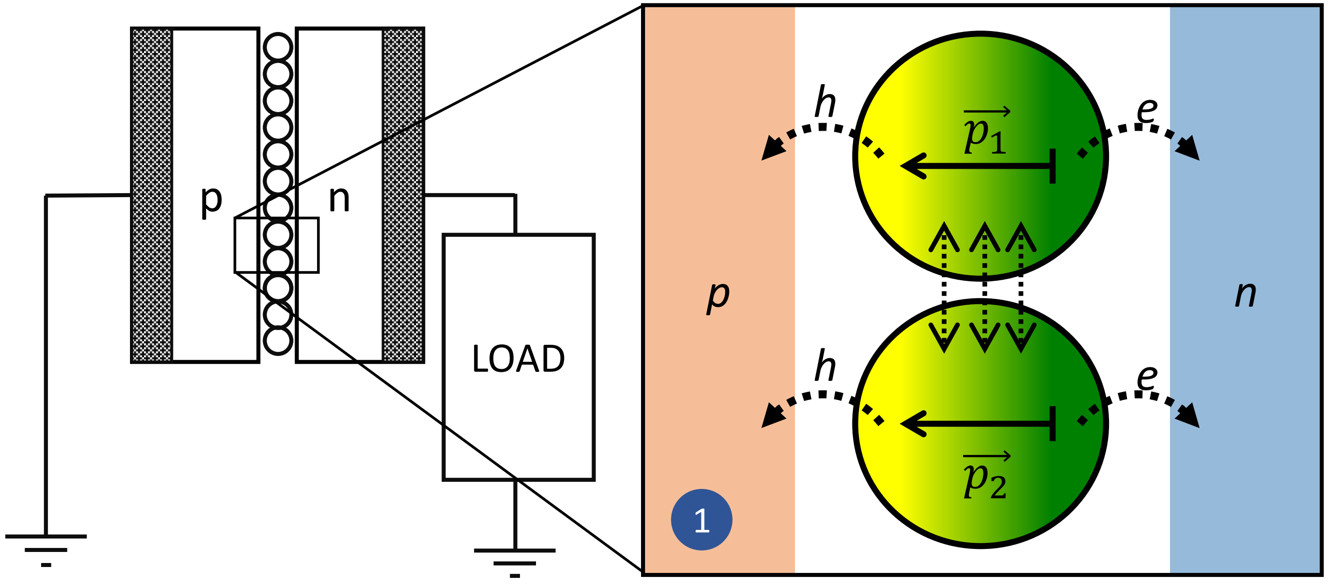
Quantum photocell based on GaN quantum dots

Abhishek Chakraborty[a] and Vishvendra Singh Poonia[a]*
[a] Indian Institute of Technology Roorkee, India
* vishvendra@ece.iitr.ac.in



- We propose a quantum biomimetic photocell based on GaN quantum dots.
- The strong built-in electric field in GaN QDs and excitonic dipole-dipole coupling between adjacent QDs are exploited to break the detailed balance.
- We show that such a photocell exhibits enhanced photo-voltage and photocurrent (~25%).
- The proposed quantum photocell (Fig. 1) could be a crucial step towards harnessing quantum effects in practical energy harvesting devices.

The model

- The proposed structure is inspired from highly efficient charge separation mechanism in the photosynthetic reaction center
  - And builds on Marlan O. Scully's idea of a quantum photocell.

Dorfman et al., PNAS, 110.8, 2013.
Marlan O. Scully, *PRL*, 104, 20, 207701, 2010.

- Photons create excitonic states in a pair of coherently coupled GaN quantum dots. The Hamiltonian looks like:

$$H = H_0 + H_1$$

$$H_0 = \sum_{j=1,2} \hbar\omega_j \sigma_j^+ \sigma_j^- \text{ and } H_1 = J_{12}(\sigma_1^+ \sigma_2^- + \mathrm{h.c.})$$

