Enhanced x-ray detection sensitivity in semiconducting polymer diodes containing metallic nanoparticles

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Abstract:

Semiconducting polymer X-radiation detectors are a completely new family of low-cost radiation detectors with potential application as beam monitors or dosimeters. These detectors are easy to process, mechanically flexible, relatively inexpensive, and able to cover large areas. However, their X-ray photocurrents are typically low as, being composed of elements of low atomic number (Z), they attenuate X-rays weakly. Here, the addition of high-Z nanoparticles is used to increase the X-ray attenuation without sacrificing the attractive properties of the host polymer. Two types of nanoparticles (NPs) are compared: metallic tantalum and electrically-insulating bismuth oxide. The detection sensitivity of 5 μm thick semiconducting poly([9,9-dioctylfluorenyl-2,7-diyl]-co-bithiophene) diodes containing tantalum NPs is four times greater than that for the analogous NP-free devices; it is approximately double that of diodes containing an equal volume of bismuth oxide NPs. The X-ray induced photocurrent output of the diodes increases with an increased concentration of

nanoparticles. However, contrary to the results of theoretical X-ray attenuation calculations, the experimental current output is higher for the lower-Z tantalum diodes than the bismuth oxide diodes, at the same concentration of nanoparticle loading. This result is likely due to the higher tantalum NP electrical conductivity, which increases charge transport through the semiconducting polymer, leading to increased diode conductivity.

1. Introduction

The inherent physical properties and advantageous processing characteristics of semiconducting polymers, when compared to their inorganic counterparts, have increased the range of optoelectronic applications in which they are used. [1] Device performance has been further improved using complementary materials, such as small organic molecules [2] or inorganic nanoparticles (NPs) (such as carbon nanotubes (CNT)), [3] introduced into the polymer matrix, which can increase polymer conductivity, device lifetime and stability.

Consequently, alongside a variety of potential candidates, [4] polymer semiconductors have been identified as materials of interest for the detection of high energy radiation [5] and associated imaging applications. [6] Initial experiments have used a semiconducting polymer photodetector to detect X-ray generated light from a scintillation screen, [7,8] and such detectors have been found to return more than 60% of their original photocurrent at doses of up to 4.2 kGy. [9]

Alternatively however, semiconducting polymers can be used for the direct detection of X-rays, [2,10,11] and similar direct detectors have also been produced using organic semiconductor single crystals. [12] Although these organic materials can be susceptible to radiation damage, [13] they have some advantages for their use as X-ray detectors, such as mechanical flexibility, tissue equivalence, and an ability to be coated over large areas. [13,14]

We have previously produced X-ray induced photocurrents (on the order of ten nA) in several micrometer thick semiconducting polymer films exposed to incident 17.5 keV X-ray doses of up to 70 mGy.s⁻¹. [11,14] As the dark current produced by these devices is approximately 0.1 nA, the X-ray induced photocurrent can be detected in laboratory applications using sensitive ammeters and electrical amplifiers. However, to produce devices that detect soft X-rays and produce higher photocurrents, or detect hard X-rays without the requirement for electrical amplification, the use of semiconducting polymers on their own is not optimal.

The problem arises from the relatively low X-ray attenuation (radiation stopping power [15]) of polymers (and other organic materials). The low atomic number (Z) of the component atoms in the polymer (typically C and H, combined with O, N or S) make them largely transparent to X-rays. For example, a 200 µm thick polystyrene film stops less than 2% of incident 17.5 keV (soft) X-rays. [16] (For comparison, an equivalent 200 µm thick sheet of aluminium or iron would stop 25.7% and 99.8% of the same X-rays, respectively). Consequently, only a small proportion of incident X-rays interacts with the electronic structure of a semiconducting polymer and induces a photocurrent. This places a limitation on the usefulness of polymeric direct detectors.

To increase the photocurrent, the attenuation of the polymer film needs to be raised without affecting the electronic properties of the diode, and preferably while retaining the advantageous physical properties of the polymer, such as mechanical flexibility. One possible method is to introduce high-Z elements into the polymer matrix which will attenuate the X-rays and induce a photocurrent in the host polymer chains.

Nanoparticles are ideal for this purpose. At low concentrations they introduce the advantageous properties of the nanoparticle into the semiconductor layer, without disrupting the continuous phase of the semiconductor film; which would consequently affect the properties of the diode. Such a technique has already shown promise in the production of

hybrid organic-inorganic solar cells, [3] in which the inorganic element provides an electron acceptor component and contributes to device stability.

We have previously shown that nanoparticles made from a high-Z element, bismuth (Bi), yield a higher photocurrent in a semiconducting polymer diode. [18] Here, we investigate the significance of the electrical properties of the NPs on the detector performance, by comparing the effects of metallic Ta NPs and insulating Bi₂O₃ NPs in a semiconducting poly([9,9-dioctylfluorenyl-2,7-diyl]-co-bithiophene) (F8T2) thick film, contained as the active component of a photodiode. The response of the diode to the inclusion of the NPs upon irradiation with 17.5 keV molybdenum (Mo) α X-rays is examined.

