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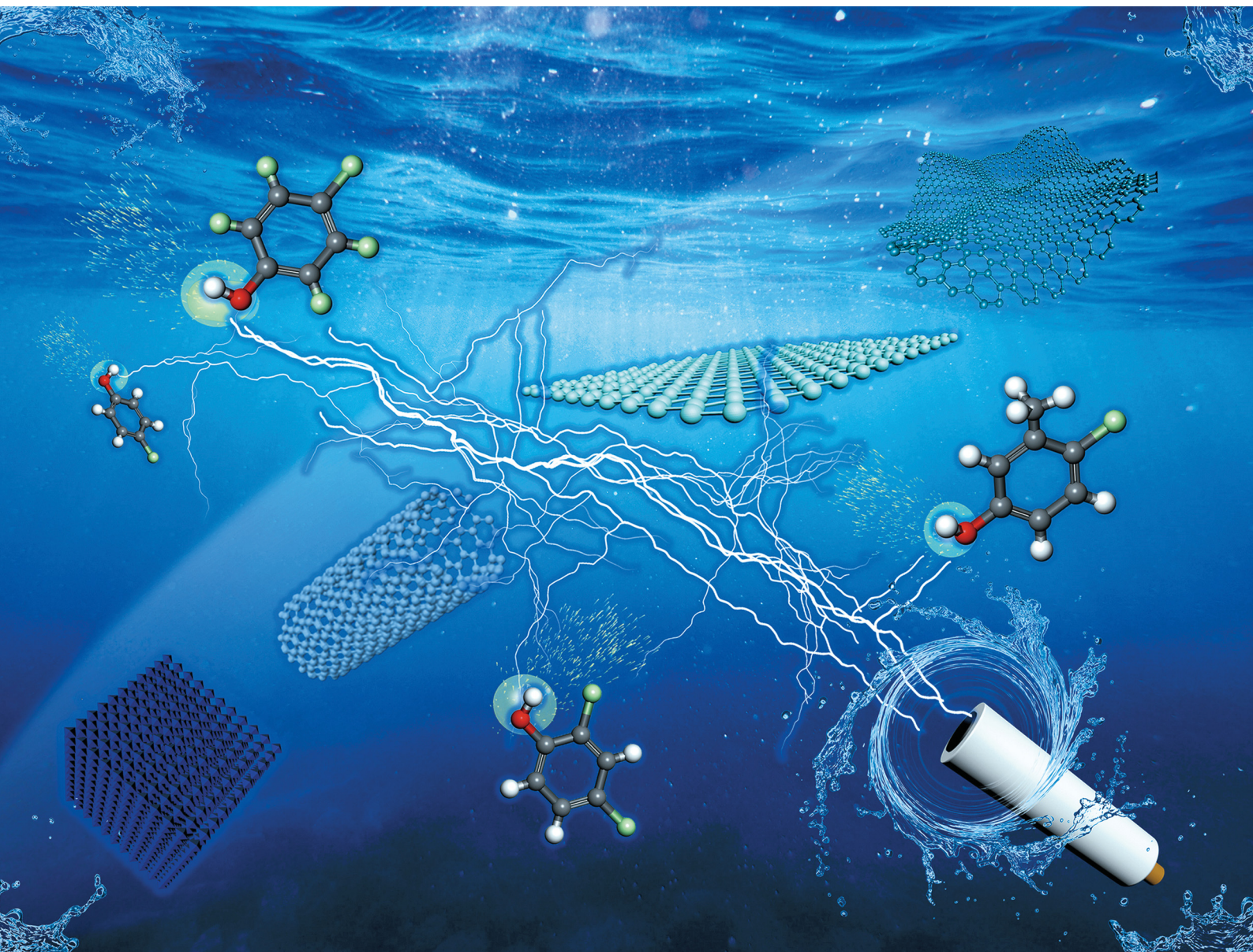
REVIEW ARTICLE
Shuai Chen, Chuanyi Wang, Ling Zang *et al.*
Tunable construction of electrochemical sensors for
chlorophenol detection

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Tunable construction of electrochemical sensors for chlorophenol detection

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As one typical class of the most persistent organic pollutants, chlorophenols (CPs) have gained growing concern because of their severe threats to the environment and public health. Effective monitoring of CPs has become an urgent and challenging issue. Electrochemical sensing has been considered as a feasible approach to meet the fast-growing demand for onsite and real-time detection of CPs. This review aims to provide a comprehensive and critical assessment of the technical advancement in developing electrochemical sensors for chlorophenol detection. It not only discusses detection systems, mechanisms and material architectures, but also places special emphasis on the tunable construction of working electrodes, which is normally based on a common working electrode (*e.g.*, noble metal, carbon-based, ITO glass or flexible types) modified with various active materials such as biomaterials, metallic materials, carbon nanomaterials, metal–organic frameworks, intrinsically conducting polymers, clays *etc*. Furthermore, a perspective on future research and technical commercialization, along with the potential challenges in the electrochemical detection of CPs is provided aiming to guide and inspire a new phase of research effort.

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1. Introduction

Chlorophenols (CPs) are a typical class of phenolic derivatives that contain a benzene ring, hydroxyl (–OH), and at least one covalently bonded chlorine atom (–Cl) on the benzene ring. Since their discovery from chlorinated coal tar in 1836, CPs have been extensively commercialized by the chlorination of phenols or hydrolyzation of chlorobenzenes, and widely applied in the areas of agriculture, pharmacy, industrial production, *etc*.[1–3] For instance, CPs are important pharmaceutical intermediates, and are also vital to pulp and paper, dyestuff, medical fungicide, disinfectant, agricultural herbicide, insecticide, and wood preservative industries.[4–14] According to the numbers of chlorine atoms and different substitutions on the benzene ring, nineteen common isomers of CPs have been found in the environment, which can be generally grouped into monochlorophenols (MCPs), dichlorophenols (DCPs), trichlorophenols (TCPs), tetrachlorophenols (TeCPs), and pentachlorophenol (PCP). Besides, there are CPs attached to other functional groups mainly including methyl-chlorophenols (M-CPs), amino-chlorophenols (A-CPs), and nitro-chlorophenols (N-CPs).[1,7] Their chemical structures are shown in Fig. 1, and some physicochemical properties are listed in Table 1.

In view of the electron withdrawing substituent (–Cl) that leads to a decrease in the electron density of the aromatic ring, CPs are more recalcitrant to oxidation and degradation in comparison with the unsubstituted phenols, and thus are more likely to accumulate in the environment. With the increase of chlorination degree on the benzene ring, CPs are less soluble in water and show a higher octanol–water partition coefficient (K_{ow}). The K_{ow} is widely employed in environmental investigations to demonstrate the distribution of an organic compound between water and the fats of aquatic organisms.[8] The higher K_{ow} value leads to a higher bioconcentration factor (BCF), implying that CPs are likely to accumulate in organisms.[9] And CPs are exogenous organic compounds formed merely by anthropogenic emissions and are difficult to degrade once they enter the biological chain. Subsequently, the migration and transformation of CPs in environmental media could bring serious health risks to aquatic life and human beings.[10] More seriously, CPs are highly carcinogenic and mutagenic, belonging to environmental endocrine-disrupting chemicals (EDCs),[11] and are classified as Group 2B carcinogens by the International Association for Research on Cancer (IARC).[8] Owing to the high stability, persistence, and perniciousness, CPs are listed as

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prioritized persistent organic pollutants by the United States Environmental Protection Agency (US EPA), the European Union (EU), and many other organizations.[3,8,12] Taking domestic water as an example, admissible concentrations of most CPs in it are restricted to the trace level (0.5 μg L^{-1} by EU, and 1 μg L^{-1} by US EPA).[13] Since CPs undertake a significant role in industrial production and day-to-day life, their distribution is thus quite ubiquitous.[14] It is urgent to take actions to monitor the low concentration of CPs in the water environment, ensuring the safety of anthropogenic emissions.

Up to now, various analytical methods and techniques such as high-performance liquid chromatography,[15] supercritical fluid chromatography,[16] gas chromatography[17] equipped with mass spectrometry,[18] and capillary electrophoresis[19] have been developed and used in the detection of CPs. However, these methods involve expensive and sophisticated instruments, and suffer from complex sample pretreatment and time-consuming operation processes, which limit their use mostly in laboratories, requiring skilled technicians and high maintenance costs. Furthermore, transferring samples from the field to

laboratory may cause sample contamination, or chemical change due to air oxidation, thermal decomposition *etc.*, leading to potential errors in measurement. Therefore, it is of great significance to develop effective sensors that can be used for the *in situ* detection or monitoring of CPs.

As a traditionally reliable chemical analysis technique, electrochemical sensing is capable of meeting the demand for frequent and regular environmental monitoring and assessment.[20] With the increasing concern over environmental security and the requirements for quick, frequent, and *in situ* quantitative pollutant analysis, developing electrochemical sensors for CP detection has been promoted greatly. Since the presence of the phenolic hydroxyl group endows CPs with great electrochemical activity, plentiful electrochemical sensors have been designed to efficiently monitor CPs, which are mainly based on voltammetry and amperometry. Several reviews related to this issue have previously been published.[21–27] In 2012, Karim *et al.*[25] reviewed the development of biosensors for CPs and other phenolic compounds. In 2016, Ndunda *et al.*[27] concentrated on the molecularly

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Qingyun Tian

Shuai Chen is an associate professor at Jiangxi Science & Technology Normal University, China. He earned his PhD degree in materials physics and chemistry from the University of Chinese Academy of Sciences in 2015 under the supervision of Prof. Chuanyi Wang, and was a postdoctoral fellow with Prof. Ling Zang at the University of Utah during 2018–2020. His current research emphasizes the design and fabrication of new organic semiconductor composites for electrochemical sensors, chemosensors and clean energy conversion applications, as well as conducting polymers, conductive coatings and their optoelectronic applications.

Shuai Chen

Jiarui Yu graduated with a major in pharmaceutical engineering from the Jingchu University of Technology, China, in 2019, and is now an MS student under the supervision of Prof. Shuai Chen at Jiangxi Science & Technology Normal University, China. She focuses on exploring PEDOT-based intrinsic conducting polymer films as well as their uses in organic electronic devices.

Jiarui Yu

Miao Zhang graduated with a major in environmental science from Shanxi Agriculture University, China, in 2019, and is now an MS student under the supervision of Prof. Ling Zang and Prof. Shuai Chen at the Shaanxi University of Science and Technology, China. Her research is focused on organic thin film chemosensors for the trace level detection of environmental pollutants in water.
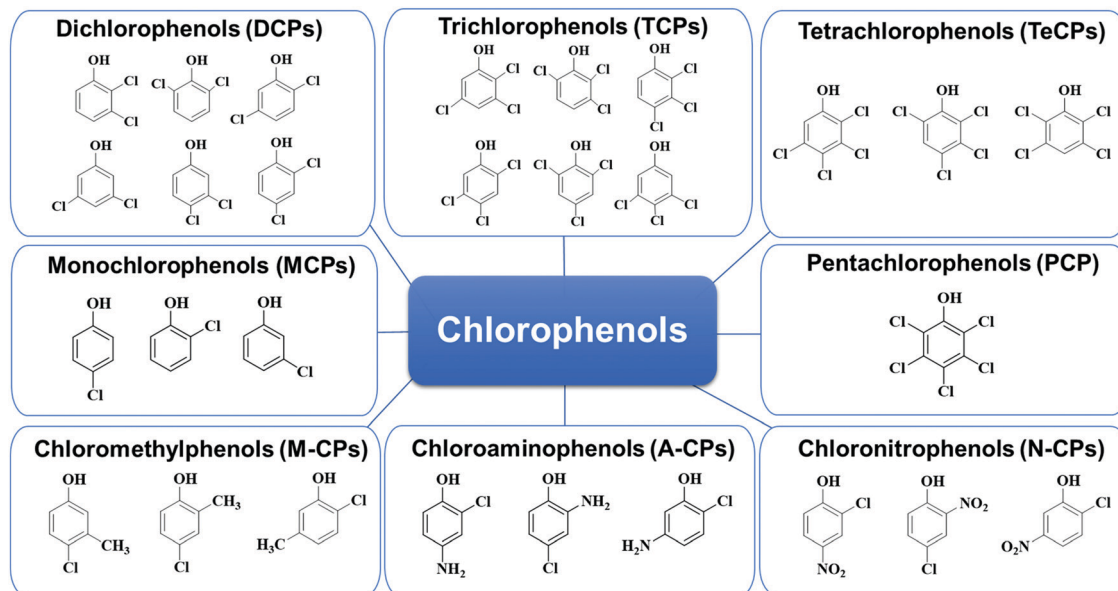
Miao Zhang

Fig. 1 Classes and chemical structures of common CPs.

imprinted polymers (MIPs) towards the electrochemical sensing of CPs and other polychlorinated aromatic pollutants. More recently in 2020, Patel and coworkers[21] summarized nanocomposite-based sensors for the voltammetric detection of phenolic pollutants including several CPs. Other related reviews focused on carbonaceous[22–24] or biosensing materials[25,26] for the electroanalysis of various pollutants including CPs. In view of the rapid progress over the past decade on the electrochemical detection of CPs and related compounds, we believe it is crucial to provide a deep and comprehensive review with a more specific focus on electrochemical sensors for CPs.