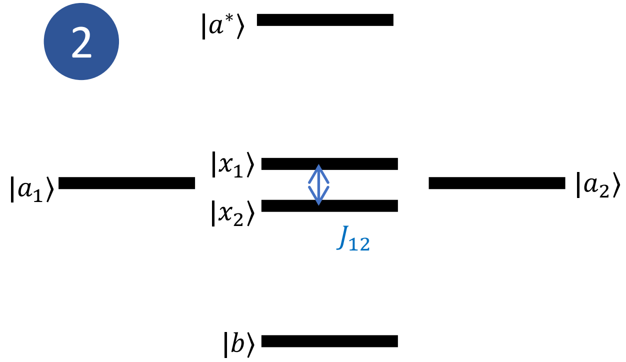
- We treat the quantum dots as excitonic two-level systems with a ground state $|b\rangle$ and degenerate excited states $|a_1\rangle$ and $|a_2\rangle$ for the two dots respectively. In presence of dipole-dipole coupling, the new eigenstates are $|x_1\rangle$ and $|x_2\rangle$. (Fig 2)

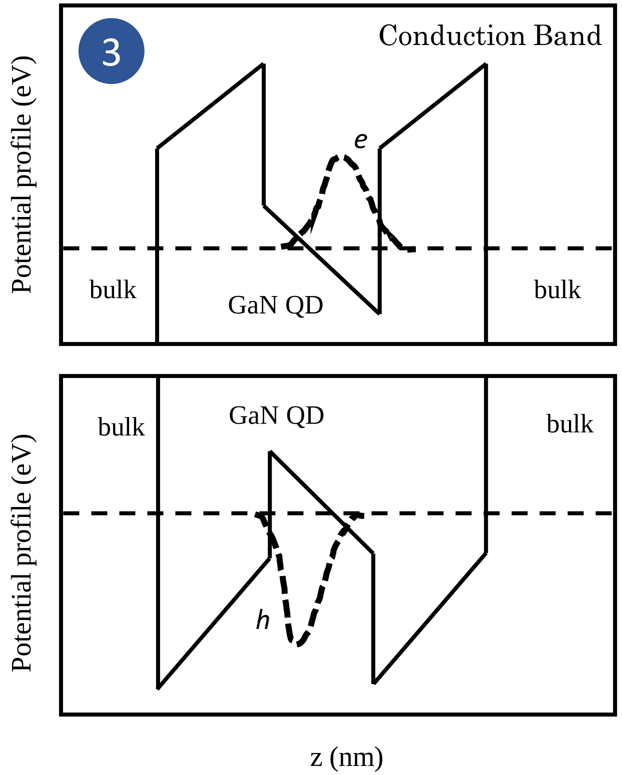
$$|x_1\rangle = \frac{1}{\sqrt{2}}(|a_1\rangle + |a_2\rangle) \text{ and } |x_2\rangle = \frac{1}{\sqrt{2}}(|a_1\rangle - |a_2\rangle)$$

$$\varepsilon_{x_{1,2}} = \varepsilon_{ab} \pm J_{12} \text{ and } \Delta\varepsilon = \frac{|\vec{\mu}|^2}{4\pi\epsilon d_\perp^3} \equiv J_{12}$$

- Electron and hole wavefunctions (Fig 3.) are spatially separated due to intrinsic electric field. The excitonic binding energy is lowered.

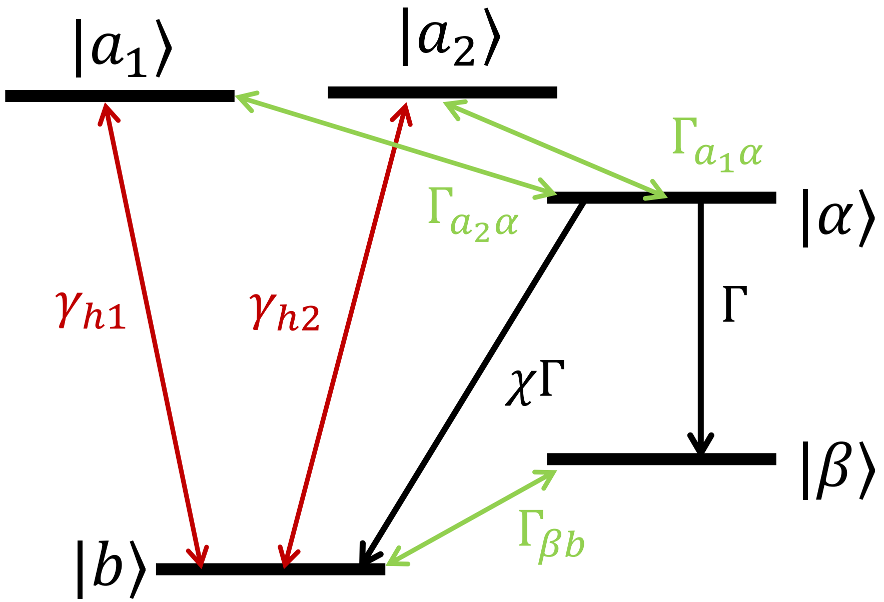
- The electron tunnels out of the QD into the bulk semiconductor. The barrier width and coupling strength determine the tunnelling rate. Band bending and confinement due to the built-in electric field in GaN quantum dots.





