Impact of Covalent Functionalization on the Aqueous Processability, Catalytic Activity and Biocompatibility of Chemically Exfoliated MoS₂ Nanosheets

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Abstract

Chemically exfoliated MoS₂ (ce-MoS₂) has emerged in recent years as an attractive two-dimensional material for use in relevant technological applications, but fully exploiting its potential and versatility will most probably require the deployment of appropriate chemical modification strategies. Here, we demonstrate that extensive covalent functionalization of ce-MoS₂ nanosheets with acetic acid groups (~0.4 groups grafted per MoS₂ unit) based on the organoiodide chemistry brings a number of benefits in terms of their processability and functionality. Specifically, the acetic acid-functionalized nanosheets were furnished with long-term (>6 months) colloidal stability in aqueous medium at relatively high concentrations, exhibited a markedly improved temporal retention of catalytic activity towards the reduction of nitroarenes and could be more effectively coupled with silver nanoparticles to form hybrid nanostructures. Furthermore, in vitro cell proliferation tests carried out with murine fibroblasts suggested that the chemical derivatization had a positive effect on the biocompatibility of ce-MoS₂. A hydrothermal annealing procedure was also implemented to promote the structural conversion of the functionalized nanosheets from the 1T phase that was induced during the chemical exfoliation step to the original 2H phase of the starting bulk material, while retaining at the same time the aqueous colloidal stability afforded by the presence of the acetic acid groups. Overall, by highlighting the benefits of this type of chemical derivatization, the present work should contribute to strengthen the position of ce-MoS₂ as a two-dimensional material of significant practical utility.

Keywords: MoS₂, two-dimensional material, transition metal dichalcogenides (TMDs), colloidal dispersion, functionalization, metal nanoparticles, catalytic reduction.

1. Introduction

Over the last decade, graphene has been the focus of intense research efforts aimed at exploiting the exceptional electronic, mechanical, thermal and optical properties of this two-dimensional (2D) carbon material towards a wide variety of different technological applications.¹ Such an interest has progressively broadened in recent years to include other 2D materials, as it has become increasingly apparent that many of them boast their own share of attractive and frequently unusual physical properties that are distinct from those of their bulk counterparts and complementary to those of graphene.^{1,2} At present, one of the most actively investigated 2D materials beyond graphene is arguably MoS₂, which belongs to the larger family of layered transition metal dichalcogenides (TMDs).^{3,4} As recent work has demonstrated, single- and few-layer sheets of MoS₂ and other TMDs are very promising platforms for use in, e.g., electronic and optoelectronic devices,⁵ catalysis,⁶ energy conversion and storage,⁷ molecular sensing⁸ or biomedicine.⁹

Similar to the case of other 2D materials, it is generally accepted that the successful implementation of atomically thin MoS₂ in real-life applications will first and foremost depend on the availability of efficient techniques for its production in large quantities. In this regard, three main approaches that show promise towards the mass production of 2D MoS₂ can be currently identified: (1) chemical vapor deposition (CVD) from molybdenum and sulfur precursor species onto appropriate substrates,¹⁰ (2) direct liquid-phase exfoliation of bulk MoS₂ assisted by ultrasound or shear forces,^{11,12} and (3) chemical exfoliation based on the intercalation of alkali metals (typically Li) into the bulk parent solid.^{13–15} Although bottom-up CVD methods appear ideally suited to attain high quality, large-area wafers of single-/few-layer MoS₂ for use in high-end electronic

or photonic applications, top-down exfoliation strategies are probably a better option when large amounts of solution-processable 2D flakes are sought after. Indeed, direct exfoliation of bulk MoS₂ powder in proper organic solvents (e.g., *N*-methyl-2-pyrrolidone) or water/surfactant solutions is known to afford stable colloidal dispersions of 2D flakes.¹² Such dispersions can then be made into useful macroscopic materials, such as thin films, coatings or composites, by straightforward processing techniques (vacuum filtration, spray-coating, solution blending, etc). However, this exfoliation approach suffers from some significant drawbacks, most notably a low exfoliation yield (< 5 wt%) and a population of exfoliated objects dominated by few- and several-layer MoS₂ flakes rather than single-layer ones.¹⁶

By contrast, chemical exfoliation based on Li intercalation has been reported to afford almost fully delaminated products, both in terms of yield (> 90 wt%) and flake thickness (mostly monolayers).¹⁷ Intercalation is typically carried out by reaction of bulk MoS₂ with an organolithium reagent (e.g., *n*-butyllithium) or by electrochemical means, which involve electron transfer to the host MoS₂ lattice.^{13,18} Such a reduction process facilitates the subsequent exfoliation of the intercalated product (Li_xMoS₂) in aqueous medium as well as the colloidal stabilization of the resulting negatively charged, chemically exfoliated MoS₂ (ce-MoS₂) nanosheets, but also triggers a conversion of the MoS₂ structure from the original semiconducting 2H phase to the metallic 1T phase.¹⁷ Albeit this semiconducting-to-metallic phase transition can be detrimental in some cases (e.g., in electronic devices), recent work has demonstrated that 1T-phase ce-MoS₂ outperforms its 2H-phase counterpart when used, for example, as a catalyst and/or co-catalyst in the electrochemical and photocatalytic production of hydrogen^{19,20} as well as in aqueous-phase organic reduction reactions,²¹ or as an

electrode material for supercapacitors.²² The utility of ce-MoS₂ in biomedicine²³ and sensing²⁴ has also been demonstrated.

While the potential of ce-MoS₂ as a valuable material towards different applications is now well established, its actual implementation faces several hurdles that require consideration. These hurdles, which mainly concern the processing and manipulation of the exfoliated nanosheets but have ramifications in different areas of interest, include the following. (1) Although Li-intercalated MoS₂ can be exfoliated and dispersed in water, the resulting colloidal dispersions lack long-term stability (< 1 month),²⁵ which seriously limits their utility as, e.g., aqueous-phase catalytic systems. (2) Conversion of 1T-phase ce-MoS₂ back to the 2H phase directly in water (to give stable aqueous dispersions of 2H-phase nanosheets) would be highly desirable for their broader applicability, but no way to do such a conversion has yet been reported. 1T-to-2H conversion has only been demonstrated for thin ce-MoS₂ films on appropriate substrates¹³ or, very recently, for ce-MoS₂ dispersions in high boiling point organic solvents.²⁶ (3) Combining ce-MoS₂ nanosheets with metallic or semiconducting nanoparticles (NPs) to yield functional hybrids is attractive for a number of applications, but generally difficult to achieve in practice due to the lack of proper chemical handles in the nanosheet surface.²⁷ (4) ce-MoS₂ nanosheets are attractive platforms for use in biomedical applications, but studies on their biocompatibility as well as on strategies to boost it have received little attention.²⁸

We hypothesize that functionalization of ce-MoS₂ with proper chemical groups could provide a unified solution to the abovementioned issues. Over the last few years, a number of functionalization schemes have been explored for both ce-MoS₂ and single-/few-layer MoS₂ obtained by other means.^{29,30} Among these, conjugation with thiols relying on the presence of structural defects in the MoS₂ lattice (mainly sulfur

vacancies) has been by far the most extensively investigated approach.^{25,27,31} Indeed, such a type of derivatization has been used to partially tackle some, though not all, of these issues.^{25,27} Very recently, covalent functionalization of ce-MoS₂ with organic groups through reaction with certain electrophiles (organoiodides³² and aryldiazonium salts)³³ has been reported. Derivatization with organoiodides, in particular, has been shown to afford very high degrees of functionalization (~0.3 organic groups grafted per MoS₂ unit), making it an especially attractive strategy for tuning the surface characteristics and, consequently, many of the properties of ce-MoS₂. However, the potential of covalent functionalization as a means to address the limitations of ce-MoS₂ towards practical uses remains mostly unexplored.

