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### Tailoring the physicochemical properties of solution-processed transition metal dichalcogenides *via* molecular approaches

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During the last five years, the scientific community has witnessed tremendous progress in solutionprocessed semiconducting 2D transition metal dichalcogenides (TMDs), in combination with the use of chemical approaches to finely tune their electrical, optical, mechanical and thermal properties. Because of the strong structure-properties relationship, the adopted production methods contribute in affecting the quality and characteristics of the nanomaterials, along with the costs, scalability and yield of the process. Nevertheless, a number of (supra)molecular approaches have been developed to meticulously tailor the properties of TMDs *via* formation of both covalent and non-covalent bonds, where small molecules, (bio)polymers or nanoparticles interact with the basal plane and/or edges of the 2D nanosheets in a controlled fashion. In this Feature Article, we will highlight the recent advancements in the development of production strategies and molecular approaches for tailoring the properties of solutionprocessed TMD nanosheets. We will also discuss opportunities and challenges towards the realization of multifunctional devices and sensors based on such novel hybrid nanomaterials.

1. Introduction

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The discovery of new materials with exploitable properties has always boosted the scientific and societal progress in the history of mankind. In this regard, the latest cornerstone

that we have faced during the past fifteen years concerns the

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so-called discovery of the outstanding physical and chemical properties of graphene and related 2D materials (2DMs) by Geim and Novoselov in 2004.<sup>1</sup> Indeed, graphene represents a veritable breakthrough in materials science: its unique and exceptional properties<sup>2</sup> may be the key to revolutionize existing technologies and to foster the development of new ones.

The ease of graphene isolation *via* micromechanical cleavage, also known as the scotch-tape method, has encouraged scientists worldwide to isolate new 2DMs starting from the related bulk counterparts.<sup>3</sup>

As a result, a variety of atomically-thin nanosystems have been produced from layered van der Waals structures, such as black phosphorus (BP), hexagonal boron nitride (h-BN) and transition metal dichalcogenides (TMDs). Unlike graphene that exhibits a semimetallic behaviour and does not possess a bandgap in its pristine form,<sup>2</sup> TMDs offer a broad portfolio of electronic and optical properties which include, for instance, tunable bandgaps in the whole visible spectrum,<sup>4,5</sup> a pivotal feature for electronic and optoelectronic applications.<sup>6</sup>

Noticeably, the properties of the single-layer materials are markedly different from those of their bulk systems because of strong quantum confinement, reduced screening and surface effects.<sup>7</sup> Therefore, the discovery of exotic quantum effects and phenomena in the atomically thin limit has promoted the ever growing diffusion of 2D materials, and TMDs in particular, for applications spanning from electronics,<sup>6</sup> optoelectronics<sup>8</sup> and (photo)catalysis<sup>9</sup> to (bio)sensing and biomedicine.<sup>10</sup>

Nevertheless, the performances of TMD-based devices are strictly connected to the inherent properties and quality of the materials, which play a paramount role in determining the final



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Paolo Samorì is a distinguished professor at the University of Strasbourg and Director of the Institut de Science et d'Ingénierie Supramoléculaires. He is a foreign member of the Royal Flemish Academy of Belgium for Sciences and Art (KVAB), Fellow of the Royal Society of Chemistry (FRSC), Fellow of the European Academy of Sciences (EURASC), Member of the Academia Europaea and Junior Member of the Institut Universitaire de France (IUF). His

research interests include supramolecular sciences, nanochemistry and materials chemistry with a specific focus on graphene and other 2D materials as well as functional organic/polymeric and hybrid nanomaterials for application in opto-electronics, energy and sensing. His work has been awarded with various prizes, including the IUPAC Prize for Young Chemists (2001), the ERC Starting Grant (2010), the CNRS Silver Medal (2012), the Surface and Interfaces Award by the RSC (2018), the Grand Prix Pierre Süe by the French Chemical Society, and the Prix the Blaise Pascal Medal by EURASC (2018). applications. More specifically, research endeavors have been devoted to the development of production techniques and successive functionalization steps to increase the quality and enhance the performance, respectively, of the afforded materials.<sup>11,12</sup> Indeed, the early stages of the research based on TMDs have relied exclusively on micromechanical exfoliation, yet, this technique has two major drawbacks concerning the lack of control during the production of samples with a specific number of layers and it is not suitable for production at a large (industrial) scale.<sup>13</sup>

Therefore, in order to overcome these limitations, various strategies have been developed and pursued during the last few years to foster the production of high-quality 2D materials. Remarkably, solution-processing approaches have stood out as efficient methods towards the synthesis or exfoliation of TMD nanosheets.<sup>14,15</sup>

Although the production steps already contribute in affecting the quality and the characteristics of solution-processed TMD materials, in the last few years many research endeavors have been devoted to the development of molecular strategies in order to further tailor their physicochemical properties.<sup>12</sup> In particular, such approaches exploit non-covalent and covalent interactions through which small molecules,<sup>16</sup> noble metal nanoparticles (epitaxial growth or self-assembly)<sup>17,18</sup> or (bio)polymers<sup>19</sup> interact with the basal plane and/or edges of TMD nanosheets. In fact, the physisorption or chemisorption process of molecular systems onto 2D structures is driven by a variety of mechanisms, whose versatility guarantees a powerful toolbox in such an exciting area of 2D materials science.

In this Feature Article, we will thoroughly discuss the foremost molecular strategies employed to finely tune the properties of solution-processed TMDs, with particular emphasis on the emerging properties of the resulting TMD-based hybrid systems and their possible applications in numerous research areas. More specifically, after a brief introduction regarding the structures and properties of TMDs (Section 2), we will explore the possibilities to employ solution-processed TMDs, obtained via both top-down and bottom-up strategies (Section 3), in functionalization steps via molecular strategies (Section 4) and leading to hybrid multifunctional materials, whose new and/or enhanced properties might be exploited in many different research fields (Section 5). Significantly, the chemical approach plays a fundamental role in designing the molecules to employ during the functionalization reactions envisaged for TMDs, tailoring à la carte the properties of the resulting ultrathin hybrid systems, bearing the new functionalities required for specific applications (Section 6).

