Layered Transition Metal Dichalcogenides for Electrochemical Energy Generation and Storage: From Bulk to Thin Layers and Single 2-Dimensional Sheets

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Layered Transition Metal Dichalcogenides for Electrochemical Energy Generation and Storage

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Layered transition metal dichalcogenides (TMDs) (MoS_2, $MoSe_2$, WS_2, WSe_2, etc.) are a chemically diverse class of compounds having band gaps from 0 to ~2 eV and remarkable electrochemical properties. The band gaps and electrochemical properties of TMDs can be tuned by exchanging the transition metal or chalcogenide elements. After a brief description of the most commonly followed synthetic routes to prepare TMDs, we wish to highlight in this review the diverse electrochemical applications of MoS_2, a representative and well-studied TMD, which span from its use as catalysts in hydrogen evolution reactions to its adoption in supercapacitors, batteries, solar cells, and hydrogen storage.

1. Introduction

Transition metal dichalcogenides (TMD) are scientifically interesting and industrially important compounds. Chalcogenides, that is S, Se, and Te (VI A group), create very stable binary compounds with transition elements forming layered crystalline structures especially with transition metals of group IV-VII B. Their layered structure resembles that of graphite with weak van der Waals interactions between the individual layers. The crystal structure varies from the hexagonal $P6_3$/mmc for molybdenite (MoS_2) and tungstenite (WS_2) to the orthorhombic structure Pmn21, as for $MoTe_2$ and WTe_2, giving rise to dramatic anisotropy and different material properties (see Figure 1). Such properties are of industrial importance. For example, due to their layered structure, MoS_2 and WS_2 can be employed as dry lubricants able to withstand higher temperatures than graphite.[1] Layered transition metal dichalcogenides are compounds of the general formula MX_2 where M is a transition element of groups IV B (Ti, Zr, Hf), V B (V, Nb, Ta), VI B (Mo, W), and VII B (Tc, Re) and X is a chalcogen atom of the VI A group (S, Se, Te). VIII B group elements create dichalcogenides, which in some cases are partially layered in structure (Co, Ni; Rh, Pd, Ir, Pt). Unlike pristine graphene, which is a semimetal with a zero band gap, TMDs exhibit a variable band gap between 0 (semimetal) to 2 eV (semiconducting) depending on the element combination, the number of layers, and the presence or lack of a doping atom. TMDs exhibit well-defined structures, unlike doped graphene, which loses its crystalline structure when covalently doped to tune its bandgap, effectively creating poorly defined amorphous graphenoid material.[2] Tuning of the band gap is important for electronic, electrochemical, and optical applications of these layered binary materials. Layered TMDs also possess catalytic properties, which can easily be tuned with selective doping. For example, MoS_2 doped with Co or Ni is used in the petrochemical industry for hydrodesulfurization processes.[3,4]

MoS_2 is found as the mineral molybdenite (mined i.e., in Norway, Australia, and North America). Some other TMDs are known from nature: WS_2 (tungstenite), $MoSe_2$ (drysdallite), ReS_2 (rheniite). However, only molybdenite, which is the main source of molybdenum, is found in nature in large amounts. Molybdenite can form large crystals in some types of geological formations (for example, granite pegmatite veins, cracks in granite and granodiorite, quartz-MoS_2-Bi veins, Sn-W greisen veins, Sn-Cu greisen veins, and disseminated porphyry with Cu-Mo and Mo mineralization). Naturally occurring crystals of MoS_2 have sufficient quality for basic research applications. The natural crystals of molybdenite and tungstenite are shown in Figure 2. The layered structure of TMDs offers the possibility of preparing well-defined ultra-thin structures and, ultimately, single layers, which possess remarkably different electronic properties than those of their counterpart bulk materials. Such tunability properties make them ideal materials for electronic or electrochemical devices. With increasing interest in layered TMDs from the research community, we wish to provide focused minireview on the representative past efforts in the use of layered TMDs in electrochemical applications. We will describe the electrochemical applications of layered TMDs from bulk materials to single-layer sheets. We hope to provide here introduction of the field to chemists and materials scientists who are new to the field as well as to provide useful discussion of the key papers to the experts. We wish to direct interested readers to more specific reviews; there are excellent extensive review articles focused on the structure and interfacial properties of bulk TMDs[5], on the use of TMDs in lithium batteries[6], general materials properties of nanosized TMDs[7], and energy storage and conversion devices.[8,9]

