A sensitive dopamine biosensor based on ultra-thin polypyrrole nanosheets decorated with Pt nanoparticles†

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A sensitive and selective electrochemical sensor to determine dopamine (DA) was successfully fabricated from ultra-thin polypyrrole nanosheets (UltraPPy) that were decorated with Pt nanoparticles (Pt/UltraPPy–GCE). The morphology and structure of the modified electrode were characterized using transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction and Fourier-transform infrared spectroscopy (FTIR). This new electrode displayed a synergistic effect of UltraPPy and Pt on the electro-oxidation of DA in phosphate buffer solution at pH 7. The Pt/UltraPPy–GCE demonstrated excellent electrochemical activity towards DA oxidation compared with the bare GCE, UltraPPy–GCE and Pt NPs–GCE, possibly because of the larger surface area of the UltraPPy, which increased the interactions between the polymer and the K2PtCl6 solution during Pt NP deposition. The small size of the deposited Pt NPs resulted in a large surface area of Pt, which is suitable for the reaction with DA. Furthermore, polypyrrole (PPy) in the nanocomposite material could crosslink to improve its stability with the Pt NPs. By applying the differential pulse voltammetry technique under optimized experimental conditions, a good linear ratio of oxidation peak currents and DA concentrations over a range of 0.01–400 μM was achieved with a limit of detection of 0.67 nM. This electrode was used to determine the DA concentration in a DA hydrochloride injection.

1. Introduction

Dopamine (DA), which is one of the most significant catecholamines in the mammalian central nervous system and biological organisms, plays an important role in cardiovascular and Parkinson’s diseases, drug addiction, and renal and hormonal systems. DA has also attracted the interest of neuroscientists and chemists because of its effects in attention span, cognition, emotions and neuronal plasticity. DA coexists in high concentrations with other molecules in biological samples, which causes poor selectivity and sensitivity in DA determinations. Therefore, accurately measuring the DA concentrations in biological systems is important. Among the various determination methods (such as mass spectrometry, fluorometry, radioenzymatic, electrochemistry, and chromatographic methods), electrochemical methods have many inherent advantages, such as economy, rapid response, sensitivity and easy miniaturization. Furthermore, DA and other catecholamines are easily oxidized; therefore, their detection is possible using electrochemical methods. Modified electrodes are the ideal candidate to solve this challenging bioanalytical problem because of their unique mechanical, chemical and physical properties.

Electrodes, such as the multi-walled carbon nanotube (MWCNT) modified carbon paste electrode, thin pyrolytic carbon films, and Pt nanoparticles (NPs) supported on reduced graphene oxide, have been used for the sensitive electrochemical determination of DA. However, nanoscale conducting polymers have attracted considerable attention over the past few years for use in electronic devices, supercapacitors, functional electrodes, rechargeable batteries and sensors because of their good stability, reproducibility, increased number of active sites, homogeneity in electrochemical deposition and strong adherence to the electrode surface. Recently, NPs of noble metals have also attracted attention from scientific and technological viewpoints because of their interesting optical, photoelectrochemical, electrochemical and electronic properties. In recent years, there has been extensive research into the electrochemical properties of metal NP-modified electrodes. Previous studies indicate that Pt NPs can increase the surface area and are conducive to the electron transfer process with strong catalytic properties, and they have attracted wide interest as materials for modified electrodes.
Research efforts have also demonstrated that nanocomposites that contain both conducting polymers and NPs of noble metals, such as silver, platinum and gold, can be used as electrochemical sensors. Among the conductive polymers, PPy is one of the most promising conducting polymers because of its ease of preparation, wide range of applications, high electrical conductivity, good redox reversibility and high stability. The conductive properties of this polymer make it an important class of material for a wide range of applications, such as chemical sensors, biosensors, supercapacitors, gas sensors, and corrosion protection, due to it being environmentally stable, electrically conductive and flexible. Moreover, UltraPPy has a larger catalytic surface area because the entire surface of UltraPPy acts as the active site. PPy has been successfully used in the conducting matrices of composite materials that incorporate Fe₃O₄, V₂O₅ and noble metals, such as Au, Pd, Ag or Pt. Recent reports show that the composites of polymers, such as poly(nicotinamide) and polyethyleneimine, with noble metal nanoparticles are good candidates for the detection of DA. The present study demonstrates the synthesis of ultrathin polypyrrole nanosheets (UltraPPy) decorated with Pt NPs. The UltraPPy nanosheets were first prepared in the presence of sodium dodecyl sulfate (SDS) and Pt NPs were deposited on the surface of UltraPPy through an in situ reduction of K₂PtCl₄. To the best of our knowledge, there are no reports on the use of a Pt/ultra-thin-PPy-nanosheet-modified glassy carbon electrode (GCE) (Pt/UltraPPy–GCE) nanocomposite for the monitoring of DA. The electrochemical behavior of DA on the Pt/UltraPPy–GCE was investigated using cyclic and differential pulse voltammetry. The stability, reproducibility and broad range of detection are the important characteristics of the prepared biosensors, which combine the properties of UltraPPy and Pt NPs. A favorable electrode performance for DA detection is described in the following sections.

