High performance Pb$^{+2}$ detection using CVD-produced high quality multilayer reduced graphene oxide

Viviana Sarmiento$^{1,2,3}$, Malcolm Lockett$^{2,4}$, Emigdia Guadalupe Sumbarda-Ramos$^1$ and Oscar Vázquez-Mena$^{2,4}$$\text{© 2021 The Author(s). Published by IOP Publishing Ltd}$

Abstract
Detection of heavy metals such as Pb$^{+2}$ is critical due to their high toxicity as even trace amounts of them pose a serious detrimental risk to human health. Pb$^{2+}$ is one of the major toxic and persistent pollutants generated from industry and commonly found in soil, drinking water, and aquatic environments. Due to its high-mobility and one-atom thickness, graphene (Gr) based materials have shown great potential for chemical sensors of heavy metals. Recently, a novel conductive reduced-GO obtained by chemical vapor deposition (CVD-rMGO) showed improved layering structure and conductivity over conventional rGO based on chemically exfoliated flakes. Herein, utilizing this novel rGO obtained from chemical vapor deposition, we showed improved Pb$^{2+}$ detection using both electrochemical and conductivity sensing. For electrochemical sensing, a CVD-rMGO film is used as working electrode and cyclic voltammetry is used to detect Pb$^{+2}$ ions accumulated on the CVD-rMGO, obtaining a sensitivity of 4.6 nA nM$^{-1}$ cm$^{-2}$ and a calculated limit of detection of 0.21 nM. For electrical sensing, the drain current through a CVD-rMGO was monitored as the film as exposed to different concentrations of Pb$^{+2}$, reaching an estimated limit of detection of 0.101 nM. This work shows that high-quality reduced graphene oxide produced by chemical vapor deposition can serve as a basis enable high-sensitivity detectors of Pb$^{+2}$.

1. Introduction
Detection of heavy metals is critical due to their high toxicity to human health [1]. Pb$^{2+}$ is one of the major toxic and persistent pollutants generated from industry and commonly found in soil, drinking water, and aquatic environments [2]. Electrochemical methods have shown great promise detecting hazardous elements due to their inherent high sensitivity and low cost and easy on-site operation [3]. The use of nanoscale systems and materials as sensing materials for heavy metals has offered new opportunities due to their larger surface area, fast time-response, and low-volume footprint, which can enable easier heavy metal detection in terms of cost and portability, as well as reaching lower detection limits [4, 5]. In particular, the use of graphene for sensing applications offers several advantages [6–8] such as ultra-high mobility and ambipolar conduction [9], one-atom thick basal planes [10], and chemical functionalization versatility [11–15]. Different forms of graphene incorporating nanomaterials and chemical functionalization have been developed in order to optimize its sensing capabilities [16–21]. In particular, graphene oxide has been widely used for sensing using oxygen functional groups to tailor the chemical interactions and sensing capabilities of graphene [22–25]. Graphene oxide (GO) production has been mainly carried out by chemical exfoliation following Hummers method.
which is similar to the methods reported by Brodie in 1859 to study graphene basal planes. However, this method results in graphene oxide films made of disordered arrays of graphene flakes, severely affecting physical properties such as electrical conductivity, which can affect the performance of graphene-based devices. As an alternative, a novel method to produce high-quality, large, continuous, and highly conductive multilayer reduced graphene oxide (rMGO) obtained by chemical vapor deposition (CVD) was reported. Compared to conventional reduced multilayered graphene oxide films based on flakes produced by chemical exfoliation (flake-rMGO), the rMGO films obtained by chemical vapor deposition (CVD-rMGO) are continuous with improved layer stacking as they are based on multilayer graphene grown by CVD (CVD-MG). CVD-rMGO reaches 40% of the original CVD-MG conductance. The use of high continuous and ordered CVD-rMGO with high conductivity is important to enable portable devices that require low power consumption and small volume footprint.

