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Research Article

Nano structured diatom frustules incorporated into TiO₂ photoelectrodes to enhance performance of quasi-solid-state dye-sensitized solar cells

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ABSTRACT

Diatom frustules are incorporated into multilayer photoelectrodes intending to enhance efficiency in dyesensitized solar cells utilizing their light interaction properties. A specific, but ubiquitous in all oceans, pennate-type diatom frustules were used to form the composite layers. Single, double, and triple-layer photoelectrodes were constructed with pure TiO_2 (control measurements) as well as with a TiO_2 /diatom frustule composite. The electrodes were prepared using TiO₂ nanoparticles of two sizes (13 and 21 nm) and were analyzed using UV visible absorption and XRD spectra. The morphology of frustules and electrodes were analyzed using scanning electron microscopy. The performance for each photoanode configuration was measured by assembling photoelectrochemical solar cells fabricated with a Pt counter electrode and a gel polymer electrolyte that excludes volatile solvents. The efficiency of the control cell is 3.37%. After replacing the topmost TiO₂ layer with a TiO₂/diatom frustule composite layer, efficiency increases to 6.78%. This is an impressive efficiency enhancement of 101%. The short circuit current density of frustule-incorporated threelayer cells is 18.1 mA cm⁻¹ while for the control cell it is 8.98 mA cm⁻¹. The enhanced efficiency of cells made with TiO₂/diatom frustule composite electrodes and a polyethylene oxide-based gel polymer electrolyte can be attributed to the improved light absorption by the photoanode due to optical scattering and light-trapping effects caused by the presence of diatom frustules. Frustules also can assist in enhancing dye adsorption by increasing the effective specific surface area of the composite photoelectrode due to their nanoporous structure.

1. Introduction

Dye-sensitized solar cell (DSSC) is a widely researched, solar energy harvesting device, which can efficiently convert solar energy to electrical energy. Although DSSCs have achieved reasonably high efficiency, further improvements in device stability, efficiency, and cell construction methods such as the exclusion of volatile liquid electrolytes in the cells are of practical and commercial interest [1–3]. In a few previous DSSCs studies, TiO₂ photoelectrodes have been improved by fabricating them with various nanostructured morphologies and including composite materials in order to increase the effective surface area. The resultant enhancement of dye adsorption, which increases the light-harvesting efficiency of the electrode, has finally improved the photoconversion efficiency of the cells [4,5]. In addition, inorganic and organic nanostructured materials having optical waveguiding effects have been integrated into photoelectrodes to achieve efficient electron excitation in the photo-electrode [6,7].

Diatoms are abundant single-cell photosynthetic algae species usually found in all aquatic habitats on earth. Diatoms have threedimensional exterior nanostructures called frustules (i.e., exoskeletons) made of biomineralized glass-like hydrous amorphous silica [8], which has a complex pattern of submicron and nanoscale pores [9, 10]. Diatom frustules exhibit good mechanical strength [11,12], impressive photonic properties [13, 14]and enhanced wavelength-specific guided modes of light absorption [15]. Moreover, the surface area of frustules is very high due to their hollow structure and the presence of a denselv distributed multilavered hierarchical pore structure. These pores in the frustule surface have been naturally

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Fig. 1. Schematic diagram (not to a scale) of control cell configurations; (a) single layer; TiO_2 (T1), (b) double layers; $1st TiO_2$ and $2nd TiO_2$ (T1/T2), and, (c) triple layers; $1st TiO_2$, 2nd TiO_2 and $3rd TiO_2$ (T1/T2/T3). Schematic diagram of test cell configurations; (d) single layer; TiO_2 /diatom frustules composite (F1), (e) double layers; $1st TiO_2$ and $2nd TiO_2$ /diatom frustules composite (T1/F2), and (f) triple layers; $1st TiO_2$, $2nd TiO_2$ and $3rd TiO_2$ / diatom frustules composite (T1/T2/F3). Here T1 = TiO_2 1st layer, T2 = TiO_2 2nd layer, T3 = TiO_2 3rd layer, F1 = Frustules added 1st layer, F2 = Frustules added 2nd layer, F3 = Frustules added 3rd layer.

evolved to facilitate a selective light capture by algae for their photosynthesis. A wide size range (1 μ m–5 mm) of frustules with pore size variation from 50 nm to 1 μ m has attracted special interest in nanotechnology and nanomaterial research [16–18].

The sizes of the complex nano-patterns and pore structures of frustules are comparable with the wavelengths of visible and UV light and frustules can be considered as photonic crystals composed of periodically variable refractive-index materials where the pore patterns are able to capture and guide light in the visible spectral range [19–21]. The hierarchically ordered micro/nanopores in frustules play an important role when developing materials with improved light trapping and scattering. Further, metal-doped (cadmium, titanium, germanium, palladium, and platinum etc.) frustules can be successfully used in anticancer treatment, filtration, fabrication of biosensing devices, and water purification [22,23]. There are very few studies in the literature on using these natural nanostructures to enhance the efficiency of DSSCs. The application of frustules in DSSCs is an interesting and inspiring area of research and the field needs further research for the optimization of the structure and composition of 3D photoelectrodes with embedded frustules to improve the efficient dye distribution, which contributes to the light-harvesting efficiency of the cells [18,24]. Photonic crystals, chemical sensors, solar cells, and optical switches are other examples where the optical features of frustules are being used [14,25].

