Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Electronic Supplementary Information (ESI)

Near infrared detectors based on HgSe and HgCdSe quantum dots generated at the liquid-liquid interface

Manoj K. Jana, [a] P. Chithaiah, [a] Banavoth Murali, [b] S. B. Krupanidhi, [b] Kanishka Biswas, [a] and C. N. R. Rao *[a]

[a] *New chemistry Unit, International Centre for Materials Science and Sheikh Saqr Laboratory, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore 560064, India*

[b] *Materials Research Centre, Indian Institute of Science, Bangalore 560012, India.*

**E-mail: cnrrao@jncasr.ac.in*

Experimental Section:

Synthesis: Mercury cupferronate ($Hg(cup)_2$) or mercury cadmium cupferronate ($Hg_{0.5}Cd_{0.5}(cup)_2$) was used as Hg or Hg-Cd sources and selenourea, as the selenium source to prepare mercury selenide (HgSe) and mercury cadmium selenide ($Hg_{0.5}Cd_{0.5}Se$) QDs.

$Hg(cup)_2$ was prepared by adding aqueous cupferron solution to the aqueous $HgCl_2$ solution at 0 ^{o}C with vigorous stirring. $Hg_{0.5}Cd_{0.5}(cup)_2$ (nominal composition) was prepared by adding cupferron solution to the stoichiometric amounts of $HgCl_2$ and $CdCl_2$ dissolved in water, at 0 ^{o}C. The products were collected by centrifugation, washed several times with distilled water and ethanol and dried in a vaccum dessicator.

For the synthesis of HgSe nanocrystalline films, 6.5 mg of selenourea was dissolved in 20 ml of water in a 50 ml beaker and 25 mg of $Hg(cup)_2$ was dissolved in 20 ml of toluene by ultrasonication. For the similar synthesis of $Hg_{0.5}Cd_{0.5}Se$ films (nominal composition), 7.1 mg of selenourea and 25 mg of $Hg_{0.5}Cd_{0.5}(cup)_2$ were used. The toluene solution was slowly added along the walls of the beaker containing aqueous solution of selenourea. The interface starts

appearing black within few minutes. The reaction was left undisturbed for 24 hrs for the complete formation of HgSe and $Hg_{0.5}Cd_{0.5}Se$ nanocrystalline films. The films were lifted on to a glass slide for further characterizations.

Characterization: Powder XRD pattern of the products were recorded on Bruker D8 Advance diffractometer with CuK_{α} radiation (1.54 Å). The average crystallite sizes obtained using the Scherrer-formula (from XRD) for HgSe and $Hg_{0.5}Cd_{0.5}Se$ are ~9.5 nm and ~6 nm respectively. The TEM and SAED were performed on JEOL TEM-3010 electron microscope at an accelerating voltage of 300 kV. The actual elemental composition of the HgCdSe QDs was determined by energy dispersive X-ray spectroscopy (EDS) and found to be close to the nominal composition. (See Fig.S8) Diffuse reflectance measurements for the solid products were performed on Perkin Elmer Lambda 900 UV-Vis-NIR spectrometer at room temperature. The reflectance was converted to absorbance by Kubelka munk function to obtain the band edge by extrapolation.

IR detection: For the fabrication of devices, two Au electrodes of 150 nm thickness were deposited on a pre-cleaned soda lime glass (SLG) by evaporating Au through electron-beam evaporation. During the deposition, a spacing of 70 μm was maintained in between the Au electrodes using a mask. The active layer was prepared by drop casting a toluene dispersion of HgSe or $Hg_{0.5}Cd_{0.5}Se$ or HgS QDs into the channel between the Au electrodes and the device was dried overnight in the vacuum. For studying the IR detection properties, the IR source constituting a monochromatic laser diode with 1550 nm peak wavelength and a beam diameter of 400 μm was focused vertically on to the channel. The Photocurrent measurements were performed under ambient conditions. The current-voltage characteristics of the devices were measured using Keithley 6430 meter and monitored through the LabVIEW program.

Table S1. Summary of the photodetection properties of various QD based vis-IR photodetectors in the literature along with our present work.

