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Mini review

Overview on the sensors for direct electrochemical detection of illicit drugs in sports

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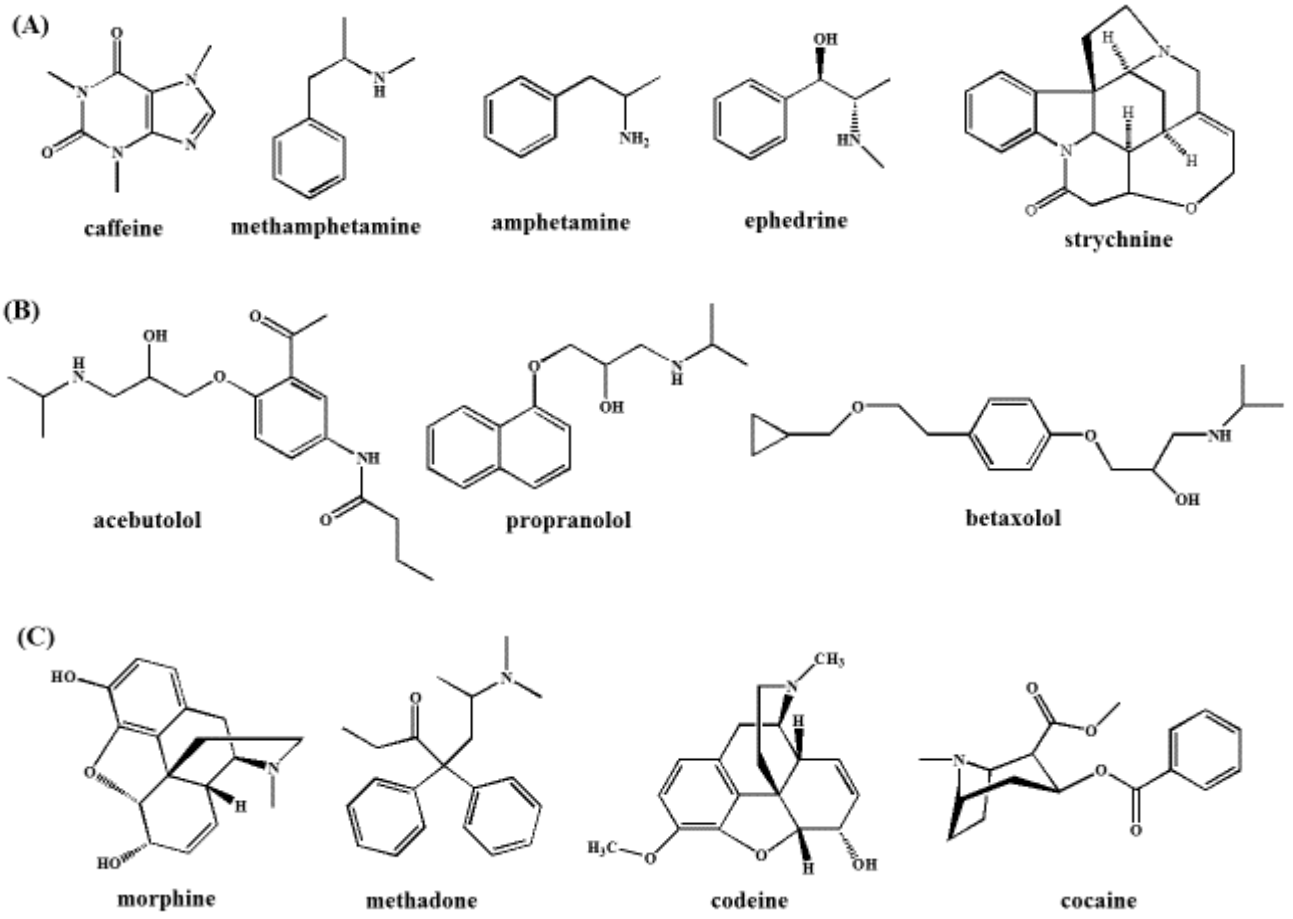
Abuse of illicit drugs seriously undermines the principle of fair and equitable competition in sports and has serious consequences for the health of athletes. Thus, it is highly desired to develop rapid, sensitive, portable and easy-to-operate methods for the detection of a variety of illicit drugs in sports. Electrochemical technique is a promising substitute for chromatographic and spectral analysis. In the past decades, the direct electrochemical detection of illicit drugs has experienced great growth due to the discovery of novel electrode materials, such as carbon materials, metal/metal oxide and polymers. In this view, the progress in electrochemical detection of illicit drugs in sports was summarized, including dopes (caffeine, (meth) amphetamine, ephedrine and strychnine), sedatives (acebutolol, propranolol and betaxolol), anesthetic (morphine, codeine, methadone and cocaine), diuretics (hydrochlorothiazide, bumetanide and mannitol), anabolic hormone nandrolone and masking agent theophylline. The work should be valuable for the development of novel electrochemical sensors for drug analysis.

Keywords: illicit drugs; electrochemical sensors; nanomaterials; sports

1. INTRODUCTION

Illicit drugs generally refer to the medicines unrelated to medical treatment, prevention and health care. The repeated and large-scale use of illegal drugs may cause a series of abnormal behaviors, such as psychological and physical dependence, mental disorder and mental excitement to users [1]. The international attention to illicit drugs in sports events began in 1988. The use of illicit drugs not only seriously undermines the principle of fair and equitable competition in sports events, but also irreversibly damages the health of athletes and brings serious long-term sequelae. Therefore, it is of great significance to accurate and quick detection of illegal drugs whether they exist in the human body for maintaining the fairness of competitive sports and combating illegal drug abuse [2-5].



Scheme 1. Chemical structures of different types of illicit drugs detected by electrochemistry: (A) dopes, (B) sedatives, (C) anesthetic, (D) diuretics, and (E) anabolic hormone nandrolone and masking agent theophylline.