We report here an investigation on the derivatization of ce-MoS₂ nanosheets with iodoacetic acid. Significantly, an extensive degree of functionalization could be attained (~0.4 acetic acid groups grafted per MoS₂ unit), which afforded a radical change in the long-term aqueous dispersibility of the nanosheets (stable dispersions for more than 6 months were attained) as well as a significantly extended shelf-life of the nanosheet dispersions when used as a catalyst for reduction reactions in water. Furthermore, a hydrothermal method for the conversion of the functionalized, 1T-phase ce-MoS₂ to 2H-phase ce-MoS₂ while retaining the long-term colloidal stability of the nanosheets was implemented, which was previously not possible. Finally, the covalent functionalization of ce-MoS₂ with acetic acid was also seen to be beneficial for the nucleation and growth of Ag NPs onto the nanosheets to form hybrid structures and in enhancing the biocompatibility of the as-prepared nanosheets, as evaluated from cell proliferation studies using murine fibroblasts. Taken together, the present results highlight the benefits of this type of derivatization in improving the processability and functionality of ce-MoS₂ towards a number of uses.

2. Results and discussion

2.1. Covalent functionalization of *ce*-MoS₂ nanosheets with acetic acid groups

Lithium intercalation of bulk MoS₂ powder based on reaction with *n*-butyllithium and subsequent ultrasound-induced exfoliation of the intercalated product (Li_xMoS₂) in water is well-known to afford colloidal dispersions of *ce*-MoS₂ nanosheets, which are mostly single-layered objects.^{13,17} Although the starting bulk MoS₂ material exhibits the thermodynamically stable, semiconducting 2H phase (trigonal prismatic coordination), charge transfer from the lithium intercalates to the host MoS₂ lattice triggers an extensive (although incomplete) structural transformation in Li_xMoS₂ to the metastable, metallic 1T phase (octahedral coordination) that is carried forward to the *ce*-MoS₂ nanosheets dispersed in aqueous medium.¹⁷ The excess electron charges present in the nanosheets are also thought to be responsible for their dispersibility in aqueous medium. However, this colloidal stability is generally rather limited, in particular when working at moderately high *ce*-MoS₂ nanosheet concentrations. For example, aqueous dispersions at a concentration of ~0.8 mg mL⁻¹ are seen to precipitate in a matter of just 3 weeks (Supporting Information, Fig. S1), whereas strong agglomeration is already observed after 1 month for ~0.1 mg mL⁻¹ suspensions. Precipitation of the *ce*-MoS₂ nanosheets is an irreversible process, as the sedimented material cannot be successfully re-dispersed even after sonication for several hours. Such a behavior is likely due to the slow reaction of water molecules with the excess electrons,³⁴ but in any case it is clearly detrimental to the manipulation and use of *ce*-MoS₂ towards different applications. We envisaged that covalent derivatization of the nanosheets with proper organoiodides could be a particularly efficient way to overcome this issue, taking into account the extensive degree of functionalization that has been previously achieved using this

particular approach for MoS₂ and other TMDs.³² Organoiodides having ionic or ionizable moieties should be well suited for the intended purpose, as the net charge associated to the covalently grafted groups would be expected to provide the nanosheets with enhanced and enduring colloidal stability. To test this hypothesis, we selected iodoacetic acid and iodomethanesulfonic acid, which possess, respectively, a pH-dependent carboxylate anion and a permanent sulfonate anion.

Addition of iodoacetic acid to a mildly acidic ce-MoS₂ dispersion in water was seen to induce a slight coagulation of the nanosheets within several hours. After being allowed to react for a total of 5 days and thoroughly washed, the nanosheets could be readily re-dispersed in neutral and basic aqueous medium (see Experimental section for details). Evidence for their successful functionalization with acetic acid groups was obtained using a suite of characterization techniques. Fig. 1a (black trace) shows the UV-vis absorption spectrum of the starting, non-functionalized ce-MoS₂ dispersion. Unlike the case of MoS₂ flakes produced by direct exfoliation of the bulk powder, the structure of which is dominated by the semiconducting 2H polymorph,^{11,35} no excitonic peaks in the 400-500 and 600-700 nm wavelength ranges were observed for ce-MoS₂. Instead, two absorption bands at ~255 and 300 nm, together with essentially featureless absorbance above 300 nm, were noticed. Such attributes are characteristic of MoS₂ with a predominance of metallic 1T phase, as expected for the as-prepared ce-MoS₂ nanosheets.¹³ The two mentioned bands, which are largely absent from 2H-phase MoS₂ flakes, can be ascribed to plasmon resonances associated to the metallic state of ce-MoS₂.³⁶ By contrast, these plasmon bands tended to disappear after treating the nanosheets with iodoacetic acid, whereas the rest of the spectrum remained essentially unaltered except for the emergence of a shoulder-like feature at about 400 nm (Fig. 1a, green trace). Such a result was indicative of changes to the electronic structure of the

nanosheets, which in turn would be consistent with derivatization having taken place. Furthermore, recent experimental and theoretical work has suggested that the originally metallic nature of the as-prepared ce-MoS₂ nanosheets becomes semiconducting upon their covalent functionalization with different chemical groups, even though the 1T phase is retained in the process.^{32,37} Thus, if the iodoacetic acid treatment was successful towards the covalent modification of ce-MoS₂, its associated plasmon resonances would be expected to disappear as a result of the loss of metallic character, and this is exactly what the absorption spectrum of the treated nanosheets indicated (Fig. 1a).

Figure 1. Spectroscopic characterization of the starting, non-functionalized ce-MoS₂ dispersion, (black trace), and the same material after treatment with iodoacetic acid (green trace), and annealing at 160 °C (red trace): (a) UV-vis absorption spectra, high resolution XPS (b) Mo 3d (and S2s, blue dotted line), (c) S 2p, (d) C1s core level spectra, and (e) ATR-FTIR spectra. Mo3d and S2p XPS core level doublet bands are deconvoluted into two components assigned to the 2H (dotted line) and 1T phases (dashed line). In the S2p core level spectra of the treated samples, an additional doublet component at binding energies of ~163–164 eV (solid violet trace) is assigned to C–S covalent bonds. Dotted lines have been added to the ATR–FTIR spectra to assist in the identification of the main peaks.

