Hard X-ray Generation from ZnO Nanowire Targets in a Non-Relativistic Regime of Laser-Solid Interactions

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New Generation of Electrochemical Sensors Based on Multi-Walled Carbon Nanotubes

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Abstract: Multi-walled carbon nanotubes (MWCNT) have provided unprecedented advances in the design of electrochemical sensors. They are composed by sp² carbon units oriented as multiple concentric tubes of rolled-up graphene, and present remarkable active surface area, chemical inertness, high strength, and low charge-transfer resistance in both aqueous and non-aqueous solutions. MWCNT are very versatile and have been boosting the development of a new generation of electrochemical sensors with application in medicine, pharmacology, food industry, forensic chemistry, and environmental fields. This work highlights the most important synthesis methods and relevant electrochemical properties of MWCNT for the construction of electrochemical sensors, and the numerous configurations and successful applications of these devices. Thousands of studies have been attesting to the exceptional electroanalytical performance of these devices, but there are still questions in MWCNT electrochemistry that deserve more investigation, aiming to provide new outlooks and advances in this field. Additionally, MWCNT-based sensors should be further explored for real industrial applications including for on-line quality control.

Keywords: nanomaterials; multi-walled carbon nanotubes; synthesis methods; electrochemical properties; electrochemical sensors; electroanalysis; sensing applications

1. Introduction

Several nanomaterials have been exploited for different purposes, but carbon nanotubes (CNT) and their composites emerged as the most exciting and versatile [1–5]. CNT are carbon allotropes with intermediate properties between graphite and fullerenes [6]. They are composed by sp² carbon units oriented as one (single-walled; SWCNT) or multiple concentric tubes (multi-walled; MWCNT) of rolled-up graphene, separated by ≈0.35 nm [4,6–8]. Both nanostructures had positive impacts for the applied sciences, but the latter has gained more attention due to the higher yield and lower production cost per unit, thermochemical stability, and ability to maintain or improve its electrical properties when submitted to different functionalization processes [9]. A general MWCNT representation and the possible π- and σ-covalent bonds established along the nanostructure are displayed in Figure 1. MWCNT also present remarkable active surface area, chemical inertness, high strength, and low charge-transfer resistance in both aqueous and non-aqueous solutions, making them suitable for numerous applications as nano-sized metallic and/or semiconducting components in transistors [10], energy storage [11], hybrid conductors [12], supercapacitors [13], thin-film coatings [2,5,6], field emitters [14], (bio)fuel cells [1–3,7], photovoltaic devices [1,3], electromagnetic shields [1,7], and electrochemical probes [1,2,5–7].
MWCNTs have remarkable applications in medicine, clinical diagnostics, pharmacology, food industry, sanitary surveillance, occupational safety, forensic chemistry, and environmental analysis [1–3,6–9,15–18]. Other promising innovations can also be found in review papers that have been published over the last decade [6–9,15–20]. The assays are performed by various electrochemical techniques (voltammetry, amperometry, potentiometry, impedance spectroscopy, and their associations), which are selected according to the nature of the target-redox process [2,6,7,15–20]. MWCNTs bring together high electronic conductivity, large specific surface area, chemical stability, biocompatibility, and ease of modification, improving the intensity and resolution at which the electroanalytical signals are observed on the working platforms [15–18]. However, the successful application requires a refined control of the sensor architecture and physicochemical properties, as well as the functionalization and/or surface modification of the carbon nanotubes [4,6–9]. Thus, in this study, these critical variables will be highlighted and discussed, addressing exciting issues from the MWCNT synthesis to their application in electrochemical biosensors design. With this goal in mind, the available literature concerning this subject in Thomson Reuters, Web of Science was reviewed from 2013 to March 2018.
2. MWCNT Synthesis Methods

Regarding synthesis methods, there are different paths that can be followed, such as electrical arch-discharge (EAD), laser ablation (LA), and numerous types of chemical vapor deposition (CVD), so that MWCNT conductor character varies according to the diameter and degree of helicity [4,7,21]. An overall layout of each system and its associated processes are shown in Figure 2. The yield rate of all aforementioned methods is more than 75% under appropriate operating conditions [22], but some questions about the structural quality, diameter uniformity, chirality, practicality, number of unitary operations, and production cost continue to divide opinions about the best strategy [4,21–24]. Researchers are continually trying to explore each possibility to optimize or innovate them for several new applications.

![Figure 2](image-url)

**Figure 2.** General layout of an (a) electrical arch-discharge (adapted by permission from Reference [23]), (b) laser ablation (adapted by permission from Reference [23]) and (c) chemical vapor deposition apparatus (adapted by permission from Reference [25]) used to synthesize multi-walled carbon nanotubes.
EAD is relatively less expensive, offers better yield quality, but involves high temperature for synthesis [21–23]. Triggering an electrical arc-discharge between two electrodes, a plasma composed by carbon and metallic catalysts vapor (iron, nickel, cobalt, yttrium, boron, cerium, among others) is formed under a rare gas atmosphere (helium or argon) [21–23]. The vapor content is a consequence of the energy transferred to the catalysts-doped anode, causing its erosion, while MWCNT are formed as a hard and consistent deposit on the cathode [23]. The LA method also represents a promising alternative to synthesize high-quality carbon nanotubes at room temperature, although it demands high instrumental and operational costs [21–23]. In this technique, a pulsed or continuous laser beam is focused on catalyst-based graphite pellet, which is placed at the center of a quartz tube filled with an inert gas and kept at 1200 °C. The radiant energy is enough to sublimate the carbon substrate, and this vapor is swept by the gas flow towards the conical water-cooled copper collector. MWCNT deposits are formed in the majority on the same collector, but appreciable amounts are also found on the quartz tube walls and graphite pellet backside. Both EAD and LA also produce in parallel other carbon phases and all products contain metallic impurities from the catalysts [23]. The small fractions of remaining metals do not compromise the performance of the electrochemical devices, and there are several purification processes proposed in the literature and by some commercial companies to remove undesirable phases [22–24]. Nevertheless, these procedures are based on oxidation under strong acidic conditions, which may significantly affect the integrity of the nanostructures.

The synthesis performed by CVD overcomes the aforementioned difficulties, guarantees large-scale production and, for these reasons, it has become more widely used to obtain MWCNT [22–25]. This technique involves either a heterogeneous (if a solid substrate is used) or a homogeneous process (supposing that reactions take place in the gas phase) [23,25]. The main synthetic route explores the catalytic decomposition of a carbon-containing source on substrates containing transition metals and their composites (Au, Ag, Cu, Cr, Co, Fe, Mn, Mo, Ni, Pt, Pd, SiO$_2$, SiC, and ceramics), which enables the growth of aligned and dense arrays of nanotubes [23,24]. Alternative energy sources such as plasma and optical excitation can also be employed, giving the possibility to synthesize MWCNT at low-temperatures (450–1000 °C) compared to EAD and LA [23–25]. The CVD method also allows greater control of selectivity/type, homogeneity and size of the nanotubes (a few tens to hundreds of micrometers) in comparison to the others, although these characteristics are strongly dependent on the nature and structure of the catalysts, and the operational conditions of the synthesis. All these aspects affect the density and speed of electron transfer through the nanostructures that, in turn, directly impact the performance of the electrochemical sensors.

3. MWCNT Electrochemical Properties

MWCNT-based electrochemical sensors have remarkable advantages for analytical applications, such as enhanced detection sensitivity, low charge-transfer resistance ($R_{tc}$), electrocatalytic effect, and reduced fouling. It is also speculated that traces of metallic catalysts can add remarkable electroanalytical characteristics (positive synergistic effect) to the nanotubes, playing a supporting role for the development of the devices [6,7,15–26]. There are still controversies about the electron transfer mechanism along the structural network: Some researchers believe that the sidewalls of the CNT are inert (i.e., the edge–plane-graphite-like open ends and defect sites control the phenomenon) [26–28], but some studies conducted with two-dimensional SWCNT have shown evidence of charge-transfer on the basal-plane [7,23,25]. Although the uncertainties about the fundamental contributions of MWCNT in electrochemical sensors, the number of MWCNT successful applications in highly complex systems does not stop growing [2,9,17,26].

