

## ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

### Large area van der Waals MoS<sub>2</sub> - WS<sub>2</sub> heterostructures for visible-light energy conversion

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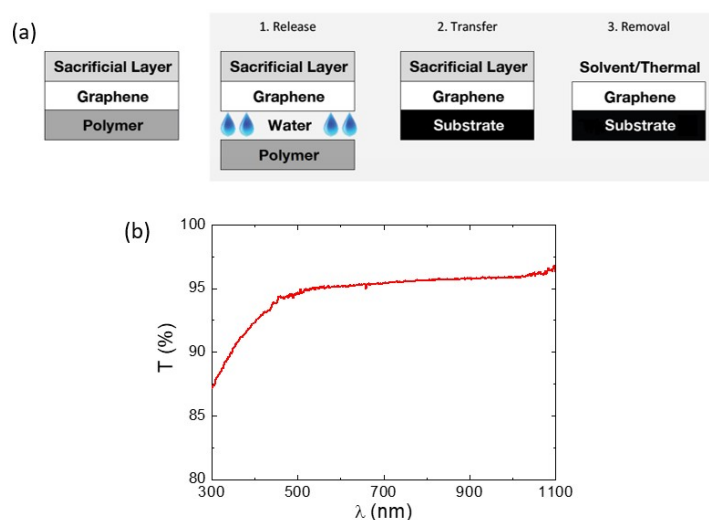
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#### S1. Graphene transfer

Large area commercial bilayer graphene electrodes (Graphenea) have been transferred on transparent silica substrates recurring to a wet transfer process in deionized water. The substrates were treated by ozone lamp to increase surface hydrophilicity to ease the transfer process, described by **Figure S1a**. Initially, the graphene is provided on a polymer film and coated by a sacrificial layer for protection. By immersion in deionized water, the graphene + sacrificial layer detach from the substrate and start floating. The surface treated silica substrate is then immersed to fish the floating graphene from below. The sample is then dried for 30 minutes in air and annealed for 1 hour at 150 °C on a hot plate. After that, it is stored in low vacuum for 1 day to increase the adhesion to the substrate. Finally, the sacrificial layer is removed by wash in hot acetone (50 °C) for 1 hour and isopropyl alcohol for another 1 hour.

**Figure S1b** shows an optical transmission spectrum acquired on a transferred bilayer graphene. Extinction in the visible range is about 5%, in agreement with the expected theoretical absorption value of 4,6% for a bilayer graphene. The high transparency is crucial for graphene application as a transparent window layer in photonic devices in superstrate configuration.

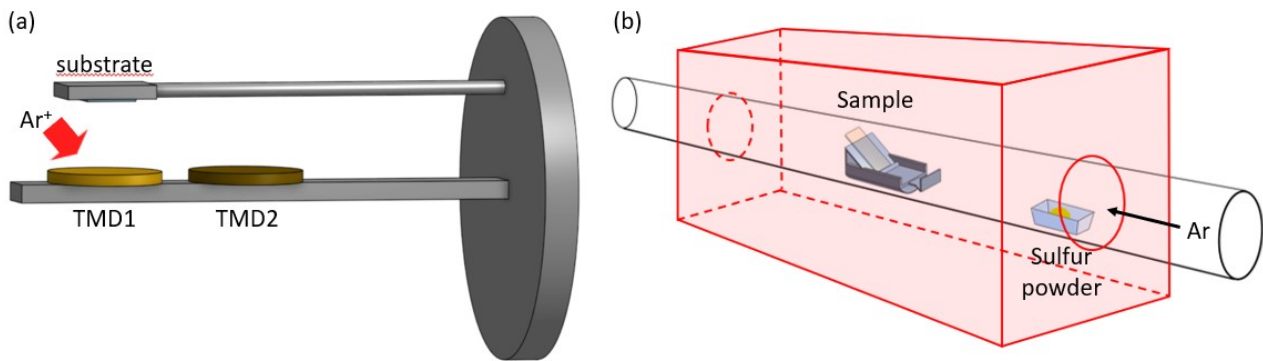


**Figure S1.** a) Graphene transfer steps, from Graphenea EasyTransfer Instructions. b) Optical transmission of a transferred bilayer graphene.

