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Towards Low-Voltage and Bendable X-ray Direct Detectors Based on Organic Semiconducting Single Crystals

--Manuscript Draft--

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Please submit a plain text version of your cover letter here. **If you are submitting a revision of your manuscript, please do not overwrite your original cover letter. There is an opportunity for you to provide your responses to the reviewers later; please do not add them here**.	Dear Editors of Advanced Materials: On behalf of my co-authors, I am pleased to submit the manuscript entitled “Towards Low-Voltage and Bendable X-ray Direct Detectors Based on Organic Semiconducting Single Crystals”, by A.Ciavatti et al., to be considered for publication as a Communication in Advanced Materials. This paper reports on advanced direct ionizing radiation detectors based on organic semiconducting single crystals (OSSCs) that possess enhanced sensitivity, low operating voltage (5V) and with a minimum detectable dose rate of 50 uGy/s. We achieved these results by reaching a deeper understanding of the critical role played by the electrodes and device geometry in the photo-generated charge transport and collection process, The here reported results indicate how OSSCs have a great potential as solid-state room-temperature and human tissue-equivalent X-ray detectors, opening the way to the development of novel large-area, thin, flexible and low-power consuming (hence potentially portable) ionizing radiation sensors. This manuscript contains original results and its content has not been submitted to other journals for publication. More specifically, we feel our work makes several important contributions to the understanding of ionizing radiation and organic semiconductors and to the design and development of novel devices for direct ionizing radiation detectors operating at room temperature: 1.The assessment of an intrinsic direct conversion mechanism of X-rays into an electrical signal in OSSCs. We have assessed how Organic Single Crystals only a few tens of microns thick grant a full photo-generated charge collection (either in the vertical or planar electrode geometry) and this opens the possibility to integrate radiation detectors based on organic crystals into flexible electronic devices, exploiting the enhanced bendability of thin crystals and the recently reported possibility to cover large areas with printed single crystalline thin films. 2.Key role played by the device geometry on the X-ray detecting performance. Device geometries that maximize the electrode/semiconductor interface active area (e.g. interdigitated electrodes with finger spacing of few tens of microns) allow to significantly increase the charge collection efficiency and the X-ray electrical photoresponse of 4HCB single crystals. The macroscopic effect is a strong increase of the output electrical signal (up to few microamperes) and a dramatic reduction of the operating bias voltage down to few Volts. 3.State-of-the-art radiation sensitivity The minimum X-ray dose able to trigger the detection in 4HCB-based devices is 50 Gy/s, in line with the typical values for diagnostic medical applications (dose rates around 25μGy/s). Moreover, the here reported sensitivity of 4HCB-based detectors (about 0.1 uC/cm2 R) is in line with that of state-of-the-art a-Se based detectors (about 0.2 uC/cm2 R).

	We would also like to underline that the here presented experiments results, being based on easy-to-grow and largely available materials (i.e. OSSCs grown from solution), can be readily repeated in not expensively equipped laboratories, thus ensuring a very wide access all over the world to this field of studies. Our results indicate how X-ray detectors based on OSSCs possess a great potential as solid-state room-temperature and tissue equivalent X-ray detectors and dosimeters, paving the way to the development of novel large-area, thin, flexible and low-power consuming ionizing radiation sensors, to be used in a vast variety of fields, spanning from medical diagnostic, to civil security and industrial applications.Therefore, the submitted paper should be considered as the seminal work opening the new field of research of direct ionizing radiations detectors based on OSSCs. Thank you in advance for your consideration of our contributed manuscript. Sincerely, Dr. Andrea Ciavatti
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Abstract:	Organic materials have been so far mainly proposed as detectors for ionizing radiation in the indirect conversion approach, i.e. as scintillators, which convert ionizing radiation into visible photons. Here we show how we realized the first thin and bendable X-ray direct detector based on Organic Semiconducting Single Crystals (OSSCs),promising candidates for the direct detection of X-ray radiation (i.e. X-photons are directly converted into an electric signal) that possess enhanced sensitivity, low operating voltage (≈5V) and with a minimum detectable dose rate of 50 Gy/s. We achieved these results by reaching a deeper understanding of the critical role played by the electrodes and device geometry in the photo-generated charge transport and collection process, The here reported results indicate how OSSCs have a great potential as solid-state room-temperature and human tissue-equivalent X-ray detectors, opening the way to the development of novel large-area, thin, flexible and low-power consuming (hence potentially portable) ionizing radiation sensors.

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Towards Low-Voltage and Bendable X-ray Direct Detectors Based on Organic Semiconducting Single Crystals

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Organic semiconductors are attracting a large interest as they allow to realize organic electronic and photonic devices spanning from field effect transistors, solar cells, light-emitting displays, smart tags and molecular sensors, that can be produced using large-area fabrication techniques, with advantages like low fabrication cost, low environmental impact and the possibility of creating transparent and flexible devices, allowing unprecedented and integrated device functions and architectures [1–5].

Organic materials have been so far mainly proposed as detectors for ionizing radiation in the indirect conversion approach, i.e. as scintillators, which convert ionizing radiation into visible

photons, or as photodiodes, which detect visible photons coming from a scintillator and convert them into an electrical signal [6]. Recent examples of organic devices used as direct photon detectors have been presented for operation in the UV-NIR range, with very interesting values for figures of merit such as photo-conversion efficiency, speed and minimum detectable signal level [7], and even though the simultaneous attainment of all these relevant parameters is demonstrated only in a limited number of papers, real applications are within reach for this technology, where the best reported photo-responsivity outperform amorphous silicon-based devices. Organic semiconductors are also very promising candidates for the detection of higher energy photons (X- and gamma rays) [8–10] and we recently reported how organic semiconducting single crystals (OSSCs) provide a direct (i.e. X-ray photons are directly converted into an electric signal within the crystal), stable and linear electrical photo-response to increasing X-rays dose rates, proving to be good ionizing radiation sensors operating at room temperature [11,12].

