Different strategies for GaN-MoS$_2$ and GaN-WS$_2$ core-shell nanowire growth

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Abstract

One-dimensional (1D) nanostructures – nanowires (NWs) – exhibit promising properties for integration in different types of functional devices. Their properties can be enhanced even further or tuned for a specific application by combining different promising materials, such as layered van der Waals materials and conventional semiconductors, into 1D-1D core-shell heterostructures. In this work, we demonstrated growth of GaN-MoS$_2$ and GaN-WS$_2$ core-shell NWs via two different methods: (1) two-step process of sputter-deposition of a sacrificial transition metal oxide coating on GaN NWs followed by sulfurization; (2) pulsed laser deposition of few-layer MoS$_2$ or WS$_2$ on GaN NWs from the respective material targets. As-prepared nanostructures were characterized via scanning and transmission electron microscopies, X-ray diffraction, micro-Raman spectroscopy and X-ray photoelectron spectroscopy. High crystalline quality core-shell NW heterostructures with few-layer MoS$_2$ and WS$_2$ shells can be prepared via both routes. The experimental results were supported by theoretical electronic structure calculations, which demonstrated the potential of the synthesised core-shell NW heterostructures as photocatalysts for efficient hydrogen production from water.

Keywords: nanowire; gallium nitride; MoS$_2$; WS$_2$; core-shell; heterostructure
1. Introduction

Layered two-dimensional (2D) van der Waals (vdW) materials have been a hot research topic since the ground-breaking experiments on graphene in 2004 [1]. 2D vdW materials, such as graphene, hexagonal boron nitride, transition metal dichalcogenides (TMDs), have been shown to exhibit promising electrical, optical and mechanical properties when their thickness is reduced to several atomic layers [2]. TMDs have a general chemical formula MeX$_2$, where Me is a periodic table Group 4 – 7 transition metal and X is S, Se or Te. Most commonly studied TMDs are typically semiconductors with indirect-to-direct bandgap transition from bulk to monolayer [3]. For example, MoS$_2$ bandgap shifts from 1.2 to 1.9 eV when reduced to monolayer, while WS$_2$ bandgap shifts from 1.3 to 2.1 eV [4]. TMDs are now being investigated for potential applications in energy [5,6], sensors [7], electronics and optoelectronics [4].

On the other hand, one-dimensional (1D) nanostructures – nanowires (NWs) – have been extensively studied for more than two decades and exhibit promising properties for integration in different types of functional devices [8,9]. By preparing hybrid material NWs, for example, various 1D-2D or axial and radial 1D heterostructures, their characteristics can be improved even further [10,11]. One type of such hybrid nanostructures are core-shell NWs, which are promising due to possible modification of NW electronic surface states [12] and even further increase of already high surface-to-volume ratio [13]. A potential way to effectively increase the NW surface is to grow layered vdW materials around the NW, since they exhibit weak interlayer bonding [14,15]. Many energy applications, e.g., photo- and electrocatalytic hydrogen evolution reactions (HER), supercapacitors and storage, require materials with large effective surface and high concentration of active sites, therefore, NW and
layered material heterostructures are promising candidates [16–23]. Furthermore, the NW core can also be a high-mobility charge carrier migration channel, if the right materials are selected [24].

Gallium nitride (GaN) nanoscale heterostructures with mono- or few-layer MoS$_2$ and WS$_2$ have recently been shown to exhibit type-II band alignment, which is suitable for optoelectronics and photoelectrocatalysis applications [25,26]. GaN is an established material for optoelectronics due to its direct bandgap ($E_g \approx 3.45$ eV) and high electron mobility in the form of thin films and NWs [27], while the thickness-dependent bandgap of layered 2D materials gives tunability for desired applications [28]. In the case of GaN-MoS$_2$ heterostructures, there have been several experimental and theoretical studies of 2D-2D (thin films or thin crystals) heterojunctions for applications as photodetectors [29–31], sensors [32] and catalysts for water splitting [33,34]. Furthermore, 1D-2D GaN-MoS$_2$ heterostructures have been demonstrated in electronic and optoelectronic devices [35–37]. As for GaN-WS$_2$, a combination of these materials shows promise in optoelectronics [38] and photocatalysis [25], since WS$_2$ can also be an efficient catalyst [39]. Regarding 1D-1D core-shell nanostructures, growth of MoS$_2$-wrapped GaN NWs has recently been demonstrated by Ji et al. via direct deposition of MoS$_2$ on GaN NWs with magnetron sputtering [40] and GaN-MoS$_x$ core-shell NWs by Zhou et al. via electrodeposition [41]. The few previous studies clearly demonstrate the potential of such heterostructures; however, the development of other versatile fabrication methods is still needed for further progress.

