

## Solution Phase Synthesis of Carbon Quantum Dots as Sensitizers for Nanocrystalline TiO<sub>2</sub> Solar Cells

Peter Mirtchev,<sup>a</sup> Eric J. Henderson,<sup>b</sup> Navid Soheilnia,<sup>a</sup> Christopher M. Yip,<sup>c</sup> and Geoffrey A. Ozin<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6

<sup>b</sup> Opalux Inc., Lash Miller Chemical Laboratories, Suite 308, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6

<sup>c</sup> Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada, M5S 3E5

### Supporting Information

#### *Experimental Section*

*Materials:*  $\gamma$ -butyrolactone (Reagent Grade, >99%), concentrated H<sub>2</sub>SO<sub>4</sub> (95-98%), and anhydrous Na<sub>2</sub>CO<sub>3</sub> (min 99.5%) were purchased from Sigma Aldrich and used as received. Deionized water (18.1 M $\Omega$ .cm) was obtained from a Millipore filtration system. Dialysis membranes (MWCO 1000) were purchased from Serva Electrophoresis. Fluorine doped tin oxide (FTO) substrates (TEC 25, ~ 15  $\Omega$  / square) were purchased from Hartford Glass Co.

*Carbon dot synthesis:* In a typical experiment, 60 mL of  $\gamma$ -butyrolactone (67.8 g, 0.79 mol) was heated to 100°C in air with mechanical stirring in a round bottom flask equipped with a reflux condenser. Once the desired temperature was obtained, 20 mL of concentrated sulfuric acid (18 M H<sub>2</sub>SO<sub>4</sub>, 0.38 mol) was added to the stirring solution. After addition of the concentrated acid, the solution quickly changed color, from clear to yellow and finally to dark brown. The temperature of the mixture was maintained at 100°C in mild reflux for 1 hour. The reaction flask was then cooled down to nearly room temperature and neutralization of residual acid was performed through gradual addition of 200 mL of aqueous Na<sub>2</sub>CO<sub>3</sub> (24 g, 1.1 M). A biphasic mixture resulted, and the amber-colored upper layer was isolated using a separation funnel. Sodium sulphate byproducts from the neutralization were collected by centrifugation at 7800 rpm for 15 minutes, and the remaining mixture of carbon dots in water/butyrolactone was dialyzed against deionized water using SpectraPor dialysis membranes (MWCO 1000) for a minimum of 18 hours. CQD solutions were concentrated to approximately 1mg/mL for solar cell fabrication using a vacuum oven operating at 60°C.

*Solar Cell Fabrication:* For solar cell fabrication, aqueous TiO<sub>2</sub> paste (25% w/w TiO<sub>2</sub>, 10% w/w polyethylene glycol (MW 20000)) was doctor bladed onto FTO substrates. The films were then calcined at 450°C for 2 hours. After cooling down to around 60°C, the substrates were immersed in the CQD solution and kept in the dark for 48 hours. Sandwich cells were prepared using platinum coated FTO as the counter electrode. The two electrodes were sealed by melting a thin transparent film of polymer gasket (Surlyn) at 80°C on a hot plate. A small amount of

electrolyte solution (Iodolyte AN 50, Solaronix ) was infiltrated through a pre-drilled hole in the Pt/FTO electrode and the cell was subsequently sealed with microscope slides and extra polymer.

