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Review paper

Conducting polymer functionalized graphene-based electrochemical sensors for sensing pollutants in water

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Abstract

Recent trends in electrochemical sensors based on conducting polymer functionalized graphene for the detection of pollutants in water are highlighted in this review. Graphene has been the subject of a lot of scientific research to be composited with conducting polymers. Researchers are interested in graphene and its variants because they have a lot of good qualities, like good electrical and mechanical properties and very high surface area. With this review, we intend to arouse interest in the important topic of graphene and conducting polymer nanocomposite that is making significant advances in electrochemical sensing, especially for sensing pollutants in water.

Keywords

Composites, voltammetry; sensing properties; water pollution

Introduction

Water is necessary for all living things to survive, although different species use it for different purposes. For example, water is an essential component of respiration for all oxygen-dependent species and serves as a solvent, temperature buffer, metabolic product, and habitat. However, water pollution has become one of the most pressing environmental problems of our time due to increasing industrialization and urbanization. Figure 1 shows the sources of emerging water pollution that may be of concern. The introduction of toxic substances into water bodies (*e.g.*, lakes, rivers, and oceans) results in water pollution, where the substances either dissolve, float, or accumulate and affect water quality. Not only is this harmful to aquatic ecosystems, but the pollutants that leach into groundwater also contaminate domestic water supplies, where water is used for a variety of activities, including drinking. Therefore, it is important to limit human exposure to contaminants through proper water quality monitoring.

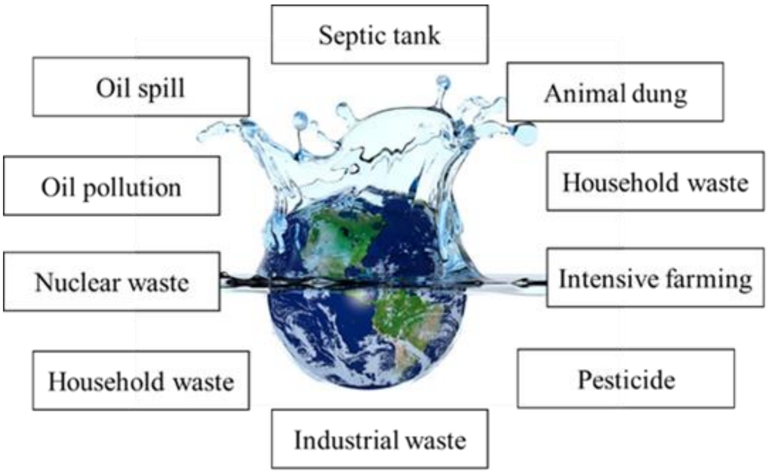

Figure 1. *Sources of emerging water contaminants that could be of concern*

World health organization (WHO) has continuously revised the guideline values for all water quality measures since 1983 (Table 1) [1]. The hazardous substances that accumulate in the human body through water are degraded only slowly. Therefore, limiting human exposure to toxins is critical and should be achieved through comprehensive water quality monitoring. Detection of water contaminants has traditionally been performed with hanging mercury drop electrodes or mercury-modified electrodes, as replacement of the mercury drop is sufficient to restore a pristine surface [2]. However, due to new regulations and the high toxicity of mercury, new alternatives for its replacement are being investigated. There are some reports of work using gold nanoparticles, microelectrodes, and also cathode stripping potential to detect heavy metals. Unfortunately, it is difficult to detect water pollutants using these methods [3,4].

Table 1. *Maximum permissible concentrations for water quality testing according to WHO* [1]

Parameter	Maximum permissible concentration
Antimony	20 ppb
Arsenic	10 ppb
Benzene	10 ppb
Chloramines	3 ppm
Chlorine	5 ppm
Chromium	50 ppb (total)
Copper	2 ppm
Fluoride	1.5 ppm
Lead	10 ppb
Mercury	6 ppb (inorganic)
Nitrate	50 ppm
Nitrite	3 ppm
Selenium	40 ppb
Toluene	0.7 ppm
Uranium	30 ppb

Recently, the electrochemical approach to water contaminant analysis has been gaining popularity due to its ease of use, low cost, rapid analysis, and high sensitivity [5,6]. In the past, electrochemical sensors have been used to monitor oxygen concentration in the industry since the 1950s, when they were first introduced [7]. At that time, the monitoring of hazardous gases and fuels in confined spaces was mandated by labour legislation, which led to an explosion in research on electrochemical sensors with high selectivity. Leland C. Clark [8] introduced an oxygen sensor that consisted of an oxygen-permeable membrane separating two electrodes in a cell, producing a current that was inversely proportional to the concentration of oxygen in the sample. Since the invention of Clark's electrochemical oxygen sensor, a variety of other sensors have followed. Despite their commercial success, Clark's oxygen sensors produce an unstable electrical current reading due to contamination or corrosion of the working electrode surface, which requires frequent recalibration of the oxygen analyzers, making them unsuitable for routine use [8].

In addition, conventional electrochemical sensors usually require a catalytic enzyme to detect impurities. With an enzyme sensor, one can achieve higher sensitivity, selectivity, and stability [9], but it also has some limitations, including enzyme denaturation and limited stability, and a difficult purification process due to weak immobilization of the enzyme on electrodes [10]. Therefore, scientists are constantly looking for ways to improve them, for example, by developing enzyme-free sensors. Non-enzymatic sensors for the detection of water contaminants that do not involve enzymes seem to be viable alternatives, but they still need significant improvements in sensitivity and selectivity before being used commercially. This is why the development of non-enzymatic sensors is so important. Therefore, scientists are investigating the aspect of more sensitive materials with novel morphologies while maintaining all the performance criteria of the sensor.

While the flexibility of polymers makes them attractive for a variety of applications, they are often undesirable for conductive applications because most polymers are insulating. In terms of their electrical and optical properties, organic polymers have comparable characteristics to inorganic semiconductors. The most important and distinctive feature of a conducting polymer is alternating single and conjugated double bonds along the main chain, with the highly delocalized, polarized, and electron-dense π-bonds providing electrical and optical properties [11]. In 1977, Shrikawa, Heeger, and MacDiarmid [12] first proposed that conjugated polymers are tailored to transmit electricity. Their study involved the removal of an electron from a delocalized bonding configuration by a halogen dopant, resulting in the formation of a hole. An electron then jumps to an adjacent site and fills the hole, creating another and allowing a charge to flow along the polymer chain. The structural properties of some conducting polymers are shown in Figure 2, including poly(3,4-ethylenedioxythiophene) (PEDOT), polyacetylene (PAC), polypyrrole (PPy), polythiophene, polyaniline (PANI), poly(p-phenylenevinylene) (PPV), polyethylene (PE) and polypropylene (PP).

Carter *et al*. [13] developed nanocomposites of elastomer-reinforced polymers with exfoliated layered silicate fillers as early as 1950, and a study published over forty years later found that mechanical properties of a clay-filled nylon-6 matrix were improved [14]. This triggered a great interest in nanocomposites both in academia and industry. Recently, there has been growing interest in functionalizing conductive polymers with nanofiller-based materials to provide new or improved properties for sensor development [15,16]. The polymer matrix filled with a variety of nanofillers, such as spherical nanoparticles, is the most basic nanocomposite system, while all kinds of anisotropy-inducing fillers, such as graphene, graphene oxide, and other graphene derivatives find their way into polymer nanocomposites.

A study by Marsden *et al*. [17] proposed conductive composites prepared by infusing the polymer matrix with graphene. When the filler loading approaches the percolation threshold (pc), the conductivity of the composite increases rapidly and the conductivity plot as a function of loading takes a typical S-shape indicating three different states: insulating, permeable and conductive.

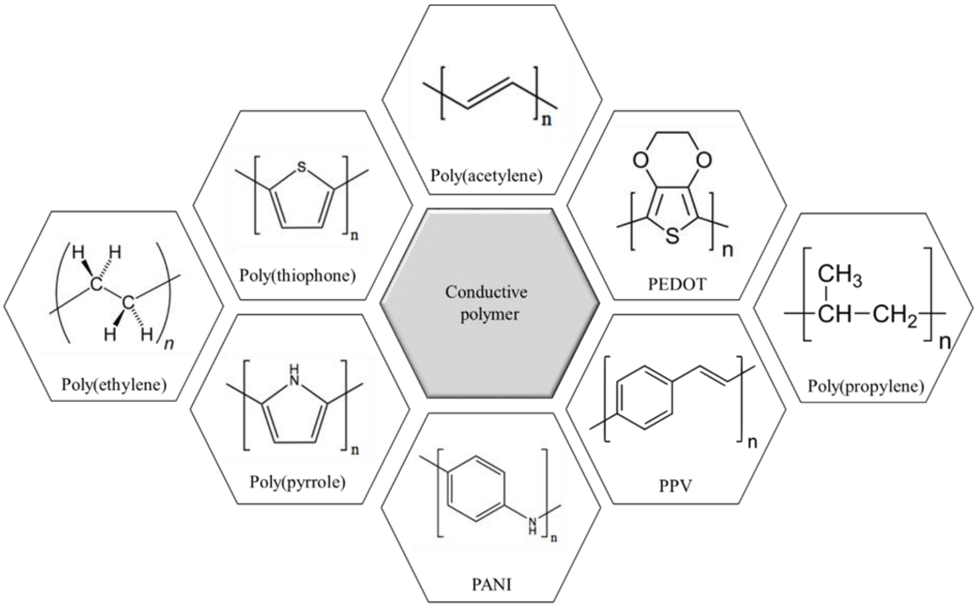

Figure 2.*-Structural properties of numerous conducting polymers*

Thus, the polymer remains insulating at minimum loading. A conductive network forms when the filler content reaches the percolation threshold. A robust network forms and the conductivity saturates with increasing loading [17]. Conducting polymer-functionalized graphene nanocomposites are more promising to improve the properties of conducting polymers, and the use of graphene and its derivatives with excellent properties has attracted the attention of researchers [18-20]. Novoselov *et al*. discovered graphene in 2004 [21], and it is a honeycomb-shaped, two-dimensional (2-D), and atomically dense material composed of sp^2 carbon atoms. Compared to carbon nanotubes, polymer molecules can easily reach the surface of 2-D graphene. As a result, more filler material can be incorporated into the graphene matrix and the final conductivity values increase. Table 2 shows someof other important physicochemical properties of graphene.