Diatom frustules also exhibit photoluminescence under UV excitation due to their porous silicon dioxide architecture [26,27]. It has been shown that nanostructured silicon (size of about 3 nm) emits photoluminescence by the quantum detention effects of trapped charges inside [28,29]. Using this unique characteristic, the properties of porous silicon can be exploited when used in novel photonic devices. Also, if frustules are placed on a semiconductor film, the light absorption from the film can be enhanced [15,30]. Assembling diatom frustules on FTO is difficult, and also diatom frustules containing amorphous silica are

transparent in the visible spectrum, however, the extracted frustules are translucent due to their nanostructures. The refractive index of pure diatom frustules is 1.4 and when frustules are incorporated into TiO₂ the refractive index of the composite layers lies between 1.7 and 2.5 which finally contributes to the efficiency enhancement in solar cells facilitating the capturing of more light through effective scattering [14,19, 31]. However, frustule incorporated TiO₂ electrodes can be prepared using various methods for DSSCs applications. When the frustules are combined with TiO2, this gives high and periodic dielectric contrast, so photonic bandgaps and enhanced light scattering within the frustule pore array can be expected [19,32,33]. TiO₂/diatom frustule photoelectrodes have been studied by Huang et al., who reported power conversion efficiency enhancement of the DSSCs due to the improvement of light-trapping and scattering. In their work, for the bare TiO₂ electrode, the efficiency of the DSSCs was 3.81%, which was increased to 5.26% when coated once with the TiO₂/diatom paste [34]. According to the authors, frustule added DSSCs exhibited a doubling of the power efficiency (9.45%) compared to the control DSSCs which were made without adding diatom frustules (4.20%) [32]. The above two studies clearly indicate that the diatom frustules incorporated in the photo-electrodes enhance the efficiency of DSSCs.

However, the liquid electrolytes in these cells can devastate the physical and chemical stability of the cells. It was reported by us that the efficiency and stability of quasi solid state DSSC with gel polymer electrolytes can be improved by adding diatom frustules to the photoelectrode [35]. In that study, single and double-layered photo-electrodes have been investigated with different frustule/TiO₂ layer combinations and conformations. The study has revealed efficiency and short circuit current density enhancements of 35% and 39% due to the incorporation of diatom frustules in quasi-solid state DSSCs along with a polyacrylonitrile (PAN) (M_w 150,000) host polymer-based iodide ion conducting electrolyte. The DSSCs based on double-layer photoelectrodes prepared by adding 1 wt% of frustules to the 2nd TiO₂ layer have shown enhanced values of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), and efficiency values of 9.58 mA cm⁻², 729 mV and 4.65% under 1000 W m⁻² irradiation.

As mentioned earlier, three-dimensional nanostructured diatom frustule incorporation into the photoelectrodes of DSSCs is a remarkable development due to their unique photonic properties such as light trapping and scattering that improve DSSC performance. In this study, TiO₂:diatom frustules are mixed according to 100:1 mass ratio and the TiO₂/diatom frustule mixture is applied as the top layer of the photoelectrode followed by assembling a quasi-solid state photoelectrochemical (PEC) cell. Multiple layered (single to triple layers) photoelectrodes were studied in this work. In addition, the effect of continuous irradiation was also investigated to study the short-term stability. The objective of this study is to explore the effect of incorporating diatom frustules in the TiO₂ multilayer photoelectrode on the performance of DSSCs while improving the physical and chemical stability by using a quasi-solid state gel polymer electrolyte.

2. Experimental techniques

2.1. Preparation of multi-layered, frustule incorporated TiO_2 photoelectrodes

The TiO₂ slurries were prepared by grinding mixtures of 13 nm (Evonik P90) or 21 nm (Evonik P25) TiO₂ powder and 0.1 M HNO₃ in an agate mortar. For the control samples, the TiO₂ slurry was spin-coated on a well-cleaned transparent conductive fluorine-doped tin oxide (FTO) (Solaronix TCO22-7) substrates (2 cm \times 1 cm) according to configurations shown in Fig. 1(a), (b), and (c). For the 1st and 2nd layer preparation, TiO₂ (13 nm) was spin-coated at 2300 RPM while the 3rd layer was prepared using TiO₂ with the particle of size 21 nm and spin-coated at 1000 RPM.

In addition to control samples a TiO2/frustule composite slurry was



Fig. 2. FTIR spectra of the constituents of the gel polymer electrolyte in the frequency range of $3000-500 \text{ cm}^{-1}$.

 Table 1

 IR transmittance band positions and their assignments for the electrolyte [38].

Peak number	Wavenumber (cm^{-1})	Band assignment
1	2930	-C-H aliphatic stretching
2	1795	-C=O stretching
3	1481	-C-H scissoring
4	1390	-C-H bending
5	1169	-C-O-C asymmetric stretching
6	1072	-C=O symmetric stretching
7	774	-C-H bending

prepared using the TiO_2 nanoparticles and diatom frustules (purified at the Swedish Algae Factory- Sweden, batch K632, freeze-dried). For this purpose, materials were mixed according to the weight ratio of TiO_2 : frustules (100:1) in 0.1 M HNO₃. Then the slurry was sonicated for about 2 h at room temperature to make a homogeneous mixture. After that, the mixture was allowed to settle down for 12 h under room temperature for the TiO_2 nanoparticles to get dispersed into the frustule pores. Finally, the mixture was spin-coated in different film conformations on FTO glass substrates as shown in Fig. 1(d), (e), and (f). For the 1st and 2nd layers, 13 nm TiO_2 was used and spin-coated at 2300 RPM while the 3rd layer was prepared using the particle size of 21 nm and spin-coated at 1000 RPM.

After spin-coating of each thin film layer, samples were allowed to sinter at room temperature for about 24 h. Subsequently, the films were annealed at 450 °C for about 2 h. Both heating and cooling rates were 1.5 °C min⁻¹.

2.2. Dye sensitization

Prepared multi-layer photoelectrodes were photo-sensitized by dipping in an ethanol solution of di-tetrabutylammonium *cis*-bis



Fig. 3. Grazing-incidence X-ray diffraction (GIXRD) patterns of phase content on T1, T1/T2, T1/T2/T3, F1, T1/F2, and T1/T2/F3 layers of films and identified SiO₂/TiO₂ peaks according to the JCPDS 75–3168. (Peaks related to Silica, Rutile and Anatase are designated as S, R, and A respectively).



Fig. 4. Powder XRD spectrum of the diatom frustule powder sample.

Table 2

The	conductivity	of the	electrolyte a	s a function	of temperature.
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Temperature/°C	25	30	35	40	45	50	55	60	65	70
Conductivity/mS $\rm cm^{-1}$	4.00	4.23	4.73	5.17	5.62	6.18	6.70	7.22	7.70	8.09

Table 3

Calculated values of the average crystallite size (*D*), strain (ε), and dislocation density (δ) for all photo-electrodes using peaks related to (101) crystal plane with 0.35 nm d spacing and (004) crystal plane with 0.24 nm d spacing.