2. Experimental methods

2.1 Electrochemical apparatus

The electrochemical measurements, which involve cyclic voltammetry (CV), differential pulse voltammetry (DPV) and chronoamperometry, were conducted using an Autolab potentiostat/galvanostat PGSTAT30 (Ecochemie Netherlands). A three-electrode system, with a platinum wire as the auxiliary electrode and Ag/AgCl (3 M NaCl) as the reference electrode, was used in the electrochemical experiments. The working electrode was either the unmodified GCE or (Pt/UltraPPy–GCE). Unless otherwise stated, all potentials are quoted with respect to the reference electrode.

2.2 Materials

DA, distilled pyrrole, ascorbic acid, uric acid and potassium tetrachloroplatinate II (K₂PtCl₄) were purchased from Sigma Aldrich. All other chemicals (E. Merck, Germany) were of analytical grade and were used without further purification. The DA hydrochloride injection was purchased from the pharmacy center in the University of Malaya hospital. Double-distilled water was used for all experimental procedures. A 0.1 M phosphate buffer (pH 7) was prepared by mixing stock solutions of KH₂PO₄ and KH₂PO₄.

2.3 Synthesis of Pt–ultra-thin PPy nanosheets

The ultra-thin PPy was prepared similarly to the previous method in the literature. In summary, chemical polymerization was performed by dissolving 2.45 g of SDS in 100 mL of distilled water in a reaction vessel; the reaction was maintained at 30 °C with continuous stirring at 800 rpm with a mechanical stirrer. Then, the solution was cooled to 0 °C. During this step, 20 mmol of the pyrrole monomer was added to this solution with continuous stirring for 30 min at 0 °C. A pre-cooled solution of 45 mmol ferric chloride (20 mL) was added drop-wise to the prepared mixture, and the white mixture gradually turned black. The stirring was continued for another 3 h at 0 °C to allow complete polymerization of the UltraPPy. The resulting product was filtered, repeatedly washed with distilled water, and dried in a vacuum oven at 50 °C for 24 h.

The synthesized UltraPPy (0.05 g) was dispersed into 20 mL of distilled water with ultrasonication. This process was followed by the addition of 0.02 M K₂PtCl₄ to the dispersed UltraPPy solution with continuous stirring for 2 h at room temperature, then reduction with hydrazine hydrate at 50 °C for 1 h. The composite was subsequently filtered and repeatedly washed with distilled water, followed by drying in a vacuum oven at 60 °C for 24 h. The Pt NPs were prepared using the aforementioned procedure without the addition of UltraPPy.