# 2. A brief overview about the structure-properties relationship in TMDs

The layered structure of TMDs is commonly indicated by the general formula  $MX_2$  and consists of an atomic layer of transition metal atoms (M = Mo, W, Re, Pt, *etc.*) sandwiched between

two atomic layers of chalcogen atoms (X = S, Se, Te).<sup>20</sup> In this regard, research endeavors in isolating thin TMD nanosheets starting from bulk systems have revealed more than 40 possible and different layered structures.<sup>21</sup> More specifically, group 4–7 TMDs are predominantly layered systems, unlike some of the group 8–10 TMDs which are non-layered. The atoms within individual nanosheets (typically 6–7 Å thick) are held together *via* strong M–X covalent bonds, whereas adjacent sheets interact through weak van der Waals (vdW) interactions, in the range of 10 and  $10^{-2}$  eV per atom, respectively.<sup>22</sup>

According to the reciprocal coordination geometry between the M and X atoms within the individual nanosheets, TMDs can manifest multiple crystal lattices and undergo phase transitions among these polymorphs triggered via physicochemical stimuli.<sup>23</sup> In particular, TMD systems exhibit a polymorphism involving three different crystal lattices (Fig. 1): hexagonal, generally indicated as 1H for single layer and 2H for multilayer (trigonal prismatic coordination for the metal center,  $D_{3h}$ ), tetragonal 1T (octahedral coordination for the metal center,  $O_{\rm h}$ ) and rhombohedral 3R.<sup>24</sup> Noteworthily, the numerical digits in 1T, 2H and 3R indicate the number of layers in the stacking sequence, whereas the letters refer to the crystal lattices. Besides general considerations about the structure of TMDs, they possess extremely versatile properties related to their electronic structure, strongly affected by the constituent transition metal and chalcogen atoms.6,24

More specifically, the electronic properties of TMDs are strongly influenced by the progressive filling of the nonbonding d bands from group 4 to group 10, located within the gap between the bonding and anti-bonding bands of M-X bonds.<sup>24</sup> In cases where the orbitals are partially filled, *e.g.*, as in 2H-NbSe<sub>2</sub> and 1T-ReS<sub>2</sub>, TMDs exhibit metallic conductivity, whereas when they are fully occupied, *e.g.*, as in 2H-MoS<sub>2</sub> and 1T-PtS<sub>2</sub>, the materials possess semiconducting properties. Moreover, even if the transition metal atoms have a major effect on the electronic properties, the bandgap between the valence and conduction band decreases when the atomic number of the chalcogen increases. Indeed, the bandgap of bulk 2H-MoS<sub>2</sub>, 2H-MoSe<sub>2</sub> and 2H-MoTe<sub>2</sub> gradually decreases from 1.2 eV down to 1.0 eV.<sup>20</sup> Nevertheless, the stability of the different polymorphs is also strongly influenced by the d-electron count of the transition metal atoms. Indeed, group 4 TMDs exhibit an octahedral structure, whereas in group 5 and 6 both the octahedral and trigonal prismatic structures are observed. Group 6 TMDs are primarily found in trigonal prismatic geometry and group 7 are typically in a distorted octahedral structure, unlike group 10 which are all in the octahedral structure.<sup>24</sup>

Moreover, the ever-growing success of TMDs is particularly related to their thickness-dependent properties, which is determined by a change in the band structure caused by quantum confinement effects and resulting variations in the orbital composition of the electronic states.<sup>25</sup> For example, the bulk and monolayer band structure for the semiconducting TMDs, e.g., MoS<sub>2</sub> and WS<sub>2</sub>, undergoes remarkable variations with the number of layers. Indeed, at the  $\Gamma$ -point of the Brillouin zone the bandgap transition is indirect for the bulk material, but it gradually shifts towards the direct one in the monolayer structure, whereas the direct transition at the K-point remains almost unaffected.<sup>26</sup> Therefore, such a phenomenon makes TMD materials prime candidates for optoelectronic and photonic applications.<sup>27</sup> An additional paramount aspect to consider whenever a 2D material is exposed to an in-depth analysis concerns the inevitable presence of defects. Although defects alter the pristine properties of TMDs,<sup>28,29</sup> they can act as chemically active sites during the chemical functionalization of TMDs, as proved by experimental and theoretical studies.<sup>30,31</sup> In particular, due to thermodynamic considerations related to the formation



**Fig. 1** Illustration of the different polymorph structures for TMDs. (a) Depiction, in side view, of the three possible TMD polymorphs and obtained *via* different stacking sequence of individual layers. (b) Representation, in top view, of the metal coordination geometry for the three possible TMD polymorphs. Atom colour legend: light blue, transition metal; yellow, chalcogen.

energies, vacancies are the most common point defects in ultrathin TMD nanosheets and they have been observed in multiple forms, such as single or double M or X vacancies, albeit the landscape of defects and disorder in TMD systems is much more complex and might also include grain boundaries, dislocations, vacancies of Mo–S complexes and antisite defects.<sup>32</sup>

Ultimately, the physicochemical properties of ultrathin TMD systems can vary dramatically with the 2D structure features, and such considerations cannot be overlooked during the molecular strategies aiming at finely tailoring their properties (Section 4).

## 3. Production of solution-processed TMDs

The successful applications of certain 2D materials are strictly related to their quality and the yield of their exfoliation processes. To date, micromechanical cleavage remains the most straightforward source of high-quality 2DMs, although it suffers from low yields and production rates that are not technologically scalable at an industrial level.

In light of such limitations, during the last decade intense research endeavors have been addressed towards the design and development of innovative solution-based strategies to achieve an efficient production of 2D structures (Fig. 2),

such as TMD nanosheets, exhibiting specific structural features and therefore electronic and spectroscopic properties. For a better understanding, the production approaches can be classified as top-down and bottom-up approaches. In the latter case, TMDs are synthesized starting from suitable precursors and by connecting atoms to each other, leading to systems characterized by minor defectivity, high chemical homogeneity and good short- and long-range ordering. In particular, this class includes processes mainly based on solvothermal,<sup>33,34</sup> colloidal<sup>35,36</sup> and secondarily electrochemical synthesis.<sup>37,38</sup> Conversely, in top-down strategies, which include among others liquid-phase exfoliation (LPE)<sup>39</sup> and electrochemical exfoliation (ECE)<sup>40</sup> approaches, TMD nanosheets are exfoliated from the bulk system under specific conditions and, due to the inherent features of the procedure, such an approach entails both the production of new defects in the nanosheets and the propagation of defects inherited from the bulk structure. Nevertheless, such a class of techniques is commonly employed because it represents the best trade-off among the pivotal parameters to assess a production strategy in 2DMs' science, such as costs, purity, yield, etc.41

The following sub-chapter describes the main characteristics for each of the aforementioned production strategies, pointing out the opportunities and challenges faced during the production and isolation of solution-processed TMD nanosheets.



**Fig. 2** Illustration of the main production strategies to obtain solution-processed TMD materials *via* top-down (left) and bottom-up approaches (right). In particular, top-down strategies mainly rely on liquid-phase exfoliation (LPE) and electrochemical exfoliation (ECE) of bulk systems, unlike bottom-up approaches which essentially entail solvothermal and hot-injection synthesis starting from appropriate precursors.

#### 3.1 Solvothermal synthesis

The first crystal growth under hydrothermal conditions was reported in 1845 by the German geologist Schafhäutl, who succeeded in the production of microscopic quartz crystals.<sup>42</sup> It is noteworthy that the term "solvothermal" refers to the procedures which exploit an organic solvent, whereas when water or aqueous solutions are involved it is referred to as a "hydrothermal" process.

