

Resonant Electronic Energy Transfer from Excitons Confined in Silicon Nanocrystals to Oxygen Molecules

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We demonstrate efficient resonant energy transfer from excitons confined in silicon nanocrystals to molecular oxygen (MO). Quenching of photoluminescence (PL) of silicon nanocrystals by MO physisorbed on their surface is found to be most efficient when the energy of excitons coincides with triplet-singlet splitting energy of oxygen molecules. The dependence of PL quenching efficiency on nanocrystal surface termination is consistent with short-range resonant electron exchange mechanism of energy transfer. A highly developed surface of silicon nanocrystal assemblies and a long radiative lifetime of excitons are favorable for achieving a high efficiency of this process.

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Photons cannot efficiently excite molecules if the electronic transitions between their ground and excited states are spin, total momentum, or parity forbidden. To achieve optically forbidden electronic excitation carefully selected intermediary-photosensitizing species are commonly used. The key idea of this indirect excitation process is that first the photosensitizer (donor) is excited optically and the energy of the electronic excitation is further transferred to acceptor molecules via resonant dipole-dipole interaction (Förster coupling [1]) or direct electron exchange mechanism (Dexter transfer [2]). In both scenarios the long lifetime of electronic excitation of the donor, overlap of donor and acceptor electron energy levels, and their small space separation are crucial for the efficiency of the energy transfer.

It is well known that the ground state of molecular oxygen (MO) $^3\Sigma$ has triplet multiplicity but not singlet multiplicity unlike most natural compounds. Chemical reactions forming singlet molecules from triplet and singlet reactants are forbidden by the spin selection rule. Thus, the triplet multiplicity is the actual reason why most reactions of oxygen with organic substances require heating or the presence of catalysts and do not proceed at room temperature. The lowest excited singlet state of O_2 ($^1\Delta$) lies 94 kJ mol^{-1} above the triplet ground state. This results in lowering of the activation barrier of the oxidation reactions. Additionally because of its singlet multiplicity no spin forbiddance exists for reactions of $O_2(^1\Delta)$. Therefore singlet oxygen is chemically extraordinary reactive. Above the $^1\Delta$ excited singlet state lies the $^1\Sigma$ singlet state of the oxygen molecule with excitation energy 157 kJ mol^{-1} . The corresponding electron spin con-

figurations and the gaps between the energy levels are indicated in the inset of Fig. 1.

The unstable, energy-rich singlet MO (1O_2) is involved in various photosensitization and photo-oxidation

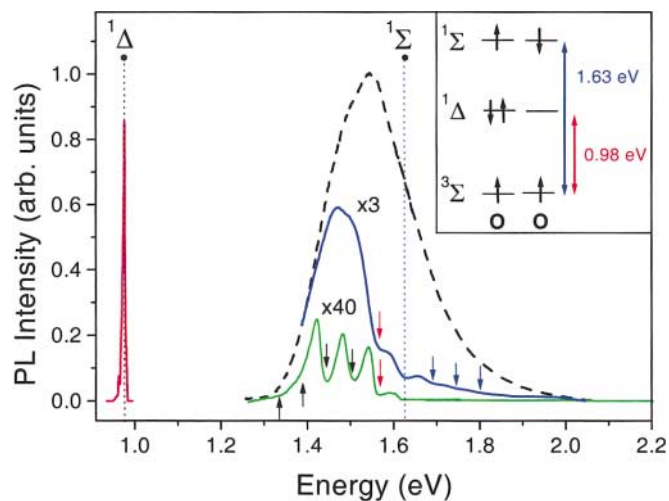


FIG. 1 (color). PL spectra from the as-prepared P*Si* layer. Excitation energy is 2.41 eV. Dashed curve: $T = 50 \text{ K}$; layer is in vacuum. Blue curve: $T = 50 \text{ K}$; MO pressure is 10^{-2} mbar . Green curve: $T = 5 \text{ K}$; MO pressure is 10^{-4} mbar . Red line is emission due to the $^1\Delta$ - $^3\Sigma$ transition. Broad weak background of the Si dangling bonds PL band is subtracted for clarity. Energies of $^1\Sigma$ and $^1\Delta$ states are shown by vertical dotted lines. Arrows indicate spectral features discussed in the text. PL scaling factors are shown. Inset: sketch of the energy levels of molecular oxygen depending on electron spin configurations. Labeling and energies of transitions are indicated.