Understanding the size-dependent features is an indispensable requirement to explore the fascinating properties of nanotubes in analytical tools and to move the electroanalytical researches forward. In this sense, it must be assumed that the electronic band structure of CNT as a hexagonal lattice, where each carbon atom is covalently bonded to three others via sp$^2$ molecular orbitals (the fourth valence electron in a p$_z$-orbital hybridizes with all others to form a delocalized π-band) [27].
Like this, an even number of electrons are contained in the basic nanotube structure, whose conduction character will depend on its behavior as metal or semiconductor. This property can be assessed through the tight-binding electronic structure calculations, considering the translational vector ($C_h$) that connects two equivalent crystallographic sites (unitary vectors $a_1$ and $a_2$) and its coefficients ($n_1$ and $n_2$), according to the following Equation (1):

$$C_h = n_1 a_1 + n_2 a_2$$

so that a metallic behavior is observed when the result is an integer multiple of three, while a non-metallic/semiconductor profile is observed for other cases; a direct consequence of the different conduction band gaps [6]. The electron-transfer along the MWCNT are also influenced by the tube diameter ($d_t$), chiral angle ($\theta$), and basic translation vector ($T$), as shown in Figure 3. Thus, the manner in which a graphene sheet is rolled determines the main electronic properties of the resulting nanotube [6,15,23,27].

Observing the referred parameters on the tubulene lattice, $d_t$ values can be determined by Equations (2) and (3), which relate this variable with the circumferential length of the nanotube ($L$) and a hexagonal network constant ($a$):

$$d_t = \frac{L}{\pi} = \frac{C_h}{\pi} = \frac{a(n_1^2 + n_1 n_2 + n_2^2)^{\frac{1}{2}}}{\pi}$$

considering $a_v = 1.42$ Å for carbon nanotubes [6]:

$$a = \sqrt{3}a_v = 2.49$$ Å

Regarding the $\theta$, the expression that describes its magnitude can be written as follows:

$$\cos \theta = \frac{2n_1 + n_2}{2\sqrt{n_1^2 + n_1 n_2 + n_2^2}}$$

The vector $T$ is used to specify the orthogonal orientation to the $C_h$ axis of the nanotube, and its value can be calculated by:
\[
T = \frac{(2n_2 + n_1)a_1 - (2n_1 + n_2)a_2}{d_k}
\] (5)

where \(d_k\) ranging from \(d\) (when \(n_1 - n_2\) and \(d_k\) is not a multiple of 3\(d\)) to 3\(d\) (when \(n_1 = n_2\) and \(d_k\) is a multiple of 3\(d\)) for chiral tubulenes, considering \(d\) the greatest common divisor for the coefficients \(n_1\) and \(n_2\) [6,15,23,27].

In addition, a translation vector (\(\tau\)) is also necessary to delimit the unitary cell of the nanotube. It can be represented by Equations (6)–(8),

\[
\tau = t_1a_1 + t_2a_2
\] (6)

\[
t_1 = \frac{(2n_2 + n_1)}{d_r}
\] (7)

\[
t_2 = \frac{-(2n_1 + n_2)}{d_r}
\] (8)

knowing that \(d_r\) (\(d\rightarrow3d\)) is the greatest common divisor of the respective coefficients. In summary, the limits of the 1D nanotube unit cell (plane segment \(OAB'BO\)) are demarcated by the vectors \(C_h\) and \(T\), whereas \(a_1\) and \(a_2\) define the area of the 2D graphene unit cell [6,27]. This sequence of equations is very important for the development of electrochemical sensors because it allows to determine the number of electric and phononic bands in the carbon nanostructures, i.e., the magnitude of the electrical conduction through the nanomaterial.

The influence of the band structure on the nanotube conduction bands is defined in the context of the Fermi velocity (\(\nu_F\)).

\[
\nu_F = \frac{\hbar k_F}{m}
\] (9)

where \(\hbar\) is the reduced Planck constant, \(k_F\) is the Fermi wavevector, and \(m\) represents the mass of the nanostructure under study. These values are not well-defined in cases where the Fermi surface is non-spherical, but it is estimated to be \(\nu_F \sim 10^6\) ms\(^{-1}\) for semiconductors or even higher for conductors [27]. This prevision corroborates the observation recorded in the density of states diagram for SWCNT with different chirality, since at the Fermi energy level (\(E_F\)) there is a finite electronic transition for metallic structures (first van Hove optical transition), but a zero-band gap for semiconductors (second van Hove optical transition). A general description of the band structures and density of states for metallic and semiconductor nanotube is presented in Figure 4. Thus, if we imagine that MWCNT are composed by several coaxial SWCNT, it might be expected that they are not strictly a 1D-type conductor [7,27]. Likewise, when the nanotubes have different chirality, the band structure undergoes alterations, and the resultant coupling between the electronic states at the \(E_F\) and phonon modes may cause superconductivity [4,7,27]. Despite the similarity with metallic materials, the carrier density in carbon nanotubes (1D quantum wires) is much lower and novel physical electron-electron phenomena (such as spin-charge separation and suppression of the electron tunneling density of states) should be considered to justify the possible discrepancies, as predicted by Luttinger liquid theory [23,26–28].

Some electrochemical studies showed a lower \(R_{tc}\) for MWCNT containing structural defects and/or traces of metallic impurities (catalyst nanoparticles), so that the current flow occurs mainly through the outer most nanotube cylinder [26–28]. Only one of the concentric tubes needs to exhibit this behavior for the overall electronic properties to be essentially metallic-low quantum capacitance values [7,27]. It is believed that if \(d_l\) is smaller than the elastic mean free path, the one-dimensional ballistic transport predominates, but the opposite characterizes a two-dimensional diffusive current flow [7,26–28]. In addition, nanotubes with larger \(d_l\) have a greater density of structural defects, besides facilitating their modification and functionalization, which are interesting requirements for the development of electroanalytical devices [2,6–9]. The mean length of the nanotubes also has a significant effect on the electron-transfer rate; they are inversely proportional
properties [22, 24, 27]. Vertically aligned structures also exhibit superior performance compared to those randomly immobilized [2, 16, 25–28].

![Diagram of band structures and density of states](image)

Figure 4. Idealized models of band structures and density of states for (a) metallic and (b) semiconducting nanotubes.

Therefore, MWCNT provide special characteristics in electrochemical sensors both in aqueous and non-aqueous electrolytes (electrocatalytic properties, high and fast electron-transfer, signal amplification and stability, among other particularities observed in different prototypes) when compared with the conventional carbonaceous electrodes (such as glassy carbon, highly-oriented pyrolytic graphite, carbon microfiber, and boron-doped diamond) [26–28]. However, the true reasons and fundamental electrochemical properties responsible for the reported performances (both when nanotubes are used alone or in (nano)composites) are still not fully elucidated and demand further research [2, 4, 6, 9, 17].

4. Overview of MWCNT Applications in Electrochemical Sensors

Different and exciting properties are obtained with macro-, micro-, and nano-structured carbon derivatives [4, 17], but the implementation of the latter in the configuration of electrochemical sensors brought new opportunities to detect trace concentrations (µmol L\(^{-1}\) to pmol L\(^{-1}\)) of numerous analytes (active principle and metabolites of drugs, personal care products, flame retardants, gases, surfactants,
industrial additives, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), hormones, pesticides, among others) in complex matrices (natural waters, soils, foodstuffs, biological fluids, fuels, wastes, and even in living organisms) [1–17]. This trend led to the development of the newest category of electroanalytical devices (third generation/way), i.e., nanotools for nanoscale analysis [2,16]. The basic mechanism for the operation of these tools is based on the conversion of redox processes, registered at the sensor/electrolyte interface, onto quantitative or semi-quantitative information. MWCNT had an important role to reach such advances, and this fact can be easily attested by the exceptional growth of scientific reports in this field [2–6,8,16,17]. MWCNT’s large active surface area, facile electron-transfer with a variety of molecules, and their use in nano-composites (mixed with conductive polymers, nanoparticles and active biomolecules), as well as their high potential for device miniaturization, have been enhancing the sensitivity of current methodologies and providing new sensing opportunities [2,17,19–22]. The multichannel electron ballistic transport and the presence of holes/defects along the structures, especially when functionalized with carboxyl groups and their derivatives, further enhance the previously mentioned properties [2,4–9]. When converting a graphene sheet to a nanotube, one electron of the carbon atoms remains in $p$-orbitals, organized between valence ($\pi$) and conduction ($\pi^*$) bands with very low bandgap (a partial $\sigma$–$\pi$ hybridization), which favors a fast electron transfer. The density of states in MWCNT structure depends on diameter ($\approx 2–100$ nm), chirality/configuration (concentric, herringbone, and bamboo) and nature (semiconductor, conductor, and superconductor) [1,7,15]. In addition, the strength of C–C bonds is among the most robust and, when they are organized in the nanotube form, these interactions also provide flexibility and resistance to rupture, increasing the versatility and number of possible applications of these nanomaterials [4,7,16].

