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Review

Research developments in carbon materials based sensors for determination of hormones

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Abstract

Various carbon-based sensors (graphene, carbon nanotubes, graphite, pencil graphite, glassy carbon, etc.) have distinctive behavior and a broad range of importance for identifying sex hormones like estriol, estradiol, estrone, progesterone, and testosterone. The current review emphasizes voltammetric, amperometric, and electrochemical impedance spectroscopic methods for detecting some of these hormones. The existence, structural aspects, nature, and biological importance of each hormone were analyzed in detail and their analysis with different electroanalytical methods was considered. Unique methodologies and innovations of electrochemical sensors for hormones based on carbon materials modified by different agents were examined. In this review, the interaction among various sensor materials and analytes in different supporting electrolyte media is premeditated. The most important significances of the electroanalytical methodologies were discussed based on sensor selectivity, sensitivity, stability, the limit of detection, repeatability, and reproducibility.

Keywords

electroanalysis; estriol; estradiol; estrone; progesterone; testosterone.

Introduction

The recent new materials based on carbon have fascinated the researchers of various fields of science and technology. Thus, different carbon-based materials have already been developed as sensing platforms for various analytes using voltammetry techniques. The choice of analytes for voltammetric analysis are based on their electroactive nature and biological significance. Hormones belong to cell-signaling molecules in multicellular organisms that transmit information between organs and tissues. They play a substantial involvement in controlling the functions and mechanisms of the living organisms and life activities like respiration, lactation, digestion, excretion, reproduction, sleep, growth development, sensory stimulation, and emotions [1-3]. Hence,

investigations of hormones are imperative. Variety of analytical methods for hormone analysis were already reported, such as bioassay [4], immunoassay [5], high-performance liquid chromatography [6], capillary electrophoresis [7], spectrophotometry [8], *etc*. All these techniques give accurate results, but they require expensive instruments with complex methodologies, what considerably restricts their application [9-12]. Electroanalytical methods, which are suitable for recognizing hormones observed in the human blood serum, urine, and plasma samples could overcome this problem. In addition, electroanalytical methods hold merits like rapid response time, easy operation, sensitivity, precision, accuracy, *etc*. [13-17]. As hormones have a significant role in human biochemistry and metabolism, assessing hormones is becoming a trending research. Rapid monitoring of hormone levels is essential as they lead to major health issues [18,19]. So, the estimation of hormones became the focus of a broad scientific investigation. Rapid testing of hormonal concentration in biological matrices is important. In this review paper, we address to some new advancements in the fabrication of electrodes for the analysis of hormones.

Carbon and its different forms occupy a special place in electroanalysis due to their unique properties like high mechanical and thermal stability, low resistance for electrons transfer, wide potential window, low price, and eco-friendliness. Carbon and its derivatives such as graphite ($3D/sp^2$), glassy carbon ($3D/sp^2$-sp^3), diamond ($3D/sp^3$), carbon nanotubes ($1D/sp^2$), graphene ($2D/sp^2$), pyrolytic graphite ($2D/sp^2$), carbon dots ($0D/sp^3$), fullerenes ($0D/sp^2$), amorphous carbon, pencil graphite, carbon black, carbon fibers, *etc*. were often used in electrochemical device assemblies. These carbon materials are abundant and low-cost but significantly improve the current/voltage characteristics in electrochemical studies because these materials possess very high surface area, low ohmic resistance, high mechanical stability, and biocompatibility [20-41]. Carbon-based electrode materials have a broad spectrum of real-time applications for detection and estimation of molecules and ions. Presently there are various reports of carbon-based electrochemical devices in investigations of vitamins [42-46], hormones [47-49], drugs [50-52], dyes [53,54], metal ions [55,56], pesticides [57,58], phenolic compounds [59,60], neurotransmitters [61-63] *etc*., and even pathogens like viruses [64] and bacteria [65]. Also, carbon-based materials have great application in the research of kinetics of electrochemical reactions and electronic states [66], supercapacitors, batteries [67], aerospace applications [68], different types of sensors [69], drug-delivery platforms, anticancer therapy, photothermal and photodynamic therapies, radiation treatment, bimolecular absorption [70] *etc*.

This review focuses on the analytical performance of electrochemical sensors based on carbon materials for estriol, estrone, estradiol, progesterone, and testosterone hormones.

Abbreviations

CV:	cyclic voltammetry
DPV:	differential pulse voltammetry
SWV:	square wave voltammetry
LSV:	linear sweep voltammetry
GCE:	glassy carbon electrode
SWAdSV:	square wave adsorptive stripping voltammetry
CPE:	carbon paste electrode
EIS:	electrochemical impedance spectroscopy
LOD:	limit of detection
LOQ:	limit of quantification
ER:	estriol

