J Mater Sci (2011) 46:5665–5671
DOI 10.1007/s10853-011-5517-5

Enlargement of diatom frustules pores by hydrofluoric acid etching at room temperature

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Received: 24 November 2010 / Accepted: 31 March 2011 / Published online: 20 April 2011

Abstract Based on the fact that SiO_2 can dissolve in HF solution, three kinds of diatom frustules were treated with 1% HF solution at room temperature. Given the proper reaction times (0–2 h for the diatoms *Coscinodiscus* and *Navicula*, and 0–3 h for the diatom *Melosira*), the size of the pores on the frustules gradually increased and the structures of the frustules remained. While HF treatment does not affect the composition, chemical bonds, or photoluminescence signature of the diatom frustules, the treatment reduces their surface areas. This method may be beneficial to diatom studies, diatom nanotechnology, and diatom device applications that make use of diatom pores.

Introduction

Diatoms are unicellular, eukaryotic, and photosynthetic algae found in both fresh and salt water. They produce 25% of the oxygen on Earth and display thousands of different morphologies at nano- to millimeter scales [1–3]. Over the last two decades, frustules, which are the cell walls of diatoms composed of amorphous silica, have become a kind of novel material in nanotechnology, attracting the attention of investigators in the fields of biology, biotechnology, physics, material science, and engineering [4–14].

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The regularly arranged pores (areola) of diatom frustules are important microstructures; the pores have sizes ranging from hundreds of nanometers to microns, and may be circular, polygonal, or elongated in shape [1]. Many studies have been carried out on these diaphanous pores with the aim of utilizing them in various applications, such as in gratings or photolithography masks [15], drug delivery with diatom frustules [10], photonic applications of diatom valves [11], fabrication of frustules morphologies by replica molding [8], solar energy uses [13], and so on. The natural propagation of diatoms increases exponentially [16, 17], and provides large quantities of frustules for the abovementioned purposes. The procreation style of diatoms insures that the size and the structure of its pores are unalterable. Thus, pores size is an important factor to be considered in diatom application studies. If the size of the pores is varying within a certain range, the design and fabrication of diatom micro-devices could be more flexible, and the number of diatom species that may be utilized could increase. Pore processing methods combined with a chemical conversion treatment [18–20], nanoparticles adsorption process [21], particle separation [22], or frustule arrangement [23] could increase the engineering value of diatom frustules.

In this article, a convenient and controllable method to enlarge the pores of diatom frustules is sought. Heat treatment is a possible method. Kazuo found that after baking at 800 °C for 2 h, the pores sizes of *Navicula* sp. frustules increased significantly [24]. However, the enlargement of pores is hard to control because long-term heating could melt porous silica and deform the frustule structures. Chemical treatment is another method of enlarging frustule pore sizes. The chemical composition of diatom frustules consists of amorphous SiO_2, which could react with HF. In industrial production, HF is usually used

to etch silicon wafer and glass. In this article, HF treatment as a rapid and controllable method of enlarging diatom frustule pores is proven.

Materials and experimental

Materials and purification

Coscinodiscus and *Melosira* diatoms were respectively obtained from Linjiang Sailite Diatomite Co. Ltd. and Shengzhou Huali Diatomite Co. Ltd. Self-cultivated *Navicula* diatoms were also used. Before the experiments, residual organic materials and metal oxides were removed by heating the diatomite/diatom mixed with sufficient H_2SO_4/H_2O_2 at a ratio of 1:1 at 95 °C for 3 h. After centrifugation, the diatomite/diatom residue was mixed with anhydrous ethanol in a beaker at a mass ratio of 1:10. After ultrasonic cleaning for 30 min at room temperature, the mixture was filtrated with filter cloth to remove micro-impurities and frustule debris. The residual mixture on the filter cloth was composed of clean frustules, and used for the experiments (see Fig. 1). The clean frustules were dried at 80 °C overnight for the following experiments.

Pore enlargement by HF etching

The diatom frustules are composed of SiO_2, which can react with HF according to the following:

$$SiO_2 + 4HF = SiF_4 \uparrow + 2H_2O \quad (1)$$

Based on the reaction above, HF may be used to enlarge the pores of frustules. The following experiment was thus carried out in a ventilated case while avoiding contact with HF acid.

Clean diatom frustules were placed in a plastic beaker mixed with sufficient amounts of 0.5–5% HF solution. After a 0.5–3 h reaction at room temperature, the supernatant was removed by a pipet and the remaining frustules were dried at 120 °C for 3 h for observation.

