Fluorescence blinking statistics from CdSe core and core-shell nanorods

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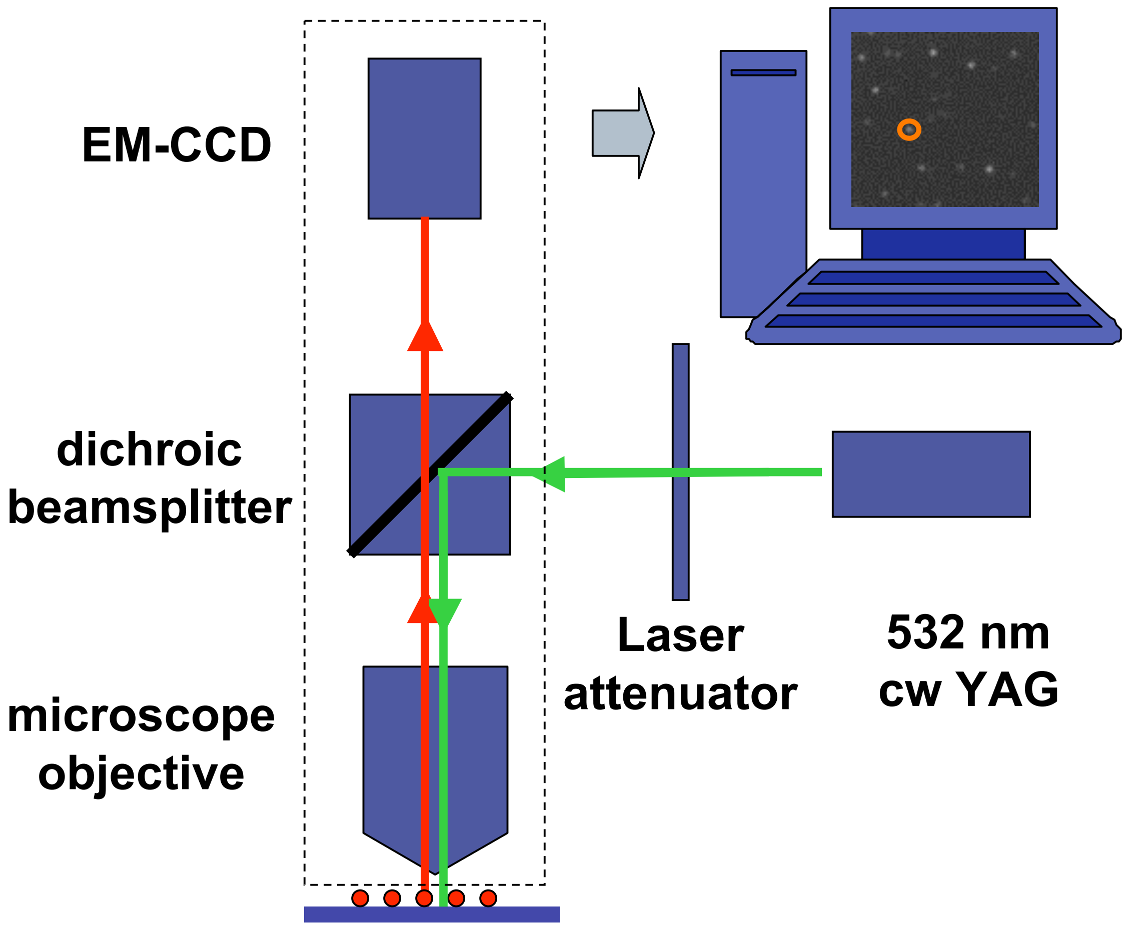
- Research goals
  - Characterize NR blinking, compare to spherical NC
  - Determine effect of aspect ratio, surface ligands
- Experiment
  - Widefield epifluorescence microscopy
- Results
  - Off-time statistics: power-law
  - On-time statistics: truncated power law
  - Aspect ratio dependence
  - Absorption rate dependence
  - Surface passivation dependence
- Conclusions