Electrochemical sensing of a wide variety of chemically, biologically, and environmentally important analytes was investigated on MWCNT (chemical purity $\geq 95\%$)—based solid electrodes, as shown in Table 1. Numerous traditional and modern pharmaceuticals, for instance, are electroactive on these sensors and relevant contributions have been reported, either in stationary or in flow-through systems. Mao et al. [29] fabricated an electrochemical sensor for metronidazole (antibacterial and anti-inflammatory compound employed for the treatment of protozoal diseases) based on MWCNT and chitosan (CTS)-nickel complex modified glassy carbon electrode (GCE) by the self-assembly technique. The polymer matrix facilitates the immobilization of the nanocomposite on the electrode support, while the association between nickel and carbon nanomaterials increases the current intensity of the electroanalytical signal. Using differential pulse voltammetry (DPV), Ni-CTS/MWCNT/GCE also showed electrocatalytic effect toward metronidazole reduction, making the method highly selective to its analysis in pharmaceutical and biological samples, with a low detection limit (LOD; 0.025 µmol L$^{-1}$) and suitable reproducibility and stability. Holanda et al. [30] reported a simple methodology to quantify acetaminophen (a compound with analgesic and antipyretic action) in commercial formulations, using a GCE modified with gold nanoparticles (Au-NP), functionalized MWCNT ($f$-MWCNT) and cobalt phthalocyanine (Co-Pht) as working sensor. Using $f$-MWCNT, a lower system capacitance and better stability of the sensor was observed. The quantification of acetaminophen on Co-Pht/$f$-MWCNT/Au-NP/GCE was carried out by square-wave voltammetry (SWV) that, in turn, showed a sensitivity (LOD = 0.135 µmol L$^{-1}$) and reproducibility similar to the standard ultraviolet-visible spectrophotometric procedure (at the wavelength of 257 nm). Montes et al. [31] studied the superior electrochemical activity of MWCNTs with shorter dimensions (diameter $\times$ length: 100–170 nm $\times$ 5–9 µm and 6–9 nm $\times$ 5 µm) towards the oxidation of propionic acid derivatives, which are drugs with analgesic, antipyretic, and anti-inflammatory properties. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetric (CV) data showed better electrocatalysis effect, $R_{tc}$ and signal amplification for the sensor constructed with the shorter diameter nanostructures due to the increased defect density revealed by Raman spectroscopic measurements. The developed sensor (MWCNT (diameter $\times$ length: 6–9 nm $\times$ 5 µm)/GCE) was adapted to a flow-injection analysis system (FIA) and provided a sensitivity and accuracy to determine ibuprofen (LOD = 1.9 µmol L$^{-1}$).
by amperometry comparable to that obtained by capillary electrophoresis. Pavinatto et al. [32] used a fluorine doped tin oxide (FTO) electrode, coated with nanostructured layer-by-layer films of CTS@MWCNT (Figure 5), as a sensor for 17-α-ethinylestradiol, that is a synthetic estrogen widely used as an oral contraceptive. The electron-transfer on the sensor reduced dramatically in the presence of the nanotubes, improving its electroanalytical performance and enabling assays at very low concentrations. Using the irreversible and adsorption-controlled oxidation process of the estrogen onto the three-bilayer CTS@MWCNT/FTO, it was possible to determine it by SWV (LOD = 0.09 μmol L⁻¹) without significant effect of the most common interfering compounds present in human urine (urea, uric, and ascorbic acids, glucose, NaCl, KCl, and NH₄Cl). Chen et al. [33] used a nanocomposite based on MWCNT and 1-octyl-3-methyl-imidazolium hexa-fluorophosphate ionic liquid (IL) to modify a GCE, to develop a chiral electrochemical sensor for the enantiomeric recognition of propranolol, using the linear sweep voltammetry (LSV) technique. The authors did not present a LOD but declared the success of the proposed method to evaluate the enantiomeric purity of reagents and wastewater treatment efficiency. Other promising MWCNT-based electrochemical devices were also reported to successfully analyze hydrochlorothiazide and triamterene [34], mangiferin and icariin [35], natamycin [36], omeprazole [37], gentamicin [38], and many other drugs [2,6,9,17–20], attesting their electroanalytical performance and effectiveness.

![Figure 5](image-url)

**Figure 5.** (a) Schematic representation of the layer-by-layer and (b) supramolecular interaction between chitosan and multi-walled carbon nanotubes (MWCNT) for 1-bilayer film (adapted by permission from Reference [32]).

The growing trend of using miniaturized systems for the electroanalysis of bioactive molecules in living organisms through less invasive tests has positive repercussion and wide acceptance [2,17]. From this perspective, glucose sensors have been receiving special attention, since these analytic tools can be used as an effective way to diagnose diabetes, hypoglycemia, and other metabolic diseases in real time, using human blood and other secreted fluids as study matrix. Başkaya et al. [39] fabricated a non-enzymatic glucose sensor using a hybrid film (composed by f-MWCNT and highly monodisperse nickel nanoparticles) immobilized on GCE, which was able to determine this target in human blood serum samples by amperometry, with sensitivity (LOD = 0.021 μmol L⁻¹) and stability similar to one of commercial enzymatic biosensors. The results also support the positive synergistic effects that are observed when different nanomaterials are associated into the same matrix, enhancing the capacity and versatility of the electrochemical sensors. Purine bases are also crucial biomolecules to the immune function and abnormal changes causes serious disorders, such as cancer, epilepsy, lupus erythematosus, renal calculi, and cardiovascular alterations. Wang et al. [40] prepared a nanocomposite by mixing...
MWCNT and copper-nickel hybrid nanoparticles (Cu@Ni-NP), which was deposited onto a GCE surface, with the goal of monitoring adenine and guanine in ds-DNA from mouse brain tissues. Using DPV under the optimized conditions, the Cu@Ni-NP/MWCNT/GCE sensor achieved a LOD of 0.17 µmol L⁻¹ and 0.33 µmol L⁻¹ for guanine and adenine, respectively, attesting to its potential to quantify purine bases in complex samples. Likewise, sensors for point-of-care detection of DNA damage in medical diagnostics are also on the rise. Li and Lee [41] investigated the performance of f-MWCNT (functionalization with oxygen-containing groups to improve the immobilization and stability of the bioelement) as an additive in electrochemical DNA sequence differentiation ability. The electroanalytical signal achieved by DPV was highly selective and modulated between the probe (5′-GTG TTG TCT CCT AGG TTG GCT CTG-3′; 24-base fraction of the p53 gene, used as a marker for breast cancer) and its complementary sequence (5′-CAG AGC CAA CCT AGG AGA CAA CAC-3′). The detection capacity (LOD = 141.2 pmol L⁻¹) was more than two orders better than the previously reported for graphene functionalized (f-Grf) based sensors, even in the presence of single (5′-CAG AGC CAA CCT AGG AGA CAA CAC-3′) and all-base mismatched pairs (5′-ATA TCG ACC TTG GCC GAG ACG GTG-3′). Great effort has also been directed towards the development of electrochemical devices capable of early detection of immune deficiency diseases, such as acquired immune deficiency syndrome (AIDS) caused by the HIV-retrovirus. Ma et al. [42] proposed a device composed by a GCE modified with MWCNT and molecularly imprinted polymers (MIPs) based on CTS for the determination of HIV-p24 protein in real human serum samples (Figure 6). Using DPV and the developed sensor (HIV-p24/CTS/MWCNT/GCE), a low limit of detection (0.083 pg cm⁻³), good selectivity, repeatability, reproducibility, stability, and accuracy were reached for the proposed electroanalysis; validation was performed by comparative studies with enzyme-linked immunosorbent assay (ELISA). The outstanding ability of MWCNT-based electrochemical sensors to simulate redox reactions that occur in vivo has also been demonstrated with the electroanalysis of hemoglobin [43], amino acids [44], cholesterol [45], bilirubin [46], neurotransmitters, and related compounds [47–49], and even microorganisms [50], in mammalian fluid samples, achieving great results and contributing to the early diagnosis and treatment of several related diseases.

