Fast-Response Single-Nanowire Photodetector Based on ZnO/WS₂ Core/Shell Heterostructures

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Supporting Information

ABSTRACT: The surface plays an exceptionally important role in nanoscale materials, exerting a strong influence on their properties. Consequently, even a very thin coating can greatly improve the optoelectronic properties of nanostructures by modifying the light absorption and spatial distribution of charge carriers. To use these advantages, 1D/1D heterostructures of ZnO/WS₂ core/shell nanowires with a-few-layers-thick WS₂ shell were fabricated. These heterostructures were thoroughly characterized by scanning and transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. Then, a single-nanowire photoresistive device was assembled by mechanically positioning ZnO/WS₂ core/shell nanowires onto gold electrodes inside a scanning electron microscope. The results show that a few layers of WS₂ significantly enhance the photosensitivity in the short wavelength range and drastically (almost 2 orders of magnitude) improve the photoresponse time of pure ZnO nanowires. The fast response time of ZnO/WS₂ core/shell nanowire was explained by electrons and holes sinking from ZnO nanowire into WS₂ shell, which serves as a charge carrier channel in the ZnO/WS₂ heterostructure. First-principles calculations suggest that the interface layer i-WS₂, bridging ZnO nanowire surface and WS₂ shell, might play a role of energy barrier, preventing the backward diffusion of charge carriers into ZnO nanowire.

KEYWORDS: core/shell nanowires, 1D/1D heterostructures, van der Waals epitaxy, transitional metal chalcogenides, photodetectors

INTRODUCTION

Nanostructured photodetectors operating from ultraviolet (UV) to terahertz frequencies have attracted much attention during the last few decades due to their appealing performance for various applications.1 Such nanodevices made of quantum dots, nanowires (NWs), nanobelts, nanotubes, or nanolayers demonstrate high integration density and sensitivity, fast response, and multifunctionality.2−5 Current developments in the field are concentrated on precisely controlling the manufacturing of nanostructured materials, modifying their properties, and developing methods for mass production.6

Photodetectors based on one-dimensional (1D) nanostructured materials have become one of the most attractive photoelectric devices that can be implemented using individual or assemblies of nanostructures.4,5 A fabrication of hybrid nanostructures composed of two or more components opens new possibilities to control their properties, in particular, in photodetection capability in a broad spectral range from UV to infrared.4 Depending on the dimensionality of the constituting components, hybrid nanostructures can be classified into six types,3 and the 1D/1D nanostructured photodetectors constitute the subject of the present study. Furthermore, they can be realized as core/shell, branched or axial heterojunctions.

Radially heterostructured core/shell nanowires (NWs) are intriguing and prospective types of nanomaterials, and these NWs have been intensively explored recently.7−10 The surface of NWs plays an important role because the surface is often the origin of structural and electronic defects. Properly chosen shell material can protect the core and significantly improve its electrical, mechanical, and optical properties.9,11,12 Therefore, the engineering of core/shell heterostructures is a versatile tool for creating a novel advanced nanostructures with desired properties.

ZnO NWs are among the most popular nanomaterials with a wide range of applications in nanoelectronics, sensorics, and nanophotonics, including the use of ZnO NWs as piezoelectric nanogenerators and ultraviolet (UV) photodetectors.13,14 At ambient conditions, the most stable phase of ZnO has n-type conductivity and is hexagonal wurtzite-type with a direct band
gap of about 3.2–3.3 eV. Cubic zinc blend and rock-salt ZnO phases can be also obtained at specific conditions. ZnO NW UV photodetectors demonstrate excellent performance and sensitivity; however, their time response is relatively slow, being in the range of seconds. There are several reasons for slow photoresponse of ZnO NW photodetectors, namely, surface charge traps and surface states related to adsorbed oxygen molecules. An obvious method to make photodetector faster is to etch and passivate NW surface layer, as was demonstrated by Mallampati et al. Cheng et al. used the electric field of Shottky barrier to increase both speed and gain of ZnO NW photodetector. In a number of works, significant improvement in ZnO NW photodetectors responsivity and speed was achieved by Au nanoparticles decoration.

