**Aqueous Exfoliation of Transition Metal Dichalcogenides Assisted by DNA/RNA
Nucleotides: Catalytically Active and Biocompatible Nanosheets Stabilized by
Acid-Base Interactions**

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Abstract

The exfoliation and colloidal stabilization of layered transition metal dichalcogenides (TMDs) in aqueous medium using functional biomolecules as dispersing agents have a number of potential benefits towards the production and practical use of the corresponding two-dimensional materials, but such a strategy has so far remained underexplored. Here, we report that DNA and RNA nucleotides are highly efficient dispersants in the preparation of stable aqueous suspensions of MoS₂ and other TMD nanosheets at significant concentrations (up to 5–10 mg mL⁻¹). Unlike the case of common surfactants, for which adsorption on 2D materials is generally based on weak dispersive forces, the exceptional colloidal stability of the TMD flakes was shown to rely on the presence of relatively strong, specific interactions of Lewis acid-base type between the DNA/RNA nucleotide molecules and the flakes. Moreover, the nucleotide-stabilized MoS₂ nanosheets were shown to be efficient catalysts in the reduction of nitroarenes (4-nitrophenol and 4-nitroaniline), thus constituting an attractive alternative to the use of expensive heterogeneous catalysts based on noble metals, and exhibited an electrocatalytic activity towards the hydrogen evolution reaction that was not impaired by the possible presence of nucleotide molecules adsorbed on their active sites. The biocompatibility of these materials was also demonstrated on the basis of cell proliferation and viability assays. Overall, the present work opens new vistas on the colloidal stabilization of 2D materials based on specific interactions that could be useful towards different practical applications.

1. Introduction

Two-dimensional (2D) solids are currently at the forefront of research developments in materials science, with potentially important ramifications in many relevant technological areas including electronics, photonics, energy conversion and storage, catalysis, chemical sensing or biomedicine.^{1–4} Aside from the well-known example of graphene, a considerable number of 2D materials have become in recent years the focus of intense interest from the scientific community. In particular, layered transition metal dichalcogenides (TMDs), such as MoS₂, WS₂, MoSe₂ or MoTe₂, are probably at present the most extensively investigated 2D solids beyond graphene.^{2,5–7} Although in their bulk form layered TMDs have been studied for decades, the emergence of new or enhanced properties and phenomena that arise when their dimensions are downscaled to the single- and few-layer level (due to, *e.g.*, quantum confinement effects or greatly increased surface areas), as well as the prospect of capitalizing on such phenomena from an applied viewpoint, have driven the current surge of activity around layered TMDs in 2D form.^{5,6,8–11}

Similar to the case of any novel nanostructured material, a critical step towards the practical implementation of 2D TMDs concerns the availability of methods for their production in large quantities and with characteristics that are specifically tailored to each intended application. In this regard, research efforts have focused so far on three main production strategies: (1) chemical vapor deposition (CVD) of inorganic precursors onto suitable substrates,¹² (2) chemical exfoliation of bulk TMD crystals based on the intercalation of Li, either by reaction with organolithium reagents (*e.g.*, *n*-butyllithium) or by electrochemical means,^{13,14} and (3) direct liquid-phase exfoliation of bulk TMDs assisted by ultrasound or shear forces.^{15,16} CVD growth methods have been shown to afford large-area, single- and few-layer films of some TMDs (mainly MoS₂

and WS₂) that could be useful in high-end electronics or photonics applications, but the need of high synthesis temperatures and relatively sophisticated transfer processes as well as the relatively poor structural quality of the films currently limit their wider utility.⁶ Regarding chemical exfoliation, its main attraction lies in the very high exfoliation yield and degree (mostly single-layer flakes are obtained) that is usually associated to such a method.¹⁷ However, the required Li intercalation process can trigger a structural phase transition and induce the generation of defects (*e.g.*, pinholes and cracks) in the resulting exfoliated products,¹⁸ which can be detrimental to their performance when used in certain materials and devices.

On the other hand, ultrasound- or shear-induced exfoliation of TMDs in the liquid phase can yield large amounts of few-layer flakes that generally preserve the structural quality of the parent layered solid.^{15,16} While the exfoliation yield provided by this approach is usually low (< 5 wt%), its simplicity and versatility, together with the fact that it naturally leads to colloidal suspensions of the 2D flakes, make it the production method of choice when large quantities of solution-processable nanosheets are required to access a range of useful materials, such as thin films, coatings or composites.¹⁶ Broadly speaking, to be effective in the exfoliation and colloidal stabilization of 2D TMD flakes, solvents have to satisfy certain surface energy requirements.^{15,19} In practice, this means that only certain single-component solvents, most notably *N*-methyl-2-pyrrolidone, are efficient in this task. Unfortunately, such successful solvents tend to be relatively toxic and possess a high boiling point, which complicates their widespread use. For environmental, safety and other practical reasons, working in aqueous medium would be preferable, but water alone is inefficacious in dispersing TMDs, which are rather hydrophobic materials. Very recent work based on the analysis of surface energies has revealed that mixtures of water and a low boiling point co-

solvent (*e.g.*, isopropanol or acetone) are effective in exfoliating and dispersing TMDs, but the fraction of co-solvent required is very large (~50-80 vol%).²⁰

Alternatively, colloidal dispersions of 2D TMD flakes can be prepared in water with the aid of some stabilizers of amphiphilic nature, such as surfactants and certain polymers.¹⁶ During the last years a number of synthetic dispersing agents, including those of cationic,²¹ anionic²¹⁻²⁴ and non-ionic²⁵⁻²⁸ nature, have demonstrated their utility towards this purpose. On the other hand, the use of stabilizers of natural origin (*i.e.*, biomolecule-based dispersants) has recently emerged as a particularly attractive option, because it offers some potential advantages over the use of synthetic amphiphiles.²⁹ Such assets include a greater sustainability and environmental friendliness associated to the production process, an improved biocompatibility of the 2D materials, or the possibility of (bio)chemical functionalization of the 2D flakes on the basis of well-established protocols for the biomolecules in question. In addition to bile salts (mostly sodium cholate), which have been used as benchmark surfactants in the development of direct liquid-phase exfoliation of TMDs,³⁰⁻³² a range of other biomolecules, mainly polysaccharides and plant extracts (cellulose,³³ chitosan,³⁴ lignin,³⁵ tannic acid,³⁶ etc) but also proteins (bovine serum albumin³⁷ and gelatin)³⁸ or DNA,³⁹ have been successfully tested in recent years towards the exfoliation and dispersion of TMDs in aqueous medium. As a particular example of the benefit of using biomolecule-based stabilizers versus synthetic ones, prior work has demonstrated that MoS₂ flakes exfoliated and stabilized by bovine serum albumin exhibit a much higher degree of biocompatibility with respect to fibroblast cells than flakes stabilized by polyacrylic acid or polyvinylpyrrolidone.³⁷

Even though significant progress in the use of biomolecules as exfoliating/dispersing agents for TMDs has been attained over the last few years, this

research area is still in an incipient stage. For instance, with the exception of bile salts, small functional biomolecules have remained essentially untapped towards such an endeavor. This is particularly the case with nucleotides, including DNA/RNA nucleotides. In addition to their wide availability, biocompatibility and environmentally friendly character, we hypothesize that the rich chemistry associated to DNA/RNA and other nucleotides could be put to good use to promote their role as efficient dispersants of TMDs (*e.g.*, by exploiting specific nucleotide-TMD interactions). However, to the best of our knowledge no previous study has addressed this topic. Indeed, only the non-DNA/RNA nucleotide flavin mononucleotide (FMN) has been used so far in the exfoliation and stabilization of 2D materials, and only for the case of graphene.^{40,41} In that prior work, encouraging results were obtained concerning the performance of FMN as a colloidal dispersant.

