modes of C-O-C, C=C and O-H bonds respectively. The major peaks can be clearly seen in the case of IL-GNP and the characteristic peak at 1588 cm^{-1} corresponds to the N-H bending vibration of NH_2. This result proved that NH_2 groups of the IL have reacted with the residual oxygen-containing functional groups of GNP, indicating successful synthesis of the composite. Of course, intercalation of the IL into the GNP as well as simple adsorption onto the platelet surface can be additionally taken into consideration of the composite formation.
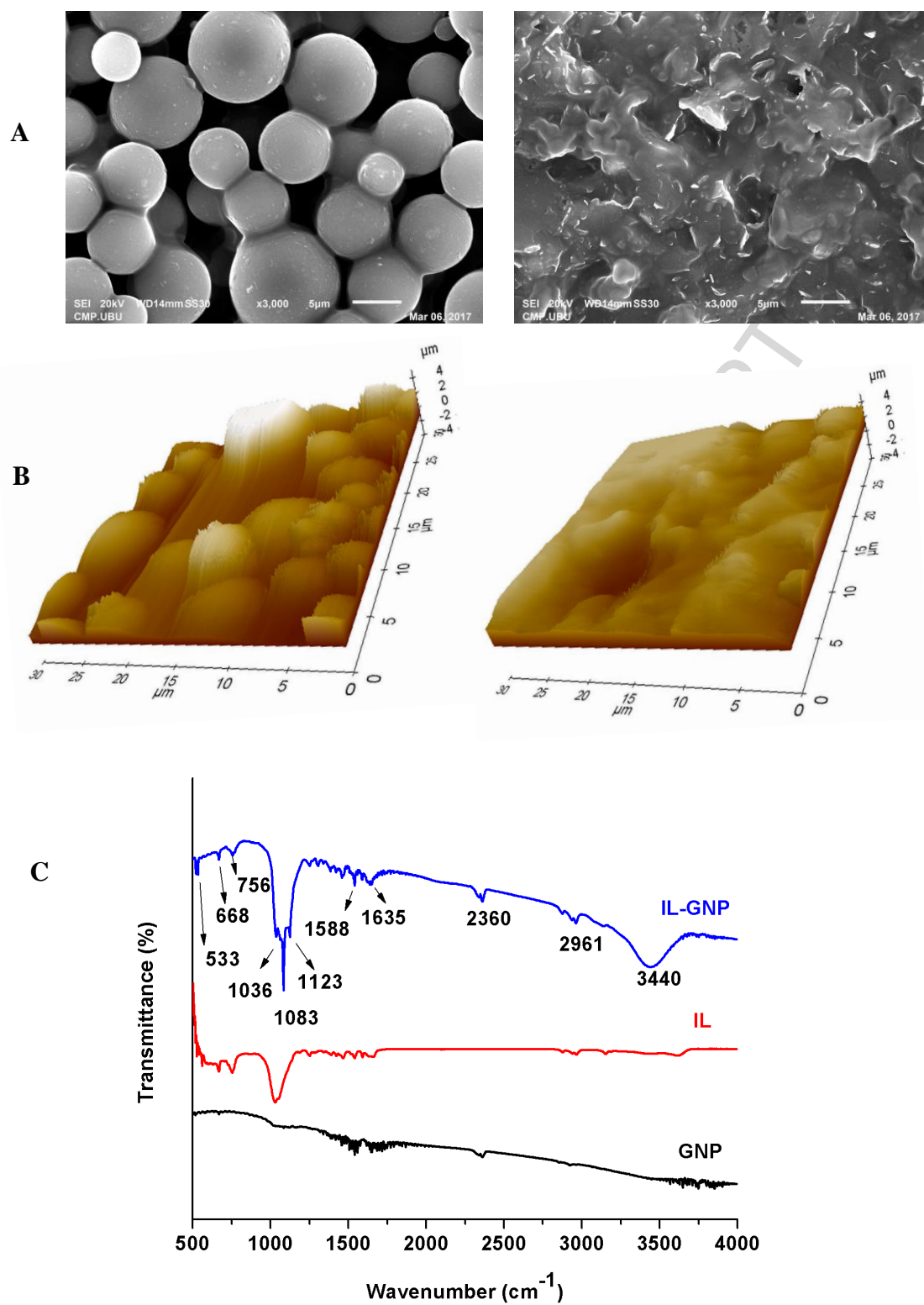
Fig. 2. (A) SEM and (B) AFM images of bare GCPE (left), IL-GNP/GCPE (right) and (C) FTIR Spectra of GNP, IL and IL-GNP

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3.2. Electrochemical characterization of IL-GNP/GCPE

The cyclic voltammetric behavior of a GCPE, unmodified and modified with IL, GNP, and IL-GNP was investigated from -0.5 to +1.0 V with a scan rate of 0.1 V.s^{-1} in a mixed solution of 5 mM K$_3$[Fe(CN)$_6$] and 5 mM K$_4$[Fe(CN)$_6$] containing 0.1 M KCl solution (Fig. 3A). A pair of well-defined quasi-reversible one-electron redox peaks of Fe(CN)$_6^{3-/4-}$ was observed on the bare GCPE, with a peak-to-peak separation (ΔE_p) of 0.49 V and a peak current (I_p) of 55.1 µA. After the electrode was modified with IL, I_p increased and ΔE_p decreased compared to the bare GCPE, which may be attributed to the ion-exchange capability and high ionic conductivity of IL. With GNP as modifier, I_p was slightly smaller compared to the IL-modified electrode showing a ΔE_p of 0.2 V, indicating that GNP possesses electron-transfer enhancing properties. In the presence of both IL and GNP, they are well-defined and enhanced redox peaked with a small peak potential separation ΔE_p of 0.12 V.

