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$EVROXWH IHPWRVHFRQG PHDVXUHPHQWV UHFRPELQDWLRQ G\QDPLFV LQ OHDG VXOI

%&KR: . 3HW9HU7/LZD$UL3 6SHQ%FHUD5Q R-Y +DQG0 ' -RQDV

'HSDUWPHQW RI &KHPLVWU\ 8QLYHUVLW\ RI &RORUDGR %RXOG
86$

$EVWUDFW 7KH SKRWRQ H[FLWDWLRQ RI KRW FDUULHUV JH
SUREHG DV D IXQFWLRQ RI WKH DEVROXWH QXPEHU RI SKR
RI $XJHU UHFRPELQDWLRQ DQDO\VHV IDLO IRU DQ DYHUDJ

,QWURGXFWLRQ

Quantum dots have attracted considerable attention because of the potentially useful properties stemming from quantum confinement [1]. For example, multiple exciton generation (MEG) has been reported in PbS dots [2]. However, there is still an on-going controversy over the mechanism and yield of MEG [3]. The reverse process to MEG is the less controversial Auger recombination (AR); a standard model based on stepwise annihilation of multiexcitons exists [4]. This Auger analysis assumes that the signal is proportional to the number of electron-hole pairs, N_{eh}, that photo-excitation follows Poisson statistics, and that there are no annihilation processes other than AR. Poisson statistics can predict the initial and final signals with the microscopic kinetic model for AR connecting the two ends of the signals. „ †'–• Š ƒ˜‡ „ƒ•†‰ƒ' †‡‰‡•‡”ƒ…› 'ˆ zâ ƒ– Š‹‰Š‹Ž‡Žš‹•‰ƒ–‹ invoked to explain a rapid Auger process not described by the standard model [5]. However, $<N_{eh}>$ was not known absolutely. For 8 nm PbS dots, we have measured pump-probe transients up to an absolutely known $<N_{eh}>=10(\pm 10\%)$, where the brackets around N_{eh} indicate a weighted average over the probe beam profile. The assumptions of the standard Auger analysis fail below $<N_{eh}> = 2$.

([SHULPHQWDO

The pump-probe experiments in Figure 1 used pulses from a home-built noncollinear optical parametric amplifier delivering 150 nJ, 35 fs, 500 nm pulses at 10 kHz repetition rate. The NOPA was pumped by a Coherent RegA seeded by a home-built Ti:Sapphire oscillator running at 76 MHz. AR experiments used a Coherent RegA delivering 750 nJ, 75 fs, 800 nm pulses at 20 kHz repetition rate. The oleate capped PbS dots were supplied by NREL and were dispersed in toluene before use. The dot samples were held in an air-tight spinning cell (1800 rpm) to ensure that the sample is refreshed after each laser shot. The pump-probe signal was measured by a Si photodiode using lock-in detection. For fluorescein, calculation of the absolute signal size utilized the steady state absorption and emission spectrum, the transverse

spatial profile of the laser beams, the pulse spectra, and the known electronic state lifetime. Figure 1 shows the calculated and measured time-dependent pump-probe signal for fluorescein at magic angle pump-probe polarization. Agreement to within 5% indicates the accuracy for N_{eh}.

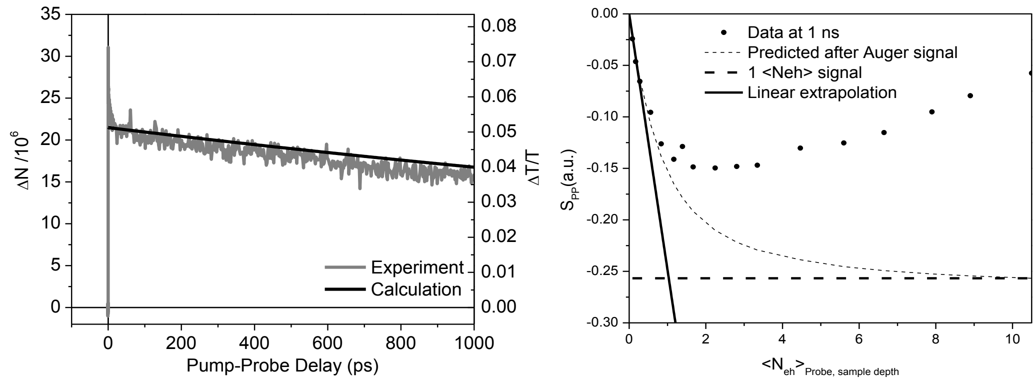

Fig.1. OHIW $EVROXWH FKDQJH LQ WKH QXPEHU RI SUREH SK
GLDQLRQ LQ EDVLF PHWKDQRO IRU D PDJLF DQJOH SXPS SUR
GHOD\ 7KH H[SHULPHQWDO PHDVXUHPHQW JUH\ LV FRPSD
DGMXVWDEOH SDUDPHWHUV EODFN YHULI\LQJ WKH DEVROX

Fig. 2 ULJKW 3XPS SUREH VLJQDO IRU QP 3E6 GRWV DYHUDJH
D IXQFWLRQ RI HK 7KH 1VROLG EODFN OLQH LV WKH OLQHDU H[WUD
7KH VKRUW GDVKHG FXUYH DVVXPHV HK DOO GHFD\ HK WR 1 GRWV
FRPSOHWH $5 HK $W KLJK 1RW GDVKHG FXUYH DSSURDFKHV RW
ORZ HK 1GDWD HK ORQJ GDVKHG KRUL]RQWDO OLQH 'DWD GR
WKH VWDQGDUG $XJHU HK DQDO\VLV IDLO EHORZ 1