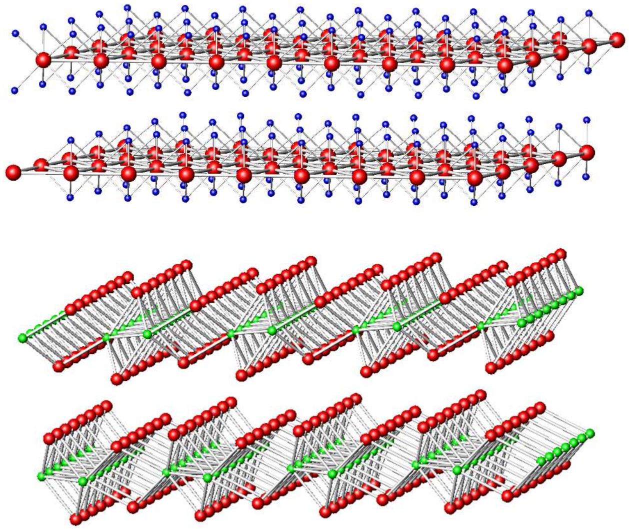

Fig. 1 Crystal structure of layered transition metal chalcogenides. Upper structures correspond to layered hexagonal structure (P63/mmc symmetry group; red atoms – Mo and W; blue atoms – S and Se). Bottom structure corresponds to layered orthorombic structure (Pmn21 symmetry group; green atoms – Mo and W; red atoms – Te).

2. Preparation methods

Prior to discussing the electrochemistry of layered TMDs, we wish to briefly mention the methods used for their preparation (Figure 3). The layered structure of TMDs suggests that methods similar to those used in the preparation of graphene can be used for preparing TMD thin layers. The methods are based on "top-down" and "bottom-up" procedures. The "top-down" procedures include mechanical exfoliation of bulk TMDs. This has similar limitations as those encountered in graphene fabrication: while it is not scalable, large sheets of high-quality, single-layer material can be obtained. Large quantities of few-layer TMDs can be prepared by lithium intercalation methods with consequent exfoliation of bulk TMDs. Lithium intercalation is performed using organometallic compounds of lithium (like butyllithium) in MoS_2 and WS_2.[10] WS_2 was prepared by unzipping WS_2 nanotubes using *n*-butyllithium in hexane.[11] Another strategy for lithium intercalation is to use TMD as a cathode for electrochemical reduction and subsequent intercalation of metallic lithium.[12] Mechanical exfoliation using ultrasonic exfoliation in various solvents are also suitable methods for large-scale production of single-layer and few-layer TMD.[13,14] This method was successfully applied for MoS_2, WS_2, WSe_2, $MoSe_2$ and many others.[12,14,15] Methods based on "bottom-up" procedures can be employed for the synthesis of single- and few-layered films as well as for bulk powders. Ultra-high quality monolayer MoS_2 has been prepared by solid-vapor deposition.[16] A different strategy is the decomposition of tetrathiomolybdate and subsequent reduction of MoS_3 to MoS_2.[17] For the CVD deposition of TMD, sufficiently volatile precursors must be used. Typical examples are halogens and oxo-halogens of Mo and W. As the sulfur source, thiols or dialkyl sulfides and dialkyl selenides[18-21] are usually used. The bulk synthesis of TMD nanostructures is based on the reaction of sulfur precursors (such as Na_2S, CH_3CSNH_2, NH_2CSNH_2, KSCN) with molybdate ions.[22] Another strategy for the "bottom-up" synthesis of TMDs is based on the thermal decomposition and subsequent reduction of thiomolybdates or thiotungstenates under hydrothermal conditions.[15]

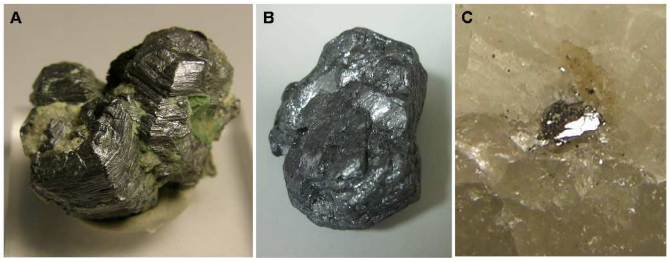

Fig. 2 Natural crystals of molybdenite (Figure 2A, Locality: Valle de Elqui, Atacama, Chille, sample size 2 cm), individual crystal of molybdenite (Figure 2B, Locality: Sörumsaasen mine, Spikkestad, Drammen, Norway, crystal size 3 cm) and natural crystals of tungstenite (Figure 2C, Locality: Crevoladossola quarry, Ossola Valley, Piedmont, Italy, crystal size 1.5 mm). Authors collection.

