High-Z nanoparticles for enhanced sensitivity in semiconducting polymer X-ray detectors

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Abstract

Semiconducting polymers have previously been used as the transduction material in X-ray dosimeters, but these devices have a rather low detection sensitivity because of the low X-ray attenuation efficiency of the organic active layer. Here, we demonstrate a way to overcome this limitation through the introduction of high density nanoparticles having a high atomic number (Z) to increase the X-ray attenuation. Specifically, bismuth oxide (Bi2O3) nanoparticles (Z = 83 for Bi) are added to a poly(triarylamine) (PTAA) semiconducting polymer in the active layer of an X-ray detector. Scanning electron microscopy (SEM) reveals that the Bi2O3 nanoparticles are reasonably distributed in the PTAA active layer. The reverse bias d.c. current-voltage characteristics for PTAA-Bi2O3 diodes (with indium tin oxide (ITO) and Al contacts) have similar leakage currents to ITO/PTAA/Al diodes. Upon irradiation with 17.5 keV X-ray beams, a PTAA device containing 60 wt.% Bi2O3 nanoparticles demonstrates a sensitivity increase of approximately 2.5 times compared to the plain PTAA sensor. These results indicate that the addition of high-Z
nanoparticles improves the performance of the dosimeters by increasing the X-ray stopping power of the active volume of the diode. Because the Bi$_2$O$_3$ has a high density, it can be used very efficiently, achieving a high weight fraction with a low volume fraction of nanoparticles. The mechanical flexibility of the polymer is not sacrificed when the inorganic nanoparticles are incorporated.

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**Keywords**: Poly(triarylamine) (PTAA), conjugated polymer, Organic electronics, high Z nanoparticles, X-ray sensors.

### 1. Introduction

Conventional silicon-based detectors are currently the first choice for X-ray radiation detection applications. However, despite excellent performance, silicon suffers from several major drawbacks. The size of the detector is limited to the size of available wafers, usually six or eight inches, and the wafer cannot bend to fit curved surfaces. Large-area, high quality silicon is relatively expensive, and it is difficult to fabricate. Hence, there is a need for new materials that offer unique solutions to overcome these problems.

The field of organic electronic devices has evolved dramatically over the past 20 years in line with the development of semiconducting polymers. Primarily, applications for these polymers utilize the organic material as an active component in a variety of electronic devices, such as light emitting diodes [1], field effect transistors [2], photovoltaic cells [3], lasers [4], and sensors [5].

The advantage of using semiconducting polymers in electronic devices is the ease of fabrication. Polymer solutions, stable under ambient conditions, can easily be obtained by dissolving conjugated polymers in common organic solvents, enabling the
possibility of large-area device production using low-cost, wet processing techniques, such as spin-casting, spray-casting, and ink-jet or roll-to-roll printing [6]. Currently, organic electronic devices are at the point at which they are beginning to rival the performance of their equivalent inorganic semiconductor-based devices.

At the current time however, only a small number of scientific publications have reported the use of conjugated polymers in the detection of ionizing radiation. For detector applications to be realized, these key requirements must be met: a low dark current at high field strength; good rectification behavior; high charge-carrier mobility; and high X-ray stopping power (i.e. strong attenuation). We have previously reported on ITO/semiconducting polymer/Al devices, with low dark currents in reverse bias operation [7, 8].

The detection of ionizing particles can be divided into two different categories, namely direct and indirect detection. Indirect detection relies on a secondary transduction method, such as the optical monitoring of turbidity or scintillation [9, 10]. For instance, the optical properties of poly(phenylene vinylene) (PPV) and its derivative (MEH-PPV) have been modulated after exposing to proton [11] or gamma radiation [12]. Direct detection, on the other hand, measures a change in current directly generated by the material upon exposure to ionizing radiation, producing the advantage of providing real-time radiation detection. Previously, direct detection of electron [13] and alpha (α) particles [14, 15] has been achieved using polymers as the active layer. We have recently shown that direct X-ray induced photocurrents can be observed in metal/semiconducting polymer/metal diode structures [7, 8, 16, 17] indicating the feasibility of using conjugated polymers in direct real-time radiation detection applications. The addition of small organic semiconducting molecules to
the polymer increased the charge-carrier mobility, which resulted in increased X-ray sensitivities [18].