Type of Photo- electrode	FWHM (deg.)		Position 2θ (deg.)		Average	Average Strain, ε ($\times 10^{-3})$	Average Dislocation density, δ ($\times \ 10^{-3}$
	101 Plane	004 Plane	101 Plane	004 Plane	Crystallite Size, D (nm)		nm ⁻²)
T1	0.63	0.50	25.39	37.91	15.61	2.36	4.11
T1/T2	0.53	0.55	25.33	37.84	16.11	2.25	3.85
T1/T2/T3	0.45	0.53	25.30	37.86	18.32	1.98	2.99
F1	0.84	0.56	25.97	37.87	13.00	2.93	5.92
T1/F2	0.74	0.54	25.39	37.90	13.22	2.81	5.72
T1/T2/F3	0.55	0.63	25.35	37.91	15.22	2.38	4.32



(c) T1/T2

(d) T1/T2



(e) T1/T2/T3

(f) T1/T2/T3



Fig. 5. SEM images of pennate diatom frustules nanostructure, extracted and purified from a diatom monoculture by the Swedish Algae factory shown at different magnifications (7.74k, 30k, 50k 100k).

(isothiocyanato)bis(2,2'-bipyridyl4,4'-dicarboxylato) ruthenium(II) dye (N719) (Solaronix). Once electrodes were dipped in the dye solution, the temperature of the dye solution and photoelectrode were both maintained at ~60 °C. After the dipping process, all electrodes were kept immersed in dye solution for about 48 h at room temperature to ensure complete dye adsorption.

2.3. Preparation of the gel polymer electrolyte

The gel polymer electrolyte utilized was composed of polyethylene oxide (PEO), ethylene carbonate (EC), propylene carbonate (PC), 4-tertbutylpyridine (4TBP), lithium iodide (LiI), tetrahexylammonium iodide (Hex₄NI), and 1-butyl-3-methylimidazolium iodide (BMII) salts. The



(a) T1

(b) T1



Fig. 6. SEM images of single layer photoelectrodes prepared without frustules, at (a) 50,000 and (b) 100,000 magnifications. SEM images of double layer photoelectrodes prepared without frustules, at (c) 50,000 and (d) 100,000 magnifications. SEM images of triple layer photoelectrodes prepared without frustules, at (e) 50,000 and (f) 100,000 magnifications.

samples were prepared using PEO (Molecular weight 4,000,000) (0.005 g), EC (0.400 g), PC (0.464 g), 4TBP (0.014 g), LiI (0.018 g), Hex₄NI (0.043 g), and BMII (0.008 g). The electrolyte consisted of PEO:EC:PC: BMII:Hex₄NI:LiI:4TBP:I₂ according to the molar ratios of the components; 10:40:40:0.25:0.8:1.2:0.85:0.2. Using the stoichiometric ratios, the electrolyte composition can be written as $(PEO)_{10}(EC)_{40}(PC)_{40}$ (BMII)_{0.25}(Hex₄NI)_{0.8}(LiI)_{1.2}4TBP_{0.85}(I₂)_{0.2} [36].

For the preparation of the electrolytes, EC, PC, and 4TBP were mixed with respective weights in a closed glass bottle under continuous stirring. The relevant amounts of iodides, LiI, Hex₄NI, and BMII were added to the mixture and stirred for a few more hours until all the compounds were well dissolved. Subsequently, 50 mg of PEO was added to the solution and stirred further to obtain a homogeneous mixture. Then the resulting mixture was heated up to 100 °C with continuous stirring until mixed well and a transparent slurry was formed. After that, the temperature of this mixture was allowed to decrease to about 40 °C, and then 0.006 g of I₂ was added and stirred until properly dissolved [36]. The resulting translucent, orange-colored slurry was allowed to form into a gel at room temperature. This gel polymer electrolyte was allowed to saturate for 2 days before applying it in DSSCs.

All control and testing DSSCs were assembled by clipping together the components under gentle pressure, according to the configuration with gel polymer electrolyte sandwiched between the dye-sensitized photoelectrode and the Pt-coated glass plate as the counter electrode.

2.4. Characterization and measurements

2.4.1. Characterization of the electrolyte

FTIR spectra of the gel-polymer electrolyte were analyzed at room temperature using a Bruker Alpha-P FTIR spectrophotometer equipped with a Platinum-ATR and a diamond crystal module. The spectra were obtained in the range $500-3000 \text{ cm}^{-1}$ with a resolution of 4 cm⁻¹. In this study, attenuated total reflection (ATR) mode was used to obtain the spectra for the gel electrolyte.

(b)





Fig. 7. SEM images of single layer photoelectrodes prepared TiO₂ (P90)/Diatom frustules at (a) 1,000, (b) 5,000, (c) 20,000, and (d) 50,000 magnification.

2.4.2. Characterization of the composite photoelectrode

A Rigaku Ultima IV X-Ray Diffractometer (XRD) (KYOWAGLAS-XATM, Japan) was used for studying the TiO₂/frustule films using grazing incidence X-ray diffraction GIXRD, Cu K α radiation with $\lambda =$ 1.54184 Å and continuous mode at generator voltage of 40 kV in a 40 mA tube. The scan step size was 0.01° with 2θ in the range of $20-80^{\circ}$. In order to get UV-visible absorption spectra of the TiO₂/frustule films, a UV-1800 Shimadzu double-beam UV-vis spectrophotometer was used in both transmittance and absorbance modes. Measurements were obtained at room temperature at normal incidence in the wavelength range from 300 to 800 nm. In order to investigate the morphology/topology of the film surface, a Zeiss EVO|LS15 scanning electron microscope was used to take scanning electron microscopy (SEM) at 50 and 100 k magnification with a 20 kV beam. To take SEM images, the samples were coated with gold.

2.4.3. Characterization of solar cells

The photovoltaic performances of DSSCs were evaluated using a source meter unit (Keithley Instruments Inc.). For this purpose, the cells were irradiated with 1000 W m^{-2} (AM 1.5) by a PEC-LO1 solar simulator, and the current-voltage (I-V) characteristics of the cells were recorded. The active area of the cell was 20 mm². Current-voltage data were measured for about 3 h (in 10 min steps) under continued irradiation.