We here report on direct X-rays detectors based on OSSCs of 4-hydroxycyanobenzene (4HCB) (Figure 1a). The X-ray energies (10-25 keV) and dose rates (0.05 – 120 mGy/s) we used to test their performance are comparable to those employed in medical diagnostic applications (typically mammography, see Figure 1b), so to assess the behaviour of OSSCs detectors in medically relevant conditions. In fact, the low effective atomic number Z of 4HCB (and of all organic compounds) constituent atoms is similar to the average human tissue-equivalent Z, and makes them ideal candidates for dosimetric purposes in radiotherapy and diagnostics applications.

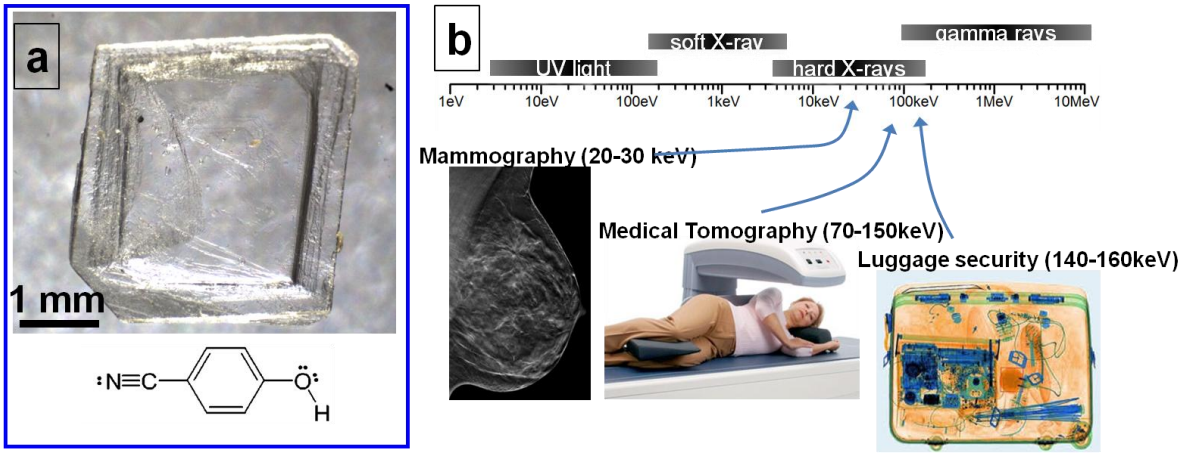

Figure 1
a) Optical microscopy image in transmission mode of solution grown 4-hydroxycyanobenzene and its building block molecule. **b)** Panoramic view of the photon energies involved in X-ray detection and their application.

Devices with different electrodes configuration, contact material, charge collection area and interaction volume have been fabricated and investigated, obtaining key information on the influence of these parameters over the detectors' performances. The measured OSSCs electrical response to X-rays is highly linear for increasing dose rates and we evidenced efficient charge carrier generation and collection in crystals with thicknesses varying from 40 to 500 microns. Finally, we fabricated bendable OSSC-based detectors onto a plastic substrate with interdigitated electrodes, that maximize the charge collection area. They show notable performances even at operating voltages <5 V and evidence no appreciable degradation neither during nor after repeated bending cycles.

These results open the way to breakthrough applications as thin, flexible X-rays detecting devices, since recent reports indicate that thin organic crystals can be reliably integrated into flexible electronic circuits thanks to their bending properties [13–15].

We have previously reported the proof of principle operation of X-ray solid state detectors based on thick (>500 μm) 4-hydroxycyanobenzene (4HCB) OSSCs, assessed in a very basic

device configuration and under a broad energy spectrum X-ray beam (Mo tube source, 35kV) [11].

4HCB is a dipolar molecule able to deliver free standing, very low cost and robust organic semiconducting single crystals upon solution growth, with tunable dimensions up to few millimeters (Figure 1a) [16]. The highly anisotropic three-dimensional molecular packing of 4HCB crystals and their transport properties have been investigated in recent years and reported in [17,18]. In particular, the measured mobilities vary of up to 4 orders of magnitude if measured along the vertical ($2x10^{-5}$ cm^2/Vs) and planar axes ($1x10^{-1}$ cm^2/Vs). This striking difference in the electronic transport properties indicates that the molecular packing anisotropy affects the transport process, as has been assessed in the case of various organic semiconducting single crystals [3,19–21].

Table 1: The three sample geometrical configurations tested in this work and their X-ray sensitivity at 50 V and 500 V (max bias value).

Sample configuration	**Electrode area**	**Crystal thickness**	**Sensitivity Mo Tube @35keV**	
			@50V	**@500V**
	mm^2	*μm*	*nC/Gy*	*nC/Gy*
S1	0.15 ± 0.02	400 ± 10	53 ± 2	170 ± 3
S2	2.0 ± 0.1	400 ± 10	87 ± 1	175 ± 2
S3	2.0 ± 0.3	40 ± 5	87 ± 2	150 ± 3

With the aim to understand and control the detection process and performance of OSSC-based detectors, we have carried out an in-depth study of their photo-response by varying the device geometry and electrodes configuration and by using both conventional X-rays sources and monochromatic synchrotron X-ray beams, working in air and at room temperature. In particular, in order to identify the role of: i) the electrode area, ii) the crystal thickness and iii)

the electrode material with respect to the X-rays detection response, we performed Current-Voltage and Current-Time analyses on 4HCB crystals, in the configurations reported in Table 1. The non-negligible contribution to the collected X-ray signal induced by electrodes and substrate has been evaluated to be ≈ 80 pA at 100 V (Supplementary Information figure SI-1) and has been subtracted from all the reported measurements.