ED:	estradiol
EN:	estrone
PN:	progesterone
TN:	testosterone
GCE:	glassy carbon electrode
SPCE:	screen-printed carbon electrode
BDDE:	boron doped diamond electrode
Co-poly (Met):	cobalt-poly (methionine)
RGO-GNPs-PS:	reduced graphene oxide-gold nanoparticles-potato starch
Lac/rGO/Sb_2O_5:	reduced graphene oxide doped with Sb_2O_5 film and with immobilized laccase enzyme
CCh/WGE:	carbamylcholine modified paraffin-impregnated graphite electrode
Pt/MWCNTs:	Pt nanoclusters/multi-wall carbon nanotubes
CNB-AgNP:	carbon black nanoballs/ silver nanoparticles
Fe_3O_4NPs:	ferrimagnetic nanoparticles
RGO/AgNPs:	reduced graphene oxide/ Silver nanoparticles,
SDSMCNTPE:	sodium dodecyl sulphate modified carbon nanotube paste electrode
OXL -9MGPE:	octoxynol-9 modified graphite paste electrode,
RGO/AgNWS/AgNPs:	reduced graphene oxide (RGO)/silver nanowires/silver nanoparticles
RGO - SbNPs:	reduced graphene oxide/antimony nanoparticles
Fe_3O_4 NPs-BMI.PF6:	magnetite nanoparticles/ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate
CNTs/PVI/ ITO:	carbon nanotubes/poly (vinylimidazole)/ indium titanium oxide
VS_2/AuNPs:	vanadium disulfide nanoflowers and Au nanoparticles
RGO/CuTthP:	reduced graphene oxide and metal porphyrin complex
Cu-BDC/CPE:	1,4-benzenedicarboxylic and copper framework,
MWCNT-Nafion:	multi-walled carbon nanotubes and Nafion
FeTPyPz:	iron tetrapyridinoporphyrazine
CuPc-P6LC-Nafion/SPEF:	screen-printed sensor modified with CuPc, Printex 6L carbon and Nafion film
DHP:	dihexadecylphosphate
ErG/AuNP/ITO:	electro-reduced graphene and gold nanoparticle on indium tin oxide
BPIDS:	1-butyl-3-[3-(N-pyrrole) propyl] imidazolium tetrafluoroborate
CuO:	copper (II) oxide
MWNT - GNP/PGE:	multi-walled carbon nanotube - gold nanoparticles modified graphite electrode
ERGO:	electrochemically reduced graphene oxide
FSCPE:	fused silica modified carbon paste electrode
CTAB - Nafion:	cetyltrimethylammonium bromide/Nafion
MWNT-[bmim]PF6/GCE:	multi-walled carbon nanotubes/1-butyl-3-methylimidazolium hexafluorophosphate
GCE/$NiFe_2O_4$-MC:	$NiFe_2O_4$ metal oxide/mesoporous carbon
GOx/AuNP/CuS:	glucose oxidase/gold nanoparticles/copper sulfide nanoparticles
A-UCPPyNT:	carboxylate polypyrrole nanotubes
AuNPs/CoS:	gold nanoparticles/cobalt sulfide nanoparticles
LSGE:	laser-scribed graphene electrode
MWNT-CR:	multi-walled carbon nanotubes/Congo red functionalized
Fe_3O_4NP-BMI PF6:	Fe_3O_4 nanoparticles / ionic liquid 1-butyl-3-methylimidazolium hexafluoro-phosphate

CCh/WGE:	carbamylcholine modified paraffin-impregnated graphite electrode
MIP:	molecularly imprinted polymers
mAb:	monoclonal antibody
BiFE:	bismuth film-plated electrode,
Anti-Prog-Au_{coll}--graphite-Teflon:	antiprogesterone/gold nanoparticles-modified graphite-Teflon composite electrode
Fe_3O_4@GQDs/f-CNT:	Fe_3O_4/graphene quantum dots/ functionalized carbon nanotubes
PEDOT/ZrO_2-NPs:	poly (3, 4- ethylenedioxythiophene)/ zirconium oxide nanoparticles
BSA/Aptamer/GQDs-NiO-AuNFs/f-MWCNTs:	bovine serum albumin/ aptamer/graphene quantum dots/ functionalized multiwalled carbon nanotubes
AuNP/AMBI:	gold nanoparticles/ 5-amino-2-mercaptobenzimidazole
HRP-P4-(P4)-anti-P4--Protein-G-MBs:	peroxidase labelled progesterone/anti-human progesterone capture antibody/protein G functionalized-magnetic microbeads
HRP-P4-(P4)-cAb--Protein G-MBs:	peroxidase-labeled progesterone/ anti-human-LH-biotin capture antibody/ protein G functionalized-magnetic microbeads
GO-IMZ:	imidazole-functionalized graphene oxide
ACN:	acetonitrile
rIgG/mAb/:	anti-progesterone monoclonal antibody /rabbit anti-sheep IgG,
Mn(III)-SB:	Mn(III) Schiff base film
CoO_x:	Cobalt oxide
SWNT modified EPPGE:	single-wall carbon nanotubes modified edge plane pyrolytic graphite electrode
Anti-testosterone--nAu/MWCNTs/Teflon:	anti-testosterone-gold nanoparticles-carbon nanotubes-Teflon composite electrodes
MBs/AbTES:	protein A-functionalized magnetic beads/anti-testosterone
NCD/silicon wafer/MIP:	nano-crystalline diamond/ silicon wafer/ molecularly imprinted polymer
SA/BSA/BiNb16:	streptavidin/ bovine serum albumin/ biotinylated nanobod

Electroanalysis of estriol at carbon based sensors

Estriol or oestriol (ER) is a sort of female sex hormones (estrogens) that belong to steroids, secreted by the placenta [71]. ER is the most dominant sex hormone in females. Its release level is enriched during pregnancy periods [72,73]. Therefore, ER is essential for women's reproductive and sexual characters. Its abnormal levels in the body leads to heart disorders, osteoporosis, hyperandrogenism, cancer, and urogenital diseases [74,75]. The central issue of ER hormone is its chemical stability resisting sewage management which might lead to serious health risks to aquatic organisms [76,77]. Therefore, it is necessary to develop fast and accurate clinical and environmental diagnostic methods. There are several literature reports on the electrochemical estimation of ER at carbon-based electrodes. The probable ER oxidation reaction at carbon-based electrode [90] is drawn in Figure 1.

In this regard, Hareesha and Manjunatha [78] examined the ER by sodium dodecyl sulfate and electropolymerized xanthacridinum carbon nanotube and graphite composite paste electrode through different voltammetric methods in buffer solutions (pH 7.0). The studied concentration of ER varied from 2.0 to 200.0 µM and 10.0 to 70.0 µM with the LOD values of 0.29 and 0.19 µM, respectively. In addition, the stability of electrodes was studied by cycling 30 CV cycles with 95.5 % current retention. Reproducibility was obtained for five measurements with RSD 3.42 % and repeatability for five measurements was obtained with an RSD of 2.57 %. For analytical application, the water samples were analyzed by standard addition method with 98.0-99.0 % recovery.