This review attempts to provide an overview of the electrochemical CP sensors mainly from three aspects: the configuration of the sensing system, construction of sensors especially working electrodes modified with active materials, and versatile strategies for sensor performance enhancement. At the end, we will outline the obstacles, challenges, and prospects of the future development of electrochemical sensors for the efficient detection of CPs. Since CPs are a representative type of persistent organic pollutant, we also believe that this review will provide new insights into the development of high-performance electrochemical sensors for other organic pollutants.

Chuanyi Wang

Chuanyi Wang, Fellow of the Royal Society of Chemistry, has been a Distinguished Professor at the Shaanxi University of Science & Technology (China) since 2017. He obtained his PhD degree from the Institute of Photographic Chemistry of Chinese Academy of Sciences (CAS) in 1998, worked in Germany as an Alexander von Humboldt research fellow with Prof. Detlef Bahnemann and in the U.S. (Tufts University and Missouri University-Kansas City) as a research faculty from 1999 to 2010, and then in the Xinjiang Technical Institute of Physics & Chemistry of CAS as a distinguished professor during 2010–2016. His research covers catalysis and photo/electro-catalysis with nanostructured materials.

Ling Zang

Ling Zang is a full professor at the University of Utah. He received his BS degree from Tsinghua University in 1991 and PhD degree from the Institute of Photographic Chemistry of Chinese Academy of Sciences (CAS) in 1995. He is a fellow of the National Academy of Inventors (NAI, 2020) and the American Association for the Advancement of Science (AAAS, 2021). His current research focuses on nanoscale imaging and molecular probing, organic semiconductors and nanostructures, optoelectronic sensors and nanodevices, with the long-term goal to achieve real applications in the areas of national security, health monitoring, renewable energy, and clean environment.

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Table 1 Physical–chemical properties of CPs[2,3,7,8,14]

	CPs	Boiling point (°C)	Melting point (°C)	Solubility (g L^{-1})	pK_a	Log K_{ow}
MCPs	2-Chlorophenol	175	8.7	28.0	8.3–8.6	2.12–2.17
	3-Chlorophenol	214	33–34	26.0	8.8–9.1	3.20–3.24
	4-Chlorophenol	217–219	42–44	27.0	9.1–9.4	2.57–2.86
DCPs	2,3-Dichlorophenol	206	57–58	NR	6.4–7.8	3.13–3.44
	2,4-Dichlorophenol	210	45	4.5	7.5–8.1	2.57–2.86
	2,5-Dichlorophenol	211	58–69	NR	6.4–7.5	3.13–3.44
	2,6-Dichlorophenol	219	68	NR	6.7–7.8	2.57–3.56
	3,4-Dichlorophenol	253–254	65–68	NR	7.4–8.7	3.13–3.44
	3,5-Dichlorophenol	233	68	NR	6.9–8.3	2.57–3.56
TCPs	2,3,4-Trichlorophenol	NR	77–84	0.22	6.5–7.7	3.49–4.07
	2,3,5-Trichlorophenol	248–255	57–62	0.22	6.8–7.4	3.84–4.56
	2,3,6-Trichlorophenol	246	58	NR	6.0–7.1	3.88
	2,4,5-Trichlorophenol	NR	67–70	0.95	7.0–7.7	3.72–4.10
	2,4,6-Trichlorophenol	243–249	69	0.43	6.0–7.4	3.60–4.05
	3,4,5-Trichlorophenol	271–277	101	NR	7.7–7.8	4.01–4.39
TeCPs	2,3,4,5-Tetrachlorophenol	NR	116–117	0.17	6.2–7.0	4.21–5.16
	2,3,4,6-Tetrachlorophenol	150	70	0.18	5.3–6.6	4.10–4.81
	2,3,5,6-Tetrachlorophenol	188	114–116	0.10	5.2–5.5	3.88–4.92
PCP	Pentachlorophenol	300	190	0.01	4.7–4.9	5.01–5.86
M-CPs	4-Chloro-3-methylphenol	235	63–65	4.0	9.5	NR
A-CPs	2-Amino-4-chlorophenol	185	136–141	NR	9.1–9.5	NR

NR: not reported.

2. Electrochemical detection systems for chlorophenols

2.1 Overall architecture and chemical mechanism

According to the operating transduction principles, electrochemical CP sensors usually use working electrodes as the transduction unit to convert the electrochemical information into electric signals, which are easily recorded and quantized. As shown in Fig. 2a, such a sensor generally consists of two basic functional units, and the signal processing normally undergoes three steps.[27–32] Firstly, the receptor unit captures the signal after its contact with target CPs. Then the transducer unit converts the signal into a useful electrochemical signal, which is finally collected by signal acquisition and processing assembly through the signal read-out techniques.

2.2 Signal read-out techniques

The signal read-out techniques for electrochemical detection can collect the electrical signals (current, potential, impedance, or charge) about every sampling interval of the reaction of target molecules in the analytical solution.[31–33] They are usually grouped into voltammetry, amperometry, potentiometry, conductometry, and impedimetry.[28–32] Among them, voltammetry and amperometry are more widely employed in electrochemical CP detection, and are described in detail in this section. In contrast, no previous literature is based on conductometry or impedimetry, and only one work reported potentiometric sensors for 2,4-DCP detection.[32]

2.2.1 Voltammetry. As the example shows in Fig. 2a, voltammetry refers to the measurement of current resulting from the application of potential.[6] According to different potential waveforms (linear, triangular, differential pulse, and square wave), voltammetry can be subdivided into linear sweep voltammetry (LSV), cyclic voltammetry (CV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV), respectively.[33–36] The measured current is the sum of faradaic current (caused by the electrochemical redox reaction of target molecules on the electrode) and non-faradaic current (triggered by the reorganization of supporting electrolytes at the electrode–solution interface and charging of the electric double layers).[37] The faradaic current is primary but when the applied potential functions are based on the linear scan and cyclic scan, the effect of non-faradaic current cannot be eliminated. To better collect the faradaic current, DPV and SWV are more general in electrochemical CP detection. The applied pulse waves consist of forward and reverse pulses, which can exhaust the capacitive current and correct the measured current. Thus, a more accurate peak current can be obtained to detect CPs in trace levels.

2.2.2 Amperometry. Amperometry (AMP) applies a constant bias potential and the change in current is monitored as a function of time (an example is shown in Fig. 2a). The applied uniform potential serves as the driving force for the redox process of CPs. And the change in current represents a molecular electron-transfer reaction, which is directly correlated with the concentration of the reacted CPs.[38] Therefore, AMP is unaffected by the background current and is easy to operate.

2.3 Response mechanism

Through signal read-out techniques, the redox process of CPs on the working electrode surface can be measured. The detection

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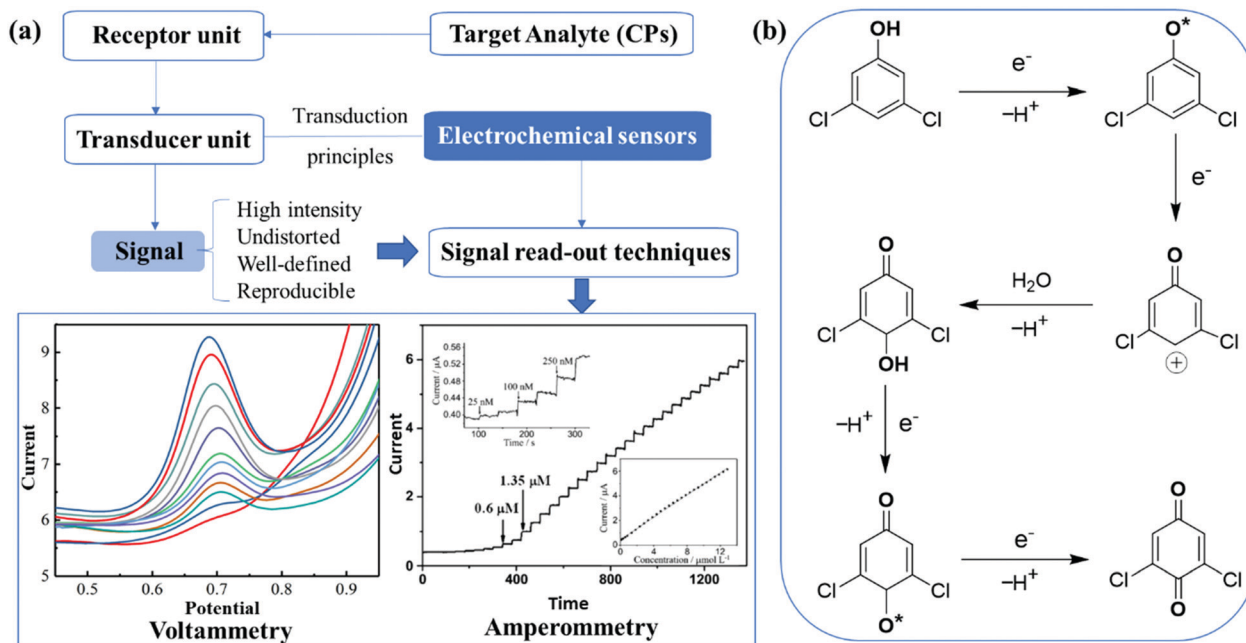This journal is © The Royal Society of Chemistry 2022

Fig. 2 (a) Illustration of the overall architecture and typical signal measurement principle for electrochemical CP sensors. Reprinted with permission, copyright 2014, Wiley.[28] (b) Typical electrochemical oxidation mechanism of CPs (taking 3,5-DCP as an example).

potentials profoundly vary depending on the number of electrophilic chlorine atoms and their position on the benzene ring with respect to the –OH group of CPs. And the redox rate decreases with an increase in the number of chlorine atoms. It's important to notice that, including CPs, the electrochemical redox process of many aromatic compounds at various types of working electrodes exhibits a remarkably sluggish redox rate.[34] As demonstrated by an example of 3,5-DCP shown in Fig. 2b, the molecule oxidation starts from producing phenoxy radicals at an impressed voltage, which could undergo further oxidation to quinones.[35] However, these radicals can continuously react with nearby radicals and quinones to form dimers, oligomers, and eventually passive insulating polymers.[36] This polymer film on the electrode surface shows low permeability and strong adhesion,[36] leading to surface fouling and passivation. Thus, the elimination of the fouling effect remains critical for fabricating high-performance electrochemical CP sensors.

2.4 Sensor performance evaluation

The large linear detection range and low limit of detection (LOD) are usually considered as the most critical performance criteria for evaluating the performances of electrochemical CP sensors. By adding standard solutions of CPs and plotting responses *versus* their concentrations, a linear detection range can be obtained which is determined by the lower and upper limits of quantification, possibly corrected with a background signal. Since the LOD is determined by both the slope of calibration curves and the standard deviation of the blank,[4] the steady background signal and desirable calibration curves are of great importance. These performances of electrochemical CP sensors mentioned in this review are summarized in

Table 2. Other performance parameters include sensitivity (which depends on the slope of the calibration curve without considering the background signal) and selectivity (which depends on whether the signal response that is supposed to change solely with CP concentrations varies with the concentration fluctuation of interfering substances). Moreover, to improve the stability, reproducibility, reversibility, and durability of these data, the construction of a stable and reliable electrochemical detection system is a precondition.

2.5 Electrochemical cell configuration

The key premise for electrochemical CP detection is the construction of an electrochemical cell that usually employs a three-electrode configuration.[39–45] No matter what signal read-out technique is used, to obtain a high intensity, undistorted, well-defined, and reproducible electric signal that is essential for a stable, reliable sensor performance, it is usually imperative to design synergistically the electrochemical cell in a configuration as shown in Fig. 3, which includes electrolytes, a reference electrode, a counter electrode, and a working electrode. More specifically for the working electrode, chemically or electrochemically active materials can be used to modify the electrode in order to improve the sensor performance.