In this work, we demonstrated growth of GaN-MoS$_2$ and GaN-WS$_2$ core-shell NWs via two different methods: (1) two-step process of sputter-deposition of a sacrificial respective transition metal oxide coating on GaN NWs followed by sulfurization; (2) pulsed laser deposition of few-layer TMDs on GaN NWs from MeS$_2$...
targets. Characterization results show that high crystalline quality core-shell NW heterostructures can be prepared through both routes. To theoretically support the experimental results, the electronic structure of a model reproducing structural properties core-shell NWs was investigated. The model used here differs from numerous models of heterostructures where (0001) MoS$_2$/WS$_2$ surface possessing the hexagonal symmetry is deposited on the GaN (0001) surface [25,28,42–44], which also exhibits hexagonal symmetry. The model previously proposed for structurally similar ZnO/WS$_2$ heterointerface [45] was used in this work. In this model GaN (11̅00) surface of GaN substrate is stacked with the outer atomic layer of MoS$_2$/WS$_2$ (0001). In contrast to the ZnO/WS$_2$ model, in which bridging atoms between the surfaces were used to stack both interfaces, here the stacking occurred directly due to a better match between the positions of the surface atoms of sulfur and gallium. This model corresponds well to the situation of TMD shell growth on a gallium nitride [0001]-oriented NW core, which is important for the correct description of nanowire electronic properties. Based on our calculations, GaN-MoS$_2$ and GaN-WS$_2$ core-shell NWs might be promising candidates for further investigation as photocatalysts for efficient hydrogen production from water.

2. Experimental details

GaN-MeX$_2$ core-shell NW preparation methods demonstrated in this work are schematically depicted in Fig. 1. GaN NWs were synthesized via atmospheric pressure chemical vapour transport method in a horizontal quartz tube reactor. 2 g metallic Ga (99.999%, Alfa Aeasar) was loaded in a ceramic boat and placed in the centre of the quartz tube, oxidized silicon wafers SiO$_2$/Si(100) (Semiconductor Wafer, Inc.) coated with spherical Au nanoparticles (NPs, Alfa Aesar, water suspension, 100 nm diameter)
Au NPs were used as a catalyst for the vapour-liquid-solid (VLS) mechanism. The reactor was heated to 940°C under a flow of carrier gas mixture Ar/H₂-35%, then gaseous NH₃ flow in 1:1 ratio to the carrier gas was introduced and maintained for 30 minutes for the gas-phase reaction and NW growth, followed by natural cooling to the room temperature under Ar/H₂ flow. As a result, 5-20 μm long GaN NWs were produced on the SiO₂/Si substrate. Characterization data for the as-grown pure GaN NWs is shown in Fig. S1.

Few-layers of MoS₂ and WS₂ on GaN NWs were obtained with two different routes. The first route consists of two steps – deposition of amorphous MoO₃ and WO₃ coating on GaN NWs via reactive DC magnetron sputtering of a metallic target in a mixed Ar/O₂ atmosphere, followed by subsequent sulfurization of the samples in a quartz tube reactor at high temperatures. The optimal sacrificial precursor film thickness (on a flat substrate) was found to be 30 nm and 40 nm for MoO₃ and WO₃, respectively. Optimal sulfurization temperature was 750°C for MoS₂ and 800°C for WO₃.
WS\textsubscript{2} coatings. The second route was pulsed laser deposition (PLD) from stoichiometric MoS\textsubscript{2} and WS\textsubscript{2} targets. 500 mJ 248 nm KrF laser beam was used for target ablation at 10 Hz repetition frequency and 10\textsuperscript{-5} Torr background pressure. A few-layer MoS\textsubscript{2} coating was obtained with 1500 pulses at 600°C substrate temperature, and WS\textsubscript{2} coating with 3000 pulses at 650°C substrate temperature.