Varying the scan rate uncovered a linear dependence of the signal on the square root of the scan rate (Fig. 3B and inset) which meant that the process was mass-transfer controlled. Nevertheless, notable currents at the intercept (0 V.s^{-1}) indicated that there were also other contributions, probably ion exchange, by the ionic liquid.

Further characterization was performed with electrochemical impedance spectroscopy to study the electron-transfer kinetics of the modified electrodes. Fig. 3C represents the results of all types of electrodes in the presence of a mixed solution of 5 mM K$_3$[Fe(CN)$_6$] and 5 mM K$_4$[Fe(CN)$_6$] containing 0.1 M KCl solution. The Nyquist plot indicated for the bare GCPE a semicircle with a charge transfer resistance (R_{ct}) of 3.14 kΩ. After modification with IL and GNP, the R_{ct} was lowered to 1.75 and 2.51 kΩ respectively. In the presence of both, IL and GNP, R_{ct} decreased dramatically to 0.53 kΩ. The results underlined that the IL-GNP composite greatly improved the conductivity and charge transfer ability.

To evaluate the electrochemical response of the sensor to BPA, the different electrodes were investigated in 0.1 M PBS (pH 7.0) containing 2 µM BPA using differential pulse voltammetry (Fig. 3D). Oxidation currents were recorded in the potential range from +0.3 to +1.0 V with all electrodes tested. The highest signal was found when both modifiers were present at the electrode surface. The increase in the anodic current was associated with the very good electron transfer activity and the increased conductivity due to GNP and IL. Moreover, this result demonstrated that the GNP can be attributed to the improved accumulation efficiency for BPA through π interaction.

The possible kinetic mechanism including the electron transfer number (n) for the oxidation of BPA in PBS pH 8.0 at IL-GNP/GCPE was investigated further by cyclic voltammetry with different scan rates of 10-150 mV.s^{-1} (Fig. 3E). The anodic current density (J_{pa}) was increased linearly with the square root of scan rate in the range (Fig. 3F). The same behavior was also observed in the case of a study of a mixed solution of 5 mM K$_3$[Fe(CN)$_6$] and 5 mM K$_4$[Fe(CN)$_6$] containing 0.1 M KCl solution (Fig. 3B), indicating that the electrochemical oxidation of BPA at the IL-GNP/GCPE was also a typical diffusion-controlled process.
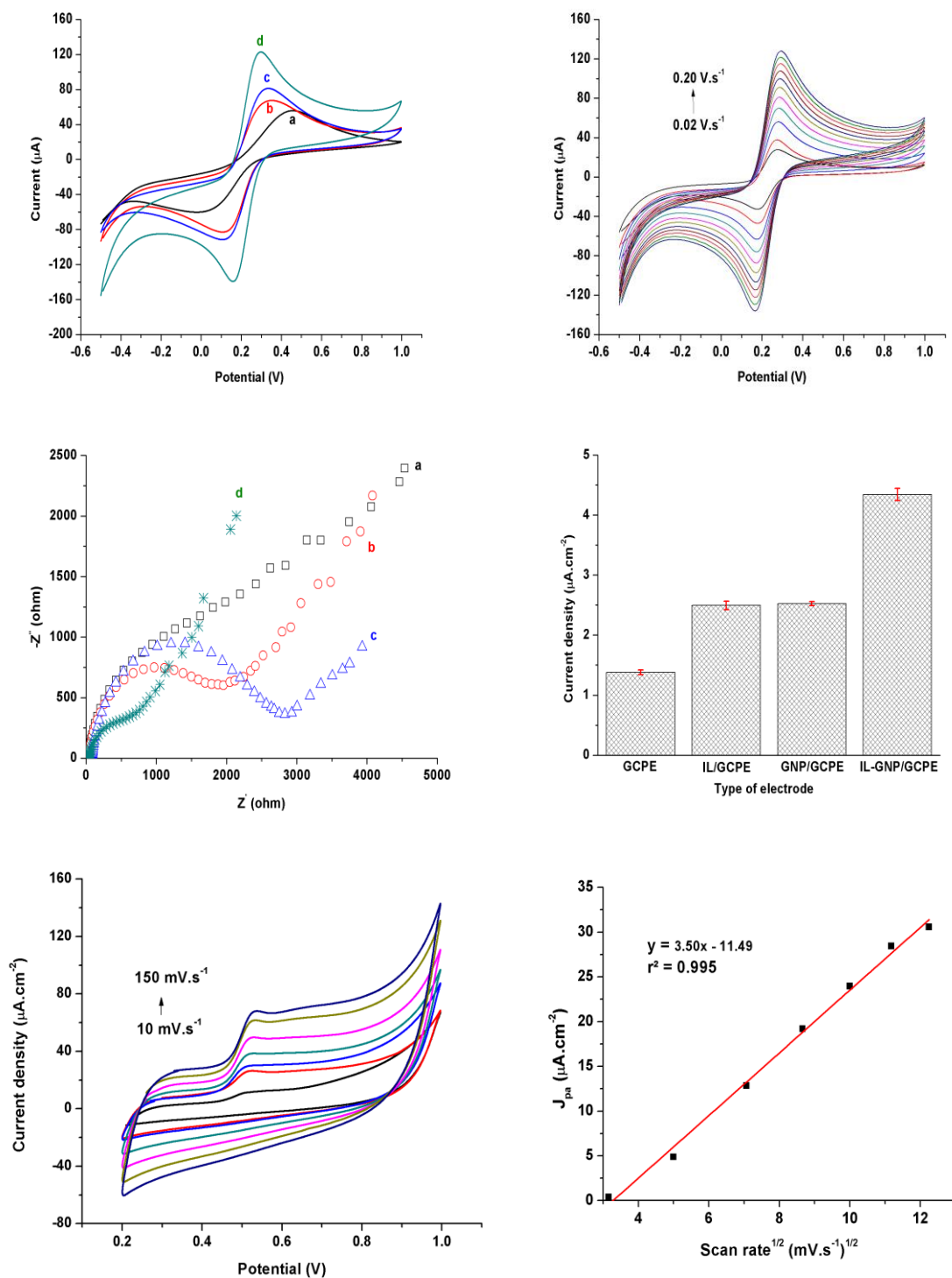
Fig. 3. (A) CV in a mixed solution of 5 mM $K_3[Fe(CN)_6]$ and 5 mM $K_4[Fe(CN)_6]$ obtained with (a) bare GCPE, (b) IL/GCPE, (c) GNP/GCPE and (d) IL-GNP/GCPE in the potential range of -0.5 to +1.0 V with a scan rate of 0.1 $V.s^{-1}$; (B) at scan rates of 0.02 to 0.20 $V.s^{-1}$ on a IL-GNP/GCPE (inset: peak current dependence on the square root of the scan rate). (C) EIS of (a) bare GCPE, (b) IL/GCPE, (c) GNP/GCPE and (d) IL-GNP/GCPE; frequencies from 10^4 to 0.1 Hz. (D) DPV of bare GCPE, IL/GCPE, GNP/GCPE and IL-GNP/GCPE; (A)-(C) KCl (0.1 M), (D) PBS (0.1 M, pH 7.0) containing 2 µM BPA and (E) CV of BPA (1 µM) at different

