Carbon-dot & quantum-dot futuristic material for sensing of arsenic: An overview of recent development

Priyanshi Dixit¹ Hritik Jha² Suman Swami³

Department of chemistry, Chandigarh University NH-05 Ludhiana-Chandigarh State Highway, Punjab 140413

Corresponding author email: dpriyanshi27@gmail.com

Graphical Abstract DIAGNOSIS THERAPY ablation **Drug Delivery** Cancer cell Gene Delivery imaging Electro Photodynamic Ultrasonic Top-Down **Nucleus targeted** chemical Therapy imaging Sensing Carbon Dots Carbonize Bottom-Up Microwave **Pvrolvsis** method

Fig 1: Demonstrating the use of carbon dots in various fields.

ABSTRACT

Arsenic is a very hazardous heavy metal that can have detrimental effects on human health if it is exposed for an extended period of time. Heart attacks, diabetes, birth defects, damage to the liver and kidneys, arenicolids, haemolysis, cancer, neurological conditions, and sore spots on the hands and feet are a few of these. Given the harmful effects on human health and the environment, it is essential to conduct routine monitoring and devise corrective measures. Recent years have seen significant efforts to develop novel analytical techniques in response to the urgent demand for efficient dangerous metal ion detection. Nanomaterials have become important participants in this endeavour, especially those based on carbon. [1,2] The investigation of quantum dots and zero-dimensional carbon dots as arsenic detection sensors is the main topic of this review. The review explores the in-depth conversation of Nanomaterials, particularly carbon-based materials, have emerged as pivotal players in this pursuit.

This review focuses on the exploration of zero-dimensional carbon dots and quantum dots as sensors for arsenic detection. The review delves into the detailed discussion of these nanomaterials, shedding light on their unique properties and applications in arsenic detection of notable significance is the emphasis on carbon quantum dots, highlighting their production processes and properties in the context of the latest advancements in arsenic detection. The synthesis of knowledge on the nanomaterials not only underscores their potential in addressing the challenges posed by arsenic toxicity but also signifies a crucial step toward ensuring the well-being of both human populations and the environment through advanced detection and remediation methodologies. [3,4]

Keywords

Carbon dot, Quantum dot, Arenicolids, haemolysis

Introduction

Carbon and quantum dot-based material play significant roles in development of material science. From traditional industrial carbon (activated carbon, carbon black) to new industrial carbon (carbon fibers, graphite) and new carbon and quantum nanomaterials such as graphene and carbon nanotubes. Nanostructured materials are of interest because they can bridge the gap between the bulk and molecular levels and leads to entirely new avenues for applications especially in electronics, optoelectronics and biology. During the last two decades, a great deal of attention has been focused on the sensing properties of nanostructured materials(carbon quantum dots) as many fundamental properties are size dependent in the nanometer range. Heavy metal contaminants are a type of dangerous waste that is frequently discovered in water sources, originating from geogenic, industrial, pharmaceutical, and agricultural activities. Smelting, mining, extraction, batteries, metal plating, foundries, and inappropriate recycling of electronic wastes are additional methods of contaminating water supplies. [5,6]

Globally, common source of water for agricultural or public use is well water as it is originated from ground, it contains heavy mineral concentration and also shows presence of heavy metals mainly arsenic and mercury. Arsenide contamination in drinking water is a major threat to global public health. Arsenide contamination has been reported in different zones around the world: Argentina, Australia, Bangladesh, Cambodia, Canada, Chile, China, Germany, Ghana, Hungary, Japan, India, Laos, Mexico & United States. Arsenic, threat to global public health found in earth's crust as naturally occurring metalloid exists in various forms(-3,0,+3,+5). The most toxic form is As³⁺ which gets incorporated in food chain. Maximum permissible level of arsenic in drinking water is 10ug/l set by World Health Organization Environmental Protection Agency (WHO) (EPA). poisoning/Arenicolids is a long-term exposure of arsenic in human body results in chronic illness. Arsenic and its components can be found in environment in several oxidation states like: (+5, -3, 0, +3). As³⁺& As⁵⁺ are present in drinking water causing threat to public health. Organic arsenic such as-dimethyl arsenic acid (DMA), trimethyl arsine Oxide (TMAO) can be generated by organisms during biological activities in water.

Contamination of arsenic in drinking water is main cause of liver, lung, prostate, kidney cancer, hyperpigmentation of skin, keratosis of feet and hands, chronic health problems. Lethal toxins include Mercury& lead not only harm the environment but also gets accumulated in food chain serving as fatal agents. This review covers the novel method for creating fluorometricapt sensors used to measure Arsenic (III), a cation i.e., extremely dangerous. Aptamers are oligonucleotide molecules (ssDNA or RNA) that attach to certain molecules or metal ions. Aptamers are like antibodies and possesses same therapeutic and diagnostic applications. The aptamer-target connection occurs through electrostatic, van der Waals, and/or hydrogen bonding interactions, or through a mixture of these interactions. The World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) state that in 2001, the maximum contamination limit (MCL) for arsenic (As) in drinking water might range from 50 to 10 ppb. [7,8,9]

Contents

•	Introduction to quantum dots
•	Raw Materials used for fabrication
•	Methods used for characterization
•	Arsenic poisoning
•	Applications
•	Conclusions
•	References

Introduction to carbon dots

Carbon dots, rising star can be defined as a fascinating class of carbon nanoparticles that mainly consists of carbon with sizes in nanometers or less than that. Due to their strong quantum confinement effect, high tunability & optoelectronic properties they are considered as fluorescent materials. Electron transfer and reservoir properties of carbon dots can be applied to separate photo-generated electrons. They possess great potential in wastewater treatment due to high stability, good biocompatibility, low toxicity, high water dispersibility, low fabrication cost as well as outstanding photo-stability.[10,11]

The need for fabricating CQD_S is one of the major man-made crisesi.e., water pollution due to discharging of approximately two million tons of different types of hazardous wastes into water bodies.