Results and discussion

The size of the frustules varies because diatoms reproduce by fission. Frustules with similar sizes and pore distributions were thus chosen as reference for observation and analysis. The reference frustules included *Coscinodiscus* frustules 40 μm in diameter, *Melosira* frustules 12 μm in diameter and 15 μm in height, and *Navicula* frustules 15 μm in length and 12 μm in width.

Experimental conditions of HF etching

The orthogonal test was adopted to determine the proper HF concentration and reaction time for pore enlargement. The mass concentration of the HF solution was 0.5–5%, and the reaction times ranged approximately 0.5–3 h. Figure 2 shows the morphological changes in *Coscinodiscus* valves after HF treatment. Figure 2a shows the primitive morphology of the diatom valves. After 2 h of 1% HF treatment, the valve mantle dissolved and the edge of the valve became incomplete (Fig. 2b). After 3 h of 1% HF treatment, the pores near the edge dehisced, and the valve lost its round shape (Fig. 2c). After 2 h reaction with 2% HF, large areas of the valve edge dissolved, and the valve became thin and small (Fig. 2d). After 2 h treatment with the 5% HF solution, the structures of the pores and valves were seriously destroyed (Fig. 2e). These results show that HF rapidly reacts with frustules, even at low mass concentrations. The 1% HF solution was chosen as an etchant for the following experiments to insure easy control of the reaction.

Figure 3 shows *Melosira* and *Navicula* frustules treated with 1% HF solution. Figure 3a and b shows *Melosira* frustules after 2 and 3 h of treatment. Compared with

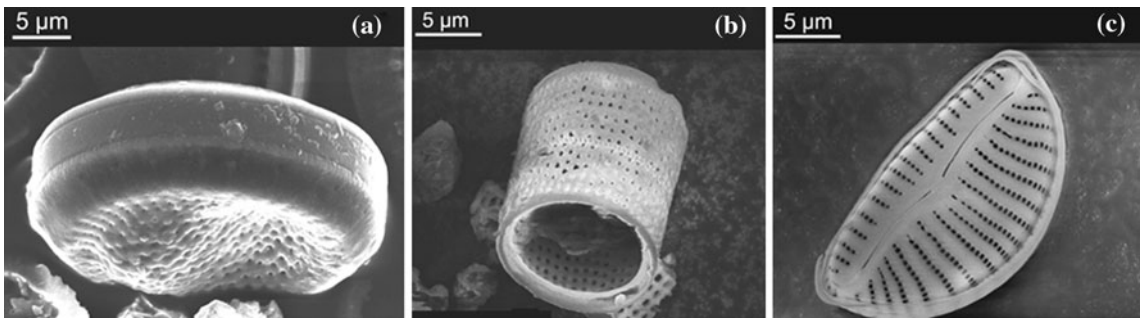

Fig. 1 SEM images of diatom frustules after purification treatment: the frustule of diatom *Coscinodiscus* sp. (**a**), *Melosira* sp. (**b**) and *Navicula* sp. (**c**)