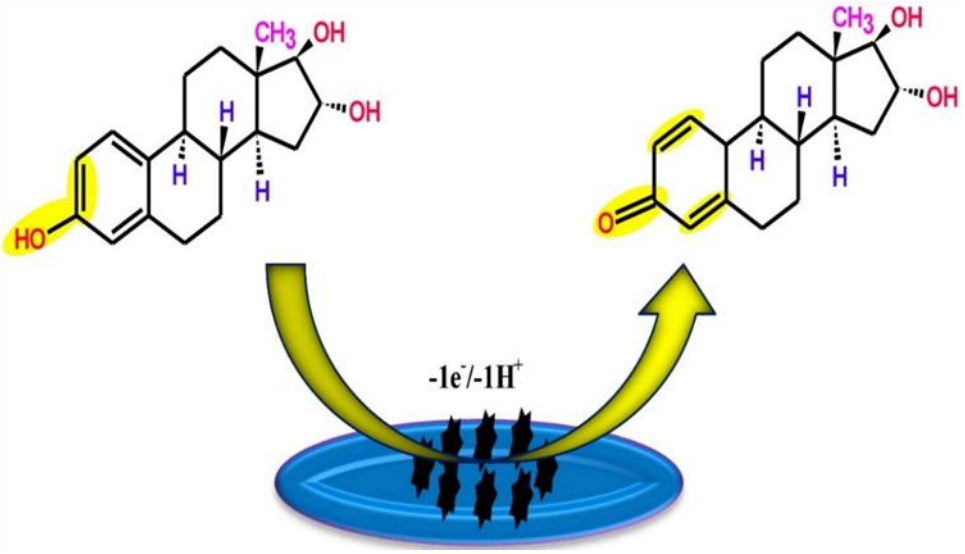

Figure 1. *Oxidation of ER at carbon incorporated electrode*

Manjunatha [79] has studied electrooxidation of ER at poly(glycine) modified CPE in phosphate buffer, pH (6.0), using DPV and CV techniques. The suitable concentration range for ER analysis was from 2.0 to 100 µM, with the LOD of 8.7×10^{-7} M and good recovery in injection samples. In addition, stability was examined after 15 days for ER sensing with 84 % current retention. Furthermore, good reproducibility towards ER detection was observed for five measurements with RSD of 4.75 %.

Charithra and Manjunatha [80] have examined ER on L-proline electropolymerized CPE using CV technique in 0.1 M phosphate buffer (pH 6.5). The linear range for ER analysis was from 6×10^{-6} - - 6×10^{-5} M with LOD of 2.2×10^{-7} M and LOQ of 7.6×10^{-7} M. Moreover, the method was stable with 92.87 % current retention even after 30 CV cycles of ER sensing, and reproducible responses for ER were observed with RSD of 4.75 %. Also, simultaneous separation of ER, folic acid, and ascorbic acid was achieved with the proposed methodology.

In addition, Ochiai *et al.* [81] effectively fabricated the SPE surface modified with carbon nanotubes as an electrochemical sensor for the amperometric estimation of ER in medicinal products. The authors defined a convenient concentration range from 1.0 to 1000 µmol L^{-1} with LOD and LOQ of 0.53 and 1.77 µmol L^{-1}, respectively. For comparison, the spectrophotometry method was also applied and the obtained results are found to be in agreement with 95 % confidence level.

The results of some other already reported works [82-97] are tabulated in Table 1. The tabulated ER sensors yield good LOD with real-time applications in pharmaceutical, biological and environmental samples. Comparatively, Xin*et al*. [85] observed the smallest LOD of 0.00693 µM in clinical and water sample applications. However, the carbon fibers, pencil graphite, activated carbon-based electrodes are still to be explored for ER sensing.

Table 1. *Analytical properties of some carbon-based sensors for ER determination using various electrochemical techniques and real samples*

Electrode	Technique	ER linear range, µM*	LOD, µM	Analytical application	Ref.
Co-poly(Met)/GCE	DPV	0.596 - 9.90	0.034	Pharmaceutical tablets and human urine	[82]
RGO-GNPs-PS/GCE	LSV	1.5-22	0.48	Water and urine samples	[83]
GCE/Lac/rGO/Sb_2O_5	Chronoamperometry	0.025 - 1.03	0.011	Human urine	[84]
N-MWCNT/GONRs	Amperometry	0.34 - 69.35	0.00693	Clinical and water samples	[85]
BDDE	SWV	0.2 - 20.0	0.17	Pharmaceutical and urine sample	[86]

Electrode	Technique	ER linear range, µM*	LOD, µM	Analytical application	Ref.
MWCNTs/Pt/GC	SWV	1.0 - 75.0	0.62	Blood serum	[87]
CNB-AgNP/GC	DPV	0.2 - 3.0	0.16	Creek water	[88]
CPE/Fe_3O_4NPs	SWV	3.0 - 110.0	2.6	Pharmaceutical sample and artificial urine	[89]
rGO/AgNPs/GCE	DPV	0.1 - 3.0	0.021	Tap water Synthetic urine	[90]
Ni-GCE	CV	5 - 100	0.1	-	[91]
OXL -9MGPE	CV	40 - 120	1.46	-	[92]
RGO/AgNWs/ AgNPs/SPCE	DPV	1 - 90	0.58	Synthetic urine	[93]
GCE/rGO - SbNPs	DPV	0.2 - 1.4	0.0005	Natural water	[94]
SDSMCNTPE	CV	6.0 - 20 and 25 - 150	0.32	ET injection	[95]
Fe_3O_4 NPs-BMI.PF6/CPE	SWV	1.0 - 10.0	0.3	Pharmaceutical samples	[96]
PVI/CNTs/ITO	DPV	2.0 - 15	0.090	Serum	[97]

