SENSING OF ARSENIC USING ZINC OXIDE (ZnO) MODIFIED WITH CURCUMIN

by

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A comprehensive project report has been submitted in partial fulfilment of the requirements for the degree of

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ABSTRACT

Zinc oxide (ZnO) has presented itself as a special material with great potential and has attracted researchers to study this semiconductor in the form of powders, single crystals, thin films etc. ZnO is used for a wide variety of applications such as, transparent conducting electrodes in solar cells, photocatalysts, UV lasers, sensors etc.

Arsenic exists in water as two major inorganic species, namely As (III) (arsenite) and As (V) (arsenate). In aerobic or oxidizing conditions arsenates are stable, whereas under anaerobic or mildly reducing conditions arsenites are more stable. Of these two redox states of arsenic, As (III) (arsenite) is the more toxic form than As (V) (arsenate).

In this project work, we have applied a simple aqueous phase chemistry method and have modified nanostructured zinc oxide surfaces with the organic compound curcumin ($C_{21}H_{20}O_6$), here referred to as Zn(cur)O. These Zn(cur)O nanostructured materials have the morphology of a grain-like wurtzite hexagonal crystal structure with good crystalline quality. The defects of ZnO, which are visible luminescence centers get filled by doping of curcumin. It in turn prolongs the electron-hole recombination, thereby causing the quenching of visible luminescence and also enhancing the exciton emission of zinc oxide. Now, Zn(cur)O is weak fluorescent. When it comes in contact with arsenic and binds with it, it becomes strongly fluorescent and shows enhanced photoluminescence. The photoluminescence of ZnO is insensitive to arsenic concentration in water. Arsenic can be sensitively sensed in the concentration range of 100 to 3000 ppb by the photoluminescence of a Zn(cur)O colloidal solution at an excitation wavelength of 425 nm.

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Chapter 1

Introduction

The advancement of nanomaterials and nanotechnology has been fuelled by the design of functional nanomaterials leading to the production of special materials with novel properties which can be effectively used for potential applications in chemical, biological, and technological domains. When the functionalities of organic systems are incorporated on the surfaces of metal oxide nanoparticles, it will yield hybrid materials with novel properties and functions. Zinc oxide (ZnO) has presented itself as a special material with great potential and has attracted researchers to study this semiconductor in the form of powders, single crystals, thin films etc. ZnO is biocompatible rendering it suitable for biomedical and environmental applications and it is used for a wide variety of applications such as, transparent conducting electrodes in solar cells, photocatalysts, UV lasers, sensors etc. ZnO has a wide band gap (≈3·37 eV at room temperature) and efficient excitionic emission can be obtained from it, even at room temperature because of its high exciton binding energy (60 meV).

Millions of people around the world get affected by arsenic contamination in natural water. Health hazards such as cancers of liver, lung, kidney, skin, and bladder, problems associated with the cardio vascular system, occur if one is exposed to arsenic over extended periods of time and it also affects the mental development of children. Arsenic can accumulate in natural water as a result of leaching from arsenic containing source rocks and sediments. Geochemical environments such as basin-fill deposits of alluvial lacustrine origin, volcanic deposits, inputs from geothermal sources, mining wastes and landfills, are generally associated with the presence of arsenic. In 2001, the US Environmental Protection Agency (EPA) lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 to 10 mg L^-1 (0·01 ppm), thereby rendering the drinking sources all over the world unacceptable. The arsenic contamination of the groundwater has been a serious problem in many countries. As a result, researchers are engaged in the development of low-cost and simple methods which would be able to detect or sense arsenic from a given sample of water.

Arsenic exists in water as two major inorganic species, namely As (III) (arsenite, AsO_3^{3-}) and As (V) (arsenate, AsO_4^{3-}). The pH and the redox conditions of the environment in which they are present are the factors which mainly determine the existence and ratio of these two forms of arsenic. In aerobic or oxidizing conditions arsenates are stable, whilst under anaerobic or mildly reducing conditions arsenites are more stable. In solution, arsenite species exists as H_3AsO_3 (arsenous acid) and $H_2AsO_3^-$ (dihydrogen arsenite) with pK_a values of 9·2 and 12·7 respectively. Arsenate species is present as $H_2AsO_4^-$ (dihydrogen arsenate) and $HAsO_4^{2-}$ (arsenate hydrogen ion) and the pK_a values for arsenic acid (H_3AsO_4) are $pK_{a1} = 2{\cdot}3$, $pK_{a2} = 6{\cdot}8$, and $pK_{a3} = 11{\cdot}6$. Of these two redox states of arsenic, As (III) (arsenite) is the more toxic form than As (V) (arsenate). Since arsenate is an ionic species in the pH range typically found in the aquatic environment, hence it is easier to remove it from water than arsenite. On the other hand, in natural water, arsenite exists in non ionic form H_3AsO_3 with pH value ranging from weakly acidic to weakly alkaline. Due to this, the adsorption performance of various adsorbents on As (III) (arsenite) is poor.

ZnO acts as a good adsorbent. The luminescence property of ZnO may be influenced by doping with an organic system. When ZnO is sensitized towards visible light then the band gap has to be narrowed or spilt into several sub-gaps. We can achieve this through a number of methods, out of which one is through the surface modification by incorporation of organic materials. The major component of curcuminoid complexes is curcumin. It is well known for its pharmaceutical applications and medicinal potential in the therapy of many diseases such as cancer, cardio vascular diseases and rheumatoid arthritis. In dye sensitized solar cells having a photocurrent density of 1·66 mA cm^2, as a sensitizer curcumin derived dye can be used. Curcumin has very exciting photophysical and fluorescence properties. Nowadays, curcumin, as fluorescence probe for developing new sensing scheme, is becoming more and more popular. It helps in the preparation of metal nanoparticles and nanorods by acting as a reducing agent and can make metal complex with various metal ions. It also forms a Zn-curcumin complex by reacting with zinc salt. ZnO-curcumin composites can also be made using curcumin. In this project work, an attempt has been made to prepare new curcumin doped ZnO nanomaterials, termed here as Zn(cur)O, and apply it for the development of new fluorescence sensing scheme for arsenic.

1.1 Objective

The primary objective of this project work is to design a sensor which would be able to detect or sense efficiently, whether arsenic in present in a sample of drinking or natural water. The metal oxide zinc oxide (ZnO), modified with the organic compound curcumin ($C_{21}H_{20}O_6$), has been used to design the required sensor. Modification of nanostructured zinc oxide surfaces with curcumin leads to the formation of Zn(cur)O. Now, Zn(cur)O is weak fluorescent. When it comes in contact with arsenic, it binds with it and becomes strongly fluorescent and shows enhanced photoluminescence. Arsenic can be sensitively sensed in the concentration range of 100 to 3000 ppb by this photoluminescence of Zn(cur)O.

1.2 Motive

Arsenic contamination in drinking water is a global problem widely seen in Bangladesh and West Bengal of the Indian sub continent. Serious health hazards are caused by arsenic and its toxic compounds. Consumption of food and water contaminated with arsenic paves the way for human exposure to arsenic. Chronic exposure to high concentrations of arsenic can cause severe health problems, collectively known as **arsenicosis**. Some of the symptoms of arsenicosis include skin lesions, nervous system disorders, gastrointestinal problems and various types of cancers. Inorganic arsenic is naturally present at high levels in the groundwater of several countries, including India, Pakistan, China, Vietnam and several parts of the United States of America. The main motive or purpose behind doing this project is to design a user-friendly and highly sensitive sensor which can efficiently and effectively detect the presence of arsenic in a sample of water and whose output would be almost error free. Analytical methods capable of detecting arsenic at low concentrations are usually based on sophisticated laboratory instrumentation. Atomic absorption spectroscopy (AAS), induced coupled plasma atomic emission spectroscopy (ICP-AES), X-ray fluorescence, and atomic fluorescence spectroscopy are examples of sensitive and selective methods used for arsenic sensing. The quality of data obtained from these methods is high, but, analyzing water samples using these methods is very expensive due to the manpower and instrumentation requirements and the overall cost of analysis. Hence, these powerful methods are not adequate for routine arsenic monitoring. The sensing mechanism described in this project work fulfils the motive of arsenic detection and regular arsenic monitoring. By using this sensor, the detection/sensing of arsenic in a drinking or groundwater sample can be done and it would serve the purpose of locating and demarcating the areas where arsenic contamination is predominant. This information can be used by the local administration to keep a regular check on the arsenic pollution and supply purified water in these areas, when necessary. Also the easy, quick, efficient and correct testing of water samples using the sensor proposed here, will lead to the identification of deep tube wells, taps etc. which are contaminated with arsenic and they can be distinguished from the other water sources in that area and the local residents can be prohibited from using those for their daily works. The analysis of the data, provided efficiently and quickly by the sensor designed here, on the quality of water obtained from various sources from different areas, will help the requisite departments of the government as well as the local administration and will easily enable them to take the necessary steps such as marking of the contaminated water sources with a particular colour, prohibiting the usage of such sources for everyday work etc, so that further spread of arsenicosis can be prevented in those areas which in turn would help to reduce the arsenic contamination and pollution. As a future prospect, this project work can be extended to the removal of arsenic from the said water sample, since Zn(cur)O can significantly improve the efficient removal of arsenic contamination from water below the maximum contaminant level (MCL).

1.3 Literature review

The advancement of nanomaterials and nanotechnology has been fuelled by the design of functional nanomaterials leading to the production of special materials with novel properties which can be effectively used for potential applications in chemical, biological, and technological domains. When the functionalities of organic systems are incorporated on the surfaces of metal oxide nanoparticles, it will yield hybrid materials with novel properties and functions. Zinc oxide (ZnO) has presented itself as a special material with great potential and has attracted researchers to study this semiconductor. ZnO is used for a wide variety of applications such as, transparent conducting electrodes in solar cells, photocatalysts, UV lasers, sensors etc. ZnO acts as a good adsorbent. The luminescence property of ZnO may be influenced by doping with an organic system. When ZnO is sensitized towards visible light then the band gap has to be narrowed or spilt into several sub-gaps. We can achieve this through a number of methods, out of which one is through the surface modification by incorporation of organic materials. Millions of people around the world get affected by arsenic contamination in natural water causing various types of health hazards. Arsenic contamination of the groundwater has become a serious problem in many countries. As a result, researchers are engaged in the development various methods which would be able to detect or sense arsenic from a given sample of water.