reactions and mediates fundamental processes in chemistry and biology [3,4]. It reacts with many organic compounds including aromatics, steroids, vitamins, amino acids, proteins, etc. It is also involved in the modification of biological structures. One important example of the medical application of $^1\Delta$ and $^1\Sigma$ states of MO is the photodynamic cancer therapy [5]. The transition from the $^3\Sigma$ ground state to one of the excited 1O_2 states and vice versa requires the change of the electron spin state (spin-flip process) and direct states conversion via absorption/emission of photons is spin forbidden [3] in the first approximation. The photosensitizing agents involved in MO excitation are commonly strongly absorbing organic dye molecules [3] or fullerenes [5]. Because of light absorption the dye molecules are excited into the singlet state and after fast relaxation they are accumulated in the long-lived triplet state. Further triplet-triplet annihilation results in the yield of 1O_2 [3].

Bulk silicon (Si) is an inefficient light emitter because of its indirect band-gap electronic structure. Recently, several Si-based nanostructures exhibiting high quantum yield have been developed. Porous Si (PSi) formed by electrochemical etching of bulk Si crystals is one of those [6–8]. PSi consists of an almost infinite number of individual absorbers (nanocrystals) having different band gaps (1.12 eV, up to 2.5 eV) due to the quantum confinement effect. The intrinsic electronic structure of the excitons confined in Si nanocrystals is very similar to that of dye molecules. The upper and lower exciton states have been shown to be optically active spin singlet and optically inactive spin triplet, respectively, with the triplet state shifted towards lower energy due to electron-hole exchange interaction [7–9]. The value of exciton singlet-triplet splitting is in the *meV* range and at elevated temperatures 75% of excitons are in the triplet state [7,8]. The radiative lifetime of triplet excitons measured at cryogenic temperatures when only triplet states are occupied is similar to that of triplet states of dye molecules and is in the millisecond range [7,8]. However, unlike dye molecules or direct band-gap nanocrystals the radiative lifetime of singlet excitons confined in Si nanocrystals is also very long (10^{-5} – 10^{-3} sec) due to the indirect nature of the radiative transitions [7,8]. Therefore despite small singlet-triplet energy gap even at room temperature excitons persist in the triplet state in this time scale. The other remarkable property of PSi is a highly developed specific surface area (up to 10^3 m²/cm³) [10] because it consists of pores and Si nanocrystals whose typical dimensions are of the order of 2–5 nm [11]. Pores network in PSi layers is continuous and the surface of the Si nanocrystals is accessible for MO in the gaseous form.

In this Letter we present observations of electronic energy transfer from excitons confined in Si nanocrystals to surrounding oxygen molecules. We measure quenching of the photoluminescence (PL) (lifetime) of Si nanocrystals

by an MO ambient and compare the energies of the spectral features with the singlet-triplet splitting energies of MO. We further present the evidence of activation of MO to singlet states. Spectroscopic analysis of PL quenching and its dependence on nanocrystal surface termination shows that energy transfer is mediated by the resonant direct electron exchange mechanism.

PSi layers have been prepared by standard anodic etching of *p*-type bulk Si wafers with a typical resistivity of 2–5 $\Omega \cdot \text{cm}$ [7]. The layers have been inserted in evacuated temperature-regulated cryostat and MO ambient pressure has been controlled by a microvalve. PL has been excited by a continuous Ar⁺ ion laser (514.5 nm) and measured with a monochromator equipped with a charge coupled device, photomultiplier, or Ge detector. Excitation intensity is in the range of 10^{-3} – 10^2 W/cm². PL decay time has been measured under excitation with second harmonic (532 nm) of fundamental radiation of a pulsed Nd:YAG laser (10^{-8} sec, 10^3 W/cm²).