2.4 Electrode preparation

The modified electrode was fabricated as follows: the GCE was polished with alumina, thoroughly rinsed with water/ethanol (V : V = 2 : 1), cleaned in an ultrasonic bath with water and finally rinsed with deionized water. Then, the cleaned GCE was dried at ambient temperature. The prepared Pt/UltraPPy (1 mg) was dispersed in 1 mL water for 1 h in an ultrasonic bath to obtain a homogenous suspension. The Pt/UltraPPy suspension (15 µL) was drop-casted on the GCE surface and dried at 25 ± 5 °C to produce the Pt/UltraPPy–GCE electrode. The Pt/UltraPPy–GCE was subsequently used for further experiments.

2.5 Characterization methods

The phase and crystallite size of the Pt NPs were characterized by X-ray powder diffraction (XRD) using an automated diffractometer (PANalytical’s Empyrean) with monochromated CuKα radiation (λ = 1.54056 Å). The particle size and structural characterization of the synthesized product were performed using a high-resolution transmission electron microscope (HRTEM-FEI-G-4020, 500 kV). The samples were ultrasonicated in distilled water before the HRTEM characterization. Using an EDAX-System (Hitachi SU8000) instrument attached to a FESEM instrument, energy dispersive X-ray (EDAX) analysis was performed to investigate the elemental composition of the samples. Atomic force microscopy (AFM, PSIA XE-100) measurements were also used to analyze the surface...
morphism of the UltraPPy. Fourier-transform infrared (FTIR) analysis was performed on a Perkin Elmer System 2000 series spectrophotometer (USA) between 4000 and 450 cm⁻¹.

2.6 Procedure
The experiments were performed by studying the cyclic voltammetric behavior of the electrode in phosphate buffer (pH 7) as the supporting electrolyte in a potential range of −0.15–0.7 V and at scan rates of 10–300 mV s⁻¹. The DPV was performed with potentials from −0.15 V to 1 V with a step potential of 2 mV, a modulation amplitude of 50 mV and a scan rate 10 mV s⁻¹. All experiments were conducted at 25 ± 5 °C.

3. Results and discussion
3.1 Characterization of Pt/UltraPPy

3.1.1 Morphological and XRD analysis of the Pt/UltraPPy. The AFM scan and corresponding depth profiles in Fig. 1a confirm that the UltraPPy surface is flat. The thickness of the top and bottom layers of the UltraPPy, shown with an arrow in Fig. 1b, is ~40 nm, which confirms the nanosheet structure of the UltraPPy.

The TEM imaging technique was used for a detailed observation of the sample morphology (Fig. 1b–d). The TEM image in Fig. 1f further supports the AFM results (Fig. 1a). Fig. 1b shows that the UltraPPy is composed of two layers of UltraPPy, which are loosely held together as ultrathin nanosheets with a large surface area. Fig. 1c and d show that the nanosheets are decorated with Pt NPs. The lower magnification TEM image in Fig. 1c clearly shows the surface coverage of UltraPPy by Pt, and indeed confirms the presence of a large number of Pt NPs as dark spots embedded in the UltraPPy matrix. Moreover, the higher magnification TEM image in Fig. 1d reveals that the Pt NPs are well distributed on the UltraPPy surface, forming a nanocomposite structure, which can enhance the electrochemical detection of DA. Fig. 1e shows the histogram of the Pt nanoparticle diameter. The results reveal that the Pt nanoparticles have a diameter of approximately 2.17 nm.

Furthermore, the EDX of the Pt/UltraPPy composite in Fig. 1f shows the existence of Pt (from the deposited nanoparticles), C and N (from Ppy) and O (from SDS). The EDX results confirm that an appropriate percentage of Pt NP deposition occurred on the UltraPPy surface. The weight percentage of each element is provided in Fig. 1f (inset).

The crystalline structure of Pt/UltraPPy was studied using XRD, as shown in Fig. 1g. A broad amorphous diffraction peak in the range of 2θ = 17–25° (ref. 39) is attributed to the scattering by the interplanar spacing among the bare polymer chains. In addition, the XRD profile of the sample shows three diffraction peaks at 2θ = 40.041, 46.535 and 67.861°, which are attributed to the (111), (200) and (220) lattice planes of cubic Pt (JCPDS card no. 00-001-1194), respectively, with the lattice constant a = b = c = 3.91 Å. This result confirms that Pt²⁺ was reduced in the presence of the UltraPPy colloids.