## S2. TMDs growth process

Large area deposition of TMD layers is achieved by means of ion beam sputtering. In **Figure S2a** we show a sketch of our custom set-up, featuring the possibility to face the substrate to multiple targets (in this case,  $\text{WS}_2$  and  $\text{MoS}_2$ ) from which the selected material can be deposited by translation of a manipulator.

The TMD layers deposited by means of physical sputtering are initially in an amorphous phase. To obtain semiconducting 2H-phase, a high temperature recrystallization process in a sulfur enriched argon atmosphere is employed. To this end, we used a single zone tube furnace set at  $750\text{ }^\circ\text{C}$  with an argon flux of  $100\text{ sccm}$ . The TMD layer is placed at the center of the furnace, while a quartz boat containing about  $300\text{ mg}$  of sulfur powder is placed upstream in a region of the oven at about  $170\text{--}200\text{ }^\circ\text{C}$ . The heating rate is set at  $20\text{ }^\circ\text{C}/\text{min}$  and a soaking of 10 minutes is performed once the final temperature is reached. After the soaking, quenching is performed by retracting the tube to quickly cool down the sample, preventing the TMD from sublimation. In **Figure S2b** a sketch of the tube furnace is shown.

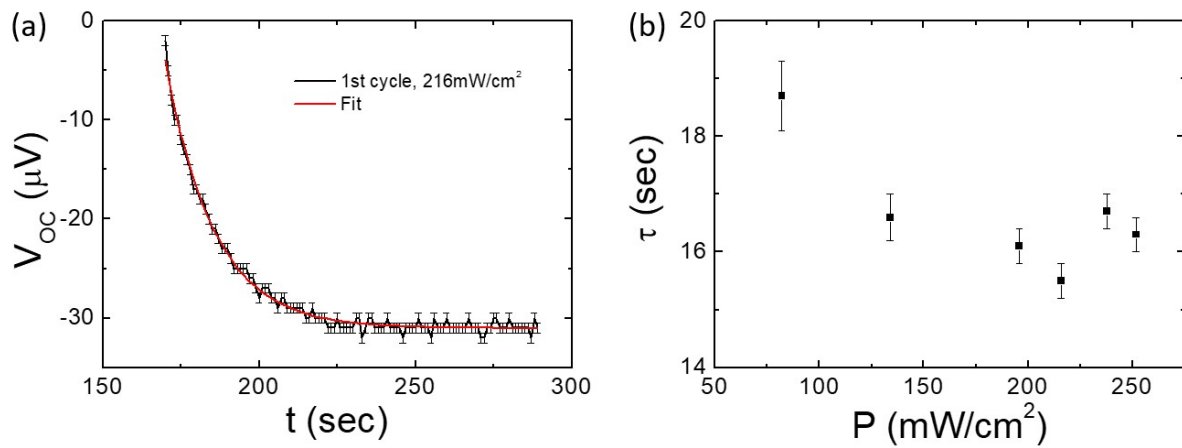


**Figure S2.** a) Sketch of the IBS deposition set-up. b) Sketch of the tube furnace used for TMD recrystallization.

## S3. Photovoltage response time

The photovoltage time dependent variation under continuous broadband illumination, shown in Figure 3a in the main text, was analyzed to extract the characteristic response time of the device. The first illumination cycle for each illumination power density level was fitted with a first-order exponential decay described by the following formula:  $V_{OC} = A_1 \cdot e^{(-t/\tau)} + V_0$ . An error bar of  $0.5\text{ }\mu\text{V}$  (noise level) has been considered for each point.

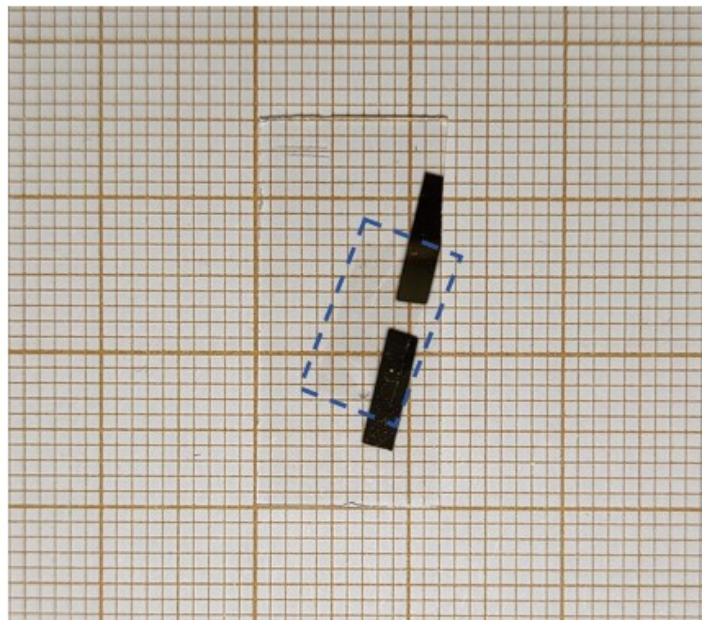
An example of one cycle fit is reported in **Figure S3a** for the power density level of  $216\text{ mW}/\text{cm}^2$ , giving a response time of  $15.5 \pm 0.3\text{ sec}$ . In **Figure S3b** the extracted response time at each power density is reported, showing an average response time of about  $16\text{ sec}$ .