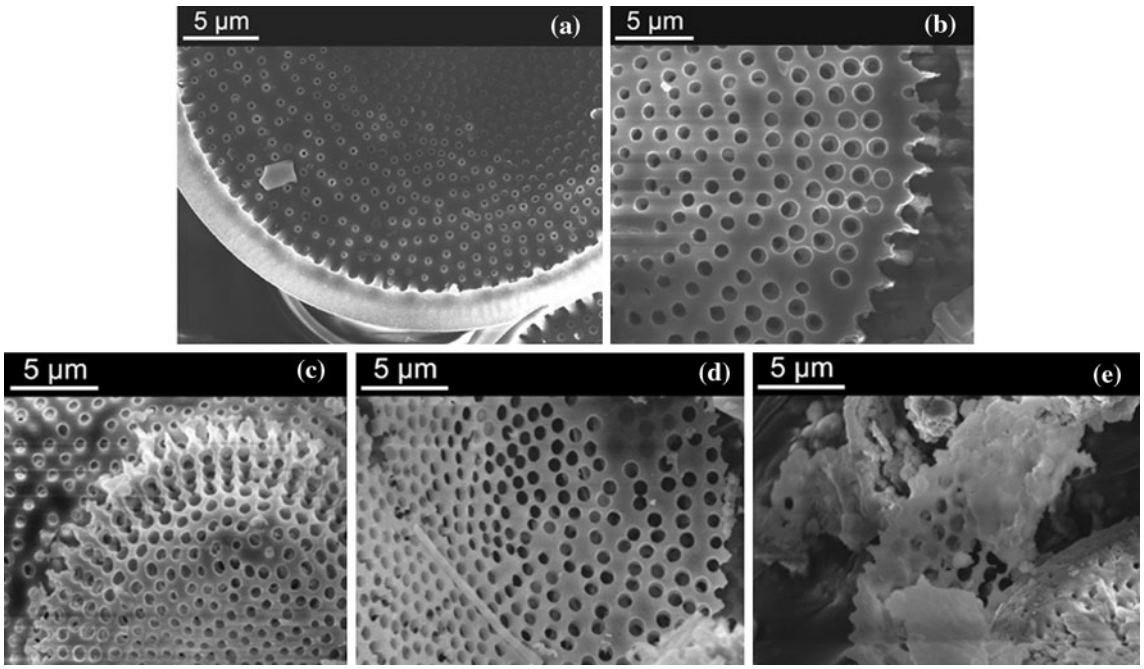

Fig. 2 SEM images of diatom frustules during HF erosion: original *Coscinodiscus* valve (**a**), valve after a 2-h reaction of 1% HF solution (**b**), valve after a 3-h reaction of 1% HF solution (**c**), valve after a 2-h reaction of 3% HF solution (**d**), valve after a 2-h reaction of 5% HF solution (**e**)

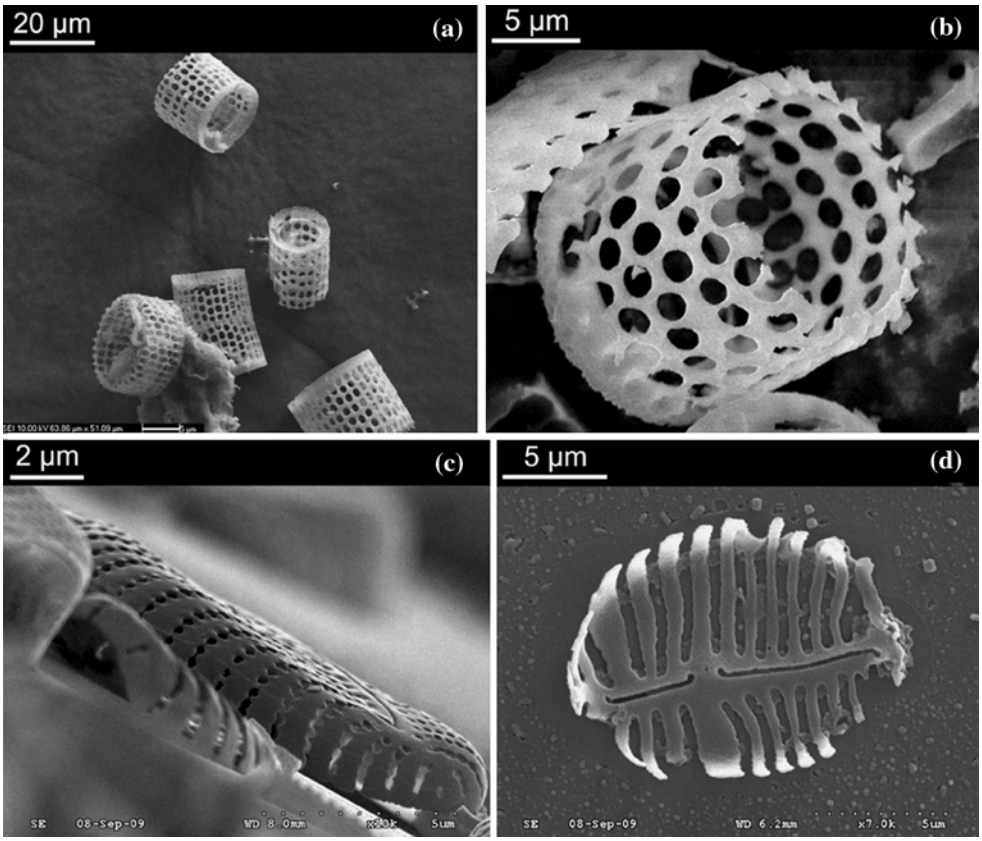

Fig. 3 SEM images of diatom frustules after 1% HF treatment: *Melosira* frustules reacted after 2 h (**a**) and 3 h (**c**), *Navicula* frustules reacted after 1 h (**c**) and 2 h (**d**)

Fig. 1b, the sizes of the pores in Fig. 3a and b increased and the thickness of the frustules decreased. The structure of the *Melosira* frustules appeared to be fragile after 3 h of HF erosion (Fig. 3b). Figure 3c and d shows *Navicula* frustules after 1 and 2 h reaction. In these images, the pores were observed to expand and join; and the frustules gradually lost their original shape.