Supporting electrolytes can be completely dissolved and ionized in aqueous solution wherein the analyte is also present. The major function of supporting electrolytes is to minimize the migration of the electroactive analytes caused by the electric field.[37] To maintain a stable system, the electrolyte used should be chemically or electrochemically inert not only on the electrode but also in the solution phase under the operating window of the electrochemical potential for CP detection, *i.e.*,

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Table 2 Sensing performance comparison of reported electrochemical CP sensors employing working electrodes modified with diverse active materials

Analytes	Working electrodes	Active materials	Techniques	Linear range (μM)	LOD (μM)	Ref.
2-CP	Au	Poly(GMA-co-MTM)/PPy/CNT/HRP	AMP	1.6–68.8	0.249	38
	Pt	TYR/PO₄–PPy	AMP	—	5.61	12
	GCE	Dicetyl phosphate/MWCNTs	DPV	0.1–20	0.004	39
	GCE	Pd/Ag/rGO	CV	0.1–80	0.0047	40
	GCE	HRP/SDBS–HT clay	AMP	0.005–0.05	0.002	41
	GCE	Acetylene black–DHP	DPV	0.2–40	0.005	42
	GCE	CS@Ag@GO	DPV	0.05–25	0.00139	43
	GCE	PVP/ZnSe QD-CTAB	DPV	0.02–10.0	0.008	44
	CPE	β-Cyclodextrin/Grs	DPV	0.5–40	0.2	45
	ITO	DNA/PPy–PVS	AMP	0.506–126.6	NR	46
3-CP	Au	Poly(GMA-co-MTM)/PPy/CNT/HRP	AMP	1.6–81.6	0.441	38
	GCE	Pd/Ag/rGO	CV	0.1–100	0.0077	40
	GCE	Er₂O₃/CuO	I–V	0.0001–10 000	0.00009	47
	CPE	β-Cyclodextrin/Grs	DPV	0.4–77	0.009	45
	ITO	DNA–PPy–PVS	CV	0.253–278	0.253	48
4-CP	Au	Poly(GMA-co-MTM)/PPy/CNT/HRP	AMP	1.6–86.4	0.336	38
	Au	CoTSPc	CV	50–1000	NR	36
	Pt	OMLG	CAMP	0.5–10	0.054	49
	GCE	CS@Ag@GO	DPV	0.1–35	0.00351	43
	GCE	Pd/Ag/rGO	CV	0.1–80	0.0075	40
	GCE	3-DOM polycysteine	DPV	0.05–3	0.00167	50
	GCE	PDDA–Gr/MIP	DPV	0.8–100	0.3	51
	GCE	Au NPs/MWCNTs–COOH	DPV	0.3–400	0.11	52
	GCE	TmPcs	LSV	0.136–150	0.041	53
	GCE	MgO 3D-flowers	CV/DPV/SWV	10–45/10–50/5–50	0.045/0.068/0.052	54
	GCE	Au NFs	AMP	200–480	110	55
	GCE	DBβ-cyclodextrin dimer/MWCNTs	DPV	0.1–200	0.028	56
	GCE	PPO/BiOx	AMP	0.015–15	0.005	57
	GCE	Au NPs@MWCNT–COOH	DPV	0.3–400	0.11	52
	GCE	SnO₂ HS@GO	DPV	0.02–20	0.0031	58
	GCE	CNTs–OH/Pt NPs/RhB	DPV	10–300	3.69	59
	GCE	PVA/F108/Au NPs/Lac	AMP	1–25	12.09	60
	GCE	Cu–BTC@GS	DPV	0.039–116.7	0.0148	61
	GCE	ZnO NPs/G/PoPD	SWV	0.2–170	0.04	62
	GCE	NNH–MWCNTs	DPV	1.0–750	0.5	63
	GCE	Pt NPs/rGO	DPV	0.1–500	0.051	122
	GCP	PPO/PTS–PPy	CAMP	3.8–85.6	2.4	64
	CPE	CTAB–MMT	DPV	0.05–10	0.02	65
	CPE	GO/NiO NPs/IL	SWV	1.0–550.0	0.7	66
	CPE	PVA/clay	SWV	1–2000	0.4	67
	CPE	2,4-DDMA–NiO/NP	SWV	1.0–600.0	0.7	68
	CFE	TYR	AMP	0.1–10	0.0051	69
	SPE	TiO₂/GO	CV	0.05–200	0.02	70
	SPE	SWCNTs/PEDOT	LSAV	0.8–500	0.339	71
	ITO	Ag–PTA/chitosan	DPV	1–400	0.34	72
	Epoxy	Expanded graphite/zeolite/Ag	DPV	20–1000	10.0	73
	Epoxy	Expanded graphite	AMP	100–500	NR	74
2,4-DCP	Graphite	PPy NT/SrCuO₂/Lac	CV/DPV	1–50	0.188	4
	GCE	Chitosan/CDs–CTAB	DPV	0.04–8.0	0.01	75
	GCE	Pd/Ag/rGO	CV	0.002–100	0.00036	40
	GCE	TYR/MWCNTs/PDDA	AMP	2–100	0.66	76
	GCE	PVA/F108/Au NPs/Lac	AMP	1–25	2.7	60
	GCE	CPANI/graphene–MWCNTs/MIP	DPV	0.05–0.6	0.0076	77
	GCE	Polydopamine/rGO/MIP	DPV	0.002–0.01/0.01–0.10	0.0008	78
	GCE	PMAA/chlorohemin/MIP	DPV	5.0–100.0	1.6	79
	GCE	CS@Ag@GO	DPV	0.05–35	0.00725	43
	GCE	MWCNTs/Nafion	DPV	1–150	0.001	80
	GCE	PVP/ZnSe QDs–CTAB	DPV	0.006–9.0	0.002	44
	GCE	MoS₂/IL/Au NRs/Ag NRs	DPV	0.01–50	0.0026	81
	CPE	Cu–BTC	DPV	0.04–1.0	0.009	82
	CFPE	PEDOT/MIP	DPV	0.00021–0.30	0.00007	13
	SPE	SWCNTs/PEDOT	LSAV	0.5–300	0.341	71
	PVC	TOMAC	Potentiometry	33–500	7.2	32
	PVC	TDMAC	Potentiometry	5.8–500	4.8	32
3,5-DCP	GCE	rGO/V₂O₅	SWV	0.019–220	0.005	29

Table 2   (continued)

Analytes	Working electrodes	Active materials	Techniques	Linear range (μM)	LOD (μM)	Ref.
2,4,6-TCP	GCE	Hemin/Cu–MOF-74	DPV	0.01–9	0.005	83
	GCE	CNTs–OH/Pt NPs/RhB	DPV	5–175	1.55	59
	GCE	PVA/F108/Au NPs/Lac	AMP	1–25	9.33	60
	GCE	CS@Ag@GO	DPV	0.03–35	0.00971	43
	GCE	Poly(bromocresol purple)/rGO	LSV	0.05–1/1–130	0.005	84
	CPE	PPD–chloroperoxidase	AMP	0.1–1	0.1	85
	CPE	UiO-66	DPV	0.01–0.5	0.00649	86
	SPE	SWCNTs/PEDOT	LSAV	0.5–300	0.311	71
	ITO	HS–β-Cyclodextrin/Au NPs	DPV	0.003–0.028	0.001	87
PCP	GCE	Ag NPs/rGO	DPV	0.008–10.0	0.001	88
	GCE	NHCNS@rGO	DPV	0.03–38.00	0.01	89
	GCE	PVP/ZnSe QDs–CTAB	DPV	0.06–8.0	0.01	44
	CPE	Al-doped mesoporous cellular foam	DPV	0.376–18.8	0.3	90
	Epoxy	MWCNTs	DPV	2–12	0.801	91
PCMC	GCE	MWCNTs	DPV	14.0–137.5	8.8	6
	GCE	UiO-66–NH_2@PEDOT/GA	DPV	0.6–18.0	0.2	93
	CCE	MWCNTs	SWV	3.0–32.0	0.7	94
	BDDE	CTAB	DPV	0.5–100.0	0.11	95

GCP: glass carbon plate; HRP/SDBS–HT clay: Horseradish peroxidase modified electrode based on a film of Co–Al layered double hydroxide modified with sodium dodecylbenzenesulfonate; PVA/F108/Au NPs/Lac: poly(vinyl alcohol)/polyethylene oxide–polyoxypropylene–polyethylene oxide/Au nanoparticles/laccase; PVC: plasticized polyvinyl chloride; TDMAC: tridodecylmethylammonium chloride; TOMAC: trioctylmonomethyl-ammonium chloride; ZnO NPs/G/PoPD: ZnO nanoparticles/graphene/poly(o-phenylenediamine); 3-DOM polycysteine: 3D ordered macroporous polycysteine; CAMP: chronoamperometry; LSAV: linear stripping anodic voltammetry; I–V: current–voltage; PCMC: 4-chloro-3-methylphenol.
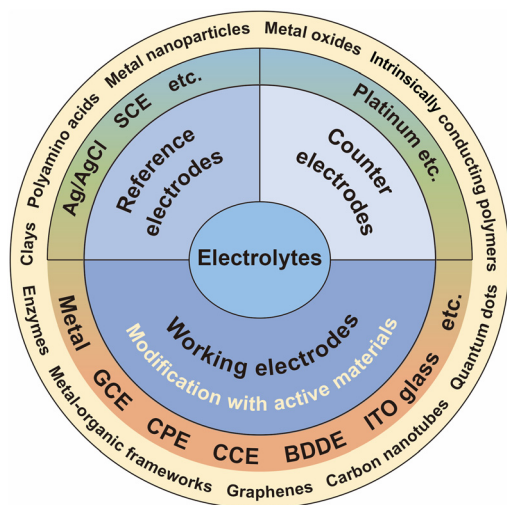
Fig. 3   Configuration of the typical three-electrode electrochemical sensor system for CPs. Listed in detail are the basic types of reference, counter and working electrodes, as well as the wide diversity of active materials used in the modification of the working electrode.

the presence of the electrolyte should not be reactive or interfere with the redox reactions of CPs.[46–52] Currently, most of the electrolytes used in this field are phosphate or sodium acetate–acetic acid buffer solution.[53–59]

The reference electrode offers a constant potential so as to control and adjust the working electrode potential accurately, which facilitates the quantitative analysis of the electrochemical system. In electrochemical sensors, the Ag/AgCl electrode and saturated calomel electrode (SCE) are the most commonly used reference electrodes.[60–64] This is mainly because they are easy to prepare, and show great stability,

working independently from the solution and working electrode during measurement. The introduction of a counter electrode completes the electrical circuit and further improves the potential stability recorded by the reference electrode in the system.[37] Platinum (Pt) and graphite electrodes are the most commonly used counter electrodes in this aspect, mainly because of their chemical and electrochemical inertness.[65–71] Employment of a counter electrode reduces the bath voltage (potential between working electrodes and counter electrodes), which helps avoid reactions occurring on the counter electrode, and the contamination caused by the reaction products generated thereof.

Compared to the reference and counter electrodes, the working electrode is usually more important in determining the sensor performance because it serves as the receptor and transducer units in the electrochemical cell, as shown in Fig. 3. There are diverse kinds of working electrodes currently in use, including the classic noble metal electrodes (Au and Pt), indium tin oxide (ITO) glass electrodes, or carbonic electrodes like the glassy carbon electrode (GCE), carbon paste electrode (CPE), carbon ceramic electrode (CCE) and boron-doped diamond electrode (BDDE), for which a wide range of active materials can be used to modify the electrochemical performance.[72–95] The modified working electrodes are highly tunable in both the structure and function that help increase the signal response of CPs and the detection selectivity. Various property and performance factors are normally considered when trying to identify the best materials for modifying a certain type of electrode, and the typical factors include the background current, potential window, electrical conductivity, response rate and electrocatalytic activity towards CPs, chemical stability, machinable properties, portability, reusability, costs, etc.

3. Construction of working electrodes

3.1 Basic working electrode

3.1.1 Noble metal electrode.

Because of their high conductivity and excellent chemical inertness against environmental corrosion, noble metals like platinum (Pt)[12,49] and gold (Au)[36,38] are widely used as working electrodes in electrochemical CP sensing systems. The high density of electronic states and the number of atomic orbitals within the noble metals enable not only free electron migration in the bulk phase, but also fast heterogeneous electron transfer on the surface,[96–98] which is conducive to facilitating the redox reactions of CPs.

However, according to the response mechanism, the oxidation of CPs can lead to the formation of phenoxy radical polymeric layers on Pt or Au electrode surfaces, leading to surface fouling and passivation.[34] As shown in Fig. 4a, there are mainly two strategies to overcome sluggish kinetics and fouling effect, one is to adjust the electrode surface itself (*e.g.*, electrochemical dealloying),[98] and another is to modify the surface with active materials (*e.g.*, phthalocyanines).[36,96] For the former, Quynh and coworkers[98] have developed a nanoporous electrode through electrochemical dealloying of silicon (Si) out of Au–Si or Pt–Si alloy thin films. With the 3D porous network of interconnected noble-metal ligaments on the order of nanometers (Fig. 4b), this electrode showed desirable properties such as a high surface area, tunable porosity, excellent conductivity, mechanical rigidity, and high chemical stability, which when combined are conducive to the electrochemical oxidation and analysis of aromatic analytes. However, when

used for detecting 2-CP, the fouling effect remained on the nano porous Au electrode, and there was no good linearity obtained for the measurement. Also, the fabrication process of the metallic porous structure is complex, tedious, and requires sophisticated operating conditions and high cost. In this regard, the surface modification with active materials has become more popular in the development of electrochemical CP sensors, and this will be discussed in detail later in Section 3.2.