**Figure S3.** a) Fit with a first order exponential decay of the first illumination cycle at 216mW/cm<sup>2</sup>. b) Response time at different power density levels.

#### S4. Graphene sheet resistance

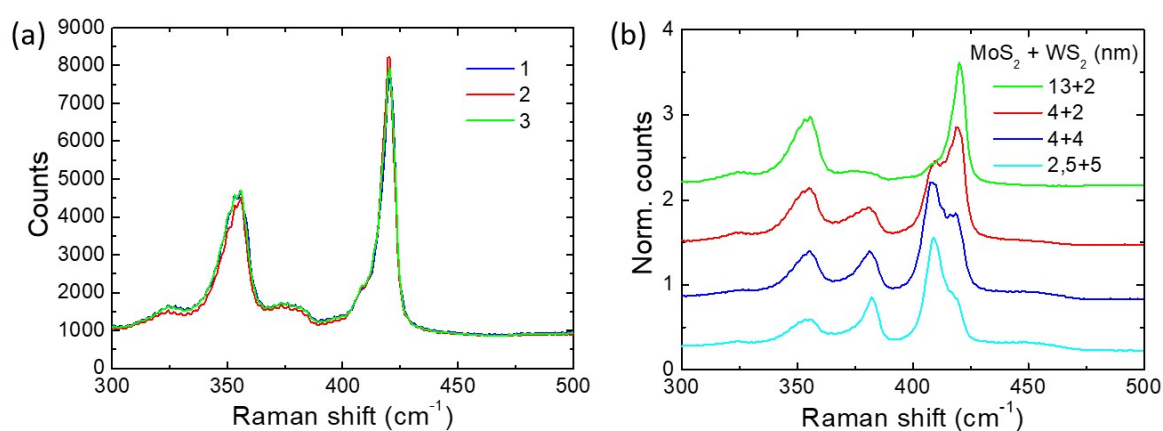
To evaluate bilayer graphene sheet resistance, a second graphene electrode was transferred on a silica substrate recurring to the same transfer process. Macroscopic Ti/Au contact (width 2 mm, gap 2 mm) were deposited on the graphene layer by ion beam sputtering using a proximity mask, as shown by the photograph of the sample in **Figure S4**. The measured resistance across the contacts measures 1.5 k $\Omega$ .



**Figure S4.** Photograph of a bilayer graphene electrode with Ti/Au contacts. The graphene layer is marked by the dashed blue rectangle.