Compound	***Responsivity (A/W)***	***Detectivity (Jones)***	***Operating range***	***References***
PbS QDs	2700	1.8×10^{13}	Vis-NIR	*Nature*, 2006, *442*, 180-183
PbS QDs	0.225	10^{12}	Vis-NIR	*Nat.Nanotechnol*. 2009, *4*, 40-44
CdSe	9.1-31	6.9×10^{10}	Vis	*ACS nano*. 2012, *6*, 5627-5634
CdSe NWs	1.30×10^{-2}	3.7×10^{9}	Vis	*ACS Nano*. 2011, *5*, 7627–7639
CdSe QD	1.80×10^{-3}	10^{7}	Vis	*Appl.Phys. Lett*. 2005, *87*, 213505.
Bi_2S_3 nanocrystals	20	10^{11}	Vis-900nm	*Nanoletter*. 2008, *8*, 4002
HgTe QDs	4.4	3×10^{10}	Mid-IR	*Adv. Mater*. 2007, *19*, 3574–3578
HgTe QDs	0.15-0.25	2×10^{9}	Mid-IR	*Nature Photonics*. 2011, *5*, 5489-493
HgCdTe bulk		10^{10}-10^{11}	NIR-LWIR	*Rep.Prog.Phy*. 2005, *68*, 2267
$Hg_{0.5}Cd_{0.5}Se$ film	0.91	3.3×10^{10}	NIR	Our work
HgSe film	0.45	1.1×10^{9}	NIR	Our work

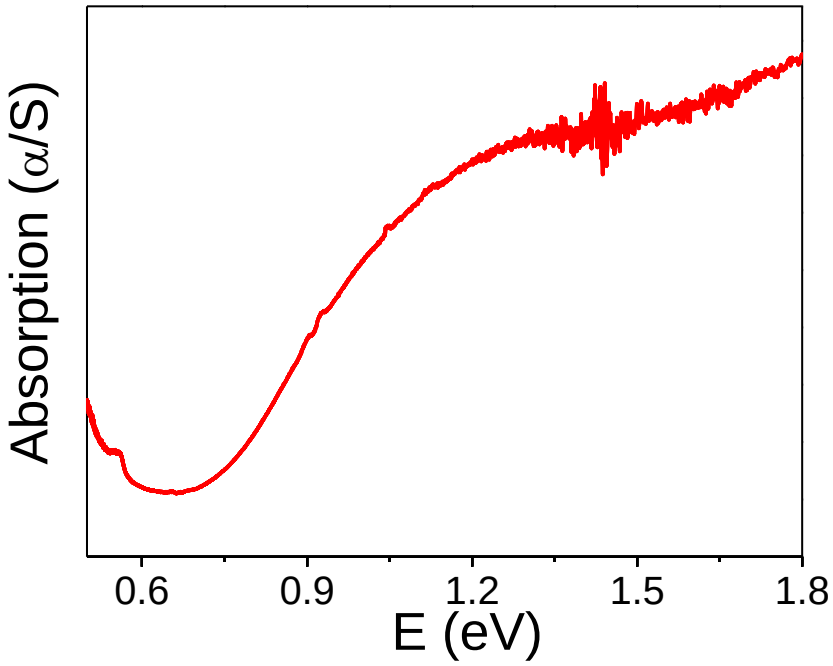

Fig. S1 Absorbance spectrum of HgSe QDs.