We have investigated the use of DNA/RNA nucleotides as exfoliating/dispersing agents of TMDs in aqueous medium, the results of which are reported here. Unlike the case of graphene, these nucleotides are shown to be highly effective stabilizers for a range of TMDs, including MoS₂, WS₂ and MoTe₂, affording aqueous dispersions of 2D flakes at considerably high concentrations (up to ~5–10 mg mL⁻¹). Significantly, we provide experimental evidence indicating that the colloidal stabilization of the flakes relies on specific, relatively strong nucleotide-flake interactions rather than just on the weak dispersive and hydrophobic forces commonly associated to the use of many surfactants. We investigate the origin of the strong adsorption of the nucleotides on the 2D TMD flakes and conclude that it arises from Lewis acid-base interactions. Concerning the potential practical utility of these aqueous dispersions, we demonstrate that the nucleotide-stabilized MoS₂ flakes obtained here are efficient catalysts in the reduction of nitroarenes and display a good electrocatalytic activity towards the

hydrogen evolution reaction (HER). Finally, with a view to their prospective use in biomedicine, we have also carried out a preliminary investigation into the proliferation and viability of murine pre-osteoblasts and human sarcoma osteoblasts in the presence of nucleotide-stabilized MoS₂ flakes, suggesting that these materials possess a high biocompatibility.

2. Results and discussion

2.1. Nucleotide-assisted exfoliation and dispersion of MoS₂ in aqueous medium

Nucleotides, the building blocks of nucleic acids (including RNA and DNA), are organic molecules that comprise a heterocyclic base, a five-carbon sugar and one or more phosphate groups.⁴² As individual entities, nucleotides are expected to possess a certain amphiphilic character that could be exploited towards the colloidal stabilization of hydrophobic substances, such as TMDs, in aqueous medium. More to the point, the nucleobase component is a planar, aromatic and essentially hydrophobic moiety that could intercalate and adsorb in the interlayer space of layered TMDs, acting as a molecular wedge and thus promoting their exfoliation, whereas the appended phosphorylated sugar has a polar, anionic nature that should favor the colloidal stability of the exfoliated layers through electrostatic repulsion. Recent theoretical calculations have indicated that DNA and RNA nucleobases (*i.e.*, adenine, thymine, guanine, cytosine and uracil) are physisorbed on the basal surface of MoS₂ and WS₂ through van der Waals interactions,⁴³ thus providing a rational basis for the use of the corresponding nucleotides as exfoliating/dispersing agents of TMDs. We therefore set out to investigate the performance of a number of nucleotides towards such a purpose, the chemical structures of which are shown in Fig. 1. Specifically, we mainly selected the four nucleotides of DNA, namely deoxyadenosine monophosphate (dAMP),

deoxyguanosine monophosphate (dGMP), deoxythymidine monophosphate (dTMP) and deoxycytidine monophosphate (dCMP), as well as the non-DNA/RNA nucleotide flavin mononucleotide (FMN). In the following, we will mainly focus on the exfoliation of MoS₂ with dAMP and dGMP because of the particular relevance of MoS₂ among TMDs⁶ and because the aforementioned theoretical report suggested that adenine and guanine adsorb more strongly on the MoS₂ and WS₂ surface than thymine and cytosine do, so that they are expected *a priori* to be more effective in their role as dispersants for these materials. However, we will also show further below that the results obtained for the dAMP- and dGMP-MoS₂ systems are generally extensible to both other TMDs and the three other nucleotides depicted in Fig. 1, which has relevant implications in the specific modes of interaction that are in place between the nucleotides and the TMDs.

Figure. 1. Chemical structures of the four nucleotides of DNA, namely deoxyadenosine monophosphate (dAMP), deoxyguanosine monophosphate (dGMP), deoxythymidine monophosphate (dTMP) and deoxycytidine monophosphate (dCMP), as well as the non-DNA/RNA nucleotide flavin mononucleotide (FMN).

Bath sonication of MoS₂ powder in aqueous solutions of either dAMP or dGMP followed by a mild centrifugation step (see Supporting Information, SI for details) typically led to supernatant dispersions that exhibited an opaque, dark green tone, as can be noticed from the digital photographs shown in the inset to Fig. 2a (dAMP-MoS₂) and b (dGMP-MoS₂), and remained colloidally stable and homogeneous to the naked eye for months. Such an appearance was consistent with the presence of exfoliated MoS₂ particles in the dispersions.^{22,31,37} Indeed, the UV-vis absorption (or extinction, to be more precise) spectra recorded for these suspensions (red plots in Fig. 2a and b for dAMP-MoS₂ and dGMP-MoS₂, respectively) revealed peaks located roughly at 670, 610, 450 and 400 nm that could be ascribed, respectively, to the A, B, C and D excitonic bands characteristic of this TMD.^{31,44,45} Additional sharp peaks in the 200–300 nm wavelength range (UV region) were observed in the spectra, which were attributed to absorption features of the nucleotides. As a matter of fact, these very same peaks were present in the spectra of aqueous dAMP and dGMP solutions in the absence of MoS₂ (black plots in Fig. 2a and b). The nucleotide-only solutions displayed negligible absorbance at wavelengths above ~300 nm.

Figure 2. UV-vis extinction spectra obtained for dispersions of (a) dAMP-MoS₂ (b) and dGMP-MoS₂ as prepared (red plots) and after two sedimentation/re-suspension cycles (green plots). The black plots correspond to UV-vis absorption spectra of solution of the corresponding nucleotides in the absence of MoS₂. Insets: digital photographs of as-prepared (left) and ten-fold diluted (right) dispersions of (a) dAMP-MoS₂ and (b) dGMP-MoS₂.

We note that sonication and subsequent centrifugation of MoS₂ powder in water alone did not yield any significant amount of TMD material in the supernatant, as expected, and also that complete sedimentation via high-speed centrifugation of the MoS₂ material suspended in the presence of either dAMP or dGMP left behind a supernatant with a nucleotide concentration lower than that of the starting aqueous solution (as evidenced by the decreased intensity of the characteristic absorption peaks). The supernatant solutions prepared in the presence of nucleotides were thus concluded to be comprised of exfoliated MoS₂ particles colloidally stabilized by adsorbed nucleotide molecules as well as of free, non-adsorbed nucleotides. However, the latter could be removed to a large extent by iterative cycles of sedimentation of the MoS₂ fraction using high-speed centrifugation and re-suspension of the sedimented material in

pure water, as detailed in the SI. For example, the green plots in Fig. 2a and b show typical extinction spectra for the MoS₂ dispersions after two sedimentation/resuspension cycles, where it is clearly noticed that the intensity of the peaks ascribed to the nucleotides decreased markedly relative to that of the MoS₂ excitonic peaks. For a limited number of iterative purification cycles (typically up to 3 or 4), the resulting MoS₂ suspensions were seen to retain their original colloidal stability. However, additional cycles usually led to agglomeration of the dispersions, probably due to an excessive desorption of nucleotides from the MoS₂ particles that caused them to be colloiddally unstable.

The effect of nucleotide concentration on key features of the exfoliated nanosheets, such as their average lateral size and thickness, was also investigated and rationalized, the detailed results being gathered in the SI. Summing up, the average lateral size and thickness of the exfoliated flakes in the nucleotide-stabilized aqueous dispersions were seen to be markedly dependent on the dispersant concentration (in a range between 0.5 and 10 mg mL⁻¹), smaller and thinner flakes being present at higher dispersant concentrations. Rather than arising from differences in the exfoliation pattern, such an outcome could be attributed to a better colloidal stability of small/thin flakes compared to large/thick ones: although similar populations of exfoliated flakes (in terms of lateral size and thickness distributions) are generated at the different nucleotide concentrations, large/thick flakes become colloiddally unstable at higher nucleotide concentrations, thus selecting dispersions towards small/thin objects.

