Nanostructure-Modified Electrodes tor Contaminants of Environmental Concern Detection

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The contaminants of environmental concern (CECs) are found in substances people all use in the daily lives such as pharmaceuticals, pesticides, flame retardants, personal care products, and so on. These contaminants pose a threat to human and environmental well being, hence the need for effective methods for the fast and sensitive detection of these contaminants in the ecosystems. The detection of these CECs can be achieved using electrodes modified with novel nanostructures that serve to increase the sensitivity and lower the detection limits.

contaminants of emerging concerns amperometry voltammetry nanostructure electrode sensor

1. Introduction

Electrode surface modification features a conductive substrate that has been modified with monolayers, electroactive thin films, nanomaterials, nanostructures, or thick coatings. Surface modifications can occur by processes such as electro-polymerization, self-assembly, ionic bonding, electrodeposition, drop-casting, or ionic hydride formation. Surface modifications are important for their effect on electrochemical interactions with the analyte during redox reactions. Furthermore, minor adjustments to the surface characteristics can determine the sensitivity of the measurements in electroanalytical applications. An attractive opportunity for the trace level identification of physiologically significant and environmentally harmful compounds with improved sensitivity and selectivity has been made possible by the modification of electrodes for use as sensors [1]. Electrode surface modification is a widely used method for enhancing the selectivity and sensitivity of electroanalytical detection by voltammetry. Electrodes are typically evaluated based on their limit of detection, which reflects their sensitivity and their ability to selectively identify the target in complex media [2]. The linear range of the response is also an essential feature.

2. Application to Detection of Bisphenol and Related Compounds

The organic molecule bisphenol A, also known as 2,2-bis (4-hydroxyphenyl) propane or BPA, is neither biodegradable nor chemically degradable, making BPA concentrations in the environment typically high. Numerous studies have demonstrated that BPA can mimic hormonal actions and interfere with such activities by interfering with growth, development, and reproduction; as a result, BPA has been classified as a significant endocrine disruptive compound (EDC) [3]. It is commonly utilized in water pipes, epoxy coatings on metal cans, food packaging materials, bottle caps, and plastics and resins. Food contamination with BPA has reportedly been found, depending on the food's kind and storage circumstances. As a result, the necessity of detecting various pollutants in food and environmental applications is rising steadily [4].

Extensive data suggest that 1–10 g mL^{-1} of BPA is acutely harmful to freshwater and marine species of aquatic creatures and causes feminization of fishes, reptiles, and birds throughout their gonadal ontogeny [5]. Exposure to high levels of BPA in humans has been linked to a variety of health problems, including but not limited to diabetes, heart disease, breast and prostate cancer, infertility, and liver damage. BPA is also dangerous to aquatic ecosystems since it disrupts the development of many aquatic organisms. Because of its impact on human health, BPA has been restricted by governments all over the world. The use of BPA in polycarbonate baby bottles has been outlawed in a number of nations [6].

An early study of electrode development for bisphenol A detection made use of mesoporous silica MCM-41 mixed with graphite powder and paraffin oil made into a paste electrode [7]. Compared with related paste electrodes of MWCNT, activated carbon, silica gel, and graphite, the electrode including MCM-41 gave the superior response for a DPV sweep in which bisphenol A was oxidized, presumably due to adsorption of bisphenol A into MCM-41 pores. An accumulation time of 3 min was used, and the optimal response was found at pH 8.0 and 20 wt.% of MCM-41 in the formulation of the paste electrode. The linear range was found to be 0.22–8.8 μM and the detection limit was 0.038 μM. Recovery from samples spiked into various local waters ranged from 91.3–107.3%.

MWCNT has proved useful for the construction of electrochemical sensors for bisphenol A [8]. A composite electrode on GCE was developed using MWCNT treated with nitric acid to introduce carboxylate groups. The treated MWCNT and Au NP were drop-cast on GCE in varying amounts for an optimization study. The DPV oxidation current on the optimally modified GCE was almost four times that seen on bare GCE. A linear range from 0.01–0.7 μM was reported with a detection limit of 4.3 nM. Reproducibility over five prepared electrodes was 1.1% and over five repeated measurements was 1.5%. Recovery of sample spiked into river water and mineral water was 95.2–102.4%.

Electrochemical sensors based on carbon nanomaterials, such as nanodiamond (boron-doped diamond) and nanocarbon, were designed by Jiang et al. to address the difficulties of monitoring trace amounts of BPA. They offered three methods: direct detection of BPA using boron-doped diamond on GCE electrodes, using disposable nanocarbon on GCE electrodes, and indirect detection of BPA using redox reaction of the by-product quinone on nanocarbon electrodes. The linear range for detection on nanodiamond/GCE was 0.1–50 mM and the detection limit was 5 nM as compared to a linear range from 0–30 mM and a detection limit of 0.5 mM on nanocarbon/GCE. A number of BPA sensors have been published in the literature, however the performance of these three approaches is superior. Recent medical advice has defined daily dose limitations for BPA, and the carbon-based sensors reported here can detect levels below them. These three sensors' key characteristic is the avoidance of surface fouling, the main issue for electrochemical BPA sensors, in addition to a lower detection limit and large detection range [9].

Niu et al. developed a practical electrochemical sensor for bisphenol A detection using stacked graphene nanofibers (SGNF) and gold nanoparticles (AuNPs) composite modified GCE. The AuNPs/SGNF modified electrode electrocatalyzed BPA oxidation, decreasing BPA oxidation overpotentials and increasing peak current compared to bare GCE and other modified electrodes. The transfer electron number (n) and charge transfer coefficient (α) for BPA were n = 4 and 0.52, indicating a four-electron and four-proton process for electrochemical oxidation on AuNPs/SGNF modified electrode. The effective surface area for the AuNPs/SGNF on GCE was 1.7-fold larger than bare GCE. The improved electrode's kinetic characteristics showed an apparent heterogeneous electron transfer rate constant (k_s) of 0.51 s^{-1}. Linear sweep voltammetry (LSV) was used to determine BPA and the linear range was found to be 0.08 to 250 nM with a detection limit of 35 nM. The modified electrode was used to detect BPA in baby bottles with good high sensitivity, long-term stability, and reproducibility [10].