Table 2. *Some of the important physicochemical properties of graphene*

Physiochemical properties	Estimated value	Reference
Large specific surface area	~2630 m^{2}g^{-1}	[22]
Excellent electrical conductivity	~1738 Siemens/m	[23]
Strong mechanical strength	Young's modulus ~1100 GPa	[24]
Good thermal conductivity	~5000 W m^{-1} K^{-1}	[25]
Mobility of charge carriers	200000 cm^2 V^{-1} s^{-1}	[26]
Ease of functionalization	π-π interaction and electrostatic interaction	[27]
Band gap	zero	[28]

The carbon atoms in graphene have a total of six electrons, two of which are in the inner shell, while four electrons are scattered in the outer shell with chemical bonding orbitals 1s^{2}2s^{2}2p^2 (Figure 3a). The two electrons in the 1s core orbital of the honeycomb crystal structure remain in this orbital, while the remaining electrons form sp^2 bonds with three other orbitals and one p$_z$ orbital and also hybridize with each other (Figure 3b). The free electron is held in the p$_z$ orbital, which is located above the plane and is thus responsible for the formation of the π-bond [29]. It is this overlap of p electrons that gives graphene its unique electronic properties, which are controlled by the bonding and counter-bonding of atoms (Figure 3c). In addition, the honeycomb structure of graphene can also be characterized as a triangular lattice, with each unit cell containing two atoms A and B as studied by Castro Neto *et al.* [30]. The sublattices A and B are connected by basis vectors in graphene (a1, a2).

The Dirac points are two unequal sites labeled K and K' at the transition of the Brillouin zone of graphene. When the valence and conduction bands cross in space, the Dirac point is reached [30].

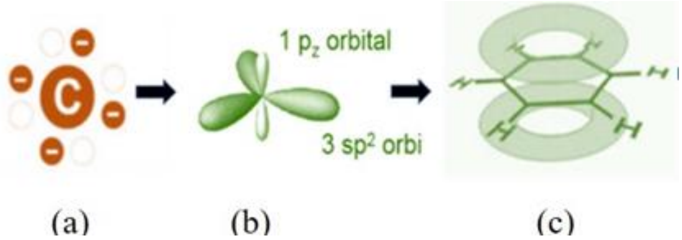

Figure 3. *(a-c) Fundamental property of graphene's bonding (with ©permission from [29])*

Analysis of the available literature shows that the surface of graphene can be easily functionalized while maintaining the quality of electron transport. This is of great importance in the field of water quality detection, as it allows selectivity towards the analyte of interest [31-34]. The use of graphene-based materials as nanofillers in polymers has the potential to take advantage of the beneficial properties of graphene but also to reduce the cost and speed up the production process of the composite. It is also possible that the polymer matrix, on the other hand, may have attractive properties such as functional groups or molecular imprinting that are of importance. This review article provides an overview of recent research and methods for the construction of electrochemical sensors based on conductive polymer-functionalized graphene for the detection of water pollutants over the past seven years. For the reader's convenience, the detection mechanisms of electrochemical sensors based on conductive polymer-functionalized graphene materials are briefly explained. Then, a series of methods for preparing nanocomposite materials of graphene and conducting polymers, including covalent and noncovalent functionalization, are discussed. Nanocomposites of graphene and conducting polymers have been shown to improve the performance of electrochemical sensors in a variety of target samples.

Figure 4 illustrates how the number of publications dealing with conductive polymer-functionalized graphene electrochemical sensors has increased from 706 in 2016 to 2,483 in 2021 and 2,470 in 2022 (ScienceDirect), showing the increasing importance of these nanocomposites. Table 3 provides a list of review articles on conductive polymers and carbon-based sensors for the detection of contaminants in water.

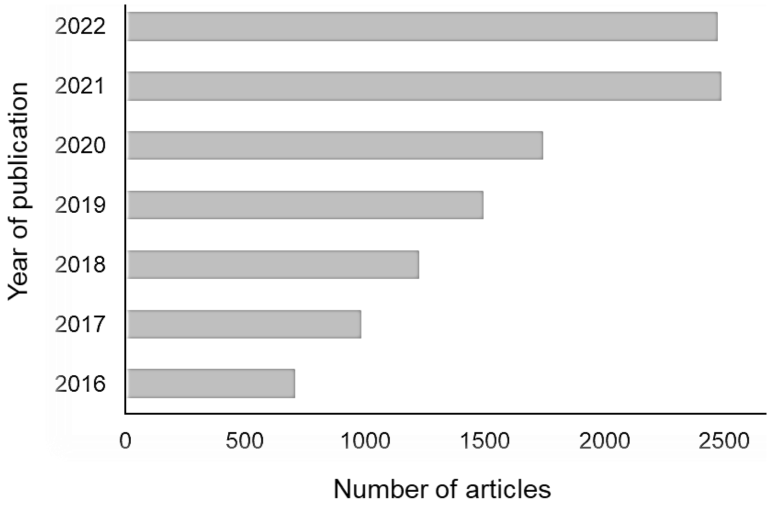

Figure 4. *Histogram illustrating the annual number of scientific articles published in the last seven years (research published on March 18, 2022 in 'Science Direct' with graphene-conducting polymer composite electrochemical sensor)*

Table 3. *List of review papers on conducting polymer and graphene-based electrochemical sensors for sensing pollutants in water*

Year of publication	Title	Main emphasis	Ref.
2021	A review of nanocomposite-modified electrochemical sensors for water quality monitoring	Surface modification of electrodes	[33]
2021	Electrochemical sensors based on conducting polymers for the aqueous detection of biologically relevant molecules	Conducting polymer	[34]
2020	Review—Graphene-Based Water Quality Sensors.	Graphene	[31]
2020	Nanocomposites (conducting polymer and nanoparticles) based electrochemical biosensor for the detection of environment pollutant: Its issues and challenges.	Conducting polymer and nanoparticles	[32]
2020	Recent trends of micro and nanostructured conducting polymers in health and environmental applications	Nanostructured conducting polymers	[35]
2019	Application of graphene-based materials for detection of nitrate and nitrite in water - a review	Graphene-based nanocomposites	[36]
2019	Polymer-based electrochemical sensing platform for heavy metal ions detection-a critical review	Polymers modified electrodes	[37]
2018	Composites based on conducting polymers and carbon nanomaterials for heavy metal ions sensing (review)	Organic conducting polymers and carbon nanotubes	[38]

A thorough analysis of the existing literature reveals a gap in knowledge regarding the combination of graphene and conductive polymer as an electrochemical nanocomposite for sensing. According to studies, the combination of graphene and conducting polymers can improve the selectivity and other important sensing parameters of electrochemical sensors, which could be due to various factors such as synergistic and geometric effects. In this article, we first review the fabrication and sensing performance of electrochemical graphene sensors functionalized with conducting polymers, which are used to detect pollutants in water.

Detection mechanism of electrochemical sensors based on conductive polymer functionalized graphene nanocomposites

A sensor is a device that detects and responds to signals. This signal must be some type of energy, such as heat, light, motion, or electrochemical reaction. A sensor will convert one or more of these signals as soon as it detects them [39]. Electrochemical sensors are gaining popularity among chemical sensors because they use an electrode as a transducer element in the presence of an analyte. Electrochemical sensor systems offer analytical techniques that are fast, accurate, selective, sensitive, and easy to use. These sensor systems are effective and suitable for detecting and monitoring contaminants in environmental samples because electrochemical analysis requires only a small amount or volume of sample, and no preparatory steps.

In electrochemical reactions, both current and voltage play a role, as well as potential and resistance. There are three types of electrochemical sensors: potentiometers, amperometers, and conductometers [40]. Table 4 lists some of the most common electrochemical processes and electrical signals they produce. At the potentiometric sensor interface, the electrode or membrane potential is recorded, and information about the composition of a sample can be obtained from the potential difference between the two electrodes. In an amperometric sensor, electroactive species can be oxidized or reduced by applying a voltage between the reference and working electrodes and recording the resulting current. Conductometric sensors, on the other hand, are used to measure conductivity at various frequencies. Coulometry and capacitive approaches, for example, derive their results from electric current and resistance [41].

Table 4. *Electrochemical methods, electrical properties, and units of measurement*

Electrochemical methods	Monitored electrical property
Potentiometry	Potential difference, V
Conductometry	Resistance, Ω
Amperometry and voltammetry	Current as a function of applied potential, A
Coulometry (Q)	Current as a function of time ($Q = I \cdot s$), A·s
Capacitance (C)	Potential load ($C = Q / V$), F

When the chemical reactions of a target species occur on electrodes, electrochemical sensors convert the chemical reactions into electrical signals. Electrochemical sensors consist of two or three electrodes, depending on the device. In a three-electrode cell, as shown in Figure 5, each electrode serves a specific purpose [42]. The reaction of interest takes place at the working electrode, which in this case, involves the reference electrode. Materials for the working electrode, such as platinum, gold, and/or carbon, have a significant impact on the performance of an amperemetric sensor. The reference electrode is responsible for maintaining a constant potential throughout the amperometric experiment [43]. Silver/silver chloride (Ag/AgCl) is the most practical reference electrode and is commonly used in an electrochemical sensor. The potential of the reference electrode is stable, reproducible, and can be calculated thermodynamically. The maximum temperature at which this type of electrode can function is about 130 °C [44].

The current flow is provided by the counter electrode, which has the opposite sign of the working electrode. The counter electrode is reduced when the working electrode undergoes oxidation and vice versa. However, this does not affect the response of the working electrode. The charge flowing through the counter electrode is always the same as at the working electrode [45]. Platinum is commonly used as a counter electrode for electrochemical sensors due to its good conductivity. In addition, platinum typically releases hydrogen or oxygen as a counter electrode in an aqueous system. This hydrogen bubbling does not lead to the dissolution of species in the electrolyte that could affect the working electrode [46]. Table 5 shows the list of conductive polymer functionalized graphene and their derivatives together with their performances in electrochemical sensors for the detection of pollutants in water.