3.1.2 FTIR spectroscopy. The FT-IR spectra of UltraPPy and Pt/UltraPPy display characteristic bands as shown in Fig. 2. In the FT-IR spectrum of the synthesized UltraPPy and Pt/UltraPPy, the peaks at 3325.42 and 3322.20 cm⁻¹, respectively, are attributed to the N–H bond. The two absorption bands at 1185.33 cm⁻¹ and 666.78 cm⁻¹ are assigned to the SO₂ stretch (and S–O stretch), which occurs because the UltraPPy is synthesized in the presence of SDS. In addition, identical characteristic bands for SO₃ and S–O are observed in the FT-IR spectrum of Pt/UltraPPy (Fig. 2b), but with a slight shift in wavenumbers. The slight shift in the wavenumbers of SO₃ at 1186.05 cm⁻¹ and S–O at 667.70 cm⁻¹ in the FT-IR spectrum of the Pt/UltraPPy compared with UltraPPy can be accounted for by the interaction between Pt and the non-bonding electron pair, similar to that from O (from SDS). The peaks at 1708.63 cm⁻¹ (Fig. 2a) and 1710.25 cm⁻¹ (Fig. 2b) are related to the C–N–C bond vibrations in UltraPPy and Pt/UltraPPy, respectively. The band at 2847.45 cm⁻¹ (Fig. 2a) and the strong band at 2850.84 cm⁻¹ (Fig. 2b) are associated with the aliphatic C–H vibrations, which also confirms that an appropriate percentage of the Pt NPs was deposited on the UltraPPy surface. The bands at 1425.47 cm⁻¹ and 1461.31 cm⁻¹ are assigned to the typical Ppy ring vibrations.

3.2 EIS studies
Electrochemical impedance spectroscopy (EIS) is a widely used technique for studying modified electrodes to obtain a deeper understanding of the electron transfer process across the electrode/electrolyte interface. The EIS experiments were performed on the bare GCE, UltraPPy–GCE, Pt NPs–GCE and Pt/UltraPPy–GCE. Fig. 3a shows the Nyquist plots in 0.1 M KCl solution with 1 mM [Fe(CN)₆]³⁻/⁴⁻ (1 : 1) in a frequency range of 0.1 to 10⁵ Hz at the formal potential of the redox probe (5 mV).

The Nyquist plot of the impedance spectra consists of a semicircle portion in the higher-frequency region, which is attributed to the electron transfer limiting process, whereas a linear portion in the lower-frequency region is attributed to a diffusion limiting process. The Pt/UltraPPy–GCE (curve a) demonstrates a much lower charge transfer resistance than the Pt NPs–GCE (curve b), UltraPPy–GCE (curve c) and bare GCE (curve d).

The electron transfer resistance (Rct) is evaluated from the semicircle diameter (see ESI Table S1). To clearly realize the electron transfer behavior across the electrode/electrolyte interface, the Randles’ equivalent circuit of Rct(Q[Rct,W]) accurately fits the experimental data (Fig. 3b) with a minimized chi square (χ²) value of 10⁻³. In this circuit, Rs represents the solution resistance, Q is the constant phase element, which is an approximation of the double-layer capacitance, and Rct is the resistance against the electron transfer process, which is parallel to the Q. In addition, the Warburg element, which represents the diffusion impedance, is in series with Rct. From the simulation of the experimental results, Rct increases in the order of Pt/UltraPPy–GCE (476.02 Ω) < Pt NPs–GCE (936.87 Ω) < UltraPPy–GCE (2236.5 Ω) < GCE (7517.4 Ω). The CV and EIS simulation results show that the electron transfer process can be improved with the presence of Pt in the nanocomposite-modified electrode (Pt/UltraPPy–GCE) compared with the
other modified electrodes. Therefore, it is concluded that the Pt/UltraPPy–GCE nanocomposite benefits from the synergistic effect of Pt and UltraPPy, and UltraPPy is an electron mediator in the electron transfer process.