Further indication of derivatization of the nanosheets with acetic acid groups was obtained by X-ray photoelectron spectroscopy (XPS). Fig. 1b (top plot) shows the high resolution Mo 3d core level spectrum for the starting ce-MoS₂ material. A doublet band corresponding to the 3d_{3/2} (located at ~232 eV) and 3d_{5/2} (~229 eV) levels of Mo⁴⁺ was observed (the weak feature at ~226.5 eV arises from the S 2s level). Following prior work on ce-MoS₂,^{13,32} each peak from this doublet band could be fitted to two components that could be associated to the 2H and 1T phases, namely, the components located at ~232.6 and 229.4 eV (dotted traces) arose from Mo atoms in the 2H phase, whereas the components at about 231.8 and 228.6 eV (dashed traces) corresponded to Mo atoms from the 1T phase (i.e, they were downshifted ~0.8 eV relative to their 2H counterparts). Such a peak-fitting allowed quantification of the percentage of each phase present in the nanosheets, revealing that the 1T polymorph was predominant (~73% 1T phase, ~27% 2H phase). This phase composition was comparable (slightly higher) to that previously reported for ce-MoS₂.³² Following treatment of the nanosheets with iodocacetic acid, the Mo 3d core level spectrum did not experience very significant changes (Fig. 1b, middle plot), which would be consistent with the idea that organoiodide functionalization takes place through sulfur but not molybdenum atoms of ce-MoS₂.³² However, a slight but clear increase in the fraction of 1T phase (up to about 79%) was noticed. We interpret this increase to be a consequence of functionalization. It has been recently reported on the basis of theoretical calculations that covalent grafting of MoS₂ with a number of chemical groups (such as -H and -CH₃) through its sulfur atoms induces stabilization of the originally metastable 1T phase, so that above a certain threshold coverage of grafted groups (estimated to be ~20% of the sulfur atoms) this phase becomes the thermodynamically stable one.³⁷ It is therefore not unreasonable to

assume that grafting of acetic acid groups triggered a partial conversion of the 2H phase remaining in the ce-MoS₂ nanosheets to the stabilized 1T polymorph.

More direct evidence of the covalent bonding of acetic acid groups to the ce-MoS₂ nanosheets was gathered from the high resolution S 2p core level spectra of the samples. The S 2p band is also a doublet, with peaks located at ~162 (2p_{1/2}) and ~163 (2p_{3/2}) eV for 2H-phase MoS₂ that are again downshifted by ~0.8 eV in the case of 1T-phase MoS₂.^{13,32} As expected, the S 2p spectrum of as-prepared, non-functionalized ce-MoS₂ (Fig. 1c, top plot) could be fitted to four components that can be associated to both the 2H and 1T polymorphs, but with a prevalence of the latter. (For simplicity, the two components of each phase in Fig. 1c are shown as a single line: dotted line for 2H, dashed line for 1T). After treatment with iodoacetic acid, the shape of the S 2p band underwent some noticeable changes (Fig. 1c, middle plot), so that in addition to the 1T- and 2H-related components, a new doublet component appeared at binding energies of ~163-164 eV (solid violet trace). Such additional doublet component can be ascribed to sulfur atoms covalently bonded to carbon,³² thus constituting direct indication of the grafting of acetic acid groups to the nanosheets. The presence of this chemical group was also made apparent from the C 1s region of the XPS spectra (Fig. 1d). For non-functionalized ce-MoS₂ (top plot), a relatively broad band centered at ~285 eV was observed. This a priori unexpected feature can be assigned to the adventitious carbon (hydrocarbon contamination) that so pervasively comes to light when samples are investigated by XPS.³⁸ By contrast, for iodoacetic acid-treated ce-MoS₂ a further component at about 288.4 eV was clearly noticed (Fig. 1d, middle plot), which could be attributed to carbon atoms in carboxylic acids, therefore substantiating the idea that acetic acid groups were incorporated to the ce-MoS₂ nanosheets. Furthermore, Fig. 1e (top plot) shows the ATR-FTIR spectrum of iodoacetic acid-treated ce-MoS₂, which

exhibited additional indication of successful functionalization. Specifically, the following features were observed: (1) a sharp peak located at $\sim 655\text{ cm}^{-1}$, ascribed to S–C stretching vibrations arising from acetic acid groups grafted onto the nanosheets via sulfur atoms), (2) a peak at $\sim 1170\text{ cm}^{-1}$, attributed to $\text{CH}_2\text{-S}$ wagging, (3) a peak at $\sim 1420\text{ cm}^{-1}$, attributed to symmetric C=O stretching of acetate groups, and to a combination of C–O stretch. and O–H deformation vibrations from the carboxylic acid group of acetic acid, (4) a peak at $\sim 1600\text{ cm}^{-1}$ assigned to asymmetric stretching for C=O bonds in acetate groups together with a shoulder on its high wavenumber side ($\sim 1680\text{ cm}^{-1}$) corresponding to C=O stretch. for H–bonded COOH groups, and (5) an intense and broad band ($2750\text{--}3400\text{ cm}^{-1}$), which can be associated to O–H stretching vibrations from H–bonded carboxylic acid groups. Thus, the ATR–FTIR spectrum of the iodoacetic acid-treated ce-MoS₂ in the solid phase indicates the presence of both acetate salts and H–bonded COOH groups. Moreover, derivatization with acetic acid groups was not seen to induce significant changes to the morphology of the ce-MoS₂ nanosheets, as evidenced from both transmission electron microscopy (TEM; Fig. 2a and c) and atomic force microscopy (AFM; Fig. 2b and d) imaging. The non-functionalized sample (Fig. 2a and b) was comprised of lamellar objects with typical lateral sizes in the 50–500 nm range and apparent thickness of $\sim 1\text{--}2\text{ nm}$, indicating that they were mainly single-layer ce-MoS₂ nanosheets.^{17,21} The acetic acid-functionalized material was 1–2 nm thicker (Fig. 2c and d), which is consistent with the presence of carboxylic acids on both sides of the nanosheets adding to their thickness.

Figure 2. TEM (a,b) and AFM (c,d) images of the starting non-functionalized material (a,c) and the acetic acid-functionalized material (b,d). (e) Digital photographs of ~ 0.2 mg mL⁻¹ dispersions of non-functionalized ce-MoS₂ (top row) and acetic acid-functionalized ce-MoS₂ (bottom row) (left column: just prepared; middle column: after 4 weeks; right column: after 4 months).

We note that iodoacetic acid could not have simply adsorbed on the ce-MoS₂ nanosheets, but instead must have reacted to form covalent bonding with this material. If the former situation had taken place, we would expect to observe the presence of iodine in the XPS survey spectrum (i.e., the I 3d_{5/2} band at ~ 621 eV), feature which is not found (see Supporting Information, Fig. S2b), as well as a component in the C 1s

region of the spectrum associated to C–I bonds (spectrum not shown). However, none of these features were noticed, but only the emergence of a component consistent with S–C bonds in the S 2p spectra (Fig. 1c). The XPS data were also used to estimate the degree of functionalization of the nanosheets. This calculation was done by two different, independent ways: (1) determining the amount of carbon atoms present in carboxylic acid groups relative to the amount of either sulfur or molybdenum atoms in the functionalized samples, taking into account that the number of carboxylic acid carbons equals the number of acetic acid groups, and (2) determining the amount of carbon-bonded sulfur atoms relative to the total amount of sulfur in the sample, using the areas of the peak-fitted components from the S 2p spectra and considering that the number of carbon-bonded sulfur atoms equals the number of grafted acetic acid groups. The values derived from these two methods were seen to be consistent with each other, yielding a functionalization degree for the nanosheets in the range of 0.17-0.20 acetic acid groups per sulfur atom, or equivalently, 0.35-0.40 groups per MoS₂ unit. This extent of derivatization is considerably larger than that reported for other functionalization schemes of ce-MoS₂. For example, covalent grafting of 4-methoxyphenyl groups based on the use of the corresponding diazonium salt has led to a functionalization degree of ~0.2 groups per MoS₂ unit,³³ whereas conjugation with 3-mercaptopropionic acid afforded ~0.1 groups per MoS₂ unit.²⁷ By comparison, the previous report on functionalization of ce-MoS₂ with organoiodides (2-iodoacetamide) attained 0.29 grafted groups per MoS₂ unit.³² Treatment of the ce-MoS₂ material prepared in the present work with 2-iodoacetamide yielded a slightly higher derivatization degree (~0.34). We interpret this difference to arise from the somewhat larger extent of 1T fraction present in our nanosheets (73 vs 65%). Considering that the covalent grafting of chemical groups appears to be energetically very favorable on the

1T phase but very weak on the 2H phase,³⁷ a larger fraction of 1T phase in ce-MoS₂ should be associated to larger numbers of readily available derivatization sites, and consequently to the possibility of higher functionalization degrees.

