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Unusual reactivity of MoS₂ nanosheets†

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The reactivity of the 2D nanosheets of MoS₂ with silver ions in solution, leading to their spontaneous morphological and chemical transformations, is reported. This unique reactivity of the nanoscale form of MoS₂ was in stark contrast to its bulk counterpart. While the gradual morphological transformation involving several steps has been captured with an electron microscope, precise chemical identification of the species involved was achieved by electron spectroscopy and mass spectrometry. The energetics of the system investigated supports the observed chemical transformation. The reaction with mercury and gold ions shows similar and dissimilar reaction products, respectively and points to the stability of the metal– sulphur bond in determining the chemical compositions of the final products.

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Introduction

Graphene and its 2D chemical analogues, such as MoS₂, WS₂, MoSe₂, etc., have shown several novel phenomena such as unusual electronic conductivity,¹⁻⁴ charge transport,⁵⁻⁸ hydrogen evolution reactivity (HER),⁹⁻¹² and optoelectric properties,13-17 and it is also used as a material in Li-ion batteries.¹⁸ Composite materials using such components show even more fascinating properties due to efficient charge separation or associated effects during photoexcitation.19-21 Water splitting is more efficient in composites such as ZnO/ MoS₂,^{22,23} CdS/MoS₂,^{24–27} TiO₂/MoS₂,^{28,29} SiC/MoS₂,³⁰ Ag/ MoS_2 ³¹ graphene/MoS₂^{32,33} etc., than in the components. In all of these processes, individual chemical properties of the constituents are utilised and the reaction occurs at the phase boundary. Although individual properties of the sub-system are examined in these processes, the chemical effects become significant at the nanoscale leading to novel chemical reactions and transformations. This has been manifested in alloying between nanoparticles³⁴ as well as cation and anion exchange in quantum dots,^{35,36} both occurring in solution. Atomic substitution in graphene is expected to be energy intensive due to its large binding energy. As a result, incorporation of hetero atoms into graphene from nanoparticles has not been reported. However, for graphene analogues such as MoS₂, the change of either Mo or S is facile due to their

reduced lattice energy.³⁷ This is also facilitated by multiple oxidation states possible for Mo which can act as a redox site, inducing chemical reactivity.

In this paper, we demonstrate the first example of the direct nanoscale reactivity of MoS_2 with silver ions leading to its spontaneous disintegration through a series of steps. These individual events involve reduction of incoming silver ions at MoS_2 nanosheets (MoS_2 NSs) forming Ag NPs combined with oxidation of Mo(rv) to Mo(v1) followed by spontaneous transformation of the Ag NPs forming Ag₂S NPs by capturing S atoms from the NSs. These processes bring about morphological changes of MoS_2 NSs. Molybdenum from MoS_2 NSs ends up in the solution in the form of molybdate ions. Such a reaction suggests the possibility of stabilizing metastable structures as well as the creation of novel phases by size control of the reactants.

Experimental

Chemicals

All the chemicals were commercially available and were used without further purification. Silver nitrate (AgNO₃), hexane and Hg(OAc)₂ were purchased from RANKEM. Molybdenum sulphide (MoS₂) and 1.6 M *n*-butyllithium in hexane were purchased from Sigma Aldrich. HAuCl₄ was bought from CDH, India.

Synthesis of MoS₂ NSs

 MoS_2 NSs were prepared from MoS_2 powder using the chemical exfoliation method.^{38–40} 3 mL of 1.6 M *n*-butyllithium was added to 300 mg of MoS_2 powder under an argon atmosphere. This solution was maintained for two days under an argon atmosphere with constant stirring. After two days, the lithium

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intercalated product was repeatedly washed with hexane to remove the unreacted *n*-butyllithium. Around 80 mL of water was then added to this product and the dispersion was sonicated for 1 h using a bath sonicator. The aqueous dispersion of MOS_2 NSs was finally centrifuged at 10 000 rpm for 10 minutes to remove the unexfoliated MOS_2 . The quality of the MOS_2 NS samples was ensured from the UV/Vis and Raman spectrum (Fig. S1†). A standard solution of Mo was prepared by dissolution of a calculated amount of MOS_2 powder. The concentration of the MOS_2 dispersion was determined by ICP MS using this standard solution. All the concentrations used for the MOS_2 NSs later in the text are given in terms of Mo concentrations.