Photocell without excitonic coupling

④



$$\dot{\rho}_{a_1a_1} = -\frac{\gamma_h}{2}\left[(1+n_h)\rho_{a_1a_1} - n_1\rho_{bb}\right] - \Gamma_{a\alpha}\rho_{a_1a_1}$$

$$\dot{\rho}_{a_2a_2} = -\frac{\gamma_h}{2}\left[(1+n_h)\rho_{a_2a_2} - n_2\rho_{bb}\right] - \Gamma_{a\alpha}\rho_{a_2a_2}$$

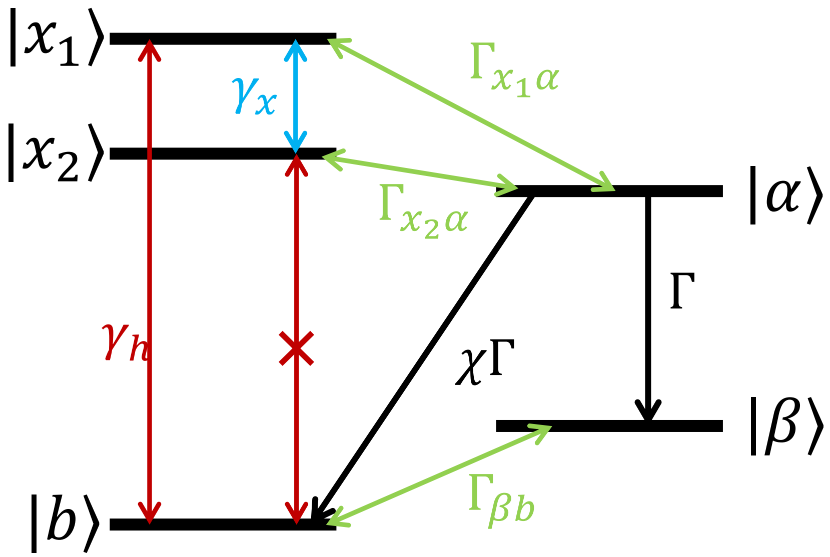
$$\dot{\rho}_{\alpha\alpha} = \Gamma_{a_1\alpha}\rho_{a_1a_1} + \Gamma_{a_2\alpha}\rho_{a_2a_2} - (\Gamma + \chi\Gamma)\rho_{\alpha\alpha}$$

$$\dot{\rho}_{\beta\beta} = \Gamma\rho_{\alpha\alpha} - \Gamma_{\beta b}\rho_{\beta\beta} \text{ and } \textstyle\sum_i \rho_{ii} = 1$$

- Each quantum dot is photoexcited from ground state $|b\rangle$ to the excited state $|a_1\rangle$ ($|a_1\rangle$) for the first (second) dot. This photoexcitation corresponds to the creation of an exciton in the dot.
- From the excited state, the electrons tunnel across the barrier into the bulk semiconductor, leaving the photocell in a charged state $|\alpha\rangle$.
- The electron is used for work relaxing the system to a state $|\beta\rangle$.
- Finally, the hole in the quantum dot recombines with an electron from the bulk semiconductor, bringing the electron back to the ground state $|b\rangle$.