We have found that the presence of an MO ambient results in a strong quenching of the PL from PSi layers having hydrogen-terminated surface. This quenching depends on the temperature and the partial pressure of MO. The essence of the effect is seen in Fig. 1. We demonstrate first the low temperature measurements because they straightforwardly identify the quenching mechanism. The dashed curve shows the PL spectrum from the PSi layer placed in vacuum at 50 K. The large variety of the shapes and sizes of Si nanocrystals causes a broad featureless PL band. Injection of MO in the cryostat results in significant quenching of the PL intensity (blue curve). The strongest PL suppression is observed at 1.63 eV (indicated by dotted drop line) what coincides with the $^1\Sigma$ state excitation energy. Local minima in the PL spectrum above this energy (marked by blue arrows) are equally spaced in energy scale; their positions with respect to the $^1\Sigma$ state are equal to an integer number times ~ 62 meV. At lower energies PL quenching is inefficient. Further reduction of temperature down to 5 K (green curve) results in the complete quenching of the PL above ~ 1.617 eV and appearance of additional sharp PL features indicated by black arrows. They are observed even if the exciting photon energy is below 1.63 eV. Their spacings with respect to excitation energy of the $^1\Delta$ state are again equal to an integer number (up to 9) times ~ 62 meV. Thus, the injection of MO introduces two specific demarcation energies inherent to the process of MO activation.

A direct proof for the generation of 1O_2 is the detection of light emission during its relaxation to the $^3\Sigma$ ground state [3]. The fast decay of the $^1\Sigma$ state to the $^1\Delta$ state prevents the observation of the $^1\Sigma$ – $^3\Sigma$ transition experimentally [3]. We found that quenching of the PL is always accompanied by the appearance of a narrow PL line at 0.98 eV (red line in Fig. 1) resulting from the $^1\Delta$ – $^3\Sigma$

transition of MO; i.e., obviously there is energy transfer from annihilated excitons to MO.

For nonresonant energy transfer additional dissipation of energy is required. In Si this process is mainly mediated by transverse optical (TO) phonon emission and should be the most efficient when the band gap of the Si nanocrystal is equal to the energy of MO transition plus an integer number of TO-phonon energies (local PL minima). The energy of the TO phonon in bulk Si having the maximal density of states is about 62 meV [12]; this coincides well with the separation of the PL minima. Otherwise, additional acoustical phonons are involved in what introduces a "bottleneck" in the energy transfer [13] (local PL maxima). Note that the local PL minimum marked by red arrows is only 56 meV below the PL onset. The reason for that is the indirect band-gap nature of Si nanocrystals. Radiative exciton recombination requires the emission of a bulk Si momentum-conserving TO phonon ($E_{\text{TO}} = 56$ meV) [13]. Thus, nanocrystals having band-gap energy in the vicinity of the excitation energy of the $^1\Sigma$ state will not contribute to the PL 56 meV below.

Further indication for the phonon cascade emission comes from the spectral dispersion of PL decay time which is found to be almost identical to the spectral shape of the PL band (see Fig. 2). The PL decay time at the energies of PL minima is about 300 μs and almost twice shorter than that measured at PL maxima energies. It is ~ 15 times shorter than triplet exciton recombination time [7,8] measured in vacuum (~ 5 ms) and, therefore, it gives the time of the energy transfer from the excitons confined in Si nanocrystals to the $^1\Delta$ state of MO (at a particular PL quenching level). These experiments show that the energy transfer rate is maximal when simultaneous emission of only TO phonons is required to fulfil the energy conservation law. At energies above 1.63 eV the decay of extremely weak remnant PL is very fast and the time of the energy transfer to the $^1\Sigma$ state is faster than our experimental time resolution (1 μs).