scan rates with a IL-GNP/GCPE in PBS pH 8.0 containing 1 µM BPA and (F) the relationship between the anodic current density and the square root of scan rate

3.3. Optimization of experimental conditions

The influence of IL functionalized on the GNP was investigated with DPV varying its surface concentration from 0.1 to 0.5 mg.cm^{-2} (Fig. 4A). The anodic peak current increased gradually from 0.1 to 0.4 mg.cm^{-2}, whereas it decreased slightly beyond. Therefore, 0.4 mg.cm^{-2} of IL was used for the functionalization on the GNP.

The amount of the IL-GNP composite at the electrode surface played a crucial role in the electrocatalytic behavior of the sensor (Fig. 4B). Maximum oxidation current of BPA was found with 14 µg.cm^{-2} of the composite. Thus, 14 µg.cm^{-2} of IL-GNP composite was used as optimum for the modification on the electrode surface.

The effect of the pH value was investigated over the range from 5.0 to 9.0 using phosphate buffer solution as shown in Fig. 4C. The oxidation peak current gradually increased when increasing the pH value from 5.0 to 8.0 whereas it decreased in more alkaline solutions. The higher current response to pH was below the pK_a of BPA (pK_a = 9.73) [31], which suggested that the non-dissociated form of BPA may be better adsorbed on the IL-GNP/GCPE surface [32]. Therefore, PBS with a pH value of 8.0 was chosen as the supporting electrolyte for the detection of BPA.

The relationship between the oxidation peak potential (E$_{pa}$) and pH indicated that the former shifted linearity with the pH (Fig. 4D) with a slope of 60 mV per concentration decade. This suggested that the same number of protons and electrons were involved in the oxidation process of BPA. A probable mechanism is given in Fig. 1B [33, 34].