At present, there are about 100 kinds of illegal drugs probably used in international competitions, including the seven categories of dopes, analgesics, sedatives, diuretics, steroids, peptide hormones and masking agents. Among them, there are about 40 kinds of dopes, including amphetamine, methylhydroxyamphetamine, caffeine, ephedrine, fluoroamphetamine, amphetamine, nikethamide and strychnine. The use of these drugs can enhance the users' spirit and physical strength, eliminate fatigue, increase the speed and agility of human response, and/or improve the competitive state in sports. There are more than 20 analgesics in total, represented by dolantin, propofol, d-propofol, mesalazine, morphine diacetate, ethyl morphine and many alkaloids. They can stimulate the nerve center of users and make the human body produce a kind of pain pleasure and psychological excitement, thus reducing pain and hallucinations. Taking such drugs for a long time will induce tumors and threaten human health. Sedatives are nerve blocking drugs, including acetylbutylphthalide, propranolol, betalol, and heartache. They can block sympathetic ganglia, reduce human blood pressure and heart rate, improve sedation, stabilize emotions, and inhibit hand tremor. Diuretics include ethanolamine, butylbenzoic acid, diuretic acid, mannitol, dihydrogram urine plug and so on. Taking of diuretics can increase the excretion of human urine and discharge the excess water accumulated in the subcutaneous abdominal cavity as far as possible, so as to achieve the goal of losing weight in a short time. Steroidal anabolic hormones have a

cyclic steroidal structure, mainly including chlorphenone, dioxidosterone and enoxalone. Taking of hormones can strengthen muscle tissue and improve competitiveness. There are four kinds of skin hormones, all of which are endogenous hormones. Such drugs can play the role of male hormones and increase the endurance of body. There are mainly two masking agents, epitestosterone and probenecid. After the use of epitestosterone, the ratio of testosterone to epitestosterone in body will decrease, thus covering up the illegal use of testosterone. The use of probenecid can inhibit the excretion of synthetic steroids in urine, thus reducing the concentration of such drugs and making their detection different.

Due to the short life span of illicit drugs in human body, monitoring of them has become increasingly difficult with the passage of time, which has brought great challenges to their detection and management. Although standard chromatography and spectral analysis technologies, such as high performance liquid chromatography, gas chromatography, mass spectrometry and Raman spectroscopy, can accurately detect the content of illicit drugs in human body, these methods usually rely on large and expensive instruments and trained personnel, and the detection processes require a lot of time and high cost [5]. Therefore, it is severely limited to use these techniques as point-of-care (POC) methods for real-time detection of illicit drugs. In recent years, with the progress of materials science and bioanalytical technology, various novel sensing techniques have developed rapidly. Electrochemical techniques show significant advantages in the analysis of illegal drugs, such as high sensitivity, fast analysis speed and low cost [6-9]. In this paper, the applications of electrochemical sensing electrodes for the direct detection of various illicit drugs in sports was summarized.

2. SENSING ELECTRODES FOR DIRECT DETECTION OF ILLICT DRUGS

Modified electrodes paly a decisive in the analytical performances of electrochemical sensing devices. In recent years, the appearance of nanoparticles and the rapid development of materials science have made great contributions to the current situation of electrochemical sensors. Because the working electrode is the most important component of electrochemical sensors, many improvements have been made to improve the selectivity and sensitivity for the detection of illegal drugs. The commonly used working electrodes for the construction of electrochemical sensors include carbon material electrodes, metal and metal oxide electrodes and polymer-based electrodes, which are separately summarized below.

2.1 Carbon material electrodes

Carbon is an inert electrode material, which can facilitate the electrochemical redox reactions in aqueous and non-aqueous solutions. Compared with metal solid electrodes, carbon electrodes show greater advantages due to their unique characteristics such as high aspect ratio, high strength to weight ratio, excellent mechanical properties, good conductivity, low background current, wide anode electrode range, chemical inertness and low cost. These characteristics promote their applications in the fields of electroanalytical chemistry, especially in sensing devices. Moreover, a variety of nanoscale carbon materials with different shape and sizes have been employed as the electrode materials to fabricate electrochemical sensors, such as carbon nanotubes and graphene. The commercial carbon material

electrodes include glassy carbon electrode, screen-printed electrode, boron doped diamond electrode and carbon paste electrode, which can used as the sensing electrodes for the direct detection of some illegal drugs or as the supports of nanoscale carbon materials to fabricate electrochemical sensors (Table 1).

Table 1. Detection performances of carbon material electrodes for the detection of illegal drugs.

Electrode	Analyte	Linear range (μM)	LOD (μM)	Ref.
CNF/GCE	caffeine	25 ~ 450	17.4	[10]
ND-DHP/GCE	codeine	0.299 ~ 10.8	0.0545	[11]
Gr-ZrO_2/GCE	caffeine	1 ~ 2000	0.0119	[12]
SmHCF/MWCNTs/GCE	codeine	0.2 ~ 20	0.06	[13]
MWCNTs/GCE	ephedrine	1 ~ 100	0.75	[14]
rGO/GCE	bumetanide	0.26 ~ 50	0.075	[15]
ED-GO/GCE	theophylline	0.8 ~ 60	0.1	[16]
CdSe/GCE	theophylline	1 ~ 700	0.4	[17]
SPE	amphetamine	50 ~ 500	22.2	[18]
MoS_2 NSs-Gr/SPCE	amlodipine	0.04 ~ 400	0.0012	[19]
FSG/SPE	codeine	0.02 ~ 200	0.0058	[20]
MWCNTs-Nafion/GNPs/SPE	methamphetamine	3 ~ 50	0.006	[21]
BDDE	methamphetamine	0.07 ~ 80	0.05	[22]
BDDE	hydrochlorothiazide and valsartan	1.97 ~ 88.1 and 9.88 ~ 220	0.639 and 0.935	[23]
BDDE	ephedrine	30 ~ 240	0.79	[24]
BDDE	theophylline	2 ~ 380	0.91	[25]
BDDE	uric acid and caffeine	9.2 ~ 95 and 4.6 ~ 95.7	3.9/2.1	[26]
Gr/Fc/CPE	captopril and hydrochlorothiazide	1 ~ 430/0.5 ~ 390	0.87/0.38	[27]
5AEB/CNTs/CPE	methyldopa	0.1 ~ 210	0.048	[28]
PGE	methamphetamine	0.075 ~ 54	0.05	[29]
MWCNT/CPE	betaxolol and atenolol	2–110 and 5–210	0.19 and 0.29	[30]
MWCNTs-PGE	methadone	0.1 ~ 15	0.087	[31]
p(Thp)/AuNPs/CCE	methadone	0.049 ~ 9.9	0.014	[32]
CFE	caffeine and theophylline	0.2 ~ 22/0.5 ~ 30	Not reported	[33]
fullerene-C60/GCE	nandrolone	1×10^{-4} ~ 50	4.2×10^{-4}	[34]

Abbreviations: CNF, carbon nanofber; GCE, glassy carbon electrode; ND-DHP, nanodiamonds-dihexadecyl phosphate; Gr, graphene; MWCNTs, multiwalled carbon nanotubes; rGO, reduced graphene oxide; SPE, screen printing electrode; MoS_2 NSs, molybdenum disulfide nanosheets; GO, graphene oxide; SPCE, screen printed carbon electrodes; FSG, adenine-functionalized spongy graphene; GNPs, gold nanoparticles; BDDE, boron-doped diamond electrode; Fc, ferrocene; CPE, carbon paste electrode; 5AEB, 5-amino-2′-ethyl-biphenyl-2-ol; PGE, pencil graphite electrode; p(Thp), polythiophene; AuNPs, gold nanoparticles; CFE, carbon fiber electrode.