2.2. Effect of functionalization on the aqueous processability, catalytic activity and use as nanoparticle support of ce-MoS₂

Functionalization with acetic acid groups was seen to drastically improve the dispersibility of the nanosheets in water, particularly in the long term. This point is illustrated in Fig. 2e, which shows digital photographs of dispersions ($\sim 0.2 \text{ mg mL}^{-1}$) of both non-functionalized (left column) and acetic acid-functionalized (right column) ce-MoS₂ following different standing times after their preparation (first row: just prepared; second row: 4 weeks; third row: 4 months). It can be noticed that the non-functionalized nanosheets precipitated in a matter of 4 weeks, whereas their acetic acid-derivatized counterparts remained colloidally stable, forming homogeneous suspensions to the naked eye well beyond 4 months (this was observed also for acetic acid-functionalized dispersions at concentrations up to 0.4 mg mL^{-1}). Such a result can be ascribed to the presence of negatively charged, deprotonated carboxylate moieties associated to the grafted acetic acid groups in the functionalized samples, which are expected to furnish the nanosheets with enhanced colloidal stability through electrostatic repulsion. In particular, we note that full deprotonation of the carboxylic acids can be expected to bestow the functionalized nanosheets with a net negative charge of $\sim 0.35\text{-}0.40e$ per MoS₂ unit. This figure is larger than the estimated value for the excess charge present in as-prepared ce-MoS₂ nanosheets ($\sim 0.15\text{-}0.25e$),³⁴ although the latter should probably depend on the particular extent of 2H-to-1T phase conversion attained for each sample in question, which differs considerably in the literature.^{13,21,32} Nevertheless, extensive

deprotonation of carboxylic acids usually takes place only under basic, neutral and very slightly acidic conditions, but not at lower pH values. In accordance with this, the acetic acid-functionalized nanosheets were seen to be colloidally stable at basic and neutral pH values, whereas they precipitated in acidified media.

In an attempt to make the nanosheets colloidally stable in a wider pH range, we tried to derivatize ce-MoS₂ with iodomethanesulfonic acid instead of iodoacetic acid, as the former organoiodide possesses a more permanent anion (the pK_a value of sulfonic acids is typically around -3). However, analysis of the nanosheets treated with iodomethanesulfonic acid suggested such an attempt to be unsuccessful. For instance, XPS (S 2p region) did not show evidence of the formation of S-C bonds in the nanosheets (spectrum not shown), but rather pointed to the presence of unreacted organoiodide molecules (iodine detected in the survey spectrum; see Supporting Information, Fig. S2a). Furthermore, the colloidal stability of as-prepared ce-MoS₂ was not changed after treatment with iodomethanesulfonic acid, so that dispersions exposed to this reagent also precipitated in 4 weeks. We believe that this functionalization reaction cannot effectively take place due to electrostatic repulsions between the nanosheets and the organoiodide, i.e. the permanent negative charge associated to the sulfonate group prevents the organoiodide from approaching the nanosheets, which are also negatively charged.

The enhanced processability of ce-MoS₂ nanosheets in water after their covalent functionalization with acetic acid groups should have a number of practical benefits. For example, it has been recently demonstrated that ce-MoS₂ is rather efficient as a catalyst in reduction reactions of several organic molecules (including nitroarenes and dyes) carried out in aqueous medium.²¹ We can expect this catalytic activity to be strongly dependent on the number of active sites that are readily available for interaction with the

reaction medium, and thus to be dependent on the degree of agglomeration of the nanosheets. Therefore, non-functionalized ce-MoS₂ should become a much less effective catalyst after a few weeks as a result of its colloidal instability in water, i.e., the shelf life of this catalyst should be quite limited. On the other hand, although we envisage the catalytic performance of acetic acid-functionalized ce-MoS₂ to be initially lower than that of its non-functionalized counterpart (due to, e.g., steric barriers to reaction associated to the presence of functional groups on the catalytically active 1T domains),²¹ the increased colloidal stability of the former should lead to a less pronounced decline in activity with time. It would thus be conceivable that the functionalized nanosheets exhibit a better catalytic performance in the long run compared to the non-functionalized nanosheets. To test this hypothesis, we compared the reduction of two nitroarenes, namely the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) and the reduction of 4-nitroaniline (4-NA) to *p*-phenylenediamine (*p*-PDA), in aqueous medium at room temperature using sodium borohydride as a reductant. In addition to their practical relevance, e.g., as key steps in the synthesis of certain drugs and polymers, these reduction reactions are frequently used to benchmark the activity of different catalytic systems.³⁹ As detailed in the Experimental section and thoroughly discussed elsewhere,^{21,40} both reactions can be readily followed using UV-vis absorption spectroscopy. For the present studies, because some ce-MoS₂ dispersions (specifically, non-functionalized ones) could be found in a precipitated state, we routinely sonicated all the aqueous samples for a few minutes to temporarily re-suspend the catalytic material and be able to perform the catalytic measurements.

Fig. 3 compares the catalytic activity (determined as number of moles of substrate converted per hour per mole of MoS₂ used) of non-functionalized and acetic acid-functionalized ce-MoS₂ in the reduction of 4-NP (a) and 4-NA (b) measured

immediately, one month and three months after preparation of the nanosheets. From these results, several points can be noticed. First, the catalytic activity of the nanosheets (either functionalized or non-functionalized) tended to be lower towards reduction of 4-NP compared to 4-NA. This outcome is probably related to the fact that under the basic pH of the reaction medium, electrostatic repulsions between the deprotonated 4-NP molecules (4-nitrophenoxide anions)⁴⁰ and the negatively charged nanosheets hinders the approach of the substrate to the active sites on the catalyst. By contrast, such electrostatic barriers are expected to be absent in the case of 4-NA because this substrate lacks a net charge. Second, as expected, the catalytic activity of acetic acid-functionalized ce-MoS₂ immediately after its preparation was lower than that of its non-functionalized counterpart for both 4-NP and 4-NA reduction. However, in relative terms the difference between non-functionalized and functionalized nanosheets was much more significant for the former reaction (~70% reduction in catalytic activity for 4-NP compared to ~30% for 4-NA). Again, electrostatic effects can be invoked to rationalize this result. The catalytically active sites of ce-MoS₂ are thought to be mostly located on its 1T domains,²¹ but such domains have been very extensively grafted with negatively charged acetate groups (~0.45-0.50 groups per MoS₂ unit from the 1T phase according to the data given above and assuming that only this phase can be covalently grafted with chemical moieties).³⁷ For the electrically neutral 4-NA molecules, the acetate groups would just constitute a steric barrier in their path to the catalytic sites on the nanosheets, but for the deprotonated 4-NP molecules both steric and electrostatic barriers would be expected to be in place at the very location of the active sites, leading to a larger degree of reduction in catalytic activity.