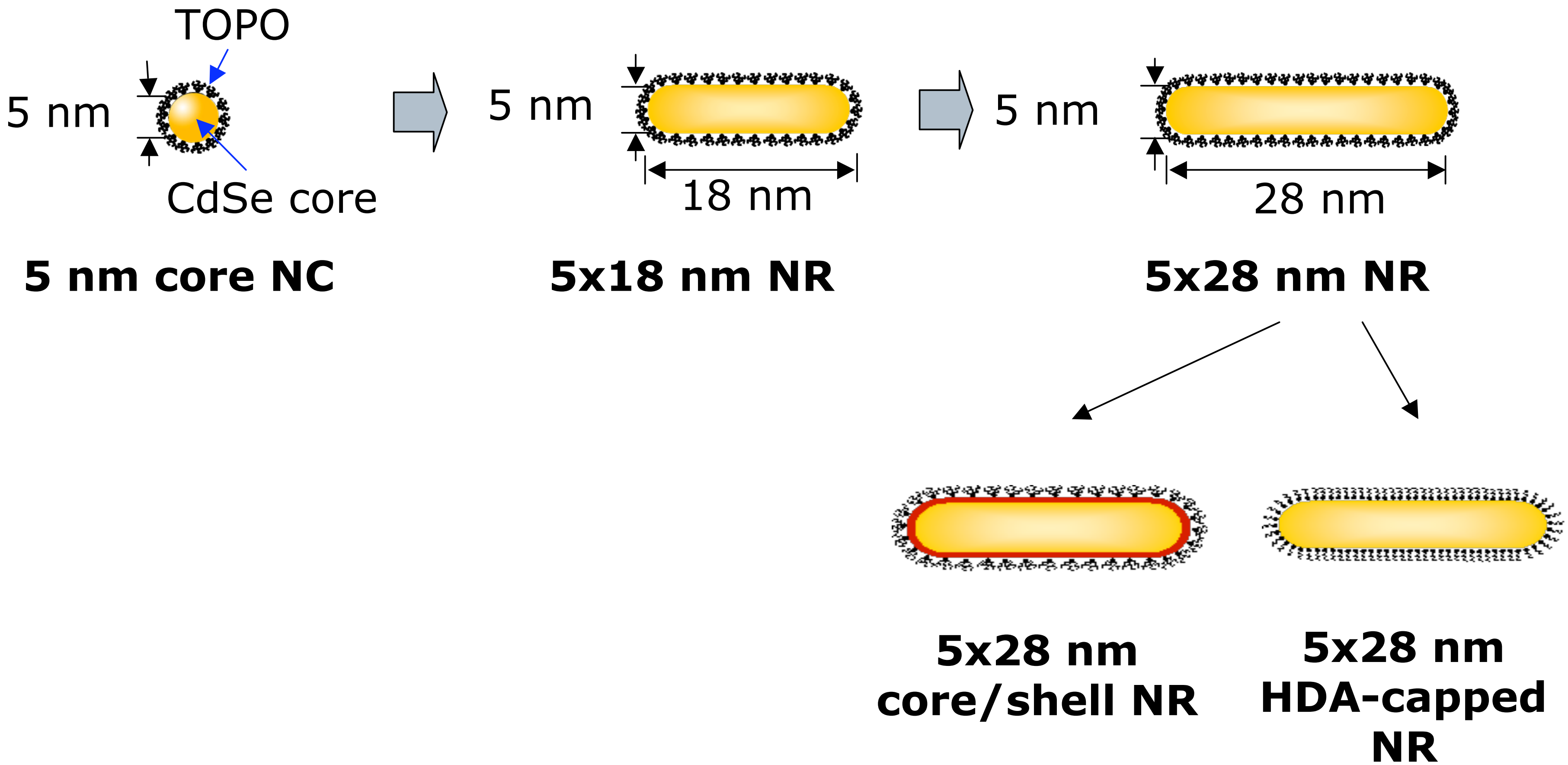
Experiment

wide-field fluorescence microscopy



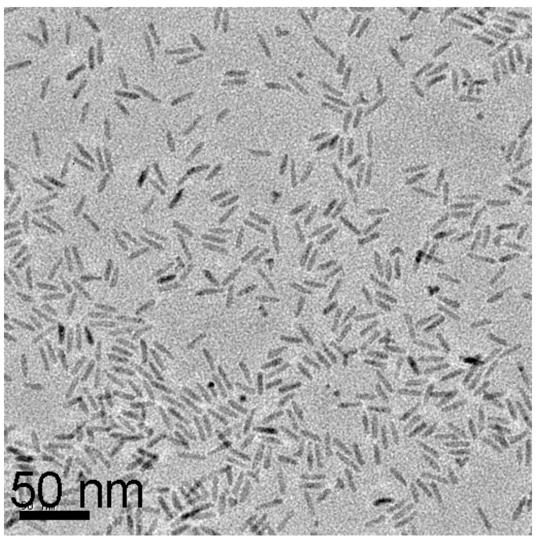
NRs spin-cast on mica substrate

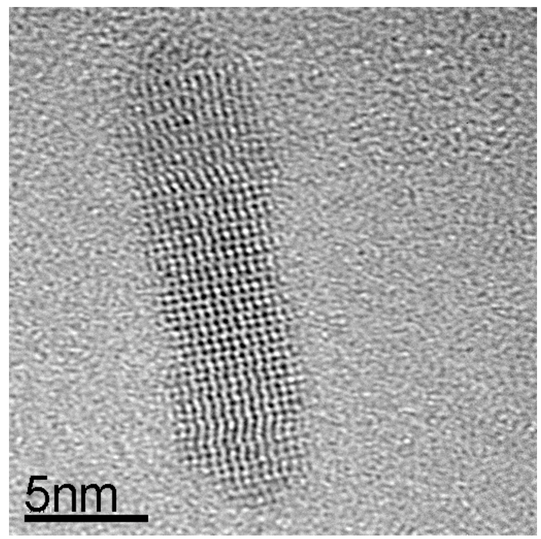
Nanorods


TOPO
5 nm
CdSe core
5 nm core NC
5 nm
18 nm
5x18 nm NR
5 nm
28 nm
5x28 nm NR
5x28 nm
core/shell NR
5x28 nm
HDA-capped
NR

Nanorods

- Seven different aspect ratios from 3 to 11
- Both CdSe core NRs and CdSe/ZnSe core/shell NRs
- Both TOPO and HDA surface ligands
- Compared to core and core/shell spherical NCs (Evident)





Sample	*d* (nm)	*l* (nm)
NC	5.2	-
NR1	3.4	18
NR2	3.5	25
NR3	3.4	38
NR4	5.2	18
NR5	5.2	28
NR6	6.1	22
NR7	6.0	31

Why examine nanorod blinking?

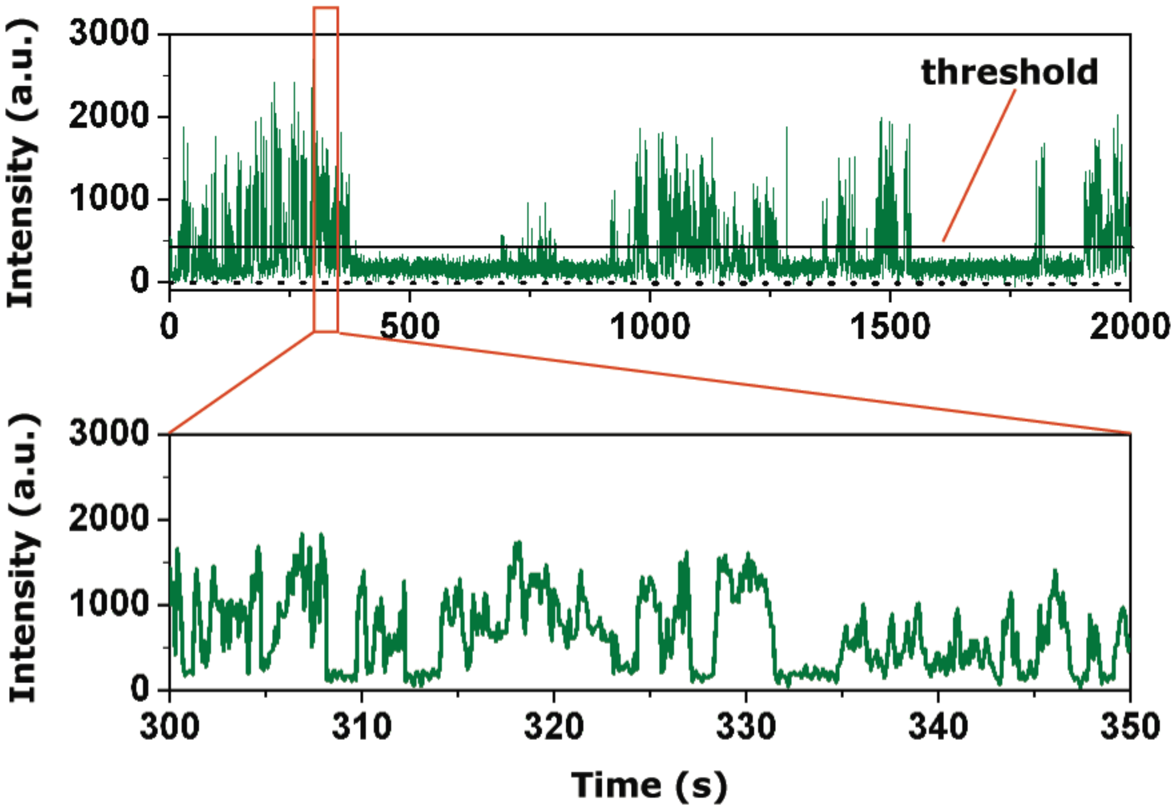
- Reduced quantum confinement along length: exciton can diffuse along the rod
- Symmetry breaking: surface charge locations are not all equivalent

Muller *et al*, PRL 93, 167402 (2004)