To selectively detect BPA, Sanko et al. created a $Mo_2Ti_2AlC_3$ and MWCNT composite. The synthesis and comprehensive characterization of transition metal carbide was performed using SEM and TEM. Based on the MAX phase material, the electrochemical sensor $Mo_2Ti_2AlC_3$ exhibited improved electrical conductivity and electrocatalytic properties, enabling more selective and sensitive detection of BPA. Because it served as a suitable channel for electron transfer, the composite with MWCNT also had enhanced sensor qualities. The linear range of BPA concentrations observed was 0.01 to 8.5 µM, with a limit of detection and a limit of quantitation (LOQ, 10 S/N) of 2.7 and 8.91 nM, respectively. In milk in plastic bottle and can samples, quantitative recoveries of 95.67–100.60% revealed sensitive detection of BPA at extremely low concentrations and with high selectivity with respect to other possible matrix chemicals [11]. Recently, copper ferrite nanoparticles have been combined with MWCNT to make a composite electrode by drop-casting a dispersion of these two components onto GCE [12]. The $CuFe_2O_4$ nanoparticles in the composite were 47 nm in diameter on the 30 nm diameter MWCNT. A detection limit from DPV of 3.2 nM was found with a linear range from 0.01–120 µM.

In order to achieve sensitive and selective measurement of BPA, Zhang et al. created a novel dual-signal sensor by connecting nanoporous gold leaf (NPGL) with thiolated beta-cyclodextrin (SH-β-CD) [13]. Electrochemical measurements, scanning electron microscopy, and energy-dispersive spectroscopy (EDS) were all used to follow the course of NPGL modification and self-assembly of SH-β-CD on gold electrode. In the dual signaling approach, signals from the target molecule BPA and the probe molecule methylene blue were simultaneously recorded in order to model the competitive host–guest interaction (MB). Since the host molecule (β-CD) binds to BPA differently than it binds to MB, the former can enter the latter's cavities, lowering the latter's oxidation peak current while increasing its own. A linear relationship was found between the total change in current and the logarithm of BPA concentration between 3×10^{-7} and 1×10^{-4} M, with a detection limit of 6×10^{-8} M. In contrast to employing just DIBPA as the response signal, the detection limit reached by dual-signaling was significantly lower. The sensor was also used to evaluate BPA in milk and municipal water supplies.

The best possible substitute for bisphenol A, bisphenol S, has been shown to be hazardous to humans. Unfortunately, no quick detection method has been developed to serve the on-site measurement of bisphenol S. In order to address this gap, Zhu et al. developed a novel electrochemical platform based on the co-reduction of graphene oxide and C_{60} nanoassembly cast onto GCE. The innovative electroanalytical platform enabled sensitive determination of bisphenol S by DPV in the range of 1–100 μM with a detection limit of 0.5 μM. The nanoassembly was generated by grinding. High electrocatalytic activity towards bisphenol S was found. This sensor was also used to identify bisphenol S in milk, with promising results for its anti-interference capacity and respectable recovery [14].

A peptide specific for binding to bisphenol A was developed as a recombinant LacI protein with the heptapeptide specific to bisphenol A (CKSLENSYC) inserted at the C-terminus end. Layer by layer assembly of the recombinant protein and reduced graphene oxide nanosheets onto quartz substrate. Denaturation of the recombinant protein yielded hydrophobic interactions necessary to immobilize the peptide sequence. The rGO thin film was 2 bilayers of rGO and 4 nm thick. EIS was used as the detection method and the increase in R_{ct} was linear from 10^{-13} M to 10^{-8} M BPA with a detection limit of 5.0 fM [15].

The polysaccharide chitosan has also proved useful as a component for the construction of nanocomposite electrodes that included also carbon nanotubes [16]. Chitosan cross-linked by glutaraldehyde was combined with carbon nanotubes and TiO_2 nanoparticles in mineral oil to make a paste for the formation of an electrode referred to as a carbon nanotube paste electrode. It was found that 10% TiO_2 nanoparticles were optimal. The linear range in DPV for the oxidation of bisphenol A was from 0.01–6.0 μM and the detection limit was 9.58 nM.

The orientation of single-walled carbon nanotubes (SWCNT) on an electrode surface was found to have a dramatic effect on the limit of detection for bisphenol A [17]. SWCNT wrapped by a special ssDNA with a terminal thiol are found to orient vertically relative to a gold electrode surface. Remarkably, the DPV detection limits for detection of oxidation of bisphenol A were 102.3, 45.8, and 11.0 nM for bare Au, Au covered by dispersed non-oriented SWCNT, and the vertically oriented SWCNT, respectively. The linear range for detection using the oriented SWCNTs was 0.5–3.8 μM. The sensitivity reported was 0.49 $\mu A\ \mu M^{-1}$ for oriented SWCNT on Au electrode and 0.24 $\mu A\ \mu M^{-1}$ for dispersed SWCNT on Au electrode. In another study, the effect of type of carbon nanotube on detection of bisphenol A was evaluated [18]. MWCNT of diameter 110–170 nm and those of diameter 20–40 nm was compared. The effect of acid treatment with HNO_3/H_2SO_4 (3:1 by volume) was also evaluated. The limit of detection and sensitivity was the best for the smaller diameter MWCNT that were acid-treated, 0.084 μM vs. 0.61 μM for the acid-treated larger diameter MWCNT. A GCE electrode modified with acid-treated MWCNT was reported to be able to electrochemically distinguish bisphenol AF from bisphenol F [19].