2. Experimental Section

2.1 Materials

Body-centered-cubic, α -form tantalum (Ta, <25 nm diameter, resistivity = 13 $\mu\Omega\text{cm}$) and tetragonal, β -form bismuth oxide (Bi₂O₃, 90-210 nm diameter, surface area = 3.2-3.5 m^2g^{-1}) NPs, and toluene (99.99%) were purchased from Sigma-Aldrich (Sigma-Aldrich Chemical Co., UK), and used as supplied. Poly([9,9-dioctylfluorenyl-2,7-diyl]-co-bithiophene) (F8T2, $M_n = 45,000 \text{ g.mol}^{-1}$, $M_w = 120,000 \text{ g.mol}^{-1}$) was prepared as previously reported. [19] Indium Tin Oxide (ITO) coated glass, with a nominal sheet resistance of 25 Ωsq^{-1} and an oxide thickness of 80-120 nm, was purchased from Delta Technology Ltd., USA (CB-60IN).

F8T2 polymer was dissolved in toluene to produce a 2 wt.% polymer solution. The solution was shaken for 4 hours (Yellowline basic shaker) to dissolve the polymer and produce a homogenous solution. Ta or Bi₂O₃ NPs were added to aliquots of the solution to produce a 60 wt.% polymer/NP solution. The solution was then exposed to a sonic water bath for 90 minutes to disperse the NPs. To produce the range of NP solution concentrations used here, the 60 wt.% polymer/NP stock solution was diluted as required. Films with target NP

concentrations of approximately 60, 45 and 30 wt.% NPs were produced for X-ray testing. For UV-visible spectroscopy a more transparent, 2 wt.% NP film was produced.

2.2 Diode production

ITO coated glass slides were cut to size (approx. $2.5 \times 2.5 \text{ cm}^2$), cleaned by repeated rinsing alternately in acetone and water, and then dried under ambient conditions. The F8T2/NP solution was spin-cast on the ITO (Headway Research Inc., model PWM32 photoresist spinner) at spin speeds of 50 rpm for the time required to produce an air-dried film (approx. 5 min.). A small area of the ITO was left uncovered to allow later electrical contact. After heating in a vacuum oven (120°C for 24 hours), approx. $5 \mu\text{m}$ thick polymer/NP films were produced, as determined by a surface profilometer (Dektak, Veeco Instruments).

Gold (Au) or aluminium (Al) electrodes (100 nm thick, 0.25 cm^2) were thermally evaporated through a shadow mask onto the F8T2 (at 10^{-6} mbar vacuum). The diodes were connected to the measurement electronics through filament wires attached by gold paste to the ITO and Au/Al electrodes. Finally, the devices were encapsulated with insulating, plasticized paraffin bonding wax (OCON-199, Logitech Ltd, UK) by dip coating the diode in the molten wax. Upon completion, the diodes were stored under nitrogen and in the dark to minimise any adverse oxidation effects.

2.3 Diode characterisation

2.3.1 Thermogravimetric analysis. Thermogravimetric analysis (TGA) was carried out (Q500, TA Instruments), under a nitrogen atmosphere, from room temperature (20°C) to 650°C with a heating rate of $10^\circ\text{C min}^{-1}$. After use in the dosimetry experiments, a small amount of the dried, NP-loaded F8T2 film was removed from the ITO using a sharp knife and deposited into TGA weighing boats, which were hermetically sealed and introduced into the TGA apparatus.

2.3.2 Optical and electrical characterisation. To examine the effects of the NPs on the optical properties of the polymer films, aliquots of F8T2 solution, with and without NPs, were spin-cast (2000 rpm, 1 min) onto soda-lime float glass, and allowed to dry in air. Comparative UV-visible spectroscopy (Camspec M350 Double Beam UV/VIS Spectrophotometer.) was undertaken (300 to 1000 nm). The samples were then annealed (180°C, 3 h) to mimic the longer, lower temperature (120 °C, 24 h) anneal used in the X-ray experiments, and the measurements repeated.

Current-voltage (I-V) characteristics of the ITO/F8T2/metal diodes (5 µm thick) were examined using a voltage source-picoammeter (487, Keithley Instruments, UK) by applying a bias voltage to the ITO electrode (from 0 to -50 V, then 0 to +50 V).

2.3.3 Dosimetry. Dosimetry measurements were performed using 17.5 keV K α X-rays from a molybdenum (Mo) target X-ray tube (XF50 11, Oxford instruments, UK). The anode current of the tube could be varied up to 500 µA at an operational anode voltage of 50 kV to provide X-ray dose rates up to 26 mGy.s⁻¹. Calibration was performed using a dosimeter (Farmer NE2670) connected to an ionisation chamber (2611A, Thermo Scientific). While applying a constant operating voltage to the ITO electrode (-50V), the detector was exposed to the X-ray beam through the metal top electrode. The induced photocurrent was then measured using a voltage source-picoammeter (487, Keithley Instruments, UK). During exposure, the detectors were mounted 10 cm from the X-ray source, in the dark and at room temperature.

3. Results

3.1 Attenuation quantum efficiency

Tantalum is a transition metal commonly used in electrical components such as capacitors, whereas Bi_2O_3 is typically used in solid fuel cells as an ionic conductor. [20] They were chosen as NP additives for the semiconducting polymer X-ray detectors due to their high Z, low cost and abundance in the Earth's crust (to ensure that any devices can be sustainably produced into the future). Bismuth's abundance is on a par with gold, and tantalum is on a par with tin. Selected physical properties and abundance data for Ta, Bi and Bi_2O_3 are given in Table 1.