To protect the original structure of the diatom frustules, the proper reaction times for pores enlargement are 0–2 h for *Coscinodiscus* and *Navicula* diatom, and 0–3 h for *Melosira* diatom in 1% HF solution at room temperature.

Pore observations after HF etching

After the selected reaction conditions were applied, SEM micrographs of the reacted frustules were taken and changes in their pore size and structure were observed.

Figure 4 shows the pores of *Coscinodiscus* frustules before and after 1% HF treatment. The resulting frustules were all 40 μm in diameter. As shown in Fig. 4a and b, the original pores were about 500 nm in diameter with light-colored rings (see arrows in Fig. 4b). After half an hour of HF treatment, the pores became slightly enlarged, and the light-colored rings disappeared, revealing it is a thin film composed of SiO_2. The thin SiO_2 ring may form a protective film over the pores, because pores expanded faster in the HF solution after the ring disappeared. As the reaction time increased, the diameter of the pores gradually expanded to 900 nm (see Fig. 4c–h) and the surface of the frustules appeared smoother.

Figure 5 shows the pores of *Melosira* and *Navicula* frustules before and after 1% HF treatment. The reference frustules are *Melosira* frustules 12 μm in diameter and 15 μm in height and *Navicula* frustules 15 μm in length

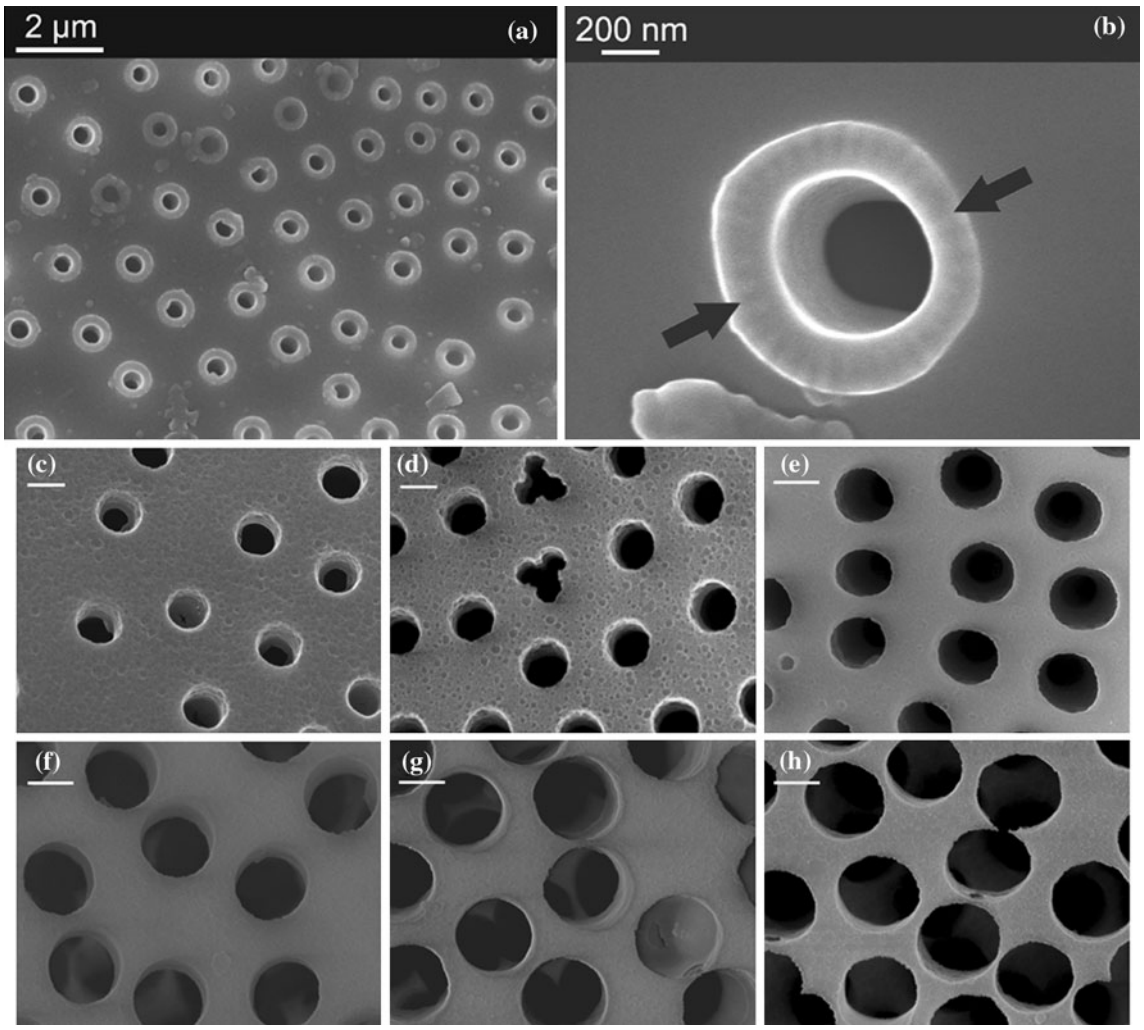

Fig. 4 SEM images of *Coscinodiscus* valves before and after 1% HF treatment. Pores of original *Coscinodiscus* frustules (**a**) and enlarged view of the pore (**b**), the *arrows* in **b** is a light-colored ring around the pore, pores after HF etching for 0.5 h (**c**), 1 h (**d**), 1.5 h (**e**), 2 h (**f**), 2.5 h (**g**) and 3 h (**h**). The *scale bars* in **c**–**h** are 500 nm