In 2014, X. Savarimuthu *et. al.* demonstrated "Implementation of electrochemical sensors in arsenic-contaminated areas of West Bengal in India toward rapid and point-of-use detection of arsenic in drinking water". In this paper, the author has described an electrochemical detection technique, capable of detecting trace amounts of arsenic in groundwater samples. The point-of-use (POU) electrochemical sensor utilizes a three-electrode system with carbon, silver, and silver/silver chloride electrodes integrated with a handheld electrochemical analyzer. The handheld electrochemical analyzer is capable of delivering quick and accurate readings at the test site. When the device is connected to the potentiostat and a small volume of water sample is deposited onto the detection zone, cyclic voltammetry or anode stripping voltammetry can be applied to the electrode surface, producing a current peak, through the range of the potential scanned. In 2015, P. Devi *et. al.* demonstrated "Novel carbon/manganese oxide nanocomposite for electrochemical detection of arsenic in water- a step towards portable real time sensor", where the author has discussed about the results on novel nanocomposite (NC) material, reduced graphene oxide (rGO)/manganese oxide (MNO_2), for sensitive and selective detection of As (III) in water. The novel MnO_x /rGO nanocomposite based working electrode is fabricated by one step electrochemical reduction method and characterized for its optical, structural and electrical properties. In this electrochemical sensor a standard three electrode system was used which included Ag/AgCl as reference electrode, a platinum wire as counter electrode and a Graphene oxide (GO)-modified glassy carbon electrode (GCE) as a working electrode. Sensing parameters such as time, pH, and deposition potential are optimized, which are recorded to design a portable embedded system for As (III) sensing. In 2010, S. Das *et. al.* showed "Design, fabrication and performance evaluation of a piezoresistive arsenic sensor", where the author has described the design, analysis and testing of a cantilever based piezoresistive arsenic sensor. Here, the technologies of anisotropic chemical etching have been utilized for the fabrication on a single crystal silicon substrate. When the sensing cantilever adsorbs arsenic on its surface which is coated with arsenic adsorbent, then the arsenic sensor, which is of resistive type, changes its resistance. Piezoresistivity describes the change in the electrical resistance of a material due to the applied mechanical stress. A model of the structure was established and the sensor characteristics were found to have high sensitivity and linearity. In 2019, Hema. R *et. al.* demonstrated "Development, Analysis and Evaluation of Arsenic (III) Sensor". In this paper, the author has described a special technique for the determination by express sensing of arsenic ionic level in water on a Smooth or Glassy carbon electrode (GCE) with nano Gold transformation in 0.5 (M) H_2SO_4. The gold nanoparticles are electrodeposited on glassy carbon electrode. The electrode was examined by Differential Pulse Voltammetry (DPV), Anodic Stripping Voltammetry (ASV), Linear Sweep Voltammetry (LSV) and cyclic Voltammetry (CV). After optimization, a Level Of Detection of 0.9 ppb was achieved. The Chemical setup consists of GC and platinum foil as working and counter electrode with MMS (Mercury Mercurious Sulphate) as standard reference electrode. Potential was applied between working and standard reference electrodes. The arsenic detector is developed using working GCE and Platinum foil counter electrode with reference to MMS standard electrode. In 2021, Haradhan Kolya *et. al.* demonstrated “Recent Advances in Colorimetric Detection of Arsenic Using Metal-Based Nanoparticles”, where the author has described the application of several metal-based nanoparticles to prepare a cost-effective and straightforward detector for arsenic (III) ions. Among the developed strategies, colorimetric detection is one of the simplest methods to detect arsenic (III) in water. Several portable digital detection technologies make nanoparticle-based colorimetric detectors useful for on-site arsenic detection. Here, several metal-based nanoparticles such as silver-based nanoparticles, metal oxide-based nanoparticles, and CNT-based nanoparticles etc that can detect arsenic (III) in water colorimetrically at a concentration of ~0.12 ppb or lower were showcased by the author. This paper also describes future directions, perspectives and challenges, which will help us in designing an effective arsenic sensor for commercial use. In 2022, S. Pandey demonstrated "Sensing Material and Design of an Optical Sensor for Detection of Arsenic-A Review". In this paper, the author has described about the challenges various optical phenomenon like absorption, scattering, fluorescence etc have in the sensing world and discussed about the different sensing materials which can be used for the sensor.

After rigorously studying and going through all of these papers, in our project work, we have applied a simple aqueous phase chemistry method and have modified the surfaces of the nanostructured particles of the metal oxide, zinc oxide with the organic compound curcumin ($C_{21}H_{20}O_6$), here referred to as Zn(cur)O. This Zn-curcumin complex is used in order to design the requisite sensor, for the sensing of arsenic. These Zn(cur)O nanostructured materials have the morphology of a grain-like wurtzite hexagonal crystal structure with good crystalline quality. The defects of ZnO, which are visible luminescence centers get filled by doping of curcumin. It in turn prolongs the electron-hole recombination, thereby causing the quenching of visible luminescence and also enhancing the exciton emission of zinc oxide. As such, Zn(cur)O is weak fluorescent. But, when it comes in contact with arsenic, it binds with it and becomes strongly fluorescent and shows enhanced photoluminescence. This fluorescence sensing technique is deployed to sense or detect the presence of arsenic in the said water sample.

Chapter 2

Definition of the work and Materials required

2.1 Definition

The surfaces of the nanostructured particles of the metal oxide zinc oxide (ZnO) are modified using the organic compound curcumin ($C_{21}H_{20}O_6$), in order to design a sensor, for the sensing of arsenic.

2.2 Materials required

The following materials are required for doing this project work.

i) Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] {98% extra pure}, which was obtained from Sigma Aldrich

ii) Acetone {$(CH_3)_2CO$}, which was obtained from Merck

iii) Potassium hydroxide (KOH), which was also obtained from Merck, and,

iv) Curcumin ($C_{21}H_{20}O_6$), which was obtained from Sigma Aldrich

2.2.1 Zinc nitrate hexahydrate: The chemical formula of Zinc nitrate hexahydrate is [$Zn(NO_3)_2.6H_2O$]. It is soluble in both water and alcohol. It is a colourless odourless solid. Its melting point is approximately 36°C. It is usually obtained in the form of white odourless crystals or powder. It is a hygroscopic compound and is hence sensitive to moisture.

Fig 1: Zinc nitrate hexahydrate crystals

It is generally used as a mordant in dyeing. It is also used for printing and dyeing textiles. Zinc nitrate hexahydrate is used in the synthesis of coordination polymers. It is utilized in the preparation of zinc oxide based nanowires. It is incompatible with powdered metals, cyanides, stannous chloride, flammable substances and strong reducing agents. Zinc nitrate hexahydrate nanorods can be synthesized by microwave heating of a mixture of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) precursors in deionised water (DI water). The figure below shows the structural formula of [$Zn(NO_3)_2.6H_2O$].

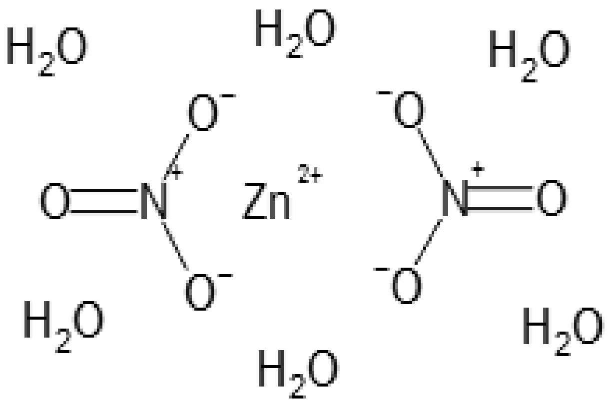


Fig 2: Structural formula of Zinc nitrate hexahydrate

2.2.2 Acetone: Acetone, propanone or dimethyl ketone is an organic compound with the chemical formula $(CH_3)_2CO$. It is the simplest and smallest ketone. It is colourless, has a characteristic pungent smell to it and is a flammable liquid. It is also highly volatile. It acts as an important organic solvent since it can be completely dissolved in water. The normal metabolic processes in the human body produce and dispose acetone. Diabetic ketoacidosis infected patients produce it in large amounts. Propylene is used for the direct or indirect production of acetone. Generally, we alkylate benzene with propylene to produce cumene, which in turn is oxidised by air to produce phenol and acetone. Earlier acetone used to be produced by the dry distillation of acetates. The keto-enol tautomerism is exhibited in acetone like in most other ketones, where the normal keto structure $(CH_3)_2C=O$ of acetone is itself in equilibrium with the enol isomer $(CH_3)C(OH)=(CH_2)$. In the presence of suitable catalysts, two acetone molecules combine to form the compound diacetone alcohol $(CH_3)C=O(CH_2)C(OH)(CH_3)_2$. Polyester resin can be thinned and super glue can be dissolved before it gets hardened, using acetone. It is used as one of the volatile components of some paints and varnishes. Acetone is widely used for the safe transportation and storage of acetylene, despite itself being inflammable. A wide variety of organic reactions, such as S_N2 reactions use acetone as a polar aprotic solvent. Due to its low cost and volatility, acetone is commonly used in academic laboratory settings for rinsing laboratory glassware. Cleaning agents such as nail polish and super glue removers contain acetone as their primary component. It is used in the pharmaceutical industry to prepare some drugs and also used for the treatment of acne.

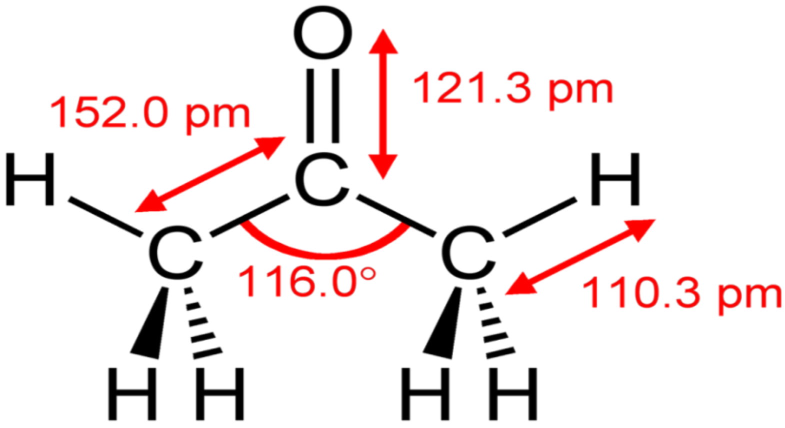
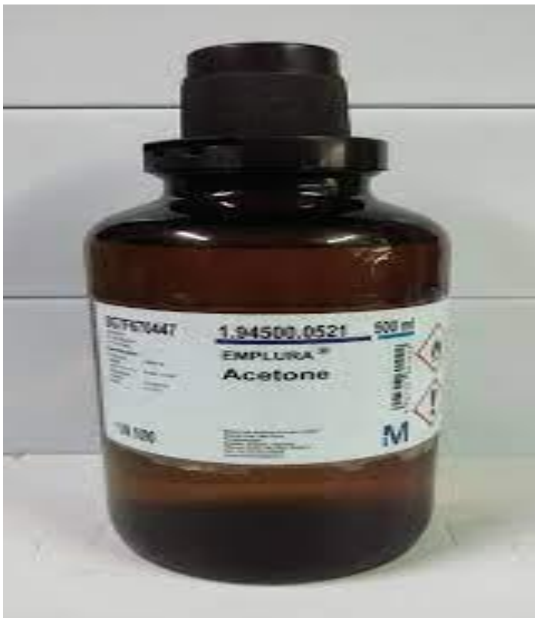


Fig 3: Structural formula of acetone



2.2.3 Potassium hydroxide: Potassium hydroxide (KOH), is an odourless, white or slightly yellow, inorganic compound commonly referred to as caustic potash. We normally get it in the form of pellets, flakes and powders. It is soluble in water, having a melting point of 360°C. It belongs to the class of inorganic compounds referred to as alkali metal hydroxides. In this class of compounds, the largest oxoanion is the hydroxide and the heaviest atom is an alkali metal. The precursor to most soft and liquid soaps is KOH. Since KOH exhibits high thermal stability and has a low melting point, it is frequently metal cast into pellets or rods which are easy to handle and have smaller surface area.