Another promising class of nanomaterials consists of layered two-dimensional (2D) transition metal dichalcogenides (TMDs), and they have recently attracted much attention. The use of 2D ZnO/WS2 heterostructures for enhanced UV photodetectors was demonstrated. For example, several state-of-the-art 1D and 2D WS2 and MoS2-based high-sensitivity UV and vis photodetectors was demonstrated. In addition, a few-layers-thick TMDs show a transition from indirect to direct band gap behavior. For example, bulk WS2 is an n-type semiconductor having an indirect band gap $\Delta E_{bg} = 1.3–1.4$ eV, whereas a monolayer has a direct optical band gap $\Delta E_{bg} = 1.7–1.9$ eV and a strong optical absorption, being able to absorb 5–10% of the incident light. Furthermore, epitaxial growth of WS2 and MoS2 is possible on sapphire wafers because the (0001) plane of c-sapphire is hexagonally arranged, matching the crystal lattice of the two sulfides. Recently, the authors have demonstrated that both WS2 and MoS2 can be epitaxially grown around ZnO NWs, producing ZnO/WS2 and ZnO/MoS2 core/shell nanostructures.

Hybrid or composite TMDs materials have recently attracted significant attention. The use of 2D ZnO/WS2 heterostructures for enhanced UV photodetectors was demonstrated by Lan et al. The heterostructured device was produced by transferring chemical vapor deposition grown WS2 monolayer onto the surface of polycrystalline ZnO film deposited by direct current (dc) magnetron sputtering on glass substrate, and, finally, the aluminum electrodes were fabricated by thermal evaporation through a shadow mask. An enhancement by 16 times (in vacuum) of UV light photodetection by ZnO/WS2 heterostructure was observed relatively to pure ZnO film. However, the photoresponse time was still measured in the range of seconds.

This study demonstrates a significantly enhanced photodetection by ZnO NWs coated with a few WS2 monolayers (ZnO/WS2 core/shell NWs) and a drastic (almost 2 orders of magnitude) improvement in the photoresponse time compared to that of pure ZnO NWs. Our results show a potential of combining layered 2D TMDs materials with semiconducting NWs to create new core/shell heterostructures with advanced optoelectronic properties.

**EXPERIMENTAL SECTION**

**Synthesis.** The synthesis of ZnO/WS2 core/shell NWs was described in the authors’ previous article. In brief, amorphous a-WO3 shell was deposited over ZnO NWs by reactive dc magnetron sputtering of a metallic tungsten target in mixed Ar/O2 atmosphere. Then, ZnO/a-WO3 NW samples were annealed in a quartz tube in a sulfur atmosphere during 0.5 h at 800 °C to convert amorphous tungsten trioxide into tungsten sulfide (WS2). This process was followed by heating for 0.5 h in an inert atmosphere to sublime excess material.

**Sample Characterization.** The phase composition of ZnO/WS2 NWs was studied by X-ray diffraction (XRD) at room temperature (20 °C) using a $\theta$–$\theta$ Bragg–Brentano powder diffractometer PANalytical X’Pert Pro MPD equipped with copper anode X-ray tube (Model PW3030, Cu Kα radiation). Micro-Raman spectroscopy measurements were performed using a confocal microscope with spectrometer Nanofinders-S (SOLAR TII). A diode pumped solid-state Nd:YAG laser ($\lambda = 532$ nm, max continuous wave power $P = 150$ mW) was used as an excitation source. The Raman spectra were recorded using the monochromator with a 520 mm focal length equipped with 600 grooves/mm diffraction grating and the edge filter to eliminate the elastic component. A Peltier-cooled back-thinned CCD camera (ProScan HS-101H) was employed as a detector of Raman spectra. All of the measurements were performed in backscattering geometry at room temperature (20 °C) through a Nikon CF Plan Apo 100x (NA = 0.95) optical objective. Furthermore, the morphology of NWs was observed by a scanning electron microscope (SEM) (Tescan Lyra XM), and the inner structure of ZnO and ZnO/WS2 NWs was characterized using a transmission electron microscope (TEM) (Tecnai GF20, FEI) operated at the accelerating voltage of 180 kV.

**Fabrication of Photodetectors.** To fabricate single-nanowire photodetectors, gold microelectrodes with the gap width of 2 μm were first obtained on an oxidized silicon wafer by the conventional photolithography technique (as shown in Figure 1). Briefly, the microelectrode pattern was obtained using a direct write laser lithography (μPG 101, Heidelberg Instruments) on SU-8 2003 photosist (MicroChem), and 5/45 nm Cr/Au film was deposited via thermal evaporation method, followed by a liftoff procedure.