In Fig. 3 we show the spectral dependencies of the PL quenching strength which, in fact, indicates the efficiency of the energy transfer from excitons to MO. To exclude the effect of the Si nanocrystal size distribution they have been evaluated via division of PL spectra measured in vacuum on those measured in the ambient of MO. At low temperatures distinct spectral features (marked by arrows in Fig. 3) that are relevant to the participation of Si TO phonons in the energy exchange process are seen. At elevated temperatures these features are smeared due to thermal broadening effects. At all temperatures the PL quenching is most efficient at the energy of the $^1\Sigma$ state. PL quenching becomes very strong below 100 K even at low MO ambient pressures. At these temperatures adsorbed MO is always present at the surface of nanocrystals, while at room temperature the energy transfer takes place during short collision events.

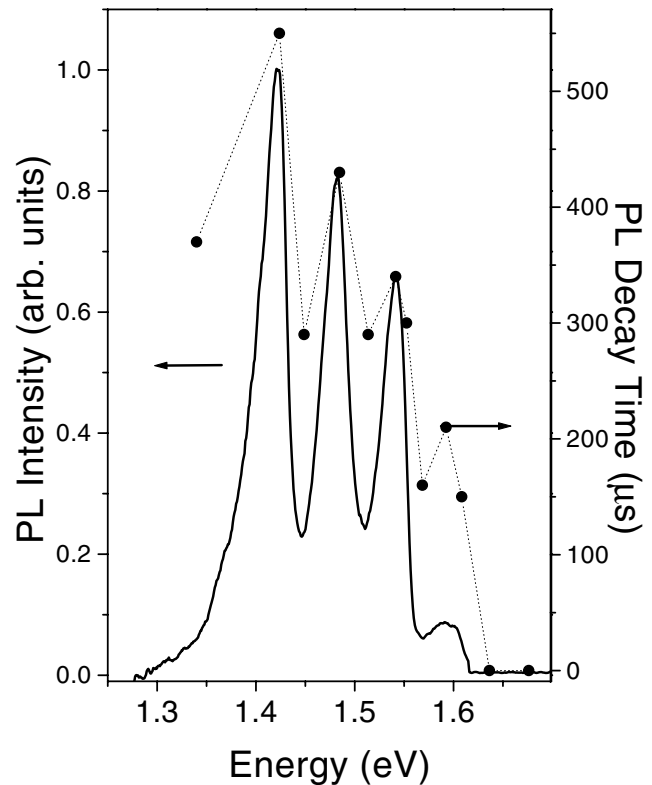


FIG. 2. PL spectrum from as-prepared PSi (solid curve) and spectral dispersion of the PL decay time (circles) at $T = 5$ K; MO pressure is 10^{-4} mbar. Measurements have been performed at a weak level of PL quenching to keep the signal-to-noise ratio on a reliable level for time-resolved measurements.

The dipole-dipole interaction [1,2] and the direct electron exchange [2] are the most suitable candidates for the energy transfer from excitons confined in Si nanocrystals to oxygen molecules. Förster showed that the dipole-dipole interaction can dominate the energy transfer mechanism only when the donor and the acceptor are characterized by dipole-allowed transitions [1]. However, in our system both radiative recombination of excitons and activation of MO are spin-forbidden processes. Dexter demonstrated that the spin states of donor and acceptor can be changed simultaneously if the energy transfer is governed by direct electron exchange [2]. Therefore simultaneous transfer of photoexcited electron to oxygen molecule and compensation of hole in an Si nanocrystal by electron from oxygen molecule, i.e., triplet exciton annihilation and spin-flip excitation of an oxygen molecule, are allowed processes. MO physisorbed on the surface of nanocrystals should play a role similar to that of midgap deep center or surface state in a bulk semiconductor. Trapping of carriers on those states is usually accompanied by phonon emission cascade [14] that is consistent with our observations.