*Linear concentration range of estriol detection

Electroanalytical estimation of estradiol

Estradiol/oestradiol ($C_{18}H_{24}O_2$) is a steroid and the most important female hormone. It participates in the process of oestrous and is involved in menstrual reproductive cycles. Estradiol (ED) is important for the growth of secondary women sexual characteristics such as the female-associated pattern of fat distribution, and widening of hips and the breasts. ED is also very much important in the protection of reproductive muscles such as the adulthood vagina during puberty, uterus, mammary glands, and pregnancy [98,99]. However, ED level in males is lower as compared to females. ED also originated in most crustaceans, vertebrates, fish and insects [100,101]. ED causes serious problems in premature puberty of children and also makes a risk in ovarian and breast cancer in women [102,103]. A deficiency of ED causes diseases such as heart diseases or menopausal symptoms and osteoporosis [104,105]. Due to this risk factor in humans, the determination of ED is necessary. Several literature reports are available for the detection of ED using voltammetric techniques, which are based on the possible electrooxidation reaction of ED [107] shown in Figure 2.

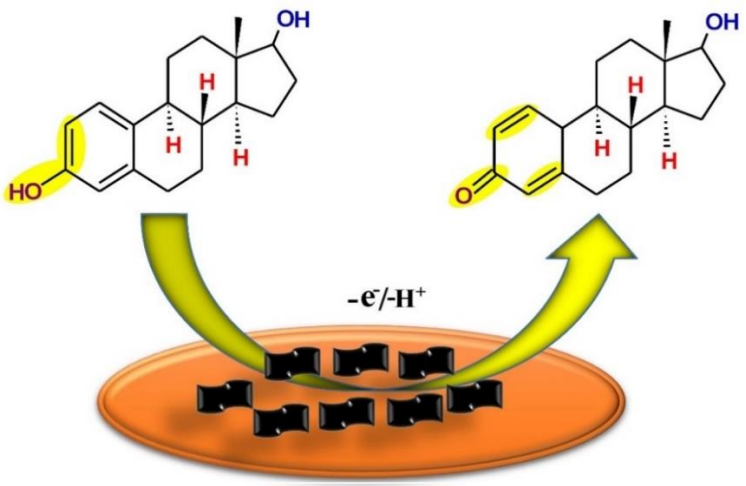

Figure 2. *Possible electrooxidation of ED at carbon-based electrode*

Chen and his research group [106] have analyzed ED by Fe_3O_4-doped nanoporous carbon (Fe_3O_4-NC), which was made through the carbonization of Fe-porous coordination polymer (Fe-PCP). Fe_3O_4-

NC was characterized with a scanning electron microscope (SEM), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. It was fabricated into an electrochemical sensor for the detection of ED in toner using Britton-Robinson buffer (pH 8.69) and concentrations range from 0.01 to 20 µM/L, with a detection limit of 4.9 nM/L were obtained. Additionally, simultaneous determination of diethylstilbestrol and ED was performed and achieved diethylstilbestrol and ED 91.2-110 % recovery in toner samples.

In addition, Masikini *et al*. [107] studied the detection of ED in environmental samples (tap water and wastewater) by electrooxidation on multi-walled carbon nanotubes (MWCNT) and gold nanoparticles (AuNP) modified glassy carbon electrode (GCE) in 0.1 M phosphate buffer solution of pH 7.0, and obtained result of a dynamic range up to 20 % $molL^{-1}$ and the value of LOD was estimated to be 7.0×10^{-8} $molL^{-1}$. Additionally, the sensor retained 79 % of its initial response even after five days after storing at 4° C, and good reproducibility was observed for ED detection with RSD of 1.7 %.

Zaid *et al.* [108] successfully analysed ED by a sensitive impedimetric aptasensor based on a screen-printed electrode /carbon nanodots/76-mer aptamer. The prepared electrode was characterized by UV-visible absorption spectra, fluorescence spectra, and transmission electron microscopy. The detection limit of 0.5×10^{-12} M in a concentration range from 1.0×10^{-7} to 1.0×10^{-12} M was achieved, using EIS. Moreover, a stable and selective sensor was applied for determination of ED in river water samples with recovery rates of 92.3 and 101.2 %.

Yuan *et al.* [109] analysed ED by electrochemical sensor based on molecularly imprinted membranes at the platinum nanoparticles-modified electrode in phosphate buffer solution pH (6.86). Under optimized conditions, DPV was applied for the determination of ED in the concentration range from 3.0×10^{-8} - 5.0×10^{-5} mol L^{-1} (R = 0.996) with the assessed LOD of 1.6×10^{-8} mol L^{-1}. Acceptable stability was observed even after ten days with 97 % of 17-estradiol response retention. Also, good reproducibility and repeatability of ED response were observed with RSD 2.9 and 2.3 %, respectively. The proposed method was utilized for ED detection in hospital wastewater with 93.9 % recovery.

Zhang *et al*. [110] determined the ED by a glassy carbon electrode (GCE) which was modified by gold nanoparticles (AuNPs) and molecular imprinted polymer (MIP) in phosphate buffer solution (PBS) (0.01 M, pH 6.97). The produced sensor was characterized by CV and EIS. The proposed sensor exhibits a linear range from 1.0×10^{-12} to 1.0×10^{-7} mg/ml, and LOD of 1.28×10^{-12} mg/ml under calibrated conditions. The stable and reproducible sensor was applied for ED detection in milk samples with a recovery of 84.7 - 102.9 %. Analytical results from some other reported works [111-134] are tabulated in Table 2. Comparatively, ErG/AuNP/ITO [121] showed a low LOD of 0.1×10^{-15} M with practical application in water and pharmaceutical samples. Finding of new modifiers with good sensitivity is still a hot topic.