Figure 3. Catalytic activity (determined as number of moles of substrate converted per hour per mole of MoS₂ used) of non-functionalized (black squares) and acetic acid-functionalized (green circles) ce-MoS₂ in the reduction of 4-NP (a) and 4-NA (b) measured immediately, one month and three months after preparation of the nanosheets.

Concerning the time evolution of catalytic activities in Fig. 3, we note that the efficiency of both non-functionalized and acetic acid-functionalized ce-MoS₂ decreased markedly in tests carried out one and three months after their preparation, but the extent of such a decline was seen to be much larger with the former material. For instance, non-functionalized ce-MoS₂ retained just ~6% (4%) of its original catalytic activity in the reduction of 4-NP (4-NA) after three months, whereas the corresponding values for acetic acid-functionalized ce-MoS₂ were ~23% (4-NP) and 29% (4-NA). The origin of the decreased activity for the functionalized nanosheets is currently not understood, as it is apparently not related to colloidal stability issues (no precipitated material was visible to the naked eye after three months), so an in-depth analysis of their partial deactivation is warranted in future studies. In any case, the long-term catalytic activities of functionalized ce-MoS₂ turned out to be either similar (for 4-NP reduction) or much higher (4-NA) than those of its non-functionalized correlative, suggesting the former to be a more convenient catalyst for extended use. Furthermore, as can be noticed from

Table 1, even such decreased, long-term activities were competitive with those reported in the literature in recent years for a considerable number of catalytic systems. For example, the catalytic activity of acetic acid-functionalized ce-MoS₂ towards 4-NP reduction after three months ($\sim 2 \text{ h}^{-1}$) lay in the lower range of values typically documented for catalysts based on expensive noble metal (e.g., Pt or Pd) NPs,^{41–46} whereas it was similar to or somewhat higher than that of non-noble metal (e.g., Cu) NP-based catalysts^{47–50} but much higher than that of novel metal-free catalysts based on heteroatom-containing carbon materials, such as nitrogen-doped reduced graphene oxide.^{51–55} In the case of 4-NA reduction, the long-term catalytic activity of the functionalized nanosheets (27.6 h^{-1}) was comparable to the values typically reported with noble metal NP-based catalysts^{56–62} and much higher than that of nitrogen-doped reduced graphene oxide²¹ (data for catalysts based exclusively on non-noble metal NPs are not available for this reaction in the literature).

Table 1. Comparison of the catalytic activity (defined as number of moles of substrate converted per hour per mole of catalyst used) of non-functionalized and acetic acid-functionalized ce-MoS₂ three months after their preparation with that of other catalysts towards the reduction of 4-NP and 4-NA.

Catalytic system	Catalytic activity (h ⁻¹)	Ref.
Reduction of 4-NP		
Non-functionalized ce-MoS ₂ (3 months)	1.8	Present work
Acetic acid-functionalized ce-MoS ₂ (3 months)	2	Present work
Pt NPs on graphene oxide/PVA/Fe ₃ O ₄ composite gel	3	41
PtPd ₃ bimetallic NPs	1.8	42
Porous Pd nanoclusters	0.3	43
Dendritic Pd NPs	6	44
Ir NPs	2.4	45
Au NPs supported on poly(ε-caprolactone) nanofibers	0.6	46
Cu NPs supported onto carbon microspheres	0.2	47
Cu and Sn sponges/dendrites	1.2-1.8	48
Cu ₂ O octahedrons supported on BN nanosheets	0.7	49
Ni NPs supported on MOF-derived mesoporous carbon	0.25	50
N-doped reduced graphene oxide	0.06	51
Hydrothermally reduced graphene oxide	0.05	52
Vitamin C-reduced graphene oxide	0.002	53
N-doped porous carbons derived from different MOFs	0.05-0.25	54,55
Reduction of 4-NA		
Non-functionalized ce-MoS ₂ (3 months)	5.4	Present work
Acetic acid-functionalized ce-MoS ₂ (3 months)	27.6	Present work
N-doped reduced graphene oxide	0.08	21
Pt NPs supported on graphene aerogel	48	56
Bimetallic Pt-Ni NPs	18	57
NiFe ₂ O ₄ -Pd NP hybrid	180	58
Polyaniline/Fe ₃ O ₄ /Pd NP hybrid	15	59

Pd NPs supported on reduced graphene oxide	25	60
Polyhedral Au NPs	1-6	61
Hollow Ag nanospheres	6	62

The abundant presence of covalently grafted acetate groups on ce-MoS₂ can also be beneficial towards the production of hybrids with metallic or semiconducting NPs, because the carboxylate moieties can act as effective anchoring sites that favor the nucleation and/or attachment of such NPs onto the nanosheets.²⁷ As a preliminary test of this possibility, we tried to synthesize Ag NPs on both non-functionalized and acetic acid-functionalized ce-MoS₂ by reduction of a metal salt (silver nitrate) with sodium borohydride in an aqueous dispersion of the corresponding nanosheets. We note that Ag⁺ ions can be directly reduced to Ag NPs in the presence of as-prepared ce-MoS₂ without the need of a reducing agent, presumably due to the transfer of the excess electrons that are present in the nanosheets. However, very recent work has demonstrated that this approach triggers the over-oxidation and finally disintegration of the nanosheets in a matter of hours.⁶³ To avoid this outcome, we included the reductant sodium borohydride in our synthetic procedure. Upon mixing the reactants in the presence of the non-functionalized ce-MoS₂ nanosheets, the solution immediately turned dark green, indicative of the formation of Ag NPs. Nonetheless, TEM inspection of the products (Fig. 4a) revealed that very few NPs were actually resting on the nanosheets, whereas stand-alone NPs were frequently observed. By contrast, large numbers of NPs (~10–15 nm in diameter) were seen to be decorating the acetic acid-functionalized nanosheets (Fig. 4b), implying a stronger interaction between the two components in this case. This result suggests the functionalized material to be a superior substrate for the synthesis of hybrids based on ce-MoS₂.

Figure 4. TEM images of hybrids of Ag NPs on both non-functionalized (a) and acetic acid-functionalized ce-MoS₂ (b).