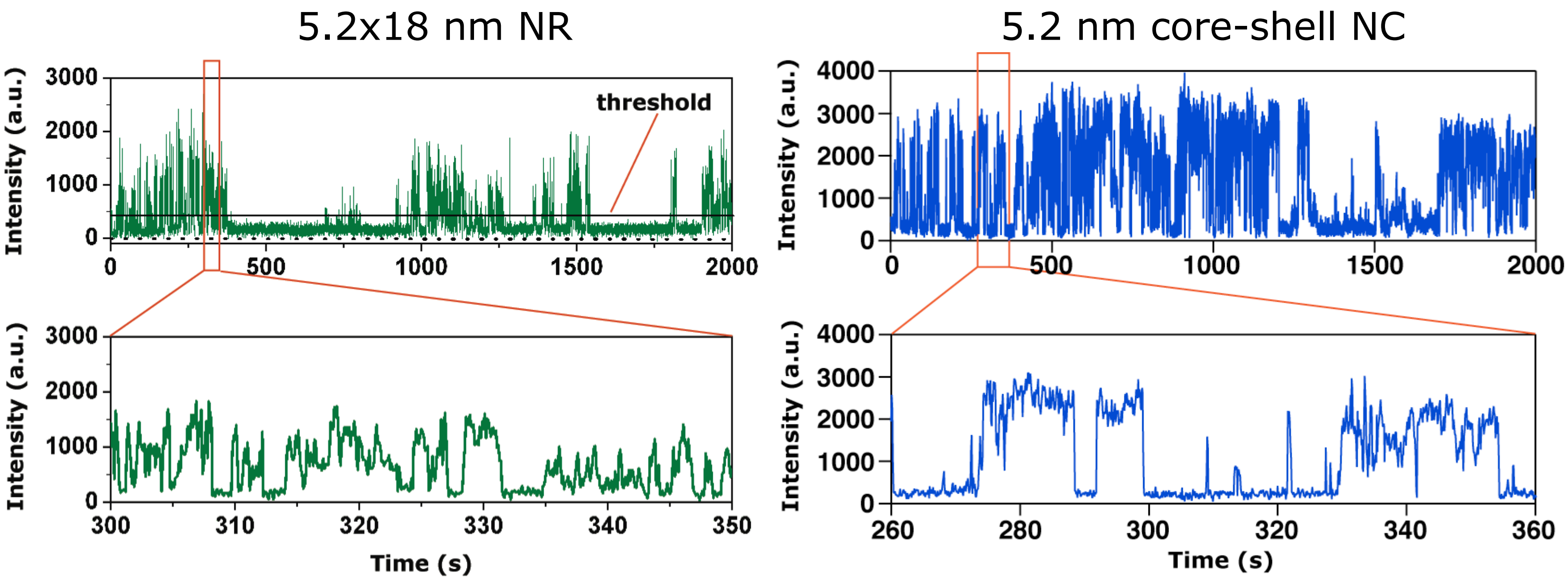
Rothenberg *et al*, Nano Letters 5, 1581 (2005)

- Blinking models involve diffusion or random walk; surface charge wandering on elongated rod may give enhanced diffusion/random walking

Nanorod blinking trajectory



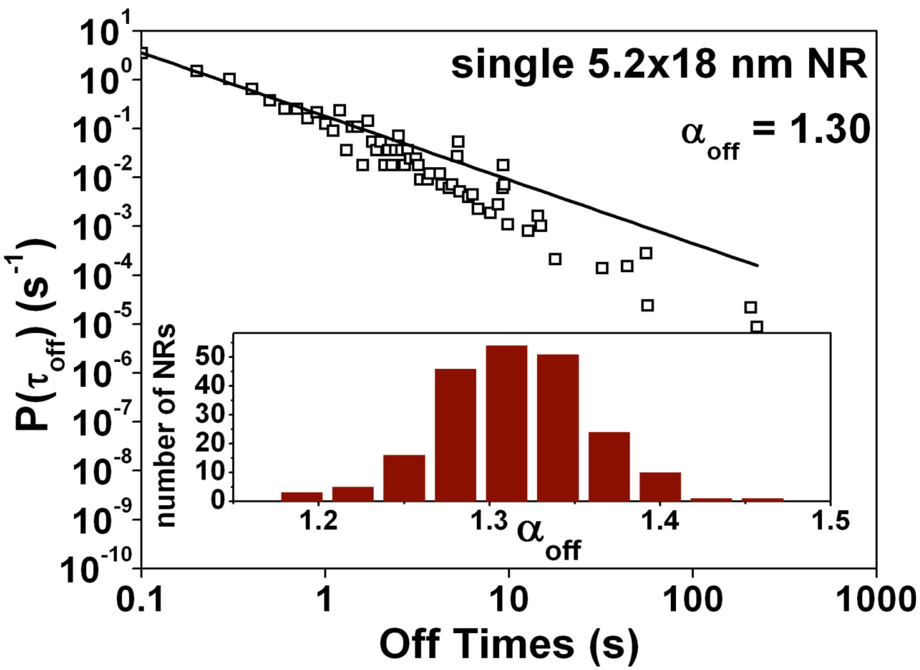
Nanorod blinking trajectory



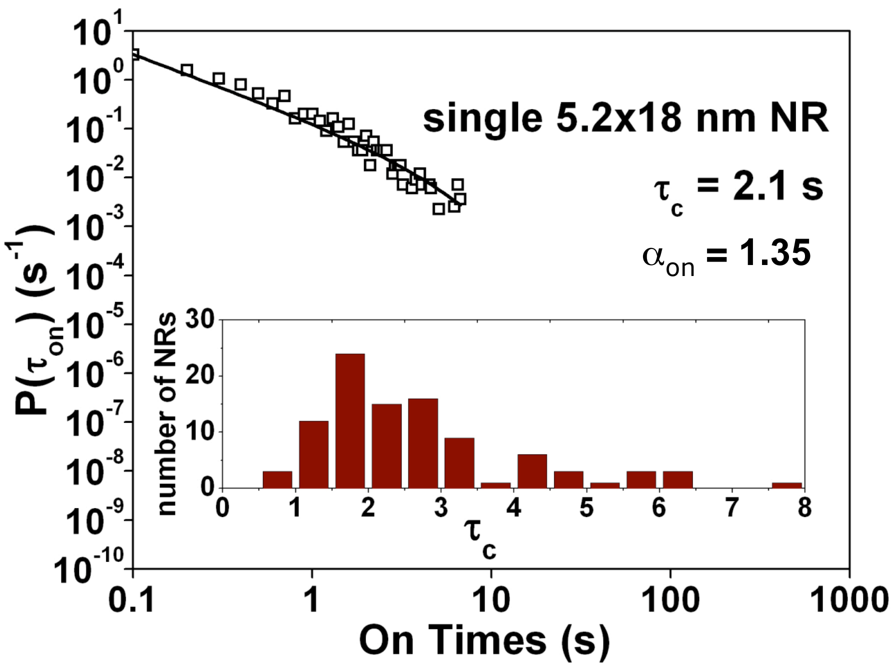
Very few long on-times
Core-shell NR gives similar traces

