Singlet oxygen generation by nanoporous silicon: photoluminescence dynamics in magnetic field

Gazi N Aliev ©, Jamaree Amonkosolpan 1 and Daniel Wolverson

University of Bath, Department of Physics, Bath, BA2 7AY, United Kingdom

E-mail: gazi.aliev@gmail.com

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Abstract

Singlet oxygen generation in porous silicon (PSi) was investigated by a magneto-optical experiment. Photoluminescence (PL) quenching due to an energy transfer (ET) process mediated by an exchange interaction was monitored in the spectral range 1.4–2.5 eV and in a magnetic field of 0–6 Tesla at different levels of oxygen concentration and excitation pump power. When a magnetic field was applied, both PL recovery and, for magnetic fields below 2 Tesla and high concentrations of oxygen, an unusual additional pump power dependent quenching of the PL was observed. A rate equation model describing the behavior of PL from PSi with oxygen adsorbed at cryogenic temperatures in magnetic field was developed. The model has been expanded to cover the ET process as a function of the nanoparticle size.

Keywords: porous silicon, singlet oxygen, energy transfer, photoluminescence, magnetic field, photosensitizing, exchange mechanism

(Some figures may appear in colour only in the online journal)

1. Introduction

Energy transfer (ET) from photoexcited silicon nanoparticles (SiNPs) to molecular oxygen generates highly reactive singlet state species that have found application in fields as diverse as medicine, photodynamic cancer therapy [1, 2] and chemical engineering, in optically activated reactors [3]. Exchange coupling between SiNP excitons and the ground triplet level of oxygen (the Dexter mechanism [4]) is believed to be the dominant process. Monitoring SiNP photoluminescence (PL) has proved particularly useful in understanding this phenomenon [5–8]. In the presence of oxygen, ET will depopulate the SiNP exciton levels and hence reduce (quench) the PL. The application of a large magnetic field at low temperature will spin polarize both the exciton and molecular triplet levels. The need to satisfy spin selection rules reduces the ET rate in this circumstance, and usually results in a partial recovery and enhancement of the PL.

The dependences of the efficiency of the process on magnetic field and oxygen concentration in terms of the dynamics of the ET and other excitation and relaxation processes were investigated in our previous work [8]. However, for simplicity, that work neglected three questions: these were (i) the NP size distribution, (ii) the pump power and (iii) the random orientation of the oxygen molecules. Here, we extend our model to take into account all of these, together with fresh experimental data to test the new model. Importantly, the revised model reproduces some experimental observations (for instance, a surprising initial quenching of the PL with increasing magnetic field) that were previously unexplained.

In detail, two major simplifications were [8]: (i) the two singlet oxygen levels, $^1\Sigma$ and $^1\Delta$ at $E_\Sigma = 1.63$ eV and $E_\Delta = 0.98$ eV, respectively, were not distinguished; and (ii)
oxygen molecules were assumed to be oriented along the magnetic field. The first simplification does not affect the singlet-to-triplet relaxation times as long as both radiative and non-radiative processes are grouped together; however, by introducing the possibility to excite $^1\Delta$ to $^1\Sigma$ by optical pumping it can modify PL dynamics. This simplification also does not affect ET rates as long as PL intensity close to either $E_a$ or $E_b$ is analyzed, because in these cases ET to either $^1\Sigma$ or $^1\Delta$ level can be neglected due to the large energy gap between these two states (see section 3.1.4). However, for the NPs emitting PL at about 1.3 eV, the ET to the $^1\Sigma$ and $^1\Delta$ levels is comparable and cannot be neglected. Furthermore, the transition rates used in the model cannot be compared straightforwardly with the literature data for those two states. Meanwhile, the assumption that the oxygen molecules are not parallel to the magnetic field has a significant effect on PL dynamics due to the relaxation of selection rules for ET as well as for intramolecular transitions.

In the present work, (i) the singlet $^1\Sigma$ and $^1\Delta$ levels of molecular oxygen were included in the model explicitly; (ii) the model was generalized for the oxygen molecules oriented randomly in the magnetic field (however the magnetic splitting of the orbital doublet $^1\Delta$, $m_\ell = \pm 2$ was not included); and, further, (iii) the ET process is now modeled as a function of NP size and excitation pump rate.

The modeling requires a large set of input parameters. Many of these are available in the literature; others have been estimated as part of the present work. Although our new analysis of the literature data (section 4.5 and the appendix) suggests a set of the parameters which are more realistic than in our previous work [8], we identify some parameters that still need clarification.

2. Experimental

The samples were produced in the form of porous silicon (PSi) layers (thickness $\sim 8 \mu m$) on bulk crystalline substrates by conventional electrochemical etching from wafers consisting typically of $p$-type boron-doped CZ (100) silicon with resistivities of 1–25 $\Omega$ cm. Room temperature anodization was performed in a 1:1 solution of 48% aqueous HF and ethanol; the porosity was controlled by variation of the current ($10–40 mA cm^{-2}$) and was typically 60%–70%. The etched layers were left attached to the substrates for better mechanical strength and were glued to a copper cold finger with heater and thermometer resistors attached. The samples were held either in a continuous-flow cryostat (base temperature $\sim 10 K$) or a superconducting magnet in superfluid helium (base temperature $\sim 1.5 K$, magnetic field up to 6 Tesla either parallel or perpendicular to the layers). In both systems, the cold finger could be raised to the top of the cryostat to expose the cold sample briefly to oxygen gas and it could be heated whilst in vacuum to desorb oxygen. PL was excited by a continuous wave solid state diode laser (wavelength $\sim 450 nm$, power $\sim 0.4-40 mW$ at the sample, with a weakly focused laser spot, size $\sim 4 mm^2$) and detected with an intensified CCD camera and compact single-grating spectrometer. The frequency-resolved spectroscopy (FRS) [9] has been used to examine the dynamics of PSi.

3. Theory (model)

3.1. Rate equations: steady state solution

The model is based on ideas about donor-acceptor recombination that were undertaken by Dunstan and Davies [10]—upon an assumption that O$_2$ molecules will be excited to their singlet states only by adjacent excitons. O$_2$ molecular vibrations are neglected.

The differences between low and high O$_2$ spectra, as well as between those for low and high pump power, point to competition between the physical processes (light absorption, radiative recombination, spin relaxation, and ET) that control the shape of the PL spectrum. These processes are indicated schematically in figures 1 and 2, and serve as a guide to the rate equation model we develop below. In this model, the photo-excited populations of the separate spin states of the excitons and the oxygen molecules are treated explicitly, taking into account the spin-dependence of the ET to O$_2$, the radiative exciton recombination rate, the processes of thermal excitation and spin-lattice relaxation that lead to population redistribution between the spin states for a given silicon NP, and the rates of relaxation from singlet to triplet and singlet to singlet oxygen states.

3.1.1. Silicon nanoparticles without oxygen. At the low measurement temperatures necessary for magneto-optical experiments, we can assume that oxygen is not mobile and we can therefore divide the NPs into two separate populations; those which are not in contact with oxygen (figure 1(c)), and those which are (represented in figure 2).
Figure 2. Schematic overview of the energy transfer from photoexcited excitons in SiNPs to adsorbed oxygen molecules. Optical excitation (blue arrows, ‘pump’) generates excitons confined in SiNPs that can recombine to emit photoluminescence (red arrows, ‘PL’) or can transfer energy to those absorbed oxygen molecules that are in the triplet ground state (orange arrows, ‘energy transfer’). Excited oxygen molecules in the singlet state can return to their ground state via emission of luminescence and/or non-radiative relaxation processes. The details about fractional populations \(n, v, w\), relaxation rates \(r, R, \gamma, \beta\), energy transfer rates \(t\) (with the corresponding indices) and pump rate \(P\) are given in the text.

