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Chemical reaction mediated by excited states of Si nanocrystals—Singlet oxygen formation in solution

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Formation of singlet oxygen in solution by using Si nanocrystals as photosensitizers has been demonstrated. It has been shown that the absorption band of 1,3-diphenylisobenzofuran (DPBF) in benzene centered at 416 nm decreases by irradiating green (514.5 nm) or red (632.8 nm) light if fresh porous Si powder is dispersed in the solution. The decomposition of DPBF was observed only when fresh porous Si was irradiated by light, i.e., without light irradiation no effects were observed. Furthermore, the effect was drastically suppressed if porous Si powder was annealed and a monolayer of oxide was formed on the surface of nanocrystals. The rate of the decomposition of DPBF was accelerated when the solution was bubbled by oxygen gas. These results indicate that electronic excitation of Si nanocrystals is transferred to molecular oxygen dissolved in solution, resulting in the formation of singlet oxygen. Generated singlet oxygen reacts with DPBF (1,4-cycloaddition reaction), forming endoperoxides, which in turn decompose to yield irreversible products. In addition to the singlet-oxygen-mediated decomposition of DPBF, the possibility of direct reaction between triplet excited states of Si nanocrystals and DPBF is discussed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1664021]

I. INTRODUCTION

Molecular oxygen is one of the most important substances on Earth. The ground state of molecular oxygen is the triplet state ($^3\Sigma_g^-$), with the two lowest-energy excited states being singlets ($^1\Delta_g$ and $^1\Sigma_g^+$). The excited state molecular oxygen is called singlet oxygen.¹ The singlet oxygen mediates important processes in chemistry and biology.^{2–4} It reacts with many organic compounds including aromatic, steroids, vitamins, amino acids, proteins, etc. It also is involved in modification of biological structures. Photodynamic cancer therapy is an example of its medical application.⁴

Formation of singlet oxygen requires the presence of a light-absorbing photosensitizer with subsequent energy transfer from electronic excitation to oxygen molecules. The energy transfer process is explained by the triplet–triplet annihilation of photosensitizers and oxygen molecules by electron exchange (Dexter transfer)⁵ coupling; annihilation of a triplet excited state of a photosensitizer is accompanied by spin-flip excitation of an oxygen molecule. Strongly light absorbing dye molecules (Rose Bengal, methylene blue, etc.) are usually employed as a photosensitizer.¹ Recently, we have demonstrated that Si nanocrystal assemblies, especially porous Si, act as an efficient photosensitizer for singlet oxygen formation.^{6,7} From detailed spectroscopic studies, we

found that a molecule-like electronic structure of excitons in Si nanocrystals, i.e., excitonic states are split into an optically active spin-singlet state and an optically inactive spin-triplet state which is lowered in energy, is essential in realizing a function as a photosensitizer. Despite a small singlet-triplet splitting being in the milli-electron-volt range, 75% of excitons reside in the threefold degenerated triplet state even at elevated temperatures. The efficient formation of triplet excitons makes triplet–triplet-annihilation type energy transfer to oxygen molecules possible.

The fundamental mechanism of the energy transfer from Si nanocrystals to oxygen molecules is now almost clarified. The next step is to demonstrate the practical usefulness of porous Si as a photosensitizer for singlet oxygen formation. For many applications in chemical and biological fields, formation of singlet oxygen in solution is required, because singlet oxygen mediated reactions proceed usually in solution. The standard method to detect singlet oxygen in solution is to use biochemical traps (singlet oxygen acceptors) and analyze a specific reaction product or monitor the decrease in the amount of acceptor materials. Typical biochemical traps are cholesterol, 1,3-diphenylisobenzofuran (DPBF), *p*-nitrosodimethylalanine, sodium azide, etc.⁸ In this work, we employed DPBF as a singlet oxygen acceptor. DPBF readily undergoes a 1,4-cycloaddition reaction with singlet oxygen forming endoperoxides, which in turn decompose to yield irreversible products (1,2-dibenzoylbenzene). This process can be monitored by the decrease in the inten-

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sity of the absorption band of DPBF centered at 416 nm.^{9,10} We will study the absorption spectra of DPBF-dissolved solution containing porous Si powder under light irradiation and demonstrate that porous Si acts as a photosensitizer for singlet oxygen generation in solution.

