Int. J. Electrochem. Sci., 13 **(2018)** 2126 – 2135, doi: 10.20964/2018.02.66

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Electrochemical Sensor Based on poly(3,4-ethylenedioxy - thiophene) Doped with Transition Metals for Detecting Rutin in Buck Wheat Tea

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Received: 15 June 2017 / *Accepted:* 18 August 2017 / *Published:* 28 December 2017

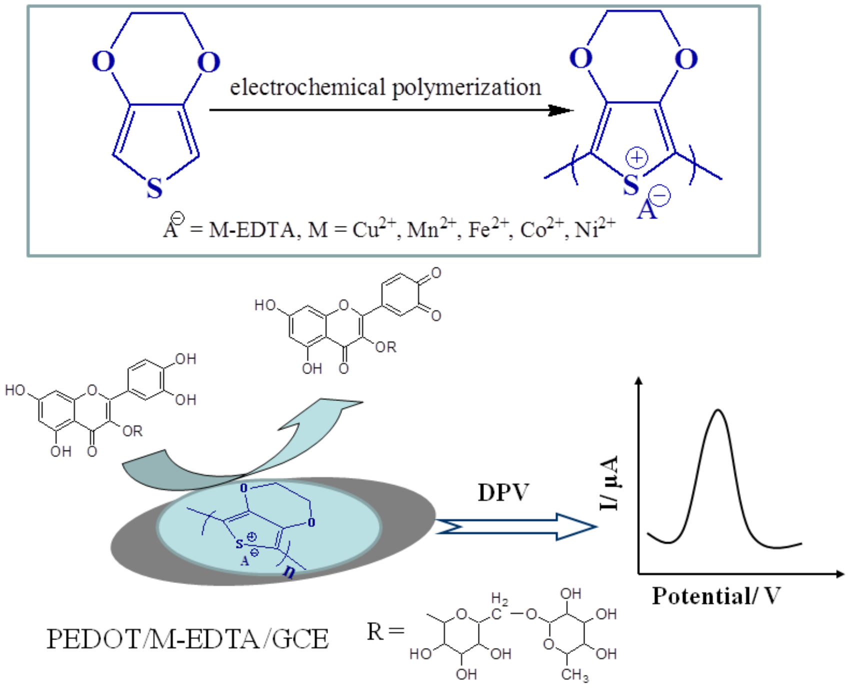
Herein, poly(3,4-ethylenedioxythiophene) (PEDOT) films doped with transition metals were electrochemically synthesized. Transition metal ions-EDTA (M-EDTA, M = Cu^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}) complexes served as dopants. Rutin as model molecular was utilized to investigate its electrochemical responses at PEDOT/M-EDTA modified electrodes. It was found the PEDOT/Co^{2+}-EDTA exhibited better electrocatalytic activity toward rutin oxidation than other PEDOT/M-EDTA modified electrodes. Thus, PEDOT/Co^{2+}-EDTA film-based electrochemical sensor was used to detect rutin. Low detection limit (1.67 nM), good reproducibility and wide linear range (5 nM-100 μM) were obtained. The sensor was employed for the determination of rutin in buckwheat tea. These results suggest that PEDOT/Co^{2+}-EDTA could be utilized as a promising sensing platform for rutin detection.

Keywords: PEDOT; Transition metals; Rutin; Electrochemical detection; Sensor

1. INTRODUCTION

Rutin, a flavonoid compound, is pharmacologically and physiologically active with anti-inflammatory, anti-tumor, anti-bacteria and anti-oxidant property [1-3]. Usually, it can be applied for clinical medicine. Capillary electrophoresis, high performance liquid chromatography, spectrophotometry, chemiluminescence and electrochemical methods have been investigated for detecting rutin [4-8]. Among them, electrochemical techniques provide an efficient method for the detection of rutin because of their simple operation, fast response, portability, and low cost instrumentation. However, for the determination of rutin, chemically modified electrodes are needed to improve adequate sensitivity, selectivity and stability.