Heavy metal pollutants are one such hazardous waste which is being found in water bodies commonly produced by geogenic, industrial, pharmaceutical and agricultural processes. Another method of water contamination includes mining, extraction, smelting, foundries, batteries, metal plating, improper recycling of electronic waste. This paper highlights the As³⁺& Hg⁺ ions contamination in drinking water. Arsenic being readily soluble in water results into leaching of groundwater. Likewise, Mercury shows its presence in rocks released during mining activities. Due to their non-biodegradable nature, they accumulate in food chain leading to increase in concentration at each trophic level of food chain. For e.g. Methylmercury, toxic form of mercury produced by bacteria absorbed by plankton and gets accumulated in food chain leading to contaminated food or water leading to serious health conditions affecting skin, nervous, respiratory, endocrinological, cancer and immune disorders. Contaminated drinking water is an issue of major concern.

There are two methods of synthesizing Carbon Quantum dots:

- Top-down approach
- Bottom-up approach(flow diagram)

Bottom-up approach includes hydrolysis, hydrothermal, solvothermal, microwave assisted pyrolysis etc. Neem, Basil and other medicinal plants extracts have been successfully synthesized Carbon Quantum Dots. CQDs found potential application in determination of toxic or heavy metals like mercury and arsenic. This paper reports the use of functionalized CQDs for selective detection of As^{3+} & Hg^{+} ions by banana leaf extract through hydrothermal growth method. CQDs based on emission spectra. CQDs with high temperature above 200-degree Celsius exhibits broad emission peaks at 480nm.

On the other hand, CQD_S synthesized at lower temperature above 120 and below 160-degree Celsius exhibits new emission peaks at 677 and 725nm. This paper covers the fabrication of carbon dots in order to detect arsenic poisoning. In order to reduce false positives and enhance the precision of measurement outcomes in environmental detection, a single-switch dual-mode nano-sensing technique should be created for in situ and real-time detection. In order to accurately detect As(III) in water, a dual-mode optical nano-sensor that combines colorimetric and fluorescent technology. The nano-sensor was made up of amino-functionalized carbon dots (NCDs) and gold nanoparticles modified by trithio-cyanuric acid (TMT-Au NPs). For the purpose of identifying dangerous materials in water, SERS detection, colorimetric detection, and fluorescence detection are frequently used. [12,13]

Multi-colored fluorescent sulfur-doped carbon dots (CNDs) has been created using sodium thiosulfate and citric acid pyrolysis with basic microwave assistance. The artificially created CNDs demonstrated high selectivity dual mode colorimetric ultrasensitive sensing for both glutathione (GSH) and arsenic [As (III)].

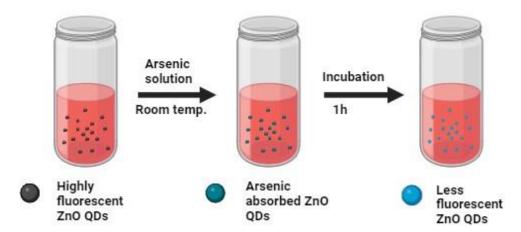
Introduction to quantum dots

Quantum dots are of interest because they can bridge the gap between the bulk and molecular levels and leads to entirely new areas for applications, especially in optoelectronics and biomedical applications. Processing, structure, properties, performance are some of the core factors on which band gaps of quantum dots depends. Quantum dots can be defined as the solid having distinct variations in optoelectronic properties and possesses size less than 100nm. These are zero dimensional structures.

Graphene quantum dots(GQD_S) are zero dimensional nanomaterials which possesses superior or physical and chemical properties like: High photostability, low toxicity, biocompatibility, high confinement effects on comparison to other quantum dots. GQDs shows higher electron mobility due to the presence of more abundant atom quantity at the edges. Surface to volume ratio in GQDs is higher than other nanoparticles due to which it shows high electron mobility and quicker reaction rate. GQDs are widely used in optical and electrical sensors due to molecular adsorption and variation. GQD_S have particle size about 10nm and fast electron transfer kinetics which increases the adsorption of molecules. GQDs possesses unique plasmonic structure, tune able surface chemistry, low intrinsic toxicity, high stability, excellent solubility and easier binding of surface with receptors. Heavy metals pose major health risks, so it's imperative to detect them in drinking water quickly and reliably in impoverished nations. The new chlorophyll-functionalized CQD (ChlCQD) is introduced in this work as a nanoprobe for the sensitive detection of As and Hg ions in aqueous solutions. The hydrothermal treatment of banana leaf extract is done in one step to create these CQDs. This study reviews that CQDs with various optical characteristics may be obtained by adjusting the hydrothermal synthesis temperature from 120°C to 230°C.Only the CQDs produced at 120°C and 160°C are embellished with functional groups of chlorophyll, whereas the CQDs produced at 200°C and 230°C lack any chlorophyll groups. A band of fluorescence near the red area is produced by these chlorophyll groups, and the presence of metal ions either enhances or quenches this band. We show that the synthesized ChlCQDs at 160°C can be used as a low-limit detection turn-on/off sensor for the selective detection of As and Hg ions. [14, 15,16]