We write the proportion of NPs which do not have adsorbed oxygen molecules and which do not currently contain an exciton as \(n_{0}g\); excitons are created in these in one of the three triplet exciton states (index \(i = 1, 2, 3\)) with equal pumping rates \(\frac{1}{2P}\) to generate fractional populations \(u_{i}\) (all populations involved in the rate equations are fractional, from here we will omit the word ‘fractional’). The photoexcited NPs can de-populate only by radiative emission (rates \(r_{1}, r_{2}, r_{3}\) for \(m_{S} = \{-1, 0, 1\}\), respectively; assuming \(r_{3} = r_{1}\)), spin-lattice relaxation to spin states lower in energy \(\gamma_{ij}\) or thermal excitation to spin states higher in energy by \(\Delta E\) \((\gamma_{ij} = \gamma_{ji} \exp(-\Delta E/kT))\). Under these assumptions, the steady-state solution of four rate equations for the populations \(u_{i}(i = 1, 2, 3)\) and \(n_{0}\) yields:

\[
-u_{1}r_{1} + \sum_{k=1}^{3} (-u_{k}g_{kk} + u_{k}g_{kk}) = \frac{1}{2}n_{0} = 0,
\]

\[
n_{0} + u_{1} + u_{2} + u_{3} = 1 - F,
\]

where \(F\) is the total fraction of NPs with bound \(O_{2}\).

The low-temperature PL intensity in the case without oxygen will be:

\[
I_{PL} = r_{1}(u_{1} + u_{3}) + r_{2}u_{2}.
\]

The influence of non-radiative transitions is found to be negligible for \(T < 100 \text{K}\) but increases substantially above \(150 \text{K}\) [11, 12]; in the latter case, the radiative contributions to decay rates \(r_{1}\) and \(r_{2}\) must be considered in (2).

3.1.2. Silicon nanoparticles with oxygen. We now consider the second population of NPs, those which are in contact with oxygen. We write the proportions of NPs which do not contain an exciton as \(n_{p}\), where \(j = 1, 2, 3\) runs over the three possible oxygen triplet states \(m_{S} = \{-1, 0, 1\}\), respectively. As above, excitons are created in these NPs in one of the three triplet exciton states (index \(i = 1, 2, 3\) corresponding to \(m_{S} = \{-1, 0, 1\}\), respectively) with equal pumping rates \(\frac{1}{2P}\) to generate coupled exciton-oxygen populations \(n_{p}\). The exciton radiative recombination and spin-lattice relaxation terms are as above, and we introduce \(\beta_{ij}\), a spin-lattice relaxation and thermal excitation term between the oxygen triplet states analogous to \(\gamma_{ij}\). We must account for NPs in which the oxygen is in the singlet state and no exciton is present. This is the state of an NP after ET and before relaxation of the oxygen molecule, at which point the oxygen states have populations \(n_{S}(^{1}\Sigma)\) and \(n_{D}(^{3}\Delta)\). We also must account for NPs in which an exciton has been created while the oxygen is still in the singlet state (populations \(v_{j}\) and \(w_{j}\) of \(^{1}\Sigma\) and \(^{3}\Delta\) levels, respectively). Also, we have to consider the possibility of optically allowed excitation of \(O_{2}\) from its lower singlet \(^{3}\Delta\) to the higher singlet \(^{1}\Sigma\) level.

Finally, we introduce the ET process which is the focus of this work through the rates \(t_{\alpha}\). For the case of an oxygen molecule which is aligned along the magnetic field, the matrix \([\alpha_{ij}]\) has a simple form in order to impose the overall conservation of spin angular momentum, \(\Delta m_{S} = 0\):

\[
[\alpha_{ij}] = \begin{pmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
1 & 0 & 0
\end{pmatrix},
\]

where \(t\) is the ET rate at \(B = 0\). However, for \(O_{2}\) tilted with an angle \(\theta\) with respect to the magnetic field, the spin states of the \(O_{2}\) triplet are mixed, the selection rules (3) are relaxed and, from Fermi’s golden rule, the matrix needs to be considered as follows:

\[
[\alpha_{ij}] = \begin{pmatrix}
\alpha_{31} & \alpha_{32} & \alpha_{33} \\
\alpha_{21} & \alpha_{22} & \alpha_{23} \\
\alpha_{11} & \alpha_{12} & \alpha_{13}
\end{pmatrix},
\]

where \(\alpha_{ij}\) are components of eigenvectors of the oxygen spin-Hamiltonian \(H_{O_{2}}\):

\[
H_{O_{2}} = \begin{pmatrix}
-g\mu_{B}B + D_{z} & \frac{D}{2} \sin \theta \cos \theta & \frac{D}{2} \sin \theta \sin \theta \\
\frac{D}{2} \sin \theta \cos \theta & -D_{z} & \frac{D}{2} \sin \theta \cos \theta \\
\frac{D}{2} \sin \theta \sin \theta & \frac{D}{2} \sin \theta \cos \theta & g\mu_{B}B + D_{z}
\end{pmatrix},
\]

where \(\mu_{B} = 0.057 8838 \text{ meV T}^{-1}\) is the Bohr magneton, \(D_{z} = (3 \cos^{2} \theta - 1)D/3\), and \(D\) is the zero field splitting shown in figure 1. Subscripts \(\Sigma\) or \(\Delta\) for the rate \(t\) and rate matrix \(t_{ij}\) used below indicate ET to \(^{1}\Sigma\) or \(^{3}\Delta\) levels, respectively (e.g. \(t_{23}, t_{31}\)).

Figure 1(a) shows the oxygen triplet states in a magnetic field, calculated according to (5), for two orthogonal directions: \(B\) parallel and perpendicular to the molecular symmetry axis, \(z\).

As in the previous sub-section, we present the steady state solutions of the resulting nineteen rate equations plus the
condition that the total number of NPs with adsorbed oxygen remains constant.

The first sets of expressions, (6), represent the generation and loss of excitons in NPs with adsorbed triplet oxygen (block 2 in figure 2); the existence of two triplet entities gives nine possible joint spin states, so that nine equations are required

\[
\frac{1}{2}(P_{i j} + S_{i j} + D_{i j}) + \sum_{k, i} \gamma_{i k} n_{i k} + \sum_{k, j} \beta_{i j} n_{i j} = r_{i} + t_{\Sigma i} + t_{\Delta i} + \sum_{k} \gamma_{i j} n_{i j} + \sum_{k, j} \beta_{i j} n_{i j} = 0, \tag{6}
\]

where \(i = 1, 2, 3, j = 1, 2, 3\)

\[
S_{j} = (a_{j}^{2} + a_{j}^{2})R_{b-x,0} + a_{j}^{2}R_{b-x,0}, \tag{7}
\]

\[
D_{j} = (a_{j}^{2} + a_{j}^{2})R_{b-x,0} + a_{j}^{2}R_{b-x,0}, \tag{8}
\]

and \(R_{b-x,0}\) (or \(R_{b-x,0}\)) and \(R_{b-x,1}\) (or \(R_{b-x,1}\)) are the relaxation rates from the singlet \(1\Sigma\) (or \(1\Delta\)) level of oxygen to un-mixed levels of triplet oxygen at \(B\|z\) with \(m_{S} = 0\) and \(m_{S} = \pm 1\), respectively.