The occurrence of pesticides in foodstuffs, natural water, soils, among other matrices of environmental relevance, constitute a worldwide concern. Sipa et al. [51] associated square-wave adsorptive stripping voltammetry (SWAdSV) and a modified sensor (β-cyclodextrins/MWCNT/GCE) to determine trace concentrations of the pesticide dichlorophen. The excellent electroanalytical performance of the system, mainly in the presence of nanotubes (LOD = 4.4 × 10⁻⁸ mol L⁻¹), allowed to monitor this vermicide in river water (Pilica River, in Poland) with good selectivity and absence of natural and anthropogenic interfering compounds. Özcan and Gürbüz [52] developed a simple and sensitive sensor for the voltammetric determination of the herbicide clopyralid in urine, river water, sugar beet, wheat, and herbicide formulations (Phaeton® and Lontrel™). This novel sensor was built by modification of a GCE with a nanocomposite containing acid-activated MWCNT (oxygen-functionalized nanostructures with very low Rct) and fumed silica, which, when associated with DPV, attained a LOD of 0.8 nmol L⁻¹, confirming the sensitivity of the proposed method. Ghodsi and Rafati [53] reported a strategy to develop a voltammetric sensor for diazinon (an organophosphate insecticide) based on TiO₂ nanoparticles (TiO₂-NP) and MWCNT nanocomposite assembled onto a GCE. Under optimum conditions, TiO₂-NP@MWCNT/GCE reached a LOD of 3.0 nmol L⁻¹, using both CV and SWV, and this performance was explored for the electroanalysis of the pesticide in well and tap water. Other mentioned advantages were the fast response time, good repeatability, stability, besides the fast and inexpensive electrode modification. Sensitive electrochemical sensors that associate the unique properties of MWCNT and metallic nanoparticles were also proposed by Wei et al. [54] and Ertan et al. [55], aiming to electroanalyzise trichlorfon insecticide (LOD = 4.0 × 10⁻⁷ mol L⁻¹, using Nafion®/TiO₂-NP@MWCNT@carboxymethyl chitosan/GCE) and simazine herbicide (LOD = 2.0 × 10⁻¹¹ mol L⁻¹, using MIP/platinum nanoparticles@polyoxometalate@f-MWCNT/GCE), respectively, reinforcing the positive synergistic effect between these nanostructures for the improvement of the electroanalytical methodologies.
orders better than the previously reported for graphene functionalized (f-Grf) based sensors, even in the presence of single (5′-CAG AGC CAA CCT CGG AGA CAA CAC-3′) and all-base mismatched pairs (5′-ATA TCG ACC TTG GCC GAG ACG GTG-3′). Great effort has also been directed towards the development of electrochemical devices capable of early detection of immune deficiency diseases, such as acquired immune deficiency syndrome (AIDS) caused by the HIV-retrovirus. Ma et al. [42] proposed a device composed by a GCE modified with MWCNT and molecularly imprinted polymers (MIPs) based on CTS for the determination of HIV-p24 protein in real human serum samples (Figure 6). Using DPV and the developed sensor (HIV-p24/CTS/MWCNT/GCE), a low limit of detection (0.083 pg cm\(^{-3}\)), good selectivity, repeatability, reproducibility, stability, and accuracy were reached for the proposed electroanalysis; validation was performed by comparative studies with enzyme-linked immunosorbent assay (ELISA). The outstanding ability of MWCNT-based electrochemical sensors to simulate redox reactions that occur in vivo has also been demonstrated with the electroanalysis of hemoglobin [43], amino acids [44], cholesterol [45], bilirubin [46], neurotransmitters, and related compounds [47–49], and even microorganisms [50], in mammalian fluid samples, achieving great results and contributing to the early diagnosis and treatment of several related diseases.

The wide active area and low \(R_{tc}\) observed for MWCNT, and related (nano)composites, have been providing important advances on the single and simultaneous electroanalytical quantification of metallic cations (\(\text{Cd}^{2+}\) [56], \(\text{Pb}^{2+}\) [56], \(\text{Mn}^{2+}\) [57], and \(\text{Na}^+\) [58]) and anions (\(\text{SO}_3^{2-}\) [59], \(\text{NO}_2^-\) [60], and \(\text{BrO}_3^-\) [60]) in varied and complex matrices (wastewater [57], drinking water [56], and groundwater [58,59]). Trace concentrations of persistent organic pollutants (sunset yellow [61], tartrazine [62], and luteolin [62] dyes), as far as gases (chlorine [63], carbon dioxide [64], and methanol vapor [65]) and industrial by-products (glycerol [66], bisphenol A [67], hydrazine [68], and hydrogen peroxide [69]) are now being monitored with MWCNT-based sensors in a quick, reproducible, reliable, and cost-effective way when compared to the traditional analytical protocols, including those based on electrochemical devices from previous generations.
| Sensor                      | Modification Procedure                                                                 | Analyte(s)                          | Technique(s)/Detection Limit | Application                  | Stability                        | Reference |
|-----------------------------|----------------------------------------------------------------------------------------|-------------------------------------|------------------------------|------------------------------|----------------------------------|-----------|
| Ni-CTS/MWCNT/GCE            | GCE modified with MWCNT and Ni-CTS complex through drop coating and self-assembly, respectively | metronidazole                      | DPV/0.025 µmol L\(^{-1}\)    | tablet and biological samples  | 81% after one month              | [29]      |
| Co-Pht@f-MWCNT/Au-NP/GCE    | suspension of Co-Pht and f-MWCNT immobilized on Au-NP modified GCE by drop coating      | acetaminophen                       | SWV/0.135 µmol L\(^{-1}\)    | commercial formulations      | n.r.                             | [30]      |
| MWCNT(shorter diameter)/GCE | MWCNT (diameter = length: 6-9 nm × 5 µm) dropped on GCE                                | ibuprofen                           | CV/1.90 µmol L\(^{-1}\)      | tablet and liquid commercial formulations | n.r.                             | [31]      |
| Three bilayer MWCNT@CTS/FTO | FTO coated with nanostructured Layer-by-Layer films of MWCNT@CTS                         | 17-a-ethynylestradiol               | SWV/0.09 µmol L\(^{-1}\)     | synthetic urine samples       | n.r.                             | [32]      |
| MWCNT@IL/GCE                | immobilization of MWCNT and IL (1-octyl-3-methyl-imidazolium hexa-fluorophosphate) nanocomposite on GCE | propranolol                         | LSV/n.r.                     | commercial reagent and wastewater | n.r.                             | [33]      |
| MWCNT/GCE                   | suspension of MWCNT dropped on GCE                                                     | hydrochlorothiazide and triamterene | ASV/2.8 × 10\(^{-8}\) and 2.9 × 10\(^{-8}\) mol L\(^{-1}\) for hydrochlorothiazide and triamterene, respectively | hemodialysis samples | n.r.                             | [34]      |
| Au@Ag-NP/MWCNT-SGS/GCE     | layer-by-layer assembly of Au@Ag-NP and MWCNT-SGSs on GCE                               | mangiferin and icariin              | DPV/0.017 µmol L\(^{-1}\) for both compounds | Rhzoma acaumarthae, Artemisia capillaris Herba and Epimedium macranthum samples | ≤95.1% after one month | [35]      |
| 3D-Grf@MWCNT/GCE            | electrodeposition of 3D-Grf@MWCNT suspension on GCE                                     | natamycin                           | LSV/1.0 × 10\(^{-6}\) mol L\(^{-1}\) | red wine and beverage samples | 94.6% after two weeks          | [36]      |
| Fe\(_3\)O\(_4\)-NP@MWCNT/PDDA/GCE | casting of PDDA modified GCE with Fe\(_3\)O\(_4\)-NP@MWCNT hybrid film                  | omeprazole                          | LSV/15 nmol L\(^{-1}\)       | tablet, capsules, wastewater, serum, and urine | 92.1% after three weeks | [37]      |
| Calixarene/MWCNT/SPE        | dip coating of graphite-based SPE in composite matrix of calixarene and MWCNT           | gentamicin sulphate                 | potentiometry/7.5 × 10\(^{-8}\) mol L\(^{-1}\) | dosage forms and spiked surface water samples | n.r.                             | [38]      |
| Ni-NP@f-MWCNTs/GCE          | drop coating of hybrid film (Ni-NP and f-MWCNT) on GCE                                  | glucose                             | CV and amperometry/0.021 µmol L\(^{-1}\) | human blood serum samples    | practically constant signal after 1000th cycle | [39]      |
| Cu@Ni-NP/MWCNT/GCE          | immobilization of hybrid film of Cu@Ni-NP and MWCNT on GCE                             | guanine and adenine                 | DPV/0.17 µmol L\(^{-1}\) and 0.33 µmol L\(^{-1}\) for guanine and adenine, respectively | ds-DNA from mice brain tissues | 96.7% for 30 days               | [40]      |
| Gold electrode              | measurements with unmodified gold electrode, keeping f/MWCNT additive and DNA sequence in electrolyte solution | breast cancer marker (5’-GTG TGT TCT CCT AGG TFG CTC CTRG-3’; 24-base fraction of the p53 gene) | DPV/141.2 pmol L\(^{-1}\) | solution containing the complementary sequence (5’-CAG AGC CAA CCT AGG AGA CAC CAC-3’) | n.r.                             | [41]      |
Table 1. Cont.