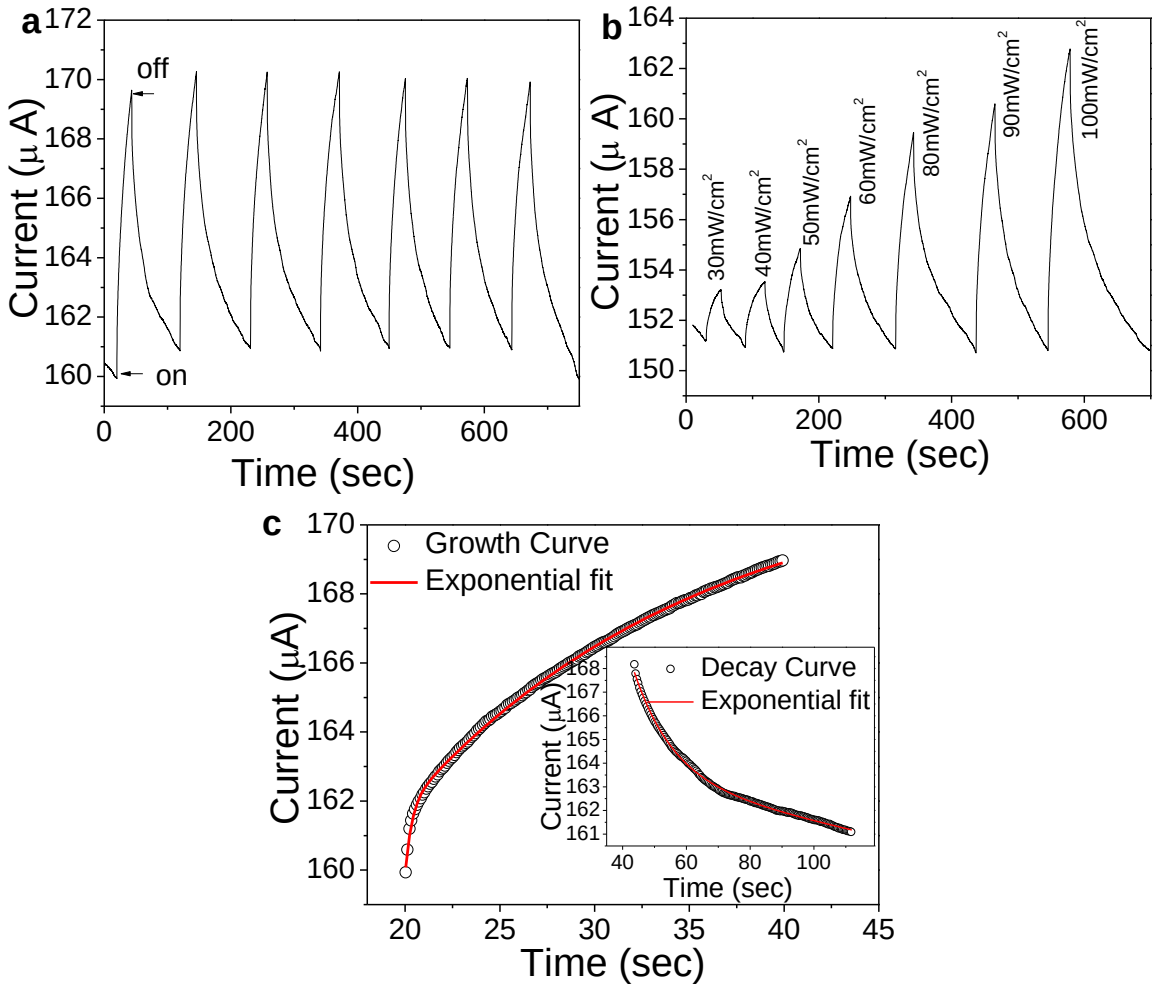

Fig. S2 a) On–off curves of photocurrent HgSe QDs with time at 2V bias and 80 mW/cm^2 intensity; b) Plot of photocurrent versus time at different illumination intensities and c) Time resolved photocurrent, growth and decay (inset) curves.