As-grown NW morphology was characterized using a scanning electron microscope (SEM, Lyra, Tescan), while their inner crystalline structure was studied using a transmission electron microscope (TEM, Tecnai GF20, FEI) operated at a 200 kV accelerating voltage. NW phase composition was studied by X-ray diffraction (XRD) using Rigaku MiniFlex 600 X-ray powder diffractometer with Bragg-Brentano 0-2θ geometry and the 600W Cu anode (Cu K\textalpha{} radiation, \( \lambda = 1.5406 \) Å) X-ray tube. Micro-Raman spectroscopy measurements were performed using a TriVista 777 confocal Raman system (Princeton Instruments, 750 mm focal length, 1800 lines/mm grating) equipped with an upright Olympus microscope with Olympus UIS2 MPlanN 100x/0.90 objective, a continuous-wave single-frequency diode-pumped laser Cobolt Samba 150 (\( \lambda = 532 \) nm) and Andor iDus DV420A-OE CCD camera. XPS measurements were performed using an X-ray photoelectron spectrometer ESCALAB Xi (ThermoFisher), and XPSPEAK41 software was used for peak fitting.

3. Theoretical background and computational model

CRYSTAL17 computer code [46,47], which employs Gaussian-type functions centred on atomic nuclei as the basis sets (BS) for an expansion of the crystalline orbitals has been used to perform the DFT calculations of GaN-MoS\textsubscript{2} heterostructures implementing hybrid HSE06 exchange-correlation functional. Heyd-Scuseria-Ernzerhof hybrid exchange-correlation functional (HSE06) [48], which uses a screened
hybrid functional and includes the exact nonlocal Fock exchange, has been used to perform the calculations of GaN, MoS$_2$, and WS$_2$ structures as well as GaN/MoS$_2$ and GaN/WS$_2$ heterostructures. Ga$_{86}$-4111d41G basis set [49] has been used for gallium atoms, N$_{6}$-31d1G basis set has been adopted for nitrogen atoms calculations [50], W_cora_1996 basis set [51] has been chosen for tungsten atoms, Mo_SC_HAYWSC-311(d31) Hay Wadt small core basis set [52] has been used to describe molybdenum atoms, and S$_{86}$-311G basis set taken from [53] has been used for sulphur atoms. To perform the calculations, the Brillouin zone has been sampled by 8×8×8 Pack-Monkhorst net [54] resulting in 75 $k$-points total. Empirical Grimme correction [55] is not used in the calculations.

In this work, we calculated the separate slabs of hexagonal 2H phase WS$_2$ (0001) and MoS$_2$ (0001) with the thickness from 1 to 3 monolayers of dichalcogenide, GaN (1$\bar{1}$00) slab with the thickness of 24 atomic layers, as well as the heterostructure formed by the 24 atomic-layer GaN slab on which 1-3 layers of WS$_2$ (0001) or MoS$_2$ (0001) were deposited. Each monolayer of dichalcogenide in the slab is formed by three atomic planes where the central plane contains only Me atoms and the outer planes contain S atoms. Neighbouring atomic monolayers of dichalcogenide consist of the inverse arrangements on the atoms. Three projections of WS$_2$ surface and GaN surface are shown in Figs. S4 and S5, correspondingly. The heterostructures formed by GaN substrate with deposited WS$_2$/MoS$_2$ layers are shown in Figs. S6 and S7.

4. Results and discussion
As-grown individual core-shell NW morphology and inner structure was characterized using TEM (see Fig. 2), while SEM was used to confirm that the NWs maintain their length after the shell deposition procedures, as can be seen in Fig. S2. Lower magnification TEM images show the typical coating morphologies obtained via each MoS$_2$ and WS$_2$ synthesis method. While with PLD approach and pre-deposited WO$_3$ sulfurization (Fig 2. (c,e,g)) it is possible to obtain a smooth and uniform shell around NWs, MoO$_3$ sulfurization at optimal conversion and crystallization temperature gives non-uniform island-like coating (see Fig. 2(a)). Uniform shell is usually paramount for good electrical properties; however, the TMD-NW hybrid nanostructures with increased surface roughness are excellent for various energy applications [56], since the TMD in this configuration provides a lot of open active edge sites, while the NW core keeps its highly crystalline structure. At higher TEM resolution (Fig. 2(b,d,f,h)) the inner crystalline structure of the nanostructures is revealed. The layers of synthesised MeX$_2$ (each consisting of X-Me-X atomic planes)

![Figure 2](image)