A novel method for creating a fluorometricapt sensor has been presented and used to measure As(III), a cation that is extremely poisonous. This technique involved the agglomeration of cationic cysteamine-stabilized CdTe/ZnS core/shell quantum dots using an aptamer, leading to the accumulation of fluorescence quenching. Aptamer and As (III) makes a complex which prevents aggregation of quantum dots which increases the quantum dot efficiency. The fluorometric assay has a low detection limit of 1.3 pmolL⁻¹As (III) and a dynamic range of 1.0×10 -11 to 1.0×10 -6 mol L-The study examined the interference effect of various cations and anions, confirming the aptasensor's good selectivity for detecting As(III). The method successfully detected As(III) in many water samples. Arsenic is a heavy metal that poses a risk to human health even at low concentrations. [17,18,19]

The fabrication of three component based aptasensor for simple, rapid and selective detection of As^{3+} ions. For this purpose, guanidium bearing poly(HPMA-s-GPMA) copolymer and MPA-CdTeCdS quantum dots was incorporated with As^{3+} specific aptamer, leaving poly(HPMA-s-GPMA) free which can interact electrostatically with QDs which quenches the fluorescent signal. This three-component system is based on quenching phenomenon displayed by QDs due to competitive binding of As^{3+} ions & cationic copolymer to the aptamer. In the absence of As^{3+} ions aptamer gets bind with poly(HPMA-s-GPMA) making copolymer inactive to affect the fluorescence signal of QDs. This aptasensor can detect As^{3+} ions with the limit of detection of 246.77pm.[20,21]



Schematic representation of showing the fluorescence quenching of ZnO quantum dots in the presence of arsenic analytes

Fig 2: Schematic representation of showing the fluorescence of Zinc Oxide Quantum dots in the presence of arsenic analytes

Raw materials used for fabrication

According to past studies, in order to accurately detect As(III) in water, a dual-mode optical Nanosensor have been created that combines colorimetric and fluorescent technology. The Nanosensor was made up of amino-functionalized carbon dots (NCDs) and gold nanoparticles modified by trithiocyanuric acid (TMT-Au NPs). When TMT-Au NPs were added to the NCD solutions, an internal filtering effect caused the overlap of the UV-vis absorption peak of the TMT-Au NPs with the emission peak of the NCDs, which reduced the fluorescence of the NCDs. As(III) was added, and As(III) coordinated with TMT-Au NP sulfhydryl groups, resulting in the fluorescence of the NCDs. The threat posed by contaminants in water is a global issue. Arsenic, one of the most harmful contaminants in water, has a detrimental effect on people's health.1. It can result in cancer and even death in extreme circumstances. This study proposes a dual-mode optical Nanosensor using colorimetry and fluorescence to detect dangerous As(III) pollutants in water. We first created amino-functionalized carbon dots (NCDs) and TMT-modified gold nanoparticles (TMT-Au NPs). The dualmode optical Nanosensor (NCDs/TMT-Au NPs) was created by introducing TMT-Au NPs into the NCDs solution, thereby quenching their fluorescence through an internal filtering effect (IFE). When As(III) is added to TMT-Au NPs, it coordinates with sulfhydryl groups (-SH) on the surface, causing aggregation and colorimetric detection by local surface plasmon resonance (LSPR). Our dualmode optical Nanosensor accurately detects As(III) in water with a detection limit of 0.66 ppb by fluorescence and 0.87 ppb by colorimetry. [22,23]

Besides that, a new one-step process for producing vivid, multicolored fluorescent sulfur-doped carbon dots (CNDs) has been created using sodium thiosulfate and citric acid pyrolysis with basic microwave assistance. The artificially created CNDs demonstrated high selectivity dual mode colorimetric ultrasensitive sensing for both glutathione (GSH) and arsenic

[As (III)]. As (III) was discovered to have a detection limit (DL) of as low as 32 p.m. using fluorometric testing. Even in the face of interference from high quantities of other metal ions, the selectivity statistics demonstrate how highly selective the recently created CNDs are for As (III). Even in blood plasma, the CNDs shown a very selective ability to detect GSH relative to other bio thiols, such as cysteine (Cys) and homo-cysteine (H-cys), with a DL of 43 nm. The current CNDs assay may be employed on-site for As (III) detection, according to the quick kinetic results.

A novel hyper selective detection using ZnS-based quantum dots capped with thiosalicylic acid, which exhibit photoluminescence "turn-on" properties exclusively when arsenic is present in the aquatic medium for the first time. It exhibits a good limit of detection for soluble arsenic down to a few ppb levels, which is significantly lower than the MCL stated value and is unaffected by other ions.