Fig 4: Potassium hydroxide pellets

It is a hygroscopic substance and its solvation in water is strongly exothermic. Potassium hydroxide gives rise to a series of crystalline hydrates, depending upon the orientation of the OH group, such as the monohydrate $KOH.H_2O$, the dihydrate $KOH.2H_2O$ as well as the tetrahydrate $KOH.4H_2O$. Since it is a hygroscopic substance, KOH serves as a desiccant in the laboratory. Often basic solvents, especially amines and pyridines are dried using it. OH^-, a highly nucleophilic anion that attacks the polar bonds in both organic and inorganic materials, is supplied by KOH. Earlier, potassium hydroxide used to be prepared by the addition of potassium carbonate to a strong solution of calcium hydroxide. Nowadays it is usually prepared by the electrolysis of potassium chloride solutions. Chip fabrications for semiconductors use potassium hydroxide. It is used in the alkametric titrations in analytical chemistry. “Potassium soaps” are prepared by the saponification of fats with KOH. Alkaline batteries employ aqueous KOH as the electrolyte based on nickel-cadmium, nickel-hydrogen, and manganese dioxide-zinc. A food thickener, a pH control agent and a food stabilizer are the different functions performed by potassium hydroxide, in food products. Potassium hydroxide makes use of its corrosive properties to emerge as a very important ingredient in agents and preparations that clean and disinfect surfaces. It is used in the manufacturing of cuticle removers which is used in manicure treatment. In the identification of some species of fungi, KOH is used. Severe irritations in the skin and other tissues are caused by potassium hydroxide and its solutions.

2.2.4 Curcumin: The plants of the *Curcuma longa* species produce a bright yellow chemical known as curcumin. Curcumin is the principal among the three curcuminoids present in turmeric (*Curcuma longa)* which is a member of the ginger family Zingiberaceae, the other two being desmethoxycurcumin and bis-desmethoxycurcumin. Curcumin gets its characteristic yellow colour from these curcuminoids.

Fig 5: Curcuminoids present in Turmeric

The dried rhizome of the turmeric plant, a long-lasting herb cultivated extensively in south and south-east Asia, is the source of curcumin. 2% to 5% curcumin is present in turmeric which is processed from the rhizome or the root of the herb. Chemically, curcumin belongs to the class of diarylheptanoid which falls under group of curcuminoids, which are phenolic pigments. A seven carbon linker and three major functional groups, one α,β-unsaturated β-diketone moiety and an aromatic O-methoxy-phenolic group, can be observed in curcumin. Two α,β-unsaturated carbonyl groups connect the aromatic ring systems, which are phenols. The chemical formula of curcumin is ($C_{21}H_{20}O_6$) and its melting point is 183°C. It is a diketone tautomer, existing in enolic form in organic solvents and in keto form in water. It is hydrophobic in nature and is hence is poorly soluble in water, but, it is easily soluble in organic solvents. The bioactivity of curcumin or its analogs is limited by factors such as chemical instability, water insolubility, absence of potent and selective target activity, low bioavailability, limited tissue distribution, and extensive metabolism. A high risk of toxicity can occur if curcumin enters the plasma in reasonable amounts, since it is promiscuous, and interacts with several proteins known to increase the risk of adverse effects. The figure given below shows the chemical structure of curcumin.

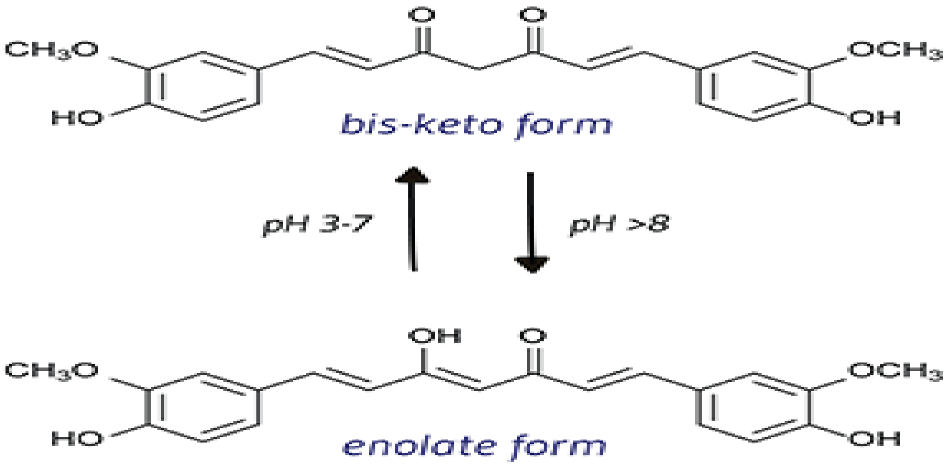


Fig 6: Chemical structure of Curcumin

Curcumin finds a wide variety of applications in dietary supplements, in cosmetics and as a flavouring of foods. Colouring for foods, such as curry powders, mustards, butters, cheeses etc. can be done using curcumin. The quantification of boron can be performed using curcumin, since it reacts with boric acid to form a red coloured compound known as rosocyanine. It has been observed from various researches that curcumin is an effective antiinflammatory agent which can reduce inflammation and plays an important role in the treatment of cancer and rheumatoid arthritis. The reduction in the transformation, proliferation and spread of tumours is facilitated by curcumin and it can be achieved through the regulation of transcription factors, inflammatory cytokines, growth factors, protein kinases and other enzymes. Curcumin interrupts the cell cycle and induces programmed cell death, thus preventing proliferation. It has been demonstrated that curcumin gives protection against the cancers of the blood, skin, mouth, lung, pancreas and intestinal tract and has significant hepatoprotective effects. Certain diseases of the oral cavity can also be treated with curcumin since it has antimicrobial properties. SARS-CoV-2 cytokine storm can be inhibited by curcumin nanoparticles. Curcumin can act as a useful antioxidant that can neutralize free radicals due to its chemical structure. Curcumin plays an important role in reducing the risk of cardio-vascular diseases and also helps in the treatment of Alzheimer's disease and type 2 diabetes mellitus.

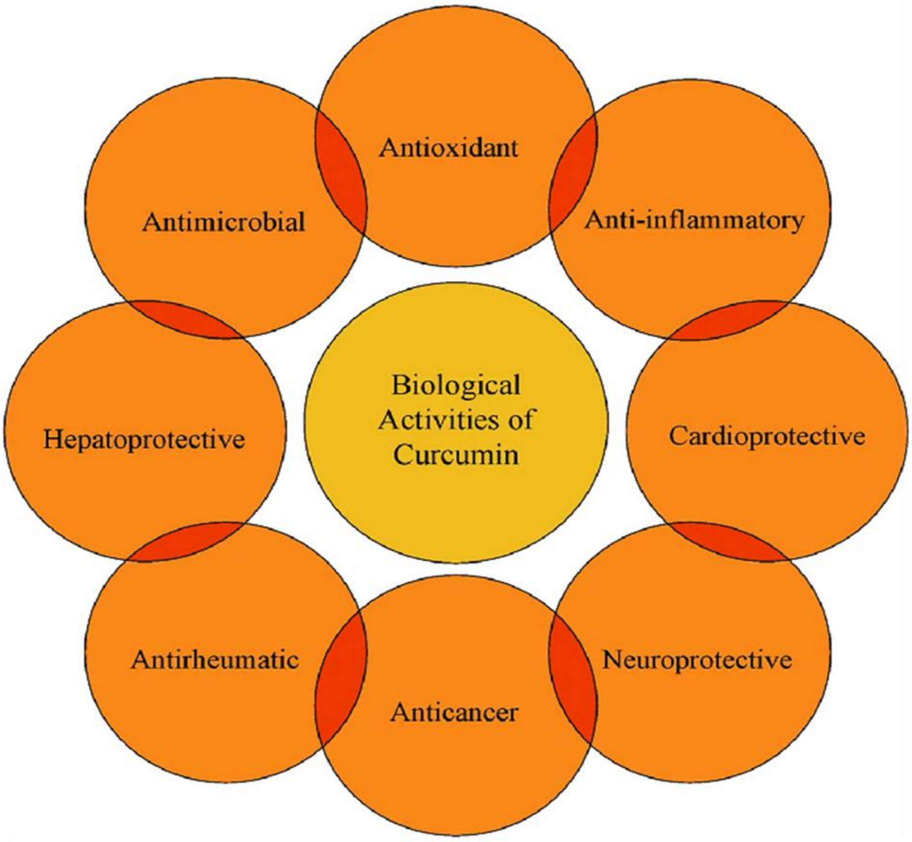


Fig 7: Biological Activities of Curcumin

It has very exciting photophysical and fluorescence properties and displays fluorescence under ultraviolet light. In the present day, researchers are examining the possibilities of using curcumin, as fluorescence probe for developing new sensing scheme. It helps in the preparation of metal nanoparticles and nanorods by acting as a reducing agent and can make metal complex with various metal ions. It also forms a Zn-curcumin complex by reacting with zinc salt.

Fig 8: Curcumin Powder

Chapter 3

Description of the work

In this project work we have designed a sensor which would be efficiently able to detect or sense, whether arsenic in present in a sample of drinking or natural water, and provide us with an almost error-free output. The surfaces of nanostructured particles of the metal oxide zinc oxide (ZnO) are modified using the organic compound curcumin ($C_{21}H_{20}O_6$), leading to the creation of Zn(cur)O. This Zn-curcumin complex is used in order to design the requisite sensor, for the sensing of arsenic. The aforementioned materials have been utilised for performing this work.

Now, in order to achieve this, we have to go through a series of steps and perform some experiments in those corresponding steps, before we can obtain the final end product, which is the required arsenic sensor. So, in the following section we will be describing and discussing each of the requisite steps, one by one.

<u>STEP 1: REQUIREMENT OF MATERIALS</u>

We require **Zinc nitrate hexahydrate** [$Zn(NO_3)_2.6H_2O$], **Acetone** [$(CH_3)_2CO$], **Potassium hydroxide** (KOH) and **Curcumin** ($C_{21}H_{20}O_6$).

Fig 9: Materials required for the project work

STEP 2: PREPARATION OF CURCUMIN SOLUTION

At first we take 2mg of curcumin. Then, we take 50 ml of double distilled water. We mix these two together to form a solution at temperature 80°C-90°C.

STEP 3: ADDITION OF ZINC NITRATE HEXAHYDRATE SOLUTION

We will have to wait for the mixture of double distilled water and curcumin to become completely soluble. Then, we have to add 50ml of 0·1M zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] solution to it.