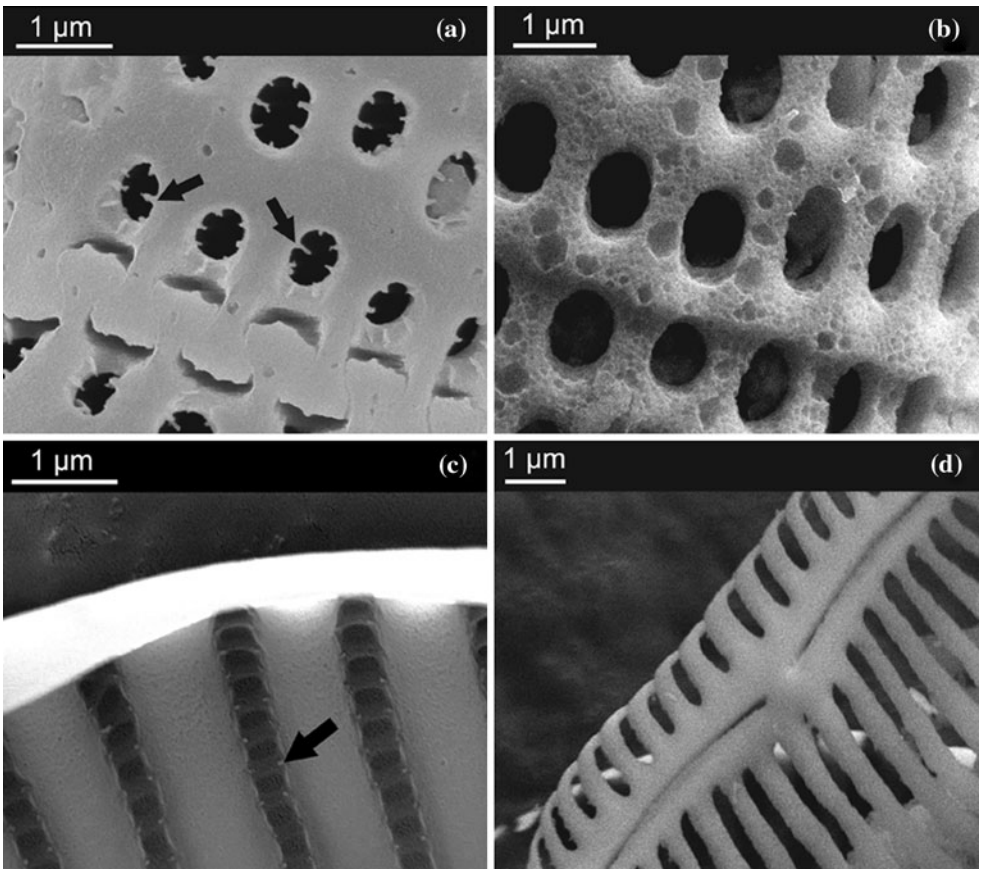

Fig. 5 SEM images of *Melosira* and *Navicula* frustules before and after 1% HF treatment. Pores of original *Melosira* frustule (**a**) and *Navicula* frustules (**c**), the *arrows* in **a** are tiny teeth in pores, the *arrow* in **c** is a septum dividing the pores. Pores of *Melosira* frustules after 1 h of 1% HF treatment (**b**), pores of *Navicula* frustules after 1 h of 1% HF treatment (**d**)

and 12 μm in width. As shown in Fig. 5a, the original pores of the *Melosira* frustules are shaped as irregular ellipses (with minor axes of about 500–600 nm), with seven inward tiny teeth (see the arrows in Fig. 5a). After 1 h of HF treatment, the pores expanded to 700–800 nm in terms of minor axis diameter (Fig. 5b), inside of which the tiny teeth vanished, and the surface of the *Melosira* frustules became rough with many small pits. Figure 5c shows the reverse side of the *Navicula* frustules, with pores about 250 nm in diameter and divided by septa less than 50 nm in thickness (see the arrow in Fig. 5c). After 1 h of HF treatment, the septa dissolved, the pores connected, and the *Navicula* frustules presented different rib-like structures.

Physical and chemical property changes of frustules after HF etching

To determine whether or not the physical and chemical properties of the frustules changed after HF treatment, a series of contrast tests was carried out, including a photoluminescence (PL) spectra scan, an infrared spectra scan, and surface area tests.

