Supporting Information

Molecular functionalization of 2H-phase MoS$_2$ nanosheets via an electrolytic route for enhanced catalytic performance

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1 Experimental section

1.1 Materials and reagents

Pieces of MoS$_2$ natural crystals (approximate dimensions: ~10×10×0.5 mm$^3$) were obtained from SPI Supplies. Platinum foil (25×25×0.025 mm$^3$) was purchased from Good Fellow. Ethanol was obtained from VWR. H$_2$SO$_4$ 25 %, KCl (>0.005% Br), isopropanol, iodoacetic acid (purity ≥98.0%), NaBH$_4$, 4-iodoaniline (≥98.0%), 4-nitrophenol (4-NP), 2-nitrophenol (2-NP), 4-nitroaniline (4-NA), 2-nitronailine (2-NA), nitrobenzene (NB), methylene blue (MB), and methyl orange (MO) were obtained from Sigma-Aldrich and used as received. Milli-Q deionized water (Millipore Corporation; resistivity: 18.2 MΩ•cm) was employed in all the experiments.

1.2 Electrochemical functionalization

The functionalization of MoS$_2$ was carried out in two consecutive electrochemical steps, both performed in cathodic conditions and in a two-electrode set-up. A ~5×5×0.5 mm$^3$ piece of MoS$_2$ was first cut from the as-received crystal, then cleaved by mechanical exfoliation with scotch tape, which removed the top-most layers of MoS$_2$, leaving a freshly exposed crystal surface. The latter was used as the working electrode and platinum foil as counter electrode, both of them being connected to a DC power supply (Agilent 6614C), using crocodile clips, and fixed at a distance of ~2 cm from each other in the solution. In this configuration, about two-thirds of the MoS$_2$ electrode was immersed in the electrolyte. In the first step, 20 mL of an aqueous 4 M KCl solution was used as the electrolyte and a negative voltage of -20 V was applied to the MoS$_2$ electrode for 30 min, to promote its delamination. Then, functionalization was carried out by substituting the electrolytic medium by 20 mL of iodoacetic acid solution and a negative voltage of -5 V was applied for 1 h. Although different solvents (ethanol, isopropanol, water and supporting electrolytes for iodoacetic acid were tested, the functionalization was considered to be optimal using an aqueous solution of 0.05 M iodoacetic acid and 0.15 M Na$_2$SO$_4$. After the electrochemical treatment, the most expanded part of the cathode, which roughly corresponded to the lower half of the MoS$_2$ piece, was recovered, thoroughly washed with water, dried overnight under reduced pressure at room temperature and finally stored in glass vials for subsequent use.
1.3 Post-processing of the functionalized products: nanosheet extraction and dispersion in water

To obtain individualized MoS$_2$ nanosheets (NSs) from the electrochemically treated material, the latter was first cut into smaller pieces with the aid of a scalpel and then transferred to water at nominal concentration of 2 mg mL$^{-1}$, where it was bath-sonicated (J.P. Selecta Ultrasound system, 40 kHz) for 3 h. After standing undisturbed for 24 h to allow sedimentation of the poorly exfoliated fraction of the material, the upper ~75% of the supernatant volume was collected from the sonicated dispersion and kept for subsequent use.

1.4 Characterization techniques

The material was characterized by UV-vis absorption spectroscopy, zeta-potential measurements, atomic force microscopy (AFM), field-emission scanning electron microscopy (FE-SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, electron paramagnetic resonance (EPR) spectroscopy as well as by measurement of its water contact angle. UV-vis absorption (extinction) spectra were obtained for colloidal dispersions of the exfoliated MoS$_2$ material in a double-beam Helios $\alpha$ spectrophotometer (Thermo Spectronic) using quartz cuvettes with an optical path length of 1 cm. The average lateral size and thickness of the dispersed NSs along with their concentration in the supernatant suspension were estimated by means of UV-vis absorption (extinction) spectroscopy using the metrics developed by Backes et al for this 2D material [1]. Zeta-potential measurements were carried out at a temperature of 25 °C with a Malvern Zetasizer Nano ZSP apparatus from Malvern Instruments Ltd. using ~1 mL of MoS$_2$ dispersion at a concentration of 0.02 mg mL$^{-1}$. AFM measurements were carried out with a Nanoscope IIIa Multimode apparatus (Veeco Instruments) in the tapping mode of operation, using silicon cantilevers with nominal spring constant and resonance frequency of ~40 N m$^{-1}$ and 250–300 kHz, respectively. Samples for AFM were prepared by drop-casting a small volume (~10 µL) of a low-concentration MoS$_2$ NS dispersion in isopropanol (~0.03 mg mL$^{-1}$) onto highly oriented pyrolytic graphite and allowing it to dry under ambient conditions first and then, under vacuum at room temperature. FE-SEM images were recorded on a Quanta FEG
apparatus (FEI Company) operated at 25 kV. Raman spectra were recorded on a Horiba Jobin-Yvon LabRam instrument at a laser excitation wavelength of 532 nm (green line). A low incident laser power (~0.2 mW) was employed to avoid damage to the NSs. XPS was accomplished on a SPECS system, working at a pressure below $10^{-7}$ Pa with a monochromatic Al K$_\alpha$ X-ray source (1486.7 eV) operated at 14.00 kV and 150 W. For Raman spectroscopy, XPS and contact angle measurement, specimens were prepared in the form of thin films by drop-casting MoS$_2$ NS dispersions (in isopropanol, in the case of the nonfunctionalized NSs and in water, in the case of the functionalized ones) onto stainless steel discs, which were allowed to dry at room temperature. ATR-FTIR spectra were registered on a Nicolet 8700 spectrometer (Thermo Scientific) with a diamond ATR crystal. Specimens for ATR-FTIR spectroscopy were prepared in the form of freestanding, paper-like films by vacuum-filtering aqueous dispersions of the functionalized MoS$_2$ material through silver membrane filters. EPR spectra were recorded with a X-Band (9.4 GHz) Bruker ELEXSYS E500 spectrometer using a magnetic field modulation amplitude of 1 G, a modulation frequency of 100 kHz and a microwave power of ~20 mW. Contact angles were measured by dropping 2 µL of water on the films with a pipette and immediately taking images of the droplet with a standard digital camera with an attached macro lens. Analysis of the recorded images with ImageJ software was carried out to determine the value of the contact angle.