Mo et al. developed an electrochemical sensor for bisphenol A using AuPd incorporated onto polymer-wrapped carboxylic multi-walled carbon nanotube [20]. Poly (diallyldimethylammonium chloride) was first allowed to assemble around MWCNT in solution followed by citrate reduction of $HAuCl_4$ and $PdCl_2$ to create AuPd nanoparticles that could assemble onto the polymer-wrapped MWCNTs. Bisphenol A was found to be best accumulated on the electrode for a time of 50 s at –0.2 V (vs. SCE). DPV was used to detect bisphenol A using the oxidation peak near 0.5 V (vs. SCE). The linear range was 0.18–18.0 μM and the limit of detection was 60 nM. Bisphenol A detection was possible when spiked in either milk or in tap water with excellent recovery.

3. Application to Detection of Estrogen-like CECs in the Environment

An ever-increasing number of people these days are eager to find ways to stop the hands of time and restore their youth. Estrogens added to cosmetics have the potential to lighten skin, improve skin suppleness, get rid of wrinkles, and slow the aging process. Use of these drugs for an extended period of time, however, has been linked to an array of health problems, including endocrine disruption and several forms of cancer (including endometrial carcinoma, cell carcinoma, breast, and ovarian cancer). The three essential steroid estrogens, estradiol, estrone, and estriol, are significant bioactive compounds that play a role in intracellular communications and affect the emergence and upkeep of sex characteristics [21].

When introduced into an organism, phenolic estrogens disrupt the endocrine system, leading to aberrant reproductive or immunological functioning, hermaphroditism, sexual instability, reproductive organ impairment, and so on. Hexestrol (HEX), diethylstilbestrol (DES), dienestrol (DE), and bisphenol A (BPA) are the most widely used phenolic estrogens (BPA) [22]. Estriol was used for the treatment and prevention of hormonal imbalance-related problems, including cardiovascular disease, cancer, hyperandrogenism, osteoporosis, and urogenital diseases in females. Because it is eliminated in the urine and is not destroyed during sewage treatment, it is also considered an endocrine disruptor that is harmful to human and animal health [23].

An electrochemical immunoassay using DPV was developed for HEX, DES, DE, and BPA by Pan et al. Au nanoparticles (20–80 nm by SEM) were formed by electrodeposition on GCE and then modified by aminoethanethiol to which HEX was conjugated using EDC/NHS coupling. The introduction of monocolonal antibodies and phenolic estrogen results in a change in the DPV peak current near 0.2 V (vs. Ag/AgCl) for the redox probe $Fe(CN)_6^{3-/4-}$. Detection limits of 0.25, 0.25, 0.15, and 0.20 ng mL^{-1} were found for HEX, DES, DE, and BPA, respectively and the linear range of response vs. log(concentration) extended up to 200, 2000, 500, and 500 ng mL^{-1}, respectively. Recovery was excellent from samples spiked into supernatant extracts from beef, pork, and milk powder samples [24].

Raymundo-Pereira et al. detailed the electrochemical detection of estriol employing carbon black nanoballs (CNB) decorated with silver nanoparticles (AgNP) formed by the reduction of $AgNO_3$ from solution and drop-cast onto GCE [25]. Uniform, porous films were produced with CNB with widths of 20–25 nm and AgNPs of 5–6 nm in width. Cyclic voltammetry and electrochemical impedance spectroscopy showed that CNB/AgNP electrodes were more effective than bare GCE and GCE/CNB in terms of electron transfer and electroactive area. Estriol was detected using DPV in 0.1 M PBS (pH 7.0) with a linear range of 0.2 to 3.0 μM and a limit of detection of 0.16 μM. In a stream water sample, the sensor detected estriol with the same sensitivity as the gold standard approach based on HPLC.

An electrochemical sensor for the simultaneous detection of diethylstilbestrol (DES) and 17-β-estradiol (E2) in skin care toner was developed by Chen et al. using Fe_3O_4-doped nanoporous carbon (Fe_3O_4-NC), which was manufactured by carbonizing Fe porous coordination polymer (Fe-PCP), also known as metal–organic framework (MOF). Since estrogens frequently interact in natural samples, the ability to precisely quantify them is of paramount practical importance [26]. By using electro-catalytic oxidation at a Fe_3O_4-NC modified GCE (Fe_3O_4-NC/GCE), the levels of two common estrogens, DES and E2, were simultaneously determined. The detection limits for DES and E2 were 4.6 and 4.9 nM, respectively, and the DPV peak currents rose linearly as the concentrations increased from 0.01 to 12 μM and from 0.01 to 20 μM, respectively.

Graphene nanoribbons (GNR) are a material prepared by ‘unzipping’ MWCNT under oxidizing conditions. A nanocomposite electrode was prepared by combining GNR with fumed silica that was decorated by Au nanoparticles modified by cysteamine and then drop-casting it over a carbon paste electrode (CPE) [27]. The fumed silica served to enhance surface area, Au NP, and GNR to increase conductivity and cysteamine to promote hydrogen-bonding. Raman spectroscopy was used to confirm the vibrational features of GNR. Using DPV, the sensor, when applied to detecting 17-β-estradiol, gave a linear range of 0.1–5.0 μM and a detection limit of 7.4 nM. The detection of 17-β-estradiol spiked into milk was successful.

17-β-Estradiol was also successfully detected using GCE modified by MWCNT that had been acid treated to produce polar and hydrophilic functional groups on the nanotube surfaces. The modified MWCNT were drop-cast onto GCE followed by drop-casting of Au NP of 20–30 nm diameter, the same as the average diameter of the nanotubes. Using linear sweep voltammetry, the optimal response was found at pH 7.0. A linear range from 1.0–20.0 μM was found with a detection limit of 70 nM. The sensor retained 79% of its initial response after 5 days. Recovery from samples spiked into wastewater, treated water, or tap water ranged from 94.7–98.5% [28].

