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Photosensitization of oxygen molecules by surface-modified hydrophilic porous Si

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Abstract. Hydrophilic porous Si is prepared by surface modification with polyethylene oxide (PEO) molecules. The surface modification is confirmed by infrared absorption spectroscopy and photoluminescence spectroscopy. The effect of surface modification on the efficiency of photosensitization of oxygen molecules, i.e., the efficiency of singlet oxygen generation, is studied. The PEO-terminated hydrophilic porous Si is shown to hold the photosensitization ability although the efficiency is reduced by the modification.

PACS. 71.35.Gg Exciton-mediated interactions – 33.50.Hv Radiationless transitions, quenching

1 Introduction

It has been demonstrated recently that nanometer-size Si crystals (Si nanocrystals) act as an efficient photosensitizer for the generation of a kind of active oxygen species, called singlet oxygen [1]. Singlet oxygen is involved in a variety of oxidation reactions in organic chemistry and biology [2–4]. One of the most important applications of singlet oxygen is the photodynamic therapy of cancer [5]. The sensitization of oxygen molecules by Si nanocrystals is made by the triplet-triplet annihilation type energy transfer from quantum-confined excitons in Si nanocrystals to oxygen molecules during the collision of oxygen molecules with the surface of Si nanocrystals in gas or in liquids [6–9]. Because of the restriction of the energy conservation rule, the energy transfer is possible only for Si nanocrystals in a particular size range, i.e., Si nanocrystals having band gap energies around 1.63 eV, which corresponds to the energy difference between the second excited $^1\Sigma$ state to the ground $^3\Sigma$ state of oxygen molecules. Therefore, the new function of Si nanocrystals, i.e, photosensitization to oxygen molecules, is a direct consequence of the quantum size effects.

Most of applications of singlet oxygen are in the environment of aqueous solution. The singlet oxygen formation by Si nanocrystals in aqueous solution has been demonstrated by two approaches. The first one is the detection of resonant quenching of photoluminescence (PL) from Si nanocrystals around 1.63 eV due to non-radiative energy transfer from excitons to oxygen molecules [9]. The other direct evidence is the observation of near-infrared (NIR) PL from singlet oxygen. In a previous work, we showed that when Si nanocrystals are put in oxygen-saturated heavy water and illuminated by light, a sharp PL peak is observed at 0.98 eV, and the intensity increases with increasing the amount of Si nanocrystals in water [14]. These results unambiguously imply that excitons in Si nanocrystals can transfer energy to O_2 molecules dissolved in water during short collision time and singlet oxygen is generated.

Until now, a variety of methods have been developed to synthesize Si nanocrystals. For the sensitization of oxygen molecules, their easy access to the surface of Si nanocrystals is required, and thus Si nanocrystals with open structures are indispensable. Si nanocrystals satisfying this condition can be prepared by both bottom-up and top-down approaches. The bottom-up approaches consist of chemical synthesis [10], laser pyrolysis of silane gas [11] and aerosol procedure [12]. The examples of top-down approaches are anodization of bulk Si wafer, i.e., porous Si [13] and stain-etching of bulk Si. Although Si nanocrystals prepared under different methods usually show similar PL properties, the quality (crystallinity) is different depending on the preparation procedure. For singlet oxygen formation by energy transfer, very high crystallinity and long exciton lifetime are required. To our experience, porous Si exhibits the highest singlet oxygen generation efficiency.

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Previous studies on singlet oxygen formation by porous Si have been done by using as-prepared H-terminated hydrophobic porous Si [9,14]. However, for biological application, they should be hydrophilic to prevent aggregation and precipitation in a biological environment. Water-soluble and luminescent Si nanocrystals have been prepared by chemical synthesis [10]. However, reported luminescence lifetime of chemically synthesized Si nanocrystals is of the order of ns, which is much faster than the energy transfer time and thus they are not suitable for the present application.

In this work, we employ porous Si, the luminescence lifetime of which is several tenth of μs at room temperature, as a starting material and realize hydrophilicity through the surface modification by organic molecules. The main purpose is to demonstrate that surface-modified and hydrophilic porous Si holds the ability to sensitize oxygen molecules. We show that although the efficiency is decreased, the surface-modified porous Si exhibits the sensitization effect.

