Growth and characterization of PbI$_2$-decorated ZnO nanowires for photodetection applications

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abstract

In this study, we demonstrated for the first time the growth of ZnO nanowires (NWs) decorated with highly crystalline few-layer PbI$_2$ and fabricated two-terminal single-nanowire photodetector devices to investigate the photoelectric properties of the hybrid nanostructures. We developed a novel two-step growth process for uniform crystalline PbI$_2$ nanosheets via reactive magnetron deposition of a lead oxide film followed by subsequent iodination to PbI$_2$ on a ZnO NW substrate, and we compared as-grown hybrid nanostructures with ones prepared via thermal evaporation method. ZnO@PbI$_2$ NWs were characterized by scanning and transmission electron microscopy, X-ray diffraction analysis and photo-luminescence measurements. By fabricating two-terminal single-nanowire photodetectors of the as-grown ZnO@PbI$_2$ nanostructures, we showed that they exhibit reduced dark current and decreased photoresponse time in comparison to pure ZnO NWs and have responsivity up to 0.6 A/W. Ab initio calculations of the electronic structure of both PbI$_2$ nanosheets and ZnO NWs have been performed, and show potential for photocatalytic hydrogen production. The obtained results show the benefits of combining layered van der Waals materials with semiconducting NWs to create novel nanostructures with enhanced properties for applications in optoelectronics or X-ray detectors.

1. Introduction

The surface plays an exceptionally important role in deter-mining nanomaterial physical and chemical properties. The impact of surface modification on nanoscale material properties has been intensively explored for the last few decades [10-13]. Nanowires (NWs) are one-dimensional (1D) nanomaterials that exhibit promising properties beneficial for integration in functional de-vices, such as photodetectors, nanolasers, LEDs, etc. [4,5], and modification of their surface can significantly improve their elec-trical, optical and mechanical characteristics [3,4,6]. Modification or decoration of a NW surface has no restrictions of material lattice mismatch and its caused stress at the interface, unlike the con-ventional thin film growth [5,7,8], therefore, opening new possi-bilities to engineer novel hybrid nanostructures with desired properties, such as photon detection capability in a broad spectral range [9]. Currently, most research in this field is focused on developing precisely controllable nanostructure fabrication methods and tuning nanostructure properties for specific applica-tions [6,7,9].

Zinc oxide (ZnO) is one of the most commonly studied NW materials due to its simple synthesis and wide field of applications, such as ultraviolet photodetectors [10,11] and piezoelectric nano-generators [12], as well as the potential to be a scintillator material for X-ray detectors [13-15]. ZnO is an n-type semiconductor with a direct bandgap around 3.2 eV and it has a high exciton binding energy (60 meV), which allows room temperature excitonic emis-sion [16]. ZnO NWs have frequently been used as template material for nanomaterial synthesis [17,18]. Furthermore, in several studies, it has been demonstrated that passivating the surface of ZnO nanostructures or decorating the NWs with specifically selected materials enhances light and gas detecting properties [19-24].

Lead (II) iodide (PbI$_2$) is a photoconductor material with 2.2 eV bandgap [25] and is typically employed in fabricating perovskite solar cells and photodetectors [26-30], and as an X-ray and g-ray detector material [31-34]. PbI$_2$ has a layered structure in which the covalently bonded PbI$_6$ repeating layers are bound by weak van der Waals (vdW) interaction [35]. Recently, it has gained more attention due to the extensive research on various 2D vdW materials, such as graphene and transition metal dichalcogenides.
There are theoretical and experimental studies that show band structure shift from direct bandgap to indirect bandgap when the PbI$_2$ thickness is reduced from bulk to monolayer [35,38], as opposed to well-studied vdW materials, MoS$_2$, for example [39]. Therefore, monolayer PbI$_2$ is not expected to be an efficient mate-rial for optoelectronics applications. In the last few years, there have been several studies that demonstrate the growth of few-layer PbI$_2$ crystals and investigate their promising photodetection properties both on rigid and flexible substrates [25,35,40,42]. The growth of 1D PbI$_2$ NWs for high-sensitivity photodetector applications has also been reported [43]. Zhang et al. proposed low-temperature heteroepitaxial growth of PbI$_2$ thin film on submeter-sized graphene/polyethylene terephthalate (PET) sub-strate and showed its applicability in light detection [44]. However, there are challenges remaining in obtaining highly-crystalline and uniform large-area PbI$_2$ films.