The sets (9) and (10) of three equations each represent the optical pumping and de-excitation of NPs with adsorbed oxygen in its singlet \(1\Sigma\) state (block 4 in figure 2) and \(1\Delta\) state (block 6 in figure 2), respectively; the three equations \((i = 1, 2, 3)\) in each of the two sets arise from the three exciton states

\[
\left[ P + R_{b-a} + \frac{1}{2}(S_{i} + S_{2} + S_{3}) + \sum_{k, i} \gamma_{i k} n_{i k} \right]w_{i} = r_{i} + R_{b-a} + \frac{1}{2}(S_{i} + S_{2} + S_{3}) + \sum_{k, i} \gamma_{i k} w_{i}, \tag{9}
\]

where \(R_{b-a}\) is the relaxation rate \(1\Sigma \rightarrow 1\Delta\).

\[
\left[ P + r_{i} + \frac{1}{2}(D_{1} + D_{2} + D_{3}) + \sum_{k} \gamma_{k} v_{k} \right]v_{i} = \frac{1}{2}Pn_{D} + R_{b-a}w_{i} + \sum_{k, i} \gamma_{v k} v_{k}, \tag{10}
\]

Here it is assumed that \(\frac{1}{4}Pn_{D}\) from block 5 comes to each of three levels of block 6, while \(\frac{1}{4}Pn_{D}\) goes to block 3.

The set of three \((j = 1, 2, 3)\) equations (11) represent the generation and loss of NPs with triplet oxygen but no exciton (block 1 in figure 2).

\[
\left[ P + \sum_{k, j} \beta_{i j} \right]n_{j} + \sum_{k, j} \beta_{i j} n_{k} + \frac{1}{2}(S_{i} + D_{i} + D_{i}) + r_{i}n_{ij} = 0. \tag{11}
\]

The two equations (12) and (13) represent the generation and loss of NPs with singlet oxygen in the \(1\Sigma\) level (block 3 in figure 2) and \(1\Delta\) level (block 5 in figure 2), respectively, but with no exciton:

\[
\left[ P + R_{b-a} + \frac{1}{2}(S_{i} + S_{2} + S_{3}) \right]n_{S}
+ \frac{1}{2}Pn_{D} + \sum_{i} \left( r_{i}w_{i} + \sum_{j} n_{ij} \right) = 0, \tag{12}
\]

\[
\left[ P + \frac{1}{3}(D_{1} + D_{2} + D_{3}) \right]n_{D}
+ R_{b-a}n_{S} + \sum_{i} \left( r_{i}v_{i} + \sum_{j} n_{ij} \right) = 0. \tag{13}
\]

With these equations, we have a fully-determined system of twenty linear equations with twenty variables, however, the balancing equation (14) is important for normalizing and cannot be omitted; so any one of the above equations can be made redundant. Thus, equation (14) imposes the requirement that the total fraction of NPs with adsorbed oxygen should remain constant at \(F\):

\[
n_{S} + n_{D} + \sum_{i} \left( n_{i} + w_{i} + v_{i} + \sum_{j} n_{ij} \right) = F. \tag{14}
\]

We can sum all the exciton radiative processes in order to obtain an expression for the low temperature PL intensity \(I_{PL}\) as follows:

\[
I_{PL} = \sum_{i} \left( v_{i} + u_{i} + w_{i} + \sum_{j} n_{ij} \right), \tag{15}
\]

and this expression can be evaluated as a function of magnetic field, pump rate or particle size. As before, a zero nonradiative contribution to \(r_{i} (= r_{3})\) and \(r_{2}\) is assumed.

We note that the probability of relaxation of the oxygen singlet to the triplet state (and also of \(1\Sigma \rightarrow 1\Delta\) transition) with the simultaneous recombination of a Si exciton (such as transitions from blocks 4 and 6 to block 1 and from block 4 to block 5 in figure 2) was not considered. These probabilities are proportional to the squares of the corresponding fractional populations and are smaller than the linear ones, and thus can be neglected. They also make the system of equations nonlinear which requires a more laborious algorithm to solve it. Exciton hopping (tunneling) processes in interconnected SiNPs are also ignored in the model.

### 3.1.3. Effect of randomly oriented \(O_{2}\)

In assuming that the oxygen molecules are randomly oriented within PSi, the number of oxygen molecules oriented with an angle \(\theta\) with respect to the magnetic field \(B\) is proportional to \(\sin \theta\). The PL intensity calculation was performed for one hemisphere of solid angle, i.e. for \(\theta\) from \(0^\circ\) to \(90^\circ\) (with the step of \(0.1^\circ\)), with the corresponding normalized weighting factor of \(\frac{1}{2} \sin \theta\).

### 3.1.4. NP size (PL energy) dependence of the ET rate

Zero phonon and phonon assisted contributions to the ET need to be considered. The contribution of each phonon replica must be summed for each PL energy. The ET rate \(i\) is proportional
to the probability of ET from confined Si excitons in the particles, where their energy levels are in resonance with $E_T = 1.63$ eV, and from Si excitons in smaller and bigger particles with the energies separated by multiple transverse optical (TO) phonon energies of $\pm n/\omega_{TO}$, $n = 1, 2, 3, \ldots$ from $E_T$. The ET rate also proportional to the number of oxygen molecules adsorbed at the surface of a NP of a certain radius $R$ (smaller for higher energies); the surface area is proportional to $R^2$. Finally, the number of oxygen molecules is proportional to frequency of appearance of this particular radius given by the radius-distribution (RD) function $\nu(R)$.

Thus:

$$t(E) = t_1(E)R_{\text{tot}}^2 \nu(E) |dR/dE|,$$

where $\nu(E)$ is the RD function with the $R$-scale converted to the $E$-scale according to the following relation between the SiNP PL peak position $E$ in eV and the particle radius $R$ in nm [13–17]:

$$E = E_g^0 + A/R^a,$$

where $E_g^0 = 1.17$ eV is the band gap of bulk Si at $T = 0$ K, and the parameters $a$ and $A$ are constants which slightly vary in the literature—we used $a=1.39$ and $A=1.42$ eV nm$^a$ [13, 17] 2. The term $|dR/dE|$ arises to conserve the distribution function normalization in the energy scale. From (17):

$$R(E) = A^{1/a}(E - E_g^0)^{-1/a},$$

$$|dR/dE| = a^{-1}(E - E_g^0)^{1/a-1}.$$  

According to (18), the PL peak positions of samples 1 and 2, 1.71 and 1.60 eV, and $E_g = 1.63$ eV, correspond to the NP radii 2.0, 2.4, and 2.3 nm, respectively.