Reaction between MoS₂ NS and AgNO₃ solution

The reaction was carried out by adding AgNO₃ solution to the aqueous dispersion of MoS₂ and the reaction mixture was kept for 6 h under stirring conditions at room temperature. Concentration dependent reactions were performed by varying the volume of the AgNO₃ solution (5.8 mM) used: (a) 50 μ L, (b) 100 μ L, (c) 200 μ L, (d) 400 μ L, (e) 800 μ L and (f) 1.6 mL keeping the concentration of MoS₂ solution the same (3.7 mM in terms of Mo, 500 μ L). The total volume of the reaction mixture was maintained to be the same (7 mL). Thus the AgNO₃ concentration of MoS₂ was 0.26 mM (in terms of Mo, as mentioned before). For time dependent reactions, a medium concentration of AgNO₃ (800 μ L, 5.8 mM) was taken with the same concentration).

Reaction of MoS₂ NSs with Hg(OAc)₂ and HAuCl₄

The reaction of MoS_2 NSs with $Hg(OAc)_2$ was performed with the same concentration that was used in the case of $AgNO_3$ and MoS_2 NSs, under the same reaction conditions. For the reaction with Au^{3+} , 15 µL of 25 mM HAuCl₄ solution was taken keeping the MoS_2 concentration the same and the reaction was performed under the same reaction conditions (overall concentrations of $HAuCl_4$ and MoS_2 NSs were 0.053 and 0.26 mM, respectively).

Results and discussion

In the course of our experiment, we explored reaction products between AgNO₃ and MoS₂, in its bulk and 2D nanoscale forms. A solution of AgNO₃, kept in contact with MoS₂ powder (under magnetic stirring), remained unreactive for extended periods (24 h) without any visible changes in the solution. Furthermore, examination of the MoS₂ powder post AgNO₃ treatment did not show any change in its chemical composition (Fig. S2†). Such a phenomenon is expected and can be explained by the bulk thermochemical values ($\Delta G_{\rm f}^{\circ}$ MoS₂ and Ag₂S are -248.7 kJ mol⁻¹ (ref. 41) and -40.67 kJ mol^{-1,42} respectively). MoS₂ NSs were synthesized by chemical exfoliation^{38,39} of bulk MoS₂ (powder) in two steps, lithium intercalation followed by exfoliation of the lithiated MoS₂ (Li_xMoS₂) through ultrasonication. Both these steps involved changes in Gibb's free energy, resulting in a different $\Delta G_{\rm f}^{\circ}$ for the NSs and they behaved differently.

Upon mixing Ag^+ with a dispersion of MoS_2 NSs, gradual changes were seen visually which were in stark contrast to the bulk. The color of the reaction mixture changed from light green to brown and finally the products started floating on the surface. These changes were also manifested in the UV-visible spectra with gradual disappearance of the peaks at 420 and 310 nm,^{38,39} which are the characteristic bands for MoS_2 NSs (Fig. S1A†). The reaction starts instantly upon addition of Ag^+ solution and this is reflected in the UV-visible spectrum obtained immediately after addition (Fig. S3†). An overall scheme of the reaction involving MoS_2 NSs and Ag^+ (AgNO₃ solution) is shown in Scheme 1.

Transmission electron microscopy (TEM), in a time dependent manner, was employed for further exploration of the phenomenon. Parent MoS₂ NSs were approximately 200 to 1000 nm in length and had an average layer thickness of 2-3 layers, typical of chemically exfoliated MoS₂ (Fig. 1A(i)). An HRTEM image of the NSs, shown in Fig. 1B(i), showed a well resolved hexagonal lattice structure with the (100) spacing of 0.27 nm.38,39 The Fast Fourier Transform (FFT) pattern of the HRTEM image [inset of Fig. 1B(i)] showed a pattern expected for graphenic equivalents. The TEM images of these MoS₂ NSs in the course of the reaction showed gradual changes in their morphology. Systematic time dependent data reveal three main steps to form the final product as indicated in Scheme 1. The initial interactions of Ag⁺ with the MoS₂ NS lead to the formation of Ag NPs on the NSs (Step 1, Scheme 1). This happens immediately after the addition of Ag⁺ and appears as small black particles on the NSs in the low magnification TEM image (Fig. 1A(ii)). Structural confirmation of these particles came from the lattice resolved HRTEM images; one such particle on MoS₂ NS (Fig. 1B(ii)) showing Ag (111) lattice of 0.23 nm is presented as an example. Simultaneous focusing



Scheme 1 Graphical outline of the reaction between Ag^+ and MoS_2 NSs elucidating the steps involved in the overall reaction.