Additional and more direct evidence of the attainment of exfoliated MoS₂ flakes in aqueous suspension assisted by the dAMP and dGMP nucleotides was gathered by a number of microscopy and spectroscopy techniques, including scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), X-ray photoelectron

spectroscopy (XPS) and Raman spectroscopy. Fig. 3a and b shows typical STEM images recorded for MoS₂ flakes from aqueous dispersions stabilized by 1 and 10 mg mL⁻¹, respectively, of the dAMP nucleotide. In all cases, the observed flakes exhibited an irregular polygonal shape. However, in agreement with the UV-vis extinction spectroscopy results (see Fig. S2c in the SI), their lateral size tended to be larger in the 1 mg mL⁻¹ suspensions (200–400 nm) compared to their 10 mg mL⁻¹ counterparts (100–200 nm). Similarly, AFM imaging revealed generally thicker flakes in MoS₂ dispersions prepared from 1 mg mL⁻¹ nucleotide solutions (apparent thicknesses of ~5–9 nm, Fig. 3c) than those from 10 mg mL⁻¹ solutions (apparent thickness of ~2–4 nm, Fig. 3d). Considering that the thickness of a MoS₂ monolayer as measured by the AFM technique is usually between 0.7 and 1 nm,^{15,46} these values were also consistent with those estimated from extinction spectroscopy (see Fig. S2d in the SI). XPS and Raman spectroscopic characterization of the exfoliated MoS₂ flakes is described in detail in the SI. Taken together, the microscopy and spectroscopy results confirmed that the nucleotide-stabilized MoS₂ dispersions were made up of few- to several-layer flakes that largely retained the chemical and structural integrity of their bulk parent material.

Figure 3. Typical STEM images recorded for MoS₂ flakes from aqueous dispersions stabilized by (a) 1 and (b) 10 mg mL⁻¹ of the dAMP nucleotide. AFM images for MoS₂ flakes from aqueous dispersions stabilized by (c) 1 and (d) 10 mg mL⁻¹ of the dAMP nucleotide.

Besides MoS₂, other TMDs could be successfully exfoliated and dispersed in aqueous medium with the aid of the dAMP and dGMP nucleotides as stabilizers. This possibility is illustrated in Fig. 4 for the case of WS₂ (a), MoTe₂ (b) and NbSe₂ (c) suspensions that were prepared using 1 mg mL⁻¹ of either dAMP (left vials) or dGMP (right vials). In agreement with previous reports from the literature,³⁰ their corresponding UV-vis extinction spectra (Fig. 4d, obtained with dAMP) exhibited features that were characteristic of exfoliated flakes of each material. Furthermore, all the prepared nucleotide-stabilized TMD dispersions were seen to possess long-term colloidal stability, appearing homogeneous to the naked eye at least for several months.

Figure 4. Digital photographs of (a) WS₂, (b) MoTe₂ and (c) NbSe₂ suspensions that were prepared using 1 mg mL⁻¹ of either dAMP (left vials) or dGMP (right vials). (d) UV-vis extinction spectra for the suspensions obtained with dAMP: WS₂ (red trace), MoTe₂ (blue) and NbSe₂ (green).

Besides, the exfoliated flakes were shown to be biocompatible by studies of proliferation and viability of murine pre-osteoblasts and human sarcoma osteoblasts in the presence of nucleotide-stabilized flakes (see SI). It is also worth mentioning that replacement of these DNA nucleotides by their RNA counterparts, *i.e.* use of adenosine monophosphate (AMP) and guanosine monophosphate (GMP) instead of dAMP and dGMP, respectively, did not have any noticeable effect on the characteristics of the resulting dispersions, as could be probably anticipated for such a minor change in the chemical make-up of the nucleotides.

2.2. Mechanism of colloidal stabilization of MoS₂ with DNA/RNA nucleotides

Based on general knowledge on the use of surfactants for the colloidal stabilization of 2D as well as other nanostructured materials^{16,47} and on previous work on the interaction of DNA nucleobases with such materials,⁴³ we have assumed that nucleotides adsorb on the TMD surface through weak, non-specific interactions of a dispersive (van der Waals) nature. However, as we show in the following, experimental evidence obtained in the present work strongly suggested that such an assumption is not correct. Drawing from basic notions of adsorption,⁴⁸ we note that the adsorption of nucleotide molecules from the aqueous phase on the TMD flake surface can be expected to be a dynamic process, whereby adsorbed nucleotides desorb from the surface at a certain rate and are then replaced by new molecules from the reservoir of free molecules

in the surrounding solution. In the equilibrium state, the surface of the exfoliated flakes will be covered by a given constant density of nucleotides, which will afford the flakes to be colloidally stable provided that such a coverage density is sufficiently high. In turn, this density will be determined by two main factors: (1) the concentration of free nucleotides in the solution, so that the higher the nucleotide concentration, the higher their coverage density on the flakes and thus the better their colloidal stability; and (2) the strength of the nucleotide-flake interaction, in such a way that, for a given concentration of free nucleotides in the solution, the higher the interaction strength, the higher the coverage density and hence the better the colloidal stability of the flakes. According to these ideas, the nucleotide-flake interaction strength can be qualitatively put to the test by preparing the corresponding aqueous suspensions in the presence of a sufficiently low concentration of free nucleotides. Under such circumstances, the colloidal stability of the flakes should be critically dependent on the magnitude of the nucleotide-flake interaction, and so we would expect to observe significant differences between the suspensions if different nucleotides interact with the flakes with differing strengths (*e.g.*, we would expect higher dispersed concentrations and/or slower sedimentation profiles for stronger nucleotide-flake interactions).

We prepared a set of aqueous MoS₂ dispersions with the 5 nucleotides shown in Fig. 1 (*i.e.*, dAMP, dGMP, dCMP, dTMP and FMN) using a starting nucleotide concentration of 3 mM in all cases, equivalent to mass concentrations slightly above or below 1 mg mL⁻¹ depending on the specific nucleotide. The as-prepared dispersions were then subjected to two cycles of sedimentation via centrifugation and re-suspension in pure water (see SI) to decrease markedly the concentration of free nucleotides in the solution. Finally, the dispersed amount of MoS₂ was measured by UV-vis extinction spectroscopy and the suspensions were stored to monitor their sedimentation behavior

with time. For comparison purposes, the same protocol was applied to prepare aqueous suspensions of graphene flakes using graphite powder as starting material. The histogram shown in Fig. 5a depicts the concentration of graphene flakes stabilized by the different nucleotides, which was measured immediately after their preparation. FMN was seen to afford the highest dispersed amount, followed closely by dAMP and dGMP. By contrast, dCMP and dTMP exhibited a rather poor dispersing ability. Furthermore, the graphene dispersions prepared with the latter two nucleotides precipitated altogether in a matter of 1–2 days, those prepared with dAMP and dGMP did so in a longer timeframe (2–3 weeks), whereas their FMN counterpart did not show visible signs of substantial precipitation over the course of at least several months. These results suggested that the interaction of graphene with FMN was the strongest among the investigated nucleotides, the interaction with dCMP and dTMP was the weakest, whereas that with dAMP and dGMP was somewhere in between in strength. Such an outcome could be rationalized by assuming that the nucleotides interact with the graphene surface exclusively through dispersive forces arising between their nucleobase moiety and the 2D material (mainly via π – π stacking). In this scenario, the interaction strength would be expected to increase with the number of aromatic rings present in the nucleobase, so that it should follow the trend FMN (three rings) > dAMP $\approx$ dGMP (two rings) > dCMP $\approx$ dTMP (one ring), which was indeed in agreement with the results of the dispersion experiments using the different nucleotides.

Figure 5. Histograms of the concentration of (a) graphene and (b) MoS₂ flakes stabilized by the different nucleotides measured immediately after their preparation. UV-vis absorption spectra of (c) dAMP and (d) dGMP aqueous solutions obtained as supernatants of nucleotide-stabilized MoS₂ dispersions that were first sedimented and then acidified (green traces) or first acidified and then sedimented (red traces).

Schematic illustrating the different mechanisms of stabilization of colloidal dispersions of graphene (e) and MoS₂ flakes (f) with DNA/RNA nucleotides.

On the other hand, the results obtained for MoS₂ were not consistent with the idea of nucleotide adsorption (and hence colloidal stability of the MoS₂ flakes) relying exclusively on dispersive interactions. If that was the case, we would expect the dispersion behavior of MoS₂ with the nucleotides to be similar to that observed for graphene. In contrast, as noticed from Fig. 5b, the following trend was found: FMN $\approx$ dAMP $\approx$ dGMP $\approx$ dCMP $>$ dTMP. Furthermore, different to the case of graphene, visual inspection revealed that MoS₂ dispersions prepared with any of these nucleotides retained their colloidal stability for months without showing significant signs of aggregation. We then have to conclude that the ability of at least some of the nucleotides (particularly those with one or two rings in their nucleobase) to colloidally stabilize MoS₂ flakes in aqueous medium must rest to a critical extent upon another, more specific type of interaction. As schematically depicted in Fig. 5e and f we believe Lewis acid-base interactions to be the main driving force behind the enhanced dispersibility of MoS₂ with DNA nucleotides compared to the case of graphene. Support for such a hypothesis was obtained on the basis of the following observations.