2 Experimental procedure

Porous Si was prepared by electrochemical etching of a (100) oriented boron-doped bulk Si wafer with a resistivity of 11–15 Ω cm in a 55:45 by volume mixture of hydrofluoric acid (46 wt% in water) and ethanol. The current density and etching time were 80 mA/cm^2 and 3 h. With this preparation condition, porous Si layers are cracked and become powder during drying. Porous Si powder was further crushed in a mortar before chemical treatments. As-prepared porous Si powder is H-terminated and shows strong hydrophobicity. Hydrophilic porous Si powder was prepared by modifying the surface Si-H bonds through reaction with 3,6,9-trioxa-dodecene-1-ol (Fig. 1a). In a typical experiment, 3 ml of 3,6,9-trioxa-dodecene-1-ol and 40 mg of Si powder were mixed with 30 ml of toluene. The mixture was then refluxed for appropriate times (5 min–8 h). After modification of the surface, the powder was purified by centrifugation using toluene (three times). The solvent was then removed using a rotary evaporator to produce polyethyleneoxide (PEO)-terminated hydrophilic Si powder.

The energy transfer from excitons in Si nanocrystals to oxygen molecules is made by triplet-triplet annihilation type electron exchange process. 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 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 5 min to 8 h.

For PL measurements in gas or in vacuum, porous Si powder was put into a small hole (1 mm in diameter) in an aluminum plate, and it 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, porous Si 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 ion laser was used. PL spectra in NIR and visible ranges were recorded using a single monochromator equipped with a liquid N_2 cooled InGaAs NIR diode array and with a liquid N_2 cooled Si charge coupled device, respectively. The surface chemical composition of Si nanocrystals was analyzed using FTIR measurements by a diffuse reflection geometry.

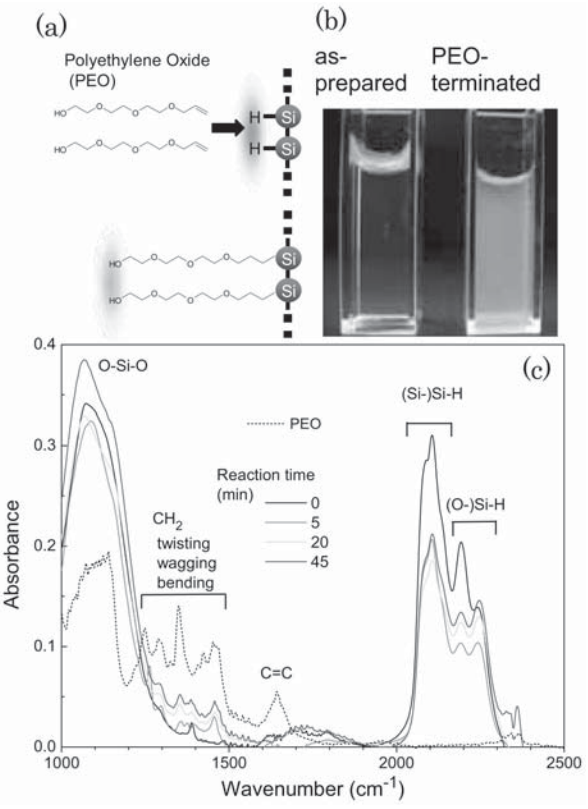

Fig. 1. (a) Schematic illustration of the procedure used to change the surface chemistry of porous Si from hydrogen to PEO (b) pictures of as-prepared (left) and PEO-terminated (right) porous Si in water. The reaction time is 5 min. (c) Infrared absorption spectra of porous Si powder. The reaction time is changed from 0 to 45 min. As a reference, the spectrum of PEO powder is shown with a dashed curve.

3 Results and discussion

As can be seen in Figure 1b, as-prepared porous Si is hydrophobic and is not dispersed in water, while after 5 min treatment, it is well dispersed, suggesting that the surface is modified. This can be confirmed by infrared (IR) absorption spectroscopy. Figure 1c shows IR absorption spectra obtained before (0 min reaction time) and after the surface modification. The reaction time is changed from 5 to 45 min. The spectrum of PEO powder is also

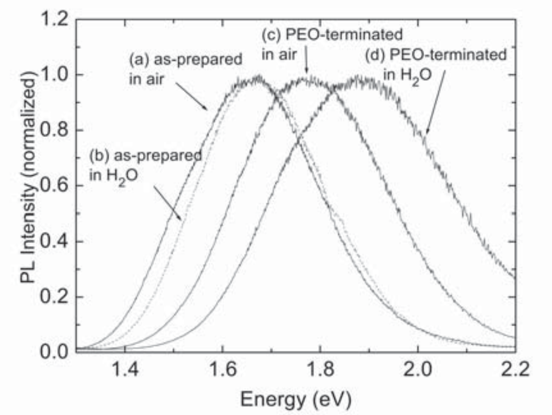

Fig. 2. PL spectra of as-prepared porous Si in air (a) and in water (b), and PEO-terminated porous Si in air (c) and in water (d). The reaction time is 45 min. The spectra are normalized at the maximum intensities.