Unfortunately, due to the typically low atomic number (Z) of their constituent atoms, conjugated polymers provide a low attenuation (stopping power) for ionizing radiation (such as X-rays) in comparison to conventional materials used for radiation detectors, such as cadmium telluride (CdTe). In order to retain the advantages of the polymer (mechanical flexibility and low dark current) but enhance the attenuation efficiency of the conjugated polymer, the inclusion of a high atomic number (high-Z) material in the polymer layer has been previously examined. For example, Wang et al have reported X-ray photoconductivity measurements on Bil3-nylon-11 high-Z composite thick films [19]. Campbell et al. have demonstrated an increase in luminescence, by more than one order of magnitude, in a blend of MEH-PPV and CdSe-ZbSe core-shell quantum dots upon electron irradiation [20]. Alternatively, composites of high-Z Bil3 and HEH-PF semiconducting polymer have demonstrated PL quenching upon gamma radiation [21]. The PL intensity produced by the composite decreased linearly with increasing dosage, while pure HEH-PF showed a stable PL intensity upon gamma irradiation.

Here, we have investigated a nanocomposite material for direct X-ray detection consisting of high-Z bismuth oxide (Bi$_2$O$_3$) nanoparticles and poly(triarylamine) (PTAA) [22-24] semiconducting polymer. Nanoparticles have been used in this study instead of the bulk material because the nanoparticles uniquely offer high cross sectional area for X-ray interaction, and potentially allow simple integration into the semiconducting polymer matrix. Use of materials with a high density ensures that a high weight concentration can be achieved with a comparatively low volume concentration. Performance parameters for device applications,
comprising the current-voltage characteristics, signal-to-noise ratio and sensitivity, have been obtained. Improvements in performance have been observed upon the introduction of Bi$_2$O$_3$ nanoparticles.

2. Materials and Methods

The details of device fabrication can be found elsewhere [7]. In brief, a 5 wt% solution of PTAA was prepared by dissolving PTAA, molecular weight ($M_w$) of $3.1 \times 10^4$ g/mol and a polydispersity (PDI) index ($M_w/M_n$) of 2.07, in toluene (Sigma-Aldrich). After adding Bi$_2$O$_3$ nanopowder (99.9% purity, diameter <100 nm, Sigma-Aldrich), the solution was homogenized for half an hour in a sonicated water bath. The blend solution was then spin-cast at 50 rpm for 30 s on top of the ITO (sheet resistance of 25 $\Omega$, Delta Technology Ltd., USA (CB-60IN)) providing a single polymeric active layer with an approximate thickness of 20 $\mu$m. The films were initially left to dry under atmospheric conditions and then were annealed under vacuum at 150°C, which is above the glass transition temperature of the polymer ($T_g \approx 103^\circ$C) [7], for 12 hours to eliminate any trapped solvent. The thickness of the active layer was then measured using a surface profilometer (Dektak, Veeco Instruments). The device fabrication was completed by thermal evaporation of aluminum (Al) contacts (100 nm thick, 0.5 x 0.5 cm$^2$) on top of the active layer to create a Schottky contact. After attaching filament wires to the respective electrodes, the devices were coated with paraffin wax (Logitech Ltd, UK) by dip-coating the diode into the molten wax. The diodes were stored under nitrogen and in the dark to reduce any oxidation effects and to limit dust contamination.

Nanocomposites were prepared with target Bi$_2$O$_3$ concentrations of 20, 40 and 60 wt.%, expressed on the total weight of the dry material. To determine the precise
concentration of Bi$_2$O$_3$ nanoparticles in the nanocomposites, thermogravimetric analysis (TGA) was carried out under a nitrogen atmosphere, using TGA apparatus (Q500, TA Instruments) from 20°C to 700°C with a heating rate of 10 °C/min. Drop-cast PTAA thick films with different weight percentages of Bi$_2$O$_3$ nanoparticles were analysed. Scanning electron microscope (SEM) was performed using a Hitachi S-4000 electron microscope with an electron energy of 10 kV. Energy dispersive X-ray (EDX) analysis was completed using a scanning electron microscope (Hitachi S-3200N) equipped with a silicon drift detector (Oxford Instrument). The current-voltage (I-V) characteristics were investigated by applying a voltage to the ITO electrode and measuring a resulting current from the Al electrode using an integrated voltage source-picoammeter (487, Keithley Instruments, UK). The X-ray photocurrent measurements of the devices were completed using 17.5 keV Kα X-rays from a molybdenum target X-ray tube (XF50 11, Oxford Instruments). The diode was placed 10 cm away from the X-ray tube, in the dark and at room temperature. The diode was then irradiated by the X-ray beam through the Al top contact. The X-ray photocurrent was recorded at a fixed reverse bias using the voltage source-picoammeter.