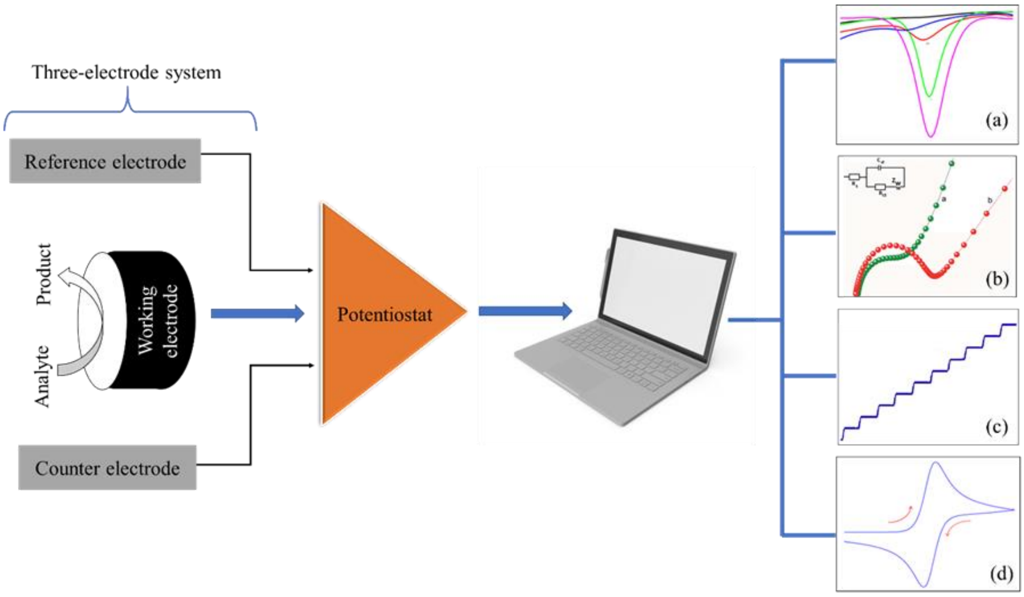

Figure 5. *Typical electrochemical measurement setup with three electrodes, a working electrode, a reference electrode, and a counter electrode for (a) square wave anodic strip voltammetry (SWASV), (b) electrochemical impedance spectroscopy (EIS), (c) amperometric, and (d) cyclic voltammetry (CV)*

Table 5. *List of graphene functionalized with conducting polymers and its derivatives and their performances in electrochemical sensors for detection of pollutants in water*

Electrode matrix	Detection technique	Linear range, µM	Detection limit, µM	Analyte	Ref.
pGO/PPy	DPSV	1 to 100	0.05	Cd^{2+}	[47]
3DGO-Py10	SWASV	5 to 400	3.6	Cd^{2+}	[48]
PANI@GO/Ag	-	10^5 to 10^2	10	Cd^{2+}	[49]
PoPD/ERGO/GCE	SWASV	10^{-3} to 50×10^{-3}	0.13×10^{-3}	Cd^{2+}	[50]
Fe_3O_4-GO-PANI	-	0.01 to 0.15	3.6×10^{-3}	Cd^{2+}	[51]
rGO-PANi-HBr	DPV	0.01 to 0.18 0.01 to 0.23	7.3×10^{-3} 6.5×10^{-3}	Cd^{2+} Pb^{2+}	[52]
PA/PPy/GO	DPV	5 to 150	2.13 0.41	Cd^{2+} Pb^{2+}	[53]
rGO/Ala/PANI	SWASV	$0.1\text{-}8 \times 10^{-5}$	3×10^{-5} 4.5×10^{-5} 6.3×10^{-5}	Cd^{2+} Pb^{2+} Cu^{2+}	[54]
PANI-GO-APTES	LSV	0.01 to 0.4	0.0053	Pb^{2+}	[55]
PPY-rGO	SWASV	5×10^{-3} to 0.75	4.7×10^{-5}	Pb^{2+}	[56]
PPy-rGO	SWASV	5×10^{-4} to 0.45	3×10^{-4}	Pb^{2+} Cd^{2+} Cu^{2+} Hg^{2+}	[57]
PGMGPE	CV	0.02 to 0.045 and 0.05 to 0.0012 0.015 to 0.0015	0.8 6.6	Pb^{2+} Hg^{2+}	[58]
polyPATT-GO/GCE	CC	1.0 - 10000.0 (ppb)	0.08 (ppb) 0.20 0.05 0.09 0.10	Cd^{2+} Pb^{2+} Zn^{2+} Cu^{2+} Hg^{2+}	[59]
EDTA_PANI/GO	DPSV	1 to 30 (ppb)	0.612 (ppb)	Hg^{2+}	[60]
PEDOT/GO/GCE	DPSV	0.01 - 3.0	2.78×10^{-3}	Hg^{2+}	[61]
p-NP-MIP-PANI/GO	CV	$6 \times 10^{-5}\text{-}14 \times 10^{-5}$	2×10^{-5}	p-nitrophenol	[62]
GCE-PANi-G-ITN	DPV	0.03×10^{-3} (i_{pa}) 0.01×10^{-4} (i_{pc})	0.0052 0.0024	4-nitrophenol	[63]
GO-PANI-AuNPs	amperometric	0.5 - 240 and 240 - 258	0.17	nitrite	[64]
GCE/RGO/PPy/NR	CV	5×10^3 - 2×10^5	275	nitrite	[65]
CG/PPy/CS/GCE	DPV	0.2 - 1000	0.02	nitrite	[66]
rGO/AgNPs/poly(PyY)	amperometric	0.1-1000	0.012	nitrite	[67]
AgNPs@PANI/rGO	DPV	2.7 – 24.4 1.0 – 28.2	0.077 0.056	sulfite nitrite	[68]
GONRs + PEDOT:PSS	amperometric	0.05 – 16.55 0.05 – 16.55 0.05 – 16.55 0.05 – 16.55	0.041 0.030 0.011 0.018	ascorbic acid uric acid dopamine nitrite	[69]
AgNPs@PPy/rGO	DPV	0.6 – 6.6	0.019 0.021	hydrazine nitrite	[70]
Gr-PANi	current-potential	10 – 200	5.880	urea	[71]

Song *et al.* [47] described the concept of the Cd(II) sensor. First, Cd^{2+} ions in an aqueous solution were simultaneously absorbed by the porous GO/PPy electrode and the carboxyl group graphene oxide. Second, Cd^{2+} was reduced to Cd under stripping voltage on the electrode surface. After reduction, cadmium was finally oxidized to Cd^{2+} *via* carboxyl groups, pGO/PPy and PPy by differential pulse voltammetry. A heavy metal sensor based on the pGO/PPy material was developed and tested for its performance. However, the authors did not test the stability of the sensor of their method in real water. Guo *et al.* [48] studied the interaction of pyrrole with graphene oxide using different characterization approaches to better understand the role of the doped pyrrole. They discovered that the reaction ratio of pyrrole and graphene oxide is crucial to improve the effect of pyrrole. It is believed that pyrrole can be used not only as a nitrogen supplier but also as a reducing agent and regulator to change the composition and structure of graphene aerogels, which will affect the electrochemical sensing performance for Cd^{2+} ions.

Eltayeb *et al*. [49] prepared a nanocomposite of GO functionalized with PANI and doped with silver to improve its thermal and electrical properties. By oxidizing it with simple persulfate while it was in solution, a very simple sol-gel method was used to make it. The GO was used as a template, while aniline was polymerized on the surface of GO by oxidation. Then, Ag nanoparticles were attached. The change in DC conductivity properties with temperature was also investigated. This showed the range between the metallic and conductive regions, but the sensor did not have a very small sensing range. The authors did not investigate how sensitive their sensor was. Aboobakri *et al*. [51] also used PANI in their work. To increase the extraction capacity and selectivity for Cd^{2+} ions, they laboriously incorporated magnetite nanoparticles into graphene oxide PANI nanocomposite (MGOPA). Since centrifugation and filtration are time-consuming processes that could be skipped, the magnetic property of the adsorbent is an essential feature that significantly increases the throughput of the method. The novel adsorbent has low toxicity and is inexpensive. It has been shown to have a high adsorption capacity with good recoveries. The total time for sample extraction and pre-concentration is less than 25 minutes, showing fast adsorption-elution kinetics for Cd^{2+} ions. Although the sensor was used as it was fabricated, the interference effect was not investigated by the authors.

Dai *et al*. [53] investigated the simultaneous measurement of Cd^{2+} and Pb^{2+} samples using a phytic acid functionalized (PPy)/graphene oxide (GO) modified electrode (PA/PPy/GO). From the electrochemical performance, they found that the electrode modified with PPy/GO nanocomposite had no detection signal for heavy ions, most likely due to the coverage of the GO nanosheets by the PPy. Oxidation current peaks of Cd(II) and Pb(II) ions at modified electrodes PA/GO and PA/PPy/GO occurred at 0.88 V and 0.64 V, respectively. The enhancement of the signals of the heavy ion stripping peaks on PA/PPy/GO may be due to two factors. First, the large surface area of GO and the better electrical conductivity of PPy may make it easier for electrons to move during the detection process. Second, the presence of functional groups with significant negative charges on PA and GO is advantageous for increasing heavy metal ion adsorption.

Alruwais *et al.* [55] used wet chemistry to create polyaniline (PANI), graphene oxide (GO), and 3-aminopropyltriethoxylsilane (APTES). In the linear range from 0.01 to 0.4 M, the lowest measurable lead concentration was 0.0053 M. The measured sensitivity was 165.71 A cm^2 M^{-1} and the response time was less than 20 s. Even though metal ions and electroactive species might have interfered, the PANIGO-APTES current response to Pb^{2+} was stable. Raril and Manjunatha [58] described the invention of an electrochemical sensor based on polyglycine-modified graphene (PGMGPE) for the determination of Hg^{2+} and Pb^{2+} ions by cyclic voltammetry (CV). The electrochemical behavior of heavy metal ions on bare and modified electrodes was studied, and it was discovered that the modified electrode improves the redox signal of these two heavy metal ions. Hashemi *et al.* [63] reinforced glassy carbon electrodes with decorated graphene oxide nanoflakes with interconnected, porous, and high-density patterns of iron tungsten nitride (GO-ITN) for the detection of 4-nitrophenol in aqueous environments. They suggested that modification of PANi with hybrid 2D

GO-ITN nanoflocks improves the conductivity/sensitivity of the created sensor by promoting protonation and active functional groups in the final platforms.

Rong *et al.* [56] and Suvina *et al.* [57] used PPy to fabricate their Pb^{2+} detecting sensors. Rong *et al.* [56] synthesised the PPY-rGO nanocomposite without difficulty by electrochemical polymerization and electrochemical reduction. Anodic stripping voltammetry was used to study the response of the electrode modified with the nanocomposite and the corresponding parameters were set. They discovered that the introduction of nanosheets of reduced graphene oxide (rGO) not only increased the effective area of the nanocomposite, but also increased the rate of electron transfer at the interface. Combined with the selective recognition of PPY, this porous three-dimensional PPY-rGO nanocomposite exhibited high Pb^{2+} selectivity. On the other hand, Suvina *et al.* [57] investigated the synthesis of hydrogels from the PPy and rGO for the simultaneous detection of four different metal ions, *i.e.,* Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}. A PPy-rGO hydrogel composite was prepared by *in situ* polymerization of pyrrole in the presence of an rGO dispersion. The authors discovered that the PPy-rGO hydrogel composite has a surface area of 21.48 m^2/g, which is more than three and a half times that of PPy (5.89 m^2/g).

Mahadik *et al.* [60] reported the electrochemical detection of Hg^{2+} using a PANI/GO composite modified with ethylenediaminetetraacetic acid (EDTA). Electrochemical detection of mercury ions was performed using differential pulse stripping voltammetry (DPSV). The EDTA-modified PANI/GO electrode showed excellent response to Hg^{2+} from 30 ppb to 1 ppb. However, the authors did not address the effects of interference even though the sensor was used in its original form. Zuo *et al.* [61] also found a way to determine Hg^{2+} using poly(3,4-ethylenedioxythiophene) nanorod/graphene oxide nanocomposite modified glassy carbon electrode (PEDOT/GO/GCE). A simple liquid-liquid interfacial polymerization method was used to propose a PEDOT/GO nanocomposite. The results showed that PEDOT with a structure like nanorods adhered to the surface of GO nanosheets, which could improve the electrically active sites of the nanocomposite. DPSV was used to find out how much Hg^{2+} was present at low concentrations on PEDOT/GO/GCE. Under the best conditions, there was a good linear relationship between the peak currents and the concentration of Hg^{2+} ions in the range of 10.0 nM - 3.0 mM. With a signal-to-noise ratio of 3, the minimum amount that could be found was estimated to be 2.78 nM.

