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Sensors and Actuators B 130 (2008) 396–399

SENSORS AND ACTUATORS B CHEMICAL

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Marine diatoms as optical chemical sensors: A time-resolved study

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Available online 15 September 2007

Abstract

Marine diatoms are microscopic algae living in aquatic environment; their skeleton, made of amorphous silica, possesses a complex geometrical structure that presents holes on different length scales in a fractal-like fashion, achieving a high surface-to-volume ratio and making them good candidates for gas detecting purposes. Indeed, different gas species can influence diatoms' photoluminescence emission according to their different polarizing abilities. In particular, to exploit marine diatoms as optical nitrogen dioxide sensors and in order to get a better insight on the nature of the photoluminescence quenching process induced by the gas molecules, continuous-wave and time-resolved photoluminescence studies have been carried out, showing that nitrogen dioxide affects only the photoluminescence yield without altering the dynamics of the recombination process.

Keywords: Natural nanostructured materials; Chemical sensing; Photoluminescence; Quenching mechanisms

1. Introduction

In the last decades a big effort has been spent in developing new techniques to design complex top-down nanostructures for chemical sensing.

A completely different point of view consists in exploiting nanostructures that nature has already realized and optimized during its evolution. In particular, diatoms are microscopic algae enclosed in amorphous silica shells that aggregate, forming complex and intricate skeletons, called *frustule*. Diatoms populate both fresh and salt water and they can be found even in damp grounds. There is plenty of different diatom species (about 10^5 different families), each possessing its own frustules morphology. Due to their peculiar structures, the large variety of different morphologies and their robustness, a widespread interest about diatoms and their possible application in nanosciences and nanotechnology has been growing [2–4]. Recently [1], gas sensitive optical properties of silica skeleton in marine diatoms *Thalassiosira Rotula Meunier* have been reported; photoluminescence (PL) emission of these nanostructures was found to be quenched or enhanced by the presence of gases or organic vapors, depending on their polarizing ability.

In the present work, we focused our attention on the *Thalassiosira Rotula*'s ability in detecting nitrogen dioxide presence; the consequent photoluminescence quenching was detected by means of continuous-wave photoluminescence (CWPL) technique. Moreover, in order to gain a deeper insight into the nature of the gas adsorption effect, a study of recombination dynamics has been carried out, using time-resolved photoluminescence (TRPL) technique.

2. Experimental

In order to analyze the optical properties of diatom's frustules, a cleaning process has been carried out. A mixture of acids of different strength has been used in order to dissolve the organic component of diatoms (it should be pointed out that in what forthcomes we will denote diatoms their frustules cleaned off the whole organic material). Some micro- and nanostructured valves and less silicified frustules may dissolve in strong acids. It is thus very important to accurately calibrate the strength of the mixture to avoid silica skeleton damages. The *Thalassiosira rotula* possesses highly silicified frustule and therefore the cleaning procedure may use highly concentrated acid. Samples analyzed in this work were cleaned using the following steps:

(i) 50 ml of a highly concentrated, fixed phytobenthos sample was centrifuged at 3000 rpm for 10 min;

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doi:10.1016/j.snb.2007.09.012

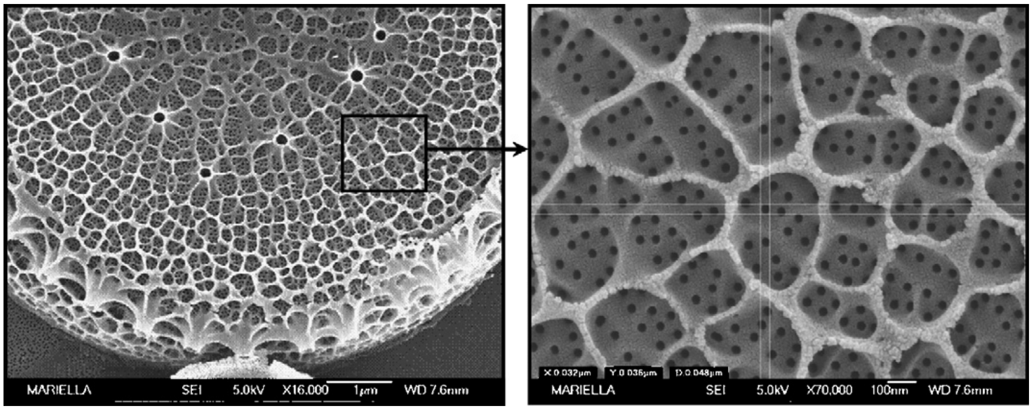

Fig. 1. Microscope photographs of the sample of *Thalassiosira Rotula Meunier* with different zooming factors. Holes do occur at different length scales.