3. Results and discussion

To produce an X-ray induced photocurrent in a semiconductor, the incident X-ray beam has to be absorbed by the material, and therefore interact with its atoms to produce free charge carriers. The ability for a certain material to attenuate X-rays is called the attenuation quantum efficiency (Q.E.) and can be expressed by this equation:

\[
Q.E. = (1 - e^{-\frac{\mu}{\rho}}) \times 100\% ,
\]

where \( \frac{\mu}{\rho} \) is the mass attenuation coefficient obtained from a photon attenuation
database [25], and $\rho$ and $x$ are the density and thickness of the material, respectively. Figure 1 shows the calculated theoretical quantum efficiency of a 20 µm thick composite film, upon irradiation with 17.5 keV X-rays, as a function of Bi$_2$O$_3$ nanoparticle concentration (by weight). The Q.E. increases exponentially, rising by a factor of 10 as the concentration of the nanoparticles increases from 10 wt.% to 60 wt.%, reaching an X-ray attenuation efficiency of 30% found for the PTAA layer blended with 60 wt% of Bi$_2$O$_3$ nanoparticles. These simulations indicated that, in principle, the attenuation quantum efficiency of the device can be raised by adding a high atomic number material into the polymer active layer.

Thermogravimetric analysis has been performed in order to confirm the weight percentage of Bi$_2$O$_3$ nanoparticles in the PTAA film. Figure 2 shows the thermogram from room temperature up to 700°C for various concentrations of Bi$_2$O$_3$ nanoparticles in the PTAA layer. The thermal decomposition regime for the PTAA film (line a) is found to be in the range of 500-550°C with a maximum weight loss of about 70%. The weight of pure Bi$_2$O$_3$ nanoparticles remains constant throughout the experimental temperature range (line e). The PTAA films loaded with an increasing concentration of Bi$_2$O$_3$ nanoparticles leave behind residuals with decreasing percentage weight loss (line b-e). The weight percentage of Bi$_2$O$_3$ nanoparticles was subsequently back-calculated (Table 1), and values of 19 wt.% (sample Bi20), 38 wt.% (sample Bi40) and 56 wt.% (sample Bi60) of Bi$_2$O$_3$ nanoparticles in the PTAA films are estimated for lines b, c and d, respectively. (The number in the sample name indicates the target Bi$_2$O$_3$ concentration, expressed as wt.% on the total dry material.)

It is noted that nanoparticle loss during film formation by spin-casting is unavoidable, and hence the weight percentages of Bi$_2$O$_3$ nanoparticles in the PTAA layer deviate from the initial solution concentration. Table 1 also lists the nanoparticle
concentrations expressed as volume percentage, estimated using a density of 8.9 g cm\(^{-3}\) for Bi\(_2\)O\(_3\) [26] and 1 g cm\(^{-3}\) for PTAA.

The distribution of Bi\(_2\)O\(_3\) nanoparticles in the PTAA layer was examined using SEM. Figure 3A shows an example of a cross-sectional SEM image of a Bi60 thick film. The majority of the nanoparticles are observed at the bottom of the polymer layer, near to the ITO electrode. This is probably because the Bi\(_2\)O\(_3\) nanoparticles are not well dispersed in common organic solvents, such as toluene in this case, and they settled to the bottom of the film during spin-casting. However, they are clearly dispersed homogeneously throughout the polymer layer in the plane of the film. No large scale aggregation of the nanoparticles is seen. The majority of the nanoparticles have a diameter well within the range from 100 to 300 nm. Larger particles are attributed to agglomeration between two or more nanoparticles and to limits in the microscope’s resolution. Figure 3B represents the elemental characteristic composition of the Bi60 sample using EDX analysis in mapping mode. The various false colours in the image correspond to the different compounds (identified through elemental analysis). This analysis confirms that the nanoparticles are mainly situated in the lower section of the PTAA film, near to the ITO substrate.