3. Electrochemical properties

3.1. Photoelectrochemistry

Interesting photoelectrochemical properties were found in thin films of MoS_2 and $MoSe_2$. Ultrathin MoS_2 sheets (thickness of 39 nm) were found to exhibit poor heterogeneous electron transfer (HET) rates (low k^0) and low faradic currents in dark environments for non-aqueous electrochemistry in acetonitrile. Upon white light irradiation, the HET rates increased dramatically for all tested compounds such as decamethylferrocene and tetrachlorobenzoquinone, tetracyanoquinodimethane (TCNQ), and tetramethylphenylenediamine (TMPD).[23] Similar photoelectrochemical behavior was observed for $MoSe_2$ bulk materials (see Figure 4).[24] Photoelectrochemical oxidation of Cl^- and Br^- on bulk MoS_2 and WS_2 in the production of Cl_2 and Br_2 was investigated. Platinized TMD showed enhanced performance than did bare layered MoS_2 and WS_2.[25] It was shown theoretically and experimentally that there are qualitative differences in the photoelectrochemistry of bulk and nanostructured MoS_2.[26]

3.2. Hydrogen evolution reaction

Layered TMDs are immensely popular for use in electrochemical hydrogen evolution reactions (HER).[27] It was contended that the edge planes of MoS_2 are the active sites for HER.[28] It was found that current density during HER scales directly with exposed edge sites of MoS_2[29] and that changing the dimensions of MoS_2 from bulk sizes to single-layer structures leads to special surface properties that can greatly improve material HER performance.[26]

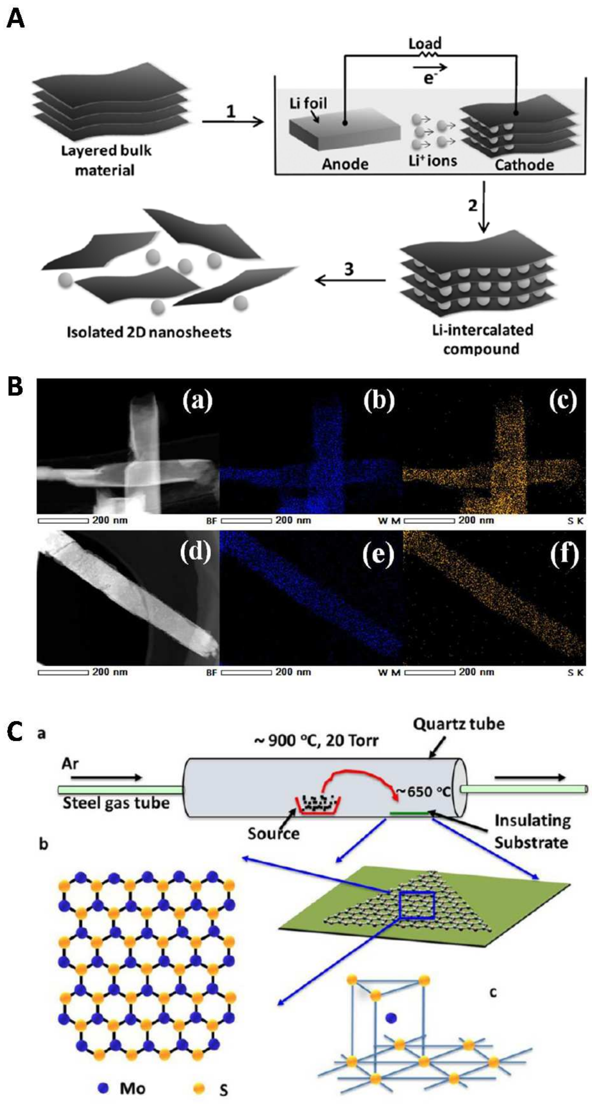

Fig. 3 Synthetic routes for fabrication of single layer TMD. (A) exfoliation by intercalation of lithium; (B) opening of WS_2 nanotube and (C) vapor deposition. Reprinted from Refs [13, 11, 16] with permission.