Now, molecular weight of zinc is 65·38g

Molecular weight of hydrogen is 1·00784g

Molecular weight of oxygen is 15·999g

Molecular weight of nitrogen is 14·0067g

∴ the molecular weight of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] = [65·38+(14·0067×2)+(15·999×3×2)+(6×1·00784×2)+(15·999×6)]g = 297·475g ≈ 297·5g

Now, 1 mole of [$Zn(NO_3)_2.6H_2O$] ≡ 1000ml of [$Zn(NO_3)_2.6H_2O$] ≡ 297·5g of [$Zn(NO_3)_2.6H_2O$]

∴ 1 mole 1ml of [$Zn(NO_3)_2.6H_2O$] = $\left(\frac{297.5}{1000}\right)$g of [$Zn(NO_3)_2.6H_2O$]

∴ 1 mole 50ml of [$Zn(NO_3)_2.6H_2O$] = $\left(\frac{297.5\times50}{1000}\right)$g of [$Zn(NO_3)_2.6H_2O$]

∴ 0·1 mole 50ml of [$Zn(NO_3)_2.6H_2O$] = $\left(\frac{297.5\times50\times0.1}{1000}\right)$g = 1·4875g ≈ 1.5g of [$Zn(NO_3)_2.6H_2O$]

Hence from this calculation we can conclude that 50ml of 0·1M [$Zn(NO_3)_2.6H_2O$] solution ≡ 1·5g of [$Zn(NO_3)_2.6H_2O$] solution

So, in this step we have added 1·5g of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] solution to the solution of curcumin and double distilled water.

STEP 4: REFLUXING OF THE RESULTANT SOLUTION

The above two solutions gets mixed together and the mixture of these two solutions gives a resultant solution which is yellowish in colour. Then, we reflux the resultant solution for 1 hour at temperature 85°C-90°C.

STEP 5: ADDITION OF POTASSIUM HYDROXIDE

This solution is then allowed to cool down. Then, to this solution we slowly add 5ml of 0·2M potassium hydroxide (KOH), at 4°C temperature.

Now, molecular weight of potassium is 39·0983g

Molecular weight of hydrogen is 1·00784g

Molecular weight of oxygen is 15·999g

∴ the molecular weight of potassium hydroxide (KOH) = (39·0983+1·00784+15.999)g = 56.105g ≈ 56g

Now, 1 mole of (KOH) ≡ 1000ml of (KOH) ≡ 56g of (KOH)

∴ 1 mole 1ml of (KOH) = $\left(\frac{56}{1000}\right)$g of (KOH)

∴ 1 mole 5ml of (KOH) = $\left(\frac{56\times5}{1000}\right)$g of (KOH)

∴ 0·2 mole 5ml of (KOH) = $\left(\frac{56\times5\times0.2}{1000}\right)$g = 0·056g of (KOH)

Now, 0.056g is a very small quantity. So, instead of using 5ml of 0·2M potassium hydroxide, we have used 20ml of 0·2M potassium hydroxide.

∴ 20ml of 0·2 mole (KOH) = (0.056×20)g = 1·12g of (KOH)

Hence from this calculation we can conclude that 20ml of 0·2M (KOH) ≡ 1·12g of (KOH)

So, in this step we have added 1·12g of potassium hydroxide (KOH) to this solution.

STEP 6: FORMATION OF GEL-LIKE SUSPENSION

20ml of 0·2M potassium hydroxide (KOH) or 1·12g of potassium hydroxide and the solution gets mixed together and after some time an orange-yellow gel-like suspension is seen.

STEP 7: CLEANING OF THE WAFER

A silicon (Si) wafer, which forms the base of the sensor, is taken and it is held with tweezers for 5 minutes above acetone vapours, for the purpose of cleaning.

STEP 8: COATING OF THE WAFER BY SPIN PROCESS

The coating of a wafer can be usually done by three processes, namely **a) Spray process**; **b) Dipping process**; **c) Spin process**. In this step, any of the three processes can be carried out such as dipping, spraying or spinning for coating the wafer. However, here we have used the spin process. We have spin coated the silicon wafer with the orange-yellow gel-like suspension obtained in Step 6 at 5000 rpm, using the spin coating unit, to obtain a uniform layer on the surface of the wafer.

STEP 9: WASHING OF THE PRECIPITATE WITH WATER

The precipitate thus obtained on the wafer as a result of the spin coating process is washed with water, until no more yellow colour is observed.

STEP 10: WASHING OF THE PRECIPITATE WITH ACETONE

Then we wash with the precipitate with acetone $[(CH_3)_2CO]$, and finally again with water. After drying of the spin coating gel-like suspension, the final precipitate obtained are very small crystals, formed on the surface of the wafer, in the nanometre range, which is the required Zn-curcumin complex, **Zn(cur)O**.

Then this Zn(cur)O is used in the water sample we have taken, to sense or detect the presence of arsenic, through a fluorescence sensing technique. The flow chart for the whole process is illustrated below.

FLOW CHART FOR ARSENIC SENSOR USING ZINC OXIDE (ZnO) MODIFIED WITH CURCUMIN

Zinc nitrate hexahydrate, Acetone, Potassium hydroxide & Curcumin are required.

↓

First take 2.0 mg of curcumin. Then take 50ml double distilled water. Mix these two together at 80-90°C temperature.

↓

After they become soluble, add 50ml of 0.1 M $[Zn(NO_3)_2.6H_2O]$ solution, to it.

↓

Mixing of these two solutions gives a yellowish colour. Then reflux the mixed solution at a temperature of 85-90°C.

↓

Allow this solution to cool down. Then slowly add, 20ml of 0.2 M potassium hydroxide at 4°C temperature, to this solution.

↓

An orange-yellow gel-like suspension is observed. A silicon (Si) wafer is taken and is cleaned using acetone vapours. Then, the orange-yellow gel-like suspension is deposited uniformly on the surface of the wafer using the spin coating process, at 5000 rpm.

↓

Wash the precipitate thus obtained with water, till no more yellow colour is seen.

↓

Wash the precipitate with acetone and finally again with water. Zn(cur)O is obtained as the final precipitate, in the form of small crystals on the surface of the wafer.

↓

Take the water sample. Add Zn(cur)O to it.

↓

Zn(cur)O will become strongly fluorescent if arsenic is present in the water sample.

Chapter 4

Result and discussion

Like the synthesis Zn(cur)O as discussed earlier, here, we have also synthesized a control ZnO through wet chemistry, making use of 50ml of 0·1M zinc nitrate [$Zn(NO_3)_2$] solution, cooling it to 0°C in an ice bath and then subsequently adding potassium hydroxide solution to it slowly. The white suspension was spin coated at 5000 rpm and washed with water, to obtain the required product.

The SEM images of ZnO and Zn(cur)O nanoparticles, which were synthesized, are shown in the figure below. The particles varied in sizes from 200-600 nm in width and 600-2000 nm in length. Particles of smaller sizes were also present. The particles were similar in structure to a grain-like wurtzite hexagonal crystal structure with good crystalline quality. Zn(cur)O nanoparticles were found to be almost similar in morphology and appearance when compared to ZnO nanoparticles.

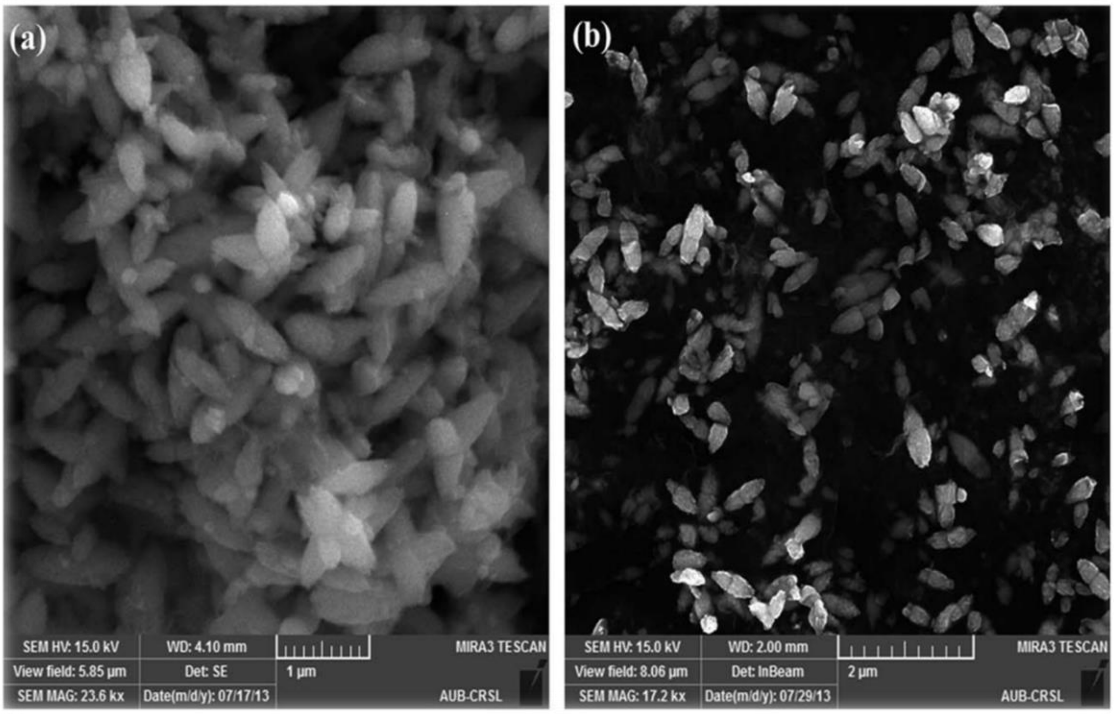


Fig 10: SEM images of (a) ZnO and (b) curcumin doped ZnO termed as Zn(cur)O

We have recorded closer SEM images of these grain shaped Zn(cur)O in 200 nm resolution and displayed them in the next figure, thereby revealing that these grain appearing particles are made up of an assembly of nano-sized particles. It should be kept in mind that as such no significant impact on the morphology of these particles was observed, by changing the concentration of curcumin during the preparation of Zn(cur)O. However, more number of smaller or half-broken particles were observed in Zn(cur)O prepared by using 2mg curcumin, than when it was prepared by using 0·5mg of curcumin.