2.3. 1T-to-2H phase transformation of acetic acid-functionalized ce-MoS₂ in aqueous colloidal suspension

As demonstrated above, the covalent functionalization of ce-MoS₂ with acetic acid groups promotes the aqueous dispersibility of the nanosheets, which in turn can bring several advantages when considering the practical use of this material. Nonetheless, similar to the case of its as-prepared, non-functionalized counterpart, the functionalized ce-MoS₂ material incorporates a majority of 1T phase in its structure. It would be desirable to be able to convert ce-MoS₂ back to its original 2H phase while retaining at the same time a good dispersibility of the nanosheets in aqueous medium. In principle, this phase conversion can be achieved by thermal annealing at moderate temperatures (150–300 °C),¹³ so that for nanosheets in aqueous dispersion a hydrothermal treatment could be a convenient way to induce the 1T-to-2H conversion. In this context, successful phase conversion of ce-MoS₂ stably dispersed in non-polar or low-polarity organic solvents has been recently reported after electrostatic binding of oleylamine to the nanosheets,²⁶ but conversion in water has not yet been achieved. As a matter of fact, we observed that hydrothermal treatment of non-functionalized ce-MoS₂ at relevant temperatures (>100 °C) led to immediate and irreversible precipitation of the

suspensions unless the process was carried out at low nanosheet concentrations (~ 0.05 mg mL⁻¹ and below), and even in the latter case the resulting annealed dispersions tended to precipitate in a matter of several hours to a few days. We note, however, that it was possible to induce conversion of the acetic acid-functionalized ce-MoS₂ nanosheets back to the 2H phase while retaining their aqueous dispersibility to a large degree. To this end, the hydrothermal annealing temperature had to be carefully chosen so as to strike a balance between the extent of phase conversion attained and the degree of defunctionalization that is also associated to the annealing process, the latter being detrimental to the aqueous colloidal stability of the nanosheets.

A suite of hydrothermal annealing experiments revealed a temperature of 160 °C to be appropriate for the intended purpose. As noticed from Fig. 1a (red trace), absorption features in the 400–500 and 600–700 nm wavelength regions, which can be ascribed to excitonic transitions in 2H-phase MoS₂, were seen to emerge after annealing the functionalized dispersions at 160 °C. Furthermore, the high resolution Mo 3d core level spectrum of this sample (Fig. 1b, bottom plot) indicated that an extensive (although incomplete) structural conversion to the 2H phase had occurred (81% 2H phase vs 21% for functionalized but non-annealed ce-MoS₂). Such an extent of phase conversion was comparable to that recently reported in non-polar/low-polarity organic solvents.²⁶ Consistent with the idea that the catalytically active sites in ce-MoS₂ are mostly located on the 1T phase (some non-negligible contribution from the nanosheet edges is also expected to be in place),²¹ the catalytic activity of the hydrothermally annealed nanosheets immediately after their preparation was seen to decrease by a factor of 3 to 5 in the reduction of 4-NP and 4-NA compared to their non-annealed counterpart (results not shown). In parallel to the phase conversion, we observed by XPS a decrease in the amount of acetic acid groups grafted onto the nanosheets, i.e., a less intense S-C

component in the S 2p region (Fig. 1c, bottom plot) as well as a weaker feature at ~288.4 eV related to carboxylic acids in the C 1s region (Fig. 1d, bottom plot). This conclusion was supported by ATR-FTIR spectroscopy (Fig. 1e, bottom plot), as the peak associated to S–C stretching vibrations became clearly less intense compared to that of the non-annealed sample (top plot).

XPS-based quantification of the functionalization degree for the dispersions annealed at 160 °C yielded a value of about 0.16 acetic acid groups grafted per MoS₂ unit. This figure was significantly lower than that estimated for the non-annealed nanosheets (0.35-0.40; see above) but nonetheless comparable to the values reported for non-annealed nanosheets functionalized via thiol conjugation or reaction with aryldiazonium salts (~0.1-0.2).^{27,33} We also note that such a degree of functionalization is consistent with the fraction of 1T phase remaining in the annealed nanosheets (19%). If the covalent attachment of chemical moieties is strongly favored at sulfur atoms from the 1T phase relative to the 2H phase,³⁷ then we would expect the degree of functionalization of the annealed sample not to be higher than 0.19 grafted groups per MoS₂ unit, which was in agreement with the actual data derived from the XPS measurements. In any case, the decreased extent of functionalization associated to the annealed nanosheets was still sufficient to afford their aqueous dispersibility at significant concentrations (e.g., 0.2–0.4 mg mL⁻¹) for reasonable periods of time. Even though the annealed suspensions tended to precipitate before then non-annealed ones, they could be re-dispersed by a simple hand-shaking procedure. We also note that different annealing temperatures either failed to induce a considerable 1T-to-2H phase conversion (<160 °C) or led to colloiddally unstable products that agglomerated immediately due to extensive defunctionalization (>160 °C), so that a temperature of 160 °C constituted a reasonable compromise between these two opposing requirements.

2.4. Biocompatibility of acetic acid-functionalized *ce*-MoS₂

Finally, we carried out a preliminary investigation on the biocompatibility of acetic acid-functionalized *ce*-MoS₂. 2D materials, including MoS₂, are currently the focus of intense research activities towards their prospective application in biomedicine, e.g., as drug carriers in different therapies or as contrast agents in diagnostic imaging.⁹ In the particular case of *ce*-MoS₂ nanosheets, previous work has explored their use as photothermal agents²³ or as drug carriers in combined photothermal, photodynamic and chemotherapy of cancer.⁶⁴ For these and other bio-related applications, it is obvious that the nanosheets need to be highly biocompatible and non-cytotoxic, and so studies on their biological interactions are highly relevant.⁶⁵ Although 2D MoS₂ (including *ce*-MoS₂) nanosheets are generally regarded to exhibit low toxicity towards mammalian cell lines,^{65,66} it is also known that their specific toxicity profile is affected by a number of physicochemical parameters associated to the material, such as its exfoliation degree, aggregation state or electrical conductivity.^{28,66} Similar to the case of graphene,⁶⁷ we also expect the biocompatibility/cytotoxicity of the *ce*-MoS₂ nanosheets to be modulated by their surface chemistry, and therefore to be sensitive to functionalization treatments, but such a point has not yet been investigated. To shed light on this question, we explored and compared the biocompatibility of the different *ce*-MoS₂ materials prepared here towards murine fibroblasts (L929 cell line) on the basis of the MTT assay. The L929 cell line is generally used as a benchmark in the biocompatibility assessment of medical devices.

Fig. 5 summarizes the results of L929 cell proliferation tests carried out on polystyrene culture plates 24 h after having seeded the cells at an initial density of 5500 cells cm⁻², in the presence of different concentrations of *ce*-MoS₂ materials in the

culture medium. For comparison purposes, tests with graphene oxide nanosheets were also performed. At the lowest nanosheet concentration ($10 \mu\text{g mL}^{-1}$), all the ce-MoS₂ materials, i.e. the non-functionalized, acetic acid-functionalized as well as functionalized and 160 °C annealed samples, displayed somewhat reduced cell proliferation values compared with the control test (no nanosheets in the culture medium, 100% proliferation), although the reduction was more significant for the two latter samples. As the nanosheet concentration was progressively increased up to $100 \mu\text{g mL}^{-1}$, cell proliferation values tended to decrease a bit in the presence of non-functionalized ce-MoS₂, whereas they increased slightly for the functionalized and annealed material. By contrast, the functionalized nanosheets (i.e., without annealing) afforded significantly enhanced proliferation. Such a result suggests that the extensive grafting of acetic acid moieties (0.35-0.40 groups per MoS₂ unit in the functionalized material compared to ~ 0.16 after annealing at 160 °C) has a clearly beneficial effect on the biocompatibility of the nanosheets. We also note that the performance of the functionalized material paralleled that of the graphene oxide nanosheets, as both appeared to stimulate substantially the proliferation of L929 cells with increasing concentration of the 2D material. On the other hand, at the highest nanosheet concentration ($150 \mu\text{g mL}^{-1}$), both non-functionalized and functionalized/annealed ce-MoS₂ became remarkably cytotoxic (~ 70 -90% reduction in proliferation compared to the control test), while proliferation in the presence of the functionalized material was also seen to decrease relative to lower concentrations, but nonetheless kept pace with that of the control. This behavior was not observed with graphene oxide, which seemingly induced further cellular proliferation at the concentration of $150 \mu\text{g mL}^{-1}$.

