

Supporting information

The effect of light intensity, temperature, and oxygen pressure on the photo-oxidation rate of bare PbS quantum dots

Huiyan Liu ^{1,2,3}, **Qian Dong** ⁴ and **Rene Lopez** ^{1,4,*}

¹ School of Physical Science and Technology, ShanghaiTech University, 393 Middle Huaxia Road, Shanghai 20210, China

² Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

³ University of Chinese Academy of Sciences, Beijing 101407, China

⁴ Department of Applied Physical Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North, Carolina 27599, United States

* Correspondence: rln@physics.unc.edu;

Section a) The Model for the oxidation is setup following the following 4 equations:

$$\left\{ \begin{array}{l} N_A + N_A^* + N_C = N_T \\ \frac{dN_A^*}{dt} = \frac{\sigma I}{h\nu} (N_A - N_A^*) - \frac{N_A^*}{\tau} - k^* N_A^* \\ \frac{dN_A}{dt} = \frac{\sigma I}{h\nu} (N_A^* - N_A) - \frac{N_A^*}{\tau} - k^* N_A \\ \frac{dN_C}{dt} = k^* N_A^* + k N_A \end{array} \right. \left\{ \begin{array}{l} \text{Where } N_A \text{ number of PbS atomic pairs,} \\ N_A^* \text{ number of PbS excited pairs (or exciton number)} \\ N_C \text{ number of PbS pairs transformed into a new oxide product} \\ \text{that cannot produce photoluminescence (PL)} \end{array} \right.$$

Additionally, the decay lifetime of the exciton

$$\tau^{-1} = \tau_R^{-1} + \tau_{NR}^{-1} \quad \begin{array}{l} \tau_R \text{ radiative lifetime of PbS exciton} \\ \tau_{NR} \text{ non-radiative lifetime of PbS exciton} \end{array}$$

Thus, the PL yield depends on the number of created excitons and the radiative and non-radiative lifetimes as:

$$PL \sim \frac{N_A^* \tau_R^{-1}}{\tau_R^{-1} + \tau_{NR}^{-1}} = \frac{N_A^*}{1 + \tau_R / \tau_{NR}}$$

As the non-radiative lifetime depends inversely with the number of defects, we propose a power function with the number of non-oxidized atoms as:

$$\tau_{NR} \sim \frac{1}{\text{Defects}} \sim \frac{1}{(N_A + N_A^*)^y} = \frac{1}{(N_T - N_C)^y}$$

As the oxidation is slow compared to the time the QD requires to reach equilibrium between N_A and N_A^* , to a first approximation the equation system is first solved taken $k^* \ll I/\tau$. k is much smaller than k^* , thus we will use $k = 0$ from here on. Thus, we proceed to solve explicitly for the fast process of photoexcitation (with neglected oxidation that is expected to happen much slower). Note τ is approximated to be constant on this part of the solution.

$$\begin{array}{l} \frac{dN_A^*}{dt} = \frac{\sigma I}{h\nu} N_A - \left(\frac{\sigma I}{h\nu} + \frac{1}{\tau} \right) N_A^* \\ \frac{dN_A}{dt} = -\alpha N_A + \beta N_A^* \\ \left(\alpha = \frac{\sigma I}{h\nu} ; \beta = \frac{\sigma I}{h\nu} + \frac{1}{\tau} \right) \end{array} \quad \rightarrow \quad \begin{array}{l} \frac{d}{dt} \begin{pmatrix} N_A^* \\ N_A \end{pmatrix} = \begin{pmatrix} -\beta & \alpha \\ \beta & -\alpha \end{pmatrix} \begin{pmatrix} N_A^* \\ N_A \end{pmatrix} \\ \begin{pmatrix} N_A^* \\ N_A \end{pmatrix}_{t=0} = \begin{pmatrix} 0 \\ N_T - N_C \end{pmatrix} \end{array}$$

$$\begin{array}{l} \det \begin{pmatrix} -\beta - \lambda & \alpha \\ \beta & -\alpha - \lambda \end{pmatrix} = (-\beta - \lambda)(-\alpha - \lambda) - \alpha\beta = 0 \\ (\beta + \lambda)(\alpha + \lambda) - \alpha\beta = 0 \\ \Rightarrow \alpha\beta + (\alpha + \beta)\lambda + \lambda^2 - \alpha\beta = 0 \\ \lambda(\lambda + (\alpha + \beta)) = 0 \end{array}$$

$$\text{characteristic values} \quad \left\{ \begin{array}{l} \lambda_1 = 0 \\ \lambda_2 = -(\alpha + \beta) \end{array} \right.$$