1.5 Catalytic tests

For the catalytic tests, aqueous aliquots (2.5 mL) containing MoS$_2$ catalyst at concentration of 7 µg mL$^{-1}$ and the substrate molecule (a nitroarene or an organic dye at a concentration of 0.12 or 0.06 mM, respectively) as well as a large excess of NaBH$_4$ (72–110 mM) were prepared in quartz cuvettes with an optical path length of 1 cm. Immediately after preparation, the cuvettes were transferred to an UV-vis absorption spectrophotometer and the reaction progress was monitored by recording the corresponding kinetic profiles. The latter were obtained by measuring the temporal evolution of absorbance at the wavelength of a characteristic peak of the substrate molecule, namely, at 400, 416, 380, 410, 270, 461 and 675 nm for 4-NP, 2-NP, 4-NA, 2-NA, NB, MB and MO, respectively. To check the performance of the catalyst at higher concentrations of substrate, 1.2 mM and 12 mM 4-NP aqueous solutions were
reduced by NaBH₄ (1.1 M) in the presence of 7 µg mL⁻¹ MoS₂ catalyst. To record the kinetic profiles, the absorbance of the catalytic medium was directly measured, without dilution, monitoring a wavelength different to that of the absorbance maximum (400 nm) to avoid saturation of the signal. Specifically, a wavelength of 455 nm was used for 1.2 mM 4-NP and 479 nm for 12 mM 4-NP. To test the catalyst for the reduction of mixtures of nitroarenes, a binary mixture of 0.12 mM 4-NA and 0.24 mM 2-NA and a ternary mixture of 0.06 mM 4-NP, 0.06 mM 4-NA and 0.12 mM 2-NA were reduced by NaBH₄ in the presence of MoS₂ catalyst at a concentration of 3.5 µg mL⁻¹. The kinetic profiles of the mixtures were followed by monitoring the absorbance at a wavelength of 400 nm. For every kinetic profile, a blank experiment, i. e., a kinetic run were no catalyst was added to the reaction medium, was recorded. To facilitate their recovery and re-use, the functionalized MoS₂ NSs were immobilized onto commercial polyurethane foam. To this end, the foam was first cut into cylinders ~1 cm in diameter and ~1 cm in height and cleaned by bath-sonication during 20 min in ethanol. After drying under vacuum, the polyurethane foam cylinders were soaked into ~10 mg L⁻¹ aqueous MoS₂ dispersion and then dried at room temperature under reduced pressure. To increase the amount of loaded NSs, the soaking/drying process was carried out several times (typically three), after which the original white color of the polyurethane foam turned into an olive green tone. For the catalytic tests, the MoS₂-loaded foam cylinders were immersed into the substrate/NaBH₄ reaction mixture. After reaction completion, the cylinders were removed from the solution, rinsed with water and allowed to dry before being used in the next catalytic cycle.
2 Additional characterization of the functionalized MoS$_2$ material

2.1 Additional XPS spectra of MoS$_2$ nanosheets functionalized with iodoacetic acid

Figure S1. XPS survey spectrum of cathodically functionalized MoS$_2$ nanosheets. The main bands are labeled for clarity. The fact that no signal was detected in the 635–615 eV binding energy range, which is characteristic of the main XPS core level of iodine (I 3d) confirmed that this element was absent from the material.

Figure S2. Background-subtracted, high resolution XPS (a) Mo 3d and (b) S 2p core level spectra of the nonfunctionalized (black trace) and functionalized (green trace) MoS$_2$ nanosheets. The symmetrical shape and position of the 3d$_{5/2}$ and 3d$_{3/2}$ components...
of the Mo 3d doublet band (~229.8 and 233 eV, respectively) and of the 2p\(_{3/2}\) and 2p\(_{1/2}\) components of the S 2p doublet band (~162.7 and 163.9 eV, respectively) was consistent with 2H phase-only materials. A downshift of ~0.8 eV in the position of all these components should be expected for the 1T′ phase.

