

Fabrication of indium tin oxides (ITO)-supported poly(3,4-ethylenedioxythiophene) electrodes coated with active IrO₂ layer for morphine electrooxidation

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Abstract Novel indium tin oxides (ITO)/PEDOT/IrO₂ composite electrodes were fabricated by dipping IrO₂ colloids onto poly(3,4-ethylenedioxythiophene) (PEDOT)-coated ITO substrate for morphine electrooxidation. Scanning electron microscopy (SEM) image showed that the active IrO₂ layer was dispersed more uniformly at PEDOT intermediate layer than at bare ITO substrate. Voltammetric measurements indicated that the as-prepared IrO₂ colloids are very active for both the oxygen evolution reactions (OER) and for reversible valance transition between lower and higher oxides. ITO/PEDOT/IrO₂ electrodes perform enhanced electrochemical activity towards the oxidation of morphine, as compared with the un-modified ITO-based PEDOT electrodes (ITO/PEDOT) or the ITO electrodes directly coated with IrO₂ (ITO/IrO₂), suggesting that the composite electrode materials are one of the potential candidates for morphine detection.

Keywords Poly(3,4-ethylenedioxythiophene) (PEDOT) · IrO₂ · Electrooxidation · Morphine

1 Introduction

Morphine is widely used in clinical anesthesia, analgesia, and treatment of drug abuse. However, it also has serious side

effects, e.g. the risk of addiction, the development of tolerance, and respiratory depression. Thereby, optimal dosing of morphine requires the monitoring of its concentration in blood. In addition, abuse of morphine is illegal in most countries, and the detection of morphine in biological fluids is also required for the purpose of law enforcement. Various techniques, such as radioimmunoassay (RIA) [1], enzyme-linked immunosorbent assay (ELISA) [2], high performance liquid chromatography (HPLC) [3, 4], gas chromatography-mass spectroscopy (GC-MS) [5, 6] have been developed for the analysis of morphine, but they require either expensive reagents or complicated equipments.

Electrochemical method, on the basis of the electrochemical oxidation of morphine, has been attracting more and more attentions for morphine detection due to its high sensitivity, low cost and low time consumption. The phenolic group in morphine molecular is responsible for its electroactivity, which has been studied by voltammetry using different electrode materials, e.g. platinum, graphite and glassy carbon (GC) electrodes [7–10]. But more often used in electrochemical detection of morphine are modified electrodes, such as cobalt hexacyanoferrate-modified [11] and multiwall carbon nanotubes-modified [12] GCs and Prussian blue (PB)-modified indium–tin oxide (ITO) glass [13]. The recent advance is the development of a so-called molecularly imprinted polymer (MIP) [14–16]. A conducting polymer, mainly made of poly(3,4-ethylenedioxythiophene) (PEDOT), was used as the cross-linking matrix. The target molecular, e.g. morphine, was incorporated into the polymer and extracted by organic solvent, leaving holes in polymer with identical size of morphine molecule. The MIP is of very high selectivity for morphine detection against its analogs. Nevertheless, PEDOT-alone was very less often used for morphine electroanalysis, although it has high activity towards morphine electrooxidation.

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In this work, we reported the improved electrochemical performance of ITO-supported PEDOT film electrodes for morphine oxidation by surface modification with IrO₂ nanoparticles. IrO₂ is metallically conductive and is a very active electrocatalyst for, in particular, the oxygen evolution reaction (OER). Nowadays this oxide has been found its merits for electrocatalytic oxidation of organic compounds due to its specific ability of selective oxidation. Up to our best knowledge, IrO₂ has never been used as the electrocatalyst for the oxidation reactions of morphine or other drugs.

2 Experimental

2.1 Sample preparation

ITO glass (from Laibao Hi-tech Co. Ltd., Shenzhen, China) embedded by epoxy resin with working area of 0.8 cm² (0.8 × 1.0 cm) was used as the substrate. The substrate was sequentially washed in acetone, ethanol and 1/1 (v/v) ammonia/H₂O₂ mixed solution via sonication for 10, 10 and 30 min, respectively. Finally it was rinsed with DI-water and dried with hot air before use.