| Sensor                             | Modification Procedure                                                                 | Analyte(s)                      | Technique(s)/Detection Limit                                         | Application                      | Stability                  | Reference |
|------------------------------------|----------------------------------------------------------------------------------------|---------------------------------|-----------------------------------------------------------------------|----------------------------------|---------------------------|-----------|
| HIV-p24/MIP/MWCNT/GCE             | HIV-p24 crosslinking MIP (acylamide functional monomer, \(N,N'\)-methylenebisacrylamide as crosslinking agent and ammonium persulphate as initiator) immobilized on MWCNT/GCE | HIV-p24 protein                 | DPV/0.083 pg cm^{-2}                                                   | real human serum samples         | 98.6% after 10 days         | [42]     |
| MIP/MWCNT/Cu                      | MIP (itaconic acid monomer, ethylene glycol dimethacrylate cross-linker and α,α'-azobisobutyronitrile as initiator) on MWCNT modified Cu electrode | hemoglobin                      | potentiometry/1.0 μg mL^{-1}                                          | human bile juice and urine samples | 6 months without significant change in the electrode performance | [43]     |
| Cu-MP@polyethylenimine/MWCNT/GCE  | Cu-MP dispersed in polyethylenimine and dropped on MWCNT/GCE                          | amino acids, albumin and glucose | SWV and amperometry/0.10-0.37 μmol L^{-1} for the amino acids (L-cystine, L-histidine and L-serine), 1.2 mg mL^{-1} for albumin; and 182 nmol L^{-1} for glucose | pharmaceutical products and beverages | 7.7% RSD after 10 successive calibration plots using the same surface | [44]     |
| MIP/Au-NP/MWCNT/GCE               | Au-NP electrodeposited on MWCNT/GCE, and assembled with MIP (tetrabutylammonium perchlorate) | cholesterol                     | DPV/3.3 × 10^{-14} mol L^{-1}                                         | n.r.                             | 91.7% after one month     | [45]     |
| MWCNT/SPE                         | MWCNT films casted onto SPE                                                             | bilirubin                       | CV/9.4 μmol L^{-1}                                                     | n.r.                             | n.r.                      | [46]     |
| Grf-Ox@MWCNT/GCE                  | drop coating of Grf-Ox@MWCNT suspension on GCE                                         | catechol and dopamine           | CV/n.r                                                               | n.r.                             | n.r.                      | [47]     |
| Phenazine methosulfate/3-aminopheny/lorbic acid/MWCNT/GCE | drop coating of phenazine methosulfate and 3-aminophenyl boronic acid on MWCNT/GCE | NADH                            | amperometry/0.16 μmol L^{-1}                                          | human serum                      | 96.7% after five consecutive measurements | [48]     |
| HPU/β-CD/MWCNT®/GCE               | layer-by-layer of HPU, β-CD and composite film (MWCNT®/Nafion®) on GCE                | uric acid                       | amperometry/n.r                                                       | n.r.                             | n.r.                      | [49]     |
| Microorganisms                     |                                                                                        |                                 |                                                                       |                                  |                           |           |
| MWCNT®/Nafion®/GCE                | dip coating of composite suspension (MWCNT®/Nafion®) on GCE                           | Enterotoxigenic Escherichia coli F4 (K88) | SWV/6 × 10^{4} CFU mL^{-1}                                             | swine stool samples              | n.r.                      | [50]     |
| Pesticides                        |                                                                                        |                                 |                                                                       |                                  |                           |           |
| β-CD/MWCNT/GCE                    | β-CD and MWCNT composite suspension dropped on GCE                                    | dichlorophen                    | SWAdS/4.4 × 10^{-5} mol L^{-1}                                         | river water                      | 93.9% after one week      | [51]     |
| Fumed silica/acid-activated MWCNT/GCE | drop coating of a nanocomposite suspension (Fumed silica and acid-activated MWCNT) on GCE | clopyralid                      | DPV/0.8 nmol L^{-1}                                                   | urine, river water, sugar beet, wheat, and herbicide formulations (Placent and Leitrot) | 91% after three weeks     | [52]     |
| TiO₂-NP®/MWCNT/GCE                | TiO₂-NP®/MWCNT nanocomposite dropped on GCE                                           | diazinon                        | CV an SWV/3.0 nmol L^{-1}                                             | well and tap water               | 89% after 28 days         | [53]     |
| Nafion®/TiO₂-NP®/MWCNT®/carboxymethyl chitosan/GCE | Nafion® assembled on composite film (TiO₂-NP®/MWCNT®/carboxymethyl chitosan) previously immobilized on GCE | trichlorfon                     | DPV/4.0 × 10^{-7} mol L^{-1}                                          | apple, mushroom, and cucumber    | 98% after one week        | [54]     |
| MIP/Pt-NP@polyoxometalate@f-MWCNT/GCE | MIP (pyrrole in the presence of the analyte) assembled on hybrid film (Pt-NP@polyoxometalate@f-MWCNT) immobilized on GCE | simazine                        | DPV/2.0 × 10^{-11} mol L^{-1}                                         | wastewater samples               | 96.9% after 45 days       | [55]     |
Table 1. Cont.

