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Freshwater Diatoms from Deepor Beel - A Ramsar Site of Assam, India Revealed Potential Photoluminescence Properties for Nanotechnological Applications

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Research Article

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ABSTRACT

Photoluminescence property of few freshwater diatoms was studied form Deepor Beel, a Ramsar site of Assam, India. Diatom, a unicellular, eukaryotic, photosynthetic alga of the class Bacillariophyceae has the natural ability biogeochemical cycling of natural silica and to deposit nanoporous silica over cell frustule. Nanoporous silica with excellent photoluminescence properties become suitable material for wider applications in IT based sector. Keeping view in mind, the present study was undertaken with some freshwater diatoms obtained from an important internationally recognized important freshwater wetland. Four diatom *viz. Navicula* sp., *Thalassiosira* sp., *Nitzschia* sp. and *Achanthes* sp., treated with acid digestion method were subjected to scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Vis spectroscopy analysis to characterize their structural properties of the frustules. Photoluminescence properties (PL) of diatom frustules excited at 250 nm, 285 nm and 329 nm showed a diverse range of PL spectra at ultraviolet, green and blue ranges that indicated their potential optoelectronic behaviours. Time-resolved photoluminescence (TRPL) analysis of the diatom frustules, excited at 375 nm revealed the decay time in the range between 3.85 eV to 2.67 eV suggesting the biexponential decay of natural diatoms.

INTRODUCTION

Diatoms are unicellular, eukaryotic, photosynthetic algae belong to Bacillariophyceae, found in both fresh and marine water. They are found in a wide variety of habitats, responsible for up to 25% of the world's net primary productivity [1]. Diatom is the only organism having genetic ability to mineralize natural silica and to deposit over the frustule in nanoporous sizes. After understanding the ultrastructural organization of frustule, diatom became excellent materials for the nanotechnologists [2].

Nanostructured silica has received significant attention due to its visible photoluminescence [3]. To address the limitations of conventional semiconductor material fabrication, there is an emergence of interest in bio-fabrication techniques to assemble nano- to micro-scale hierarchical semiconductor materials [4]. Specifically, diatoms have been touted as a paradigm for biological fabrication of nanostructured silica [5]. Diatom frustules to use as a platform for device applications, significant efforts have been made to harness the inherent optoelectronic properties of nanostructured silica [6]. The photoluminescence of biosilica frustules has been used for immunocomplex sensing, antibody detection, and gas sensing [7-9]. The biosilica has also been chemically converted to $BaTiO_3$ and $SrTiO_3$ and coated in $ZnSiO_4$: Mn, Zn_2SiO_4, TiO_2, CdS, and gold, all in an effort to enhance the optoelectronic properties [10]. An enormous amount of effort has been made in the development of science and technology in the micro and nanoscale level due to the novel optical and electrical properties nanostructured materials, which can be applied for fabrication of optoelectronic and photonic devices [11]. In the world there are more than 200000 diatom species of unique frustule architecture in their nano-sized features [12]. These naturally synthesized 3D nanostructured materials are of great importance in research in nanotechnology from various points of view, which include their morphology, mechanical properties, optical and electrical properties [13]. Diatom frustules possess strong blue photoluminescence which is ascribed to the quantum confinement of electron-hole pairs in silicon nanopores [14,15].

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Deepor Beel, a freshwater wetland of Assam, India is an internationally recognized Ramsar site. Characterization of diatom frustule of this important wetland is thought to be important for identification of potential materials with photoluminescence properties.

EXPERIMENTAL SECTION

Water and semi-aquatic soil samples were collected from Deepor Beel on the basis of habitat stratification in the month of June, 2012. Freshly collected samples were immediately transferred in the DM (diatom media), standardized with slight modification [16]. The cultures were allowed to grow in a BOD incubator at 3 K light and 18-20°C under 50 μMol photons m^{-2} sec^{-1} on a 14:10 hr L:D (Light:Dark) cycle until its exponential phase for 15-20 days. Repeated subcultures were done on solid diatom medium to obtain pure cultures of diatom species.