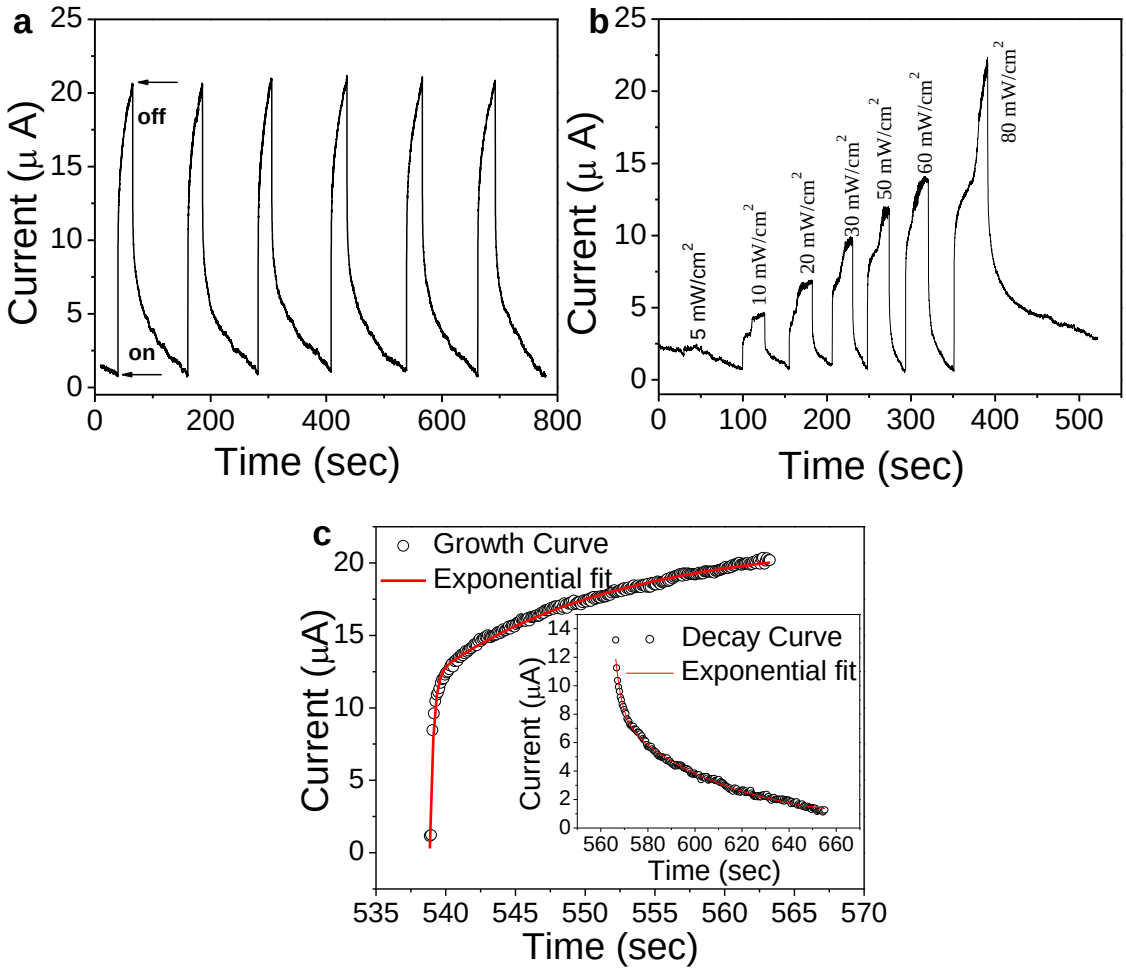

Fig. S3 a) On–off curves of photocurrent $Hg_{0.5}Cd_{0.5}Se$ QDs with time at 2V bias and 80 mW/cm^2 intensity; b) Plot of photocurrent verses time at different illumination intensities and c) Time resolved photocurrent, growth and decay (inset) curves.

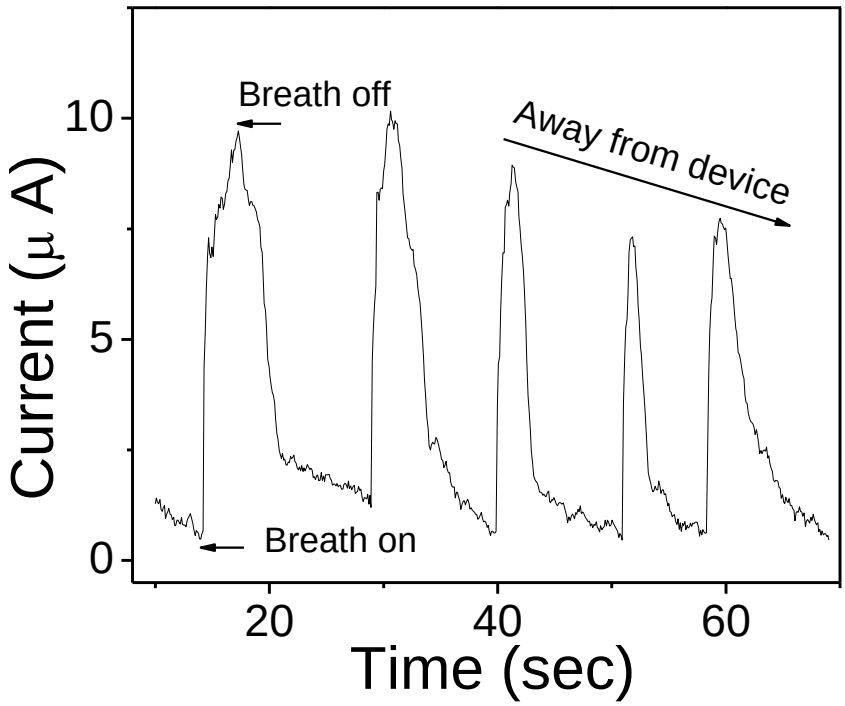

Fig. S4 Photoresponse to the human breath at 0.1 V bias for $Hg_{0.5}Cd_{0.5}Se$ QDs.