First, although relatively weak in magnitude, DNA nucleobases are known to possess a basic character.⁴² Second, the actual degree of basicity of a nucleobase depends sensitively on the specific substituents present in the purine or pyrimidine unit that makes up the scaffold of the nucleobase (*e.g.*, electron donating amine groups increase the nucleobase basicity, whereas electron withdrawing carbonyl substituents decrease its basicity). More specifically, adenine, guanine and cytosine exhibit a similar degree of basicity: the pK_a values of their corresponding conjugate acids, pK_{aH}, are 4.3,

3.3 and 4.6, respectively, which are substantially higher than that of thymine ($\text{pK}_{\text{aH}} < 1.3$).⁴² Therefore, compared with dTMP, the nucleotides dAMP, dGMP and dCMP should be able to establish stronger acid-base interactions with prospective acidic sites on MoS_2 . Significantly, the three latter nucleotides were seen to be much more efficient as dispersants for MoS_2 flakes than dTMP was (Fig. 5b). Third, if the hypothesis of nucleotide adsorption on the MoS_2 flakes relying to a large extent on acid-base interactions is correct, then we would expect to observe significant desorption from the flakes when such nucleotide-flake interactions are suppressed, for example by protonating the nucleobase moiety at a sufficiently low pH value.

To test this idea, we prepared aqueous MoS_2 dispersions using either dAMP or dGMP (1 mg mL^{-1}) as a stabilizer, which were then subjected to four cycles of sedimentation via centrifugation and re-suspension in pure water to drastically reduce the concentration of free, non-adsorbed nucleotide molecules. Subsequently, the dispersions were divided into two aliquots. The pH of one aliquot was decreased to a value of ~ 2 by addition of HCl to ensure protonation of the nucleobases in the nucleotides, and the acidified dispersion was centrifuged at 20000 g for 2 h to completely sediment the MoS_2 fraction. The other aliquot was first centrifuged at 20000 g for 2 h and then the pH of the resulting supernatant was adjusted to ~ 2 . If nucleotides desorb from the MoS_2 flakes upon acidification of the aqueous dispersion as a result of acid-base interactions being suppressed, then the nucleotide concentration in the supernatant from the aliquot that was first acidified and then centrifuged should be higher than that in the supernatant from the aliquot that was first centrifuged and then acidified. To compare the nucleotide concentrations we used UV-vis extinction spectroscopy, as shown in Fig. 5c and d for the case of dAMP and dGMP, respectively. It was consistently observed that the absorption peaks associated to the nucleotides

[e.g., the peak at ~ 260 (255) nm for dAMP (dGMP)] were more intense in the supernatants from aliquots that were acidified in the first place (red traces in Fig. 5c and d) relative to those that were acidified after centrifugation (black traces). This result provided strong indication that acid-base interactions play a significant role in the adsorption of nucleotides on MoS₂ flakes and would explain, for instance, the different dispersing ability of dTMP compared to the other three DNA nucleotides: the much weaker basic character of dTMP should lead to its having weaker adsorption on MoS₂ and finally to its poorer dispersing ability for this material, as it was actually observed (Fig. 5b).

Finally, we note that the hypothesis of acid-base interactions arising between MoS₂ and the nucleotides obviously requires the presence of acidic sites on the former. Acidic sites do indeed exist in MoS₂ in the form of sulfur vacancies, which in turn are known to be a common type of defect for this material. Indeed, it has been demonstrated that natural MoS₂ samples⁴⁹ as well as MoS₂ flakes and sheets produced either by micromechanical cleavage,^{50,51} direct liquid-phase exfoliation^{52,53} or CVD methods^{51,54} contain significant concentrations of sulfur vacancies as a result of their relatively low formation energy. In our case, XPS analysis of the nucleotide-exfoliated MoS₂ samples revealed S/Mo atomic ratios of ~ 1.9 thus suggesting a sulfur vacancy concentration of $\sim 5\%$. Furthermore, prior studies from the field of catalysis have established that the coordinately unsaturated molybdenum sites associated to sulfur vacancies possess a Lewis acid nature, so that basic molecules such as pyridine and ammonia adsorb selectively onto these sites.⁵⁵ It is therefore quite likely that the enhanced colloidal stability of MoS₂ flakes afforded by DNA nucleotides stems from Lewis acid-base interactions between the basic nucleobases of the nucleotides and the acidic sulfur vacancies of MoS₂. Likewise, in this scenario the sugar moiety of the nucleotide does

not appear to play a critical role in the colloidal stabilization of the MoS₂ flakes, so it is not surprising that use of the DNA or RNA version of a given nucleotide (*e.g.*, dAMP vs. AMP) yielded dispersions with virtually the same characteristics.

2.3. Catalytic activity of nucleotide-stabilized MoS₂ flakes in the reduction of nitroarenes

Very recent work has demonstrated that nanosheets/nanostructures of MoS₂ and other TMDs prepared by different means are catalytically active towards a number of reduction reactions (most notably, nitroarene reduction) carried out in the aqueous phase with sodium borohydride as the reductant.^{56–59} MoS₂ nanosheets obtained by the lithium intercalation/exfoliation approach were seen to be particularly efficient in such a role, probably due to the structural transformation from the semiconducting 2H phase to the metallic 1T phase that is induced by intercalation.⁵⁶ However, lithium-exfoliated MoS₂ nanosheets are known to lack long-term colloidal stability in water (they tend to agglomerate and precipitate in a few weeks altogether), which seriously limits their practical utility as catalysts for the mentioned reactions. In this regard, MoS₂ flakes produced in aqueous dispersion by direct exfoliation methods using suitable dispersants, such as the present nucleotides, could be an attractive alternative, but their catalytic activity has not yet been tested. We therefore investigated the ability of our nucleotide-stabilized MoS₂ suspensions to catalyze the room-temperature reduction of two nitroarenes, namely the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and of 4-nitroaniline (4-NA) to *p*-phenylenediamine (*p*-PDA) with sodium borohydride. Both reactions are thermodynamically downhill but kinetically hampered by relatively large activation barriers, so they require the use of suitable catalysts to proceed rapidly at room temperature.⁶⁰ In addition to their status as model reactions to probe the

performance of many catalysts (mainly metal-based), these reduction reactions are relevant from a practical point of view, for instance, as important steps in the synthesis of certain drugs and polymers.^{60,61} As detailed elsewhere,^{41,56} the kinetics of both reactions can be readily followed using UV-vis extinction spectroscopy, specifically by monitoring the evolution of the intensity of bands that are characteristic of each substrate (*i.e.*, bands at ~400 and 382 nm for 4-NP and 4-NA, respectively) and thus reflect their concentration in the reaction medium.

Fig. 6a and b shows typical kinetic profiles measured for the reduction of 4-NP (a) and 4-NA (b) with MoS₂ flakes that were prepared with two different concentrations of dGMP, namely 1 (blue traces) and 10 (red traces) mg mL⁻¹. An induction period of several minutes, which can be ascribed to dissolved oxygen in the solution being depleted by sodium borohydride or to the catalytic sites being conditioned by the reactants^{62,63} was usually observed. After the induction period, the reduction reaction proper set in, which was reflected in a continuous decrease in the extinction values (and hence in the concentration) associated to both 4-NP and 4-NA. Because the kinetic profiles could be fitted to exponential decay functions and sodium borohydride was used in a large excess relative to either 4-NP or 4-NA, the reduction reactions were concluded to obey a pseudo-first-order kinetic behavior with respect to the substrate concentration, so that

$$\frac{d[subs]}{dt} = -k_{app}[subs] \quad (1)$$

, where [subs] is the substrate (4-NP or 4-NA) concentration and k_{app} is the apparent reaction rate constant. It was also determined that the exfoliated MoS₂ flakes were the catalytically active element in the as-prepared, nucleotide-stabilized aqueous dispersions rather than any molecular species that could be present in such dispersions (*e.g.*, the nucleotide itself or species leached from the MoS₂ flakes). Indeed, when the

flakes were removed from the as-prepared MoS₂ dispersions by means of centrifugation (20000 g, 2 h) and the resulting supernatants were added to the reaction medium instead of the full-fledged MoS₂ dispersions, no reduction was seen to take place.