Table 2. *Analytical properties of some carbon-based sensors for ED determination using various electrochemical techniques and real samples*

Electrode materials	Method	ED linear range, M*	LOD, M	Real sample	Ref.
GCE	DPV	4×10^{-5} - 1×10^{-3}	1.21×10^{-5}	Tablet and serum	[111]
Aptamer/AuNPs/VS_2/GCE	DPV	1.0×10^{-11} - 1.0×10^{-8}	1.0×10^{-12}	Human urine	[112]
RGO/CuTthP/GCE	DPV	1×10^{-7} - 1.0×10^{-6}	5.3×10^{-9}	River water sample	[113]
Cu-BDC/CPE	DPV	5.0×10^{-9} - 6.5×10^{-7}	3.8×10^{-9}	Water samples	[114]
MWCNT-Nafion/GCE	SWV	2.5×10^{-7} - 1.0×10^{-5}	1.0×10^{-8}	----	[115]
FeTPyPz/CPE	-----	4.5×10^{-5} - 4.5×10^{-4}	13.0×10^{-6}	Injection	[116]
CuPc-P6LC-Nafion/SPEF	DPV	8.0×10^{-8} - 7.3×10^{-6}	5.0×10^{-9}	Environmental and synthetic urine samples	[117]
RGO-DHP/GCE	LSV	4.0×10^{-7} - 2×10^{-5}	7.7×10^{-8}	Synthetic urine	[118]

Electrode materials	Method	ED linear range, M*	LOD, M	Real sample	Ref.
Poly(L-serine)/GCE	LSV	0.1×10^{-6} - 30×10^{-6}	20×10^{-8}	Human blood serum	[119]
Al_2O_3/GCE	LSV	4.0×10^{-7} - 4×10^{-5}	8.0×10^{-8}	---	[120]
ErG/AuNP/ITO	CV	1×10^{-3} - 0.1×10^{-12}	0.1×10^{-15}	---	[121]
CNT - Ni(cyclam)-GC	SWV	5.0×10^{-7} - 4×10^{-5}	60×10^{-9}	Human serum	[122]
BPIDS/GCE	DPV	1.0×10^{-7} - 1.0×10^{-5}	5.0×10^{-8}		[123]
CuO/CPE	SWV	60×10^{-9} - 800×10^{-9}	21×10^{-9}	Urine and buttermilk samples	[124]
MWNT - GNP/PGE	LSV	$7.0\ 10^{-8}$ - $4.2\ 10^{-5}$	1×10^{-8}	Blood serums	[125]
ERGO/GCE	SWV	1.0×10^{-15} - -2.3×10^{-10}	0.5×10^{-15}	Wastewater and pharmaceutical samples	[126]
FSCPE	DPV	$0.1\times10^{-6}$and 15.0×10^{-6}	2.3×10^{-8}	Milk and pharmaceutical samples	[127]
CTAB - Nafion/GCE	LSV	2.5×10^{-8} to 1.5×10^{-6}	1.0×10^{-9}	Blood serum	[128]
MWNT-[bmim]PF6/GCE		1.0×10^{-8} to 1.0×10^{-6} 1.0×10^{-6} - 7.5×10^{-6}	5.0×10^{-9}	Rabbit blood serum and environmental water	[129]
GCE/NiFe2O4-MC	SWV	20.0×10^{-9}-56.6×10^{-8}	6.88×10^{-9}	Tablet samples	[130]
GOx/Aptamer/AuNPs/ /GOx/AuNPs/CuS/GCE	DPV	5.0×10^{-13} to 5.0×10^{-9}	6.0×10^{-14}	Urine samples	[131]
Fe3O4@Au-GSH/MIPs/GCE	DPV	0.025×10^{-6} - 10×10^{-6}	2.76×10^{-9}	Pharmacological product	[132]
cDNA/aptamer/AuNPs/ /CoS/GCE	DPV	1.0×10^{-12} to 1.0×10^{-9}	7.0×10^{-13}	Urine samples	[133]
LSGE	DPV	1.0×10^{-13} to 1.0×10^{-9}	6.31×10^{-14}	Milk samples	[134]

*Linear concentration range of estradiol detection

Electrochemical sensing of estrone

Estrone (E1) is also known as 3-hydroxyestra-1,3,5(10)-trien-17-one/oestrone. It is a minor women's sex hormone that plays a substantial role in female sexual growth and functions. Estrone (EN) is produced from gonads, adrenal androgens, and adipose tissue. It is used in menopausal hormone therapy and prostate cancer control, and is excreted through urine and feces. EN is an endocrine-disrupting chemical that affects endocrine systems and can lead to carcinogenic effects, birth faults, and other growth issues [135-140]. So, its detection is important for human health and environmental concern. Possible electrochemical oxidation of EN at carbon electrode [144] is shown in Figure 3.

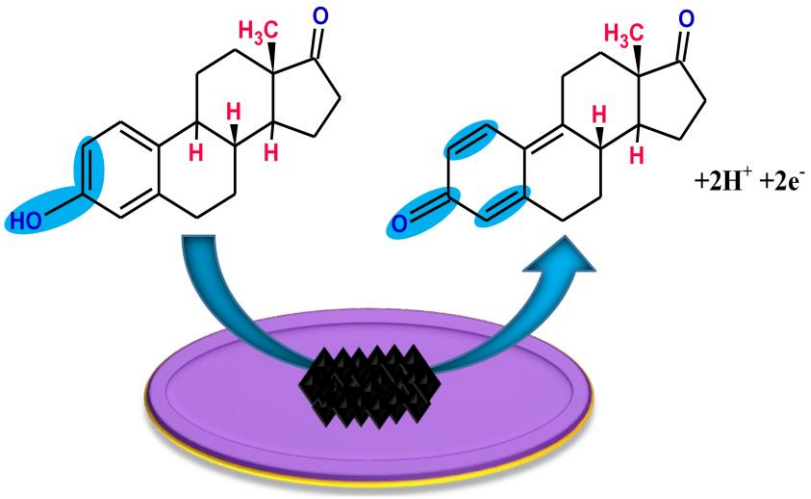

Figure 3. *Oxidation of EN at carbon incorporated electrode*

In this perspective, Okina *et al.* [141] described a sensor for EN, based on a glassy carbon electrode incorporated MWNTs, functionalized with carboxylic groups. The reported sensor detects