Diatom frustules were cleaned with acid digestion method to remove the organic materials before subjected to SEM, XRD, UV-Vis spectroscopy, PL and TRPL spectroscopy analyses [17]. The cleaned frustule valves were then stored in ethanol to avoid contamination and bacterial growth. To determine the structural morphology of diatoms, cleaned frustules were partly mounted on brass stubs and coated with gold for SEM analysis (Leo 1430vp).

X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex diffractometer with CuKα radiation (λ=1.5405 Å). UV-vis spectroscopy was performed using a Shimadzu 2450 UV-vis spectrophotometer. PL and TRPL spectroscopy were also carried out to investigate the optical properties of the freshwater diatom frustules. Perkin Elmer LS55 is used to measure PL which uses Xenon discharge lamp as the excitation source. The TRPL was measured by using Edinburgh Instruments, UK, Model- LifeSpec II.

RESULTS

Pure cultures of freshwater diatoms from Deepor Beel revealed the presence of 12 diatom species, belonging to 4 genera of which 3 were pennate and 1 centric type which were identified as *Navicula* sp., *Thalassiosira* sp., *Nitzschia* sp., *Acanthus* sp. respectively. These four diatom species were used for further investigations.

SEM micrograph of the diatom revealed that the frustules of *Navicula* sp. were rhombic-lanceolate with cuneate apices, 76.2- 95 μm long, 16.7- 20.7 μm wide and with the silica nanopores sizes 120-150 nm **(Figure 1A and 1B)** showed circular shape (*Thalassiosira* sp.) of average diameter 12 μm and has a symmetric array of stubs of length 2.5 μm and width 0.25 μm approximately. From the SEM images, the nanoporous silica structures were found to be ~100 nm sizes. Frustule structure of *Nitzschia* sp. revealed biraphid, symmetrical to apical and transapical axes, raphe marginal to nearly central, crossed transapically by fibulae **Figure 1C**. Raphe system of one valve positioned diagonally opposite of other valve of a frustule. Striae unresolved to distinctly punctate. The silicon nanoporous sizes of the *Nitzschia* sp. was measured as ~100 nm. **Figure 1D** of *Achanthes* sp. showed that the valves were elliptic to linear-elliptic with broadly rounded apices. The central area was large and orbicular with a length of 22-62 μm and width of 12.5-23.0 μm. The silica nanoporous structure of frustule of *Achanthes* sp. revealed ~60- 100 nm in sizes.

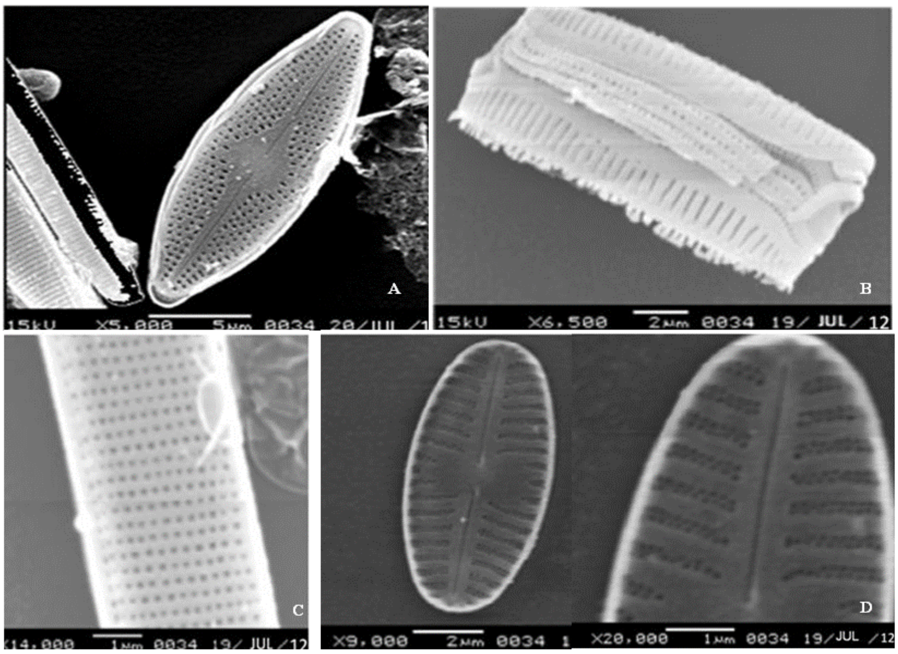

Figure 1. SEM photograph of diatom species of Deepor Beel used in the study. A: *Navicula* sp.; B: *Thalassiosira* sp.; C: *Nitzschia* sp.; D: *Achanthes* sp.