Blinking statistics: 5 x 18 nm NR

off times



on times



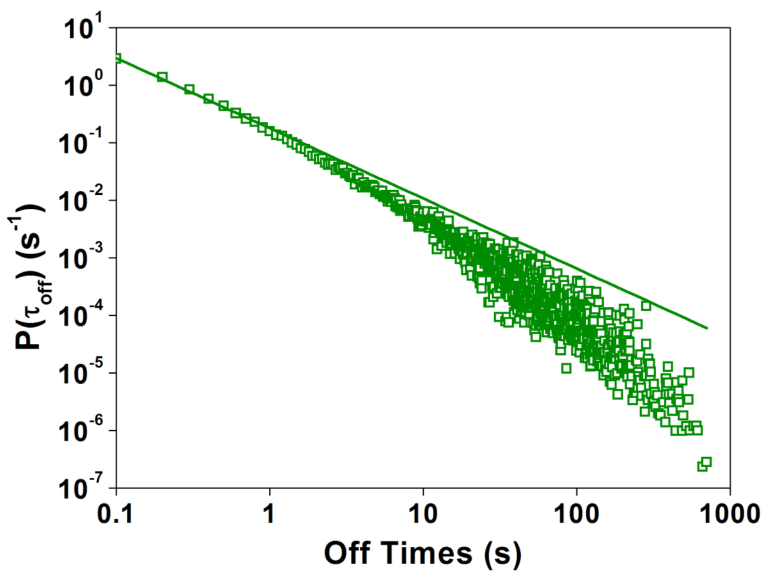
power law: $P\left(\tau_{off}\right) \propto \tau_{off}^{-\alpha_{off}}$

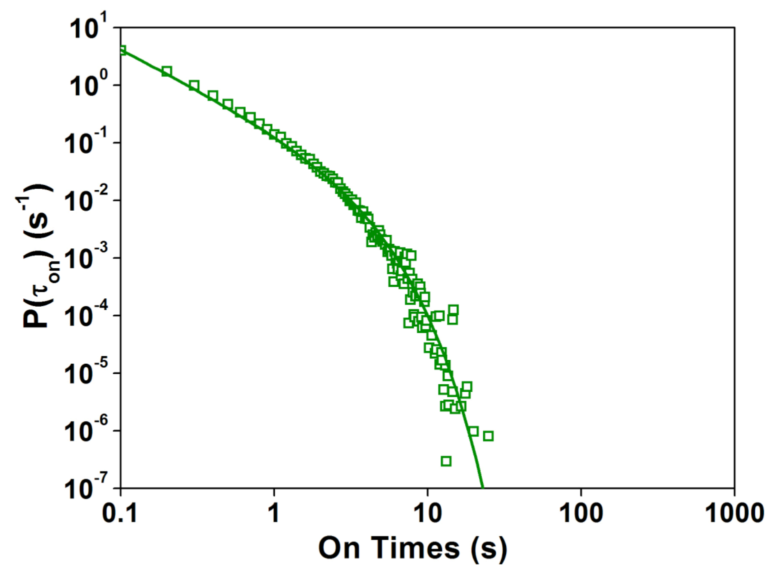
truncated power law:

$$P\left(\tau_{on}\right) \propto \tau_{on}^{-\alpha_{on}} e^{-\tau_{on}/\tau_c}$$

Data aggregation

- Individual NRs: few long on-times in 2000 s experiment
- Aggregate data from 100 NRs to get better statistical representation
- Aggregated statistics are reproducible
- Obtain same results with 2000 or 4000 s experiment





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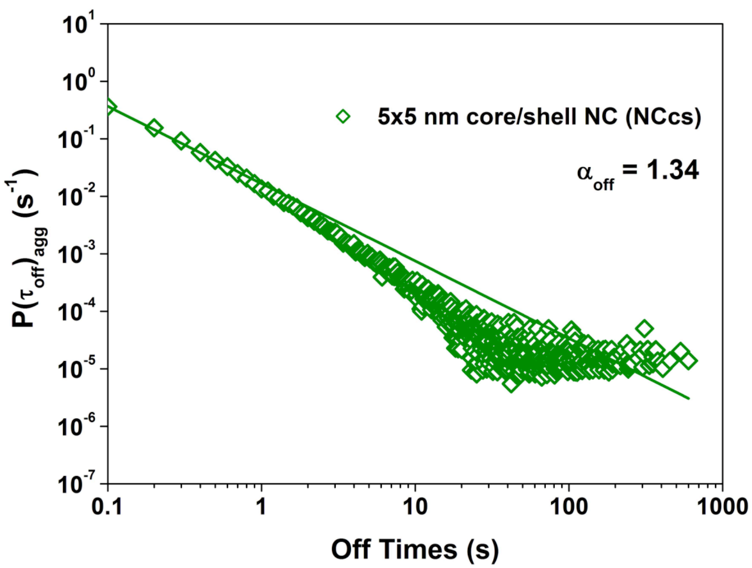
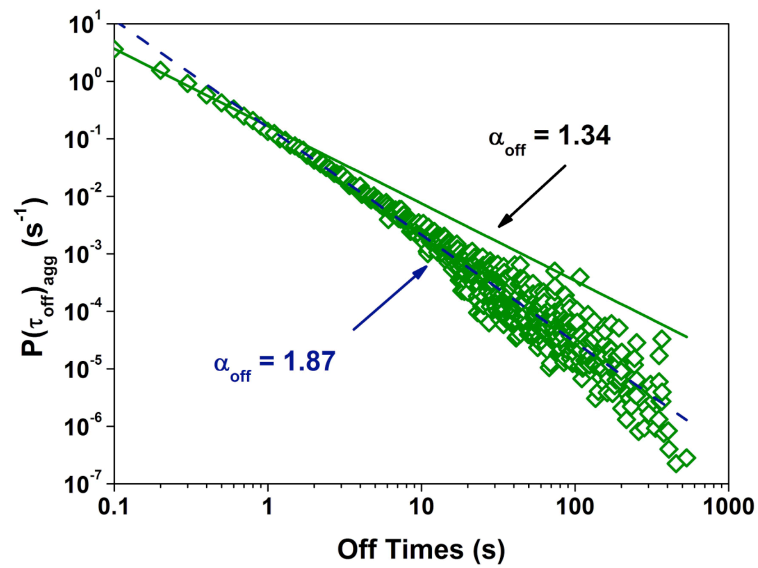
Weighting and fitting

Aggregated core-shell NC off-times





unweighted

$$P(\tau) = \frac{N(\tau)}{N_{tot}} \times \frac{1}{\Delta t}$$

nearest-neighbor weighting

$$P(\tau) = \frac{N(\tau)}{N_{tot}} \times \frac{1}{\Delta t_{ave}} \quad \text{with } \Delta t_{ave} = (a+b)/2$$

