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UV-Light Photoelectrochemical Sensor Based on the Copper Tetraamino-Phthalocyanine-modified ITO Electrode for the Detection of Nifedipine in Drugs and Human Serum

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In this study, a new photoelectrochemical (PEC) sensor based on the copper tetraamino-phthalocyanine-modified ITO electrode (CuTAPc/ITO) was designed for the determination of nifedipine. The prepared CuTAPc materials were characterized using UV–Visible spectrophotometry (UVS), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). Then, the CuTAPc solution was coated on the ITO electrode surface to fabricate a simple PEC sensing platform. Then, the photoelectrochemical behavior of nifedipine at the CuTAPc/ITO electrode was investigated by chronoamperometry under ultraviolet light irradiation. The obtained results indicated that the modified electrode showed a higher response signal than the blank electrode. The photocurrent of CuTAPc/ITO increased with the increasing concentration of nifedipine. The peak photocurrents were linearly dependent on the nifedipine concentration in the range of 0.25–18.0 μmol/L, thereby providing the detection limit of 0.15 μmol/L ($S/N = 3$). Due to the good responses for the determination of nifedipine, this sensor can be used as an alternative analysis tool for the detection of nifedipine in various real samples with high sensitivity, low detection limit, and wide linearity range.

Keywords: Photoelectrochemical sensor, Copper tetraamino-phthalocyanine, Nifedipine

Introduction

Nifedipine [1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)-3,5-pyridinedicarboxylic acid dimethyl ester] (NP) is a dihydropyridine calcium antagonist that is used for the treatment of angina pectoris due to coronary heart disease, and in particular for variant angina pectoris and angina pectoris caused by coronary artery spasm, high blood pressure and cardiovascular disease.[1–3] The NP dosage must be strictly controlled. Excessive use of NP can trigger hypotension and proarrhythmic effects.[4] Therefore, the determination of NP level in pharmaceutical formulations is indispensable for the control of industrial product quality and for ensuring the suitable dose for the patients. Modern instrumental analysis techniques such as high-performance liquid chromatography (HPLC),[5,6] gas chromatography,[7,8] capillary gas chromatography,[9] and spectrophotometry[10,11] were established and applied to the determination of NP. Although HPLC and other combination technologies[12–14] have high sensitivity and selectivity, these analytical methods involve costly and time-consuming processes. It is urgently necessary to develop a method with simple operation, fast response, and low cost for use in NP detection.

Photoelectrochemical (PEC) sensors are an emerging analytical tool that is operated with an electrochemical workstation and a photoelectric instrument.[15] The light source is used to irradiate the photoactive materials to give rise to charge transfer and the electrochemical workstation is responsible for performing tasks and recording the strength of the photocurrent signal.[16] PEC sensors combine the advantages of optical methods and chemical sensors due to their simultaneous application of light irradiation and electrochemical detection.[17] Moreover, due to the separation of the light source and the detection signal, PEC sensors effectively reduce the background signal interference and improves the detection sensitivity.[18] PEC sensors have been successfully applied to the detection of environmental pollutants,[19] food additives,[20] drug content,[21] pesticide residues,[22,23] and enzymes.[24] Generally, PCE sensors have bright prospects for use in a wide range of applications.

As the paramount tetrapyrrole derivatives, metallophthalocyanine (MPc) compounds have been intensively studied in the recent years. MPc compounds have a highly delocalized 18 π-electron macrocyclic conjugate system with special optical, conductive, electron-donor, and electron-acceptor properties.[25] In addition, MPc shows unique thermal and chemical stability and photosensitivity and has also been widely used in the fabrication of photoelectrochemical sensors.[26] MPc also possesses a strong modifiable structure[27] that can accommodate different substituents that are introduced to improve its functions and overcome the disadvantage of poor solubility. For example, the properties of metal tetraamino-phthalocyanine (MTAPc) are not only superior to those of MPc, but MTAPc is also soluble in general organic solvents.[28] MTAPc compounds have been used in various applications, such as electrochemical sensors,[29] light-effect transistor,[30] optical sensor,[31] and solar cells.[32]

In this work, CuTAPc was dripped onto the ITO-coated glass electrode, producing a uniform, highly conductive, robust and strongly adherent coating. The modified electrode served as the working electrode of the PEC sensor for nifedipine detection. The PEC sensors exhibited high sensitivity, good selectivity, and low detection limits with satisfactory results.