The PL and infrared spectra of the frustule samples before and after HF treatment were scanned to determine whether or not the chemical compositions and bonds of the frustules changed. Correlation studies have shown that both the optical intensity and peak positions of the PL emission from the diatom frustules are affected by surrounding gases and organic vapors [25]. Figure 6 shows a set of room temperature PL spectra from *Melosira* frustule samples. Induced by ultraviolet light at a wavelength of 256 nm, the PL spectra of the original frustules and treated frustules present similar peak positions and similar optical intensities. The PL spectra of the *Coscinodiscus* and *Navicula* frustules present similar results. No SiF_4 or other substances were found to have adsorbed onto the frustules after HF treatment, and the PL spectra of the diatom frustules were not affected by changes in pore size or frustule structures. Figure 7 shows a set of infrared spectra obtained from *Coscinodiscus* frustules before and after HF treatment. A comparison of the spectra indicates that no chemical bonds changed during the HF treatment. The infrared spectra of the *Melosira* and *Navicula* frustules conform to those in Fig. 7.

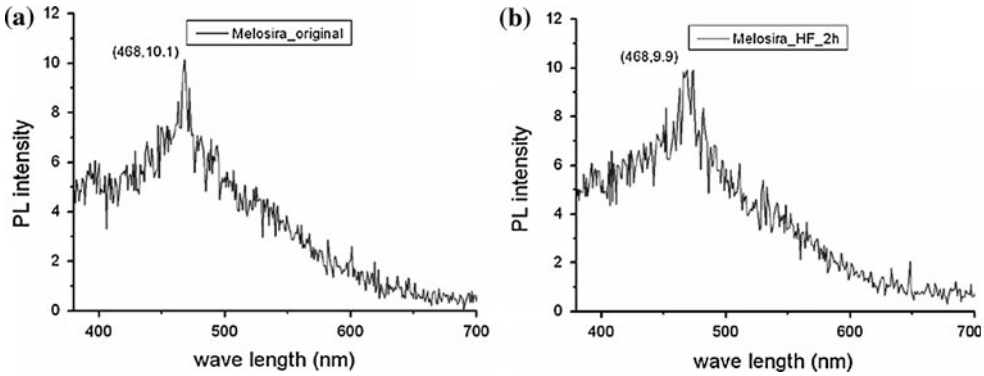

Fig. 6 Photoluminescence spectra of the *Melosira* frustules in air. The samples for spectrum **a** are original *Melosira* frustules, the samples for spectrum **b** are *Melosira* frustules treated by 1% HF for 2 h