Conducting polymers are of intense interests for chemical modification of electrodes by virtue of their high stability, good conductivity, reproducibility and homogeneity, and high adherence to electrode surface. Of various conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most promising polymers for its interesting transparency, good conductivity, biocompatibility and environmental stability [9]. These properties make PEDOT suitable candidate as an electronic material, especially for constructing various sensors [10-13]. Moreover, the catalytic and electronic properties of PEDOT could be improved by doping different types of active materials, such as ferricyanide and ferrocenecarboxylic acid [14,15]. Transition metal complexes as redox species have attracted considerable attentions in the area of electroanalysis. They have been widely employed as electrode materials for detecting varieties of environmental and biological substances, including H_2O_2 [16], nitrite [17], uric acid [18], l-glutathione [19], and peroxyacetic acid [20]. The combination of PEDOT and Ni-EDTA could result in synergistic properties between the disparate components. In our previous work, PEDOT doped Ni-EDTA as electrochemical sensing platform has been used for detecting luteolin and good analytical results were obtained [21]. However, till now, PEDOT/transition metal ions-EDTA nanocomposite has not been found in detecting rutin.



Scheme 1. The preparation process of doped PEDOT films (PEDOT/M-EDTA) and the electrochemical detection of Rutin.

In this study, five kinds of M-EDTA complexes (Cu^{2+}-EDTA, Mn^{2+}-EDTA, Fe^{3+}-EDTA, Co^{2+}-EDTA and Ni^{2+}-EDTA) were selected as doping species to prepare PEDOT films using electrodeposition method (as shown in Scheme 1). FTIR and UV/vis were used to characterize the doped PEDOT films and the electrocatalytic performance towards rutin was investigated by cyclic voltammogram (CV) at different PEDOT/M-EDTA modified electrodes. Among them, PEDOT/Co^{2+}-EDTA modified electrode showed higher catalytic peak currents due to the synergetic effects between PEDOT and Co^{2+}-EDTA complex. The PEDOT/Co^{2+}-EDTA modified electrode displayed high selectivity and sensitivity. The sensor has been applied for the determination of rutin in buckwheat tea sample.

2. EXPERIMENTAL

2.1 Chemicals

Buckwheat tea was supplied by Sichuan reagent factory. Na_2EDTA was purchased from Shanghai reagent factory. $CoCl_2$, $MnCl_2$, $FeCl_3$, $CuCl_2$ and $NiCl_2$ were purchased from Aldrich. EDOT was supplied by Tianjin Damao Chemical Factory. The solution of phosphate buffer consisting of 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4 served as supporting electrolyte. All reagents were of analytical grade.

2.2 Apparatus

The UV-vis and FT-IR measurements were operated on UV-vis spectrometer (Agilent 8453) and FTIR spectrophotometer (Nexus 670). Electrochemical tests were conducted on CHI660E electrochemical workstation (ChenHua Instruments Co., Shanghai, China). Three-electrode system was involved, where bare GCE ($\Phi = 3$ mm) and saturated calomel electrode (SCE) served as working and reference electrodes. Counter electrode was platinum foil electrode. All potentials were measured versus the SCE.

2.3 Preparation of the modified electrodes

GCE was polished using 0.05 μm Al_2O_3 slurry. It was then ultrasonically cleaned in double distilled water.

The PEDOT/GCE was electrochemically synthesized by immersing bare GCE in 10 mM EDOT and 30 mM NaCl deposition solution using chronoamperometry. Similarly, the PEDOT/EDTA/GCE was obtained by dipping the cleaned GCE in solution containing 10 mM EDOT and 10 mM Na_2EDTA. Other PEDOT/Cu^{2+}-EDTA, PEDOT/Mn^{2+}-EDTA, PEDOT/Fe^{3+}-EDTA, PEDOT/Co^{2+} -EDTA and PEDOT/Ni^{2+}-EDTA modified GCEs were obtained immersing bare GCEs in 10 mM EDOT and 10 mM Na_2EDTA solution containing 15 mM $CuCl_2$, 15 mM $MnCl_2$, 15 mM $FeCl_3$, 15 mM $CoCl_2$ and 15 mM $NiCl_2$, respectively. All the deposition potential is 1.05 V and deposition time is 90 s.