The parameters for DPV measurements were optimized and yielded the following values: pulse potential of 0.075 V, step potential of 0.030 V, scan rate of 0.050 V.s^{-1}. These parameters present voltammograms of high sensitivity, well-shaped waves, and best peak morphology.
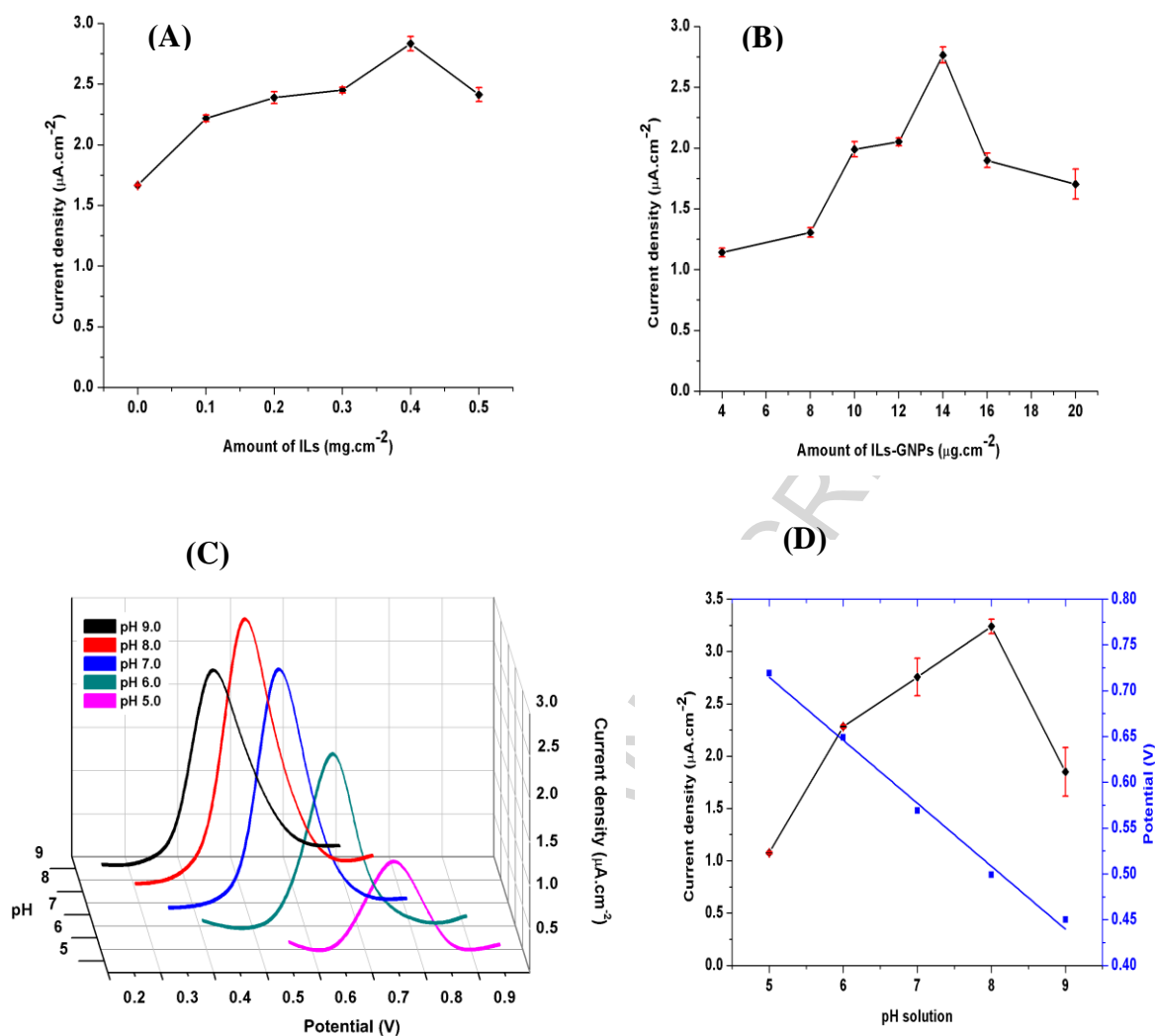
Fig. 4. Effect (A) IL and (B) IL-GNP on the sensor response to 1 µM BPA in 0.1 M PBS pH 7.0. (C) DPV of 1 µM BPA in PBS with different pH values and (D) dependence of the peak potential and peak current on pH

3.4. Analytical performance

The DPV behaviors of a GCPE, unmodified and modified with IL, GNP, and IL-GNP were investigated from -0.2 to +1.0 V with a scan rate of 0.05 $V.s^{-1}$ in 1.2 µM BPA (Fig. 5A). The result obtained that BPA response is the highest sensitivity to GCPE modified with IL-GNP. In addition, the analytical performance of the IL-GNP/GCPE for the determination of BPA was evaluated with DPV under optimized experimental conditions. The oxidation peak current increased linearly with the increasing of BPA concentration in the range from 0.02 µM to 5.0 µM (Fig. 5B), with a linear regression of I $[µA.cm^{-2}]$ = 6.25 C [µM] + 0.734 (r^2 = 0.990). With BPA concentrations higher than 5.0 µM, the peak current leveled off. The sensitivity was determined as 6.25 $µA.µM^{-1}cm^{-2}$, which is about 2 times that of a bare GCPE, IL/GCPE and GNP/GCPE as shown in Fig. 5C. The detection limit (3 σ) and quantification limit (10 σ) were calculated as 6.4 nM and 0.02 µM respectively.