| Sensor| Modification Procedure| Analyte(s)| Technique(s)/Detection Limit| Application| Stability| Reference |
|-------|------------------------|------------|-----------------------------|------------|----------|-----------|
| **Metallic cations** | | | | | | |
| BiF/Grf-Red/MWCNT/SPE | layer-by-layer of BiF, Gfr-Red and MWCNT on SPE (gold support) | Cd$^{2+}$ and Pb$^{2+}$ | SWV/0.6 ppb for Cd and 0.2 ppb for Pb | drinking water | n.r. | [56] |
| Mn$^{2+}$-imprinted polymer /IL@CTS@MWCNT/GCE | thermal immobilization of Mn$^{2+}$-imprinted polymer on composite layer (IL@CTS@MWCNT) dropped on GCE | Mn$^{2+}$ | SWAdSV/0.15 μmol L$^{-1}$ | wastewater | 94.8% after two weeks | [57] |
| β-NiO$_3$/MWCNT-modified CPE | electrodeposition of hybrid film of β-NiO$_3$ on MWCNT-modified CPE | Na$^+$ | SWV/9.86 × 10$^{-8}$ mol L$^{-1}$ | groundwater | practically constant signal for more than five hundred consecutive cycles | [58] |
| **Anions** | | | | | | |
| f-MWCNT/GCE | drop coating of f-MWCNT (COOH-functionalized structures) as suspension on GCE | SO$_3^{2-}$ and NO$_2^-$ | DPV/215 nmol L$^{-1}$ for SO$_3^{2-}$ and 565 nmol L$^{-1}$ for NO$_2^-$ | groundwater | ≥96.4% after one week | [59] |
| Ag-NP@MWCNT/GCE | drop coating of nanocomposite (Ag-NP@MWCNT) on GCE | BrO$_3^-$ | amperometry/n.r. | n.r. | n.r. | [60] |
| **Dyes** | | | | | | |
| Grf-Oxo@MWCNT/GCE | suspension of Grf-Oxo@MWCNT immobilized on GCE by drop coating | sunset yellow and tartarazine | LSV/0.025 μmol L$^{-1}$ for sunset yellow and 0.010 μmol L$^{-1}$ for tartarazine | orange juice | 89–93% after one month | [61] |
| Poly(crisal violet)/MWCNT/GCE | electropolymerization of crystal violet on MWCNT/GCE | luteolin | DPV/5.0 × 10$^{-9}$ mol L$^{-1}$ | Chrysanthemum samples | 93% after one month | [62] |
| **Gas/Vapor** | | | | | | |
| Hexa-decafluorinated zinc phthalocyanine @f-MWCNT/SPE (gold support) | drop coating of the composite (Hexa-decafluorinated zinc phthalocyanine@f-MWCNT) on SPE | Cl$_2$ | resistance/0.06 ppb | n.r. | n.r. | [63] |
| SbSI@CNTs/Au-microelectrode | ultrasonic bonding of SbSI@CNTs composite on Au-microelectrode | CO$_2$ | amperometry/n.r. | n.r. | n.r. | [64] |
| MWCNT@polyaniline/FTO | drop coating of MWCNT@polyaniline nanocomposite on FTO | methanol vapor | resistance/50 ppm | n.r. | the signal remained almost constant for up to 20 days | [65] |
| **Industrial by-products** | | | | | | |
| CuO-NP/MWCNT/GCE | electodeposition of CuO-NP on MWCNT/GCE | glycerol | amperometry/5.8 × 10$^{-6}$ g dm$^{-3}$ | biodiesel samples | n.r. | [66] |
| Au-NP/Gfr-Red@MWCNT/GCE | electodeposition of Au-NP on Gfr-Red@MWCNT/GCE | bisphenol A | DPV/1.0 × 10$^{-9}$ mol L$^{-1}$ | river water and shopping receipt samples | 98% after 30 days | [67] |
| Pd-NP/Gfr-Red@MWCNT/GCE | electodeposition of Pd-NP on Gfr-Red@MWCNT/GCE | hydrazine | amperometry/0.15 μmol L$^{-1}$ | tap water spiked with hydrazine | n.r. | [68] |
| Prussian blue/CTS@MWCNT/GCE | electodeposition of Prussian blue complex on GCE Modified with CTS@MWCNT nanocomposite | hydrogen peroxide | amperometry/0.10 μmol L$^{-1}$ | routine analysis in pure electrolyte | 90.5–92.6% after two weeks | [69] |

Au-NP: gold nanoparticles; Ag-NP: silver nanoparticles; Cu-MP: copper microparticles; CuO-NP: copper oxide nanoparticles; Pd-NP: palladium nanoparticles; CTS: chitosan; Co-Pht: cobalt phthalocyanine; IL: ionic liquid; HPUs: hydrothane polyurethane; β-CD: β-cyclodextrin; BiF: bismuth film; MIP: molecular imprinted polymer; MWCNT: multi-walled carbon nanotubes; f-MWCNT: functionalized multi-walled carbon nanotubes; 3D-Grf: three-dimensional graphene; Grf-Ox: graphene oxide; Grf-Red: reduced graphene; HIV-p24: retrovirus of the AIDS; GCE: glassy carbon electrode; SPE: screen-printed electrode; CPE: carbon paste electrode; FTO: fluorine doped thin oxide electrode; LSV: linear sweep voltammetry; CV: cyclic voltammetry; DPV: differential pulse voltammetry; SWV: square-wave voltammetry; ASV: adsorptive stripping voltammetry; SWAdSV: square-wave adsorptive stripping voltammetry; n.r.: no reported.
5. Final Remarks

MWCNT and their (nano)composites have been the origin for exciting and versatile sensing platforms due to their inherent advantages, namely large active surface area, electrocatalytic properties, high and fast electron-transfer, signal enlargement, reduction of the overpotential, chemical inertness, among others. Their incorporation into electrochemical sensors has been improving the electroanalytical performance of these devices and simultaneously widening their scope and range of applications. However, some limitations related to the high cost of production of high purity MWCNT have been restricting their large-scale and industrial utilization. Thus, improvements on the current synthetic routes and purification methods or/and development of novel low cost and effective techniques are clearly needed. In addition, comprehensive characterization of the toxicity of MWCNT is another requirement to expand their application to in vivo assays. These achievements will contribute to the construction of reliable and reproducible MWCNT-based electrochemical sensors enlarging sensors exploitation in real in vivo monitoring and in on-line manufacturing applications.

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References

1. Sudha, P.N.; Sangeetha, K.; Vijayalakshmi, K.; Barhoum, A. Nanomaterials history, classification, unique properties, production and market. In Emerging Applications of Nanoparticles and Architecture Nanostructures—Current Prospects and Future Trends; A Volume in Micro and Nano Technologies; Makhlouf, A.S.H., Barhoum, A., Eds.; Elsevier: Cambridge, MA, USA, 2018; pp. 341–384, ISBN 978-0-323-51254-1.
2. Soriano, M.S.; Zougagh, M.; Valcarcel, M.; Rios, Á. Analytical Nanoscience and Nanotechnology: Where we are and where we are heading. *Talanta* 2018, 177, 104–121. [CrossRef] [PubMed]
3. Adams, F.C.; Barbante, C. Nanoscience, nanotechnology and spectrometry. *Spectrochim. Acta Part B* 2013, 86, 3–13. [CrossRef]
4. Liu, J.; Liu, L.; Lu, J.; Zhu, H. The formation mechanism of chiral carbon nanotubes. *Physica B* 2018, 530, 277–282. [CrossRef]
5. Kurkowska, M.; Awietjan, S.; Kozera, R.; Jeziierska, E.; Boczkowska, A. Application of electroless deposition for surface modification of the multiwall carbon nanotubes. *Chem. Phys. Lett.* 2018, 702, 38–43. [CrossRef]
6. Zaporotskova, I.V.; Borozrina, N.P.; Parkhomenko, Y.N.; Kozhitov, L.V. Carbon nanotubes: Sensor properties. A review. *Mod. Electron. Mater.* 2016, 2, 95–105. [CrossRef]
7. Dumitrescu, I.; Unwin, P.R.; Macpherson, J.V. Electrochemistry at carbon nanotubes: Perspective and issues. *Chem. Commun.* 2009, 6886–6901. [CrossRef] [PubMed]
8. Hamada, N.; Sawada, S.-I.; Oshiyama, A. New one-dimensional conductors: Graphitic microtubules. *Phys. Rev. Lett.* 1992, 68, 1579–1581. [CrossRef] [PubMed]
9. Mao, J.; Wang, Y.; Zhu, J.; Yu, J.; Hu, Z. Thiol functionalized carbon nanotubes: Synthesis by sulfur chemistry and their multi-purpose applications. *Appl. Surf. Sci.* 2018, 447, 235–243. [CrossRef]
10. Xiao, Z.; Elke, J.; Reynolds, A.; Moten, R.; Zhao, X. The fabrication of carbon nanotube electronic circuits with dielectrophoresis. *Microelectron. Eng.* 2016, 164, 123–127. [CrossRef]
11. Su, L.; Wang, X.; Wang, Y.; Zhang, Q. Roles of carbon nanotubes in novel energy storage devices. *Carbon* 2017, 122, 462–474. [CrossRef]
12. Guo, Y.; Shen, G.; Sun, X.; Wang, X. Electrochemical aptasensor based on multiwalled carbon nanotubes and graphene for tetracycline detection. *IEEE Sens. J.* 2015, 15, 1951–1958. [CrossRef]

13. Liu, L.; Niu, Z.; Chen, J. Flexible supercapacitors based on carbon nanotubes. *Chin. Chem. Lett.* 2018, 29, 571–581. [CrossRef]

14. Parveen, S.; Kumar, A.; Husain, S.; Husain, M. Fowler–Nordheim theory of carbon nanotube based field emitters. *Phys. B Condens. Matter.* 2017, 505, 1–8. [CrossRef]