Glassy carbon electrode has the advantages of good conductivity, high hardness and hydrogen overpotential, wide polarization range, and excellent chemical stability. Therefore, GCE is one of the

widely used electrodes for the development of electrochemical sensors to detect illegal drugs. For example, Sebokolodi et al. developed an electrochemical sensor based on carbon nanorods (CNFs)-modified glassy carbon electrode to detect caffeine [10]. Cyclic voltammetry, electrochemical impedance spectroscopy and square wave voltammetry were used to study the electrochemical behaviors of caffeine and $[Fe(CN)_6]^{3-/4-}$ on the CNF-modified electrode under acidic conditions. The results showed that the sensing electrode significantly increased the peak oxidation current of caffeine (about twice than that of bare glassy carbon electrode), and the oxidation potential decreased from 1.44 to 1.35 V. This is due to the high conductivity and large surface area of CNF. In addition, Simoni et al. developed an electrochemical sensor for the determination of codeine in drugs and biological liquid samples using nanodiamond/hexahexyl phosphate-modified glassy carbon electrode (ND-DPH/GCE) [11]. The redox activity of codeine on GCE, DPH/GCE and ND-DPH/GCE was investigated by cyclic voltammetry. The sensitivity for codeine detection was improved by modifying the electrode with ND-DPH, which is due to its excellent characteristics, such as mechanical resistance, conductivity, thermal conductivity and compatibility with carbon nanomaterials.

Graphene has attracted extensive interest in the preparation of electrochemical sensors due to its unique two-dimensional structure, electronic properties, mechanical properties and thermal properties. Thus, graphene oxide (GO) and reduced graphene oxide (rGO) have been widely used to modify the electrode for the design of electrochemical sensors. The rGO with better conductivity than GO restores the unique properties found in the original graphene. Phong et al. realized the simultaneous determination of ascorbic acid, paracetamol and caffeine by electrodeposition and electro-reduction of GO on the glassy carbon electrode with cyclic voltammetry [35]. The results showed that the modified electrode had high electrocatalytic activity for the electro-oxidation of ascorbic acid, paracetamol and caffeine. Yigit et al. developed an electrochemical sensor based on graphene-modified glassy carbon electrode for the detection of 5-O-caffeoylquinic acid (5-CQA), vanillin and caffeine [36]. Cyclic voltammetry and square wave stripping voltammetry were used to study the electrochemical behaviors of the three analytes on the modified electrode. They showed an oxidation peaks at 0.53, 0.83 and 1.39 V, respectively. Okutan et al. prepared a caffeine electrochemical sensor by using graphene/ZrO_2 nanocomposites synthesized by a simple one-pot method to modify glassy carbon electrode [12]. The results indicated that the graphene-based ZrO_2 nanoparticle-modified electrode exhibited high sensitivity and good response to caffeine in real samples.

Carbon nanotubes with quantum effect, nano-size effect and large specific surface area are another type of carbon nanomaterials, which can be used as the electrode modifiers to exhibit excellent conductivity and catalytic activity [37-39]. For example, Karimi et al. developed an electrochemical sensor for simultaneous determination of hydrochlorothiazide and triamterene by modifying the glassy carbon electrode with rGO and multi-walled carbon nanotubes (MWCNTs) [40]. The synergistic effect between MWCNTs and rGO was helpful to improve the performances of the sensor and catalyzed the oxidation reaction of the two drugs. Compared with bare and MWCNTs-modified glassy carbon electrodes, the rGO/MWCNTs-modified electrode enhanced the anodic reaction of triamterene and hydrochlorothiazide. The results show that the sensor has good sensitivity, wide dynamic range and acceptable selectivity. Moreover, the good adhesion performance of MWCNTs improved the stability and durability of the sensor. Based on this property, Mashadizadeh et al. achieved the high sensitive and

selective detection of codeine by using organic-inorganic hybrid (SmHCF/MWCNT)-modified glassy carbon electrode [13]. Compared with the bare glassy carbon electrode, SmHCF/MWCNT-modified electrode showed good stability, conductivity and durability. In addition, electrochemical sensors based on graphene or MWCNT-modified glassy carbon electrode have been developed for the detection of ephedrine hydrochloride [14], cocaine [41] and theophylline [16, 17].