Aptamers have also been employed as highly specific binding agents for 17-β-estradiol as part of a nanostructured electrode. Boron-doped diamond thin films were first formed by chemical vapor deposition onto p-Si(100) which was then treated with aqua regia to yield an –OH terminated surface. Using the hydrogen bubble template method, Zn nanoparticles were formed on the surface. The Zn nanoparticles served as templates for the electrodeposition of Au nanostructures in the form of tree-like dendrites. The gold surfaces were then modified at ssDNA 76-mer aptamer that was thiolated on one terminal end. The increase in charge transfer resistance upon binding of 17-β-estradiol to the aptamer was linear vs log([17-β-estradiol]) over the range 10^{-14}–10^{-9} M. A remarkably low detection limit of 5×10^{-15} (5.0 fM) was found [29].

Javaid et al. described the electrochemical detection of methylparaben using a GCE modified with zinc oxide nanoparticles [30]. The chemicals in parabens have both estrogenic and antiandrogenic properties. As was already established, these molecules have been linked to male infertility and cancers, including breast tumors. As a result, parabens are being considered as a possible health danger. The usage of medicinal items and cosmetics are the main ways that people are exposed to parabens. The ZnO nanoparticles were prepared using a sol–gel method and then mixed with carbon black and Nafion to prepare a paste that was drop-cast onto GCE. The ZnO nanoparticles were prepared as nanospheres (at pH 12), nanocuboids (at pH 10), and nanowires (at pH 8). ZnO nanowires performed best with a linear range from 0.02–12 mM and a detection limit of 7.25 μM.

The use of screen-printed electrodes for developing sensors for estrogens has been reviewed recently [31] and progress in the development biosensors, including those based on optical and spectroscopic approaches, has also recently been reviewed [32]. Molecular imprinting combined with nanoparticle layers has been another avenue for development. Other strategies reported for electrode modification have included GCE modified with Pt nanoparticles and then by a molecularly imprinted polymer layer [33]. PtNP were first formed on the GCE by electrodeposition and then the layer of PtNP surface modified by the monomer 6-mercaptonicotinic acid which also served as the monomer for electropolymerization. The electropolymerization took place in the presence of the 17β-estradiol, which was subsequently washed out, leaving behind a molecularly imprinted surface. Ten cycles of electropolymerization gave a layer with a thickness that gave the optimal response. A ratio of monomer:E2 of 24:1 was found to produce a surface of optimal response. An incubation time of 4 min was found to be optimal. A linear range in DPV response was found for oxidation of E2 just below 0.7 V (vs. SCE) over a range of 0.03–50.0 μM with a detection limit of 0.016 μM. GCE modified by electrodeposited Au nanoparticles and then covered by a molecularly imprinted polymer layer was used to develop and electrode for estradiol detection [34]. In a similar strategy, 4-aminothiophenol was self-assembled onto the layer of AuNPs and then used as the monomer for electropolymerization in the presence of estradiol that was subsequently washed out. An incubation time of 8 min was found to be optimal with a range from 1–15 min tested for maximum current in chronoamperometric detection (−0.3 V vs. Ag/AgCl, 200 s). The imprinted sensor was characterized using CV and EIS and the $Fe(CN)_6^{3-/4-}$. The linear range was reported as 1.0×10^{-12} mg mL^{-1} to 1.0×10^{-8} mg mL^{-1} with a detection limit of 1.28×10^{-12} mg mL^{-1}. Milk samples spiked with E2 showed recoveries from 84.7–102.9%.

Oral contraceptives also constitute a problem for environmental contamination and cause endocrine-disrupting effects. 17-α-ethynylestradiol (EE2) is used in contraceptives and hormone replacement and is a potentially significant environmental contaminant [35]. Magnetic nanoparticles of Fe_3O_4 (10–15 nm) modified by molecularly imprinted siloxane polymer (mag@MIP) were used to capture EE2 from solution and then these particles were magnetically bound to an SPCE modified by graphene that had been treated with strong acid (functionalized graphene) and by graphene quantum dots to enhance electrical conductivity. The surface area of the magnetic nanoparticles was enhanced by about 50% due to the imprinting step. An analyte adsorption time onto dispersed mag@MIP of 3.0 min was found to be optimal. The amount of dispersed mag@MIP was also optimized. SWV showed an oxidation peak for EE2 near 0.26 V (vs. Ag/AgCl) and a limit of detection of 2.6 nM was found with a linear range from 10 nM to 2.5 μM. Recovery of samples from EE2 spiked into urine, serum, and river water was found to be excellent.

4. Application to Detection of Pharmaceutical CECs

Antibiotics are essential to human health as antiseptic and anti-inflammatory medications. However, a growing number of issues have come to light as a result of prolonged antibiotic use. Clinically, drug overdose can result in a variety of negative side effects, including nausea, vomiting, abdominal pain, and lack of appetite. The quantity of antibiotics is especially crucial. The liver or kidneys are typically where many antibiotics are processed, which may cause organ damage [36]. Unneeded or outdated products from the pharmaceutical industry and clinics were presumably being immediately dumped to ecosystems and water bodies. Due to their poor solubility over time, the metabolites of micropollutants pose a serious health danger to both aquatic life and people [37].

The antibiotic tinidazole, which is 1-(2-ethyl sulfonyl ethyl)-2-methyl-5-nitro-imidazole, can be an environmental contaminant and be cytotoxic, carcinogenic, and mutagenic in humans. An electrochemical sensor for tinidazole was developed using an Ag-Co_3O_4 nanomaterial as an electrocatalyst to modify a GCE [38]. Under SEM, the prepared nanomaterial showed ‘carrom coin’ disc-like structures of Co_3O_4 decorated by silver nanoparticles. EIS confirmed a much lower charge transfer resistance on the modified GCE. An irreversible reduction reaction was used to detect tinidazole using amperometry and the modified GCE as a rotating disc electrode in pH 7.0 N_2 saturated phosphate buffer. Two linear segments in the cathodic current density vs. concentration were observed with linearity up to 388 μM and detection limit of 0.035 μM. The sensor was selective against a range of likely interferent species and recovery was excellent for tinidazole spiked into a range of aqueous media, including drinking water, sewage water, lake water, and tap water.