Figure 6. Typical kinetic profiles measured for the catalyzed reduction of 4-NP (a) and 4-NA (b) with MoS₂ flakes prepared with two different concentrations of dGMP, namely, 1 (blue traces) and 10 (red traces) mg mL⁻¹.

A comparison of the catalytic activity (calculated as the number of substrate moles converted per unit time per mole of catalyst used) of the present dGMP-stabilized MoS₂ flakes for both 4-NP and 4-NA reduction to that of other catalysts recently reported in the literature for the same reactions is provided in the SI (see Table S1 and the accompanying text for a detailed discussion). Overall, we conclude that nucleotide-stabilized MoS₂ flakes can be competitive catalysts for the reduction of nitroarenes, as they strike a good balance between catalytic activity, simplicity and environmental friendliness of their preparation (compared to, *e.g.*, reduced graphene oxide or lithium-exfoliated MoS₂) and cost-effectiveness (compared to noble metal-based catalysts).

2.4. Electrocatalytic activity of nucleotide-stabilized MoS₂ flakes towards HER

MoS₂ and other TMDs are known to possess a considerable electrocatalytic activity towards the HER, and are currently investigated as a prospective, non-noble metal-based replacement for the highly effective but very scarce and expensive Pt-based electrocatalysts for such a purpose.^{64,65} It has also been demonstrated that, at least in the case of MoS₂, the catalytically active sites are located at edges and chalcogen vacancies of the layered structure, so that different nanostructuring strategies aimed at increasing the fraction of edges and defects in TMDs have been pursued in recent years as a way to enhance their HER performance.^{64,66} In this context, the direct liquid-phase exfoliation of TMDs can be regarded as a straightforward and efficient nanostructuring methodology towards HER because it can afford exfoliated flakes of a relatively small lateral size and thus with a relatively large fraction of edges.⁶⁷ However, for the MoS₂ flakes investigated here we have concluded that the nucleotides are strongly adsorbed at coordinately unsaturated molybdenum sites (*i.e.*, at sulfur vacancies but also probably at edges) through acid-base interactions, so there is the possibility that their HER activity is impaired by the adsorbed nucleotides blocking their active sites. It was therefore important to evaluate the HER electrocatalytic performance of these nucleotide-stabilized MoS₂ samples. To this end, we deposited different MoS₂ dispersions onto the surface of glassy carbon electrodes (GCEs) at a constant MoS₂ amount of $\sim 35 \mu\text{g cm}^{-2}$ and then tested their electrocatalytic activity towards HER by linear sweep voltammetry (LSV) in a 0.5 M H₂SO₄ solution.

Fig. 7a shows typical polarization curves obtained for MoS₂ flakes prepared with the nucleotides dAMP and dGMP at two different concentrations (1 and 10 mg mL⁻¹) and deposited onto a GCE. As could be expected, lower values of onset potential (defined as the potential required to attain a current density of -1 mA cm^{-2}) were

observed for MoS₂ samples comprised of flakes with smaller average lateral size, *i.e.* samples prepared at a nucleotide concentration of 10 mg mL⁻¹ (average size ~130–150 nm compared to ~260–280 nm for a nucleotide concentration of 1 mg mL⁻¹). Specifically, the following onset potentials were measured: -0.44 V (1 mg mL⁻¹ dAMP), -0.39 V (10 mg mL⁻¹ dAMP), -0.43 V (1 mg mL⁻¹ dGMP) and -0.37 V (10 mg mL⁻¹ dGMP). These values were similar to those previously reported for liquid-phase exfoliated MoS₂ flakes of comparable size and deposited on the working electrode at amounts similar to those used here. For example, MoS₂ flakes exfoliated in water with sodium cholate as a dispersant having a mean lateral size of ~190 nm and deposited at an amount of 30 µg cm⁻² yielded an onset potential of about -0.43 V,³¹ whereas it was -0.34 V for flakes with an average size of ~122 nm and deposited at ~60 µg cm⁻².⁶⁸ Tafel plots (*i.e.*, plots of overpotential vs log of current density) for the different nucleotide-stabilized samples are given in Fig. 7b. The corresponding Tafel slopes, which indicate the increase in overpotential required to raise the current density by one order of magnitude, were (in mV per decade) 178 for 1 mg mL⁻¹ dAMP, 158 for 10 mg mL⁻¹ dAMP, 132 for 1 mg mL⁻¹ dGMP and 127 for 10 mg mL⁻¹ dGMP. On one hand, we note that for a given nucleotide concentration the Tafel slopes were smaller (indicative of better HER performance) for MoS₂ flakes prepared with dGMP compared to dAMP, even though the average flake lateral size and thickness obtained using these two dispersants were very similar (see Fig. S2c and d in the SI). This observation suggests that some blockage of the catalytically active sites by the nucleotides (especially in the case of dAMP) could indeed take place. On the other hand, the Tafel slopes derived here lay for the most part within the range of values that have been typically documented for liquid-phase exfoliated MoS₂ flakes of comparable or not very different size (115–164 mV per decade for flakes with average sizes between 75 and 146 nm) and

more generally for 2H MoS₂ materials (between ~100 and 150 mV per decade).^{32,67,68} Therefore, although a certain degree of active site blockage by the nucleotides should not be ruled out, we can conclude that such an effect must be rather limited so that the HER performance of the MoS₂ flakes does not become seriously affected.

Figure 7. (a) Typical polarization curves obtained for MoS₂ flakes prepared with the nucleotides dAMP and dGMP at two different concentrations (1 and 10 mg mL⁻¹) and deposited onto a GCE. (b) Tafel plots for the different nucleotide-stabilized samples with indication of the corresponding Tafel slopes. The color code is: GCE (black trace), dAMP at 1 mg mL⁻¹ (orange), dAMP at 10 mg mL⁻¹ (red), dGMP at 1 mg mL⁻¹ (cyan), and dGMP at 10 mg mL⁻¹ (blue).

3. Conclusions

We have demonstrated that DNA and RNA nucleotides are highly efficient dispersants towards the exfoliation and colloidal stabilization of MoS₂ and other transition metal dichalcogenides (TMDs) in aqueous medium at significant concentrations (up to ~5-10 mg mL⁻¹). This behavior was in contrast to the case of graphene, for which the DNA/RNA nucleotides were shown to be rather mediocre dispersants. The results of a

suite of experiments suggested that the remarkable ability of these nucleotides to colloidally stabilize the MoS₂ flakes relies on the establishment of relatively strong, specific nucleotide-flake interactions, which were believed to be of Lewis acid-base nature, in such a way that the nucleobase moiety of the nucleotide molecule is preferentially adsorbed onto the Lewis acidic sites associated to sulfur vacancies in MoS₂. Furthermore, the average lateral size and thickness of the exfoliated flakes in the nucleotide-stabilized aqueous dispersions were found to be notably dependent on the dispersant concentration, smaller and thinner flakes being present at higher dispersant concentrations. The nucleotide-stabilized MoS₂ flakes were also demonstrated to possess a remarkable catalytic activity in the reduction of nitroarenes (4-nitrophenol and 4-nitroaniline), which was comparable to that of many non-noble and even noble metal-based catalysts documented in the literature. Likewise, their electrocatalytic performance towards the hydrogen evolution reaction was not significantly impaired by the possible presence of nucleotide molecules adsorbed on the active sites of MoS₂ (edges, sulfur vacancies). A high biocompatibility of the nucleotide-stabilized MoS₂ flakes towards murine pre-osteoblasts and human sarcoma osteoblasts was deduced from preliminary studies as well. Finally, in addition to the more direct benefits of using DNA/RNA nucleotides as dispersants for TMD flakes (simplicity, environmental friendliness, biocompatibility, etc), we note that the knowledge generated here could open new avenues for the exploitation of these flakes. For instance, because cancer cells are usually associated to low pH values, one can envisage small MoS₂ flakes as drug delivery vehicles where the molecular cargo is loaded by taking advantage of acid-base interactions with the flakes and then released selectively at the cancer tissue as triggered by its acidic environment.