Herein, we report a new platform for high-performing detection of heavy metal Pb²⁺ ions based on CVD produced high-quality rMGO, enabling both electrochemical and conductivity sensing of heavy metals such as Pb⁺². First we show that Pb²⁺ is detected by electrochemical sensing using cyclic voltammetries (CV), showing that the CVD-rMGO based chip detects traces of Pb²⁺ lower than the recommended limit for Pb²⁺ contamination in drinking water provided by the World Health Organization (WHO). Then, we also demonstrate Pb⁺² sensing based on electrical conduction using the CVD-rMGO chips for electrical detection of

![Figure 1. Measuring setups for Pb²⁺ detection using CVD-rMGO. (a) For the electrochemical setup, the working electrode was assembled using a Golden foil (Au), a copper (Cu) wire, the CVD-rMGO chip, and Polytetrafluoroethylene (PTFE) tape. (b) Diagram of the three-electrode electrochemical cell (80 ml) used in electrochemical analysis, consisting of a working electrode (WE), a Pt foil counter electrode (CE) and an Ag/AgCl electrode as reference electrode (RE). (c), (d) Optical images of the working electrode showing the copper wire and after PTFE wrapping. (e) Electrical conduction setup to test Pb²⁺ detection using the CVD-rMGO chip on a SiO₂ chip with predefined electrodes. (f) Optical images of the chip for electrical conduction sensing, showing the chip and rGO films. The active sensing area between the Au electrodes is 100 × 100 μm².](image-url)
metal ions in aqueous solutions. Thus, the CVD-rMGO chip might represent a new electrochemical/electrical platform for designing sensors of practical analysis which could be useful for the environmental analysis and biological applications, as well as for wearable and flexible devices.

2. Methods

2.1. Materials
CVD Multilayer Graphene (CVD-MG) with a thickness in the 500–800 nm range on Nickel foils (25 μm thick) was purchased from Graphene Supermarket. Analytical reagent grade H₂SO₄ (98%), H₃PO₄ (85%), KMnO₄, and HCl (10%) solution was purchased from Spectrum. Ethanol (90%) was purchased from Alfa Aesar. Buffer used for Pb²⁺ detections was 50 mM ammonium acetate (pH 6.3) containing 50 mM KCl (from Merck Millipore). The pH was adjusted with NaOH or acetic acid that were purchased from Sigma Aldrich. The stock Pb²⁺ solution (0.1 M) was prepared using Pb(NO₃)₂ from Sigma-Aldrich in Milli-Q water, and ammonium acetate buffer (pH 6.3) was used to make the diluted Pb²⁺ solutions with different concentrations for electrochemical analysis and 50 mM KCl solution was used for electrical experiments. All glassware was rinsed with 6 M HNO₃ and Milli-Q water to remove contamination by metal ions.

2.2. Fabrication of the CVD-rMGO chips
We have previously reported the fabrication of the CVD-rMGO chip used in this work which consists of a reduced chemical vapor deposited multilayer graphene oxide (CVD-MGO) [33]. The fabrication began with direct chemical conversion of large, highly ordered and continuous multilayer graphene (CVD-MG) into multilayer graphene-oxide (CVD-MGO) by our direct CVD-Hummers method. Our method prevents exfoliation by using the mechanical support of the CVD Ni foil and a more gentle acidic solution for oxidation. Then, the newly synthesized CVD-MGO was pre-treated with hydrazine hydrate vapor for initial reduction before implementing thermal reduction in a CVD chamber to obtain reduced CVD-GO (CVD-rMGO). Detailed information regarding CVD-rMGO fabrication and characterization of the films through oxidation and reduction is included in the supporting information SI.1 (figures SI-1 and SI-2) (available online at stacks.iop.org/NANOX/2/010023/mmedia).