Nowadays, hydro/solvothermal synthesis represents a valuable bottom-up approach to produce TMDs, starting from specific precursors and taking advantage of sealed autoclaves operating at high temperatures  $(10-10^2 \, ^\circ C)$  and controlled pressure  $(1-10 \, Pa).^{43-45}$  The main advantages of this strategy lie with the superior aptitude of materials in being induced to solubility *via* suitable temperature and pressure conditions, along with the more accurate control of the operating parameters, which might influence the quality and crystal structure of the final systems.<sup>46</sup> Nevertheless, such an approach envisages some drawbacks related to the need of expensive autoclaves able to withstand the operating conditions (temperature, pressure, pH, solvent, *etc.*) and the lack of a real-time monitoring of the crystal growth ("black box").<sup>47</sup>

As already mentioned, the operating parameters play a fundamental role in determining the successful and efficient growth of TMDs. A prime example is represented by the solvent, whose nature might strongly affect the morphology of MoS<sub>2</sub> nanosheets because of the structure-directing ability of organic molecules, as reported by Feng et al.<sup>33</sup> Furthermore, Xie and co-workers succeeded with the growth of defect-rich MoS<sub>2</sub> nanosheets by adjusting the concentration of the precursors, namely ammonium molybdate and thiourea, stabilizing ultrathin structures and enhancing their electrocatalytic activity towards hydrogen evolution reactions (HERs).<sup>48</sup> Interestingly, solvothermal operating conditions have also been exploited to intercalate TMDs with solvent molecules,49 lithium ions50 or oxygen molecules,<sup>51</sup> promoting the subsequent exfoliation procedures. Finally, solvothermal synthesis can also be exploited to grow TMD-based hybrid systems, by making use of the synergetic effects of the components and enhancing the proprieties and performances of the resulting materials.<sup>52,53</sup>

#### 3.2 Hot-injection synthesis

Hot-injection synthesis, also known as colloidal synthesis, represents an additional valuable option among the wet bottom-up chemical methods to produce TMD systems.

In particular, such an approach provides a versatile strategy towards the synthesis of nanocrystals with tunable shape, lateral size and thickness. From this perspective, the choices concerning the precursors, the potential coordinating ligands (to ensure stability and control over the size and shape) and the solvent (which provides an homogeneous reaction medium and might act as a capping ligand as well) are crucial.<sup>54</sup> Nevertheless, the hot-injection method possesses some major drawbacks related to the use of expensive, hazardous and toxic precursors and solvents, such as organometallic and phosphine-based compounds, respectively, which have hindered large-scale synthesis for commercial production.  $^{\rm 55}$ 

In most cases, the method involves the use of a chalcogen precursor solution rapidly injected into a hot mixture (150-300 °C) of metal precursors and capping agents, where an accurate control over the structural features of the growing materials can be achieved by adjusting the operating conditions and the chemical species involved in the process. In particular, besides general protocols mainly adopted in the synthesis of group 4 and 5 TMDs with specific lateral size and thickness,<sup>56,57</sup> researchers have developed versatile approaches to obtain materials with specific physicochemical characteristics. For instance, the lateral size of TMD nanosheets can be tuned by playing with reaction time while keeping the thickness constant, as reported by Jang et al. about  $ZrS_2$  nanodisc synthesis by injecting carbon disulfide ( $CS_2$ ) into a mixture of zirconium(IV) chloride (ZrCl<sub>4</sub>) and oleylamine at 300 °C under an argon atmosphere.<sup>58</sup> Analogously, even the final thickness of TMD systems can be finely tuned by either adjusting the precursor concentration,<sup>59</sup> or more interestingly, by changing the functional groups of the capping ligands, to exploit the different binding affinities with the TMD nanosheet edges.<sup>35</sup> Moreover, the reaction temperature can be adjusted to produce TMD defectrich nanoflakes, as reported by Cheng and co-workers, who exploited the abundant presence of edges to obtain a WS<sub>2</sub>-based material characterized by high catalytic activity for HERs in acids.<sup>60</sup> Finally, the presence of templating agents can steer the growth of TMDs towards specific structural features, introducing external chemical species<sup>61</sup> or performing the reaction under a controlled atmosphere.62

Ultimately, colloidal synthesis represents an intriguing and versatile class of reactions towards the bottom-up production of TMDs, and recently some innovative variations have been established in order to employ single precursors,<sup>63</sup> produce hybrid systems<sup>64</sup> and use nontoxic phosphine-free solvents.<sup>65</sup>

#### 3.3 Liquid-phase exfoliation (LPE)

The overwhelming majority of solution-processed TMD systems produced by top-down approaches derives from liquid-phase exfoliation techniques. Indeed, the seminal work published by Coleman and co-workers in 2008, on the first LPE of graphite towards graphene,<sup>66</sup> paved the way to this new method for the isolation of thin 2DMs, such as TMD nanosheets.

LPE entails the use of a liquid sample containing the bulk TMD crystals and a transfer of energy thereto, in order to overcome the weak vdW interactions acting within the layered systems and promote their exfoliation. Towards this end, mechanical energy is a suitable choice because of several advantages, such as low cost, user-friendliness and versatility among others. In this regard, mechanical energy can be transferred to the bulk TMD crystal *via* different strategies and forms (the latter is related to the different forces acting on the bulk structure). More specifically, shear and compression forces arise during the exfoliation steps by means of ball milling and shearing methods, fostering the separation of thinner systems.<sup>67–69</sup> Additionally, ultrasonication approaches can also be employed to guarantee an energetic agitation of the system

and the transfer of energy from the solution to the layered structure. In particular, the ultrasound waves propagate within the solvent causing alternating high- and low-pressure cycles that promote the exfoliation because of two main forms of energy inputs, namely vibration and cavitation forces. Vibrational energy arises from the generation and propagation of transverse waves through the solvent, causing vibrational modes within the layered structure with enough energy to peel the nanosheets apart. Moreover, the increase of ultrasonication power allows the generation of cavitation forces, more energetic than vibrational forces. In fact, the formation and implosion of cavitation bubbles within the solvent promotes fast and energetic shock waves that induce high local temperature (10<sup>2</sup>-10<sup>3</sup> °C) and pressure (from kPa to MPa) conditions. Nevertheless, such high energy cavitation forces have detrimental effects on the lateral size of the nanosheets, although they exfoliate far more effectively than vibration ones, leading to higher concentrations of dispersed material.<sup>70</sup> Therefore, since vibration forces help in maintaining the nanosheet size,<sup>71</sup> a balanced trade-off between the two modes is required to tune the final structural features of the material.