Saadati *et al.* [62] and Hashem *et al*. [63] used PANI in their studies for the detection of nitrophenol. Saadati *et al*. [62] developed an electrochemical sensor for the detection of p-nitrophenol (p-NP) based on a molecularly imprinted polymer (MIP) on GO. The sensor host molecule and initiator, aniline and ammonium persulfate, were precipitation polymerized to create the sensor. The variable functional groups (*i.e.,* hydroxyl, carboxyl, and epoxide groups), high surface area, outstanding mechanical properties, and good compatibility with polymers make GO a suitable material for the synthesis of nanocomposites. In the presence of related phenol chemicals, such as 4-chlorophenol, 4-bromophenol, 2,4-dinitrophenol, and 2-nitrophenol, the sensor demonstrated high selectivity for nitrophenol. Hashemi *et al.* [63] improved the polymer structure and sensitivity of PANI by reinforcing it with decorated GO nanoflocks with an interconnected, porous and dense pattern of iron tungsten nitride (GO-ITN) for the detection of nitrophenol in aqueous media. They reported that the surface of a GCE electrode was modified with a PANI -based nanocomposite containing 50 wt.% GO -ITN and then subjected to various studies. In addition to improved protonation, the prepared nanocomposite showed superior sensitivity with a detection limit, quantification limit and sensitivity of 5.2 nM, 18.2 nM, and 253.08 A cm^{-2} M^{-1} for the oxidation peak current, and 2.4 nM, 7.1 nM and 354.92 A cm^{-2} M^{-1} for the reduction peak current, respectively.

Umar and Nasar [65] developed a sensor (GCE/RGO/PPy/NR) based on a nanocomposite of reduced graphene oxide (RGO) and PPy immobilized on a glassy carbon electrode (GCE) by nitrate reductase (NR). Acidic *in situ* oxidative polymerization of pyrrole in the presence of RGO was used to create the conductive nanocomposite (RGO/PPy). Direct electron transport from nitrate to the electrode was realized by nitrate reductase on the GCE/RGO/PPy. Nitrate reductase is an enzyme that helps electrons to move directly from the active site of the RGO/PPy electrode surface. This causes the current density to go up to 4.24 mA cm^{-2}. However, the linear range of their study was not very broad. PPy was also used by Xiao *et al*. [66] in their study to detect nitrite. An electrochemical sensor based on n-carboxyl graphene (CG), PPy and a GCE nanocomposite modified with chitosan (CS) was prepared using differential pulse voltammetry (DPV). The combination of PPy and CG provides a large surface area and numerous active sites and increases the charge transfer between the electrode and the reagent. At the same time, the many amino groups in CS attract negatively charged nitrite, which makes it easier for nitrite to build up on the surface of the electrode.

Some researchers have also used PPy for the detection of hydrazine and nitrite. Kaladavi *et al.* [70] generated AgNPs@PPy/rGO composite using the interfacial polymerization technique employing an organic solvent dispersion of pyrrole as the GO reducing agent. An aqueous solution of silver nitrate was utilized as a precursor for Ag nanoparticles and oxidizing agent to commence the polymerization reaction at the interface. The nanocomposite film electrode was used for the electrochemical oxidation of inorganic pollutants, hydrazine and nitrite, and their oxidation potentials in the phosphate buffer were +0.53 and +0.76 V (*vs*. Ag/AgCl). Significantly, the electrochemical sensor was synthesized by means of interfacial polymerization without the use of any powerful oxidizing chemical, such as ammonium persulfate. The believability of the proposed system as an electrochemical sensor is supported by the absence of interference from specific inorganic contaminants and other biomolecules.

Fabrication of conducting polymer-functionalized graphene nanocomposites

The fabrication of graphene hybrid nanocomposites to modify materials is one of the highlights of graphene research. It is obvious that graphene, as a component of polymer nanocomposites leads to better material properties than conventional fillers. A high degree of graphene dispersion in a matrix solvent is required for better integration between graphene and polymer material particles. Graphene oxide is the most commonly used dispersant in water for graphene dispersion. It is possible to produce large amounts of graphene oxide by exfoliating graphite under highly acidic and oxidative conditions, resulting in a high concentration of hydroxyl, epoxy, and carboxyl groups in the resulting material [72]. Moreover, both covalent and noncovalent functionalization can help to improve the graphene dispersibility in conducting polymers, increasing their interfacial contacts and enabling graphene dispersion in a polymer matrix.

Covalent functionalization approach

Chemical modification, also known as covalent functionalization, is a straightforward technique for forming covalent bonds between graphene oxide or graphene in conducting polymers. Two unique approaches are widely used for the covalent modification of graphene with a conducting polymer, *i.e.,* either by connecting end-functionalized polymer chains to the solid substrate, which is referred to as 'grafting on', or by polymerization from the surface where the grafting process can occur, which is also referred to as 'grafting off' [73]. In short, the 'grafting on' preserves the graphite lattice by connecting polymer chains and functional groups to the graphene oxide edge. As shown by the significantly reduced dispersed phase size and high current values, Tan *et al.* [74] discovered that conductive polymers grafted onto modified, reduced graphene oxide significantly increase electrical conductivity and compatibility.

Vallés *et al*. [75] prepared graphene with a polymer functionalized covalently bonded polymer by coupling a diazonium addition reaction to produce -NH_2-terminated NH_2-GNPs with an amidation between the NH_2-graphene nanoplatelets (NH_2-GNPs) and poly(methyl methacrylate) (PMMA) chains to produce PMMA-grafted NH_2-GNPs. The polymer grafted onto chemically reduced graphene oxide sheets by emulsion polymerization improves the dispersion and contact between the sheets and the matrix, resulting in effective stress transfer. However, current research in the grafting and subsequent fabrication of conducting polymer and graphene composites is limited due to difficulties in matching the unique surface chemistry of graphene oxide with the specific functions of polymer chains. In addition, the selectivity of the chemical reactions between the active sites on the prefabricated polymers and GO cannot be controlled, which is essential to consider. As a result, the final structure of the composite is not clear [76].

In the 'grafting of' process, a polymer backbone functionalized with initiation sites serves as a macroinitiator from which the side chains are subsequently prepared [77]. This method demonstrates the advantages of making grafted polymer brushes that are both thick and well-controlled. Most graphene-polymer composites have been prepared by the grafting method based primarily on the controlled free radical live polymerization, radical transferred atom polymerization (ATRP) [78-81], reversible chain transfer polymerization (RAFT) [82-86], radical polymerization with a single electron transfer (SET-LRP) [87,88], polymerization by ring opening [89-91], polymerization by free radicals [92,93], grafting by electrochemical methods [94], polymerization process triggered by ultrasound [95-97], and polymerization mediated by copper and triggered by light [98]. Park *et al.* [99] presented the 'grafting of' covalent graphene- PANI nanocomposites. The perfluorophenyl nitrene generated by photochemical or thermal activation of PFPA reacts with graphene to form a covalent adduct. In this study, the aniline derivative PFPA-ANI was used to add aniline groups to graphene and found to be effective. *In situ* polymerization of aniline was used to prepare PANI, which was then grafted onto the graphene surface.

By functionalizing graphene nanoplatelets with poly(methyl methacrylate) (PMMA), Rubio *et al*. [100] contrasted the 'grafting from' and 'grafting to' approaches. According to their results, grafting rates were much higher for ’grafting from’ (44.6 to 126.5 %) than for ‘grafting to’ (12.6 to 20.3 %). ‘Grafting to’ products resulted in higher absolute grafting rates and improved dispersibility in acetone as monomer supply increased, while ‘grafting to’ products due to steric effects resulted in lower absolute grafting rates and a decreasing trend as polymer molecular weight increased.

Noncovalent functionalization approach

The noncovalent functionalization of graphene can improve its dispersion without affecting its structure or electronic network, which means that crucial properties such as electrical conductivity and mechanical strength are not affected [101]. In this process, the surface of graphene is modified by the physical absorption of modifiers on the surface of the material to improve its dispersibility in various solvents. These modifiers are usually substances that have the potential to develop different interactions with graphene layers, such as π-π, cation-π, and anion-π interactions [102]. To understand the energetic and geometric significance of π-interactions, studies were conducted in which Apatiga *et al*. [103] discovered that polymers with aromatic rings in their structure are more compatible with graphene nanoparticles to maximize conductivity by inducing a π-π-stacking effect that increases the transport of electrons from graphene to the polymer and *vice versa*. Noncovalent interactions are present in polymers with linear architecture and are mainly affected by the CH /π-stacking. Even though electrons are not accelerated as in aromatic polymers, electronic mobility is still promoted in these materials.

It has been discovered that the use of surfactants can be an effective approach to improving the mechanical and thermal properties of polymer nanocomposites. Examples of surfactants such as sodium dodecylbenzene sulfonate (SDBS) [104-106], sodium dodecyl sulfate (SDS) [107,108], and cetyltrimethylammonium bromide (CTAB) [109] are among the most commonly used noncovalent modifiers for graphene-filled polymer composites. Stankovich *et al*. [110] proposed that the adsorption of the surfactant polymer onto the graphene sheets should be due to the π-π interaction between the PSS benzene rings and the graphene sheets, which reduces the interactions between the graphene sheets and thus prevents aggregation [110]. The use of PEDOT:PSS was demonstrated by Nardes *et al.* [111] and Hakimi *et al.* [112] due to its large electrical conductivity, high transparency, excellent processability and low redox potential. Unfortunately, the process is difficult because PSS-modified graphene can only be dispersed in water. As an alternative to PSS-modified graphene, solution coagulation can be used to combine water-insoluble polymers with PSS-modified graphene [113].

Noncovalent graphene-polymer nanocomposites can be synthesized by other methods, such as solution mixing, melting, and *in situ* polymerization [114]. The final characteristics and properties of the nanocomposites are affected by the particular method. The solution mixing method is widely used and particularly effective in the synthesis of polymer-graphene nanocomposites. The chemically or thermally reduced graphene oxide can be well dispersed in organic solvents due to oxygen-containing groups, which are not removed from the graphene oxide by this technique [115]. Three processes are involved in the mixing of the solution. Ultrasonic dispersion of the graphene fillers in a suitable solvent is the first step. The next step is the addition of polymer to an ultrasonically prepared premix of graphene and solvent. The entire mixture is then vortexed to ensure that the graphene is well dispersed in the polymer matrix. The solvent must then be removed in the final stage by evaporation, filtration, precipitation or distillation. This step determines the quality of the polymer-graphene nanocomposite produced on a solid support, as well as the effectiveness of the overall solution mixing process and solvent compatibility.