5HVXOWV DQG 'LVFXVVLRQ

Ordinarily, the PbS dot emission lifetime is ~300 ns and biexciton Auger recombination lifetime is ~200 ps. Figure 2 shows pump-probe signals at 1 ns delay (after AR is complete but before population loss is expected) as a function of $\langle N_{eh} \rangle$. Because $\langle N_{eh} \rangle$ is absolutely known, the height of the long dashed line is known *a priori*, and a discrepancy with the standard Auger analysis assumptions is revealed by $\langle N_{eh} \rangle = 1.5$. Figure 3 shows that the pump-probe signal at 100fs delay is linear in $\langle N_{eh} \rangle$ up to $\langle N_{eh} \rangle = 10$. This likely indicates that photo-excitation generates a Poisson distribution and that the signal is proportional to N_{eh} before relaxation. This is an advantage of exciting hot carriers that interact only weakly; these assumptions of the Auger analysis do not hold for band edge excitation of excitons. A likely explanation for the discrepancies in Figure 2 is charge ejection from the dot into a surface or ligand trap[6, 7]. Charge separated dots have an emission lifetime of ~300 ps; the signal at 1 ns can be explained by assuming charge separation in ~4/5 of the dots at $\langle N_{eh} \rangle = 10$

Figure 3 also shows that the pump-probe signal at 1.5 ps (after carrier cooling) starts to saturate at $\langle N_{eh} \rangle \approx 4$. The early time development of this saturation is shown as a function of initial $\langle N_{eh} \rangle$ and pump-probe delay on Figure 4. This is possible because the signal is linear in $\langle N_{eh} \rangle$ up to ~ 200 fs delay. At present it is not yet clear whether these fast saturation dynamics are connected to charge separated states (which could arise from persistent charge separated states with lifetimes greatly exceeding the 30 ms time required for the sample to rotate back into the beam) or band-filling.

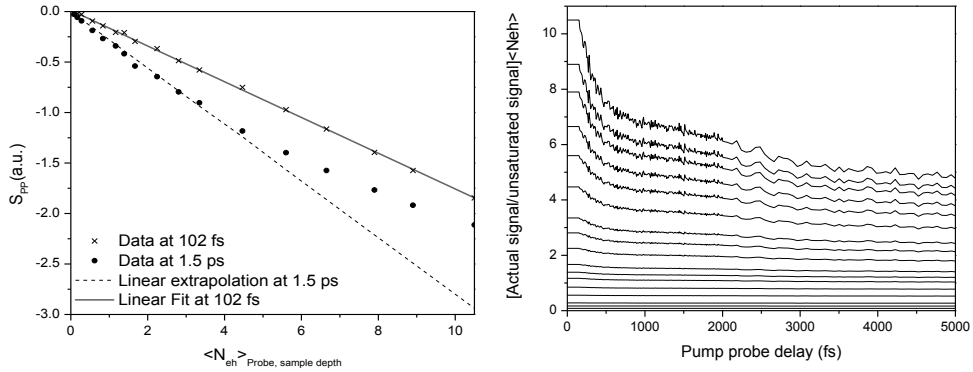

Fig.3 OHIW QP GLDPHWHU 3E6 GRW SXPS SUREH VLJQDOV DV DV D IXQFWLRQ RI 1

Fig.4 ULJKW 6DWXUDWLRQ RI WKH SXPS SUREH VLJQDO VLJ IURP WKH ORZ SRZHU VLJQDO DW HDFK SXPS SUREH GHOD\ WKH VLJQDO IRU GHOD\V QHDU LQLWLDO

&RQFOXVLRQ

Multiexciton dynamics with an absolute N_{eh} scale shows that the assumptions of the standard Auger analysis have limited validity beyond $\langle N_{eh} \rangle = 1$. The dot quenching processes revealed by scanning to 1 ns delay and absolutely calibrating $\langle N_{eh} \rangle$ may affect the early time dynamics previously attributed to band filling. Close inspection of Fig. 3 indicates time-dependent saturation within 1 ps at around $\langle N_{eh} \rangle = 0.5$; this is faster than ordinary AR or trion decay.

$FNQRZOHGJPHQW

7KLV ZRUN ZDV IXQGHG E\ WKH 'LYLVLRQ RI &KHPLFDO 6FL RI %DVLF (QHUJ\ 6FLHQFHV RI WKH 8 6 'HSDUWPHQW RI (Q

5HIHUHQFHV

) : :LVH $FF &KHP 5HV
$ - 1R]LN 0 & %HDUG - 0 /XWKHU 0 /DZ 5 - (OOL
110
3 7\DJL DQG 3 .DPEKDPSDWL - &KHP 3K\V
9 , .OLPRY - $ 0F*XLUH 5 ' 6FKDOOHU 77 DQG 9 , 5XSD
(,VWUDWH 6 +RRJODQG 9 6XNKRYDWNLQ / /HYLQD
&KHP
$ * 0LGJHWW + : +LOOKRXVH % . +XJHV $ - 1R]LN
114,
/ $ 3DGLOKD , 5REHO ' & /HH 3 1DJSDO - 3LHW