In the Bi60 material with a high weight concentration of nanoparticles, the overall volume concentration is only 12.5% (although locally the concentration is higher). The high density of the Bi\(_2\)O\(_3\) provides a high efficiency of nanoparticle loading. Mono-sized hard spheres reach random close-packing at volume concentrations of approximately 60% [27]. At higher nanoparticle concentrations, there would not be enough polymer available to bind randomly-packed particles and hence voids would develop in the composite. At nanoparticle concentrations of 60 wt.%, however, the loading is far below this limit.
Dark current-voltage characteristics for the PTAA-Bi$_2$O$_3$ nanoparticle diodes are presented in Figure 4A. In all cases, the thickness of the active layer is approximately 20 µm, according to surface profilometry. Voltages ranging from -100 V to 100 V were applied to the ITO electrode. For the ITO/pristine PTAA/Al diode, the I-V curve shows a rectifying behavior with a reverse bias leakage current density of 0.65 nA cm$^{-2}$ at -100 V (field strength of 50 kV cm$^{-1}$). Reverse bias operation is achieved when the ITO is negatively biased. I-V curves for the diodes containing Bi$_2$O$_3$ nanoparticles still show a low reverse bias leakage current density (0.25-0.9 nA cm$^{-2}$ at -100 V). However, the rectifying behavior for these devices is deteriorated in the presence of the nanoparticles. The rectification ratio is reduced from 40 in the PTAA device to values between 1.5 and 4 in the blend devices. However, only the dark current in the forward bias is affected by the addition of the nanoparticles, while the dark current in reverse bias gives a similar value to that of the pure PTAA-based diode. This shows that the presence of high-Z nanoparticles does not alter the electrical performance of the PTAA diodes in reverse bias operation. A low leakage current at a high field strength is critical for detector applications to ensure the maximum drift photocurrent.

Figure 4B displays the time-dependent corrected X-ray response as a function of increasing dose rate (from 13 to 66 mGy s$^{-1}$) (after subtraction of the dark current) for various concentrations of Bi$_2$O$_3$ nanoparticles in the PTAA film. The devices in this case were operated at -150 V (reverse bias). The X-ray source was alternately switched on and off for periods of 90 s for each applied dose rate. Note that the reverse bias operation creates an X-ray photocurrent with a negative value, but typically data presented in the literature are reversed in order to provide a positive current value. The X-ray photocurrent from the detectors increases as the dose rate of
the incident X-ray increases. It is clear that the induced X-ray photocurrent depends on the concentration of the doped Bi$_2$O$_3$ nanoparticles included in the polymer matrix. For instance, at the X-ray dose rate of 66 mGy s$^{-1}$ the X-ray photocurrent increases from 2.4 nA for the ITO/PTAA/Al device to 6.4 nA for the ITO/Bi60/Al device. This holds true for all applied dose rates and voltages. (See Figure S1 in the Supplementary data.)

The signal-to-noise ratio is defined by the ratio between the corrected X-ray photocurrent and the dark current. Figure 4C shows the signal-to-noise ratio as a function of applied voltage for the ITO/pure PTAA/Al and the ITO/Bi60/Al devices at an X-ray dose rate of 66 mGy s$^{-1}$. Although the dark current from both samples is similar (Figure 4A), the signal-to-noise ratio for the Bi60 device is higher than that of the PTAA device. However, the signal-to-noise ratio for both devices diminishes at a high operational voltage as the dark currents of the devices increase. The lowest value of the signal-to-noise ratios are 28 for the ITO/Bi60/Al device and 12 for the ITO/pure PTAA/Al device. Both of these ratios are greater than 1, which means that the generated photocurrent signal is still greater than the leakage current. One of the major requirements for the material to be realised in detector applications is a high signal-to-noise ratio.