Kuno *et al*, J. Chem. Phys. 2001

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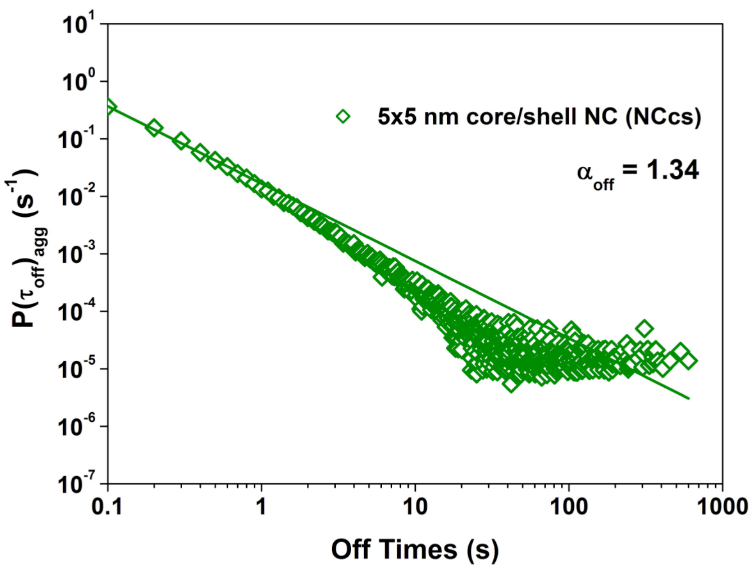
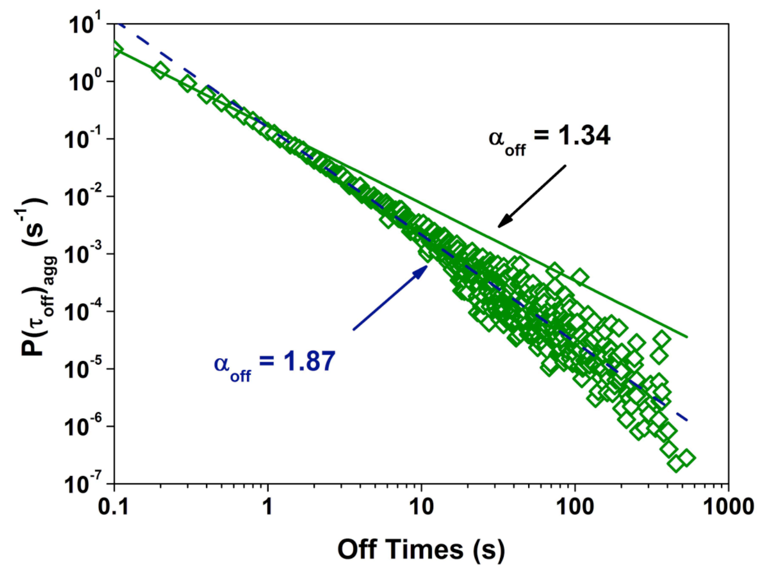
Weighting and fitting

Aggregated core-shell NC off-times



unweighted



nearest-neighbor weighting

Solid line: power law fit

Dashed line: Linear fit to log[$P(\tau)$] vs. log[τ]

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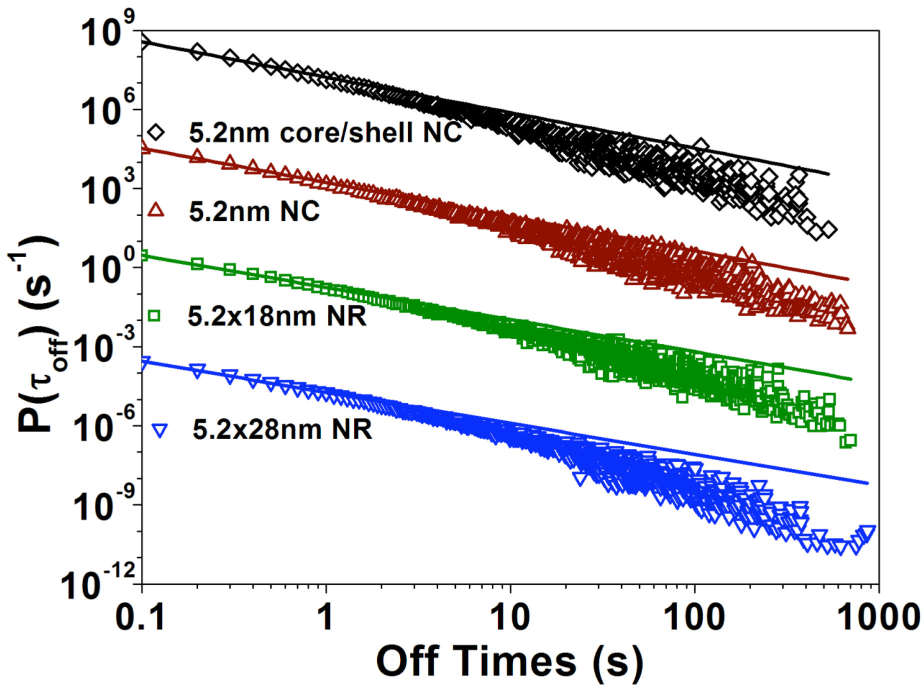
Nanorod off-time statistics

Aggregated data (100 individual NRs)



Sample	α_{off}
5.2 nm NC	1.3 ± 0.1
3.4 x 18 nm	1.2 ± 0.1
3.5 x 25 nm	1.1 ± 0.1
3.4 x 38 nm	1.2 ± 0.1
5.2 x 18 nm	1.2 ± 0.1
5.2 x 28 nm	1.2 ± 0.1
6.4 x 22 nm	1.2 ± 0.1
6.9 x 34 nm	1.2 ± 0.1

Power law fit (weights short times most)
Adding ZnSe shell or changing ligands has no effect

Nanorods vs. nanocrystals

Off-time distributions:

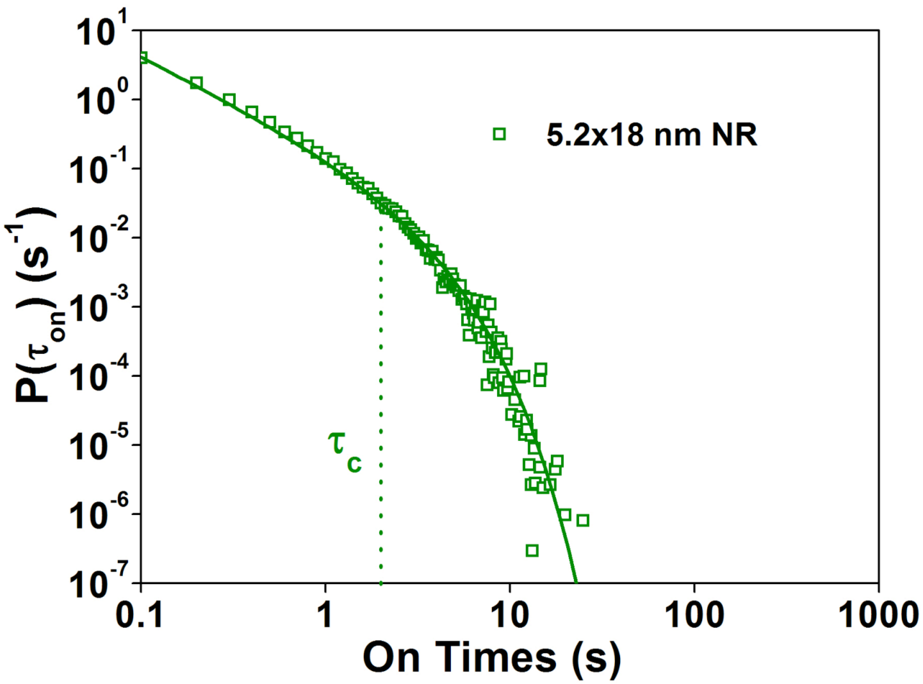
- Same power-law behavior for NRs and NCs (slightly smaller exponent for NRs)
- No difference among NRs with different aspect ratio or surface composition
- Independent of excitation intensity

Dark state returns to bright by same mechanism for NRs and NCs

Differences appear in on-time distributions

On-times: truncated power law

Aggregated data (100 individual NRs)



$$P(\tau_{on}) \propto \tau_{on}^{-\alpha_{on}} e^{-\tau_{on}/\tau_c}$$

5 x 18 nm NRs:

α_{on} = 1.35

τ_c = 2.2 s ± 0.2 s

Truncated power law fits better than power law, stretched exponential

Tang and Marcus, *J. Chem. Phys.* 2005, *Phys. Rev. Lett.* 2005

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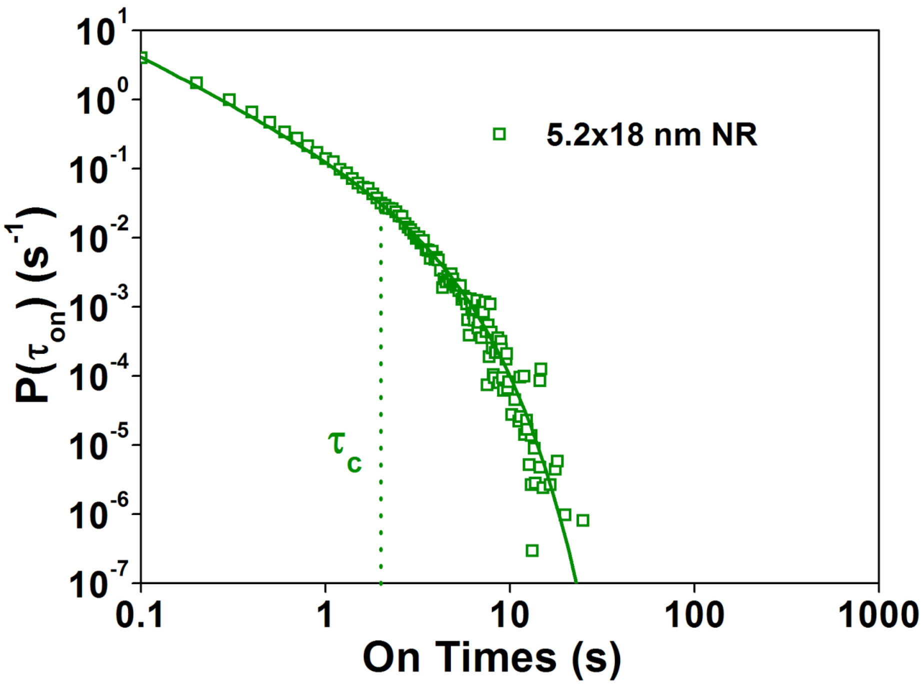
On-times: truncated power law

Aggregated data (100 individual NRs)



$$P(\tau_{on}) \propto \tau_{on}^{-\alpha_{on}} e^{-\tau_{on}/\tau_c}$$

5 x 18 nm NRs:

$\alpha_{on} = 1.35$

$\tau_c = 2.2$ s $\pm$ 0.2 s

Find α_{on} from power law fit to first four points, then find τ_c from logarithmic fit (Tang)

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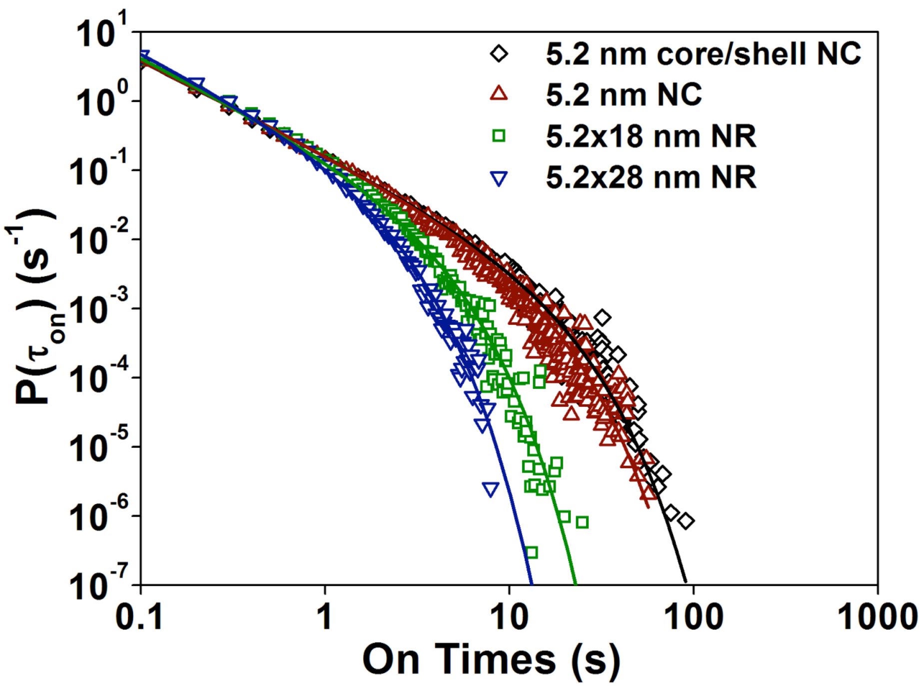
τ_c depends on shape

Aggregated data (100 NRs)



Sample	τ_c (s)
5.2 nm NC	10 ± 1
3.4 x 18 nm	1.2 ± 0.1
3.5 x 25 nm	0.72 ± 0.2
3.4 x 38 nm	0.90 ± 0.2
5.2 x 18 nm	2.2 ± 0.2
5.2 x 28 nm	1.2 ± 0.1
6.1 x 22 nm	2.5 ± 0.2
6.0 x 31 nm	1.3 ± 0.1

increasing aspect ratio
decreasing quantum confinement
decreasing τ_c

←

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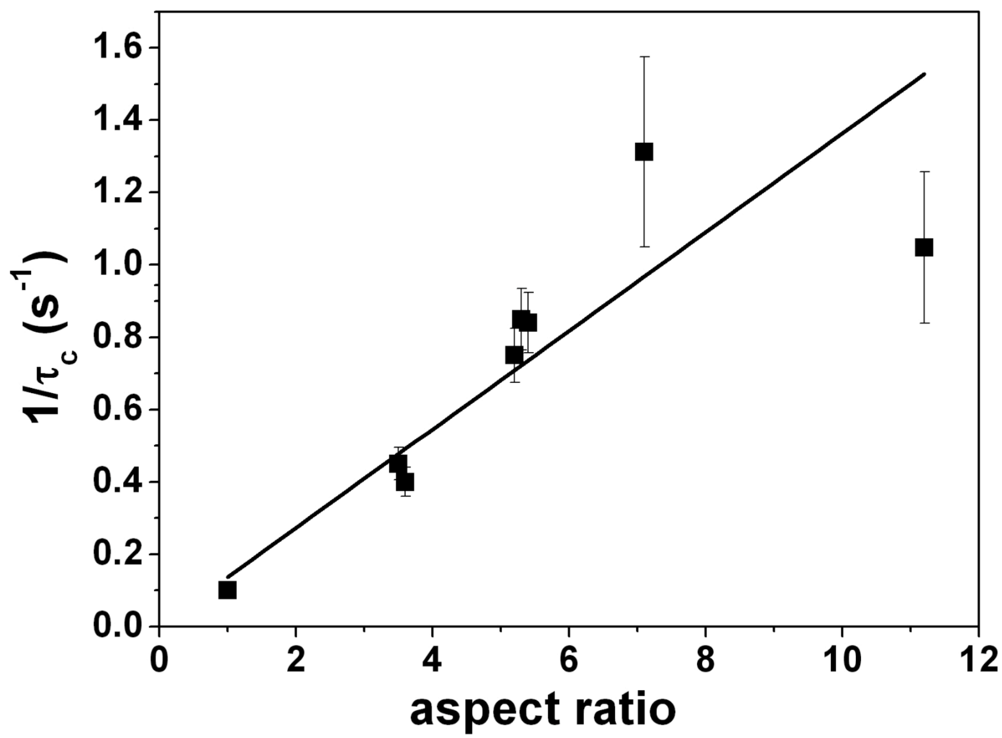
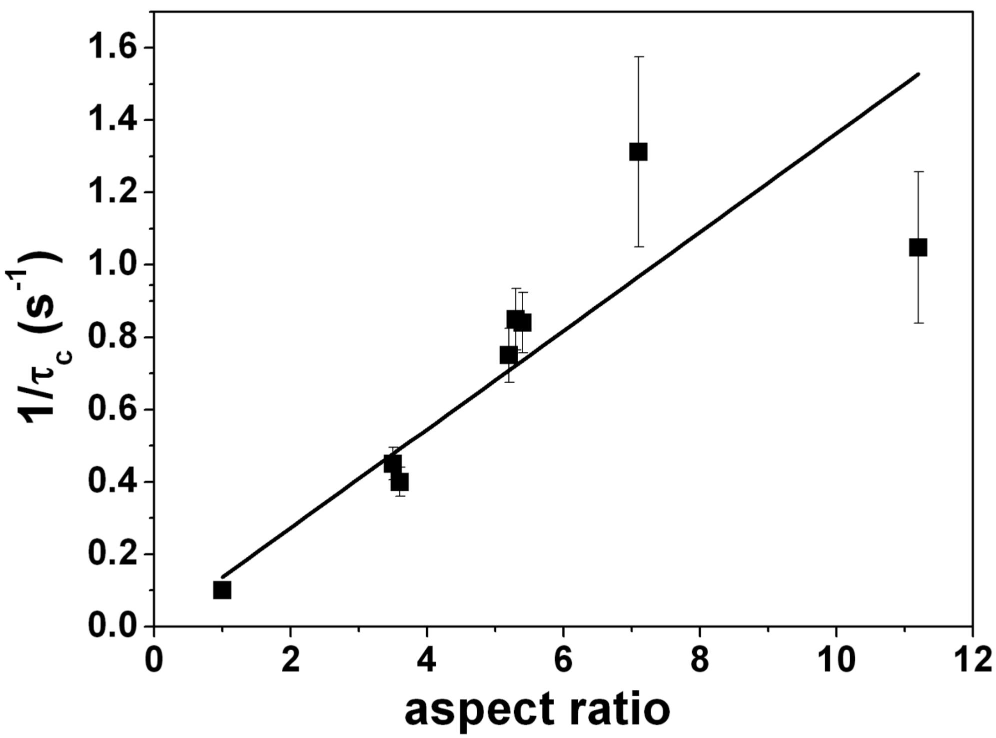
Aspect ratio dependence



aspect ratio	sample
1	5.2 nm NC
3.5	5.2x18 nm NR
3.6	6.1x22 nm NR
5.2	6.0x31 nm NR
5.3	3.5x18 nm NR
5.4	5.2x28 nm NR
7.1	3.5x25 nm NR
11	3.5x38 nm NR

Data for 3.5 nm NRs acquired for 1200 s (600 s for 3.5 x 25) due to rapid bleaching

Aspect ratio dependence



$1/\tau_c$ increases approximately linearly with NR aspect ratio

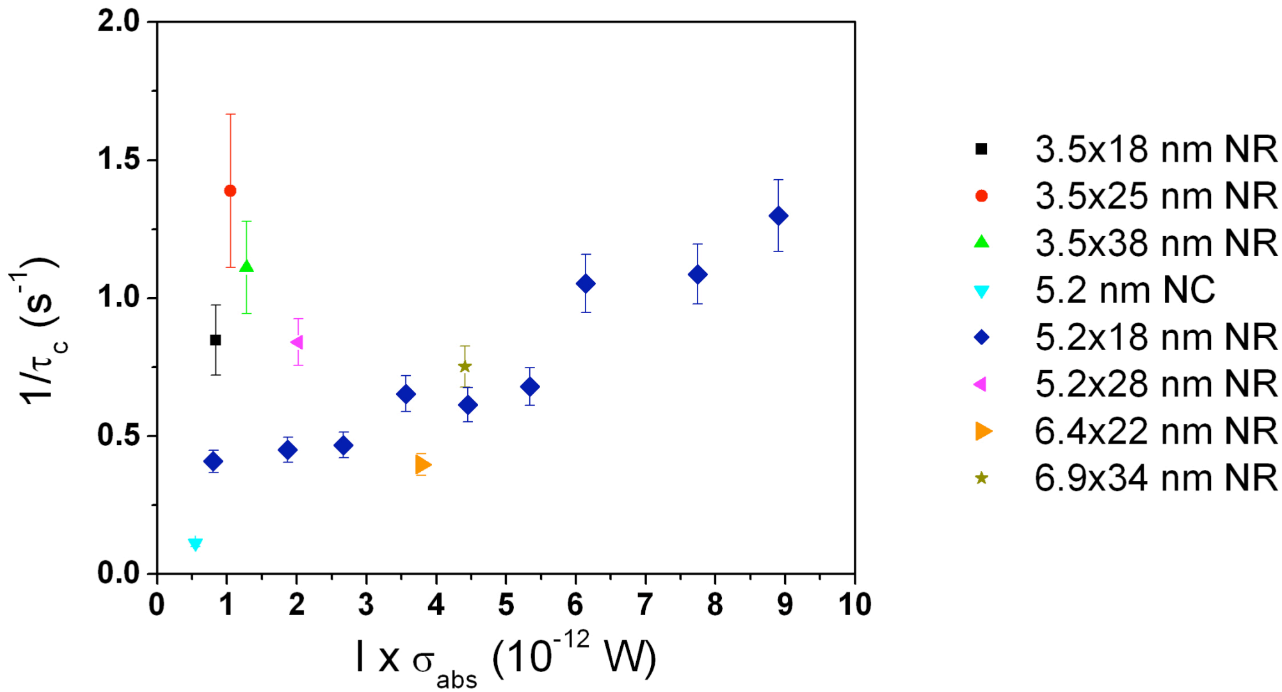
$$1/\tau_C = 0.14(l/d)$$

Aspect ratio dependence

- Absorption cross-section increases with volume
- Expect τ_c to decrease as illumination intensity increases (Shimizu experiments, Tang and Marcus, Frantzusov and Marcus)
- Is aspect ratio dependence just due to absorption rate changes?

Absorption rate dependence

$1/\tau_c$ increases gradually with intensity



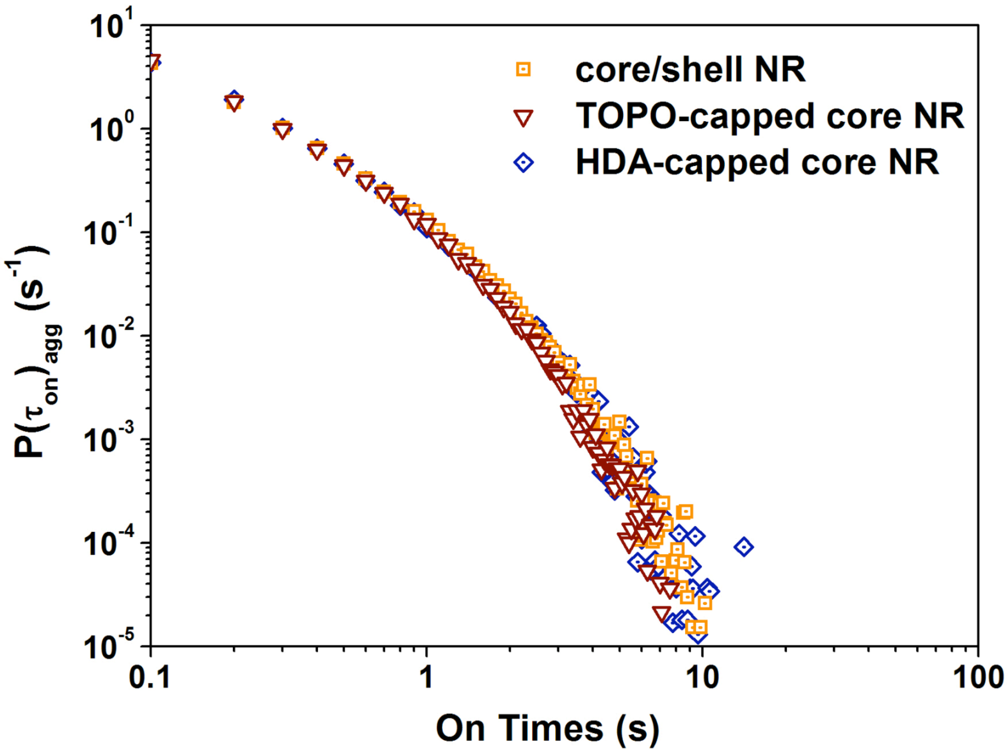
Changes in absorption cross-section cannot account for all of the variation in τ_c.

Why aspect ratio?

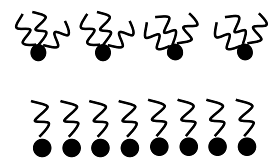
Some speculation:

- Stacking faults or other internal defects in NRs
- Motion of exciton along rod: longer rods sample environment more rapidly
- Surface charge migration produces greater fluctuations

Surface passivation: 5×28 NRs



Surface coverage:



TOPO ~ 36%

HDA ~ 100%

Sample	τ_c (s)
TOPO	1.2 ± 0.1
HDA	1.6 ± 0.1
Core-shell	1.5 ± 0.1
5×18	2.2 ± 0.1

Surface has only a small effect!

Do internal faults matter more than surface traps?

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Summary

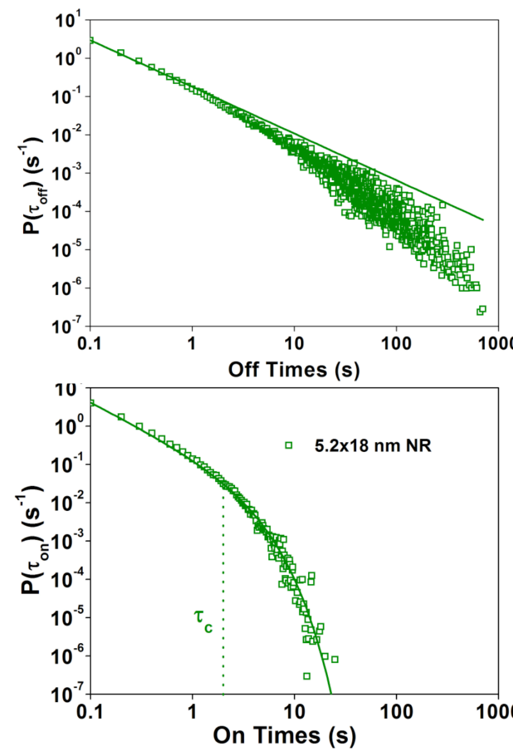
NRs: power-law off-time distribution (α_{off} = 1.2)

- independent of shape, intensity, surface
- same mechanism as NCs

Truncated power law on-time distribution

- shorter τ_c than NCs
- τ_c decreases with increasing intensity
- τ_c decreases with increasing aspect ratio (not just due to changing cross-section)
- Surface affects τ_c little
- 1D exciton? Internal faults?

Absorption rate dependence of three NC sizes



Outlook

- Shorter timescales
- Lifetime measurements
- Spectral diffusion
- Confirm single NRs

Acknowledgements

- Funding: ONR (Penn), NSF (Penn), HHMI (Swarthmore), and Swarthmore College
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Wang, S. *et al*, *J. Phys. Chem. B*; **2006;** *110* (46), 23221 - 23227.

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Thank you, Boldizsar and Ken, and Mimi!