Besides mechanistic considerations, several parameters play a fundamental role in determining the quality and efficiency of the exfoliation procedures, such as the power, time and type of sonication (e.g., sonic baths or sonic probes), along with the exfoliation solvent.<sup>72,73</sup> Indeed, the choice of solvent is crucial, since it plays three main roles:  $^{11}(1)$  it is a medium designed for transferring acoustic power during the ultrasonication steps; (2) it must exhibit the correct parameters to minimize the mixing enthalpy between the liquid and the layered structure, in some cases allowing the solvent intercalation;<sup>72</sup> (3) it stabilizes the exfoliated material by providing a steric barrier with consequent inhibition of the reaggregation phenomena.<sup>74</sup> In this regard, new liquid-phase exfoliation approaches have been developed to employ less hazardous and lower boiling point solvents, leading to the use of solvent/surfactant mixtures.<sup>75</sup> The additives play a double role by modulating the surface tension of the solvent, improving the dispersibility, and creating an additional repulsive force that inhibits the reaggregation process, such as in the case of polymer solutions.<sup>76,77</sup> Although the use of stabilizers provides some benefits, it is difficult to remove them completely from the exfoliated materials and this can affects their properties, especially the electrical performances.<sup>78</sup> Moreover, liquid-phase as-exfoliated TMD nanosheets display a broad polydispersity in terms of thickness and lateral size, requiring several size-sorting steps to achieve the desired structural features.<sup>79</sup> Ultimately, LPE strategies might possess suitable features to scale-up the production of TMDs to an industrial level, paving the way to their application in several research fields.

#### 3.4 Electrochemical exfoliation (ECE)

An additional and extremely powerful top-down approach to exfoliate bulk TMD crystals exploits the intercalation of chemical species within the layers, leading to an expansion of the structure and a weakening of the interlayer vdW interactions.

Lithium-ion intercalation in TMDs has been studied since the 1980s<sup>80,81</sup> and the original method is still widely adopted to

produce single- and few-layer TMD nanosheets. It involves the formation of an intercalated intermediate [Li<sub>x</sub>MoS<sub>2</sub>] by soaking bulk TMD powder in a solution of *n*-butyllithium (*n*-BuLi) for 2-3 days under an inert atmosphere, generally argon or nitrogen, at increased temperature (ca. 80 °C). Subsequently, the intercalated material is transferred into an aqueous or lowboiling point solvent solution and exposed to ultrasound waves to complete the exfoliation, even promoting the potential reaction between lithium ions and water to form gaseous hydrogen, which boosts the separation of thin nanoflakes.<sup>81</sup> However, some TMDs undergo structural and electronic changes during lithium-ion intercalation (lithiation process), and therefore they are often referred to as chemically exfoliated TMDs (ce-TMDs).<sup>82</sup> Nevertheless, such a technique presents considerable hazards related to the use of n-BuLi and safer approaches have been developed in the last few years.

A promising variation of such an exfoliation technique is the electrochemically-assisted process,<sup>83,84</sup> which guarantees fine control over the lithium intercalation within the bulk TMD crystals. One of the possible lithium sources is represented by lithium foils, usually employed as the anode of the electrolytic cell, along with the TMD crystal acting as the cathode of the system (cathodic exfoliation). It is worth mentioning that electrochemical exfoliation exhibits many advantages due to the more favorable operating conditions, such as room temperature, shorter production time and safer chemicals. Nevertheless, in order to tackle the costs concerning the use of lithium foils, new techniques exploiting different lithium sources, such as electrolytes,<sup>85</sup> have been explored. By taking advantage of that, the electrochemical exfoliation can be performed using aqueous solutions<sup>86</sup> and under ambient conditions,<sup>87</sup> thus representing an appealing and cutting-edge technique to produce thin TMD nanosheets.

It is worth mentioning that the lithium intercalation is not just a mechanical process in which an expansion of the structure is achieved. In fact, an electron transfer process takes place from the metal ion to the lowest lying unoccupied energy level of the metallic d-bands for the MX<sub>2</sub> crystal.<sup>88,89</sup> The effects of this charge transfer depend on the resulting d-electron count of the metal center and they are particularly significant in group 6 TMDs, such as  $MoS_2$ ,<sup>90</sup> WS<sub>2</sub>,<sup>91</sup> etc. More specifically, the energy penalty encountered due to the electron transfer is minimized by forcing a change in the metal coordination geometry, from trigonal prismatic (2H polymorph) to the charge-stabilizing octahedral geometry (1T polymorph). As a consequence, the changes in the electronic structure result in significant alterations of the properties: in the MoS<sub>2</sub> case, the change from the 2H polymorph to the 1T polymorph, upon lithium-ion intercalation, induces a change from semiconducting to metallic behavior, respectively. However, the pristine 2H structure and its related properties can be preserved by either converting the metastable 1T phase, obtained via a lithiation process, by means of physicochemical stimuli<sup>92,93</sup> or using different intercalating chemical species,94,95 which promote the retention of the starting crystal structure. Therefore, electrochemical exfoliation approaches represent an efficient and

versatile tool to achieve the production of thin TMD systems with specific structural features and properties.

# 4. TMD functionalization strategies *via* molecular approaches

As extensively discussed in Section 3, synthesis and production processes already contribute in determining the final properties of exfoliated TMD nanosheets. Nevertheless, post-exfoliation treatments have arisen lately to meticulously customize the physical and chemical properties of two-dimensional TMD materials (Fig. 3), where the final goal seeks the matching with the requisites envisaged for a certain type of application.

In particular, many excellent review articles<sup>96,97</sup> have been published on solution-based approaches to exfoliate TMD materials, although they do not provide additional information about a possible further tailoring of the physicochemical properties using molecular approaches. For this purpose, in the following paragraphs, we report on the diverse classes of functionalization strategies envisaged for solution-processed TMDs, exploiting different mechanisms and interactions (Fig. 4).

#### 4.1 Physisorption

TMD nanosheets, like all others 2DMs, are characterized by a high surface area, hence non-covalent functionalization *via* physisorption of various molecular systems is a promising strategy to produce TMD-based hybrid structures (Fig. 5).

Such an approach is mainly adopted to increase the dispersibility of TMD nanosheets in a certain solvent, preventing aggregation of 2D sheets after the exfoliation procedures. Specifically, organic functional groups are adsorbed onto the nanosheet surface of 2DMs *via* vdW and electrostatic interactions,<sup>98,99</sup> modulating the solubility parameters. From a mechanistic point of view, the stabilization in an aqueous environment by means of ionic surfactants is achieved because of steric hindrance and Coulombic repulsion, which can be described within the Derjaguin-Landau-Verwey-Overbeek



**Fig. 3** The image illustrates the main functionalization strategies for TMD materials *via* molecular approaches. In particular, they rely on the physisorption and chemisorption phenomena of (supra)molecular species by means of diverse mechanisms/interactions.



#### Coordinative

**Fig. 4** Functionalization strategies *via* molecular approaches for solutionprocessed TMD nanosheets. The plethora of possible functionalizing molecules to succeed in the formation of functional TMD-based hybrid systems guarantees a wide range of possible combinations, and the different methods can be divided into five classes: physisorption, covalent, coordinative, coordinate-defects and defects.