Thermogravimetric analysis (TGA) measurements were used to calculate the concentration of NPs in the F8T2 films after they had been used for X-ray detection. The F8T2 decomposes at approx. 450 °C leaving behind the added NPs and any polymer decomposition products, the weight of which is given as a percentage of the total film weight. When the data are normalised to that of the weight of the decomposition products for pristine F8T2, weight percentage estimations for the NPs can be calculated. Experimental weight percentages are taken as the average of the weight measurement values at $T > 500$ °C. The weight percentage concentrations of the NPs are approx. 30, 42, and 57 wt.% respectively. When converted into volume percentage, this corresponds to 4.6, 7.5 and 13.0 vol.% for Bi_2O_3 , and 2.5, 4.2 and 7.4 vol% for Ta, respectively. The weight of Bi_2O_3 NPs has previously been shown to be stable across the measurement range. [18]

Figure 1 shows the attenuation quantum efficiency (QE) of 17.5 keV X-rays incident on 5 μm thick F8T2 films, loaded with increasing concentrations of Bi_2O_3 and Ta NPs. The transmitted radiation intensity, as a function of photon energy, was calculated using the equation:

$$I_{(x)} = I_0 e^{-(\mu/\rho)\rho x}, \quad (1)$$

where I_0 and $I_{(x)}$ are the incident and transmitted radiation intensities, respectively, and μ , x and ρ are the linear attenuation coefficient, the thickness, and the density of the polymer film, respectively. For F8T2, ρ was assumed to be 1 g.cm^{-3} . Values of the mass attenuation

coefficient (μ/ρ) for the NP-loaded polymer films were obtained from a photon attenuation database. [16] The database uses the weight fraction of each of the components (polymer and NP) to calculate μ/ρ for the film. The QE of the NP-loaded polymer films, were then calculated using,

$$QE = 1 - \frac{I_{(x)}}{I_0} \quad (2)$$

The graph shows that QE increases with increasing NP concentration, and that the attenuation should be higher in F8T2 films containing the higher densities of Ta NPs.

The inset in Figure 1 gives the chemical structure of F8T2. The extensive conjugation through the polymer chain gives F8T2 its semiconducting properties, while the alkane chains in the fluorene moiety allow the polymer to be dissolved in organic solvents, such as toluene.

3.2 Electrical and optical properties

UV-visible spectra of pristine F8T2, and when loaded with 2 wt% Ta NPs, were measured when the film was newly deposited and after vacuum annealing at 180 °C for 3h. The spectra are similar for both the pristine and NP-loaded polymer. After annealing, the spectra are largely unchanged apart from a small 2 nm bathochromic shift. Measurements on increasingly loaded polymer films displayed similar spectra, although with lower transmitted light intensities.

Figure 2 shows the peaks in the UV-visible spectra at $\lambda < 500$ nm. The newly-deposited polymer films (pristine and NP loaded) display a prominent peak at 464 nm and a shoulder to this peak at 485 nm. After annealing, the peak at 485-490 nm becomes more prominent. In the pristine film the peak at 464 nm remains prominent, but in the NP-loaded polymer films, this peak decreases in relative intensity. The relative difference in absorbance

between the two peaks increases in the order: pristine polymer < Ta loaded polymer < Bi₂O₃ loaded polymer.

The appearance of similar peaks in the UV-visible spectra, and their shift in prominence with annealing, has been seen previously in conjugated polymers when poly(3-octylthiophene) films have been reduced using hydrazine. [21] The appearance of two peaks in the absorption spectra can be attributed to the pristine polymer (low wavelength peak) and areas of the polymer in which partial, higher order chain alignment occurs (higher wavelength peak). The relative proportion of aligned chains increases during annealing because the greater chain mobility allows rearrangement of the polymer chains: the higher wavelength peak increases because of greater chain-chain interaction. Solvent loss will additionally cause chain relaxation in the polymer matrix, via relaxation of the structure and densification of the film, and again produce greater contact between chains. [14] Nano-objects (such as carbon nanotubes) [22,23] and “hard walls” [24] are also known to affect local chain conformation.

Figure 3 shows typical current-voltage (I-V) curves for an ITO/F8T2 (5 µm)/Al diode, and an analogous diode with a 30 wt.% Bi₂O₃-loaded F8T2 layer. In each case, the diodes display similar rectifying behaviour with dark currents, at negative bias, of the order of 0.1 nA. The similarity in the DC characteristics suggests that the electrical conductivity of the polymer is unaffected by the inclusion of the NPs, at least when not illuminated or irradiated. Similar results are found for Ta-loaded F8T2 diodes, although their dark currents tend to be higher (Table 2). The DC characteristics mirror those found for similar diodes incorporating poly(triarylamine) (PTAA) polymer, which have been examined elsewhere. [11]

3.3 X-ray induced photocurrent

3.3.1 Nanoparticle effects. Figure 4 presents the photocurrent produced when NP-loaded F8T2 diodes with different top electrodes (Aluminium [Al] or Gold [Au]) are irradiated with 17.5 keV X-rays. Figure 4A shows the photocurrent induced in F8T2 (5 µm thick) diodes

incorporating 30, 42 and 57 wt.% Bi_2O_3 NPs. The induced photocurrent increases as the concentration of added NPs increases, when compared to an equivalent pristine F8T2 diode (dashed line). Ionisation of these high molecular mass NPs upon interaction with the incident radiation will cause them to act as electron acceptors within the semiconducting polymer matrix. This will oxidatively dope the polymer, making it increasingly p-type, and inducing an increased photocurrent in the diode. [25]

Diodes containing Ta NPs also induce a photocurrent (Figure 4B), which is larger than for the equivalent Bi_2O_3 -loaded polymer diodes. The Ta-loaded polymer diodes have a sensitivity (Table 2) approx. double that of the Bi_2O_3 diodes, and approximately four times that of the NP-free diodes.