Next, single NW photoresistors were fabricated using in situ nanomanipulations inside SEM-FIB Tescan Lyra XM. The as-grown ZnO and ZnO/WS2 NWs were mechanically transferred from the Si substrate to the as-prepared gold microelectrodes by welding a single NW to the tungsten (W) nanomanipulator probe using an electron-beam-assisted platinum (Pt) deposition. Finally, the NW was aligned and placed on top of the microelectrodes, following its cutting off from the W probe with gallium (Ga) ion beam and welding to the electrodes using Pt deposition to ensure the electric contact and fixed position. A SEM image of a typical as-prepared photoresistor is shown in Figure 1c, where the narrow dark strip is the gap between the electrodes, two small rectangles on the NW are the deposited Pt fixed points, and the trench is visible where the NW was cut by the ion beam.

For comparison, WS2 water suspension was prepared using an ultrasound exfoliation of WS2 powder (Sigma-Aldrich). A small amount (36 mg) of WS2 powder in 6 mL of pure deionized water was ultrasonically processed at 100 W for 3 h. After 1 day, water suspension of WS2 was centrifuged and resuspended in 1 mL tube. A droplet of WS2 suspension was cast on gold electrodes and heated at 150 °C during 5 min.

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**Figure 1.** Schematics of ZnO/WS2 core/shell nanowire-based photodetector (a). Optical microscope image of gold microelectrodes on the oxidized silicon substrate (b). SEM image of a typical nanowire photoresistor (c).
Device Measurements. Current–voltage ($I-V$) characteristics and photoresponse of the fabricated single-NW photodetectors were measured with a two-contact microprobe station connected to a Model 6485 Keithley Picoammeter, a Model 2000 Keithley multimeter, and a voltage source (33220A Waveform Generator, Agilent). Semiconductor diode lasers with the wavelengths of 405, 532, and 660 nm and the power of 0.5 W/cm$^2$ were used as illumination sources for the photoresponse measurements. Optical beam shutter Thorlabs SH05 was employed for time-resolved measurements, and all of the measurements were performed at room temperature in air.

Computational Details. In this study, hybrid density functional theory (DFT) calculations have been performed using the CRYSTAL computer code,$^{34}$ and the code utilizes localized Gaussian type functions (GTFs) in the form of a basis set (BS) centered on atomic nuclei to expand the crystalline orbitals as linear combinations of atomic orbitals. Fully relaxed ZnO/WS$_2$ 2D interfaces were calculated by means of hybrid exchange correlation functional PBE0 according to the derivations by Perdew et al. and Adamo and Barone.$^{35,36}$ For oxygen atoms, the all-valence BSs of atomic GTFs (constructed using pure s- and hybrid sp-AOs) in the form of 8s-411sp were used, and for zinc atoms, the all-valence BS in the form 8s-6411sp-41d were used. In addition, the BS adopted for sulfur atoms had the form of ECP-111sp-31d56, whereas for tungsten atoms, the BS that had the form of ECP-11sp-31d56 was used, where ECP represents the effective core pseudopotentials employed to accelerate computation. To provide a balanced summation in both direct and reciprocal lattices, the reciprocal space integration was performed by sampling the interface Brillouin zone (BZ) with the 12 $\times$ 12 Monkhorst–Pack mesh$^{38}$ that gives in total 16 k-points evenly distributed at the BZ. The calculations were considered as converged only when the total energy differs by less than 10$^{-9}$ au in two successive cycles of the self-consistent field procedure.

RESULTS AND DISCUSSION

The phase composition of as-prepared ZnO/WS$_2$ core/shell NWs on the silicon substrate was studied by X-ray diffraction using the Rietveld method and implemented in the PROFEX code.$^{39}$ The result of the Rietveld refinement is shown in Figure 2a. Four crystalline phases corresponding to the Si substrate, ZnO NWs, WS$_2$ shell, and ZnS were detected. Although the amount of ZnS on the substrate was high enough to be detected in the XRD measurements, only a sub-monolayer was present inside the ZnO/WS$_2$ core/shell nanowires.$^{31}$

Figure 2. Rietveld refinement (solid line) of the X-ray diffraction pattern (open circles) of the ZnO/WS$_2$ sample (a). Raman spectrum of the ZnO/WS$_2$ core/shell nanowire (inset: confocal microscope image of the nanowire) (b).

