Chapter 1

Introduction

1.1 Diatoms

Diatoms are unique living organisms. They appear in a huge variety of species (up to ten thousand known and classified species), shapes and dimensions (2 microns-500 microns in diameter) [1, 2]. They sometimes form colonies and are generally found abundantly in all oceans and freshwater bodies [3]. The protoplasm of every monocellular diatom is enclosed by an external wall, called the frustule, made of porous hydrogenated silica formed by two valves interconnected by a lateral girdle [4, 5].The biomineralised cell wall (the frustule) of diatoms consists of amorphous silica. Each cell consists of two halves, the thecae, which can be divided into a valve and one or more girdle bands. The thecae overlap like a petri dish and separate during cell division. In the cell wall of valves and girdles, regular arrays of chambers (called the areolae) and pores (called the cribra) form three dimensional periodic patterns. The formation of patterns is reported to proceed via self-organized phase separation. The hierarchical order present in the structure leads to the self-similarity of the patterns down to small length scales [4, 6, 7, 8]. The different families of diatoms can be classified into two main categories: *Centrales*, characterized by a radial symmetry of the frustules, and *Pennates*, which are bilaterally symmetric [9]. The dimension of the frustule pores ranges from nanometer to micrometer scale (depending on species and position in the cell wall structure) and they interact efficiently with light by means of diffractive processes [1, 5]. Diatom frustules and their complex pore architecture not only serve as mechanical protection and filter against external environment because of which diatoms can survive in very harsh environmental conditions, but also have high photosynthesis efficiency [1, 10, 11]. Diatoms are responsible for 20-25% of global oxygen produced by photosynthesis process [1, 2].

1.2 Scope of the thesis

1.2.1 Adverse effect of dye pollutants and its control by using photocatalyst

Lots of textile and color industries like leather, rubber, plastic, wool, food, cosmetics, drugs, ink, paper, art and craft etc. use many synthetic dyes for coloring. Dyes are one of the major causes of water pollution due to direct dumping of dyes into water bodies and open environment in large amounts by the industries without proper degradation of these dyes [12, 13]. World Bank reported that nearly 20% water pollution is caused by textile industries [14, 15]. Many of these are creating serious problems not only because of their color but also their non-biodegradable and complex structures which give them thermal and photo stability [15]. Most of them are highly toxic, carcinogenic or mutagenic to human life. Therefore, proper degradation of these dyes is necessary to keep the environment safe. Also removal of dyes from water sources has to be done. Several conventional physical, biological and chemical techniques have been used for efficient and effective removal of persistent dyes released into aquatic environments. Physical methods like filtration, absorption, coagulation-flocculation, solvent extraction, electro-chemical techniques, reverse osmosis, membrane filtration etc. are used to degrade dyes [13, 16]. Again, advanced oxidation process (AOP) is also gaining importance for dye degradation [13, 17]. Most of the techniques are highly expensive, low in efficiency, require high power consumption and have undesirable effects on the environment, while some are incapable of completely removing dyes. Therefore for transforming harmful organic dyes into eco-friendly benign products, more efficient and cost effective methods are needed. Amongst them, photocatalysis is a promising and potentially strong, complex multi-step process for complete degradation of dyes to benign substances with high cost effectiveness. It is also an eco-friendly, green process in which light is used as energy-source to operate the dye degradation by the conversion of solar energy into chemical energy [18,19]. Varieties of semiconducting materials photocatalysts like TiO_2, WO_3 etc. have been studied by researchers. Metal organic framework (MOF) based novel photocatalysts have also been discovered [20]. The main demerit of single semiconductor photocatalysts is that they have high electron-hole (e^--h^+) recombination rate, low capability of harvesting solar energy and poor selective adsorption [21]. Therefore to improve and exploit the advantageous photocatalytic activity of semiconductors, hybrids of two or more semiconductor systems have been developed to utilize solar radiation effectively [22]. The benchmark material in the field of photocatalysis is pristine TiO_2 [18, 20]. It is photo reactive to light of wavelength $\lambda \leq 3875$ Å that lies in the UV range (about 3-5% of solar energy) due to its large band gap (BG) [23]. Still TiO_2 is extensively used in the field of photocatalysis. TiO_2 possesses high photo-reactivity, good time stability, low cost and not only these; it is also environmentally friendly. From ancient times it has been used as white pigment in foods, cosmetics, medicines, etc, and is safe for both humans and the environment [20]. To increase the light utilization beyond the UV range, use of light harvesting natural organisms in the field of photocatalysis is very promising. Moreover, hybrids of two or more semiconductor systems, called hetero structures, are more efficient than a solitary phase semiconductor photocatalyst in utilization of solar radiation along with these natural organisms [24]. These hybrid materials are expected to improve photocatalytic activity and increase light utilization over a wide range of visible light spectra which is about 45% of solar spectra [24].