Supporting Information. Materials and methods. XPS and Raman characterization of the exfoliated MoS₂ flakes. Investigation on the effect of nucleotide concentration on the average lateral size and thickness of the exfoliated nanosheets. Comparison of the catalytic activity of the nucleotide-stabilized MoS₂ flakes for both 4-NP and 4-NA reduction to that of other catalysts recently reported in the literature for the same reactions. Demonstration of the biocompatibility of nucleotide-stabilized MoS₂ dispersions on the basis of cell proliferation and viability assays carried out with murine pre-osteoblasts and human sarcoma osteoblasts.

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References

- (1) Ferrari, A.C.; Bonaccorso, F.; Falko, V.; Novoselov, K. S.; Roche, S.; Bøggild, P.; Borini, S.; Koppens, F.; Palermo, V.; Pugno N.; Garrido, J. A.; Sordan, R.; Bianco, A.; Ballerini, L.; Prato, M.; Lidorikis, E.; Kivioja, J.; Marinelli, C.; Ryhänen, T.; Morpurgo, A.; Coleman, J. N.; Nicolosi, V.; Colombo, L.; Fert, A.; Garcia-Hernandez, M.; Bachtold, A.; Schneider, G. F.; Guinea, F.; Dekker, C.; Barbone, M.; Galiotis, C.; Grigorenko, A.; Konstantatos, G.; Kis, A.; Katsnelson, M.; Beenakker, C. W. J.; Vandersypen, L.; Loiseau, A.; Morandi, V.; Neumaier, D.; Treossi, E.; Pellegrini, V.; Polini, M.; Tredicucci, A.; Williams, G. M.; Hong, B. H.; Ahn, J. H.; Kim, J. M.; Zirath, H.; van Wees, B. J.; van der Zant, H.; Occhipinti, L.; Di Matteo, A.; Kinloch, I. A.; Seyller, T.; Quesnel, E.; Feng, X.; Teo, K.; Rupesinghe, N.; Hakonen, P.; Neil, S. R. T.; Tannock, Q.; Löfwander, T.; Kinaret, J. Science and Technology Roadmap for Graphene, Related Two-Dimensional Crystals, and Hybrid Systems. *Nanoscale* **2015**, *7*, 4598–4810.
- (2) Gravagnuolo, A. M.; Morales-Narváez, E.; Longobardi, S.; da Silva, E. T.; Giardina, P.; Merkoçi, A. In Situ Production of Biofunctionalized Few-Layer Defect-Free Microsheets of Graphene. *Adv. Funct. Mater.* **2015**, *25*, 2771–2779.
- (3) Peng, L.; Zhu, Y.; Chen, D.; Ruoff, R.S.; Yu, G. Two-Dimensional Materials for beyond-Lithium-Ion Batteries. *Adv. Energy Mater.* **2016**, *6*, 1600025.
- (4) Bhimanapati, G. R.; Lin, Z.; Meunier, V.; Jung, Y.; Cha, J.; Das, S.; Xiao, D.; Son, Y.; Strano, M. S.; Cooper, V. R.; Liang, L.; Louie, S. G.; Ringe, E.; Zhou, W.; Kim, S. S.; Naik, R. R.; Sumpter, B. G.; Terrones, H.; Xia, F.; Wang, Y.; Zhu, J.; Akinwande, D.; Alem, N.; Schuller, J. A.; Schaak, R. E. Terrones, M.; Robinson, J. A. Recent Advances in Two-Dimensional Materials Beyond Graphene. *ACS Nano* **2015**, *9*, 11509–11539.
- (5) Duan, X.; Wang, C.; Pan, A.; Yu, R.; Duan, X. Two-Dimensional Transition Metal Dichalcogenides as Atomically Thin Semiconductors: Opportunities and Challenges. *Chem. Soc. Rev.* **2015**, *44*, 8859–8876.
- (6) Subbaiah, Y.P.V.; Saji, K.J.; Tiwari, A., A Versatile Nongraphene 2D Material. *Adv. Funct. Mater.* **2016**, *26*, 2046–2069.
- (7) Zhang, X.; Hou, L.; Ciesielski, A.; Samorì, P. 2D Materials beyond Graphene for High-Performance Energy Storage Applications. *Adv. Energy Mater.* **2016**, *6*, 1600671.

- (8) Kannan, P.K.; Late, D.J.; Morgan, H.; Rout, C.S. Recent Developments in 2D Layered Inorganic Nanomaterials for Sensing. *Nanoscale* **2015**, *7*, 13293–13312.
- (9) Li, H.; Shi, Y.; Chiu M.-H.; Li, L.-J. Emerging Energy Applications of Two-Dimensional Layered Transition Metal Dichalcogenides. *Nano Energy* **2015**, *18*, 293–305.
- (10) Zhang, G.; Liu, H.; Qu, J.; Li, J. Two-Dimensional Layered MoS₂: Rational Design, Properties and Electrochemical Applications. *Energy Environ. Sci.* **2016**, *9*, 1190–1209.
- (11) Mak, K.F.; Shan, J. Photonics and Optoelectronics of 2D Semiconductor Transition Metal Dichalcogenides. *Nat. Photon.* **2016**, *10*, 216–226.
- (12) Shi, Y.; Li, H.; Li, L.-J. Recent Advances in Controlled Synthesis of Two-Dimensional Transition Metal Dichalcogenides via Vapour Deposition Techniques. *Chem. Soc. Rev.* **2015**, *44*, 2744–2756.
- (13) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS₂. *Nano Lett.* **2011**, *11*, 5111–5116.
- (14) Zeng, Z.; Yin, Z.; Huang, X.; Li, H.; He, Q.; Lu, G.; Boey, F.; Zhang, H. Single-Layer Semiconducting Nanosheets: High-Yield Preparation and Device Fabrication. *Angew. Chem. Int. Ed.* **2011**, *50*, 11093–11097.
- (15) Coleman, J. N.; Lotya, M.; O'Neill, A.; Bergin, S. D.; King, P. J.; Khan, U.; Young, K.; Gaucher, A.; De, S.; Smith, R. J.; Shvets, I. V.; Arora, S. K.; Stanton, G.; Kim, H. Y.; Lee, K.; Kim, G. T.; Duesberg, G. S.; Hallam, T.; Boland, J. J.; Wang, J. J.; Donegan, J. F.; Grunlan, J. C.; Moriarty, G.; Shmeliov, A.; Nicholls, R. J.; Perkins, J. M.; Grievson, E. M.; Theuwissen, K.; McComb, D. W.; Nellist, P. D.; Nicolosi, V. Two-Dimensional Nanosheets Produced by Liquid Exfoliation Of Layered Materials. *Science* **2011**, *331*, 568–571.
- (16) Niu, L.; Coleman, J. N.; Zhang, H.; Shin, H.; Chhowalla, M.; Zheng, Z. Production of Two-Dimensional Nanomaterials via Liquid-Based Direct Exfoliation. *Small* **2016**, *12*, 272–293.
- (17) Chhowalla, M.; Shin, H. K.; Eda, G.; Li, L.-J.; Loh, K.P.; Zhang, H. The Chemistry of Two-Dimensional Layered Transition Metal Dichalcogenide Nanosheets. *Nat. Chem.* **2013**, *5*, 263–275.