The photocurrent produced by the diodes (Figure 4A) can be compared to the theoretical calculations of X-ray Q.E. (Figure 1). The increase in photocurrent with NP loading (Figure 4A) doubles when progressing from 30 to 57 wt.% Bi_2O_3 . This compares to a three-fold increase predicted by the theoretical Q.E. results. The measured photocurrent increase is therefore approximately 66% of that expected from the attenuation of the films.

Similarly, looking at the difference in photocurrent produced from diodes containing 30 wt.% Bi_2O_3 and Ta NPs (Figure 4B), the photocurrent is approx. 35% greater from the Ta-loaded diodes compared to their Bi_2O_3 analogues. In comparison, the theoretical attenuation results (Figure 1) suggest that the difference should be in the region of 26% for 30 wt.% NP loaded devices (see discussion for explanation).

3.3.2 Electrode effects. A comparison of diodes with equivalent Bi_2O_3 loaded polymer matrixes, but different metallic top contacts, either Al or Au, shows that the induced photocurrent for either contact electrode is similar for a given concentration of NPs (Figure 4A). The diodes containing Ta NPs, with Al and Au top contacts, also produce similar photocurrents (Figure 4B). The diode sensitivity (Table 3) is similar for both diodes (Al and

Au), for the dose rates used in these experiments, with the sensitivity of the Al diodes being slightly higher than those for the Au diodes.

These results can also be compared (Table 4) with previous results for Bi₂O₃ loaded poly(triarylamine) (PTAA) diodes. [18] The diodes produced using F8T2 (5 µm thick, Bi₂O₃) and PTAA (20 µm thick, Bi₂O₃) have similar NP concentrations (approx. 40 wt.%) and give similar X-ray photocurrents (1 nA at approx. -50V) when irradiated (17.5 keV X-rays, 27 mGy dose). However, the F8T2 analogues produce a higher sensitivity due in part to the smaller volume of the polymer active area. Comparitively however, even with a lower NP concentration (30 wt.%), F8T2/Ta diodes display a higher photocurrent, and consequently a higher sensitivity than their Bi₂O₃-loaded analogues.

4. Discussion

4.1 Electromagnetic energy deposition

To explain the photocurrent data further, we simulated the interaction of the X-rays with the polymer matrix in the diode systems using FLUKA Monte Carlo simulations (Figure 5). [26] The model calculates the electromagnetic (E.M.) energy, deposited in the NP-loaded F8T2, by interaction of the incident 17.5 keV X-rays with the components in the polymer matrix (i.e. the F8T2 and NPs) and the peripheral diode materials (i.e. the paraffin wax, the electrode materials and the glass support). The E.M. energy in this case is defined as the secondary X-rays and electrons (such as Auger electrons) produced in the diode components by interaction of those components with the incident primary X-rays. The majority of ionization produced will not primarily be the result of direct interaction with the incident, high-energy X-ray photons, but rather of interactions of these less energetic electrons with the diode materials.

The polymer was modelled as a finite volume, defined by the thickness of the polymer and the area of the top metal electrode, which corresponds to the volume of polymer sandwiched between the electrodes of the diode subjected to an applied bias during the measurement of the X-ray induced photocurrent. The electrodes of the diode were modelled using their component thicknesses and their constituent atomic composition.

Whereas the experiments were performed in air, for simplicity the model diode structure was irradiated in vacuum. The vacuum negates any possibility of X-rays re-entering the model diodes from the surrounding environment. X-rays exiting the model system are terminated to ensure they do not re-enter the diode structure. The devices were modelled as a sandwich structure consisting of paraffin wax/electrode/F8T2 (NP)/ITO/soda-lime float glass diode, where the electrode was Al, Au, or omitted for comparison. Further details of the model are given in the supplementary information.

4.1.1 Nanoparticle effects. Figure 5A shows the amount of E.M. energy deposited in a 5 μm thick polymer matrix, with increasing concentrations of added NPs. The amount of deposited energy increases as the concentration of the NPs increases and corresponds to the masses of the constituent materials, as evidenced by the greater deposition in the (higher molecular mass) Bi_2O_3 -loaded polymer when compared to the Ta-loaded polymer. The amount of E.M. energy deposited in the polymer does not appear to change greatly with the different top electrodes (Al and Au). Rather, it depends more on the concentration of the NPs deposited in the polymer film, with the higher molecular mass Bi_2O_3 causing more of the incident X-rays to be attenuated.

Contrary to this however, Figure 4B shows that, experimentally, the current produced by the Ta-loaded diodes is higher than that from the Bi_2O_3 -loaded diodes. This contradicts the theoretical results in Figure 5, which show that more E.M. energy should be deposited in the Bi_2O_3 diodes. This discrepancy may be explained by examining the electrical conductivity of

the respective NPs. Ta is a metallic element with a conductivity of $8.2 \times 10^6 \text{ S.m}^{-1}$, [27] whereas Bi_2O_3 is more insulating with a conductivity of $10^3\text{-}10^4 \text{ S.m}^{-1}$. [28] The metallic Ta NPs will more readily act as doping agents within the polymer matrix by ionising when exposed to the incident X-rays.

The increased charge produced on the F8T2 polymer chains by the ionised Ta consequently produces a higher photocurrent in the diode, compared to the Bi_2O_3 -loaded diodes. This may explain the lower than expected output of the Bi_2O_3 diodes (Figure 4A) when compared to that expected from their Q.E. (Figure 1). It can also explain the unexpectedly inferior output from the Bi_2O_3 devices (Figure 4B) when compared to the theoretical deposition of energy in the diode active materials (Figure 5A).