(DLVO) theory.<sup>100</sup> In this regard, Gupta et al. provided evidence on the structure and organization of ionic surfactants onto MoS<sub>2</sub> nanosheets, focusing on the cationic amphiphile cetyltrimethyl ammonium bromide (CTAB) and the anionic sodium dodecyl sulfate (SDS). It was demonstrated that the surfactant chains physisorbed flat, randomly arranged on the basal plane of the MoS<sub>2</sub> nanosheets, with their charged headgroup pointing out from the MoS<sub>2</sub> surface. Furthermore, by means of the Nuclear Overhauser Effect (NOE) spectroscopy, the authors studied the dynamic interaction between the organic physisorbed molecules and the inorganic TMD nanosheets, where the former are rapidly exchanged with the free surfactant molecules in the aqueous environment.<sup>101</sup> In the case of non-ionic surfactants or polymers being added as stabilizers to nanosheet dispersions,<sup>102</sup> the stabilization process can be described in the framework of solution thermodynamics. Nevertheless, the presence of polymers during the exfoliation process can negatively affect the efficiency of the process, in terms of mean layer number and concentration. Indeed, the presence of polymers in solution influences the surface tension of the solvent (in particular, it increases with the polymer concentration), therefore some authors suggested to add gradually the polymeric system during the exfoliation procedure to overcome such an issue.<sup>103</sup>

Another common non-covalent approach relies on the use of electrostatic interactions between ionic molecules and negatively charged ce-1T-TMD nanosheets, promoting the stabilization of their liquid dispersions ("inks") as well.<sup>104</sup> Taking advantage of the aforementioned interactions, ce-1T-TMD systems can be dispersed in high boiling point solvents, *e.g.*, octadecene and *o*-dichlorobenzene, and undergo phase transition by heating,



**Fig. 5** (a) Cartoon of MoS<sub>2</sub> nanosheets with surfactant molecules, containing ionic head-groups (in blue). (b) Zeta-potential distribution of the as-prepared MoS<sub>2</sub>-CTAB and MoS<sub>2</sub>-SDS dispersions. Reproduced with permission from ref. 100, copyright 2015 American Chemical Society. (c) Illustration of phase-transfer processes for ce-MoS<sub>2</sub> nanosheets from water to organic solvents. (e) XPS spectra evolution of MoS<sub>2</sub> annealed at different temperatures, with corresponding phase percentage (d). Reproduced with permission from ref. 105, copyright 2015 American Chemical Society.

preventing any aggregation phenomena.<sup>105</sup> Additionally, electrostatic interactions can represent a fruitful tool to produce multi-layered structures. On this view, a layer-by-layer method allows the formation of assemblies made of TMD systems regularly spaced by polyelectrolyte layers, and where the photoluminescence properties of the nanosheets depend on the number and functional groups of the ionic layers.<sup>106</sup>

#### 4.2 Covalent

Besides physisorption phenomena, solution-processed TMD nanosheets, obtained *via* both LPE and ECE, can be chemically functionalized by taking advantage of chemisorption mechanisms (Fig. 6).

In particular, covalent modification of TMDs refers to a reductive functionalization of nanosheets with electrophiles and involves the formation of a new carbon-chalcogen bond.<sup>107</sup> The pioneering work in this direction was published by Voiry *et al.*, who exploited the reaction between ce-1T-MoS<sub>2</sub>, WS<sub>2</sub> and MoSe<sub>2</sub> with alkyl halides and aryl diazonium salts, leading to dramatic changes in the optoelectronic properties of the involved TMD nanosheets.<sup>108</sup> More specifically, the authors reported on the reaction through which the electrophile species attack the negatively charged nanosheets and a new carbon-chalcogen bond is formed, with a degree of functionalization around 20%. The successful functionalization was proved by means of <sup>13</sup>C-NMR, XPS, PL and IR spectroscopy, highlighting the retention of the 1T structural polymorph but exhibiting the semiconducting properties of the material after the covalent modification, due to the charge neutralization phenomenon.



**Fig. 6** (a) Illustration of the functionalization reaction for ce-MoS<sub>2</sub> nanosheets using R–I, such as iodomethane or 2-iodoacetamide. (b) ATR-FTIR spectra of iodomethane (1) and functionalized 1T-MoS<sub>2</sub> (2), 1T-WS<sub>2</sub> (3) and 1T-MoSe<sub>2</sub> (4). Reprinted with permission from ref. 108, copyright 2014 Nature Publishing Group. (d) Representation of ce-MoS<sub>2</sub> functionalization with  $[Ru^{II}(bpy)_3]^{2+}$ . (c) Chronoamperometry measurements of pristine ce-MoS<sub>2</sub> (black) and  $[Ru^{II}(bpy)_3]$ –MoS<sub>2</sub> (red). Reproduced with permission from ref. 111, copyright 2017 Wiley-VCH.

Taking inspiration from the aforementioned work, the covalent modification of solution-processed TMD materials has been mainly achieved by making use of alkyl/aryl halides and aryl diazonium salts. In particular, the latter approach shows a great feasibility because it exploits the inherent high reactivity of the negatively charged TMD nanosheets, obtained via ECE, and the diazo group, consisting of two linked nitrogen atoms at the terminal position of a molecule. In this regard, Backes and co-workers succeeded in the covalent grafting of organic moieties onto the basal plane of MoS2 nanosheets, via the formation of new C-S bonds. Remarkably, DFT calculation revealed that the grafting of the functional groups to the sulfur atoms of MoS<sub>2</sub> is energetically favorable and C-S bonds are indeed formed.<sup>109</sup> Furthermore, such an approach can be also adopted to tune the surface energy of ce-TMD nanosheets with fundamental consequences on their electrocatalytic activity towards HERs.110

Covalent modification *via* of alkyl/aryl halides represents an additional and efficient approach to tune the physicochemical properties of ce-TMD nanosheets. A prime example comes from the work published by Chen *et al.*, who functionalized 1T-MoS<sub>2</sub> nanosheets with light-sensitive Ru(II) complexes, leading to the formation of TMD-based hybrid systems characterized by higher photoresponsivity and notable performances in HERs.<sup>111</sup>

Even though negatively charged ce-TMD nanosheets present higher reactivity, and therefore superior aptitude to undergo covalent functionalization, some recent works have been published on TMDs obtained *via* LPE as well. Among them, an elegant approach was published by McAdams, concerning the simultaneous covalent modification of  $MoS_2$  nanosheets with Eu(m) and Gd(m) complexes, to form a stable luminescent and paramagnetic hybrid material.<sup>112</sup> Ultimately, the covalent approach is a paramount tool which allows meticulous control over the TMD properties.

#### 4.3 Coordinative

a)

An intriguing additional strategy to chemically functionalized solution-processed TMD nanosheets relies on the coordination chemistry of cationic metal complexes (Fig. 7). Although the coordinative strategy is still at its infancy, some interesting studies have been published in this regard, proving the high potential of such an approach.