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A comparison of various different electrochemical methods for the determination of BPA is presented in Table 1. The proposed sensor shows the lower detection limit and the wider linear range. The advantages of the current one are an acceptable linear range combined with a simple way of preparation and handling of the sensor. The electrochemical sensor is essentially superior or comparable to previously reported devices for the determination of BPA. These results suggest that the electrochemical sensor based on the IL-GNP composite is a good candidate for the ultrasensitive and rapid detection of the target analyte.
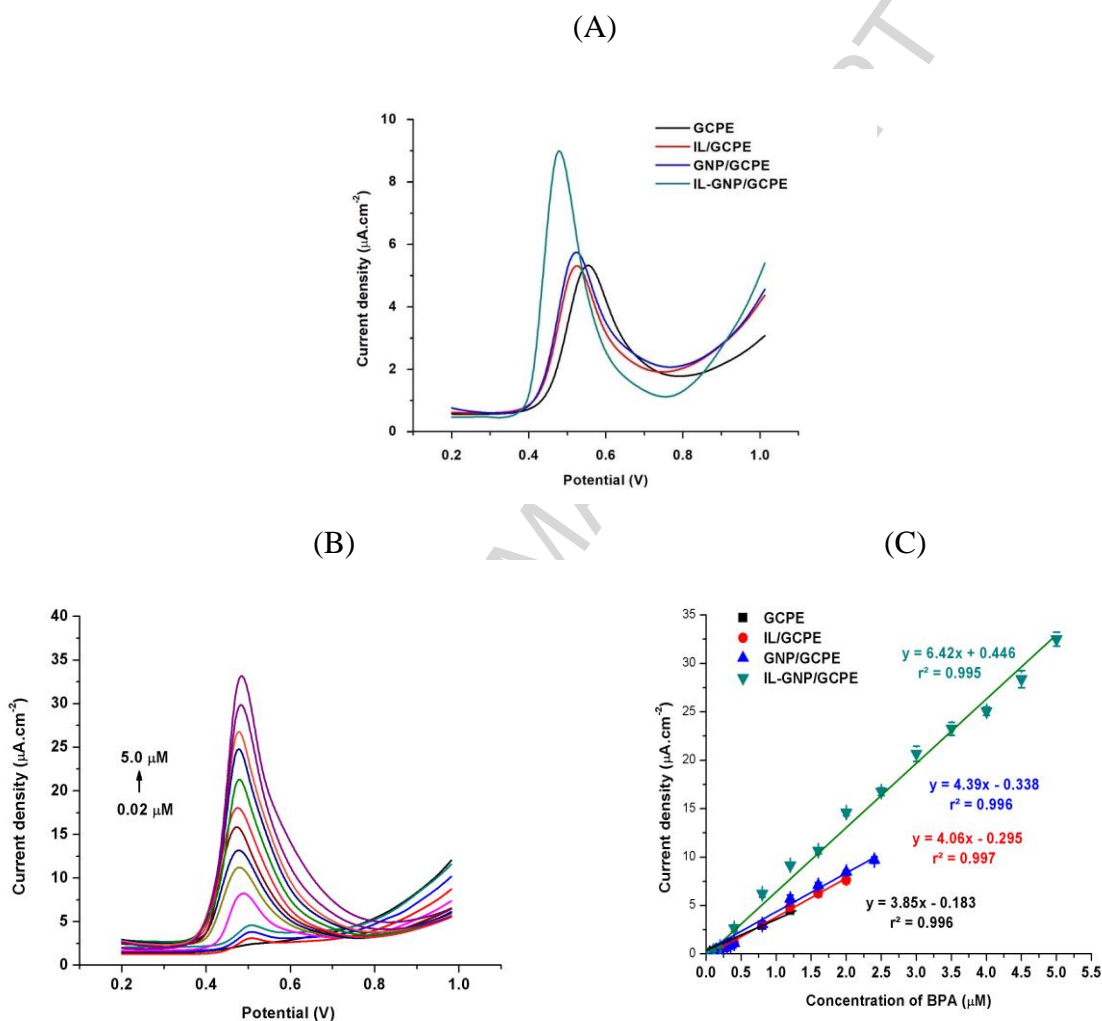
(A)

(B)   (C)

Fig. 5. (A) DP voltammograms in 1.20 µM BPA obtained with (a) bare GCPE, (b) IL/GCPE, (c) GNP/GCPE and (d) IL-GNP/GCPE in the potential range of -0.2 to +1.0 V with a scan rate of 0.05 V.s^{-1}; (B) DPV curves of BPA recorded with an IL-GNP/GCPE; (C) calibration plots of BPA obtained with the electrodes under consideration

3.5. Repeatability, reproducibility, stability, and selectivity of the IL-GNP/GCPE

The repeatability and reproducibility of the IL-GNP/GCPE for the detection of 1 μM BPA were investigated. A relative standard deviation (RSD) value of 3.3% for five successive measurements and 3.8% for five different freshly-prepared electrodes were found, indicating an acceptable repeatability and reproducibility of the modified electrode. The developed sensor retained 80% of its original response after storage at 4°C for 2 weeks (*n*=42), demonstrating acceptable long-term stability of IL-GNP composites on the surface of the GCPE.

The influences of some potential interferents on the BPA detection were examined to evaluate the selectivity of the IL-GNP based-sensor. Common interferences in the detection of BPA, including phenol, 1-napthol, and 4-nitrophenol, had little influence on the electrochemical response of BPA at the same concentration but did interfere when being in excess. However, this finding does not seem serious in relation to the practical application with plastics because phenolic chemicals, except BPA, are not commonly used in the production of plastics [16]. In addition, some possible interfering substances in natural water samples, such as organic compounds like glucose and sucrose with a concentration 100-fold higher, and some inorganic ions, such as 100-fold concentration of Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+}, and Cd^{2+}, had no obvious influence on BPA determination**.** These results indicated that the specificity and selectivity toward BPA detection of the proposed sensor was acceptable.