Figure 5. Results of L929 cell proliferation tests, based on the MTT assay, for aqueous dispersions of ce-MoS₂ (black), acetic acid-functionalized ce-MoS₂ (green), hydrothermally treated acetic acid-functionalized ce-MoS₂ (red), and graphene oxide (orange) at different concentrations. The light blue bar corresponds to the blank experiment. Significant statistical differences between the different materials according to the concentration data groups are indicated by the use of the different symbols *, † and •.

Overall, the L929 cell proliferation studies suggested the presence of acetic acid groups on the surface of the functionalized ce-MoS₂ nanosheets, and more specifically their associated carboxylic acid groups, to be a major driver in boosting the biocompatibility of this material. This conclusion would be in line with previous results obtained using other nanostructured materials. For example, comparison between unreduced and reduced forms of graphene oxide, which only differ in the amount of oxygen functional groups (hydroxyl, epoxy, carboxylic) grafted onto the carbon lattice, revealed that the unreduced, heavily functionalized nanosheets were more biocompatible towards L929 cells than their reduced counterparts.⁶⁷ Similarly, functionalization of carbon nanotubes with either carboxylic or sulfonic acid groups was

demonstrated to drastically reduce their in vitro cytotoxicity towards human dermal fibroblasts.⁶⁸ Despite the very different chemical composition and structure of the starting material in question, the present results indicate that covalent functionalization can be an effective strategy to improve the biocompatibility also in the case of ce-MoS₂.

3. Conclusions

In conclusion, the extensive covalent derivatization of chemically exfoliated MoS₂ (ce-MoS₂) nanosheets with acetic acid groups has been made possible based on reaction of the nanosheets with the corresponding organoiodide (i.e., iodoacetic acid). Analysis of the resulting products indicated that a high degree of functionalization can be attained with this approach (0.35-0.40 acetic acid groups grafted per MoS₂ unit). The ensuing presence of a very high density of carboxylic acid groups on the surface of the functionalized ce-MoS₂ nanosheets has demonstrated a number of practical benefits regarding the processing and practical use of this two-dimensional material. More to the point, the functionalized nanosheets exhibited greatly improved long-term (>6 months) colloidal dispersibility in aqueous medium, a much higher temporal retention of catalytic activity towards the reduction of nitroarenes as well as an enhanced ability to anchor silver nanoparticles and form hybrid structures in comparison with their non-functionalized counterpart. Likewise, hydrothermal treatment of the acetic acid-functionalized, 1T-phase ce-MoS₂ material at an appropriate temperature (160 °C) afforded its extensive conversion to the original 2H phase while retaining at the same time a significant aqueous colloidal dispersibility in the phase-reversed nanosheets, which was not previously possible. Functionalization with acetic acid groups was also seen to significantly improve the in vitro biocompatibility of the ce-MoS₂ nanosheets, as evaluated by cell proliferation tests using murine fibroblasts. Finally, we anticipate that

the abundant presence of carboxylic acid moieties on this functionalized material can be exploited, e.g., towards the covalent attachment of biomolecules (DNA, proteins, etc) on the ce-MoS₂ nanosheets through well-developed chemistries, giving rise to hybrid structures with potential utility in biomedicine or biosensing.

4. Experimental

4.1. Materials and reagents

The following chemicals were obtained from Sigma-Aldrich and used as received: MoS₂ powder, *n*-hexane, 1.6 M *n*-butyllithium solution in *n*-hexane, 2-iodoacetamide, iodoacetic acid, iodomethanesulfonic acid, isopropanol, ethanol, silver nitrate, 4-nitrophenol, 4-nitroaniline, sodium borohydride and sodium hydroxide. Cellulose ester dialysis membranes (molecular weight cutoff: 14000 Da) were also acquired from Sigma-Aldrich, whereas alumina membrane filters (pore size: 0.2 µm; diameter: 25 mm) were purchased from Whatman. Milli-Q water (resistivity: 18.2 MΩ cm) was used throughout the studies.

4.2. Preparation of ce-MoS₂ nanosheets

The method originally described by Morrison and co-workers,⁶⁹ based on the intercalation of MoS₂ through reaction with *n*-butyllithium, was used for the preparation of ce-MoS₂ nanosheets. Caution must be exercised in dealing with such a highly pyrophoric reagent such as *n*-butyllithium. Specifically, a solution of *n*-butyllithium in *n*-hexane (1.6 M, 3 mL) was poured into MoS₂ powder (300 mg) in an argon-filled glovebox, and the mixture was left to stand for 48 h at room temperature under static conditions to obtain a lithium-intercalated product (Li_xMoS₂). The latter was then washed with *n*-hexane (60 mL) through filter paper to remove unreacted *n*-butyllithium

as well as residues from its reaction with MoS₂, and immediately dispersed in water under bath sonication (JP Selecta Ultrasons system, frequency: 40 kHz, ultrasound power: 22 W L⁻¹) for 1 h to exfoliate the Li_xMoS₂ powder into individual nanosheets. The resulting aqueous dispersion of ce-MoS₂ nanosheets was purified by dialyzing it against water for 2 days and subsequently stored for further use. The concentration of the as-prepared ce-MoS₂ suspensions was estimated by UV-vis absorption spectroscopy on the basis of the Lambert-Beer law ($A/l = \alpha C$), where, A/l is the absorbance per unit length of optical path, C is the concentration and α is the extinction coefficient. The measurements were carried out at a wavelength of 450 nm, for which the extinction coefficient of ce-MoS₂ had been previously determined ($\alpha_{450} = 5045 \text{ m}^{-1} \text{ g}^{-1} \text{ L}$).²¹

4.3. Covalent functionalization of ce-MoS₂ nanosheets with acetic acid groups

Derivatization of ce-MoS₂ nanosheets with acetic acid groups was accomplished through a slight modification of the general scheme recently developed by Voiry *et al* for functionalization with acetamide and methyl groups, which is based on reaction of the nanosheets with the corresponding electrophilic organoiodides.³² More to the point, iodoacetic acid ($1.1 \times 10^{-3} \text{ mol}$) was added to a mildly acidic (pH~ 4) aqueous dispersion of ce-MoS₂ nanosheets (40 mL, 0.44 mg mL⁻¹), and the mixture was left to stand for 5 days at room temperature. Afterwards, the dispersion was washed consecutively with isopropanol, ethanol and water via repeated cycles of sedimentation via centrifugation (1743g, 30 min) and re-suspension in the corresponding solvent (3 cycles for each solvent). Following completion of this washing procedure, the functionalized nanosheets were obtained in aqueous dispersion, which was dialyzed for 2 days against water to further remove unreacted species. For comparison purposes, treatment of ce-

MoS₂ with either 2-iodoacetamide or iodomethanesulfonic acid instead of iodoacetic acid was also carried out, using the same molar amounts in all cases.