The ITO-based PEDOT electrodes (denoted “ITO/PEDOT electrodes”) were prepared by anodically electropolymerizing 3,4-ethylenedioxythiophene (EDOT, purchased from Aldrich) onto ITO substrates. 0.025 mol L⁻¹ EDOT aqueous solution with 0.1 mol L⁻¹ LiClO₄ as the supporting electrolyte was used. The electropolymerization was conducted using a three-electrode compartment, using an Ag/AgCl electrode as the reference and a Pt plate as the counter. The PEDOT films were potentiostatically electrodeposited at 1.2 V (vs. Ag/AgCl) until the charge of 20 mC was passed. Finally they were washed by DI water and dried in the air at room temperature.

The ITO-based PEDOT electrodes modified with IrO₂ layer (denoted “ITO/PEDOT/IrO₂ electrodes”) were fabricated by simply spreading a certain amount of IrO₂ colloid onto ITO/PEDOT electrodes prepared above. The IrO₂ colloid (6.2 × 10⁻⁴ mol L⁻¹) with the diameter of IrO₂ particles in the range of 10–20 nm was prepared by hydrolysis of H₂IrCl₆ in the presence of citrate ions as the stabilizer, as described elsewhere [17]. Different volumes (3, 10, 20, 40, 60, 80 μL, respectively) of IrO₂ colloid were dropped onto ITO/PEDOT electrodes, getting the ITO/PEDOT/IrO₂ electrodes with 0.52, 1.74, 3.47, 6.94, 10.42, 13.89 μg cm⁻² IrO₂, respectively. Finally the electrodes were dried at 50 °C for 2 h to remove the excessive solvents.

2.2 Characterizations

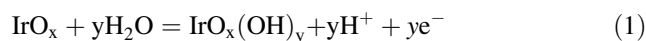
Electrochemical measurements were carried out at a three-electrode cell as described in Sect. 2.1. Voltammograms in

0.5 mol L⁻¹ Na₂SO₄ solution (pH 2.0 after adjusted by H₂SO₄) were recorded from 0 to 1.3 V (vs. Ag/AgCl) with a scan rate of 50 mV s⁻¹. Cyclic voltammograms (CVs) were performed in 0.1 mol L⁻¹ KCl + 4 mmol L⁻¹ morphine (in the form of morphine hydrochloride, 99.1%, purchased from Qinghai Pharmaceutical Factory Co. Ltd., with the authorized permission of Zhejiang Food and Drug Administration, China) between 0 and 1.0 V with a scan rate of 50 mV s⁻¹. All the electrochemical measurements were carried out at 20 °C on a CHI630B electrochemical workstation (CH Instruments). The electrode surface morphology was observed on a SIRION field emission scanning electron microscopy (SEM) (FEI Co. Ltd).

3 Results and discussion

Figure 1 shows the SEM images of ITO/PEDOT, ITO/IrO₂ (3.47 μg cm⁻²) and ITO/PEDOT/IrO₂ (3.47 μg cm⁻²) electrodes. A rough island-like morphology is observed for the ITO/PEDOT electrode (Fig. 1a), which is in agreement with the literature reports [18]. It is interesting that IrO₂ particles (white highlight as determined by Energy Dispersive X-ray Spectroscopy, EDS) aggregate seriously on ITO surface (Fig. 1b), but disperse much better on PEDOT-covered substrate (Fig. 1c). The reason for the merit of the latter substrate is still unclear, but may come from its higher hydrophobicity, while the bare ITO surface is highly hydrophilic.

The presence of IrO₂ on ITO/PEDOT/IrO₂ electrodes was further verified by voltammetric measurements in Na₂SO₄ aqueous solution (Fig. 2a). The bare ITO substrate nearly has no current response in the whole potential range, while the current measured at the ITO electrode coated with 3.47 μg cm⁻³ IrO₂ sharply increases when the potential reaches 1.16 V due to the occurrence of the OER [17, 19, 20]. However, at the ITO/PEDOT electrode, obvious Faradaic currents are observed at much lower potentials (E ≥ 0.6 V), corresponding to the oxidation of PEDOT film itself [21, 22]. Moreover, for IrO₂-containing electrodes (ITO/IrO₂ and ITO/PEDOT/IrO₂), an oxidation peak, which was believed to be attributed to the reversible transition between lower iridium oxides and higher iridium oxides (reaction 1) [23, 24], is observed in a broad potential range of 0.4–0.8 V (see enlarged plots in Fig. 2a: red and green curves).