For room-temperature micro-Raman measurements, the NWs were transferred onto a clean silicon substrate. The Raman spectrum and confocal image (see the inset) of typical individual ZnO/WS$_2$ core/shell NW are shown in Figure 2b. Two main bands at 354 and 419 cm$^{-1}$ were detected and attributed to the WS$_2$ phase. In contrast, no Raman signal from the ZnO NW core was observed because of its very weak intensity when excited at 532 nm. The Raman spectrum of bulk WS$_2$ measured in a backscattering geometry includes the second-order $1E_{2g} (\Gamma) \approx 355$ cm$^{-1}$ and out-of-plane $A_{2g} (\Gamma) \approx 420$ cm$^{-1}$, a zone-edge longitudinal acoustic mode $LA (M) \approx 350$ cm$^{-1}$, and several multphonon combinations of these modes.$^{40-42}$ When the thickness of WS$_2$ was reduced to a monolayer, the resonant Raman scattering occurs under 532 nm excitation, enhancing the second-order effects significantly, and the spectrum became very rich in the region of $LA (M) - 1E_{2g} (\Gamma)$ modes.$^{41,42}$ In this case, the intensity of the strongest second-order Raman peak, $2LA (M)$ mode at 354 cm$^{-1}$ (Figure 2b), became dominant, and it overlaps strongly with the first-order $1E_{2g} (\Gamma)$ mode. Thus, the intensity ratio between 354 and 419 cm$^{-1}$ bands in the Raman spectrum of the ZnO/WS$_2$ core/shell NW implies the thickness of the WS$_2$ shell to be on the order of a monolayer.

The TEM images of pure ZnO NW, ZnO/WS$_2$ core/shell NW after annealing for 0.5 h in a sulfur atmosphere and after additional annealing in inert atmosphere are shown in Figure 3. Pure ZnO NWs have a smooth surface and a single-crystalline structure (Figure 3b). After annealing in a sulfur atmosphere, many WS$_2$ layers and protruding WS$_2$ microplates can be seen on the surface of the NW (Figure 3c,d). However, after annealing in an inert atmosphere, only a few layers of WS$_2$ remain in agreement with the results of Raman spectroscopy (Figure 2b): the layers appear as black lines parallel to the ZnO NW surface (Figure 3e,f). A more detailed description of the TEM investigation of ZnO/WS$_2$ core/shell NWs and related theoretical models have been published by the authors previously.$^{31}$

Figure 4 shows the measured current–voltage characteristics of photodetectors built using pure ZnO and ZnO/WS$_2$ core/shell NWs, as well as pure WS$_2$ flakes. At least five photodetectors of each material were fabricated and measured. The ZnO photoresistor demonstrates a nonsymmetric current–voltage $I(V)$ curve (Figure 4a), and this is typical for the Schottky barrier of ZnO NWs on gold contacts.$^{43}$ At the same time, a nearly symmetric response was obtained for WS$_2$ flakes and ZnO/WS$_2$ devices (Figure 4b,c).

On-off photoresponse measurements were performed at the bias voltage of 1 V, laser wavelengths of 405, 532, and 660 nm, and laser power of 0.5 W/cm$^2$. The typical photoresponse measurements of pure ZnO and ZnO/WS$_2$ core/shell NWs and WS$_2$ flakes-based devices are shown in Figure 5. Pure ZnO NWs respond only to the illumination at a wavelength of 405 nm and do not respond to the wavelengths of 532 and 660 nm (Figure 5a). In addition, the photoresponse of WS$_2$ flakes is almost identical at the wavelengths of 405, 532, and 660 nm (Figure 5b). In particular, the photoresponses of ZnO/WS$_2$ core/shell NWs are similar at 532 and 660 nm but significantly
stronger at 405 nm (Figure 5c). Because pure ZnO NWs do not respond to green 532 nm (2.33 eV) and red 660 nm (1.88 eV) light owing to their wide band gap ($E_g = 3.2 - 3.3$ eV), the photoresponse of ZnO/WS$_2$ core/shell NWs to red and green light is caused by the WS$_2$ shell. For violet light (405 nm), both ZnO core and WS$_2$ shell contribute proportionally to the photoresponse of ZnO/WS$_2$ core/shell NWs.