Experimental

Apparatus. The photoelectrochemical experiments were carried out using a CHI 760E Electrochemical Workstation (Chenhua Instrument Co., Shanghai, China) and a PEAC 200A photoelectric alignment collimator (Tjaida Instrument Co., Tianjin, China) equipped with a 10-W light-emitting diode (LED). The LED provided the source of a 375-nm UV-light. The electrochemical workstation was directly connected to a three-electrode cell system. The CuTAPc/ITO electrode was used as the working electrode. A Pt wire was employed as the counter electrode and a saturated Ag/AgCl served as the reference electrode. The sizes and structures of the experimental materials were characterized by SEM (Hitachi S-4800, Tokyo, Japan; 5 kV), UVS (UV-6100S, Metash, Shanghai, China), FT-IR (Spectrum 65, Perkin Elmer, Santa Clara, CA, USA), and FS (RF-5301PC, Shimadzu, Japan) techniques. A pH meter (pHS—3C, Rex, Shanghai, China) was used to measure the pH of the solutions.

Chemicals and Materials. NP was purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). The human serum sample was originally obtained from Chongzuo People's Hospital (Guangxi, China). Sodium sulfate, copper chloride [$CuCl_2{\cdot}2H_2O$], and ammonium molybdate were provided by Xilong Scientific Co., Ltd. (Guangdong, China). Concentrated sulfuric acid, fuming nitric acid and *N*,*N*-dimethylformamide (DMF), and other chemicals used in this work were obtained from the Chengdu Kelong chemical reagent plant (Chengdu, China). All of the reagents used in this study were of analytical grade. All of the solutions were prepared using double distilled water. Britton-Robinson (B-R) buffer solution (0.04 mol/L) was prepared by mixing phosphoric acid, boric acid, and glacial acetic acid. A 0.2 mol/L NaOH solution was used to adjust the pH of the buffer solution. ITO-coated glass slices (6 Ω, 50 × 5 × 1.1 mm) were provided by Xiangcheng Technology Co., Ltd. (Shenzhen, China). All of the experiments were carried out under the National Law and Related Institutional Committee Regulations. Patients who provided blood samples were given the right to know about and to agree to participate in the trials.

Synthesis of CuTAPc materials. Following the reports in the literature[33,34,] the CuTAPc materials were synthesized as follows.

Synthesis of Copper Tetranitro-Phthalocyanine. 4-nitrophthalimide (4.10 g), urea (10.15 g), and molybdic acid (0.05 g) were ground evenly in a mortar. The resulting powder was then placed in a 250-mL flask and placed in an electric heating jacket to heat and melt. After all of the solid had melted, ground copper chloride powder (1.40 g) was added to the flask under stirring. The reaction temperature was maintained at 160 °C for 1 h. The solid product was ground and boiled for 1 h with an HCl solution (1 mol/L, 300 mL) and a NaOH solution (1 mol/L, 300 mL), respectively. The product was vacuum filtered, neutralized with water, and dried.

Synthesis of Copper Tetraamino-Phthalocyanine. CuTNPc (1.05 g) and sodium sulfide (7.14 g) were placed into a 250-mL three-necked flask, and then DMF (45 mL) was added. The temperature was kept at 60 °C under stirring for 1 h. The solid product was separated from the reaction mixture by centrifuging and was treated with a 1 mol/L HCl solution followed by the treatment with a 1 mol/L of NaOH solution. The suction filtered CuTAPc was washed to neutral with distilled water and dried to get obtain a dark green solid.

Construction of the Modified ITO-coated Glass Electrode. The ITO-coated glass electrode was ultrasonically washed with acetone, then anhydrous ethanol, and then distilled water, and then was dried under an infrared lamp. The modifier was prepared with CuTAPc (1 mg) and DMF (1 mL) and ultrasonically dispersed for 30 min. Then, 10 μL of the modifier was dripped onto the ITO electrode. The area of the material covering the electrode is 5×15 mm^2. After the modified electrode was dried naturally, a green film was formed on the surface.

NP sample preparation. The solutions were prepared in a darkened room. The coating of the NP tablets was removed, and the tablets were ground, and weighed precisely. An appropriate amount of methanol was added, and NPs were dissolved by ultrasonication. The initial solution of the sample (contains 1×10^{-3} mol/L NP) was diluted with the B-R buffer solution to the scale. The filtrate was collected for the filtration. The pretreatment process of the serum refers to the previous studies reported in the literature.[35] The serum samples were thawed at room temperature. Serum and methanol were placed in centrifuge tubes to precipitate the proteins at a volume ratio of 1: 3. The mixture was shaken vigorously for 2 min and then was centrifuged at 10000 rpm for 20 min.