3. RESULTS AND DISCUSSION

3.1 Structural characterizations of the doped PEDOT films

Fig. 1A shows the FT-IR spectrum of as-prepared PEDOT/M-EDTA films. As shown, three typical peaks for PEDOT (a) are observed at 1621, 1358 and 1145 cm^{-1}. The absorption peak at 1621 cm^{-1} represents the doping level of PEDOT [22]. The peak at 1358 cm^{-1} belongs to C=C stretching vibration of thiophene ring and 1145 cm^{-1} is attributed to C-O-C stretching vibrations in ethylenedioxy group. The peaks at 982, 835 and 698 cm^{-1} are ascribed to the C-S stretching mode in thiophene ring. Other characteristic peaks at 1204 and 1051 cm^{-1} are attributed to the stretching modes of ethylenedioxy group [23,24]. In Fig. 1A(b), apart from the similar peaks derived from PEDOT, new bands at 1604 cm^{-1} and 1390 cm^{-1} are associated to the symmetric vibration of carboxyl group of EDTA [25]. For the spectrums of PEDOT/Cu^{2+}-EDTA (c), PEDOT/Mn^{2+}-EDTA (d), PEDOT/Fe^{3+}-EDTA (e), PEDOT/Co^{2+}-EDTA (f) and PEDOT/Ni^{2+}-EDTA (g), the obvious blue-shifts are observed in relative with PEDOT/EDTA (b), indicating EDTA-metal ions complexes were doped in these PEDOT films.

Furthermore, the structural characterization of PEDOT/M-EDTA films was investigated using UV-vis spectrum (Fig. 1B). The characteristic peaks at about 360 nm corresponds to π-π^* transitions in the benzenoid units of PEDOT chain [26]. Other broad absorption peaks at 623, 636, 704, 723, 752, 781, 818, 846 and 861 nm were observed at PEDOT (a), PEDOT/EDTA (b), PEDOT/Cu^{2+}-EDTA (c), PEDOT/Mn^{2+}-EDTA (d), PEDOT/Fe^{3+}-EDTA (e), PEDOT/Co^{2+}-EDTA (f) and PEDOT/Ni^{2+}-EDTA (g), respectively. These typical bands can be found in partially doped PEDOT [27,28].

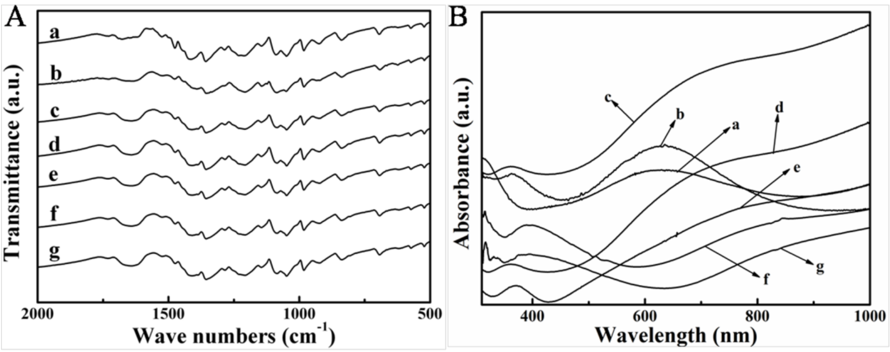


Figure 1. (A) FT-IR spectrum of PEDOT (a), PEDOT/EDTA (b), PEDOT/Cu^{2+}-EDTA (c), PEDOT/Mn^{2+}-EDTA (d), PEDOT/Fe^{3+}-EDTA (e), PEDOT/Co^{2+}-EDTA (f) and PEDOT/Ni^{2+}-EDTA (g). (B) UV-vis spectrum of PEDOT (a), PEDOT/EDTA (b), PEDOT/Cu^{2+}-EDTA (c), PEDOT/Mn^{2+}-EDTA (d), PEDOT/Fe^{3+}-EDTA (e), PEDOT/Co^{2+}-EDTA (f) and PEDOT/Ni^{2+}-EDTA (g).