Electrochemical impedance spectroscopy (EIS) data of the solar cells were recorded by a Potentiostat (Autolab PGSTAT128 N) frequency response analyzer (FRA) module. Impedance measurements were collected with NOVA 1.1 software. For the measurements, the cells were placed in a Faraday cage and data were collected at room temperature in dark conditions. The measurements were conducted by applying a bias voltage similar to the $V_{\rm oc}$ of the respective cells. The measurement frequency window was 0.1 Hz-1000 kHz and scanning was conducted with 80 steps.

3. Results and discussion

3.1. Characterization of the electrolyte

3.1.1. FTIR analysis of the electrolyte

Fig. 2 shows the FTIR spectrum of the electrolyte containing PEO, EC, PC, 4TBP, BMII, and iodine and that of the basic components of the complex electrolyte, namely PC, EC, PC + EC, PEO, and PC + EC + PEO. Peaks at different wavenumbers and their corresponding vibrational modes were identified considering the FTIR results. The wavenumber and the respective bond vibrations of the significant peaks are shown in Table 1.

The intense characteristic absorption band at 2930 cm⁻¹ corresponds to -CH₂ aliphatic asymmetrical stretching. The peak is significant in PEO spectra, and it appears as a less intensive peak in the electrolyte spectra. The clear band shown around the peak at 1795 $\rm cm^{-1}$ is attributed to -C=O (carbonyl group) stretch. In EC spectra corresponding band appears as a double peak and in PC spectra it appears as a single peak. In the mixed systems, the bands appear as a single peak and any shift of peaks is not observed due to the mixing of components [37]. The bands (a)

(b)



Fig. 8. SEM images of double layer photoelectrodes prepared with top layer TiO_2 (P90)/Diatom frustules at (a) 1,000, (b) 5,000, (c) 20,000, and (d) 50,000 magnification.

appearing around 1389 cm^{-1} and 1353 cm^{-1} are related to –CH aliphatic bending group with symmetric stretching which can be clearly observed in the spectra of EC, PC and their mixtures.

The less intense peak appearing at 1481 cm^{-1} is the -CH₂ scissor mode and the set of spiky bands at 1072 cm⁻¹ and 972 cm⁻¹ can be attributed to -C=O symmetric stretching [38,39]. The bending of the -C-O-H group in -CH₂OH can be observed at 1481 cm⁻¹ [40,41]. The C–O stretching of the primary alcohol is shown at 1119 cm^{-1} . The 973 cm^{-1} band is a result of a strong C=C bending. As shown in Fig. 2, the significant absorption bands in the spectra of the electrolyte are related to the vibration modes of the components in the electrolyte but a redistribution of vibrational energies by mixing EC and PC can be observed. The FTIR data does not show the presence of any impurities or any changes in the chemical composition of the electrolyte by reactions or coordination between the components in the electrolytes. All the peaks observed in the electrolytes are related to the FTIR bands of the solvating materials, with the exception of the EC/PC mixture and thus the formation of any new chemical bonds between polymer, solvent, or salt species can be ruled out.

3.1.2. Conductivity in the electrolyte

The ionic conductivities of the electrolyte with increasing temperature were calculated using bulk resistances determined using Nyquist plots. The conductivities of the electrolyte at different temperatures are given in Table 2. The room temperature conductivity of the electrolyte is 4.00 mS cm^{-1} and it increases to 8.09 mS cm^{-1} when the temperature increases to 70 $^{\circ}$ C. However, the temperature dependency of conductivity does not exhibit Arrhenius-type behavior. Therefore, the conductivity data of the electrolyte were fitted to the Vogel Taman Fulcher (VTF) equation,

$$\sigma = AT^{-1/2} \exp\left(-\frac{E_{a}}{k_{\rm B}(T - T_{\rm g})}\right) \tag{1}$$

where σ , *T*, *A*, *E*_a, and *T*_g represent the conductivity, absolute temperature, pre-exponential factor, pseudo activation energy and the equilibrium state glass transition temperature, respectively. The values determined for *E*_a, *A* and *T*_g by fitting the data to VTF equation are 0.034 meV, 152.1 S m⁻¹ K^{1/2} and 173 K, respectively.

3.2. Characterization of photoelectrodes

3.2.1. Structural peculiarities

Fig. 3 shows the GIXRD patterns of all the photoelectrodes prepared using TiO₂ and TiO₂/diatom frustule mixtures in different configurations. The observed XRD patterns were compared with standard JCPDS data files 75–2544 and 75–3168 by matching the observed 2θ values with references [42,43]. Diffraction peaks were observed at $2\theta = 25.32^{\circ}$, 37.90°, 48.10°, 51.67°, 54.63°, 55.21°, 61.74°, and 65.94° positions. The most conspicuous peak was found at 25.32° reflection plane orientation (101). This describes that the formation of nanocrystals has a preferred crystallographic orientation at (101). It can be observed that

(b)





Fig. 9. SEM images of triple layer photoelectrodes prepared with top layer TiO₂ (P25)/diatom frustules at (a) 1,000, (b) 5,000, (c) 20,000, and (d) 50,000 magnification.

Table 4

Thickness values of the photoelectrodes investigated and calculated using transverse SEM images.

	Photoelectrode configuration	Thickness/µm
Control	T1	0.66
	T1/T2	1.08
	T1/T2/T3	2.23
Test	F1	0.85
	T1/F2	1.51
	T1/T2/F3	2.68

the relative intensity of the peak related to (101) plane increases while that of (004) decreases. Therefore, it is evident that the compact layers prepared by TiO2 of particle size 13 nm (P90) prefer (004) orientation. Thus, the weighted average crystallite size was estimated from the peak area and the peak width of (101) and (004) using the Scherrer equation. The crystallite size, lattice strain, and dislocation density were calculated using more dominant peaks only. Based on this it was confirmed that TiO₂ was predominantly in the tetragonal anatase phase. The small peak at 23° is related to reflections from rutile (110) planes. The rest of the peaks correspond to Anatase phase TiO2 (004), (200), (105), (211), (204), and (215) crystallographic planes. Any peaks related to SiO2 from Diatom frustules were not visible in the XRD spectra possibly due to the low concentration (1 wt%) of frustules and the amorphous nature of this SiO2. In order to get a clear picture XRD of pure frustules also were measured.