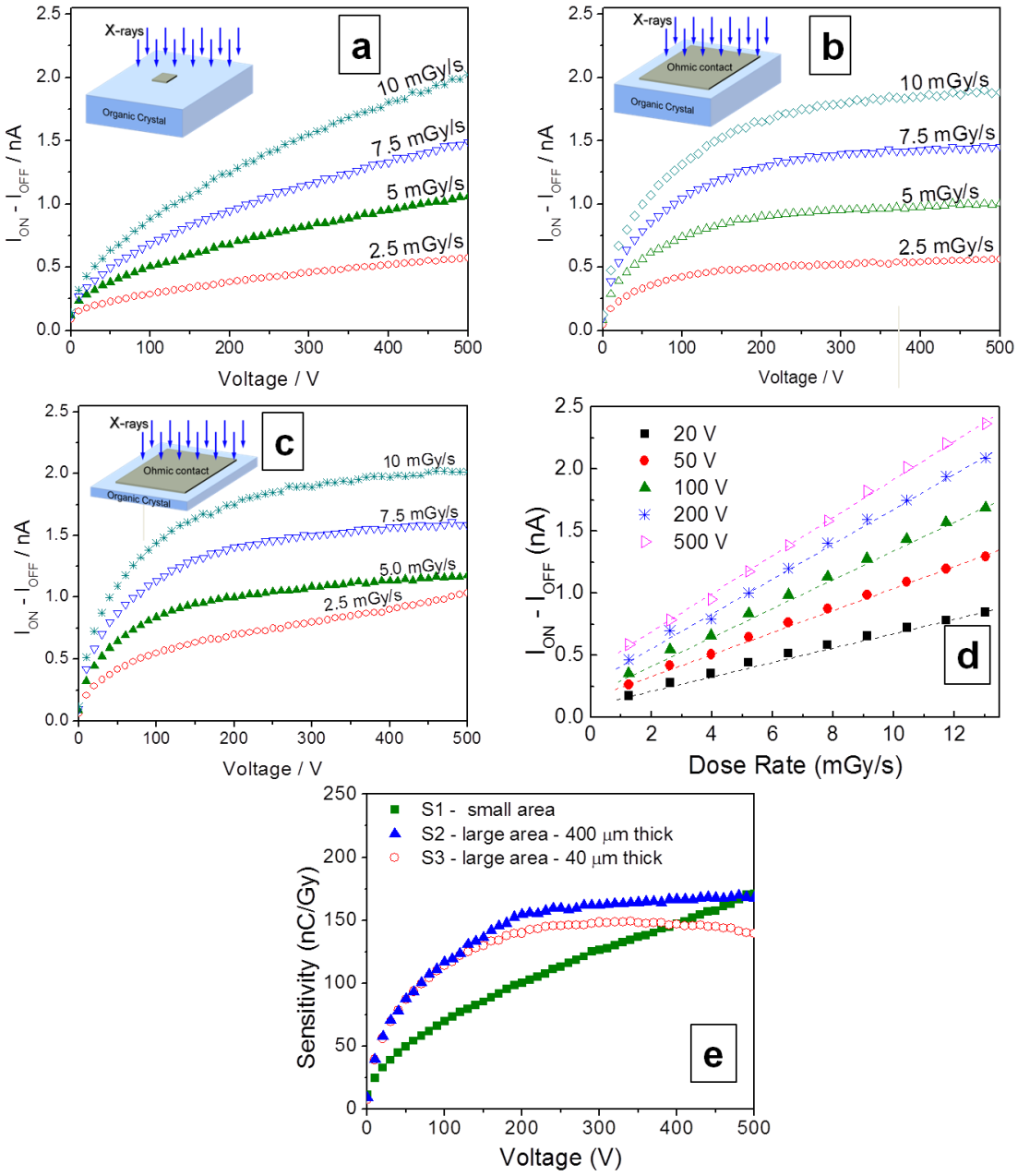

Figure 2
Current-Voltage characteristics of 4HCB organic crystals under X-ray exposure (measured along the vertical axis). The X-ray source is a Mo tube with a 35 kVp accelerating voltage and dose rates up to 13 mGy/s. The photo-response of three different sample configurations is

reported in (**a)** for small top contact area (0.15 mm^2) and thick (400 μm) crystal, in (**b)** for a large area (2 mm^2) and thick (400 μm) crystal and in (**c)** for large area and thin (40 μm) crystal.
A typical linear photo-response trend, i.e. ΔI=Ion-Ioff reported as a function of increasing dose rate, is shown in (**d)**. From the linear fit of these curves the sensitivity is extracted and reported as a function of applied bias in (**e)**, for a small area and 400 μm thick sample (green squares), for a large area and 400 μm thick sample (blue solid triangles), and for a large area and 40 μm thin sample (red open triangles). The maximum obtained sensitivity for large electrode area samples is 175 nC/Gy.

Figure 2a shows the electrical photo-response $\Delta I = I_{ON} - I_{OFF}$ induced by the X-ray beam generated from a Mo tube and impinging on a 400 μm thick crystal with a small top electrode (configuration S1). This response is in good agreement with previously reported results [11]. The observed photo-current response is linear across all dose rates and does not reach saturation at high bias, indicating an incomplete collection of the photo-generated charge carriers. Figure 2b shows identical measurements carried out on a crystal with the same thickness but with a much larger (one order of magnitude, see Table 1) top electrode area (configuration S2): the collected current signal reaches a saturation regime at lower bias voltages (< 200 V). Figure 2c reports the X-ray photo-response obtained from a much thinner crystal (40 μm) with the same large electrode area of the previous case (configuration S3), showing that also in this configuration the collected current tends to saturate at lower bias values.

It is noteworthy that the current saturation value achieved with the large electrode configuration devices S2 and S3 is comparable between the 400 μm and 40 μm thick crystals (Figure 2b and 2c), providing a strong evidence that the crystal thickness can be reduced down to few tens of microns without affecting the charge generation and collection properties of the sensor. This observation can be interpreted with the recently reported values of several microns for exciton diffusion length, that were directly measured by optoelectronic analyses in organic single crystals [22], suggesting that only the charge carriers photo-generated within a few microns from the electrode would be effectively collected. However, diffusion processes

alone would not generate such a significant photocurrent and the charge collection geometry used plays a key role in the detector performance . In fact, the equivalent performance of configurations S2 and S3 clearly indicates that there is a trade-off between the attenuated fraction of the incident X-ray beam (i.e. the X-photon quantum efficiency, see Table II for quantitative discussion), which is higher in the thicker devices thanks to the larger X-ray beam-crystal interaction volume, and the magnitude of the collected signal, which is optimized in thinner devices thanks to the stronger electric field at a given applied bias.

Table 2: X-ray absorption parameters at different X-ray energies. Mass absorption coefficient of 4HCB, quantum efficiency of 400 μm thick crystal and sensitivity under synchrotron radiation (bias at 50V) are reported.