Screen-printing or thick film technology is a well-known method for manufacturing disposable and low-cost electrochemical sensors and biosensors. Screen-printed electrode has the advantages such as small size, low cost and customizability. It has become more and more important to use screen-printed electrode for sensor applications and electrochemical analysis in the field of pharmaceutical, environmental and food analysis. Amphetamine is one of the commonly abused drugs in the illegal market, but it shows no electroactivity. Parrilla et al., for the first time, reported that amphetamine could be quickly and accurately determined with graphene screen-printed electrode (Figure 1) [18]. In this work, square wave voltammetry technology was used to study the electrochemical characteristics of the electroactive products derived from 1,2-naphtoquinone-4-sulfonate (NQS) and amphetamine. After NQS was reacted with amphetamine for 2.5 minutes in a buffer solution (pH 10), the NQS-amphetamine complex showed a significant oxidation peak at 0.66 V at screen-printed electrode. Mohammadi et al. proposed an electrochemical strategy for the determination of amlodipine by modifying the screen-printed carbon electrode with MoS_2 nanosheets /graphene hybrid nanostructures [19]. Graphene flakes, as excellent substrates and structure directing agents, promoted the formation of well-dispersed ultra-thin MoS_2 nanosheets and restrict their aggregation. The MoS_2 nanosheets were well dispersed and arranged, resulting in the exposure of more nano edges. The synergistic effect between MoS_2 nanosheets and graphene significantly increased the electrocatalytic performances of sensing electrode. With differential pulse voltammetry (DPV), the modified electrode showed an enhanced oxidation activity to amlodipine. Muzetti Ribeiro et al. used $[UO_2(4\text{-MeOSalen})(H_2O)]\cdot H_2O$ films to modify screen-printed electrode for voltammetric determination of cocaine [42]. According to the experimental results, cocaine showed a clear irreversible anodic peak current at 0.85 V, and the current was proportional to the concentration of cocaine. Mohamed et al. used adenine-functionalized spongy graphene (FSG) composite-modified screen-printed electrode to determine codeine in the presence of paracetamol and caffeine [20]. Adenine can inhibit the re-stacking of graphene sheets, leading to three-dimensional interconnection and permeable arrangement. This three-dimensional aligned structure can produce the exposed edge plane positions/defects, allowing optimal charge transfer/electrode dynamics. This is the first report that FSG is used for electrochemical sensing. Compared with the unmodified graphite screen-printed electrode, the modification of FSG can improve the electrochemical response by reducing the oxidation potential of codeine. Rafiee et al. reported the detection of methamphetamine using gold nanoparticles (AuNPs)/MWCNT/Nafion-modified screen-printed electrode [21]. The electrochemical behavior of methamphetamine was studied by cyclic voltammetry, and the sub-nanomolar methamphetamine in the samples was determined by square wave stripping voltammetry. The synergistic effect of MWCNTs and AuNPs significantly improved the performance for electrocatalytic oxidation of methamphetamine in sodium hydroxide electrolyte.

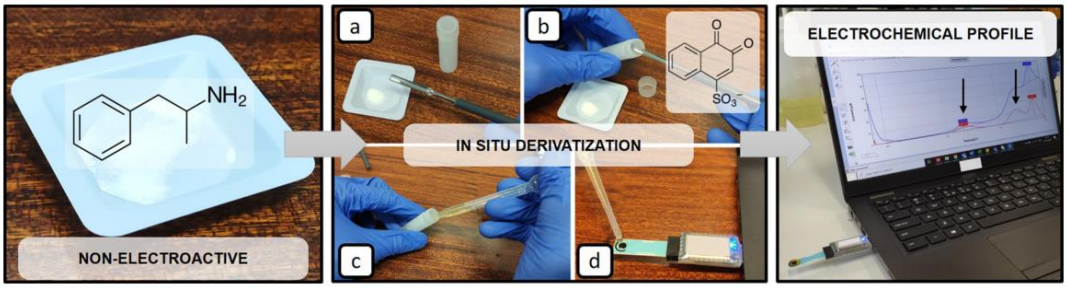


Figure 1. Schematics of the concept for the on-site screening of amphetamine (AMP). (a) A suspicious powder is mixed (b) with sodium 1,2-naphthoquinone-4-sulfo-nate (NQS) in hydrogen carbonate buffer pH 10, (c) thoroughly shaken for in situ derivatization, and (d) deposited on a SPE for the SWV interrogation by a portable potentiostat. The characteristic electrochemical profile is displayed in a laptop or smartphone exhibiting the illicit compound found in the suspicious sample aiming for a confiscation. Copyright 2021 Elsevier from reference [18].

Captopril and hydrochlorothiazide have good electrochemical activity, which can be oxidized on the surface of solid electrode. Gholivand et al. reported a voltammetric method for simultaneous determination of captopril and hydrochlorothiazide based on graphene/ferrocene composite carbon paste electrode [27]. In this paper, the paste electrode has a very effective catalytic activity for the electrochemical oxidation of captopril, reducing the anode overpotential of hydrochlorothiazide and increasing its anode current. The full resolution between the DPV peak potentials of captopril and hydrochlorothiazide (more than 600 mV) provided a very suitable and effective method for the simultaneous determination of the two compounds. Tajik et al. developed an electrochemical voltammetric sensor for simultaneous determination of methylopa and hydrochlorothiazide based on 5-amino-2′-ethyl-biphenyl-2-ol (5AEB) and carbon nanotube (CNTs)-modified carbon paste electrode [28]. Compared with the unmodified electrode, the voltammetric response on the electrode surface was significantly improved, and the oxidation potential was reduced by 220 mV. Moreover, Silva et al. reported the simultaneous determination of pindolol, acebutolol and metoprolol by using amino-functionalized hexagonal mesoporous silica (HMS-NH_2)-incorporated carbon paste electrode [43]. The sensing electrode showed strong adsorption activity for the oxidation of these three drugs at the potential of 0.85, 1.11 and 1.45 V, respectively. The detection limits are 0.1, 0.046 and 0.23 μM for pindolol, acebutolol and metoprolol, respectively.

Electrochemical sensors with carbon-based electrodes play an important role in the detection of illegal drugs. Besides the aforementioned electrodes, other carbon-based electrodes such as carbon paste electrode [43], pencil graphite electrode [29, 31], flexible carbon cloth electrode [32], carbon fiber electrode [33], GO sheet paste electrode [44] and fullerene-C60-modifed electrode [34] have also been reported to detect various illegal drugs. For example, strychnine can be electrochemically oxidized [45], which has been detected by different carbon material electrodes [46-49]. Khairy et al. reported the simultaneous electrochemical detection of propranolol and hydrochlorothiazide or amlodipine with disposable screen-printed electrode [50]. The electrochemical experiments were conducted in sulphuric acid for propranolol/hydrochlorothiazide and in sodium dodecyl sulfate (SDS)-contained Britton Robinson buffer for propranolol/amlodipine. The detection limits in the two systems are 0.0817/0.546 μM for propranolol/hydrochlorothiazide and 0.013/0.075 μM for propranolol/amlodipine. In addition,

other materials have been used to modify the electrodes for propranolol detection with high sensitivity, including MWCNTs/CdS@ZnS, cysteine-AuNPs, MWCNT, carbon black, GO, CuNPs, graphene/ionic liquid/AgNPs and so on [51-59].