Peaks at 37.50° (020) and 51.63° (121) correspond to the FTO substrate on which films were deposited [43,44] (Fig. 3). The intensity of the peaks at 37.90° and 51.67° decrease with the increasing number of TiO2 layers (1,2, or 3) in a directly proportional manner.

Fig. 4 shows powder XRD of diatom frustules that exhibit a more or less amorphous nature. Diatom is mainly formed with SiO2 and shows a broad and weak peak in the 20-30° range which corresponds (001) plane of the hexagonal structure [45]. The GIXRD pattern of photoelectrodes containing frustules (annealed at 450 °C), F1, T1/F2, and T1/T2/F3, are shown in Fig. 3. As shown in Figs. 3 and 4 XRD results do not exhibit clear peaks pertaining to SiO₂, and this may be due to the very low frustule content (1 wt%) which are more or less amorphous.

Particle size, lattice strain, and dislocation density of the TiO₂ in films were calculated for the major peak (101) crystal plane of anatase. These parameters, given in Table 3, were calculated based on Debye Scherrer relationships given in Equations (1), (2), and (3) [46],

$$D = \frac{0.94 \times \lambda}{W \times \cos \theta} \tag{1}$$

$$\varepsilon = \frac{W \times \cos \theta}{4} \tag{2}$$

$$\delta = \frac{1}{D^2} \tag{3}$$



Fig. 10. UV–vis spectra of optical (a) transmittance vs. wavelength (b) absorbance vs. wavelength for all photoelectrodes studied in this work.

 Table 5

 Calculated values of the bandgap for photoelectrode layers.

Type of photoelectrodes	Experimental E_g /eV		
T1	3.31		
T1/T2	3.29		
F1	3.32		
T1/F2	3.29		

where, *D* indicates the crystallite size, λ is the X-ray wavelength, θ is Bragg's angle, and *W* is the Full Width at Half Maximum (FWHM) of the peak. The lattice strain, ε , and the dislocation density, δ , were calculated using the above formulas as well.

The crystallite size (*D*), strain (ε), and dislocation density (δ) for all photo-electrodes using peaks related to (101) crystal plane with 0.35 nm d spacing and (004) and crystal plane with 0.24 nm d spacing were calculated and given in the Supplementary Tables S1 and S2, respectively. Calculated weighted (considering peak intensity) average values of *D*, ε , and δ for all photo-electrodes are given in Table 3. The variation of crystallite size with respect to different layer configurations is shown in Table 3. For layers with TiO₂ only, the crystallite sizes in 1st and 2nd layers were 15.61 nm and 16.11 nm, respectively (in agreement with the manufacturer's specification of P90, average particle size ~13 nm). The higher crystallite size shown by the double layer film can be due to the calcination (since T1/T2 was calcined twice). In addition, the 1st layer is

prepared on the smoother FTO substrate, and the 2nd layer is prepared on the rougher TiO₂ substrate (i.e., 1st layer) and thus larger particles can escape more easily from the FTO substrate due to centrifugal force while spinning. In the case of the 1st and 2nd layers coated with TiO₂/ diatom frustule mixture, the respective crystallite sizes were 13.00 nm and 13.22 nm. These results are comparable with the manufacturer's specification of P90 powder (average particle size~13 nm). The small deviations shown can be due to the effect of added frustules which shows an XRD peak in the same region. Further, frustules also influence the TiO₂ film formation and aggregation. The additional 3rd layer with TiO₂ showed the 18.32 nm average crystallite size, which agrees with the specifications because the electrode contains two P90 (~13 nm) and one P25 (~21 nm) layers. Moreover, the internal strain of the layers decreases with increasing layer thickness. Lattice strain is a measure of the dispersion of lattice constant values arising from crystal imperfections, such as lattice dislocations. This decrease of the strain with increasing thickness can be connected to the decrease of cohesive force between the film and the substrate material. Due to that, there can be a decrease in the concentration of lattice imperfections with the increase in layer thickness (as well as an increase in the crystallite size) [47]. In general, crystallite size usually increases with the increase in thickness while the lattice strain decreases [48]. On the other hand, diatom frustule incorporated TiO₂ layers resulted in smaller crystallite sizes and higher lattice strain compared to the pure TiO₂ layers.

The XRD spectra have been taken via the reflections from the surface, therefore the thickness and morphological artifacts of film surfaces have affected the peak intensities. Transformations of the morphology of these films can be seen via the SEM images. Other observed properties such as grain size and dislocation density would also affect the electrical and optical properties of the films.

3.2.2. Morphological peculiarities

This study is based on pennate diatom frustules, processed, and purified from a diatom monoculture by the Swedish Algae Factory. SEM images taken at different magnifications (7.74k, 30k, 50k, and 100k) are shown in Fig. 5. Fig. 5(a), shows a single frustule with micro-scale size (6.16 µm in width and 34.41 µm in length) with an elongated needleshape, having bilateral symmetry. The diatoms consist of either solitary or patterned colonies attached to the end of a substrate [49]. Unicellular diatoms can form colonies, which can take the shape of filaments or ribbons, fans, zigzags, or stars. Individual cells range in size from 2 to 200 µm [50]. Fig. 5(b) shows the 'frustule valve' feature. Fig. 5 (c) and (d) reveal the internal structures. Fig. 5(c) shows foramen, with approximately 139 nm pore hole size. Fig. 5(d) shows the second level, sieved pores with spines. Using ImageJ® software (for biological-image analysis), the number of pore holes on the frustule surface was estimated to roughly about 3500 pore holes on a frustule. When diatom frustules are mixed with TiO₂ nanoparticles, these nanoscale pore holes get filled with TiO₂, increasing the effective TiO₂ surface area.