3.1.2 Indium tin oxide (ITO) glass electrode.

ITO, a conductive metal oxide, is another working electrode material for fabricating electrochemical CP sensors. This is because ITO exhibits comparatively low sheet resistance and mechanical hardness. Uniquely, ITO has excellent optical transparency in the visible region arising from its wide bandgap and strong adhesive force with glass. Indeed, ITO has been recognized as the best transparent conductive oxide (TCO) coating onto a soda-lime glass substrate forming the mostly used glass electrode in electrochemical sensors. However, just like Pt and Au, ITO glass by itself suffers from some technical challenges when used for electrochemical CP sensing, such as the slow mass transport rate of CPs and fouling problem. To solve these problems, the ITO electrode can be modified with various active materials, *e.g.*, the DNA entrapped polypyrrole–polyvinyl sulfonate (PPy–PVS) film,[46,48] Ag–phosphotungstic acid loaded chitosan (Ag–PTA/chitosan),[72] and Au nanoparticles functionalized with hydrosulfuryl–β-cyclodextrin (Au NPs/HS–β-cyclodextrin). As shown in Fig. 4c, the Au NPs/HS–β-cyclodextrin modified ITO glass electrode brought a LOD of 1.0 nM for the detection
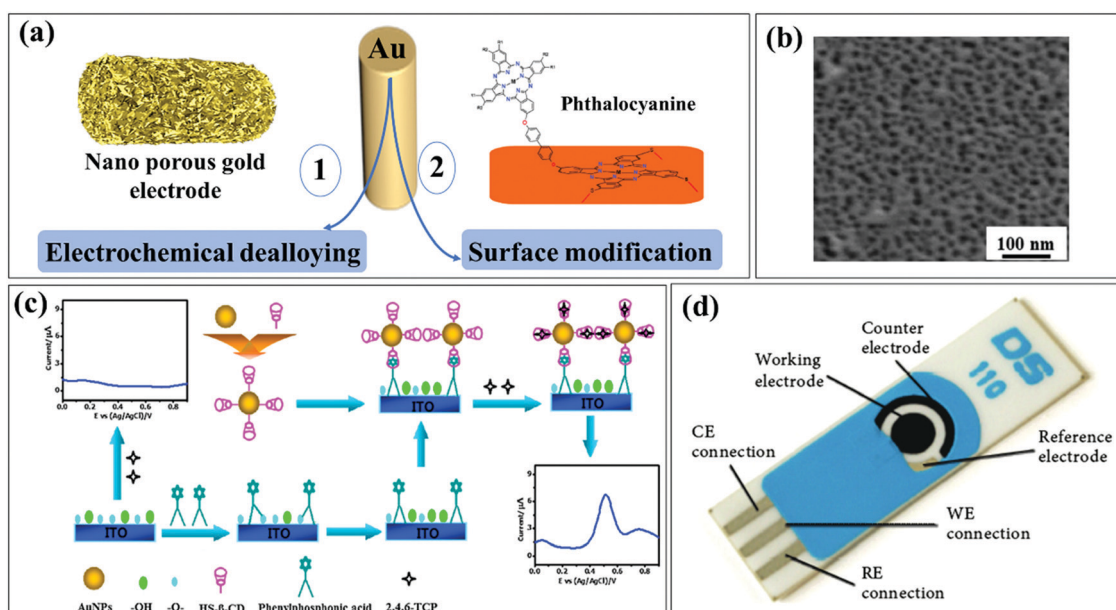

Fig. 4 (a) Illustration of different modification strategies of Au electrodes taking electrochemical dealloying and surface modification with phthalocyanine as an example. Reprinted with permission, copyright 2018, Elsevier.[96] (b) SEM images of a nanoporous Pt electrode. Reprinted with permission, copyright 2018, IOP Publishing.[98] (c) Illustration of the preparation of an Au NPs/HS–β-cyclodextrin modified ITO glass electrode for electrochemical sensing of 2,4,6-TCP. Reprinted with permission, copyright 2015, Elsevier.[87] (d) A three-electrode SPE with SWCNT/PEDOT/carbon ink as the working electrode, carbon as the counter electrode and Ag as the reference electrode. Reprinted with permission, open access article, copyright 2015, Negussie Negash *et al.*[71]

of 2,4,6-TCP.[87] And, after electrochemically depositing with the PPy–PVS film (and pre-loaded with double-stranded DNA), the ITO glass electrode showed great stability for detecting 2-CP, with a shelf life of about 4 months when stored at 25 °C.[46] Compared to the noble metals or below-mentioned carbon-based electrodes, the ITO glass electrode also shows superiority in surface cleaning and renewing.[72] However, indium metal is relatively rare and very dispersive on earth, and commercial ITO is nearly monopolistic with a high cost like noble metals. Currently the ITO glass is mostly fabricated with magnetron sputtering or vacuum evaporation deposition methods. Its high cost, together with its fragile nature, has dramatically limited its practical application as an electrochemical electrode. It remains essential to develop simple, low-cost fabrication techniques for ITO glass, or replace the ITO coating with other feasible TCO materials like fluorine doped tin oxide (FTO), antimony tin oxide (ATO), *etc.*

3.1.3 Carbon-based electrode.

Due to the relatively low cost and wide availability of carbon materials, carbon-based electrodes have been widely used ever since graphite electrodes were introduced for electrochemical production of alkali metals.[94–99] Diverse carbon-based electrodes emerge, benefiting from the presence of abundant allotropes of carbon including the sp^2 hybridized graphitic carbon materials (graphite, glassy carbon, carbon black, *etc.*), and the completely sp^3 hybridized tetrahedral diamond. The currently used carbon-based electrodes for electrochemical CP sensing are based on a glassy carbon electrode (GCE), a carbon paste electrode (CPE), a carbon ceramic electrode (CCE) and a boron-doped diamond electrode (BDDE), and others in composite with other materials. These electrodes have a relatively high proton reduction overpotential and stronger propensity to adsorb molecules from solution than noble metal electrodes, showing a fast mass transfer rate towards CPs, which are otherwise more difficult to absorb on metal electrodes.[97]

A GCE, usually obtained from pyrolysis of polyacrylonitrile, has a structure with randomly intertwined graphitic ribbons and abundant voids.[97] As the commonly used working electrode in electrochemical sensors (especially for the detection of CPs as listed in Table 1), the GCE is widely commercially available, and has many advantages including low background current, high conductivity, a wide potential window, and ease of surface modification.[99] However, the surface of the GCE is prone to oxidation, thus requiring appropriate surface preprocessing, usually by pretreatment with the Al_2O_3 powder or treatment with a laser, electrochemistry, or heat under vacuum. These pretreatment processes are often time-consuming and costly.

The CPE generally consists of a mixture of carbon powder, especially the polycrystalline graphite powder, and a binder (pasting liquid).[100] The advantages of the CPE stem from the following aspects:[101,102] great surface renewability, increased active sites originating from the randomly exposed edge and the basal plane of the graphite powder, low background current due to the less exposed area and low capacitance, efficient mass transport of electroactive molecules, and great potential to incorporate diverse active materials into the paste composite.

Not only carbonaceous materials but also surfactants,[102] metals,[90] metal oxides,[68] ionic liquids,[66] enzymes,[85,103] and metal–organic frameworks (MOFs)[82] can be incorporated into the CPE to improve the sensing performance towards CPs. One technical drawback of the CPE lies in the fact that the electrocatalytic materials used usually have high leachability from the CPE surface after continuous work, causing concern for the stability and reproducibility.

The CCE is generally produced from carbon sol–gel silicate precursors, and similarly to the CPE, it can also be composited with other active materials such as enzymes and multiwall carbon nanotubes (MWCNTs) to construct electrodes with renewable surfaces.[104–106] In view of its easy fabrication at room temperature at low cost, and more robust and higher stability than CPEs, CCEs are expected to be explored more in the future, especially regarding the optimization of material composition in order to maximize the electrochemical sensor performance towards CPs.

The BDDE is a representative sp^3 hybridized carbon-based electrode. The undoped diamond shows completely sp^3 hybridized tetrahedral bonding, resulting in no electronic states within its band gap.[97] Doping with boron introduces mid-gap states, increasing both the conductivity and electron transfer reactivity of the material. The boron doping level is vital to its electrochemical performance.[95,97] Compared with sp^2 hybridized carbons mentioned above, the BDDE has extremely high chemical stability, exhibiting a longer lifetime, better reproducibility, and a wider electrochemical potential window.[19] Particularly, the BDDE shows great anti-oxidation capability, which can be used with little surface pretreatment after a long period of storage in ambient air. By using a BDDE, Rahmah and coworkers reported a linear range of 0.5–100 μM for detecting PCMC.[95] Currently, the BDDE remains at a relatively high price, and this may prevent it from becoming popular in electrochemical sensors unless some breakthrough in synthesis can be achieved in the future to significantly reduce the material cost.

Composite electrodes fabricated by compositing carbon-based materials (usually graphite, carbon nanotubes, *etc.*) with polymers like epoxy resins have also attracted great attention in the last few decades.[73,74,91] For example, Adriana and coworkers[91] fabricated a stable MWCNT–epoxy composite electrode *via* an easy insertion process and successfully applied it for the electrochemical detection of PCP with a LOD of 0.801 μM. In addition, epoxy resin composites with expanded graphite, a special low-density graphite prepared by the thermal expansion of randomly oriented natural graphite, were also used for the fabrication of electrodes for 4-CP detection.[73,74] The commercial availability and easy processability of epoxy resins bring great convenience for the encapsulation of conductive carbon materials to fabricate working electrodes.

In general, there remains a great need for further research to explore more active materials for surface and structure modification of carbon-based electrodes. Many of the currently used modification materials are either sensitive to the change of electrolyte acidity, or the surface passivation by organic compounds (including the target analytes).

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3.1.4 Flexible electrodes. Flexible electrodes are a special type of electrode that consist of conductive materials coated on substrates with significant flexibility, usually polymers or fabric.[107–115] Carbon-based materials and intrinsically conducting polymers (ICPs) are among the most used conductive materials for fabricating flexible electrodes.[108–110] These working electrodes can be further modified with active materials to enhance the specific electrochemical responses towards analytes like CPs. Flexible electrodes deserve more attention and research effort as they have attracted increasing interest in constructing portable or wearable sensors and related electronic devices, which represent a promising direction for both fundamental research and technical development for the electrochemical CP sensors.

Existing attempts to apply flexible electrodes in the electrochemical detection of CPs include a carbon fiber paper electrode (CFPE) for 2,4-DCP,[13] a carbon felt electrode (CFE) for 4-CP,[69,112] etc. These electrodes have high porosity and wettability, providing a hydrophilic surface and abundant active redox sites. Moreover, the randomly oriented 3D porous structure, along with the high surface area, functions as an ideal matrix for immobilizing active components like enzymes and amine compounds that are essential for enabling or enhancing the electrochemical detection of CPs.

Furthermore, screen-printed electrodes (SPEs) based on carbon ink and flexible plastic substrates such as the polyimide film have also been studied in electrochemical CP sensors.[70,113–115] As shown in Fig. 4d, a carbon ink electrode modified with single-wall carbon nanotube/poly(3,4-ethylenedioxythiophene) (SWCNT/PEDOT) shows great field detection potential and rapid response.[71] As an alternative to conventional electrodes, SPEs possess several features such as simplicity, miniaturization, disposability, and exemption from surface passivation aroused by the fouling effect of analytes like CPs. A combination of these features provides SPEs with good economical practicality and portability to be integrated with smart electronic devices, for which the current major technical drawback would be the manufacturing reproducibility between different batches of electrodes. Moreover, taking advantage of the structural tunability of carbon inks, the SPE could be modified with varying active materials to enable different electrochemical responses, and the different electrodes thus fabricated can be integrated into an array to enhance the detection capacity (through differential sensing) for complex samples containing multiple CPs and other chemicals.

The development and application of flexible working electrodes in the fields of electrochemical CP sensors remain to be further investigated, particularly with the aim of technical practices that synergistically concern mechanical flexibility and reliability, electrical conductivity, system miniaturization, and integration into portable or disposable devices.

3.2 Working electrodes modified with active materials

Without appropriate surface or structural modification, the basic working electrodes (all commercially available) often suffer from sluggish surface kinetics, resulting in unsatisfactory signals such as peak broadening, weak response, low sensitivity, and/or poor selectivity among different CPs or against other analytes that have very close redox potentials.[92] Besides, the unmodified electrodes require high potential to proceed with the redox reaction of CPs at high rates.[94] Thus, in practical use, modification of the working electrodes with specific active materials is necessary. Such modification facilitates both the interface contact with target CPs and the interfacial charge transfer therein. In this regard, the modification materials used are usually considered as electrocatalysts helping expedite the electrochemical reaction and altering the redox potential of CPs.

There are generally two strategies to improve the electrocatalytic performance of the active materials for the electrochemical detection of CPs. One is to increase the active site number of working electrodes via morphology or architecture control, while the other is to increase the intrinsic activity via composition or structure change of the electrode. The current active materials employed include biomaterials, metallic materials, carbon nanomaterials, MOFs, ICPs, and clays. Modification of basic working electrodes with these materials via versatile strategies is described in this section.

3.2.1 Biomaterials. Biomaterials such as enzymes, polyaminoacids, and deoxyribonucleic acids (DNA) have earned special attention for being used in the modification of working electrodes of electrochemical CP sensors. The electrodes constructed with biomaterials as receptor or transducer units benefit from their intrinsic biological recognition towards target analytes, environmental friendliness, catalytic activity, as well as electrocatalytic amplification of response signals.[116–121]

3.2.1.1 Enzymes. Enzymes, as well-known biocatalysts, can be modulated onto the surface of basic electrodes to serve as binding recognition receptors in electrochemical sensors. CPs can serve as electron donors for oxidized enzymes such as tyrosinase (TYR),[12,71] polyphenol oxidase,[57,64,118] laccase (Lac),[4,60,119] horseradish peroxidase (HRP),[38,41,62,120] chloroperoxidase,[85] and microsomal cytochrome,[11] among others. As shown in Fig. 5a and b, the enzyme mediated electrochemical sensing of CPs generally occurs in four steps: (1) transfer of CPs from the electrolyte solution to the working electrode surface; (2) distribution of CPs between the enzyme layer and the solution phase; (3) diffusion and reaction of CPs in the enzyme layer; and (4) charge transfer from the oxidation of CPs to the base electrode to generate an electrochemical signal.[12] Overall, the sensing performance is determined by the intrinsic electrocatalytic ability of the enzyme, as well as the surface immobilization, operational stability, and long-time stability of the enzymes.