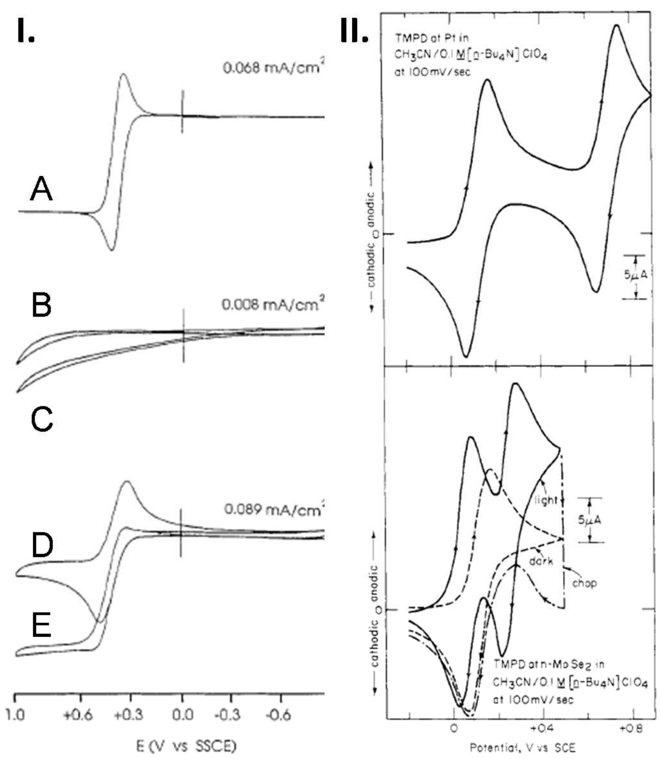

Fig. 4 Photoelectrochemistry on MoS_2 and $MoSe_2$. (I.) Cyclic voltammogram of 1.0 mM ferrocene/0.10 M TBAP in acetonitrile at 20 mV/s. Working electrodes: (A) Pt; (B) TiO_2/Ti in the dark, (C) TiO_2/Ti under white illumination; (D) MoS_2 thin film in the dark; (E) MoS_2 thin film under white illumination. (II.) Comparison of cyclic voltammetry for TMPD at Pt and $MoSe_2$ (dark and illuminated and illumination discontinued at the anodic limit). Illumination was with 632.8 nm light at 50 mW/cm^2. Reprinted from Ref [23] and [24] with permission.

In contrast, other groups found that there is very little difference between bulk and ultra-thin films of MoS_2 for HER.[30] It was shown that metallic single layer 1T-MoS_2 polymorph exhibits highly favorable HER properties.[31] Doping bulk MoS_2 with other transition metals was found to tune the reduction potential towards H^+.[32] MoS_2 was found to be beneficial as an electrode material for HER in microbial electrolysis cells to replace Pt.[33] Few-layer MoS_2 sheets were synthesized on carbon nanospheres and used for HER.[34] In order to combine the catalytic properties of MoS_2 nanostructured materials with the favorable electrical properties of carbon materials, systems with enhanced performance have recently been obtained by synthesizing MoS_2 nanostructures over carbon nanotubes[35] and graphene.[36] Specifically, the solvothermal synthesis of MoS_2 in the presence of reduced graphene generated a composite with a high concentration of edge-plane structures of MoS_2, which generated an overpotential as small as ~0.1 V.[37] MoS_2 nanoparticles (of 1.47 nm) were deposited on an Au electrode and exhibited favorable HER properties.[37] In other work, MoS_2 deposited on 3D Ni foam was reported to be highly efficient in HER.[38] Core-shell MoO_3/MoS_2 nanotube arrays exhibited highly efficient hydrogen evolution due to the high surface area.[39] Research on hydrogen evolution is theoretically well supported. It was shown that MoS_2 exhibits much more favorable reaction coordinates for H_2 evolution than do many other catalysts and is similar to those of the hydrogenase and nitrogenase enzymes (Figure 5).[40] MoS_3 particles (non-layered structure) were shown to demosntrate lower reduction potentials (that is, more favourable) than MoS_2 microcrystals.[41] In depth review on the HER on MoS_2 can be found in Ref.42. Strained single-sheet WS_2 were prepared by chemical exfoliation and exhibited very high catalytic activty towards HER.[43] MoS_2 can act as enhancer of photocatalyst efficiency. CdSe nanoribbons are photocatalytic materials capable of induction of H_2 evolution from aqueous solution. When MoS_2 was linked to CdSe nanoribbons, the efficiency of the compsoite material increased about 4 times due to the participation of MoS_2 in hydrogen reduction. Interestingly, CdSe-Pt hybrids showed lower performance than CdSe-MoS_2 hybrids.[44]