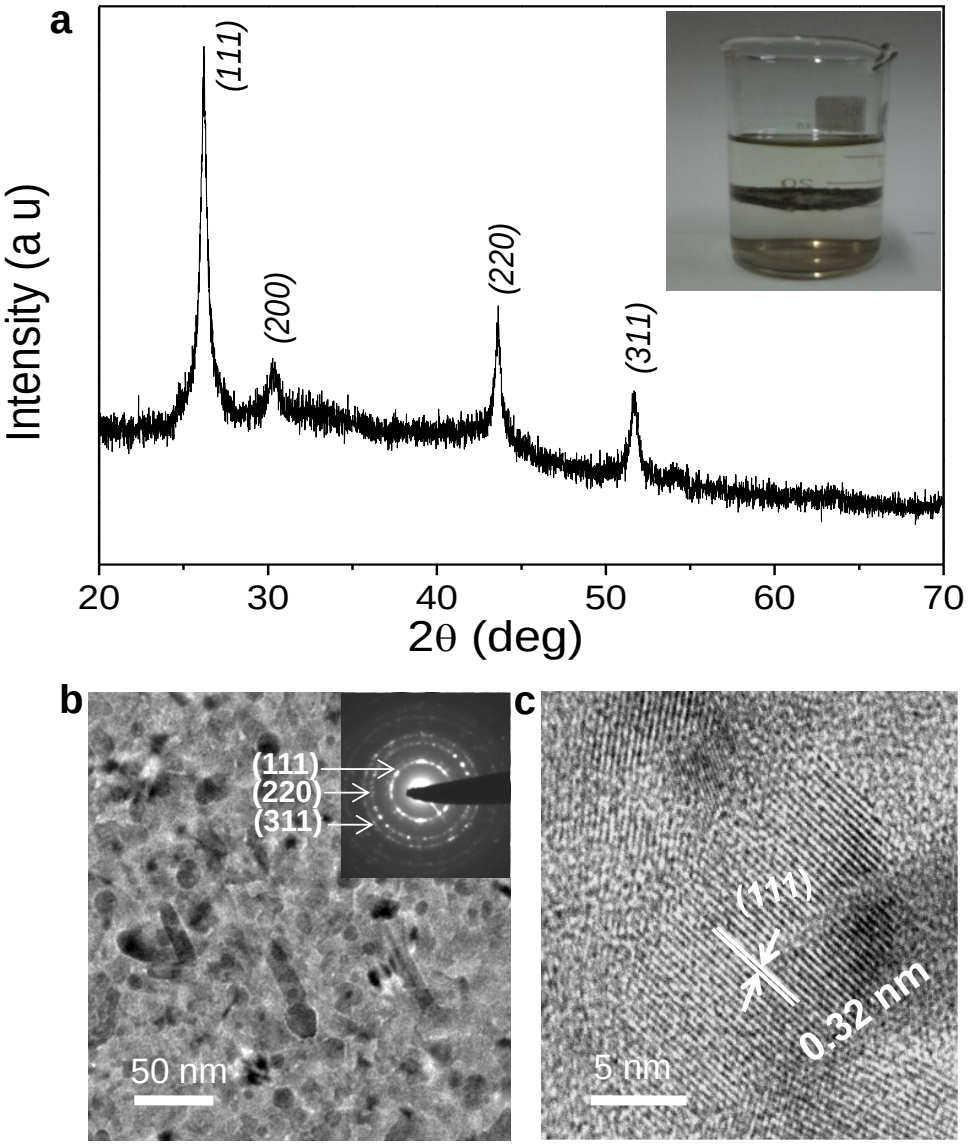

Fig. S5 a) XRD pattern and the photograph of the nanocrystalline film (inset) of HgS QDs formed at the toluene-water interface; b) TEM image, SAED pattern (inset) and c) HRTEM image of HgS QDs.