The antibiotic metronidazole (MNZ) has been used in animal feed but in humans can cause seizures, ataxia, and peripheral neuropathy. An electrochemical sensor for metronidazole was assembled using molecular imprinting and the superior electrical conductivity properties of graphene quantum dots [39]. Graphene nanoplatelets were drop-cast onto GCE to improve surface conductivity. A nanocomposite of graphene quantum dots and molecularly imprinted siloxane polymer was then drop-cast. MNZ was removed by solvent wash until it was no longer detected by UV-visible spectrometry. In CVs, the peak current was 2.1× higher for the modified electrode than for MNZ on bare GCE. MNZ was found to undergo a $4H^+$, $4e^-$ reduction reaction on the electrode. An accumulation time of 80 s was found to be optimal with no further current increase at longer times. A detection limit of 0.52 nM was found with a linear range in two regions from 0.005–0.75 and 0.75–10.0 μM.

Antibiotics released into the environment can put animals at risk of cancer. The antibiotics sulfamethoxazole and trimethoprim are frequently used together in a synergistic manner. A GCE modified with a 3:1 by weight mixture of ZnO nanorods (~180–250 nm diameter and 1.4 μm in length) and graphene by drop-casting was found to perform well for simultaneous detection of these two antibiotics [40]. The ZnO nanorods possessed good electron transport properties and prevented the graphene sheets from aggregating by intercalation between the ZnO nanorods. EIS showed that the addition of graphene greatly reduced the charge transfer resistance relative to that of GCE modified only with ZnO nanorods. The detection using DPV showed two oxidation peaks for each compound, with one peak much larger than the other. Two linear ranges were observed, with the second extending to 220 μM for sulfamethoxazole and to 180 μM for trimethoprim. Detection limits of 0.4 μM for sulfamethoxazole and 0.3 μM for trimethoprim were reported. Excellent recovery was found when samples were spiked into aqueous media, including lake water. While lower limits of detection for these two antibiotics have been reported, this approach produced a wider linear range.

Sulfamethoxazole and trimethoprim are both antibiotics of concern as environmental contaminants and their residues can cause thyroid cancer. A sensor for sulfamethoxazole (SMX) and trimethoprim (TMP) was developed by first preparing Fe_3O_4 nanoparticles in the presence of a dispersion of MWCNT by precipitation by reaction of $FeCl_3$ and Fe_3O_4 with NH_4OH. The MWCNT and Fe_3O_4 nanoparticles were then drop-cast onto GCE. EIS showed that GCE/MWCNT/ Fe_3O_4 nanoparticles electrode had the best electron transfer properties with low charge transfer resistance and low phase angle in a Bode plot. CV on GCE showed well-separated irreversible anodic peaks for SMX (914 mV, vs. Ag/AgCl) and TMP (1150 mV, vs. Ag/AgCl) that were amplified by a factor of 3.5 upon modification with MWCNT/ Fe_3O_4 and were at a lower potential by a few hundred mV than seen on bare GCE. DPV was used for simultaneous determination of SMX and TMP and measured up to 0.5 μM. The detection limit for SMX was found to be 11.0 nM and that for TMP was 21.0 nM [41].

The detection of acetaminophen and estrogen in water was achieved using GCE modified by multi-walled carbon nanotubes (MWCNT) modified with β-cyclodextrin in four different ways: physical mixing, use of a click chemistry reaction, esterification using thionyl chloride, and a one-step Steglich esterification. 4-ethynylaniline was used to modify MWCNTs to present alkyne groups. The goal was to take advantage of the complexation ability of β-cyclodextrin and the excellent conductivity of MWCNTs. The MWCNT dispersions were drop-cast on GCE, followed by heating at 80 °C. Linear sweep voltammetry was applied to detection of acetaminophen over the range 0.005–20 μM and of estrogen (17β-estradiol) over the range 0.01–15 μM. The greatest slope for peak current versus concentration was found for the electrode prepared using MWCNT linked to β-cyclodextrin using the one-step Steglich esterification that makes use of the reagents dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). The slope was 1.8 $\mu A\ \mu M^{-1}$ for these electrodes versus 1.27 $\mu A\ \mu M^{-1}$ for the electrode modified by MWCNT and β-cyclodextrin physically mixed. Detection limits of 3.3 and 2.5 nM were found for acetaminophen and 17β-estradiol, respectively [42].

Non-steroidal anti-inflammatory drugs (NSAIDs) such as naproxen when released into aquatic ecosystems pose a serious threat to aquatic animals. GCE modified by a ternary nanocomposite of Au nanoparticles with carbon nanotubes surface-modified to present carboxylic acid groups and graphene oxide [43]. SEM indicated Au nanoparticles situated around the edges of the –COOH functionalized carbon nanotubes and next to graphene oxide sheets. EIS showed that the full ternary nanocomposite modified electrode showed the lowest charge transfer resistance. Chronoamperometry was applied to naproxen in 0.1 M PBS over the range of concentration of 0.1–113.6 μM at 1.1 V (vs. Ag/AgCl) and a limit of detection of 14 nM was found. The selectivity was found to be good in the presence of excess concentrations of potential interferents such as fructose, sucrose, glucose, acetaminophen, chloramphenicol, nitrite, and NaCl. Recovery from samples spiked into media including tap water, sea water, river water, and pond water was near 100%.

The detection of the antibiotic ciprofloxacin and the anti-pyretic and analgesic paracetamol was reported using a graphite electrode modified with TiO_2 sol also containing CMK-3 mesoporous silica, gold nanoparticles and Nafion. Mesoporous silica was used to enhance the surface area and gold nanoparticles and Nafion contributed excellent conductivity [44]. Using currents in CV measured at 400 mV and at 700 mV (vs. Ag/AgCl) in solution, two linear ranges of 1–10 μM and then 10–52 μM were reported for each compound. Detection limits of the 0.108 and 0.210

μM were determined for ciprofloxacin and paracetamol, respectively. Recovery was excellent for samples spiked into river water or wastewater.