4.1.2 Electrode effects. Although the type of NP has a dominant effect on the amount of E.M. energy deposited in the diode, the electrode materials also contribute. The E.M. energy deposited in the F8T2 behind the metal electrodes is less than in the polymer without a metal electrode present. Due to the relative atomic masses of the electrode materials, the amount of deposited energy is on average 5% lower (at $[\text{NP}] > 20 \text{ wt.}\%$) in the Au electrode diode than the Al diode and the F8T2 film alone: the latter cases retain similar amounts of E.M. energy (Figure 5B). When $[\text{NP}] < 20 \text{ wt.}\%$, the error in the mean values for the deposited E.M. energy are typically in excess of 5% (Supplementary information: Table S4) which may explain differences in deposited E.M. energy of greater than 100% (Figure 5B).

The model assumes that the higher mass Au stops more of the X-rays entering the polymer. Al, on the other hand, has a mass similar to the atoms in the polymer, and consequently the energy deposited in the polymer behind the Al is similar to that in the pristine polymer, given the thickness of the metal electrode layer (100 nm). If we compare the results of the modelling with the experimental results in Figure 4, we see that there is very

little difference in the currents produced by the NP loaded F8T2 diodes using either Al or Au electrodes as the dose rate increases.

Comparison of the sensitivities of the devices (Table 2) does however show that the Al diodes are more sensitive to the incident radiation. This suggests that more E.M. energy is deposited in Al diodes with equivalent NP loadings. However, this effect may be masked in our experiments by the effect of the metal electrode on the diode. Al produces a better ohmic contact to the polymer than Au, resulting in more efficient extraction of charges. [29] This in turn may contribute to the higher current seen in the Al diodes, rather than any effect due to the electrode material.

Modelling of the attenuation of the materials in the respective diodes confirms that, not only do the NPs affect the output current, but to a lesser extent so do the metallic contacts used to complete the diodes. Although the difference in attenuation due to the contact metal is small, compared to that due to the presence of the NPs, consideration must therefore be given to the construction of the diode when producing these X-ray detectors.

Examining the literature, similar attenuation effects have been observed in NP loaded polymer films for a number of applications. Photoluminescence quenching has been observed in Bismuth Iodide (BiI_3)-loaded polymer diodes upon irradiation with gamma (γ) rays. [30] The authors postulated that the BiI_3 NPs form aggregates upon irradiation which quench excitons formed on the polymer chain. Wang *et. Al.* [31] have demonstrated increased photoconductivity in thick (100's μm to mm), non-conducting nylon-11 films, doped with BiI_3 NPs, and examined using X-ray induced discharge techniques. In this case, the increased photoconductivity is assigned to an increased percolation conduction through the high concentration (50 wt.%) of NPs.

In our polymer/NP composites, the low output currents, and the stepwise increase in conduction with increasing NP concentration, suggest that percolation through the NPs does

not occur in the range of NP concentrations studied. This is expected as the volume percentage of NPs is small (<13 vol. %) and below the percolation threshold. An examination of the potential for sedimentation has been completed for the nanoparticles in a toluene solution (see supplementary information). Given an estimated thickness of the wet film (250 μm), and using an evaporation rate, E , for toluene of $1.14 \times 10^{-7} \text{ ms}^{-1}$, [32] the sedimentation number, N_s , and the sedimentation Péclet number, Pe_{sed} , can be calculated. [33] For Ta NPs in toluene, $N_s = 1.28$ and $Pe_{\text{sed}} = 5.0$. A value of $N_s > 1$ suggests that sedimentation of the Ta NPs is significant with respect to evaporation of the toluene, and similarly a $Pe_{\text{sed}} > 1$ suggests that the sedimentation is significant with respect to the diffusion of the NPs in the solvent, given:

$$N_s = \frac{Pe_{\text{sed}}}{Pe} \quad (3)$$

where, Pe is the Péclet number, which describes the significance of evaporation with respect to diffusion. Consequently, it may be expected that the nanoparticles will sediment in the polymer film, and the spatial distribution of the NPs in the F8T2 films used herein is expected to be similar to that seen elsewhere in PTAA diodes, [18] where the NPs are predominately positioned near the bottom ITO electrode.

If we assume F8T2 is p-type, as with many conducting polymers, the polymer Fermi level, E_f , typically lies just above the highest occupied molecular orbital (HOMO) at the top of the valence band (E_v) (Figure 6a). Upon contact the Al electrode produces a rectifying contact with the F8T2; at equilibrium band bending occurs and a depletion layer forms (Figure 6b). Although the sedimentation of the nanoparticles is not ideal, especially when considering the fact that the depletion region in the diode is positioned at the opposite, metallic contact, [14] the diodes still have potential for use as X-ray detectors, as evidenced by the increase in device photocurrent with NP inclusion. In the future, improved distribution of the NPs in the polymer matrix may produce greater increases in photocurrent as more

charges in the polymer are deposited in, and more easily removed from, the depletion region of the diode.

