Utilization of semiconducting bismuthene, antimonene and V_2O_5 2D nanosheets in electrochemical sensing

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Abstract: 2D inorganic layered materials have been on the forefront of energy related applications for almost two decades. However, their impact on electroanalysis should not be underestimated, since they have undoubtedly invigorated the field due to their enhanced electrocatalytic properties, great surface to volume ratio and direct electron transfer between the modified electrode surface and the redox centers of biomolecules [1]. Our research fixes upon the implementation of 2D inorganic nanosheets, produced via various top-down approaches, and their use, as electrocatalysts, for the determination of heavy metal ions, explosive and highly toxic compounds or pharmaceutical compounds. It should be stressed out that the majority of inorganic nanosheets are low to wide band gap semiconductors with some exceptions illustrating metallic properties [such as 1T polymorph of dichalcogenides, MXene-core (not taking into consideration electronic state deviations originating from various etching procedures), etc.]. This leads to the necessity of creating conjugated or composite forms of those materials with more conducting phases to ameliorate sensor sensitivity. Our first endeavor is the production shear-force exfoliated bismuthene which is a low band gap semiconductor (bilayer bismuthene ranges from 0.18 to 0.23 eV) and its conjugation with similarly produced few-layer graphene for the anodic stripping voltammetric determination of Cd(II) and Pb(II) at the sub-ppb level (LODs of 0.33 ppb). Our second effort was the production of few-layer antimonene, which is a wide band gap semiconductor with an indirect band gap of 2.28 eV (predicted for monolayer β-Sb), with probe sonication and the in-situ formation of a semi-conducting heterostructure with poly(3,4ethylenedioxy thiophene):poly(styrene sulfonate) for the nanomolar cathodic determination of 4-nitrotoluene (LOD 16.7 nM) and 2,4-dinitrotoluene (LOD 33.3 nM). Finally, we have successfully utilized few-layer V_2O_5 nanosheets, which have a very wide band gap, predicted to be 4 eV for a monolayer, via a simple bath sonication procedure. Admittedly, while this great a band gap partially hampers electronic transfer, it can provide a great electroanalytical platform through the intercalation/deintercalation of ionic species which can enhance proton related redox reactions. This is proven by the nanomolar determination of diclofenac (a widely administered non-steroidal anti-inflammatory drug), via the quantification of its electrochemically active oxidation product, thus reaching an LOD of 6.6 nM. The analytical utility of the respective screen-printed sensors was evaluated in real-world samples, in which excellent recovery values were obtained.

Reference

[1] A.C. Lazanas, M.I. Prodromidis, Two-dimensional inorganic nanosheets: production and utility in the development of novel electrochemical (bio)sensors and gas-sensing applications, Microchim. Acta. 188 (2021)