15. Hulanicki, A.; Glab, S.; Ingman, F. Chemical sensors: Definitions and classification. *Pure Appl. Chem.* 1991, 63, 1247–1250. [CrossRef]

16. Kim, S.N.; Rusling, J.F.; Papadimitrakopoulos, F. Carbon nanotubes for electronic and electrochemical detection of biomolecules. *Adv. Mater.* 2007, 19, 3214–3228. [CrossRef] [PubMed]

17. López-Lorente, Á.; Valcárcel, M. The third way in analytical nanoscience and nanotechnology: Involvement of nanotools and nanoanalytes in the same analytical process. *Trends Anal. Chem.* 2016, 75, 1–9. [CrossRef]

18. Harris, P.J. Engineering carbon materials with electricity. *Carbon* 2017, 122, 504–513. [CrossRef]

19. Abdalla, S.; Al-Marzouki, F.; Al-Ghamdi, A.A.; Abdel-Daim, A. Different technical applications of carbon nanotubes. *Nanoscale Res. Lett.* 2015, 10, 1–10. [CrossRef] [PubMed]

20. Park, S.; Vosguerchian, M.; Zhenan Bao, Z. A review of fabrication and applications of carbon nanotube film-based flexible electronics. *Nanoscale* 2013, 5, 1727–1752. [CrossRef] [PubMed]

21. Rezaee, S.; Ghaderi, A.; Boochani, A.; Solaymani, S. Synthesis of multiwalled carbon nanotubes on Cu-Fe nano-catalyst substrate. *Res. Phys.* 2017, 7, 3640–3644. [CrossRef]

22. Dhore, V.G.; Rathod, W.S.; Patil, K.N. Synthesis and characterization of high yield multiwalled carbon nanotubes by ternary catalyst. *Mater. Today Proc.* 2018, 5, 3432–3437. [CrossRef]

23. Monthioux, M.; Serp, P.; Flahaut, E.; Razafimananana, M.; Laurent, C.; Peigney, A.; Bacsa, W.; Broto, J.-M. Introduction to carbon nanotubes. In *Springer Handbook of Nanotechnology*, 2nd ed.; Bhushan, B., Ed.; Springer: Berlin, Germany, 2007; pp. 47–118, ISBN 3-540-29855-X.

24. Araga, R.; Sharma, C.S. One step direct synthesis of multiwalled carbon nanotubes from coconut shell derived charcoal. *Mater. Today* 2017, 188, 205–207. [CrossRef]

25. Rius, G.; Baldi, A.; Ziaie, B.; Atashbar, M.Z. Introduction to micro-/nanofabrication. In *Springer Handbook of Nanotechnology*, 4th ed.; Bhushan, B., Ed.; Springer: Berlin, Germany, 2017; pp. 51–86, ISBN 978-3-662-54355-9.

26. Yañez-Sedeño, P.; Pingarrón, J.M.; Riu, J.; Rius, F.X. Electrochemical sensing based on carbon nanotubes. *Trends Anal. Chem.* 2010, 29, 939–953. [CrossRef]

27. Bandaru, P.R. Electrical properties and applications of carbon nanotube structures. *J. Nanosci. Nanotechnol.* 2007, 7, 1–29. [CrossRef]

28. Ahammad, A.J.S.; Lee, J.-J.; Rahman, M.A. Electrochemical sensors based on carbon nanotubes. *Sensors* 2009, 9, 2289–2319. [CrossRef] [PubMed]

29. Mao, A.; Li, H.; Yu, L.; Hu, X. Electrochemical sensor based on multi-walled carbon nanotubes and chitosan-nickel complex for sensitive determination of metronidazole. *J. Electroanal. Chem.* 2017, 799, 257–262. [CrossRef]

30. Holanda, L.F.; Ribeiro, F.W.P.; Sousa, C.P.; Casciano, P.N.S.; De Lima-Neto, P.; Correia, A.N. Multi-walled carbon nanotubes-cobalt phthalocyanine modified electrode for electroanalytical determination of acetaminophen. *J. Electroanal. Chem.* 2016, 772, 9–16. [CrossRef]

31. Montes, R.H.O.; Lima, A.P.; Cunha, R.R.; Guedes, T.J.; Dos Santos, W.T.P.; Nosso, E.; Richter, E.M.; Munoz, R.A.A. Size effects of multi-walled carbon nanotubes on the electrochemical oxidation of propionic acid derivative drugs: Ibuprofen and naproxen. *J. Electroanal. Chem.* 2016, 775, 9–16. [CrossRef]

32. Pavinatto, A.; Mercante, L.A.; Leandro, C.S.; Mattoso, L.H.C.; Correa, D.S. Layer-by-Layer assembled films of chitosan and multi-walled carbon nanotubes for the electrochemical detection of 17α-ethinylestradiol. *J. Electroanal. Chem.* 2015, 755, 215–220. [CrossRef]

33. Chen, L.; Li, K.; Zhu, H.; Meng, L.; Chen, J.; Li, M.; Zhu, Z. A chiral electrochemical sensor for propanolol based on multi-walled carbon nanotubes/ionic liquids nanocomposite. *Talanta* 2013, 105, 250–254. [CrossRef] [PubMed]

34. Hundari, F.F.; Soza, J.C.; Zanoni, M.V.B. Adsorptive stripping voltammetry for simultaneous determination of hydrochlorothiazide and triamterene in hemodialysis samples using a multi-walled carbon nanotube-modified glassy carbon electrode. *Talanta* 2018, 179, 652–657. [CrossRef] [PubMed]

35. Zhai, H.; Wang, H.; Wang, S.; Chen, Z.; Wang, S.; Zhou, Q.; Fan, Y. Electrochemical determination of mangiferin and icariin based on Au-AgNPs/MWNTs-SGSs modified glassy carbon electrode. *Sensors Actuators B Chem.* 2018, 255, 1771–1780. [CrossRef]
36. Yang, X.; Yu, X.; Heng, Y.; Wang, F. Facile fabrication of 3D graphene-multi walled carbon nanotubes network and its use as a platform for natamycin detection. J. Electroanal. Chem. 2018, 816, 54–61. [CrossRef]

37. Deng, K.; Liu, X.; Li, C.; Hou, Z.; Huang, H. An electrochemical omeprazole sensor based on shortened multi-walled carbon nanotubes-Fe₃O₄ nanoparticles and poly(2,6-pyridinedicarboxylic acid). Sens. Actuators B Chem. 2017, 253, 1–9. [CrossRef]

38. Khaled, E.; Khalil, M.M.; El Aziz, G.M.A. Calixarene/carbon nanotubes based screen printed sensors for potentiometric determination of gentamicin sulphate in pharmaceutical preparations and spiked surface water samples. Sens. Actuators B Chem. 2017, 244, 876–884. [CrossRef]

39. Ba˘kaya, G.; Yıldız, Y.; Savk, A.; Okyay, T.O.; Eri˘s, S.; Sert, H.; Şen, F. Rapid, sensitive, and reusable detection of glucose by highly monodisperse nickel nanoparticles decorated functionalized multi-walled carbon nanotubes. Biosens. Bioelectron. 2017, 91, 728–733. [CrossRef] [PubMed]

40. Wang, D.; Huang, B.; Liu, J.; Guo, X.; Abudukeyoumu, G.; Zhang, Y.; Ye, B.-C.; Li, Y. A novel electrochemical sensor based on Cu@Ni/MWCNTs nanocomposite for simultaneous determination of guanine and adenine. Biosens. Bioelectron. 2018, 102, 389–395. [CrossRef] [PubMed]

41. Li, J.; Lee, E.-C. Functionalized multi-wall carbon nanotubes as an efficient additive for electrochemical DNA sensor. Sens. Actuators B Chem. 2017, 239, 652–659. [CrossRef]

42. Ma, Y.; Shen, X.-L.; Zeng, Q.; Wang, H.-S.; Wang, L.-S. A multi-walled carbon nanotubes based molecularly imprinted polymers electrochemical sensor for the sensitive determination of HIV-p24. Talanta 2017, 164, 121–127. [CrossRef] [PubMed]

43. Anirudhan, T.S.; Alexander, S. A potentiometric sensor for the trace level determination of hemoglobin in real samples using multiwalled carbon nanotube based molecular imprinted polymer. Eur. Polym. J. 2017, 97, 84–93. [CrossRef]