2.2 Metal and metal oxide electrodes

The most commonly used metal solid electrodes include gold, platinum, nickel and aluminum. Metal electrodes have been widely used to prepare electrochemical sensing devices because the high-purity metals can be readily obtained and processed into electrode modifiers with various configurations, such as wires, rods, plates and nets. Moreover, metal/metal oxide nanoparticles promote the development of electrochemical sensors with high sensitivity and selectivity. At present, AuNPs, ZnO nanoparticles, platinum nanoparticles, manganese dioxide, ferric oxide, aluminum oxide, nickel oxide, cadmium oxide, titanium platinum/cobalt alloy nanowire arrays have been successfully used to modify the sensing electrodes for the determination of various illegal drugs (Table 2) [60].

AuNPs as the modifiers can improve the conductivity and catalytic activity and increase the specific surface area of sensing electrodes. Haghighi et al. developed an electrochemical sensor for the determination of methamphetamine [61]. The sensor was prepared by modifying MWCNT-NH_2 on the surface of glassy carbon electrode for the deposition of AuNPs, followed by further deposition of Fe_3O_4@SiO_2-Si-$(CH_2)_3$-SH nanomagnetic core shell. The obtained GCE/MWCNT/AuNPs-SH-$(CH_2)_3$-Si-SiO_2@Fe_3O_4 electrode was used to study the detection performance for methamphetamine by cyclic voltammetry. The detection limit of the sensor for methamphetamine was as low as 16 nM obtained by square wave voltammetry. Silva et al. constructed a sensing platform for electrochemical determination of theophylline with AuNPs/MWCNTs-modified glassy carbon electrode [62]. The sensing electrode was characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The results showed that the modified electrode had a good promotion effect on the electrochemical oxidation of theophylline, and showed good selectivity and reproducibility. Zhang et al. developed a highly sensitive electrochemical sensor for theophylline detection based on glassy carbon electrode modified with dopamine-melanin nanosphere-gold nanoparticles (DMN-AuNPs) nanocomposite [63]. The electrochemical oxidation behavior of theophylline on DMN-AuNPs modified electrode was studied by cyclic voltammetry and differential pulse voltammetry. In 0.1 M sulfuric acid medium, the developed electrochemical sensor has good electrocatalytic activity for the oxidation of theophylline. In addition, Allahnouri et al. decorated gold copper bimetallic nanostructures (Au-CuNPs) on the surface of porous silicon by using the electric displacement reaction between metal ions and porous silicon, and then used the prepared nanocomposites for the modification of screen-printed electrode for simultaneous determination of codeine and acetaminophen [40]. The combination of porous silicon and metal nanoparticles provides a porous high surface area with good conductivity, which reduced the peak potential of the analytes on the surface of sensor and enhanced the oxidation peak currents of codeine and acetaminophen. The sensor has achieved satisfactory results in the aspect of anti-interference, reproducibility, stability and recovery. Recently, Chen and co-workers reported an electrochemical strategy for morphine detection with the electrode covered with Au@Pt-centered and multi-G-quadruplex/hemin wire-surrounded electroactive super-nanostructures (Figure 2) [64]. The sensing

electrode showed a high electrochemical signal. However, the he super-nanostructures would be destroyed by morphine, thus greatly decreasing the signal due to the competitive effect.

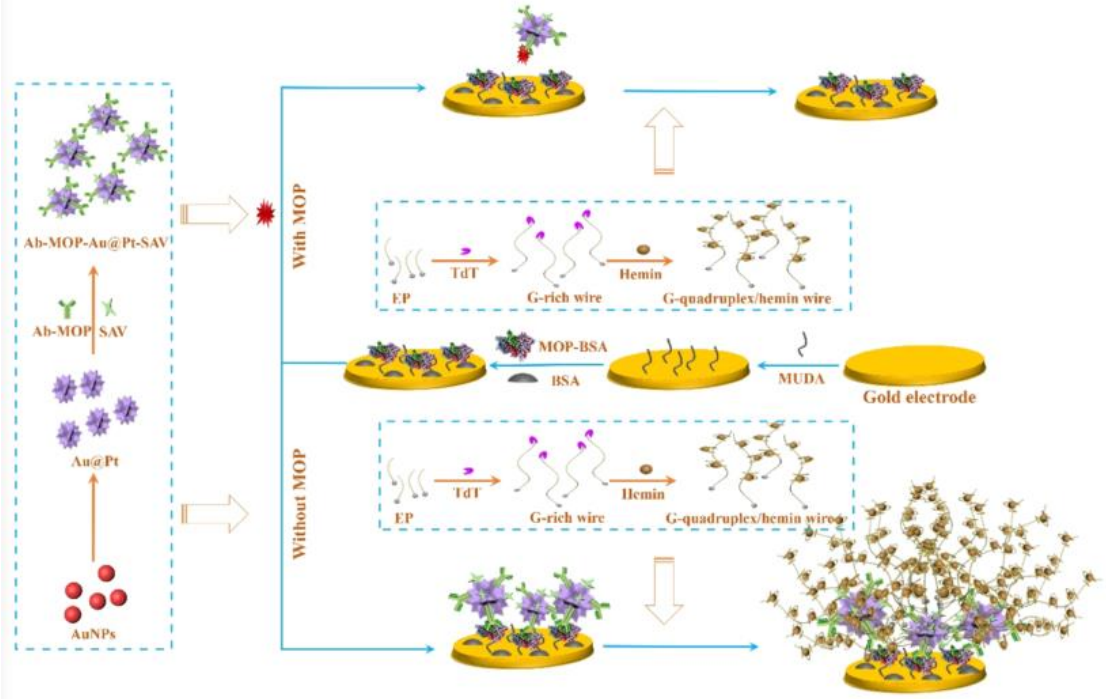


Figure 2. Schematic illustration of the electrochemical biosensor based on surface-confined building of Au@Pt-centered and multi-G-quadruplex/hemin wire-surrounded electroactive super-nanostructures for "signal-off" electrochemical determination of MOP. Copyright 2020 American Chemical Society from reference [64].

