Graphitic Carbon Nitride Derived Probes for the Recognition of Heavy Metal Pollutants of Environmental Concern in Water-bodies

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Abstract

Graphitic carbon nitride (g-CN) has a number of valuable features that have been recognized during the studies related to its photocatalytic activity enhancement derived by visible-light. Because of these characteristics, g-CN can be used as a detecting signal transducer with different transmission modalities. The latest up-to-date detection capabilities of modified g-CN nanoarchitectures are covered in this study. The structural features and synthetic methodologies have been discussed in a number of reports. Herein, employment of the g-CN as a promising probing modality for the recognition of different toxic heavy metals is the promising feature of the present study.

Keywords; Graphitic carbon nitride; nanomaterials; naked eye detector; toxic metals; aqueous matrices

1. Introduction

Water is the basic need of human life and is required for various activities like drinking, cooking, human recreation, agriculture, industries and waste disposal. The quantity and quality of water are the two issues that people are now dealing with. Demand for pure water is increasing with global increases in population (Masood et al., 2015). However, with industrialization and urbanization, fresh water is turning to contaminated water as the effluents of the industries like textile, leather tanning, agriculture research, hair coloring, light harvesting array, paper production and food technology are discharged without proper treatment (Mansha, Waheed, Ahmad, Kazi, & Ullah, 2020; Tahir Rasheed, Bilal, Li, & Iqbal, 2017). Discharge of various industries contains heavy metal ions (Z. Xu et al., 2019), dyes (Mansha, Kazi, et al., 2020) (Waheed, Kazi, et al., 2020) and antibiotics (Manzar et al., 2022). This makes the water unsuitable for human use as well harmful for aquatic life. Moreover, it also suppresses the microbial activity leading to decreased soil fertility (Valapil, Kadagathur, & Shankaraiah, 2021).

Heavy metals are a serious threat to the environment as they are non-biodegradable metallic elements (Tahir Rasheed, Bilal, Nabeel, Adeel, & Iqbal, 2019; Tahir Rasheed, Bilal, et al., 2018; Tahir Rasheed, Li, Bilal, Yu, & Iqbal, 2018; Tahir Rasheed & Nabeel, 2019). Even low concentrations of the heavy metals possess deleterious effects due to their carcinogenicity and genotoxicity abilities (Bjørklund, Bengtsson, Chirumbolo, & Kern, 2017). For example, mercury is used in various industries like paints, ammunition, (Hu & Pan, 2012) pesticides, mining etc.(Cabecinhas et al., 2015). As a result, it discharged and pollute air and water in diverse forms together with metallic (Hg^{o}), mercuric (Hg^{2+}), organic mercury (phenyl and alkyl mercury) and inorganic mercurous (Hg^{2+}). However, high volatility, bonding with sulfur containing amino acids, higher water solubility and easy transfer to food chain makes the Hg^{2+} an acute toxic analyte (J. Zhang et al., 2015). Because of this, drinking of water even with low concentration of Hg^{2+} can damage endocrine, immune system, central nervous system, reproductive system, cardiovascular, gastrointestinal and renal system of the human which is characterized by memory loss, lack of coordination, deafness and vision problem (Chemnasiri & Hernandez, 2012). The environmental protection agency and World health organization have stipulated the Hg^{2+} amount in drinking water to be 30 and 10 mg/L respectively (Aragay, Pons, & Merkoçi, 2011). Furthermore, arsenic, lead and cadmium pose stern health and environmental hazards. Arsenic is fatal if exposed to their higher concentration. It is carcinogenic in all oxidation states and can hinder the formation of adenosine triphosphate during respiration (Chini, Kumar, Javed, & Satapathi, 2019). Long exposure to cadmium could result in lung damage, renal failure and bone weakening. It is also documented that lead causes teratogenic effects abnormality of kidney and inhibition of hemoglobin synthesis.(Chini et al., 2019). This demands continuous tracking of heavy metal ions in the water for which there is a need of highly sensitive, selective, cost effective and fast response sensors (Nabeel & Rasheed, 2020; Nabeel, Rasheed, Mahmood, & Khan, 2020; T Rasheed, 2022; Tahir Rasheed, Hassan, Bilal, Hussain, & Rizwan, 2020; Tahir Rasheed et al., 2022; Tahir Rasheed, Nabeel, Adeel, Bilal, & Iqbal, 2019; Tahir Rasheed, Nabeel, Adeel, Rizwan, et al., 2019; Tahir Rasheed, Nabeel, Li, & Bilal, 2019; Tahir Rasheed, Nabeel, Li, & Zhang, 2019; Tahir Rasheed, Nabeel, Shafi, Bilal, & Rizwan, 2019; Tahir Rasheed & Rizwan, 2022). Conventionally analytical strategies and instruments like high performance liquid chromatography, electrochemical sensing, atomic absorption spectroscopy and fluorescence spectroscopy, are used for the detection of heavy metal ions. They are effective in sensing heavy metal, but they suffer from limitations like laborious sample preparation, expensive and heavy instrumentation, which makes them time consuming and unfit for onsite applications.(Waheed, Ahmad, Haroon, & Ullah, 2020). In this regard carbon based nanomaterials have attracted great attraction due to their high efficiency, signal visibility, portability, low cost and short response time (Amanulla, Perumal, & Ramaraj, 2019).

Carbon based materials have received great attention for the sensing of heavy metal ions due to their high surface area, chemical stability, unique physiochemical and mechanical properties(Xing et al., 2016). Much graphene based electrochemical sensors are developed for the sensing of heavy metal ions. For example, Zhao et al. used electrode modified with polypyrrole-reduced graphene oxide nanocomposite for the trace level detection of Pb(II) through electroanalytical method (Zhao, Chen, Yang, Liu, & Huang, 2012). Carbon dots and carbon nanomaterials have grabbed the attraction for biological applications due to their low toxicity which makes them biocompatible. Their outstanding electron donor and electron acceptor properties makes them suitable for the electrochemical and fluorescent based sensing of heavy metal ions.(Simpson et al., 2018). Detection of heavy metal is important for the well-being of the human. C-dots are mainly used due to their fluorescent properties. For example, mercury ion in water sample was detected due to fluorescence quenching of the fluorescent C-dots with the addition of the metal ions (Barman & Sadhukhan, 2012). B. Amanullah et al. used composite of gold NPs accumulated on Sulphur doped on g-CN for the sensing of Hg^{2+} in water samples. Limits of detection was calculated to 0.275 nm (Amanulla et al., 2019).