2.3. Pb²⁺ detection

2.3.1. Electrochemical Pb²⁺ analysis
An electrochemical analyzer (910 PSTAT, Metrohm AG) was used for the electrochemical experiments at room temperature on the fabricated electrode with a three-electrode system. The working electrode was a CVD-rMGO chip contacted to a gold foil that was assembled into a copper wire as shown in figure 1(A). Then the electrode was coated using polytetrafluoroethylene (PTFE) film tape exposing a graphene area (1 × 2 mm²). Figure 1(B) shows a schematic of the electrochemical measuring setup. An Ag/AgCl electrode with 3 M of NaCl and a Pt wire were utilized as the reference and counter electrodes, respectively. Figures 1(C) and (D) show optical images of the working electrode assembly. For Pb²⁺ analysis, lead ions were accumulated on the CVD-rMGO surface by immersing the working electrode into 80 ml of a stirred solution of different concentration of Pb²⁺ in 50 mM ammonium acetate (pH 6.3) for 60 s. The electrode was removed, rinsed with ammonium acetate (pH 6.3) and transferred to an electrochemical cell with 50 mM ammonium acetate (pH 6.3) containing the electrolyte of 50 mM KCl for electrochemical measurements by cyclic voltammetry (CV). CV was conducted at a sweep rate of 0.1 Vs⁻¹ between −1.5 V and +1.5 V, and carried in triplicates on separate days using freshly prepared reagents for all cases. Statistical analysis was made comparing the mean of cathodic peaks of each experiment, using one-way ANOVA test with post hoc Tukey tests. Significance level was set at p < 0.05. Tukey’s tests are shown in tables SI.1 and SI.2 in the supporting information.

2.3.2. Electrical measurements
CVD-rMGO chips (figures 1(E) and (F)) were electrically contacted by pre-deposited gold electrodes on the Si/SiO₂ chip for electrical measurements using a probe station with a Keithley Sourcemeter at room temperature. The electrical conductance was recorded by monitoring the change in the drain current (I_DS) for a fixed source–drain voltage (V_DS) when the CVD-rMGO chip was exposed to 10 μl of different concentrations of Pb²⁺ solutions. A rubber ring was used to place the samples on the CVD-rMGO surface. In order to improve wettability of the CVD-rMGO chip we diluted Pb²⁺ solutions with 50 mM KCl. To further confirm the sensor repeatability, the detection process was repeated using 3 – 4 sensors, which showed similar sensing responses.
3. Results and discussion

A highly ordered and continuous multilayer graphene growth by CVD (CVD-MG) was converted into multilayer graphene oxide (CVD-MGO) using a direct CVD-Hummer method that relies on a gentle acidic solution for oxidation based on H$_2$SO$_4$ (98%), H$_3$PO$_4$ (85%) and KMnO$_4$ as described previously [33]. This method also allows to transfer the film onto a SiO$_2$/Si substrate. The film was then reduced to recover the conductive properties of the graphene basal planes using hydrazine hydrate vapor followed by thermal reduction to obtained CVD-reduced multilayer graphene oxide (CVD-rMGO). Detailed information regarding CVD-rMGO synthesis and characterization is included in the Supporting Information (figures SI-1 and SI-2). Cyclic voltammetry (CV) was employed to investigate the electrochemical properties of the CVD-rMGO using ammonium acetate:KCl solution at pH 6.3. The analysis was carried out at the potential window from $-1.5$ to $+1.5$ at scan rate of $0.1$ V s$^{-1}$. The experiments to determine optimal pH conditions are shown in the supporting information SI.2 (figures SI-3). The cyclic voltammograms are shown in figure 2(A), using CVD-rMGO as working electrode for ammonium acetate:KCl solution at pH 6.3 without Pb$^{2+}$ (rGO black line) and ammonium acetate: KCl with molarities from 5 to 110 nM Pb$^{2+}$ (color lines). The background voltammogram for the ammonium acetate:KCl solution (black line) shows cathodic and anodic waves from $-1.5$ V to $+1.5$ V. Addition of Pb$^{2+}$ reduced the current density of CVD-rMGO CV peaks (color lines).

To investigate the stability of the CVD-rMGO sensor prior to Pb$^{2+}$ detection, the electrical current behavior was studied before and after 6 cycles in acetate:KCl solution varying the pH in the 3.3–10.3 range with a scan rate...
of 100 mV s⁻¹. It was observed that even after 6 cycles, 100% of the initial current was retained. No significant differences between independent experiments performed in triplicates were observed (p < 0.05) (tables SI-1 and SI-2, supporting information), showing that the CVD-rMGO has good stability. The long-term storage stability of CVD-rMGO was tested by subjecting the same chip to Pb²⁺ detection with an electrolyte containing 110 nM Pb to 7 days. Interestingly, the magnitude of the current did not change. The underlying reason for this was that Pb²⁺ complexes with different oxygen-containing functional groups on CVD-rMGO surface, making it hard to desorb the target metal ions. Even by cleaning in nitric acid (0.1 M), the CVD-rMGO surface following electrochemical Pb²⁺ detection was no longer the same as prior to any Pb²⁺ deposition (figure SI-5, supporting information). These results clearly indicate that the chip with after Pb²⁺ detection cannot be reused conveniently.