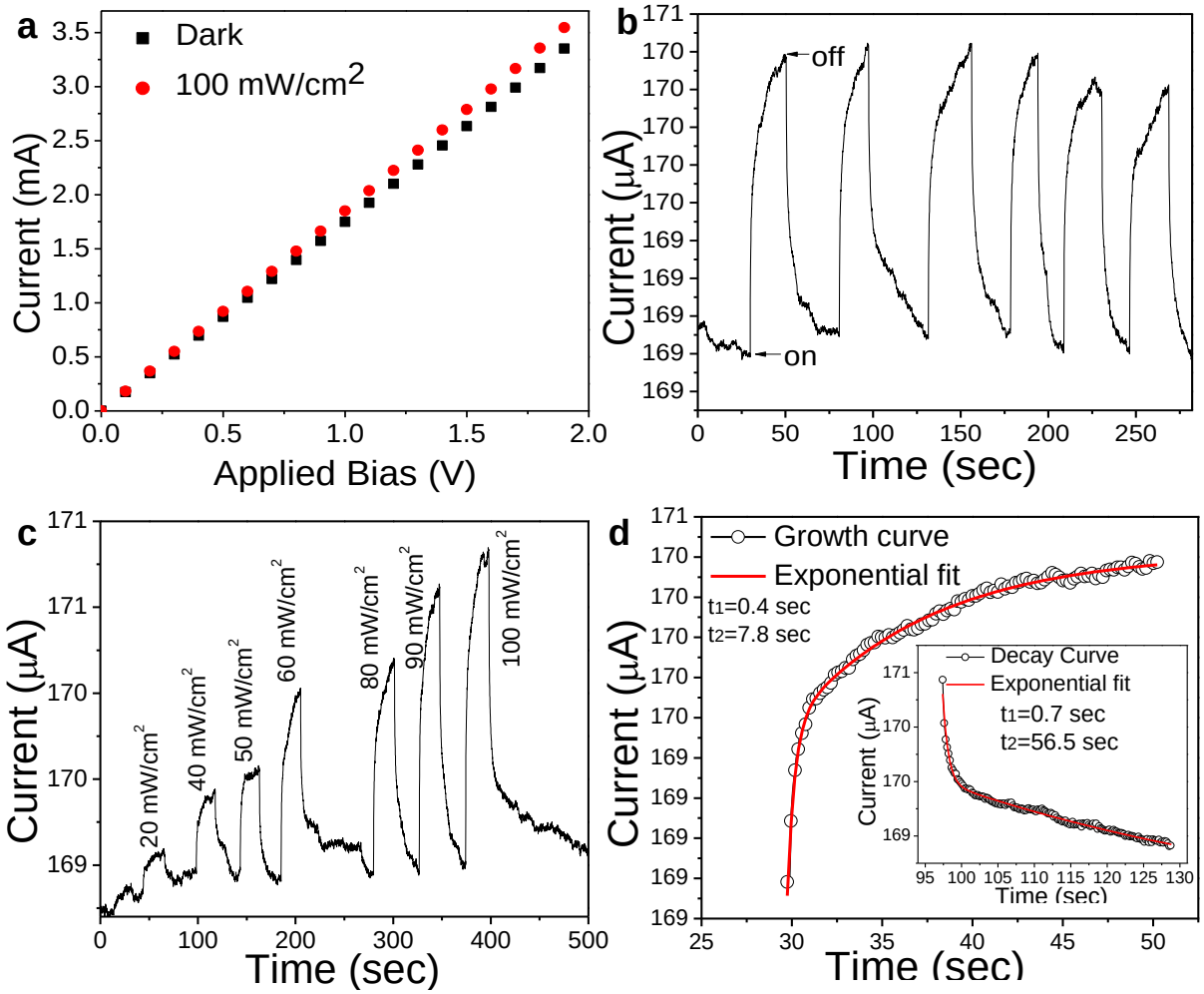

Fig. S6 a) I-V characteristics of HgS QDs in the dark and under 1550 nm-laser illumination intensities of 100 mW/cm^2; b) On–off curves of photocurrent with time at 0.1V bias and 100 mW/cm^2 intensity, showing the reproducibility; c) Plot of photocurrent verses time as a function of different illumination intensities and d) Time resolved photocurrent, growth and decay (inset) curves.