Alternatively, NWs can be used as a template for growth and easier manipulation of layered vdW materials, such as WS$_2$ and MoS$_2$, while maintaining the high crystallinity of the materials used and even enhancing their properties [20,45,47]. Large-scale printing of NWs at specified locations on flexible substrates via roll-to-roll transfer has been demonstrated [48], therefore enabling the advancement of all-printed layered material- and NW-based electronic and optoelectronic devices in the future. Furthermore, some research has been done on the development of high-resolution NW-arrays for X-ray imaging [49,50]. There are also few reports on using single-nanowire devices for X-ray detection and beam shape characterization [51,53].

Consequently, using ZnO and PbI$_2$ materials in 1D hybrid nanostructures could potentially lead to next-generation high-resolution direct-conversion digital X-ray detector devices with advanced properties.

In this work, we demonstrate two different approaches to syn-thise novel 1D ZnO@PbI$_2$ nanostructures. Highly crystalline few-layer PbI$_2$ was grown on ZnO NWs by: (1) direct thermal evapo-ration of PbI$_2$ powder, and (2) the conversion of a sputter-deposited lead oxide coating in iodine vapour at an elevated temperature. Two-terminal single-nanowire photodetectors were fabricated to show their enhanced photoelectric properties compared to pure ZnO NWs. The results show the potential of combining layered vdW materials with semiconducting nanowires to create novel nano-structures with advanced properties for potential photodetection applications. From our ab initio modelling, nanosized ZnO@PbI$_2$ heterostructures might be used for efficient photocatalytic hydrogen production from water.

2. Experimental details

2.1. Nanostructure synthesis and characterization

ZnO NWs were synthesised on oxidized silicon wafers SiO$_2$/ Si(100) (Semiconductor Wafer, Inc.) via atmospheric pressure chemical vapour transport in an open-end horizontal quartz tube reactor using spherical Au nanoparticles (Smart materials, water suspension, 100 nm diameter) as a catalyst for the vapour-liquid-solid mechanism [54]. In short, 0.5 g of a 1:1 mixture of ZnO and carbon powders was loaded in a ceramic boat in the centre of the quartz tube at 900°C. The vapour was transported downstream to the Au/Si substrate at a lower temperature region using N$_2$ as a carrier gas. The temperature was held constant for 90 min, followed by natural cooling to the room temperature. See Fig. S1 for the scanning electron microscope (SEM) images and X-ray diffraction (XRD) pattern of the as-grown ZnO NWs.

In the next step, a few layers of PbI$_2$ were deposited on the as-grown ZnO NW arrays via two different approaches: (1) thermal evaporation of a PbI$_2$ powder and (2) sputter deposition of a lead oxide coating followed by iodination at elevated temperatures. Both evaporation and sputtering were carried out in a Sidrabe SAF25/50 multifunctional cluster tool. In the first method, a simple thermal evaporation process was carried out in a vacuum chamber at 10$^{-5}$ torr while rotating the ZnO NW sample (60 mg PbI$_2$ powder was evaporated from an Al$_2$O$_3$ crucible). The second method con-sists of two steps. First, a lead oxide PbO$_x$ coating (consisting of different phases, including PbO and PbO$_2$ as shown by the XRD data in Fig. S2) was obtained by reactive DC magnetron sputtering of a metallic lead target in a mixed Ar/O$_2$ atmosphere (20s$\mathrm{litre}$ of Ar and 10 sccm O$_2$ gas flows, 5 min of sputtering at 100 W DC power). Second, as-prepared ZnO-PbO$_x$ samples were annealed in a quartz tube in an iodine atmosphere for 15 min using an Ar/H$_2$ 5% mixture as the carrier gas to convert lead oxide to lead iodide. An iodine-rich atmosphere was obtained by placing 0.25 g iodine powder upstream of the sample at 120°C. The optimal annealing temperature was found to be 420°C, and the lead oxide conversion to PbI$_2$ starts around 350°C. One must optimize between a high coating crystallinity and the sublimation rate of the converted PbI$_2$ film, which increases rapidly above 400°C. As a reference sample for comparison, a PbI$_2$ thin film on SiO$_2$/Si substrate was prepared using the second approach.