Electrochemical detection of Pb²⁺ by CVD-rMGO involved a two-step process: chemical adsorption of Pb²⁺ ions on the working electrode surface, followed by the voltammetric analysis. During the adsorption step (60 s in a stirred sample), Pb²⁺ was accumulated on CVD-rMGO, which was immobilized on the surface by complexation chemistry (figure 3). As expected, the pH of the solution has significant influence on the adsorption process. To remove the residual ions, the working electrode was rinsed with ammonium acetate. We believe that the carboxylic and hydroxyl groups act as anchor sites to adsorb heavy metal ions on CVD-rMGO surface [35], similar to those on carbon nanotubes surface [36]. Moreover, the precipitation will occur between Pb²⁺ and OH⁻ as the pH exceeds pH 7.0 [37], and CVD-rMGO displayed optimal electrochemical performance at pH 6.3 [SI.2, Supporting Information]. Thus, pH 6.3 was selected for the Pb²⁺ electrochemical detection. This step allowed the preconcentration of metal ions without electrolyte, applied potential, or degassing of the solution. CVD-rMGO readily detected Pb²⁺ without significant sample pretreatment other than adjusting the sample pH to 6.3.

The electrochemical response of Pb²⁺ involved reduction-oxidation reactions. The CVD-rMGO before the addition of Pb²⁺ gives the well-defined peak current, attributed to the presence of functional groups including hydroxyl, carboxyl groups, which favors the facile diffusion of electrolytes by improving wettability and resulting in an increased specific capacitance [38]. Consequently, the blocking of the active sites (carboxylic and hydroxyl groups) by chemical adsorption of Pb²⁺ ions lead to a significant inhibition of the electron transfer. Therefore, a decrease in oxidation peaks, with increasing Pb²⁺ concentration indicates the irreversible deposition/intercalation of Pb²⁺ directly onto the working electrode surface (CVD-rMGO). The cathodic peaks decrease with increasing Pb²⁺ concentration can be ascribed to the reduction of electrochemically active oxygen-containing groups on the surface of CVD-rMGO as carboxyl groups interact with metal ions. To gain deep insight into the adsorption mechanism, it is important to clarify the fundamental principle of generation of the current observed in our experiment. During the electrochemical detection of Pb²⁺ the following reactions may have taken place on electrode surface. In the first step, lead divalent ions (Pb²⁺) are deposited on the CVD-rMGO surface and then in the forward scan they may be reduced to neutral lead (Pb⁰). When Pb⁰ atoms reacted with the hydroxyl generated from the electrochemical reduction of different oxygen-containing functional groups (carboxyl and hydroxyl) on CVD-rMGO, these interactions can lead to the formation of a Pb-O bond on the electrode surface [39].

The effect of Pb²⁺ concentration on the CVD-rMGO was examined by recording the CV at each concentration from 5 to 110 nM Pb²⁺ and plotting current density versus concentration for either the anodic peak (Ipa) or the cathodic peak (Ipc). The relationship between concentration and cathodic current peaks was linear. (figure 2(B)) However, the anodic waves (Ipa) the concentrations of the Pb²⁺ ions exhibited a nonlinear relationship as shown in figure SI-4 (supporting information). Thus, for the analysis, cathodic signals were chosen, studying the shift in cathodic peak current (ΔIpc), corresponding the difference in Ip between the signal due to the presence of Pb²⁺ and the recovery CV obtained by cleaning of the chip before each measurement cycle. The resulted calibration is shown figure 2(C), showing a linear behavior in the ΔIpc versus Pb²⁺ concentration curve in the range from 5 to 110 nM and a sensitivity of 4.6 nA nM⁻¹ cm⁻² with a correlation coefficient of R² = 0.998. The limit of detection (LOD), described as the smallest concentration of an analyte that can be reliably measured by an analytical procedure, was calculated on the basis of 3 sB criterion (LOD = 3sB/m), where m was the slope of calibration curve and sB the standard deviation of 9 successive measurements of blank (CVD-rMGO before Pb²⁺ additions) [40, 41]. A lower LOD for Pb²⁺ ions as low as 0.21 nM was achieved, which is much lower than the maximum contaminant level (MCL) for Pb²⁺ ions in drinking water recommended by the World Health Organization (WHO) [34].