**Figure 2.** Transmission electron microscope images at different magnifications of individual (a-b) GaN-MoS$_2$ NW prepared via MoO$_3$ coating sulfurization, (c-d) GaN-MoS$_2$ NW prepared via pulsed laser deposition, (e-f) GaN-WS$_2$ NW prepared via WO$_3$ coating sulfurization, (g-h) GaN-WS$_2$ NW prepared via pulsed laser deposition; the insets show the measured d-spacings.
shells can be distinguished as parallel black and white lines along the surface of NWs. The typical thickness of the uniform coatings varies from 4 to 10 monolayers, however, with some limitations it is possible to achieve thickness control including single monolayer deposition (see Fig. S3). Interplanar distance values (d-spacings) were measured to be around 6.4 – 6.6 Å for MoS$_2$ and 6.2 – 6.5 Å for WS$_2$, which are in good agreement with the lattice parameters for bulk MoS$_2$ (a = 6.16 Å, ICDD-PDF #37-1492) and WS$_2$ (a = 6.18 Å, ICDD-PDF #08-0237), respectively. Furthermore, the single-crystalline nature of the GaN NW core is clearly visible; the measured interplanar distance is 2.7 – 2.8 Å, closely matching hexagonal GaN (a = 2.76 Å, ICDD-PDF #50-0792). The TEM measurements show the high crystalline quality of the prepared core-shell NWs.

To confirm the presence of the respective phases in the as-grown core-shell NW samples, XRD measurements were performed on the NW arrays on the Si(100)/SiO$_2$ substrates (see Fig. 3(a,c)). Here and later on, for the sake of clarity, measurement results are shown only for the nanostructures prepared by the two-step sacrificial

![Figure 3](image)

**Figure 3.** (a) X-ray diffraction and (b) micro-Raman spectrum of GaN-MoS$_2$ NW arrays on a Si/SiO$_2$ substrate; (c) X-ray diffraction and (d) micro-Raman spectrum of GaN-WS$_2$ NW arrays on a Si/SiO$_2$ substrate.
coating method, since the PLD samples gave qualitatively identical results. Both XRD patterns for each sample exhibit Bragg peaks of the desired crystalline phases: hexagonal GaN NWs (ICDD-PDF #50-0792), MoS$_2$ shell (ICDD-PDF #37-1492) and WS$_2$ shell (ICDD-PDF #08-0237), supporting the TEM measurements. Bragg peak at $20 \approx 33^\circ$ can be attributed to the Si(100) substrate (forbidden Si(200) reflection). Peaks at $38.1^\circ$ and $44.3^\circ$ belong to the Au NPs used for the VLS growth (ICDD-PDF #04-0784). Furthermore, room-temperature micro-Raman spectroscopy was used to confirm the presence of the WS$_2$ and MoS$_2$ layers in the as-prepared nanostructures. The measured Raman spectrum of GaN-MoS$_2$ core-shell NW contains the in-plane E$_{12g}$ mode at 383 cm$^{-1}$ and the out-of-plane A$_{1g}$ mode at 408 cm$^{-1}$ (see Fig. 3(b)), thus confirming the formation of MoS$_2$ on GaN NWs [57]. Similarly, in the obtained GaN-WS$_2$ NW spectra, two bands at 352 cm$^{-1}$ and 420 cm$^{-1}$ were measured and attributed to the E$_{12g}$ and A$_{1g}$ modes in WS$_2$ [45], respectively (Fig. 3(d)).

An XPS analysis was performed in order to verify the chemical composition of the core-shell NW arrays on the Si(100)/SiO$_2$ substrates (see Fig. 4). High-resolution spectra of Mo 3d, W 4f, S 2p, Ga 3d and N 1s peaks were acquired and calibrated relative

![Figure 4](image.png)

**Figure 4.** High-resolution XPS core-level spectra and peak fits of GaN-MoS$_2$ core-shell NWs for (a) Mo 3d, (b) S 2p, (c) Ga 3d and (d) N 1s. High-resolution XPS core-level spectra and peak fits of GaN-WS$_2$ core-shell NWs for (a) W 4f, (b) S 2p, (c) Ga 3d and (d) N 1s.
to adventitious C 1s peak at 285 eV binding energy. Ga and N characteristic peaks for all samples confirmed the presence of GaN chemical state as was expected from GaN NWs: Ga 3d scan consists of Ga-N peak at 20.2 eV together with O 2s contribution at around 24.0 eV, while N 1s scan shows Ga-N peak at 397.8 eV and strong overlapping with Ga LMM peak. For both – GaN-MoS$_2$ and GaN-WS$_2$ – samples S 2p peaks consist of spin-orbit doublets ($\Delta_{3/2-1/2}=1.2$ eV) with 2p$_{3/2}$ peak measured at 161.8 eV, which is consistent with MoS$_2$ and WS$_2$ compounds. In the case of GaN-MoS$_2$ NWs, Mo 3d peak shows spin-orbit splitting ($\Delta_{5/2-3/2}=3.2$ eV) with Mo 3d$_{5/2}$ component being at 229.0 eV, corresponding to the MoS$_2$ chemical state [41]. Overlapping S 2s peak at 226.2 eV can also be observed in the scan. As for GaN-WS$_2$ NWs, the characteristic W 4f$_{7/2}$ peak position for WS$_2$ chemical state was measured at 32.0 eV ($\Delta_{7/2-5/2}=2.2$ eV) [39].