In our research work, we have used diatoms frustules as templates for producing titania structures which are developed to increase the photo activity in the visible light range as a potent photocatalyst. Periodic nanopores contained in the frustules of diatoms are efficient light collectors, capitalize on solar energy, can interact effectively with light photons and have high photosynthesis efficiency due to their internally located chloroplast [1-4]. Furthermore diatom frustules can be regarded as photonic crystal slab waveguides which can control light propagation and can utilize a wide range of solar light [1,4]. Syntheses of photocatalyst using diatom frustules and titania, which act as hetero-semiconducting-systems, is able to utilize a wide range of visible light solar energy more effectively and thus become sustainable solution to environmental problems. Another advantage is that calcined diatom frustules can absorb light from ultra violet to a broad range of visible light [24].

Methyl orange (MO) and methylene blue (MB) are considered as model dyes in our study, because both dyes belong to azo dye group having undesirable consequences on the environment [25, 26]. Aromatic structured azo group dyes are resistant to degradation [27]. But MO has various uses in textile industry, printing industry, coloring certain items, pharmaceutical industries, leather industry, etc. However, above a certain quantity it is toxic if swallowed, harmful if inhaled, even is mutagenic and carcinogenic. It can cause eye irritation, skin irritation and irritation of the digestive tract; also can increase the heart rate, cause vomiting, damage of lung tissue, etc. [17, 25, 28]. It can cause burning of the skin, and also can cause mental disorders [26]. Lots of works have been reported on the photocatalytic degradation of MO and MB under UV light. It has been observed that the time required for MO and MB degradation is also very high. In this present work, our aim is not only to reduce the required time for complete degradation of MO and MB dye but also use visible light instead of UV light for photocatalysis by using our as prepared titania coated diatom frustules as catalyst with various dye concentrations.

1.2.2 Diatoms as a precursor for green synthesis of nanoparticles and sensing of ammonia

Naturally occurring micro-organisms like algae, bacteria, fungi, yeasts, etc. are becoming increasingly used as base materials for the synthesis of nanoparticles, which is called green synthesis process, without application of external reducing and capping agents [29, 30]. The green synthesis process of nanoparticles (NPs), which is a simple, high yield, environment friendly, cost effective, one step and reproducible technique, is a needed solution of global problems in conjunction with environmental issues that gives advancement over conventional methods [29-33]. Due to the applications of silver nano material in various field like biosensing, biomedical applications, drug delivery, water treatment, agriculture applications, high sensitivity biomolecular detection, catalytic properties**,** photography application, biological labeling, photonics, opto-electronics, surface-enhanced Raman scattering (SERS) detection, cancer detection etc. its production is evolving as one of the most important needs[29-36]. Researchers reported that silver NPs also possess anti-bacterial, anti-fungal, anti-viral, anti-microbial, anti-inflammatory, anti-angiogenesis, anti-oxidant and anti-biofilm properties [30, 33, 37, 38]. There are lots of physio-chemical techniques for synthesis of silver NPs such as chemical reduction, laser ablation, ion sputtering, sol gel, gamma ray radiation, photochemical reduction, electrochemical methods, microwave, autoclave method etc.[30, 34]. In chemical reduction methods toxic chemical reagents are used that releases non-biodegradable wasteful products and are hazardous to eco-systems and most of these methods are costly and consume high energy [30, 31, 34, 37]. So green synthesis process is a better way for synthesis of NPs based on bottom up process, where NPs are built from smaller structures, such as metal ions, and are highly acceptable in this regard [29]. The host material used in this work, that is, diatoms possesses some photosynthetic pigments, chlorophyll-protein molecular complexes and fucoxanthin that can harvest solar light [3, 39]. Their reducing and stabilizing properties are employed to prepare silver NPs in this present work. The diatom of species *Navicula* has been used for bioconversion of metal ions into NPs, which is a green biological technique, in this work. Further as-synthesized hybrid nano-material has been used in this work for monitoring and sensing water dissolved ammonia at room temperature for the first time. Sensing and monitoring of dissolved ammonia is an important issue. There are lots of techniques to monitor ammonia gas, but techniques for detection of dissolved ammonia are rare. Only a few works are reported for dissolved ammonia sensing [40, 41]. Ammonia is used extensively in industries like fertilizer, explosive, pharmaceutical, manufacture of plastic, synthetic fiber, paper, refrigeration of large scale foods etc. [42, 43]. It is corrosive to human health, creates skin and eye irritation, its high concentration causes permanent blindness, lung disorder; it is hazardous to aquatic species and crustaceans even in very low concentrations and more importantly it cannot be converted into less toxic compounds. Moreover, presence of ammonia in human body is an indicator of disorder or disease like liver and kidney collapse, stomach infection of bacteria, cancer, ulcer, diabetes etc. [40-46]. The detection and sensing of dissolved ammonia, in this present work, is based on color change of reagent in presence of ammonia and is characterized by UV-visible absorption spectrometer. The as-prepared material possesses following significant features:

(i) has no need of any other chemical reducing/stabilizing reagent,

(ii) works in ambient environment and has no need of air or oxygen supply,

(iii) requires no external stimulus such as Joule heating or UV illumination for reaction to initiate,

(iv) operates at room temperature,

(v) is eco-friendly,

(vi) has low detection limit,

(vii) has a fast response time,

(vii) is low cost and is abundantly available.

Hierarchical structures of diatoms are obtained by natural self assembly process which encourages and facilitates bio-inspired approach for synthesis of semiconductor and metal oxide nanoparticles with metabolic insertion of impurities like TiO_2, Ge etc. into biosilica frustules [47-49]. Diatoms also have unique optical, morphological and mechanical properties [50]. Fortunately for research work, diatoms can be grown in a large scale at ambient conditions in the laboratory by following simple culture procedures [51] and thereby opening a pathway for the controlled production of nanostructured silica with unique photonic properties. Few focused research areas on diatom frustules include luminescent bio-sensing, photonic sensing, biochemical sensing, filtration, micro-fluidics, optical transducers for biosensors, optical nanotechnology, micro-capsule for drug delivery, fluorescent biosensors, template for photonic crystal slabs, dye-sensitized solar cells, nanostructured battery electrodes, and electroluminescent display devices etc.[52-59]. The light scattering properties of diatoms are also studied and can be determined not only by the refractive indices of diatoms and the medium but also by their shape, size, density along with the scattering angle and polarization state of the incident and scattered light [60].

1.2.3 Diatoms as a material for the detection of arsenic

In this research work the modification of the chemical composition of a representative diatom *Cosmioneis Reimeri* by the arsenic compounds has also been reported. This work is conducted to investigate the ability of diatom frustules to incorporate arsenic into the diatom frustules in their growth process. Moreover, the optical properties of diatom frustules, when arsenic compounds are involved, are found to be changed and this result finds new application in arsenic detection in water bodies.

1.3 Objectives of the thesis

In summary the main objectives of this research work are as follows:

a) Synthesis of photocatalysts having different nanophases of titania synthesized by diatom frustule templates.

b) Green synthesis of silver nanoparticles using diatom cells.

c) Preparation of arsenic functionalized diatoms.

d) Characterization of the as-synthesized materials using different analytical techniques such as XRD, SEM, EDX, TEM, Raman spectroscopy, UV-visible spectroscopy, FTIR, N_2-adsorption-desorption isotherm analysis etc.

e) Study of photocatalytic behavior of the as-synthesized photocatalysts using different dye materials.

f) Study of sensing behavior of silver nanoparticles synthesized via green synthesis technique of water dissolved ammonia.

g) Study of optical property of arsenic functionalized diatoms.

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