- (18) Voiry, D.; Mohite, A.; Chhowalla, M. Phase Engineering of Transition Metal Dichalcogenides. *Chem. Soc. Rev.* **2015**, *44*, 2702–2712.
- (19) Cunningham, G.; Lotya, M.; Cucinotta, C. S.; Sanvito, S.; Bergin, S. D.; Menzel, R.; Shaffer, M. S. P.; Coleman, J. N. Solvent Exfoliation of Transition Metal Dichalcogenides: Dispersibility of Exfoliated Nanosheets Varies Only Weakly Between Compounds. *ACS Nano* **2012**, *6*, 3468–3480.
- (20) Shen, J.; Wu, J.; Wang, M.; Dong, P.; Xu, J.; Li, X.; Zhang, X.; Yuan, J.; Wang, X.; Ye, M.; Vajtai, R.; Lou, J.; Ajayan, P. M. Surface Tension Components Based Selection of Cosolvents for Efficient Liquid Phase Exfoliation of 2D Materials. *Small* **2016**, *12*, 2741–2749.
- (21) Gupta, A.; Arunachalam V.; Vasudevan, S. Water Dispersible, Positively and Negatively Charged MoS₂ Nanosheets: Surface Chemistry and the Role of Surfactant Binding. *J. Phys. Chem. Lett.*, **2015**, *6*, 739–744.
- (22) Yang, H.; Withers, F.; Gebremedhn, E.; Lewis, E.; Britnell, L.; Felten, A.; Palermo, V.; Haigh, S.; Beljonne D.; Casiraghi, C. Dielectric Nanosheets Made by Liquid-Phase Exfoliation in Water and Their Use in Graphene-Based Electronics. *2D Mater.* **2014**, *1*, 011012.
- (23) Bindhu, B.; Sharu, B. K.; Gopika, M.S.; Praseetha, P. K.; Veluraja, K. Molybdenum Disulfide Nanoflakes through Li-AHA Assisted Exfoliation in an Aqueous Medium. *RSC Adv.* **2016**, *6*, 22026–22033.
- (24) Chen, X.; Boulos, R. A.; Eggers, P. K.; Raston, C. L. *p*-Phosphonic Acid Calix(8)arene assisted Exfoliation and Stabilization of 2D Materials in Water, *Chem. Commun.* **2012**, *48*, 11407–11409.
- (25) Guardia, L.; Paredes, J. I.; Rozada, R.; Villar-Rodil, S.; Martínez-Alonso, A.; Tascón, J. M. D. Production of Aqueous Dispersions of Inorganic Graphene Analogues by Exfoliation and Stabilization with Non-Ionic Surfactants. *RSC Adv.* **2014**, *4*, 14115–14127.
- (26) Bari, R.; Parviz, D.; Khabaz, F.; Klaassen, C. D.; Metzler, S. D.; Hansen, M. J.; Khare, R.; Green, M. J. Liquid Phase Exfoliation and Crumpling of Inorganic Nanosheets. *Phys. Chem. Chem. Phys.* **2015**, *17*, 9383–9393.

- (27) Quinn, M. D. J.; Ho, N. H.; Notley, S. M. Aqueous Dispersions of Exfoliated Molybdenum Disulfide for Use in Visible-Light Photocatalysis. *ACS Appl. Mater. Interfaces* **2013**, *5*, 12751–12756.
- (28) Mansukhani, N. D.; Guiney, L. M.; Kim, P. J.; Zhao, Y.; Alducin, D.; Ponce, A.; Larios, E.; Yacaman, M. J.; Hersam, M. C. High-Concentration Aqueous Dispersions of Nanoscale 2D Materials Using Nonionic, Biocompatible Block Copolymers. *Small* **2016**, *12*, 294–300.
- (29) Paredes, J. I.; Villar-Rodil, S. Biomolecule-Assisted Exfoliation and Dispersion of Graphene and Other Two-Dimensional Materials: a Review of Recent Progress and Applications. *Nanoscale* **2016**, *8*, 15389–15413.
- (30) Smith, R. J.; King, P. J.; Lotya, M.; Wirtz, C.; Khan, U.; De, S.; O'Neill, A.; Duesberg, G. S.; Grunlan, J. C.; Moriarty, G.; Chen, J.; Wang, J.; Minett, A. I.; Nicolosi, V.; Coleman, J. N. Large-Scale Exfoliation of Inorganic Layered Compounds in Aqueous Surfactant Solutions. *Adv. Mater.* **2011**, *23*, 3944–3948.
- (31) Backes, C.; Smith, R. J.; McEvoy, N.; Berner, N. C.; McCloskey, D.; Nerl, H. C.; O'Neill, A.; King, P. J.; Higgins, T.; Hanlon, D.; Scheuschner, N.; Maultzsch, J.; Houben, L.; Duesberg, G. S.; Donegan, J. F.; Nicolosi, V.; Coleman, J. N. Edge and Confinement Effects Allow in Situ Measurement of Size and Thickness of Liquid-Exfoliated Nanosheets. *Nat. Commun.* **2014**, *5*, 4576.
- (32) Varrla, E.; Backes, C.; Paton, K. R.; Harvey, A.; Gholamvand, Z.; McCauley, J.; Coleman, J.N. Large-Scale Production of Size-Controlled MoS₂ Nanosheets by Shear Exfoliation. *Chem. Mater.* **2015**, *27*, 1129–1139.
- (33) Li, Y.; Zhua, H.; Shen, F.; Wan, J.; Lacey, S.; Fang, Z.; Dai, H.; Hu, L. Nanocellulose as Green Dispersant for Two-Dimensional Energy Materials. *Nano Energy* **2015**, *13*, 346–354.
- (34) Feng, X.; Wang, X.; Xing, W.; Zhou, K.; Song, L.; Hu, Y. Liquid-Exfoliated MoS₂ by Chitosan and Enhanced Mechanical and Thermal Properties of Chitosan/MoS₂ Composites. *Compos. Sci. Technol.* **2014**, *93*, 76–82.
- (35) Liu, W.; Zhao, C.; Zhou, R.; Zhou, D.; Liu Z.; Lu, X. Lignin-Assisted Exfoliation of Molybdenum Disulfide in Aqueous Media and Its Application in Lithium Ion Batteries. *Nanoscale* **2015**, *7*, 9919–9926.

- (36) Ravula, S.; Baker, S. N.; Kamath, G.; Baker, G. A., Ionic Liquid-Assisted Exfoliation and Dispersion: Stripping Graphene and Its Two-Dimensional Layered Inorganic Counterparts of Their Inhibitions. *Nanoscale* **2015**, *7*, 4338-4353.
- (37) Guan, G.; Zhang, S.; Liu, S.; Cai, Y.; Low, M.; Teng, C. P.; Phang, I. Y.; Cheng, Y.; Duei, K. L.; Srinivasan, B. M.; Zheng, Y.; Zhang, Y.-W.; Han, M.-Y. Protein Induces Layer-by-Layer Exfoliation of Transition Metal Dichalcogenides. *J. Am. Chem. Soc.* **2015**, *137*, 6152–6155.
- (38) Ge, Y.; Wang, J.; Shi, Z.; Yin, J. Gelatin-Assisted Fabrication of Water-Dispersible Graphene and Its Inorganic Analogues. *J. Mater. Chem.* **2012**, *22*, 17619–17624.
- (39) Bang, G.S.; Cho, S.; Son, N.; Shim, G.W.; Cho, B.-K.; Choi, S.-Y. DNA-Assisted Exfoliation of Tungsten Dichalcogenides and Their Antibacterial Effect. *ACS Appl. Mater. Interfaces* **2016**, *8*, 1943–1950.
- (40) Yoon, W.; Lee, Y.; Jang, H.; Jang, M.; Kim, J. S.; Lee, H. S.; Im, S.; Boo, D. W.; Park, J.; Ju, S.-Y. Graphene Nanoribbons Formed by a Sonochemical Graphene Unzipping Using Flavin Mononucleotide as a Template. *Carbon* **2015**, *81*, 629–638.
- (41) Ayán-Varela, M.; Paredes, J. I.; Guardia, L.; Villar-Rodil, S.; Munuera, J. M.; Díaz-González, M.; Fernández-Sánchez, C.; Martínez-Alonso, A.; Tascón, J. M. D. Achieving Extremely Concentrated Aqueous Dispersions of Graphene Flakes And Catalytically Efficient Graphene-Metal Nanoparticle Hybrids with Flavin Mononucleotide as a High-Performance Stabilizer. *ACS Appl. Mater. Interfaces* **2015**, *7*, 10293–10307.
- (42) Dewick, P.M. Essentials of Organic Chemistry, John Wiley & Sons Ltd, Chichester, 2006, chapters 11 and 14.
- (43) Vovusha, H.; Sanyal, B. Adsorption of Nucleobases on 2D Transition-Metal Dichalcogenides and Graphene Sheet: a First Principles Density Functional Theory Study. *RSC Adv.* **2015**, *5*, 67427–67434.
- (44) Vella, D.; Vega-Mayoral, V.; Gadermaier, C.; Vujicic, N.; Borzda, T.; Topolovsek, P.; Prijatelj, M.; Tempra, I.; Pogna E. A. A.; Cerullo, G. Femtosecond Spectroscopy on MoS₂ Flakes from Liquid Exfoliation: Surfactant Independent Exciton Dynamics. *J. Nanophotonics* **2016**, *10*, 012508.
- (45) Li, B. L.; Zou, H. L.; Lu, L.; Yang, Y.; Lei, J. L.; Luo, H. Q.; Li, N. B. Dependent Optical Absorption of Layered MoS₂ and DNA Oligonucleotides Induced Dispersion

Behavior for Label-Free Detection of Single-Nucleotide Polymorphism. *Adv. Funct. Mater.* **2015**, 25, 3541–3450.