Results and Discussion

Characterization of CuTAPc Materials. The characteristic functional groups of CuTAPc were identified by FT-IR spectroscopy (Figure 1(a)). A double peak was observed in the wavelength range of 3500–3200 cm^{-1} that corresponds to the presence of amino groups (ν_{NH2}).[34] The sharp peak at 1606 cm^{-1} (δ_{NH}) further proved the presence of amino groups.[36] The absorption peaks observed at 1136, 1083, 1047, 939, 817, and 743 cm^{-1} were due to the vibrations of the phthalocyanine skeleton.[37]

The UV–Vis spectra of CuTAPc in DMF are shown in Figure 1(b). Two absorption bands, the B band (341 nm), and the Q band (730 nm), appeared in the representative spectrum. Both of these absorption peaks are due to the π-electron transition on the ring of the tetraamine copper phthalocyanine. The B band is due to the $4a_{2u} \rightarrow 6e_g$ transition, and the Q band is due to the $2a_{1u} \rightarrow 6e_g$ transition. This finding is consistent with the previous reports in the literature.[28,38]

XRD was used to characterize and analyze the CuTAPc crystal structure. The XRD patterns of the CuTAPc powders showed diffraction peaks in the 2θ range of 10–80° (Figure 1(c)). The peaks were observed at the 28° plane. This peak corresponds to the characteristic peak of the CuTAPc materials.[39]

Electrochemical impedance spectroscopy. The electrochemical system examined in this work can be viewed as an equivalent circuit that is a combination of the resistance of the solution (R_s, R_{et}), double-layer capacitance (C_{dI}), and Warburg impedance (Z_w) in series and in parallel.[18] Electrochemical impedance spectroscopy (EIS) is a useful analysis technique for investigating the electrode surface dependent charge transfer process and efficiency.[40] EIS was carried out in a 3.0 mmol/L $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ solution containing 0.1 mol/L KCl for the characterization of the ITO and the CuTAPc/ITO electrodes. A small-amplitude alternating current signal at different frequencies was applied to the electrochemical system, with the highest frequency of 100 000 Hz, the lowest frequency of 1 Hz, and the amplitude of 0.005 V. As seen in Figure 2(a), the ITO electrode exhibited a larger semicircle diameter than the CuTAP/ITO electrode in the EIS. The electron-transfer resistance is equal to the semicircle diameter.[41] The results showed that the modified electrode has a lower resistance than the ITO electrode. This finding may be because the CuTAPc film has a reduced mass-transfer resistance of $[Fe(CN)_6]^{3-/4-}$ and, as a result, shows an accelerated electron transfer between the electrolyte and the electrode surface. The successful modification of the CuTAPc material onto the surface of the ITO electrode was confirmed.

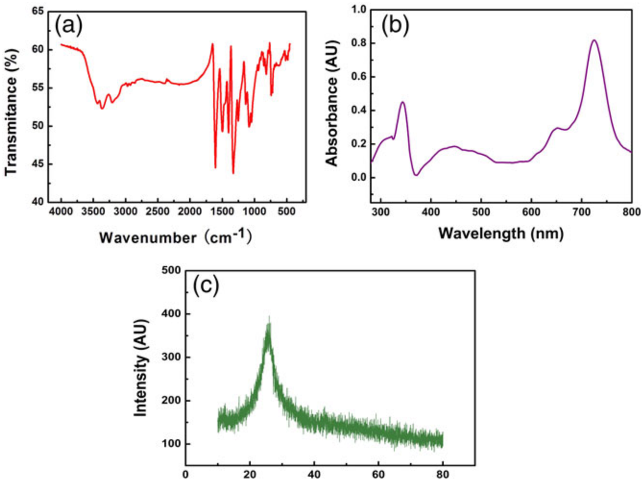


Figure 1. FT-IR spectrum (a), UV-Vis spectrum (b), and X-ray diffraction (c).