For each eigenvalue, we obtain a characteristic vector

$$\lambda = 0$$

$$\begin{pmatrix} -\beta & \alpha \\ \beta & -\alpha \end{pmatrix} \begin{pmatrix} N_A^* \\ N_A \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \longrightarrow V_1 = \begin{pmatrix} \frac{1}{\beta} \\ \frac{1}{\alpha} \end{pmatrix}$$

$$\lambda = -(\alpha + \beta)$$

$$\begin{pmatrix} \alpha & \alpha \\ \beta & \beta \end{pmatrix} \begin{pmatrix} N_A^* \\ N_A \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \longrightarrow V_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

$$\begin{pmatrix} N_A^* \\ N_A \end{pmatrix} = C_1 \begin{pmatrix} \frac{1}{\beta} \\ \frac{1}{\alpha} \end{pmatrix} e^0 + C_2 \begin{pmatrix} 1 \\ -1 \end{pmatrix} e^{-(\beta+\alpha)t}$$

Applying the initial conditions at the moment lights are turned on, ie. All atoms are not excited

$$\begin{pmatrix} 0 \\ N_T - N_C \end{pmatrix} = \begin{pmatrix} \frac{C_1}{\beta} \\ \frac{C_1}{\alpha} \end{pmatrix} + \begin{pmatrix} C_2 \\ -C_2 \end{pmatrix} \longrightarrow \begin{array}{l} 0 = \frac{C_1}{\beta} + C_2 \longrightarrow C_2 = -\frac{C_1}{\beta} \\ N_T - N_C = \frac{C_1}{\alpha} - C_2 = C_1 \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) = C_1 \frac{\beta + \alpha}{\alpha\beta} \end{array} \left\{ \begin{array}{l} C_1 = \frac{(N_T - N_C)\alpha\beta}{(\beta + \alpha)} \\ C_2 = \frac{-(N_T - N_C)\alpha}{(\beta + \alpha)} \end{array} \right.$$

$$N_A^* = -C_2 + C_2 e^{-(\beta+\alpha)t} = -C_2(1 - e^{-(\beta+\alpha)t})$$

$$N_A = -\frac{C_1}{\alpha} + \frac{C_1}{\beta} e^{-(\beta+\alpha)t} = C_1 \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) e^{-(\beta+\alpha)t}$$

Arriving to time dependent explicit formulas

$$N_A^* = \frac{(N_T - N_C)\alpha\beta}{(\beta + \alpha)} \alpha (1 - e^{-(\beta+\alpha)t})$$

$$N_A = \frac{(N_T - N_C)\alpha\beta}{(\beta + \alpha)} \left(\frac{1}{\alpha} + \frac{1}{\beta} \right) e^{-(\beta+\alpha)t}$$

Under constant illumination equilibrium values of N_A^* and N_A are established rapidly (in microseconds or less). It is upon these “quasi-static” steady state values of N_A^* and N_A that the slower oxidation process (seconds to hours) proceeds. Thus, the “quasi-static” values must not be interpreted as N_A and N_A^* have constant values over the whole experiment. The equations explicitly show both depend on $(N_T - N_C)$ which will slowly decrease as N_C (the oxidized PbSO_x) grows. All along the light emitted is always proportional to N_A^* and a function of the radiative and non-radiative recombination paths.