*Characterization:* PL measurements were carried out on a Varian Cary Eclipse fluorescence spectrometer. FTIR spectra of the CQDs in EtOH were obtained neat on NaCl disks on a Perkin Elmer Spectrum One FTIR Spectrometer. Raman spectroscopy was performed using a 532nm diode laser and calibrated using a crystalline silicon wafer. TEM images were obtained on a Hitachi HD2000 operating at 200 kV. UV-VIS absorbance spectra were recorded with a Perkin Elmer Lambda 900 UV/Vis/NIR spectrophotometer. Zeta potential measurements were conducted on a Malvern ZetaSizer 3000 HSa. NMR spectra were collected on a Varian Mercury 400 MHz spectrometer in D<sub>2</sub>O. Powder X-Ray diffraction was performed using a Siemens D5000 with the CuK $\alpha$  line as excitation source. Samples for AFM and XPS analysis were prepared by spin coating a CQD thin film onto a plasma-cleaned Si wafer for 60s at 3000 rpm using a Lauriel spin coater. All AFM imaging was performed using a Digital Instruments Multimode Scanning Probe Microscope equipped with a Nanoscope IIIA controller and a vertical engage J-scanner. The AFM images were acquired as 512 x 512 pixel data sets in intermittent contact mode using TESPAs diving board cantilevers in air at a scan rate of 1 Hz and a drive frequency of ~ 350 kHz. Image analysis was performed using the Nanoscope software version 5.12. X-ray photoelectron spectra were acquired on a Thermo Scientific Theta Probe utilizing monochromatic Al K $\alpha$  radiation. Solar cell measurements were performed using an Oriel Sol 1A solar simulator as the excitation source with an incident light intensity of 1000 W/m<sup>2</sup> calibrated using a standard Si solar cell. A Keithley 2400 source meter was used as the power supply. The absolute quantum yield measurement was performed using a 365 nm LED (Thorlabs, Inc.) as the excitation source, a custom-made integrating sphere (Gigahertz Optik), and a Maya 2000 spectrometer (Ocean Optics) as the detector. The AQY value was calculated using custom-made Labview software.