II. EXPERIMENTAL DETAILS

DPBF can be dissolved in variety of organic solvents. In this work, benzene (99.8%) was employed as a solvent because the lifetime of singlet oxygen in it is relatively long (the lifetime of $^1\Delta$ state is 24 μ s)¹ and thus a larger probability of the interaction with DPBF is expected. Furthermore, compared to other organic solvents, e.g., methanol, benzene does not quench luminescence of porous Si so much, leading to a smaller probability of nonradiative recombination of excitons before transferring energy to oxygen molecules and higher efficiency of singlet oxygen formation. DPBF was dissolved into benzene with the concentration of about 40 μ mol/l. The maximum absorbance [$-\ln(\text{transmittance})$] of the solution was about 4.8. Oxygen was not intentionally dissolved but benzene was exposed to air for a long period before DPBF was dissolved.

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.¹¹ The current density and etching time were 54 mA/cm² and 3 h, respectively. After the electrochemical etching process, porous Si layers were rinsed with ethanol several times to reduce the amount of residual fluorine as small as possible. With this preparation condition, porous Si layers are cracked and become powder during drying. The powder was then corrected and 10 mg of it was put into a quartz cell filled with DPBF-dissolved benzene. Since the powder is not ground down, the size of the powder was distributed in a wide size range.

As has been discussed in previous papers,^{6,7} the ability of singlet oxygen formation depends strongly on the band gap energy of Si nanocrystals comprising porous Si. The efficiency of singlet oxygen formation is the best for nanocrystals having a luminescence (band gap) energy at around 1.63 eV, which corresponds to the energy separation of the second excited singlet state of oxygen molecules ($^1\Sigma$) and the triplet ground state ($^3\Sigma$); these nanocrystals can resonantly transfer their electronic excitation to oxygen molecules staying on the surface. On the other hand, if the band gap energy is far from 1.63 eV, emission or absorption of phonons are required during the energy transfer process to satisfy the energy conservation rule. The requirement of the phonon participation drastically reduces the energy transfer rate, and efficient formation of singlet oxygen is not expected. The band gap energy of porous Si can be controlled by the resistivity of Si wafers, etching current density, concentration of hydrofluoric acid in etching solution, etc. We have tuned the sample preparation condition so that porous Si powder exhibits photoluminescence (PL) maximum at around 1.63 eV.

The schematic illustration of the quartz cell ($1 \times 1 \times 4.5$ cm³) containing porous Si powder is shown in the in-

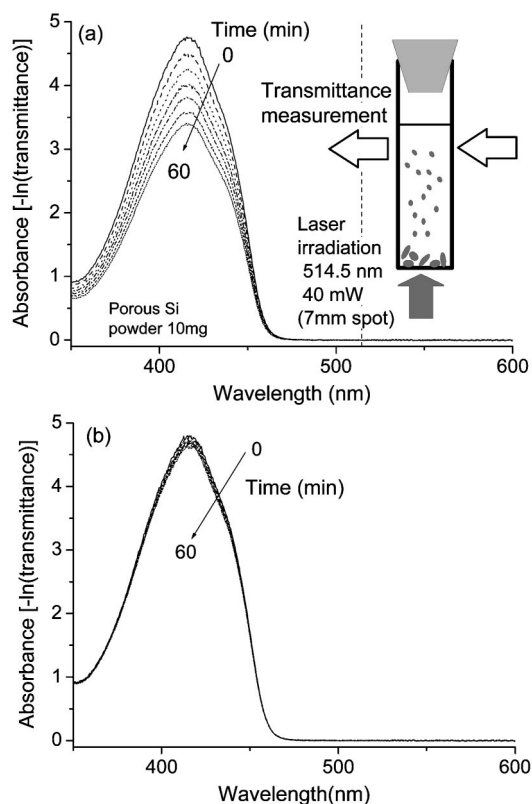


FIG. 1. Absorption spectra of DPBF-dissolved benzene as a function of irradiation time. The wavelength and power of the irradiation light are 514.5 nm and 40 mW, respectively, with the spot size of about 7 mm in diameter, (a) with porous Si powder, and (b) without porous Si powder. Inset in (a) is the configuration of experiments.

set of Fig. 1(a). Large powder which can be seen easily by naked eyes sink down to the bottom, and only a portion of small powder wanders in the solution. Existence of small powder in solution can easily be recognized by the red luminescence of powder if we irradiate the cell with green light. Light transmittance measurements of the cell were made by a double-beam spectrophotometer equipped with a double monochromator (Shimadzu UV-3101PC) by using a quartz cell filled with pure benzene as a reference. DPBF easily degrades by absorbing blue light. To make the degradation during the measurements as small as possible, a fast scan mode was employed, i.e., the total measurement time was about 30 s for each scan, and samples were treated in a dark room. No degradation of DPBF was observed during measurements.