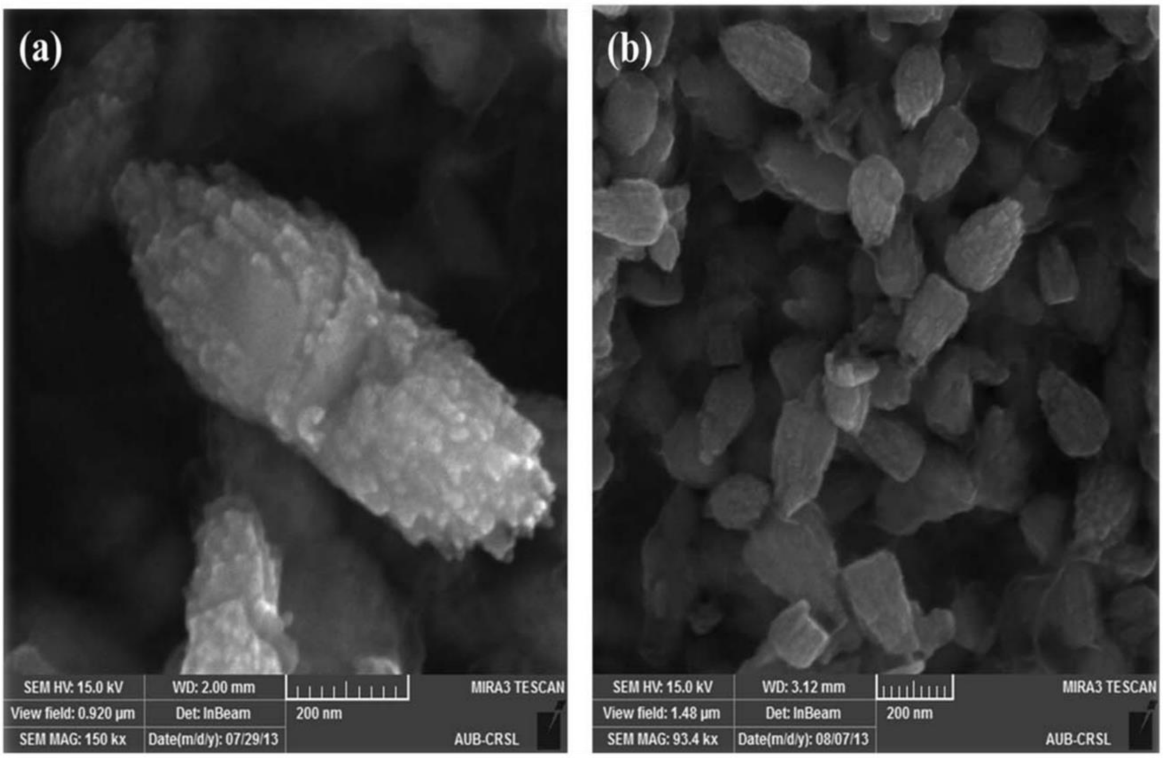


Fig 11: SEM images of Zn(cur)O where (a) [cur] = 0·5mg and (b) [cur] = 2·0mg

Zn(cur)O was added to the water sample contaminated with arsenic. The arsenic solution was shaken to disperse Zn(cur)O particles and ensure its good contact with the arsenic contamination. As such, Zn(cur)O is weak fluorescent. But, when it comes in contact with arsenic, it binds with it and becomes strongly fluorescent and shows enhanced photoluminescence. This fluorescence sensing technique is deployed to sense or detect the presence of arsenic in the said water sample.

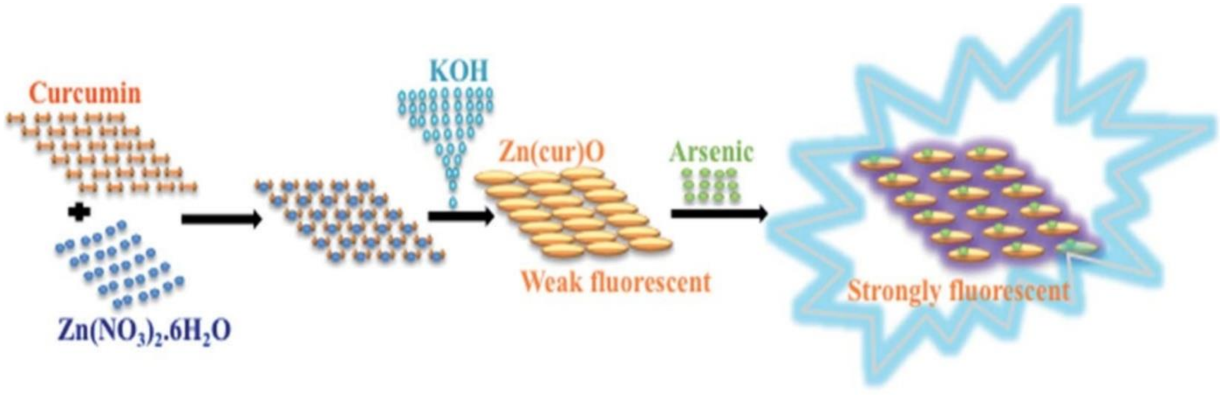


Fig 12: Fluorescence enhancement of Zn(cur)O upon binding with arsenic in water

A strong fluorescence coming out from the whole region leads us to conclude that curcumin is present all over the particle in Zn(cur)O. As we have already stated, next this Zn(cur)O will come in contact with the arsenic present in water sample and will bind with it, leading to the enhancement in the fluorescence. This is how we have made use of the fluorescence sensing scheme of Zn(cur)O in order to detect or sense the presence of arsenic in the water sample that we have used. For conformation, we have captured the fluorescence image using a high sensitive STED confocal set up comprising confocal microscope, APD detector and an argon laser with an excitation wavelength of 430 nm. A wavelength of 430 nm was used to excite Zn(cur)O. The STED fluorescence image of Zn(cur)O upon binding with arsenic present in the water sample is shown below.

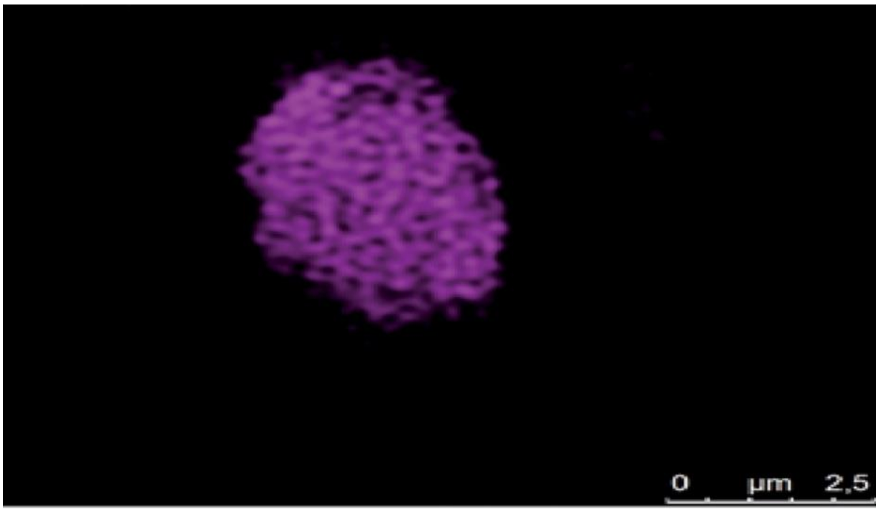


Fig 13: STED fluorescence image of Zn(cur)O, after its binding with arsenic

We have also recorded the X-ray diffraction pattern of ZnO and Zn(cur)O. It is interesting to note that at 2θ of 31·80° (h k l, 100), 34·51° (h k l, 002), 36·26° (h k l, 101), 47·49° (h k l, 102), 56·61° (h k l, 110), 62·99° (h k l, 103), 66·55° (h k l, 200), 67·84° (h k l, 112), 69·19° (h k l, 201), and 77·53° (h k l, 202), we have located all the Zn-O hexagonal phase diffraction peaks. The peaks observed here agree quite well with the peaks which are observed for hexagonal ZnO with wurzite structure. The presence of curcumin accounts for the additional peaks which can be seen at 37·03°, 37·80°, 43·23° and 64·35°. The sharp diffraction peaks signify the good crystalinity of the ZnO nanoparticles. We have not observed the characteristic peaks of any impurities or of any other phase of ZnO. This indicates that the compounds are relatively pure. The pattern of pure curcumin showed sharp characteristic peaks at 2θ of 20°–30°. But, no characteristic peaks of curcumin were viewed in the XRD patterns of Zn(0·5cur)O and Zn(1·0cur)O, when curcumin was coated on ZnO and only three characteristic peaks of curcumin were viewed in the XRD pattern of Zn(2·0cur)O at 26·0°, 26·8°, and 29·45°, which attributed to the curcumin in this range. The XRD pattern of ZnO and Zn(cur)O at different quantities of curcumin is illustrated in the figure below.

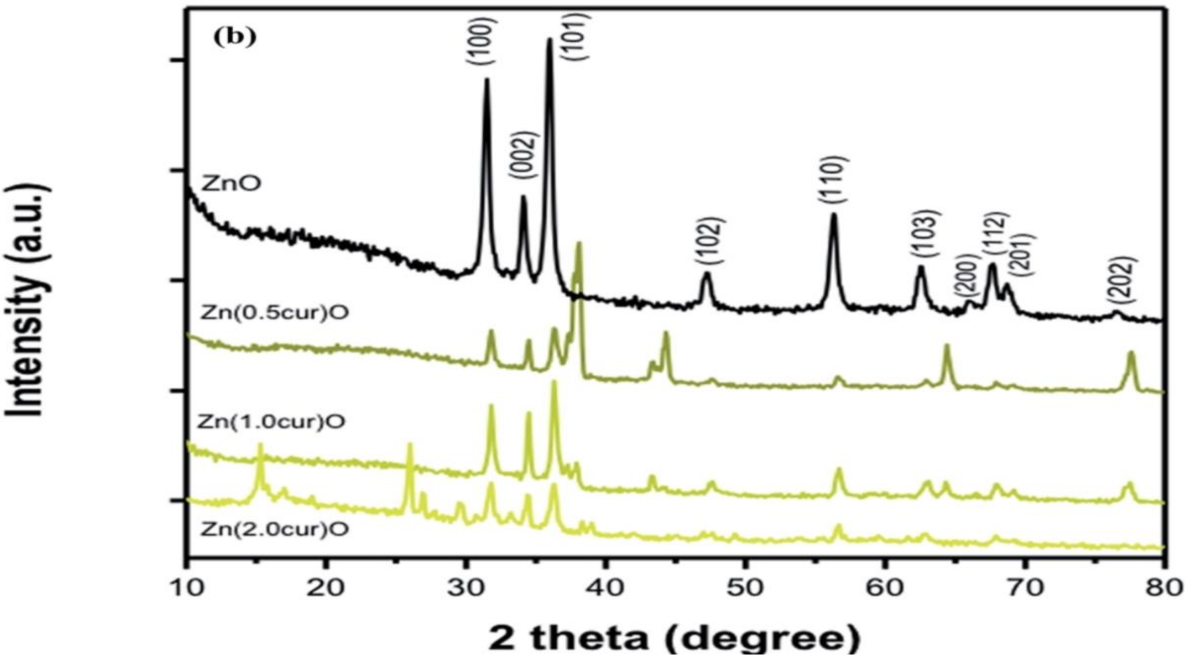


Fig 14: X-ray diffraction patterns of ZnO nanoparticles and Zn(cur)O nanoparticles at different quantities of curcumin

The line broadening at full width at half maximum (FWHM) is related to the average crystallite size of the sample through the **Scherrer equation**. We use this equation to determine the average crystallite sizes of the samples. The Scherrer equation is given as $\mathbf{D_{XRD} = 0.9\lambda\beta/\cos\theta}$, where $\mathbf{D_{XRD}}$ is the average crystallite sizes in nanometres, $\boldsymbol{\lambda}$ is the X-ray wavelength ($\lambda = 1{\cdot}5406$ Å), $\boldsymbol{\beta}$ is the full-width at FWHM of the highest intensity peak in radians, and $\boldsymbol{\theta}$ is half of the diffraction peak angle. In order to evaluate the relative crystallite size with respect to curcumin concentration used during the synthesis of Zn(cur)O, we have studied the peak of the [100] plane which is one of the strongest peaks. For ZnO, Zn(0·5cur)O, Zn(1·0cur)O, and Zn(2·0cur)O, we obtained crystallite sizes of 24·63 nm, 20·18 nm, 26·06 nm, and 20·04 nm respectively. As such, we do not obtain any specific relationship between the crystalline structures and the amount of curcumin used in the synthesis Zn(cur)O.