3.3 Electrochemical behavior of DA

The performance of the Pt/UltraPPy–GCE was investigated using cyclic voltammetry in 0.1 M phosphate buffer solution (pH 7) in the presence of 100 μM DA. The broad redox couple peaks of DA on the bare GCE, UltraPPy–GCE and Pt NPs–GCE (Fig. 4a–c) indicate a slow electron transfer process. The UltraPPy–GCE (Fig. 4b) has a larger peak current than the bare GCE because of over-oxidation phenomena, which can occur for PPy during the oxidation of DA and causes the direct oxidation of DA in the presence of PPy. The high surface area of UltraPPy increases the interaction with Pt²⁺ ions and the direct oxidation of DA by PPy. The peak current improvement is more noticeable on the surface of the Pt NPs–GCE (Fig. 4c) compared with the bare GCE and UltraPPy–GCE because Pt has superior catalytic activity for DA oxidation.

A larger peak current response for the electrochemical oxidation of DA was obtained on the Pt/UltraPPy–GCE (Fig. 4d). It is observed that the Pt/UltraPPy–GCE has a considerable effect, with an approximately 5 times improvement in peak current compared to the UltraPPy–GCE.

Fig. 1 (a) AFM image and the corresponding depth profile of UltraPPy; TEM images of (b) UltraPPy, UltraPPy deposited with Pt NPs in (c) low magnification and (d) high magnification; (e) size distribution diagram of the Pt/UltraPPy composite; (f) EDX of UltraPPy deposited with Pt NPs; (g) XRD pattern of UltraPPy deposited with Pt NPs.
The Pt/UltraPPy–GCE obviously has the largest peak current compared with the UltraPPy–GCE because there are Pt NPs on the UltraPPy. The UltraPPy morphology can create a large surface area for Pt$^{2+}$ to interact with the polymer nanosheets during the Pt NP deposition. The lower electrical conductivity of the UltraPPy can be improved by the presence of Pt NPs, and together they act synergistically in the DA oxidation. The TEM results (Fig. 1c and d) show a large number of deposited Pt nanoparticles on the surface of the UltraPPy; thus, a large catalytic current can be produced on the Pt/UltraPPy–GCE.

3.4 Effects of the pH of the solution

The effect of pH on the electrochemical response of the Pt/UltraPPy–GCE on addition of 100 μM DA was investigated using CV. The change in peak current with pH (pH range of 4–7.8) is shown in Fig. S1A (ESI†). It is observed that $I_{\text{pa}}$ (anodic peak current) increases with pH up to pH 7. However, in Fig. 4, the $I_{\text{pa}}$ of DA in the phosphate buffer (pH 7) is higher than the reduction peak current $I_{\text{pc}}$ (cathodic peak current), which indicates a quasi-reversible electrode process. Consequently, the buffering at pH 7, which is near physiological pH, is used for the remainder of the work. Smaller currents were detected when the pH value of the solution was either lower or higher than 7. The effect of the phosphate buffer pH on $E_{\text{pa}}$ (anodic peak potential) was investigated, and the results show that $E_{\text{pa}}$ was shifted toward negative potentials with a slope of $-58$ mV per decade. A linear relationship of $E_{\text{pa}}$ (mV) = $-58.9$ pH + 657.1 was obtained with $R^2 = 0.997$ (Fig. S1B, ESI†). The slope is notably close to the Nernstian value of $-59$ mV per decade, which suggests that the numbers of protons and electrons transferred in the redox reaction of DA are equal.$^{14,46}$ Two electrons and two protons are involved in the oxidation of DA. Thus, the mechanism of the redox process of DA is proposed in Scheme 1† (ESI†).