Figure 5A presents the relationship between the corrected X-ray photocurrent and X-ray dose rate for all devices at an operational voltage of -150 V. (See Figure S2 in the Supplementary Data for other applied voltages). All devices show a linear response with an increasing incident X-ray dose rate. Figure 5B shows the sensitivity of the devices as a function of the applied voltage. The device sensitivity to ionizing X-rays was obtained at a particular voltage by dividing the slope of the graph of X-ray photocurrent versus dose rate by the active volume of the sensor. All devices exhibit a
similar behavior in which the sensitivity increases as the applied reverse bias increases, and it approaches saturation at high applied voltages. For devices with a low concentration of Bi$_2$O$_3$ nanoparticles (e.g. 20 wt.%), the calculated sensitivities are similar to those obtained from the PTAA device. There is a clear increase in the device sensitivity when the PTAA layer is loaded with a high concentration of Bi$_2$O$_3$ nanoparticles (e.g. 60 wt.%). An increase in the sensitivity by approximately 2.5 times, from 78 nC mGy$^{-1}$ cm$^{-3}$ in the PTAA device to 200 nC mGy$^{-1}$ cm$^{-3}$ in the Bi60 device, has been observed (when operated at -200 V). The experimental increase in the photocurrent can be compared with the theoretical increase in quantum efficiency (Figure 1). The photocurrent (Figure 5A) increases from 3 nA to 6.7 nA for the 20 wt% Bi$_2$O$_3$ and 60 wt% Bi$_2$O$_3$ samples, respectively, indicating an approximately 2.5 times increase in output current with the increase in Bi$_2$O$_3$ nanoparticle concentration. By comparison, the theoretical quantum efficiency increases six-fold, from 5.5% to 28.6%, for the equivalent concentrations. The observed increase in output current is therefore approximately 40% of that expected from the quantum efficiency calculations. After the addition of the Bi$_2$O$_3$ nanoparticles, the polymer retains its mechanical flexibility, as is illustrated visually in Figure 6. In comparison to inorganic detectors, such as Si or CdTe, the polymer/inorganic composite offers a clear advantage for applications that require flexibility. Although our present study used rigid ITO/glass substrates, devices could be fabricated with metal-coated polymer substrates, as we reported previously [17], to create a flexible detector.

Our results clearly show that adding the high-Z nanoparticles into the active layer of the devices leads to an improvement of the device performance by providing a higher induced X-ray photocurrent and sensitivity due to increased X-ray quantum efficiency while retaining mechanical flexibility. The theoretical result is consistent
with a higher sensitivity observed in the device with Bi$_2$O$_3$ nanoparticles. Without the nanoparticles, the majority of X-rays pass through the device without interacting with the polymer matrix. Only a small proportion of them are attenuated by the PTAA layer, resulting in a relatively poor sensitivity. The high-Z nanoparticles act as X-ray absorbers, which then produce secondary, lower energy X-ray and electron showers, which are more likely to interact directly with the polymer, or alternatively they become charged, inducing the formation of charge on the polymer in a typical semiconductor donor/acceptor method.

The comparison of the output current with the theoretical quantum efficiency suggests that the output current achieved with these devices should be somewhat better. One explanation may come from Figure 3, which shows that the majority of the nanoparticles in our devices are positioned closer to the ITO electrode, onto which the PTAA is spun down, rather than near the Al electrode. Our previous work on PTAA X-ray detectors, [7] has identified that the depletion layer in these diodes lies adjacent to the Al electrode. Charges produced in this region are swiftly removed from the diode, reducing the possibility of recombination effects that may reduce diode efficiency. Consequently, the effect of the nanoparticles in the diode may be diluted by their positioning away from the depletion region, and device performance may be enhanced if the nanoparticles can be more effectively dispersed throughout the polymer.

Finally, the diodes produced here were the most simple possible, consisting merely of a nanoparticle-loaded semiconducting polymer sandwiched between two electrodes, to ensure that any enhancement seen in diode performance was due only to the presence of the nanoparticles. Detector performance may be improved further by designing the diodes to enhance charge production and transfer through the diode. For
example, the addition of charge transport layers at the electrodes will facilitate the transfer of charged species out of the detector and improve the output current. Enhanced diode architecture such as this, allied to the addition of the nanoparticles, will likely further improve device performance. Finally, we have previously found that the addition of small organic molecules into the semiconducting polymer layer increases the charge carrier mobility by a factor of 17, which results in an increase in the sensitivity of four times [18]. A promising strategy is therefore to combine high-Z nanoparticles and small organic molecules into a single device. An even higher sensitivity is expected, provided that the effects of greater attenuation and faster charge transport in the device are additive.