Table 1
Electrochemical sensing assays for the determination of BPA

Modified electrode	Linear range (μM)	LOD (nM)	Reference
GN-IL/GCE	0.02-2	8	[4]
CS/N-GS/GCE	0.01-1.3	5	[14]
CS/MNPs-rGO/GCE	0.06-11	17	[16]
Tyrosinase-NGP/GCE	0.1-2	33	[35]
GN/GCE	0.05-1	46	[36]
EG/GCE	1.56-50	760	[37]
GN-CNT/GCE	0.06-10	42	[38]
Fe_3O_4NPs-$Si_4Pic^+Cl^-$/AuNPs$Si_4Pic^+Cl^-$/GCE	0.02-1.4	7	[39]
AuNP/MWCNT/GCE	0.01-0.7	4	[40]
IL-Zn-Al LDH/GCE	0.02-3.0	4.6	[41]
Ni_2Al LDH/GCE	0.02-1.5	6.8	[42]
IL-GNP/GCPE	0.02-5.0	6.4	This work

GN: graphene, EG: exfoliated graphite, GS: graphene sheet, rGO: reduced graphene oxide, NGP: hydrophilic nanographene, GNP: graphene nanoplatelet, MWCNT: multiwalled carbon nanotube, IL: ionic liquid, CS: chitosan, N: nitrogen doped, CNT: carbon nanotube, AuNP: gold nanoparticles, MNPs: magnetic nanoparticles, Fe_3O_4NPs: ferroferric oxide nanoparticles, $Si_4Pic^+Cl^-$: 3-*n*-propyl-4-picolinium silsesquioxanechloride polymer, LDH: layered double hydroxide

3.6. Practical application

The IL-GNP/GCPE was further used to determine BPA in three commercial plastic products for water storage and in water samples in contact with them. A certain volume of sample solution was added to a 5 mL electrochemical cell containing PBS solution (pH 8.0), and then detected by DPV under optimized conditions (Table 2). Each sample solution underwent three parallel determinations by the standard addition method. To evaluate the accuracy of the proposed sensor, recovery studies with spiked plastic and water samples were performed. Recoveries ranged within 95.3-104.5%, indicating that the IL-GNP/GCPE was sensitive, selective, and reliable for practical application.

The particular DP voltammograms of analysis of BPA with the graphical evaluation of the multiple standard addition methods are given in Fig.6A. Results from comparative analyses with HPLC with external calibration plot, peak area evaluation, and analyte concentrations from 0.05-200 mg.L^{-1} (Fig. 6B and 6C) were in very good agreement with results obtained with the sensor achieving recoveries of 95.0-102.5% upon spiking. Paired t-test analysis at a confidence interval of 95% probability suggests that the two methods provide results which are not statistically significantly different.
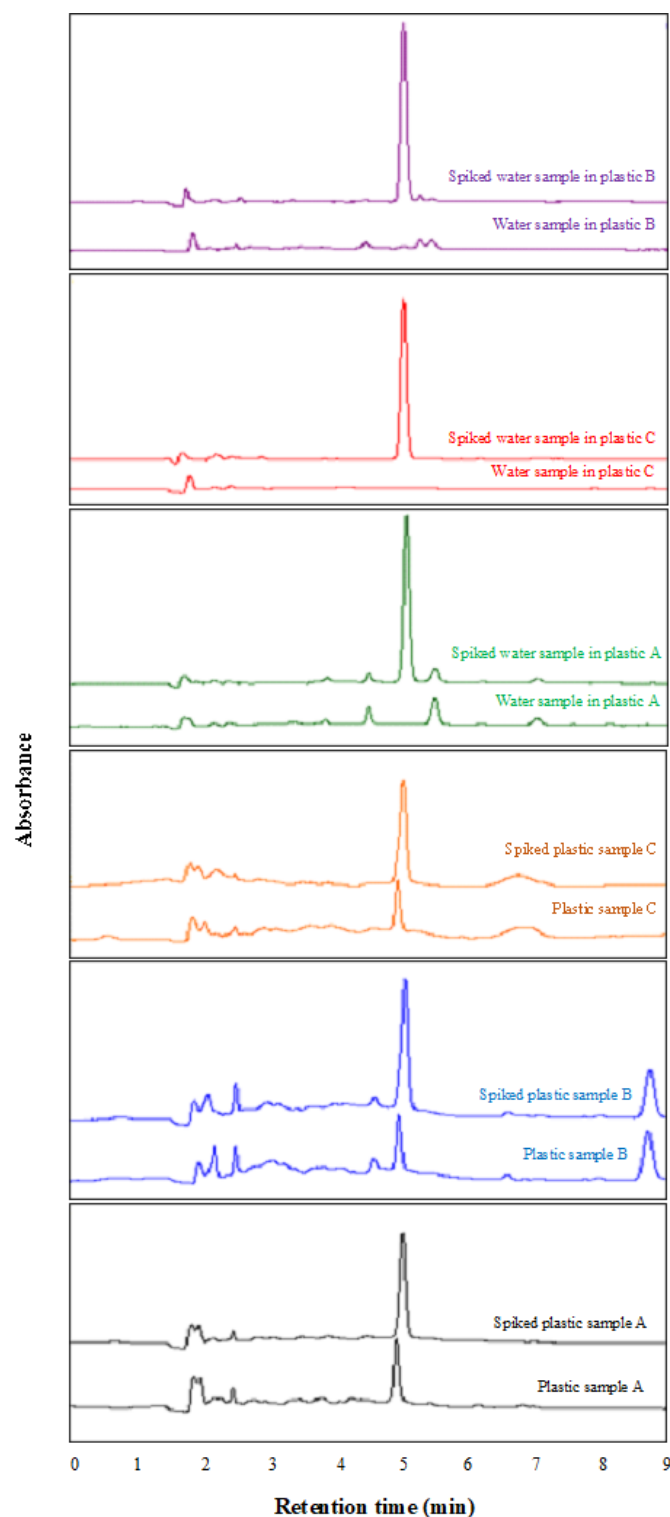
(A)