4.4. 1T-to-2H phase conversion of acetic acid-functionalized ce-MoS₂ nanosheets in aqueous dispersion

A hydrothermal treatment was implemented to induce conversion of the acetic acid-functionalized ce-MoS₂ from the 1T phase that was brought about by the lithium intercalation step back to the original 2H phase, while attaining at the same time a long-term colloidal stability in water of the converted nanosheets. Briefly, an aqueous dispersion of acetic acid-functionalized, 1T-phase ce-MoS₂ (20 mL, 0.2 mg mL⁻¹) was first purged with an argon flow (45 mL min⁻¹) for 30 min and then transferred to a Teflon-lined stainless steel autoclave (50 mL in capacity), where it was heated at 160 °C for 4 h. After cooling down to room temperature, the dispersion was collected and its pH was adjusted to ~8 with addition of NH₃ to promote the colloidal stability of the nanosheets.

4.5. Testing of the catalytic activity of non-functionalized and acetic acid-functionalized ce-MoS₂ nanosheets

The catalytic activity of non-functionalized and acetic acid-functionalized ce-MoS₂ was evaluated on the basis of two reduction reactions, namely, the reduction of 4-nitrophenol (4-NP) and 4-nitroaniline (4-NA) to 4-aminophenol (4-AP) and *p*-phenylenediamine (*p*-PDA), respectively, carried out with sodium borohydride as a reducing agent at room temperature. It has been previously shown that as-prepared ce-MoS₂ nanosheets are rather efficient catalysts for both reactions.²¹ To this end, an aqueous mixed solution (2.5 mL) containing either non-functionalized or acetic acid-

functionalized ce-MoS₂ nanosheets (concentration of ce-MoS₂ component: ~0.015 mg mL⁻¹), either 4-NP (0.12 mM) or 4-NA (0.11 mM), as well as sodium borohydride [72 mM (for 4-NP) or 110 mM (for 4-NA)] was prepared and then the reaction progress was monitored through UV-vis absorption spectroscopy by measuring the intensity of the peak located either at ~400 nm (characteristic of 4-NP) or at ~382 nm (characteristic of 4-NA).

4.6. Growth of Ag NPs onto non-functionalized and acetic acid-functionalized ce-MoS₂ nanosheets

The growth of Ag NPs onto ce-MoS₂ nanosheets was carried out in the aqueous phase and was based on the reduction of a metal precursor (silver nitrate) with sodium borohydride in the presence of the nanosheets. Specifically, mixed aqueous solutions containing 0.5 mM silver nitrate, 22.5 mM sodium borohydride and 0.1 mg mL⁻¹ ce-MoS₂ were prepared and left to react undisturbed for 2 h. Subsequently, the reacted product was purified by two cycles of sedimentation through centrifugation (20000 g, 20 min) and re-dispersion in water.

4.7. Biocompatibility testing of ce-MoS₂ materials

Murine fibroblasts (L929 cell line, ECACC 85011425) were chosen to evaluate the biocompatibility of the different ce-MoS₂ materials, as these fibroblasts are highly stable, fast-growing and commonly used in cell culture studies for cytotoxicity assessment. The fibroblasts were seeded at a density of 5500 cells cm⁻² onto 96-well tissue culture polystyrene plates. The culture medium used was Dulbecco's modified Eagle's medium (DMEM) supplemented with 10% fetal bovine serum (FBS), penicillin (100 U mL⁻¹), and streptomycin (100 mg mL⁻¹), and incubation was carried out at 37 °C

in a 5% CO₂ atmosphere. 72 hours after seeding, the culture medium was replaced by fresh medium that also contained a given type of ce-MoS₂ (non-functionalized, acetic acid-functionalized as well as functionalized and hydrothermally treated) at different concentrations: 10, 25, 50, 100 and 150 µg mL⁻¹. For comparison purposes, graphene oxide (obtained from Graphenea) was also assayed at the same concentrations. The cell proliferation tests were carried out 24 h after addition of the MoS₂-containing media by means of the MTT assay (Sigma-Aldrich). This assay is based on the enzymatic reduction of the tetrazolium dye 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) to its water-insoluble formazan derivative.⁷⁰ To this end, the MoS₂-containing culture medium was taken out from each seeded well and then 200 µL of aqueous MTT solution (1 mg mL⁻¹) were added to each well. To exclude interference of the MoS₂ material on the MTT assay, special emphasis was placed on thoroughly removing the MoS₂-containing medium from the wells. After incubation at 37 °C under 5% CO₂ atmosphere for 4 h, the MTT solution was carefully removed, 100 µL of dimethyl sulfoxide were added to solubilize the generated formazan crystals and finally the absorbance of this reaction product was measured with a BMG FLUOstar Galaxy microplate reader (MTX Lab Systems, Inc.) at 570 nm and the reference wavelength of 690 nm. Statistical analysis of the results was performed with the SPSS Statistics software. When data followed the normality and homogeneity of variance requirements, their means were compared by the parametric test ANOVA followed by Bonferroni's post hoc multiple *t*-test. The significance level was set to a *p*-value < 0.05.

4.8. Characterization techniques

The different ce-MoS₂ materials were characterized by UV-vis absorption spectroscopy, X-ray photoelectron spectroscopy (XPS), attenuated total reflection

Fourier transform infrared (ATR-FTIR) spectroscopy, atomic force microscopy (AFM) and transmission electron microscopy (TEM). UV-vis absorption spectra were recorded on a double-beam Helios α spectrophotometer (Thermo Spectronics). XPS was carried out with a SPECS system at a pressure of 10^{-7} Pa with a non-monochromatic Mg K_{α} X-ray source operated at a power of 100 W. The high resolution spectra were taken at pass energy of 10 eV with an energy step of 0.1 eV. The binding energy scale of all spectra was referenced to the maximum of the C1s band for adventitious carbon. ATR-FTIR spectroscopy was accomplished on a Nicolet 8700 spectrometer (Thermo Scientific) with a diamond ATR crystal. Specimens for XPS and ATR-FTIR spectroscopy were prepared in the form of free-standing, paper-like films by vacuum-filtering aqueous dispersions of the corresponding ce-MoS₂ sample (60 mL, 0.1 mg mL⁻¹) through anodic alumina membrane filters. AFM imaging of the ce-MoS₂ nanosheets was performed with a Nanoscope IIIa Multimode apparatus (Veeco Instruments) in the tapping mode of operation, using silicon cantilevers (spring constant ~ 40 N m⁻¹; resonance frequency ~ 250 -300 kHz). To this end, a small volume of a diluted aqueous dispersion of the nanosheets (~ 10 μ L, ~ 0.05 mg mL⁻¹) was drop-cast onto a freshly cleaved mica substrate and allowed to dry under ambient conditions. TEM images were recorded on a JEOL 2000 EX-II microscope operated at 160 kV. In this case, the aqueous ce-MoS₂ dispersion was diluted with an equal volume of ethanol, and then 50 μ L of the resulting suspension were drop-cast onto a copper grid (200 mesh) covered with a continuous amorphous carbon film and allowed to dry under ambient conditions.

Supporting Information. Evidence for the limited colloidal stability of as-prepared aqueous dispersions of ce-MoS₂; survey XPS spectra of ce-MoS₂ treated with iodomethanesulfonic and iodoacetic acid.

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