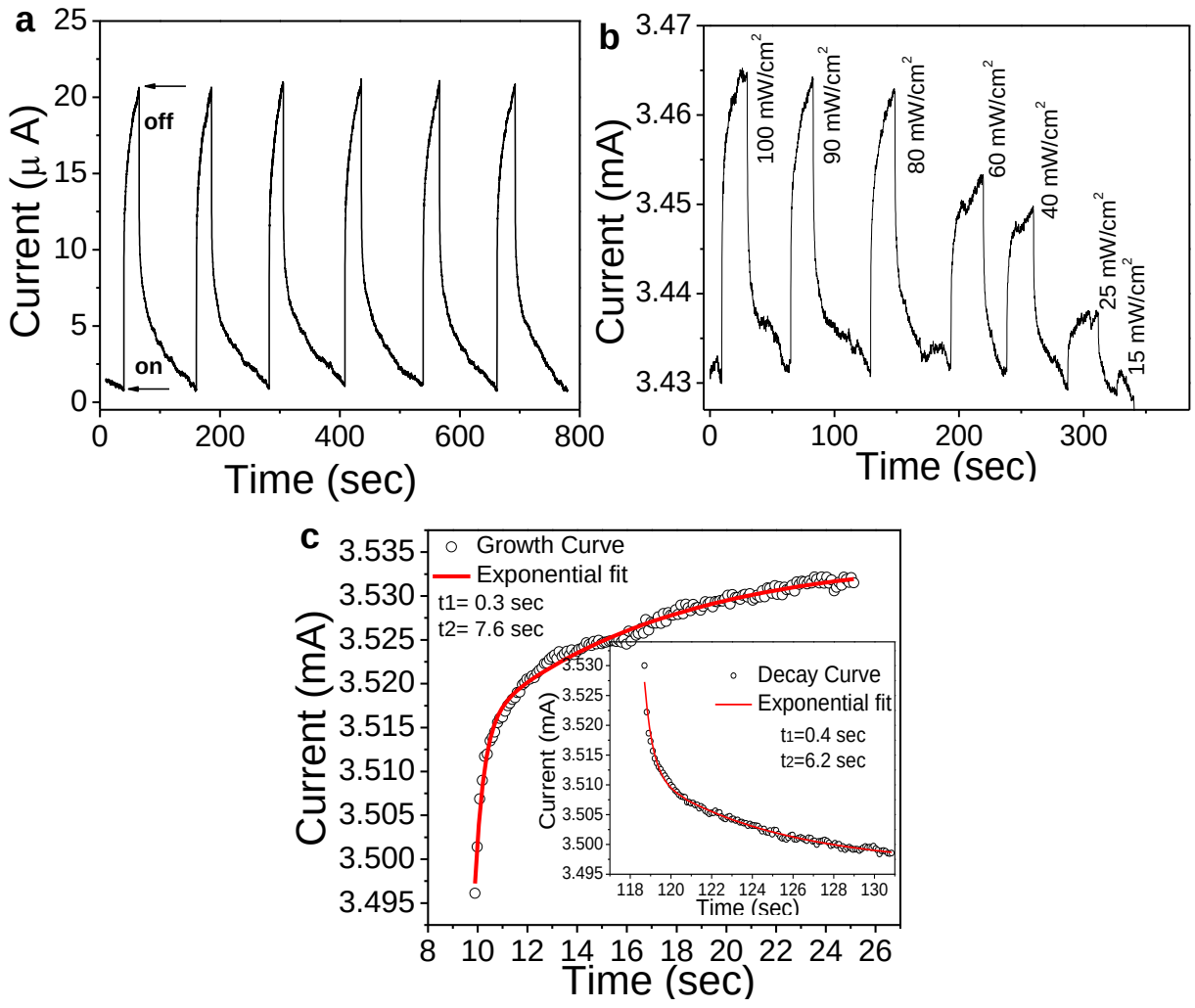

Fig. S7: a) On–off curves of photocurrent HgS QDs with time at 2V bias and 100 mW/cm^2 intensity; b) Plot of photocurrent verses time at different illumination intensities and c) Time resolved photocurrent, growth and decay (inset) curves.