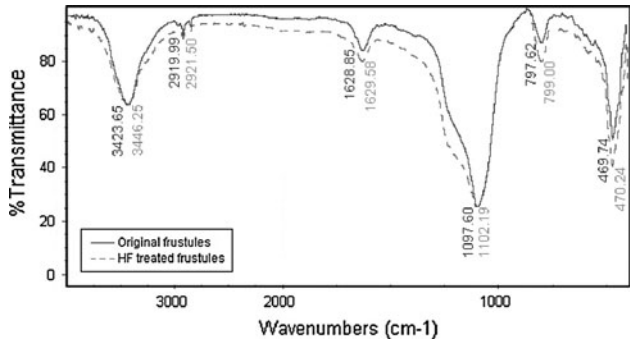

Fig. 7 Infrared spectrum of *Coscinodiscus* frustules before and after HF treatment. The two samples are separately original *Coscinodiscus* frustules and *Coscinodiscus* frustules treated by 1% HF for 2 h

Surface area is an important property that affects the adsorption capacity of the diatom frustules. The surface areas of the *Coscinodiscus* and *Melosira* frustule samples were measured from nitrogen gas adsorption using the BET method. Figure 8 shows that the surface area of the original

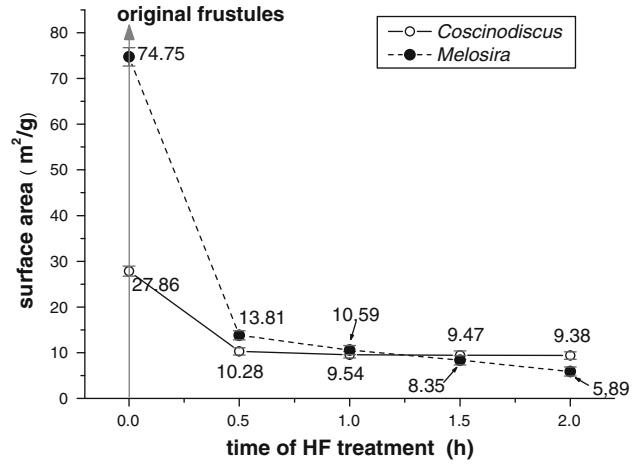

Fig. 8 The surface areas of the diatom frustules (*Coscinodiscus* and *Melosira* sp.) before and after HF treatment. The *error bars* indicate the range of surface area calculated for each sample

Coscinodiscus frustules was 27.86 m^2/g, sharply decreasing to 10.28 m^2/g after 0.5 h, and slowly decreasing to 9.38 m^2/g over the next 1.5 h. The *Melosira* frustules had an original surface area of 74.7 m2/g, sharply decreasing to 13.8 m^2/g after 0.5 h, and slowly decreasing to 5.9 m^2/g over the next 1.5 h. Original *Melosira* samples had larger specific surface areas because they had smaller and thinner frustules and more complex pore structures compared with *Coscinodiscus* samples. The declines in the two lines at 0.5 h indicate that the nanopores on the surfaces of frustules suffered extensive damage after short periods of HF treatment. As the reaction time increased, the inner wall of the pores increased and the quality of a single frustule decreased, thereby increasing the specific surface area of the frustule samples. Meanwhile, the area of the frustule surface (excluding the inner wall of the pores) decreased (Figs. 4a–h, 5a, b) and the nanopores inside the frustules damaged, reducing the surface area of the sample. The two factors work together to slowly reduce the surface area of a frustule sample. In conclusion, the HF treatment reduced the surface areas of the frustules within a short span of time and weakened their adsorption capacity.

The tests above indicate that HF treatment does not change the chemical composition and chemical bonds of the diatom frustules but reduces their surface area.

Conclusions

HF etching is an effective method of enlarging the pores on diatom frustules. Pores treated with 1 wt% HF solution at room temperature gradually increased in size. The structure of the frustules was maintained under the proper reaction times (0–2 h for *Coscinodiscus* and *Navicula* diatoms, and 0–3 h for *Melosira* diatom). HF treatment was found to have no effect on the composition, chemical bonds, and photoluminescence signatures of diatom frustules aside from reduction of their surface area. The method proposed here might be useful in the study of diatom pores, diatom nanotechnology, and device applications that make use of diatom pores.

Acknowledgements This work was supported by the National Science Foundation of China (No. 50805005), the 863 Project of China (No. 2007AA04Z353, 2009AA043804), and the Innovation Fund Project for Graduate Student of Beihang University.

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