Such a characteristic redox pair for IrO₂ electrocatalyst is also observed in KCl solution in the potential range of ~0.3–0.7 V (curves 3 and 4 in Fig. 2b). In addition, it is clearly shown that the capacitive currents at PEDOT-containing electrodes (ITO/PEDOT and ITO/PEDOT/IrO₂)

Fig. 1 SEM images of ITO coated with PEDOT (a), IrO₂ (b) and PEDOT/IrO₂ (c)

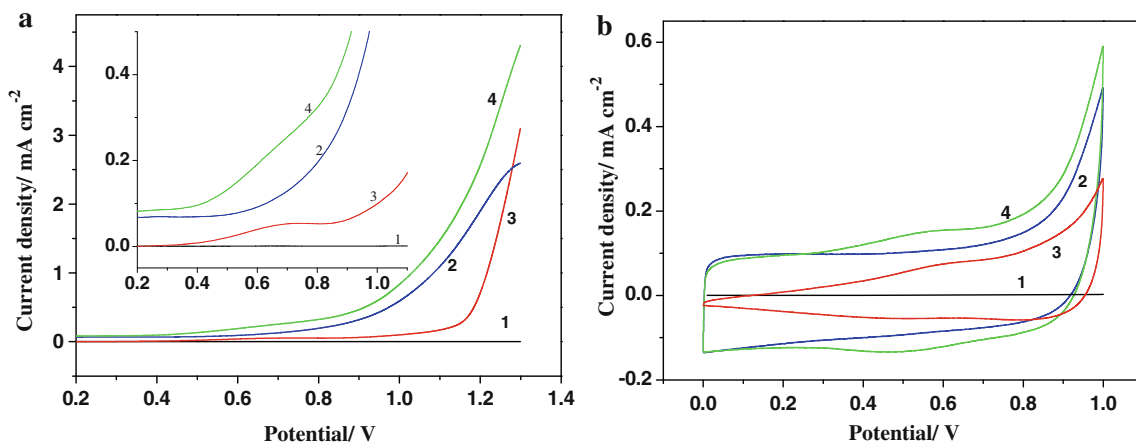
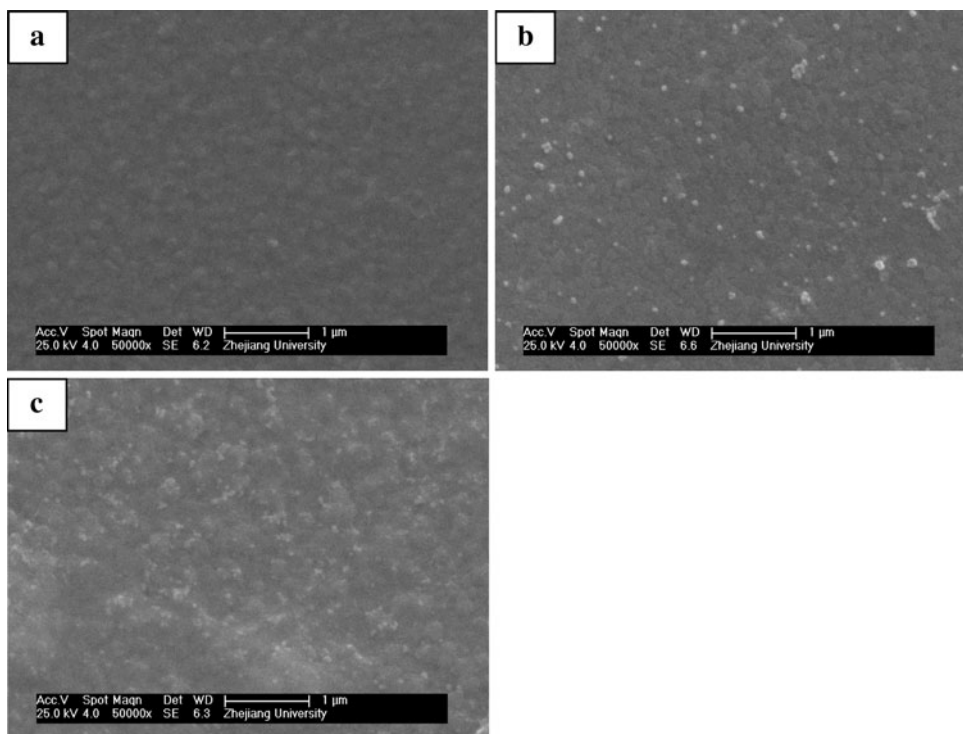