As shown by Suemoto et al [18] and further discussed by Yorikawa and Muramatsu [16, 19] (see also [20]), an RD function of an ensemble of NPs of different size can be deduced from the PL spectrum of the ensemble excited at an energy $E_{\text{exc}}$ with an intensity $I(E_{\text{exc}})$:

$$I_{\text{PL}}(E) = C\nu(E) \nu(E) |dR/dE| I(E_{\text{exc}}),$$

where $C$ is a constant including the quantum yield and $I_{\text{tot}}$ is the total absorption of exciting laser light by the ensemble. At low temperature and for sufficiently large gap between $E_{\text{exc}}$ and the PL energy $E$, $\nu(E)$ is a simple parabola as a function of $(E_{\text{exc}} - E)^2$ [18]. The function $\nu(R)$ is usually fitted by a lognormal or a Gaussian function as commonly observed for colloid or granular particle size distributions [12, 16, 20, 21]. A lognormal function of the following form was found to be preferable in most of the cases [12, 16]:

$$\nu(R) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left(-\frac{1}{2}\left(\ln R/R_0 \right)^2\sigma^{-2}\right),$$

where $R_0$ is the median, $\sigma$ is the standard deviation and $R_0$ is the minimal radius. The RD maximum (mode) is at $R_p = R_0 + R_0\exp(-\sigma^2)$ and the full width at half-maximum is given by $R_p = 2R_0\exp(-\sigma^2)\sinh(\sigma\sqrt{\ln 4})$.

Figure 3(c), (d) shows that the PL quenching occurs far from $E_\Sigma$, to the both sides of the spectra. This is because, as mentioned above, the phonon replicas of the ET resonance are involved. The probabilities of these replicas decrease exponentially with an increasing gap between the replica.
and the resonance energy as follows from the theory by Miyakawa and Dexter [22]:

$$t_\xi(E) = t_\xi(0) \exp(-\chi E), \quad \text{where } E = n \hbar \omega_{\text{TO}}, \quad (21)$$

n = 1, 2, 3, ...

In our model, we approximated t_\xi(E) per a single oxygen molecule by sum of multiple lorentzians: the first lorentzian positioned at E_\Sigma (or E_\Delta) and the others at the distance of ±n\hbar\omega_{\text{TO}} from the first, with the amplitudes decreasing exponentially according to (21). For brevity, only one TO phonon, namely the energy-conserving TO phonon with energy 63 meV having the highest density of states and located at the Γ point of the silicon phonon dispersion was considered in our model for NPs emitting above as well as below the triplet to singlet transition energy thresholds. However, as reported in [6, 7, 23] and seen in figure 3(b), the phonon replicas associated with the momentum-conserving TO phonon with energy 57 meV located at the X point of the Brillouin zone can also contribute in the ET process; this momentum-conserving phonon was reported in [6, 7, 23] to be dominant for the 1st replica below the triplet to singlet transition energy. However it does not seem to be a common rule. Our results (figure 3) demonstrate the gap of 63.4 meV between the resonant dip at 1.6207 eV and the 1st dip below it at 1.5573 eV for sample 1 and the gap of 57.2 meV between the resonant dip at 1.63 eV and the 1st dip below it at 1.5728 eV for sample 2. Thus, only sample 2 reveals ET assisted dominantly by the momentum-conserving TO phonon. This 1st replica below the resonance is interesting also from the other point of view: due to the indirect character of a Si exciton in NP, ET at one phonon below the resonance occurs as no-phonon process [24].

The resulting size (PL energy) dependent ET rate was normalized to the value t(E_\Sigma) obtained from fitting the experimental data in figure 4.

4. Experimental results and discussion

4.1. Low temperature PL spectra: effects of magnetic field, pump power and O_2 concentration

Typical PL spectra at 1.6 K for two PSi samples exposed to zero, low and high O_2 concentrations are shown in figure 3. PL from samples 1 (figure 3(a)) and 2 (figure 3(b)) were excited with a laser power I_{\text{exc}} of about 0.4 and 17.5 mW, respectively (see details above, section 2). The broad PL band corresponding to a wide distribution of SiNP sizes [20, 25–27] is observed for the cases of low and zero O_2 concentration. Zero-oxygen PL for samples 1 and 2 peaked at about 1.71 and 1.60 eV have linewidths of about 0.34 and 0.36 eV, respectively. The low O_2 spectra in figure 3(a), (b) are of a similar shape to those obtained in the absence of oxygen but are lower in intensity. The high O_2 spectra demonstrate much stronger quenching with severe deformation of the PL shape. It is not possible to measure quantitatively the concentration of oxygen adsorbed on the SiNPs but the stronger quenching of the PL (with the other conditions, e.g. pump power, kept the same) gives a clear indication that the concentration is higher than in the case of the weaker quenching. The strongest quenching of the PL occurs precisely (as seen more clearly in figures 3(c), (d)) for NPs having an exciton energy equal to E_\Sigma = 1.63 eV [28–30]. We note that the dip position at 1.621 eV for sample 1 is lower than that expected for gaseous oxygen, 1.63 eV. The spectra show a number of other sharp downward-pointing peaks or dips part of which originate from the enhanced ET to oxygen for NPs whose exciton energies differ from 1.63 eV by energies corresponding to one or more momentum- and energy-conserving phonons (located, as mentioned above, at the X and Γ points of the silicon phonon dispersion, respectively). These phonon related dips are partly masked by the dips whose energies differ by phonon energies of 1.96 and 1.74 eV, which correspond to ET to the oxygen dimer state 2\Delta_{(0,0)} and the stretched dimer state 2\Delta_{(0,1)}, respectively [23, 24]. Significant PL is observed above the threshold for ET to the 1\Sigma state, even at these higher O_2 concentrations.

Figure 3(c), (d) demonstrates the dependence of PL quenching strength (QS), defined by the ratio

$$\frac{I_{\text{E(O_2)}}(B - 0)}{I_{\text{E(O_2)}}(B) - 0}$$

3 As discussed in [6], the weak van der Waals interaction of adsorbed O_2 molecules with Si surface atoms lowers the energy of the excited states of molecular oxygen and slightly broadens the transitions.

Figure 4. Normalized PL at E_\Sigma: magnetic field dependence. Points: the ratio of the PL intensity at E_\Sigma at magnetic field B to that at zero field B = 0 for high (circle) and low (square) O_2 concentrations; lines: predictions of the rate equation model for B/0. (a) Inset: I(B) slope deviation at B = D/\mu B.
on photon energy for $B = 0$, 3 and 6 T at $T = 1.6$ K. An abrupt (in log scale) rise near 1.63 eV is followed by a more gentle slope prolonged until about 2.4 eV. The dimer and phonon related features manifest here as peaks. QS at zero magnetic field at 1.63 eV for sample 2 (figure 3(d)) is about 30 times weaker than that for sample 1 (figure 3(c)).

4.2. PL intensity at $E_2$: magnetic field dependence

We extract PL intensities at $E_2$, 1.621 eV (sample 1) and 1.63 eV (sample 2), from the spectra of figure 3(a), (b) and plot them in figure 4 as a function of magnetic field $B$, normalized to the PL intensity at $B = 0$ T. This normalization eliminates the difficulties associated with considering absolute PL intensities and will facilitate the comparison of data from different samples.

The high O$_2$ PL in figure 3(a) both above and below the 1.63 eV threshold shows a much stronger recovery of intensity as the magnetic field is increased, by a factor of about three times (figure 4(a), right scale) and, unlike the case of low O$_2$ coverage (figure 4(e), left scale), the recovery of the PL has not saturated up to $B = 6$ T. The enhanced quenching at $B = 0.5$ T is not an artefact. Rather different behaviors are exhibited by sample 2, when excited by higher pump power (figure 4(b)); (i) the level of PL recovery in a magnetic field for the specimen with high O$_2$ is smaller than that for the specimen with low O$_2$; (ii) in the case of high O$_2$, PL is additionally quenched in the wider range (up to $B = 2$ T) than that for sample 1 (below 1 T) and deeper$^4$; (iii) further increasing pump power leads to decreasing PL recovery at higher fields with simultaneous shallowing the dip of additional quenching at lower fields (not shown).