SEM images of single, double, and triple layer photoelectrodes prepared without frustules, are shown in Fig. 6. All images captured the surface morphology top layer of the photoelectrodes, and pinhole- or crack-free films were observed. TiO₂ nanoparticles have spread uniformly without voids. Fig. 6(a)–(d) show single- and double-layer films coated with the same TiO₂ particle size (13 nm). Here, only the thickness has increased, with no other structure or morphological changes observed. Triple-layer film (Fig. 6(e)-(f)) composed of TiO₂ particles of average size 21 nm agrees with the standard particle size of P25, is confirmed by XRD measurements as well. A uniform film surface, highly porous with mesopores can be seen in the images. They exhibit high porosity and large effective surface area, and all the considered films indicate that the composite, multilayer electrodes are suitable for DSSC applications.

Fig. 7 shows SEM images of the three photoelectrodes prepared with $TiO_2/diatom$ frustule composites which demonstrate their top layer morphology. Images in Fig. 7 clearly show the distribution and



Fig. 11. The photocurrent density versus potential as a function of time for the DSSC containing different TiO_2 and $TiO_2/Frustules$ layer configurations in photoelectrode under continuous irradiation of 1000 W m⁻² (1.5 a.m.) for 3 h. The photocurrent density versus the potential for the DSSC containing the TiO_2 (a) single, (c) double, and (e) triple layer configurations (control cells). The photocurrent density versus the potential for the DSSC containing the $TiO_2/Frustules$ (a) single, (c) double, and (e) triple layer configurations (test cells).

orientation of TiO₂/diatom frustule films. Fig. 7(a) shows how the TiO₂ spread and covers the frustules well from all directions. However, the entire surface is not covered by frustules, and frustules are not placed in any regular pattern (sparse and random coverage). However, since TiO₂/Diatom frustule weight ratio is 100:1, an appreciable amount of frustule appears on the surface. Fig. 7(b–d) depicts how the TiO₂ particles envelop the frustule to fill and cover the pores thoroughly. Moreover, as seen from Fig. 7(b–d), no pinholes appear either on the surface of the frustule, or on the surrounding TiO₂ area. Fig. 7(b) and (c) show cracks on the frustule and near the frustule surface. Frustules in the top layer of photoelectrodes are well covered by TiO₂ nanoparticles, according to Fig. 7(c) and (d). The edge between a frustule and TiO₂ area is magnified in Fig. 7(d), showing how both regions are uniformly covered.

Fig. 8 shows the SEM images of double layer photoelectrodes prepared with top layer $TiO_2/diatom$ frustules. Double layer samples consist of a bottom layer of pure TiO_2 and a top layer of $TiO_2/diatom$ frustule precursor, coated under the same conditions as the single-layer samples explained above. Therefore, considering the top layer $(TiO_2/diatom frustules)$ surface images of Fig. 8(a), (b), (c), and (d), the morphology is similar to the single-layer counterparts. Pinholes or voids are not present on any SEM image in Fig. 8 series either. Fig. 8(c) and (d) capture TiO₂-covered frustules with the cracked area. These cracks may increase cell performance by improving dye adsorption since these layers are prepared on a compact 1st layer.

Fig. 9 shows the SEM images of triple layer photoelectrodes prepared with top layer $TiO_2/diatom$ frustules. Note that the spin coating speed for the 3rd ($TiO_2/diatom$ frustules) layer is different from the two (TiO_2) layers below, however, the same $TiO_2/diatom$ frustule precursor was used to prepare frustule containing samples. Compared to previous images, the triple-layer specimen in Fig. 9 shows more frustules than the single and double layer specimens.

Moreover, in all the SEM images of (Figs. 7–9) frustule precursorcoated layers, the sharp edges of frustules are visible. These bright

(b) F1



(u:)

(a) T1

Fig. 12. The power density versus potential as a function of time for the DSSC containing the TiO_2 and $TiO_2/frustules$ layer configurations in photoelectrode under continuous irradiation of 1000 W m⁻² (1.5 a.m.) for 3 h. The power density versus the potential for the DSSC containing the TiO_2 (a) single, (c) double, and (e) triple layer configurations (control cells). The power density versus the potential for the DSSC containing the $TiO_2/frustules$ (a) single, (c) double, and (e) triple layer configurations (test cells).

demarcations in the SEM images may be due to the sharp frustule edges accumulating charge or due to the presence of radial striae (thin parallel streaks or ridges on the frustule surface) with higher TiO₂ concentration.

Transverse SEM images of film cross-sections were taken to determine the film thickness and the results obtained are given in Table 4. The thickness has obviously increased with the number of layers. Also, the higher the layer count, the greater the cell efficiency in the measured configurations (up to three layers). When comparing electrodes with equivalent layer configurations thicknesses were consistently higher for the films with TiO₂/frustule composites compared to the pure TiO₂ coated films (reference films).

3.2.3. Optical absorption

Fig. 10(a) and (b) show the UV-visible optical transmittance and

absorbance spectra of the multilayer photoelectrode films. Lower transmittance suggests higher light absorption, leading to better lightharvesting by the film. In general, films with lower thicknesses are expected to result in higher transmittance. According to Fig. 10(a) a singlelayer film shows the highest transmittance as expected. Moreover, films coated with a TiO2/diatom frustule mixture show an overall reduction of transmittance compared to pure TiO2 coated films. Absorbance spectra, as expected, are inversely proportional to the logarithm of the transmittance, Fig. 10(b) clearly shows that the absorbance is increased when the thickness of the electrode increases, and thus the data follows the Beer Lambert law [51]. Compared to pure TiO₂ control samples, TiO₂/diatom frustule incorporated photoelectrodes consistently exhibit higher optical absorption which can be due to the increased film thickness and the multiple scattering effects caused by the presence of



Fig. 13. The characteristic solar cell parameters of triple-layer TiO_2 and $TiO_2/$ diatom frustule based DSSCs vs. time.

Table 6

The average values for characteristic parameters in different DSSCs constructed using photoelectrodes with TiO_2 and TiO_2 /diatom frustules.