X-ray energy	**μ/ρ**	**Q.E.**	**Sensitivity**
keV	*cm^2/g*	*%*	*nC/Gy*
10	3.0 ± 0.1	14.0 ± 0.8	17.2 ± 0.4
13	1.5 ± 0.1	7.1 ± 0.6	15.0 ± 0.2
15	1.0 ± 0.1	5.0 ± 0.6	19.9 ± 0.4
17	0.7 ± 0.1	3.7 ± 0.6	21.7 ± 0.9
19	0.6 ± 0.1	2.9 ± 0.6	30.6 ± 0.3
21	0.5 ± 0.1	2.4 ± 0.5	32.1 ± 0.9

In more detail, we can observe that devices with a small contact electrode (configuration S1, Figure 2a) show a photocurrent signal ΔI comparable to that of large electrode devices (configurations S2 and S3, Figures 2b,c) at voltages of about 500 V, indicating that the electric field profile within configuration S1 can drift a comparable number of charge carriers to the small electrode only at high voltages. In conclusion, OSSCs that are only a few tens of microns thick can detect X-ray as effectively as much thicker (400 μm) crystals, provided an appropriate charge collection geometry is used.

We have further assessed that in all the three tested configurations, S1, S2 and S3, organic semiconducting single crystals provide a perfectly linear response to an X-ray beam, with dose rates varying in the range 0.05-120 mGy/s and at different bias voltages in the range 10-500 V. Figure 2d reports the linear response in the 1-15 mGy/s dose rate range. In a linear regime it is possible to determine the device sensitivity, defined as $S = (I_{ON} - I_{OFF})/\text{Dose Rate}$, i.e. the slope of each curve of Figure 2d, for different bias voltages.

Figure 2e shows a direct comparison between the sensitivity of crystals with large area contacts (blue and red triangles, configurations S2 and S3, respectively), hence with optimized charge collection, and that of crystals with small electrode area (green squares, configuration S1), reported as a function of increasing bias voltage. These results clearly confirm that thin (40 μm) and thick (400 μm) crystals with large area electrodes have comparable sensitivity values.

It is remarkable that crystals with large area electrodes (S2, S3) reach saturation at voltages <150 V, while samples with small contact area (configuration S1) reach the same sensitivity of large electrode area ones only at biases as high as 500 V. Interestingly, identical results have been obtained also using different electrode materials (gold, silver epoxy and graphite), and no major differences have been observed in the measured photocurrent variation within the statistical sample variation error (about 15%) over about five tested crystals for each configuration type and for different electrode materials (Supplementary Information figure SI-2).

The above described findings clearly indicate that the electrodes surface area and their separation are crucial parameters to control the collection process of the photo-generated charge, and that the charge carrier drift length is less than 40 μm, the minimum crystal thickness tested. Therefore, by properly designing the electrode geometry (area and channel distance) the sensor photo-response can be significantly enhanced at lower (<150 V)

operating voltages (Figure 2e) and this compares very favourably with the high biases currently needed for inorganic based dosimeters.

Overall, the here reported devices show a maximum sensitivity of 175 nC/Gy at 500 V, a value that is four-times higher than the first and currently only reported values for X-ray direct detectors based on organic single crystals [11] and thin film polymers with metal nanoparticles [10]. This value is comparable to those reported for inorganic semiconductor based dosimeters (e.g. 150 nC/Gy for Silicon)[23–26] and confirms the potential of OSSC-based devices for practical applications. The effective detector efficiency, that takes into account both the charge carriers pair production efficiency and the collection efficiency, has been estimated, as reported in[11], as $f = \Delta I/[\Phi\beta(2e)]$, where ΔI is the current variation, Φ is the photon absorption rate, b is the number of photogenerated carriers per photon. In the optimized detector geometry the effective efficiency is enhanced from 2% of the first published results[11] to 20%. Most interestingly, since recently reported work indicate how organic crystals less than 50 μm thick can be reliably used in flexible electronic devices thanks to their bending properties [13–15], the above described findings suggest that 4HCB crystals can be excellently used to fabricate flexible X-rays detecting devices.

