

MoS₂ Defect Healing for High-Performance Sensing of Polycyclic Aromatic Hydrocarbons and Mercury Ions

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The increasing population, societal and industrial development represent major environmental problems. Nowadays various governmental agencies decided to pose limits for the maximum permitted levels of pollutants in water, soil and air. For example, among toxic chemicals, heavy metals such as mercury ions (Hg²⁺) and polycyclic aromatic hydrocarbons (PAHs) are poisoning contaminants which could lead to serious health problems. The Environmental Protection Agency (EPA) defined as 10 nM and 0.2 ppb the maximum allowed levels of Hg²⁺ ions and PAHs in drinkable water, respectively. For this reason, the development of fast and reliable sensors for air and water quality monitoring became a hot-topic in science. Low-dimensional materials have attracted great attention as ideal sensory materials, combining high surface-to-volume ratio with unique optical and electrical properties. [1] Among them, two-dimensional semiconductors, such as transition metal dichalcogenides (TMDCs) are characterized by physical and chemical properties that are hugely susceptible to environmental changes. TMDCs can be integrated in field-effect transistors (FETs), which can operate as high-performance chemical detectors of the (non-)covalent interaction with small molecules. Here, we have developed MoS₂-based FETs as platforms for PAHs sensing, relying on the affinity of the planar polyaromatic molecules for the basal plane of MoS₂ and the structural defects in its lattice. X-ray photoelectron spectroscopy (XPS) analysis, photoluminescence (PL) measurements and transfer characteristics in FETs showed a notable reduction in the defectiveness of MoS₂ and a p-type doping upon exposure to PAHs containing solutions, with a magnitude determined by the correlation between the ionization energies (E_i) of the PAH target and that of MoS₂. Naphthalene, endowed with the higher E_i among the studied PAHs, exhibited the greatest output. Remarkably, we observed a log-log correlation between MoS₂ doping and naphthalene concentration in water in a wide range (10⁻⁹-10⁻⁶ M). Naphthalene concentrations as low as 0.128 ppb were detected (Figure 1a), being below the limits imposed by health regulations for drinking water. When performing several exposure/washing cycles,

the sensor was also able to switch among two different doping levels. Furthermore, our MoS₂ devices can reversibly detect vapors of naphthalene both with an electrical and optical readout: overall, our device architecture could operate as a dual platform for the electrical sensing and Raman identification of the analyte. [2]

In another work, we have fabricated MoS₂-based FETs with a similar architecture and exploited them as platforms for Hg²⁺ sensing, relying on the affinity of heavy metal ions for both point defects in TMDCs and sulfur atoms in the MoS₂ lattice. XPS characterization showed both a significant reduction of the defectiveness of MoS₂ when exposed to Hg²⁺ ions with increasing concentration and a shift in binding energy of 0.2 eV suggesting a p-type doping of the 2D semiconductor. The efficient defect healing has been confirmed also by low-temperature PL measurements by monitoring the attenuation of defect-related bands after Hg²⁺ exposure. Transfer characteristics in the MoS₂ FETs provided further evidence that Hg(II) acts as a p-dopant of MoS₂. Interestingly, we observed a strict correlation of the doping with the concentration of Hg²⁺ ions, following a semi-log trend. Hg(II) concentrations as low as 1 pM can be detected (Figure 1b), being below the limits imposed by EPA regulations. Electrical characterizations also revealed that the sensor can be washed and used multiple times, efficiently switching among two different doping levels. Moreover, the developed devices displayed a markedly high selectivity for Hg(II) against other metal ions as ruled by soft/soft interaction among chemical systems with appropriate redox potentials. In conclusion, we propose a generally applicable approach to develop chemical sensing devices combining a highly sensitivity, selectivity and reversibility to meet technological needs. [3]

References

- [1] C. Anichini, W. Czepa, D. Pakulski, A. Aliprandi, A. Ciesielski, P. Samorì, *Chemical Society Reviews*, 47, 13, (2018), 4860-4908
- [2] F. J. Urbanos†, S. Gullace†, and P. Samorì, *ACS Nano*, submitted
- [3] F. J. Urbanos, S. Gullace, P. Samorì, *Nanoscale*, 13, (2021), 19682-19689

Figures

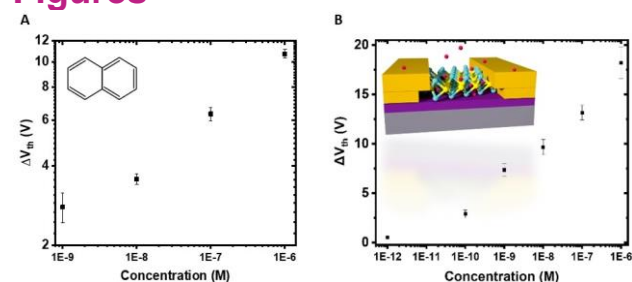


Figure 1. Variation of the threshold voltage (ΔV_{th}) of the fabricated field effect transistors (FETs) as a function of **A)** naphthalene and **B)** mercury ions, in water. The inset shows a representative scheme of the interaction among Hg(II) ions and a MoS₂-based FET.