One critical requirement for constructing the sensors as illustrated in Fig. 5a and b is effective surface immobilization of the enzyme on the working electrode so that the enzyme still maintains enough active sites exposable to analytes like CPs. For TYR, the most frequently employed enzyme,[103] several types of surface modification have been developed. For example, layer-by-layer assembly of oppositely charged materials, like the positively charged polydiallyldimethylammonium chloride (PDDA) and negatively charged MWCNTs as shown in Fig. 5a,
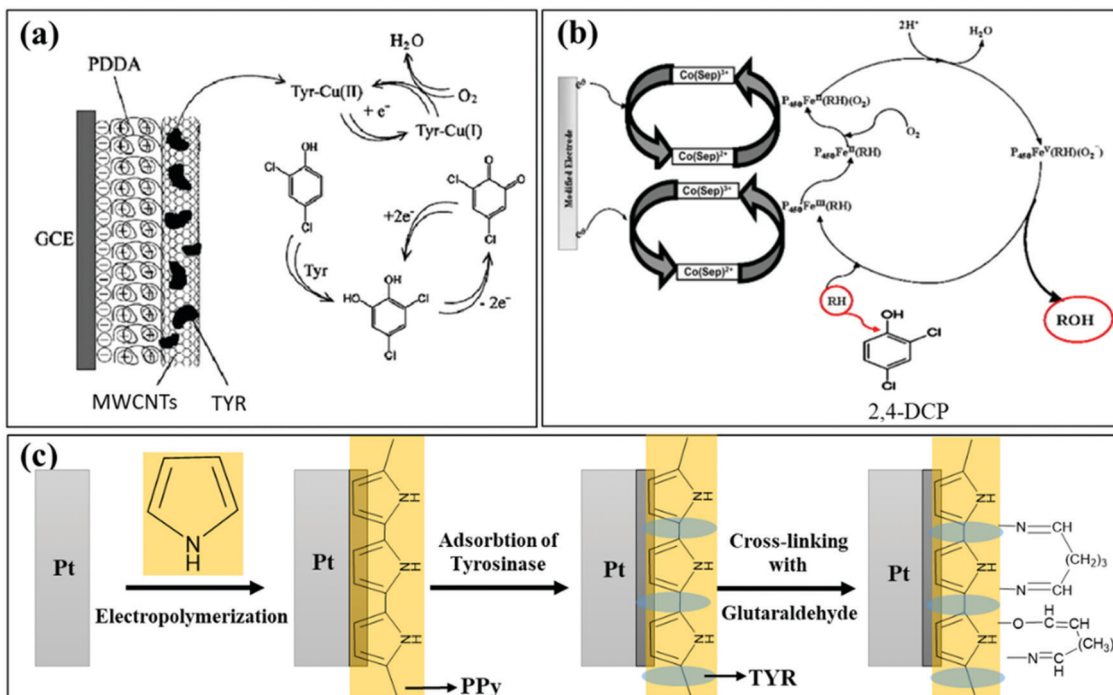
Fig. 5 The electrochemical oxidation process of CPs (2,4-DCP as an example) on (a) TYR. Reprinted with permission, copyright 2009, Springer[76] or (b) monooxygenase enzyme (microsomal cytochrome CYP3A4) modified GCE. Reprinted with permission, copyright 2008, Elsevier.[11] (c) Immobilization of TYR into the PPy film and cross-linking with glutaraldehyde for fabricating the biologically active layer on the Pt electrode. Reprinted with permission, copyright 2011, Elsevier.[12]

can provide a good immobilization matrix for TYR, which facilitates the electron transfer between the active sites of the TYR and GCE surface.[117] Alternatively, Au nanoparticles (Au NPs) can be first electrodeposited onto the GCE surface to form a self-assembled monolayer for TYR immobilization, helping in increasing the exposure of TYR to CPs, leading to a significant enhancement of signal response.[121] Another efficient enzyme immobilization matrix is PPy. As shown in Fig. 5c, the electro-polymerized PPy film can act as a matrix to adsorb and immobilize TYR through hydrogen bonding and electrostatic interactions. Further cross-linking with glutaraldehyde helps stabilization of TYR within the matrix of PPy, while retaining the intrinsic enzyme activity to a large extent. The TYR/PPy system demonstrated a fast, highly sensitive and stable response in the electrochemical sensing of 2-CP.[12] Similarly, the porous carbon felt can also serve as an effective immobilization matrix to retain the intrinsic enzyme activity of TYR, thus enhancing the sensor stability.[69,112]

Despite working well under certain conditions, the enzyme-based electrochemical sensors described above are often affected by temperature, pH, and passivation of CPs, which in combination may reduce the performance stability in the long term. Some additives like triblock copolymer PEO–PPO–PEO (polyethylene oxide–polyoxypropylene–polyethylene oxide, F108) have been utilized with the aim to further stabilize the performance of enzymes, e.g., Lac, which retained 65.8% of its initial sensor response (in terms of current) after 30 days of use.[60] Apparently, plenty of work remains to be done to further improve the long-term performance robustness of enzyme-based electrochemical sensors. Additional challenges of employing enzymes in the sensors include the decrease in conductivity of electrodes and the complicated procedure involved in surface modification. For some enzymes, these two challenges may become so serious that they will prevent the practical application of the sensor system. Therefore, it is alternatively imperative to develop non-enzymatic biological active materials that can be used to modify the working electrodes to achieve better environmental stability and long-term performance.

3.2.1.2 Polyaminoacid and DNA. Polyaminoacid and DNA show greater stability than enzymes, and have been used as alternatives for constructing electrochemical CP sensors. However, in comparison to enzymes, these two biomaterials often lack sufficient exposure sites to analytes like CPs. To overcome this problem, Zhang and coworkers[50] reported a unique approach to fabricate a 3D ordered macroporous film by electropolymerization of cysteine on the surface of polystyrene spheres as templates. The structure thus fabricated provides a large specific surface area, uniform porosity, and 3D network access to the active sites. This electrode showed good recovery (99.6–107.0%) of sensor performance when tested for the detection of 4-CP, which gave a LOD as low as 0.0167 nM. As a robust, precisely controlled structure, DNA has also gained attention for electrode surface modification, taking advantage of the strong binding affinity towards some organic pollutants,

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especially those that are subject to bioaccumulation.[48,116] With physical adsorption of DNA onto the PPy–PVS film electrochemically polymerized on the ITO glass electrode, the electrochemical sensor performance was significantly improved, showing a wide linear detection range for 2-CP, 0.506–126.6 μM.[46]

3.2.2 Metallic materials. Metallic materials (nanostructured metals, metal oxides, metallophthalocyanines, *etc.*) are proven to be efficient and stable electrocatalysts when modified onto electrodes, and such surface catalysis can be applied to the redox reactions of CPs. The large surface-to-volume ratio of nanoscale morphology (as for nanoparticles, nanorods, quantum dots, *etc.*) provides abundant active sites. Metals can be doped into mesoporous materials to synthesize composites with a large specific area, providing a high density of active sites that are accessible to CPs for electrocatalytic reactions.[40] Ya *et al.*[90] reported on a CPE modified with Al-doped mesoporous cellular foam, which demonstrated an enhanced electrochemical oxidation peak towards PCP with a linear detection range of 0.376–18.8 μM and a LOD of 0.3 μM.[90] Besides, Pd can be doped into Ag to form heterostructured Pd/Ag bimetallic alloys, enhancing the intrinsic electrochemical activity.[40] Such alloys can be composited with rGO, and used to modify the GCE, enabling quick detection of multiple CPs such as 2-CP, 3-CP, 4-CP, and 2,4-DCP, for which LODs of 4.7, 7.7, 7.5, and 0.36 nM were obtained, respectively.[40] This type of composite approach provides unique potential for detecting multiple analogues of CPs at the trace level.

3.2.2.1 Nanostructured metals. Nanostructured metallic materials have been attracting considerable attention owing to their large surface area, special binding sites, fast electron transfer rate, good electrocatalytic activity, and enrichment effect on the target analyte. These features have been extensively incorporated in improving the relatively poor catalytic activity of the basic working electrodes when used in the electrochemical detection of CPs. Nanostructure engineering of metal electrodes can also help reduce the over-potential, which is conducive to the electrochemical oxidation of CPs.[68] Qiu and coworkers[55] reported on an electrodeposition method, which can be used to modify the surface of the GCE with Au nanofilms (Au NFs), thus enabling fast amperometric detection of 4-CP. However, the linear detection range (0.2–4.8 mM) and LOD (0.11 mM) are not as good as compared to other types of electrodes. This could be due to the poor dispersion of metal NPs, which are unable to form an efficient electronic transmission network. Therefore, further incorporation with other active materials that have a large surface area and efficient electronic network could be a feasible strategy to solve the problem. As shown in Fig. 6a, Au NPs were loaded onto carboxyl functionalized MWCNTs (MWCNT–COOH) to achieve a network nanostructure, which possesses abundant active sites and superior electrocatalytic activity.[52] The nanocomposite thus fabricated, Au NPs/MWCNTs–COOH can be used to modify the GCE to enhance the electrochemical sensing performance towards 4-CP, for which a linear detection range of 0.3–400 μM and a LOD of 0.11 μM were obtained. Similarly, Wang *et al.*[88] loaded

Ag NPs on rGO to increase the surface area and electron-transfer rate. The obtained Ag NPs/rGO/GCE can also help enrich analytes like PCP on the electrode interface, as indicated by the low LOD (1 nM) and wide linear detection range (8 nM–10 μM), which are suited for the direct detection of real samples. Sun *et al.*[122] distributed Pt NPs on rGO *via* a facile *in situ* electrochemical reduction method. The fabricated Pt NPs/rGO/GCE exhibited excellent electrocatalytic properties, which amplified the oxidation peak current as well as lowering the oxidation over-potential of 4-CP, both helping to enhance the detection efficiency.

The two constituents in bimetallic NPs usually interact, therefore, in comparison to the corresponding single metals, the alloy generally has improved properties regarding catalytic activity and selectivity, resistance to deactivation and so on, which are all essential for the enhancement of electrochemical sensing.[123] Yang *et al.*[123] fabricated a sensitive 4-CP sensor *via* loading Cu–Au NPs on rGO. Huang *et al.*[81] modified the GCE with MoS_2, Au NRs/Ag NRs and ionic liquids (IL), and the obtained electrode demonstrated a low LOD of 2.6 nM when tested for the detection of 2,4-DCP.

Besides, quantum dots (QDs) of metallic chalcogenides are also attractive for electrochemical sensing due to their high electron-transfer efficiency and surface reaction activity. Li *et al.*[44] reported on an electrochemical CP sensor based on ZnSe QDs, which can be electrostatically self-assembled with cetyltrimethyl ammonium bromide (CTAB) and modified on the GCE. The composite electrode thus fabricated, ZnSe QDs–CTAB/GCE, showed excellent electrocatalytic activity and thus sensing performance towards CPs, with LODs of 8 nM, 2 nM, and 10 nM, achieved for 2-CP, 2,4-DCP, and PCP, respectively.

3.2.2.2 Metal oxides. Distinguished from pure metals, metal oxides have a semiconductor nature, that is, metal nodes can exist in two or more oxidation states, showing unique electromagnetic properties, electrocatalytic properties, and photocatalytic properties.[57] To increase the active sites, various nanostructured metal oxide materials such as $CuWO_4$ NPs,[124] NiO NPs,[68] ZnO NPs,[62] Bi_2O_3 nanofilms (NFs),[57] and MgO 3D-flowers have been fabricated using various chemical and physical methods, and employed for modification of the working electrode used in electrochemical sensors.