44. Gutierrez, F.A.; Rubianes, M.D.; Rivas, G.A. Electrochemical sensor for amino acids and glucose based on glassy carbon electrodes modified with multi-walled carbon nanotubes and copper microparticles dispersed in polyethyleneimine. J. Electroanal. Chem. 2016, 765, 16–21. [CrossRef]

45. Ji, J.; Zhou, Z.; Zhao, X.; Sun, J.; Sun, X. Electrochemical sensor based on molecularly imprinted film at Au nanoparticles-carbon nanotubes modified electrode for determination of cholesterol. Biosens. Bioelectron. 2015, 66, 590–595. [CrossRef] [PubMed]

46. Taurino, I.; Van Hooft, V.; De Micheli, G.; Carrara, S. Superior sensing performance of multi-walled carbon nanotube-based electrodes to detect unconjugated bilirubin. Thin Solid Films 2013, 548, 546–550. [CrossRef]

47. Sharma, V.V.; Gualandi, I.; Vlamidis, Y.; Tonelli, D. Electrochemical behavior of reduced graphene oxide and multi-walled carbon nanotubes composites for catechol and dopamine oxidation. Electrochim. Acta 2017, 246, 415–423. [CrossRef]

48. Li, J.; Sun, Q.; Mao, Y.; Bai, Z.; Ning, X.; Zheng, J. Sensitive and low-potential detection of NADH based on boronic acid functionalized multi-walled carbon nanotubes coupling with an electrocatalysis. J. Electroanal. Chem. 2017, 794, 1–7. [CrossRef]

49. Wayu, M.B.; DiPasquale, L.T.; Schwarzmann, M.A.; Gillespie, S.D.; Leopold, M.C. Electropolymerization of β-cyclodextrin onto multi-walled carbon nanotube composite films for enhanced selective detection of uric acid. J. Electroanal. Chem. 2016, 783, 192–200. [CrossRef]

50. Tarditto, L.V.; Arévalo, F.J.; Zon, M.A.; Ovando, H.G.; Vettorazzi, N.R.; Fernández, H. Electrochemical sensor for the determination of enterotoxigenic Escherichia coli in swine feces using glassy carbon electrodes modified with multi-walled carbon nanotubes. Microchem. J. 2016, 127, 220–225. [CrossRef]

51. Sipa, K.; Brycht, M.; Leniart, A.; Urbaniak, P.; Nosal-Wiercińska, A.; Palecz, B.; Skrzypek, S. β-Cyclodextrins incorporated multi-walled carbon nanotubes modified electrode for the voltammetric determination of the pesticide dichlorphen. Talanta 2018, 176, 625–634. [CrossRef] [PubMed]

52. Özcan, A.; Gürbüz, M. Development of a modified electrode by using a nanocomposite containing acid-activated multi-walled carbon nanotube and fumed silica for the voltammetric determination of clopyralid. Sens. Actuators B Chem. 2018, 255, 262–267. [CrossRef]

53. Ghodsi, J.; Rafati, A.A. A voltammetric sensor for diazinon pesticide based on electrode modified with TiO₂ nanoparticles covered multi walled carbon nanotube nanocomposite. J. Electroanal. Chem. 2017, 807, 1–9. [CrossRef]
54. Wei, X.-P.; Luo, Y.-L.; Xu, F.; Chen, Y.-S.; Yang, L.H. In-situ non-covalent dressing of multi-walled carbon nanotubes@titanium dioxides with carboxymethyl chitosan nanocomposite electrochemical sensors for detection of pesticide residues. *Mater. Des.* **2016**, *111*, 445-452. [CrossRef] [PubMed]

55. Ertan, B.; Eren, T.; Ermiş, I.; Saral, H.; Atar, N.; Yola, M.L. Sensitive analysis of simazine based on platinum nanoparticles on polyoxometalate/multi-walled carbon nanotubes. *J. Colloid. Interface Sci.* **2016**, *470*, 14-21. [CrossRef] [PubMed]

56. Firmino, M.L.M.; Morais, S.; Correia, A.N.; De Lima-Neto, P.; Carvalho, F.A.O.; Castro, S.S.L.; Oliveira, T.M.B.F. Sensor based on β-NiO hybrid film/multi-walled carbon nanotubes composite electrode for groundwater salinization inspection. *Chem. Eng. J.* **2017**, *323*, 47-55. [CrossRef]

57. Sudha, V.; Kumar, S.M.S.; Thangamuthu, R. Simultaneous electrochemical sensing of sulphite and nitrite on acid-functionalized multi-walled carbon nanotubes modified electrodes. *J. Alloys Compl.* **2018**, *749*, 990-999. [CrossRef]

58. Li, Q.; Zhang, Q.; Ding, L.; Zhou, D.; Cui, H.; Wei, Z.; Zhai, J. Synthesis of silver/multi-walled carbon nanotubes composite and its application for electrocatalytic reduction of bromate. *Chem. Eng. J.* **2015**, *217*, 28-33. [CrossRef]

59. Xuan, X.; Park, J.Y. A miniaturized and flexible cadmium and lead ion detection sensor based on micro-patterned reduced graphene oxide/carbon nanotube/bismuth composite electrodes. *Sens. Actuators B Chem.* **2018**, *255*, 1220-1227. [CrossRef]

60. Roushani, M.; Saedi, Z.; Hamdi, F.; Dizajdizi, B.Z. Preparation an electrochemical sensor for detection of manganese (II) ions using glassy carbon electrode modified with multi walled carbon nanotube-chitosan-ionic liquid nanocomposite decorated with ion imprinted polymer. *J. Electroanal. Chem.* **2017**, *804*, 1-6. [CrossRef]

61. Li, Q.; Zhang, Q.; Ding, L.; Zhou, D.; Cui, H.; Wei, Z.; Zhai, J. Synthesis of silver/multi-walled carbon nanotubes composite and its application for electrocatalytic reduction of bromate. *Chem. Eng. J.* **2015**, *217*, 28-33. [CrossRef]

62. Qu, X.; Lu, L.; Leng, J.; Yu, Y.; Wang, W.; Jiang, M.; Bai, L. An enhanced electrochemical platform based on graphene oxide and multi-walled carbon nanotubes nanocomposite for sensitive determination of sunset yellow and tartrazine. *Food Chem.* **2019**, *190*, 889-895. [CrossRef] [PubMed]

63. Tang, J.; Jin, B. Poly (crystal violet)-Multi-walled carbon nanotubes modified electrode for electroanalytical determination of luteolin. *J. Electroanal. Chem.* **2016**, *780*, 46-52. [CrossRef]

64. Sharma, A.K.; Mahajan, A.; Bedi, R.K.; Kumar, S.; Debnath, A.K.; Aswal, D.K. Non-covalently anchored multi-walled carbon nanotubes with hexa-decafluorinated zinc phthalocyanine as ppb level chemiresistive chlorine sensor. *Appl. Surf. Sci.* **2018**, *427*, 202-209. [CrossRef]

65. Bora, A.; Mohan, K.; Pegu, D.; Gohain, C.B.; Dolui, S.K. A room temperature methanol vapor sensor based on highlyconductive carboxylated multi-walled carbon nanotube/polyanilinenanotube composite. *Sens. Actuators B Chem.* **2017**, *233*, 255-266. [CrossRef]

66. Arévalo, F.J.; Osuna-Sánchez, Y.; Sandoval-Cortés, J.; Tocco, A.D.; Granero, A.M.; Robledo, S.N.; Zon, M.A.; Vettorazzi, N.R.; Martínez, J.L.; Segura, E.P.; et al. Development of an electrochemical sensor for the determination of glycerol based on glassy carbon electrodes modified with a copper oxide nanoparticles/multiwalled carbon nanotubes/pectin composite. *Sens. Actuators B Chem.* **2017**, *244*, 949-957. [CrossRef]

67. Wang, C.; Zhang, K.; Zhang, N.; Zhang, L.; Wang, H.; Xu, J.; Shi, H.; Zhuo, X.; Qin, M.; Wu, X. A simple strategy for fabricating a prussian blue/chitosan/carbon nanotube composite and its application for the sensitive determination of hydrogen peroxide. *Micro Nano Lett.* **2016**, *12*, 23-26. [CrossRef]