2.2 Estimation from the degree of functionalization from XPS data

2.2.1 Photoelectron emission cross-section of MoS\(_2\) for electrons from S 2p core level as a function of emission depth

When photo-emitted electrons pass through a layer of material with thickness \(d\), the intensity of the corresponding signal, \(I_0\), is exponentially attenuated according to the following equation, often referred to as the Beer–Lambert law or the straight-line approximation:

\[
I = I_0 \exp\left(-\frac{d}{L \cos \theta}\right)
\]

where \(\theta\) is the angle of emission of the electrons from the surface normal and \(L\) is the attenuation length, which gathers both elastic and inelastic scattering effects. By considering electrons that emerge at \(\theta=90^\circ\) to the sample surface, which was the configuration used for the XPS measurements reported here, the equation simplifies to:

\[
I = I_0 \exp\left(-\frac{d}{L}\right)
\]

Incidentally, the approximate probe depth or information depth (ID) is defined as the sample thickness from which a specified percentage (e.g., 95%) of the detected signal originates. From eq. (2), some 95% of the signal will emanate from a depth lower than 3\(L\) and thus:

\[
ID = 3L
\]

In earlier approaches to estimate \(L\), the inelastic mean free path (\(\lambda\)) was calculated first and then, in a simplistic way, \(L\) was considered to be 10 per cent less than \(\lambda\). [2]:

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More recently, independent universal curves for $\lambda$ [3] and $L$ [4] have been derived, which display the lowest deviations from the experimental data reported to this day amongst the different available equations [including the well-known TPM-2M equation by Tanuma, Powell and Penn [5], which is offered as an option for the calculation of $\lambda$ for inorganic compounds in the NIST electron inelastic mean free path database from predictive formulae [6]]. Specifically, the equation of the universal curve for $L$ is:

$$L = \left(\frac{5.8 + 0.0041Z^{1.7} + 0.088E^{0.93}a^{1.82}}{Z^{0.38}(1-W)}\right)^{0.38}, \tag{5}$$

Apart from the energy of the photo-emitted electrons $E$, the only parameters involved in the calculation of $L$ are the average atomic number $Z$ and the average atomic size $a$ for the corresponding material. In addition, for strongly bonded materials, such as oxides and alkali halides, a small extra term is included for the heat of formation $H$ (where $W=0.06H$). In the case of 2H-MoS$_2$, $H=276.14$ KJ mol$^{-1}$.

The simplest approach to estimate $Z$ for an inorganic compound with chemical formula $G_gH_h$ is to calculate an average $Z$ from the molecular formula as follows:

$$Z = \frac{gZ_g + hZ_h}{g + h} \tag{6}$$

In the case of MoS$_2$, $Z \sim 24.67$ Da.

The atomic size $a$ is deduced from the relation:

$$a^3 = \frac{10^{2+M}}{\rho N_A(g+h)} (nm^3) \tag{7}$$

where $\rho$ is the density in g cm$^{-3}$, $N_A$ is Avogadro’s number, and $g$ and $h$ are the stoichiometric coefficients in the molecular formula $G_gH_h$ of a molecule with molecular mass $M$. In the case of 2H-MoS$_2$, using $M=160.07$ Da and $\rho=5.03$ g cm$^{-3}$ yields $a \sim 0.26$ nm.

The kinetic energy of the electrons photo-emitted from the S 2p core level using an Al K$_\alpha$ X-ray source is 1326.6 eV. Substituting $E$ by the latter value and the aforementioned
values of $H$, $Z$ and $a$ for 2H-MoS$_2$ in the expression for $L$ (eq. 5) yields a value of ~2.1 nm (probe depth of ~6.3 nm by eq. 3). We note that a similar value for $L$ (~2.2 nm) is obtained by first calculating $\lambda$ by the TPM-2M equation (using the values for $M$ and $\rho$ specified above, number of valence electrons of 18 and a band gap of 1.2 eV), and then $L$ through eq. 4.

2.2.2 Contribution of the outermost sulfur atoms to the total sulfur signal

Once $L$ for the S 2p sulfur signal is calculated, eq. 2 can be used to estimate how much the outermost sulfur atoms contribute to the total sulfur signal. As mentioned above, only electrons that emerge at $\theta=90^\circ$ to the sample surface are considered. The surface of the 2H-MoS$_2$ crystal will be constituted by its topmost (0001) basal plane, the Z axis of the crystalline structure being parallel to the photoemission. An ideal 2H-MoS$_2$ crystal shows sulfur planes every 3.186 Å (intra trilayer, i.e., distance between sulfur planes in a S-Mo-S sandwich) and every 2.959 Å (inter trilayer, i.e., distance between sulfur planes of adjacent S-Mo-S sandwiches) along its Z axis. To calculate the contribution of each sulfur plane to the total intensity of photo-emitted S 2p electrons, eq. 2 was used to calculate the percentage of out-coming, nonattenuated signal at the corresponding depth of each plane, except for the topmost sulfur plane, for which no attenuation was considered. The ratio of the contribution of the outer plane to that from all the sulfur planes which contribute to the signal amounts to ~14 %.

2.2.3 C1s core level XPS spectrum of bulk MoS$_2$ crystal functionalized with iodoacetic acid

If we consider, as explained in the main text, that all the acetic groups are grafted to the outermost sulfur atoms, then the ratio of the signal corresponding to COOH (component at ~289 eV in the C 1s core level band depicted in Fig. S3 below these lines) to that corresponding to topmost sulfur plane can be taken as an indication of the extent of functionalization. This yields a value of ~0.10 molecular groups inserted per surface sulfur atom.
Figure S3. Background-subtracted, high resolution XPS C 1s core level spectrum of bulk MoS$_2$ crystal functionalized through cathodic treatment with iodoacetic acid.