Photoelectrode	J_{sc} /mA cm ⁻²	V _{oc} /mV	FF/%	Efficiency/%
T1 T1/T2 T1/T2/T3 F1 T1/F2 T1/T2/F3	$\begin{array}{c} 3.38 \pm 0.12 \\ 6.47 \pm 0.05 \\ 8.98 \pm 0.05 \\ 4.21 \pm 0.06 \\ 8.22 \pm 0.12 \\ 18.08 \pm 0.08 \end{array}$	$\begin{array}{c} 755 \pm 30 \\ 704 \pm 42 \\ 716 \pm 34 \\ 707 \pm 19 \\ 665 \pm 58 \\ 677 \pm 28 \end{array}$	$\begin{array}{c} 63.1 \pm 1.3 \\ 62.5 \pm 4.1 \\ 61.3 \pm 7 \\ 61.3 \pm 1.3 \\ 58.7 \pm 7.8 \\ 55.9 \pm 7 \end{array}$	$\begin{array}{c} 1.46 \pm 0.01 \\ 2.41 \pm 0.02 \\ 3.37 \pm 0.02 \\ 1.87 \pm 0.01 \\ 3.03 \pm 0.04 \\ 6.78 \pm 0.03 \end{array}$

frustules.

The optical energy bandgap (E_g) is an important parameter to analyze the performance of electrodes prepared for DSSCs. The method introduced by Jan Tauc to calculate the bandgap energy of amorphous semiconductors using optical absorption spectra is used in this study [52]. The Tauc equation is;

$$\alpha h v = A \left(h v - E_g \right)^n \tag{4}$$

where, α is an energy-dependent absorption coefficient, *h* is the Planck constant, ν is the photon frequency, E_g is the bandgap energy, and *A* is a proportionality constant. The factor *n* depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition bandgaps, respectively. A plot of $(\alpha h \nu)^{1/2}$ verses $h\nu$ (Supplementary Fig. 1) is used to calculate bandgaps (bandgap of anatase is indirect, thus n = 2) given in Table 5. In general, optical bandgap energy for TiO₂ semiconductor material is within the 3.2 eV–3.8 eV range and therefore the bandgaps of the films are in agreement with the literature [53]. According to the Tauc plot (Supplementary Fig. 1), the energy bandgap of the films investigated in this work were 3.32 eV and 3.29 eV for the F1 and T1/F2 films, respectively. This shows that the energy bandgap of TiO₂ layers has not changed significantly due to the presence of 1 wt% of Frustules.

In any material, the refractive index is directly involved in the reflection, transmission, and absorption of light. The connection between the refractive index and the bandgap is essential in explaining the optical absorption of the films [54]. The refractive index of pure TiO_2 material is 2.26 [55] and in diatom frustules, it is 1.43 [14], and when diatoms combine with TiO_2 , the average refractive index spans of the composite range from 1.7 to 2.5 [31,33]. Due to the contrast in refractive index, the light can be scattered by frustules (total internal reflection) facilitating the effective absorption of light.

We can compare the contribution to the scattering by the surface texture, evident by having a lesser transmitted energy and drop of bandgap value compared to the reference. Moreover, microscale diatom frustules along with nanoscale porous features, frustule valves can help absorb more visible light than pure TiO_2 nanoparticles [56]. Also, the girdles may help in modulating light inside the frustules. Therefore, TiO_2 /Diatom frustules layer can enhance the light trapping, optical scattering, and the porous-textured surface increases the crystalline defects, which contribute to the lowering of the conduction band of the material.

3.3. DSSC potentiostatic measurements

Fig. 11 depicts the time evolution of current density versus potential (*J-V*) curves within a 3 h irradiation period for the DSSCs investigated in this study. Fig. 11(a), (c) and (e) represent single, double and triple layers cells prepared without frustules (control cells). The *J-V* curves of the DSSC containing the TiO₂/Frustules composites electrode are shown in Fig. 11(b) for single, (d) double and (f) triple layer configurations, respectively (test cells). As visible in these graphs, all cells exhibited excellent stability within this 3 h measurement period.

The choice of TiO_2 particle size and their structural configuration in photoanode is crucial to achieve higher performance for DSSCs. Larger TiO_2 particles are often used in the bottom layer (in this case 3rd layer) of the photoanode due to several reasons.

- 1) Larger TiO_2 particles have a higher light-scattering ability. This means that when light strikes the photoanode, larger particles scatter the light, increasing the chances of the dye molecules absorbing more photons [57–59]. This helps to enhance the overall light absorption efficiency of the DSSC.
- 2) Larger TiO₂ particles can facilitate better charge transport across the photoanode [60,61]. Electrons generated by the dye molecules need to move through the TiO₂ matrix to reach the conductive substrate. Larger particles can provide a more continuous pathway for electron transport, reducing the likelihood of electron recombination and improving the overall efficiency of the DSSC [62,63]. For instance, Nakade et al. have shown that the electron diffusion coefficient increases with the TiO₂ particle size [64].
- 3) In DSSCs, the electrolyte typically contains iodide/triiodide ions. Larger TiO₂ particles can reduce the likelihood of recombination between electrons in the TiO₂ and triiodide ions in the electrolyte since larger particles at the interface reduce the effective contact area [65]. This is because larger particles may provide more difficult and limited pathways for the triiodide ions, decreasing the chances of contact with electrons and reducing recombination losses.

3.3.1. DSSC with single layer photoanodes

Fig. 11(a) and (b) depict the time evolution of *J*-*V* curves within 3 h irradiation period for the single layer photoelectrodes made with and without frustules, respectively. Fig. 12(a) and (b) show the variation of power density versus potential (P-V) for 3 h. These curves represent the single layer electrodes prepared by TiO_2 and TiO_2 /diatom mixture, respectively. Furthermore, J_{sc} increased with irradiation time, from 3.0 mA cm⁻² to 3.5 mA cm^{-2} for the frustule free cells. Similarly, for cells with added frustules, J_{sc} increases from 3.8 mA cm⁻² to 4.8 mA cm⁻² with irradiation time. This might be a result of heating due to prolonged irradiation. Charge transport kinetics can get amplified when the temperature is increased, by suppressing $V_{\rm oc}$ [66–68]. Observed average energy conversion efficiencies for single layered configuration were 1.36% and 1.87%, and the average $J_{\rm sc}$ values were 3.38 mA cm⁻² and 4.21 mA \mbox{cm}^{-2} for \mbox{TiO}_2 and $\mbox{TiO}_2/\mbox{diatom}$ systems, respectively at the thermal equilibrium. Comparing results for these DSSC containing single layer photoelectrodes, a significant performance enhancement due to the incorporation of diatom frustules is apparent. The added frustules have increased current density by 24.6% while the efficiency increased by 37.5%.