Screen-printed carbon electrodes modified by carbon nanofibers were used to develop a sensor for paracetamol based on analyte adsorption followed by stripping voltammetry for detection [45]. Linear ranges from 2.0–50 nM and from 0.1–2.0 μM were observed, and a very low detection limit of 0.54 nM was reported. Theoretical modeling found that the paracetamol adsorbed parallel to the carbon surface with a binding energy of −68 kJ/mol. Selectivity against common interferents, including a range of metal ions, ibuprofen, and caffeine, was very good, and recovery from samples spiked into sea and river water was near 100%.

Antidepressants such as citalopram are also known as dangerous contaminants of aquatic environments. A nanocomposite of metal–organic framework (JUK-2 MOF), together with MWCNTs and Au nanoparticles, was used to modify GCE to create a sensor for citalopram [46]. JUK-2 is a proton-conducting MOF. The lowest charge transfer resistance was found for GCE modified with the complete nanocomposite layer. Staircase voltammetry was found to be the most suitable method of detection, and the anodic peak current for irreversible oxidation was found to display three distinct and successive linear ranges of 0.05–1.0 μM, 1.0–10 μM, and 15.0–115 μM, with sensitivities of 38.0, 15.89, and 3.32 $\mu A\ \mu M^{-1}$, respectively. The reported detection limit was 0.011 μM. The recovery for samples spiked in river, surface, and wastewater was excellent.

Chlorpromazine is an antipsychotic drug which, upon continued exposure, can lead to many disorders such as tardive dyskinesia, vision changes, neuromuscular problems, and contact dermatitis. An electrochemical sensor for this drug was developed, taking advantage of the cubic β-phase of stannous tungstate since it has high catalytic activity and was used in the form of one-dimensional nanorods prepared using a sonochemical method. TEM showed the nanorods to be 40 nm wide and 300–350 nm long, and the material was further characterized by EDS mapping, FTIR, XPS, and powder XRD. The β-$SnWO_4$ nanorods were drop-coated over the GCE [47]. The amperometric current versus concentration was increased by successive additions of chlorpromazine in pH 7.0 phosphate buffer, measured using the modified GCE as a rotating disc electrode at 1200 rpm and 0.65 V (vs. Ag/AgCl). This current was found to increase linearly from 0.01 to 457 μM chlorpromazine with a detection limit of 0.003 μM. Selectivity against a range of common interferents was excellent, and so was reproducibility among five different prepared electrodes and ten trial runs using the same electrode.

Cobalt oxide, Co_3O_4, is a p-type semiconductor with high electrochemical activity. Nanocubes of Co_3O_4 doped with La^{3+} were prepared by autoclaving a solution of the precursor salts together with polyvinylpyrrolidone (PVP). The nanocubes were about 70 nm in size and were drop-cast over a screen-printed electrode and used to make a sensor for the antidepressant drug venlafaxine. Cyclic voltammograms of venlafaxine in pH 7.0 PBS showed an irreversible oxidation near 0.70 V (vs. Ag/AgCl). The peak current increased linearly with the square root of the scan rate as expected for diffusion-controlled behavior. Using DPV, a linear range from 1.0–500 μM was found with a detection limit of 0.5 μM. Recovery of samples spiked into drinking water, wastewater, and river water was near 100%. Interference of less than 5% was reported for a wide range of potential interfering species including, based on obtained results, Mg^{2+}, Al^{3+}, NH^{4+}, F^{-}, $SO4^{2-}$, S^{2-}, caffeine, urea, ethanol, methanol, benzoic acid, fructose, saccharose, tyrosine, lactose, L-phenylalanine, L-tryptophan, L-glycine, L-histidine, L-proline, L-threonine, L-serine, L-asparagine, uric acid, acetaminophen, NADH, dopamine, ascorbic acid, epinephrine, norepinephrine, glucose, and L-lysine [48].

5. Application to Detection of CECs of Agricultural Use

Horticulturists and farmers commonly employ insecticides to keep unwanted critters at bay. Pesticides have many practical applications in agriculture, but they are not without their downsides. The massive use of pesticides and the lack of expertise in their application have contaminated land and water. Dosage limits and monitoring at the trace level are essential for lessening pesticides' negative effects. The development of new, sensitive, selective, and straightforward methods for determining the lowest feasible concentrations of pesticides is thus critically important [49]. Detection of the pesticide carbofuran was achieved using DPV and a GCE modified with a composite of reduced graphene oxide (rGO) and Au nanoparticles subsequently covered by a layer of a molecularly imprinted polymer. The rGO/Au nanoparticles were dispersed in Nafion before a small volume was drop-cast onto GCE. Methyl acrylic acid, ethylene glycol maleicrosinate acrylate as cross-linker, and AIBN as free radical initiator in toluene along with carbofuran were drop-cast over the composite and allowed to react at 353 K in a vacuum oven for 4 h, followed by washing out the carbofuran template. Upon incubation with carbofuran, the current due to the $Fe(CN)_6^{3-/4-}$ redox couple was reduced as the pesticide molecule bound into the imprinted sites and hindered electron transfer of the redox probe. The calibration curve was found to decrease from 50 nM to 20 µM, and a detection limit of 20 nM was reported. The sensor was selective against structurally-related analogs of carbofuran [50].

A sensor for organophosphorous pesticides was achieved by forming CuO nanoflowers on ITO electrodes using a hydrothermal synthesis. The distinct microns-wide flower-like morphology was composed of units of nano-beads in the 20–70 nm size range. Pimelic acid was added to act as an agent to direct the orientation of the CuO nuclei. SEM observation showed full coverage of the ITO surface by CuO nanoflowers of about 34 µm thickness. Pralidoxime chloride was immobilized over the pimelic acid on the CuO nanoflowers. The oxidation of the aldoxime group of pralidoxime to carbonyl near 0.6 V (vs. Ag/AgCl) was inhibited by interaction with the pesticide molecules. Using the decrease in the oxidation current in DPV as the sensor response, calibration plots were determined for chlorpyrifos, methyl parathion, and fenthion over the range 0.01–0.16 µM. Detection limits of 1.6, 6.7, and 2.5 nM were found for chlorpyrifos, methyl parathion, and fenthion, respectively, which was lower than others reported, except for one for fenthion using pralidoxime on graphene quantum dots-modified electrodes [51].