Fig. 2 Voltammograms of bare ITO (1), ITO/PEDOT (2), ITO/IrO₂ (3) and ITO/PEDOT/IrO₂ (4) electrodes in 0.5 mol L⁻¹ Na₂SO₄ (pH 2.0) (a) and 0.1 mol L⁻¹ KCl (pH 5.0) (b) solutions. Potential

scan rate: 0.05 V s⁻¹; IrO₂ loading: 3.47 μg cm⁻². *Inset in a* shows the enlarged plots before the OER

in the both solutions are significantly higher (~0.07–0.08 mA cm⁻² in Na₂SO₄ and ~0.1 mA cm⁻² in KCl solution) than those at electrodes without PEDOT layer (bare ITO and ITO/IrO₂). The non-faradic capacitive current (*i_c*), as a result of charging process of double-layer capacitor, is proportional to double layer capacitance (*C_{dl}*, C cm⁻²) and potential scan rate (*v*) by the following equation:

$$i_c = C_{dl} \cdot v \tag{2}$$

while *C_{dl}* is a function of effective surface area (*S_r*) and thickness (*d*) of capacitor:

$$C_{dl} = \epsilon \epsilon_0 S_r / (S_a d) \tag{3}$$

where ϵ and ϵ_0 are dielectric coefficient (~78.5 at 298 K for water) and dielectric constant of vacuum (8.85×10^{-14} F cm⁻¹), respectively, and *S_a* is the apparent surface area (here is 0.8 cm²). *d* is an approximate value of Debye length (κ^{-1}), which is mainly determined by the ionic strength of testing solution. Thereby, the dramatically increased capacitive currents suggest that after pre-coated with a conducting polymer PEDOT layer, the effective electro-active area of ITO electrode is increased

accordingly. This may facilitate its electrochemical activity toward organic oxidation reactions.

Figure 3 shows the cyclic voltammograms of different ITO electrodes in $0.1 \text{ mol dm}^{-3} \text{ KCl} + 4 \times 10^{-3} \text{ mol dm}^{-3}$ morphine solution (denoted “morphine solution”). Anodic peaks at $\sim 0.79 \text{ V}$ (P1) corresponding to the oxidation of morphine are found at both the ITO/PEDOT and ITO/ IrO_2 electrodes. Better peak-shaped current response is observed at ITO/PEDOT/ IrO_2 electrode. More interestingly, compared with the former two electrodes, the ITO/PEDOT/ IrO_2 electrode performs a negative shift in the peak potential (from ~ 0.79 to $\sim 0.73 \text{ V}$, P2), accompanying with obvious enhancement in the current response. These phenomena indicate that the ITO/PEDOT/ IrO_2 electrodes have better electrocatalytic activity for morphine oxidation than ITO/