Scientists' processes Chlorophyll synthesized Carbon Quantum Dots for detection of heavy metals like As³⁺& Hg⁺ ion in drinking water or aqueous solutions. These CQD_S synthesized from banana leaf extract which shows different optical properties in correspondence to changing temperature. Chlorophyll functional groups are present in CQD_S designed at **120&160 degree** Celsius while absent in CQD_S synthesized at **200&230 degree** Celsius. Chlorophyll included CQD_S can be utilized as sensors for selective detection of Hg⁺ & As³⁺ ions. The use of functionalized CQD_S for selective detection of As³⁺ & Hg⁺ ions by banana leaf extract through hydrothermal growth method. CQD_S based on emission spectra. CQD_S with high temperature above 200-degree Celsius exhibits broad emission peaks at 480nm. On the other hand, CQD_S synthesized at lower temperature above 120 and below 160-degree Celsius exhibits new emission peaks at 677 and 725nm.

Aptasensors based on quantum dots show a change in their fluorescent response proportional to a particular analyte concentration proves to be a simple method for arsenic sensing. Aptamers are the specialized class of molecules of nucleic acid that are chemically equivalent to antibodies and use for investigation in clinical purposes. Recently, it is reported that Aptasensors can sense As³⁺ions. QD based aptasensors requires aggregates of QD_S needs to be induced with an aptamer that possesses opposite net charge reducing their fluorescence response, then added As³⁺attached to aptamer leaving free QD_S and recovering proportionally their fluorescent response. QD aptasensors finds numerous applications due to optical properties, high stability, wide absorption spectra, high quantum yield and photochemical stability.Small found potential copper nanoparticles applications field nanoecotoxicology due to their low cost, least toxicity, stable size photoluminescence. It has been discovered recently that functionalized Cu₂S QD_S can be obtained easily in aqueous media, their cytotoxicity & colloidal stability can be easily altered by biomolecules having potential application in ion sensing. LCIS(L-cysteine) QD stabilizer binds to the crystal through sulfur bonds, that benefits water solubility and colloidal stability. LCIS behaves as reducing agent, least toxic, in-situ functionalization with an inert atmosphere Cu(II) reduction to Cu(I).

This study shows the synthesis of water soluble Cu₂S QD_S with red emission for As³⁺ sensing using LCIS as an stabilizer in an aqueous solution at ambient temperature and neutral Ph (7). Higher ph values can decrease repulsion between quantum dots resulting in aggregation.

This fluorometric test in the presence of aptamer shows a shift in intensity of fluorescence when As³⁺ ions incorporated and used aptamer makes a complex leaving the quantum dots and recovering the fluorescence response. This paper concludes that QD based aptasensors and LCIS based QD_S finds potential application in As³⁺ ion sensing in drinking water and thereby prevent major health conditions. [24,25,26]

The fabrication of three component based aptasensor for simple, rapid and selective detection of As^{3+} ions. For this purpose, guanidium bearing poly(HPMA-s-GPMA) copolymer and MPA-Cd-TeCdS quantum dots was incorporated with As^{3+} specific aptamer, leaving poly(HPMA-s-GPMA) free which can interact electrostatically with QD_S which quenches the fluorescent signal. This three-component system is based on quenching phenomenon displayed by QD_S due to competitive binding of As^{3+} ions & cationic copolymer to the aptamer. In the absence of As^{3+} ions aptamer gets bind with poly(HPMA-s-GPMA) making copolymer inactive to affect the fluorescence signal of QD_S. This aptasensor can detect As^{3+} ions with the limit of detection of 246.77pm.

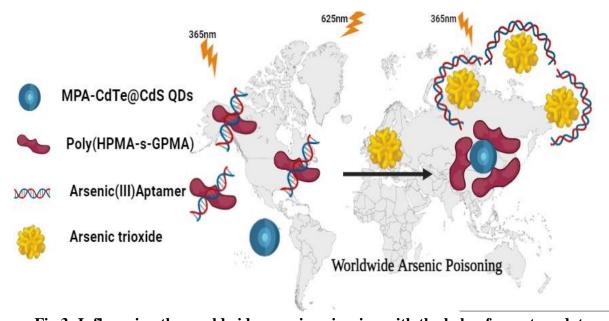


Fig 3: Influencing the worldwide arsenic poisoning with the help of quantum dots.

The new chlorophyll-functionalized CQD (ChlCQD) is introduced in this work as a nanoprobe for the sensitive detection of As and Hg ions in aqueous solutions. The hydrothermal treatment of banana leaf extract is done in one step to create these CQDs. This study reviews that CQDs with various optical characteristics may be obtained by adjusting the hydrothermal synthesis temperature from 120°C to 230°C. Only the CQDs produced at 120°C and 160°C are embellished with functional groups of chlorophyll, whereas the CQDs produced at 200°C and 230°C lack any chlorophyll groups. A band of fluorescence near the red area is produced by these chlorophyll groups, and the presence of metal ions either enhances or quenches this band. We show that the synthesized ChlCQDs at 160°C can be used as a low-limit detection turn-on/off sensor for the selective detection of As and Hg ions. [27,28]

Density Functional Theory (DFT) computations were carried out theoretically to obtain atomic-level insight into the interactions between As and Hg and the surface of ChlCQD (low-temperature model surface). significant overlap between the Arsenic and CQD surfaces causes a significant absorption peak at 660 nm; for Hg, however, there is no such peak because there is very little overlap between the orbitals of Hg and the ChlCQD surface. According to similar experimental absorption spectra for both metals, As and Hg interact similarly with various locations on the CQD (high-temperature model structure). One of the main man-made problems that is currently endangering the earth's environment is water pollution. Worldwide, an estimated 2 million tons of industrial and agricultural sewage waste are dumped into water bodies each day, endangering people, vegetation, and wildlife. Numerous substances can contaminate water, including chemicals, household trash, pesticides, herbicides, waste from food processing, volatile organic compounds (VOCs), and heavy metals (such as lead, arsenic, mercury, cadmium, and chromium). Groundwater contamination with heavy metals has also been a new issue brought on by inappropriate recycling of technological waste. Natural processes can introduce heavy metals from the Earth's crust into water resources. Over 200 minerals include arsenic, which is extensively distributed in them. Some of these minerals are volatile and easily soluble in water, which causes arsenic to gradually leach into groundwater.