EN at 0.59 V as an irreversible electrode process. SWV results showed 2.5 times higher current of EN oxidation reaction as compared to bare glassy carbon electrode. The proposed electrode offers a lower LOD of 0.117 and LOQ of 0.392 µM L^{-1} with a sensitivity of 0.1521 µA/M L^{-1}. Moreover, the sensor electrode showed a good recovery (91 %) in seawater samples.

In addition, Chai *et al*. [142] described sequential ion-exchange and in-situ chemical reduction strategy synthesis of Au nanoparticles ornamented bimetallic metal-organic framework, and its sensing application towards endocrine-disrupting chemical EN. The prepared sensor material exhibits high sensing performance towords EN. The authors showed a low LOD of 12.3 nM in a linear range of concentrations from 0.05 - 5 µM with a sensitivity of 101.3 A M^{-1} cm^{-2}.

The results of some other literature reports [143-147] are listed in Table 3. It is obvious that in comparison to other sensors, MIP/CPE [147] showed significantly lower LOD of 1.18×10^{-12} M with real-time application in pregnant mare urine. The carbon materials like pencil graphite, carbon dots, carbon fibers, fullerenes, pyrolytic graphite, *etc*., are yet to be explored.

Table 3. *Analytical properties of some carbon-based sensors for EN determination using various electrochemical techniques and real samples*

Sensor	Method	EN linear range, M/l*	LOD, M/L	Real sample	Ref.
MWNT-CR/GCE	LSV	5.0×10^{-8} - 2.0×10^{-5}	5.0×10^{-9}	Tablets	[143]
CPE/Fe3O4NP-BMI.PF6	SWV	4.0×10^{-6} - 9.0×10^{-6} & 9.0×10^{-6} - 100.0×10^{-6}	4.7×10^{-7}	Pork meat	[144]
CCh/WGE	SWV	0.3×10^{-6} - 30.0×10^{-6}	0.10×10^{-6}	Blood serum	[145]
CPE in presence CTAB	--	9.0×10^{-8} - 8.0×10^{-6}	4.0×10^{-8}	Tablets	[146]
MIP/CPE	CV	4.0×10^{-12} - 6.0×10^{-9}	1.18×10^{-12}	Pregnant mare urine	[147]

*Linear concentration range of estrone detection

Electrochemical determination of progesterone at carbon-based electrodes

Progesterone (PN) is an unsaturated α,β-ketone hormone derived from cholesterol, which is shaped by 21 carbon hydrophobic steroids framed by the corpus luteum in the ovary during pregnancy [148-150]. PN hormone has a vital contribution to pregnancy maintenance, synthesis of sex hormones, cognitive development, monthly menstrual cycle, growth of breast, *etc*. The imbalance of PN can cause severe problems in the body. It forms infertility and abnormality of the reproductive system. In humans, it causes the secretion of gonadotropin-releasing hormone (GnRH), which may give rise to a decline of released testosterone and affect male behavior. Therefore, it is necessary to determine PN in mammals for clinical diagnosis [151,152]. There are several literature reports on the voltammetric determination of PN using carbon-based electrode. Possible Reduction process of PN at carbon-based electrode [157] is schematically presented in Figure 4.

In this perspective, Naderi and Jalali [153] have successfully determined PN at glassy carbon electrode modified with MWCNT, Au nanoparticles, and poly-L-serine. It was characterized by FESEM, energy dispersive X-ray spectroscopy (EDS), CV, and EIS techniques. The modified electrode showed improved current response as compared to the bare electrode by lowering overpotential. Under optimized conditions, sensor exhibits lower LOD of 0.2 nM (0.063 ng ml^{-1}) in a concentration range of 0.001 - 2.0 µM (0.31 to 636 ng ml^{-1}) using PBS buffer 0.1 M with pH (7.4). A reproducible and stable sensor was utilized for PN in pharmaceutical and blood serum samples.

Esmaeili *et al.* [154] have successfully examined determination of PN using a gadolinium(III) tungstate nanoparticles modified carbon paste electrode in 0.1 M Britton - Robinson buffer (BRB) solution at pH 11.5, using fast Fourier transformed SWV technique. Under optimized conditions, the sensor detects PN in the concentration domain of 0.1 to 1.0 µM (31.45-314.47 ng ml^{-1}) with

acceptable sensitivity of 485.64 A M^{-1} and LOD of 50 nM (15.72 ng ml^{-1}). The stable and selective sensor was used for estimation of PN in human blood plasma with a recovery of 103.7 %.