Finally, the performance of X-ray detectors based on thin films of polymer-NP composites may be improved if they are flexible enough to be folded or rolled. The attenuation QE of a 5 μm thick 50 wt.% Ta/F8T2 film can be increased by folding or rolling to make a thicker layer. The efficiency increases from approx. 20% for the 5 μm thick film to more than 70% for a 5 μm thick film folded or rolled in such a way that the incident X-rays pass through 6 layers (30 μm) of the material (Supplementary information: Figure S1). We have previously demonstrated the flexibility of these composite NP-polymer films alone. [18] The remaining challenge is to produce diodes, and their associated electrodes, with such flexibility that they may be much more tightly rolled or folded. [14]

5. Conclusions

Nanoparticle-loaded semiconducting polymer diodes have been shown to produce an increased output current under X-radiation when compared to their unloaded polymer analogues. The increased sensitivity to radiation is found to depend somewhat on the electrical conductivity of the NP and the associated transfer of charge to the surrounding semiconducting polymer matrix. The conducting Ta NPs induce more current output from the X-ray irradiated polymer diode than their more insulating Bi_2O_3 analogues. Although the X-ray attenuation suggests that the Ta-loaded diodes should attenuate more of the incident X-rays, theoretical studies of the energy deposited in the diodes suggest that more energy (as secondary X-rays and Auger electrons) should be deposited in the higher mass Bi_2O_3 NP diodes. If all this deposited energy is converted to charge carriers, the Bi_2O_3 diodes could be expected to produce a higher photocurrent. However, the experimental results show that it is the Ta-loaded diodes that produce the higher X-ray photocurrent, probably due to the increased metallic character of the Ta.

The addition of the NPs at concentrations up to 30 wt.% has not been shown to adversely affect the electrical properties of the diodes, neither have low concentrations (approx. 2 wt.%) been found to affect the optical properties. Although the photocurrents produced here are small, improvements to diode architecture (such as the introduction of electron and hole transport layers between the F8T2 and the electrodes), and a better dispersion of the NPs throughout the F8T2 film should see the produced photocurrent improve. The photocurrent may be further improved by folding or rolling a flexible all-polymer diode so that the incident X-rays pass more than once through the NP-loaded F8T2 layer.

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Figures:

Figure 1 Quantum Efficiency (Q.E.) of 5 μm thick F8T2 films incorporating Bi₂O₃ (●) and Ta (▲) nanoparticles of increasing concentration, calculated using equation 2. Inset: chemical structure of F8T2.

Figure 2 Normalised UV-visible absorption spectra of thin films of F8T2 measured immediately after preparation (A) and after annealing at 180°C for 3h (B). The curves are plotted for pristine polymer (solid lines), F8T2 loaded with 2 wt.% Ta (dashed lines) and 2 wt.% Bi₂O₃ (dash-dot lines) nanoparticles.

Figure 3 Current-voltage plots for (solid line) ITO/F8T2/Al and (dashed line) ITO/F8T2 (30 wt.% Bi₂O₃)/Al diodes, with the bias voltage applied to the ITO electrode. The dotted line in each case indicates the approximate position of the current minima, at values below the measurement limit of the picoammeter (10^{-12} A). Inset is a diagram depicting the energy levels (in eV) in the ITO/F8T2/Al diode.

Figure 4 (A) Induced photocurrent in ITO/F8T2/Au (solid symbols) and ITO/F8T2/Al (open symbols) diodes, incorporating 30 wt.% (■), 42 wt.% (●), and 57 wt.% (▲) Bi₂O₃ nanoparticles (NP) in 5 μm thick F8T2 films, irradiated with 17.5 keV Mo K α X-rays. (B) Induced photocurrent in ITO/F8T2 (NP)/Au (solid symbols) and ITO/F8T2 (NP)/Al (open symbols) diodes, incorporating 30 wt.% Bi₂O₃ (■) and 30 wt.% Ta (▲) NPs in 5 μm thick F8T2 films, irradiated with 17.5 keV Mo K α X-rays. In each figure, the dashed line shows the induced photocurrent produced in a NP-free 5 μm thick ITO/F8T2/Al diode.

Figure 5 (A) Linear trend lines fitted to mean data produced by a Monte Carlo simulation (Fluka [26]) of electromagnetic energy (E.M. energy) deposited in the F8T2 when irradiated by 17.5 keV Mo $K\alpha$ X-rays originating 10 cm from the polymer layer. The 5 μm thick F8T2 film, incorporating increasing concentrations (wt.%) of Ta (lower lines) and Bi₂O₃ (upper lines) nanoparticles (NP), is incorporated in a paraffin wax/electrode/F8T2 (NP)/ITO/soda-lime float glass diode, where the electrode is: Al (red line), Au (blue line), or no electrode (dashed green line). The data plotted is tabulated in the supporting information (Table ST4). (B) Percentage E. M. energy deposited in F8T2 diodes with Al (filled symbols) and Au (open symbols) electrodes compared to devices with no metal electrode, for increasing concentrations (wt.%) of Ta (▲) and Bi₂O₃ (●) NPs. Data taken from figure 5A. The 100% level (equivalent to a diode with no metal electrode) is indicated by a dashed line.

Figure 6. (A) Energy levels in the Al/F8T2/ITO diode, indicating the estimated position of the F8T2 Fermi level. (B) Band bending at the rectifying Al/F8T2 interface, showing the maximum possible built-in voltage (V_{bi}). Key: E_F = Fermi level, E_V = Valence band, W = depletion layer width. Energy levels are given in electron volts (eV).

Tables**Table 1** Selected physical properties and abundance of Ta, Bi and Bi₂O₃.