A novel method for creating a fluorometric aptasensor has been presented and used to measure As(III), a cation that is extremely poisonous. This technique involved the agglomeration of cationic cysteamine-stabilized CdTe/ZnS core/shell quantum dots using an aptamer, leading to the accumulation of fluorescence quenching. Aptamer and As(III) makes a complex which prevents aggregation of quantum dots which increases the quantum dot efficiency. The fluorometric assay has a low detection limit of 1.3 pmol L-1 As(III) and a dynamic range of 1.0×10 -11 to 1.0×10 -6 molL⁻¹. The study examined the interference effect of various cations and anions, confirming the aptasensor's good selectivity for detecting As(III). The method successfully detected As(III) in many water samples. Arsenic is a heavy metal that poses a risk to human health even at low concentrations. Aptamers are oligonucleotide molecules (ssDNA or RNA) that attach to certain molecules or metal ions. Aptamers are like antibodies and possesses same therapeutic and diagnostic applications. The aptamer-target connection occurs through electrostatic, van der Waals, or hydrogen bonding interactions, or through a mixture of these interactions. The past several decades has seen a growth in the usage of aptamers in various scientific domains due to their advantages, which include ease of synthesis, specificity to targets, and simplicity in detection and analysis. Due to their benefits over organic dyes, such as their narrow emission, size-dependent optical characteristics, and resistance to light bleaching, quantum dots (QDs) have drawn a lot of interest. The aptamer and As(III) combine to create a complex in the presence of As(III), preventing the quantum dots from aggregating. As a result, when the quantum dots deaggregated—a process that is dependent on the As(III) concentration—their fluorescence intensity increased. The highly selective aptasensor method for As(III) detection is the suggested approach. The current assay was effectively used to measure As(III) in a number of water samples. Selective detection of additional metal ions, proteins, and tiny molecules can be achieved by simply substituting the utilized aptamer with another aptamer. [29,30]

A novel hyperselective detection using ZnS-based quantum dots capped with thiosalicylic acid, which exhibit photoluminescence "turn-on" properties exclusively when arsenic is present in the aquatic medium for the first time. It exhibits a good limit of detection for soluble arsenic down to a few ppb levels, which is significantly lower than the MCL stated value and is unaffected by other ions. Therefore, In order to identify the hazardous arsenic alone, it makes sense to design extremely straightforward yet dependable and affordable sensing technologies, free from outside interference. Due to their decreased toxicity compared to other II-VI semiconductor QDs (such as CdS, CdSe, and CdTe), zinc sulfide quantum dots (ZnS QDs) can be very suitable for applications in biological sectors. The high ionic potential of arsenic (the first ionization potential is 9.81 eV) makes it prone to bind Odonor ligands. This is the reason for the urgency in developing sensors that can detect arsenic and have free oxygen donor sites. To create ZnS QDs for the selective detection of arsenic, we utilized thiosalicylic acid (TSA), an aromatic thiol, as a capping ligand. The majority of research, revolves around the development of arsenite or arsenate. For the purpose of detecting arsenate (LOD: 1.32 µM) and arsenite (LOD: 0.23 µM), Ali and colleagues have created a di-oxime-based turn-on blue emission fluorescent probe. However, the probe is not entirely interference-free, as Co(II), Ni(II), and Cu(II) are found to slightly interfere with the arsenic sensing, and the limit of detection (LOD) for arsenate is in the micromolar range (quite high). [31,32]

Harrop et al. reported using an organic THF solvent to work with a fluorescent probe that had a good limit of detection (LOD) for As (III). In light of this, it would seem imperative to search for any harmful material in a purely aqueous medium rather than in an organic one when addressing biological and environmental problems. This study presents a novel, easy to understand and highly reliable synthetic methodology for the synthesis of water-soluble thiosalicylic acid (TSA)-capped ZnS-based QDs. The QDs can be used for the highly selective detection and estimation of arsenic using the fluorescence turn-on protocol, all without interference from other coexisting ions in an aquatic system. The behavior of these QDs in the presence of arsenic (As) can be explained by very selective aggregation-enhanced emission (AEE), according to the findings of several tests. It is crucial to have the right pH for a successful probe in biological applications. We used phosphate buffer (10 mm) to determine the PL intensities of our chemo sensor in the presence and absence of arsenic at various pH values. [33,34]

Methods used for characterization

Several instruments or analysis techniques are commonly used to characterize carbon-quantum dots. Following mentioned are the techniques:

- Fourier transform infrared spectroscopy
- UV-visible spectroscopy
- Atomic absorption spectroscopy
- Atomic emission spectroscopy
- Fluorescence spectroscopy

Fourier transform infrared spectroscopy:

It is a powerful technique used to identify and analyze the molecular structure of materials. FTIR based on the principle, measures the absorption of infra red radiation by molecules, which causes molecular vibrations. It converts raw data into spectrum which provides a fingerprint of the molecular structure.