Among other carbon-based materials, Graphitic carbon nitride (g-C_3N_4) has emerged as a promising material for sensing heavy metals due to its exceptional properties such as high surface area, tunable electronic structure, and chemical stability. However, its application in heavy metal sensing is not without limitations. One significant constraint is its inherent selectivity towards specific heavy metal ions, as g-C_3N_4-based sensors may exhibit varying degrees of sensitivity and response to different heavy metals. Additionally, the relatively low conductivity of g-C3N4 can lead to limited charge transfer and sluggish kinetics at the sensor-electrode interface, affecting the real-time monitoring of heavy metal concentrations. Furthermore, the interaction mechanism between g-C_3N_4 and heavy metal ions needs further elucidation, as a comprehensive understanding is essential to enhance sensor performance and selectivity. As g-C_3N_4-based sensing technologies continue to evolve, addressing these limitations is crucial to unlock its full potential for accurate, reliable, and selective detection of heavy metals in diverse environmental and industrial settings.

In the following sections the applications of carbon-based nanomaterials for the detection of toxic heavy metals are summarized.

2. Sensing applications of nanostructured g-CN.

Nanostructured g-CN played an essential role for designing sensors to identify several analytes exhibiting numerous exciting properties (stability, light and electricity conversion capability, excellent fluorescence quenching abilities, biocompatibility etc.) significant for sensing applications (Y. Wang et al., 2018). Specifically, the outstanding fluorescence quenching phenomena of g-CN nanomaterials revealed new potentials to the recognition of heavy metal ions. Recent developments for sensing of metal ions with nanostructured g-CN are mentioned in the subsequent sub-sections.

2.1. Sensing of copper ions (Cu^{2+})

Sensors are presently gaining popularity for detecting copper ions (Cu^{2+}) because of their promising properties such as simple, facile operation, high sensitivity and selectivity. The larger surface area and narrow energy bandgap ($E_g \approx 2.7$ eV) developed g-CN as an outstanding ion detection material. Cupric (Cu^{2+}) ion is an important micronutrient which is involved in numerous physiological procedures in the human body. However, gastrointestinal disturbances and different injuries such as renal or hepatic might be result of excess Cu^{2+} in the body. Its absence has also been related to cardiovascular disease, colon cancer, myelodysplastic syndrome, and Menkes disease, etc. As a consequence, it is important to keep track of Cu^{2+} concentrations in environmental and biological samples. Nanostructures g-CN are appealing fluorescent components for metal ions sensing due to its superior fluorescence-quenching ability. Tian et al. stated an extremely efficient Cu^{2+} detection fluoro-sensor focused on ultra-thin g-CN nanosheets (Tian, Liu, Asiri, Al-Youbi, & Sun, 2013). The bulk g-CN was ultrasonically spread in water and resulted in nanosheets formation, which showed the Tyndall effect while moving through the nanosheets. The nanosheets were well isolated from one another and had a distance of ∼1.0 nm. Cu^{2+} was detected selectively and sensitively using ultra-thin nanosheets as a fluorescent probe with a LOD of 0.5 nM. Cu^{2+} binding on g-CN nanosheets effectively quenched the fluorescence, as evidenced by the decrease in fluorescence strength (Figure 1).

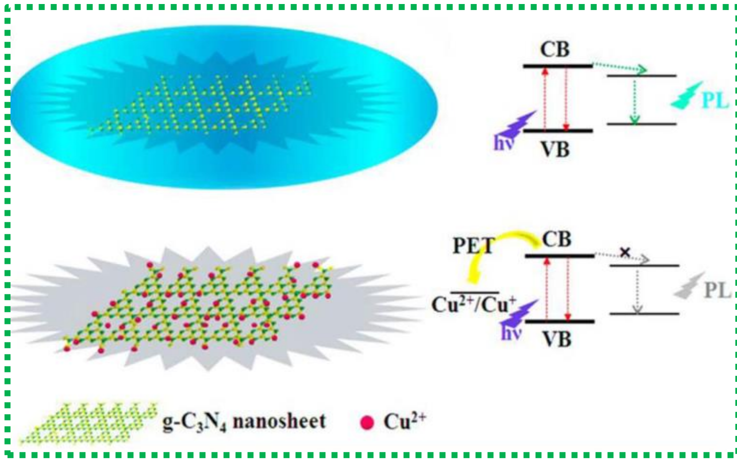

Figure 1. Corresponding section analysis of random nanosheets, Images reprinted from Ref. (Tian et al., 2013) with permission from the American Chemical Society, copyright 2013.

Furthermore, g-CN nanosheets were utilized to make a paper-based optical sensor for Cu^{2+} detection. The test paper color was shifted to light yellowish after a greater percentage of Cu^{2+} was applied. Under UV light, these strips also fluoresced (365 nm). In the presence of sunlight and UV light, the paper sensor produced limit of detection values of 0.1 nM and 5 nM, respectively. This paper strip-based sensor had several benefits, including the fact that it did not entail any pre-modification of the test paper, that it could be produced using widely available filter paper, that it was inexpensive, and that it was environmentally friendly. Additionally, Huang and colleagues showed that g-CN nanosheets can be used to make a Cu^{2+} fluorescence sensor. Exfoliation of bulk g-CN in water was used to make g-CN nanosheets, which were then used to make a Cu^{2+} fluorescence sensor with layered double hydroxides (LDH) and g-CN nanosheets (H. Huang et al., 2014). The LOD of the senor was 20 nM. Guo et al. upgraded the g-CN nanosheets through exfoliation, protonation and pyrolysis of urea (Guo, Wang, Wu, Ni, & Kokot, 2016). The Cu^{2+}