3.3. Capacitive behaviour

Since MoS_2 has a layered structure similar to graphite, it exhibits two key crystal features: a basal plane and an edge plane. The edge plane of MoS_2 has been found to be more electroactive. To create a surface with high-energy storage capacity, edge-oriented nanowall films were fabricated by chemical vapor deposition (Figure 6). It was found that MoS_2 nanowall films exhibited excellent supercapacitor properties, similar to those of carbon nanotubes.[45] Spray painting of MoS_2 with consequent laser patterning was developed for the construction of micro-supercapacitors which exhibited the high area capacitance of 8 mF cm^{-2}. [46] Recently, porous tubular C/MoS_2 composites have been fabricated using anodic aluminum oxide film as template. The capacitor assembled using this nanocomposite material exhibited good gravimetric capacitance of 210 mF g^{-1} and excellent cycling stability.[47]

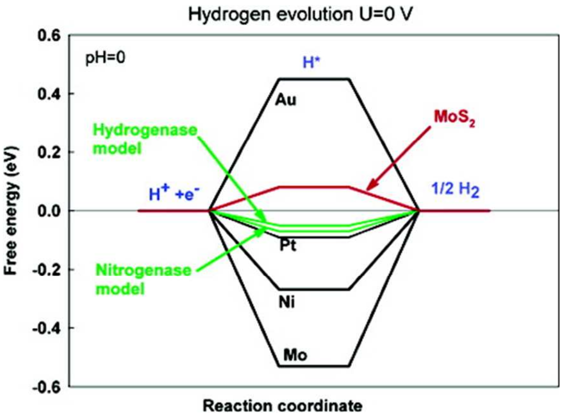

Fig. 5 Calculated free energy diagram for hydrogen evolution at a potential $U = 0$ relative to the standard hydrogen electrode at pH = 0. The free energy of $H^+ + e^-$ is by definition the same as that of $^1/_2$ H_2 at standard conditions. The free energy of H atoms bound to different catalysts is then found by calculating the free energy with respect to molecular hydrogen including zero-point energies and entropy terms. Reprinted with permission from [40].

3.4. Batteries

Layered TMDs, especially MoS_2, is used in lithium batteries as anodes. It was shown that hollow MoS_2 particles have better stability than do solid MoS_2 nanoparticles.[48] MoS_2 composites layered with graphene exhibited highly stable cycling performance and a high specific capacity of ~1100 mAh/g at a current of 100 mA/g[49] and 350 mA h/g at a current of 2000 mA/g.[50] Three-dimensional MoS_2 flower-like nanoarchitectures anchored on graphene layers were prepared via the hydrothermal route. Such MoS_2 nanoflowers resulted in the highly spaced MoS_2 nanosheets (spacing 13.8 A, compare to bulk MoS_2 with spacing of 6.2 A), which was useful for the intercalation of Li^+ ions. This material has capacity of 813.5 mAh/g at a current density of 1000 mA/g. It was found that it was possible to achieve specific capacity of 600 mAh/g even at a high current density of 4000 mA/g.[51] An interesting approach was taken to provide sulfur in lithium-sulfur batteries. To avoid the instability of Li_2S, a mixture of elemental Li and MoS_2 was electrochemically converted to Li_2S and elemental Mo. The authors claim that the resulting cell has very high stability.[52] In a manner similar to Ref [50], where MoS_2 and graphene were utilized, composites of MoS_2 with single-walled carbon nanotubes and MoS_2 nanorods coated by amorphous carbon exhibited very high capacity in Li batteries: 992 mAh/g[53] and 621 mAh/g.[54] Mesoporous WS_2 was also used as an electrode in Li batteries.[55] MoS_2/carbon composites are used in rechargeable Mg batteries.[56] The layered structure of bulk MoS_2 was found to be an attractive material for novel Na^+ batteries.[57]

3.5. Solar cells

TMDs can play several roles in solar cell energy conversion. The TiO_2 used in solar cells can be sensitized by WS_2 nanosheets, resulting in much better performance than non-sensitized TiO_2.[58] The authors found that the S-W-S layers of WS_2 are not perfectly aligned in the direction of the c-axis, emphasizing the role of lateral electron transfer. Another way to sensitize TiO_2 is the use of organic dyes. [59] WS_2 has been found to be very useful for replacement of Pt in dye-sensitized solar cells.[60] MoS_2/graphene nanocomposite was used as counter electrode in dye-sensitized solar cells with high power conversion efficiency of >6%.[61]