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X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex Diffractometer with CuKα radiation (λ=1.5405 Å).

Figure 2A-2D showed the XRD pattern of the frustule of diatoms used in this study, which confirmed peaks of α-quartz, a crystalline form of quartz. Using the Scherer formula we calculated the particle size of silica having an average grain size of 46 nm and crystallizing in a tetragonal structure. From earlier literature, it could be depicted that marine diatom frustules possess amorphous silica whereas in our case, we obtained peaks of α-quartz in XRD patterns (2θ=10°-30°) of the freshwater diatoms [18].

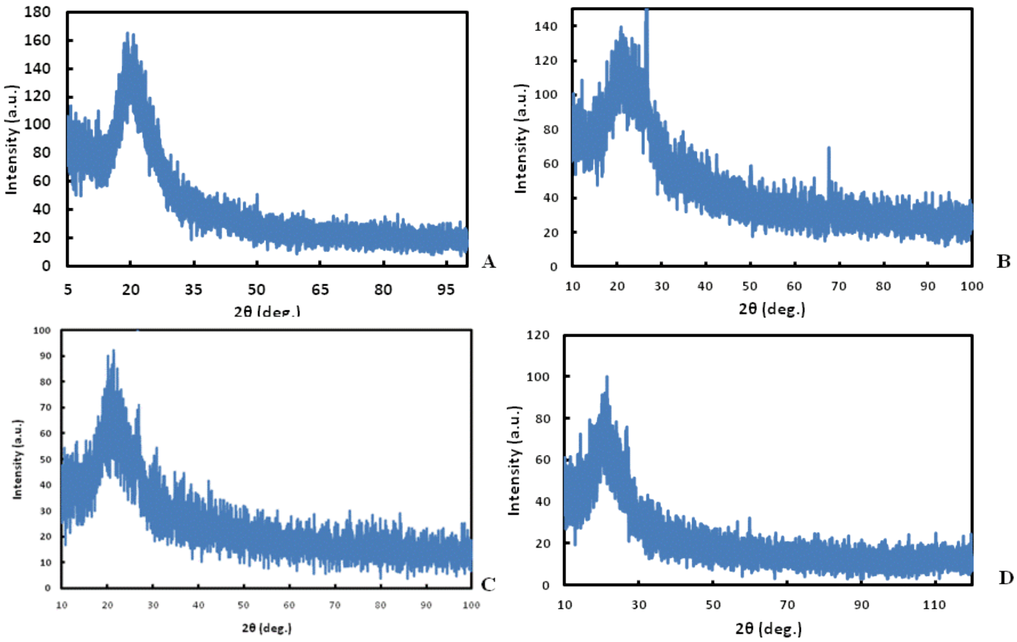

Figure 2. XRD pattern of diatoms. A: *Navicula* sp.; B: *Thalassiosira* sp.; C: *Nitzschia* sp.; D: *Achanthes* sp.

UV-Vis spectra of the diatom species was shown in **Figure 3A**. It was seen that all the four diatom species absorbed UV light with peak absorption at ~250 nm and found to be more prominent in case of *Thalassiosira* sp. followed by *Achanthes* sp., *Nitzschia* sp. and *Navicula* sp. respectively. Absorption of UV range spectra by all the diatoms species used in this study was the evidence for the presence of nanoporous silica with ideal sizes. Interestingly, *Thalassiosira* sp. was found to reveal sharp absorption peak as compared with others.