To clarify the energy exchange mechanism we performed similar experiments on naturally and thermally oxidized PSi layers having one monolayer of oxygen

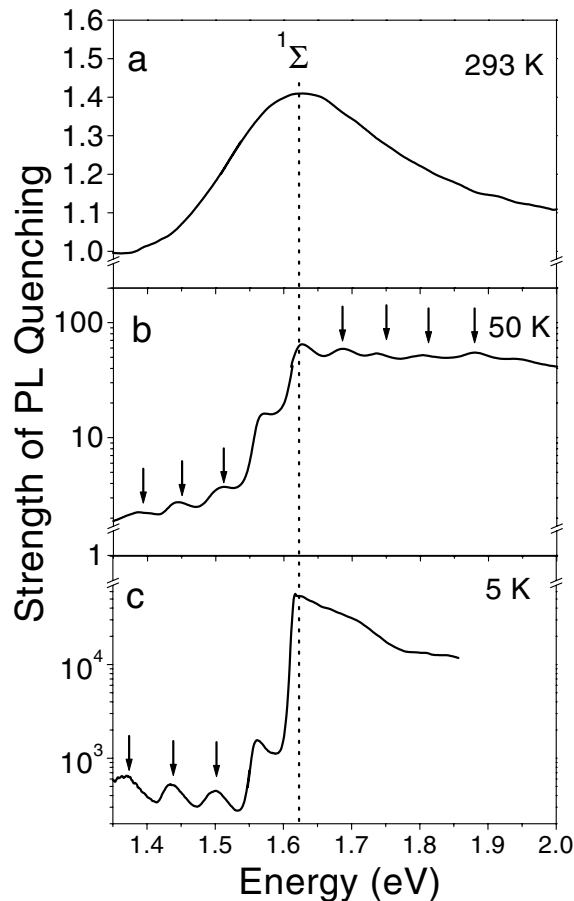


FIG. 3. The spectral dependencies of the PL quenching strength for hydrogen-terminated porous Si layers. (a) $T = 293$ K, MO pressure is 1 bar. (b) $T = 50$ K, MO pressure is 10^{-2} mbar. (c) $T = 5$ K, MO pressure is 10^{-4} mbar. TO-phonon-related spectral signatures are indicated by arrows.

atoms backbonded to the surface Si atoms [7]. Their emission properties are almost identical to those of the as-prepared layers. While all spectral features relevant to $^1\Delta$ and $^1\Sigma$ states are still present at low temperatures, the PL quenching efficiency is found to be almost 3 orders of magnitude weaker. Introduction of the monolayer of backbonded oxygen should be crucial for the electron exchange rate which depends exponentially on the spacing between interacting species. Our crude estimates based on Si-H and Si-O bond lengths show that for oxidized Si surfaces this separation is about 3 times larger and our observations are qualitatively in accord with predictions of a simple model of electron exchange rate [3]. This evidences that MO activation is governed by the direct exchange of electrons between MO and photoexcited Si nanocrystals. Furthermore, because the quenching of the PL from hydrogenated PSi layers is mainly mediated by the $^1\Sigma$ state the electron exchange seems to

proceed via one particular oxygen atom of the oxygen molecule (see the inset of Fig. 1).

From spectral behavior of the PL quenching level it follows that if an exciton does not contribute to the light emission it necessarily activates a 1O_2 state. This allows one to estimate the generation rate of 1O_2 in the pores of PSi layers. For ambient MO pressure, room temperature, and 1 W/cm^2 excitation intensity, it is $\sim 10^{20} \text{ } ^1O_2/\text{cm}^3 \cdot \text{sec}$. From analysis of the integral PL quenching behavior at 5 K the efficiency of the energy transfer (number of generated 1O_2 per photoexcited exciton) is almost equal to 1.

To summarize, we presented spectroscopic evidence of the efficient energy transfer from excitons confined in Si nanocrystals to MO. The experiments show that PSi layers have remarkable photosensitizing properties due to a broad energy spectrum of photoexcited excitons expanding over entire near-IR and visible spectral range, long exciton lifetime, and large internal surface area. Because singlet oxygen is generated in the gas phase, PSi layers can be employed as catalysts for a variety of oxidation reactions. We believe that the result of this research offers a novel area of further application of silicon.

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