Within the framework of this study the calculations of GaN, WS$_2$ and MoS$_2$ bulk crystals, free-standing GaN, WS$_2$ and MoS$_2$ 2D slabs, as well as WS$_2$@GaN and MoS$_2$@GaN 2D nanoheterointerfaces have been performed. The calculated lattice constants of the GaN bulk are $a=3.189$ Å and $c=5.162$ Å, which are in a good agreement with experimental data $a=3.189$Å and $c=5.186$ Å [doi.org/10.1016/S0022-0248(96)00341-7]. The distance between the Ga atoms in the middle of the slab is 3.17Å, while the relaxation causes noticeable distortion of the atomic positions at termination edges of the slab, where the distance between the closest Ga atoms varies from 2.93 Å to 3.24 Å. The similar atomic shifts are calculated for the distances between Ga and N atoms, as well as between N atoms. The distance between Ga and N atoms as the 1st nearest neighbor in the middle of the slab is around 1.94-1.95Å, while the distance at the termination edges of the slab reduces to 1.80-1.94 Å during the relaxation. Similarly, the distance between N atoms is around 3.17 Å in the middle of
the slab slightly decreasing to 3.14-3.15 Å at the termination edges. The calculated lattice constants of dichalcogenides in a bulk phase: \(a = 3.13\) Å and 3.14 Å for bulk WS\(_2\) and MoS\(_2\), respectively. These values are in good agreement with experimental data [58,59]. The calculated value of \(c\) constant: \(c = 12.44\) Å and \(c = 12.59\) Å for WS\(_2\) and MoS\(_2\), respectively. The negligible differences between calculated and measured values (\(c=12.323\) Å for WS\(_2\) [58] and \(c = 12.3\) Å for MoS\(_2\) [59]) could be explained by not using of empirical Grimme correction in the calculations. The reason for this is a poor SCF convergence of 2D nanoheterointerfaces if Grimme correction is in use.

Due to very close lattice constants \(a\) of GaN substrate and both dichalcogenides the geometrical matching of the materials is good. The mismatch in the lattice constant during the stacking is 1.8%. The analysis of the atom positions after the relaxation reveals a certain alignment between Ga and S atoms and form a similar spatial arrangement as observed between Ga and N atoms in the bulk region similarly to Ref. [41]. For the constructed 2D nanoheterostructure the distances between Ga atoms in the middle of the slab are almost the same as in a perfect GaN slab and are equal to 3.18 Å, which indicates that the substrate thickness selected in the constructed model is sufficient. The relaxation of the atomic positions is larger at the termination edges of GaN substrate in comparison with the middle part of 2D heterostructure and are in the range from 3.02 Å to 3.21 Å. The relaxation of the interface of both WS\(_2\)@GaN and MoS\(_2\)@GaN heterostructures occurs similarly with almost identical atomic displacements. The difference between the heterostructures of WS\(_2\)@GaN and MoS\(_2\)@GaN is in the distance between GaN and WS\(_2\) or MoS\(_2\) layers, which slightly decreases from 4.25 Å to 4.24 Å for WS\(_2\)@GaN heterostructure and slightly increases from 4.25 Å to 4.27 Å for MoS\(_2\)@GaN heterostructure with the increase of the number of layers.
Fig. 5 shows total densities of states (DOS) calculated for [0001]-oriented monolayered (1ML), bi-layered (2ML), and three-layered (3ML) WS$_2$ and MoS$_2$ nanofilms deposited atop of [1-100] oriented GaN NW. DOS calculated for free-standing GaN(1-100) slab to mimic the NW surface, as well as free-standing WS$_2$ and MoS$_2$ nanofilms are shown to elucidate changes in electronic structures induced by the core-shell interface formation. The top of the valence band (VB) of free-standing GaN(1-100) substrate (uppermost graph in Figs. 5(a) and 5(b)) is located at -6 eV with