(46) Li, H.; Lu, G.; Yin, Z.; He, Q.; Li, H.; Zhang, Q.; Zhang, H. Optical Identification of Single- and Few-Layer MoS₂ Sheets. *Small* **2012**, 8, 682–686.

(47) Di Crescenzo, A.; Di Profio, P.; Siani, G.; Zappacosta, R.; Fontana, A. Optimizing the Interactions of Surfactants with Graphitic Surfaces and Clathrate Hydrates. *Langmuir* **2016**, 32, 6559–6570.

(48) Butt, H.-J.; Graf, K.; Kappl, M. Physics and Chemistry of Interfaces, Wiley-VCH, Weinheim, 2003, chapter 9.

(49) Addou, R.; Colombo, L.; Wallace, R.M. Surface Defects on Natural MoS₂. *ACS Appl. Mater. Interfaces* **2015**, 7, 11921–11929.

(50) Sim, D. M.; Kim, M.; Yim, S.; Choi, M.-J.; Choi, J.; Yoo, S.; Jung, Y. S. Controlled Doping of Vacancy-Containing Few-Layer MoS₂ via Highly Stable Thiol-Based Molecular Chemisorption. *ACS Nano* **2015**, 9, 12115–12123.

(51) Hong, J.; Hu, Z.; Probert, M.; Li, K.; Lv, D.; Yang, X.; Gu, L.; Mao, N.; Feng, Q.; Xie, L.; Zhang, J.; Wu, D.; Zhang, Z.; Jin, C.; Ji, W.; Zhang, X.; Yuan, J.; Zhang, Z. Exploring Atomic Defects in Molybdenum Disulphide Monolayers. *Nat. Commun.* **2015**, 6, 6293.

(52) Kim, J.-S.; Yoo, H.-W.; Choi, H. O.; Jung, H.-T. Tunable Volatile Organic Compounds Sensor by Using Thiolated Ligand Conjugation on MoS₂. *Nano Lett.* **2014**, 14, 5941–5947.

(53) Nguyen, E. P.; Carey, B. J.; Ou, J. Z.; van Embden, J.; Gaspera, E. D.; Chrimes, A. F.; Spencer, M. J. S.; Zhuiykov, S.; Kalantar-zadeh K.; Daeneke, T. Electronic Tuning of 2D MoS₂ through Surface Functionalization. *Adv. Mater.* **2015**, 27, 6225–6229.

(54) Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Idrobo, J.-C. Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. *Nano Lett.* **2013**, 13, 2615–2622.

(55) Tanabe, K.; Misono, M.; Ono, Y.; Hattori, H. New Solid Acids and Bases: Their Catalytic Properties, Elsevier Science Publishers B.V., Amsterdam, 1989, chapter 3.

(56) Guardia, L.; Paredes, J. I.; Munuera, J. M.; Villar-Rodil, S.; Ayán-Varela, M.; Martínez-Alonso, A.; Tascón, J. M. D. Chemically Exfoliated MoS₂ Nanosheets as an

Efficient Catalyst for Reduction Reactions in the Aqueous Phase. *ACS Appl. Mater. Interfaces*, **2014**, *6*, 21702–21710.

(57) Wen, Y.; Zhang, H.; Zhang, S. One-Step Gas–Solid Reaction Synthesis of W@WS₂ Nanorattles and Their Novel Catalytic Activity. *Nanoscale* **2014**, *6*, 13090–13096.

(58) Lin, T.; Wang, J.; Guo L.; Fu, F. Fe₃O₄@MoS₂ Core–Shell Composites: Preparation, Characterization, and Catalytic Application *J. Phys. Chem. C* **2015**, *119*, 13658–13664.

(59) Peng, K.; Fu, L.; Ouyang J.; Yang, H. Emerging Parallel Dual 2D Composites: Natural Clay Mineral Hybridizing MoS₂ and Interfacial Structure. *Adv. Funct. Mater.* **2016**, *26*, 2666–2675.

(60) Aditya, T.; Pal, A.; Pal, T. Nitroarene Reduction: a Trusted Model Reaction to Test Nanoparticle Catalysts. *Chem. Commun.* **2015**, *51*, 9410–9431.

(61) Hu, H.; Xin, J. H.; Hu, H.; Wang, X.; Miao, D.; Liu, Y. Synthesis and Stabilization of Metal Nanocatalysts for Reduction Reactions – a Review. *J. Mater. Chem. A* **2015**, *3*, 11157–11182.

(62) Lu, Y.; Mei, Y.; Ballauff, M.; Drechsler, M. Metal–Organic Framework-Templated Porous Carbon for Highly Efficient Catalysis: The Critical Role of Pyrrolic Nitrogen Species. *J. Phys. Chem. B* **2006**, *110*, 3930–3937.

(63) Hervés, P.; Pérez-Lorenzo, M.; Liz-Marzán, L. M.; Dzubiella, J.; Lu, Y.; Ballauff, M. Catalysis by Metallic Nanoparticles in Aqueous Solution: Model Reactions. *Chem. Soc. Rev.* **2012**, *41*, 5577–5587.

(64) Benck, J. D.; Hellstern, T. R.; Kibsgaard, J.; Chakthranont, P.; Jaramillo, T. F. Catalyzing the Hydrogen Evolution Reaction (HER) with Molybdenum Sulfide Nanomaterials. *ACS Catal.* **2014**, *4*, 3957–3971.

(65) Chia, X.; Eng, A. Y. S.; Ambrosi, A.; Tan, S. M.; Pumera, M. Electrochemistry of Nanostructured Layered Transition-Metal Dichalcogenides. *Chem. Rev.* **2015**, *115*, 11941–11966.

(66) Li, H.; Tsai, C.; Koh, A. L.; Cai, L.; Contryman, A. W.; Fragapane, A. H.; Zhao, J.; Han, H. S.; Manoharan, H. C.; Abild-Pedersen, F.; Nørskov, J. K.; Zheng, X. Activating and Optimizing MoS₂ Basal Planes for Hydrogen Evolution through the Formation of Strained Sulphur Vacancies. *Nat. Mater.* **2016**, *15*, 48–53.

- (67) Gholamvand, Z.; McAteer, D.; Backes, C.; McEvoy, N.; Harvey, A.; Berner, N. C.; Hanlon, D.; Bradley, C.; Godwin, I.; Rovetta, A.; Lyons, M. E. G.; Duesberg, G. S.; Coleman, J. N. Comparison of Liquid Exfoliated Transition Metal Dichalcogenides Reveals MoSe₂ to Be the Most Effective Hydrogen Evolution Catalyst. *Nanoscale* **2016**, *8*, 5737–5749.
- (68) McAteer, D.; Gholamvand, Z.; McEvoy, N.; Harvey, A.; O'Malley, E.; Duesberg, G. S.; Coleman, J. N. Thickness Dependence and Percolation Scaling of Hydrogen Production Rate in MoS₂ Nanosheet and Nanosheet–Carbon Nanotube Composite Catalytic Electrodes. *ACS Nano* **2016**, *10*, 672–683.

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