After an initial transmittance measurement, the solution was irradiated by a 514.5 nm line of an Ar ion laser or a 632.8 nm line of a He–Ne laser for 10 min from the bottom of a quartz cell. The laser power was 40 mW with the spot size of about 7 mm in diameter. The cycle of light irradiation and transmittance measurements was repeated until total irradiation time becomes 60 min.

III. RESULTS AND DISCUSSION

Figure 1(a) shows absorption spectra of DPBF-dissolved benzene containing fresh porous Si powder. A strong absorption band centered at 416 nm is due to DPBF. Porous Si

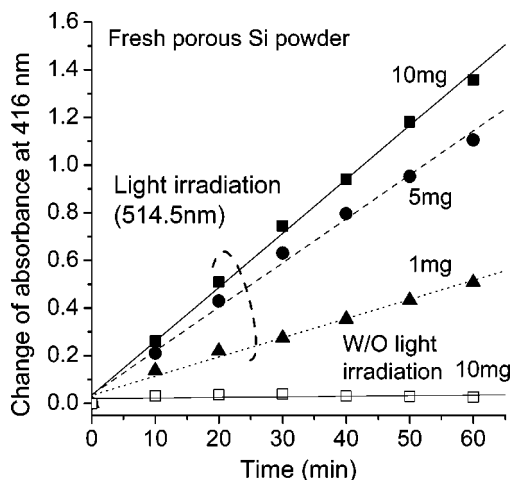


FIG. 2. Change of absorbance at 416 nm as a function of laser irradiation time for DPBF-dissolved benzene solution containing different amount of porous Si powder. \square is the data obtained without light irradiation, while others are obtained under light irradiation.

shows a broad absorption band starting from a red region.¹² However, the absorption by porous Si does not appear on the spectra in Fig. 1(a) because of a small amount of powder in a light pass during the transmittance measurements [see the inset of Fig. 1(a)].

After an initial transmittance measurement, the solution was irradiated by a 514.5 nm line of an Ar ion laser. In Fig. 1(a), by irradiating the solution with 514.5 nm light, the absorbance decreases, implying that DPBF is decomposed. It should be stressed here that the change in the absorbance was observed only when porous Si powder is added to the solution; without porous Si, the absorbance change is negligibly small [see Fig. 1(b)].

In Fig. 2, the degree of the absorbance change is plotted as a function of irradiation time for cells containing different amount of porous Si. The data plotted by \square are obtained without light irradiation. Without irradiation, porous Si powder does not exert any effects on DPBF. This implies that the observed decomposition of DPBF is not due to chemical reaction with porous Si or with impurities in porous Si. Porous Si in the photoexcited states is crucial for the observed phenomena.

Under irradiation, the change in the absorbance is larger for the solution containing a larger amount of porous Si powder. However, the degree of the change is not proportional to the amount. This may be due to the fact that all Si nanocrystals are not uniformly excited; the bottom of the cell is covered by large powder and they prevent excitation light to illuminate the cell uniformly.

The degree of absorbance change depends also on the wavelength of excitation light. Under 632.8 nm irradiation, the change was smaller than that under 514.5 nm light irradiation. The absorption coefficient of porous Si at 632.8 nm is about one order of magnitude smaller than that at 514.5 nm.¹² The difference in the absorption coefficient may result in the different rate of DPBF decomposition. The excitation wavelength dependence of the decomposition rate is another