The comparison of the detection limit of the present work with other works is shown in table 1. Bismuth-based electrochemical sensors have been reported for Pb²⁺ detection using Square wave anodic stripping voltammetry (SWASV) [42–44]. These methods have shown good detection for different metals and exhibit higher sensitivity than our method (See table 1), but they require prior functionalization with bismuth. Wang et al [45], reported a LOD of 0.2 ng ml⁻¹, using graphene oxide reduced sheets to detect Pb²⁺ and Hg²⁺ by differential pulse anodic stripping voltammetry (DPASV). The two-step approach used to obtain the working
electrode, in which the sensing surface was assembled on a glassy carbon electrode, requires more time and materials, increasing consequently costs, unlike the simplicity of our method.

In addition to electrochemical detection, we also used CVD-rMGO for Pb²⁺ detection by measuring the change in conductivity of the CVD-rMGO on a chip, achieving the detection of the Pb²⁺ that was bound onto CVD-rMGO surface. The electrical conductance was recorded by monitoring the change in the drain current ($I_{ds}$) for a fixed source–drain voltage ($V_{ds}$) when the CVD-rMGO chip was exposed to 10 μl of different concentrations of Pb²⁺ solutions (figure 4(A)). It is clear that higher concentrations of Pb²⁺ result in higher conductance through the CVD-rMGO. The changes in current ($I_{ds}$) normalized to the current of the rGO in water ($I_{r}$) at 0.9 Volts are reported in the calibration curve as $\Delta I_{ds}/I_{r}$ versus $[\text{Pb}^{2+}]$ in figure 4(B), showing the values for multiple repetition measurements recorded for each Pb²⁺ concentration. The LOD was evaluated according to the $3s_b/m$ criteria, where $s_b$ is the standard deviation of the blank and $m$ is the slope of the linear calibration curve, reaching a LOD = 0.101 nM. We suggest that the CVD-rMGO conductance changed its sensitivity due to the electron donating and withdrawing effect of target ions. The deposition/intercalation of Pb²⁺ enhanced the drain current of the CVD-rMGO chip, which might have triggered the electrons transfer.

Table 1. Comparison of analytical results of different method for Pb²⁺ detection. SWASV: Square-wave anodic stripping voltammetry; CV: Cyclic Voltammetry; FET: field-effect transistor.

| Type of interface | LOD          | Sensitivity       | Detection | Method | References |
|------------------|--------------|-------------------|-----------|--------|------------|
| rGO microsensor  | 0.2 ppb      | 926 nA/ppbcm²     | Pb²⁺      | SWASV  | [18]       |
|                  | 0.6 ppb      | 262 nA/ppbcm²     | Cd²⁺      |        |            |
|                  | 1 ng ml⁻¹    | —                 | Hg²⁺      |        |            |
| rGO/Bi nanocomposite | 17 μg l⁻¹ | —                 | Zn²⁺      | SWASV  | [19]       |
|                  | 26 μg l⁻¹    | —                 | Cu²⁺      |        |            |
|                  | 0.55 μg l⁻¹  | —                 | Pb²⁺      |        |            |
|                  | 2.8 μg l⁻¹   | —                 | Cd²⁺      |        |            |
| Gr-NPAu-DNA      | 20 pM        | —                 | Pb²⁺      | FET    | [21]       |
| EG/SiC microfluidic cell | 95 nM | 0.101 nM /μM⁻¹ | Pb²⁺      | SWASV  | [17]       |
|                  | 1 nM         | —                 | Hg²⁺      | FET    | [22]       |
| rGO-protein microfluidic cell | 1 nM | —                 | Cd²⁺      | FET    | [23]       |
| rGr-O-NPAu       | <1 ppb       | —                 | Pb²⁺      | FET    |            |
| CVD-rMGO         | <0.21 nM     | 4.6 nA nm⁻¹ cm⁻² | Pb²⁺      | FET    | Our work   |