The pioneering work in this direction was reported by Tahir *et al.*,<sup>113</sup> who succeeded in the functionalization of hybrid



**Fig. 7** (a) Illustration of the Cu<sup>II</sup>-coordinated MoS<sub>2</sub>/PMMA paper and (b) comparison of its tensile strength, Young's modulus and elongation at the break with bare MoS<sub>2</sub> and MoS<sub>2</sub>/PMMA paper. Reproduced with permission from ref. 114, copyright 2012 Wiley-VCH. (c) Depiction of MoS<sub>2</sub>-rGO hybrid paper cross-linked by PEO. (d) Cycling performance of MoS<sub>2</sub>-rGO–PEO film anodes at different wt ratios. (e) Rate capability of the MoS<sub>2</sub>-rGO–PEO film anode with wt ratio 6/3/1. Reproduced with permission from ref. 115, copyright 2013 Royal Society of Chemistry.

MoS<sub>2</sub>/fullerene nanoparticles using the inherent principles of coordination chemistry and Lewis theory of acid–base reactions. More specifically, the authors exploited a multifunctional polymer possessing a tetradentate ligand capable of anchoring Ni<sup>2+</sup> ions, whose octahedral coordination is completely blocked on one side with an umbrella-type chelating ligand (polymer), while the other part of the coordination sphere remains open to bind the sulfur layer of the MoS<sub>2</sub>/fullerene system. Therefore, the coordination geometry and sulfur affinity are crucial parameter to allow the transition metal ions to simultaneously bridge the inorganic (MoS<sub>2</sub>/fullerene nanoparticles) and organic (polymer) moieties, and so promoting the formation of the hybrid system.

In the same vein, Xie and co-workers have reported the production of MoS<sub>2</sub>-based nanocomposites<sup>114</sup> and hybrid systems<sup>115</sup> exploiting the coordination chemistry of Cu<sup>2+</sup> ions and their interaction between sulfur layers and oxygen functionalities, found in polymer matrices or graphene-related materials, such as graphene oxide (GO) and reduced graphene oxide (rGO). Indeed, MoS<sub>2</sub>-graphene hybrid paper, cross-linked by polyethylene oxide (PEO) and Cu<sup>2+</sup> ions, can be exploited to fabricate high-performance anode materials that show great potential for lithium-ion batteries.<sup>115</sup> Furthermore, it has been proved that a similar approach could be adopted to enhance the mechanical properties of nanocomposites, due to the direct and strong nanofiller/matrix interaction. Hence, solutionprocessed MoS<sub>2</sub> nanosheets can be dispersed in a polymer matrix of PMMA (polymethyl methacrylate), along with  $Cu^{2+}$  ions, to increase the Young's modulus of the resulting hybrid systems thanks to the bridging action of the inorganic cations between the organic and inorganic moieties.114

Recently, Backes et al. developed a facile approach to functionalize solution-processed 2H-MoS<sub>2</sub> nanosheets, taking advantage of their reaction with a variety of metal carboxylate salts.<sup>116</sup> In particular, the successful functionalization was proved by XPS, Diffuse Reflectance Infrared Fourier Transform spectroscopy (DRIFT-IR) and Thermogravimetric Analysis (TGA), thereby showing strong evidence about the coordination interaction between the sulfur atoms in the MoS<sub>2</sub> nanosheets and the Lewis acid metal atoms of the organic molecular systems. Moreover, the functionalization approach guarantees the retention of the initial semiconducting crystal phase and a tuning of the surface energy, proved by the superior dispersibility of the material in non-conventional solvents such as acetone and isopropanol. Finally, a coordinative strategy has been recently adopted to tune the optoelectronic properties of mechanically exfoliated TMD materials,<sup>117</sup> encouraging the use of a similar approach to solution-processed materials as well, aiming at meticulously tuning and enhancing their electrical performances.

#### 4.4 Coordinative-defect

The majority of the chemisorption-based functionalization approaches for solution-processed TMD nanosheets exploits the inevitable presence of chalcogen atom vacancies, mainly produced during the exfoliation procedures (Fig. 8).



**Fig. 8** (a) Graphical illustration depicting the ligand conjugation of ce-MoS<sub>2</sub> nanosheets with different thiolated molecules by means of sulfur vacancies. (b) Zeta potential of ce-MoS<sub>2</sub> nanosheets functionalized with thiolated molecules bearing diverse functional groups. (c) FT-IR spectra showing all the peaks and (d) zoomed-in view of the region of S-H stretching for native ce-MoS<sub>2</sub>, functionalizated-MoS<sub>2</sub> and free ligand species. Reproduced with permission from ref. 118, copyright 2013 American Chemical Society.

The seminal work was published by Dravid and co-workers in 2013,<sup>118</sup> where ce-1T-MoS<sub>2</sub> nanosheets were subjected to reactions with several different thiol-terminated polyethylene glycol derivatives bearing ionic and non-ionic headgroups. More specifically, the authors exploited the high reactivity of ce-MoS<sub>2</sub> nanosheets and their structural defects, especially sulfur vacancies located at both internal and perimeter edges. The outcome of the ligand affinity tests shows that the thiol group of the molecular systems explored is responsible for the

MoS<sub>2</sub> modifications, as proved by XPS, FT-IR and Dynamic Light Scattering (DLS) measurements. Alongside, the authors have explored the effects of the ligand structure on the properties of the 2D systems, changing the polarity of the headgroup (neutral, cationic or anionic) and the ligand conjugation. In this manner, fundamental knowledge over the colloidal stability, catalytic activity and chemical affinity towards specific molecules could be achieved, promoting a vast use of functionalized TMD materials in many different research fields. To functionalize TMD nanosheets via a coordinative-defect approach two main distinct strategies can be adopted, dealing with either the direct functionalization of TMD liquid dispersions containing the exfoliated materials,<sup>119,120</sup> or the simultaneous exfoliation of the bulk TMD crystals and functionalization of the resulting exfoliated systems.<sup>121</sup> Nevertheless, some studies have also been published about the functionalization of substrate-supported solution-processed TMD nanosheets.87 To date, the majority of studies reported in the literature involve treating the exfoliated materials with the functionalizing molecular systems after the exfoliation steps.

In this regard, 2D transition metal disulfide systems have drawn great attention because of their versatility and aptitude to undergo healing reactions, in which thiolated molecules are exploited to fill the sulfur vacancies contained in the crystal structure and produced during the exfoliation procedures. In particular, transition metal disulfide have been extensively studied and processed with dithiolane derivatives and thiolated molecules, in order to produce hybrid systems characterized by new or enhanced physicochemical properties and superior performances, for applications spanning from biosensing<sup>122</sup> to electronics.<sup>87</sup>

Nevertheless, the sulfur healing phenomenon is not always the most favorable process. Indeed, McDonald and co-workers demonstrated that the disappearance of the S-H vibration in the IR spectra, considered the main proof of the functionalization reaction, can also be due to a TMD-mediated dimerization of thiolated molecules to form disulfide species.<sup>123</sup> In this light, no chemisorption phenomena take place, and disulfide molecules are just physisorbed onto the TMD nanosheets via weak vdW interactions. This was demonstrated by DFT calculations and recent theoretical studies,<sup>124,125</sup> showing how the nature and the amount of defects influence the interaction between thiolated molecules and sulfur vacancies. Therefore, the aforementioned process, whose mechanism is still under debate, can result in either chalcogen defect healing or the formation of disulfide and hydrosulfide molecules weakly interacting with the 2D TMD systems.