Mahanthappa et al. prepared a highly selective caffeine sensor by using CuS nanoparticles-modified carbon paste electrode [65]. Compared with bare carbon paste electrode, the modified electrode exhibited higher catalytic activity for caffeine oxidation. The electrochemical impedance results showed that the charge transfer resistance at the modified electrode was significantly lower than that at the bare carbon paste electrode, indicating that CuS NPs improved the charge transfer ability of sensing electrode. Under the experimental conditions, the oxidation current was correlated with 2 ~ 120 μM of caffeine and the detection limit was 18 nM. In addition, Gao et al. prepared a new ternary nanocomposite by one-pot synthesis method and developed an electrochemical sensor for caffeine determination with Fe_2O_3/PEDOT/rGO-modified glassy carbon electrode [66]. Metal oxide/graphene composites have attracted extensive attention in the field of sensors due to their excellent electrochemical performances. Poly(3,4-ethyldioxythiophene) (PEDOT) is a good conductive polymer with stable physical and chemical properties. In this study, the authors used Fe_2O_3/PEDOT/rGO as the electrode modifiers for the first time. The results showed that the sensor has excellent sensitivity and electrocatalytic activity toward caffeine. Moreover, Santhosh et al. developed an electrochemical sensor for caffeine detection based on CeO_2 nanoparticles-modified carbon paste electrode, which showed good sensitivity, stability and high electrochemical analysis activity for caffeine [67]. The electrochemical behavior of caffeine at the sensing electrode was studied by cyclic voltammetry and differential pulse voltammetry. The modified electrode could detect caffeine in the range of 5 ~80 μM with a detection limit of 0.036 μM. Rezvani et al. constructed a highly sensitive sensor for theophylline detection by modifying glass carbon

electrode with the nanocomposites of tungsten trioxide (WO_3) nanoparticles and MWCNTs [68]. WO_3 nanoparticles were synthesized by precipitation reaction in acidic medium. Theophylline was quantitatively analyzed by adsorption stripping voltammetry. In order to obtain the best electrochemical response, the effects of different scanning rates, electrolyte solution conditions, pH value and accumulation conditions were investigated. In addition, the WO_3/MWCNTs-modified glassy carbon electrode has also been used for the detection of codeine [45].

Table 2. Detection performances of metal/metal oxide electrodes for the detection of illegal drugs.

Electrode	Analyte	Linear range (μM)	LOD (nM)	Ref.
AuNPs-SH-$(CH_2)_3$-Si-SiO_2@Fe_3O_4/MWCNT/GCE	methamphetamine	0.05 ~ 50	16	[61]
AuNPs-MWCNT/GCE	theophylline	0.5 ~ 20	90	[62]
AuNPs/ITO	nandrolone	0.05 ~ 1.5	136	[69]
DMN-AuNPs/GCE	theophylline	0.05 ~ 2	9.6	[63]
AuNPs/CPE	betaxolol	0.5 ~ 125	46	[70]
Au-CuNPs@PSI/SPCE	codeine/acetaminophen	0.6 ~ 550	350/300	[71]
Au@Pt/G-quadruplex/hemin	morphine	3.5×10^{-3} ~ 1.75	2.4×10^{-3}	[64]
TbFeO 3 /CuO/SPE	morphine	0.07 ~ 300	10	[72]
CuS NPs/CPE	caffeine	2 ~ 120	18	[65]
Fe_2O_3/PEDOT/rGO/GCE	caffeine	1 ~ 800	330	[66]
CeO_2 NPs/CPE	caffeine	5 ~ 80	36	[67]
WO_3/MWCNT/GCE	theophylline	0.025 ~ 2.6	8	[68]
WO_3/MWCNT/GCE	codeine	0.005 ~ 20	20	[73]
La^{3+}/ZnO/SPE	hydrochlorothiazide	1 ~ 600	600	[74]
La^{3+}/ZnO/CPE	codeine,	Not reported	10	[75]
ZnO-Zn_2SnO_4-SnO_2/Gr/CPE	ascorbic acid, acetaminophen and caffeine	0.02 ~ 120, 0.018 ~ 85.3 and 0.02 ~ 97.5	8.9, 6.6 and 7.1	[76]
ZnO/GCE	caffeine	2 ~ 100	38	[77]
Pt-GR/GCE	caffeine	Not reported	112.9	[78]
CuO-NP/CPE	theophylline	0.004 ~ 0.07	1.2	[79]
TiO_2NP-MCPE	codeine/acetaminophen	0.07 ~ 100	18 and 50	[80]
$CoFe_2O_4$/CPE	codeine and oxycodone	0.06 ~ 38	20 and 50	[81]
Gr/$CoFe_2O_4$/CPE	acetaminophen/codeine	0.03 ~ 12	25/11	[82]

Abbreviations: AuNPs, gold nanoparticles; ITO, indium tin oxide; DMN, dopamine-melanin nanosphere; Au-CuNPs, gold-copper nanoparticles; PSI, porous silicon; CuS NPs, copper sulphide nanoparticles; PEDOT, poly(3,4-ethylene-dioxythiophene).

Rezaei et al. suggested that the La^{3+}/ZnO nanoflower-modified screen-printed electrode could be used for the selective and sensitive detection of hydrochlorothiazide [74]. The La^{3+}/ZnO nanoflower as the electrocatalyst showed good electrocatalytic activity for hydrochlorothiazide. The results showed that the detection limit of this method for hydrochlorothiazide detection was 0.6 μM in the range of 1.0 to 600 μM. Meanwhile, Nia et al. reported that the La^{3+}/ZnO nanoflower-modified carbon paste electrode

could be used to simultaneously detect codeine and diclofenac [75]. Nikpanje et al. developed an electrochemical method for simultaneous detection of acetaminophen, caffeine and ascorbic acid based on ZnO-Zn_2SnO_4-SnO_2 and graphene-modified carbon paste electrode [76]. Jagadish et al. developed a highly sensitive electrochemical sensor for the detection of caffeine based on a glassy carbon electrode modified with ZnO nanoparticles [77]. The electrochemical property of caffeine was studied by cyclic voltammetry and differential pulse voltammetry. The modified electrode has strong electrocatalytic activity, good selectivity and high sensitivity. Qiao et al. reported a simple, rapid and low-cost electrochemical caffeine sensor by modifying the glassy carbon electrode with platinum-graphene hybrid nanosheets [78]. Graphene has the characteristics of fast electron transfer rate, mechanical strength, high electrochemical stability and large surface area, which make it an excellent carrier for the synthesis of uniformly dispersed metal nanoparticles. The modified electrode showed good electrocatalytic activity for caffeine oxidation. Acebutolol shows an excellent oxidation peak at about 0.85 V. Several nanomaterials-modified electrodes have been used to determine acebutolol with good performances [15, 83-87]. For example, Chen et al. reported the detection of acebutolol using petal-like yttrium molybdate nanosheets ($YMoO_4$ NSs)-modified glassy carbon electrode (Figure 3) [87]. The sensing electrode showed excellent electrocatalytic activity for acebutolol oxidation with a linear response range of 0.01 ~ 1632 μM and a detection limit of 2.5 nM. In short, metal oxides and their nanomaterials as electrode modifiers provide good conductivity and high sensitivity for sensors, and play an important role in the detection of illicit drugs in various complex systems such as serum, urine, beverages, pharmaceutical industrial products and wastewater [79-82].

