





Research paper

Sensitive and selective detection of Cu²⁺ and Pb²⁺ ions using Field Effect Transistor (FET) based on L-Cysteine anchored PEDOT:PSS/rGO composite

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Highlights

- The Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)/reduced graphene oxide/L-Cysteine (PEDOT:PSS/rGO/LC) synthesized successfully.
- Field-Effect Transistor (FET) sensor for the sensitive and selective detection of copper and lead (Cu²⁺ and Pb²⁺) ions are discussed.
- Sensor device responded within 2–3 s after incubation of the Cu²⁺ and Pb²⁺ ions solution over PEDOT:PSS/rGO/LC Channel.

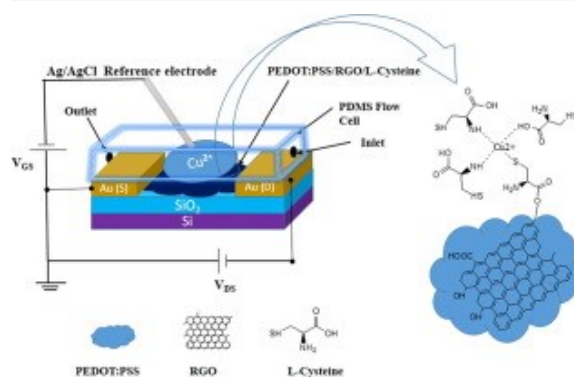
Abstract

Herein, Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/reduced graphene oxide (rGO) (PEDOT:PSS/rGO) composite was prepared and further functionalized with L-Cysteine

(LC) to manifest sensitive and selective detection of copper (Cu²⁺) and lead (Pb²⁺) ions using Field Effect Transistor (FET) in the concentration range of 1–60 µg/L. The sensor (PEDOT:PSS/rGO/L-Cysteine) exhibits low-voltage operations, highly sensitive and selective towards target metal ions (Cu²⁺ and Pb²⁺). The lower detection limits for Cu²⁺ and Pb²⁺ were found to be 0.33 µg/L and 2.36 µg/L, which is well below the World Health Organization WHO recommendations (2 mg/L (2 ppm) for Cu²⁺ ions and 10 µg/L (10 ppb) for Pb²⁺ ions.

Graphical abstract

An architecture of FET sensor for the detection of heavy metal ions.



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Introduction

Water contamination due to heavy metal ions is the ground reality, and it is one of the grand challenges in environmental monitoring. Although some of the heavy metal ions are essential nutrients to human beings, plants, animals, and living organisms, the higher concentration than optimal values will result in toxicity [1], [2], [3]. The exposure to a higher concentration of heavy metal ions leads to the effect on human health and aquatic animals [4], [5]. Among the heavy metal ions, copper (Cu) is one of the toxic heavy metals that potentially affects humans, leading to adverse effects on neurodegenerative diseases, respiratory system, hepatic damage, acute hemolytic anemia, and neurotoxicity [6], [7], [8]. Whereas, lead (Pb) is ubiquitous, non-biodegradable, widely distributed, and its presence in drinking water causes more significant risks to human health and animals [9], [10], [11]. The maximum acceptable concentration for copper and lead in drinking water should be 2 mg/L (2 ppm) and 10 µg/L (10 ppb) according to the guidelines of the World Health Organization (WHO) and U.S. EPA [2], [12]. The risk of toxicity due to heavy metal ions can be minimized by monitoring aqueous phase pollutants using stable polymeric materials. Among the conducting polymers, the commercially available PEDOT:PSS has proven its stability in

an aqueous environment and possesses excellent potential applications in FET due to its low cost, high transparency, and excellent processability [13], [14], [15], [16], [17]. But the application in sensor technology may be limited due to the low conductivity or mobility of the PEDOT:PSS conducting polymer. Hence, efforts have been carried out to enhance the conductivity of commercially available PEDOT:PSS conducting polymer by adding the solvent additives and organic molecules [18], [19], [20], [21]. Reduced graphene oxide (rGO) has high carrier mobility, high electrical and thermal conductivity, good mechanical strength, and optical transparency [22], [23], [24], [25]. Moreover, the assembling of PEDOT:PSS chains over the surfaces of rGO sheets through π -stacking interactions between both the materials was reported [26]. Therefore, the mobility in the conducting polymer can be enhanced by incorporating chemically reduced GO into the commercially available PEDOT:PSS stable matrix. Hence, the PEDOT:PSS/rGO composite can be functionalized with LC for FET sensing of heavy metal ions. The functionalization of the conducting polymer materials plays an important role due to aqueous medium stability, high affinity to the target analyte, reduced aggregation, and good specific chemical reactivity to facilitate the accumulation of target ions [27].

