2D gallium selenide (GaSe) and gallium sulfide (GaS) nanoflakes for photoelectrochemical (PEC)-type photodetectors

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Two-dimensional (2D) transition metal monochalcogenides (TMMCs) have been recently predicted to be potential photo(electro)catalysts for water splitting and photoelectrochemical (PEC) reactions [1]. In particular, 2D gallium selenide (GaSe) and gallium sulphide (GaS) are emerging as promising candidates for these applications [2][3]. In fact, their 2D nature intrinsically guarantees that the charge carriers are directly photogenerated at the interface with the electrolyte, in which redox reactions take place before charge recombination. Moreover, their electronic structure can be tuned by controlling the number of the layers to fulfil the fundamental requirements for water splitting photocatalysts, *i.e.*: 1) conduction band minimum energy (E_{CBM}) > reduction potential of H^+/H_2 ($E(H^+/H_2)$); 2) valence band maximum energy (E_{VBM}) < reduction potential of O_2/H_2O ($E(O_2/H_2O)$). In this work, we report the first experimental characterization of the PEC water splitting activity of single-/few-layer flakes of GaSe and GaS produced in inks form through scalable liquid-phase exfoliation (LPE) approach [4,5,6] in non-toxic solvents. The as-produced dispersions were deposited by spray-coating technique to conceive solution processed self-powered PEC-type photodetectors. The PEC behaviour of TMMCs-based photoelectrodes were evaluated in different aqueous media, ranging from acidic to alkaline solutions under different illumination wavelengths in the visible spectral range, namely 275, 455, 505 and 625 nm. GaSe photoelectrodes reached a responsivity of 0.16 A W^{-1} upon 455 nm illumination at a light intensity of 63.5 μW cm^{-2} and applied potential of −0.3 V *versus* reversible hydrogen electrode (RHE). Meanwhile, due to its large band gap, GaS photoelectrodes show a relevant UV selective PEC photoresponse, attaining responsivities of 1.8 mA W^{-1} in 1 M H_2SO_4 (at 0.8 V *vs.* RHE), 4.6 mA W^{-1} in 1 M Na_2SO_4 (at 0.9 V *vs*. RHE), and 6.8 mA W^{-1} in 1 M KOH (at 1.1. V *vs*. RHE) under 275 nm illumination wavelength with an intensity of 1.3 mW cm^{-2}. Our results open the way towards the use of 2D TMMCs in innovative PEC systems, (bio)sensors and other innovative optoelectronics devices.

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"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement GrapheneCore3 - 881603"