In “steady state” →

$$N_A^* = \frac{(N_T - N_C)\alpha}{(\beta + \alpha)} \quad N_A = \frac{(N_T - N_C)\beta}{(\beta + \alpha)}$$

$$\frac{N_A^*}{N_A} = \frac{\alpha}{\beta}$$

The number of oxidized atoms then can be calculated from:

$$\frac{dN_C}{dt} = k^*N_A^* + kN_A \quad (\text{the } kN_A \text{ term is much smaller and thus will be taken as zero})$$

$$\frac{dN_C}{dt} = \frac{k^*(N_T - N_C)\alpha}{(\beta + \alpha)}$$

$$\frac{dN_C}{dt} = BN_T - BN_C \quad \text{and} \quad B = \frac{k^*\alpha}{(\beta + \alpha)}$$

$$\int_0^{N_C} \frac{dN_C}{N_T - N_C} = \int_0^t B dt'$$

$$-\ln(N_T - N_C)_0^{N_C} = Bt$$

$$-\ln(N_T - N_C) + \ln(N_T) = -Bt$$

$$\ln\left(\frac{N_T - N_C}{N_T}\right) = -Bt$$

$$N_T - N_C = N_T e^{-Bt}$$

Following our stated phenomenological dependance of the non-radiative lifetime on the oxidation:

$$\tau_{NR} = \frac{1}{(N_T - N_C)^\gamma} = \frac{1}{(N_T e^{-Bt})^\gamma} \Rightarrow \tau_{NR} = \tau_{NR}^0 e^{\gamma Bt}$$

Allowing for the explicit evolution of τ_{NR} be used in the PL expression, then the PL yield can be compactly expressed as:

$$PL \sim \frac{N_A^*}{1 + \tau_R/\tau_{NR}} = \frac{(N_T - N_C)\alpha}{(\beta + \alpha)\left(1 + \frac{\tau_R}{\tau_{NR}^0 e^{\gamma Bt}}\right)} = \frac{\alpha N_T e^{-Bt}}{(\beta + \alpha)\left(1 + \frac{\tau_R}{\tau_{NR}^0} e^{-\gamma Bt}\right)}$$

$$PL = M \frac{\alpha}{\beta + \alpha} \frac{e^{-Bt}}{\left(1 + \frac{\tau_R}{\tau_{NR}^0} e^{-\gamma Bt}\right)} = A \frac{e^{-Bt}}{(1 + Ce^{-\gamma Bt})}$$

M: microscope train constant

$$A = M \frac{\alpha}{\beta + \alpha}; \quad B = \frac{k^*\alpha}{(\beta + \alpha)}; \quad C = \frac{\tau_R}{\tau_{NR}^0}$$

Section b) numeric constants used in the model:

PbS pairs in 1 QD

$$\rho_{\text{PbS}} * V_{\text{QD}} = \text{Mass of QD}$$

$$(7.6 \text{ g/cm}^3) \frac{4}{3} \pi (1.25 \text{ nm})^3 = 6.1 \times 10^{-20} \text{ g}$$

$$6.1 \times 10^{-20} \text{ g} = M * n$$

$$6.1 \times 10^{-20} \text{ g} = \frac{239.3 \text{ g}}{\text{mol}} * n$$

$$2.59 \times 10^{-22} \text{ mol} = n$$

$$2.59 \times 10^{-22} * N_{\text{A}} = \text{PbS pairs}$$

$$156 = \text{PbS pairs}$$

σ = "area" of one PbS pair

$$\sigma = \frac{1 \text{ QD in } 5 \times 5 \text{ nm}^2}{\text{PbS pairs in 1 QD}} \times 0.06$$

$$\sigma = \frac{25 \times 10^{-14} \text{ cm}^2}{156 \text{ pairs}}$$

$$\sigma = 9.6 \times 10^{-17} \text{ cm}^2$$

Experimental absorption

Thus, the α will be defined as:

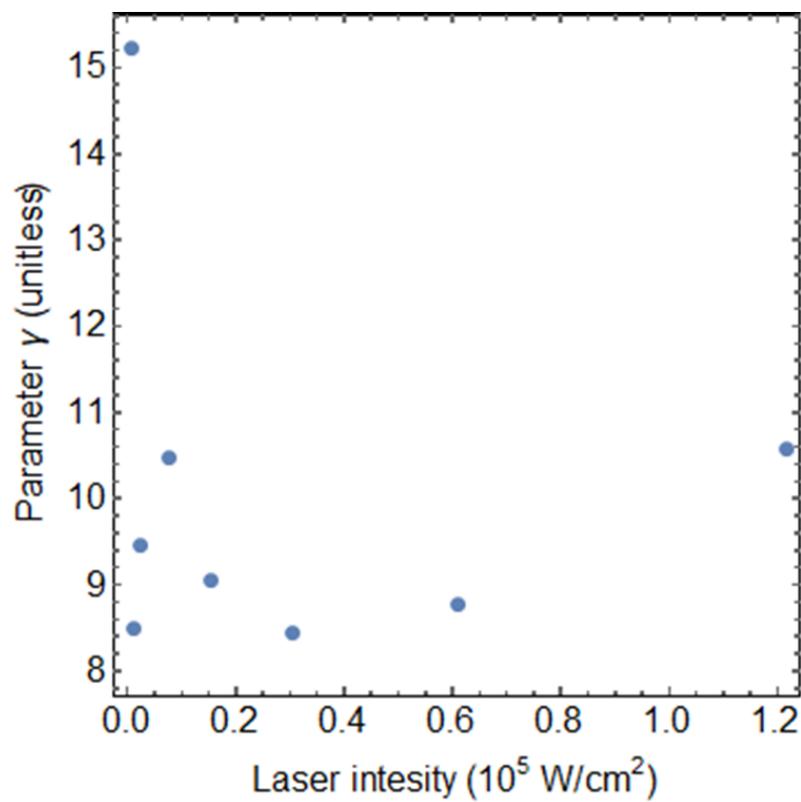
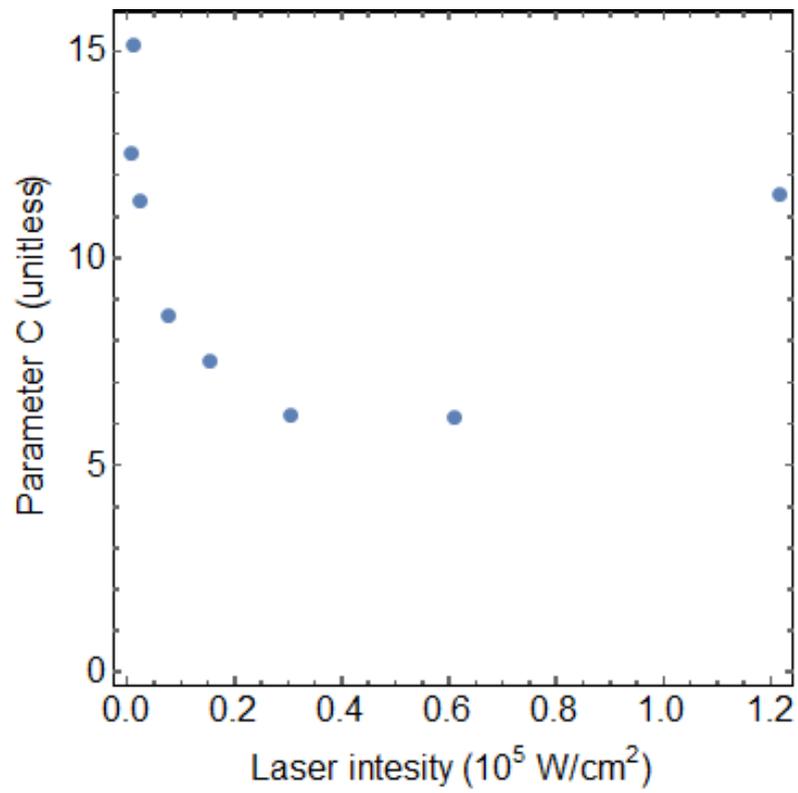
$$h\nu = (2.33 \text{ eV})(1.6 \times 10^{-19} \frac{\text{J}}{\text{eV}})$$