binding quenched the emission of fluorescence through fluorescent g-CN nanosheets. Different functional group present in g-CN nanosheets like oxygen and nitrogen sites that rapidly bind with Cu^{2+} and resulting an oxidation/reduction potential between the valence-conduction bands, and accredited photo-induced electron transfer. Zhang and colleagues designed a simple and environmentally friendly method to fabricate fluorescent nanodots of g-CN by employing the bulk g-CN through hydro-thermal process (Zhang et al., 2014). The as prepared nanodots were employed for the recognition of Fe^{3+} and Cu^{2+}ions because of their great quantum yield and blue emission property. Cu^{2+} was detected selectively in the presence of Fe^{3+} using sodium hexametaphosphate as a Fe^{3+} masking agent. Furthermore, sensing applications were put to the test in real-world aqueous samples. Huang et al. stated the fabrication of a fluorescent Cu^{2+} detection system using g-CN nanofibrous hydrogel (Z. Huang, Yan, & Yuan, 2017). After applying various concentrations of Cu^{2+} to graphitic carbon nitride based nanofibrous hydrogel in a buffer solution, the fluorescence approach was used to detect Cu^{2+}. With rising Cu^{2+} concentration, the fluorescence intensity decreases. Because of the superior interaction of low conc. Furthermore, after the reduction of the reactive sites, the Cu^{2+} ions interacted with the weaker sites. The as prepared probe demonstrated good performance in real water samples with a lower limit of detection of 60 nM. Doping/modification were used to improve the fluorescent effect of g-CN nanostructures (W. Chen et al., 2019; Rong, Song, et al., 2015). To enhance the fluorescent effect of nanohybrid composite, the Chen and coworkers recently employed ZIF-8 in combination with g-CN (W. Chen et al., 2019). The sensitivity of nanocomposite to Cu^{2+} and Ag^{+} was significantly improved as a result of modification in the fluorescence based quenching effect. Rong and coworkers developed fluorescent oxygen and phosphorus-doped based g-CN nanodots, followed by hydrothermal etching and chemical oxidation process (Rong, Song, et al., 2015). The group used sensitive fluorescence quenching and photo-induced electron transference approach to detect Cu^{2+} using a fluorescence sensing strategy. Cu^{2+} was detected in low concentrations by the sensor, suggesting that it could be used in natural aqueous samples. Wang and his colleagues described the fabrication of fluorescent g-CN quantum dots doped with sulfur and oxygen that were employed to detect Cu^{2+} ions (H. Wang et al., 2018). They improved sensing ability and stability of the as prepared quantum dots against Cu^{2+} by enhancing dispersion in the aqueous media. In addition, more carbon atoms have been introduced into the g-CN structures, that helps to alter the fluorescence spectra (L. Chen et al., 2018). Chen and coworkers used barbituric acid to modify graphitic carbon nitride based nanosheets for tuning the fluorescence spectra. The fluorescence of altered graphitic carbon nitride based nanosheets was quenched during the Cu^{2+} detection phase. Further, Cu^{2+} could also be detected with the naked eye using the sensor. Cheng and colleagues described the electro-generated chemiluminescence feature of g-CN immobilized together with $K_2S_2O_8$ and carbon paste electrode (C. Cheng et al., 2012). Furthermore, melamine can also be used for the preparation of g-CN by the single step Thermo-induced self-condensation. Under the potential of cathode, g-CN receive an electron as of the probe and was subsequently undergoes oxidation in excited state by the heavy oxidizing agent (SO_4). As excited g-CN reverted to its ground state, blue emission appeared. The chemiluminescence sensor seems to have a strong detection sensitivity to find the intensity of Cu^{2+} with a 2.5 -100 nM linear range and a small LOD of 0.9 nM. In addition, in industrial wastewater tests, the sensor was shown to be accurate and analytically reliable. Cheng and co-workers found the first large-scale production of g-CN nanosheets using a one-step process (N. Cheng et al., 2014). For Cu^{2+}, the fluoro-sensor based on g-CN nanosheets had LOD of 0.5 nM and excellent sensitivity. But, LOD was s higher in lake samples. A 3D g-CN was utilized to sense a trace amount of Cu^{2+} by increasing the surface area

(Lee, Jun, Hong, Thomas, & Jin, 2010). While using the drop-casting approach to mount g-CN nanorods on ITO electrodes, Xu and coworkers engineered a Cu^{2+} sensor working on the principle of photoelectrochemical (L. Xu et al., 2014). The g-CN nanorods were not specifically fabricated in this study, but after employing hydrothermal strategy, the morphology of nanosheets modified to nanorods. Pertinently, g-CN nanorods exhibited improved conductivity, charge separation, and light absorption, all of which have been beneficial for improving photo-current. Established sensor has a LOD value of 6.2 nM with great selectivity and sensitivity for identification of Cu^{2+}. In addition, detection moieties are being used to detect Cu^{2+} in human hairs, confirming the sensor's possible use. To improve charge transfer properties and effectively separate photo-generated electron-hole pairs, g-CN nanomaterial combined with the different nanomaterials to fabricate the nano-composites (S. Chen et al., 2017; Xia et al., 2015). Chen et al. synthesized the g-CN/quantum dots/Bi_2MoO_6 nanohybrid composite and applied it to detect Cu^{2+} photo-electrochemically. The engineered working electrode demonstrated significant increase in photocurrent intensity with increasing Cu^{2+} concentration, which was contributed to Cu^{2+} chelation with the nitrogen and oxygen functional moieties of the nanohybrid composite. The sensor's outstanding efficiency, selectivity, and stability were used to decide whether it could be used in real water samples. Xia et al. developed g-CN/graphene oxide hybrid composite and applied it to achieve an ultrasensitive electro-chemiluminescence Cu^{2+} sensor (Xia et al., 2015). The addition of graphene oxide to g-CN improved dramatically the sensor's electro-chemiluminescence response when contrasted to that provided by g-CN alone. The sensor had an excellent sensitivity, feasibility, and ultrasensitive performance, with a LOD of 0.01 nM.

2.2. Mercury (Hg^{2+}) ions sensing

Heavy metal (Hg^{2+}) is a really dangerous pollutant that has a negative impact on the nervous systems, endocrine, kidney, and brain even at small concentration. As a result, it is critical to check and observe the levels of mercury in the food as well as drinking water to avoid excessive utilization. Because of their promising properties such as a simple detection phase, rapidity, and small size, sensors are progressively being used to track mercury levels (Tahir Rasheed, Li, Fu, et al., 2018[Rasheed, 2019 #188[Rasheed, 2019 #189; Tahir Rasheed, Li, Nabeel, et al., 2018). Nanomaterials have been used extensively in the fabrication of sensors. Owing to the unique features of g-CN-based sensors have currently received significant interest, primarily for heavy metal ion detection. Zhuang et al. recently developed g-CN nanosheets by using hydrothermal technique in a single phase with sodium citrate and melamine precursors as a quencher of fluorescence to fabricate sensor for the recognition of Hg^{2+} ions (Figure 2) (Zhuang, Sun, & Ni, 2017).

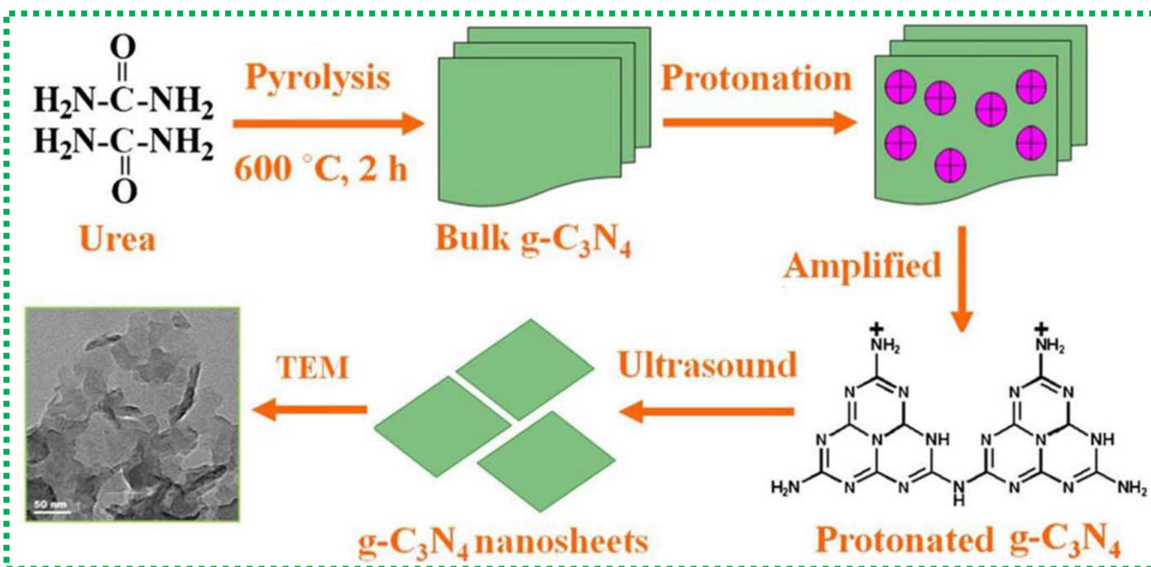

Figure 2. Schematic description of synthesis process using protonation and sonication methods. Images reprinted from Ref. (Guo et al., 2016) with permission from Springer Nature, copyright 2016.

The g-CN nanosheets produced were spherical, mono-dispersed, and two/three-layered. Various concentrations of mercury applied to the solution mixture possessing the g-CN nanosheets for Hg^{2+} detection and their fluorescence emission spectra were obtained. The intensity of fluorescence was steadily quenched with increasing Hg^{2+} amounts. Static quenching or transfer of electron from the higher energy state of g-CN nano-sheets caused such quenching. The LOD was 0.3 nM, which was sufficient for monitoring Hg^{2+} concentrations in aqueous samples with Hg^{2+} below its tolerable range. Zhang et al. utilized ultrasonic technology to prepare g-CN nanosheets using strong acid (H. Zhang et al., 2015). The g-CN nano-sheets were utilized as a fluorescence based probe for a “switc-off and switch-on” probe, and they demonstrated great sensing features as well as reasonable selectivity and sensitivity for Hg^{2+} in aqueous samples. Duan et al. suggested a g-CN nanosheet-based “on-off-on” fluorescent sensor for detecting Hg^{2+} and 6-thioguanine (6-TG) (Duan et al., 2018). The 6-TG was applied to the g-CN nanosheets solution, that quenched the fluorescence engendered by the g-CN nano-sheets. The quenching effect is because of π- π interaction and H-bonding between 6-TG and g-CN which originates the excited electrons to be transferred to 6-TG. Since 6-TG and Hg^{2+} ions have a high affinity, the quenched fluorescence may be retrieved through introduction of Hg^{2+}. Hg^{2+}-induced regeneration effect induces a new pathway and strong detecting capacity of a 6-TG/g-CN nano-sheets dependent colorimetric sensor for Hg^{2+} recognition (Figure 3).

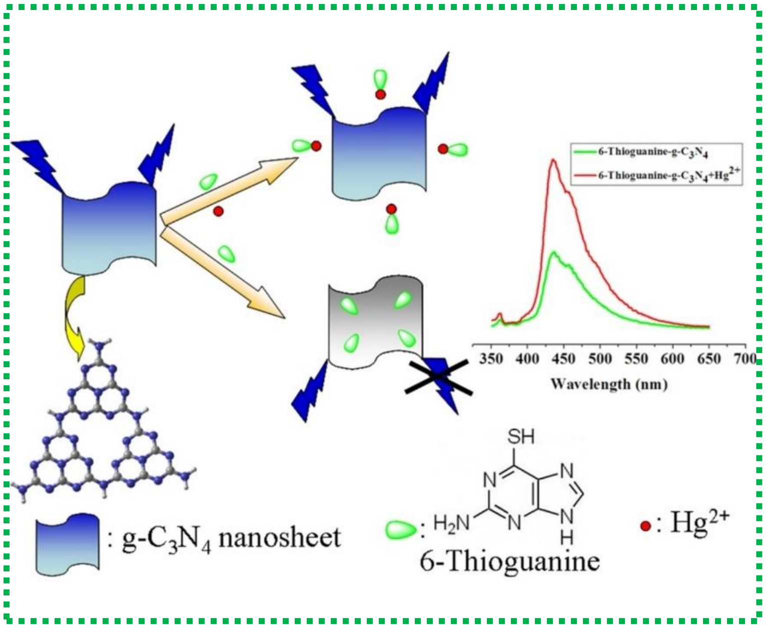

Figure 3. Schematic representation of the sensing mechanism of the g-C_3N_4 nanosheets as an "on-off-on" fluorescent sensor for the detection of 6-TG and Hg^{2+}; (a) Fluorescence spectra of g-C_3N_4 nanosheets after addition of 30 μM 6-TG and (b) 6-TG-g-C_3N_4 nanosheets upon adding 25 μM Hg^{2+}. Reproduce from Ref. (Duan et al., 2018) with permission from Elsevier, copyright 2018.

A linear array of 0 - 65 µM can be seen, with a LOD value of 65 nM, and better sensitivity in contrast of miscellaneous metal ions is exhibited. Additionally, the fluorescent sensor's sensing capacity and reliability have been performed in a controlled water sample. Li et al. newly developed multifunctional g-CN based nanosensors that had been altered with trithiocyanuric acid (M. Li et al., 2019). The fluorescence of the probe was quenched by the trithiocyanuric acid, and it was recovered when Hg^{2+} was applied. Both trithiocyanuric acid and Hg^{2+} were detected using this approach.

2.3. Iron (Fe^{3+}) ions sensing

Iron (Fe^{3+}) is a critical trace element needed for the biological process among heavy metal ions. The EPA of the United States has established a maximum safer ingestion level of 5.4 μM in drinkable water (Annie Ho, Chang, & Su, 2012). Since most physiological processes need Fe^{3+}, a sufficient intake of this ion is needed. An accumulation of Fe^{3+} can disrupt biological processes, resulting in diseases like even cancer, Parkinson's or Alzheimer's syndrome (Altamura & Muckenthaler, 2009; Wang, Yu, Liu, & Chen, 2012). As a result, assessing water quality is an active problem in reducing Fe^{3+} use. Sensors have a superiority over other methods in this context because their great sensitivity, ease of operation and fast detection performance. A number of nanomaterials have been used in the production of Fe^{3+} sensors, but little attention was paid to the g-CN nanomaterial (Yin et al., 2017; Zhou et al., 2015). Recently, for Fe^{3+} detection, Yin and coworkers utilized the g-CN/quantum dots (Yin et al., 2017). In just 5 minutes, they were able to make g-CN/quantum dots using a green synthesis method (microwave assisted evaporation-condensation). The schematic pathway of the procedure and TEM and SEM pictographs of the generated g-CNQDs and g-CN are shown in Figure 4.

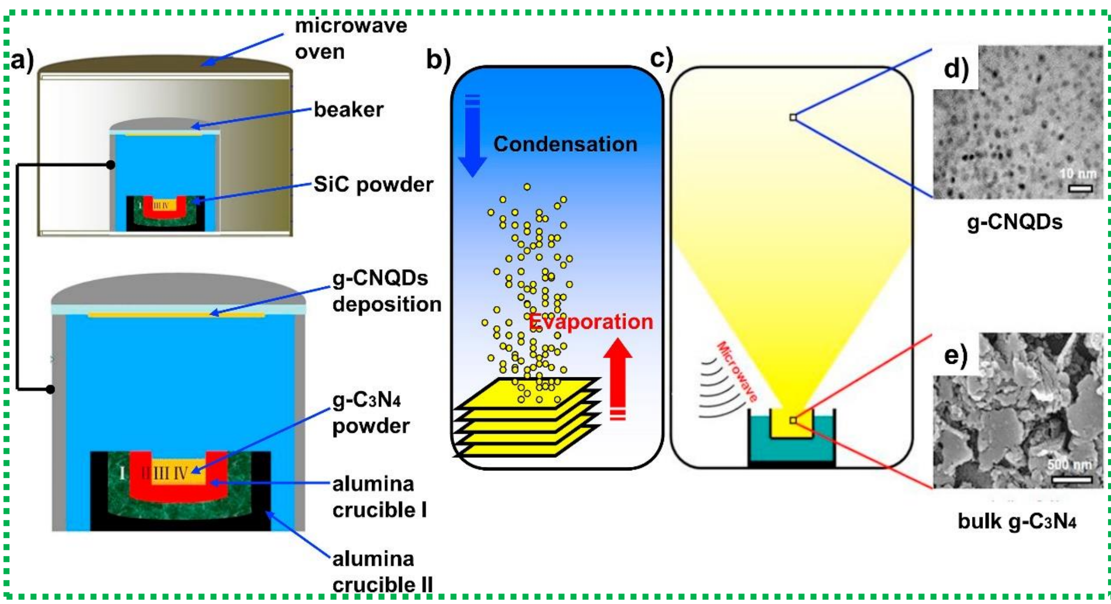

Figure 4. Schematic illustration of (a) the fabrication device, (b) the evaporation–condensation process, and (c) distribution of g-C_3N_4(g) during the transport process. (d) TEM image of the as-

prepared g-CNQDs. (e) SEM image of the bulk g-C_3N_4. Reproduce from Ref. (Yin et al., 2017) with permission from Elsevier, copyright 2017.

The synthesized g-CN/Q-dots have small diameter of 3.5 nm, with excellent crystalline consistency and had outstanding fluorescent features. With increasing Fe^{3+} concentration, the fluorescent response showed linear intensity quenching, low LOD value of 2 nM and high selectivity and sensitivity for Fe^{3+} sensing in the vicinity of miscellaneous species. Studies were also carried out to see whether g-CN/Q-dots could be used as a biolabeling agent. This study demonstrated the use of g-CN/Q-dots as an exceptional biocompatible cataloguing agent throughout liver-cell imaging. In addition, the fast, large-scale, and simple preparation of g-CN/Q-dots provide a good opportunity for other applications. For Fe^{3+} identification, Li et al. utilized the g-CN/quantum dots (Y. Li et al., 2018). While g-CN is a potential material for the Fe^{3+} detection on its own, it can be broken down chemically to produce different nanostructures with similar Fe^{3+} sensing properties (Zhou et al., 2015).

2.4. Silver (Ag^+) ions sensing

Silver ions are less dangerous metal ion in general, these ions are only harmful for human health at higher concentrations level up-to a value of greater than 0.9 mM in drinkable water. Excessive Ag^+ consumption generates a variety of health problems (including renal, and neurologic and hepatic toxicity) and can prevent protein activity. As a result, determining Ag^+ in industrial and environmental water samples became important. Nanomaterials-based sensors are extensively used for Ag^+ analysis because they are inexpensive, effective, extremely sensitive, selective, and versatile (Bian et al., 2016; Cao et al., 2016; M. Li et al., 2018). Recently, Li and coworkers applied radical polymerization to create a g-CN/polyacrylamide/polyacrylic acid composite hydrogel (M. Li et al., 2018). The potential fluorescent characteristics of the composite based hydrogel to be served as a fluorescent probe appeared in greater sensitivity and selectivity in detecting Ag^{+} ions. Some prior work stated that the detection of Ag^{+} was also carried out with g-CN nano-sheets (Cao et al., 2016; S. Chen et al., 2017). These investigations demonstrate the LODs values of 3.3, 27, and 52.7 nM respectively, which are considered to be much higher. Further, the Cu^{2+} can mainly interfere with Ag^{+} identification, that is one of the critical problems when detecting Ag^{+} in the vicinity of interfering organisms. Moreover, Tang and fellow researchers attempted to develop LOD by using a hybrid material composed of Pt-NPs and g-CN (Tang et al., 2018). According to this study, the hybrid material imitates peroxidase behavior. Because of the greater catalytic ability of the composite material, the detection system showed lower LOD value of 22 pM, that is superior to other systems. The experiment was validated using real aqueous samples.

2.5. Miscellaneous metal ions sensing

Other essential ions were observed using g-CN nanomaterials include nickel, chromium, lead and cadmium ions (Ding et al., 2018; Fang, Yang, Zhang, & Gong, 2016; Gao et al., 2016; Hatamie, Jalilian, Rezvani, Kakavand, & Simchi, 2019; Rahbar, Salehnezhad, Hatamie, & Babapour, 2018; Rong, Lin, et al., 2015; Shang et al., 2015; X. Wang et al., 2018; Zhou et al., 2016). When taken in high enough concentrations, these ions, like other heavy metal ions, can be harmful. Recently, because of their simple and label-free detection method, fluorescent sensors have gotten more attention. Using g-CN nanosheets, Rong and his colleagues developed a Cr(VI) sensor (Rong, Lin, et al., 2015). The sensing technique was built on the fluorescence quenching by the introduction of Cr^{6+}, which effectively turned it off. Surprisingly, the fluorescence strength was triggered by the introduction of ascorbic acid (Figure 5).

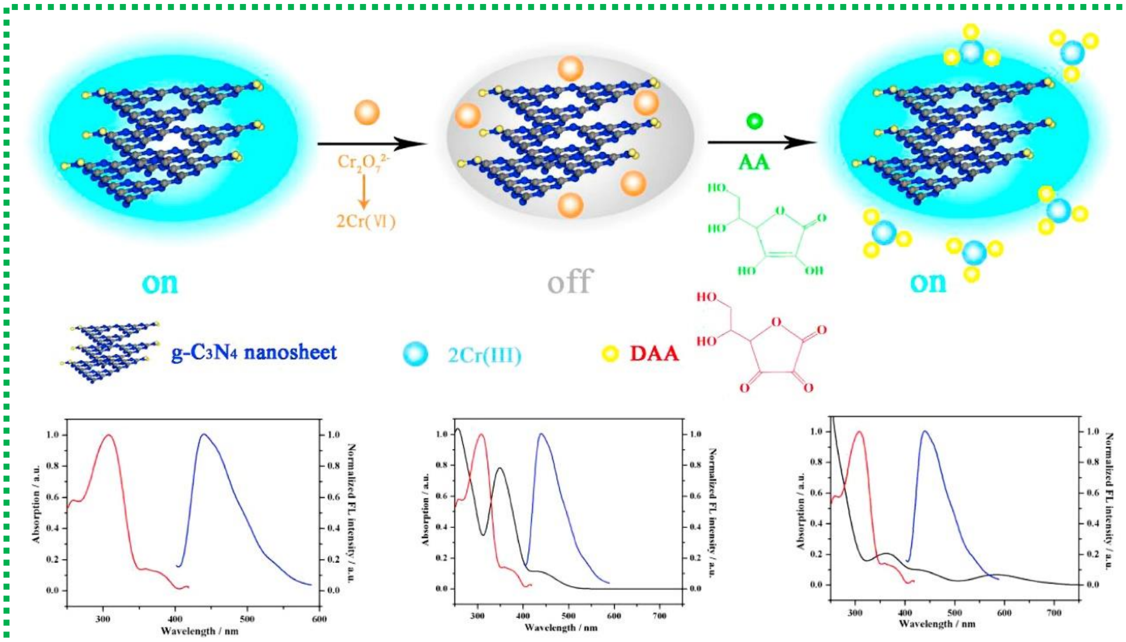

Figure 5. Schematic illustration of fluorescence "on–off" assay for Cr(VI) and "on–off–on" assay. Reproduce with permission from reference (Rong, Lin, et al., 2015) Elsevier, copyright 2015.

Rahbar and coworkers also used g-CN nano-sheets for Cr(VI) detection, but their LOD was only 3 nM owing to the use of high-temperature-prepared g-CN nano-sheets (Rahbar et al., 2018). Fang and coworkers formed a nanostructured g-CN nanosheets with incorporation of hybrid Cr(VI) ion-imprinted/formate anion (Fang et al., 2016). The nanohybrid contributed to improved charge separation and photoelectrochemical performance. During Cr(VI) determination, the ion-imprinted polymer and nanostructured hybrid demonstrated high sensitivity and selectivity. With increasing Cr(VI) concentrations, the sensor showed a linear response. The sensor efficiently captures the photogenerated holes when combined with format anions as well as the suppression of created charge transfer was observed as a recombination electron-hole pair and in result improvement in photocurrent due to the separation of photogenerated carriers produced and metal ions were employed to examine the selectivity of the sensor. This technique has been applied in raw-water samples and has been found to be effective. Graphite-phase of the polymeric CN-nanosheets was used for the Ni^{2+} detection, which exhibited lower value 1.13 nM of LOD , selectivity in the existence of interfering species, and greatly enhanced the real-world applications (Shang et al., 2015). Gao's group investigated Cd^{2+} detection by building a voltametric sensor out of g-CN nanosheets and Nafion (Gao et al., 2016). Wang and colleagues recently developed a novel aptamer and graphene/g-CN nanocomposite for Cd^{2+} detection (X. Wang et al., 2018). The hydrothermal treatment of graphene/g-CN resulted in a composite that was capable to fix with aptamers due to C=O/O-H groups on graphene (Figure 6).

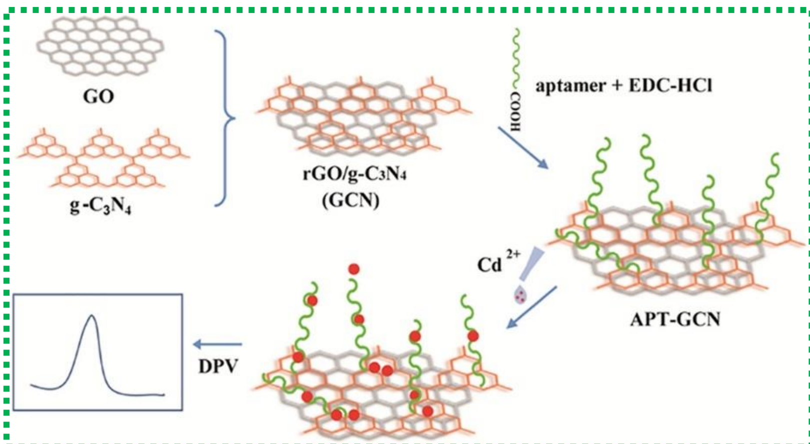

Figure 6. Schematic Illustration of the Fabrication of the APT-GCN Aptasensor and Its Detection of the Cadmium Cation. Reproduced from Ref. (X. Wang et al., 2018) with permission from American Chemical society 2018.

In 2018, Zhou and coworkers presented a facile and efficient technique for the synthesis of multicolor carbon dot materials. The multicolor CDs constructed from food waste materials through hydrothermal carbonization process were utilized for the detection of heavy metal Fe^{+3} with excellent efficiency. The developed CDs comprised of four colors for instance blue, green, yellow and red were successfully employed in fluorescence probes with remarkable performance for the detection of iron ion. Notably, the florescence intensity of the CDs diminished with the enhancement in the concentration of Fe^{+3}, however a better linear response was obtained when the concentration of Fe^{+3} varying from 1 to 50 nM with a correlation coefficient of 0.9968. Moreover, they used transmission electron microscopy and atomic force microscopy to investigate the structure and morphology of the synthesized CDs. Further, Fourier transform infrared (IR) spectroscopy and Bruker Vertex (70v) techniques were applied for the identification of various functionalities in the multicolor CDs (Y. Wang et al., 2018). In 2018, Simpson *et al.* first time reported the formation of carbon nanoparticles (CNPs) and showed their applicability in the electrochemical detection of heavy metal ions such as Pb^{2+}, Cu^{+2} in aqueous solution. The synthesized CNPs of 66 nm diameter were constructed by heating glycerol in the presence of phosphoric acid with their surface bearing important functionalities of alcohol and carboxylic acid. The CNPs modified glassy carbon electrodes were examined under different concentration of metals ions with the sensitivity of the calibration curves of 13.8 µA/ppm and 40.4 µA/ppm but the value of detection limits obtained for Pb^{2+} and Cu^{2+} were 0.50 ppm and 0.30 ppm respectively. The practical utility of the method was displayed through detection of Pb^{+2} and Cu^{+2} in the samples taken from the spiked tap water. Interestingly, the average values of Pb^{+2} and Cu^{+2} recovered from were 97.7% and 98.2% with relative standard deviations of 8.5% and 7.4% correspondingly. Further, for the characterization of CNPs different techniques were employed which confirmed their formation (Simpson et al., 2018). In 2018, Li and coworkers first time reported the application of a novel glass carbon electrode modified with N-doped carbon quantum dots-graphene oxide hybrid (NCQDs-GO) for the detection of Cd^{+2} and Pb^{+2}. It was found that the presence of oxygen bearing moieties on the surfaces of both NCQDs and GO enhanced the sensing abilities of sensors via electrostatic interaction and thus played an effective role for adsorption of heavy metals ions. Further, the uniform dispersion of NCQDs over the surface area of GO assisted the re-oxidation of metal ions and increased the sensitivity. Owing to these advantages, the glassy carbon electrode functionalized with NCQDs-GO hybrid showed excellent detection power as compared to NCQDs on GCE and GO on GCE with a large linear range (Cd^{+2}: 11.24-11241 µg/L, Pb^{+2}: 20.72-10360 µg/L), low values of detection limit (Cd^{+2}: 7.45 µg/L, Pb^{+2}: 1.17 µg/L) and high repeatability. Furthermore, the practical demonstration of the method was displayed through detection of Cd^{+2} and Pb^{+2} in lake and tap water with excellent selectivity (L. Li, Liu, Shi, & You, 2018).