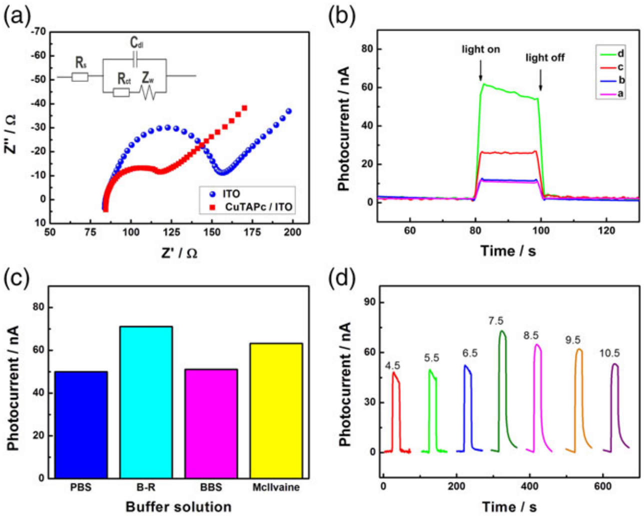


Figure 2. (a) Nyquist plots at ITO and CuTAPc/ITO in the presence of 3 mmol/L $[Fe(CN)_6]^{3-/4-}$ in 0.1 mol/L KCl. (b) Amperometric i-t curve for 15.0 μmol/L NP on the surfaces of various electrodes; ITO in the absence (a) and presence of analyte (b), CuTAPc/ITO in the absence (c), and presence of the analyte (d). (c) Effect of the electrolyte on the photocurrent in response to 15.0 μmol/L NP, and (d) effect of pH (4.5–10.5).

Photoelectrochemical Responses of NP on CuTAPc/ITO and ITO. The photoelectrochemical responses of NP on CuTAPc/ITO and ITO were studied under UV-light irradiation. As shown in Figure 2(b), the photocurrent of the bare ITO electrode in the blank solution is 9.1 nA (curve a), whereas it is 9.9 nA (curve b) in the electrolyte containing 15.0 μmol/L NP. The bare ITO electrode exhibited a weak response signal. By contrast, the CuTAPc/ITO electrode showed a good response signal. The photocurrent of the CuTAPc/ITO electrode in the blank solution is 22.4 nA (curve c), while in the electrolyte containing 15.0 μmol/L NP, the photocurrent is 60.2 nA (curve d). It is found that the signal of NP at CuTAPc/ITO increased significantly compared to that of ITO, due to the excellent photoelectric activity and sensitivity of CuTAPc.

Optimization of Experimental Conditions. To obtain the best photoelectrochemical responses, the experimental conditions, including the bias voltage, material concentration, electrolyte and pH, were investigated and optimized.

In this work, the concentrations of the introduced CuTAPc suspensions were 0.5, 1.0, 1.5, and 2.0 mg/mL.

The results indicated that the highest analytical signals were obtained for the concentration of 1.0 mg/mL. A higher concentration of CuTAPc suspension led to an increase in the background photocurrent. The bias voltage was also optimized by the examination of the voltages of 0, 0.1, 0.15, 0.2, 0.25, 0.3, and 0.35 V. Under the voltage of 0.25 V, the working electrode showed the largest response signal, but the i-t baseline was not stable. The baseline was more stable under the open-circuit voltage of 0.26 v. Moreover, there was no significant difference between the response signals obtained at 0.26 V and those obtained at 0.25 V.

In addition, the photoelectric effect of NP at the CuTAPc/ITO was studied in different media such as a phosphate buffer solution (PBS), Britton-Robinson buffer solution (B-R), McIlvaine buffer solution, and borate buffer solution (BBS). As shown in Figure 2(c), it was found that the highest photocurrent was for detecting NP was obtained in the B-R buffer solution. Chronoamperometry studies of NP at the CuTAPc/ITO were carried out in the B-R buffer solution with different pH values in the 4.5–10.5 range. It was found that the NP photocurrent increased gradually with increasing pH and reached the maximum value at pH 7.5 (Figure 2(d)). Then, the photocurrent decreased gradually until pH 10.5. Therefore, subsequent measurements were performed in pH 7.5 B-R buffer solution.

PEC Sensor Detection of NP. A PEC sensor was used for the determination of NP, with pH 7.5 B-R buffer solution. The photocurrents for different concentrations of NP on the CuTAPc/ITO were recorded, as shown in Figure 3(a). The NP photocurrent increases steadily as its concentration increased from 0.25 to 18.0 μmol/L. The data were fit with a linear regression equation given as I (nA) = 21.46 + 2.45C_{NP} (μmol/L), with the correlation coefficient of 0.9987. The limit detection of the sensor was 0.15 μmol/L (S/N = 3).