rGO: Reduced graphene oxide.
GCE: Glassy carbon electrode.
Bi: Bismute.
Gr-NPAu: Gold nanoparticle and DNAzyme functionalized graphene device.
TGA-AuNP: Thioglycolic functionalized gold nanoparticles.
EG: Epitaxial graphene on Silicon face.
from the CVD-rMGO to the Pb\textsuperscript{2+}, increasing the density of holes in the CVD-rMGO film and thereby increasing the drain current.

The conductivity-based sensors for heavy metal ion detection have achieved very low detection limits and potentially provides opportunities for compact systems. However, they require labels and other specific reagents such as gold nanoparticles \cite{46, 47}, proteins and DNA \cite{46–48}, that will potentially limit the test environment (pH, ionic strength). Our approach is label free, offering a simpler and easier method. Our method might be similar to that method reported by Santangelo \textit{et al} \cite{42}, to detect Pb\textsuperscript{2+} and Cd\textsuperscript{2+} in which they achieve higher sensitivity (LOD = 95 nM) than ours (LOD = 0.101 nM), but their device was based on epitaxial graphene layers that are not suitable for large scale implementation. Here, we have demonstrated that a facile CVD-rMGO conduction device can be utilized to rapidly detect and label free Pb\textsuperscript{2+} ions in solution with good sensitivity and achieving larger areas due CVD growth method. This nanoelectronic approach is amenable for the development of lab-on-a-chip devices.

4. Conclusions

In this study, we have obtained a sensitive electrochemical and electrical sensor using the recently developd CVD-rMGO for chip Pb\textsuperscript{2+} determination, achieving high sensitivity for Pb\textsuperscript{2+} and exhibited broad linearity, low detection limit, and satisfactory reproducibility and stability. The CVD-rMGO chip was able to detect low traces of Pb\textsuperscript{2+} ions, which is lower than the recommended limit for Pb\textsuperscript{2+} contamination in water provided by WHO (For Drinking water below 5 µg\textsuperscript{L\textsuperscript{-1}}). Under our conditions, the limit of detection (LOD) for the CVD-rMGO toward Pb\textsuperscript{2+} were 0.21 nM and 0.101 nM for electrochemical and electrical analysis respectively. Selectivity with regard to other heavy metals such as Cd and Hg remains to be explored as it is important to study the heavy-metal profile in relevant situations. This CVD-rMGO chip is amenable for the development of electrical detectors that have a simpler and compact integration. Furthermore, the chemical and mechanical stability of graphene can also open the path to use graphene as flexible or wearable device with high-sensitivity.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Oscar Vázquez-Mena @ https://orcid.org/0000-0001-9054-5183