In 2019, Yarur *et al.* described a dual absorbing and fluorescing system based on carbon dots for the detection of heavy metal ions for instance Fe^{+3}, Pb^{+2}, Co^{+2} and Hg^{+2} in water. The developed system concurrently absorbs and gives fluorescence in the areas of both blue and red shifts of the spectrum. Owing to the different metal cation concentration, the optical absorbance varies significantly and the same phenomenon was also observed in the fluorescence in which the quenching of the red fluorescence occurred selectively. They also demonstrated that the interaction aroused between the fluorescent areas of the carbon dot and metal, was responsible for the quenching property. Further, for the detection of metals ions in solution such as Co^{+2}, Fe^{+3}, Hg^{+2}, Pb^{+2}, detection limits of 96.8, 61.7, 39.5, 37.1 nM was achieved correspondingly in the nanomolar range (1-961 nM) (Yarur, Macairan, & Naccache, 2019). In 2020, Yi *et al.* reported an efficient and economical fluorescent carbon nanodots based microarray connected with a smartphone linked portable fluorescence reader for the detection of Hg^{2+}, Pb^{2+} and Cu^{2+} in the Pearl River. They prepared three different types of carbon nanodots such as CDs-1, CDs-2 and CDs-3 with excellent emission properties and versatile surface groups for the sensing of Hg^{2+}, Pb^{2+} and Cu^{2+} respectively. In order to receive signals quantitatively from microarrays, a smartphone-linked portable reader (SBR) was manufactured and interlinked with a custom designed APP which generates the results with high accuracy and reproducibility. Samples of water were taken from different sites of Pearl River and were tested for detection of Hg^{2+}, Pb^{2+} and Cu^{2+}. All the tested samples showed no evidence of Hg^{2+}, however Pb^{2+} and Cu^{2+} were obtained in the range of 0.078-0.31 and 0.257-0.38 μM respectively. Further, the results obtained were in close agreement with those of the tested samples with ICP-MS which demonstrated the reliability and practicability of SBR based carbon nanodots microarray for the on-site detection of different heavy metal ions (Figure 7) (Xiao et al., 2020).

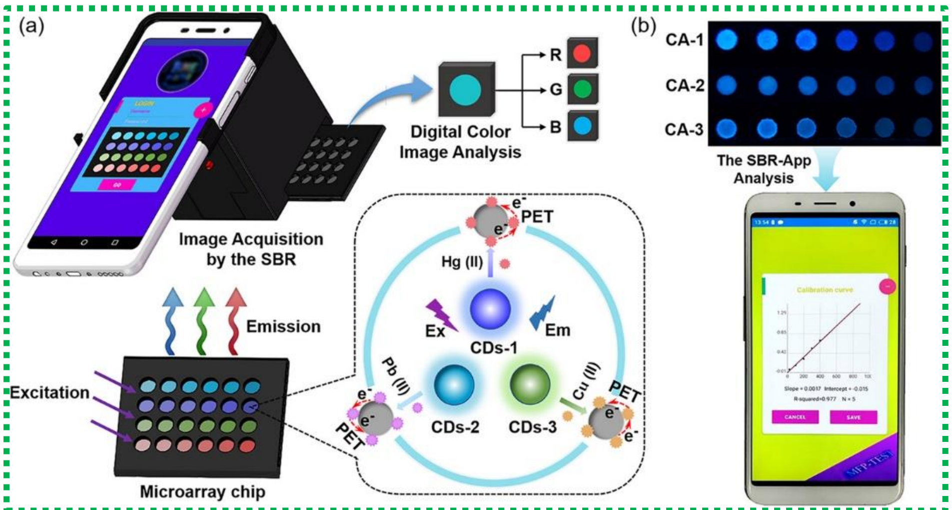

Figure 7. Illustration of Rational of the Fluorescent CDs-Based Microarrays Fabricated on Filter Papers toward Simultaneous Detection of Multiple Metal Ions and Design of a Stand-Alone Smartphone-Based Portable Reader (SBR) Installed with a Custom-Designed APP (SBR-App) for Acquiring Fluorescence Change from the Microarray and Automatically Report the Results (Xiao et al., 2020).

In 2020, Boobalan *et al.* reported the convenient approach for the synthesis of highly fluorescent blue/green CDs derived from the oyster mushroom. The grinded oyster mushroom after thoroughly mixing with 100 mL of water and sulfuric acid (5%) in autoclave was then heated up to 120 ºC to prepare CDs. These synthesized CDs were used for the detection of different toxic metal ions; however, a promising result were achieved only for the detection of Pb^{+2} with limits of detection and quantification of 58.63 µM and 177.69 µM respectively. Additionally, to get insights about ion sensing mechanism further, binding constant (k) was calculated for the interaction between CDs and Pb^{+2} by employing the Benesi-Hilderbrand equation which demonstrated that the binding constant (K = 248 µM, when N = 10) is in approximate accordance with the limit of detection value (Boobalan et al., 2020). In 2021, Xiong *et al.* reported the formation of carbon nanospheres and explored its utility in the detection of heavy metal ions such as Cu^{2+} and Hg^{2+}. The smooth carbon nanospheres having a diameter of approximately 485 nm were synthesized by hydrothermal process without using catalyst. However, at low concentration the electrostatic and hydrogen bonding interactions played a significant role in the spontaneous construction of colloidal spherical carbon precursors. Further, the accumulation of spherical colloidal structures was effectively controlled by the incorporation of octaphenyl polyoxyethyiene-30 moiety which resulted in the synthesis of octaphenyl polyoxyethyiene-30 micelles and reduced the size of the carbon nanospheres. Subsequently, the glassy carbon electrode was functionalized with carbon nanometerials and applied for the electrochemical sensing of Cu^{2+} and Hg^{2+} with limit of detection of 4.5 nM and 12.5 nM respectively. Interestingly, they observed that by introducing other metal ions, vigorous changes occurred and the limit of detection obtained for Cu^{2+} and Hg^{2+} (9.8 nM and 30.3 nM) was double of the simultaneous detection. The results obtained clearly indicated that incorporation of low concentration of other ions effectively enhanced the selectivity and sensitivity of electrochemical detection of heavy metals ions (Xiong, Zhang, Liu, Lv, & Zhang, 2021). In 2022, El-Wakil and coworkers developed a new melamine thiourea based activated carbon (MT-BAC) materials for the elimination of heavy metal ions for instance Hg^{2+}, Cd^{2+} and Pb^{2+} from waste water (Figure 8).