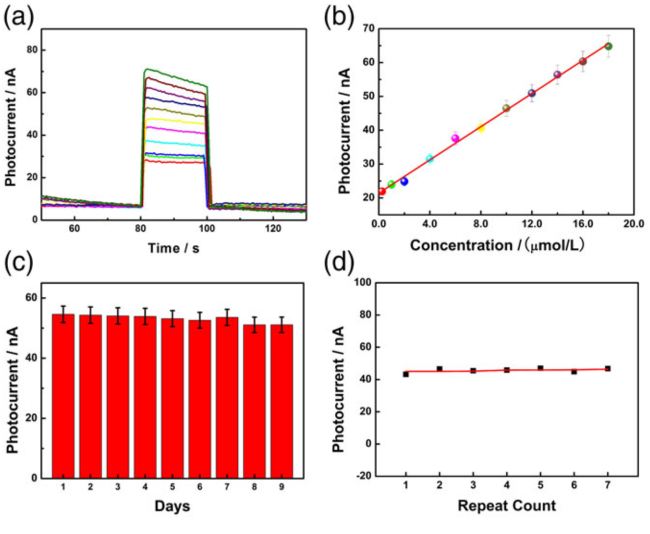


Figure 3. (a) Response of the PEC sensor under optimized conditions for detection of NP, with NP concentration ranging from 0.25 to 18.0 μmol/L. (b) The linear analytical curve. (c) Stability of the PEC sensor during continuous detection of 12.0 μmol/L NP for 9 days. (d) Detection of the same concentration of NP performed seven times. The applied bias voltage was 0.26 V (vs. Ag/AgCl).

Stability and Reproducibility of the CuTAPc/ITO. The modified electrode was stored in a refrigerator at 4 °C for 9 days, and the stability of the PEC sensor was evaluated by detection of NP in a standard solution at optimal conditions. The experimental results are shown in Figure 3(c), and the relative standard deviation (RSD) was 2.5%. This result indicates the stability of the PEC sensor. The reproducibility (Figure 3(d)) of the PEC sensor was also examined by detecting the photocurrent of NP in the B-R buffer solution (pH = 7.5) using seven electrodes. The photocurrent remained stable after seven consecutive measurements, and an RSD of 2.9% was obtained, thereby demonstrating the advantageous reproducibility of the PEC sensor.

Interference Studies. The selectivity and utility of the sensor were explored by performing the measurement in the presence of the interfering substances in the actual sample. The maximum tolerated interference limit is defined as the variation of the photocurrent value of a certain concentration of NP being smaller than 5% before and after the addition of the interfering substance. As shown in Table 1, the photocurrents of NP were not affected by most species. However, the photocurrent is more sensitive to oxalic acid and is susceptible to its interference. This outcome is because NP hydrolyzes easily in acidic conditions, thereby hindering the process of electron transfer to the electrode surface.

Detection of NP in Real Samples. To examine the practical value of the PEC sensor for detecting NP in clinical samples, content detection was tested in human serum and tablets. The samples were collected and pretreated, as described in the NP sample preparation section. For the human serum samples, the accuracy of the experimental results was expressed in terms of recovery (Table 2). For clinical drugs, the results were compared with the labeled amount (Table 3). NP levels obtained by the PEC sensors were also compared with the results obtained by HPLC. The recovery of NP in the serum, the percentage of NP in

Table 1. Interference study of some species for the simultaneous determination of 0.5 μmol/L of NP.

Foreign species	Molar ratio (foreign species/NP)
Mg^{2+}, Cl^-, maltose, urea	400
Mannitol	300
Neomycin sulfate	250
Ba^{2+}, NO_3^-, Ca^{2+}, Cu^{2+}, Sucrose	200
Al^{3+}, Zn^{2+}, SO_4^{2+}, K^+, $S_2O_3^{2-}$, Br^-, NH_4^+, CO_3^{2-}, Ni^{2+},Mn^{2+}, CH_3COO^-, Chloramphenicol	100
Theophylline	50
SO_3^{2-}	30
Oxalic acid	20

Table 2. Results for the NP determination in urine samples under the optimal conditions.

Sample	Added (μmol/L)	Found (μmol/L)	Recovery (%, n = 5)	RSD (%)
Serum	15.0	14.7	97.9	4.2

Table 3. Results for the NP determination in the drug under the optimal conditions.