Figure 4 also shows results calculated using (15), in which we take a set of parameters based on the recent literature and our measurements. These are summarized in table 2. For the two sets of experimental data, we maintain all parameters at the same values, except for those associated with pump power and the ET process itself: these are $P$, the pump rate of Si excitons, $F$, which expresses the fraction of NPs with O$_2$, and the ET rate $t$, which decreases as the number of NPs having multiple O$_2$ molecules available decreases. The ratio of the pump rates used in simulation of the magnetic field dependences for samples 1 and 2 (figure 4) was kept equal to the ratio of the actual power used in our experiment: 1750 s$^{-1}$/40 s$^{-1} = 17.5$ mW/0.4 mW (the exact fitting numbers are incidental, they can be scaled together with the other rates). The parameters $r_1$, $r_2$ and $r_3$ in the model can be magnetic field-dependent, however, with the lack of the literature data for these quantities, we fitted the data with field-independent $r_1 = r_2$ and $r_3$. There is also the lack of knowledge about the actual difference between $r_1$ and $r_2$ (see more details about the justification of parameters in the appendix).

$^4$ Similar behavior of PL from bulk Si with considerable decrease (as much as 10%–40%) in weak magnetic field $B < 0.25$ T was observed by Chen et al [31] and was attributed to strong enhancement of surface recombination due to magnetic-field-induced confinement of photoexcited free carriers near the surface.

| # | $R_e$, nm | $\sigma$ | $R_m$, nm | $R_{av}$, nm |
|---|---|---|---|---|
| 1 | 1.83 (1.79) | 0.20 (0.39) | 1.76 (1.79) | 0.84 (0.92) |
| 2 | 1.99 (1.84) | 0.28 (0.67) | 1.84 (1.84) | 1.24 (1.58) |

Having more than a dozen parameters which can be varied, it is possible to fit the magnetic field dependence of PL recovery with different sets of parameters. Two more experimental dependences—power dependence and size (PL energy) dependence (see sections 4.3.3 and 4.4.1 and figures 6 and 7)—allowed us to iterate those sets of parameters to get overall self-consistent agreement of simulated curves with the experiment. Thus, we get not only excellent fits of $I(B)$ dependences for two different pump rates and oxygen coverage (figures 4 and 7(c), (d)), but also prediction of QS (figure 7(b)) and reasonable good fit of size (energy) dependence (figure 6(b)).

We note, that (i) the $I(B)$ for sample 2 with the additional quenching below 2 T (figure 4(b)) can be fitted well if $r_2 = r_1$; (ii) this fitting (sample 2) is sensitive to the spin-lattice relaxation times $\gamma^{-1}$ and $\beta^{-1}$, which are comparable to the lifetimes $\tau^{-1}_1$, $\tau^{-1}_2$, $R_n^{-1}_p \chi$ and $R_n^{-1}_o$ (table 2), thus the system is not fully thermalized; (iii) the transfer rate $t_2$ at $E_2$ is slightly faster than that previously reported [23], however, this gives the subsequent good agreement of power dependence estimation with the experimental results; (iv) some rates, such as $t_2$ and $R_n^{-1}_o$, are too slow in comparison with the others, thus the system is not sensitive to their variation up to some extent.

In the simulations, the temperature also can be varied, since the field at which the PL recovery approaches saturation is sensitive to the relationship between $g\mu_B B$ and $kT$ (see the previous publication [8]).

4.3. Size (PL energy) dependence

4.3.1. Radius distribution function. RD functions of samples 1 and 2 deduced from their PL spectra at 1.6 K (without O$_2$) excited with 2.755 eV (figure 3(a), (b)) are well fitted by (20); the parameters are summarized in table 1. We note that our samples can be fitted reasonably well by Gaussians with sample 2 fitted better than sample 1; the Gaussian parameters are given in table 1 in brackets. In figure 5(a), the function $\nu(E) dR/dE$ (deduced from PL as well as calculated), the radius $R(E)$ and the normalized PL of sample 1 without O$_2$ are shown plotted versus energy.

4.3.2. ET rate. From 1.63 to 2.4 eV, the calculated ET rate (see section 3.1.4 above) exponentially drops by about five orders of magnitude; the exponential coefficient $\chi = 15$ eV$^{-1}$ in (21) was chosen from fitting the experimental results shown in figure 6(b). The linewidth of the replicas of 35 meV was roughly estimated from the shape of dips in figures 3(a),
rEd E

\[ \text{values of samples 1 half the energy of the TO phonon, 63 meV.} \]

\[ \text{magnitude slower than the resonant process of the non-resonant ET process is about four orders} \]

\[ \text{of 1.4–2.4 eV for 1, 3 and 6 Tesla are shown. Dashed lines depict} \]

\[ \text{for SiNPs with high and low O2 in samples 1, 3 and 6 Tesla are shown. Dashed lines depict} \]

\[ \text{versus photon energy.} \]

\[ \text{Figure 6. Size (PL energy) dependence. Thin lines: the ratio of experimental PL spectra at magnetic field} \]

\[ \text{at 0 \text{T and} B = 1.6 \text{K. Points: experimental results for the ET rate dependence on the detected PL energy} \]

\[ \text{in PSi at} B = 300 \text{K from} [23]. \]

\[ \text{(b) and overall spectral shape in figure 6(b) and it is close to} \]

\[ \text{half the energy of the TO phonon, 63 meV.} \]

\[ \text{The ET rate} t_\Delta \text{from Si excitons in NPs, emitting PL at} \]

\[ \text{at 1.4–2.5 eV range, to oxygen \^1A level was calculated as above with the same} \]

\[ \text{and corresponding energy distance} \varepsilon \text{from} E_\Delta = 0.98 \text{eV. The calculation shows that, at} E_{\nu} \text{, the rate} t_\Delta \text{of} \]

\[ \text{the} \]

\[ \text{In the literature, the energy dependence of} \tau \text{in PSi, obtained for the range 1.5–1.85 eV at} 300 \text{K and 1 bar} \]

\[ \text{ambient, has been reported in} [23] \text{(points in figure 5(b)). In the range 1.63–1.85 eV it is simply proportional to} R_{\text{et}}. \]

\[ \text{Comparison to experiment.} \]

\[ \text{Figure 6 shows the experimental and calculated ratio} I(B)/I(B = 0) \text{for samples 1 and 2 plotted for the spectral range of} \]

\[ \text{for sample 2 and (almost) no additional quenching for sample 1. The discrepancy between} \]

\[ \text{between the experimental and simulated curves for low O2 is larger than that for high O2 in figure 6—} \]

\[ \text{simulated and experimental QS versus pump power, i.e.} \]

\[ \text{Figure 7(a) demonstrates the PL intensity,} I(P), \text{simulated at} E_{\nu}. \]

\[ \text{All parameters in (15) were kept the same as for the simulation of} I(B) \text{shown in figure 4 for high O2 with varying} \]

\[ \text{Two curves for} B = 0 \text{~T and} B = 6 \text{~T for each sample are shown. Also,} I(P) \text{for the NPs without O2, i.e. simulated with} \]

\[ \text{parameters} F = 0, \text{is shown (thin black lines).} \]

\[ \text{from specimens without O2 is typical for two-level system at steady state: linear at lower} P \text{saturation at higher} P, \text{the kink is} \]