$$h\nu = 3.72 \times 10^{-19} \text{ J}$$

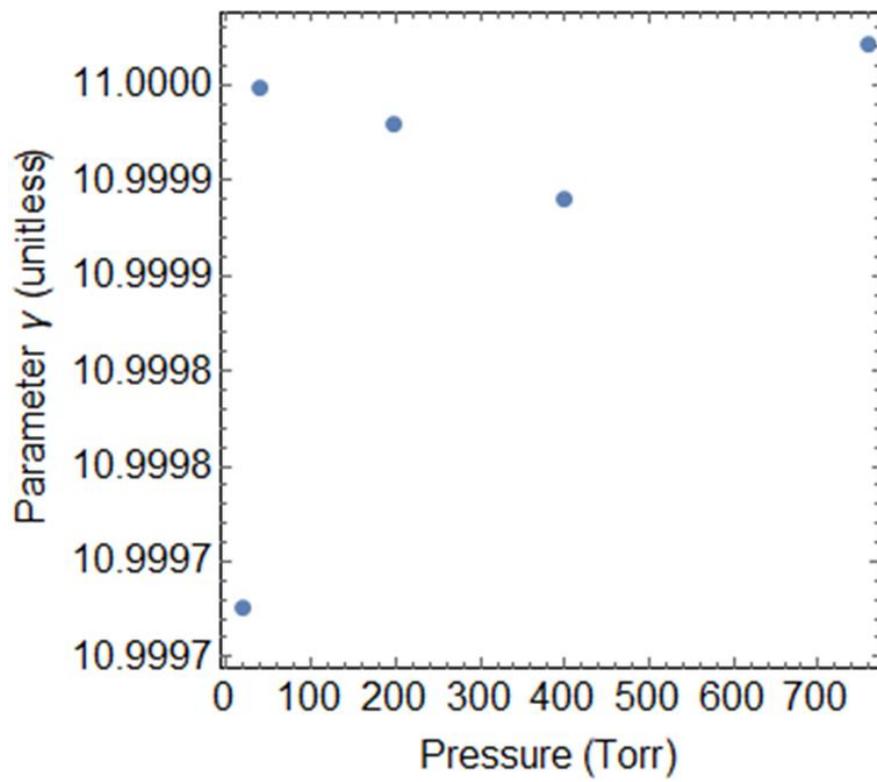
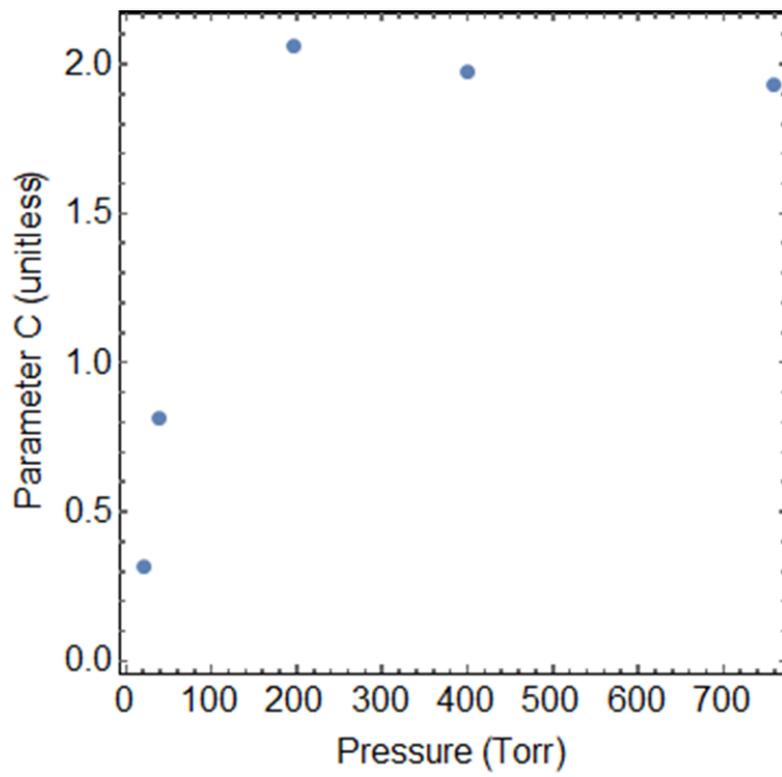
$$\alpha = \frac{\sigma I}{h\nu} = 258 \frac{\text{cm}^2}{\text{J}} \times I$$

Section c) fit of other parameters:

On light intensity:



On gas pressure:



On temperature:

