Electronic Supplementary Information

Shell and Ligand-Dependent Blinking of CdSe-Based Core/Shell Nanocrystals

Bonghwan Chon,[a] Sung Jun Lim,[a] Wonjung Kim,[a] Jongcheol Seo,[a] Hyeonggon Kang,[b] Taiha Joo,[a] Jeeseong Hwang[b] and Seung Koo Shin*[a]

[a] *Bio-Nanotechnology Center, Department of Chemistry, Pohang University of Science and Technology, San31 Hyoja-dong Nam-gu, Pohang, Kyungbuk 790-784, Korea. Fax: +82 54 279 3399; Tel: +82 54 279 2123; E-mail: skshin@postech.ac.kr*

[b] *National Institute of Standards and Technology, Physics Laboratory, Optical Technology Division, 100 Bureau Drive, Gaithersburg, MD 20899, USA Fax: +1 301 975 4580; Tel:+1 307 975 6991*

*To whom all correspondence should be addressed.

Figure Caption

Figure S1. Powder X-ray diffraction of CdSe/ZnS(6ML), CdSe/ZnSe(2ML)/ZnS(4ML) and CdSe/CdS(2ML)/ZnS(4ML) nanocrystals. The shell thickness is denoted in parenthesis in units of monolayer (ML). Vertical lines represent the diffraction patterns for bulk ZB compounds.

Figure S2. (a) The on-time duration following the *N*th off-period for CdSe/ZnS(6ML), CdSe/ZnSe(2ML)/ZnS(4ML) and CdSe/CdS(2ML)/ZnS(4ML) organic-soluble nanocrystals; (b) the off-time duration following the *N*th on-period.

Figure S3. (a) Blinking time trace (0–6 min, 4 ms bin) and intensity histogram of a water-soluble CdSe/ZnSe/ZnS nanocrystal. The on/off threshold was varied from two to seven times the standard deviation (σ) of average dark count. (b) On- and (c) off-time probability distributions in log-log scale at various thresholds. Each probability distribution was fit to the power law to extract α_{on} and α_{off}. Threshold dependence of (d) on- and (e) off-time exponents: The power-law exponents obtained from threshold of 3–6σ are comparable within errors.

Figure S4. (a) Blinking time trace (0–6 min, 4 ms bin) and intensity histogram of an organic-soluble CdSe/CdS/ZnS nanocrystal with increasing integration bin time; 4 ms (green), 8 ms (blue), 16 ms (red) and 32 ms (black). (b) Blinking time trace expanded between 165 and 177 s. The on/off threshold of 3σ is denoted by dotted line.

Figure S5. On- and off-probability distributions of an organic-soluble CdSe/CdS/ZnS nanocrystal with increasing integration bin time; 4 ms (green), 8 ms (blue), 16 ms (red) and 32 ms (black). (a) On-time and (b) off-time on log–log scales; (c) on-time and (d) off-time in log–linear scales. The power-law exponents are assigned to the data in log–log plots. Each line shown in semi-log plots represents the three-component exponential fit to the data. A single exponential does not fit the data.

List of Table

Table S1. Mean and error (95% confidence limit) of the power exponents (α_{on}, α_{off}) for organic and water-soluble nanocrystals, *N* is the number of nanocrystals.

Table S2. Previously reported power-law exponents of CdSe-based nanocrystals under various substrates and surface passivation conditions.

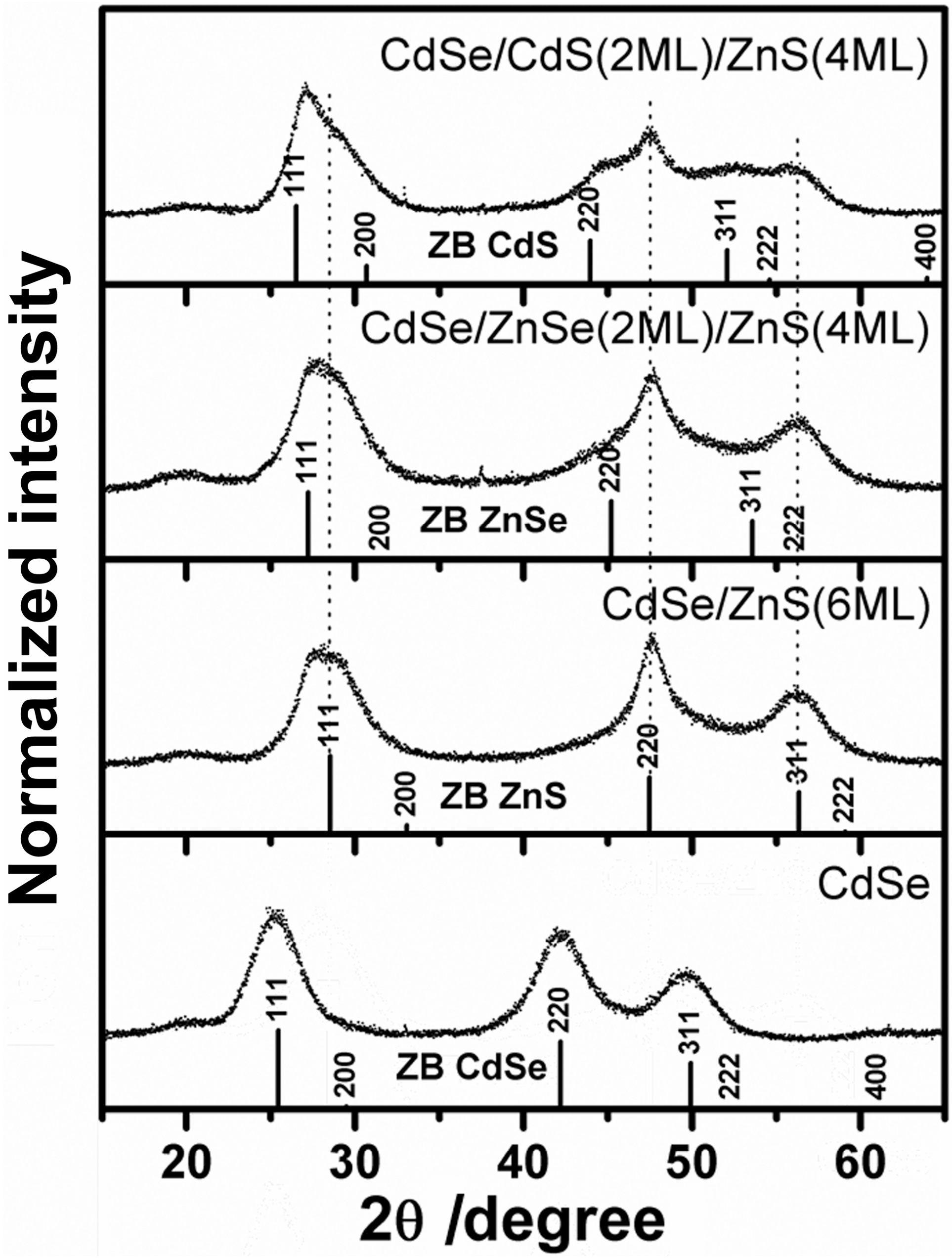
CdSe/CdS(2ML)/ZnS(4ML)
ZB CdS
111
200
220
311
222
400
CdSe/ZnSe(2ML)/ZnS(4ML)
ZB ZnSe
111
200
220
311
222
CdSe/ZnS(6ML)
ZB ZnS
111
200
220
311
222
CdSe
ZB CdSe
111
200
220
311
222
400
Normalized intensity
20
30
40
50
60
2θ /degree

Figure S1

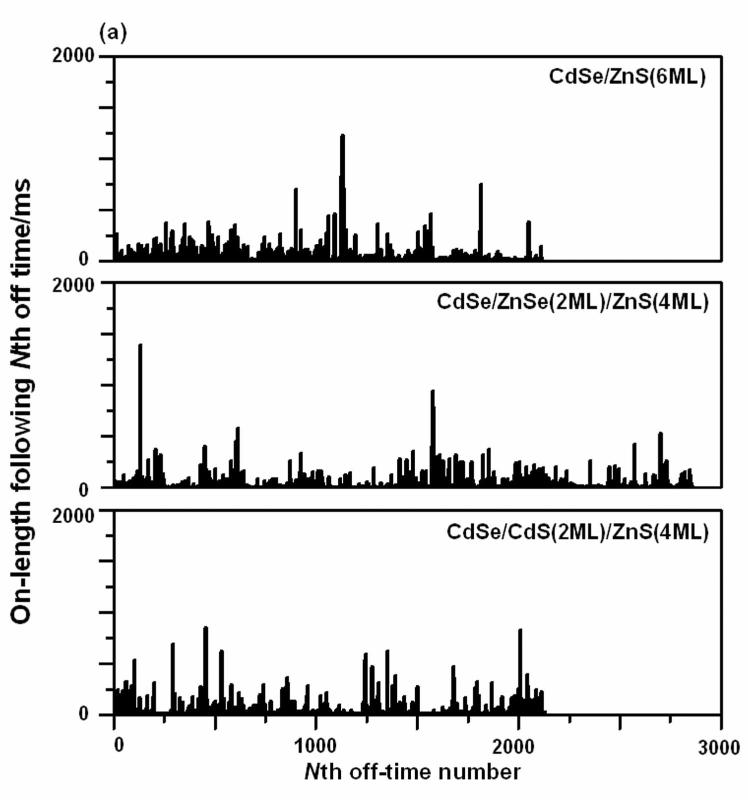

Figure S2a

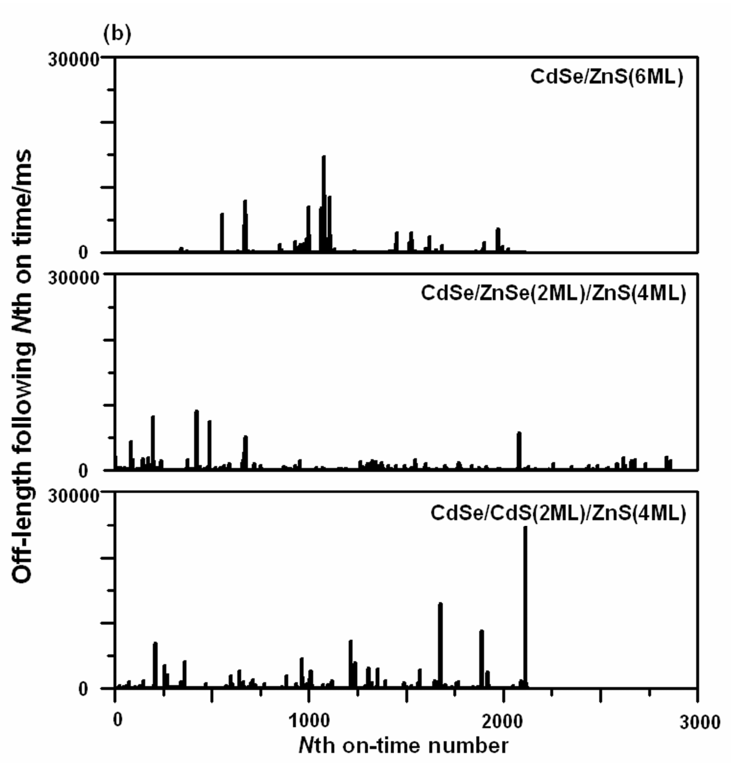

Figure S2b

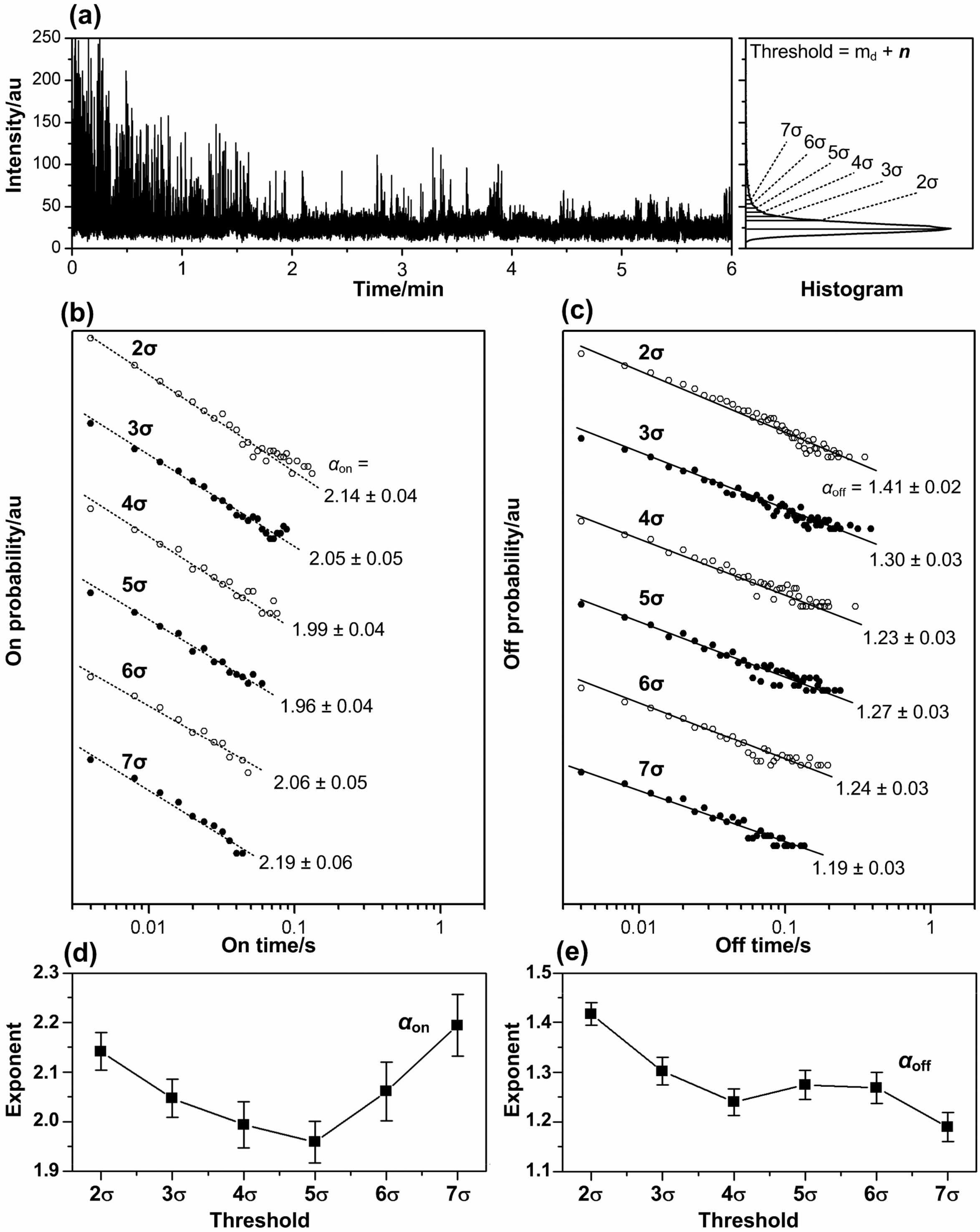
(a)
Intensity/au
Time/min
Threshold = m_d + n
7σ 6σ 5σ 4σ 3σ 2σ
Histogram
(b)
On probability/au
2σ
3σ
4σ
5σ
6σ
7σ
α_on =
2.14 ± 0.04
2.05 ± 0.05
1.99 ± 0.04
1.96 ± 0.04
2.06 ± 0.05
2.19 ± 0.06
On time/s
(c)
Off probability/au
α_off = 1.41 ± 0.02
1.30 ± 0.03
1.23 ± 0.03
1.27 ± 0.03
1.24 ± 0.03
1.19 ± 0.03
Off time/s
(d)
Exponent
α_on
Threshold
(e)
α_off
Threshold

Figure S3

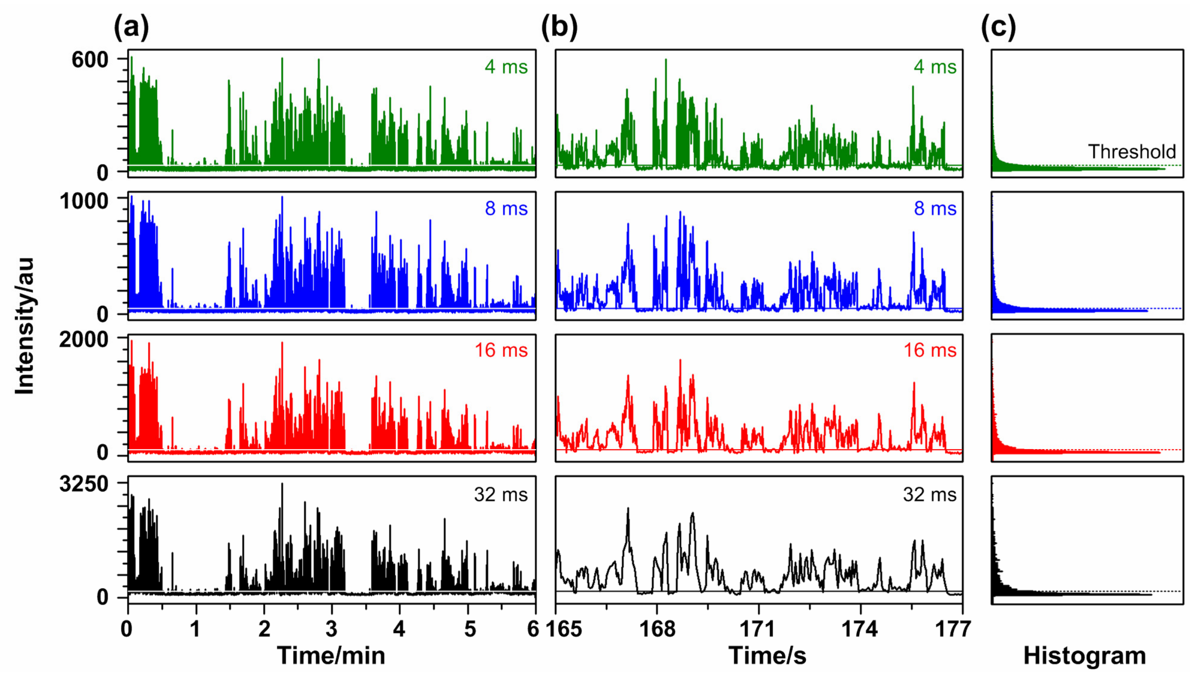
(a)
(b)
(c)
600
0
1000
0
2000
0
3250
0
Intensity/au
4 ms
8 ms
16 ms
32 ms
Threshold
0
1
2
3
4
5
6
Time/min
165
168
171
174
177
Time/s
Histogram

Figure S4

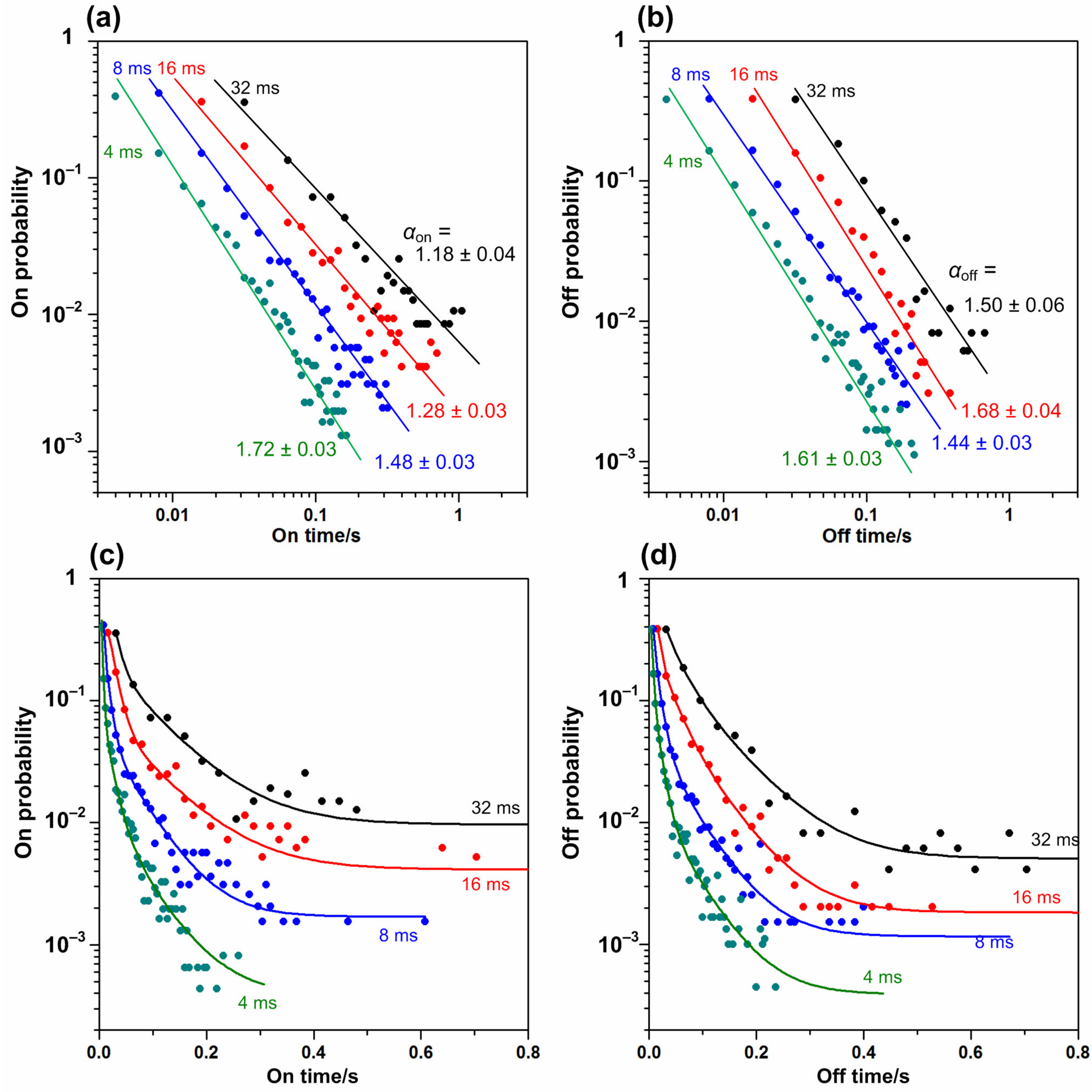
(a)
(b)
(c)
(d)
On probability
Off probability
On time/s
Off time/s
4 ms
8 ms
16 ms
32 ms
α_{on} = 1.18 ± 0.04
1.28 ± 0.03
1.48 ± 0.03
1.72 ± 0.03
α_{off} = 1.50 ± 0.06
1.68 ± 0.04
1.44 ± 0.03
1.61 ± 0.03

Figure S5

Table S1. Mean and error (95% confidence limit) of the power exponents (α_{on}, α_{off}) for organic and water-soluble nanocrystals, N is the number of nanocrystals

core/shell nanocrystals	organic-soluble[a]			water-soluble[b]		
	N	$\alpha_{on} \pm \sigma$	$\alpha_{off} \pm \sigma$	N	$\alpha_{on} \pm \sigma$	$\alpha_{off} \pm \sigma$
CdSe/ZnS(6ML)	12	1.86 ± 0.13	1.38 ± 0.10	12	2.17 ± 0.11	1.33 ± 0.08
CdSe/ZnSe(2ML)/ZnS(4ML)	15	1.75 ± 0.12	1.36 ± 0.07	7	2.11 ± 0.13	1.25 ± 0.06
CdSe/CdS(2ML)/ZnS(4ML)	33	1.53 ± 0.08	1.55 ± 0.03	15	1.85 ± 0.14	1.37 ± 0.06

[a] Stearate-covered nanocrystals in chloroform.

[b] MPA (3-mercaptopropionic acid)-capped nanocrystals in water.

Table S2. Previously reported power-law exponents of CdSe-based nanocrystals under various substrates and surface passivation conditions

nanocrystal	organic-soluble		water-soluble		substrate	ref.
	α_{on}	α_{off}	α_{on}	α_{off}		
CdSe	1.70	1.29			glass slide	1
	1.54[a]	1.35[a]			glass slide	1
CdSe/CdS	1.42	1.54			polymer film	1
CdSe/ZnS		1.37–1.79			glass slide	2
	1.73	1.38	2.29[b]	1.39[b]	glass slide	3
			2.27[c]	1.64[c]	glass slide	3
			1.48[d]	1.64[d]	glass slide	3
			1.71[e]	1.64[e]	glass slide	4
			2.04[e]	1.57[e]	gel	4
		1.46–1.77			polymer film	5
	1.71	1.63	2.16[f]	1.72[f]	polymer film	6
			2.25[g]	1.66[g]	polymer film	6
	1.61	1.74			fused silica cover slip	7

[a] octylamine-covered

[b] carboxy-functionalized

[c] amine-functionalized

[d] mercaptoundecanoic acid-capped

[e] strepavidin-conjugated

[f] AET (aminoethanethiol)-capped

[g] MPA (3-mercaptopropionic acid)-capped

REFERENCES

1. D. E. Gómez, J. van Embden, J. Jasieniak, T. A. Smith and P. Mulvaney, *Small*, 2006, **2**, 204–208.
2. M. Kuno, D. P. Fromm, H. F. Hamann, A. Gallagher and D. J. Nesbitt, *J. Chem. Phys.*, 2001, **115**, 1028–1040.
3. J. R. Krogmeier, H. Kang, M. L. Clarke, P. Yim and J. Hwang, *Opt. Commun.*, 2008, **281**, 1781–1788.
4. J. Yao, D. R. Larson, H. D. Vishwasrao, W. R. Zipfel and W. W. Webb, *Proc. Natl. Acad. Sci.USA*, 2005, **102**, 14284-14289.
5. A. Issac, C. von Borczyskowski and F. Cichos, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 161302(R).
6. Y. Kim, N. W. Song, H. Yu, D. W. Moon, S. J. Lim, W. Kim, H.-J. Yoon and S. K. Shin, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3497–3502.
7. M. Kuno, D. P. Fromm, S. T. Johnson, A. Gallagher and D. J. Nesbitt, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2003, **67**, 125304.