In order to inspect the interaction of curcumin with ZnO through fingerprint vibrations of both curcumin and ZnO and of Zn(cur)O, we have performed FTIR spectroscopy. At around 442 cm^{-1}, strong and broad absorption peak was shown by bare ZnO. The O-H stretching vibration peak of the hydroxyl functional group is usually closely related to the appearance of bands at around 3500 cm^{-1} or at 1600 cm^{-1}. However, neither at around 3500 cm^{-1} nor at around 1600 cm^{-1}, such bands were observed by us. In ZnO, the peak at 442 cm^{-1} got shifted in Zn(cur)O to 484 cm^{-1} and became less pronounced which suggested the presence of an altered Zn-O bond due to its interaction with curcumin. We have computed the frequency region of both phenolic ν(OH) vibrations of the curcumin to be at around 3595 cm^{-1}, but due to the intramolecular and intermolecular H-bonding in curcumin, this frequency region is shifted to a lower frequency at around 3510 cm^{-1}. These phenolic hydroxyls interact with ZnO which in turn leads to the shifting of the location of the band to 3430 cm^{-1} in Zn(cur)O. At the centre of the curcumin molecule the β-diketone group is present, which is one of the most prominent functional group. This functional group has the driving force to form chealtion with metal ions.

We can get a four coordination zinc-curcumin complex through this β-diketone system. This could be due to the existence of both keto and enol groups in curcumin molecules. So, whether be it weak or strong, it is not surprising to expect an interaction between this β-diketone moiety and Zn atom at the bulk surface of ZnO. We can conclude that curcumin exists mainly in the enol form, from the fact that the curcumin spectra did not show any peak in the carbonyl region (1800-1650 cm^{-1}), neither in the solid state nor in solutions. But, for Zn(cur)O two peaks were obtained in this region at ~1650 cm^{-1} and at 1756 cm^{-1}. The peak at ~1650 cm^{-1} could be due to ν(C=O) of curcumin whereas, the carbonyl's asymmetric mode of vibration in its diketo solid form has a relation with formation of the other peak at 1756 cm^{-1}. The enolic ν(OH) mode is seen at 2979 cm^{-1}. Experimentally, it has been observed that this band usually appears to be weak and broad. The dependence of the intensity and broadness of the enol band on the strength of the intramolecular hydrogen bond, causes this. From this we can infer that the band would decrease in intensity and increase in broadness as the strength of the hydrogen bond increases. Even stronger hydrogen bond effects are caused by the electron donating hydroxyl and methoxy groups, present on the phenyl rings of curcumin.

The formation of bonds or conjugation with other moieties causes the weakening of these groups' electronegativity (the phenyl ring and/or the existing methoxy and hydroxyl groups on it) which in turn leads to the decrease in the hydrogen bond strength thereby allowing a clearer visibility of the enol peak. However, the chelation of curcumin with metal ions for the zinc-curcumin complex could also lead to the generation of prominent enol peak. A predominantly mixed ν(C=C) and ν(C=O) character is present in the peak in curcumin at ~1630 cm^{-1}, as seen in our FT-IR measurement. In the curcumin spectrum, the most prominent band was found at 1510 cm^{-1}. As a result of deformation vibrations of the two methyl groups, IR bands occur in the frequency region 1430-1460 cm^{-1}. Most bands in the frequency region 1450-1300 cm^{-1} are highly mixed. The carbonyl and hydroxyl groups of curcumin can form chelate with zinc. The disappearance and shifting of the IR bands in Zn(cur)O at 960 and 855 cm^{-1}, supports this, which can be mainly attributed to ν(C-O) vibrations. Through its enol form, curcumin chelates with zinc, however, at the same time a weak link exists between the hydroxyl and methoxy groups on the phenyl ring and ZnO.

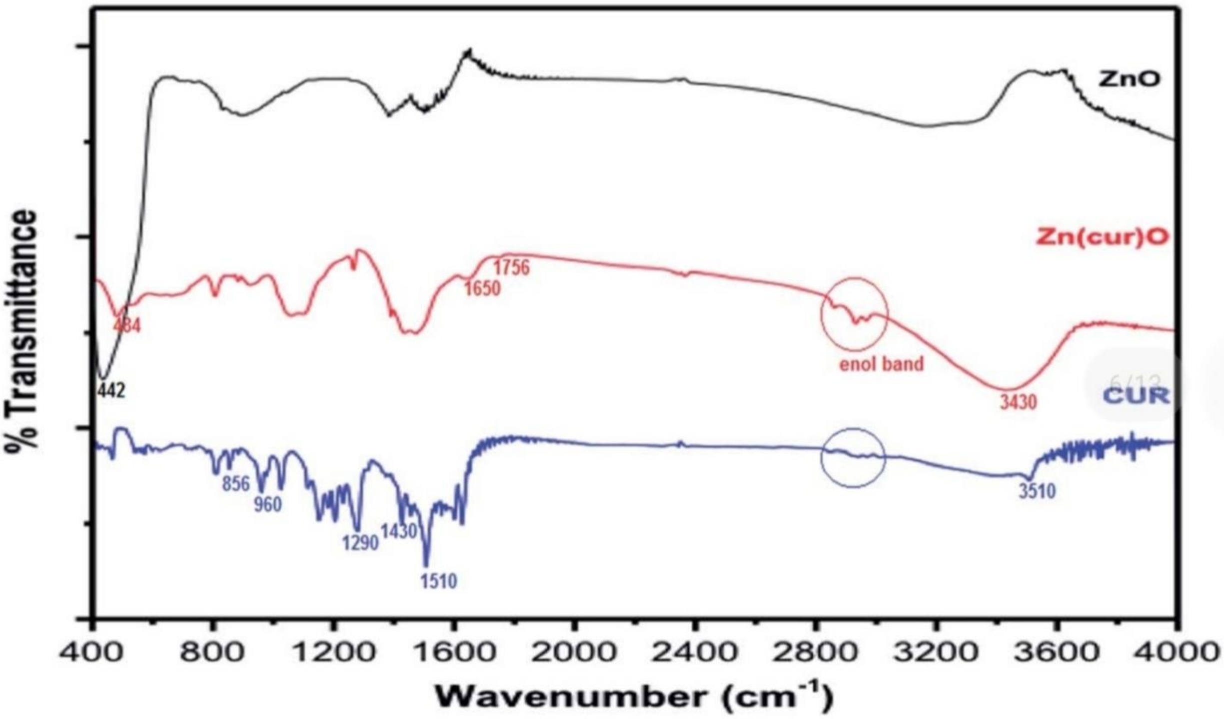
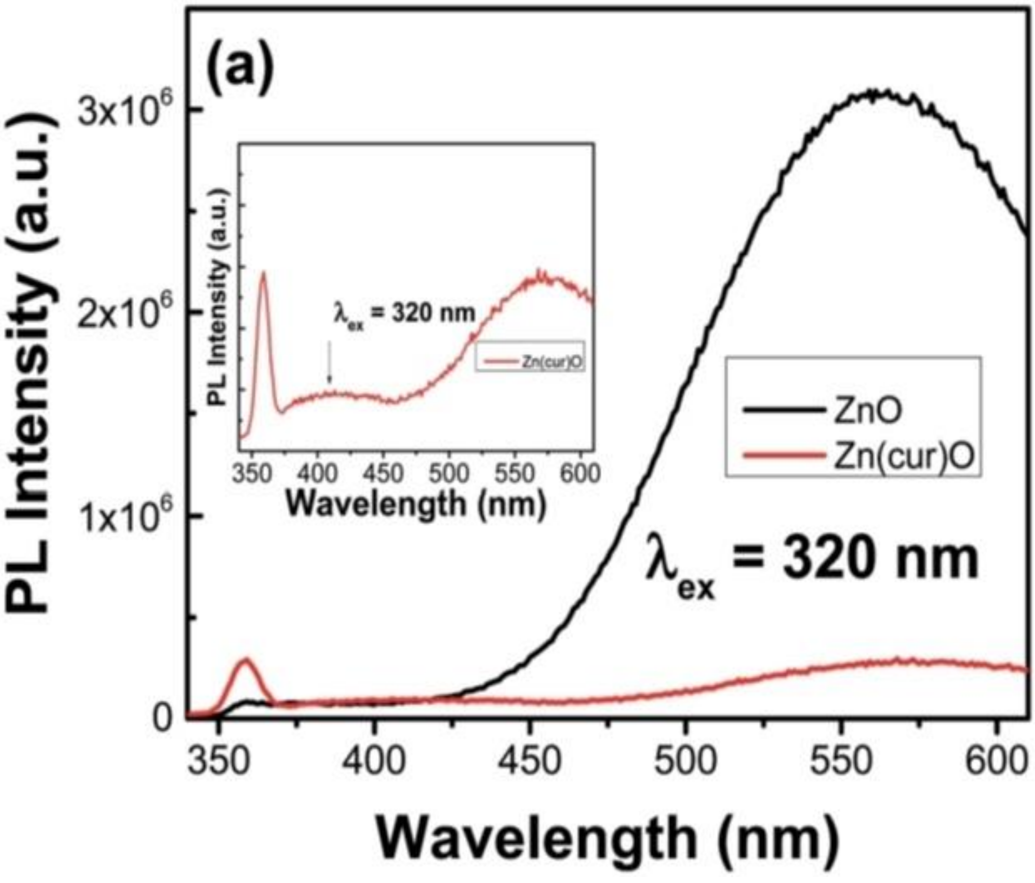


Fig 15: FTIR spectra of the as-synthesized ZnO, curcumin and Zn(cur)O nanostructures at room temperature

We have made a comparison of the photoluminescence (PL)/fluorescence of Zn(cur)O and ZnO, by measuring it at two excitation wavelengths: 320 nm (for the excitation of ZnO) and 425 nm (for the excitation of curcumin), in water. Two emission bands, one in the UV range at around 358 nm, associated with exciton emission and another in the visible range at around 560 nm, formed as a result of the electron-hole (e-h) recombination at deep level caused due to oxygen vacancy or zinc interstitial defects, were seen in ZnO, at the excitation wavelength of 320 nm. A visible photoluminescence is observed in water which in itself is an unconventional and interesting phenomenon because of the fact that even small amounts of water would kill the ZnO photoluminescence, namely visible fluorescence, as hydroxyl groups coordinate on the surface of ZnO nanoparticles. At around 530 nm, fluorescence is usually shown by curcumin, although its contribution in Zn(cur)O was negligible. A reduction by ≈10 folds occurred in the visible photoluminescence of Zn(cur)O when compared to naked ZnO. However, at 358 nm an increase by ≈4 folds occurred in the UV emission of Zn(cur)O, in comparison to ZnO. The defects on the surface of ZnO, which act as visible luminescence centers, are assumed to be filled up by some polymers and/or organic ligands, thereby resulting in quenching the ZnO visible emission and improving the UV emission. Through several studies and researches, we are almost certain that here, this is being done by curcumin. In comparison to that of ZnO, the visible emission band of Zn(cur)O was red shifted by 10 nm. At around 405 nm Zn(cur)O gave an additional band, which was absent in ZnO. The defect emission caused by curcumin could be related to the emergence of the emission line at 405 nm, because no such peak was seen in ZnO. Due to poor light absorption, ZnO is not expected to have good photoluminescence behaviour at an excitation wavelength of 425 nm. However, at this wavelength, Zn(cur)O, has a strong light absorption due to curcumin. Thus at this excitation wavelength, a substantial contribution of fluorescence is provided by Zn(cur)O relative to ZnO and the emission is largely due to curcumin rather than ZnO. Due to scattering, the peak at 495 nm was observed in both the cases. The two succeeding figures clearly depict the above facts and statements.