For example, Lego *et al*. [116] have developed a solution mixing approach for the preparation of polycarbonate/graphene composite pellets from 1,3-dioxolane-based dispersion that serves a dual function by acting as a dispersant for the graphene flakes and simultaneously dissolving the polycarbonate to obtain the final polymer composite. The addition of graphene flakes to a polymer increases the mechanical and thermal properties of the polymer as well as its electrical conductivity. The approach of Iqbal *et al.* [117] to improve the dispersion of graphene in PE by mixing the polymer with oxidized PE (OPE) was successful. Nanocomposites of graphene with PE and graphene with OPE blends were prepared by solvent mixing. Compared to pure PE nanocomposites (1 and 0.29 vol.%), they discovered improved dispersion of graphene in PE/OPE blends, significantly reducing percolation in both rheological (0.3 vol.%) and electrical (0.13 vol.%) measurements, indicating improved dispersion and exfoliation of graphene sheets in the blends compared to pure PE nanocomposites. Unfavourably, large amounts of organic solvents were required for the preparation of the blended solutions during industrial production, which pollutes the environment. The use of organic solvents also led to a significant increase in production costs. Therefore, this process is less frequently used for production on an industrial scale compared to the melt blending process.

Compared to solution mixing, melt mixing is more practical, clean, and adaptable because no solvent is required for the process of conductive polymer with graphene fillings [118]. Thus, melt blending is not only safe for the environment but also straightforward and cost-effective. Many polymer manufacturers prefer this technology for commercial production. However, care must be taken during the mixing process to prevent the polymer from disintegrating due to the high temperatures required to produce a homogeneous blend [119]. According to Tu *et al*. the electrical conductivity of graphene-filled PE/PP blends was affected by the processing sequence during melt blending [120]. In their study, they fabricated graphene-filled composites from high-density PE and PP by melt compounding and compared the electrical conductivity of the composites fabricated in three different processing sequences. It was found that the graphene, PE and PP processing sequences affect the graphene localization, affecting the observed electrical conductivity of the composites.

Graziano *et al.* [121] compared high-density PE-functionalized graphene enhanced by the melt mixing method with the solvent reaction method. For comparison, high-density PE-reduced functionalized graphene oxide composites were prepared by solvent reaction, while melt blending and solvent reaction were used for high-density PE-reduced functionalized graphene oxide composites. High-density PE-functionalized graphene has better mechanical properties than high-density PE and high-density PE-functionalized graphene oxide. This is because graphene was well distributed in the polymer matrix and had strong interactions with the polymer, allowing stresses to be transferred more easily, heat to be distributed more uniformly, and crystals to grow faster [121]. Melt compounding is more flexible, less expensive, and less environmentally harmful than the solvent reaction because no solvents or chemicals are needed. The performance improvements of the nanocomposite (prepared by melt compounding) were identical to those of the nanocomposite (prepared by solvent reaction) except for the mechanical properties [121].

Another approach to the preparation of conductive polymer-functionalized graphene is extremely useful, and known as *in situ* polymerization. The main advantage of this method is that it allows the polymerization of monomers located inside and outside the graphene interlayers. This leads to polymer nanocomposites with delaminated graphene platelets at the nanoscale. However, the problem of lack of distribution of graphene fillers in this process remains, leading to a lower polymerization rate in the later phases [122]. In a study by Qi *et al*. [123], it was found that the lamellar thickness and crystallinity of nanocomposites, as well as their crystallization temperature, are increased by the heterogeneous nucleation effect of graphene. The thermal stability of the composites was improved by the ability of graphene to absorb free radicals generated during the decomposition of high-density PE. A good interfacial polarization effect in the materials was also demonstrated by an increase in the dielectric constant and conductivity of the composites when the graphene concentration was increased.

Based on spherical and sandwich graphene/SiO_2 supports, Su *et al.* prepared a high molecular weight PE/graphene nanocomposite using *in situ* polymerization method [124]. The porous spherical graphene support offers more advantages for this technology than conventional methods and could preserve the intrinsic graphene performance in nanocomposites. When the Ziegler-Natta (Z-N) catalyst is loaded onto the support, the active components adhere to the surface and inside the pores. When ethylene molecules contact the active sites, a regular and well-organized chain of molecular bonds is formed on the surface and inside the catalytic sites. Cheng *et al.* [125] proposed a noncovalent functionalization approach to prepare graphene PANI nanocomposites to improve the electrical conductivity, mechanical and electromagnetic shielding properties of the polyimide composite film. The polymerization of graphene in the PANI matrix helps to distribute the graphene sheets uniformly in the matrix. Due to the van der Waals forces, the graphene sheets tend to clump together during the stirring process without PANI and π-π noncovalent interactions between the graphene sheets, resulting in an irregular and discontinuous network. The graphene sheets were welded together by noncovalent bonding between adjacent graphene sheets, avoiding aggregation of graphene sheets in organic solvents. Once the polymer matrix is thermally imidized, electrons can move more efficiently through the graphene PANI network. The high conductivity of graphene is not affected by the presence of noncovalent interactions in this mixture of graphene and PANI [125].

Conclusions and perspectives

This review attempts to provide an overview of current trends in conductive polymer functionalized graphene-based electrochemical sensors for the detection of contaminants in water. Electrochemical sensors are very promising because they are portable, fast, inexpensive, have good stability, sensitivity and selectivity, and are also suitable for in situ measurements. Conducting polymers are extensively studied for their superior properties, including tunable electrical properties, optical and high mechanical properties, easy synthesis and effortless fabrication, and high environmental stability compared to conventional inorganic materials. Although conducting polymers have many limitations in their original form, these are overcome by functionalization with other materials. Graphene has recently attracted much attention due to its potential as a conductive filler for polymer matrix composites. The synergistic effects of conductive polymer and graphene composites can be successfully used to overcome the limitations of each material. In this review, it has been suggested that methods for preparing graphene functionalized with conducting polymers include covalent and noncovalent functionalization. Both have a number of advantages and disadvantages that need to be considered. We compared graphene functionalized with conducting polymers and its derivatives and their performances in electrochemical sensors for the detection of contaminants in water in terms of detection technique, linear range, detection limit, and target analytes. Among different electrochemical techniques, SWASV, DPASV, CV, DPV, current potential and amperometry were used for the detection of water pollutants with conductive polymer functionalized graphene-based sensors. These results spark interest and illuminate key areas where graphene and conductive polymer nanocomposites are making significant advances in electrochemical sensing applications.

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References

[1] *Guidelines for Drinking-water Quality*, *4th edition incorporating the 1st addendum*, World Health Organization (Ed.), 2017, pp. 631. ISBN: 978-92-4-154995-0

[2] X.-S. Zhu, C. Gao, J.-W. Choi, P.L. Bishopb, C.H. Ahn, On-chip generated mercury microelectrode for heavy metal ion detection, *Lab on a Chip* **5** (2005) 212-217. https://doi.org/10.1039/B410006A

[3] X. Xuan, M.F. Hossain, J.Y. Park, A fully integrated and miniaturized heavy-metal-detection sensor based on micro-patterned reduced graphene oxide, *Scientific Reports* **6** (2016) 33125. http://doi.org/10.1038/srep33125

[4] P. Podešva, I. Gablech, P. Neužil, Nanostructured gold microelectrode array for ultrasensitive detection of heavy metal contamination, *Analytical Chemistry* **90** (2018) 1161-1167. https://doi.org/10.1021/acs.analchem.7b03725

[5] J. Bobacka, Electrochemical sensors for real-world applications, *Journal of Solid State Electrochemistry* **24** (2020) 2039-2040. https://doi.org/10.1007/s10008-020-04700-4

[6] T. Gan, S. Hu, Electrochemical sensors based on graphene materials, *Microchimica Acta* **175** (2011) 1. https://doi.org/10.1007/s00604-011-0639-7

[7] L. Neia, Milestones in the 50-year history of electrochemical oxygen sensor development, *ECS Trans* **2** (2007) 33-38. https://doi.org/10.1149/1.2409016

[8] M.L. Hitchman, *Measurement of Dissolved Oxygen*, Wiley Interscience, New York, 1978, p. 99. ISBN: 0471038857

[9] W. C. Lee, K. B. Kim, N. G. Gurudatt, K. Hussain, C. S. Choi, D. S. Park, Y. B. Shim, Comparison of enzymatic and non-enzymatic glucose sensors based on hierarchical Au-Ni alloy with conductive polymer, *Biosensors and Bioelectronics* **130** (2019) 48-54. https://doi.org/10.1016/j.bios.2019.01.028

[10] A. Economou, S. K. Karapetis, G.-P. Nikoleli, D. P. Nikolelis, S. Bratakou, T. H. Varzakas, *Enzyme based sensors,* in: *Advances in Food Diagnostics*, Second Edition, F. Toldrá, L.M.L. Nollet (Eds.), J. Wiley & Sons, New York, 2017, pp. 231-250.

[11] H.L. Thanh, K. Yukyung Y. Hyeonseok, Electrical and electrochemical properties of conducting polymers, *Polymers* **9** (2017) 150. https://doi.org/10.3390/polym9040150

[12] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$, *Journal of the Chemical Society* **16** (1977) 578-580. https://doi.org/10.1039/C39770000578

[13] L. W. Carter, J. G. Hendricks, D. S. Bolley, D. S. Elastomer Reinforced with Modified Clay (Assigned to National Lead Co.). 1950. U. S. Pat. No. 2,531,396.