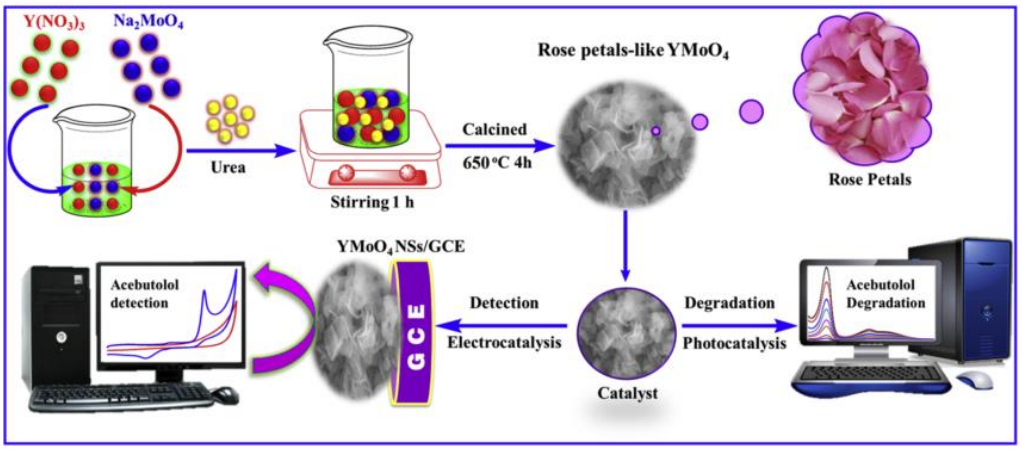


Figure 3. Overall synthesis route and the bifunctional catalytic activity of YM NSs nanosheets towards acebutolol. Copyright 2019 Elsevier from reference [87].

2.3 Polymer-based electrodes

The application of polymers in sensor devices has become a widely concerned field due to their excellent characteristics such as low cost, easy processing, recyclability and applicability. Electroactive polymers-based sensors for detecting certain narcotic drugs are used in clinical applications. Such electroactive polymers have become attractive candidates for biomolecular sensing due to their unique electrochemical, electrical and optical properties. The presence of these π-conjugated organic substances

will change when it was exposed to a low concentration of chemical substance. Atom transfer radical polymerization (ATRP) is an important method to synthesize complex polymers. The polymerization products have high potential in design of signal-amplified strategies because of their excellent properties such as controllable molecular weight, low dispersion, fidelity of high-end groups and continuous chain growth ability, thus promoting the development of electrochemical sensors for drug analysis (Table 3). Sun et al. developed a sensor for the detection of methamphetamine with high sensitivity and selectivity based on the aptamer recognition probe and ATRP signal amplification mechanism [88]. First, the aptamer and its complementary DNA strand were attached to the electrode surface. In the presence of methamphetamine, the preferential binding of methamphetamine and aptamer extracted the DNA strand from the double-stranded DNA, so that the azide-modified third DNA could be successfully modified to the electrode surface. Through click chemistry and ATRP polymerization, the monomer containing ferrocene was polymerized into a long chain, and the signal was amplified to achieve highly sensitive detection of methamphetamine. Nafion is an ionic polymer, which has been widely used in the preparation of electrochemical sensors with excellent properties, such as high conductivity, catalytic activity, antifouling ability and chemical inertness. Sadok et al reported a voltammetric sensor for the detection of paracetamol and caffeine using bismuth and Nafion film-modified boron-doped diamond electrode [89]. The sensor could simultaneously determine paracetamol and caffeine in acidic medium. The advantage of Nafion-modified electrode is related to the preconcentration of caffeine in the polymer layer. Bismuth deposited in-situ on Nafion-covered electrode effectively increased the peak current of the two substances. The adsorption ability of caffeine on the modified electrode was higher than that of paracetamol. In most cases, the detection limit is low or equivalent to that obtained by other voltammetric sensors for the simultaneous detection of paracetamol and caffeine. Yigit et al. developed an electrochemical sensor for simultaneous determination of paracetamol, aspirin and caffeine based on graphene/Nafion composite film-modified glass carbon electrode [90]. The electrochemical behaviors of the three analytes were studied by cyclic voltammetry and square wave stripping voltammetry. The oxidation peaks appeared at 0.64, 1.04 and 1.44 V, respectively. Kalaiyarasi et al. studied the electrochemical behaviors of paracetamol and caffeine at glassy carbon electrode modified with Nafion-protected halloysite nanotubular clay [91]. In the acetic acid buffer (pH 4.5), the oxidation potential of paracetamol is 0.21 V, and that of caffeine is 1.0 V. Because of the obvious difference in the peak potential between the two compounds, the sensor successfully realized the determination of them in drug formulations and human urine samples. Recently, Verrinder et al. proposed a disposable single-use electrochemical sensor strip by using Nafion to immobilize SWCNT for the direct electrochemical detection of morphine in whole blood (Figure 4) [92]. The disposable device achieved the detection of morphine with a linear range of 0.5 ~ 10 μM and a detection limit of 0.48 μM.