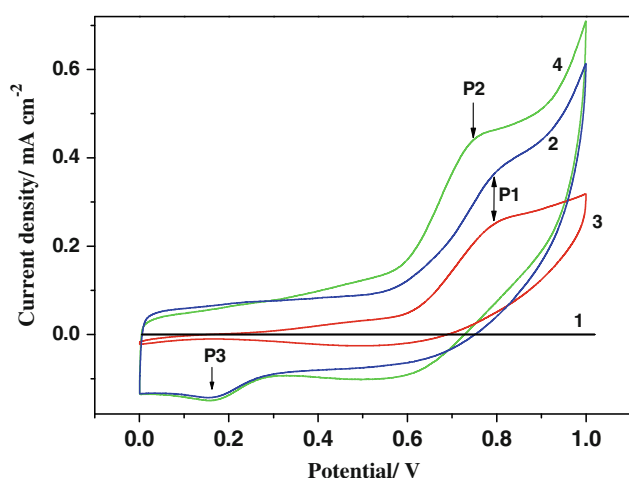


Fig. 3 Cyclic voltammograms of ITO (1), ITO/PEDOT (2), ITO/ IrO_2 (3), and ITO/PEDOT/ IrO_2 (4) electrodes in $0.1 \text{ mol L}^{-1} \text{ KCl} + 4 \text{ mmol L}^{-1}$ morphine (pH 5.0). IrO_2 loading: $3.47 \mu\text{g cm}^{-2}$; potential scan rate: 0.05 V s^{-1}

PEDOT and ITO/ IrO_2 electrodes. At $\sim 0.15 \text{ V}$ a reduction peak (P3) appears at PEDOT-containing electrode. Its origination is still unclear, but is probably attributed to the reduction reaction of PEDOT layer under the specific condition of morphine existence.

As the IrO_2 content in ITO/PEDOT/ IrO_2 electrodes increases, the peak potential remains unchangeable (not shown in context), but the background-subtracted peak current response for morphine oxidation increases until the IrO_2 loading reaches $3.47 \mu\text{g cm}^{-2}$, after then remains approximately constant (Fig. 4a). The peak current data are read at 0.79 V for ITO/PEDOT (without IrO_2), but at 0.73 V for ITO/PEDOT/ IrO_2 electrodes, and then subtracted by the measured current in KCl control solution at the same potential. For the purpose of comparison, in Fig. 4a also provides the net peak oxidation current at ITO/ IrO_2 ($6.94 \mu\text{g cm}^{-2}$) electrode, whose lower current response (0.16 mA cm^{-2}) indicates the positive contribution of PEDOT intermediate layer on the reaction kinetics of morphine oxidation. This result is in good agreement with the enhanced effective electro-active area of PEDOT-coated ITO electrodes, as mentioned above.

According to reaction 1, the integrated charge (q^*) used for de-protonation or proton insertion process can in situ evaluate the number of active sites of IrO_2 active layer [25]. Shown in Fig. 4b is the q^* value as a function of IrO_2 loading at ITO/PEDOT electrodes, as obtained from cyclic voltammetric measurements in $0.1 \text{ mol dm}^{-3} \text{ KCl}$ solution. It is shown that q^* constantly increases as the IrO_2 loading increases up to $3.47 \mu\text{g cm}^{-2}$, after that q^* almost remains unchangeable. This trend is very similar to that of current response for morphine oxidation as a function of IrO_2 loading (see Fig. 4a), indicating that the enhancement of current response at IrO_2 -modified ITO/PEDOT electrodes could be mainly attributed to the increase in electroactive

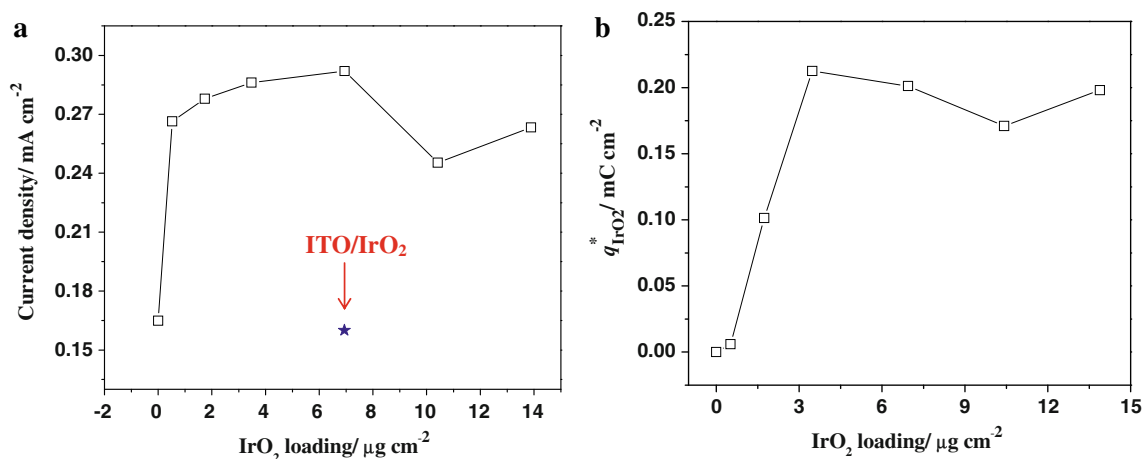
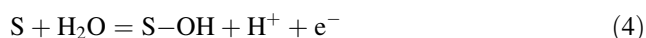