The as-prepared nanostructure morphology was characterized using SEM-FIB (Lyra, Tescan), while the crystalline structure of the PbI$_2$ coating and ZnO NW was using a transmission electron mi-croscope (TEM, Tecnai GF20, FEI) operated at 200 kV accelerating voltage. The phase composition of the samples was studied using XRD (Q Q Bragg Brentano powder diffractometer PANalytical X’Pert Pro) with monochromatic Cu Kα irradiation and the spectra were analysed using PDXL2 software. Room-temperature photo-luminescence (PL, Hamamatsu R922 PMT) spectra with a 266 nm excitation wavelength (fourth harmonic of CryLas Nd:YAG laser, 0.3 mJ power, 1 ns pulse duration, 5 kHz repetition rate) were measured to investigate the as-prepared nanostructure optical properties.

2.2. Single nanowire two-terminal photodetector device fabrication

To fabricate two-terminal single-nanowire photodetectors, first, gold microelectrodes with a 2 μm gap width were prepared on an oxidized silicon wafer by a conventional photolithography tech-nique (see Fig. S3). The microelectrode array pattern was obtained using direct-write laser lithography (μPG101, Heidelberg In-struments) on Megaposit SPR700 photoresist (Rohm and Haas Electronic Materials), 5/45 nm Cr/Au film was deposited via thermal evaporation method followed by a lift-off procedure. Second, NWs were transferred onto the electrode array by mechanically pressing it to the substrate with the as-grown nanostructures, followed by welding selected single NWs to the corresponding underlying gold microelectrodes using electron-beam-assisted platinum deposition inside SEM-FIB to ensure the electric contact and fixed position. At least ten single-nanowire photodetectors (more than five for each synthesis method) were fabricated so consistent conclusions could be made.

2.3. Device measurements

Current voltage (I–V) characteristics and photoresponse of the fabricated single-NW photodetector devices were measured with a two-contact microprobe station connected to a low-noise current preamplifier (SR570, Stanford Research Systems) and oscilloscope (TDS2004B, Tektronix). A 405 nm wavelength semiconductor diode laser (CNI Laser) with 1 W/cm$^2$ power was the illumination source for the photoresponse measurements. An optical beam shutter (Thorlabs SH05) was used for time-resolved measurements. All the
measurements were performed at room temperature and in air.

2.4. Computational details

Total energy first-principle calculations for [0001]-oriented mono- (ML), bi- (2 ML) and three-layered (3 ML) PbI$_2$ nanosheets, and 24-layer thick [10100] oriented slabs, to mimic the surface of ZnO nanowires, were performed using the HSE06 hybrid exchange-correlational functional [55] within the density functional theory (DFT), as implemented in the computer code CRYSTAL17 [56]. Localized Gaussian type functions (GTFs) in the form of atom-centred basis sets (BSs) for expansion of periodic crystalline orbitals for Zn and O were taken in the form of full electron Triple-Zeta pseudopotential BS were taken for Pb and I [56]. The reliability of the chosen theoretical method were proven by calculations of bandgap energy (d) for bulk phase ZnO and PbI$_2$ crystals (see Fig. S5). The calculated bandgaps for all materials under study are in good agreement with those experimentally observed. To provide a balanced summation in both direct and indirect bandgaps for all materials under study are in good agreement with those when the total energy differed by less than $10^7$ a.u. in two successive cycles of the self-consistent field (SCF) procedure [56]. Full geometry optimization was performed for all nanostructures considered in this study.

3. Results and discussion

3.1. Morphology, structure and photoluminescence measurements

SEM was used to image as-grown individual NWs and NW arrays and study their morphology. Pure ZnO NWs are typically 200~300 nm long with a diameter around 100 nm and exhibit a smooth surface (see Figs. S1(a and b)). Fig. 1(a and b) shows ZnO NWs with a thermally deposited PbI$_2$ coating. No significant change in diameter is observed; however, a very fine increase in surface roughness is visible. NWs with a sputter-deposited lead oxide coating with a fine roughness are shown in Fig. 1(c and d), where a considerable (up to 100 nm) increase in diameter can be seen. After annealing such NWs in iodine vapour at elevated temperatures, the surface roughness greatly increased; however the diameter is significantly reduced as a fraction of the coated material is sublimated after the transformation (see Fig. 1(e and f)). The final coating is not uniform over the entire length of NWs as some thicker particles and islands can be observed. SEM images of the reference sample, PbI$_2$ thin film converted from sputter-deposited lead oxide, are shown in Fig. 1(g and h). The film exhibits hexagonal domains, presumably highly crystalline as PbI$_2$ typically crystallizes in a hexagonal structure.