#### 4.5 Defects

An additional and appealing molecular strategy commonly used to functionalize solution-processed TMD nanosheets envisages the growth of noble metal nanoparticles (NPs), mainly Au,<sup>126,127</sup> Pd,<sup>128,129</sup> Pt<sup>130</sup> and AgNPs,<sup>131,132</sup> and their interactions with the 2D systems (Fig. 9).

In fact, NPs can interact with both liquid-phase exfoliated and ce-TMDs *via* covalent<sup>133</sup> and non-covalent<sup>127</sup> interactions,



**Fig. 9** (a and b) TEM images of (a)  $MoS_2$  and (b)  $WS_2$  nanosheets decorated by AuNPs. (c) HER performances of hybrid  $MoS_2/AuNPs$  show a decrease of the overpotential and increase of current density when the gold loading level increases, along with a decrease of the charge-transport impedance (*Z'*), as reported in (d). Reproduced with permission from ref. 127, copyright 2013 American Chemical Society.

resulting in hybrid systems characterized by exceptional performances for (photo)catalysis<sup>134,135</sup> and biomedicine<sup>131,136</sup> applications. The growth of NPs takes place after the reduction of a noble metal precursor salt,<sup>17</sup> due to an addition of reducing agent<sup>137</sup> or spontaneous formation.<sup>127</sup> In the latter case, Kim et al. succeeded in decorating ce-MoS<sub>2</sub> and ce-WS<sub>2</sub> nanosheets with AuNPs, using hexachloroauric acid (HAuCl<sub>4</sub>) in water as a precursor.<sup>127</sup> The functionalization takes place preferentially on the defect sites, located at the edges and basal plane of the nanosheets, which are in general more reactive than bulk crystals. More specifically, a redox reaction is involved between gold ions and TMD materials, encouraged by the position of the TMD Fermi level (5.2 eV and 5.1 eV for MoS<sub>2</sub> and WS<sub>2</sub>, respectively),<sup>138,139</sup> well above the reduction potential of the trivalent gold ions (+1.0 V vs. SHE). Remarkably, it was found that AuNPs play a double role, acting as a spacer to inhibit restacking phenomena in ce-TMDs and improve the charge transport among adjacent nanosheets, as proved by impedance spectroscopy.

As a consequence, the resulting  $MoS_2/AuNPs$  and  $WS_2/AuNPs$  hybrid systems possess superior electrocatalytic performances toward HERs.

Nevertheless, the synthesis and growth of noble metal NPs can also be induced by the use of a suitable reducing agent. In this regard, Huang *et al.* exploited solution-processed MoS<sub>2</sub> nanosheets to direct the epitaxial growth of Pd, Pt and Ag nanoclusters under ambient conditions, using different reduction methods according to the metal precursor.<sup>17</sup> Interestingly, the TMD nanosheets are able to address NPs towards an epitaxial growth and the major orientations arising are (100) and (111). Moreover, besides providing plenty of nucleation

sites in the defective areas, 2D epitaxial templates stabilize small NPs and prevent them from aggregating. It is worth mentioning that in the case of MoS<sub>2</sub>/PtNPs hybrid systems, the nanomaterials had been tested as promising catalysts for HERs and exhibited much better electrocatalytic activity than the commercial Pt catalyst, at the same Pt loading, likely due to the presence of additional {110} and {311} facets which promote the catalytic reactions.<sup>140</sup> Ultimately, solution-processed TMD nanosheets might be also subjected to prior functionalization exploiting thiol<sup>132</sup> or organohalide<sup>131</sup> chemistry, in order to activate the 2D structure and make it more reactive during the following growth of NPs. Finally, such an approach represents a cutting-edge molecular strategy to produce novel versatile hybrid functional materials.

# 5. Paramount applications of multifunctional and hybrid materials based on solution-processed TMDs

#### 5.1 (Opto-)electronics

Semiconducting single- and few-layer TMD nanosheets are very attractive for the fabrication of electronic devices, such as metal-oxide–semiconductor field-effect transistors (MOSFETs), photodetectors and photodiodes, exhibiting great potential for (opto-)electronic applications (Fig. 10).<sup>141</sup> Solution-processing techniques possess high exfoliation yield and a superior control over the final thickness, which is crucial in determining the electronic properties and the related electrical properties and performances of TMD-based devices (see Section 2).<sup>142</sup>

In particular, during the last few years many works have been published about the possible applications of LPE and ce-TMDs in (opto-)electronics, with intriguing results coming from the fabrication of devices such as transistors,<sup>143</sup> saturable absorbers for lasers,<sup>144,145</sup> photodetectors<sup>146</sup> and Mg/Li-ion batteries.<sup>147</sup> However, solution-processed TMDs can undergo subsequent functionalization steps *via* molecular strategies in order to meticulously tailor and/or further enhance their physicochemical properties. More specifically, many scientific endeavors have been devoted to the production of lightsensitive hybrid structures, whose performances could boost the evolution of the current technologies.

In this regard, Yin *et al.* functionalized ce-MoS<sub>2</sub> nanosheets with AuNPs, increasing the device photocurrent with a maximum located at the wavelength corresponding to the AuNPs plasmon resonance.<sup>148</sup> From a mechanistic point of view, the localized surface plasmon resonance enhances the local optical field and thus the light absorption of the MoS<sub>2</sub> layer underneath the AuNPs. Moreover, the collective electron oscillation of neighboring AuNPs can increase the photocurrent due to coupling events, leading to better device electrical performances. Additionally, Au–MoS<sub>2</sub> hybrid systems have been tested as a photoanode for water splitting applications, exhibiting higher photocatalytic activity than pristine MoS<sub>2</sub>, due to the presence of AuNPs which promote the photo-generated charge separation.



**Fig. 10** Illustration of the main applications envisaged for solutionprocessed TMD nanosheets, both in the pristine and functionalized forms. In particular, (opto-)electronics, (bio-)sensing and (photo-)catalysis represent the most influential topics covered in the literature so far. From this perspective, the areas of the different sectors reported in the graph take into account the amount of studies published in the last few years. To facilitate the comprehension of the graph, a small legend is reported below: MOSFETs = Metal-Oxide-Semiconductor Field-Effect Transistors, TCEs = Transparent Conductive Electrodes, SCs = Solar Cells, LEDs = Light Emitting Diodes, HERs = Hydrogen Evolution Reactions, Biomol. = Biomolecules, Press. = Pressure, Temp. = Temperature.