2.3 XPS spectra of MoS$_2$ nanosheets functionalized with iodoaniline

Figure S4. MoS$_2$ nanosheets functionalized with iodoaniline (a) Digital photograph of the aqueous dispersion obtained by sonication in water of cathodically expanded MoS$_2$ with a subsequent electrochemical treatment at -5 V with 0.25 M iododoaniline in ethanol. (b) Background-subtracted, normalized high resolution XPS spectra of the nonfunctionalized MoS$_2$ NSs (black trace) and MoS$_2$ functionalized with iodoaniline (red trace) in the binding energy range from 404 to 391.5 eV. In this range, only the main component of the Mo 3p doublet band, Mo 3p$_{3/2}$, which is symmetrical and centered at 395.4 eV, was detected for the nonfunctionalized NSs (black trace). However, the functionalized material displayed two additional bands which correspond to nitrogen in aniline moieties. Specifically, the two N 1s components detected at
~399.4 and ~401.7 eV were assigned to amine in neutral and positively charged form, respectively [7]. (c) I 3d binding energy range for the MoS$_2$ nanosheets functionalized with iodoaniline. The absence of the main band of iodine in the MoS$_2$ NSs treated with iodoaniline that any un-reacted iodoaniline had been effectively removed from the surface by the purification process and thus confirmed that the detected aniline groups were grafted on MoS$_2$ surface, instead of just adsorbed on it.

2.4 Functionalization using a reducing agent as an electron source

![Image](image)

**Figure S5.** (a) Digital photograph and (b) UV-vis extinction spectrum for the dispersion obtained by sonication during 1 h of a cathodically expanded MoS$_2$ crystal in an aqueous solution of 0.25 M iodoacetic acid and 0.25 M sodium borohydride.

2.5 Presence of bismuth in some of the MoS$_2$ materials

It has been recently reported that geological MoS$_2$ crystals, such as the starting material in this work, contain bismuth impurities in concentrations high enough to be detected by XPS [8]. Specifically, the bismuth impurity has been found to appear mainly as the most thermodynamically stable form of bismuth oxide, Bi$_2$O$_3$. In the present work, the presence of micron-size clusters of bismuth in the MoS$_2$ starting material was indeed confirmed by EDX. Correspondingly, bismuth was detected in some of the samples analyzed by XPS. Bi$^{3+}$ 4f$_{5/2}$ spin-orbit component appears in a similar range to that where the S 2p component for S-C bond is expected to appear (~163-164 eV) [9,10]. Thus, special care was taken not to mistake Bi$^{3+}$ 4f$_{5/2}$ for the S-C component in S 2p spectrum, by widening the acquired range for the S 2p spectrum downwards to include Bi$^{3+}$ 4f$_{7/2}$ as well, thus confirming the presence of bismuth.
Figure S6. Background-subtracted, high resolution XPS S 2p and Bi 4f core level spectra for one of the batches where bismuth was detected. As expected for an ideal sulfur signal, the S 2p spin–orbit doublet consists of S 2p$_{3/2}$ (light green trace) and S 2p$_{1/2}$ (dark green trace) components with a 1:2 peak area ratio between and spin-orbit splitting constant of 1.2 eV. The position of the of S 2p$_{3/2}$ and S 2p$_{1/2}$ components of the S 2p doublet band (~163.9 and 162.7 eV, respectively) as well as their full width at half maximum (FWHM) of just 0.7 eV was consistent with a 2H phase-only material. The Bi 4f doublet displayed Bi 4f$_{7/2}$ and Bi 4f$_{5/2}$ components split apart by 5.3 eV and in 3:4 area ratio, as expected, which were centered at binding energy of 164.3 eV and 159.3 eV, respectively, which corresponded to Bi(III).

2.6 Difference C 1s spectrum of functionalized and nonfunctionalized MoS$_2$
**Figure S7.** Difference C 1s XPS spectrum of the functionalized and the nonfunctionalized MoS$_2$ nanosheets (green and black traces in Figure 2g of the main text, respectively).

2.7 **ATR-FTIR spectrum of functionalized MoS$_2$**

The ATR-FTIR spectrum of functionalized MoS$_2$ exhibited some additional indication of functionalization.

![ATR-FTIR spectrum of functionalized MoS$_2$](image)

**Figure S8.** ATR-FTIR spectrum of the functionalized MoS$_2$ NSs.

Specifically, a weak band located at $\sim630$ cm$^{-1}$ can be ascribed to S–C stretching vibrations [9,11] arising from acetic acid groups grafted onto the NSs via sulfur atoms. This band was not very intense even in the case of functionalized 1T-phase MoS$_2$ monolayers, where the degree of derivatization with iodoacetic acid was $\sim20$ percent [10]. Thus, it is expected to be weak for the current materials, where, as explained in the main text, the multi-layered nature of the MoS$_2$ NSs implies that the percentage of (surface) sulfur atoms that are covalently bonded to carbon must be very small.

The sharp absorption peak at $\sim470$ cm$^{-1}$ is due to the A$_{2u}^1$ phonon of 2H-MoS$_2$, which involves asymmetric translation of both Mo and S atoms parallel to the c axis [12]. The bands associated to the acetic group were also observed (range not shown) but they
would be compatible with just adsorption (noncovalent functionalization) of iodoacetic acid.