Fig. 1 (A). TEM images from different stages of the reaction; (i) exfoliated $MoS_2 NS_5$, (ii) Ag NP decorated NSs, (iii) Ag-reacted NSs where the network of Ag_2S structures can be seen protruding from the NS edges and (iv) a closer view of the branched morphology of the Ag_2S network. (B) HRTEM images confirming the structures as shown in Scheme 1 (i) structure of a $MoS_2 NS$ (corresponding FFT pattern is shown in the inset; the lattice plane is marked); (ii) an expanded view of an Ag NP on the MoS_2 sheet (characteristic lattice planes are marked) and (iii) an $Ag-Ag_2S NP$ on NS. This represents the initial stage of the transformation of Ag into Ag_2S by extraction and capture of sulphur from the NSs. Scale bars are indicated on all images.

on both Ag NPs and MoS_2 NSs was difficult as they occur at different depths and that's the reason for the apparent loss of resolution in the image B(ii). However, HRTEM images taken from the same area by focusing separately on Ag (Fig. S4A†) and MoS_2 (Fig. S4B†) confirm their well-crystalline nature. The mechanism of transformation of Ag(I) to Ag(0) and subsequent formation of these Ag NPs will be addressed later in the manuscript.

The TEM images of samples collected after 1 h of mixing showed network like structures protruding out from NSs along with the presence of particles on the NS surface (Fig. 1A(iii)). The expanded TEM image of these network-like structures is shown in Fig. 1A(iv) and the EDS spectrum obtained from these (Fig. S5A^{\dagger}) hinted at the chemical composition of Ag₂S. The particles present on the NSs at this stage appeared to be of 'Janus' type from the TEM image (Fig. S5B[†]). Two different regions of the same particle offer different contrasts in the HRTEM image and a slight difference in lattice distances between these two regions was also observed (Fig. 1B(iii)). Lattice distances in the darker part of the particle match with the (111) distances of Ag while that in the lighter part of the particle matches with the (112) plane of Ag_2S (marked in Fig. 1B(iii)). We believe that S atoms from the MoS₂ NSs diffuse into the Ag lattice to transform into the Ag₂S phase

which first leads to the formation of Ag–Ag₂S Janus particles and then complete transformation of Ag into Ag₂S gives rise to the protrusions of network-like structures out of NSs (Step 2, Scheme 1). A closer inspection of the Ag–Ag₂S interphase in the HRTEM image in Fig. 1B(iii) (marked with a red box and expanded view shown in Fig. S5C†) shows the presence of crystal defects, indicative of atomic diffusion and growth of a new phase across that region.

The third and final step of the reaction deals with the time dependent transformation of network like structures of Ag₂S (Step 3, Scheme 1) and is presented in Fig. 2. The network-like structures formed after 1 h of reaction (Fig. 2A) slowly broke apart and formed particles of various sizes after 6 h of reaction (Fig. 2C). An intermediate state of this process can be observed from the TEM image taken after 4 h of the reaction (Fig. 2B). HRTEM image of one such particle (Fig. 2D) showed a lattice spacing corresponding to the (112) planes of α -Ag₂S mentioned earlier while the EDS spectrum confirms a Ag:S ratio of 2:1. To confirm whether these particles indeed are Ag_2S , the final product was subjected to powder X-ray diffraction (PXRD) analysis. The obtained pattern (Fig. 2E) was an exact match with that of the monoclinic acanthite (α form) phase of Ag₂S (Fig. 2E, JCPDS card no. 14-0072). Acanthite is the Ag₂S phase stable at room temperature.43



Fig. 2 TEM images taken after (A) 1 h, (B) 4 h and (C) 6 h of reaction showing the time dependent evolution of the network-like morphology of Ag_2S into differently sized NPs. (D) HRTEM image of one such Ag_2S NP is shown in (C) confirming the phase. EDS spectrum, shown in the inset, confirms the chemical composition. (E) Standard peaks of Ag_2S (acanthite phase, JCPDS no. 14-0072) plotted along with the observed XRD pattern of the final reaction product. Scale bars are indicated on all images.