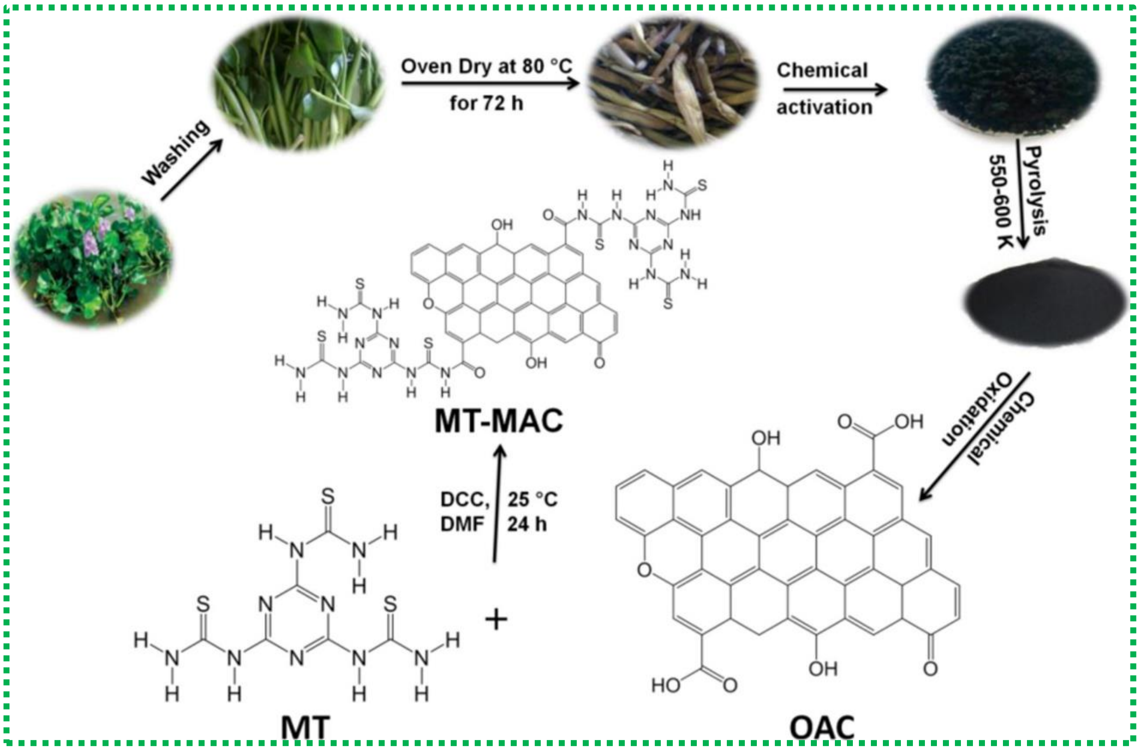

Figure 8. General Process for the Synthesis of Melamine Thiourea-Chemically Modified Activated Carbon (MT-AMC) (El-Wakil et al., 2022).

The functionalized activated carbon materials synthesized from water hyacinth and melamine thiourea showed remarkable adsorption capacity for the removal of Hg^{2+} (292.6 mg/g), Cd^{2+} (97.9 mg/g) and Pb^{2+} (237.46 mg/g) respectively. Notable, at extremely lower concentration (25-1000) with pH 5.5, complete removal efficacy was examined. Moreover, the experimental results obtained perfectly matched with the Langmuir isotherm model, thus demonstrating a monolayer adsorption nature. However, when a mixed solution of different metal ions (50 ppm each) is used, exceptionally high removal efficiency was obtained for Hg^{2+} (97%). In addition, the MT-BAC materials are not only environmentally friendly and highly potent but also displayed greater stability despite utilized in three cycles of adsorption-desorption process (El-Wakil et al., 2022).

3. Conclusion and future Prospects

In conclusion, the deployment of graphitic carbon nitride (g-C_3N_4) derived probes holds significant promise in addressing the critical issue of heavy metal pollutants in water bodies. The unique physicochemical properties of g-C_3N_4, such as its high surface area, chemical stability, and tunable electronic structure, make it a desirable candidate for heavy metal sensing. However, certain limitations must be acknowledged and addressed to fully harness its potential.

Future research should focus on enhancing the selectivity of g-C_3N_4 probes toward specific heavy metal ions. Surface functionalization techniques, such as tailored ligand modifications, could be explored to create selective binding sites for target ions, minimizing cross-reactivity and interference from other contaminants. Additionally, the integration of g-C_3N_4 with complementary materials in composite structures might synergistically enhance selectivity and sensitivity while also improving the overall sensor stability.

To overcome the conductivity challenge, innovative strategies such as introducing conductive additives or designing hierarchical nanostructures could be pursued. These approaches could expedite charge transfer kinetics and reduce response times, enabling real-time monitoring of heavy metal concentrations even at trace levels.

Furthermore, elucidating the underlying interaction mechanisms between g-C_3N_4 and heavy metal ions is pivotal. Advanced analytical techniques, such as spectroscopic and computational methods, can provide insights into the binding modes and the factors influencing the sensor response. This knowledge will facilitate the rational design of g-C_3N_4-based sensors and contribute to their improved performance.

Collaboration between research disciplines is vital for driving these advancements. Interdisciplinary teams involving materials scientists, chemists, environmental engineers, and toxicologists can provide a holistic perspective, addressing both the sensor design challenges and the broader environmental implications of heavy metal pollution.

In conclusion, while challenges exist, g-C_3N_4-based probes present a transformative opportunity to revolutionize heavy metal sensing in water bodies. Through strategic innovation, research collaboration, and a commitment to sustainable water management, g-C_3N_4 sensors could become pivotal tools for safeguarding aquatic ecosystems and ensuring the health and well-being of both the environment and human populations.

Declarations

Ethical Approval

Not applicable

Competing interests

The authors have declared no competing interests exist. All the authors have read and approve the submission.

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Not Applicable

Authors' Contributions

Tahir Rasheed, Tauqir Ahmad, Sardaraz Khan and Darim Badur Ferry: Data analysis, Curation, Project administration, Writing - original draft, review & editing. **Tahir Rasheed:** Supervision, Validation, Investigation, Methodology & Data analysis & Curation. **Tahir Rasheed, Farooq Sher and Saadat Majeed and Amjad Ali:** Conceptualization, Validation, Designing, analysis, Art work, software, Formatting, Writing - review & editing. **Tahir Rasheed:** Supervised overall review formation.

Availability of data and materials

Data will be made available on reasonable request.

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