Property	Ta [27]	Bi [27]	Bi ₂ O ₃
Density (ρ) / g.cm ⁻³	16.40	9.79	8.90 [27]
RMM / g.mol ⁻¹	180.95	208.98	465.96 [27]
Electrical resistivity (ρ) / Ω m ⁻¹	1.22x10 ⁻⁷	1.07x10 ⁻⁵	10 ⁻³ to 10 ⁻⁴ [28]
Abundance in Earth's crust / mg.kg ⁻¹	2.00	5x10 ⁻³	-

Table 2 Dark current values for 30 wt.% nanoparticle loaded F8T2 diodes, with Al/Au top electrodes, at -50 V applied to the ITO electrode.

NP	metal	I / nA
Ta	Al	0.665
	Au	0.215
Bi ₂ O ₃	Al	0.0375
	Au	0.0269

Table 3 Diode sensitivity to incident 17.5 keV Mo $K\alpha$ X-rays using the data from figure 4.

		Sensitivity / nC.mGy ⁻¹ .cm ⁻³	
		Al	Au
Bi₂O₃ concentration	30 wt. %	288	223
	(Figure 4A)		
	42 wt. %	377	323
	57 wt. %	468	408
Nanoparticle (30 wt. %)	Bi ₂ O ₃	288	223
	(Figure 4B)		
	Ta	434	439
Nanoparticle-free	-	141	-

Table 4 Comparison of device performance for polymer-nanoparticle diodes of F8T2 and PTAA irradiated with 27 mGy, 17.5 keV X-rays. PTAA data taken from [18].

	F8T2		PTAA	
Thickness / μm	5		20	
Nanoparticle	Bi_2O_3	Ta	Bi_2O_3	
Nanoparticle concentration / wt. %	42	30	38	
Applied voltage / V	-50	-50	-40	-100
X-ray Photocurrent / nA	1.4	1.7	1*	2*
Sensitivity / nC/mGy/cm^3	377	434	40**	75**

*Approx. data taken from supplementary figure S2C of [18]

** Approx. data taken from figure 5B of [18]

Enhanced X-ray Detection Sensitivity in Semiconducting Polymer Diodes Containing Metallic Nanoparticles

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Supplementary information:

Figure S1: Graph of X-ray attenuation quantum efficiency for increasingly thick 50 wt.% Ta nanoparticle/F8T2 films theoretically achieved by folding or rolling a 5 μm thick film multiple times. Inset: diagrams of X-rays passing through 1 layer (5 μm thick, left) and 6 layers (30 μm thick, right) achieved by folding or rolling the 5 μm thick film. I_0 and I denote the incident and transmitted X-ray intensity respectively.

Fluka model

Figure S2: (A) Diagram of the Fluka model for the experimental set-up used to calculate the data given in figure 5. Dimensions of the constituent components are given in table ST1 (Note that the components in the diagram are not to scale). The substrate glass is modelled as soda-lime silica (float) glass with a chemical composition as given in table ST2. (B) The X-ray source is modelled as a point source positioned at a distance (x) of 10 cm from the front polymer surface. The X-rays diverge from the source at a cone angle (θ) of 25° , as defined by the construction of the X-ray tube, in a uniform distribution. The diameter (d) of the irradiated spot at 10 cm distance from the source, as defined by the diverging X-rays, is 4.44 cm, somewhat larger than the width of the electrode (0.5 cm) on the diode.

Table ST1: Dimensions of the Fluka modelling components used to produce the data presented in Figure 5.

Identifier	Material	Dimensions		
		x	y	z
Black hole	Black hole	>10 km	>10 km	>10 km
Vacuum	Vacuum	10 km	10 km	10 km
1	Wax*	0.5 cm	0.5 cm	1 cm
2	Metal (Al or Au)	0.5 cm	0.5 cm	100 nm
3	Polymer** (NP)	0.5 cm	0.5 cm	5 μ m
4	ITO	0.5 cm	0.5 cm	100 nm
5	Soda-lime float glass	0.5 cm	0.5 cm	1 cm

* C_nH_{2n+2} ($n = 25$), $\rho = 0.9 \text{ gcm}^{-3}$

** $C_{37}H_{44}S_2$, $\rho = 1.0 \text{ gcm}^{-3}$

Table ST2: Chemical composition of soda-lime float glass, used to model the substrate support in the Fluka modelling.

Chemical constituent	Composition (wt.%)
Silica (SiO_2)	72.7
Sodium oxide (Na_2O)	14.2
Lime (CaO)	10.0
Magnesia (MgO)	2.5
Alumina (Al_2O_3)	0.6

Table ST3: Chemical composition of indium tin oxide (90 wt.% In_2O_3 , 10 wt.% SnO_2), used to model the electrode in the Fluka modelling.

Chemical constituent	Composition (wt.%)
In	91.5
Sn	8.47
O	0.03

Table ST4: Theoretical values of electromagnetic energy deposited in the polymer layer of paraffin wax/electrode/F8T2 (NP)/ITO diodes when irradiated by 17.5 keV Mo α X-rays, with Al and Au electrodes, and with no metal electrode. Linear trend lines fitted to the mean data are plotted in Figure 5A.