Changes in the structure of NSs during the course of reaction have also been looked at in detail through TEM and are presented in Fig. 3. Fig. 3A is a representation of the initial stages of the reaction, where sheet-like structures can be seen clearly although network-like Ag₂S structures have started to protrude out from the edges, probably due to higher edge-reactivity of MoS_2 NSs.^{44,45} A higher magnification image taken from the surface of the NSs at this stage shows the presence of Ag NPs on them (Fig. 3B). As the reaction proceeds, these Ag NPs transform into a branched network of Ag₂S and cover the entire surface of the NSs (Fig. 3C). The magnified TEM image (Fig. 3D) shows Ag₂S structures which are darker. However, perforated sheet-like structures, appearing with a different contrast can be observed clearly in the marked regions of the image. As the reaction completes, Ag₂S network structures convert into Ag₂S NPs and segregate on the TEM grid. At this point, these perforated sheet-like structures can be seen clearly (Fig. 3E) and appear as a holey film in the higher magnification image (Fig. 3F). These structures were found to be sensitive to electron beam irradiation and appeared amorphous. They being amorphous is the reason for the observation of only Ag₂S in the XRD of the final product of the reaction (Fig. 2E). A comparison between the EDS spectra of MoS₂ NS (a) and NSs after the reaction (b) is shown in the insets of Fig. 3F. The depletion of S content in the reacted NSs is apparent from the difference in the shape in the EDS spectra as one would expect from the extraction of S from the MoS₂ NS by Ag to form Ag₂S.

X-ray photoelectron spectroscopy (XPS) of the samples at different times during the course of the reaction was performed to understand the redox chemistry involved. The XPS survey spectrum at the end of the reaction showed the expected elements (Fig. S6†). The specific scans for Mo 3d, Ag 3d and



Fig. 3 Changes of the MoS_2 sheet structure as the reaction proceeds. (A) TEM image of MoS_2 NSs after 0.5 h of reaction. Ag₂S protrusions can be seen to stem out of NS edges. (B) HRTEM image of NS; at this stage Ag NPs are present on the surface of MoS_2 NS. (C) TEM image of reacted MoS_2 NSs after 3 h of reaction. Surface Ag NPs converted into a Ag₂S network which has encapsulated the NSs. (D) Higher magnification image of the marked region of (C), a porous sheet morphology can be seen underneath the Ag₂S network. (E) TEM image of the porous sheet formed after 6 h of reaction. (F) Higher magnification image of the marked region from (C), showing the pores on the NS. Insets show the collected EDS spectra for MoS_2 and reacted- MoS_2 NSs, respectively showing a decrease in the amount of S after the reaction. Scale bars are indicated on all images.

S 2p regions from the reactants and products at two different reaction times are presented in Fig. 5A–C, respectively. The parent MoS_2 NSs show two peaks for Mo(v) at 228.9 eV and 232.0 eV corresponding to $3d_{5/2}$ and $3d_{3/2}$, respectively [Fig. 4A (i)]. The XPS spectrum of the Mo 3d region taken after the addition of Ag^+ (0.4 mL of 5.8 mM AgNO₃) showed the emergence of two new peaks at 233.1 eV and 236.2 eV [Fig. 4A(ii)]. The peak around 236.2 eV was attributed to the $3d_{3/2}$ Mo(vı) state, confirming oxidation of Mo(v) to Mo(vı) in the reaction. An increase in the relative intensity of the peak around 236.2 eV with respect to the peak at 228.9 eV with the increasing reaction time [Fig. 4A(iii) *vs.* Fig. 4A(ii)] validates this assignment. Deconvolution of the peaks around 233.1 eV into individual Mo(v) and Mo(vı) components further supports oxidation. The corresponding change in the oxidation state of

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Fig. 4 Time dependent XPS to support the proposed mechanism. A (i–iii), B (i–iii), and C (i–iii) correspond to time dependent XPS in the Mo 3d, Ag 3d, S 2p regions, during the reaction. A(i–iii) show the change in the oxidation state and the increase in intensity for a particular oxidation state of Mo. B(i–iii) Change in the oxidation state of Ag with time and with change in the oxidation state of Mo. C(i–iii) show the shift in the binding energy with time for a particular oxidation state of S.

silver [Ag (i) in Fig. 4B(i) transforms into Ag (0) in Fig. 4B(ii)] completes the redox reaction and accounts for the formation of Ag NP decorated NSs in the first step.

$$Mo(IV) + 2Ag^+ \rightarrow Mo(VI) + 2Ag(0)$$
 (1)

However, in the final product Ag_2S , the oxidation state of silver again becomes Ag(i) (Fig. 4C(ii)). A marked change was noticed in the S 2p binding energies in due course of the reaction as well. The peaks at 162.2 eV and 163.5 eV are assigned to $2p_{3/2}$ and $2p_{1/2}$, respectively of S^{2-} (Fig. 4C(i)) in MoS₂ which moved to a relatively lower binding energy at 161.5 eV and 162.8 eV, due to the formation of Ag_2S (Fig. 4C(iii)). The relatively higher binding energy of sulphur before the reaction is because sulphur is bridging (S_2^{2-}) and/or apical (S^{2-}) in MoS₂ while a relatively lower binding energy after the reaction is in good agreement with S^{2-} in Ag_2S . Thus the overall reaction for the second step is:

$$Ag NPs + S^{2-} \rightarrow Ag_2S + 2e^{-}$$
(2)

To prove that silver nanoparticles indeed are capable of taking part in such reactions, a reaction was performed with the as-synthesized citrate protected nanoparticles. Interestingly, the same chemistry, albeit with a longer reaction time scale, was noticed (Fig. S7†) which resulted in a porous and amorphous net-like structure and Ag_2S NPs.