**Figure 5.** Density of states (DOS) as calculated for (a) WS$_2$@GaN and (b) MoS$_2$@GaN interfaces and their constituents. Zero corresponds to vacuum level. Each curve is normalized so that the maximum of each curve corresponds to 10 a.u.
the band gap width of 3.9 eV. DOSes calculated for layered WS$_2$ nanofilm (three graphs situated at the bottom in Fig. 5(a)) exhibit the top of VB positioned at -6.7 eV for all free-standing WS$_2$ nanofilms. As the number of WS$_2$ layers increases, there is a certain decrease of the band gap width due to the quantum confinement effect. The calculated band gap for 1ML-, 2-ML, and 3ML-WS$_2$ reduces in the following sequence: 2.6, 1.96, and 1.83 eV, respectively, with well-pronounced shift of the bottom of the conduction band (CB). Formation of WS$_2$@GaN interface results in further narrowing of the band gap width due to corresponding shift of both top of VB and bottom of the CB calculated for all 1ML-, 2ML-, and 3-ML-WS$_2$@GaN interfaces. The top of the VB calculated for all three WS$_2$@GaN interfaces under study remains mostly unchanged with respect to the number of nanofilm monolayers (-6.2 eV), while a more pronounced shift of the CB bottom leads to the gap of 1.32, 1.22, and 1.19 eV for 1ML-, 2ML-, and 3-ML-WS$_2$@GaN interfaces, respectively. DOS calculated for MoS$_2$@GaN interfaces (Fig. 5(b)) demonstrate a very similar behaviour of the band edges. Due to the quantum confinement effect the band gap of free-standing MoS$_2$ nanofilms increases with the decrease of the number of layers with the following sequence: 2.05, 2.23, and 2.72 eV for 3ML-, 2ML-, and 1ML-MoS$_2$, respectively. The shift of the VB top due to the formation of MoS$_2$@GaN interfaces leads to the further lowering of the band gap, while the CB bottom remains mainly unchanged. Band gaps calculated for 1ML-, 2ML-, and 3ML-MoS$_2$@GaN are 1.28, 1.19, and 1.17 eV, respectively.

According to the band edge diagram (Fig. 6) calculated for WS$_2$@GaN and MoS$_2$@GaN nanoheterostructures the free-standing WS$_2$ and MoS$_2$ monolayers have top of VB positioned below O$_2$/H$_2$O redox potential, while CB bottom is properly positioned above standard hydrogen electrode (SHE). Increased number of both WS$_2$ and MoS$_2$ monolayers shifts VB top closer to oxygen redox potential. GaN substrate
has VB top positioned at oxygen redox potential, while its CB bottom is located far above SHE. As soon as MoS$_2$ or WS$_2$ MLs are in contact with surface of GaN NW the CB bottom is positioned ~0.5 eV above SHE suitable for efficient hydrogen evolution within watersplitting reaction. VB top of both WS$_2$@GaN and MoS$_2$@GaN nanoheterostructures is located ~1 eV above O$_2$/H$_2$O redox level potentially making water splitting possible under red and near infrared irradiation. Thus, based on our calculations, WS$_2$@GaN and MoS$_2$@GaN core-shell NWs might be promising candidates for further investigation as photocatalysts for efficient hydrogen production from water.

5. Conclusions

In this work, we demonstrated growth of GaN-MoS$_2$ and GaN-WS$_2$ core-shell NWs via two different methods: (1) two-step process of sputter-deposition of a sacrificial transition metal oxide coating on GaN NWs followed by sulfurization; (2) pulsed laser deposition of few-layer MoS$_2$ or WS$_2$ on GaN NWs from the respective
material targets. As-prepared nanostructures were characterized via scanning and transmission electron microscopies, X-ray diffraction, micro-Raman spectroscopy and X-ray photoelectron spectroscopy. GaN NWs are close to an ideal substrate for MoS₂ and WS₂ growth due to the very well matching crystal lattice and high chemical stability in the corrosive sulfur atmosphere. By changing the process parameters, it was possible to obtain either a smooth and uniform shell around the NWs, which is paramount for good electrical properties, or non-uniform island-like coating with increased surface roughness that could be beneficial for various energy applications. DFT calculations showed that such GaN-MoS₂ and GaN-WS₂ core-shell NWs might be promising candidates for further investigation as photocatalysts for efficient hydrogen production from water.

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Supplementary information
Supplementary information is available and contains characterization data on pure GaN NWs, SEM images of GaN-MeS$_2$ NWs, TEM images of heterostructured NWs with various shell thickness, and projections of atomic structural models used in DFT calculations.

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