Photocell with excitonic coupling

5



$$\begin{aligned}\dot{\rho}_{x_1x_1} &= -\gamma_x\big[(1+n_x)\rho_{x_1x_1} - n_x\rho_{x_2x_2}\big] \\ &\quad -\gamma_h\big[(1+n_h)\rho_{x_1x_1} - n_h\rho_{bb}\big] - \Gamma_{x_1\alpha}\rho_{x_1x_1}\end{aligned}$$

$$\dot{\rho}_{x_2x_2} = \gamma_h\big[(1+n_h)\rho_{x_1x_1} - n_h\rho_{bb}\big] - \Gamma_{x_2\alpha}\rho_{x_2x_2}$$

$$\dot{\rho}_{\alpha\alpha} = \Gamma_{x_1\alpha}\rho_{x_1x_1} + \Gamma_{x_2\alpha}\rho_{x_2x_2} - (\Gamma + \chi\Gamma)\rho_{\alpha\alpha}$$

$$\dot{\rho}_{\beta\beta} = \Gamma\rho_{\alpha\alpha} - \Gamma_{\beta b}\rho_{\beta\beta} \text{ and } \textstyle\sum_i \rho_{ii} = 1$$

- The symmetric superposition state is a bright state and the anti-symmetric superposition state is a dark state
  - As the net dipole moment for that state is zero:

$$|\mu_{1,2}| = \frac{1}{\sqrt{2}}|\mu_1 \pm \mu_2|$$

The transition rates $\gamma \propto |\vec{\boldsymbol{\mu}}|^2$

$$\gamma_h = \frac{2\,\omega_{1b}^3|\mu|^2}{\hbar\pi\epsilon_0 c^3}$$

- No radiation recombination is possible from this dark state with zero dipole moment. This can act as a *shelving state.*

- Strong coupling and rapid phonon-mediated between the $|x_1\rangle$ and $|x_2\rangle$ transfer further reduces radiative recombination. We assume this is mediated by thermal phonons with occupation

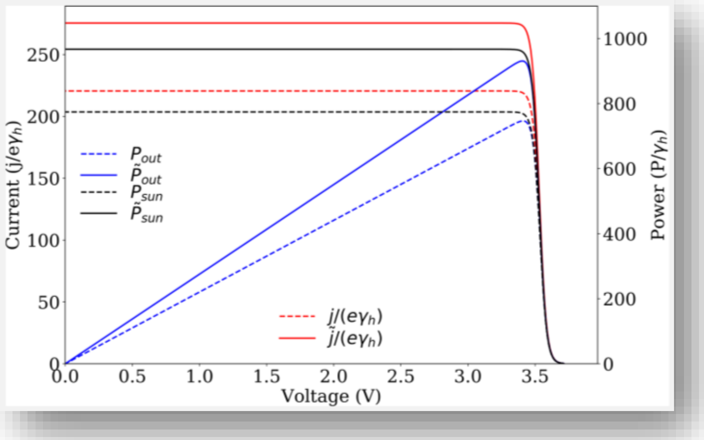
$$\bar{n} = \frac{1}{e^{\Delta\varepsilon/(k_b T_a)} - 1}$$