3.3.2. DSSC with double layer photoanodes

Fig. 11(c) and (d) show J-V curves as functions of irradiation time up to 3 h for the DSSCs containing double layers of TiO2 and TiO2/diatom mixture respectively. The P-V curves of these cells are shown in Fig. 12 (c) and (d). These curves represent the double layer electrodes prepared by TiO2 and TiO2/diatom mixture, respectively. Furthermore, in the double layered cell made without frustules, J_{sc} increases from 5.5 mA cm^{-2} to 7.5 mA cm^{-2} , as a result of heating effects due to prolonged irradiation and that for frustules added cell is from 8.5 mA $\rm cm^{-2}$ to 11.9 mA cm⁻². The observed average energy conversion efficiencies for double layered configuration were 2.41% and 3.03%, and the average $J_{\rm sc}$ values were 6.47 mA cm⁻² and 8.22 mA cm⁻² for TiO₂ and TiO₂/ diatom systems, respectively. Comparing results for these DSSC containing single layer photoelectrodes, a significant performance enhancement due to the incorporation of diatom frustules is apparent. The added frustules have increased the current density by 27.1% while the efficiency increased by 25.7%.

3.3.3. DSSC with triple layer photoanode

Fig. 11(e) and (f) show J-V as functions of irradiation time up to 3 h for the DSSCs containing triple layers of TiO₂ and TiO₂/diatom mixture, respectively. The *P*–*V* curves of the cells are shown in Fig. 12(e) and (f). Both photoelectrode types (TiO₂ only and TiO₂/diatom frustule mixed) with triple coated layers, when used in DSSCs, gave higher efficiency compared to single- and double-layer configurations. The highest efficiency was 3.37% (for TiO2 only) and 6.78% (for TiO2/diatom frustule mixed). The observed average J_{sc} values were 9.0 mA cm⁻² and 18.1 mA cm⁻² for TiO₂ and TiO₂/diatom systems, respectively. Despite the overall steady performance of DSSCs, the time variations of cell parameters can be attributed to the small temperature increase over a prolonged period of illumination. The current density increased from 7.9 mA cm⁻² to 9.9 mA cm⁻², while V_{oc} showed a small drop from 769 mV to 652 mV with prolonged illumination in the frustule free cell. In frustule added triple layers cells $J_{\rm sc}$ increased from 16.0 mA cm⁻² to 20.0 mA cm⁻² while V_{oc} showed a small drop from 723 mV to 623 mV with illumination time. The added frustules thus increased both the current density and the efficiency by 101%.

As described above, solar cell performance testing was done for about 3 h. The variation of solar cell parameters with time is shown in Fig. 13. The calculated average values of characteristic parameters obtained within 3 h are given in Table 6. According to Table 6, the singlelayer photoelectrode corresponds to the maximum Voc observed. This might be due to the relatively low recombination rate of conduction band electrons. With the available larger space for photogenerated electrons in photoelectrode with the layer thickness, the number density of electrons in the conduction band would decrease, resulting in a drop in Voc [68,69]. Therefore, the thicker film should give a lower V_{oc} . In contrast, double layer photoelectrodes resulted in lower Voc than triple layer photoelectrodes. The thickness of a double-layer film is comparatively lower than a triple layer film due to the layer fabrication method discussed above (the use of larger particle size for 3rd layer). This can be results of a relatively higher charge generation rate compared to that of electron recombination in three-layer photoanode with respect to the double layer ones. The results of the tradeoff between the open circuit voltage and film thickness are shown in Table 6.

 $J_{\rm sc}$ and efficiency followed a similar trend when layer thickness was increased. Film resistance and dye adsorption of the film depend on the film thickness and are directly related to the photocurrent. Specifically, dye absorption is essential for light-harvesting efficiency [70]. Thus, a means of increasing the efficiency of any single, double, or triple layer DSSC is by increasing the photocurrent via improvement of the surface density of dye molecules. Table 6 indicates appreciable efficiencies and $J_{\rm sc}$ values while the fill factor remains comparably low ^[70]. This behavior is due to the incorporation of diatom frustules into TiO₂. The light trapping and scattering effect due to the frustules in the top layer can improve the photocurrent yield compared to frustule free DSSCs and

frustule incorporated DSSCs exhibit higher solar cell performances.

4. Conclusions

The DSSCs made with the triple-layered photoanode that had frustules incorporated into the top layer showed the best cell performance. The highest efficiency of 6.78% shown by the frustules added solar cell reflects an impressive 101% increase compared to the control cell, implying the effective light harnessing effect of the triple-layer photoelectrode due to the added frustules. The light harvesting efficiency of low-cost DSSC is greatly increased by adding naturally occurring diatom frustules with light-trapping capabilities to the top TiO₂ layer of the photoelectrodes, without degrading the solar cell stability and the photovoltaic characteristics. This study has shown the possibilities and advantages of incorporating diatom frustules in the photoelectrode of DSSC and perhaps also in other areas where light trapping and increased light harvesting is important, such as, optoelectronics, photonics, and photocatalysis. Diatom species with various geometries and symmetries can be researched and contrasted for such applications. Infusing nanostructures of biological origin could open up a new ecofriendly and economically feasible pathway for harnessing solar energy. The study of regular and systematic frustule configurations could thus be interesting, notwithstanding its difficulty.

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CRediT authorship contribution statement

Bandara T.M.W.J.: Conceptualization, Methodology, Project administration, Supervision. S.S. Withanage: Data collection and measurement, 1st draft preparation. K.B. Wijayaratne: Writing – review & editing, Formal analysis. M.A.K.L. Dissanayake: Writing – review & editing, Formal analysis. K.M.S.P. Bandara: Writing – review & editing, Formal analysis. B.-E. Mellander: Writing – review & editing, Formal analysis. M. Furlani: Writing – review & editing, Formal analysis. I. Albinsson: Writing – review & editing, Formal analysis.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:I. Albinsson reports financial support was provided by Swedish Research Council.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.optmat.2023.114514.

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