A deeper insight into the nanostructures’ inner structure was obtained using TEM. Fig. 2(a and c) shows TEM images of ZnO@PbI$_2$ NWs obtained by the thermal evaporation method at different magnifications. The lower resolution images show noticeable contrast between the two NW sides (PbI$_2$ layers correspond to the darker region), indicating non-uniform coating deposition, which is expected from the thermal evaporation approach since it is a line-of-sight method. At a high resolution, the crystalline structure of the nanostructure is revealed. The layers of PbI$_2$ grown on the ZnO NW surface are distinguishable as parallel black lines. Typically, the thickness of the coating varies between 5 and 10 monolayers (each consisting of 10PbI$_6$ atomic planes), with interlayer distance measured around 7 Å, which is in good agreement with the lattice constant (a $\frac{1}{4}$ 6.979 Å) of bulk hexagonal PbI$_2$ (ICDD-PDF #070235). Furthermore, the single-crystalline nature of the ZnO NWs is clearly visible; the measured interplanar distance is 2.8 Å, corresponding to hexagonal ZnO wurtzite (ICDD-PDF #361451), as confirmed by the XRD pattern (see Fig. S1(c)). The TEM images of the ZnO@PbI$_2$ nanostructures obtained by conversion of sputter-deposited lead oxide coating are shown in Fig. 2(d and f). In this case, the PbI$_2$ coating is uniformly distributed over the entire ZnO NW surface; however, the surface roughness is significantly increased. The thickness of the coating typically varies between 5 and 15 monolayers, with some islands being even thicker. As in to the first approach, the measured interlayer distance is around 7 Å.

To complement TEM structural investigations and confirm the presence of phases, XRD measurements were performed on the as-prepared samples. Fig. 3(a and b) show XRD patterns of NW arrays prepared by the two approaches: thermal evaporation and converting the magnetron-sputtered lead oxide coating, respectively.

Fig. 1. Scanning electron microscope images of (a,b) ZnO@PbI$_2$ NWs made using the thermal evaporation approach; (c,d) ZnO NWs covered by lead oxide deposited by magnetron sputtering; (e,f) ZnO@PbI$_2$ NWs made by converting the lead oxide coating; (g,h) PbI$_2$ thin film made by converting a lead oxide film.
Both patterns indicate highly crystalline hexagonal ZnO wurtzite (ICDD-PDF #36-1451) and hexagonal PbI₂ (ICDD-PDF #07-0235) phases. No other phases were observed, confirming the high crystallinity of the as-prepared nanostructures, as did the TEM investigations. It is worth noting that the ratio between PbI₂ and ZnO peak intensity is not only related to the amount of PbI₂ on ZnO NWs but also the amount of PbI₂ crystallites on the Si/SiO₂ substrate. Therefore, spectra cannot be properly used to describe the phase composition ratio in the nanostructures. Furthermore, ZnO NW Bragg peak intensities vary between the samples - due to an inhomogeneous gold nanoparticle catalyst deposition from colloid on the silicon substrate; the density of as-grown ZnO nanowires arrays was also not homogeneous while the PbI₂ layer is relatively homogeneous over the substrate due to the precisely controllable deposition method. In Fig. 3(b), the Bragg peak at 33 is attributed to diffraction in the Si(100) substrate (forbidden Si(200) reflection).

The XRD pattern of pure ZnO NWs is given in Fig. S1(c). The XRD pattern of the PbI₂ thin film reference sample shows its highly crystalline structure (see Fig. 3(c)), confirming that the conversion of a lead oxide film in iodine vapour is a viable method how to obtain crystalline PbI₂ thin films.

To study the optical properties, room temperature PL in the as-prepared samples was measured in a wavelength range from 400 to 650 nm, excited by a 266 nm laser. Generally, PbI₂ has a direct band-to-band transition at around 495 nm (~2.5 eV) [58]; however, a broad band peaked at 510-525 nm has been previously observed and attributed to recombination through defects, such as iodine and lead vacancies [25]. The PL spectrum of pure ZnO NWs exhibits a defect-related band at ~520 nm [16]. Therefore, the interpretation of the ZnO:PbI₂ nanostructure spectra might be ambiguous due to this ZnO and PbI₂ PL band overlapping, since higher ZnO PL intensities might lead to indistinguishable PbI₂ PL peaks or vice versa.
Room temperature photoluminescence (PL) spectra at 266 nm excitation wavelength for the different as-prepared samples. The PL intensity is depicted in arbitrary units and does not contain information about relative intensities between the measured spectra.