(B)

(C)
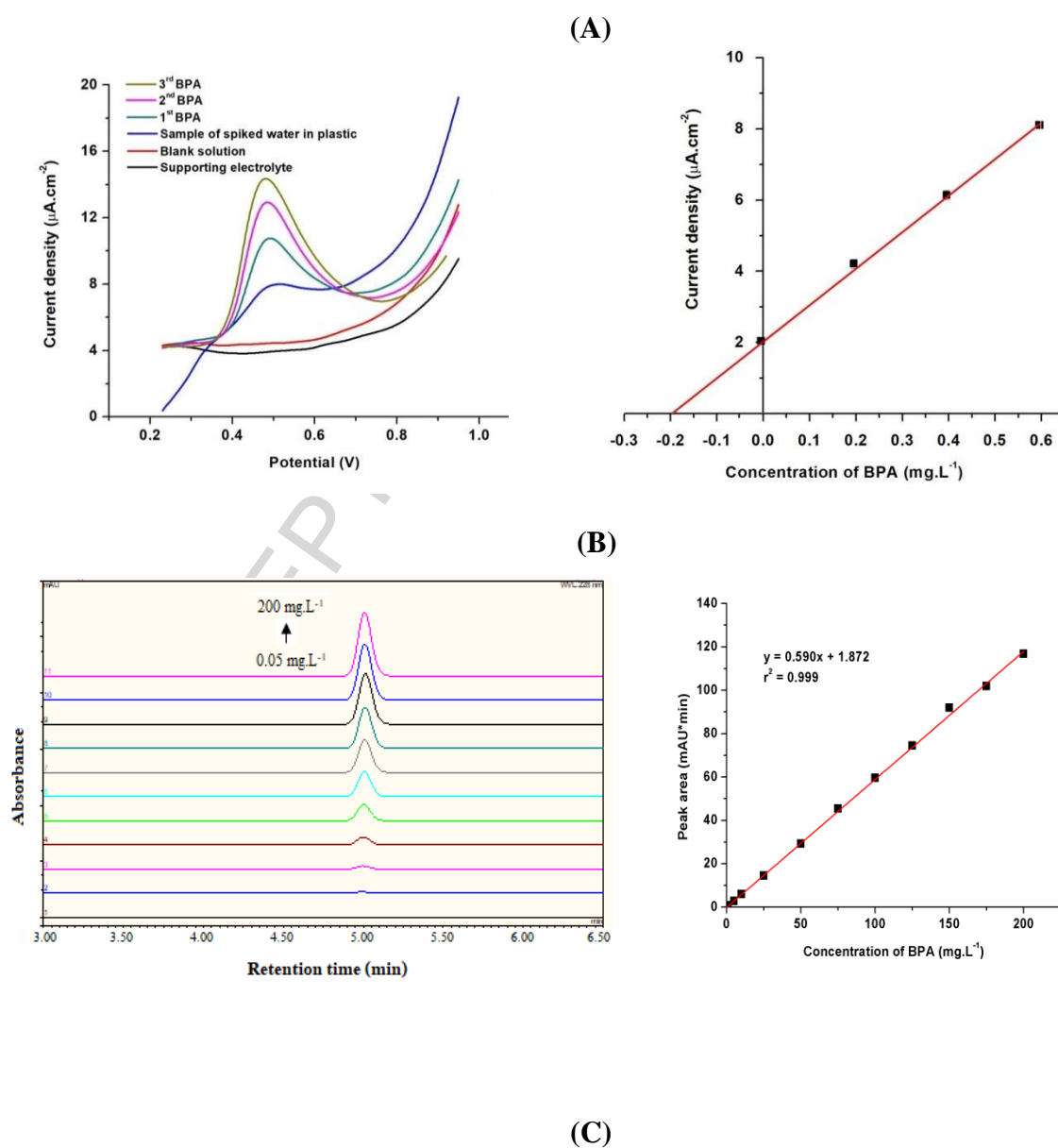
Fig. 6. (A) DPVs of analysis of BPA in water sample using standard addition method on IL-GNP/GCPE(left) and stand addition plot (right); (B) Chromatograms of BPA standards in the range from 0.05-200 mg.L^{-1} (left) and calibration plots of peak area versus BPA concentration (right); (C) chromatograms of non-spiked samples and spiked samples.