3.2 Electrochemical behavior of PEDOT/Co^{2+}-EDTA/GCE

Fig. 2 depicted the cyclic voltammograms (CVs) of various electrodes in 0.1 M PBS (pH 3.0) containing 100 μM rutin. As shown, the redox peak currents at bare GCE (a) are weak, which is due to slow electron transfer on GCE. Compared with bare GCE (a), PEDOT/GCE (b) and

PEDOT/EDTA/GCE (c) show increased redox peak currents, indicating PEDOT films has good conductivity. In contrast, the peak currents of rutin on PEDOT/Cu^{2+}-EDTA/GCE (d), PEDOT/Mn^{2+}-EDTA/GCE (e), PEDOT/Fe^{3+}-EDTA/GCE (f), PEDOT/Co^{2+}-EDTA/GCE (g) and PEDOT/Ni^{2+}-EDTA/GCE (h) are dramatically enhanced. This is probably caused by the synergetic effects from PEDOT (high electrical conductivity) and transition metal complexes (high redox activity). Particularly, it is clearly observed that PEDOT/Co^{2+}-EDTA/GCE shows a higher electrocatalytic current for rutin.

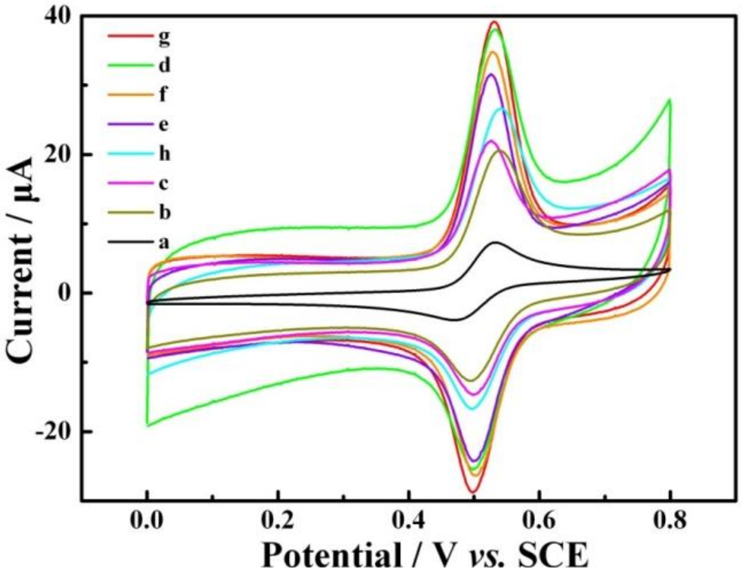


Figure 2. CVs of bare (a), PEDOT (b), PEDOT/EDTA (c), PEDOT/Cu^{2+}-EDTA (d), PEDOT/Mn^{2+}-EDTA (e), PEDOT/Fe^{3+}-EDTA (f), PEDOT/Co^{2+}-EDTA (g) and PEDOT/Ni^{2+}-EDTA (h) modified GCEs in 0.1 M PBS (pH 3.0) containing 100 µM rutin; Scan rate: 50 mV s^{-1}.

3.3 Influence of pH value

The dependence of solution pH value on the electrochemical response towards 100 µM rutin (0.1 M PBS) at PEDOT/Co^{2+}-EDTA/GCE was studied. As illustrated in Fig. 3, with the increasement of pH value from 2.0 to 8.0, both the anodic and the cathodic peaks shifte negatively, implying that protons participated in the electro-oxidation process. Furthermore, there is a good linear relationship between the anodic peak potential and pH. The corresponding regression equation is Ep = -0.061 pH + 0.7 (R^2= 0.9978) (inset of Fig. 3). The slope value of -61 mV/pH is close to the theortical value (-59 mV/pH), suggesting the oxidation processes of rutin on PEDOT/Co^{2+}-EDTA/GCE involved equal numbers of electrons and protons [29]. In addition, the maximum value of peak current was observed at pH 3.0. Thus, pH 3.0 was chosen for detecting rutin in this work.