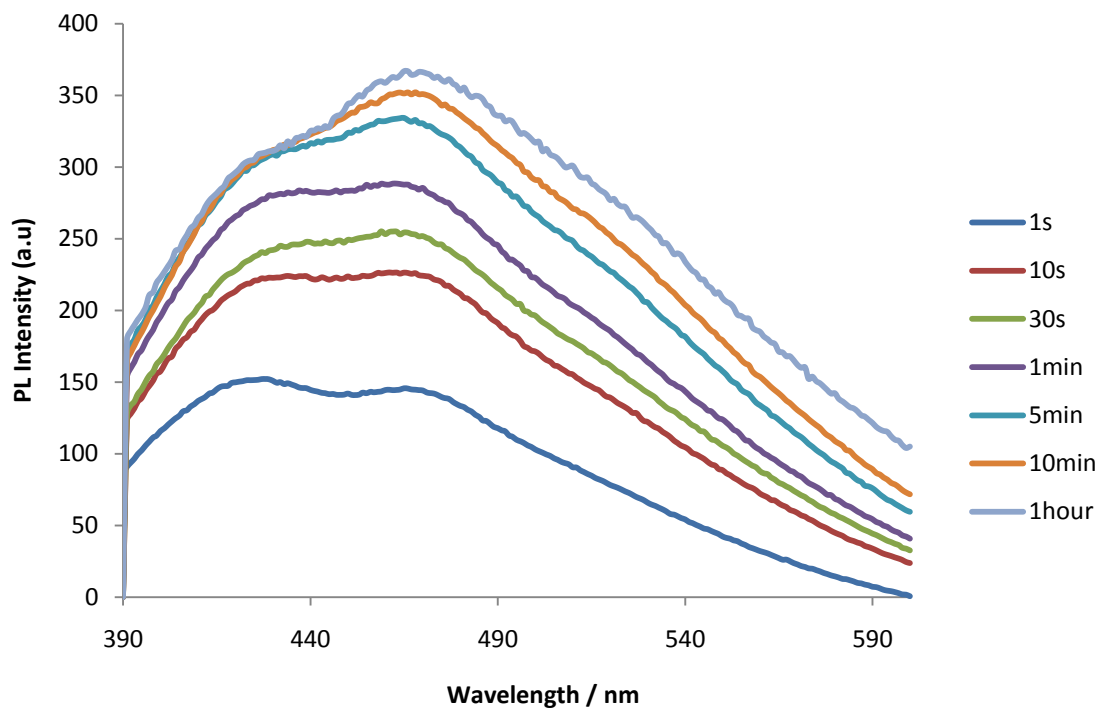


Figure S1. Evolution of CQD photoluminescence as a function of reaction time

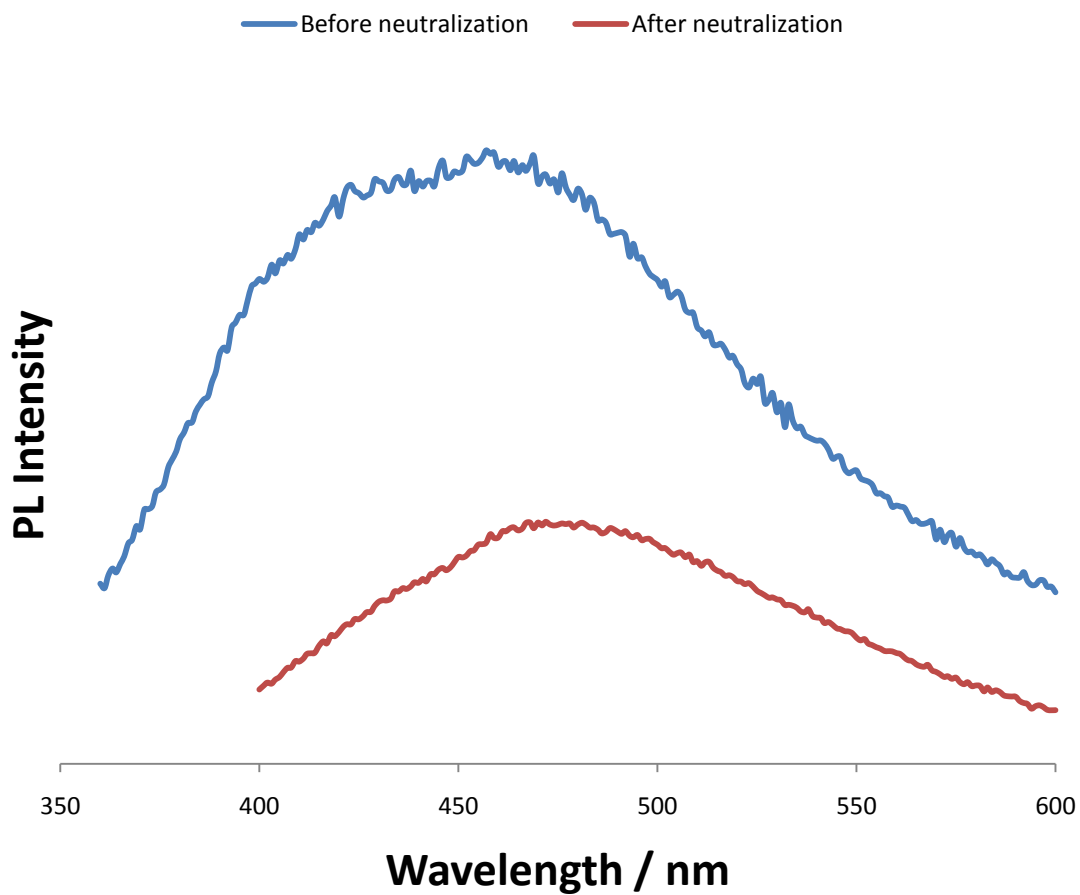


Figure S2. CQD PL spectra before and after neutralization with aqueous  $\text{Na}_2\text{CO}_3$