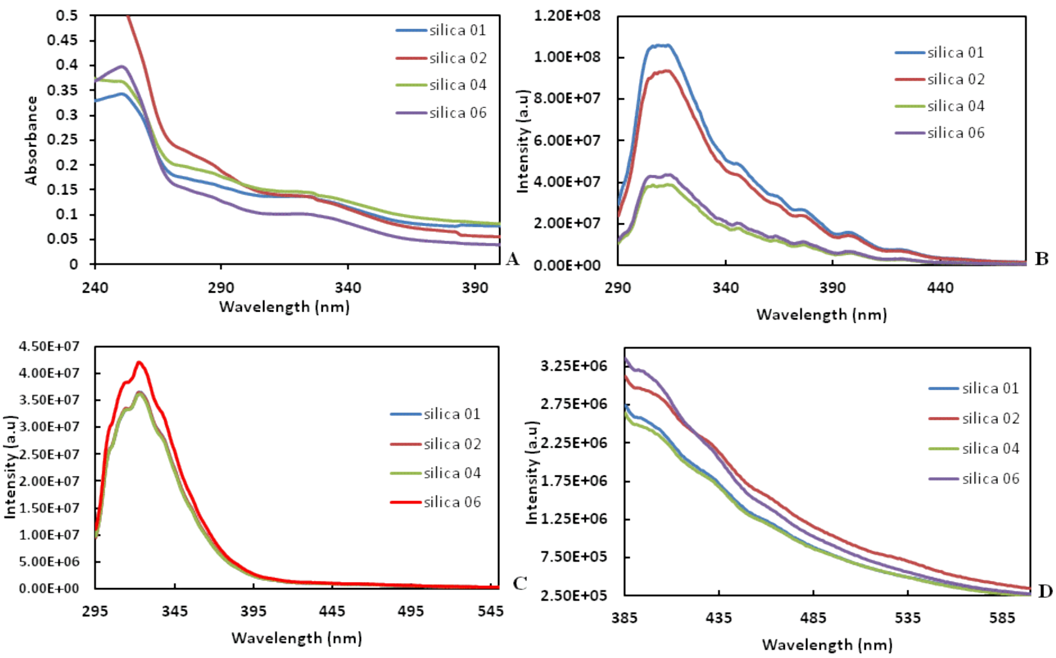

Figure 3. A: UV-Vis spectroscopy of diatoms; PL spectra under different laser excitation and excitation spectra at the peak of the PL spectrum in four different diatoms B: 250 nm C: 285 nm D: 329 nm (silica 01- *Navicula* sp.,"silica 02- *Thalassiosira* sp., silica 04- *Nitzschia* sp., and silica 06- *Achanthes* sp.).

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For PL analysis, diatoms frustules were excited with 250 nm, 285 nm and 329 nm and the PL peaks were observed at ultraviolet, blue and green region. Here, photoluminescence properties of the diatom frustules revealed similar properties to those of porous silicon which, supported the most of the recent model developed for porous silicon (PS) and taking into account the quantum-confinement (QC) in the silicon nanoscale, followed by de-excitation via light emitters in SiO_2-passivated layers.

In this study, the diatom frustules did not show any PL activities at higher excitation wavelengths suggesting that the light scattering spectra at these wavelengths were not interfered by PL. However, under 329 nm excitation, the diatoms emitted a strong blue PL that was clearly visible **Figure 3D**. The PL spectrum of the material was collected and was found to have a broad peak at 430 nm (2.9 eV). The PL peak at 430 nm was found to be more prominent in case of all the diatom frustules excited at 329 nm. Although consideration of luminescence in general did not form the main aim of this study, it might be pointed out that the relatively large amount of PL obtained here might be used for fabricating efficient luminescence devices in UV range.

Photoluminescence from nanoporous amorphous SiO_2 allowed to identify three PL bands peaked in the ultraviolet (~3.81 eV), green (~2.35 eV), and blue (~2.85 eV) spectral ranges. In few cases, the green and blue bands were found to be overlapped in conventional scan measurements, giving no way for determining their exact peak positions. Green and blue PL bands were observed for the diatoms whereas the blue band extends toward the higher-energy range and were peaked at 3.25 eV.