Sample	Labeled amount (mg)	Found (mg)	Percentage of labeled amount (%, n = 5)	RSD (%)
S1[a]	10.0	9.7	96.6	1.2
S2[b]	20.0	20.6	103.1	3.2

[a] NP tablets, Shanxi Taiyuan Pharmaceutical Co., Ltd.

[b] NP sustained—release tablets, Shanxi Yunpeng Pharmaceutical Co., Ltd.

the tablets, and the percentage of NP in the sustained-release tablets were 95.8, 89.1, and 101.2%, respectively. There is no significant difference between the results obtained by the two techniques. Finally, the obtained good recoveries and RSD values indicated that the PEC sensor has great practical significance in the detection of NP in real clinical samples.

The developed method was compared with a variety of methods that have been reported in the literature for NP detection. The distinct features of the proposed method are shown in Table 4. It is clear that the CuTAPc/ITO PEC sensor has excellent limit of detection and linear range for NP.

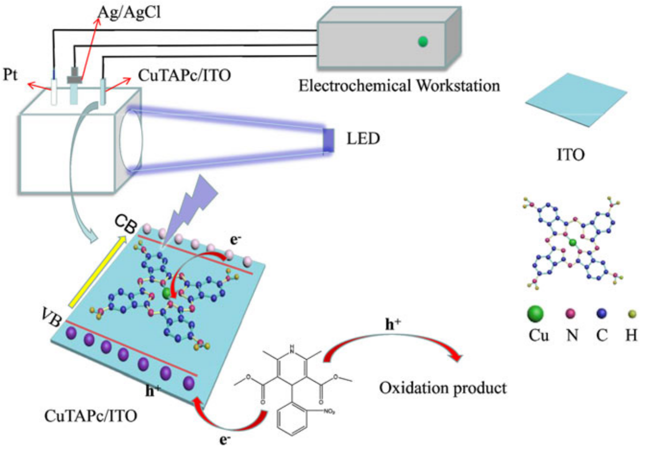
PEC Sensor Detection Mechanism. The electron-transfer mechanism of the PEC sensor with CuTAPc/IT as the working electrode was proposed for the NP-containing B-R electrolyte (Scheme 1). The UV irradiation source was turned ON/OFF every 20 s. The sensitivity (A/V) was 10^{-6}, and the applied potential was 0.26 V. When CuTAPc/ITO was stimulated by the UV irradiation source, the photogenerated electrons transferred from the CuTAPc valence band (VB) to its conduction band (CB), resulting in the separation of the photogenerated electrons and holes. The CB electrons were then transferred to the ITO electrode. Meanwhile, NP served as an outstanding electron donor and transferred electrons to the holes in the valence band simultaneously; thus, photocurrent signals were generated and further prevented the reorganization of the photogenerated electrons and holes.[26,44] The photocurrent of the modified electrode will change based on the NP content. According to the above mechanism, the PEC sensor based on the CuTAPc/ITO electrode was developed for NP detection.

Table 4. Comparison between this work and other reported methods for NP determination in real samples.

Method	Linear rang	Detection limit	References
UVS	2.0–12.0 μg/mL	1.4 μg/mL	11
DPV[a]	0.8–60.0 μmol/L	0.72 μmol/L	42
CV[b]	20–600 μmol/L 80–1000 μmol/L	11 μmol/L 43 μmol/L	43
PEC	0.25–18 μmol/L	0.15 μmol/L	This work

[a] Differential pulse voltammetry.

[b] Cyclic voltammetry.



Scheme 1. Schematic of electron transfer of the PEC sensor based on the CuTAPc/ITO electrode.

Conclusion

The establishment of accurate, rapid, and sensitive methods for the detection of drugs is highly important. In this work, it was shown that the CuTAPc materials accelerate the electron transfer on the electrode surface and enhance the photocurrent signal of the sensor. A PEC sensor based on the semiconductor CuTAPc materials for NP detection with low limit of detection and good linear range in real samples was reported for the first time. The sensor presented in this work is likely to be widely used due to its small volume and low cost. Moreover, the proposed method does not exhibit interference by coexisting ions in biological samples and drug samples that were obtained without complicated pretreatment processes. Due to its excellent selectivity and good stability and reproducibility, the novel PEC sensor is expected to be an alternative analytical tool in the fields of analytical detection and photoelectrochemistry.

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