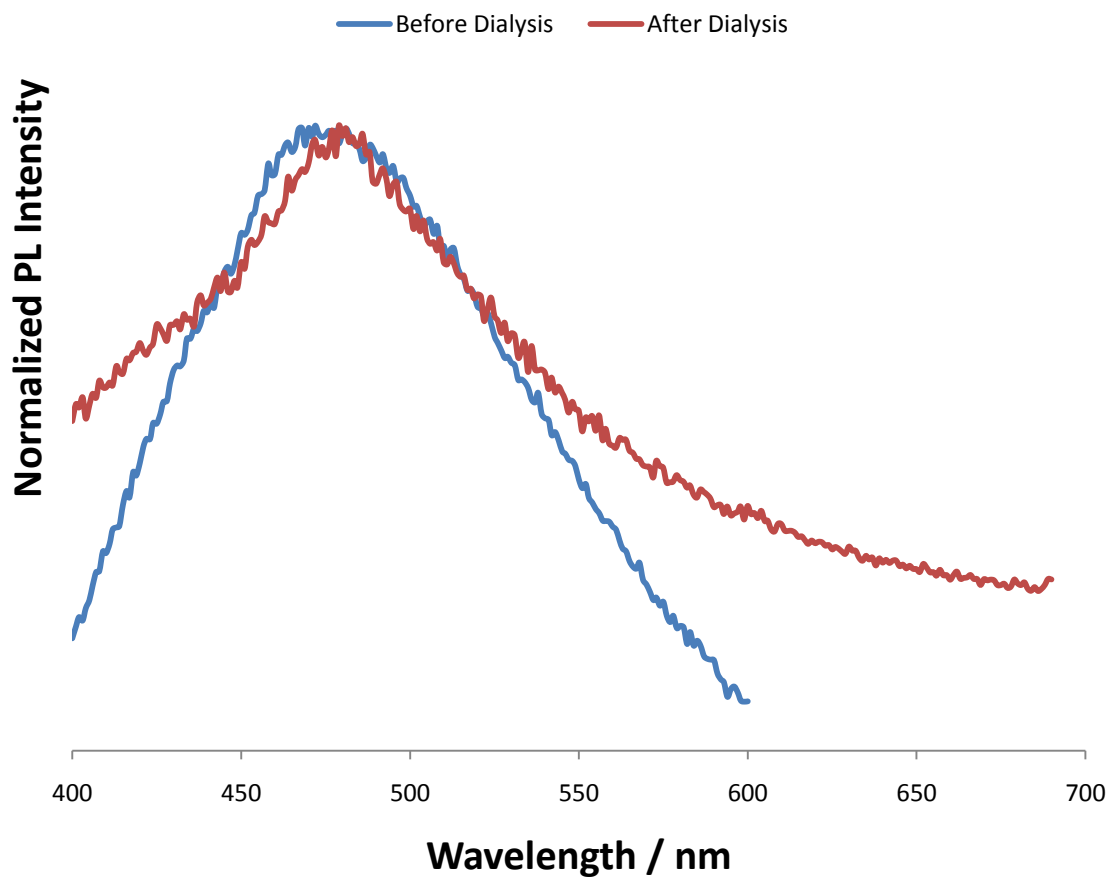


Figure S3. Normalized CQD PL spectra before and after dialysis of neutralized CQDs

Run	Pos.	KCps	Mob.	Zeta	Width	Time
1	17.0	489.0	-1.218	-15.4	6.4	14:43:14
2	17.0	466.3	-0.296	-3.7	6.5	14:46:29
3	17.0	466.2	-1.220	-15.4	6.5	14:49:22
4	17.0	461.6	-2.297	-29.0	6.5	14:52:10
5	17.0	474.4	-1.184	-14.9	6.5	14:55:36
Average		471.5	-1.243	-15.7	6.5	
+/-		10.8	0.709	9.0	0.0	