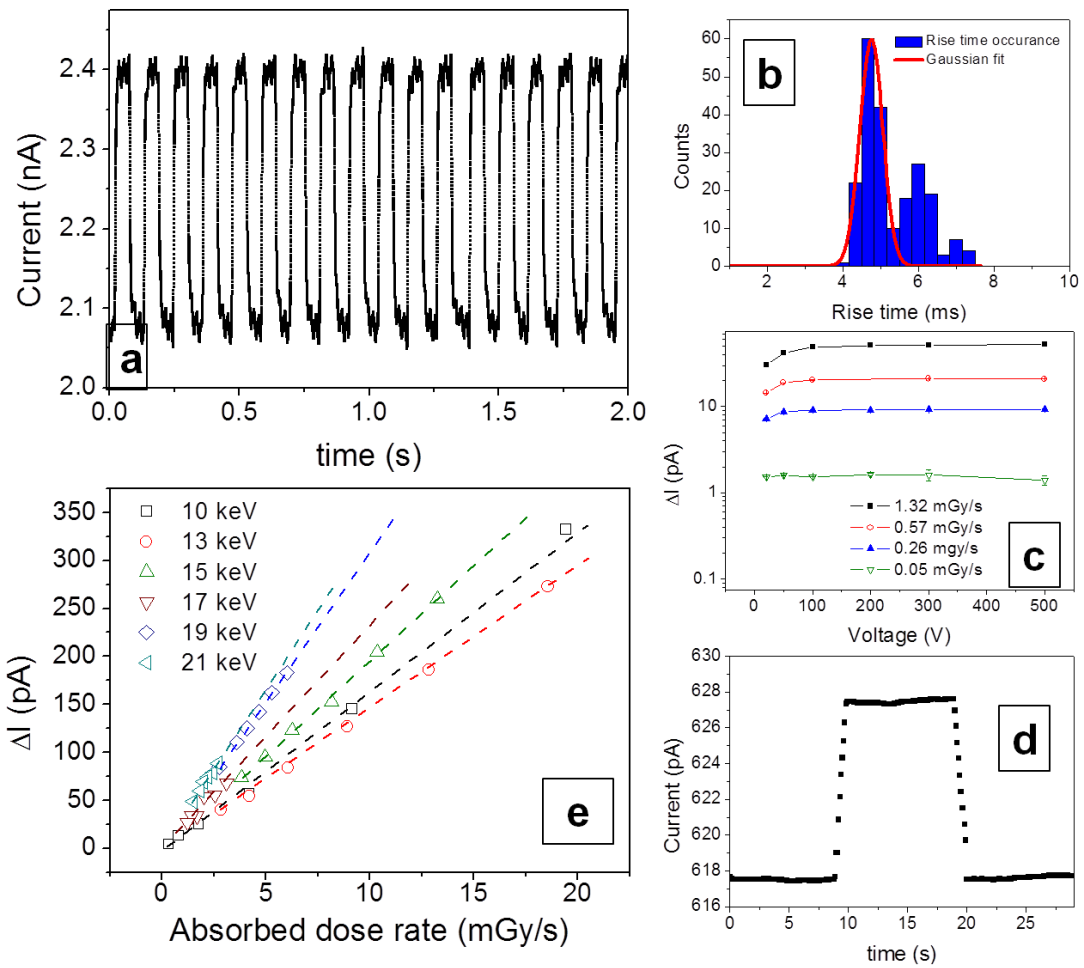

Figure 3

a) photo-response of a 4HCB detector under an on/off switching X-ray beam (Synchrotron monochromatic beam with energy 10 keV, dose rate 40 mGy/s and 20 V applied bias), showing the fast rise time, < 5 ms, as better detailed in **(b)**, and good repeatability and stability of response.

c) X-ray induced photocurrent measured for a thin crystal (40 μm) with large electrode area (configuration S3) under a monochromatic 10 keV Synchrotron X-ray beam. Very low dose rates are tested, down to the minimum detectable dose rate of 50 μGy/s. The signal-to-noise-ratio is very good also at this very low dose rate, thanks to the extremely stable and low dark current, as shown in **(d)** for an on/off switched X-ray beam.

e) the electrical photo-response, i.e. ΔI=Ion-Ioff, is reported as a function of increasing dose rate for a 4HCB single crystal detector under synchrotron X-ray monochromatic beams of different energies (from 10 to 21 keV), with an applied bias of 50 V (configuration S3). The calculated sensitivity is reported on each curve.

We took advantage of the enhanced photo-response achieved with large area electrode devices to investigate at greater depth the performance of 4HCB-based detectors using the Synchrotron X-ray source at ELETTRA (SYRMEP Beamline), that allowed to deliver onto a 4HCB-based device focused monochromatic X-ray beams with energies in the range 10-21

keV (with $4x10^{-3}$ ΔE/E energy bandwidth) and highly controlled dose rates, avoiding all spurious effects due to the classically used broad molybdenum X-ray emission spectrum. Moreover, the SYRMEP beamline setup is well suited to obtain very low dose rate values (≈ 50 μGy/s). Exploiting these peculiarities, we explored the stability, the minimum detectable dose rate and the time response of OSSCs detectors. In Figures 3a and 3b it is possible to appreciate that the signal rise and decay time is below 5 ms, and that the overall response presents a very good stability and repeatability, with a baseline shift below 5% after up to 50 on/off cycles.

Figure 3c shows the photo-response of a large area electrode device that reaches saturation when exposed to doses down to 50 μGy/s, using 10 keV synchrotron X-rays. As shown in Figure 3d, the signal-to-noise ratio is very good even at these extremely low dose rates. The minimum detectable dose rate sensitivity in 4HCB-based devices of 50 μGy/s is in line with the typical values for medical imaging and clinical analysis (presently dose rates around 25 μGy/s are required for such applications[27]), indicating that the performance of X-ray sensors based on OSSCs satisfies the requirements for their application as ionizing radiation dosimeters. State-of-the-art detectors based on a-Se, that can be considered a benchmark photoconductor material for dosimetry applications, have a sensitivity of about 0.2 $\mu C/cm^2/R$, that is not so far from the performance of the here reported 4HCB detectors (about 0.1 $\mu C/cm^2/R$, if converted in the same unit of measure). This result, together with the established robustness and reproducibility of the overall device performance, points to the great potential for practical applications of these novel devices in X-rays monitoring systems for biomedical and environmental tasks.

Taking further advantage of synchrotron radiation peculiarities @SYRMEP beamline, we measured the electrical output signal, ΔI, for an OSSC detector exposed to focused monochromatic X-ray beams of different energies, varying in the range 10-21 keV. Figure 3e

shows the ΔI vs. absorbed dose rate for selected energies. The absorbed dose rate has been determined as the product between the dose rate and the X-rays attenuated fraction in the crystal, i.e. the quantum efficiency. The quantum efficiency has been calculated as Q.E. = 1 – exp[-μ/ρ·ρ·t] , where μ/ρ is the mass attenuation coefficient obtained with the XCOM code [28], ρ is the material density and t the crystal thickness. The quantum efficiency at 10 keV for a 400 μm thick 4HCB crystal results to be 14%, while for a 40 μm thick crystal is 1.5% in the same conditions. The observed change in gradient of the data reported as a function of photon energy indicates a decrease in X-ray sensitivity as the photon energy decreases (see Fig. 3e), from 32.1 nC/mGy at 21 keV to 17.2 nC/mGy at 10 keV (Table 2). Table 2 also shows the corresponding increase in quantum efficiency as the photon energy is decreased. This different response to different incident photon energies suggests that 4HCB crystals could be used also as active components in energy-discriminating devices.