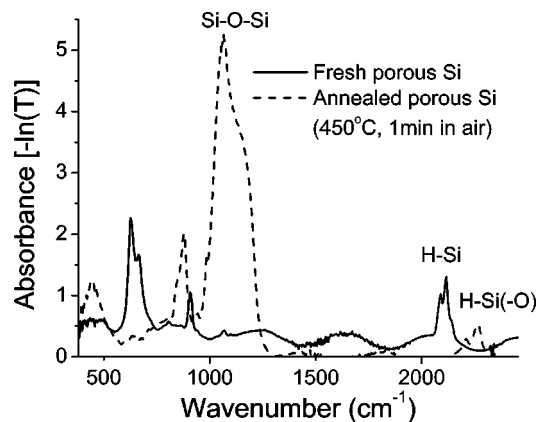


FIG. 3. Infrared absorption spectra of fresh (solid curve) and annealed (dashed curve) porous Si.

evidence that photoexcited states of porous Si is responsible for the decomposition of DPBF.

To understand the role of porous Si more in detail, we annealed porous Si at 450° for 1 min in air. The infrared absorption spectra before and after the annealing are shown in Fig. 3. As-prepared (fresh) porous Si has a hydrogen-terminated surface with characteristic absorption lines of the vibrational modes of the H-Si bonds at around 2100 cm⁻¹ (Fig. 3, solid curve). Annealing the porous Si introduces a monolayer of backbonded oxygen on the nanocrystal surface, while the hydrogen passivation of the surface is partially preserved.¹³ The chemically modified surrounding of the H-Si bonds shifts the infrared absorption lines to higher wave numbers (Fig. 3, dashed curve). The shift is accompanied by the decrease in the integrated intensity of the H-Si vibration modes and strong growth of the Si-O-Si mode at around 1080 cm⁻¹, suggesting that a part of surface hydrogen atoms are effused, and the surface is partly oxidized.

The change in the absorbance of DPBF is studied for the annealed porous Si powder. The result is shown in Fig. 4. In contrast to fresh porous Si powder, the annealed powder exerts no effects on DPBF. This is considered to be due to a poor ability of singlet oxygen formation for the annealed

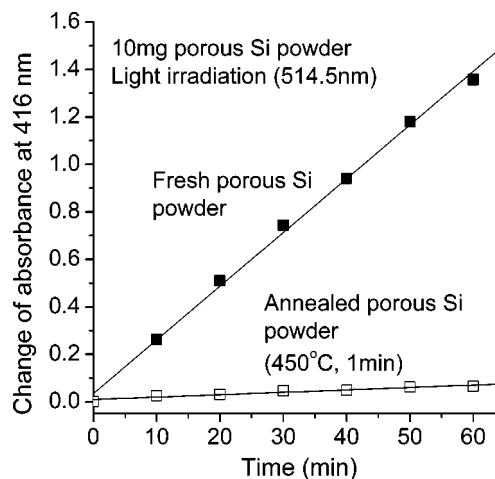


FIG. 4. Comparison of absorbance change between fresh and annealed porous Si powder under the same experimental condition.

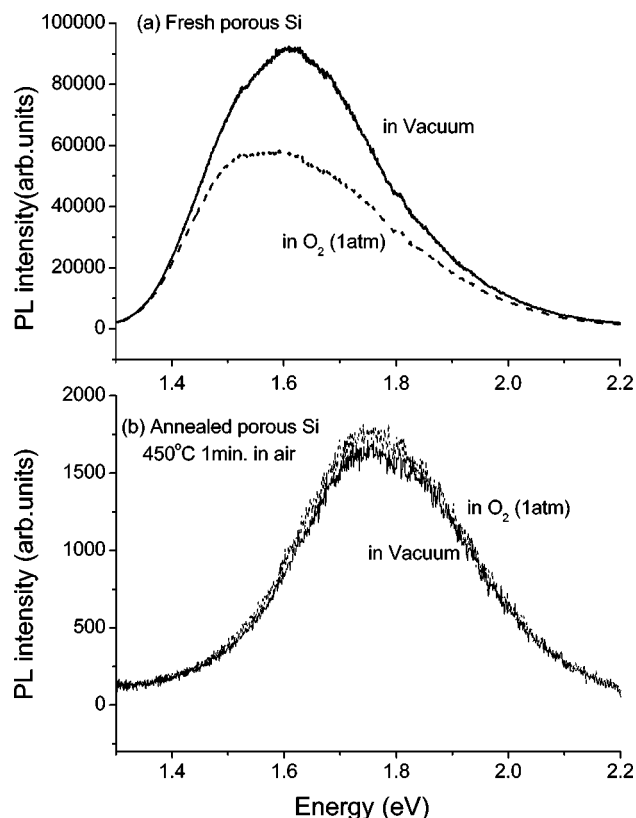


FIG. 5. PL spectra of (a) fresh and (b) annealed porous Si measured in vacuum (solid curve) and in O_2 gas (1 atm) (dashed curve) at room temperature.