As shown in Fig. 6b, Ahmad *et al.*[54] synthesized MgO 3D-flowers *via* a simple reflux method. The flowers were used to modify the GCE, resulting in a greatly improved electrochemical sensing response for 4-CP with a LOD of 0.045 μM. The improved sensing response was mainly due to the high surface area and low charge resistance of the flower structure, which in turn enhanced the electrocatalytic activity. As a common electrode material, SnO_2 possesses high surface reactivity. However, SnO_2 usually suffers from severe signal drifts when employed in electrochemical sensors.[58] To solve this problem, GO sheets were used to wrap the SnO_2 particles, specifically hollow spheres, as presented in Fig. 6c. The hierarchical nanostructured materials thus fabricated were used to modify the GCE, which demonstrated excellent electrochemical
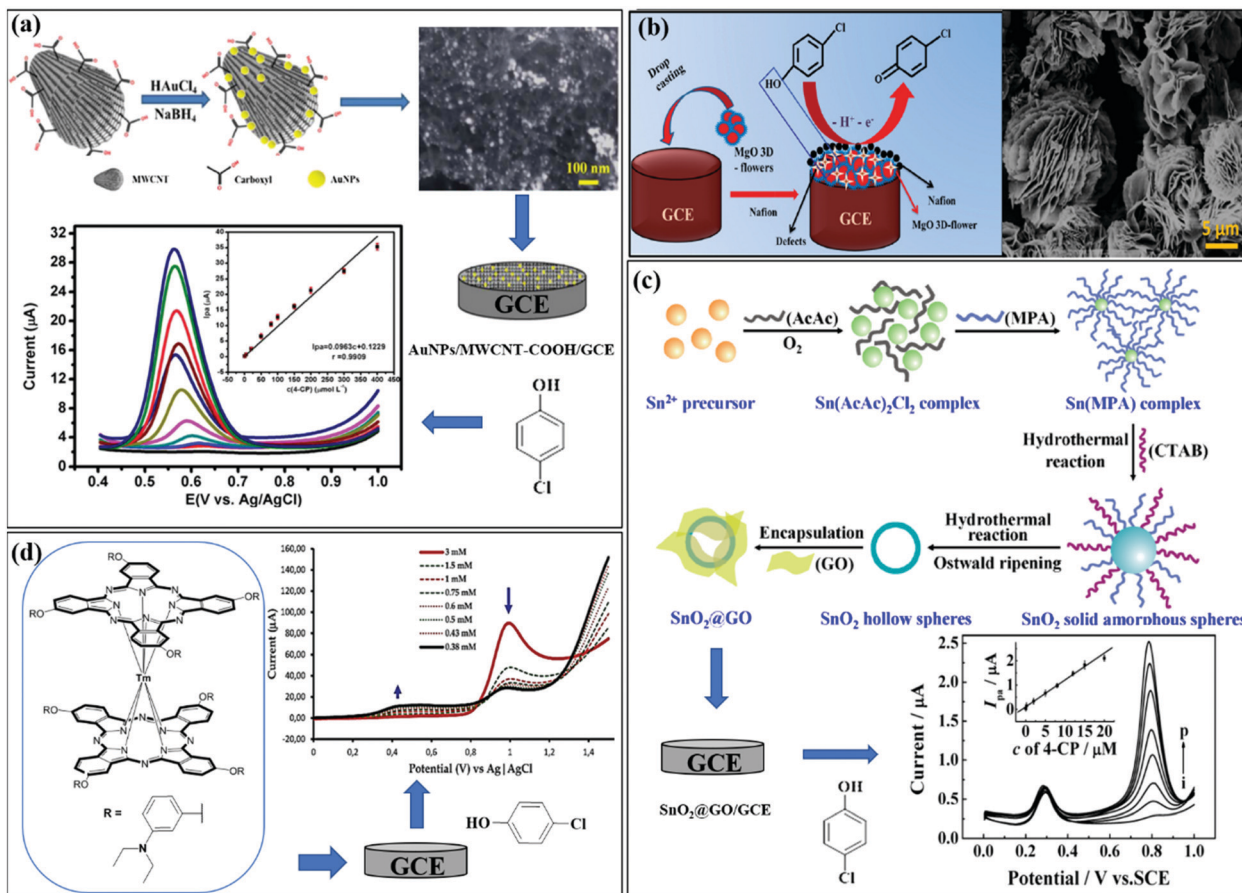
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Fig. 6 (a) Fabrication of the Au NPs/MWCNT−COOH/GCE and its SEM image and DPV responses towards 4-CP at different concentrations. Reprinted with permission, copyright 2013, Royal Society of Chemistry.[52] (b) Fabrication of the GCE modified with MgO 3D-flowers (SEM image shown) for the electrochemical detection of 4-CP. Reprinted with permission, copyright 2019, Royal Society of Chemistry.[54] (c) Fabrication process of SnO₂@GO/GCE and its DPV responses towards 4-CP at different concentrations. Reprinted with permission, copyright 2017, Elsevier.[58] (d) Chemical structure of TmPcs and LSV responses of the TmPcs modified GCE towards 4-CP at different concentrations. Reprinted with permission, copyright 2019, Wiley.[53]

response for 4-CP detection with a wide linear detection range of 0.02–20 μM and a low LOD of 3.1 nM.[58] Furthermore, bimetal oxide nanomaterials like Er_2O_3/CuO were also proven suitable for the modification of the GCE as tested in electrochemical sensing of 3-CP, which gave a LOD as low as 0.09 nM.[47]

3.2.2.3 Metallophthalocyanines. Metallophthalocyanines bearing varying functional groups are suitable for working electrode modification through forming closely packed monolayers *via* self-assembly on the surface.[36] As shown in Fig. 6d, Sekhosana *et al.* modified GCE surfaces with a thulium double-decker phthalocyanine (TmPcs), which possesses great electrocatalytic activity.[53] The surface modification resulted in the enhancement of the LSV response towards 4-CP, with a LOD of 0.0416 μM.[53]

Metallophthalocyanines can also form a bimetallic system suitable for surface modification of electrodes.[96] Makinde *et al.*[96] reported on an Au electrode modified with cobalt binuclear phthalocyanine (CoBiPc) bearing thio substituents for binding to gold. The modified Au electrode showed an enhanced peak current and lower electrocatalytic potentials compared to unmodified electrodes towards CPs.

3.2.3 Carbon nanomaterials. Carbon nanomaterials have several advantages in modifying the working electrodes of electrochemical CP sensors. Generally, they improve surface kinetics, enhance the adsorption of CPs on the electrode surface and accelerate the redox process through the provision of the enhanced electroactive surface area. According to the structural dimensionality, carbon nanomaterials can be generally classified into four groups: (a) zero-dimension (0D), *e.g.*, carbon dots (CDs) and carbon spheres (CSs); (b) one-dimension (1D) represented by carbon nanotubes (CNTs); (c) two-dimension (2D) including graphene oxide (GO) and reduced graphene oxide (rGO); and (d) three-dimension (3D), *e.g.*, aerogels consisting of entangled stacks of graphene sheets.

3.2.3.1 Carbon dots. CDs were accidentally discovered during the separation and purification of SWCNTs.[75] CDs have several advantages such as low toxicity, environmental friendliness, good water-solubility, and chemical stability. More importantly, they display great electrocatalytic activity, and surface functionalization feasibility enabling tunable control of their physicochemical properties, providing great potential for the construction of electrochemical CP sensors. As shown in

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Fig. 7a, Yu et al.[75] reported on a CD surface capped with a layer of positively charged CTAB. The addition of chitosan helped fix and stabilize the CD composite on the GCE surface. The CDs–CTAB/chitosan/GCE electrode thus fabricated showed significant electrocatalytic activity toward 2,4-DCP resulting in a LOD of 0.01 μM.

3.2.3.2 Carbon spheres. For the electrochemical sensing of CPs, CSs present several advantages such as mono-dispersity, excellent conductivity, and controlled size and shape. Also, their surface can be functionalized with various hydroxyl groups, which can be tuned to form ionized sites (–O⁻ groups) under certain alkaline conditions. These ionized sites can interact with other functional shells, enabling a potential core–shell strategy to enhance the signal response of CP sensing. As shown in Fig. 7b, Yi et al.[89] synthesized nitrogen-doped hollow CSs wrapped with a graphene nanostructure (NHCNS@rGO) for the highly sensitive sensing of PCP. The NHCNS@rGO/GCE showed a wide linear detection range of 0.03–38.00 μM and a LOD of 0.01 μM. Besides, Gan and coworkers[43] used a similar core–shell strategy to develop carbon sphere@silver spheres wrapped with GO, and the CS@Ag@GO/GCE can simultaneously detect 2-CP, 4-CP, 2,4-DCP and 2,4,6-TCP.

3.2.3.3 Carbon nanotubes. CNTs have drawn great interest in electrochemical sensors and broadly many other types of chemical sensors since their discovery in 1991,[125] mainly due to their unique features such as large, open surface area, high conductivity, and ease of surface functionalization with other active species like metallic materials[52,63] and organic molecules[126] to further improve the sensing performance. The main characteristic of CNTs in the electrochemical sensing of CPs is their rapid response and low oxidation potential for CPs, which is mainly due to their high surface area, low over-voltage, and rapid electrode kinetics.

However, the intrinsic van der Waals interaction between the nanotubes makes CNTs tend to bundle together on a large scale and insoluble in routine solvents.[56] Surface modification with surfactants or oxidative treatment to form oxygen-containing functional groups such as –OH or –COOH is an efficient strategy for CNTs to improve their solubility and thus to be further applied in electrochemical sensors. As shown in Fig. 8a, Zhu and coworkers[59] used hydroxylated nanotubes (CNTs–OH) to overcome the poor solution processability of CNTs. After loading with Pt NPs and rhodamine B (RhB) to enhance the electrocatalytic activity, the 3D-structured CNTs–OH/Pt NPs/RhB modified GCE can simultaneously determine 2,4,6-TCP and 4-CP. A large peak potential separation of about
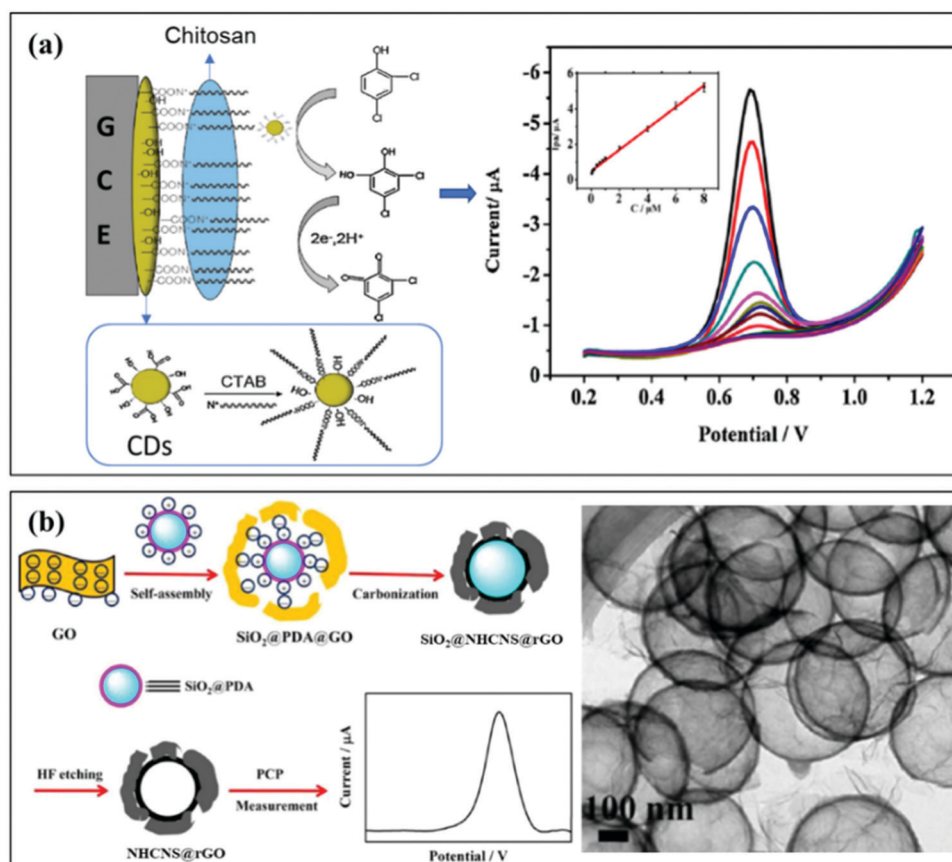

Fig. 7 (a) Construction of a chitosan/CDs–CTAB/GCE used in the detection of 2,4-DCP and the oxidation current measured at varying concentrations of 2,4-DCP. Reprinted with permission, copyright 2016, Elsevier.[75] (b) Construction of NHCNS@rGO (with the TEM image shown) that can be employed for the surface modification of the GCE for PCP detection. Reprinted with permission, copyright 2016, Elsevier.[89]
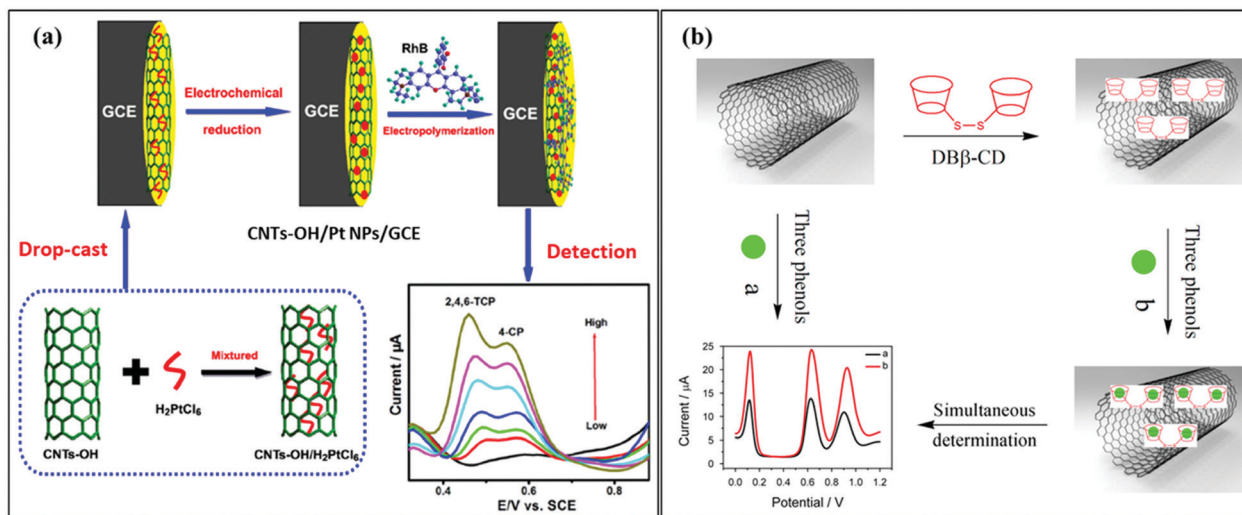
Fig. 8   (a) Construction of a CNTs−OH/Pt NPs/RhB/GCE for simultaneous determination of 2,4,6-TCP and 4-CP. Reprinted with permission, copyright 2018, Elsevier.[59] (b) Preparation of a DBβ-cyclodextrin dimer/MWCNTs/GCE and its comparison with MWCNTs/GCE for the simultaneous detection of three phenols (including 4-CP). Reprinted with permission, copyright 2015, Elsevier.[56]

91 mV was achieved by DPV, and the linear detection range for 2,4,6-TCP and 4-CP were 5.0–175.0 μM and 10.0–300.0 μM, respectively. Similarly, Zhu et al.[126] oxidized CNTs with H_2SO_4/HNO_3 to form the –COOH, –OH and C–O–C groups on the surface. These functionalized CNTs are negatively charged, showing improved solubility in water and can be further applied in 2-CP detection. Besides, Al-Qasmi et al.[80] combined the acid-treated MWCNTs with Nafion to modify the GCE. The functionalized MWCNTs/Nafion/GCE showed an anti-passivating ability and excellent catalytic properties, resulting in rapid and direct determination of 2,4-DCP with a linear detection range of 1–150 μM and a LOD of 0.01 μM.