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Table 2 Determination of BPA in plastic products and in water in contact with them by the proposed sensor and HPLC (n=3)

Sample	Added ($mg.Kg^{-1}$)	Added ($mg.L^{-1}$)	Determined by sensor Measured ($mg.Kg^{-1}$)	Measured ($mg.L^{-1}$)	Recovery (%)	Determined by HPLC Measured ($mg.Kg^{-1}$)	Measured ($mg.L^{-1}$)	Recovery (%)	t-test[b]
Plastic sample A	-		3.48 ± 0.27		-	3.44 ± 0.03		-	0.3
Plastic sample B	-		2.53 ± 0.01		-	2.59 ± 0.06		-	2.1
Plastic sample C	-		1.98 ± 0.21		-	1.91 ± 0.02		-	0.6
Spiked plastic sample A	4.00		7.62 ± 0.20		103.5	7.24 ± 0.42		95.0	1.1
Spiked plastic sample B	4.00		6.44 ± 0.59		97.8	6.54 ± 0.56		98.8	0.2
Spiked plastic sample C	4.00		6.16 ± 0.03		104.5	6.01 ± 0.23		102.5	1.0
Water sample in plastic A		-		n.d.[a]	-		n.d.	-	-
Water sample in plastic B		-		n.d.	-		n.d.	-	-
Water sample in plastic C		-		n.d.	-		n.d.	-	-
Spiked water sample in plastic A		1.00		0.95 ± 0.03	95.3		0.99 ± 0.03	98.7	1.0
Spiked water sample in plastic B		1.00		0.99 ± 0.02	98.5		1.02 ± 0.01	102.2	2.7
Spiked water sample in plastic C		1.00		0.97 ± 0.02	97.0		1.01 ± 0.01	101.3	3.6

[a] n.d. means "not detectable"

[b] t-test at a confidence level of 95% probability and degree of freedom of 2

4. Conclusion

In this work, a simple and sensitive electrochemical sensor based on IL-GNP modified GCPEs was developed for the detection of BPA. The oxidation current of BPA was significantly enhanced by modification compared to a plain GCPE. The proposed sensor displayed an acceptable wide linear range, high sensitivity, and a low detection limit with satisfactory repeatability, reproducibility, selectivity, and acceptable stability. The proposed sensor was successfully applied to determine BPA in plastic samples and water samples. Moreover, the data agreed well with results obtained by HPLC. Therefore, the proposed method may be used in sensing applications, food safety control, and environmental monitoring.

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Graphical abstract

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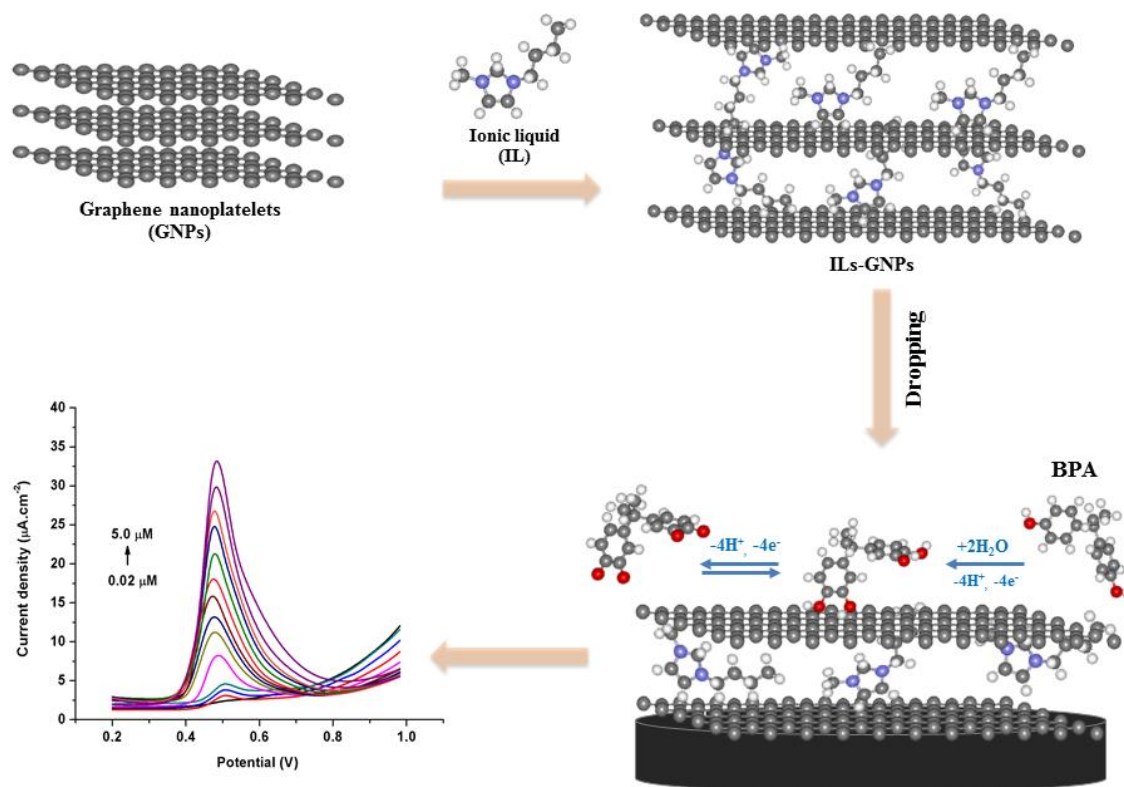
Highlights

-   Graphene nanoplatelets (GNPs) and 1-butyl-2, 3-dimethylimidazolium tetrafluoroborate (ionic liquid, IL) modified on glassy carbon paste electrode were introduced to improve current response.

-   The modified electrochemical sensor is satisfied for direct and sensitive electrochemical detection of bisphenol A.