Fig. 4 depicts our measured PL spectra of pure ZnO NWs, the PbI$_2$ thin film reference sample, and the ZnO$_x$PbI$_2$ nanostructures prepared via both approaches. It is worth noting that the PL intensity is depicted in arbitrary units and does not contain information about the relative intensities between the obtained spectra. The ZnO NW spectrum exhibits the typical defect band at 520 nm and the PbI$_2$ thin film sample (prepared by converting lead oxide film) shows two emission peaks: the direct band-to-band transition at around 495 nm and the defect-related band at around 530 nm. The ZnO$_x$PbI$_2$ nanostructures (prepared by thermal evaporation approach) exhibit two peaks at 495 nm and 525 nm; however, the nanostructures prepared via lead oxide conversion exhibit only one band with a peak at 530 nm due to the higher intensity overlapping ZnO peak. One can see and interpret the difference between the PbI$_2$ peak ratio for samples prepared with different methods due to the defect-related peak maximum shift. For example, the defect/ band-to-band peak intensity ratio for thermally evaporated PbI$_2$ is ~2, while for lead oxide converted PbI$_2$, it is ~1.33. Therefore, by also considering the ZnO peak contribution, one can qualitatively assume that lead oxide conversion via iodination leads to fewer defects in PbI$_2$ coatings than the thermal evaporation approach.

3.2. Device photoresponse measurements

Two-terminal single-nanowire photodetectors were fabricated from the nanostructures prepared via both approaches, and pure ZnO NWs. Fig. 5(a)-(c) shows the characteristics of the ZnO$_x$PbI$_2$ single NW devices made using the thermal evaporation approach, while Fig. 5(d)-(f) shows the characteristics of the ZnO$_x$PbI$_2$ single NW devices made by converting the magnetron-sputtered lead oxide coating (more than five single-nanowire photodetectors for each synthesis method were fabricated so that consistent conclusions could be made). The inset contains an SEM image of a typical as-prepared NW device. Both dark state current-voltage (I-V) characteristics of ZnO$_x$PbI$_2$ NWs in Fig. 5(a) and (d) exhibit linear behaviour, indicating that ohmic contacts formed between the nanostructures and the electrodes, as is expected for PbI$_2$ on gold [40, 59] and which is beneficial for efficient photogenerated carrier collection. In contrast, pure ZnO NWs typically form Schottky contact with gold electrodes (see the nonsymmetric I-V curve in Fig. S4(a)) [60]. The devices were illuminated with 405 nm wavelength light in a periodic fashion to study their photoresponse properties as shown in Fig. 5(b) and (e). All the devices were also tested for 532 nm and 660 nm light.
is well known that adsorbed oxygen species influence electrical properties (electrical conductivity decreases with exposure to oxygen) of metal oxide nanostructures [11,64,66]. Consequently, band bending, induced by adsorbed oxygen molecules that cap-ture free electrons, causes an efficient photogenerated electron-hole separation that leads to high gain in single-nanowire photodetectors. The presence of the PbI$_2$ layers in our nanostructures protects the ZnO surface from oxygen adsorption that might in-fluence surface-related photoinduced processes and decrease the number of charge carrier trapping centres.

The thickness of PbI$_2$ on ZnO NWs, which were used in the as-fabricated photodetector devices, was typically 6013 layers. No significant changes in the photodetector characteristics, such as spectral responsivity $R_I$, response time or current enhancement ratios ($I_{on}/I_{off}$), were observed between the samples in this PbI$_2$ thickness range. It is worth noting, that there are theoretical and experimental studies that show a band structure shift from direct bandgap to indirect bandgap when the PbI$_2$ thickness is reduced from bulk to monolayer [35,38]; therefore, monolayer PbI$_2$ is not expected to be an efficient material for optoelectronics applications and few-layer PbI$_2$ should be used instead.

Spectral responsivity ($R_I$) and external quantum efficiency (EQE) are used to evaluate photoconductive properties of a mate-rial. $R_I$ and EQE are respectively defined as $R_I = \frac{1}{4} \frac{D}{I(PS)}$ and EQE $= \frac{1}{4} \frac{hcR_I}{eD}$ [40], where $D$ is the difference between the photocurrent $I_{on}$ and the dark current $I_{off}$, $P$ is the light power density, $S$ is the effective illumination area (estimated as the electrode gap width NW diameter), $h$ is Planck’s constant, $c$ is the speed of light, $e$ is the electron charge and $l$ is the light wavelength. Large $R_I$ and EQE values correspond to high photodetector sensiti-ty. A responsivity as high as ~0.6 A/W (EQE ~180%) was calcu-lated for the ZnO:PbI$_2$ single NW devices made using the thermal evaporation approach and ~0.3 A/W (EQE ~90%) for the ones made by converting the magnetron-sputtered lead oxide coating; how-ever, it is not valid to compare the two different synthesis ap-proaches based only on the responsivity values as the value range for all as-fabricated devices overlapped no matter which method was used. The obtained $R_I$ and EQE values are comparable to other typical state-of-the-art 1D nanostructure [61] and 2D PbI$_2$ [41,42,44,59] photodetectors.

