

# Visible to Long-Wave Infrared Photodetectors based on Copper Tetracyanoquinodimethane (CuTCNQ) Crystals

Sivacarendran Balendhran<sup>1,\*</sup>, Zakir Hussain<sup>2</sup>, Vivek Shrestha<sup>1</sup>, Jasper Cadusch<sup>3</sup>, Ming Ye<sup>3</sup>, Hyungjin Kim<sup>4,5</sup>, Rajesh Ramanathan<sup>2</sup>, James Bullock<sup>3</sup>, Ali Javey<sup>4,5</sup>, Vipul Bansal<sup>2</sup>, and Kenneth B. Crozier<sup>1,3,6,\*</sup>

<sup>1</sup>*School of Physics, The University of Melbourne, Victoria-3010, Australia.*

<sup>2</sup>*Sir Ian Potter NanoBioSensing Facility, NanoBiotechnology Research Laboratory (NBRL), School of Science, RMIT University, Melbourne, Victoria-3001, Australia.*

<sup>3</sup>*Department of Electrical and Electronic Engineering, The University of Melbourne, Victoria-3010, Australia.*

<sup>4</sup>*Electrical Engineering and Computer Sciences, University of California at Berkeley, Berkeley, California-94720, USA.*

<sup>5</sup>*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

<sup>6</sup>*ARC Centre of Excellence for Transformative Meta-Optical Systems, University of Melbourne, Victoria-3010, Australia.*

*Author e-mail address: sbalendhran@unimelb.edu.au, kcrozier@unimelb.edu.au*

**Abstract:** We demonstrate room-temperature photodetectors at wavelengths from visible (450 nm, 532 nm) to near- (850 nm), short-wave (1550 nm), mid-wave (4.5  $\mu\text{m}$ ) and long-wave (8.35  $\mu\text{m}$ ) infrared. These are based on drop-cast Cu TCNQ crystals. © 2019 The Author(s)

## 1. Introduction

Semiconductor photodetectors play critical roles in applications that range from imaging to telecommunications, medical sensors and environmental monitoring. These applications span wavelengths from the visible to the long-wave infrared. For commercial systems, typical materials choices for photodetectors are Si for visible wavelengths, InGaAs for optical fiber telecommunication wavelengths and HgCdTe for the mid- and long-wave infrared (IR) [1]. For the latter, commercial photodetectors often require expensive/complex fabrication processes and the devices typically operate at cryogenic temperatures [2]. Many applications would benefit from photodetectors that operate over a wide range of wavelengths at room temperature and that can be manufactured in a simple and cost-effective manner. It has been shown that graphene-based photodetectors deliver broadband high-speed operation [3]. These devices, however, often have modest responsivities and fabrication can be complex.

In this work, we investigate copper tetracyanoquinodimethane (CuTCNQ), a narrow bandgap ( $\sim 0.137$  eV) metal-organic semiconductor [4], for broadband photodetection. Our devices are photoconductors, and show room-temperature photoresponse for various wavelengths that span from the visible (450 nm, 532 nm) to the near-infrared (850 nm), short-wave infrared (1550 nm), the mid-wave infrared (4.5  $\mu\text{m}$ ) and the long-wave infrared (8.35  $\mu\text{m}$ ). We characterize these devices with modulated illumination and find that their rise time (step response) is on average sub-millisecond (754  $\mu\text{s}$ ).

## 2. Results and Discussions

Fabrication of the device is performed as follows. Interdigitated electrode (IDE) structures are formed on a layer of SiO<sub>2</sub> on an Si substrate by optical lithography, Cr/Au evaporation and the lift-off process. Cu TCNQ crystals are grown through a simple wet-chemical reaction between copper iodide and TCNQ solution in acetonitrile. The as-grown crystals suspended in acetonitrile are drop cast onto the IDE structures. Optical microscope images of the device are shown as Fig. 1a. An IDE architecture (with an electrode gap of 15  $\mu\text{m}$ ) is adopted to reduce the transit time of the photogenerated carriers. We next measure the temporal response of the device. The device is illuminated with light from a quantum cascade laser (QCL) at a wavelength of 8.35  $\mu\text{m}$ . The laser is pulsed at a frequency of 20 Hz and has an average power of 26 mW. The temporal response is shown as Fig. 1b. The average rise and fall times are found to be 754  $\mu\text{s}$  and 1.6 ms, respectively. In Fig. 1c, we plot the photocurrent and dark current as a function of bias voltage. The linear trend for the dark current indicates that CuTCNQ forms an Ohmic contact with the electrodes. We observe a slight degradation in channel conductivity, upon prolonged high-power illumination ( $>20$  mW). Consequently, the device bias is varied between experiments (1.32-1.5 V), to achieve a constant dark current. We next characterize the device at additional wavelengths. In Fig. 1d, we show the measured photocurrent as a function of optical power when the device is biased at  $\sim 1.5$  V, for illumination the following visible and near-infrared wavelengths: 450 nm, 532 nm and 850 nm. In Fig. 1e, we show the photoresponse in the short-wave to the long-wave infrared (1.55, 4.50 and 8.35  $\mu\text{m}$ ). The responsivity is calculated by obtaining the gradient of the linear fit to the power-dependent photoresponse and presented as a function of wavelength (Fig. 1f). The peak value responsivity occurs at a wavelength of 850 nm and takes a value of 75.46  $\mu\text{A/W}$ .