2.8 EPR spectrum of functionalized MoS$_2$

![EPR spectrum](image)

**Figure S9.** Representative first-derivative X-band EPR spectrum of the functionalized MoS$_2$ NSs. The unsaturated molybdenum atoms in edges and sulfur vacancies give rise to an EPR signal with $g \approx 2$ [13,14].

3 Additional information on the performance of functionalized MoS$_2$ nanosheets as catalysts

3.1 UV-vis spectra of reactants and products
Figure S10. Chemical structure and UV-vis spectra of the reactants and products involved in the different reduction reactions where functionalized MoS$_2$ NSs have been tested as catalyst: (a) 4-NP (brown trace), 4-nitrophenoalte (pink trace) and 4-aminophenol (cyan trace); (b) 2-NP (green trace), 2-nitrophenoalte (red trace) and 2-aminophenol (blue trace); (c) 4-NA (gray trace) and its reduction product, $p$-phenylenediamine (fuchsia trace); (d) 2-NA (navy trace) and its reduction product, $o$-phenylenediamine (dark yellow trace); (e) nitrobenzene (olive trace) and aniline (black trace); (f) MO (orange trace), which is first reduced to the corresponding azo product (not shown) [15], which is followed by -HN-NH- bond dissociation to yield N,N-dimethyl-benzene-1,4-diamine and 4-amino-benzenesulfonate (both shown in violet trace) [16]; (g) MB (cyan trace), MB in the basic medium provided by NaBH$_4$ (blue trace) and its reduction product, leucomethylene blue (purple trace) [17,18]. The wavelength chosen to follow the kinetics of the corresponding reactions, which was in all cases the location of an absorption maximum of the reactant, is indicated for clarity.

3.2 Extinction spectrum of the catalyst

Figure S11. Extinction spectrum of the catalyst at a concentration of 7 mg L$^{-1}$. The extinction value for the catalyst at the wavelengths monitored for the reduction reactions of the different substrates was $\sim$0.6 for all the substrates except for MB, for which it was 0.4 (as expected from the extinction value at $\lambda_{\text{max}}$ $\sim$400 and $\sim$675 nm, respectively).
3.3 Comparison of the catalytic activities of functionalized MoS₂ nanosheets with those reported in the literature for other MoS₂- and non-noble metal-based catalysts

Table S1. Catalytic activity (defined as number of moles of reactant converted per mole of catalyst used per unit time) of the functionalized MoS₂ NSs towards the reduction of 4-nitrophenol compared with that of different types of MoS₂ nanostructures, graphene-derived materials and non-noble metal-based catalysts reported in the literature.

| Catalytic system                                                                 | Catalytic activity (h⁻¹) | Ref. |
|---------------------------------------------------------------------------------|--------------------------|-----|
| Functionalized-2H MoS₂ NSs                                                     | 63                       | Present work |
| S vacancy-decorated, ultrasound-exfoliated 2H MoS₂ NSs                         | 6.6                      | 19  |
| Li-exfoliated 2H-phase MoS₂ NSs                                                | 0.9                      | 20  |
| Li-exfoliated 1T-phase MoS₂ NSs                                                | 44.4                     | 20  |
| Hydrothermally synthesized 2H MoS₂ NSs supported onto Fe₃O₄ particles          | 2.4                      | 21  |
| GMP-stabilized sonicated 2H MoS₂ NSs                                            | 2.6–7.8                  | 22  |
| GMP-stabilized cathodically exfoliated 2H MoS₂ NSs                             | 21.4                     | 23  |
| N-doped RGO foam                                                               | 0.07                     | 24  |
| RGO NSs capped with poly(diallyldimethylammonium chloride)                      | 0.10                     | 25  |
| Hydrothermally synthesized 2H MoS₂ NSs                                          | 5.4                      | 26  |
| Hydrothermally synthesized MoS₂ NSs intercalated in pillared montomorillonite  | 24                       | 26  |
| Hydrothermally synthesized 1T MoS₂ NSs                                          | 21                       | 27  |
| Bi₂Te₃-hydrothermally synthesized 1T MoS₂ heterostructure                      | 67.2–100.8               | 27  |
| Hydrogel network with embedded Co nanoparticles (NPs)                          | 16.2                     | 28  |
| Material Description                                                                 | Value 1 | Value 2 |
|-------------------------------------------------------------------------------------|---------|---------|
| Ni nanoparticles on silica nanotubes                                                | 1.8     | 29      |
| Hybrid Ni nanoparticles/N doping carbon on diatomite                                | 0.85    | 30      |
| Cu NPs on carbon microspheres                                                      | 0.2     | 31      |
| Cu and Sn sponges/dendrites                                                        | 1.2–1.8 | 32      |
| Co particles-decorated carbon microspheres                                          | 0.06–0.24| 33      |
| Co nanocrystals on reduced graphene oxide (RGO)                                     | 0.6     | 34      |
| Ni NPs supported onto carbon black                                                  | 26.4    | 35      |
| Nanostructured zero-valent iron                                                    | 78      | 36      |
| Graphene stabilized CuNi nanocomposite                                             | 12      | 37      |
| MOF-derived Ni based N-doped mesoporous carbon                                     | 2.4     | 38      |
| Co NPs embedded in hierarchically porous N-doped carbon frameworks                 | 18      | 39      |
| Hexagonal Ni plates on RGO                                                          | 0.44    | 40      |
| Hollow porous Cu particles from silica-encapsulated Cu₂O nanoparticle aggregates  | 3       | 41      |
| Co@BN core–shell nanoparticles                                                     | 0.38    | 42      |
| Co NPs embedded into ordered mesoporous carbon                                     | 7.8     | 43      |
| NiO hollow nanospheres                                                             | 4.2     | 44      |
| Ultrafine Cu₂O nanoparticles on cubic mesoporous carbon                            | 9.6     | 45      |
| Cu NPs on oxidized boron nitride                                                   | 27      | 46      |
| Cu NPs immobilized by layered Ti₃C₂ MXene                                         | 51      | 47      |
| Cu and Co NPs doped N-containing carbon frameworks                                 | 63      | 48      |
**Table S2.** Catalytic activity of the functionalized MoS₂ NSs towards the reduction of other nitroarenes and organic dyes compared with that of different types of MoS₂ nanostructures, and non-noble metal-based catalysts reported in the literature.