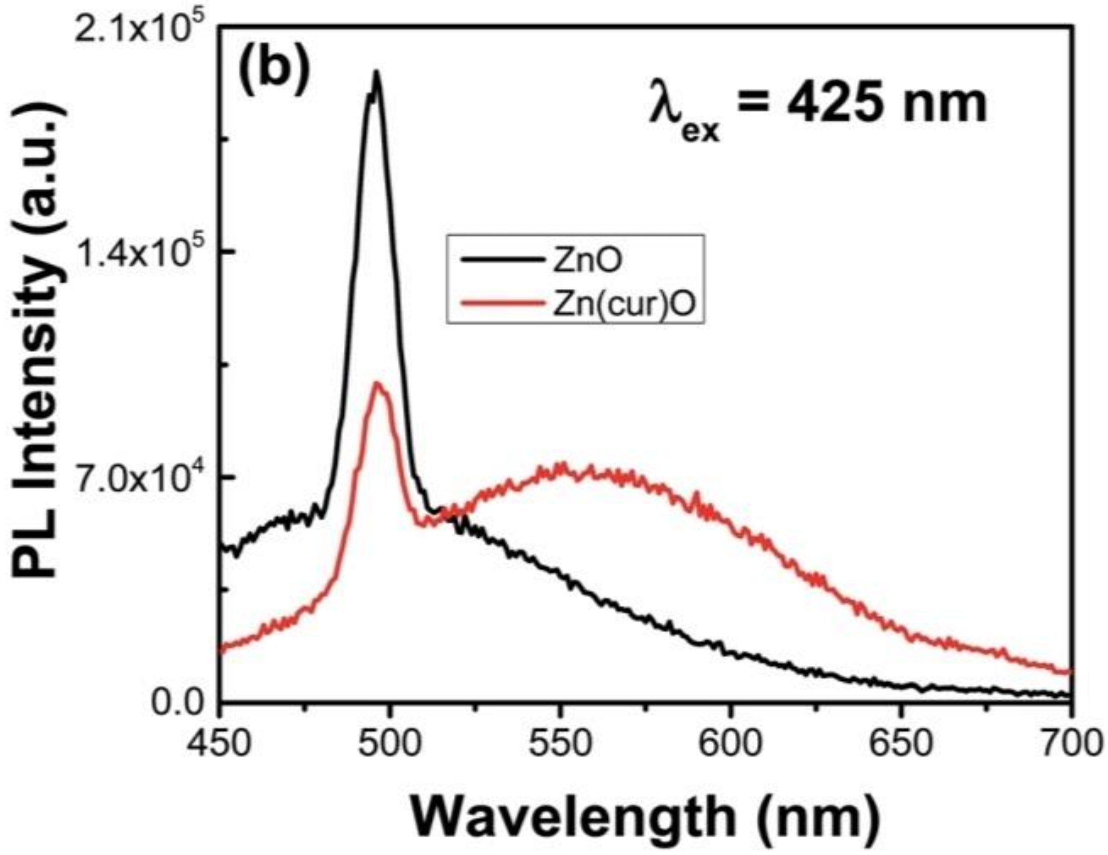


Fig 16(a) & (b): Photoluminescence/fluorescence spectra of the synthesized ZnO and Zn(cur)O nanostructures in water

Next, the photoluminescence behaviour of ZnO and Zn(cur)O was tested, for the determination of arsenic. Two concentration ranges, one from 0 to 1000 ppb(1 ppm) and another from 1 ppm to 10 ppm, were used for the sensing of arsenic. Thus, for this purpose we have used respectively 3000 ppb and 30 ppm of arsenic in water. In both these ranges of arsenic concentration used by us, no systematic photoluminescence alteration was shown by zinc oxide, at excitation wavelengths of 280 nm and 425 nm. This clearly indicates the limitation of ZnO to sense arsenic. But, when the arsenic concentration was gradually increased from 1 to 10 ppm, we observed that Zn(cur)O displayed an enhancement in the fluorescence intensity, which is shown in the next figure. From several researches it has been inferred that **surface adsorption** is the main cause for As(III) binding on ZnO surface. Here, in this project work, As(III) is facilitated to come near to curcumin, which is present in Zn(cur)O surfaces, and interact on the phenyl rings and/or the hydroxyls groups due to the surface adsorption of As(III) on Zn-O surfaces. The enhancement of fluorescence could be linked with absorption of arsenic with Zn(cur)O surfaces.

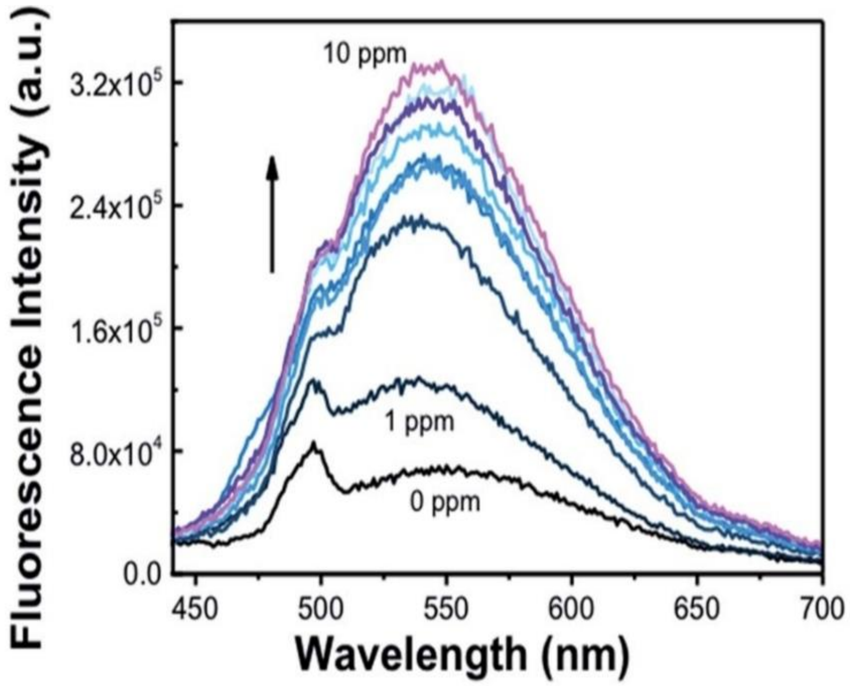


Fig 17: Fluorescence sensing of arsenic in the concentration range 1 to 10 ppm using Zn(cur)O

A comparison was made for the response of Zn(1.0cur)O and Zn(2.0cur)O, in order to get an idea and clearly understand the effect of curcumin concentration in Zn(cur)O. In the concentration range of 0 to 1000 ppb, both of them showed good linear change in fluorescence signal, as shown in Fig 18(a). In comparison to Zn(1.0cur)O, Zn(2.0cur)O showed higher fluorescence which results in the higher sensitivity of Zn(2.0cur)O, because of the prescence of higher amount of curcumin in Zn(2.0cur)O. Moreover, the higher sensitivity of Zn(2.0cur)O played an important role for its selection, and the response was extended upto 10,000 ppb(10 ppm) using Zn(2.0cur)O as the fluorescence sensing probe for sensing applications. An exponential increase was depicted by the fluorescence response as shown in Fig 18(b) and at further higher concentration, it started saturating. We can estimate from this figure that the linear changes for sensing applications is valid till around 3000 ppb of arsenic, where we can deploy the method discussed in this project work, in order to detect or sense the presence of arsenic in water samples. The limit of detection was 100 ppb.

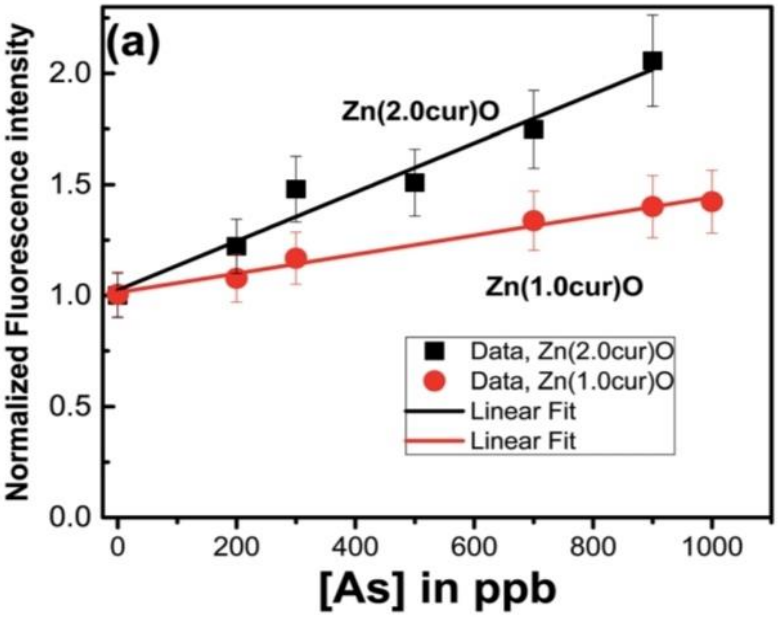


Fig 18(a): Fluorescence intensity response of Zn(1.0cur)O and Zn(2.0cur)O in the arsenic concentration range of 0 to 1000 ppb

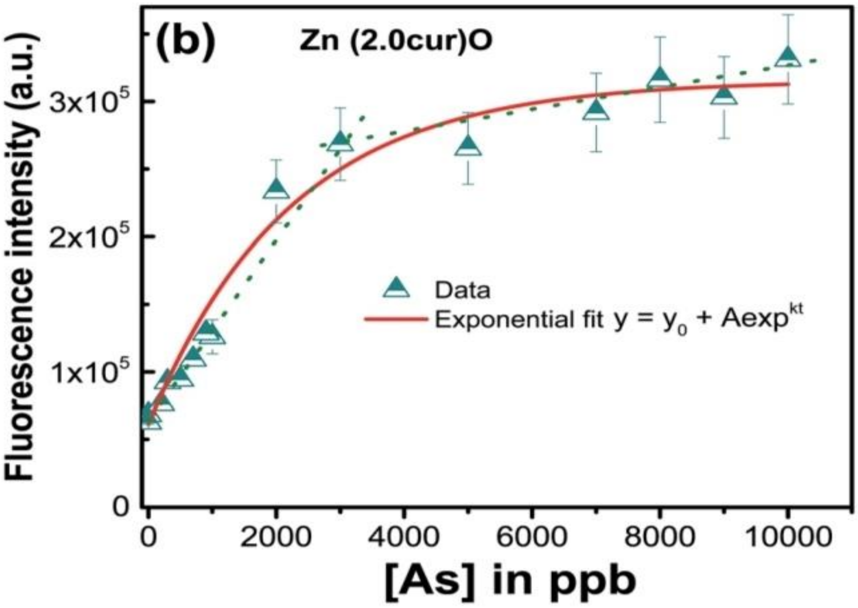


Fig 18(b): Fluorescence intensity response of Zn(2.0cur)O in the arsenic concentration range of 0 to 10,000 ppb

We have taken help of the Lagergren pseudo first-order and Lagergren pseudo second-order equations to test the experimental data of different curcumin content in Zn(cur)O adsorbent, in order to investigate the mechanism of arsenic adsorption. The linearized pseudo first-order equation can be presented as: **$\ln(q_e - q_t) = -k_1 t + \ln q_e$** , where q_e and q_t are the capacities in mg g^{-1} of the arsenic adsorbed at equilibrium and at time t_1 respectively and k_1 is the pseudo first-order rate adsorption constant (mg g^{-1} min^{-1}). The first 20-30 minutes of the interaction is usually governed by a straight line which is obtained from the plot of $\ln(q_e - q_t)$ vs t for an adsorbant. However, the correlation coefficient (R) was poorer, as shown in the figure below.