shown. Before the treatment, two strong IR absorption bands can be seen. The band around 2100 cm^{-1} is due to Si-H bonds on the surface of Si nanocrystals, while that around 1100 cm^{-1} is due to Si-O stretching vibration [15]. The comparable intensities of the two bands imply that the surface of Si nanocrystals is almost completely H-terminated because the oscillator strength of the Si-H vibration modes is much smaller than that of the Si-O stretching mode. The small peak around 1380 cm^{-1} is due to a small amount of hydroxy-group on the surface. After the surface modification, the intensity of the Si-O mode does not change significantly, implying that Si nanocrystals are not oxidized. On the other hand, the intensity of the Si-H vibration modes becomes smaller and new peaks appear in the range between 1200 and 1500 cm^{-1}. These peaks correspond quite well to CH$_2$ vibration modes of PEO powder. The close comparison between the spectra of PEO powder and PEO terminated porous Si reveals that the signal from the C=C double bond of PEO powder at 1550 cm^{-1} disappears in the surface modified porous Si. The disappearance of the double bond and the existence of the CH$_2$ vibration modes are the direct evidence that the surface of Si nanocrystals is terminated by PEO as schematically shown in Figure 1a. It is worth noting that even after 45 min of reaction, the substantial amounts of Si-H bonds remain. The surface of porous Si is thus only partially modified.

Figure 2 shows PL spectra of as-prepared and PEO-terminated porous Si in air and in water. By the surface modification, the spectrum shifts to higher energy. The shift of the spectrum also provides the evidence that the surface of majority of Si nanocrystals constructing porous Si is modified. However, the mechanism of the shift is not clear. One of the possible explanations is that the potential barrier for exciton confinement is different between H- and PEO terminated Si nanocrystals. In as-prepared porous Si, the spectrum in air and that in water are nearly identical. On the other hand, the spectrum of the PEO-terminated porous Si shifts to higher energy in water. This shift is probably due to different exciton binding energy arising from different static dielectric constants between air and water. The effect is not strong for as-prepared porous Si because the surface is hydrophobic and majority of nanocrystals constructing porous Si do not have interaction with water, i.e., water does not penetrate into the pore. For singlet oxygen formation by energy transfer, the exciton energy should be around 1.63 eV. Therefore, for practical application of singlet oxygen generation in water, we have to take into account the energy shift and prepare larger Si nanocrystals.

As mentioned above, the direct evidence of singlet oxygen generation is the observation of the PL at 0.98 eV. In the present PEO-terminated porous Si, the emission was not detected, suggesting that singlet oxygen formation efficiency is reduced. One of the reasons for this is the increased distance between excitons in Si nanocrystals and oxygen molecules by the existence of long molecules on the surface of Si nanocrystals. The modified electronic structure of Si nanocrystals may also cause the decrease of the energy transfer efficiency. As discussed above, the PL band shifts significantly to higher energy and the PL maximum after surface modification exists far above the resonant energy. The deviation of the PL maximum from the resonant energy reduces the singlet oxygen formation efficiency. Furthermore, although not shown here, exciton lifetime is shortened due probably to the modification of exciton wavefunctions by the surface treatment and also due to defect formation. The shortened exciton lifetime reduces the efficiency of energy transfer, resulting in the decrease of the singlet oxygen formation efficiency.

Although NIR emission from singlet oxygen was not detected, this does not always mean that the sensitization effect is completely lost. Another method to demonstrate the sensitization effect is to observe resonant quenching of PL from Si nanocrystals due to energy transfer from excitons to oxygen molecules [1]. 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 3a shows PL spectra of as-prepared porous Si in vacuum and in O$_2$ gas (300 Torr) at 150 K. We can clearly see the quenching of PL centered around 1.6 eV. Similarly PL quenching can be seen for PEO-terminated porous Si. Figure 3b shows the result obtained for the sample with the reaction time of 5 min (the same sample as shown in Fig. 1b). The resonant quenching can clearly be seen when PL spectra in O$_2$ gas ambient (I_{oxygen}) are divided by those in vacuum (I_{vac}) (Fig. 3c). The observation of the resonant quenching provides the evidence that singlet oxygen is generated by the energy transfer from PEO-terminated porous Si in water. However, the level of quenching is much reduced by the surface modification, and it becomes smaller with increasing the reaction time.