powder.^{6,7} The ability for the formation of singlet oxygen can be examined by PL spectroscopy. Figure 5 compares PL spectra of fresh and annealed porous Si measured in vacuum and in oxygen gas ambient. By annealing, PL intensity is significantly dropped due probably to the formation of dangling bonds. In addition, the effect of ambient on the PL spectrum is different between the fresh and annealed porous Si. In the case of fresh porous Si, PL is quenched by introducing oxygen gas, while in annealed porous Si, PL spectrum does not depend on the ambient. Figure 6 shows the ratio of PL spectra measured in vacuum to that in oxygen gas ambient (strength of PL quenching). In fresh porous Si, the strength of PL quenching has a maximum at around 1.63 eV, while the annealed porous Si does not have any structure. Since the energy of 1.63 eV corresponds to the energy separation between the second excited state ($^1\Sigma$) of oxygen molecules and the ground state ($^3\Sigma$), the PL quenching observed for the fresh porous Si is due to the energy transfer from Si nanocrystals to oxygen molecules, i.e., the singlet oxygen formation. On the other hand, singlet oxygen is not generated by annealed porous Si, and thus the decomposition of DPBF with the interaction of singlet oxygen does not occur.

If singlet oxygen generated by the energy transfer from Si nanocrystals is involved in the decomposition of DPBF, the rate of the absorbance change should depend on the concentration of oxygen dissolved in benzene. To see the effect of oxygen concentration, we bubbled DPBF-dissolved benzene solution containing porous Si powder with nitrogen and oxygen gases and compared the degree of the absorbance

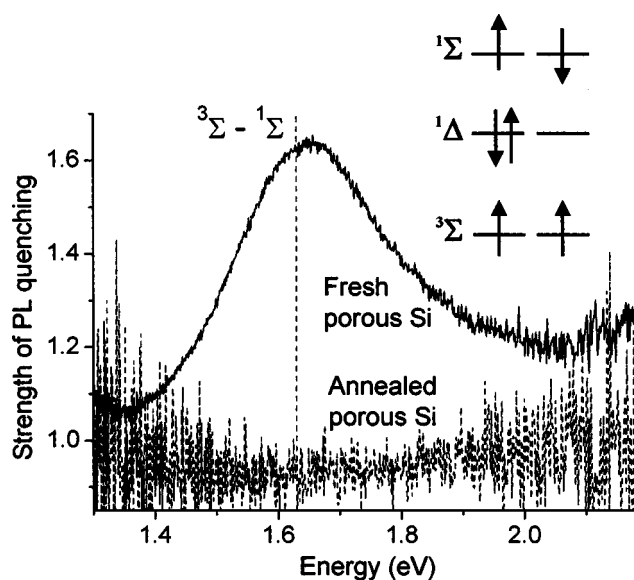


FIG. 6. PL quenching strength, i.e., the ratio of a PL spectrum in vacuum to that in oxygen ambient, of fresh (solid curve) and annealed (dashed curve) porous Si. The spectral position of the excited state of an oxygen molecule is indicated ($^3\Sigma \rightarrow ^1\Sigma$). Electron-spin configurations and spectroscopic labeling of molecular oxygen states are shown in the inset.

change. In Fig. 7(a), we first bubbled the solution with oxygen gas, put a cap on the cell and irradiated the cell for 30 min, then bubbled the same solution with nitrogen gas and again irradiated the cell for 30 min. In spite of the very rough procedure, we can clearly see the change in slope depending on the kind of gases used for bubbling; the slope becomes smaller after the nitrogen gas bubbling. In Fig. 7(b), the procedure is vice versa, i.e., first nitrogen gas bubbling and then oxygen gas bubbling. In this case, we can see an enhancement of the slope after the oxygen gas bubbling. These observations are the evidence that oxygen is involved in the decomposition of DPBF. By combining all the results ob-