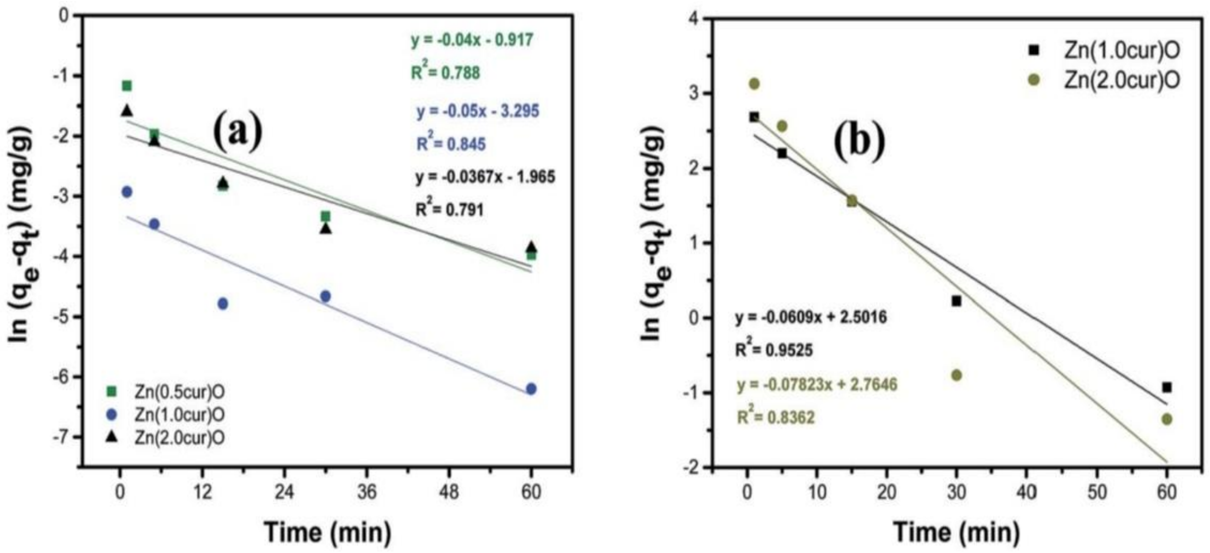


Fig 19: (a) and (b) are pseudo first-order rate kinetic model fitting of the adsorption kinetics studies of As on Zn(xcur)O and ZnO [x = 0·5, 1·0, 2·0]

The linearized pseudo second-order equation is given as: **$t/q_t = t/q_e + 1/(k_2 q_e^2)$** where k_2 is the pseudo second-order rate constant. The operating conditions on which it depends are initial pH and solution concentration, temperature, agitation rate etc. Increase in the initial concentration of the solution would lead to the decrease of k_2, as a longer time is required to reach equillibrium. A plot of t/q_t vs t would be linear, if the adsorption system follows a pseudo second-order kinetics and we can determine k_2 and q_e from the intercept and slope of the linearized pseudo second-order equation.

In the project work that we have undertaken, a pseudo second-order rate kinetic model best fits the kinetic study results as portrayed in the next figure.

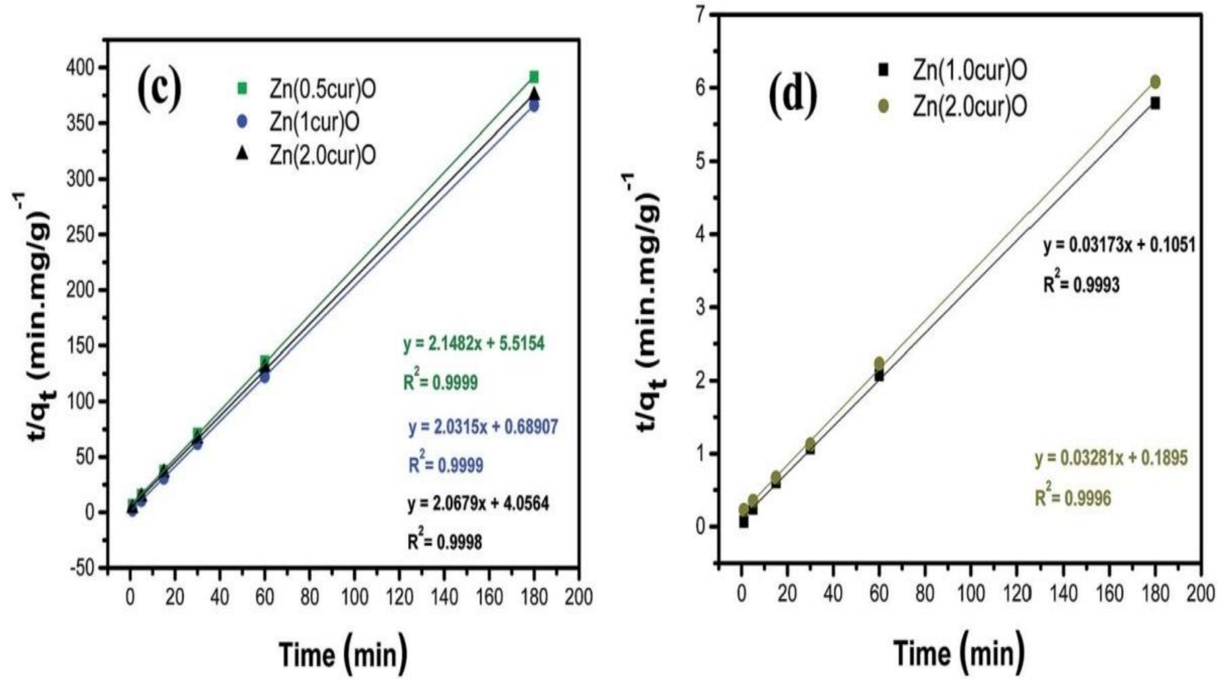


Fig 20: (c) and (d) are pseudo second-order rate kinetic model fitting of the adsorption kinetics studies of As on Zn(xcur)O and ZnO [x = 0·5, 1·0, 2·0]

The square of the of the correlation coefficient (R^2) evaluates the applicability of the pseudo second-order rate model, and its closeness to 1 indicates that the model fits the experimental data accurately. The correlation coefficients for the second-order kinetic model were greater than 0.999, which is better than first-order kinetic model. The efficiency of the adsorbent does not only depend on the surface area of the adsorbent. There are also other factors on which it dpends such as the the type and number of surface functional groups present on the adsorbents. Since the surface area of these nanostructures is no greater than ZnO microtubes, these notable results suggest that, due to the functionalities of curcumin, curcumin conjugated ZnO nanostructures possess an excellent affiliation to As(III). The adsorption capacity is proportional to the number of active sites occupied on the adsorbent, because the rate of the reaction obeys pseudo second-order kinetic model. It is quite common to assume that a higher content of curcumin would lead to a higher adsorption capacity, but it is not so. In fact, the adsorption of As(III) could be prevented due to the blocking of the adsorption sites by stacking of phenyl rings or H-bonding of hydroxyl groups as a result of the higher curcumin content incorporated within ZnO.

Chapter 5

Conclusion

Making use of some chemical reactions which are a part of the wet chemistry procedure, we have successfully synthesized curcumin-ZnO hybrid materials. Sub-micron grain-like morphology and wurtzite hexagonal crystal structure of ZnO were observed in these nanostructures. They showed very good crystalline quality. The FTIR spectra revealed that curcumin chelates with zinc through the enol form, however, at the same time a weak link between the hydroxyl or methoxy groups on the phenyl ring and ZnO is also present. At around 358 nm, an enhancement of the exciton emission occurred as a result of the doping of curcumin into ZnO and it also caused the substantial decrease of the visible emission at around 560 nm in comparison to ZnO photoluminescence. The defects, which were the visible luminescence centers, are thought to be filled up by curcumin. At the same time, curcumin also prolonged the electron-hole (e-h) recombination. In the concentration ranges from 1 to 3000 ppb in water, Zn(cur)O can function as an efficient and effective fluorescence probe for arsenic sensing, in contrast to naked ZnO. But, after 3000 ppb of arsenic in water, the fluorescence started saturating. The kinetics of the adsorption of curcumin on the surface of ZnO fits quite well to the pseudo second-order model and the high affinity of the compound to As(III) is clearly reflected by the exceptional adsorption rates. Although Zn(cur)O could sense arsenic in the 0–3000 ppb concentration range by the fluorescence method enabling it to be used as a possible optical sensing material, a further improvement in such capabilities and applications can be achieved, if we can somehow control the size and shape of such synthesized Zn(cur)O nanomaterials. As a future prospect, we can extend this project work for the removal of arsenic from a given sample of water, since, below the maximum contaminant level (MCL) from 100 ppb samples within 30 minutes, to almost zero within 3 hours, Zn(cur)O nanostructures are capable of removing the As(III) contamination, with a very low material loading.

Fig 21: The orange-yellow gel like suspension which was spin coated on the silicon wafer in order to obtain the desired Zn-curcumin complex

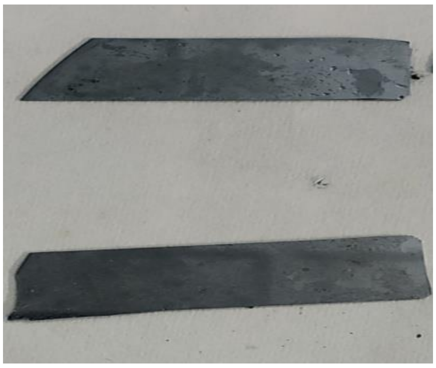


Fig 22: The silicon wafer containing nanoparticles of the desired Zn-curcumin complex, Zn(cur)O, on its surface, which is used for the sensing purpose

Fig 23: Binding of Zn(cur)O nanoparticles with arsenic present in the water sample under UV light in order to show the photoluminescence/fluorescence

Chapter 6

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