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Sol-gel based TiO$_2$ thin film deposition on frustules towards facile and scalable manufacturing

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Abstract. Diatom frustules have drawn a lot of attention from engineering researchers in the past decades. As a type of biomaterial, diatom frustules have been applied in a variety of areas such as biosensors and solar cells due to their excellent material and optical properties. Titanium dioxide (TiO$_2$), on the other hand, is also a semiconductor material and photocatalyst, and nanoparticles of which can be found in applications such as dye sensitized solar cells (DSSC). It has been demonstrated that by using diatom frustule-TiO$_2$ composite particles in DSSCs, the performance of the solar cells could be increased. In this paper, we introduce a sol-gel based method to deposit TiO$_2$ layers on the surface of diatom frustules. TiO$_2$ nanoparticles were deposited on the surface of the frustules. After a subsequent annealing process, TiO$_2$ crystal grains were formed. The method in this paper has the potential for scalable manufacturing of frustule-TiO$_2$ composite materials for future solar cell applications.

1. Introduction
Diatoms, photosynthetic microalgae that are ubiquitous in aquatic systems, have attracted significant attention from researchers over the past several decades [1]. The exoskeleton structures (frustules) that enclose their cytoplasm consist of hierarchical micro/nanostructures that are composed of pure silica. The morphology of these structures gives rise to their outstanding mechanical strength, surface area and optical properties [1].

Frustules have been directly employed in applications ranging from sensors in chemical/biosensing [2] to light scatterers [3] in solar cells because of their advanced properties and their compatibility with existing device fabrication techniques [1]. It has been reported that diatom frustules have been used in multiple types of sensors [2], in which the large surface area of diatom frustules was used for effective sensing areas enabling improved performance. Specifically, in energy applications, it has also been reported that diatom frustules were coated with TiO$_2$ nanoparticles and added in dye sensitized solar cells (DSSCs) for enhanced energy harvesting performance [3]. It was believed that diatom frustules acted as “light traps” in these solar cells for scattering light and worked together with the deposited photocatalyst titanium dioxide to increase the efficiency of these devices.

It is believed, however, that the TiO$_2$ nanowires and nanotubes are superior to TiO$_2$ nanoparticles. Furthermore, in studies of nanowire/tube structures, it has been shown that the performance of those containing higher degrees of crystallinities were superior [4]. Compared with the randomly organized TiO$_2$, highly organized crystals of TiO$_2$ can provide more direct channels for electron transmission [4]. To simultaneously take advantage of the light scattering property of diatom frustules and the superior
electron collection/transmission properties of TiO$_2$ nanocrystals, we designed a facile method for TiO$_2$ nanowire growth on diatom frustule’s surface.

Herein, we report the method to deposit thin titanium dioxide layers on the surface of diatom frustules via sol-gel process, and to consecutively anneal the TiO$_2$ layers yielding crystalline structures. The reported method differs from prior work [5] in that a) diatomite was used as the starting material, which is economic and readily available, b) a one-step deposition technique with minimum chemical reaction steps was employed, and c) nanowire structures were formed within the hollow structures of the frustules. The thusly-produced composite particles are believed to have great potential in enhancing DSSC performance.

2. Experimental

![Figure 1](image1)

**Figure 1.** Fabrication of the frustule-TiO$_2$ composite particles. (a) Filtration of the diatomite. (b) TiO$_2$ precursor deposition process. (c) Schematic of the thermal treatment setup.

In this paper, diatomaceous earth (Celite 289, Almeria, Mexico) was initially suspended in deionized water (DI water) and then filtered to obtain diatom frustules (diameter 38 $\mu$m-63 $\mu$m). The frustules were then heat-dried (Figure 1(a)).

To prepare titanium oxide sol-gel, titanium isopropoxide (TIP, 99.999%), ethyl alcohol ($\geqslant$ 99.5%) and oxalic acid ($\geqslant$ 99%) were used (all purchased from Sigma Aldrich). 2.5 ml ethyl alcohol and 25 $\mu$l water were first mixed for 5 min, then 250 $\mu$l TIP was added to the solution. 2 ml of saturated oxalic acid solution was then added slowly as the solution was vigorously mixed at 700 rpm (sol-gel A).

In a slightly different process, sol-gel B was made for comparison purposes. In this process, 500 $\mu$l TIP was first mixed with 5 ml of ethyl alcohol. A mixture of 5 ml alcohol, 100 $\mu$l acetic acid, and 50 $\mu$l water was consecutively added in the as prepared TIP solution. After 5 min of mixing (700 rpm), 2 ml of water was added to the solution drop by drop to form sol-gel B.