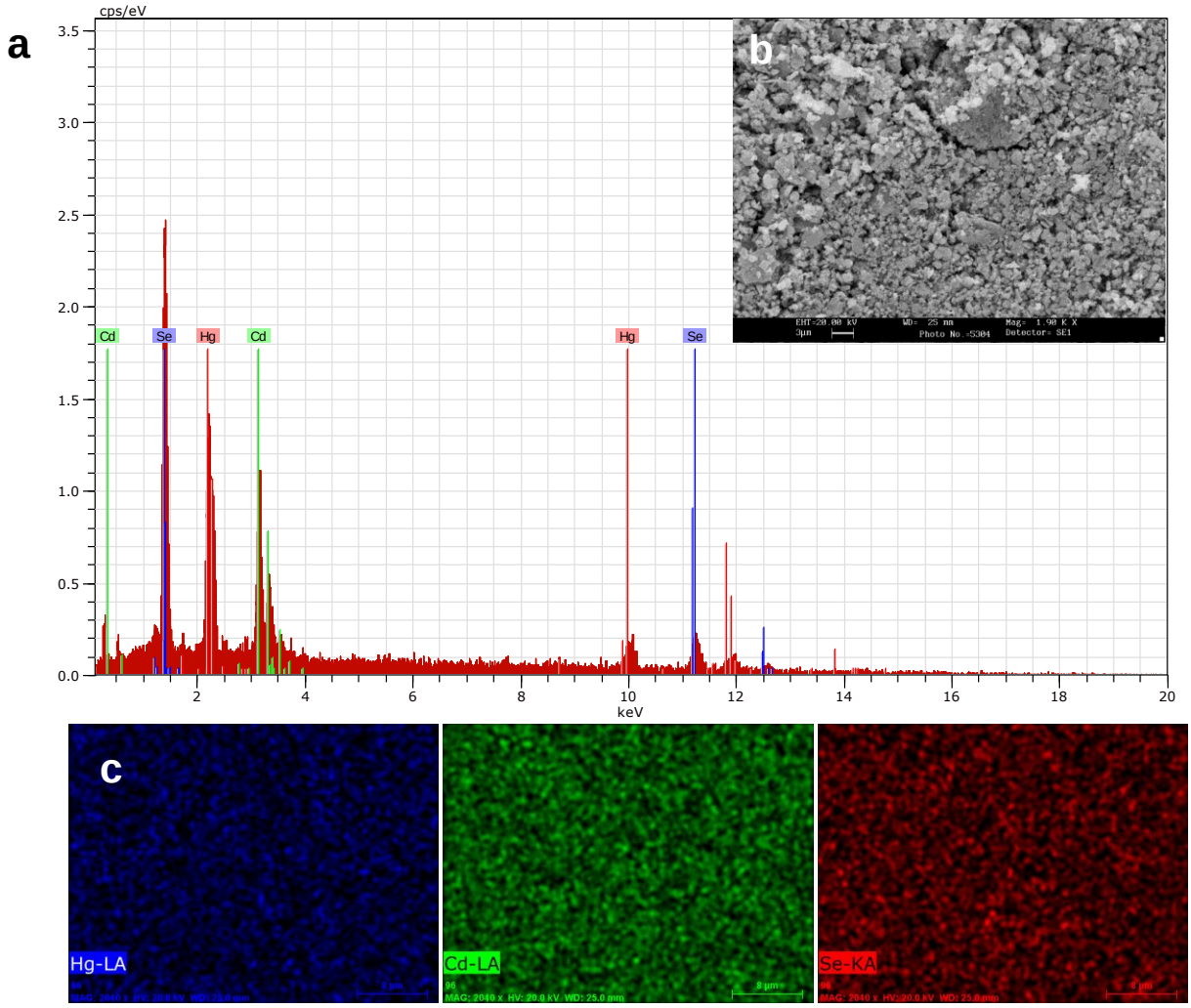

Figure S8: (a) EDAX spectrum of $Hg_{0.5}Cd_{0.5}Se$ QDs (nominal composition). (b) corresponding SEM image of the solid sample (c) elemental mapping of the image b, showing the distribution of elements. The composition determined form EDAX anlaysis is Hg:Cd:Se = 0.48:0.52:1 which is close to the nominal composition.