However, acid-treated oxidation methods inevitably cause structural damage to CNTs, leading to lower electrical conductivity, and thus poor electrochemical performance. In this respect, a non-destructive strategy to functionalize CNTs becomes more desirable. For example, Li et al.[39] used surfactant dicetyl phosphate to improve the solubility of MWCNTs. The modified electrode, dicetyl phosphate/MWCNTs/GCE, showed a LOD of 0.04 μM towards 2-CP. Yang et al.[56] used a disulfide bridged β-cyclodextrin dimer (DBβ-cyclodextrin dimer) to functionalize MWCNTs without structural damage to the nanotubes as shown in Fig. 8b. The modified electrode, DBβ-cyclodextrin dimer/MWCNTs/GCE, demonstrated a linear detection range of 0.1–200 μM and a LOD of 0.028 μM towards 4-CP.

3.2.3.4 Graphene. Graphene is a 2D nanosheet comprised of sp^2 bonded carbon atoms, showing extraordinary physical and chemical properties.[127] The exceptionally large surface-to-volume ratio, extraordinary carrier mobility, and high electron transfer rate endow graphene with both numerous active sites and intrinsic catalytic activity, arousing great interest in the field of electrochemical sensors.[51] The properties of graphene can be adjusted by regulating the synthetic conditions, dimensions, number of layers, and doping constituents.[45]

In general, graphene consists of two structural regions including the basal and edge planes. In the basal plane, sp^2 conjugated carbon atoms are arranged two-dimensionally, while the edge plane has a defective graphitic line of carbon atoms with dangling bonds and is usually functionalized with moieties like –COOH and –OH. The presence of dangling bonds is responsible for the interaction between graphene and target analytes. It has been reported that graphene samples with edge planes show an order of magnitude higher electron transfer rate constant than that of the basal plane.[49] As shown in Fig. 9a, Kannan et al.[49] reported on an electrochemical sensor for 4-CP employing the photolithography patterned Pt electrode modified with oxygen plasma-treated multilayer graphene (OMLG). Compared to pristine graphene, OMLG showed an improved electron transfer reaction rate and mass transport rate. As a result, the LOD of OMLG/Pt towards 4-CP was decreased to 0.054 μM because the oxygen plasma treatment resulted in large numbers of controlled edge defects and dangling bonds on the graphene sheet.

Because of the strong tendency for aggregation, it is difficult to directly use pristine graphene electrochemical sensors. It is necessary to functionalize the graphene by incorporating functional groups or creating large numbers of edge defects. Wang et al.[51] developed PDDA-functionalized graphene to modify the GCE for the selective determination of 4-CP. Wei et al.[45] employed a β-cyclodextrin to functionalize graphene, overcoming the aggregation and improving dispersibility. The β-cyclodextrin/graphene/GCE can simultaneously detect 2-CP and 3-CP, with a LOD of 0.2 μM and 0.09 μM, respectively. The widely commercialized GO has multiple oxygen-containing functional groups and defects on the bottom surface and edge plane, making the graphene both soluble and stable. But GO suffers from low conductivity and a lower electron transfer rate, which is undesirable for constructing high-performance electrochemical CP sensors. Two approaches have been adopted to
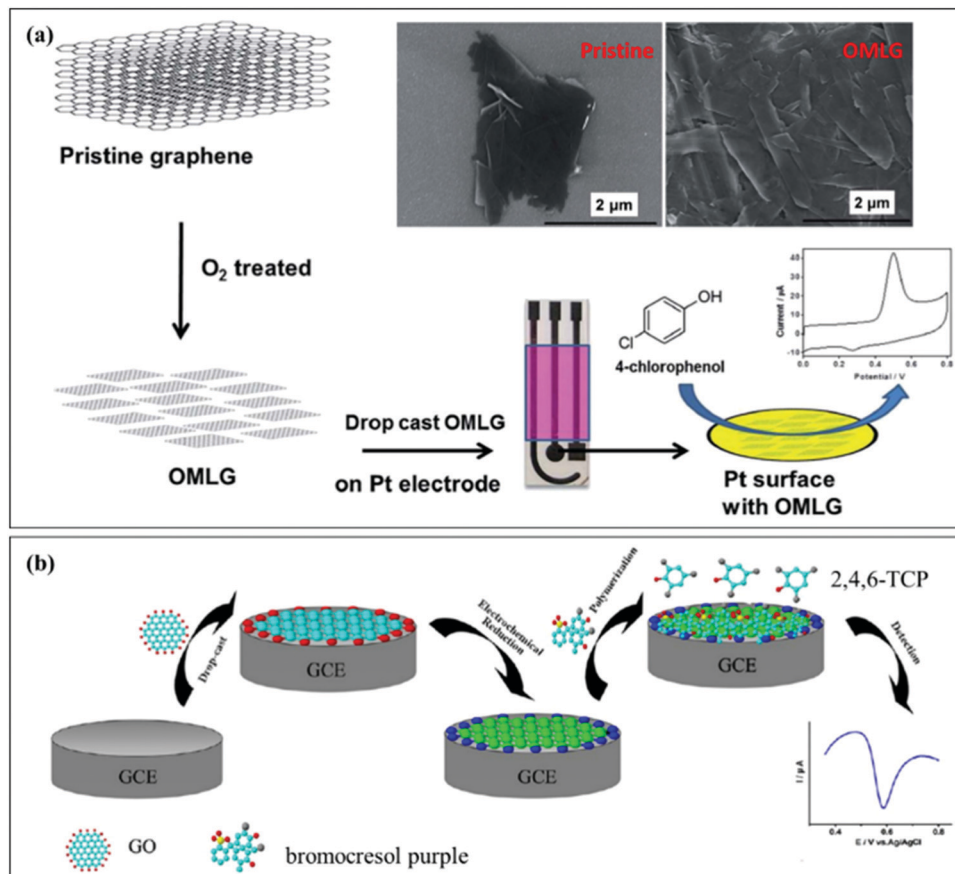
Fig. 9 (a) Preparation of OMLG/Pt for 4-CP detection and SEM images of pristine graphene and OMLG. Reprinted with permission, copyright 2016, Royal Society of Chemistry.[49] (b) Construction of a poly(bromocresol purple)/rGO/GCE for 2,4,6-TCP detection. Reprinted with permission, copyright 2015, Royal Society of Chemistry.[84]

meet this issue. One is the electrochemical reduction of GO to rGO,[58,70,78,122] which can significantly improve the signal response. Another is taking GO as a supporting matrix to disperse and stabilize different active materials such as TiO_2 NPs,[70] poly(bromocresol purple)[84] and V_2O_5 nanosheets.[29] Fig. 9b shows, for example, the construction process of the poly(bromocresol purple)/rGO/GCE including the electrochemical reduction of GO. The composite electrode was thus fabricated and demonstrated a LOD of 5 nM for 2,4,6-TCP detection.[84]

3.2.3.5 Graphene aerogels. Graphene aerogels (GAs) are another good choice that can efficiently overcome the drawback of graphene on self-aggregation. The 3D porous structures and intrinsic graphene properties enable GAs with high specific surface areas, large pore volumes, and fast mass and electron transport rates. These advantages make GAs an efficient electron transfer network, which is ideal for electrochemical sensors by providing high electrocatalytic activity and abundant active sites. For example, GAs have been used to load nanostructured PEDOT[93] and *in situ* polymerized PPy[128] to detect CPs. The effective surface area for GAs/GCE can reach 0.103 cm^2, which is superior to that of the bare GCE (0.066 cm^2).[93] The large surface area provides more active sites, which is crucial to

the improvement of sensing performance. The combination of GAs and various active materials for the high-performance sensing of CPs is still in progress.

3.2.3.6 Acetylene black. Acetylene black (AB) is a special type of carbon black synthesized from controlled combustion of acetylene, having excellent electric conductivity, large specific surface area and strong adsorptive ability.[42] However, similar to graphene, the poor dispersity hinders further application of AB to modify the working electrode in electrochemical sensors. To overcome this, Sun *et al.*[42] used a surfactant doping strategy, with the addition of dihexadecyl hydrogen phosphate (DHP), to obtain a homogeneous and stable AB–DHP suspension. As tested for 2-CP detection, the AB–DHP/GCE demonstrated a linear detection range of 0.2–40 μM and a LOD of 0.05 μM.

3.2.4 Metal–organic frameworks. Metal–organic frameworks (MOFs) are known as crystalline porous coordination polymer materials and have been widely applied in electrochemical sensors.[129] MOFs are built up from metallic bricks and organic complexing molecules acting as spacers. This combination offers ultrahigh pore volumes and large specific surface areas. Furthermore, the hybrid architecture and tunable intra-framework chemical functionality make MOFs able to display abundant functionality.[130] MOFs can serve as a stiff template[93]
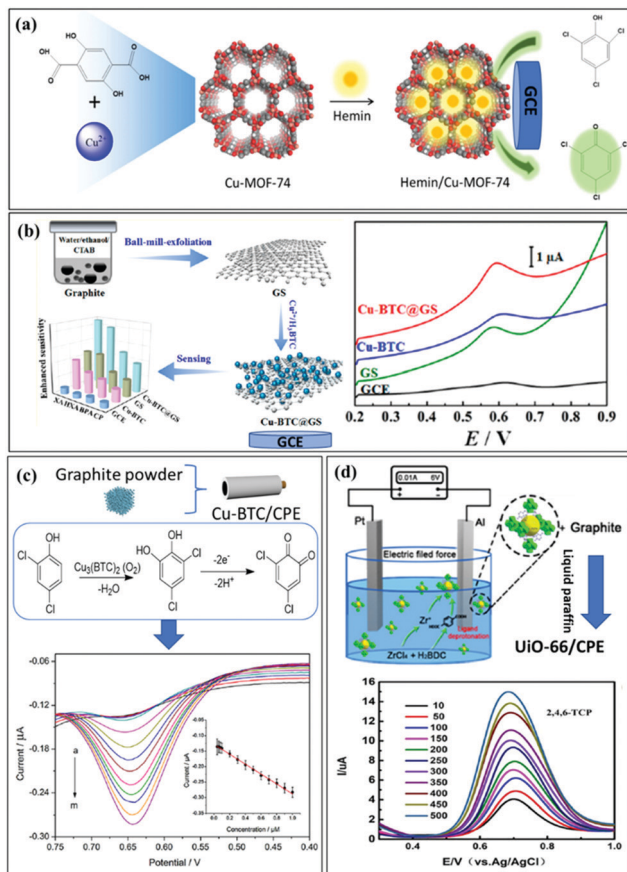
Fig. 10 (a) Construction of a hemin/Cu–MOF-74/GCE for 2,4,6-TCP detection. Reprinted with permission, copyright 2018, IOP Publishing.[83] (b) Preparation of a Cu–BTC@GS modified GCE and comparison of different DPV curves for a Cu–BTC@GS/GCE, Cu–BTC/GCE, GS/GCE, and bare GCE. Reprinted with permission, copyright 2019, American Chemical Society.[61] (c) Preparation of a Cu–BTC/CPE for 2,4-CP detection and the oxidation currents obtained at varying concentrations of 2,4-CP. Reprinted with permission, copyright 2015, Elsevier.[82] (d) Preparation process of a UiO-66/CPE via an electrochemical cathode method and its performance for 2,4,6-TCP detection. Reprinted with permission, copyright 2019, Elsevier.[86]

or substrate[83] to provide a large specific surface area and abundant active sites to enhance the sensing performance. As shown in Fig. 10a, hemin can be incorporated into the pores of Cu–MOF-74, which in turn can be used to modify the surface of the GCE. The composite electrode thus fabricated, hemin/Cu–MOF-74/GCE, demonstrated efficient detection of 2,4,6-TCP with a LOD of 5 nM.[83] Nonetheless, the electrochemical sensing performance of most MOFs could be negatively affected by their poor conductivity.[131] A rational strategy to solve this problem is to combine MOFs with other conducting materials. As shown in Fig. 10b, Li et al.[61] fabricated a highly sensitive electrochemical sensing material via in situ integration of Cu-based MOFs and high-conductivity ball-mill-exfoliated graphene nanosheets (Cu–BTC@GS). The material was highly compatible for surface modification of the GCE, and the Cu–BTC@GS/GCE showed a low LOD of 14.8 nM and an

exceptionally wide linear detection range of 39 nM–116.7 μM for 4-CP detection.

MOFs could also effectively improve the detection selectivity towards CPs due to the π–π interactions between the aromatic groups of CPs and ligands existing in MOFs. For example, Dong et al.[82] achieved highly selective detection of 2,4-DCP by introducing various amounts of Cu–BTC into the CPE (Fig. 10c). Apart from a low LOD (9 nM), the Cu–BTC/CPE showed a weak signal change (≤5%) in the presence of 16 kinds of possible interfering substances including resorcinol and phenol when the concentration of the interfering substances is lower than 1.0 μM. In addition, MOFs can be prepared by in situ electrochemical deposition to modify basic electrodes for electrochemical CP sensors. As shown in Fig. 10d, the Zr-based MOF (UiO-66) can be in situ deposited on the CPE by the electrochemical cathode method, which is suitable for detecting 2,4,6-TCP at a trace level with a LOD of 6.49 nM, and the linear range is 0.01–0.5 μM.[86] Thus, once the issues regarding the chemical stability and electrical conductivity of MOFs are addressed, it is expected that more applications of MOFs in electrochemical sensors for CPs can be achieved regarding both detection sensitivity and selectivity, taking advantage of the synthesis volatility, and structural and chemical tunability of MOF materials.