| Catalytic system                                                                 | Catalytic activity (h⁻¹) | Ref.   |
|---------------------------------------------------------------------------------|--------------------------|--------|
| **2-nitrophenol**                                                               |                          |        |
| Acetic acid-functionalized, cathodically exfoliated 2H MoS₂ NSs                 | 340                      | Present work |
| N/O-doped, hydrothermally synthesized MoS₂ NSs                                  | 0.3                      | 49     |
| Li-exfoliated 1T MoS₂ NS-RGO hybrid paper                                        | 3 (*)                    | 50     |
| NiO NSs                                                                         | 0.2                      | 49     |
| NiMoO₄ NPs                                                                      | 0.3                      | 51     |
| CuFe₂O₄ NPs                                                                     | 133                      | 52     |
| NiFe₂O₄ NPs                                                                     | 17                       | 52     |
| CuO NPs supported on γ-Al₂O₃                                                     | 0.5                      | 53     |
| Carbon black-supported Ni NPs                                                   | 27                       | 54     |
| Fe₂(MoO₄)₃ NPs                                                                  | 7                        | 55     |
| RGO-supported Ni NPs                                                            | 176 (*)                  | 56     |
| Fe@SiO₂-supported Ni NPs                                                        | 60.84                    | 57     |
| Poly(methacrylic acid)-supported Cu NPs                                         | 217                      | 58     |
| **4-nitroaniline**                                                              |                          |        |
| Acetic acid-functionalized, cathodically exfoliated 2H MoS₂ NSs                 | 180                      | Present work |
| S vacancy-decorated, ultrasound-exfoliated 2H MoS₂ NSs                          | 43                       | 19     |
| Li-exfoliated 1T MoS₂ NSs                                                        | 83.4                     | 20     |
| GMP-stabilized, cathodically exfoliated 2H MoS₂ NSs                             | 140                      | 23     |
| Bi₂Te₃-hydrothermally synthesized 1T MoS₂ heterostructure                        | 106.8                    | 27     |
| Li-exfoliated 1T MoS₂ NS-RGO hybrid paper                                       | 6                        | 50     |

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| Material Description | Value | Reference |
|----------------------|-------|-----------|
| Carbon-embedded Cu NPs | 1 | 59 |
| RGO-supported Ni NPs | 0.1 | 60 |
| MnO$_2$ NSs | 0.7 | 61 |
| Fe$_3$O$_4$ NPs | 0.9 | 61 |
| Fe@SiO$_2$-supported Ni NPs | 179.8 | 57 |
| Mesoporous polyaniline-supported Cu NPs | 84 | 62 |
| Pectin-capped Cu NPs | 90 | 63 |
| Poly(methacrylic acid)-supported Cu NPs | 54 | 58 |
| Fe$_3$O$_4$@Cu NPs | 21 | 64 |

**2-nitroaniline**

| Material Description | Value | Reference |
|----------------------|-------|-----------|
| Acetic acid-functionalized, cathodically exfoliated 2H MoS$_2$ NSs | 90 | Present work |
| Li-exfoliated 1T MoS$_2$ NS-RGO hybrid paper | 6 (*) | 50 |
| Bi$_2$O$_2$CO$_3$/CoFe$_2$O$_4$ hybrid nanostructures | 0.1 | 65 |
| DNA-supported Ni NPs | 17 | 66 |
| RGO-supported Ni NPs | 44(*) | 56 |
| Fe@SiO$_2$-supported Ni NPs | 146.7 | 57 |
| Pectin-capped Cu NPs | 22.5 | 63 |