In this study, we used a diverse range of excitation spectra to have a comprehensive data on PL activities for diatoms. Excitation at 4.96 eV (250 nm), the diatoms emitted PL spectra at UV range (315 nm) but *Navicula* sp. and *Thalassiosira* sp. emitted a strong ultraviolet PL that was clearly visible in **Figure 3B**. Excitation at 285 nm in silica frustules showed the PL spectra at 325 nm (UV range) but, here *Achanthes* sp. showed more intense peak comparing with the others **Figure 3C**. Excitation at 329 nm showed very interesting results to the diatom species, where PL peak was observed at blue spectral range i.e., ~410 nm **(Figure 3D)**. The observed peaks showed no special characteristic changes except for increase in peak intensity in case of *Thalassiosira* sp. and *Achanthes* sp. with decrease in detection wavelength in case of *Navicula* sp. and *Nitzschia* sp. respectively. The emission of blue PL bands confirmed the presence of non-bridging oxygen hole centres, hydrogen-related species, and self-trapped excitons ~STE's respectively over the diatom frustules. Hence, this PL behaviour confirmed the potentiality of diatoms used in our study to be used in fabrication of semiconductors for IT-based industries.

The time-resolved PL of nanoporous Si of freshwater diatoms were measured using pulsed N_2 laser excitation (λ_{exc}=375 nm) with a pulse duration and a peak power density of 4 $kW.cm^{-2}$. **Figure 4A-4D** demonstrated the decay time in the range between 3.85 eV to 2.67 eV. It was found after fitting the parameters that the decay best fitted for biexponential decay in diatoms. In diatoms, the PL spectra consisted of two contributions located in the ultraviolet and blue spectral range, whereas, overall PL spectra consisted of two contributions located in blue and green spectral ranges which were in good agreement with some previous reports [19].

The results of decay time measurement of the diatoms were listed in **Table 1**. Here the excitation wave length was 375 nm. The decay times were presented in table for diatom species in ns (nano-second). It was found that the χ^2 values of diatoms was ~1. As a system of coupled electron spins (electron and hole), the STE has a triplet with a long lifetime and a singlet with a fast lifetime. The lifetimes of TRPL spectroscopy are due to these two components, which could be claimed as best for the diatom samples used in this study.

Table 1. Life time data for silica nanoparticles extracted from diatom living species, τ_1 and τ_2 are their lifetimes; Si-Ge 01 (*Navicula* sp.), Si-Ge 02 (*Thalassiosira* sp.), Si-Ge 04 (*Nitzschia* sp.) and Si-Ge 06 (*Achanthes* sp.)

Sample No.	Wavelength (nm)	τ_1	τ_2	χ^2
Si-01	322	0.430 (40.79)	4.785 (59.21)	1.079
	463	1.445 (68.48)	6.400 (31.52)	1.017
Si-02	322	0.451 (56.69)	3.751 (43.31)	1.052
	463	3.295 (100.0)	4.091 (80.22)	1.032
Si-04	322	0.451 (50.36)	7.198 (49.64)	1.160
	463	1.248 (64.51)	2.710 (35.49)	0.995
Si-06	322	0.431 (40.8)	4.786 (59.22)	1.08
	463	3.296 (100.0)	4.093 (80.42)	1.052

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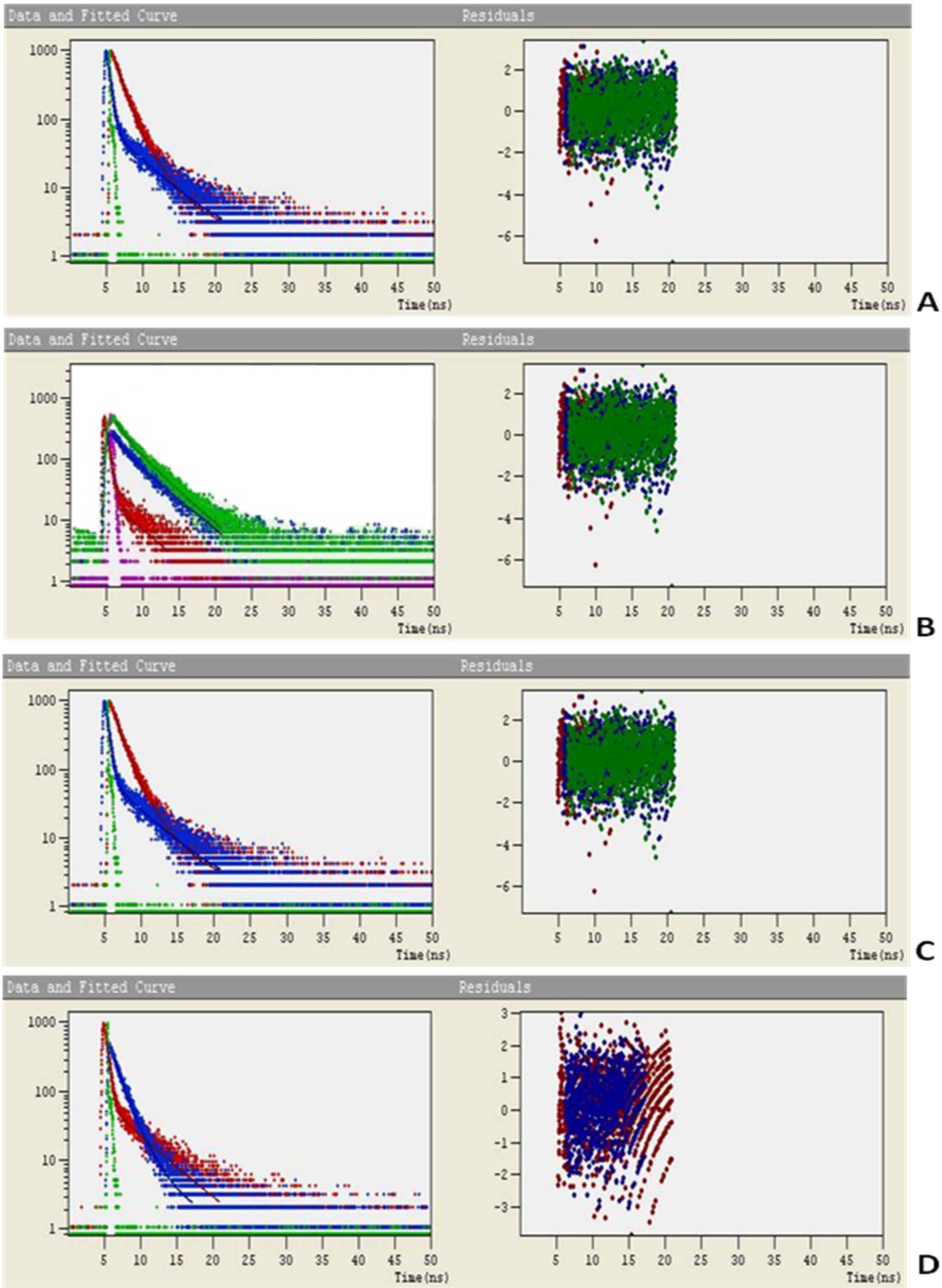

Figure 4. TRPL decay curves of diatoms corresponding to the emission wavelength 322 nm and 463 nm showing fitted curve and residuals; A: *Navicula* sp, the data were best fitted by bi-exponential decay time (χ^2=1.079 and 1.017); B: *Thalassiosira* sp. (χ^2=1.052 and 1.032); C: *Nitzschia* sp. (χ^2=1.160 and 0.995); D: *Achanthes* sp. (χ^2=1.08 and 1.052) (λ_{exc}=375 nm).

DISCUSSION

We have demonstrated the culture of the freshwater diatoms from Deepor Beel of Assam, India and 4 diatom species were selected for characterization of their photoluminescence behaviour. The efficient luminescence properties from porous silicon of diatom frustules in the visible spectral range as reported by other workers mostly in marine diatoms accelerated the material scientists. Presently wide investigations have been devoted to study silicon-based nanostructures for possible applications as light emitting devices [20].

SEM analysis revealed the presence of Si nanopores ranging from ~60-120 nm, which is acceptable by different workers to be used in various aspects [21].

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The PL spectra for the diatom frustules showed a diverse range of PL peaks at ultraviolet, blue and green ranges. The PL showed in the visible range when irradiated with UV light for all the diatoms used in this study. This species of diatoms showed PL peaks mainly in the ultraviolet and blue spectral range, due to the non-uniform pore size of nanostructures in the diatom frustules. In most of the literature it was stated that diatoms have amorphous silica frustules; however, the frustules of the species that we cultured were found to be composed of crystalline α-quartz [22].

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