3.5 Effects of scan rate

The scan rate dependency of the modified electrode in 100 μM DA was also investigated (Fig. 5). The redox peak current of the Pt/UltraPPy–GCE in the DA solution increases linearly with the increase in scan rate from 10 to 300 mV s$^{-1}$. In addition, $E_{\text{pa}}$ is
slightly shifted towards the positive region, whereas $E_{pc}$ (cathodic peak potential) is shifted to the negative region, possibly because of the changes in electrocatalytic activity and the kinetic effect of the Pt/UltraPPy–GCE surface towards the DA oxidation, particularly at scan rates higher than 100 mV s$^{-1}$. In other words, at scan rates greater than 100 mV s$^{-1}$, the DA oxidation becomes slower because of the short timescales, which decreases the facile electron transfer process. The linear relationship between the peak current and the scan rate is expressed using the following linear regression equation: $I_{pa}/\mu A = 3.39X + 107.38$ (with $R^2 = 0.994$) and $I_{pc}/\mu A = -3.75X - 103.99$ (with $R^2 = 0.995$). These results indicate that the electrochemical reaction of DA on the Pt/UltraPPy–GCE is a surface-controlled process.48,49

3.6 Determination of DA using differential pulse voltammetry

Fig. 6 shows the differential pulse voltammogram of different concentrations of DA in 0.1 M phosphate buffer (pH 7) between −0.15–1 V with a step potential of 2 mV, a modulation amplitude of 50 mV and a scan rate of 10 mV s$^{-1}$. $I_{pa}$ is linearly proportional to the DA concentration in the range of 0.01–400 μM. A linear equation of $I_{pa}$ (μA) = 0.9239[DA] (μM) + 29.292 with ($R^2 = 0.998$) was obtained (Fig. 6). The detection limit of DA at the Pt/UltraPPy–GCE is 0.67 nM. Table 1 shows a comparison between the results of this work and other results for DA detection. The limit of detection of DA at the Pt/UltraPPy–GCE shows better sensitivity than those in previous reports.

3.7 Interference effects

Ascorbic acid (AA) and uric acid (UA) are common compounds found with DA in real samples, such as biological fluids. Because the oxidation potentials of these three compounds are always close, the overlap of the oxidation peaks and interferences from the other two compounds are major problems that are encountered in DA detection. Therefore, the effects of AA and UA on the DA measurements were investigated using the amperometric response of successive additions of 100 μM DA and 100 μM of AA and UA in a phosphate buffer solution (pH 7.0) at 200 mV (Fig. 7a). However, the results demonstrate that the presence of AA and UA does not affect the DA response. Nonetheless, when 100 μM DA is spiked into the phosphate buffer solution with AA and UA, $I_{pa}$ sharply increases. The results indicate that the Pt/UltraPPy–GCE has high selectivity towards DA detection, even in the presence of some common interfering compounds that are normally found in biological samples.

The effects of AA and UA on the DA measurement were also investigated on the Pt/UltraPPy–GCE using DPV method. The electrooxidation processes of DA, AA and UA in the mixture are evaluated when the concentration of one species is changed and the other two are kept constant. Fig. 7b illustrates the DPV curves of various DA concentrations at the Pt/UltraPPy–GCE in the presence of 100 μM AA and 100 μM UA. The results indicate that the peak current response for the oxidation of DA increases linearly with the increase in the DA concentration in the range 0.01–400 μM, while the peak current for AA and UA oxidation is almost unchanged. The results obtained are similar with a previous study on the effects of AA and UA on DA determination.16,44 These results confirm that there are no significant interferences for the detection of DA in the presence of AA and UA.
Table 1  Electrochemical response of some DA sensors constructed from various materials