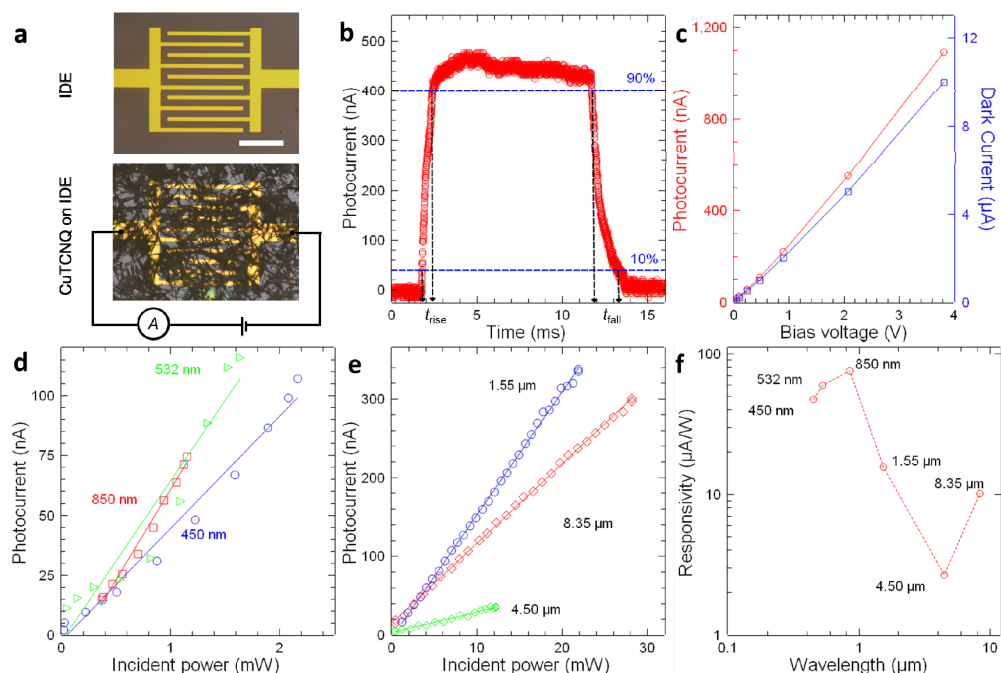


Fig. 1. (a) Optical microscope images of interdigitated electrode (IDE) device before (top) and after (bottom) applications of Cu TCNQ. Scalebar 100  $\mu\text{m}$ . (b) Time resolved photoresponse for pulsed illumination at a wavelength of 8.35  $\mu\text{m}$ . (c) Photocurrent and dark current as a function of bias voltage, for pulsed illumination at 8.35  $\mu\text{m}$ . (d) Photocurrent vs incident optical power for device at visible and near-infrared wavelengths. (e) Photocurrent at short-wave, mid-wave and long-wave infrared wavelengths. (f) Responsivity of device vs wavelength, as calculated from linear fit of photoresponse.

### 3. Conclusions

In summary, we have demonstrated the applicability of CuTCNQ, for room temperature broadband photo detection. The material synthesis and the device fabrication processes are facile. The devices show relatively fast rise times (754  $\mu\text{s}$ ). With further improvements to the device architecture (such as p-n heterojunctions), we envision a low-cost photodetector for a wider range of wavelengths, spanning from visible to long-wave infrared.

### 4. Methods

**Material Synthesis:** Phase I CuTCNQ crystals are synthesized via a wet chemical reaction between 5 mM each of copper iodide and TCNQ solution in acetonitrile at 75  $^{\circ}\text{C}$  for 3 min [5]. The dark blue crystals are washed with acetonitrile, followed by de-ionized water and dried at room temperature under vacuum.

**IDE Device Fabrication:** Photolithography is carried out on 300 nm  $\text{SiO}_2$  (thermal oxide) on doped Si substrates. Electron beam evaporation of Cr/Au (10/100 nm), followed by a lift-off process, is employed to realise the IDE structures. CuTCNQ crystals, suspended in acetonitrile, are drop cast onto the IDE surface. The IDE chip is then packaged into a 28-pin chip carrier.

**Device Characterization:** IDE devices are biased using a transimpedance amplifier (SRS 570), with the dark current offset to zero. The devices are illuminated using an optically chopped/pulsed light source, and the photocurrent is measured with a lock-in amplifier (SRS 860). Sixteen measurements are obtained at each incident power value. These are averaged. The output optical power of the lasers is attenuated using a linear polariser (450-850 nm lasers) or by varying the laser driving current (1.55-8.35  $\mu\text{m}$  lasers). The optical power incident upon the IDE device is measured using a power meter (Thorlabs, PM100D) equipped with a broad band thermal sensor (Thorlabs, S401C).

### 5. References

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