[14] A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito, Synthesis of nylon 6-clay hybrid, *Journal of Materials Research* **8** (1993) 1179-1184. https://doi.org/10.1557/JMR.1993.1179

[15] G. C. Chan, A. S. M. A. Haseeb, Recent trends and developments in graphene/conducting polymer nanocomposites chemiresistive sensors, *Materials* **13** (2020) 3311. https://doi.org/10.3390/ma13153311

[16] M. H. Naveen, N. G. Gurudatt, Y. B. Shim, Applications of conducting polymer composites to electrochemical sensors: A review, *Applied Materials Today* **9** (2017) 419-433. https://doi.org/10.1016/j.apmt.2017.09.001

[17] A. Marsden, D. Papageorgiou, C. Valles, A. Liscio, V. Palermo, M. A. Bissett, R. J. Young, I. Kinloch, *2D Materials* **5** (2018) 032003. https://doi.org/10.1088/2053-1583/aac055

[18] T. Vinod Kumar, M. Chandrasekaran, P. Mohanraj, R. Balasubramanian, R. Muraliraja, S. V. Shaisundaram, Fillers preparation for polymer composite and its properties, *International Journal of Engineering and Technology* **7** (2018) 212-217. https://doi.org/10.14419/ijet.v7i2.33.13889

[19] Y. J. Kwon, J. B. Park, J. P. Jeon, J. Y. Hong, H. S. Park, J. U. Lee, A review of polymer composites based on carbon fillers for thermal management applications: design, preparation, and properties, *Polymers* **13** (2021) 1312. https://doi.org/10.3390/polym13081312

[20] J. Yao, H. Wang, M. Chen, M. Yang, Recent advances in graphene-based nanomaterials: properties, toxicity and applications in chemistry, biology and medicine, *Microchimica Acta* **186** (2019) 395. https://doi.org/10.1007/s00604-019-3458-x

[21] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Electric field effect in atomically thin carbon films, *Science* **306** (2004) 666-669. https://doi.org/10.1126/science.1102896

[22] M. J. McAllister, J. L. Li, D.H. Adamson, H. C. Schniepp, A. A. Abdala, J. Liu, M. Herrera-Alonso, D. L. Milius, R. Car, R. K. Prud'homme, K. Robert, Single Sheet Functionalized Graphene by Oxidation and Thermal Expansion of Graphite, *Journal of the American Chemical Society* **19** (2007) 4396-4404. https://doi.org/10.1021/cm0630800

[23] N. O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, X. Duan, Graphene: an emerging electronic material, *Advanced Materials* **24** (2012) 5782-5825. https://doi.org/10.1002/adma.201201482

[24] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, D. Obergfell, S. Roth, C. Girit, A. Zettl, On the roughness of single- and bi-layer graphene membranes, *Solid State Communications* **143** (2007) 101-109. https://doi.org/10.1016/j.ssc.2007.02.047

[25] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C. N. Lau, Superior thermal conductivity of single-layer graphene, *Nano Letters* **8** (2008) 902-907 https://doi.org/10.1021/nl0731872

[26] K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, H. L. Stormer, Ultrahigh electron mobility in suspended graphene, *Solid State Communications* **146** (2008) 351-355. https://doi.org/10.1016/j.ssc.2008.02.024

[27] G. Shi, Y. Ding, H. Fang, Unexpectedly strong anion-π interactions on the graphene flakes, *Journal of Computational Chemistry* **33** (2012) 1328-1337. https://doi.org/10.1002/jcc.22964

[28] X. L. Wang, S. X. Dou, C. Zhang, Zero-gap materials for future spintronics, electronics and optics, *NPG Asia Materials* **2** (2010) 31-38. https://doi.org/10.1038/asiamat.2010.7

[29] S. K. Tiwari, S. Sahoo, W. Nannan, A. Huczko, Graphene research and their outputs: status and prospect, *Journal of Science: Advanced Materials and Devices* **5** (2020) 10-29. https://doi.org/10.1016/j.jsamd.2020.01.006

[30] A. H. Castro Neto, N.M.R. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, *Reviews of Modern Physics* **81** (2009) 109-162. https://doi.org/10.1103/RevModPhys.81.109

[31] A. Zubiarrain-Laserna, P. Kruse, Review—graphene-based water quality sensors, *Journal of The Electrochemical Society* **167** (2020) 037539. https://doi.org/10.1149/1945-7111/ab67a5

[32] H. Kumar, N. Kumari, R. Sharma, Nanocomposites (conducting polymer and nanoparticles) based electrochemical biosensor for the detection of environment pollutant: Its issues and challenges, *Environmental Impact Assessment Review* **85** (2020) 106438. https://doi.org/10.1016/j.eiar.2020.106438

[33] O. Kanoun, T. Lazarević-Pašti, I. Pašti, S. Nasraoui, M. Talbi, A. Brahem, A. Adiraju, E. Sheremet, R. D. Rodruguez, M. B. Ali, A. Al-Hamry, A review of nanocomposite-modified electrochemical sensors for water quality monitoring, *Sensors* **21** (2021) 4131. https://doi.org/10.3390/s21124131

[34] A. Terán-Alcocer, F. Bravo-Plascencia, C. Cevallos-Morillo, A. Palma-Cando, Electrochemical sensors based on conducting polymers for the aqueous detection of biologically relevant molecules, *Nanomaterials* **11** (2021) 252. https://doi.org/10.3390/nano11010252

[35] G. De Alvarenga, B. M. Hryniewicz, I. Jasper, R.J. Silva, V. Klobukoski, F. S. Costa, T. N. M. Cervantes, C. D. B. Amaral, J. T. Schneider, L. Bach-Toledo, P. Peralta-Zamora, T. L. Valerio, F. Soares, S. Frederico, J. G. Bruno, M. Vidotti, Recent trends of micro and nanostructured conducting polymers in health and environmental applications, *Journal of Electroanalytical Chemistry* **879** (2020) 114754. https://doi.org/10.1016/j.jelechem.2020.114754

[36] D. Li, T. Wang, Z. Li, X. Xu, C. Wang, Y. Duan, Application of graphene-based materials for detection of nitrate and nitrite in water—a review, *Sensors* **20** (2019) 54. https://doi.org/10.3390/s20010054

[37] H. Wang, Polymer-based electrochemical sensing platform for heavy metal ions detection - a critical review, *International Journal of Electrochemical Science* **14** (2019) 8760-8771. https://doi.org/10.20964/2019.09.22

[38] M.A. Deshmukh, M.D. Shirsat, A. Ramanaviciene, Composites based on conducting polymers and carbon nanomaterials for heavy metal ion sensing (review), *Critical Reviews in Analytical Chemistry* **48** (2018) 293-304. https://doi.org/10.1080/10408347.2017.1422966

[39] B. C . Patel, G. R. Sinha, N. Goel, *Introduction to Sensors* in *Advances in Modern Sensors,* G. R. Sinha Ed., IOP Publishing Ltd, United Kingdom, 2020, pp. 1-21. https://iopscience.iop.org/book/edit/978-0-7503-2707-7/chapter/bk978-0-7503-2707-7ch1

[40] N. R. Stradiotto, H. Yamanaka, M.V.B. Zanoni, Electrochemical sensors: a powerful tool in analytical chemistry, *Journal of the Brazilian Chemical Society* **14** (2003) 159-173. https://doi.org/10.1590/S0103-50532003000200003

[41] A. Yavarinasab, M. Abedini, H. Tahmooressi, S. Janfaza, N. Tasnim, M. Hoorfar, Potentiodynamic Electrochemical Impedance Spectroscopy of Polyaniline-Modified Pencil Graphite Electrodes for Selective Detection of Biochemical Trace Elements, *Polymers* **14** (2022) 31. https://doi.org/10.3390/polym14010031

[42] H. Karimi-Maleh, F. Fatemeh, M. Alizadeh, A. L. Sanati, Electrochemical sensors, a bright future in the fabrication of portable kits in analytical systems, *Chemical Record* **20** (2019) 682-692. https://doi.org/10.1002/tcr.201900092

[43] J. Giner, A practical reference electrode, *Journal of the Electrochemical Society* **111** (1964) 376-377. https://doi.org/10.1149/1.2426125

[44] R. C. Alkire, C. W. Tobias, *Advances in Electrochemical Science and Engineering,* VCH Publishers Inc, New York, 2008, pp. 1-74.

[45] D.W. Kimmel, G. LeBlanc, M.E. Meschievitz, D.E. Cliffel, Electrochemical sensors and biosensors, *Journal of Analytical Chemistry* **84** (2012) 685-707. https://doi.org/10.1021/ac202878q

[46] K.K. Kasem, S. Jones, Platinum as a reference electrode in electrochemical measurements, *Platinum Metals Review* **52** (2008) 100-106. https://doi.org/10.1595/147106708x297855

[47] Y. Song, C. Bian, J. Hu, Y. Li, J. Tong, J. Sun, G. Gao, S. Xia, Porous polypyrrole/graphene oxide functionalized with carboxyl composite for electrochemical sensor of trace cadmium (II), *Journal of The Electrochemical Society* **166** (2019) B95-B102. https://doi.org/10.1149/2.0801902jes

[48] X. Guo, R. Cui, H. Huang, Y. Li, B. Liu, J. Wang, D. Zhao, J. Dong, B. Sun, Insights into the role of pyrrole doped in three-dimensional graphene aerogels for electrochemical sensing Cd(II), *Journal of Electroanalytical Chemistry* **871** (2020) 114323. https://doi.org/10.1016/j.jelechem.2020.114323

[49] N. E. Eltayeb, A. Khan, Preparation and properties of newly synthesized Polyaniline@Graphene oxide/Ag nanocomposite for highly selective sensor application, *Journal of Materials Research and Technology* **9** (2020) 10459-10467. https://doi.org/10.1016/j.jmrt.2020.07.031

[50] J. Wang, J. Hu, S. Hu, G. Gao, Y. Song, A novel electrochemical sensor based on electropolymerized ion imprinted PoPD/ERGO composite for trace Cd(II) determination in water, *Sensors* **20** (2020) 1004. https://doi.org/10.3390/s20041004

[51] E. Aboobakri, M. Jahani, Graphene oxide/Fe_3O_4/polyaniline nanocomposite as an efficient adsorbent for the extraction and preconcentration of ultra-trace levels of cadmium in rice

and tea samples, *Research on Chemical Intermediates* **46** (2020) 5181-5198. https://doi.org/10.1007/s11164-020-04256-y

[52] S. A. Hashemi, S. Bahrani, S. M. Mousavi, N. Omidifar, M. Arjmand, K. B. Lankarani, S. Ramakrishna, Simultaneous electrochemical detection of Cd and Pb in aquatic samples via coupled graphene with brominated white polyaniline flakes, *European Polymer Journal* **162** (2022) 110926. https://doi.org/10.1016/j.eurpolymj.2021.110926

[53] H. Dai, N. Wang, D. Wang, H. Ma, M. Lin, An electrochemical sensor based on phytic acid functionalized polypyrrole/graphene oxide nanocomposites for simultaneous determination of Cd(II) and Pb(II). *Chemical Engineering Journal* **299** (2016) 150-155. https://doi.org/10.1016/j.cej.2016.04.083

[54] M. Akhtar, A. Tahir, S. Zulfiqar, F. Hanif, M. F. Warsi, P. O. Agboola, I. Shakir, Ternary hybrid of polyaniline-alanine-reduced graphene oxide for electrochemical sensing of heavy metal ions, *Synthetic Metals* **265** (2020) 116410. https://doi.org/10.1016/j.synthmet.2020.116410

[55] R. S. Alruwais, W. A. Adeosun, H. M. Marwani, M. Jawaid, A. M. Asiri, A. Khan, Novel aminosilane (APTES)-grafted polyaniline@graphene oxide (PANI-GO) nanocomposite for electrochemical sensor, *Polymers* **13** (2021) 2562. https://doi.org/10.3390/polym13152562

[56] R. Rong; H. Zhao, X. Gan, S. Chen, X. Quan, An electrochemical sensor based on graphene-polypyrrole nanocomposite for the specific detection of Pb (II), *Nano* **12** (2017) 1750008. https://doi.org/10.1142/S1793292017500084

[57] V. Suvina, S. M. Krishna, D. H. Nagaraju, J. S. Melo, R. G. Balakrishna, Polypyrrole-reduced graphene oxide nanocomposite hydrogels: a promising electrode material for the simultaneous detection of multiple heavy metal ions, *Materials Letters* **232** (2018) 209-212. https://doi.org/10.1016/j.matlet.2018.08.096

