Supporting Information

Scalable synthesis of WS$_2$ on graphene and h-BN:
an all-2D platform for light-matter transduction

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Additional Methods

Graphene growth, h-BN transfer, SiC and quartz preparation: The substrates used in this work were: (i) h-BN exfoliated flakes on quartz; (ii) monolayer graphene obtained via chemical vapor deposition and transferred onto quartz; (iii) epitaxial monolayer graphene on SiC(0001). Details about their preparation follow.

(i) h-BN flakes were obtained via mechanical exfoliation on quartz substrates by scotch tape method$^{[1]}$. Before exfoliation, the quartz substrate was cleaned in acetone and isopropanol, and in O$_2$ plasma (5 min, 80W). After the exfoliation, the sample was cleaned again in acetone and isopropanol, and treated with oxygen to remove possible scotch tape residue.

(ii) Growth of large single-crystals of monolayer graphene was performed on Cu foil as reported in Ref.$^{[2]}$. Graphene was then transferred onto quartz substrate via dry transfer.
(iii) Monolayer graphene was grown on nominally on-axis 6H–SiC(0001). The SiC substrate was first subjected to HF treatment to remove native oxides, and then hydrogen etched at ~1250°C to prepare an atomically-flat 6H–SiC(0001) surface\(^3\). Graphene was subsequently obtained by annealing the atomically-flat sample for several minutes in argon atmosphere of 780 mbar at about 1700 K in a resistively heated cold-wall reactor (BM, Aixtron)\(^4\).

*Raman spectroscopy and SEM imaging:* Raman characterization was performed using a standard Renishaw inVia system equipped with a 532 nm green laser and 100x objective lens. The laser spot size was ~1μm and the accumulation time was 1s. Scanning Electron Microscopy (SEM) imaging was performed at 5 keV using a Zeiss Merlin microscope, equipped with a field emission gun.

*Transmission electron microscopy:* Transmission electron microscopy was carried out on a Zeiss Libra 120 transmission electron microscope operating at 120 kV and equipped with an in-column Omega filter for energy filtered imaging. Both electron diffraction patterns and bright field images were recorded energy filtered, with a 20 eV slit centered on the zero loss peak. Electron diffraction patterns were collected with a parallel beam in micro-diffraction mode, by selecting the diffracting area through the appropriate condenser aperture. For sample preparation, graphene was transferred on a gold grid\(^2\). Subsequently, WS\(_2\) was directly grown onto this system.
Additional Raman data

Raman analysis is a powerful tool to reveal the number of layer of WS$_2$ and also to test the quality of the substrate such as graphene. Fig. S1(a) shows typical Raman spectra of WS$_2$ on h-BN and epitaxial graphene, highlighting the 310 cm$^{-1}$ peak. The Raman spectra collected for mono- and bilayer WS$_2$ regions grown on CVD graphene are shown in panel (b). Fig. S1(c) shows the spectra measured for CVD graphene before and after WS$_2$ growth, demonstrating that graphene is not damaged by the growth process. Fig. S1(d) shows typical Raman spectra taken from the zerolayer and monolayer graphene regions. The 2D peak is significantly lowered in the latter.

![Raman spectra](image)

**Figure S1 : Raman Analysis:** (a) Raman peak in the 310 cm$^{-1}$ range of WS$_2$ on h-BN and Graphene on Silicon Carbide. (b) Raman spectra of WS$_2$ on CVD graphene taken in area mostly bilayer (blue) and monolayer (red). (c) Graphene Raman spectrum before (red) and after the growth (blue), indicating that graphene is intact also after the process. (d) Raman spectrum of epitaxial graphene (red) and buffer layer (blue), taken within the same substrate.
**AFM analysis of WS$_2$ on hBN**

In order to gain information about the thickness and morphology of WS$_2$ on exfoliated hBN, we performed AFM analysis on a sample with partial WS$_2$ growth as that depicted in the SEM micrograph reported in Fig. S2(a). The white areas in the SEM micrograph are representative of exposed hBN, whereas the dark ones indicate the presence of the WS$_2$ film. Representative AFM micrograph and related line profiles for such partial growth are reported in panels (b) and (c). Line profiles collected atop of holes (e.g., red line in panel (c)) consistently show that they are $1.6 \pm 0.3$ nm in height, which confirms the bilayer nature of our film. Between holes the film is flat within a range of a few Angstroms (black line in panel(c)). A root mean square (rms) roughness of a few Angstroms was similarly retrieved on AFM micrographs performed on films with complete coverage as reported in Fig. 1(a) of the main text.