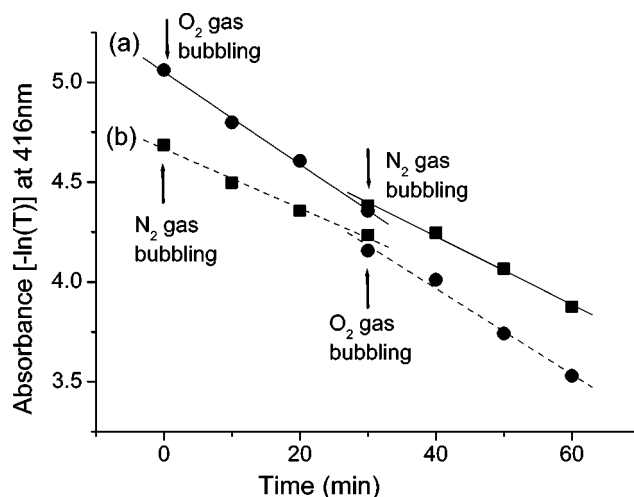


FIG. 7. Change of absorbance of DPBF as a function of time. (a) (solid line) DPBF-dissolved benzene solution was bubbled by oxygen gas before starting the measurement/irradiation cycles. After 30 min of irradiation, the solution was bubbled by nitrogen gas. (b) (dashed line) The solution was first bubbled by nitrogen gas, and after 30 min irradiation bubbled by oxygen gas.

tained, the whole process can be summarized as follows. First, Si nanocrystals are excited by light irradiation and excitons are formed. Part of them stay in the triplet states. The triplet exciton transfers energy to a ground state triplet oxygen molecule dissolved in the solution by the triplet-triplet annihilation process, resulting in the formation of singlet oxygen. Generated singlet oxygen reacts with DPBF, undergoes a 1,4-cycloaddition reaction forming endoperoxides, which in turn decompose to yield irreversible products.

Although it is clear that singlet oxygen is involved in the decomposition of DPBF in the present experiments, we cannot completely rule out the possibility that triplet excited states of Si nanocrystals interact directly with DPBF. In organic photosensitizers, two types of pathways (types I and II) are generally considered in the chemical reaction assisted by excited triplet states.⁸ The type I pathway is a direct reaction with acceptor materials by donating and accepting hydrogen or electrons and producing free radicals or free-radical ions. The type II pathway is the process we have discussed so far; excited triplet sensitizer reacts with ground state triplet oxygen to form singlet oxygen by triplet-triplet annihilation. The rate of the type II pathway is mostly dependent on the concentration of oxygen molecules in solution. As the oxygen in a system becomes depleted, the shift from type II to I mechanism is favored. In the present work, relatively small difference in the slope of the absorbance change between oxygen gas bubbled and nitrogen gas bubbled solution (Fig. 7) might suggest that, in addition to the type II mechanism, type-I-like direct interaction between triplet excitons and DPBF exists.

IV. CONCLUSION

We have succeeded in demonstrating singlet oxygen formation in solution by using porous Si as a photosensitizer. Porous Si has extremely large accessible internal surface area (up to 1000 m²/cm³) that permits a direct contact between the whole Si nanocrystals and substances in the pore. The structure is thus ideal in realizing efficient energy transfer from excitons in Si nanocrystals to oxygen molecules. Furthermore, a very broad absorption band of porous Si covering all the visible range implies that porous Si can utilize light in all visible range for singlet oxygen formation. This is a good advantage from the point of view of practical application as a photosensitizer. The nontoxicity of porous Si could allow it

to be used in biological and medical fields. Therefore, the present results offer further application of the most commercially used semiconductors.

However, in the present work, quantitative discussion on the formation rate of singlet oxygen was not made. The quantitative discussion is difficult because of the inhomogeneity of the present system. Since pores of porous Si are very narrow and have a very high aspect ratio, the availability of oxygen molecules and DPBF is not equal for all nanocrystals, and the reaction speed is considered to be quite different between nanocrystals on the surface of porous Si powder and those deep inside narrow pores. In fact, if we intentionally crashed porous Si powder, the reaction speed was changed significantly. In order to make quantitative discussion, colloidal Si nanocrystals which can be uniformly dispersed in solution may be required.

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