Sensitive detection of the pesticide malathion was achieved using GCE modified with Pd@Au core-shell nanowires then covered by the enzyme acetylcholinesterase in a chitosan film. The Pd@Au nanowires were 7 nm wide and about a micron in length and formed a network-like pattern when drop-cast on GCE. DPV was used to detect the decrease in peak current for oxidation of thiocholine produced by the action of the enzyme on acetylthiocholine substrate upon inhibition by increasing amounts of malathion. A linear range of 0.1 pM–100 nM was found with a detection limit of 0.037 pM. Recovery of malathion spiked in tap water was near 100% [52].

Acetaprimid is a broad-spectrum insecticide and is of concern as an environmental contaminant. Although acetaprimid is electrochemically inactive, a sensor could be developed using EIS. Au nanoparticles of 50 nm diameter were formed by electrodeposition onto an Au electrode surface. The aptamer specific for acetaprimid was thiol-terminated, and the formation of the Au nanoparticles on the Au electrode increased the surface loading of the aptamer ten-fold over that on the plain Au electrode [53]. 6-mercaptohexanol was used as a filler in-between immobilized aptamers. The charge transfer resistance (R_{ct}) using redox probe $Fe(CN)_6^{3-/4-}$ increased linearly with log C over the range 5–600 nM. The detection limit was found to be 1 nM. The sensor was highly selective in the presence of a variety of pesticides, and recovery for samples spiked into wastewater was close to 100%.

A sensor for the herbicide aminotriazole was developed based on TiO_2 nanoparticles and surfactant cetyltrimethylammonium bromide (CTAB) added onto a carbon paste electrode (CPE) prepared from carbon powder and paraffin oil. The TiO_2 particles were just below 100 nm in size. An irreversible anodic wave due to oxidation of aminotriazole (3-amino-1,2,4-triazole) to 3-amino-1,2,4-triazolone was seen near 0.91 V (vs. Ag/AgCl) and was about five-fold enhanced for the modified CPE than for unmodified CPE. A detection limit of 2.53 nM was reported, lower than almost all other electrochemical detection schemes previously reported for aminotriazole. The recovery of aminotriazole spiked into dam, pond, lake, and tap water, and RO (reverse osmosis) water was excellent [54].

Pralidoxime serves as an antidote for pesticide inhibition of acetylcholinesterase and is electrochemically active. The binding of non-electroactive organophosphorus pesticides (OPP) to pralidoxime prevents the irreversible oxidation of the aldoxime group, and this can be used as the basis for an electrochemical sensor [55]. The pralidoxime is a nucleophile and a nucleophilic substitution reaction with OPP occurs. An electrochemical sensor for non-electroactive OPP was constructed by drop-casting graphene quantum dots (average size 4.2 nm) in solution with chitosan onto GCE, followed by adsorption of pralidoxime which strongly was adsorbed by π-π stacking and electrostatic interactions. The addition of OPP such as fenthion progressively suppresses the current peak for the oxidation of the aldoxime. Using the approach for the detection of fenthion with DPV gave a linear dependence of change in current (μI) with log C from 10^{-11} to 5×10^{-7} M and a detection limit of 6.8 pM. Dichlone is a broad-spectrum fungicide and is also used as an algicide that is of environmental concern. The doping of ZnO nanoparticles with Ca^{2+} increases the conductivity and enhances the number of adsorption sites. Ca^{2+}-doped ZnO nanoparticles of near 200 nm diameter were prepared by co-precipitation followed by calcining and then mixed with carbon powder and paraffin oil to create a carbon paste electrode (CPE) [56]. Dichlone was added to soil samples that were then immersed in water and were added to natural water samples. In CV experiments, dichlone showed reversible redox behavior associated with 2e, $2H^+$ reaction between the quinone and dihydroxy forms. Detection on CPE using SWV resulted in a detection limit of 59.8 nM and a linear range up to near 0.3 μM.

Nanoporous gold prepared by dealloying of 12 karat Au leaf (50% Au) was fixed on the surface of a GCE and used to create a sensor for fungicide carbendazim (CBM) and pesticide methyl parathion (MP) [57]. The NPG layer was about 100 nm thick with pores of 35 nm size. DPV in pH 4.0 acetate buffer that was deoxygenated showed oxidation peaks at 0.25 V for MP and 0.95 V for CBM (vs. SCE). The linear range used was 0.5–150 μM for MP and 3–120 μM for CBM. Detection limits of 0.02 μM were found for MP and of 0.24 μM for CBM. The sensor was applied to samples spiked into wastewater and seawater and selectivity in the presence of five other pesticides was excellent, as was sample recovery.

6. Applications to Other CECs

It is imperative that efficient, fast, and reliable analytical techniques with adequate detectability to quantify a variety of synthetic pigments and dyes, which are becoming increasingly dispersed throughout the environment, be developed. This is because they have a substantial impact on the environment and can cause toxic effects. Electrochemical detection of reactive Red 195 from industrial waste samples was performed on a graphene-modified GCE utilizing bare and surface-altered GCE at pH values ranging from 1.0 to 13.0 with 4.0 found to be the optimal pH. At pH 4.0, RR 195 showed strong linear responses on both electrodes. Calibration plots were also created varying concentration of the dye, and other parameters including accumulation potential, accumulation time, initial scan potential, pulse height, pulse breadth, and potential scan increment and scan rate were optimized. The stripping voltammetric activity of the dye on a graphene-coated electrode had an extremely low detection threshold of 30 ppb. Atomic force microscopy verified the compound's adsorption on GCE and graphene-coated GCE [58].