Fig. 4 **a** Peak current for morphine oxidation at ITO/PEDOT/ IrO_2 electrodes as a function of IrO_2 loading; **b** integrated charge of redox pair of ITO/PEDOT/ IrO_2 electrodes in $0.1 \text{ mol L}^{-1} \text{ KCl}$ solution (pH 5.0). Scanning rate: 50 mV s^{-1}

surface area. Considering the particle size of IrO_2 colloid (10–20 nm) and the unit cell parameters of rutile-structured IrO_2 ($a = 4.50 \text{ \AA}$ and $c = 3.16 \text{ \AA}$) [26], one can approximately estimate that $2.44\text{--}4.87 \mu\text{g cm}^{-2}$ IrO_2 is required for the entire coverage on PEDOT substrate by a single layer of IrO_2 particles (10–20 nm). This prediction is in agreement with the optimal value ($3.47 \mu\text{g cm}^{-2}$) as observed in Fig. 4a and b.

However, for ITO/PEDOT/ IrO_2 electrodes, the higher electrochemically active area of IrO_2 layer could not well explain the negative shift in peak potential compared with the ITO/PEDOT electrodes, suggesting that one need to consider more insight into the oxidation kinetics of morphine on composite electrodes. Electrochemical oxidation of morphine is very complex and depends on a variety of parameter such as electrode materials, potential and pH of solution. Several intermediates and products that were related to the oxidation of phenol and tertiary amine groups, have been detected [10]. Clearly determining the oxidation products on PEDOT and IrO_2 electrodes is beyond the range of the present work. To explain the ease of oxidation (negative shift in oxidation potential) at IrO_2 -coated PEDOT electrode in general aspect, one needs to realize the specific oxidation mechanism of an organic compound, R (here represents morphine molecule), at IrO_2 electrode. According to Comninellis' theory [25], for active oxides (e.g. IrO_2 and RuO_2) the anodically formed higher oxides act as the chemical oxidant for organics oxidation. The general description is rewritten as follows [25, 27]:



where S stands for the active sites of IrO_2 component, S-OH and S-O are two higher oxidation states. If simply assuming that the product for morphine oxidation at PEDOT film is R' , and taking into account the general de-protonation process for morphine oxidation at conventional electrodes [10], i.e.:



it is reasonable to expect that the reaction 7 will be facilitated since the product R' can be further oxidized by S-O by the following chemical reaction:



This additional reaction can probably explain the synergetic effect at IrO_2 plus PEDOT hybrid electrocatalyst for morphine oxidation (negative shift in oxidation potential and enhanced detection current).

The de-protonation process in morphine oxidation implies a Nernst relation between the oxidation peak potential and the solution pH. However, the measured peak potentials at IrO_2 -covered electrode ($\sim 0.73 \text{ V}$) and at PEDOT-alone electrode ($\sim 0.79 \text{ V}$) are both pH independent (not shown). This result clearly suggests the indirect electrooxidation reaction of morphine at IrO_2 electrode, which is consistent with the characteristic mechanism for organic oxidation at this type electrode (reactions 6 and 8). The fact of pH-independent peak potential discriminates the pH influence of the real sample (e.g. urine and blood), which is one important advantage for the suitable application of IrO_2 -modified layer in morphine detection. The peak currents measured in solutions with various pHs all indicate a pronounced improvement in electrochemical activity for morphine oxidation at IrO_2 -modified electrode (Fig. 5).

