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Sensitized Generation of Singlet Oxygen by Allylamine-Terminated Hydrophilic Porous Si

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We studied the sensitized generation of singlet oxygen by surface-modified hydrophilic porous Si. Porous Si consisting of a network of Si nanocrystals acts as an efficient photosensitizer for the generation of exited state molecular oxygen called singlet oxygen. Singlet oxygen is widely used in chemistry and biology. One of the possible applications of it is photodynamic therapy of cancer (PDT). However, as-prepared porous Si is hydrophobic and thus cannot be used as singlet oxygen photosensitizer in aqueous solution. Therefore, in this work, we modified the surface of porous Si by organic molecules (allylamine). We found that allylamine-terminated hydrophilic porous Si holds the photosensitization ability, although the efficiency of singlet oxygen generation is reduced by the modification.
Key words: singlet oxygen, silicon nanocrystals, porous silicon, surface modification

1. Introduction

Porous Si (PSi) consisting the network of nanometer-size Si crystals (Si nanocrystals) acts as an efficient photosensitizer for the generation of excited state molecular oxygen called singlet oxygen [1]. Singlet oxygen is highly chemically reactive and widely used for chemical, biological and medical applications such as photodynamic therapy (PDT) [2]. Sensitized generation of singlet oxygen by Si nanocrystals is caused by triplet-triplet annihilation type energy transfer from quantum-confined excitons in Si nanocrystals to oxygen molecules. The energy transfer is the most efficient at 1.63 eV, which corresponds to the energy between the ground triplet state ($^3\Sigma$) and the second lowest excited singlet state ($^1\Sigma$) of oxygen molecules.

Most of applications of singlet oxygen mentioned above is required its generation in aqueous solutions. However, fresh PSi is strongly hydrophobic due to H-termination. In our previous work [3], we prepared hydrophilic PSi by modification of the surface with polyethylene oxide (PEO). However, the singlet oxygen generation efficiency was drastically reduced. An increased distance between Si nanocrystals and oxygen molecules by PEO molecules is considered to prevent the energy transfer. To shorten the distance, in this work, we choose allylamine as organic molecules for the surface modification [4]. Allylamine is much shorter than PEO and efficient singlet oxygen generation composed to PEO-terminated PSi is expected.

2. Experimental Setup

PSi powder was prepared by electrochemical etching of a (100) oriented B-doped Si wafer with a resistivity of 10-15 Ω cm. The etching solution was a 55:45 by volume mixture of hyfrofluoric acid (49 wt.% in water) and ethanol. The etching current density and etching time were 60 mA/cm^2 and 3 h, respectively. As-prepared PSi powder is H-terminated. To realize hydrophilic PSi powder, we modified the surface termination with allylamine molecules following the procedure in a literature [4]. In a typical case, 0.05 M H_2PtCl_6 (240 μL) in isopropanol as the catalyst, 12 mL of allylamine and 50 mg of PSi powder were mixed with 85 mL of isopropanol. The mixture was stirred with a magnetic stirrer in Ar gas flow for appropriate times (0-60 min). The solvent was then removed by a suction filtration and a desiccator.

The surface modification is expected to decrease the energy transfer efficiency, because it increases the distance between excitons and oxygen molecules. Therefore, complete covering of the surface by organic

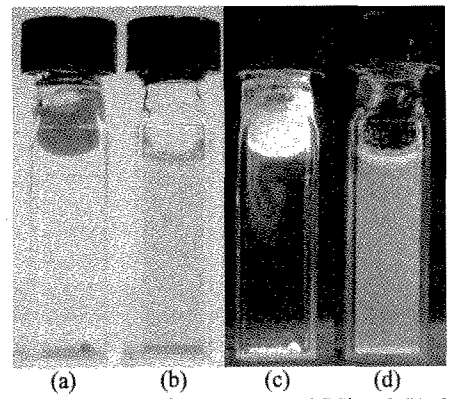

Fig.1. Photographs of (a) as-prepared PSi and (b) the PSi with reaction time of 5 min in water under day light. Photographs of (c) as-prepared PSi and (d) PSi with reaction time of 5 min in water under UV irradiation.