An additional example is provided by the work published by Zaumseil and co-workers, who exploited liquid-phase exfoliated TMD nanosheets to fabricate promising IR-photodetectors.<sup>149</sup> Indeed, combining  $MoS_2$  and  $WS_2$  nanosheets with PbSe QDs, the authors reported the fabrication of photodetectors with near-IR photosensitivity and long-term air stability. Moreover, the epitaxial growth of PbSe QDs on TMDs allows a defined and direct interface between the two systems without the use of any molecular linker. Such a condition guarantees an optimal charge transfer process and remarkable performances in hybrid systems characterized by excellent mechanical stability and therefore great potential in low-cost flexible optoelectronics.

#### 5.2 (Photo-)catalysis

Solution-processed TMDs have also attracted the attention of the worldwide scientific community because of their great aptitude to fabricate hybrid systems characterized by superior (photo)catalytic activity, with consequent many interesting possible applications (Fig. 10). More specifically, TMDs have been widely used to catalyze reactions involving organic molecular systems<sup>150–152</sup> or the production of molecular hydrogen during electrocatalytic<sup>153</sup> or photocatalytic<sup>154</sup> water splitting processes. In fact, hydrogen is one of the most important clean and renewable energy vectors for future sustainability. Nowadays, the most efficient manners to convert sustainable energy

to clean energy carriers envisage photocatalytic and electrocatalytic approaches, such as HERs.<sup>155</sup> In this regard, catalysts based on TMDs represent promising substitutes for noble metal-based systems, commonly adopted so far. Furthermore, the device performances might be further improved by combining TMDs with other nanomaterials, such as oxides, <sup>156</sup> QDs and carbon-based materials.<sup>157</sup> From this perspective, Chen et al. reported the production of high performance hybrid systems in HERs, consisting of CdS nanocrystals grown on the surface of solution-processed MoS<sub>2</sub>/graphene hybrids.<sup>157</sup> Indeed, graphene could match with MoS<sub>2</sub> and enhances its conductivity, promoting fast charge transfer and boosting the catalytic performances. In particular, under visible light, the photogenerated excited electrons of CdS are transferred to the surface, where some of them, reaching the edges of MoS<sub>2</sub> systems, directly react with H<sup>+</sup> in H<sub>2</sub>O to form H<sub>2</sub>, under the cocatalytic activity of unsaturated active S atoms. Other electrons, in the MoS<sub>2</sub>/graphene basal plane, can be transferred to the MoS<sub>2</sub> edges via graphene sheets and then react with H<sup>+</sup> following the aforementioned mechanism. Also, the nanosized MoS<sub>2</sub>/graphene hybrid systems possess an abundant number of active edges, which shorten the path for electron transfer. Finally, the overall CdS/MoS<sub>2</sub>/graphene hybrid system shows enhanced electron transfer ability and retards the recombination of electron-hole pairs, improving the photocatalytic activity in HERs.

Ultimately, the synergetic effects among the components in a hybrid system allow an increase in performances, overcoming the individual weaknesses and raising the technological level of the final materials.

#### 5.3 (Bio-)sensing

In the last few years, solution-processed TMDs have led to wide ranging and diversified technological applications because of their intriguing and versatile properties. More specifically, favorable branches involve (bio-)sensing and nanomedicine (Fig. 10) applications, taking advantage of the large surface area of 2D materials.<sup>158,159</sup> Indeed, TMDs represent forefront sensing platforms on which suitable and versatile receptors might also be anchored, *via* covalent and non-covalent interactions, in order to detect environmental parameters (*e.g.*, temperature, pressure, humidity) or specific (bio-)analytes, spanning from small molecules to complex molecular (bio-)structures.<sup>160–162</sup>

In this regard, many different TMD-based sensors have been designed, taking advantage of different interactions, properties and techniques, in order to expand the sensing fields with the consequent discovery of a great potential. Electrochemical<sup>163,164</sup> and colorimetric<sup>165</sup> sensors based on solution-processed TMD pristine or hybrid materials represent a typical example, proving how this class of 2D systems could be of paramount importance in supporting the future technological progress.

Furthermore, the optical properties of solution-processed TMDs contributed in supporting their application for imaging purposes, even though some crucial aspects must be tackled to encourage massive use, such as the poor stability of colloidal dispersions, and the lack of strategies to selectively functionalize ultrathin layered nanosheets and control the functionalization degree. From this perspective, many novel molecular strategies have been conceived in the last few years, aiming at overcoming the aforementioned limitations by means of the fabrication of hybrid materials. Notably, Liu and co-workers developed a new generation of promising theranostic and contrast agents based on TMD nanosheets functionalized with biocompatible polymer (polyethylene glycol, PEG)<sup>166</sup> and iron oxide nanoparticles along with the <sup>64</sup>Cu radioisotope.<sup>167</sup> Therefore, the functionalization of solution-processed TMD systems with molecular receptors is a promising and cutting-edge strategy to detect specific analytes with a high degree of selectivity and sensitivity, besides fast response.<sup>159</sup>

#### 6. Conclusions and outlook

The unique and versatile physicochemical properties of TMDs render them unique 2D functional scaffolds for developing new fundamental science with a great potential for technological applications. In this regard, achieving full control over the various production methods represents the first crucial task since the final properties of TMDs depend on the presence and type of defects along with the flake lateral size and thickness. Such characteristics need to be tuned in view of the application of interest. Hereof, solution-phase methods are promising for scalable, efficient and controlled production of TMDs, thus enabling widespread exploration and application. Although TMDs possess an extraordinary versatility, their properties could be further tuned via meticulous molecular strategies, by designing ad hoc functionalizing molecules to tailor on demand the properties of the resulting hybrid systems via covalent and non-covalent interactions. More specifically, the virtually-infinite number of functional molecular systems, made available by means of chemical synthesis, provides an appealing opportunity to develop new disrupting technologies. Therefore, such an approach allows the fabrication of TMDbased hybrid devices characterized by multiresponsive nature, where external stimuli, such as heat, light and/or magnetic fields, can be exploited to trigger changes in the physicochemical properties of the molecules interacting with the 2D structures. However, to succeed in this direction, a prior and challenging aspect to tackle concerns the choice of a suitable functionalization strategy to adopt, along with suitable operating conditions, in order to achieve accurate control over the fabrication of the hybrid systems. In particular, the nature of the interacting species and the related forces involved in the process are of paramount importance, managing the functionalization yield as well.

Ultimately, the fine tuning of TMD properties could result in a smart and elegant alternative to develop new, disrupting and exotic hybrid technologies based on solution-processed TMDs. In particular, the forthcoming technological progress shall exploit the enormous potential of these emerging materials, flagship systems in 2DM science, with possible and engaging applications in flexible and wearable (opto-)electronics, (bio-)sensing and (photo-)catalysis.

#### Conflicts of interest

The authors declare no conflict of interest.

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