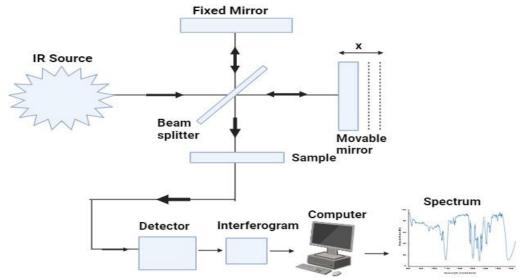


Fig4: Schematic diagram showing the FTIR spectroscopy.

UV-visible spectroscopy

It is a widely used technique that measures the absorption of ultraviolet and visible light by molecules. Principle of UV-visible spectroscopy states that molecules absorb light at specific wavelengths, resulting in transitions between electronic energy levels. Transition of molecules takes place from ground state to excited state when light energy is absorbed by them. [35]

Atomic absorption spectroscopy:

Atomic absorption spectroscopy is an analytical technique to determine and analyze the quantitative elements in a solution. It is a Spectro analytical procedure. It relies on beer-lambert's law. [36]

Atomic emission spectroscopy:

Atomic emission spectroscopy is a method used for chemical analysis that uses the intensity of light emitted from a flame, plasma, arc or spark at a particular wavelength to determine the quantity of an element in a sample. [37]

Fluorescence spectroscopy:

It is a highly sensitive and selective analytical technique that measures the emission of light by molecules that have absorbed light at a specific wavelength. Fluorescence is a type of luminescence caused by photons exciting a molecule, raising it to an electronic excited state.

Expensive and bulky techniques include: ICP-MS, XRD, SEM, TEM etc.

Surface Plasmon Resonance technique has been used and described in this paper as Surface Plasmon Resonance (SPR) sensor, an accurate & versatile technique to analyze chemical and biochemical molecules.

SPR phenomenon occurs due to optical properties and dielectric metal layers depends on charge density oscillation at the interface of metal and dielectric layer. SPR have a high potential to recognize the toxic chemical like: Arsenic due to detection of variation of optical properties. Matrix-method and effective-medium theoryg(EMT) for 2D structure were presented for analysis. The common metal used to design SPR sensor is gold. Sensing layers like: nanolayer, polymer & polymer composite layers have been used to enhance sensitivity & selectivity of SPR sensor. Carbon-based nanomaterials including graphene oxide, graphene quantum dots use to improve the gold layer. [38,39]

Arsenic Poisoning

Heavy metal contaminants are a type of dangerous waste that is frequently discovered in water sources, originating from geogenic, industrial, pharmaceutical, and agricultural activities. Smelting, mining, extraction, batteries, metal plating, foundries, and inappropriate recycling of electronic wastes are additional methods of contaminating water supplies. Arsenic being readily soluble in water results into leaching of groundwater. Likewise, Mercury shows its presence in rocks released during mining activities. Due to their nonbiodegradable nature, they accumulate in food chain leading to increase in concentration at each trophic level of food chain. For e.g. Methylmercury, toxic form of mercury produced by bacteria absorbed by plankton and gets accumulated in food chain leading to contaminated food or water leading to serious health conditions affecting skin, nervous, respiratory, endocrinological, cancer and immune disorders. Arsenite contamination in drinking water is a major threat to global public health. Arsenite contamination has been reported in different zones around the world: Argentina, Australia, Bangladesh, Cambodia, Canada, Chile, China, Germany, Ghana, Hungary, Japan, India, Laos, Mexico & United States. Arsenic is classified as a cancer-causing agent(carcinogen) by IARC(International Agency for Research in Cancer) and its presence in drinking water results in harmful disorders like: skin damage, disturbances in circulatory system, tumor growth in skin, lungs, bladder, liver or kidneys. Arsenic also known as Clastogenic(mutating agent in genetic material) and A eugenic (irregular chromosomic division) agent. WHO(World Health Organization) decides a safe limit for amount of arsenic in drinking water is 10ug/l. As³⁺ is most toxic form of arsenic which requires relevant detection and quantification. Maximum permissible level of arsenic in drinking water is 10ug/l set by World Health Organization(WHO) & Environmental Protection Agency(EPA). Arsenic poisoning/Arsenicosis is a long-term exposure of arsenic in human body results in chronic illness. The International Agency for Research on Cancer (IARC) has classified arsenic and its compounds as carcinogenic to humans, including those found in drinking water. Drinking arsenic-contaminated water can cause skin damage, interruption of circulation, and even death in extreme situations. It has been linked to cancer in the skin, lung, urinary bladder, liver, and kidney. Many regions of the world, particularly South Asia, have naturally high levels of arsenic contamination in their groundwater. [40,41,42]

Applications

Carbon and quantum dots found numerous applications not only in the field of sensing but also possesses biomedical applications, drug delivery etc. Some of the applications are discussed below:

- Imaging and sensing
- Drug delivery
- Photocatalysis, solar cells
- Fluorescent biological labeling
- Lighting and medical imaging
- Additives in food industry, antioxidants & antimicrobials

Conclusion

Arsenic poisoning in drinking water causes major health threat worldwide. Herein we have reviewed the methods for preparing fluorescent, aptamers, synthetic and green methods for carbon quantum dots preparation and found their use as arsenic sensors in drinking water. We have analyzed various factors, properties and applications of carbon quantum dots.

