## <u>Abstract</u>

In nature, among the phytoplanktons, monocellular and photosynthetic algae diatoms are dominant species having up to ten thousand known and classified species of huge variety of shapes and dimensions [1, 2]. According to researchers' reports diatoms produce oxygen, about 40% in oceans and about 20-25% in the world, through the photosynthesis process [1-3]. The frustules of diatoms are found abundantly in all oceans and freshwater bodies. They appear in a huge variety of species possessing unique frustule morphologies, shapes and dimensions. The dimensions of frustule pores, called the areolae, can range from 2000 nanometer to micrometer scale (from 2 microns to 500 microns in diameter, depending on species and position in the cell wall structure) and they interact very efficiently with light by means of diffractive processes [3]. Fortunately, diatoms can be grown in a large scale at ambient conditions in the laboratory following simple culture procedures and thereby opening a pathway for the controlled production of nanostructured silica with unique photonic properties. Due to the self-assembly into hierarchical structures of diatoms, increasing interests in bio-inspired approach for synthesis of semiconductor and metal oxide nanoparticles with metabolic insertion of impurities like TiO<sub>2</sub>, Ge, etc. into biosilica frustules have been observed [5-7]. Semiconductor embedded diatom frustules are a reliable way to degrade polluting dyes via a photocatalytic mechanism. The diatom cell contains photosynthetic pigments, fucoxanthin and chlorophyll-protein molecular complexes that have reducing and stabilizing properties [1, 8]. Due to this, diatoms have also the potentiality to synthesize silver nanoparticles by a simple, environment friendly, cost effective, high yield and one step green synthesis process.

The first chapter of this doctoral thesis is an introductory chapter that gives an extensive description about freshwater diatoms. The works done by other researchers have been thoroughly reviewed and reported here. We have discussed some important properties and findings of diatom frustules and their applications in various research fields from researcher's reports. We have also discussed the advantage of these natural nanostructures over manmade nano structures in this chapter.

In chapter 2, we have described the culture process of diatom species by using reference medium "WC" in laboratory. The diatom cell isolation and cleaning process have been reported elaborately in this chapter. Eventually the diatom frustule acts as a template for synthesis of nanoparticles. We have described the synthesis of single anatase phase  $TiO_2$  nanoparticles (named as DT500) and mixed phase  $TiO_2$  nanoparticles (named DT800) that have been synthesized by the diatom frustule templates. The green biosynthesis of silver nanoparticles using diatom cells

containing fucoxanthin, acting as a reducing and stabilizing agent, have also been described. The process of metabolic insertion of arsenic in diatom cells has also been discussed in this chapter.

In chapter 3, Different characteristic techniques e.g. X-ray diffraction, Raman spectroscopy, optical microscopy, scanning electron microscopy, transmission electron microscopy, dispersive X-ray spectroscopy, FTIR energy spectroscopy and  $N_2$ adsorption/desorption isotherm analysis were employed to study morphology and compositional properties of the as-synthesized diatom frustules based materials and raw diatom frustules. The optical properties of the materials were investigated using UV-Visible spectroscopy. These assynthesized materials, DT500 and DT800, show broad absorption of visible light as compared to bare TiO<sub>2</sub> nanoparticles. In this chapter, a comparative study of photocatalytic behavior of the assynthesized materials was also presented. DT800 shows better visible light photocatalytic activity as compared to DT500. The reusability and durability properties of DT800 catalyst were also studied.

In chapter 4, the structural and optical characterizations of the as-synthesized silver nanoparticles deposited on diatom frustules (SND) via the green synthesis technique have been reported. The synthesized material shows a broad spectrum of absorbance in the visible range. Further, the sensing behavior of this SND material on dissolved ammonia at room temperature has been investigated.

In chapter 5, a comparative study of arsenic treated diatom frustules with untreated ones is done. We have found some distinct evidence of the presence of arsenic in the arsenic treated diatom frustules and this indicated probable application of diatoms in the detection of arsenic in water bodies.

In the concluding chapter 6, we have highlighted the conclusions taken from the present investigation. We have summarized several important findings and noted their relevance in probable future works.

## References

- Tommasi, E. D. Light Manipulation by Single Cells: The Case of Diatoms. *Journal of Spectroscopy*, 2016:1-13, 2016. DOI:10.1155/2016/2490128
- [2] Hsu, S. H., Paoletti, C., Torres, M., Ritchie, R. J., Larkum, A. W. D. and Grillet, C. Light transmission of the marine diatom Coscinodiscus wailesii. In *Proc. of SPIE, Bioinspiration, Biomimetics, and Bioreplication 2012*, Volume 8339, pages 83390F-1-8. DOI: 10.1117/12.915044
- [3] Tommasi, E. D., Rea, I., Stefano, L. D., Dardano, P., Caprio, G. D., Ferrara, M. A. and Coppola, G. Optics with diatoms: towards efficient, bioinspired photonic devices at the micro-scale. Proc. SPIE 2013; 8792: 879200-6. DOI:10.1117/12.2021613
- [4] Fuhrmann-Lieker, T., Landwehr, S., Rharbi-Kucki, M. E. and Sumper, M. Diatoms as living photonic crystals. *Appl. Phys. B-Lasers O.*, 78:257-260, 2004.
  DOI: 10.1007/s00340-004-1419-4
- [5] Shian, S., Cai, Y., Weatherspoon, M R., Allan, S. M. and Sandhage, K. H. Three-Dimensional Assemblies of Zirconia Nanocrystals Via Shape-Preserving Reactive Conversion of Diatom Microshells. J. Am. Ceram. Soc., 89:694-698, 2006. DOI: 10.1111/j.1551-2916.2005.00734.x
- [6] Jeffryes, C., Gutu, T., Jiao, J. and Rorrer, G. L.Metabolic Insertion of Nanostructured TiO2into the Patterned Biosilica of the Diatom Pinnulariasp. by a Two-Stage Bioreactor Cultivation Process. ACS Nano., 2: 2103-2112, 2008. DOI: 10.1021/nn800470x
- [7] Jeffryes, C., Solanki, R., Rangineni, Y., Wang, W., Chang, C. H. and Rorrer, G. L. Electroluminescence and Photoluminescence from Nanostructured Diatom Frustules Containing Metabolically Inserted Germanium. *Adv. Mater.*, 20:2633- 2637, 2008. DOI: 10.1002/adma.200800292
- [8] Jena, J., Pradhan, N., Dash, B. P., Panda, P. K. and Mishra, B. K. Pigment mediated biogenic synthesis of silver nanoparticles using diatom Amphora sp. and its antimicrobial activity. J. Saudi Chem. Soc., 19:661–666, 2015. DOI:10.1016/j.jscs.2014.06.005