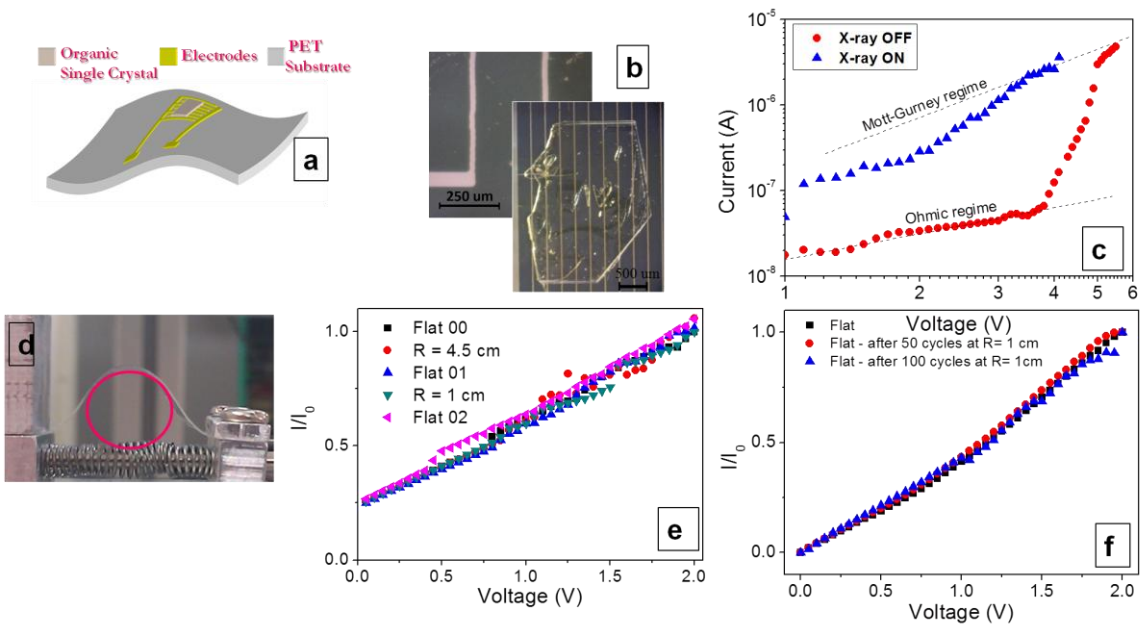

Figure 4
a) Schematic layout of the flexible X-ray detector fabricated with interdigitated Au electrodes patterned onto a thin and flexible PET substrate. The electrodes distance is 50 μm, shown in (**b**). **c**) the electrical photoresponse of a 4HCB crystal in the dark (red circles) and under a monochromatic X-ray beam (energy 17 keV and dose rate 50 mGy/s) (blue triangles) is reported in as a function of the remarkably low applied bias voltage. **d**) assessment of the bending properties of 4HCB flexible detectors via the imaged tool , capable of bending the device to a radius R. **e)** stability of the detector electrical response for different bending radii

and for subsequent bending-flat-bending operation; **f)** stability of the detectors electrical response for repetitive bending cycles

We combined two of the above described results (i.e. thin crystals are excellent detectors and a large electrode area improves their performance) by bonding thin 4HCB crystals onto an Au interdigitated electrode pattern (electrode separation 25 μm) defined on top of a flexible and transparent PET substrate, as shown in Figure 4a and 4b. The X-ray induced photo-current response of this device, using a Synchrotron monochromatic 17 keV beam, is shown in Figure 4c, together with the current-voltage curve measured in the dark. The curve in the dark follows the Space-Charge Limited Current trend typically observed in high resistivity semiconductors and in organic single crystals [29–31],[32], with the ohmic region, the SCLC regime and the trap-filled limit voltage (V_{TFL}) easily identified. Notably, all these regimes are found within 5 V of bias, which is exceptionally low, and to the best of our knowledge yet unreported. The current-voltage curve recorded under X-ray irradiation shows much higher current values (almost one order of magnitude, as usual for this type of devices), that reach the Mott-Gurney quadratic behaviour at bias voltages above V_{FTL}, which again remarkably is below 4 V. A further point of interest is that the photo-current value is of the order of μA, as is the ΔI=Ion-Ioff output signal, already at 3 V.

The bendability of these detectors has been assessed by repetitively bending the devices with the dedicated setup shown in Figure 4d. The devices were subjected to continuous changes of the bending radius (from 1 to 100 cm) for up to 100 cycles while a bias sweep between 0 V and 2 V was applied. This repeated bending procedure did not appreciably alter the electrical performance of the device, neither during the bending operation (Figure 4e) nor after repeated bending cycles (Figure 4f). These results strongly support the full feasibility for very low-voltage and flexible X-ray detectors based on organic single crystals.

In conclusion, solution-grown organic semiconducting single crystals are robust and easy to handle materials that can reliably detect X-rays in the direct approach, operating at room temperature and in air, providing a linear response to increasing X-ray dose rates. They present the following features:

1. The organic crystal thickness does not have an effect on the detector performance and sensitivity down to thicknesses of few tens of micrometers. Indeed, the charge carriers (excitons) diffusion length is quite short in thin film organic semiconductors (< 50 nm [32,33]), but recent direct measurements in organic single crystals report top values of up to 8 μm [22]. Crystals only a few tens of microns thick thus grant a full photo-generated charge collection (either in the vertical or planar electrode geometry) and this opens the possibility to integrate radiation detectors based on organic crystals into flexible electronic devices, exploiting the enhanced bendability of thin crystals [13–15] and the recently reported possibility to cover large areas with inkjet printed single crystalline thin films[33,34].
2. Device geometries that maximize the electrode/semiconductor interface active area (e.g. interdigitated electrodes with finger spacing of few tens of microns) allow to significantly increase the charge collection efficiency and the X-ray electrical photoresponse of 4HCB single crystals. The macroscopic effect is a strong increase of the output electrical signal (up to few microamperes) and a dramatic reduction of the operating bias voltage down to few Volts (large bias voltages are required to operate room temperature inorganic semiconductor detectors).
3. The minimum X-ray dose able to trigger the detection in 4HCB-based devices is 50 μGy/s, in line with the typical values for diagnostic medical applications (dose rates around 25 μGy/s [27]). Moreover, the here reported sensitivity of 4HCB-based

detectors (about 0.1 μC/cm^2 R) is in line with that of state-of-the-art a-Se based detectors (about 0.2 μC/cm^2 R)

By reaching a deeper understanding of the critical role played by the electrodes configuration and geometry in the charge collection efficiency, we succeeded in realizing the first thin and bendable X-ray direct detector based on organic semiconducting single crystals, significantly enhancing its sensitivity and its minimum detectable dose rate, These results indicate how X-ray detectors based on OSSCs possess a great potential as solid-state room-temperature and tissue equivalent X-ray detectors and dosimeters, paving the way to the development of novel large-area, thin, flexible and low-power consuming ionizing radiation sensors, to be used in a vast variety of fields, spanning from medical diagnostic, to civil security and industrial applications.