4. Conclusions

In conclusion, X-ray detectors have been successfully fabricated using poly(triarylamine)-Bi$_2$O$_3$ nanocomposites as an active material. With the introduction of high-Z Bi$_2$O$_3$ nanoparticles, the diodes retain a low reverse bias leakage current density (<1 nA/cm$^2$ at -100 V), and are used to detect X-rays at dose rates ranging from 13 to 66 mGy s$^{-1}$. The performance of the devices, including induced X-ray photocurrent, signal-to-noise ratio and sensitivity, is improved by inclusion of the high-Z nanoparticles. Owing to the high density of the Bi$_2$O$_3$, high nanoparticle loadings can be achieved with a low volume concentration, such that the mechanical flexibility of the polymer is not sacrificed. These results indicate that devices made with PTAA/Bi$_2$O$_3$ nanocomposites, when deposited on flexible substrates, are very promising candidates for use as next-generation flexible X-ray detectors.
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Figures

**Figure 1.** Theoretical quantum efficiency of a 20 µm thick film of PTAA blended with different percentage concentrations of Bi$_2$O$_3$ nanoparticles.

**Figure 2.** Thermogravimetric analysis of (a) pure PTAA film, (b) PTAA blended with 20 wt% of Bi$_2$O$_3$ (Bi20), (c) PTAA blended with 40 wt.% of Bi$_2$O$_3$ (Bi40), (d) PTAA blended with 60 wt.% of Bi$_2$O$_3$ (Bi60) and (e) pure Bi$_2$O$_3$ nanoparticles.
Figure 3  (A) An SEM image (10,000 times magnification, scale bar = 3 µm) and
(B) EDX analysis of the cross-section of a Bi60 sample on an ITO substrate. The
materials are represented as follows: PTTA is red; Bi$_2$O$_3$ is green; and ITO is violet.
The two white lines are drawn to designate the top and bottom edges of the cross-
section.
Figure 4  (A) Semi-log current-voltage characteristics for the ITO/pure PTAA/Al (—), ITO/Bi20/Al (---), ITO/Bi40/Al (□) and ITO/Bi60/Al (▲) diodes. (B) Time-dependent X-ray response for the PTAA-based dosimeters, with 20 µm thick active layers, at an operational voltage of -150 V, when active materials are (a) pure PTAA, (b) Bi20, (c) Bi40 and (d) Bi60. Irradiation of 17.5 keV X-rays is achieved with increasing dose rates (13, 27, 40, 54 and 66 mGy/s) through the Al contact. (C)
Signal-to-noise ratio versus voltage plot for the devices with pure PTAA (○) and Bi60 (▲) active layers irradiated at an X-ray dose rate of 66 mGy/s.

**Figure 5**  
(A) The X-ray photocurrent as a function of dose rate at an applied voltage of -150 V. (B) Sensitivity, calculated using data from Figure 4B, as a function of applied voltage for the ITO/pure PTAA/Al (●), ITO/Bi20/Al (□), ITO/Bi40/Al (▲) and ITO/Bi60/Al (◇) diodes.
Figure 6  Photograph of a PTAA-Bi2O3 film (Bi60) after peeling off of an ITO/glass substrate. The polymer retains its mechanical flexibility after the addition of the inorganic nanoparticles.
Table 1. Measured Bi$_2$O$_3$ nanoparticle concentration in the PTAA films obtained using TGA

<table>
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<tr>
<th>Sample Name</th>
<th>Bi$_2$O$_3$ Concentration in Dry Film</th>
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<tr>
<td></td>
<td>Weight %</td>
</tr>
<tr>
<td>Bi20</td>
<td>19</td>
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<td>Bi40</td>
<td>38</td>
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<tr>
<td>Bi60</td>
<td>56</td>
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Supplementary data, Figure S1. Time-dependent X-ray responses for the PTAA-based dosimeters with no Bi$_2$O$_3$ (black line), 20 wt.% Bi$_2$O$_3$ (red line), 40 wt.% Bi$_2$O$_3$ (green line) and 60 wt.% Bi$_2$O$_3$ (blue line) nanoparticles when operated at (A) -10 V, (B) -20 V, (C) -40 V, (D) -100 V, (E) -150 V and (F) -200 V. The devices were irradiated using 17.5 keV X-rays through the Al electrode with increasing dose rates (13, 27, 40, 54 and 66 mGy/s).
Supplementary data, Figure S2. Corrected X-ray photocurrent versus X-ray dose rate for (A) ITO/PTAA/Al, (B) ITO/Bi20/Al, (C) ITO/Bi40/Al and (D) ITO/Bi60/Al dosimeters. The data was taken from Figure S1. The straight line shows the best linear fit for the graph.