## S5. TMDs growth reproducibility

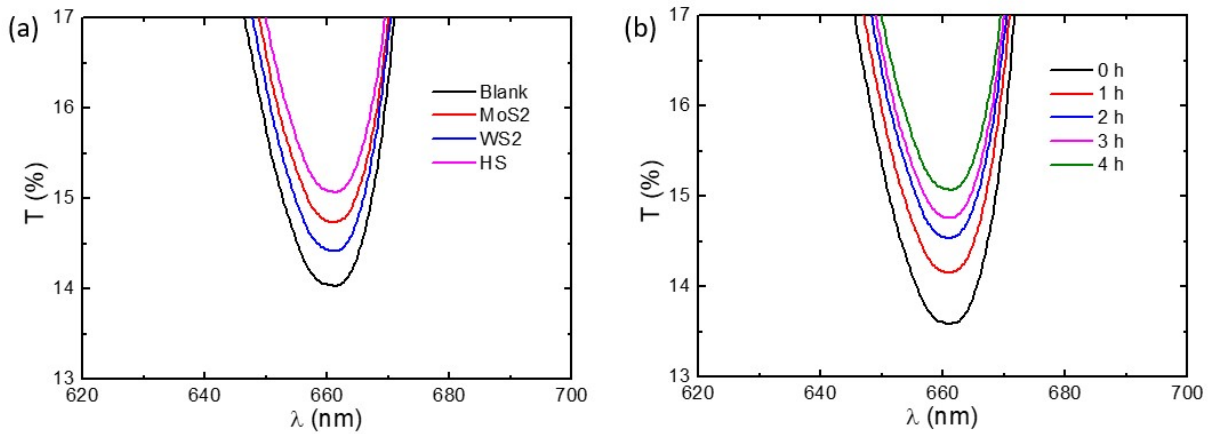
We verified the reproducibility of our single-step synthesis of large area  $\text{WS}_2/\text{MoS}_2$  heterostacks by fabricating three nominally identical samples on silica substrates in the same simple configuration adopted in the photocatalysis experiments, i.e. without the top and bottom contacts. In **Figure S5a**, the Raman characterization of the three nominally equivalent samples (13 nm  $\text{WS}_2$  and 2 nm  $\text{MoS}_2$ ) is reported, demonstrating the high degree of reproducibility of our growth process. In **Figure S5b** instead we show the Raman spectra of nominally different samples, obtained by varying the relative thickness of the  $\text{WS}_2$  and  $\text{MoS}_2$  layers. The counts have been normalized to the  $\text{WS}_2$  E mode peak and an offset has been added for the sake of clarity. The ratio between the  $\text{WS}_2$  and  $\text{MoS}_2$  peaks is in agreement with the relative  $\text{MoS}_2/\text{WS}_2$  thickness, confirming the robustness of our single-step synthesis process.



**Figure S5.** a) Raman spectra of three nominally identical  $\text{WS}_2/\text{MoS}_2$  samples, demonstrating the high degree of reproducibility of the single-step synthesis. b) Raman spectra of nominally different heterostructure samples, showing a different TMD signal ratio according to the thickness.

## S6: MB photodegradation

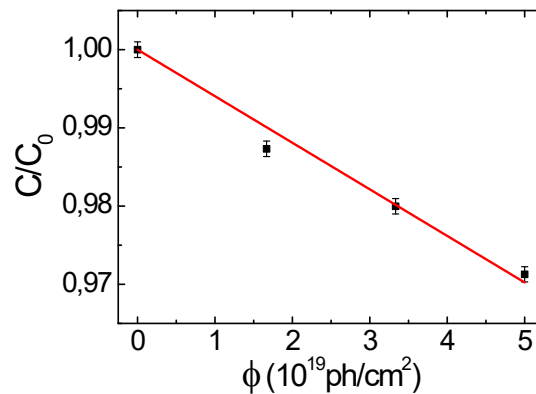
The MB concentration is evaluated by the solution optical transmission in correspondence to the absorption dip at  $\lambda = 660\text{nm}$ . In **Figure S6a** the optical transmission of the MB solution after a fixed dose is reported for the different samples, showing higher degradation in the case of  $\text{MoS}_2\text{-WS}_2$  heterostack. For the latter, exposure dose dependent evolution of the optical transmittance is reported in **Figure S6b**. By normalizing the transmission to the value for the initial solution with concentration  $C_0 = 1.3 \times 10^{-5} \text{ mol L}^{-1}$ , the concentration evolution is determined.



**Figure S6.** a) MB solution transmittance after same dose exposure with different samples. b) MB solution transmittance as a function of exposure dose for the heterostack MoS<sub>2</sub>-WS<sub>2</sub> sample.

### S7: Kinetic constant calculation

For each sample, the kinetic constant of MB photodegradation reaction is calculated by a linear fitting of the concentration evolution as a function of the photon incident dose. In **Figure S7** we show the linear fit for the case of the blank MB solution, from which we extract a kinetic constant  $k = 0.0060 \pm 0.0003 \text{ s}^{-1}$  with a  $\chi^2 = 6$ . The same procedure was repeated for each sample, and the  $k$  values were normalized to the highest value to obtain the graph reported in the main text (Figure 4d).



**Figure S7.** Linear fit of the MB concentration evolution as a function of the photon incident dose in the case of the blank solution. From the fitting we extract the kinetic constant  $k$ .