Parameters and Results

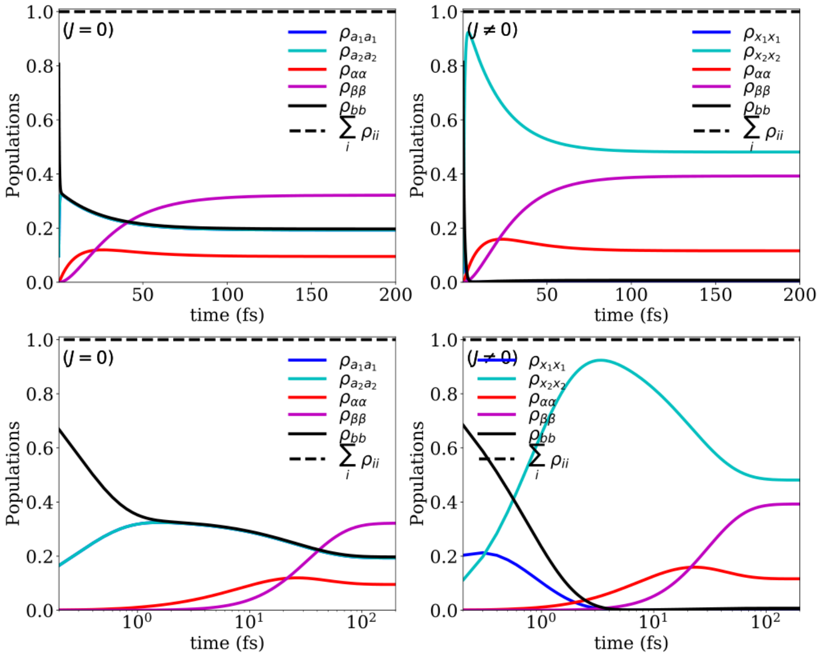
6

Quantity	Symbol	Value	Unit
GaN Bandgap	E_g	3.51	eV
Conduction band dislocation	ΔE_c	2.0	eV
Valence band dislocation	ΔE_v	0.7	eV
Electron effective mass	m_e^*	0.2	m_e
Hole effective mass	m_h^*	1.0	m_e
Relative permittivity	ϵ	9.6	
Quantum dot width	w_d	2.7	nm
QD intrinsic electric field	F_d	0.54	V nm^{-1}
Barrier intrinsic electric field	F_{br}	0.57	V nm^{-1}
Radiative recombination rate	χ	0.20	
Ambient phonon temperature	T_a	300	K
Exciton excitation energy	E_{1b}	3.25	eV
Number of solar photons	n_h	60000	

8



7



Population dynamics in the proposed photocell in the uncoupled (left) and coupled (right) models respectively.

I-V and P-V Characteristics

$$j = \Gamma \rho_{\alpha\alpha}$$

$$eV = E_{\alpha\beta} + k_b T_a \ln\left(\frac{\rho_{\alpha\alpha}}{\rho_{\beta\beta}}\right)$$

$$P_{out} = j \cdot V$$

$$P_{sun} = \frac{j}{e}\left(E_{x_1/a_1} - E_b\right)$$

$$w_{br} = 0.5 \text{ nm}$$

$$d_\perp = 1.5 \text{ nm}$$

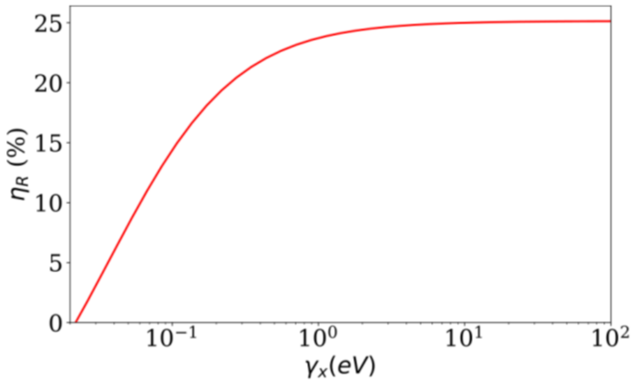
$$J_{12} \sim 200 \text{ meV}$$

Relative power enhancement

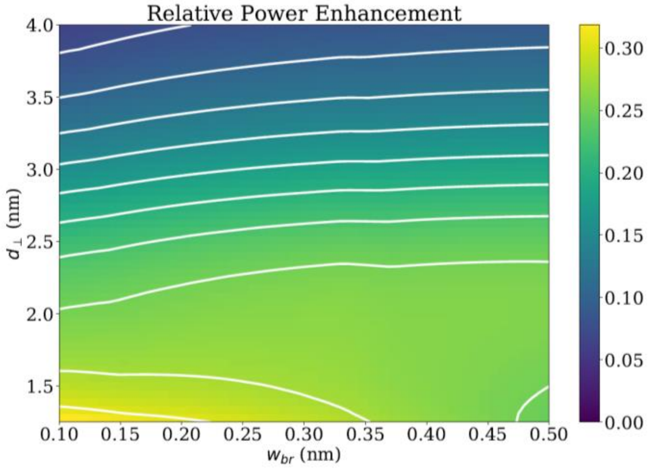
$$\eta_R = \frac{\tilde{P}_{out}^{max} - P_{out}^{max}}{P_{out}^{max}}$$

Results (contd.)

9



10



- Relative power enhancement

$$\boxed{\eta_R = \frac{\tilde{P}_{out}^{max} - P_{out}^{max}}{P_{out}^{max}}}$$

- Power enhancement upto 25% is observed due to excitonic delocalization.

Some observations:

- Greater spacing between dots leads to poorer coupling and reduces efficiency.
- Another mechanism of charge carrier extraction must be found to augment the low tunnelling rates.
  - Phonon mediated transfers could be the key to this.
- The phonon spectrum of GaN quantum dots needs to be studied in detail
  - This and variation of the geometry of the photocell may be done through DFT/tight-binding methods.