\[ \text{at} P \sim r, \text{and the saturation occurs when} P \text{overwhelms} r. \]

\[ \text{The behavior of the system with O2 is different: (i) the linear} I(P) \text{at lower} P \text{saturates at} P \text{higher than that for the case} \]

\[ \text{without O2; (ii) there is one more kink between the linear dependence and the saturation. Those kink positions} \]

\[ \text{are conditioned by the complex relation between the pump, ET and relaxation rates involved (see section 3.1). The saturation} \]

\[ \text{level of} I(P) \text{(with and without O2) is magnetic field dependent due to} r_1 = r_2 (table 2).} \]

\[ \text{In figure 7(b), the simulated QS versus pump power, i.e. the ratio} \]

\[ \text{at} B = 0 \text{~T (figure 7(b), solid lines) approaches} \]

\[ \text{which means that no oxygen-induced PL quenching} \]

\[ \text{for sample 1 and 2 plotted for the spectral range of} 1.4–2.4 \text{eV for} 1, 3 \text{and 6 Tesla. Each spectral point was calculated using} \]

\[ \text{with the energy-dependent parameters being normalized} \]

\[ \text{by their values at} E_{\nu}, \text{obtained from fitting the experimental results in figure 4. It is seen from} \]

\[ \text{the additional quenching beginning from some energy level (for low O2 above 1.8 eV), whereas the ratios for sample 1} \]

\[ \text{demonstrate negligible additional PL quenching at high energies (figure 6(a), (b)). Despite some quantitative} \]

\[ \text{discrepancies, qualitatively the simulated spectra reveal all the main features in the spectrum such as the overall} \]

\[ \text{and the additional PL quenching for sample 2 and} \]

\[ \text{for high O2 in} \]

\[ \text{simulated and experimental curves for low O2; the neglect of ET to oxygen dimer states, and the breakdown of the assumption of the number of adsorbed O2 molecules being proportional to the surface area} \]

\[ \text{at low concentrations.} \]

\[ \text{4.4. Pump power dependence} \]

\[ \text{Figure 7(a) demonstrates the PL intensity,} I(P), \text{simulated at} E_{\nu}. \]

\[ \text{All parameters in (15) were kept the same as for the simulation of} I(B) \text{shown in figure 4 for high O2 with varying} \]

\[ \text{Two curves for} B = 0 \text{~T and} B = 6 \text{~T for each sample are shown. Also,} I(P) \text{for the NPs without O2, i.e. simulated with} \]

\[ \text{the parameter} F = 0, \text{is shown (thin black lines).} \]

\[ \text{from specimens without O2 is typical for two-level system at steady state: linear at lower} P \text{saturation at higher} P, \text{the kink is} \]

\[ \text{at} P \sim r, \text{and the saturation occurs when} P \text{overwhelms} r. \]

\[ \text{The behavior of the system with O2 is different: (i) the linear} I(P) \text{at lower} P \text{saturates at} P \text{higher than that for the case} \]

\[ \text{without O2; (ii) there is one more kink between the linear dependence and the saturation. Those kink positions} \]

\[ \text{are conditioned by the complex relation between the pump, ET and relaxation rates involved (see section 3.1). The saturation} \]

\[ \text{level of} I(P) \text{(with and without O2) is magnetic field dependent due to} r_1 = r_2 (table 2).} \]

\[ \text{In figure 7(b), the simulated QS versus pump power, i.e. the ratio} \]

\[ \text{at} B = 0 \text{~T (figure 7(b), solid lines) approaches} \]

\[ \text{which means that no oxygen-induced PL quenching} \]
Table 2. Parameters used in modeling low temperature PL at $E_2$ for sample 1 (2); inverse rates in seconds, zero-field splitting $D$ in meV, and $F$ is dimensionless. The given system of the inverse rates is scalable with no effect to the modeled PL dynamics.

| Silicon NP | This work | Typical | Source |
|------------|-----------|---------|--------|
| Low O$_2$  | High O$_2$ |         |        |
| $\kappa^{-1}$ | $4 \times 10^{-3}$ | $4 \times 10^{-3}$ | $10^{-5}$--$10^{-2}$ | [11, 12, 27, 32–42] |
| $\kappa_2^{-1}$ | $10^{-3}$ | $10^{-3}$ |         |        |
| $\gamma^{-1}$ | $7 \times 10^{-4}$ | $7 \times 10^{-4}$ |         |        |
| $P^{-1}$ | $1/40 (1/1750)$ | $1/40 (1/1750)$ |         |        |
| $D$ | 0 | 0 | 0.0055 | [43] |

Oxygen

| $F$ | 0.62 (0.9) | 1 |
| $R_{C\perp,x,1}$ | 1 | 1 | 0.53–11.65 | [44–48] |
| $R_{C\perp,x,0}$ | 60 | 60 | 58.8 | [48, 49] |
| $R_{C\perp,x,1}$ | $2 \times 10^{-4}$ | $2 \times 10^{-4}$ | $7.9 \times 10^{-6}$–79 | [30, 47, 48, 50, 51] |
| $R_{C\perp,x,0}$ | $2 \times 10^{-3}$ | $2 \times 10^{-3}$ |         |        |
| $\beta^{-1}$ | $10^{-4}$ | $10^{-4}$ | $2.5 \times 10^{-5}$–$4.6 \times 10^{-2}$ | [30, 47, 48, 51–53] |
| $\Delta_0^{-1}$ | $9.6 \times 10^{-4}$ | $(4.2 \times 10^{-5})$ | $9 \times 10^{-8}$ $(3 \times 10^{-6})$ | $2.6 \times 10^{-6}$ per molecule | [23] |
| $\Delta_0^{-1}$ | 15.1 (0.75) | $1.4 \times 10^{-3}$ | $(5.4 \times 10^{-3})$ |         |        |
| $D$ | 0.4429 | 0.4429 | 0.43–0.49 | [54–64] |

Figure 7. PL intensity and quantum yield versus pump power. (a) Lines: predictions of the model for $P$ (solid) and with the high O$_2$ coverage (dashed) at $B = 0$ T (dotted) and $B = 6$ T (solid) for samples 1 (red) and 2 (blue). Points: PL intensity from figure 3(a), 2(b) (normalized to that for $B = 0$ T) for samples 1 (closed) and 2 (open) at $E_2$. (b) Lines: calculated ratios $I(P)$ at $B = 0$ T (solid) and $B = 6$ T (dashed) for samples 1 and 2; the ratios are shown by dots. Dashed horizontal line is an eye guide for the unit value of QS. Points: QS from figure 3(c), (d) for samples 1 (closed) and 2 (open) at $E_2$ and magnetic field 0 and 6 Tesla. (c), (d) Lines: calculated ratios $I(P)$ for the low (a) and high (b) O$_2$ coverage for samples 1 (solid) and 2 (dots) at magnetic field 0.5, 1, 3 and 6 Tesla. Points: the corresponding experimental ratios from figure 4 for samples 1 (closed) and 2 (open).