The enhanced electrochemical property of IrO_2 -modified electrode toward the oxidation of morphine was also evaluated by potential step experiment from 0.2 V, where morphine cannot be oxidized, to an anodic potential, say 0.65 V, where intensive oxidation reaction occurs. Higher current response is obtained at IrO_2 -modified electrode than at un-modified PEDOT electrode during the long measuring time (Fig. 6), in spite of the fact that the former electrode is more likely to be de-activated, probably due to the dissolution of active IrO_2 layer during the measurement.

The improved electrochemical activity for morphine oxidation suggests that the IrO_2 -coated PEDOT electrode may be a good candidate for morphine detection. The investigation of morphine detection at this novel electrode is now on-going in our lab. The detailed report will be appeared in the further work.

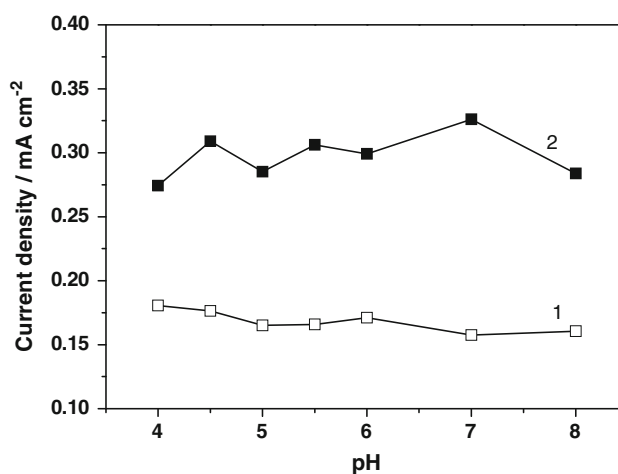


Fig. 5 Influence of solution pH on the peak current for morphine oxidation in 0.1 mol L^{-1} KCl + 4 mmol L^{-1} morphine at ITO/PEDOT (1) and ITO/PEDOT/ IrO_2 (2) electrodes

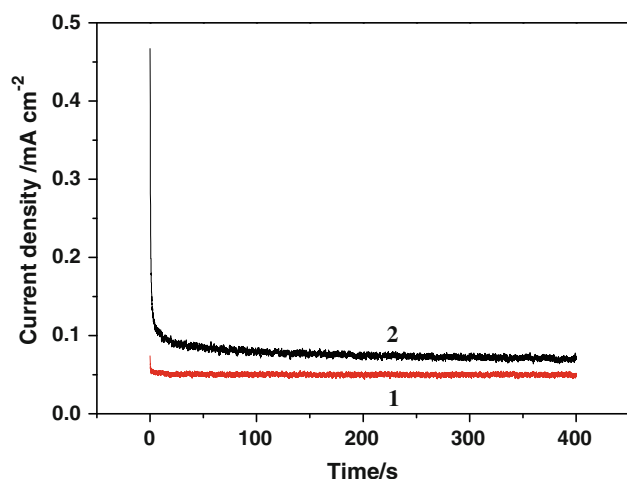


Fig. 6 Current–time responses in 0.1 mol L⁻¹ KCl + 0.6 mmol L⁻¹ morphine (pH 5.0) at PEDOT (1) and IrO₂ (3.47 μg cm⁻²)/PEDOT (2)-modified ITO. Applied potential, 0.65 V

4 Conclusions

After dip-coating IrO₂ colloid layer, the electrochemical activity for morphine oxidation at ITO-supported PEDOT electrodes is apparently enhanced, due to the additional oxidation reactions of morphine and its intermediate products taken place at active IrO₂ sites. Here, PEDOT conducting layer acts as an intermediate layer, which not only has high active area but also provide a uniformly dispersed IrO₂ layer thereon. The merit of IrO₂ modification implies its potential application in morphine detection.

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