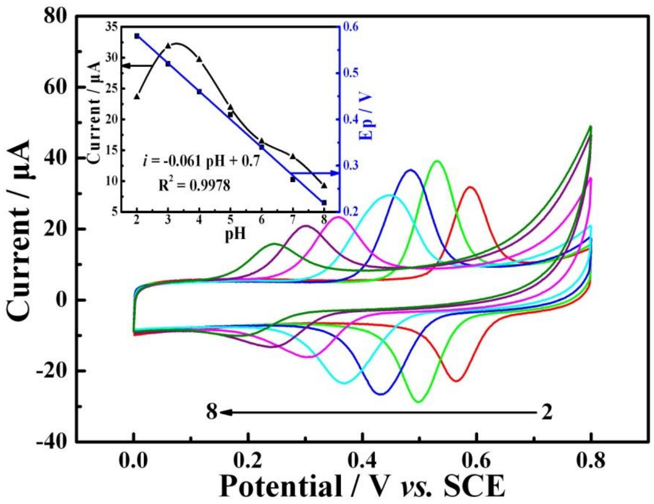


Figure 3. CVs of PEDOT/Co^{2+}-EDTA/GCE at different pH values (2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0) in PBS containing100 μM rutin. Scan rate: 50 mV s^{-1}; Inset: the influences of pH on the oxidative peak current and oxidative peak potential of 100 μM rutin.

3.4 Influence of scan rate

The effect of scan rate was studied by CV (Fig. 4). As the scan rates increased from 10 to 400 mV s^{-1}, the anode (Epa) and cathode (Epc) peak currents increase accompanied with the shift of the redox peaks potentials. The linear relationships between Epa and Epc peak currents and scan rates are observed as Ipa (μA) = 0.45 v (mV s^{-1}) + 16.23 (R^2 = 0.9902) and Ipc (μA) = -0.37 v (mV s^{-1}) - 9.03 (R^2 = 0.9949). This means that the electrode reaction of rutin on PEDOT/Co^{2+}-EDTA/GCE was dominated by the surface adsorption-controlled process.

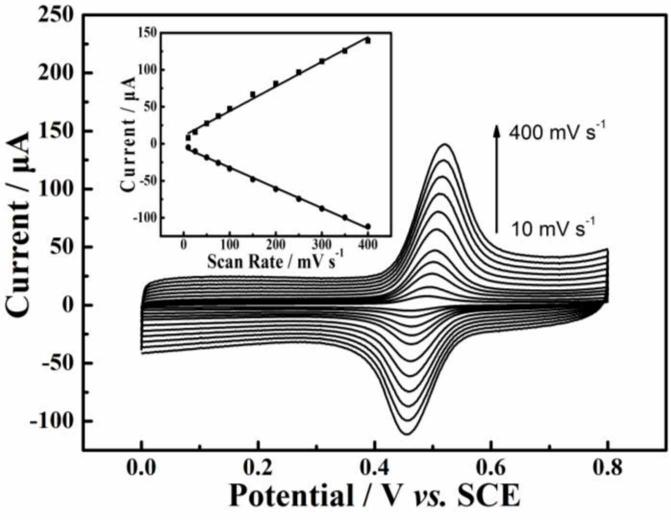


Figure 4. CVs of PEDOT/Co^{2+}-EDTA/GCE in PBS containing100 μM rutin at with different scan rates: 10, 25, 50, 75, 100, 150, 200, 250, 300, 350, 400 mV s^{-1}; Inset: Plots of redox peak currents vs potential scan rates.