Fire suppression foams, nonstick cookware, water-resistant clothes, and personal care items can all include per- and polyfluoroalkyl substances (PFAS), a new and persistent class of environmental micropollutant. Due to the durability of their network of carbon-fluorine linkages, PFAS have very slow biodegradation kinetics. Mammals exposed to PFAS have been proven to experience a wide range of harmful health effects, including hypertension, thyroid disturbance, immunotoxicity, reproductive toxicity, and hepatotoxicity. Additionally, it has been discovered that PFOS, PFOA, and other PFAS exhibit many of the essential traits of carcinogens, including changing oxidative stress, immunosuppression, and modification of receptor-mediated effects [59]. Approaches to detection of PFAS using electrochemical methods have so far focused on molecularly imprinted polymer layers and not yet on nanomaterials.

Sodium dodecyl sulfate (SDS) is an anionic surfactant that may be toxic to aquatic organisms, especially during fish fertilization, and also affects the health of the kidneys and spleen. To detect SDS, Faradilla et al. developed electrochemical sensing based on screen-printed carbon electrode (SPCE) modified with ZnO NPs/MIP. The ZnO NPs/MIP were manufactured on the SPCE substrate using a straightforward and efficient drop-casting process. On the developed electrode, the linear dynamic range for detection of SDS was 1–10 µM, and the limit of detection was 0.652 µM. Similar responses after 10 iterations of DPV testing confirm the designed electrode's repeatability performance. Perhaps most intriguingly, coupling the MIP with ZnO NPs increases the current response of SDS by a factor of up to four. The suggested SPCE-ZnO NPs/MIP shows promise for direct environmental monitoring of SDS due to its high percentage recovery of SDS from real samples [60].

Bansal et al. conducted research on electrochemical sensors based on ZrO_2 NPs/Au electrode sensing layer for monitoring hydrazine and catechol in real water samples [61]. Toxicity and limited degradability make them environmental dangers. Hydrazine is an EPA-listed neurotoxic and carcinogen. Pharmaceuticals, photography, fuel cells, insecticides, corrosion protection, and rocket propellant use it. CT is used to make insecticides, fragrances, and drugs. The purpose of the study is to investigate the electroanalytical uses of ZrO_2 NPs for the detection of hazardous compounds in industrial effluent stream and other sources. Using a highly effective ZrO_2/Au hybrid electrode, catechol and hydrazine were electrochemically detected using chronoamperometry. The fabricated system's limit of detection, sensitivity, and reaction time were all found to be excellent. With respect to hydrazine and catechol, the sensor showed good sensitivity, measuring 8.99 and 0.14 $\mu A\ \mu M^{-1}\ cm^{-2}$, respectively. It was discovered that the ZrO_2 NPs catalyzed the oxidation and reduction of catechol. It was found that the sensor was selective for hydrazine and catechol. The sensing platform was also shown to be an effective method for detecting catechol and hydrazine in samples spiked into water. The limits of detection for hydrazine and catechol were found to be 1.05 and 7.68 μM, respectively.

Shetti and coworkers developed a modified electrode for the detection of triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), which is used in personal care products, including lotions, soaps, and shampoos, amongst many others, and serves as a antimicrobial, antifungal, and antibacterial agent [62]. Triclosan is stable and lipophilic and toxic to aquatic life and can also cause adverse reactions in humans. A carbon paste electrode was developed using WO_3 nanorod structures (100–700 nm long and 50–100 nm wide) combined with reduced graphene oxide nanoparticles. The electrocatalytic properties of WO_3 that arise from the presence of oxygen vacancies were combined with the excellent conductivity of rGO nanoparticles. The WO_3 nanomaterials were characterized using XPS, SEM, and STEM (scanning transmission electron microscopy).

Brominated flame retardants have been the targeted analyte for a few studies to develop nanostructure modified electrodes. These compounds are used to reduce risk of fire but, when released into the environment, can have endocrine-disrupting properties, immunotoxicity, and neurotoxicity. A sensor for monobrominated 3-bromobiphenyl (3-BB) was constructed using an antibody specifically produced in inoculated rabbits [63]. An ITO electrode was modified with Au nanoclusters and then modified with polydopamine, followed by conjugation to the antigen by Michael addition reaction. A competitive electrochemical immunoassay was then performed by incubation with antigen and carbon hollow nanochains modified with horseradish peroxidase and anti-3-BB antibody. A linear response of the current due to HRP activity to 1 mM hydroquinone versus log [3-BB] was found over the range 1 pM to 2 nM with a detection limit of 0.5 pM. The nanostructured surface and the increased enzyme loading on a nanocarrier each served to increase the response. A sensor for polybrominated tetrabromobisphenol A (TBBPA) was developed using a carbon electrode first modified with aniline and then covered by graphene oxide reduced to graphene and then covered by electrodeposited nickel nanoparticles [64]. Molecular imprinting was carried out using pyrrole and TBBPA. The sensor used DPV and $Fe(CN)_6^{3-/4-}$ as a probe, achieving a reduction in current with TBBPA concentration that was linear in log[TBBPA] over the range from 0.5 nM–10 μM, and with a detection limit of 0.13 nM. Recovery from samples in tap, rain, and lakewater was excellent.

The detection of monohydroxylated polyaromatic hydrocarbons was achieved using a screen-printed carbon electrode onto which graphene oxide had been reduced resulting in a porous nanostructure [65]. The three analytes were 2-hydroxynapthalene, 3-hydroxyphenanthrene, and 1-hydroxypyrene, and all found to be electroactive and with distinct potentials such that all three could be distinguished when mixed. The compounds underwent π-π stacking interactions on the electrode surface and the effect of accumulation time up to 60 min was investigated finding saturation after 40 min. Using DPV, linear ranges for 50–800 nM, 50–1150 nM, and 100–1000 nM were found for 2-hydroxynapthalene, 3-hydroxyphenanthrene, and 1-hydroxypyrene, respectively. Detection limits of 10.1 nM, 15.3 nM, and 20.4 nM were found, respectively.

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