**nitrobenzene**

| Material Description | Value | Reference |
|----------------------|-------|-----------|
| Acetic acid-functionalized, cathodically exfoliated 2H MoS$_2$ NSs | 78 | Present work |
| S vacancy-decorated, ultrasound-exfoliated 2H MoS$_2$ NSs | 11 | 19 |
| Li-exfoliated 1T MoS$_2$ NS-RGO hybrid paper | 7.8 (*) | 50 |
| Bi$_2$Te$_3$-hydrothermally synthesized 1T MoS$_2$ heterostructure | 960 (**) | 27 |
| Ni NP-polyvinylamine/SBA-15 hybrid | 1.3 | 67 |
| Fe$_3$O$_4$/β-alanine-acrylamide-Ni nanocomposite | 770 | 68 |
| DNA-supported Ni NPs | 25 | 66 |
| RGO-supported Ni NPs | 59 (*) | 56 |
| Mesoporous polyaniline-supported Cu NPs | 4.2 | 62 |
methyl orange

| Component                                                                 | Formulation                                | Current work |
|---------------------------------------------------------------------------|---------------------------------------------|--------------|
| Acetic acid-functionalized, cathodically exfoliated 2H MoS₂ NSs            | 71                                          | Present work |
| S vacancy-decorated, ultrasound-exfoliated 2H MoS₂ NSs                    | 24                                          | 19           |
| Li-exfoliated 1T MoS₂ NSs                                                 | 150                                         | 20           |
| Hydrothermally synthesized 2H MoS₂ NSs intercalated in pillared montmorillonite | 13                                          | 69           |
| Poly(methacrylic acid)-supported Cu NPs                                   | 35                                          | 58           |
| Fe₃O₄@Cu NPs                                                             | 10                                          | 64           |
| Fe₃O₄-cellulose-Cu nanocomposite                                          | 0.9                                         | 70           |

methylen blue

| Component                                                                 | Formulation                                | Current work |
|---------------------------------------------------------------------------|---------------------------------------------|--------------|
| Acetic acid-functionalized, cathodically exfoliated 2H MoS₂ NSs            | 44                                          | Present work |
| S vacancy-decorated, ultrasound-exfoliated 2H MoS₂ NSs                    | 16                                          | 19           |
| Fe₃O₄@Cu NPs                                                             | 86                                          | 64           |
| Spherical montmorillonite-supported MoS₂ NSs                              | 70                                          | 71           |
| Solvothermally synthesized, amorphous MoS₂ NPs                            | 0.01                                        | 72           |
| α-MnO₂ nanorods                                                           | 0.2                                         | 73           |
| Cu NPs supported onto Si nanowire array                                   | 66                                          | 74           |

(*) in 1:1 water/methanol solvent.

(***) in methanol solvent

3.4 Reaction mechanism

The mechanism of nitroarene and dye reduction catalyzed by the present functionalized MoS₂ is expected to be the same that we previously proposed for vacancy-decorated 2H-MoS₂ [19], i. e., a mechanism involving the catalytically active sites in the NSs, such as sulfur vacancies and edges, which possess local metallic character. The fact that the functionalization takes place near an active site of the MoS₂ NSs does not promote the deactivation or blocking of the latter. As the acetic moiety is bonded to the NSs via a sulfur atom near a sulfur vacancy, the sulfur vacancy remains “vacant”, and it is thus
preserved and active. In contrast, a usual passivation method would involve filling of the vacancy with a sulfur atom provided by an external source, e.g., through chemical reaction with alkanethiols [75–77]. Indeed, the EPR signal of the functionalized MoS$_2$ NSs (Fig. S9) is indicative of the presence of Mo-S dangling bonds. The presence of the negatively charged acetic moiety near the active site does affect the process in some way, as discussed below and in the main text, but the reaction mechanism remains basically the same.

When nanoparticles (NPs) of certain noble metals such as gold are used as catalysts for the catalytic reduction of nitroarenes with NaBH$_4$, the BH$_4^-$ anion readily oxidizes, injecting electrons to the NPs, which thereby become a reservoir of excess electrons [78]. Upon adsorption of the substrate molecules onto the NPs, the excess electrons trigger their reduction. In such case, the catalytic reaction is insensitive to the pH of the aqueous medium [79]. In contrast, when metallic 1T-MoS$_2$ NSs are used as catalyst for the same type of reaction, the reduction does not occur at pH values above $\sim$11 [80], which is the pH range where the spontaneous hydrolysis of BH$_4^-$ anion becomes arrested [81,82]. This implies that, in the latter case, some product of the hydrolysis of the BH$_4^-$ anion, rather than BH$_4^-$ anion itself, is involved in the reduction reaction. As the active sites in 2H-MoS$_2$ (sulfur vacancies and edges) possess a locally metallic character, the same mechanism proposed for 1T-MoS$_2$ applies for 2H-MoS$_2$, as has been indeed reported before for vacancy-decorated 2H-MoS$_2$ [19].

In basic solution below pH~11 the BH$_4^-$ anion hydrolyzes spontaneously to give molecular hydrogen and BH$_3$OH$^-$ species as reaction products.

$$\text{BH}_4^- + \text{H}_2\text{O} \rightarrow \text{BH}_3\text{OH}^- + \text{H}_2 \quad (1)$$

H$_2$ molecule undergoes dissociative adsorption at sulfur vacancies in MoS$_2$ [83,84]. Although the resulting adsorbed H atoms could in principle react with a nitroarene/dye molecule to trigger its reduction, such a reduction reaction is inhibited by the fast recombination of the adsorbed H atoms into H$_2$ molecules, which is a very favorable process at the catalytic sites of MoS$_2$ (i.e., the Tafel step of hydrogen evolution reaction, HER) [85,86]. Indeed, previously reported control experiments in which a H$_2$ gas flow several orders of magnitude larger than the hydrolysis rate of BH$_4^-$ was passed through a nitroarene solution in the presence of MoS$_2$ NSs showed that no reduction of the substrate took place [20].
In addition to H₂, the spontaneous hydrolysis of NaBH₄ yields the BH₃OH⁻ anion as a rather stable intermediate. In the basic medium of the reaction, the BH₃OH⁻ species is oxidized at a sulfur vacancy site on the MoS₂ surface with the assistance of hydroxide anions, to release the metaborate anion (BO₂⁻), water, hydrogen and electrons [reaction (1) in Fig. S12] [87]:

\[
2\text{BH}_3\text{OH}^- + 6\text{OH}^- \rightarrow \text{BO}_2^- + 4\text{H}_2\text{O} + 3\text{H}_2 + 6\text{e}^- \tag{2}
\]