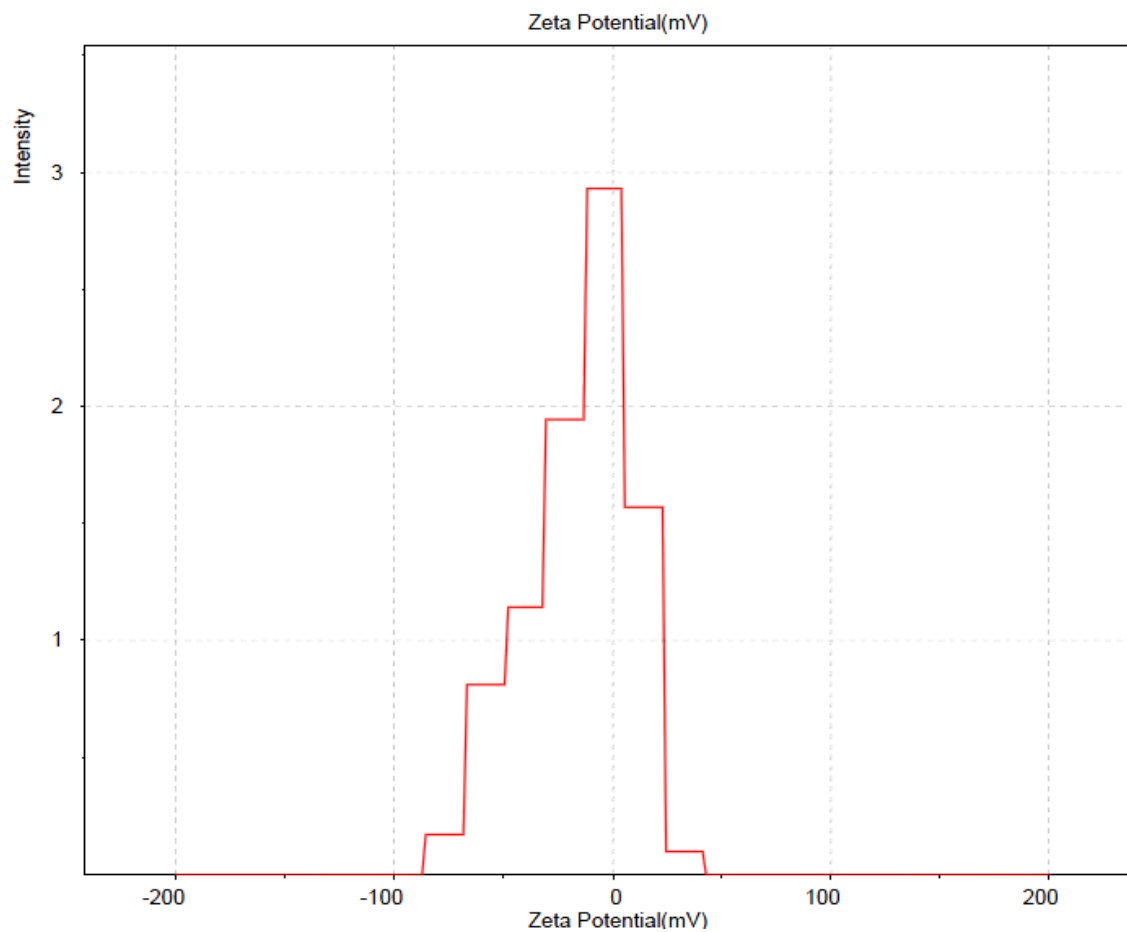


Figure S4. Sample zeta potential measurements on CQD aqueous solutions

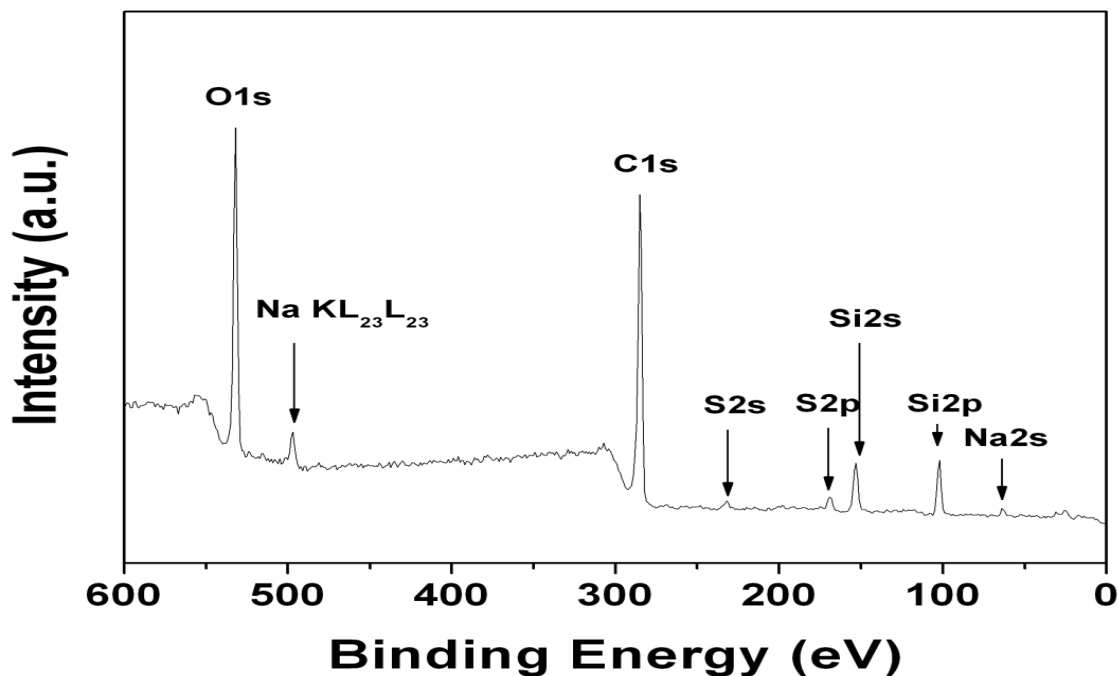


Figure S5 XPS survey scan showing the presence of sulphur species and sodium counter-ions