Time-resolved photoresponse measurements are presented in Figure 5d–f, and the corresponding data are given in Table 1. A slow response of pure ZnO NWs on the timescale of seconds is typical for this material.$^{16-18}$ The photoresponse time of WS$_2$ flake devices is significantly faster than that of ZnO-based devices: it depends on the material fabrication method and the number of WS$_2$ layers.$^{45,46}$ Perea-López et al. reported the response time of a few-layer WS$_2$ photodetector to be as fast as 5.3 ms,$^{45}$ whereas Huo et al. reported the response time of a multilayer WS$_2$ photodetector to be faster than 20 ms.$^{46}$ The time response of the proposed 1D ZnO/WS$_2$ core/shell NWs is significantly faster than that of 2D ZnO/WS$_2$-based heterostructured thin-film devices.$^{33}$ We believe that the faster response time of 1D ZnO/WS$_2$ NWs in comparison to 2D heterostructures can be explained by a good quality of ZnO–WS$_2$ interface (perfect match and close contact between WS$_2$ and ZnO), which allows a fast transfer of photogenerated charge carriers from ZnO to WS$_2$. The quality of the interface is achieved by the direct growth of WS$_2$ layer on the ZnO nanowire surface.

The influence of oxygen molecules on the surface states of ZnO NW and their effect on photoresponse kinetics were widely discussed in the literature.$^{19,20}$ The presence of WS$_2$ shell protects the ZnO surface from oxygen adsorption and might influence surface-related photoinduced processes. Moreover, WS$_2$ shell might passivate ZnO surface leading to a decrease in charge carrier trapping centers in ZnO NW and be responsible for faster photodetector kinetics. A comparison of the positions of valence and conduction bands of ZnO and WS$_2$ shows that both electrons and holes should sink into the WS$_2$ shell$^{31}$ and serve as a charge carrier channel in ZnO/WS$_2$ heterostructure (Figure 6). This conclusion is supported by the electronic density of states (DOSs) calculated for the ZnO/WS$_2$ interface layer by means of the density functional theory (Figure 6c–e). The DOS calculated for pristine n-type ZnO (T100) surface of the bare ZnO NW yields a band gap of 3.36 eV (Figure 6c), in good agreement with the experimental observation ($3.3$ eV$^{15}$). The doping of the surface of NWs with sulfur is the initial stage of ZnO/WS$_2$ interface formation.$^{31}$

![Figure 3. TEM images of pure ZnO nanowire (a, b), ZnO/WS$_2$ nanowire annealed in sulfur atmosphere (c, d), and ZnO/WS$_2$ nanowire additionally annealed in an inert atmosphere (e, f).](image1)

![Figure 4. I–V characteristics of pure ZnO NW (a) and WS$_2$ flakes drop-casted on electrodes (b) and annealed ZnO/WS$_2$ NW (c).](image2)
The surface of NWs doped with sulfur has a narrower band gap of 1.42 eV due to the presence of occupied in-gap sulfur levels located at 1−2 eV above the top of the valence band of pristine ZnO (1̅00), as shown in Figure 6d. The formation of a net of WS2 bridges as precursors for complete interface formation31 makes the band gap even more narrow at 1.14 eV (Figure 6e) due to the presence of a sharp peak containing an admixture of W and S states at the top of the valence band. Therefore, according to the DFT calculations, the interface layer i-WS2, bridging the ZnO surface and WS2 shell, has an even more narrow gap than WS2 itself, leading to the formation of energy barrier that is able to prevent backward diffusion of charge carriers into ZnO NW.