The advantages of synthesizing carbon quantum dots from above discussed methods includes feasibility and availability of raw materials on large scale production, from banana leave extract, easily available and simple. QD based aptasensors and LCIS based QD_S finds potential application in As³⁺ ion sensing in drinking water and thereby prevent major health conditions. It was proven that the affinity of As³⁺in bonding with polypyrene graphene quantum dots layer was higher than Hg²⁺and Pb²⁺ions which signifies that the limit of sensor and response time were restricted to a concentration of 0.005ppm and 380s respectively. Carbon quantum dots have also been prepared by neem, basil, Tulsi extract as studies showed they are the best capacitors. The employed aptamer can be readily substituted with alternative aptamers, hence enabling the selective identification of additional metal ions, proteins, and small molecules. Many benefits come with the newly developed aptasensor, including great selectivity and sensitivity, low cost, ease of use, a very low detection limit, and a broad linear range for the As(III) determination. In conclusion, dual-mode optical sensor is successfully employed to detect As(III) in water using IFE and LSPR. TMT-Au NPs significantly reduce the fluorescence of NCDs, creating a dual-mode Nano sensor with a pink solution color and a dim cyan fluorescence. [43,44,45]

References

- 1. Hall AH. Chronic arsenic poisoning. Toxicology letters. 2002 Mar 10;128(1-3):69-72.
- 2. Hu, H., 2008. Heavy metal poisoning.
- 3. Martinson CA, Reddy KJ. Adsorption of arsenic (III) and arsenic (V) by cupric oxide nanoparticles. Journal of colloid and interface science. 2009 Aug 15;336(2):406-11.
- 4. Goswami A, Raul PK, Purkait MK. Arsenic adsorption using copper (II) oxide nanoparticles. Chemical engineering research and design. 2012 Sep 1;90(9):1387-96.
- 5. Tuerhong M, Yang XU, Xue-Bo YI. Review on carbon dots and their applications. Chinese Journal of Analytical Chemistry. 2017 Jan 1;45(1):139-50.

6. Kang Z, Lee ST. Carbon dots: advances in nanocarbon applications. Nanoscale. 2019;11(41):19214-24.

- 7. Saha JC, Dikshit AK, Bandyopadhyay M, Saha KC. A review of arsenic poisoning and its effects on human health. Critical reviews in environmental science and technology. 1999 Jul 1;29(3):281-313.
- 8. Ullah H, Hussain S, Ahmad A. Study on arsenic poisoning by worldwide drinking water, its effects and prevention. International Journal of Economic and Environmental Geology. 2019 Sep 4;10(2):72-8.
- 9. Zaldivar R. Arsenic contamination of drinking water and foodstuffs causing endemic chronic poisoning. BeiträgePathologie. 1974 Jan 1;151(4):384-400.
- 10. Fiorito S, Serafino A, Andreola F, Togna A, Togna G. Toxicity and biocompatibility of carbon nanoparticles. Journal of Nanoscience and Nanotechnology. 2006 Mar 1;6(3):591-9.
- 11. Asadian E, Ghalkhani M, Shahrokhian S. Electrochemical sensing based on carbon nanoparticles: A review. Sensors and Actuators B: Chemical. 2019 Aug 15;293:183-209.
- 12. de Oliveira PF, Torresi RM, Emmerling F, Camargo PH. Challenges and opportunities in the bottom-up mechanochemical synthesis of noble metal nanoparticles. Journal of Materials Chemistry A. 2020;8(32):16114-41.
- 13. Sau TK, Rogach AL, editors. Complex-shaped metal nanoparticles: bottom-up syntheses and applications. John Wiley & Sons; 2012 May 7.
- 14. Jacak L, Hawrylak P, Wojs A. Quantum dots. Springer Science & Business Media; 2013 Jun 29
- 15. Reed MA. Quantum dots. Scientific American. 1993 Jan 1;268(1):118-23.
- 16. Lim, S. Y., Shen, W., & Gao, Z. (2015). Carbon quantum dots and their applications. *Chemical Society Reviews*, 44(1), 362-381.
- 17. Zheng R. The development of an aptamer-based surface plasmon resonance (spr) sensor for the real-time detection of glycated protein. The University of Toledo; 2012.
- 18. Kailasa SK, Koduru JR. Perspectives of magnetic nature carbon dots in analytical chemistry: From separation to detection and bioimaging. Trends in Environmental Analytical Chemistry. 2022 Mar 1;33:00153.
- 19. Chaturvedi A, Cruz Corella J, Robbins C, Loha A, Menin L, Gasilova N, Masclaux FG, Lee SJ, Sanders IR. The methylome of the model arbuscular mycorrhizal fungus, Rhizophagusirregularis, shares characteristics with early diverging fungi and Dikarya. Communications Biology. 2021 Jul 22;4(1):901.
- 20. Kumar SG, Rao KK. Physics and chemistry of CdTe/CdS thin film heterojunction photovoltaic devices: fundamental and critical aspects. Energy & Environmental Science. 2014;7(1):45-102.
- 21. Romeo N, Bosio A, Canevari V, Podesta A. Recent progress on CdTe/CdS thin film solar cells. Solar Energy. 2004 Dec 1;77(6):795-801.
- 22. Romeo N, Bosio A, Canevari V, Podesta A. Recent progress on CdTe/CdS thin film solar cells. Solar Energy. 2004 Dec 1;77(6):795-801.
- 23. Kundelev EV, Tepliakov NV, Leonov MY, Maslov VG, Baranov AV, Fedorov AV, Rukhlenko ID, Rogach AL. Amino functionalization of carbon dots leads to red emission enhancement. The Journal of Physical Chemistry Letters. 2019 Aug 8;10(17):5111-6.