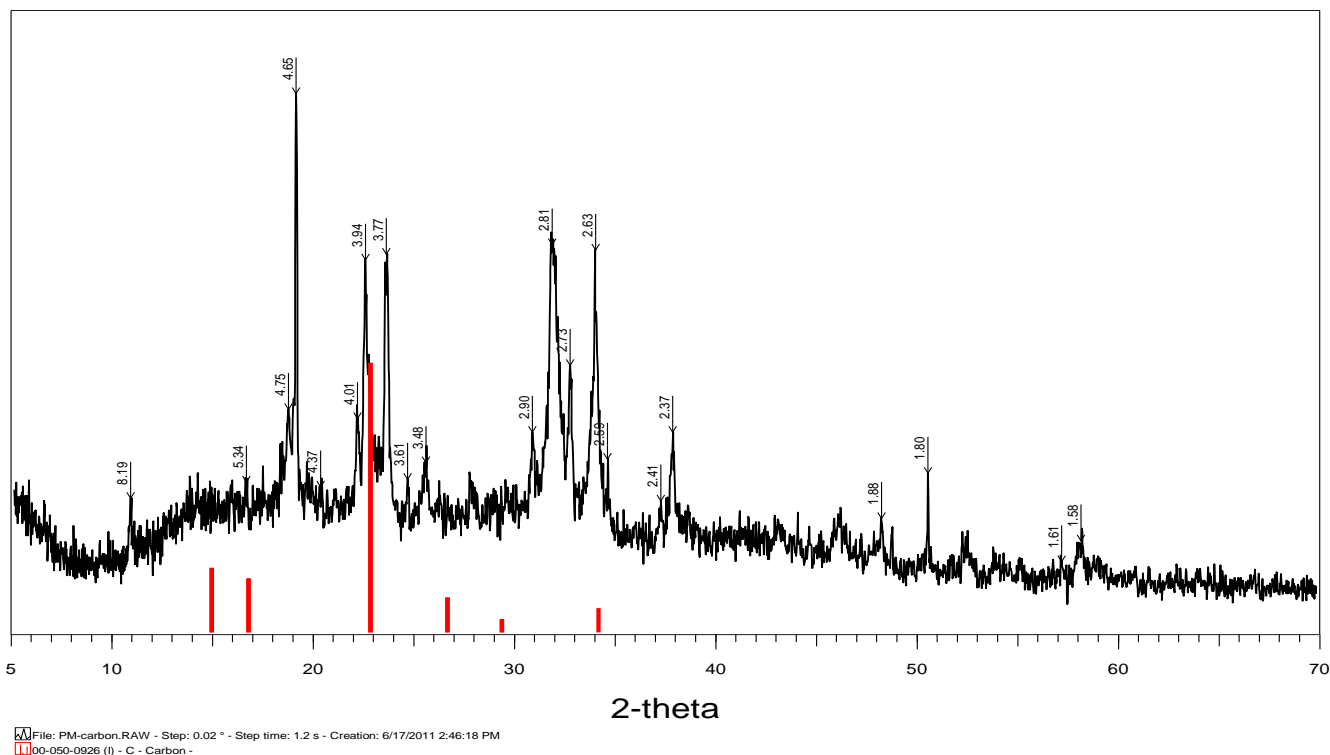


Figure S6. Powder X-ray diffractogram of dried CQD powder obtained by evaporating CQD aqueous solutions to dryness. The diffraction pattern did not