Experimental Section

Crystal growth: 4HCB single crystals have been grown from a 4 mg/mL solution composed by pre-purified 4HCB, ethylic ether, tetrahydrofurane, and toulene (50:45:5 V/V) by slow solvent evaporation following the methods described in ref. [16], in a beacker kept at 6°C. At the end of the growth the crystals have been gently removed from the beacker using a spatula, and used for the described experiments with no further treatment.

Detectors fabrication: free-standing solution grown 4HCB single crystal, millimeter-size, large area (up to 10 mm^2) and thickness 40 – 500 microns have been mounted on quartz or copper substrate. The electrode contact was fabricated with different materials: a bi-component epoxy silver paste (EPO-TEK E415G), colloidal graphite (AGAR SCIENTIFIC "AQUADAG" AGG303), gold from chloride solution (SIGMA ALDRICH 334049 $AuCl_3$). Two different electrode areas have been tested: a small area electrode (≈ 0.15 cm^2) and a large area one (2 mm^2). Interdigitated electrodes have been deposited by gold photolithography on

flexible PET (poly (ethylene terephthalate)) substrates to test the effects of a maximized electrode collection area and to assess the performance of flexible devices. The electrodes separation is 25 μm. 4HCB crystals have been bonded onto the electrode with a small drop of tetrahydrofuran (THF) that partially dissolves the crystal surface and allows for a re-crystallization onto the electrode, ensuring a good electrical contact with the interdigitated electrode. All the used materials have been chosen taking into account that the p-type conductivity of 4HCB crystals [18], provide good ohmic contacts to 4HCB OSSCs (Supplementary Information figure SI-3) and have comparable electrical performance (Supplementary Information figure SI-2).

X-ray response characterization: we performed a complete characterization of the organic crystal's electrical photo-response under two different X-ray beam sources: a) a Molybdenum tube X-ray broad spectrum with accelerating voltage of 35 kV and dose rates 2.5 – 120 mGy/s, and b) a monochromatic and aligned synchrotron X-ray beam with energies between 8.3-25 keV and dose rate 0.05-35 mGy/s. Synchrotron measurements have been carried out at ELETTRA – Trieste, in the SYRMEP beamline that is equipped with a ionization chamber for real-time dose rate monitoring. Using this beamline we have been able to explore sensitivity and X-ray detection at very low dose rates, down to 50 μGy/s and a lead-based chopper with a frequency of 9 Hz was placed in front of the X-rays beam in order to explore the time response of the device. All the reported measurements are made in air at room temperature.

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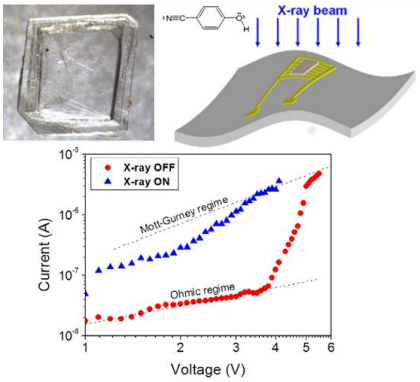
The table of contents

Keyword: Organic single crystals direct radiation detectors

A. Ciavatti, E. Capria, A. Fraleoni-Morgera, G. Tromba, D. Dreossi, P.Sellin, P.Cosseddu, A.Bonfiglio, B. Fraboni

Towards Low-Voltage and Bendable X-ray Direct Detectors Based on Organic Semiconducting Single Crystals

Organic materials have been so far mainly proposed as detectors for ionizing radiation in the indirect conversion approach, i.e. as scintillators. Her we realized the first thin and bendable X-ray direct detector based on Organic Semiconducting Single Crystals (OSSCs), promising candidates for the direct detection of X-ray radiation (i.e. X-photons are directly converted into an electric signal) that possess enhanced sensitivity, low operating voltage (≈5V) and with a minimum detectable dose rate of 50 μGy/s.



Supporting Information

Towards Low-Voltage and Bendable X-ray Direct Detectors Based on Organic Semiconducting Single Crystals

A. Ciavatti, E. Capria, A. Fraleoni-Morgera, G. Tromba, D. Dreossi, P.Sellin, P.Cosseddu, A.Bonfiglio, B. Fraboni

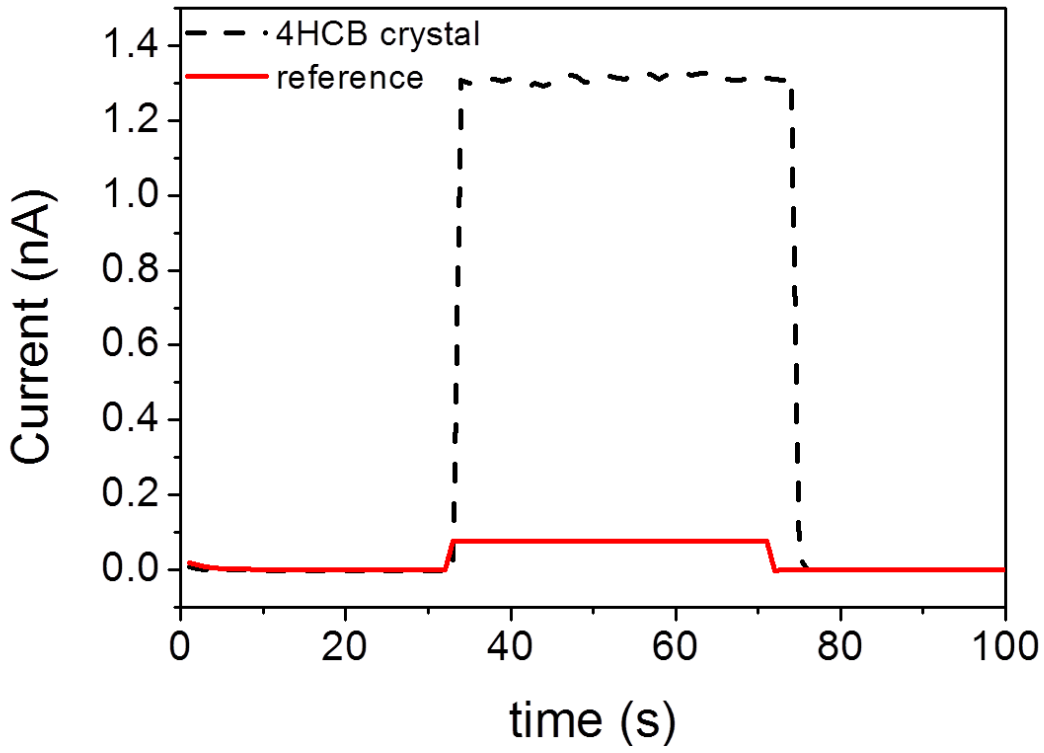


Figure SI-1: X-ray contribution collected from the substrate and electrodes

X-ray photocurrent vs time for a thick crystal with a large electrode area and (black line) compared to the measured contribution of electrodes and substrate (red line). Mo tube X-ray source (35kV) , bias of 100V and dose rate of 13 mGy/s.