[NP] / wt. %	Electrode material / Nanoparticle											
	Deposited E.M. energy (mean $\pm$ standard deviation) / eV											
	Au / Ta		Al / Ta		None / Ta		Au / Bi ₂ O ₃		Al / Bi ₂ O ₃		None/Bi ₂ O ₃	
0	0.336	± 0.261	0.336	± 0.261	0.336	± 0.261	0.336	± 0.261	0.336	± 0.261	0.336	± 0.261
5	2.232	± 0.455	2.086	± 0.329	2.086	± 0.266	2.360	± 0.542	2.189	± 0.246	2.181	± 0.225
10	3.611	± 0.313	3.505	± 0.419	3.460	± 0.267	4.180	± 0.230	4.043	± 0.449	3.950	± 0.544
15	4.254	± 2.387	5.166	± 0.323	5.230	± 0.231	6.098	± 0.394	5.897	± 0.422	5.955	± 0.336
20	6.875	± 0.254	6.841	± 0.540	6.841	± 0.490	7.409	± 0.591	7.600	± 0.442	7.631	± 0.441
25	7.968	± 0.279	8.319	± 0.467	8.319	± 0.376	9.056	± 0.445	9.573	± 0.609	9.596	± 0.536
30	9.520	± 0.209	10.038	± 0.201	9.793	± 0.406	11.013	± 0.560	11.750	± 0.830	11.813	± 0.805
35	10.832	± 0.474	11.450	± 0.389	11.493	± 0.362	12.763	± 0.498	13.362	± 0.503	13.426	± 0.505
40	12.469	± 0.671	12.968	± 0.412	12.969	± 0.424	14.392	± 0.432	15.139	± 0.613	15.136	± 0.558
45	13.797	± 0.606	14.470	± 0.371	14.470	± 0.417	16.136	± 1.029	17.118	± 0.710	17.122	± 0.751
50	15.171	± 0.680	16.042	± 0.559	16.086	± 0.531	17.779	± 0.925	18.954	± 0.719	19.084	± 0.688
55	16.451	± 0.542	17.424	± 0.930	17.492	± 0.912	19.450	± 1.279	20.350	± 0.693	20.468	± 0.658
60	18.118	± 1.099	18.952	± 1.205	18.973	± 1.097	21.133	± 1.499	22.038	± 1.018	22.095	± 0.978
65	19.405	± 1.121	20.739	± 1.102	20.741	± 0.932	22.851	± 1.414	23.966	± 0.832	24.065	± 0.873
70	20.720	± 0.979	22.038	± 1.021	22.152	± 1.048	24.730	± 1.639	25.800	± 1.012	25.855	± 0.834
75	22.019	± 1.257	23.315	± 1.040	23.316	± 1.027	26.590	± 1.697	27.427	± 0.681	27.475	± 0.620
80	23.642	± 1.214	24.920	± 1.304	24.951	± 1.285	28.158	± 1.995	28.970	± 0.995	29.025	± 0.929
85	24.907	± 1.416	26.339	± 1.294	26.317	± 1.387	29.358	± 1.585	30.654	± 1.207	30.671	± 1.002
90	26.293	± 1.516	28.717	± 1.764	27.753	± 1.217	31.093	± 1.339	32.496	± 1.385	32.533	± 1.173
95	27.531	± 1.538	29.142	± 1.223	29.141	± 1.209	32.629	± 0.928	33.997	± 1.478	34.050	± 1.369

Sedimentation analysis

Sedimentation analysis [33] has been performed using the following parameters for Ta nanoparticles in toluene:

Particle size	= 100 nm diameter
Particle radius	R = 50 nm = 5×10^{-8} m
Density (Toluene)	ρ_{Tol} = 0.87 gcm ⁻³ = 8.7×10^2 kgm ⁻³
Density (Ta)	ρ_{Ta} = 16.69 gcm ⁻³ = 1.669×10^4 kgm ⁻³
Difference	$\Delta\rho$ = 1.582×10^4 kgm ⁻³
Viscosity (Toluene)	μ = 0.59 cP = 5.9×10^{-4} kgm ⁻¹ s ⁻¹
Evaporation rate [32]	E = 1.14×10^{-7} ms ⁻¹
Acceleration due to Gravity	g₀ = 9.80665 ms ⁻²
Thickness (wet)	H = 250 μ m = 2.5×10^{-4} m
Thickness (dry)	= 5 μ m = 5×10^{-6} m

Estimated wet thickness:

$$2 \text{ wt\% F8T2 solution} \approx 2 \text{ vol\% F8T2 solution}$$

$$100 \text{ vol \% solution} = \times 50$$

$$5 \mu\text{m thick dry F8T2 film} \times 50 = 250 \mu\text{m thick when wet}$$

Gravitational force:

$$F_g = \frac{4}{3}\pi R^3 \Delta\rho g_0 = \frac{4}{3} * \pi * (5 \times 10^{-8})^3 * 1.582 \times 10^4 * 9.80665 = 8.12 \times 10^{-17} \text{ kgms}^{-2}$$

Stokes settling velocity:

$$U_0 = \frac{2R^2 \Delta\rho g_0}{9\mu} = \frac{2 * (5 \times 10^{-8})^2 * 1.582 \times 10^4 * 9.80665}{9 * 5.9 \times 10^{-4}} = 1.46 \times 10^{-7} \text{ ms}^{-1}$$

Sedimentation number:

$$N_s = \frac{U_0}{E} = \frac{1.46 \times 10^{-7}}{1.14 \times 10^{-7}} = \underline{1.28}$$

Stokes-Einstein diffusion coefficient:

$$D_0 = \frac{kT}{6\pi\mu R} = \frac{1.38 \times 10^{-23} * 294}{6 * 3.142 * 5.9 \times 10^{-4} * 5 \times 10^{-8}} = 7.30 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$$

Péclet number for sedimentation effects:

$$Pe_{sed} = \frac{HU_0}{D_0} = \frac{2.5 \times 10^{-4} * 1.46 \times 10^{-7}}{7.30 \times 10^{-12}} = \underline{5.0}$$