(ii) the pellet was washed in distilled water five times to remove the excess of fixative;
(iii) 2 ml of pellet was mixed with a similar volume of 97% sulphuric acid for 5 min at 60 °C;
(iv) the acid was removed and the pellet washed again in distilled water five times.

Since their high robustness, frustules are not damaged by the cleaning process, after which the silica skeletons are suspended in distilled water. Samples were finally obtained by dropping the suspension on a silicon substrate and waiting until the complete evaporation of water (microscope photographs of our samples are reported in Fig. 1).

The samples were then placed on a hot finger and enclosed inside a test chamber equipped with quartz windows in order to optically access the sample. The volume of the test chamber is of 0.2 l and during the whole experiment the gas flux was kept constant at 0.3 l/min, in order to avoid turbulences within the test chamber atmosphere. The working temperature during the whole experiment was kept constant at the room temperature (RT). A mass flow control system provided calibrated mixing of synthetic air and NO_2 inside the chamber, allowing to change the NO_2 concentration inside the chamber.

CWPL spectra were obtained by using the UV spectral line of an He–Cd laser (325 nm wavelength) as excitation source. The emission light spectra of the samples were collected by using a focusing lens system and the spectral intensity was acquired by means of a spectrometer equipped with a 600 grooves/mm grating, blazed at 500 nm and coupled with a Peltier cooled CCD camera. In time-resolved photoluminescence experiment the frequency tripled pulses of a mode-locked Nd-YAG laser (355 nm wavelength, 25 ps time duration) were employed for exciting the sample and the temporal profile of the spontaneous emission was acquired by means of a streak camera. The emission wavelength was selected using a set of bandpass filters with a spectral width of 40 nm.

3. Results and discussion

As already mentioned above, in a recent work [1], PL emission of *Thalassiosira Rotula* skeletons has been observed, paying attention to the spectrum alterations due to the interaction with electrophilic and nucleophilic gases with different polarizing abilities. In the present work we focused our attention on the photoluminescence quenching due to the *Thalassiosira*'s interaction with a polluting chemical species, the nitrogen dioxide, paying some attention to its optical detecting ability.

In Fig. 2 the PL spectra are reported for different NO_2 dilution in dry air: without gas (only dry air), 167 ppb and 10 ppm. The system strongly reacts to the gas presence, quenching its photoluminescence, even at the slightest gas concentrations. In Fig. 3 the maxima of the PL spectrum (normalized by the maximum value in dry air) *versus* NO_2 concentration are reported. As previously pointed out, it is possible to recognize that the PL is sensibly quenched even by gas amounts of about 100 ppb (see the inset in Fig. 3), making thus *Thalassiosira* a highly sensitive and reactive candidate for optical gas sensing purposes.

In order to investigate the nature of the quenching mechanism resulting by the interaction between the nanostructure and the gas species, we further performed TRPL measurements. As a matter of fact, the quenching process can follow two different pathways [9], known as *static* and *dynamic* quenching. If the quencher gas molecules lower the probability of the photoexcitation event the quenching is said to be *static* while if they

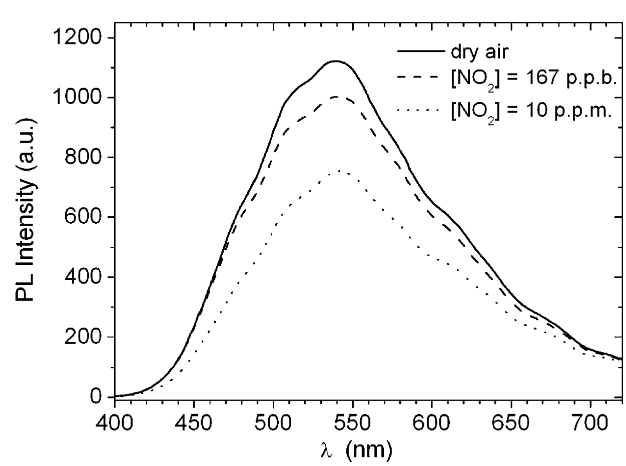

Fig. 2. *Thalassiosira*'s photoluminescence spectrum in dry air (continuous line), in 167 ppb of NO_2 in dry air (dashed line) and in 10 ppm of NO_2 in dry air (dotted line).