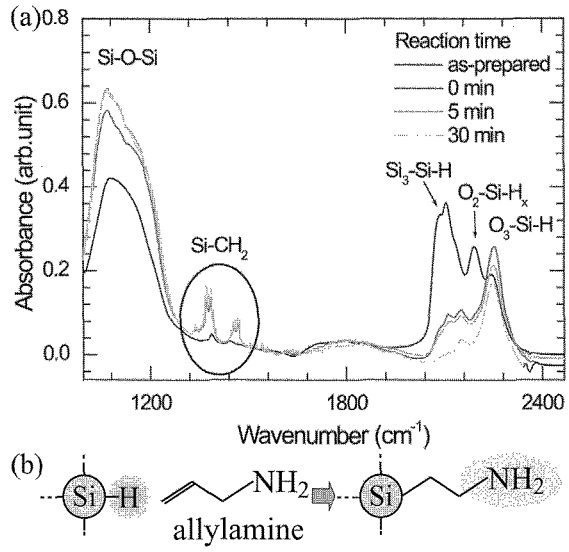

Fig.2. (a) Infrared absorption spectra of allylamine-treated PSi. The reaction time is shown in the figure. (b) Schematic illustration of surface modification by allylamine.

molecules is considered to be not appropriate to reconcile hydrophilicity and photosensitization ability. To find an optimal coverage to compromise these requirements, we changed the reaction time from 0 to 60 min.

For photoluminescence (PL) measurements in gas or in vacuum, PSi powder was put into a small hole (1 mm in diameter) in an aluminum plate, and the plate was mounted on a cold-finger of a cryostat. For low temperature PL measurements, the cryostat was first evacuated to 5×10^{-4} torr and then filled by O_2 gas to 300 torr at 150 K. For PL measurements in water, PSi powder was inserted into a quartz cuvette filled with distilled water. During optical measurements water was permanently mixed using a magnetic stirrer. For the excitation of PL spectra, the 457.9 nm line of an Ar^+ laser was used. PL spectra in near-infrared (NIR) and visible ranges were recorded using a single monochromator equipped with a liquid N_2 cooled InGaAs near-infrared diode array and with a liquid N_2 cooled charge-coupled device, respectively. The surface chemical composition of Si nanocrystals was analyzed using fourier transform infrared spectroscopy (FTIR) by a diffuse reflection geometry.

3. Results and Discussion

Figure 1 shows photographs of (a)(c) as-prepared PSi and (b)(d) the sample with reaction time of 5 min in day light ((a),(b)), and under UV irradiation ((c),(d)) in water. As-prepared PSi ((a),(c)) is not dispersed in water, while after 5 min treatment, it is well dispersed ((b),(d)). This suggests that the surface is modified. As can be seen in Figure 1(d), allylamine-treated PSi shows strong luminescence in visible range. Surface modification can also be confirmed by infrared (IR) absorption spectroscopy. Figure 2(a) shows IR absorption spectra obtained for as-prepared and surface modified PSi. The reaction time is changed from 0 (dipped into reaction solution for a very short period) to 30 min. The band around 1080 cm^{-1} is due to Si-O-Si stretching mode and that around 2100 cm^{-1} is due to vibration modes of Si-H bonds on the surface of PSi [4]. After the surface

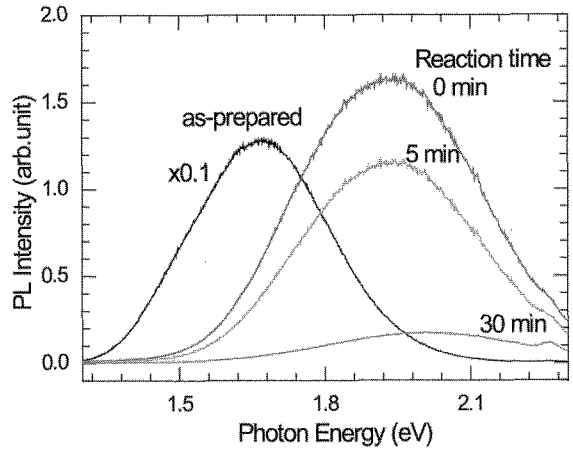

Fig.3 PL spectra of as-prepared PSi and allylamine-treated PSi with various reaction time in water.