The diatom frustules were then submerged in both types of sol-gel and mixed thoroughly for 5 min, followed by filtering and drying for further processing. This process was repeated for 3 times to achieve higher deposition thicknesses. The prepared samples were then annealed under 500 °C with a continuous O$_2$ flow (108 sccm) for 1 h. The heating rate was 20 °C/min. Diatoms processed by sol-gel A were heated with a high temperature (HT) of 750 °C. Diatoms processed by sol-gel B were heated with 980 °C. In both high temperature treatments, 30 min of Ar flow (40 sccm) and 40 min of O$_2$ flow (65 sccm) were used during the annealing process.

3. Results and discussion

Through SEM observation, it was found that most of the debris associated with the diatomaceous earth was filtered out and the remaining frustules were mostly circular micro particles, the size of which ranged from 36.5 $\mu$m to 61.9 $\mu$m. The sub-structures include nano pores with sizes of 20.1±4.2 nm and hierarchical sub-micron pores with sizes ranging from 373.3 nm to 435.8 nm (Figure 2).
The prepared sol-gels differ in their final states. Sol-gel A’s pH value was 1-1.5, while sol-gel B’s pH value was 3. With a higher pH, sol-gel B was more viscous and opaque while A is more liquid-like and transparent.

With both types of sol-gels, thick layers of TiO$_2$ were deposited on the surface of frustules after initial annealing (Figure 3). With sol-gel A, the TiO$_2$ films (type A films) are dense compared with films formed from sol-gel B (type B films) (Figure 3(c) and (f)). In type B films, TiO$_2$ nanoparticles’ diameter was down to ~10 nm, while in type A films, no obvious nanoparticle structures were observed. With sol-gel A, nanowires (diameter ~ 15 nm) and films were formed in the pores (Figure 3(a)). It was also observed that some of the sub-micron pores were blocked. Although a portion of the nano pores were also blocked, they were not affected to the same degree when compared with other pore structures. The pore-filling phenomenon was not observed in the frustules treated with sol-gel B. After high temperature treatments, both types of films showed clear crystal growth (Figure 4). In type A films, crystal grain sizes range from 30 nm to 272 nm. In type B films, the sizes range from 30 nm to 360 nm.

**Figure 2.** Morphology of the extracted frustules. The 3D structure of a frustule is dish-like. (a) Concave side of a frustule. (b, c) Sub-micron pores and nano pores on the concave side of the frustule (zoomed view of (a)). (d) Convex side of a frustule. (e) Sub-micron pores on the convex side of the frustule (zoomed view of (d)).

**Figure 3.** Deposited TiO$_2$ micro/nanostructures after 500 °C annealing. (a)-(d) show type A nano structures in frustule pores ((a) and (b)), thick films on frustule surface ((c)), and corresponding EDX analysis ((d)). (e)-(g) show type B films ((e) and (f)) on frustule and EDX analysis ((g)).
Energy dispersive X-ray spectroscopy (EDX) was performed for initial analysis of the resultant composite particles (Figure 3 and 4). The atomic ratios between oxygen, titanium and silicon varied in the different processes and films. For type A films, before HT treatment, atomic ratios (O:(Ti+Si)) ranged from 2.07 to 2.32, while after HT treatment, the ratio changed to 1.65-1.81, indicating that oxygen deficits may have been created during the HT treatment process. In type B films, this ratio was 1.70-1.91 before HT treatment, and remained relatively static after the HT treatment (1.68-1.88). In type A sol-gel, the excessive hydrogen ions likely inhibited the hydrolysis process between TIP and water molecules, and thusly significantly reduced the consecutive gelation. This property of the solution likely lead to increased diffusion into the nano pores of the diatom frustules, which may have contributed to the formation of nanowires/films in the pores.

4. Conclusion

In this work, a sol-gel based TiO$_2$ deposition technique was introduced for fabricating diatom frustule-TiO$_2$ composite particles. Two types of sol-gel were employed. With a lower pH, the sol-gel solution was able to diffuse into the sub-micro pores to form nanowire/film structures. TiO$_2$ nanoparticles and nanocrystals were formed on diatom frustules’ surfaces. The material preparation method introduced herein has the potential for scalable frustule-TiO$_2$ nanocrystal fabrications, which may be further applicable to a broad range of research areas and novel technologies.

References