References

\begin{enumerate}
\item Bradham K and Randall W 2010 Scientific Issues in the U.S. EPA Framework for Metals Risk Assessment \textit{J. Toxicol. Environ. Health Part A}, 73 108–13
\item Ara A and Usmani J A 2015 Lead toxicity: a review \textit{Interdisciplinary Toxicology}. 8 55–64
\item Bansod B, Kumar I, Thakur R, Rana S and Singh I 2017 A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms \textit{Biosens. Bioelectron.}, 94 443–55
\item Chang J, Zhou G, Christensen E R, Heideman R and Chen J 2014 Graphene-based sensors for detection of heavy metals in water: a review \textit{Anal. Bioanal. Chem.} 406 3957–75
\item Aragay G, Pons J and Merkoçi A 2011 Recent trends in macro-, micro-, and nanomaterial-based tools and strategies for heavy-metal detection \textit{Chem. Rev.} 111 3433–58
\item Nag A, Mitra A and Mukhopadhyay S C 2018 Graphene and its sensor-based applications: a review \textit{Sens. Actuators, A} 270 177–94
\item Coro$ş$ M, Pruneau S and Stefan-van Staden R-I 2019 Recent progress in the graphene-based electrochemical sensors and biosensors \textit{J. Electrochem. Soc.} 167 037528
\item Shao Y, Wang J, Wu H, Liu J, Aksay I A and Lin Y 2010 Graphene based electrochemical sensors and biosensors: a review \textit{Electroanal.} 22 1027–36
\item Novoselov K S \textit{et al} 2005 Two-dimensional gas of massless Dirac fermions in graphene \textit{Nature} 438 197–200
\item Novoselov K S \textit{et al} 2004 Electric field effect in atomically thin carbon films \textit{Science} 306 666–9
\item Torres T 2017 Graphene chemistry \textit{Chem. Soc. Rev.} 46 4385–6
\item Balandin A A 2011 Thermal properties of graphene and nanostructured carbon materials \textit{Nat. Mater.} 10 569–81
\item Craciun M F, Russo S, Yamamoto M and Tarucha S 2011 Tuneable electronic properties in graphene \textit{Nano Today.} 6 42–60
\item Rochefort A and Wuest J D 2009 Interaction of substituted aromatic compounds with graphene \textit{Langmuir} 25 210–5
\item Luo L L, Gu X X, Wu J, Zhong S X and Chen J R 2012 Advances in Graphene for Adsorption of Heavy Metals in Wastewater \textit{J. Adv. Mater. Res.} 550–553 2121–4
\item Zeng R, Luo Z, Zhang L and Tang D 2018 Platinum nanosymeye–catalyzed gas generation for pressure–based bioassay using polyaniline nanowires–functionalized graphene oxide framework \textit{Anal. Chem.} 90 12299–306
\item Shu J, Qiu Z and Tang D 2018 Self-referenced smartphone imaging for visual screening of H2S using Cu x O-polypyrrole conductive aerogel doped with graphene oxide framework \textit{Anal. Chem.} 90 9691–4
\end{enumerate}
[18] Cai G, Yu Z, Ren R and Tang D 2018 Exciton–plasmon interaction between AuNPs/graphene nanohybrids and CdS quantum dots/TiO₂ for photoelectrochemical aptasensing of prostate-specific antigen ACS Sens. 3 632–9

[19] Zhou Q, Lin Y, Zhang K, Li M and Tang D 2018 Reduced graphene oxide/BiFeO₃ nanohybrids-based signal-on photoelectrochemical sensing system for prostate-specific antigen detection coupling with magnetic microfluidic device Biosens. Bioelectron. 101 146–52

[20] Zhou Q, Lin Y, Shu J, Zhang K, Yu Z and Tang D 2017 Reduced graphene oxide-functionalized FeOOH for signal-on photoelectrochemical sensing of prostate-specific antigen with bioresponsive controlled release system Biosens. Bioelectron. 98 15–21

[21] Lin Y et al 2016 Magnetic graphene nanosheet-based microfluidic device for homogeneous real-time electronic monitoring of pyrophosphatase activity using enzymatic hydrolysis-induced release of copper ion Anal. Chem. 88 1030–8

[22] Pumera M 2011 Graphene in Biosensing Mater. Today 14 308–15

[23] Suvarnaphat P and Pechprasarn S 2017 Graphene-based materials for biosensors: a review Sensors 17 2161

[24] Chen D, Feng H and Li J 2012 Graphene oxide: preparation, functionalization, and electrochemical applications Chem. Rev. 112 6027–53

[25] Eigler S and Dimiev A M 2017 Functionalization and reduction of graphene oxide Graphene Oxide. 175–229

[26] Chen J, Yao B, Li C and Shi G 2013 An improved Hummers method for eco-friendly synthesis of graphene oxide Carbon 64 225–9

[27] Marcano D C, Kosynkin D V B, Sinitskii J M, Sun A, Slesarev Z, Alemany A, Lu L B and Tour J M 2010 Improved synthesis of graphene oxide ACS Nano. 4 4806

[28] Zaaba N I, Foo K L, Hashim U, Tan S J, Liu W-W and Voon C H 2017 Synthesis of graphene oxide using modified hummers method: solvent influence Procedia Engineering. 184 469–77