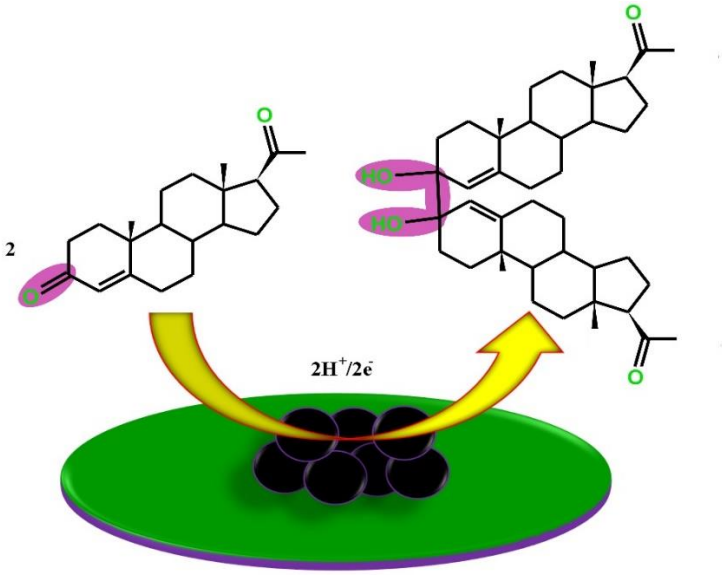

Figure 4. *Reduction of PN at carbon-based electrode*

Analytical results of some other sensors from already reported works [155-169] are tabulated in Table 4. Reported sensors provide lower LOD values with practical applicability in complicated matrices such as serum, urine, and milk samples. Comparatively, GCE/Mn(III)-SB [169] offers LOD of 0.00000314 ng ml^{-1}.

Table 4. *Analytical properties of some carbon-based sensors for PN determination using various electrochemical techniques and real samples*

Electrode	Technique	PN linear range, ng/ml*	LOD, ng/ml	Real sample	Ref.
Microfluidic immunosensor	Amperometry	0.5 - 12.5	0.2	Serum	[155]
mAb - SPCEs	Amperometry	1.56 - 15.75	0.315	Cow milk	[156]
Ex - situ BiFE	SWAdSV	125 - 2485	56.61	Pharmaceutic products	[157]
Anti - Prog - Au_{coll} - graphite - Teflon electrode	Amperometry	0 - 30	0.84	Milk	[158]
Fe3O4@GQDs/f-CNT/GCE	DPV	3.15 - 945	0.63	Serum and commercial ampoules	[159]
PEDOT/ZrO2-NPs/GCE	DPV	0.314 - 1886.8	0.102	Human blood serum & pharmaceutical products	[160]
BSA/Aptamer/GQDs - NiO-AuNFs/f-MWCNTs/SPCE	DPV	0.00314 - 314.46	0.00058		[161]
AuNP/AMBI/rGO/SPCE	SWV	0.28 to 8490.57	88.0	-	[162]
HRP-P4-(P4)-anti-P4-Protein-G-MBs/SPCE	Amperometry	0.02 - 100	0.005	Saliva	[163]
HRP-P4-(P4)-cAb-Protein G-MBs/SPCE	Amperometry	0.01 - 1000	0.0017	Saliva	[164]
GO-IMZ/GCE	SWV	69.18- 4402.52	20.13	Pharmaceutical samples	[165]
ACN /GCE	CV and SWV	1257.86-314465.41	157.23	-	[166]
rIgG/mAb/Screen - printed carbon electrodes	CV	0-5	---	Cow's milk	[167]
Sn-modified GC	DPV	1572.3 - 25156.8	35.74	Pharmaceutical commercial samples	[168]
GCE/Mn(III)-SB	CV	$3.1445\ 10^{-6}$ - $31.446\ 10^{-6}$	$3.1445\ 10^{-6}$	Milk	[169]

*Linear concentration range of progesterone detection

Electrochemical determination of testosterone

Testosterone/7β-hydroxy-4-androsten-3-one pleiotropic hormone plays a substantial role in human health. It is predominantly produced in men from testes and adrenalin glands, and has a vital role in the growth of the testes and prostate. It is also involved in the development of muscles, bones and stimulates sexual desire. Abnormal testosterone (TN) concentration in the body may lead to hypogonadism, prostate cancer, metabolic syndrome, depression, obesity, anxiety, cardio-vascular diseases, memory loss, hair loss, loss of muscle mass, *etc*. TN has also been abused for enhanced sports performance, but the World Anti-Doping Agency (WADA) prohibited its use. So, it is important to have a fast and accurate analytical method for TN detection [170-178]. Possible mechanism of electroreduction reaction of TN [179] at carbon electrode is shown in Figure 5.

In this regard, Levent *et al.* [179] reported a bismuth-film coated glassy carbon electrode for the determination of TN in Britton-Robinson buffer, pH 5.0, containing 3 mmol L^{-1}cetyltrimethyl-ammonium bromide. TN showed an irreversible, adsorption-controlled reduction peak at the electrode. The authors obtained LOD of 0.3 nM. The electrode responses were reproduced and repeated with RSD not exceeding 5 %. Finally, a sensor was utilized for the recognition of TN in medicinal and bio-samples.

Bulut *et al*. [180] introduced a sensor based on poly(benzenediamine-bis[(2-ethylhexyl) oxy]ben-zodithiophene)/testosterone antibodies *via* glutaraldehyde/screen-printed carbon electrode for the determination of TN. The surface morphology of the modified electrode was studied with atomic force microscopy. The modifications in the exterior topography due to TN binding were inspected through electrochemical techniques. The amperometric studies were conducted to measure TN in the range of 10 - 500 ng/ml with LOD of 17 ng/ml. Finally, a sensor was utilized for the analysis of TN in synthetic urine (recovery 103.4 ± 1.0 and 98.0 ± 5.3 %) and serum samples (113.8 ± 1.1 and 105.6 ± 2.2 %). Additionally, repeatability of electrode response towards TN was studied by 10 measurements, showing RSD of 0.433 %.