[58] C. Raril, J. G. Manjunatha, Fabrication of novel polymer-modified graphene-based electrochemical sensor for the determination of mercury and lead ions in water and biological samples, *Journal of Analytical Science and Technology* **11** (2020) 3. https://doi.org/10.1186/s40543-019-0194-0

[59] M. O. Park, H. B. Noh, D. S. Park, J. H. Yoon, Y. B. Shim, Long-life heavy metal ions sensor based on graphene oxide-anchored conducting polymer, *Electroanalysis* **19** (2016) 514-520. https://doi.org/10.1002/elan.201600494

[60] M. Mahadik. H. Patil, G. Bodkhe, N. Ingle. P. Sayyad, T. Al-gahaouri, S. Shirsat , M. D. Shirsat, EDTA modified PANI/GO composite based detection of Hg (II) ions. *Frontiers in Materials* **7** (2019) 81. https://doi.org/10.3389/fmats.2020.00081

[61] Y. Zuo, J. Xu, X. Zhu, D. Xuemin, L. Lu, Y. Gao, H, Xing, T. Yang, G. Ye, Y. Yu, Poly(3,4-ethylenedioxythiophene) nanorods/graphene oxide nanocomposite as a new electrode material for the selective electrochemical detection of mercury (II), *Synthetic Metals* **220** (2016) 14-19. https://doi.org/10.1016/j.synthmet.2016.05.022

[62] F. Saadati, F. Ghahramani, H. Shayani-jam, F. Piri, M. R. Yaftian, Synthesis and characterization of nanostructure molecularly imprinted polyaniline/graphene oxide composite as highly selective electrochemical sensor for detection of p -nitrophenol, *Journal of the Taiwan Institute of Chemical Engineers* **86** (2018) 213-221. https://doi.org/10.1016/j.jtice.2018.02.019

[63] S. A. Hashemi, S. M. Mousavi, S. Bahrani, S. Ramakrishna, Integrated polyaniline with graphene oxide-iron tungsten nitride nanoflakes as ultrasensitive electrochemical sensor for precise detection of 4-nitrophenol within aquatic media, *Journal of Electroanalytical Chemistry* **873** (2020) 114406. https://doi.org/10.1016/j.jelechem.2020.114406

[64] G. Chen, J. Zheng, Non-enzymatic electrochemical sensor for nitrite based on a graphene oxide-polyaniline-Au nanoparticles nanocomposite, *Microchemical Journal* **164** (2021) 106034. https://doi.org/10.1016/j.microc.2021.106034

[65] M. F. Umar, A. Nasar, Reduced graphene oxide/polypyrrole/nitrate reductase deposited glassy carbon electrode (GCE/RGO/PPy/NR): biosensor for the detection of nitrate in wastewater, *Applied Water Science* **8** (2018) 211. https://doi.org/10.1007/s13201-018-0860-1

[66] Q. Xiao, M. Feng, Y. Liu, S. Lu, Y. He, S. Huang, The graphene/polypyrrole/chitosan-modified glassy carbon electrode for electrochemical nitrite detection, *Ionics* **24** (2017) 845-859. https://doi.org/10.1007/s11581-017-2247-y

[67] K. Dagci, M. Alanyalioglu, Preparation of free-standing and flexible graphene/Ag nanoparticles/poly(pyronin Y) hybrid paper electrode for amperometric determination of nitrite, *ACS Applied Materials and Interfaces* **8** (2016) 2713-2722. https://doi.org/10.1021/acsami.5b10973

[68] G. Kaladevi, P. Wilson, K. Pandian, Simultaneous and selective electrochemical detection of sulfite and nitrite in water sources using homogeneously dispersed Ag nanoparticles over PANI/rGO nanocomposite, *Journal of The Electrochemical Society* **167** (2020) 027514. https://doi.org/10.1149/1945-7111/ab6973

[69] C. H. Su, C. L. Sun, Y. C. Liao, Printed combinatorial sensors for simultaneous detection of ascorbic acid, uric acid, dopamine, and nitrite, *ACS Omega* **2** (2017) 4245-4252. https://doi.org/10.1021/acsomega.7b00681

[70] G. Kaladevi, S. Meenakshi, K. Pandian, P. Wilson, Synthesis of well-dispersed silver nanoparticles on polypyrrole/reduced graphene oxide nanocomposite for simultaneous detection of toxic hydrazine and nitrite in water sources, *Journal of The Electrochemical Society* **164** (2017) B620-B631. https://doi.org/10.1149/2.0611713jes

[71] R. Sha, K. Kikuo, S. Badhulika, Graphene-polyaniline composite based ultra-sensitive electrochemical sensor for non-enzymatic detection of urea. *Electrochimica Acta* **233** (2017) 44-51. https://doi.org/10.1016/j.electacta.2017.03.043

[72] A. Jiříčková, O. Jankovský, Z. Sofer, D. Sedmidubský, Synthesis and applications of graphene oxide, *Materials* **15** (2022) 920. https://doi.org/10.3390/ma15030920

[73] J. S. Horacio M. Gerardo E. Gary Ellis, Recent advances in the covalent modification of graphene with polymers, *Macromolecular Rapid Communications* **32** (2011) 1771-1789. https://doi.org/10.1002/marc.201100527

[74] Y. Tan, L. Fang, J. Xiao, Y. Song, Q. Zheng, Grafting of copolymers onto graphene by miniemulsion polymerization for conductive polymer composites: improved electrical conductivity and compatibility induced by interfacial distribution of graphene, *Polymer Chemistry* **4** (2013) 2939 -2944. https://doi.org/10.1039/C3PY00164D

[75] C. Vallés, D. G. Papageorgiou, F. Lin, Z. Li, B. F. Spencer, R. J. Young, I. A. Kinloch, PMMA-grafted graphene nanoplatelets to reinforce the mechanical and thermal properties of PMMA composites, *Carbon* **157** (2019) 750-760. https://doi.org/10.1016/j.carbon.2019.10.075

[76] H. Du, Z. Li, H. Li, Y. Zhao, X. Li, J. Liu, Z. Ji, Preparation of polymer composite selective permeable membrane with graphene oxide and application for chemical protective clothing, *Processes* **10** (2022) 471. https://doi.org/10.3390/pr10030471

[77] B. Yuan, B. Wang, Y. Hu, X. Mu, N. Hong, K. M. Liew, Y. Hu, Electrical conductive and graphitizable polymer nanofibers grafted on graphene nanosheets: improving electrical conductivity and flame retardancy of polypropylene, *Composites Part A: Applied Science and Manufacturing* **84** (2016) 76-86. https://doi.org/10.1016/j.compositesa.2016.01.003

[78] M. Zygo, M. Mrlik, M. Ilcikova, M. Hrabalikova, J. Osicka, M. Cvek, M. Sedlacik, B. Hanulikova, L. Munster, D. Skoda, P. UrbÃ¡nek, J. Pietrasik, M. Jaroslav, Effect of structure of polymers grafted from graphene oxide on the compatibility of particles with a silicone-based environment and the stimuli-responsive capabilities of their composites, *Nanomaterials* **10** (2020) 591. https://doi.org/10.3390/nano10030591

[79] S. Wang, H. Chi, L. Chen, W. Li, Y. LI, G. Li, X. Ge, Surface functionalization of graphene oxide with polymer brushes for improving thermal properties of the polymer matrix, *Advances in Polymer Technology* **2021** (2021) 5591420. https://doi.org/10.1155/2021/5591420

[80] P. Eskandari, Z. Abousalman-Rezvani, H. Roghani-Mamaqani, M. Salami-Kalajahi, H. Mardani, Polymer grafting on graphene layers by controlled radical polymerization, *Advances in Colloid and Interface Science* **273** (2019) 102021 https://doi.org/10.1016/j.cis.2019.102021

[81] Ł. A. Łukasz, C. Z. Kamil Goc, Z. Szczepan, C. Kapusta, S. Zapotoczny, Enhanced thermal conductivity of polyamide-based nanocomposites containing graphene oxide sheets decorated with compatible polymer brushes, *Materials* **14** (2021) 751. https://doi.org/10.3390/ma14040751

[82] L. Yang, W. Zhen, Synthesis of graphene oxide-polystyrene graft polymer based on reversible addition fragmentation chain transfer and its effect on properties, crystallization, and rheological behavior of poly (lactic acid), *Advances in Polymer Technology* **2020** (2020) 9364657. https://doi.org/10.1155/2020/9364657

[83] K. Khezri, M. Najafi, H. Roghani-Mamaqani, Reversible addition fragmentation chain transfer polymerization of styrene from the edge of graphene oxide nanolayers, *Journal of Polymer Research* **24** (2017) 34. https://doi.org/10.1007/s10965-017-1193-8

[84] H. Mardani, H. Roghani-Mamaqani, K. Khezri, M. Salami-Kalajahi, Polystyrene-attached graphene oxide with different graft densities via reversible addition-fragmentation chain transfer polymerization and grafting through approach, *Applied Physics A* **126** (2020) 251. https://doi.org/10.1007/s00339-020-3428-5

[85] M. Qiao, S. Wu, Y. Wang, Q. Ran, Brush-like block copolymer synthesized via RAFT polymerization for graphene oxide aqueous suspensions, *RSC Advances* **7** (2017) 4776-4782. https://doi.org/10.1039/C6RA27480C

[86] M. Namvari, C. S. Biswas, M. Galluzzi, Q. Wang, B. Du, F.J. Stadler, Reduced graphene oxide composites with water soluble copolymers having tailored lower critical solution temperatures and unique tube-like structure, *Scientific Reports* **7** (2017) 44508. https://doi.org/10.1038/srep44508

[87] A. Murali, S. Sampath, A. B. Appukutti, M. Sakar, S. Chandrasekaran, V. N. Suthanthira, R. Joseph Bensingh, M. Abdul Kader, S. N. Jaisankar, Copper (0) mediated single electron transfer-living radical polymerization of methyl methacrylate: functionalized graphene as a convenient tool for radical initiator, *Polymers* **12** (2020) 874. https://doi.org/10.3390/polym12040874

[88] S. T. SIoannis, K. M. Triantafyllos, S. A. Dimitris S. Achilias, Effect of graphene oxide on the reaction kinetics of methyl methacrylate in situ radical polymerization via the bulk or solution technique, *Polymers* **9** (2017) 432. https://doi.org/10.3390/polym9090432

[89] S. Colonna, O. Monticelli, J. Gomez, G. Saracco, A. Fina, Morphology and properties evolution upon ring-opening polymerization during extrusion of cyclic butylene terephthalate and graphene-related-materials into thermally conductive nanocomposites, *European Polymer Journal* **89** (2017) 57-66. https://doi.org/10.48550/arXiv.1703.00805

[90] S. Colonna, M.M. Bernal, G. Gavoci, J. Gomez, C. Novara, G. Saracco, A. Fina, Effect of processing conditions on the thermal and electrical conductivity of poly (butylene

terephthalate) nanocomposites prepared via ring-opening polymerization, *Materials and Design* **119** (2017) 124-132. https://doi.org/10.1016/j.matdes.2017.01.067