[29] Alam S N, Sharma N and Kumar L 2017 Synthesis of graphene oxide (GO) by modified hummers method and its thermal reduction to obtain reduced graphene oxide (rGO) Graphene. 6 1–18

[30] Chang C-I, Chang K-H, Shen H-H and Hu C-C 2014 A unique two-step Hummers method for fabricating low-defect graphene oxide nanoribbons through exfoliating multiwalled carbon nanotubes J. Taiwan Inst. Chem. Eng. 45 2762–9

[31] Brodie B C 1859 XIII. On the atomic weight of graphite Philosophical Transactions of the Royal Society of London 149 249–59

[32] Dong L, Yang J, Chhowalla M and Loh K P 2010 Improved synthesis and reduction of large sized graphene oxide sheets Chem. Soc. Rev. 39 7306–16

[33] Lockett M, Sarmiento V, Balingit M, Oropeza-Guzmán M T and Vázquez-Mena O 2020 Direct chemical conversion of continuous CVD graphene/graphite films to graphene oxide without exfoliation Carbon 158 202–9

[34] World Health Organization 2003 Lead in Drinking Water: background document for development of WHO guidelines for drinking-water quality WHO/SE/WSH/03.04/09 World Health Organization www.who.int/en

[35] Yang Set al 2015 Competitive adsorption of PbII, NiII, and SrII ions on graphene oxides: a combined experimental and theoretical study Chem. Plus Chem. 80 480–4

[36] Perez-Aguilar N V, Munoz-Sandoval E, Diaz-Flores P E and Rangel-Mendoza J R 2010 Adsorption of cadmium and lead onto oxidized nitrogen-doped multiwall carbon nanotubes in aqueous solution: equilibrium and kinetics J. Nanopart. Res. 12 467–80

[37] Li Y-H, Di Z, Ding J, Wu D, Luan Z and Zhu Y 2005 Adsorption thermodynamic, kinetic and desorption studies of Pb²⁺ on carbon nanotubes Water Res. 39 605–9

[38] Bleda-Martínez M, Macía-Agullo J A, Lozano-Castelló D, Morallón E, Cazorla-Amorós D and Linarese-Solano A 2005 Role of surface chemistry on electric double layer capacitance of carbon materials Carbon 43 6777–84

[39] Ramesha G K and Sampath S 2011 In-situ formation of graphene–lead oxide composite and its use in trace arsenic detection Sensors Actuators B 160 308–11

[40] Manjunath J G 2018 A novel voltammetric method for the enhanced detection of the food additive tartrazine using an electrochemical sensor Heliyon. 4 e00986

[41] Manjunath J G 2018 A novel polyylic biosensor towards the detection of indigo carmine: a voltammetric study Journal of Food and Drug Analysis. 26 292–9

[42] Santangelo M F et al 2019 Epitaxial Graphene sensors combined with 3D-printed microfluidic chip for heavy metals detection Sensors 19 2393

[43] Xuan X, Hossain M F and Park J Y 2016 A fully integrated and miniaturized heavy-metal-detection sensor based on micro-patterned reduced graphene oxide Sci. Rep. 6 33125

[44] Sahoo P K, Panagrahy B, Sahoo S, Satpati A K, Li D and Bahadur D 2013 In situ synthesis and properties of reduced graphene oxide/Bi nanocomposites as an electroactive material for analysis of heavy metals Biosens. Bioelectron. 43 239–46

[45] Wang S et al 2018 Simultaneously detection of Pb²⁺ and Hg²⁺ using electrochemically reduced graphene oxide Int. J. Electrochem. Sci. 13 785–96

[46] Wen Y, Li F Y, Dong X, Zhang J, Xiong Q and Chen P 2013 The electrical detection of lead ions using gold-nanoparticle and DNAzyme-functionalized graphene device Adv. Healthc. Mater. 2 271–4

[47] Sudhibya H G, He Q, Zhang H and Chen P 2011 Electrical detection of metal ions using field-effect transistors based on micropatterned reduced graphene oxide films ACS Nano. 5 1990–4

[48] Matty A et al 2017 Pulse-driven capacitive lead ion detection with reduced graphene oxide field-effect transistor integrated with an analyzing device for rapid water quality monitoring ACS Sens. 2 1653–61