To evaluate the parameters of photoconducting materials, spectral responsivity $R_\lambda$ and external quantum efficiency (EQE) were calculated according to the following formulas:

$$R_\lambda = \frac{I_\lambda}{P_\lambda S},$$

where $I_\lambda$ represents the photocurrent, $P_\lambda$ represents the light intensity, and $S$ represents the effective illuminated area; and

$$EQE = \frac{hcR_\lambda}{e\lambda},$$

where $h$ represents Planck’s constant, $c$ represents the velocity of light, $e$ represents the charge of electron, and $\lambda$ represents the wavelength. In addition, a higher $R_\lambda$ and EQE corresponds to a higher light sensitivity of a material. The calculated values of $R_\lambda$ and EQE for our photodetectors are given in Table 2, and the obtained data are comparable to other state-of-the-art ZnO nanowire- and WS2 nanotube-based photodetectors. For example, Guo et al. demonstrated the high responsivity of a ZnO nanowire-based UV photodetector having 40 A/W; however, at 10 V, the kinetics of the photodetector was measured in the range of seconds.17 In contrast, Zhang et al. demonstrated a multiwall WS2 nanotube-based photodetector with $R_\lambda = 3.14$ A/W (at 0.5 V) and EQE = 615% for 633 nm light.26

Finally, ZnO/WS2 core/shell NWs with a few WS2 layers thickness are considered as a WS2 nanotube wrapped around a ZnO NW core. However, such WS2 nanotubes with the same diameter collapse without an inner ZnO core because the ZnO core can be etched away in template-assisted synthesis methods.47,48 Therefore, 1D/1D ZnO/WS2 core/shell NWs were considered as a convenient object (where ZnO may be a sacrificial template if necessary49 to manipulate a few-layers-thick 2D materials (WS2, MoS2, and others)), and similar materials can be useful in nanoelectronic and optoelectronic devices.

### CONCLUSIONS

In summary, an effective photodetector based on ZnO/WS2 core/shell nanowire (with a few layers of WS2) is demonstrated in this work. The photodetector responds to illumination at the wavelengths of 660 nm ($R_\lambda = 1.75$), 532 nm ($R_\lambda = 2.25$), and 405 nm ($R_\lambda = 7$). The ZnO/WS2 core/shell nanowire-based device shows a clear advantage over pure ZnO nanowire-based photodetector in terms of both higher responsivity (4.6-fold) and faster operation (90-fold) for 405 nm illumination. The photodetector band diagram was supported by the first-principles calculations, suggesting that the interface layer i-WS2, bridging ZnO nanowire surface, and WS2 shell, might play an important role in preventing backward diffusion of charge carriers into the ZnO nanowire, whereas WS2 shell serves as a charge carrier channel in the ZnO/WS2 heterostructure. The obtained results clearly show the potential of combining ZnO NWs with WS2 flakes or WS2 nanotubes for achieving high-performance photodetectors.

![Figure 5.](image_url)

**Table 1. Photoresponse (Rise and Decay) Time of Photodetectors Fabricated from Pure ZnO and ZnO/WS2 Core/Shell NWs as well as WS2 Flakes**

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<th>WS2 flakes</th>
<th>ZnO/WS2 NWs</th>
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<td>decay (s)</td>
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layeread 2D TMDs materials with semiconducting nanowires to create novel core/shell heterostructures with advanced optoelectronic properties.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b02241.

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### Table 2. Characteristic Parameters of Photodetectors Fabricated from Pure ZnO and ZnO/WS₂ Core/Shell NWs as well as WS₂ flakes

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<th>WS₂ flakes</th>
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**Figure 6.** Simplified band diagram of the ZnO/WS₂ core–shell NW (a). Atomic structure of ZnO/WS₂ interface (b). Total and projected densities of states (DOSs) of (c) n-type ZnO (1100) substrate, (d) S-doped ZnO (1100) substrate, and (e) WS₂ covered S-doped ZnO (1100) substrate as calculated by means of density functional theory. Zero energy corresponds to the top of the valence band.

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**Author Contributions**

The manuscript was written through contributions of all the authors. All the authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Latvian National Research Program IMIS2 and ISSP project for Students and Young Researchers Nr. SJZ/2016/6. S.P. is grateful to the ERA.Net RUS Plus WATERSPLIT project no. 237 for the financial support.

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On-off photoresponse graphs for selected ZnO/WS₂- and ZnO-based photodetector devices (PDF)
support. S.V. is grateful for partial support by the Estonian Science Foundation grant PUT1689.

**ABBREVIATIONS**

1D, one-dimensional; 2D, two-dimensional; NW, nanowire; TMD, transitional metal dichalcogenide; CVD, chemical vapor deposition; SEM, scanning electron microscope; TEM, transmission electron microscope; XRD, X-ray diffraction; DFT, density functional theory; EQE, external quantum efficiency

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