<table>
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<tr>
<th>Electrode materials</th>
<th>Technique</th>
<th>Detection limit [µM]</th>
<th>Linear range [µM]</th>
<th>Ref.</th>
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<tr>
<td>Multilwall carbon nanotubes/5-amino-3',4'-dimethoxy-biphenyl-2-ol modified carbon paste electrode</td>
<td>Square wave voltammetry</td>
<td>0.16</td>
<td>1.2–800</td>
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<td>Pt-reduced graphene/GCE</td>
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<td>10–170</td>
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<td>Electrochemically reduced graphene oxide</td>
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<td>0.5 µM</td>
<td>0.5–60</td>
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<td>Graphene modified electrode</td>
<td>DPV</td>
<td>2.64 µM</td>
<td>4–100</td>
<td>52</td>
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<tr>
<td>GC/CNT–silver hexacyanoferrate nanoparticle-modified electrode</td>
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<td>Graphene flower-modified carbon fiber</td>
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<td>Graphene nanosheets/polyethyleneimine/gold nanoparticle</td>
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<td>Au-carbon dots–chitosan-modified GCE</td>
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<td>DPV</td>
<td>0.67 nM</td>
<td>0.01–400</td>
<td>This work</td>
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![Image](67x251 to 267x484)

**Fig. 7** (a) Amperometric response of Pt/UltraPPy–GCE towards interference in phosphate buffer (pH 7) at 200 mV with successive additions of 100 µM DA, AA and UA, as indicated. (b) DPV of Pt/UltraPPy–GCE in 0.1 M phosphate buffer (pH 7) containing 100 µM AA and UA in the presence of different concentrations of DA: 0.01, 5, 10, 50, 125, 250, 300, 400; inset (b₁): DPV curve of AA in the presence of DA. Inset (b₂): plot of oxidation currents versus the concentration of DA.

3.8 Analysis of the real samples

3.8.1 DA determination in DA hydrochloride injection. To evaluate the validity of the method to analyze DA in pharmaceutical products, the Pt/UltraPPy–GCE was further tested for the DA measurement in DA hydrochloride injection (concentration of DA 10 mg mL⁻¹, 2 mL per injection). The injection solution was diluted to 50 mL with distilled water. Then, 100 µL of this solution was transferred to a 50 mL volumetric flask and diluted with 0.1 M phosphate buffer (pH 7). A portion of the resulting solution (5 mL) was subsequently removed to be the sample for the DA determination using DPV. The recovery was obtained by using DPV to evaluate the method accuracy. Based on the replicates (n = 5), the relative standard deviation of this method is presented in Table S2 (ESI†). The satisfactory recoveries of DA at the Pt/UltraPPy–GCE in the range of 0.01–400 µM show that this method is effective and reliable. These findings indicate that this method is rapid and simple for the selective and sensitive analysis of DA in pharmaceutical preparations.

3.9 Reproducibility and stability of the Pt/UltraPPy–GCE

The electrode reproducibility was examined using cyclic voltammetry studies of seven electrodes, which were constructed using the same procedure, in seven DA samples. The relative standard deviation (RSD) of Iₚa is 3.43% (n = 7), which indicates good reproducibility. In addition, the operational and storage stabilities of the Pt/UltraPPy–GCE for the oxidation of 100 µM DA in both synthetic and real samples were also studied. Long-term stability is obtained when the modified electrode is maintained in 0.1 M phosphate buffer (pH 7) at 4 °C when not in use. The operational stability is retained at 99% of the initial current when constantly used for two months.

4. Conclusion

A new electrode based on Pt/UltraPPy–GCE was prepared and investigated using various characterization methods such as FT-IR, XRD, TEM and AFM. The results confirm that the Pt NPs were deposited on the UltraPPy surface. The electrode displays higher electrocatalytic activity toward DA oxidation than the GCE, UltraPPy–GCE and Pt NPs–GCE. The incorporation of Pt into the UltraPPy composite significantly increases the conductivity and effective electroactive surface area of the
electrode. The ultra PPy provides a larger surface area for the deposition of Pt$^{2+}$ NPs, where Pt$^{2+}$ NPs can provide a suitable surface area for the electrocatalytic reaction of DA. Additionally, the Pt/UltraPPy–GCE exhibits a low detection limit for DA oxidation with improvement in the anodic peak current. The electrode is not interfered with by common physiological interferences, such as AA and UA. The proposed sensor was successfully applied to determine DA in a DA hydrochloride injection with good precision and accuracy.

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