To detect Cu²⁺ and Pb²⁺ ions from aqueous media, there are several techniques based on spectrometric, fluorescent, electrochemical, colorimetric, and optical methods that have been reported to date. However, it has certain drawbacks, e.g. low-cost, easy-to-use, and reliable device fabrication are not possible. The FET based heavy metal ions/gas sensors received much attention due to its convenient and low-cost fabrication, good sensitivity, mechanical flexibility, portability, biocompatibility, and properties tunability [28], [29], [30], [31], [32], [33]. Heavy metal ions (Cu²⁺ and Pb²⁺) have a good affinity towards -SH moiety in LC which can be employed as a base for the detection of heavy metal ions from aqueous media. Therefore, we combined the advantages of a high affinity of LC to anchor over PEDOT:PSS/rGO composite for the sensitive and selective detection of Cu²⁺ and Pb²⁺ [34]. The detection limit achieved for Cu²⁺ and Pb²⁺ is 0.33 μ g/L and 2.36 μ g/L which is much below than the reported literature [35], [36], [37], [38], [39], [40], [41], [42], [43], [44] and WHO recommendations [45], [46].

Section snippets

Chemicals

All the chemicals required for the synthesis of materials were of high purity grades ($\geq 99\%$) and used without further purification. Graphite powder, acetone ((CH₃)₂CO), isopropyl alcohol (C₃H₈O) was procured from Molychem, phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), potassium permanganate (KMnO₄) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) which has a concentration of 1.3 wt% were procured from Sigma Aldrich. Hydrazine hydrate (N₂H₄) and...

X-ray diffraction

X-ray diffraction (XRD) pattern of PEDOT:PSS, rGO, PEDOT:PSS/rGO and LC modified PEDOT:PSS/rGO composite is shown in Fig. 2. The XRD pattern of all these materials in the present investigation was recorded with 0D operation mode in high-resolution parallel-beam geometry. There were no peaks observed in PEDOT:PSS due to its poor crystalline structure [48]. Whereas, chemically reduce GO was well-matched with previously reported data [49], [50], [51]. The modification of PEDOT:PSS/rGO composite...

Conclusions

L-Cysteine modified PEDOT:PSS/rGO FET sensor was developed for the detection of Cu²⁺ and Pb²⁺ ions with the detection limit of 0.33 µg/L and 2.36 µg/L in ambient temperature. Enhancement in mobility was achieved after modification of PEDOT:PSS/rGO with L-Cysteine, which was suitable for sensitive and selective detection of Cu²⁺ and Pb²⁺ in an aqueous medium for environmental monitoring. The detection limits were achieved well below the WHO recommendations. A high affinity of L-Cysteine towards...

CRediT authorship contribution statement

Pasha W. Sayyad: Project administration, Investigation, Methodology, Software, Writing - original draft, Data curation. **Nikesh N. Ingle:** Visualization, Data curation. **Theeazen Al-Gahouari:** Formal analysis. **Manasi M. Mahadik:** Formal analysis. **Gajanan A. Bodkhe:** Software. **Sumedh M. Shirsat:** Formal analysis. **Mahendra D. Shirsat:** Resources, Conceptualization, Supervision, Validation, Funding acquisition, Project administration....

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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2023, Case Studies in Chemical and Environmental Engineering

Citation Excerpt :

...Also, it can quickly get into the food chain and cause long-term, toxic effects on living organisms. According to the World Health Organization (WHO) guidelines for drinking water, the acceptable concentration limits for Copper (II) (Cu²⁺) are 0.003 mg/L to 0.01 mg/L [1]. One of the methods that have been used to remove Cu²⁺ effectively is because it is simple, effective, and cheap [2]....

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...Recently, incorporating rGO into conducting polymer (CPs) composites has been deemed a practical approach to overcome this shortcoming. Researchers have demonstrated that hybridizing CPs with GO and rGO enhances the selectivity and sensitivity of the sensors compared with GO and rGO sensors [17–19]. CPs and their nanocomposite are widely adopted as effective sensing materials due to their inexpensive, selectivity, and high sensitivity towards gas species and volatile organic compounds (VOCs)....

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Citation Excerpt :

...Nowadays, designing functional nanomaterials with peptides exhibits excellent performance to improve the sensitivity, selectivity, and stability of electrochemical sensing. It is still the frontier and hotspot of electrochemical sensor research [34]. The hypothesis of this study was to detect Cd(II) ions selectively and with high sensitivity at low concentrations....

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...The detection limit (LOD) and quantification detection limits (LOQ) can be calculated as 0.138 μM, 0.461 μM, respectively by the following equations: LOD = 3σ/KSV, LOQ 10σ/KSV (σ: standard error). The lower detection limit for Cu²⁺ is well below the World Health Organization WHO recommendations (2 mg/L (2 ppm) (31.5 μM)) for Cu²⁺ ions [54]. Therefore, it was concluded that BGWO:0.10 mol Eu³⁺ exhibited selective and sensitive performance for detecting and recognizing Cu²⁺ ions....

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...Graphene, a single layer of sp² hybridized carbon atoms tightly packed into a hexagonal honeycomb lattice, has attracted considerable attention from both theoretical and experimental scientists [1,2]. Moreover, graphene has been extensively explored in multiple potential applications, including energy-related fields [3], electronic sensors [4,5], and biomedical applications [6]. Many efforts have been done to obtain graphene and graphene-like materials....

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