Isolating Exciton Extraction Pathways with Electric Field-Dependent Ultrafast Photocurrent Microscopy

Kyle Vogt[1], Sufei Shi[2,3], Feng Wang[3] and Matt W. Graham[1]

[1.] *Department of Physics, Oregon State University, Corvallis, OR 97331, USA*
[2.] *Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy 12180, NY USA*
[3.] *Department of Physics, University of California, Berkeley 94720, CA USA*

graham@physics.oregonstate.edu

Abstract: We develop a new, systematic approach to determine a material's intrinsic photocurrent generation efficiency through $\vec{E}_{Field}$-dependent ultrafast photocurrent and transient absorption microscopy. For WSe_2 devices, we find both measurements yield the same high efficiency.

OCIS codes: 320.7130 Ultrafast processes in condensed matter, 160.5140 Photoconductive materials.

For most nanoscale materials, photoexcited electrons recombine at a time, τ_r which is far faster than electron-hole pair dissociation and escape time [1], τ_e, resulting in inherently poor photocurrent generation efficiency given by, $\varepsilon = \frac{1/\tau_e}{1/\tau_e+1/\tau_r}$. Presently, there exists no *in-situ* time-resolved method that definitively provides the $1/\tau_r$ and $1/\tau_e$ rates. Transport based measurements lack the required time resolution, while purely optical measurement give a convoluted weighted-average of all electronic dynamics, offering no selectivity for photocurrent generating pathways. Recently, ultrafast photocurrent (U-PC) methods have successfully measured the rate limiting electronic relaxation processes in materials such as graphene [2], carbon nanotubes [3], and transition metal dichalcogenide (TMD) materials [4]. However, there exists no standard response function to understand the U-PC response. Here, we unambiguously understand the U-PC response by simultaneously resolving the transient absorption (TA) and U-PC response in highly-efficient WSe_2 devices shown in Fig. 1a. By systematically varying the applied E-field bias (V), we definitively show for the first time that both optical TA and electrical U-PC responses give the same electronic escape times, and show how they determine a material's intrinsic PC generation efficiency.

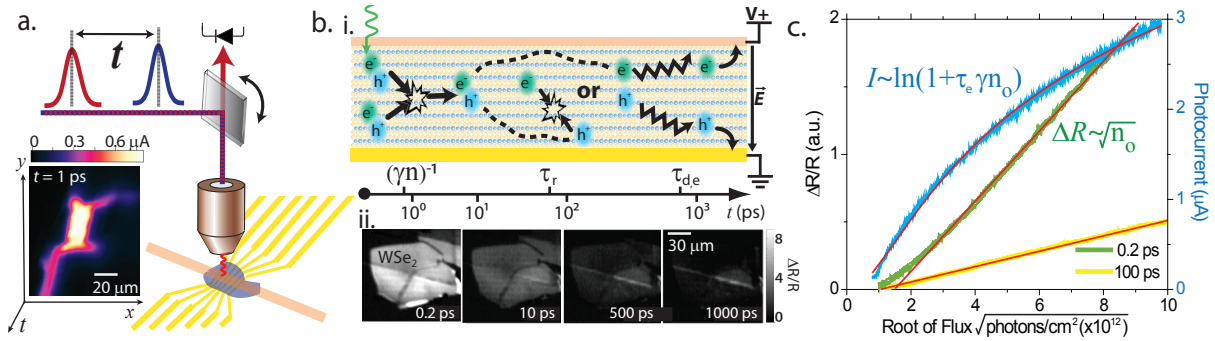

Fig. 1. (a) We measure the dynamics ($\Delta I(t,V)$ and $\Delta R(t,V)$) of exciton extraction in the WSe_2 device shown . (*inset*) $t = 1$ ps ultrafast photoconductance map. (b) *i*. Cutaway of device geometry, with transparent top gate held at voltage V, showing a timeline of photocharge extraction events measured. *ii*. TA microscopy movie of recombination rate. (c) TA (green, yellow) vs. square root of photon flux fits to a linear trend. PC fits to time-integrated response of $n(t)$.

By placing TMDs between optically translucent capacitive plates (Fig. 1a), we find that electrons resonantly excited with 120 fs pulses in WSe_2 can be harvested at efficiencies that approach a maximum of 52%. Fig 1b illustrates how we can exploit the highly nonlinear PC response to obtain a complete timeline of electronic events; from light absorption to photocurrent collection. Specifically, through analysis of the combined TA and U-PC response (Fig. 2), we extract all the kinetic rates; exciton-exciton annihilation rate ($\gamma n(t)$), recombination ($1/\tau_r$), electric field assisted diffusion and escape rates ($1/\tau_d$,$1/\tau_e$).