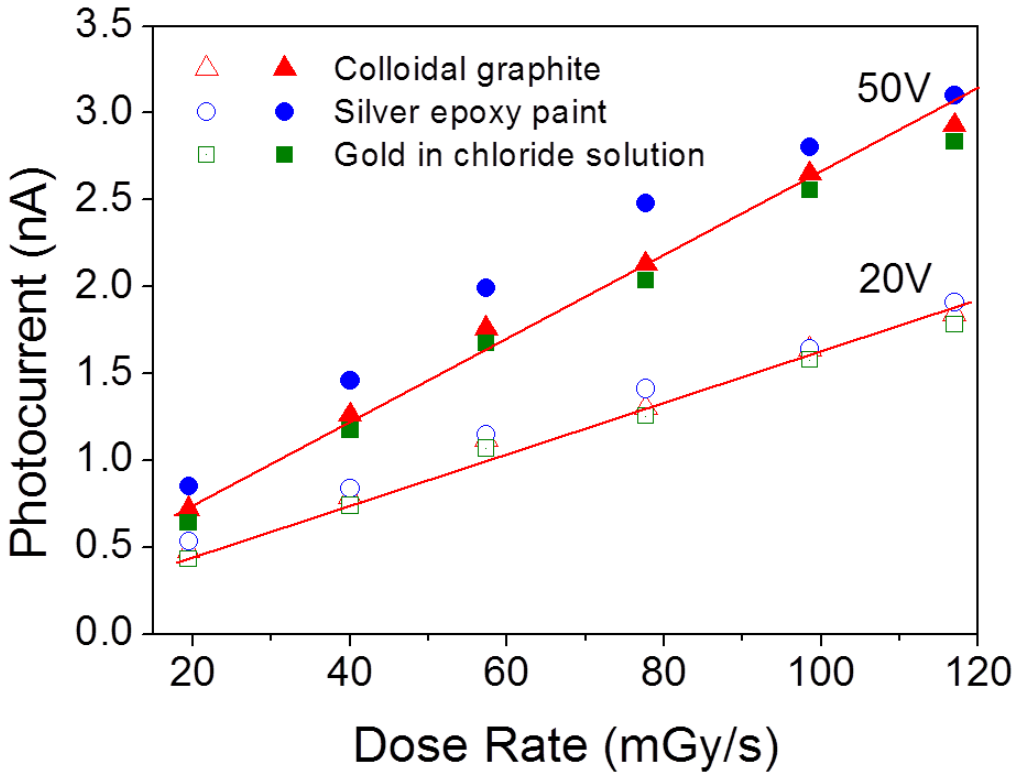


Figure SI-2: Role of electrode material

Photocurrent vs Dose Rate plot for three different electrode materials. Shows linear response for all tested electrodes materials, colloidal graphite (red upper triangle), silver epoxy paint (blue circle) and gold deposited from chloride solution (green square), and for two typical bias 20V (open symbols) and 50V (filled symbols). Linearity and sensitivity aren't affected by contact materials.

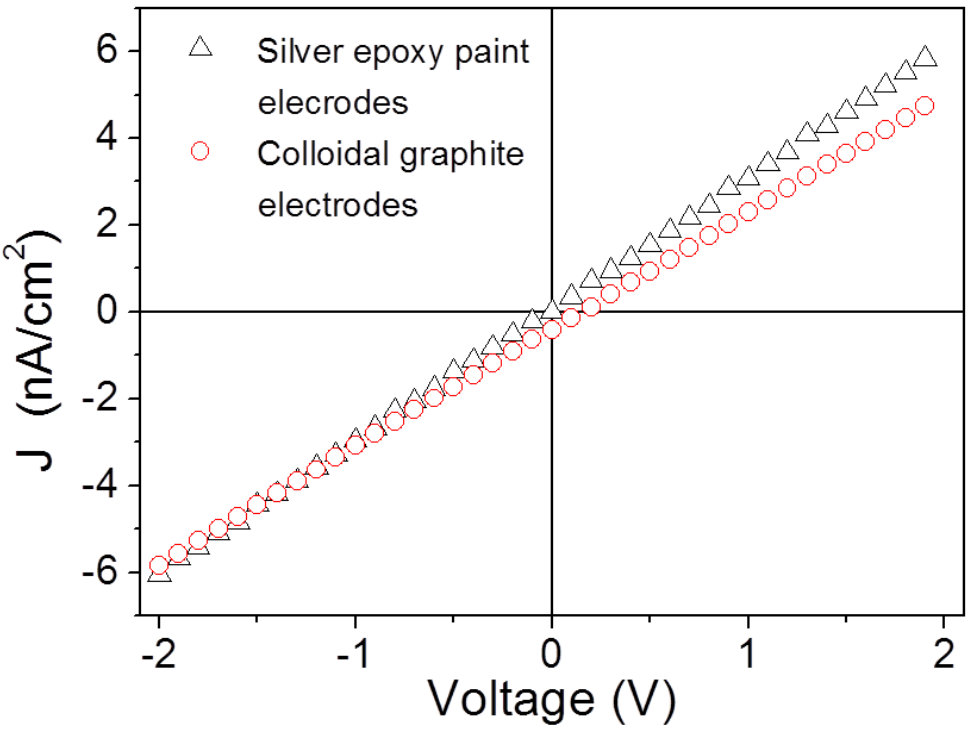


Figure SI-3: Ohmic behavior of electrodes

Current-Voltage characteristics of 4HCB crystal, showing ohmic behavior for reported electrode materials.