3.5 Determination of rutin on PEDOT/Co^{2+}-EDTA/GCE

Differential pulse voltammetry (DPV) was used to study the detection performance of the PEDOT/Co^{2+}-EDTA/GCE towards rutin. The anodic peak currents increased with increasing the concentrations of rutin (Fig. 5). The inset in Fig. 5 displays that the resulting calibration plots are linear over the range from 0.005 to 100 μM. The calibration equation was I (μA) = 0.089 C(μM) + 0.21 (R^2 = 0.9981). The detection limit was found to be 1.67 nM (S/N = 3), which is lower than the values from the previous modified electrodes (Table 1) [30-35]. The low detection limit of PEDOT/Co^{2+}-EDTA/GCE can be ascribed to the promoted electron transfer and superb catalytic activity afforded by PEDOT and Co^{2+}-EDTA.

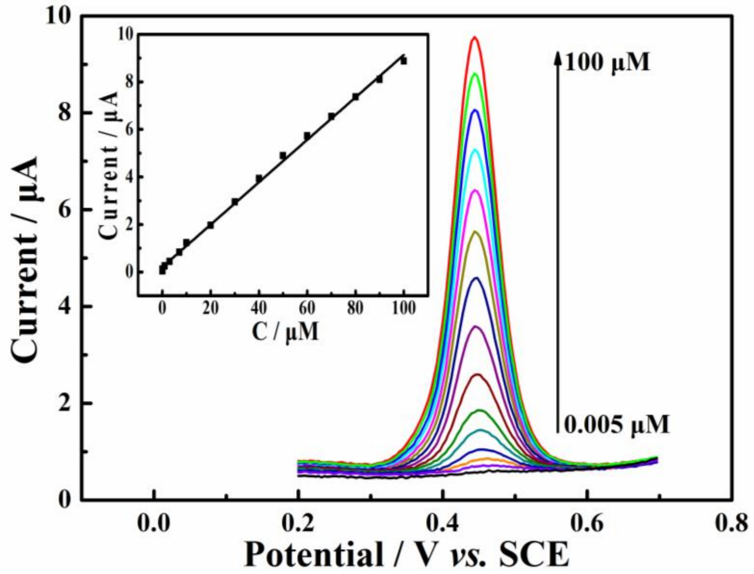


Figure. 5. DPVs of PEDOT/Co^{2+}-EDTA modified GCE in PBS (pH 3.0) containing various concentration of rutin; Inset: plot of i vs. concentration of rutin.

Table 1. The comparison of the fabricated sensor with reported electrochemical methods for the detection of rutin.

Electrodes	Linear range	Detection limit	Reference
Graphene/carbon ionic liquid	70 nM-100 μM	24 nM	[30]
Polypyrrole-graphene-MWCNTs	10 nM-1 μM	5 nM	[31]
Cu_2O-Au/ nitrogen-doped graphene	60 nM-512.9 μM	30 nM	[32]
$NiCo_2O_4$-decorated reduced graphene oxide	100 nM-150 μM	10 nM	[33]
β-cyclodextrin/MWNTs	400 nM-1 mM	200 nM	[34]
Graphene/carbon ionic liquid electrode	70 nM-100 μM	24 nM	[35]
PEDOT/Co^{2+}-EDTA	5 nM -100 μM	1.67 nM	This work

3.6. Reproducibility, stability and selectivity of PEDOT/Co^{2+}-EDTA/GCE

The reproducibility of PEDOT/Co^{2+}-EDTA/GCE was studied by repetitively detecting 50 μM rutin for 20 times. The relative standard deviation (RSD) was 1.47% (n= 5) (Fig. 6A), suggesting the modified electrode has good reproducibility. To study the stability of the electrode, PEDOT/Co^{2+}-EDTA/GCE was used to measure 50 μM rutin every few days. From Fig. 6B, we can see that the anodic peak current decreases less than 5% from its original value for 30 days, demonstrating the proposed method possesses good stability.

Possible interferences for rutin determination were also investigated. A fixed amount of 50 μM rutin was mixed with possible interfering substances. The results demonstrated that Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, in a 200-fold concentration, ascorbic acid, cysteine, glycine, citric acid and glucose in a 50-fold concentration, did not interfere the electrochemical determination of rutin according to the relative error <±5%.