The data in Figure 3c is obtained at 150 K. In general, singlet oxygen generation efficiency is larger at lower temperatures because of two reasons [7]. The first one is larger probability of exciton occupation at the spin triplet state. The other reason is a larger probability of finding oxygen molecules on the surface of Si nanocrystals at lower

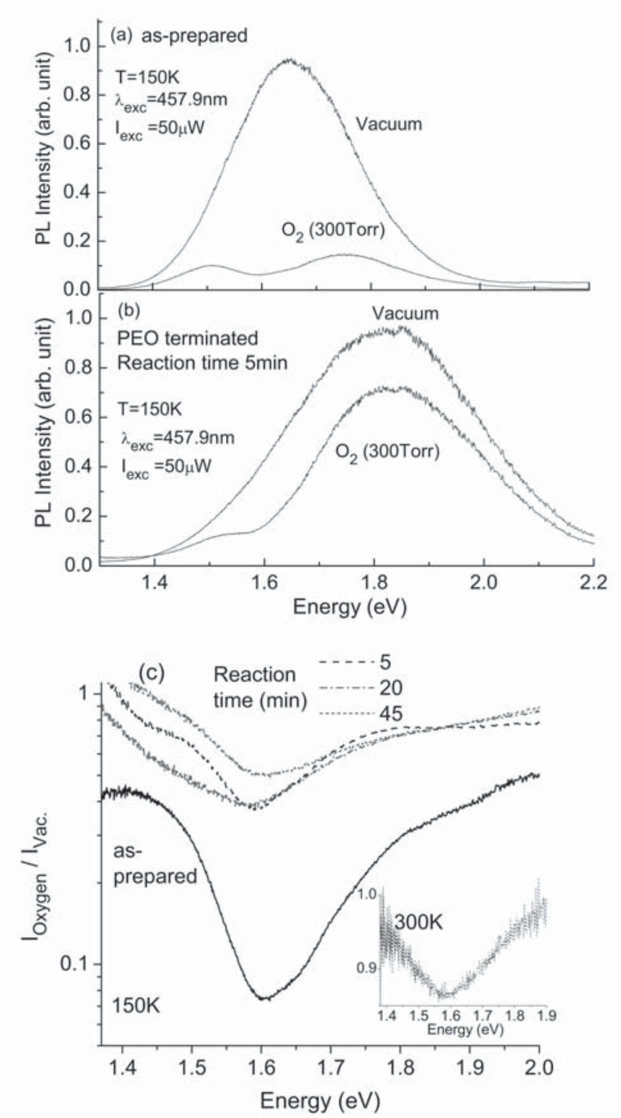

Fig. 3. (a) PL spectra of as-prepared porous Si at 150 K in vacuum and in O_2 gas 300 Torr ambient. (b) PL spectra of PEO-terminated porous Si at 150 K in vacuum and in O_2 gas 300 Torr ambient. The reaction time is 5 min. $I_{exc} = 50$ μW, $\lambda_{exc} = 457.9$ nm. (c) PL spectra of porous Si in O_2 gas 300 Torr divided by those of porous Si in vacuum (I_{oxygen}/I_{vac}) at 150 K. The data for as-prepared porous Si and PEO terminated porous Si are shown. The reaction time is 5, 20, and 40 min. In the inset, I_{oxygen}/I_{vac} at 300 K for PEO-terminated porous Si is shown (reaction time 5 min).

temperatures. Although, the singlet oxygen generation efficiency is reduced from 150 K to room temperature, the resonant quenching can also be seen at room temperature for PEO-terminated porous Si. The experimental result at room temperature is shown in the inset of Figure 3c for the sample with the reaction time of 5 min.

4 Conclusions

We prepared porous Si with hydrophilic surface by surface modification and demonstrated that the hydrophilic porous Si has photosensitization ability for O_2 molecules, although the efficiency of the sensitization is reduced. 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. One possible approach to improve the sensitization efficiency is simply to shorten the reaction time. Another approach is to employ shorter molecules, i.e., NH_3 for surface modification. Porous Si powder used in this work is an aggregate of a large amount of Si nanocrystals. Although the access of oxygen molecules to Si nanocrystals deep inside the aggregate is in principle possible via interconnected pores, extraction of generated singlet oxygen from the pore is very difficult because singlet oxygen relaxes to ground triplet oxygen during collision with pore walls. Therefore, an ideal system for singlet oxygen generation is that isolated Si nanocrystals are dispersed in water.

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