As previously reported control experiments where NaBH₄ was substituted by NaBO₂ in the reaction medium have shown, the generated BO₂⁻ is inactive as a reductant and thus will not participate in the catalytic reduction [20]. Molecular hydrogen is activated by the released electrons to give a negatively charged hydride (H⁻) [88], which is very unstable, and thus would not form on the surface of defect-free MoS₂, but becomes stabilized when it adsorbs at sulfur vacancies by transferring excess electron charge to their neighboring unsaturated molybdenum atoms [89] [reaction (2)]. The vacancy-anchored, negatively charged hydride should readily trigger the hydrogenation of the nitro group in the nitroarene molecules through the well-known three-step sequence [36,90]; i.e., the nitro group is first converted to the nitroso group [reaction (3)], which is then reduced to a hydroxylamine species [reaction (4)] and finally to the amino group [reaction (5)]. In the case of the dyes, the generation of highly active hydride species at the sulfur vacancy sites by way of reactions (1) and (2) in Fig. S12 would subsequently trigger hydrogenation of the substrate.
**Figure S12. Proposed reaction mechanism for the reduction of 4-NP at the active sites of the MoS\(_2\) nanosheets.** Reaction (1): \(2\text{BH}_3\text{OH}^- + 6\text{OH}^- \rightarrow 2\text{BO}_2^- + 4\text{H}_2\text{O} + 3\text{H}_2 + 6\text{e}^-\)

(2) \(2\text{BH}_3\text{OH}^- + 2\text{e}^- + \text{H}_2 \rightarrow \text{BH}_4^+ + 3\text{H}_2\text{O}\)

(3) \(\text{BH}_4^+ + \text{H}_2\text{O} + \text{HO}-\text{NO} \rightarrow \text{BH}_3\text{OH}^- + \text{H}_2 + 2\text{OH}^- + \text{HO}-\text{NO}^-\)

(4) \(\text{BH}_3\text{OH}^- + 2\text{H}_2\text{O} + \text{HO}-\text{NO} \rightarrow \text{BH}_2\text{OH}^- + \text{H}_2 + 2\text{OH}^- + \text{HO}-\text{NOH}\)

(5) \(\text{BH}_2\text{OH}^- + \text{H}_2\text{O} + \text{HO}-\text{NOH} \rightarrow \text{BH}_2\text{O}^- + \text{H}_2 + 2\text{OH}^- + \text{HO}-\text{N}^\cdot\)

Overall reaction:

\[2\text{BH}_3\text{OH}^- + 6\text{OH}^- \rightarrow 2\text{BO}_2^- + 4\text{H}_2\text{O} + 3\text{H}_2 + 6\text{e}^-\]
As aforementioned, according to the proposed mechanism, the catalytic activity of a MoS$_2$ NS relies on the availability of stable adsorption sites for the H$^-$ species, that is, unsaturated molybdenum atoms in MoS$_2$ edges and sulfur vacancies. Thus, the colloidal stability of the MoS$_2$ catalyst will have a major influence on the catalytic activity, as the adsorption sites for the H$^-$ species in the MoS$_2$ layers will only be available as long as their surface remains exposed to the aqueous medium where catalysis takes place. If the layers aggregate, catalytic activity will consequently decrease. The fact that the current materials perform better as catalysts in aqueous medium than previously reported surfactant-stabilized MoS$_2$ catalysts [19] could be partly related to the different way in which colloidal stabilization affects the catalytic sites in one and the other. In the present case, the covalently attached acetic group which imparts colloidal stability is grafted to a sulfur atom near the sulfur vacancy/edge, and thus the unsaturated molybdenum atoms remain available for adsorption of H$^-$ at any time. However, in the surfactant-assisted stabilization, guanosine monophosphate (GMP) molecules adsorbed on the surface of MoS$_2$ by acid-base interaction between their nucleobase and some of the unsaturated molybdenum sites [22], thus blocking them. Hence, in the latter case, colloidal stability is attained at the expense of catalytic activity although not all catalytic centers will be blocked with GMP and, even those with GMP on, will be temporally available for catalysis as GMP is not irreversibly adsorbed. This was confirmed by the fact that the surfactant-stabilized MoS$_2$ NSs aggregated if many washing cycles were done, as washing led to their progressive removal from the NS surface and thus to a loss of colloidal stability. Thus, GMP will be desorbing and adsorbing from the surface of surfactant-stabilized MoS$_2$ NSs and unsaturated molybdenum sites will be available for catalysis when GMP eventually desorbs. We note that, in the case of the current functionalized MoS$_2$ NSs, the presence of the acetic group near the sulfur vacancy could introduce some steric impediment for the approaching substrate molecules. However, this effect will be minor in the case of diatomic vacancies, which are easily formed and stabilized [91].
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