![Fig. 6](image_url)  
Fig. 6. Total and projected densities of states (PDOS) calculated for (a) 3-monolayer thick PbI$_2$ nanosheet, (b) monolayer thick PbI$_2$ nanosheet, and (c) ZnO (1e100) slab. The 24-layer thick slab of ZnO substrate is symmetrically terminated to mimic the surface of the nanowires. PDOS projected onto all orbitals of corresponding metal or non-metal atoms. The energy scale is shown with respect to the vacuum level.

### 3.3. Electronic structure calculations

Fig. 6 compares the total and projected densities of states (PDOS) calculated for [0001]-oriented monolayered (ML) and three-layered (3 ML) PbI$_2$ nanosheets, Fig. 6(a) and (b), respectively, and the PDOS calculated for slab models of [1e100] oriented ZnO NW (Fig. 6(c)). The PDOS calculated for bi-layered (2 ML) PbI$_2$ nanosheet is not presented in Fig. 6 since its electronic structure does not practically differ from that calculated for 3 ML PbI$_2$. For all PbI$_2$ nanosheets under study, the upper part of the valence band (VB) is predominantly formed by the iodine (5p) orbitals with significant contributions from lead (6s) orbitals. The bottom of the conduction band (CB) of PbI$_2$ nanosheets is formed mainly from Pb (6p) states. In the case of ZnO (1e100) surfaces, the VB top is formed by oxygen 2p states, while 3d orbitals of Zn mainly form the CB bottom. The band edge positions of ML and 3 ML PbI$_2$ differ from those of bulk (Fig. 5S(a)). The bottom of the CB is shifted down, closer to the hydrogen evolution potential of 4.44 eV. The position of the top of the VB calculated for (1e100) ZnO NW surfaces is located near 5.67 eV oxygen reduction potential, which allows us to conclude that the hybrid ZnO:OePbI$_2$ NWs can be considered as promising potential materials for efficient solar-driven photo (electro)catalytic water splitting.
4. Conclusions

In this paper, we demonstrated for the first time the growth of ZnO NWs decorated with highly crystalline few-layer PbI₂ and fabricated two-terminal single-nanowire photodetector devices to investigate the photoelectric properties of the hybrid ZnO: PbI₂ nanostructures. We developed a novel two-step growth process for uniform crystalline PbI₂ nanosheets via reactive magnetron deposition of a lead oxide film followed by subsequent iodination in iodine vapour to PbI₂ at 420°C on a ZnO NW substrate, and we compared as-grown hybrid nanostructures with ones prepared via thermal evaporation method. As-prepared two-terminal single-nanowire ZnO: PbI₂ photodetectors are comparable to state-of-the-art 1D nanostructure and 2D PbI₂ photodetectors and exhibit enhanced photoelectric characteristics, such as reduced dark current and significantly decreased photoresponse time compared to pure ZnO NWs, and have responsivity up to 0.6 A/W. We found that the preparation method does not significantly affect the photoelectric properties of the nanostructures; however, PbI₂ obtained by thermal evaporation benefits from a smoother coating and, presumably, less optical defect states, but lacks the uniform coverage of PbI₂ converted from lead oxide coating. First principle DFT calculations on few-layer PbI₂ nanosheets, thin slabs to mimic the surface of ZnO NWs, and bulk phase ZnO and PbI₂ crystals, were performed to obtain the electronic structure of the materials under study. The results show the potential of combining layered vdW materials with semiconducting nanowires to create novel nano-structures with enhanced properties for applications in optoelectronics or X-ray detectors. Our ab initio modelling also shows that nanosized ZnO: PbI₂ heterostructures might be used for efficient photocatalytic and electrocatalytic hydrogen production from water.

Declaration of competing interest

There are no conflicts of interest to declare.

CRediT authorship contribution statement

Edgars Butanovs: Methodology, Validation, Investigation, Visualization, Writing - original draft. Sergei Piskunov: Method-ology, Formal analysis, Visualization. Aleksejs Zolotarjovs: Inves-tigation, Boris Polyakov: Conceptualization, Supervision, Investigation, Writing - review & editing.

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