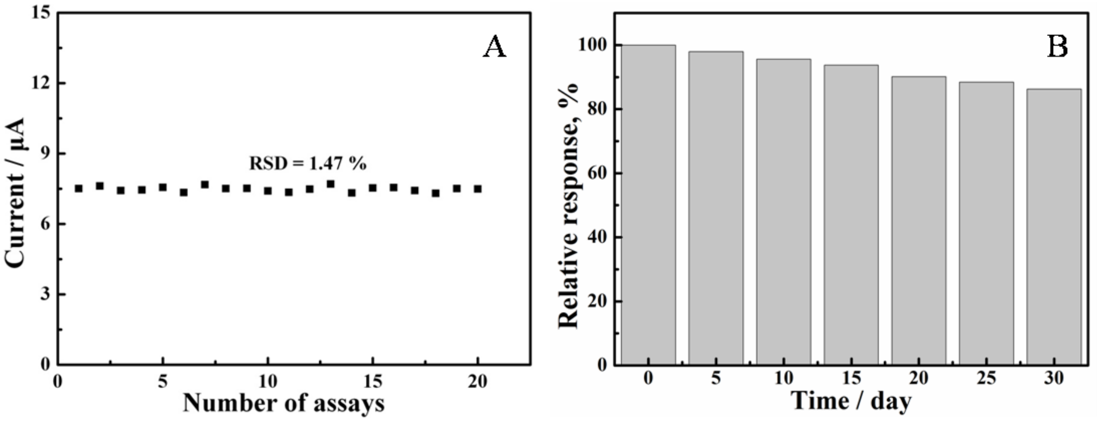


Figure 6. (A) The repeatability of the current response of the PEDOT/Co^{2+}-EDTA in 0.1 M PBS (pH 3.0) containing 50 μM rutin for 20 successive assays. (B) Long-term storage stability of the sensor.

3.7 Determination of rutin in buckwheat tea

Table 2. Determination of rutin in buckwheat tea samples (n= 3).

Sample	Detected (mg g-1)	Added (μM)	Found (μM)	Average recovery (%)	RSD recovery (%)
buckwheat tea	14.86 ± 0.46	10	9.83 ± 0.38	98.3	2.78
		20	21.16 ± 0.56	105.8	2.17
		50	49.87 ± 0.45	99.74	1.94

To study the practicability of PEDOT/Co^{2+}-EDTA/GCE, the recovery of rutin in buckwheat tea was measured by a standard addition method. Buckwheat tea was firstly triturated and dissolved in redistilled water. The sample solution was then filtered to remove insoluble impurities. After that, it was diluted and determined. Results were given in Table 2. The rutin content in the buckwheat tea was calculated to be 14.86 ± 0.46 mg g^{-1}, which was in consonance with the contents stated by manufacturer. The recovery was found to be 98.3-105.8%, indicating the prepared sensor can be efficiently utilized for detecting rutin in buckwheat tea.

4. CONCLUSIONS

In summary, PEDOT film doped Co^{2+}-EDTA complexe was electrochemically synthesized and was used as modified material for fabricating electrochemical sensor. Owing to the excellent electrical conductivity of PEDOT film and good redox activity of Co^{2+}-EDTA complex, PEDOT/Co^{2+}-EDTA electrode showed higher catalytic peak currents towards the determination of rutin. The rutin sensor based on PEDOT/Co^{2+}-EDTA electrode showed wide linear range, high reproducibility, selectivity and stability. In addition, PEDOT/Co^{2+}-EDTA electrode has been successfully used to determine rutin in buckwheat tea.

ACKNOWLEDGEMENTS
We are grateful to the National Natural Science Foundation of China (21665010 and 51302117), the outstanding youth fund of Jiangxi Province (20162BCB23027), the Natural Science Foundation of Jiangxi Province (20171BAB203015, 20151BAB203018, 2014BBF60002), and State Key Laboratory of Chemical Biosensing & Chemometrics (2015010) for their financial support of this work.

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