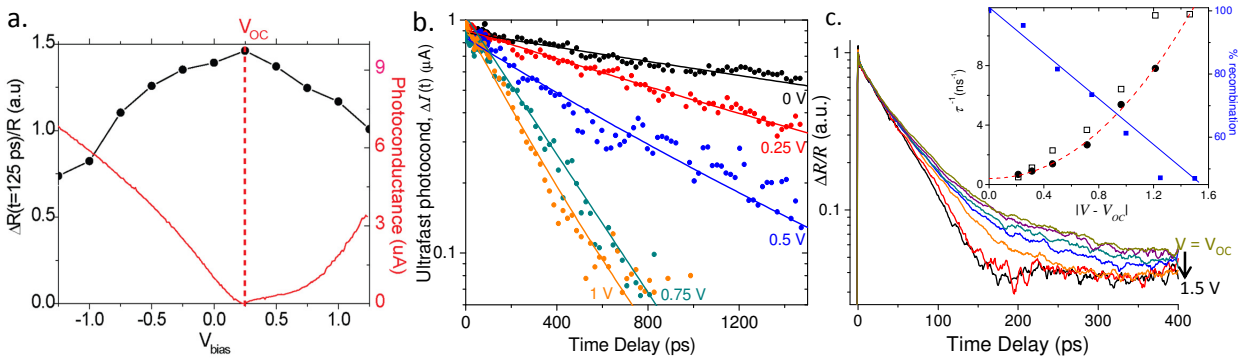

Fig. 2. Bias-dependent dynamics. (a) PC and TA amplitude at 125 ps scale symmetrically with bias about the open circuit voltage, V_{OC}. (b) Normalized U-PC WSe_2 response and model fits accelerate with increasing bias. (c) WSe_2 TA at biases ranging from 0 to 1.5 V. (*inset*) the U-PC electron drift times (τ_d, circles) and the TA electron-escape time (τ_e, open squares) give the same quadratic dependence with applied field. Fraction of electrons lost to recombination ($\%_{loss}$ =(1-ε)×100, blue squares).

Unlike typical bulk photodectors, in few-layer semiconductors like WSe_2 we find many-body electronic interactions, most notably exciton-exciton annihilation, dominate the the short-time kinetic behavior, as demonstrated by the square root scaling of the $\Delta R/R$ TA signal in Fig. 1c. If we assume an overall kinetic rate law is given as, $\frac{dn}{dt} = \delta(t)n_o - (\frac{1}{\tau_r} + \frac{1}{\tau_e})n - \gamma(t)n^2$, we obtain a photocurrent power dependence, $I(n_o) \propto \int_o^\infty n(t)dt \propto \ln(1+\gamma\tau_e n_o)$ that fits (red line) the observed response in Fig. 1c (blue). Continuing from this observation, the two-pulse U-PC response function is obtained by simply integrating piecewise about our delay time t', giving:

$$\Delta I(t) = \frac{1}{\tau_e}\int_o^t n(t', n_o)dt' + \frac{1}{\tau_e}\int_t^\infty n(t', n_o + n(t))dt' \quad (1)$$

In Fig. 2b we use the above response function to fit (solid lines) the U-PC kinetics decay, which accelerates rapidly with increasing applied voltage. The electron extraction rates (Fig. 2c (inset), solid circles) increase quadratically with voltage. The field-dependent TA kinetics rate component also increases quadratically (dashed line fit to open squares) with the applied field, showing these carriers are escaping the device as PC. We find the TA kinetics are the summation of all kinetic processes in Fig. 1b. Accordingly, both field-dependent escape time, τ_e and the field independent recombination time, τ_r can be readily extracted. In Fig. 2c (inset) we show that the field dependent TA optical escape rates ($1/\tau_e$, open squares) have excellent agreement with the rates independently extracted from the U-PC response function. The fraction of electrons that are lost to electronic recombination are further plotted (blue) via calculation of material's intrinsic photocurrent efficiency, ε. This shows the intrinsic photocurrent efficiency of WSe_2 approaches 52%. We find the material efficiency is ultimately limited by field-independent electron-hole dissociation that occurs on the timescale of 47 ps.

In summary, few-layer semiconducting TMDs like WSe_2, have long carrier lifetimes, but challenging mobility and exciton dissociation bottlenecks that inhibit photocurrent generation. By combining femtosecond resolved photocurrent microscopy with ultrafast transient absorption [1,2,4], we have selectively imaged the dominant kinetics bottlenecks that inhibit photocurrent production in devices made from WSe_2 TMD materials. Using these ultrafast space-time maps of the electron-hole dissociation dynamics, we have a new methodology to intelligently engineer 2D material heterostructures devices to avoid efficiency-destroying, carrier recombination bottlenecks and maximize photocurrent yield.

[1] M.W. Graham, S. Shi, D.C. Ralph, J. Park, P.L. McEuen, "Transient Absorption and Photocurrent Microscopy Show That Hot Electron Supercollisions Describe the Rate-Limiting Relaxation Step in Graphene" Nano Letters, 13, 5497-5502 (2013).
[2] M.W. Graham, S. Shi, D.C. Ralph, J. Park, P.L. McEuen, "Photocurrent measurements of supercollision cooling in graphene," Nature Physics, 9, 103 (2013).
[3] N. M. Gabor, Z. Zhong, K. Bosnick, and P. L. McEuen, "Ultrafast Photocurrent Measurement of the Escape Time of Electrons and Holes from Carbon Nanotube p-i-n Photodiodes," Phys. Rev. Lett., 108, 8, 087404 (2012).
[4] M. Massicotte, P. Schmidt, F. Vialla, K. G. Schdler, A. Reserbat-Plantey, K. Watanabe, T. Taniguchi, K.-J. Tielrooij, and F. H. L. Koppens (2015), "Picosecond photodetection in vander Waals heterostructures," Nature Nanotech., 11, 42-46 (2015).