24. Alam MB, Hassan N, Sahoo K, Kumar M, Sharma M, Lahiri J, Parmar AS. Deciphering interaction between chlorophyll functionalized carbon quantum dots with arsenic and mercury toxic metals in water as highly sensitive dual-probe sensor. Journal of Photochemistry and Photobiology A: Chemistry. 2022 Oct 1;431:114059.

- 25. Alam MB, Hassan N, Sahoo K, Kumar M, Sharma M, Lahiri J, Parmar AS. Deciphering interaction between chlorophyll functionalized carbon quantum dots with arsenic and mercury toxic metals in water as highly sensitive dual-probe sensor. Journal of Photochemistry and Photobiology A: Chemistry. 2022 Oct 1;431:114059.
- 26. Liu Y, Yan K, Okoth OK, Zhang J. A label-free photoelectrochemical aptasensor based on nitrogen-doped graphene quantum dots for chloramphenical determination. Biosensors and Bioelectronics. 2015 Dec 15;74:1016-21.
- 27. Kopeček J, Kopečková P. HPMA copolymers: origins, early developments, present, and future. Advanced drug delivery reviews. 2010 Feb 17;62(2):122-49.
- 28. Talelli M, Rijcken CJ, Van Nostrum CF, Storm G, Hennink WE. Micelles based on HPMA copolymers. Advanced drug delivery reviews. 2010 Feb 17;62(2):231-9.
- 29. Bagayoko D. Understanding density functional theory (DFT) and completing it in practice. AIP Advances. 2014 Dec 1;4(12).
- 30. Burke K, Wagner LO. DFT in a nutshell. International Journal of Quantum Chemistry. 2013 Jan 15;113(2):96-101.
- 31. Sharma K, Raizada P, Hasija V, Singh P, Bajpai A, Nguyen VH, Rangabhashiyam S, Kumar P, Nadda AK, Kim SY, Varma RS. ZnS-based quantum dots as photocatalysts for water purification. Journal of Water Process Engineering. 2021 Oct 1;43:102217.
- 32. Godavarti UD, Nagaraju P, Yelsani V, Pushukuri Y, Reddy PS, Dasari M. Synthesis and characterization of ZnS-based quantum dots to trace low concentration of ammonia. Journal of Semiconductors. 2021 Dec 1;42(12):122901.
- 33. Pan J, Ma J, Liu L, Li D, Huo Y, Liu H. A novel carbazole-based highly sensitive and selective turn-on fluorescent probe for mercury (II) ions in aqueous THF. Journal of Photochemistry and Photobiology A: Chemistry. 2021 Jul 1;416:113322.
- 34. Li C, Zhang X, Zhang W, Qin X, Zhu C. Carbon quantum dots derived from pure solvent tetrahydrofuran as a fluorescent probe to detect pH and silver ion. Journal of Photochemistry and Photobiology A: Chemistry. 2019 Sep 1;382:111981.
- 35. Perkampus HH. UV-VIS Spectroscopy and its Applications. Springer Science & Business Media; 2013 Mar 8.
- 36. Lagalante AF. Atomic absorption spectroscopy: A tutorial review. Applied Spectroscopy Reviews. 2004 Sep 27;34(3):173-89.
- 37. Lagalante AF. Atomic absorption spectroscopy: A tutorial review. Applied Spectroscopy Reviews. 2004 Sep 27;34(3):173-89.
- 38. Royer CA. Fluorescence spectroscopy. Protein stability and folding: Theory and practice. 1995:65-89.
- 39. Weiss S. Fluorescence spectroscopy of single biomolecules. Science. 1999 Mar 12;283(5408):1676-83.
- 40. Schoolmeester WL, White DR. Arsenic poisoning. Southern medical journal. 1980 Feb 1;73(2):198-208.

41. Nickson R, McArthur J, Burgess W, Ahmed KM, Ravenscroft P, Rahmanñ M. Arsenic poisoning of Bangladesh groundwater. Nature. 1998 Sep 24;395(6700):338-.

- 42. Nriagu JO. Arsenic poisoning through the ages. Environmental chemistry of arsenic. 2002;1:1-26.
- 43. Pourmadadi M, Nouralishahi A, Shalbaf M, Shabani Shayeh J, Nouralishahi A. An electrochemical aptasensor for detection of prostate-specific antigen-based on carbon quantum dots-gold nanoparticles. Biotechnology and Applied Biochemistry. 2023 Feb;70(1):175-83.
- 44. Jia M, Jia B, Liao X, Shi L, Zhang Z, Liu M, Zhou L, Li D, Kong W. A CdSe@ CdS quantum dots based electrochemiluminescence aptasensor for sensitive detection of ochratoxin A. Chemosphere. 2022 Jan 1;287:131994.
- 45. Huang H, Tan Y, Shi J, Liang G, Zhu JJ. DNA aptasensor for the detection of ATP based on quantum dots electrochemiluminescence. Nanoscale. 2010;2(4):606-12.