3.2.5 Intrinsically conducting polymers. Intrinsically conducting polymers (ICPs) possess an extended π-conjugation system, which expedites electron transport from one end of the polymer chain to the other.[132] Through doping or grafting, it is easy to adjust the redox activity of ICPs, making them attractive active materials for electrode modification in electrochemical sensors.[133,134] The advantages such as high electrical conductivity, mechanical flexibility, and easy solution processability promote the application of ICPs in electrochemical sensors for CPs by providing an increased current signal and better signal transduction. The most common ICPs such as PEDOT, PANI, and PPy (Fig. 11a) have not only been used to accelerate the electron transfer rate of the electrochemical redox process, but also acted as molecular imprinted polymers (MIPs) to achieve sufficient selectivity for the detection of CPs. The MIP preparation mechanisms mainly include free-radical polymerization and sol–gel processes.[135] Free-radical polymerization is the most frequently used mechanism for the preparation of MIPs.[136] Compared to other imprinting methods based on free-radical polymerization, for example, bulk polymerization, electrochemical polymerization can be a one-step and in situ process, which tends to directly form homogeneous modified layers on electrode surfaces.[13,137] Besides, the thickness of modified layers can be controlled precisely. Therefore, electrochemical polymerization has an advantage over other methods in the fabrication of electrochemical MIP sensors.[13] As shown in Fig. 11a, ICPs can form MIPs by electrochemical polymerization in the presence of target CP molecules as templates. Then, the templates are rinsed off the polymer matrix, leaving their complementary imprint sites with the same size and shape as those of the CPs. The specific cavity structure thus formed can recognize CPs by preferential rebinding, leading to enhanced selectivity, as well as sensitivity.[27]
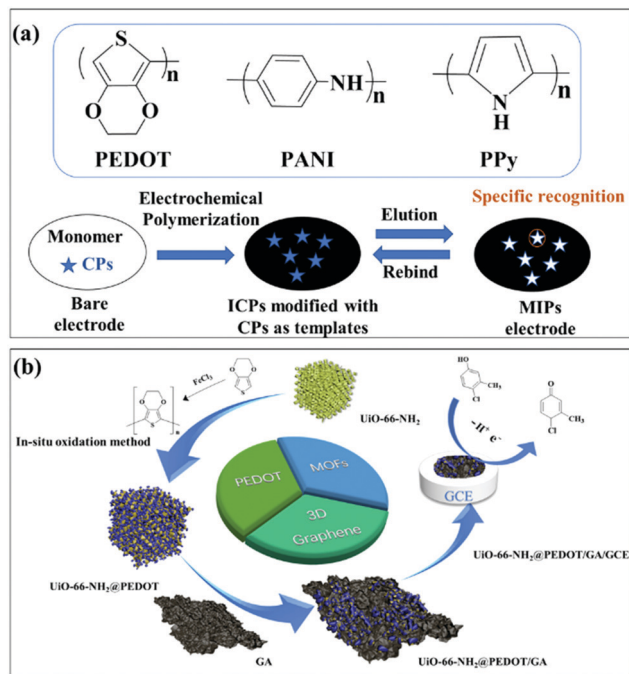
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Fig. 11 (a) Illustration of the chemical structures of PEDOT, PANI, and PPy and the electropolymerized preparation process of the MIP electrode using the ICP film for specific recognition of CPs. (b) Construction process of the UiO-66–NH₂@PEDOT/GAs/GCE and its use in PCMC detection. Reprinted with permission, copyright 2019, Elsevier.[93]

3.2.5.1 Polypyrrole. Polypyrrole (PPy) has gained special attention in serving as a matrix for the immobilization of enzymes when fabricating enzyme-based electrochemical CP sensors, as illustrated in Fig. 5c.[12] Besides, the synthesis of nanostructured PPy through a template method and its application as an active material to modify working electrodes in this field were also reported. Yashas *et al.*[4] developed a PPy material in the nanotube structure (PPy NT) by co-growing with methyl orange as the template. The PPy NT was then used as the matrix to immobilize Lac and perovskite micro-seeds ($SrCuO_2$) on GCEs. The composite electrode thus fabricated, PPy NT/$SrCuO_2$/Lac/GCE, exhibited enhanced electrocatalytic activity when employed for the electrochemical detection of 2,4-DCP, which produced a linear detection range of 1–50 μM and a LOD of 0.1878 μM.[4]

3.2.5.2 Poly(3,4-ethylenedioxythiophene). Just like PPy NT, nano-structured poly(3,4-ethylenedioxythiophene) (PEDOT) with increased exposure area can be obtained through *in situ* polymerization when using other nanomaterials as templates. As shown in Fig. 11b, Tian *et al.*[93] employed Zr-based MOFs (UiO-66–NH₂) as a template for *in situ* polymerization of PEDOT, which generated a core–shell nanostructure. After compositing with gas, the porous material thus fabricated is suitable for modification onto the GCE, which demonstrates a LOD of 0.2 μM for the detection of PCMCs.

Besides, PEDOT possesses excellent mechanical flexibility and solution processability, making it appropriate for coating not only on solid electrodes but also on flexible electrodes.[71] Maria *et al.*[13] reported on an *in situ* electropolymerization of EDOT on the surface of a flexible CFPE in the presence of 2,4-DCP, and the MIP based PEDOT/CFPE electrode thus obtained exhibited a specific recognition ability towards 2,4-DCP with an extremely low LOD of 0.07 nM, implying great potential for the surface modification of flexible electrodes to enable trace-level detection of CPs.

3.2.5.3 Polyaniline. Polyaniline (PANI) has been utilized to construct MIPs as well, and the charge-transport characteristics of PANI can be significantly adjusted by introducing conjugated crosslinkers between the conductive macromolecule chains. Based on this, Katowah *et al.*[77] used the cross-linked PANI (CPANI) to composite with graphene–MWCNTs to form a core–shell MIP and modified it onto a GCE. This modified electrode showed improvement in both charge-transport rate and detecting selectivity when tested for 2,4-DCP, for which the linear detection range was 0.05–0.6 μM and LOD was 7.6 nM. Moreover, the detection of 2,4-DCP could even be performed in fish farm water with a good recovery of 94.95–105.3%.

However, the working electrode modified with MIPs employing PEDOT or PANI still has some technical limitations concerning selectivity towards different CPs, mainly because CPs are small molecules and have limited numbers of functional groups for specific recognition.[135] Further investigation could pay more attention to the enhancement of imprint site numbers or creating imprint sites more accurately regarding molecular geometry match, for example, using core–shell structure MIPs to create an intrinsic nanostructure and porous dispersion (rather than a simple compact layer).[136,137]

3.2.6 Clays. Clays belong to the class of phyllosilicate-layered hydrous aluminosilicates.[136] Montmorillonite is one of the most often used clays, which is abundant in nature and easy to modify with a surfactant to efficiently enhance the affinity towards CPs.[41,65,67] As shown in Fig. 12, the large cationic exchange capacity of montmorillonite makes it easy to modify with CTAB.[65] The CTAB-modified montmorillonite calcium (CTAB–MMT) thus formed was used in the construction of the CPE, which showed a high detection efficiency towards 4-CP, with a linear detection range and a LOD of 0.05–10 μM and 0.02 μM, respectively.[65] Fernández *et al.*[41] found that hydrotalcite-like clay (HT clay) can be modified with surfactant sodium dodecylbenzene sulfonate (SDBS), and composited with HRP. The HRP/SDBS–HT clay/GCE was found to be capable of enhancing both the sensitivity and stability for the detection of 2-CP, showing improved stability compared to other enzyme-based electrochemical sensors. The sensor response retained 95–98% of the original value after 2 weeks of storage. Furthermore, Marinović *et al.*[67] synthesized organic–inorganic hybrid composites based on a type of montmorillonite-rich clay and poly(vinyl alcohol) (PVA), and used the polymer/clay composite to modify the GCE for 4-CP detection. The modified electrode demonstrated a wide linear detection range of 1–2000 μM, and was successfully used in the analysis of real water samples with good recovery.
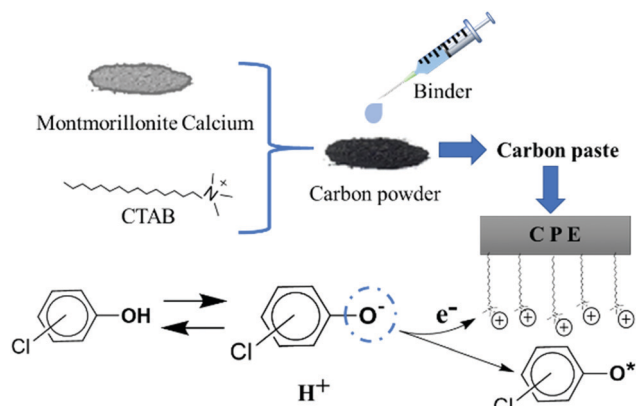
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Fig. 12 Illustration of the construction of a CTAB−MMT/CPE and its use for the electrochemical detection of CPs.

Since the modification process of clays is not technologically demanding and the synthesis of clay-based composite materials with designed properties is feasible, such low-cost and green materials provide enormous potential for development as electrochemical sensors for CP monitoring. Besides montmorillonite, other clay minerals such as vermiculite, kaolinite, sepiolite, *etc.* remain for further exploitation in this field.[138]

4. Conclusions and prospects

This review presents an overview of the tunable construction of electrochemical sensor systems for the detection of CPs, with a special focus on diverse working electrodes and their modification with various active materials. A wide range of modification strategies, such as adjusting composite architecture, increasing more active sites, strengthening intrinsic electrocatalytic activity, as well as tuning the properties and structures of active materials to match those of certain substrate electrodes, have been given critical attention. Challenges and possible solutions related to the sluggishness in kinetics, high oxidative potential, fouling effect, poor sensing performances, and other aspects towards CP detection have also been discussed on the basis of different kinds of electrodes.

Generally speaking, although recently reported working electrode materials are abundant and complex, to achieve highly effective electrochemical sensors for CPs and to promote their future development, there are several aspects that should be significantly considered. (1) Having effective adsorption and electrochemical reactivity towards CPs. For example, the utilization of π–π interactions or electrostatic binding between active materials and CP molecules can improve the enrichment and mass transport of CPs. And, carbonic, metallic and ICP materials that exhibit conductive and electrocatalytic activity, and enzymes that have excellent biocatalytic activity, are still the main choice as active probes to CPs. (2) Increasing the specific surface area or porosity. If the modified electrode surface, where the sensing reaction occurs, can provide more active sites and great permeability, it generally means an increased electrochemical signal and rapid response. In addition to the porous active materials mentioned above, other emerging materials like covalent organic frameworks (COFs) and porous organic polymers (POPs) may bring promising results in the sensing sensitivity and selectivity in the future, especially considering their great structural and chemical tunability through both molecular synthesis and nanoscale engineering. (3) Possessing nanostructured morphology. Nanostructured materials not only have a larger specific surface area and abundant active sites, but also take advantage of electrocatalytic effects which could facilitate the essential electron and proton conduction in electrochemical CP sensing systems. (4) Constructing a composite material system. The composition of different materials can overcome some weaknesses of single material systems, like certain sensor performance, limited selectivity, agglomeration of nanostructured materials, *etc.* In addition to the tunable constructing strategy, the composite systems can bring good electrochemical activity and thus synergistic enhancement of sensor performances.

It is worth noting that the practical and commercial use of these electrochemical CP sensors is still in its infancy. Recent studies focus on the exploitation of novel active materials and relative working electrodes, mostly highlighting the optimization of the linear detection range to obtain a lower LOD. Other performance criteria, particularly selectivity, still face a severe challenge to meet practical requirements, especially for complex or real environmental analyte samples. Moreover, the reproducibility and reversibility of most reported sensors are not satisfactory and lack enough investigation in view of widely used composite material architectures and special construction techniques. At the same time, there is a lack of unified and effective evaluation, which makes the horizontal comparison between different sensors difficult. This greatly limits the large-scale production and practical application of electrochemical electrodes for detecting environmental analytes including but not limited to CPs. Thus, in the future, a comprehensive and unified evaluation standard and system for the performances of electrochemical CP sensors should be established. On the basis of these comparative evaluation systems, the sensor materials and architectures can be further selected and modified. Others, in line with the fabrication convenience and lost cost, and the stability and durability of these sensors during their working process and storage, should also be taken into account.

Nevertheless, for long time, no matter in research or commercial exploitation, electrochemical sensors for chlorophenol detection will still rely on current working electrode systems (especially metallic materials, carbon nanomaterials or ICP modified GCEs) due to their comprehensive performance advantages. In line with the development of molecular imprinting, screen printing, microfluidics, and other relevant nanofabrication techniques, these electrochemical CP sensors can potentially be constructed into an electrode array and then incorporated with a smart device for quicker and more reliable analysis, which may be the most critical strategy to solve the current problems on detection selectivity, and may ideally distinguish different CP molecules.

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Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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