occurs, while the QS at $B = 6$ T becomes slightly less than unity at $P \sim 5 \times 10^5$ (figure 7b, dashed lines) before it approaches 1 at $P \sim 10^5$. However, if QS is defined as $I(P)$ with O$_2$ = 0 $I(P)$ without O$_2$ (as shown in figure 3(c), (d)), then the value of QS at $B = 6$ T at the PL saturation level is about 1.6 (figure 7b, dotted lines). Also, the ratio $I(P)B = 0$ $I(P)B = 0$ (with oxygen) becomes less than unity at some points (see line crossings at about $P = 5 \times 10^3$ s$^{-1}$, figure 7a), which means that instead of a magnetic field-induced PL recovery, an additional, magnetic field-induced PL quenching occurs. This is more clearly demonstrated in figure 7c, (d) for magnetic fields 0.5, 1, 3 and 6 Tesla for low (figure 7c) and high (figure 7d) O$_2$ concentrations. Depending on parameters $\Delta_0$ and $B$, the ratio $I(P)$ crosses unity at some point on the $P$-axis. For a weak $B \leq 0.5$ T, the additional quenching occurs at lower $P$ at the linear regime, whereas for stronger $B > 0.5$ T the additional quenching occurs at higher powers. Note, in figure 7c in the linear part of $I(P)$, the ratio $I(P)B = 0$ $I(P)B = 0$ is a unimodal function of $t^{-1}$ (not shown), peaked at about $t^{-1} = 10 \mu$s, thus values of 960 and 42 $\mu$s for low O$_2$ fall at one side of the peak (positive derivative), whereas 0.09 and 0.3 $\mu$s for high O$_2$ fall at the other side of the peak (negative derivative).

4.4.1 Comparison to experiment. We do not show the detailed power dependence data in the present work; however, we can compare the experimental values of $I(E)$, $I(E)$ with O$_2$ = 0 $I(E)$ with O$_2$ = 0 and $I(E)B = 0$ $I(E)B = 0$ for samples 1 and 2 excited by different power with those predicted by our model at $E_2$. The pump rate values of 40 and 1750 s$^{-1}$ chosen as parameters for fitting the curves in figure 4(a) and (b), respectively, indicate that the system is in the almost linear regime with and without
O₂ at P = 40 s⁻¹ and in the strongly nonlinear regime with and without O₂ at P = 1750 s⁻¹.

The QS (high O₂) predicted by the model (figure 7(b)) is about 100 at P = 40 s⁻¹ and about 4 at P = 1750 s⁻¹, and these values are in good agreement with the experimental values of 119 and 4.4 (shown by points) obtained from figure 3(c) and (d), respectively for B = 0 T. Also, the dramatic transformation of magnetic field dependence (compare figure 4(a) with (b)) and size dependence (compare figure 6(a), (b) with (c), (d)) with change of power are predicted well. Figure 7(c), (d) helps with the better understanding the differences between figure 4(a) and (b).

4.5. Parameters used for the calculations

The justification of the parameters used in the calculations is given in the appendix. The final set of parameters used is summarized in table 2.

5. Conclusions

A rate equation model was developed to describe PL dynamics in silicon nanoparticles with adsorbed O₂ in an external magnetic field. The key feature of the dynamics is the ET to oxygen molecules by an exchange mechanism, accompanied by singlet oxygen generation. This was validated by a magneto-optical experiment.

Excellent fits of the magnetic field dependence of the PL intensity at the energy E₂ = 1.63 eV, resonant with the transition energy from oxygen triplet (3Σg) to singlet (1Σg) state, were demonstrated for different levels of pump power and oxygen concentration.

Phonon-assisted ET processes at the energies non-resonant with E₂ and E₃ were considered. Good agreement with the theoretical model was demonstrated for the magnetic field dependence of the broad PL band generated by the distribution of nanoparticle sizes in PSi. It was found that the PL quenching (and its partial recovery in a magnetic field) far from E₃ was still mediated by size-dependent non-resonant phonon-assisted ET processes competing with the relaxation and pump rates.

Importantly, this new model describes well the unusual, magnetic field-induced additional PL quenching observed (i) at the high-energy wing of the PL band at higher pump levels and (ii) in the magnetic field dependence below 2 Tesla for higher as well as at lower pump levels.

The dependence of the PL intensity at E₂ on pump power was analyzed. An excellent prediction of the PL QS for the different pump rates was demonstrated. The quenching vanishes at higher pump rates at the PL saturation level.

The same set of parameters was used to fit the magnetic field, pump and O₂ concentration dependences of the PL intensity and only those parameters directly related to the dependences, i.e. magnetic field, pump power and the ET rate, respectively, were varied.

The zero-field splitting parameter D of oxygen molecule frozen on the SiNP surface was roughly estimated from the experiment to be of 0.4476 meV.

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Appendix A. Appendix. Justification of parameters

A.1. Si exciton recombination times: r⁻¹ and r⁻¹

In this work (see blue points in figure A1), a PL lifetime, τₚ, of about 1 ms at T = 10 K and of about 0.1 ms at T = 50 K was measured in the spectral range 1.52–1.91 eV by mean of FRS (see also [42]). The low temperature τₚ of SiNPs in PSi—which at cryogenic temperatures is equal to the radiative decay time, τ—one as measured in previous works [11, 27, 32–40] to be from 0.25 to 10 ms, with the average value of about 3 ms (in the temperature range of 1.5–50 K and in the spectral range of 1.55–2.2 eV). In the recent work by Lütjohann et al [41], the PL decay time of SiNPs with mean radius of 2.4 nm was measured to be about 0.2 ms at 5 K; a similar value was predicted theoretically for SiNPs of 2 nm radius in [12]. The low temperature (1.5–20 K) literature data are summarized in figure A1. In our model calculations at T = 1.6 K, values of r⁻¹ = 1 ms and r⁻¹ = 4 ms (i.e.
A.4. Transition rates between levels of the oxygen molecule: $R_{b^{-}\rightarrow X,1}$, $R_{b^{-}\rightarrow 0}$, $R_{a^{-}\rightarrow X,1}$, $R_{a^{-}\rightarrow X,0}$, and $R_{b^{-}\rightarrow a}$

Figure A2 shows the triplet ($X, 1^3\Sigma$) and two singlet (a, $1\Delta$ and b, $1\Sigma$) levels of molecular oxygen.

For unperturbed gaseous $O_2$, $R_{b^{-}\rightarrow X,1} = R_{b^{-}\rightarrow X,0} = 10 \text{ s}^{-1}$, $R_{a^{-}\rightarrow X,0} = 0.5 \text{ ms}^{-1}$, $R_{a^{-}\rightarrow X,0} = 5 \times 10^3 \text{ s}^{-1}$, and $R_{b^{-}\rightarrow a} = 5 \times 10^2 \text{ s}^{-1}$ [48].

For perturbed $O_2$ in condense phase environments, the transition rates are significantly increased [48]. At $4$–$6 \text{ K}$, the transition times between the energy levels of oxygen in solid matrices of four different noble gases was measured to be: $\tau_{b^{-}\rightarrow a} = 9.5–45.5 \text{ ms}$, $\tau_{b^{-}\rightarrow X} = 3.3–7.7 \text{ s}$, and $\tau_{a^{-}\rightarrow X} = 11.5 - 142.9 \text{ s}$ [47, 52]. The room temperature value for $\tau_{b^{-}\rightarrow X,0}$ in a H$_2$O$_2$ collision complex was calculated to be $58.8 \text{ s}$ [48]. For oxygen adsorbed on PSi at $5 \text{ K}$, a $\tau_{a^{-}\rightarrow X} = 7 \text{ s}$ was reported [51] (this is close to the value reported for oxygen in a Xe matrix [47], 11.5s). A value smaller than the latter by an order of magnitude, $\tau_{b^{-}\rightarrow a} = 0.3–0.8 \text{ ms}$, was found for oxygen in different solvents (such as CCl$_4$ etc) at $300 \text{ K}$ [48]. $\tau_{1^3\Sigma} = 25 \mu\text{s}$ and $\tau_{1^3\Delta}$ from 46 to 126 $\mu\text{s}$ were reported by Jockusch et al [30] for condensed oxygen at $77 \text{ K}$. $\tau_{1^3\Delta}$ from 7.9 to $64 \mu\text{s}$ was measured for gaseous oxygen in a zeolite and porous silica [50], $3 \mu\text{s}$ in water [51], and 3.9–15 ms in PSi [51, 53]. For $O_2$ adsorbed on PSi at $5 \text{ K}$, $\tau_{1^3\Delta} = 0.5 \text{ ms}$ was reported [51].