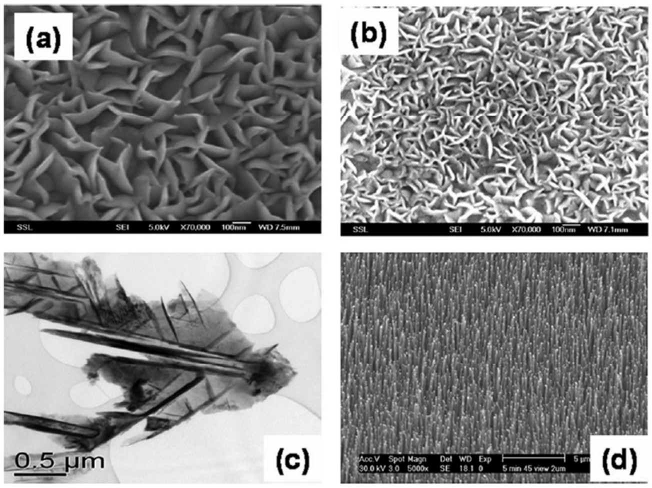

Fig. 6 SEM images of edge-oriented MoS_2 nanowall films, deposited by single source precursor CVD at (a) 550°C and (b) 650°C. (c) TEM image showing triangular nanosheets; (d) SEM image of carbon nanotube array electrode used for comparison. Reprinted from Ref [45] with permission.

In such cases, TMDs are used as replacements of the limiting factor of such cells, the counter electrode, which typically uses a Pt catalyst on a conductive support. MoS_2 films on a carbon support were suggested as Pt-free counter electrodes in dye-sensitized solar cells.[62] Similarly, MoS_2 nanosheets were deposited on multiwall carbon nanotubes and used as a replacement for Pt in solar cells.[63]

3.6. Other electrochemical energy applications

Electrochemical hydrogen storage in MoS_2 nanotubes was reported, up to 0.97% wt. of H_2.[64] Such adsorption was reported from the electrochemical reduction of water according to eq. (1)

$$H_2O + Ni/MoS_2 + e^- \rightarrow Ni/H_{ad}/MoS_2 + OH^- \rightarrow Ni/H_{ab}/MoS_2 + OH^- \quad (1)$$

Later, the same authors improved the hydrogen storage capacity by up to 1.2% wt. by treating MoS_2 nanotubes with KOH. It should be noted that as a control material, polycrystalline MoS_2 was used and exhibited a hydrogen storage capacity of <0.3% wt.[65]

Conclusions

Layered transition metal dichalcogenides exhibit tunable band gap properties, interesting photoelectrochemistry, and versatile applications for hydrogen reduction, supercapacitors, batteries, and solar cells. Layered TMDs exhibit crystalline structure and their electrochemical properties can be tuned by exchanging transition metal or chalcogenide atoms. It can be expected that there will be a dramatic increase in the number of applications of these two-dimensional materials in electrochemistry.

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Biography

Prof. Martin Pumera *is a faculty member at Nanyang Technological University, Singapore since 2010. He received his PhD at Charles University, Czech Republic, in 2001. After two postdoctoral stays (in the USA, Spain), he joined the National Institute for Materials Science, Japan, in 2006 for a tenure-track arrangement and stayed there until Spring 2008 when he accepted a tenured position at NIMS. In 2009, Prof. Pumera received a ERC-StG award. Prof. Pumera has broad interests in nanomaterials and microsystems, in the specific areas of electrochemistry and synthetic chemistry of 2D nanomaterials, nanomotors, nanotoxicity, and energy storage devices. He is associate editor of Science and Technology of Advanced Materials, member of Editorial board of Chem. Eur. J., Electrochem. Commun., Electrophoresis, Electroanalysis, The Chemical Records, ChemElectroChem and eight other journals. He published over 250 peer-reviewed articles and has h-index 43.*

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Dr. Adriano Ambrosi *received his PhD degree from Dublin City University, Ireland in 2007. As postdoctoral researcher he firstly worked for two years at ICN (Spain), and then, in 2009, at NIMS (Japan). In 2010 he joined the research group of Prof. Martin Pumera at Nanyang Technological University (Singapore) where he currently works as Senior Research Fellow. His research interests include the application of nanomaterials to electrochemical biosensors, synthesis and fundamental electrochemical studies of graphene and other 2D materials for biosensing and energy storage devices, and synthetic nanomotors.*

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