In recent years, molecularly imprinted polymers (MIPs) have been widely used in the construction of electrochemical sensors. MIP, based on the copolymerization of functional monomers and cross-linkers in the presence of template molecules, has become a powerful technology for the design and synthesis of specific artificial receptors. Bagheri et al. developed a new electrochemical sensor for the detection of ephedrine using Fe_3O_4@SiO_2@TiO_2-MIP nanocomposite-modified carbon paste electrode [93]. MIP was prepared by microwave heating with methyl methacrylate as a functional monomer. Fe_3O_4@SiO_2@TiO_2 was introduced into MIP as imprinting carrier and conductive material,

which effectively improved the signal conduction on the electrode surface and the recognition of ephedrine. Based on the formation of MIP on the surface of Nafion/MWCNTs-modified glassy carbon electrode, Jia et al. reported an electrochemical switch sensor for ephedrine detection [94]. The sensor has fast response and good anti-interference ability toward coexisting substances. Beluomini et al. developed an electrochemical sensor for the determination of mannitol using AuNPs/rGO modified MIP [95]. MIP was formed by electropolymerization of o-phenylenediamine. The AuNPs/rGO significantly improved the electron transport and increased the fixed site of mannitol, which are the key to improve the sensitivity and stability of the sensor. Zhang et al. proposed a new electrochemical biosensor for the detection of a bronchodilator drug theophylline [96]. With thiophene-3-acid acid as the functional monomer and theophylline as template, molecular recognition sites were generated by electropolymerization of molecularly imprinted polymer, and initiator-conjugated theophylline was immobilized on the electrode surface. Subsequently, surface initiated polymerization (SI-ATRP) was triggered to realize signal amplification. The growth of the polymer was directly monitored by atomic force microscopy. Acrylamide as a growth chain unit was accumulated in situ, providing a large number of amino groups for the attachment of electrochemical label (sodium phenothiazinesulfonate, PTZ-343), thus improving the detection sensitivity. This MIP with the ability to recognize target molecules effectively avoids some shortcomings of natural receptors and is expected to become an effective strategy for biomarker detection. In addition, Kan et al. used cyclic voltammetry to electropolymerize o-phenylenediamine on the surface of glass carbon electrode and prepared an electrochemical sensor for the detection of theophylline by electrodeposition of AuNPs [97]. The prepared sensor not only has a special recognition ability for theophylline, but also has a high sensitivity for the determination of theophylline. The effective fix of MIP on the electrode surface is one of the key joints to improve the sensitivity and stability of the sensing system. To this end, Bates et al. proposed a theophylline sensor by using graphite as the conductive medium to fix unmodified MIP particles on the surface of carbon electrode [98]. This is the first report of electrochemical measurement using standard methacrylate-based MIP by sol-gel immobilization method. The response of the sensor to theophylline was tested by differential pulse voltammetry, and the detection limit was as low as 1 μM.

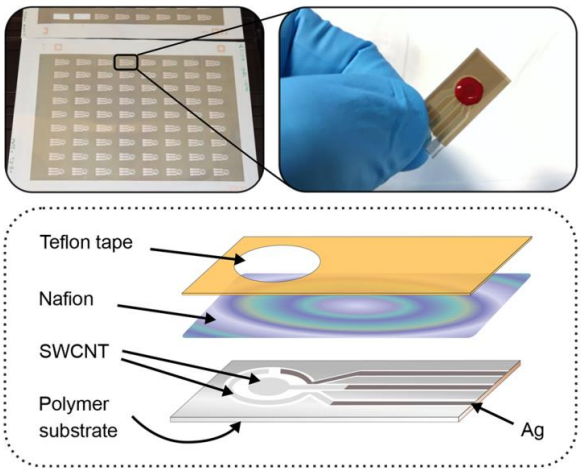


Figure 4. Photos of the sensor sheet on the polymer substrate, a close-up of the prepared sensor, and a schematic figure of the layered sensor structure. Copyright 2020 American Chemical Society from reference [92].

Table 3. Detection performances of polymers-based electrodes for the detection of illegal drugs.

Modified electrode	Analyte	Linear range (μM)	LOD (nM)	Ref.
FMMA/PgBiB/MCH/DsDNA/Au	methamphetamine	1×10^{-6} ~ 0.1	1.7×10^{-5}	[88]
Bi/Nafion/BDDE	caffeine	0.01 ~ 20	1.14	[89]
Nafion®HNT/GCE	acetaminophen/caffeine	0.6 ~ 14/0.6 ~ 20	11/173	[91]
Nafion/SWCNT	morphine	0.5 ~ 10 μM	480	[92]
Nafion/SWCNT	morphine and codeine	0.05 ~ 50 and 0.1 ~ 50	71 and 277	[99]
FST-MIP/CPE	ephedrine	0.009 ~ 2.8	3.6	[93]
MIP/Nafion/MWCNTs/GCE	ephedrine	0.18 ~ 75	0.072	[94]
MIP/AuNPs/rGO-GCE	mannitol	1×10^{-6} ~ 2×10^{-5}	7.7×10^{-4}	[95]
PTZ-343/PAM/E-MIP/Au	theophylline	2×10^{-5} ~ 30	0.011	[96]
MAA/EGDMA	theophylline	Not reported	1	[98]
CuO–PANI/GCE	hydrochlorothiazide	8 ~ 52	800	[100]
PCPE-PAA	ephedrine	60 ~ 1000	350	[101]
P(L-Pal)/rGO/GCE	theophylline and caffeine	1 ~ 260	350 and 500	[102]
Gr-PCL	amlodipine, hydrochlorothiazide	0.73 ~ 2.6 and 2.4 ~ 22	68 and 270	[103]
CNF/PSA/GCE	theophylline	0.6 ~ 137	200	[104]

Abbreviations: FMMA: ferrocenylmethyl methacrylate; PgBiB, propargyl-2-bromoisobutyrate; MCH, 6-mercapto-1-hexanol; HNT, halloysite; CuO–PANI, cupric oxide–polyaniline; Gr-PCL, graphite-polycaprolactone; PCPE, pseudo-carbon paste electrode; PAA, poly(acrylic) acid; poly(CTAB), poly(cetyltrimethylammoniumbromide); FST-MIP, Fe_3O_4@SiO_2@TiO_2-molecularly imprinted polymer; PTZ-343, phenothiazine sodium sulfonate; MAA, methacrylic acid; EGDMA, ethylene glycol dimethyl acrylate; CNF, carbon fibers; PSA, polymerized sulfosalicylic acid.

3. CONCLUSION

Various electrochemical sensors for the determination of illegal drugs are reviewed in this paper. The comparison of detection limit, linearity and method is shown in the tables. One of the main challenges in the design of electrochemical sensors is the choice of electrode modifiers. It is necessary to understand the relationship between sensing interface and reactivity at the molecular level for the design of electrochemical sensors. The idea of interfacial reaction kinetics and sensing mechanism can contribute to the performances of selectivity, sensitivity and detection limit. Therefore, the future research on the electrode materials should focus on studying the interfacial reaction kinetics in order to develop new sensors for practical application. Moreover, the integration of artificial and natural recognition elements in the sensing system may increase the sensitivity and specificity.

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