In our fits, we used $R_{b^{-}\rightarrow X,1} = 1 \text{ s}$, $R_{b^{-}\rightarrow X,0} = 60 \text{ s}$, $R_{a^{-}\rightarrow X,0} = 0.2 \text{ ms}$, $R_{a^{-}\rightarrow X,0} = 2 \text{ ms}$, and $R_{b^{-}\rightarrow a} = 0.1 \text{ ms}$ (see table 2). These values are within the wide span of the literature data. As mentioned above, these rates are included in the model not necessarily as radiative only rates.

A.5. Zero field splitting $D$

The zero field splitting parameter $D$ ($2\lambda_0$ or $3D_{zz}$/2 in alternative notations) of the spin-Hamiltonian (5) was obtained in earlier works [54–59, 62] to be of $0.492 \text{ 16 meV}$ for a oxygen molecule in the gas phase. However, for condensed oxygen, slightly reduced values were obtained: $0.4429 \text{ meV}$ for oxygen molecules formed as defects in single crystals at $26 \text{ K}$ [61, in solid N$_2$ at 4 K [60] and in solid air [63], and $0.4336 \text{ meV}$ in a N$_2$ matrix [64].

In our calculations, we used the value $D = 0.4429 \text{ meV}$ which is the closest literature value to that roughly estimated in our experiment. In the inset of figure 4, it is clearly seen that PL varies almost linearly in the regions 1.5–4 T and 4–5.5 T. The kink (intersection of these regions) at 3.867 T is attributed to the level crossing (see figure 1(a), at which $D = g\mu_B B$. This gives $D = 0.4476 \text{ meV}$.

$D$ for the Si triplet exciton was calculated to be of $0.0055 \text{ meV}$ [43] and has been neglected in the model.

A.6. $O_2$ spin-lattice relaxation time, $\beta^{-1}$

We were unable to find the literature value for $\beta^{-1}$. A magnetic field independent $\beta^{-1} = 0.12 \text{ ms}$ for oxygen triplet (table 2) was used.
A.7. ET rate

At 1.63 eV, the ET rate \( r^{-1} = 2.56 \mu s \) at 5 K and \( r^{-1} = 17 \mu s \) at 300 K from Si exciton to a single oxygen molecule adsorbed on PSi was reported [23]. The latter results are shown in figure 5(b). It was assumed in [6, 23] that about 8 molecules of \( O_2 \) were adsorbed on PSi per one NP (emitting PL at 1.63 eV) at low temperature. Given the evidence that PL above the 1.63 eV threshold is less suppressed (quenched) in our case than that of the low temperature case in [6, 23], we can conclude that the number of \( O_2 \) molecules per NP in our case is less than 8 (or at least less than that in [6, 23]). The values for the ET rate of \( r^{-1} = 0.09 \mu s \) and 0.3 \( \mu s \), which we have used in our model to fit magnetic field dependence of PL from sample 1 and 2, respectively, for high \( O_2 \) coverage in figure 4 and simultaneously power dependence of QS in figure 7, suggest about 2.56/0.09 = 28 and 2.56/0.3 = 9 \( O_2 \) molecules per NP in these cases assuming \( r \) proportional to the number of molecules per NP. Thus, our fitting for sample 2 is in better agreement with the assumption of 8 molecules per NP (or with the value of 2.56 \( \mu s \) per molecule) than for sample 1. The values \( r^{-1} \) of 960 \( \mu s \) and 42 \( \mu s \), used to fit PL for low \( O_2 \) coverage for samples 1 and 2, respectively, suggest 2.56/960 = 0.003 and 2.56/42 = 0.06 \( O_2 \) molecules per NP. With fraction of NPs with adsorbed \( O_2 \) \( F = 0.68 \) and \( F = 0.9 \) for sample 1 and 2, respectively, it suggests 0.003/0.68 = 0.004 and 0.06/0.9 = 0.07 \( O_2 \) molecules per NP in the group of NPs with oxygen. In the ideal case it must be at least 1 molecule per NP in the group of NPs with oxygen, however, further decreasing of \( F \) leads to the worse fit, so we compromised between further reducing \( t \) and/or reducing \( F \) for the best fit of \( I(B) \) for low \( O_2 \) concentration. Also, the reported in [23] rise of \( r^{-1} \) from 0.32 to 0.45 \( \mu s \) when one TO phonon involved in the ET process implies \( \chi = 5.5 \) eV\(^{-1} \) in (21), which is about 3 times smaller than that used in our model, 15 eV\(^{-1} \).

We note that the system of rate equations is scalable, thus, multiplication of all reciprocal rates in table 2 by the same factor will not effect the resulting fit. Therefore, we can scale the ET rate down by the factor of, say, four, bringing it for sample 1 to 8 ‘molecule’ limit and still keeping the other rates within the range of the literature data (e.g. \( r_1^{-1} = 16 \) ms and \( r_2^{-1} = 4 \) ms).

The ET rate from SiNP to a dimer (again, by the exchange mechanism) was proposed to be similar to that to an \( O_2 \) monomer [23], however, this process is not included in the model.

The recent theoretical calculation [72, 73] of the rate of ET (due to the exchange only mechanism) from 2D excitons in a 1.2 \( \mu m \) thick Si layer to an adsorbed \( O_2 \) molecule gives the value of \( t = 10^3 - 10^4 \) s\(^{-1} \), which is close to \( r^{-1} = 17 \mu s \) reported for 300 K [23] (see above).

The other ET mechanisms, e.g. charge transfer, can also be involved [74] and they may result in the experimentally observed ET efficiency, however, we believe that the exchange mechanism is dominant and we do not consider those charge transfer related processes in our model. The good agreement of our experimental results with the theoretical model validates the exchange mechanism of ET.

A.8. NP size (energy) dependence of the absorption coefficient

In the case of SiNPs, the pump rate \( P \propto \sigma(R) \), where \( \sigma \) is absorption cross-section per NP of radius \( R \). Kovalev et al [75] reported \( \sigma \) versus the detected energy \( E(eV) \) of PL from PSi excited at 2.7 eV, which can be fit by \( \sigma(cm^2) \approx 3.75 \times 10^{-16} \exp(3.22E - 2.16E^2) \). The excitation energy level in our case (2.76 eV) was higher than that in [75], so we could expect weaker dependence of \( P \) on \( \sigma(R) \) and, also, constant \( P \) gave the better fit of energy (size) dependence of PL in figure 6. Therefore, we used a constant \( P \) in our simulations.

ORCID IDs

Gazi N Aliev @ https://orcid.org/0000-0002-0529-5165

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