[91] A. Babaie, M. Rezaei, R. L. M. Sofla, Investigation of the effects of polycaprolactone molecular weight and graphene content on crystallinity, mechanical properties and shape memory behavior of polyurethane/graphene nanocomposites, *Journal of the Mechanical Behavior of Biomedical Materials* **96** (2019) 53-68. https://doi.org/10.1016/j.jmbbm.2019.04.034

[92] E.B. Ko, D.-E. Lee, K.-B. Yoon, Investigation of the effects of polycaprolactone molecular weight and graphene content on crystallinity, mechanical properties and shape memory behavior of polyurethane/graphene nanocomposites, *Polymers* **12** (2020) 1221. https://doi.org/10.3390/polym12061221

[93] A. Ouadah, T. Luo, J. Wang, S. Gao, X. Wang, X. Zhang, Z. Fang, Z. Wu, J. Wang, C. Zhu, Imidazolium-grafted graphene oxide via free radical polymerization: An efficient and simple method for an interpenetrating polymer network as electrolyte membrane*, Composites Science and Technology* **164** (2018) 204-213. https://doi.org/10.1016/j.compscitech.2018.05.003

[94] A. A. Hassan, I. Abdulazeez, O. A. Salawu, A. R. Al-Betar, Electrochemical deposition and characterization of polyaniline-grafted graphene oxide on a glassy carbon electrode, *SN Applied Sciences* **2** (2020) 1257. https://doi.org/10.1007/s42452-020-3074-8

[95] S. Cohen E. Zelikman R. Y. Suckeveriene, Ultrasonically induced polymerization and polymer grafting in the presence of carbonaceous nanoparticles, *Processes* **8** (2020) 1680. https://doi.org/10.3390/pr8121680

[96] Y. Yu, J. Wang, Preparation of graphene/PMMA composites with assistance of ultrasonic wave under supercritical CO_2 conditions, *Ultrasonics Sonochemistry* **73** (2021) 105487. https://doi.org/10.1016/j.ultsonch.2021.105487

[97] R. S. Chen, M. F. H. Mohd Ruf, D. Shahdan, S. Ahmad, D. Madan, Enhanced mechanical and thermal properties of electrically conductive TPNR/GNP nanocomposites assisted with ultrasonication, *PLOS ONE* **14** (2019) e0222662. https://doi.org/10.1371/journal.pone.0222662

[98] S. Railian, J. J. Haven, L. Maes, D. De Sloovere, V. Trouillet, A. Welle, P. Adriaensens, M. K. Van Bael, A. Hardy, W. Deferme, T. Junkers. Photo-induced copper-mediated (meth)acrylate polymerization towards graphene oxide and reduced graphene oxide modification, *European Polymer Journal* **134** (2020) 109810. https://doi.org/10.1016/j.eurpolymj.2020.109810

[99] J. Park, X. Yang, D. Wickramasinghe, M. Sundhoro, N. Orbey, K.F. Chow, M. Yan, Functionalization of pristine graphene for the synthesis of covalent graphene-polyaniline nanocomposite, *RSC Advances* **10** (2020) 26486-26493. https://doi.org/10.1039/D0RA03579C

[100] N. Rubio, H. Au, H. S. Leese, S. Hu, A.J. Clancy, M. S. P. Shaffer, Grafting from versus grafting to approaches for the functionalization of graphene nanoplatelets with poly(methyl methacrylate), *Macromolecules* **50** (2017) 7070-7079. https://doi.org/10.1021/acs.macromol.7b01047

[101] V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril, K. S. Kim, Functionalization of graphene: covalent and noncovalent approaches, derivatives and applications, *Chemical Reviews* **112** (2012) 6156-6214. https://doi.org/10.1021/cr3000412

[102] D. W. Johnson, B. P. Dobson, K. S. Coleman, S. Karl, A manufacturing perspective on graphene dispersions, *Current Opinion in Colloid and Interface Science* **20** (2015) 367-382. https://doi.org/10.1016/j.cocis.2015.11.004

[103] J. L. Apátiga, R. M. del Castillo, L. F. del Castillo, A. G. Calles, R. Espejel-Morales, J. F. Favela, V. Compañ, Noncovalent interactions on polymer-graphene nanocomposites and their effects on the electrical conductivity, *Polymers* **13** (2021) 1714. https://doi.org/10.3390/polym13111714

[104] A. Vipul, F. Yasemin, W. Alice, M. Namrata, N. T. Bich, A. M. N. Rabiatul, B. Saroj, B. Joanna, L. Sean, P. B. Zetterlund, Influence of anionic surfactants on the fundamental properties of polymer/reduced graphene oxide nanocomposite films, *ACS Applied Materials and Interfaces* **13** (2021) 18338-18347. https://doi.org/10.1021/acsami.1c02379

[105] L. C. O. Adrian, M. Mariatti, Z. Lockman, Effect of dodecylbenzenesulfonic acid as a surfactant on the properties of polyaniline/graphene nanocomposites. *Materials Today: Proceedings* **17** (2019) 864-870. https://doi.org/10.1016/j.matpr.2019.06.382

[106] A. Ahmad, PVC/rice straw/SDBS-modified graphene oxide sustainable nanocomposites, *Composites Part A: Applied Science and Manufacturing* **134** (2020) 105902. https://doi.org/10.1016/j.compositesa.2020.105902

[107] J. Wei, I. Fawad, Effects of surfactants on the properties of epoxy/graphene nanocomposites*, Journal of Reinforced Plastics and Composites* **37(14)** (2018) 960-967 https://doi.org/10.1177/0731684418765369

[108] A. B. Hector, C. C. Ahirton, A. N. Carrillo, M. L. Manchado, Removal of surfactant from nanocomposites films based on thermally reduced graphene oxide and natural rubber, *Journal of Composites Science* **3** (2019) 31. https://doi.org/10.3390/jcs3020031

[109] Q. Liu, W. Luo, Y. Chen, H. Zou, M. Liang, Enhanced mechanical and thermal properties of CTAB-functionalized graphene oxide-polyphenylene sulphide composites, *High Performance Polymers* **29(8)** (2017) 889-898. https://doi.org/10.1177/0954008316663810

[110] S. Stankovich, R. D. Piner, X. Chen, N. Wu, S. T. Nguyen, R. S. Ruoff, Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate), *Journal of Materials Chemistry A* **16** (2006) 155-158. https://doi.org/10.1039/B512799H

[111] A. Nardes M. Kemerink, K. M. De, E. Vinken, K. Maturova, R. Janssen, Conductivity, work function, and environmental stability of PEDOT:PSS thin films treated with sorbitol, *Organic Electronics* **9** (2008) 727-734. https://doi.org/10.1016/j.orgel.2008.05.006

[112] M. Hakimi, A. Salehi, F. Boroumand, Fabrication and characterization of an ammonia gas sensor based on PEDOT-PSS with N-doped graphene quantum dots dopant, *Journal of Sensors* **16** (2016) 6149-6154. https://doi.org/10.1109/JSEN.2016.2585461

[113] M. Wang, X. Y. Deng, A. K. Du, T. H. Zhao, J. B. Zeng, Poly(sodium 4-styrenesulfonate) modified graphene for reinforced biodegradable poly(ε-caprolactone) nanocomposites, *RSC Advances* **5** (2015) 73146-73154. https://doi.org/10.1039/C5RA15252F

[114] R. Verdejo, M. M. Bernal, L. J. Romasanta, M. A. Lopez-Manchado, Graphene filled polymer nanocomposites, *Journal of Materials Chemistry A* **21** (2011) 3301-3310. https://doi.org/10.1039/C0JM02708A

[115] M. Zhang, Y. Li, Z. Su, G. Wei, Recent advances in the synthesis and applications of graphene-polymer nanocomposites, *Polymer Chemistry* **6** (2015) 6107-6124. https://doi.org/10.1039/C5PY00777A

[116] E. Lago, P. S. Toth, G. Pugliese, V. Pellegrini, F. Bonaccorso, Solution blending preparation of polycarbonate/graphene composite: boosting the mechanical and electrical properties, *RSC Advances* **6** (2016) 97931. https://doi.org/10.1039/C6RA21962D

[117] M. Z. Iqbal, A. A. Abdala, V. Mittal, S. Seifert, A. M. Herring, M. W. Liberatore, Processable conductive graphene/polyethylene nanocomposites: Effects of graphene dispersion and polyethylene blending with oxidized polyethylene on rheology and microstructure, *Polymer* **98** (2016) 143-155. https://doi.org/10.1016/j.polymer.2016.06.021

[118] W. Chen, H. Weimin, D. Li, S. Chen, Z. Dai, Zhongxu, A critical review on the development and performance of polymer/graphene nanocomposites, *Science and Engineering of Composite Materials* **25** (2018) 1059-1073. https://doi.org/10.1515/secm-2017-0199

[119] C. Feng, D. Zhu, Y. Wang, S. Jin, Electromechanical behaviors of graphene reinforced polymer composites: a review, *Materials* **13** (2020) 528. https://doi.org/10.3390/ma13030528

[120] C. Tu, K. Nagata, S. Yan, Influence of melt-mixing processing sequence on electrical conductivity of polyethylene/polypropylene blends filled with graphene, *Polymer Bulletin* **74** (2017) 1237-1252. https://doi.org/10.1007/s00289-016-1774-4

[121] A. Graziano, S. Jaffer, M. Sain, Graphene oxide modification for enhancing high-density polyethylene properties: a comparison between solvent reaction and melt mixing, *Journal of Polymer Engineering* **39** (2019) 85-93. https://doi.org/10.1515/polyeng-2018-0106

[122] M. Šupová, G. S. Martynková, K. Barabaszová, Effect of nanofillers dispersion in polymer matrices: a review, *Science of Advanced Materials* **3** (2011) 1-25. https://doi.org/10.1166/sam.2011.1136

[123] L. Qi, Y. Li, J. Weng, B. Liu, X. He, The mechanical properties of polyethylene/graphene nanocomposites by in-situ synthesis, *Materials Research Express* **6** (2019) 065324. https://doi.org/10.1088/2053-1591/ab102b

[124] E. Su, W. Gao, X. Hu, C. Zhang, B. Zhu, J. Jia, A. Huang, Y. Bai, Preparation of ultrahigh molecular weight polyethylene/graphene nanocomposite in situ polymerization via spherical and sandwich structure graphene/SiO_2 support, *Nanoscale Research Letters* **13** (2018) 105. https://doi.org/10.1186/s11671-018-2515-4

[125] C. Kui, L. Haoliang, Z. Mohan, Q. Hanxun, Y. Junhe, In situ polymerization of graphene-polyaniline@polyimide composite films with high EMI shielding and electrical properties, *RSC Advances* **10** (2020) 2368-2377. https://doi.org/10.1039/C9RA08026K