![AFM analysis of WS$_2$ on hBN](image)

**Figure S2: AFM analysis of WS$_2$ on hBN**: (a) SEM image of a selected hBN flake, showing partial growth of WS$_2$ (black areas). (b) 1x1 µm AFM topography micrograph displaying partial WS$_2$ growth (holes in the film are visible as darker regions). The micrograph is a zoom-in of the larger area reported in the figure inset. Dashed lines indicate the position of the line profiles reported in panel (c). (c) The red line indicates that the hole depth matches that of a bilayer WS$_2$, whereas the continuous area appears to be flat in the order of a few Angstroms (black line).
AFM analysis of WS$_2$ on CVD-graphene

AFM analysis and line profile for continuous WS$_2$ films grown on top of CVD-graphene allow for WS$_2$ thickness estimation and morphology evaluation. Different from the case of exfoliated hBN flakes, where the thickness of the flake is unknown, in this case thickness of the supporting graphene layer is known (i.e. a monolayer). Hence, the thickness of WS$_2$ can be simply extracted by measuring the height of the heterostack. The line profile reported in Fig. S3(b) indicates a height of 2.3 ± 0.5 nm, compatible with that of a graphene monolayer with atop a WS$_2$ bilayer. The morphology of the film is in this case rougher (see Fig. S3(a)), with a rms roughness of 5.3 nm, which is due to contaminations brought by the transfer process.

Figure S3: AFM analysis of WS$_2$ on CVD graphene: (a) AFM topography micrograph of a flake of CVD graphene transferred on quartz with a WS$_2$ film grown on top. The number of layers of the system is estimated by tracking a line profile at the edge of the flake (b). The height measured matches the sum of one layer of graphene plus two layers of WS$_2$.

AFM analysis of WS$_2$ on epitaxial graphene on SiC

The epitaxial graphene topography was investigated before and after WS$_2$ growth. Fig. S4(a) is a characteristic AFM micrograph of an atomically flat SiC surface presenting step bunching (single steps of about 10 nm height) after graphene growth. The phase image reported in the inset of Fig. S4(a) shows typical monolayer (darker) and zerolayer (brighter) graphene regions
along the atomic terraces of SiC\textsuperscript{5,6}. Fig. S4(b) shows the sample after the growth of WS\textsubscript{2}. The morphology of the sample appears overall unaltered, although finer structures can be detected within the atomic terraces. Indeed, a more detailed analysis of the WS\textsubscript{2} film is possible by analysing the region within the atomic terraces, as shown in panel (c). The merging WS\textsubscript{2} islands, showing a triangular symmetry, present a mono to bilayer WS\textsubscript{2} height (see relative line profile in panel (d)).

**Figure S4**: AFM analysis of WS\textsubscript{2} on epitaxial graphene: (a) Representative AFM micrograph showing a typical topography of epitaxial graphene on SiC. The inset shows the phase trace, highlighting the difference between zero layer (bright) and monolayer (dark) graphene. (b) Topography of the surface after the growth of WS\textsubscript{2}. Terraces are not affected by the growth process. (c) Height scan of the same sample in the dashed area in panel (b) after WS\textsubscript{2} growth. (d) Profile of the highlighted line, showing monolayer and bilayer regions.
1. N. Mishra, V. Miseikis, D. Convertino, M. Gemmi, V. Piazza, C. Coletti, *Carbon* **2016**, *96*, 497-502.

2. V. Miseikis, D. Convertino, N. Mishra, M. Gemmi, T. Mashoff, S. Heun, N. Haghighian, F. Bisio, M. Canepa, V. Piazza, *2D Materials* **2015**, *2*, (1), 014006.

3. C. Coletti, C. L. Frewin, S. E. Saddow, M. Hetzel, C. Virojanadara, U. Starke, *Applied Physics Letters* **2007**, *91*, 61914.

4. Bianco, F.; Perenzoni, D.; Convertino, D.; De Bonis, S. L.; Spirito, D.; Perenzoni, M.; Coletti, C.; Vitiello, M. S.; Tredicucci, A. *Applied Physics Letters* **2015**, *107*, (13), 131104.

5. S. Goler, C. Coletti, V. Piazza, P. Pingue, F. Colangelo, V. Pellegrini, K.V. Emtsev, S. Forti, U. Starke, F. Beltram, *Carbon* **2013**, *51*, 249-254

6. S. Frewin, C. Coletti, C. Riedl, U. Starke, S.E. Saddow, *Mater. Sci. Forum* **2009**, *615–617*, 589.