yield a match when compared to literature spectra of graphite, few-layer graphene, and carbon black.

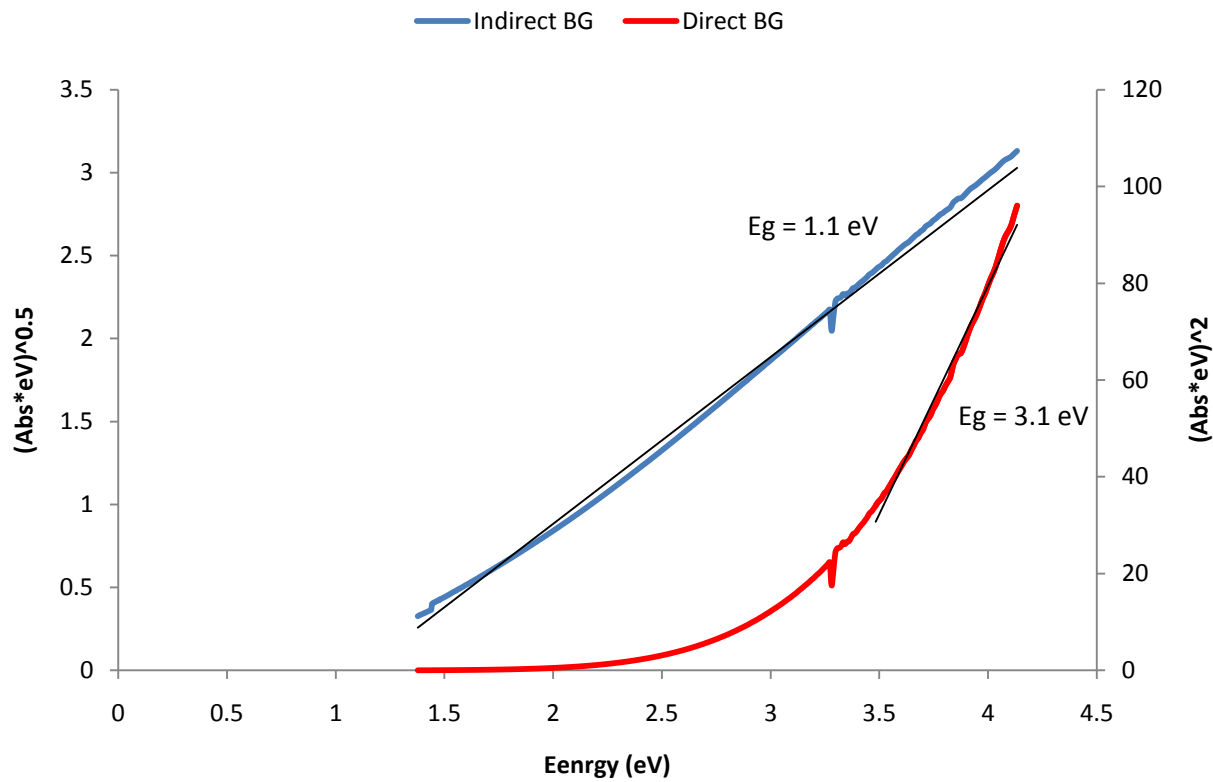


Figure S7 Tauc Plots Used for Bandgap Determination