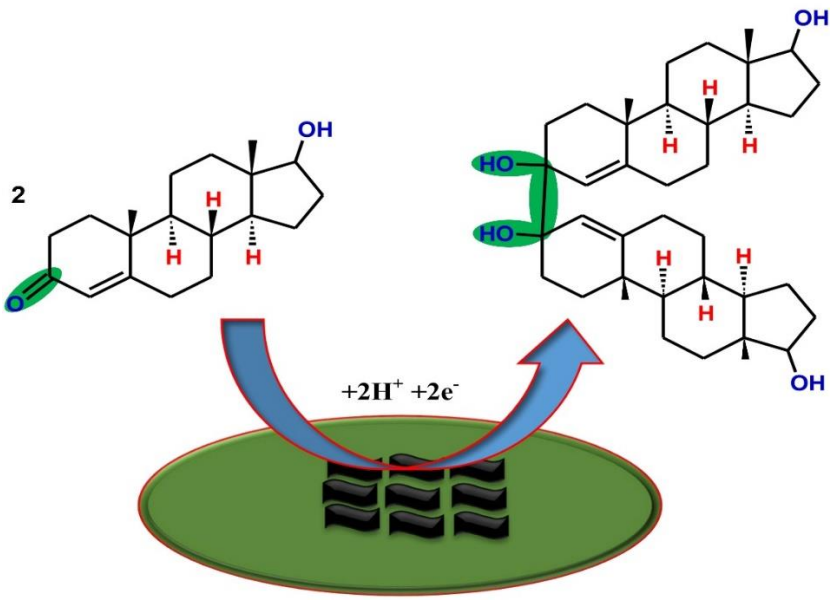

Figure 5. *Possible mechanism of TN electroreduction at carbon electrode*

Liu *et al*. [181] developed a sensor for TN based on nanosized molecularly imprinted polymer (MIP) film that was electrochemically grafted on graphene oxide sheets modified electrode. Measurement of TN was performed using EIS technique in the range 1.0 fM to 1.0 µM with LOD of

0.4 fM. Moreover, stability was good with 93.4 % retention of the initial response of electrode towards TN even after 30-day storage at room temperature. Also good reproducibility and repeatability were observed with RSD not exceeding 5 %. Practical application of sensor was carried in human serum samples with recovery 98.6 to 104.2 %, and RSD not exceeding 5 %.

Data in Table 5. [182-190] shows the comparison between different electrochemical sensors for TN. Results given by Liu *et al*. [181] for molecularly imprinted polymer /electrochemically grafted on graphene-oxide sheets modified electrode provide the lowest LOD of 0.4 fM.

Table 5. *Analytical properties of some carbon-based sensors for TN determination using various electrochemical techniques and real samples*

Electrode	Technique	TN linear range, M*	LOD, M	Real sample	Ref.
GCE/CoO_x	CV	$0.33 - 2.00 \times 10^{-6}$	1.6×10^{-7}	---	[182]
Surfactant/glassy carbon	SWV	$10 – 70 \times 10^{-9}$	1.18×10^{-9}	Human urine	[183]
SWNT modified EPPGE	SWV	$5 – 1000 \times 10^{-9}$	2.8×10^{-9}	Female urine	[184]
rGO/GCE	DPV	$2.0 – 210.0 \times 10^{-9}$	0.1×10^{-9}	Human plasma & urine	[185]
Anti-testosterone-nAu/MWCNTs/Teflon	Amperometry	0.4 and 34.67×10^{-9}	0.29×10^{-9}	Human serum	[186]
SPCE/MBs/AbTES	Amperometry	$0.0174 – 173.35 \times 10^{-9}$	0.0059×10^{-9}	Human serum	[187]
NCD/silicon wafer/MIP	EIS	$0.5 – 20\times10^{-9}$	0.5×10^{-9}	Human urine &saliva	[188]
GCE/SA/BSA/BiNb16	EIS	$0.1734 – 17.336\times10^{-9}$	0.156×10^{-9}	Human serum	[189]
CuO/CeO_2/GCE	Electrochemical (I - V) approach	$0.01 – 0.01 \times 10^{-3}$	9.30×10^{-12}	Human, mouse, and rabbit serum	[190]

*Linear concentration range of testosterone detection

Future perspectives

In the last decade, many carbon-based sensors and biosensors for the determination of hormones have been probed. However, the simultaneous determination of sex hormones seems to be a challenge manifested in a significantly lower number of literature reports. Hormones like pregnenolone, allopregnanedione, allopregnanolone, 17α-hydroxy pregnenolone, 17α-hydroxyprogesterone, dehydroepiandrosterone, androstenedione, androstanedione, androsterone, androstenediol, dihydrotestosterone, androstanediol, 2-hydroxyestrone, 16α-hydroxyestrone, 2-hydroxyestradiol, and estetrol are still waiting to be analyzed electrochemically. Carbon materials like activated carbon, carbon derived from biomass, carbon fibers, pencil graphite electrode, pin-based electrodes, fullerenes, carbon nanohornes, graphyne, carbon nanomaterials, *etc.* could be possibly utilized to achieve this goal. Breakthrough in analytical methods with new materials is always important in the field of analytical science and technology.

Conclusions

Electroanalytical methods for biomolecular diagnosis have increased widely in recent years, especially for hormone determinations. Electrochemical techniques are used for the detection of various hormones because of their excellent response, easy instrumentation, minimal sample pre-treatment criteria, rapid and satisfactory sensitivity, and low cost. Recent developments include use of graphene, graphite, carbon paste, carbon nanotubes (multi-walled, single-walled, *etc*.), glassy carbon electrodes, and other combinations, mostly due to their high effective surface area and distinct electrochemical properties. Also, these materials substantially improve analytical signals, decrease overpotentials of hormone oxidation or reduction, and solve peak overlapping problems

in complex samples. The characteristics of the sensor constituents and functionalized groups and their interfaces with analyte molecules greatly stimulates degree of electrooxidation/reduction, pH, p*K*a of the background electrolyte, and peak voltage and current. The interface and degree of electrooxidation/reduction depend extremely on the following aspects: alteration of the sensor assembly, pre-treatment of the electrode, exterior functionalities, pH, background electrolyte, and presence of other molecules. For determining the electrooxidation or reduction rate and electrode efficiency, the communication (reaction) between the respective type of analyte (targeted molecule) present at some pH value (range) and the oxygen functionalities and other groups on the sensor are found to be vital.

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