modification, the intensity of Si-O stretching mode does not change significantly which indicates that PSi is not oxidized during the surface treatment. On the other hand, Si-H vibration modes, especially Si_3-Si-H mode, become weaker and new peaks appear around 1400 cm^{-1} due to Si-CH_2 symmetric bending vibration [5]. This is the evidence that the surface of PSi is modified with allylamine molecules. The schematic illustration of surface modification by allylamine is shown in Figure 2(b). After 30 min treatment, Si-H vibration modes still remain, indicating that the surface of PSi is only partially modified.

Figure 3 shows PL spectra in water of as-prepared and allylamine-treated PSi after various reaction time. After the surface modification, PL intensity becomes weaker and the spectrum shifts to higher energy even after 0 min treatment. This is possibly caused by the modification of dielectric constant around the PSi by allylamine. After 30 min treatment, PL intensity is much weaker than that of 0 and 5 min treated PSi, while their IR absorption spectra are nearly identical. One possible reason for the PL quenching is the increment of dangling bonds during the allylamine treatment. Dangling bonds act as channels for non-radiative recombination of excitons resulting in the PL quenching[6].

The direct evidence of singlet oxygen generation is the observation of the NIR PL at 0.98 eV, which corresponds to the transition from $^1\Delta$ state to $^3\Sigma$ state of oxygen molecules. In the present allylamine-treated PSi, the PL was not detected. This suggests that singlet oxygen generation efficiency is decreased by the modification.

Although NIR emission from singlet oxygen was not detected, this does not always mean that the sensitization effect is completely lost. The indirect evidence of singlet oxygen generation is the observation of resonant quenching of PL from Si nanocrystals due to energy transfer from excitons to oxygen molecules. Resonant energy transfer to the $^1\Sigma$ state of O_2 molecules results in the quenching of PL from Si nanocrystals around the energy of the $^1\Sigma$ state (1.63 eV).

Figure 4 shows the PL spectra of allylamine-treated PSi in O_2 gas (300 Torr) divided by those in vacuum (I_{oxygen}/I_{vac}) at 150 K. We can clearly see the quenching centered around 1.6 eV. The observation of the resonant quenching provides the evidence that singlet oxygen is

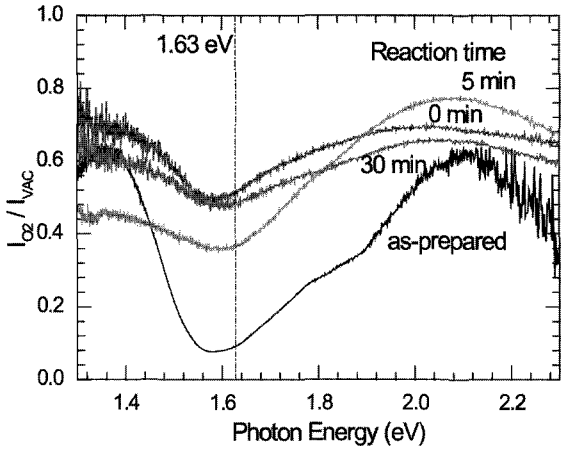

Fig.4. PL spectra taken in O_2 atmosphere divided by that in vacuum (I_{oxygen}/I_{vac}) at 150 K. The reaction time is shown in the figure.

generated by the energy transfer from allylamine-treated PSi in gas atmosphere. The resonant quenching is the most significant for 5 min treated PSi. However, the level of the quenching is decreased by the modification, and it was not detected in aqueous solution.

4. Conclusion

We prepared PSi with hydrophilic surface by surface modification with allylamine and demonstrated that the hydrophilic PSi has photosensitization ability for O_2 molecules, although the efficiency of the sensitization is reduced. There was no drastic improvement of the efficiency compared with modification by PEO. The next step is to improve the sensitization efficiency by keeping the hydrophilicity and to demonstrate the formation of singlet oxygen in aqueous solution directly by detecting NIR PL. In order to realize it, defect density should be decreased by improving the surface treatment process. This work is now under way.

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