The formation of Ag₂S by the reaction of S^{2-} with Ag NPs can be rationalized in terms of the higher bond energy of Ag–S over Mo–S [bond energy(Ag–S) = 217.1 kJ mol⁻¹ in Ag₂S and bond energy(Mo–S) = 47 kJ mol⁻¹ in MoS₂]. Oxidation of Ag NPs to Ag⁺ (Ag₂S) is also favorable from the electrochemical point of view (2Ag + S²⁻ = Ag₂S + 2e⁻ 0.691V).

Although it was established from the XPS spectra that MO(rv) oxidises to MO(vi) during the reaction, the molecular nature of the Mo containing species formed was not possible to be identified using XPS. To understand the fate of Mo after the completion of the reaction, the final mixture was subjected to electrospray ionization mass spectrometry (ESI MS). The negative mode mass spectrum (Fig. S8A†) showed a series of peaks which matches exactly with the mass spectrum of ammonium molybdate (Fig. S8B†). An expanded view of the marked region of the mass spectrum is shown in Fig. 5A where clear isotope patterns of MOO_3^- , $HMOO_4^-$ and MOO_5^- ions could be observed. The identity of the MOO_5^- ion was confirmed from



Fig. 5 (A) Negative mode ESI mass spectrum of the final reaction mixture confirming the presence of the molybdate ion. Assignment of peaks to various isotopes of Mo is shown only for MOO_5^{-} .(B) Ion current vs. time plots for N_2^+ and NO_2^+ ions to prove the evolution of NO_2 in the course of reaction.

 $\rm MS^2$ spectra where an increase in the intensity of $\rm MOO_3^-$ ions was observed with the increasing collision energy (Fig. S8C†). The ESI MS analysis unambiguously proves the formation of molybdate from $\rm MOS_2$ NSs. While we do observe a slight increase in the $\rm Mo(v_1)$ intensity in the XPS spectrum of the Mo region after 6 h of reaction (Fig. 4A(iii)), this increase was not very large as $\rm Mo(v_1)$ stayed as the molybdate ion in solution while only solid residues comprising of unreacted or partially reacted NSs were analysed in XPS.

We conjecture that NO_3^- ions (coming from AgNO₃) reduce to NO_2 in the course of the reaction to account for the charge balance. The formation of NO_2 was proved by *in situ* mass spectrometric detection. At first, solutions of both the reactants were purged separately with argon (Ar) to remove the dissolved O_2 and the reaction was initiated by injecting the AgNO₃ solution into the dispersion of MOS_2 NSs taken in an enclosed vessel. The mixture of gaseous components inside the vessel after 6 h of reaction was analysed by a residual gas analyser. The gas sampling was similar to our previous experiment on carbon nanotube reactions.⁴⁶ This resulted in an increase in the ion current for both N_2^+ and NO_2^+ due to an increase in partial pressures of the corresponding gases, in the course of time. But when a control analysis was performed, a lesser increase in ion-current for NO_2^+ was observed whereas the increase for N_2^+ (background gas) remained the same. The control followed identical reaction conditions, leading to the same extent of unavoidable leakage and corresponding changes in background gases. This supports the evolution of NO_2 in the following reaction:

$$2NO_{3}^{-} + Mo(v_{1}) + 2H_{2}O + 2e^{-}$$

$$\rightarrow MoO_{4}^{2-} + 2NO_{2} + 4H^{+}$$
(3)

The experiment suggests the formation of an acid in the reaction, which was again supported by the decrease in the pH of the solution with the increasing reaction time (Fig. S9[†]).

Thus, the overall reaction for the second step (after the formation of Ag nanoparticles) can be given as:

$$Ag + S^{2-} + Mo(v_{I}) + 2NO_{3}^{-} + 2H_{2}O \rightarrow Ag_{2}S + MoO_{4}^{2-} + NO_{2} + 4H^{+}$$
(4)

The reaction between MoS_2 and silver acetate was also performed. This too happens as in the case of $AgNO_3$ (Fig. S10[†]). Most probably, the acetate ion is getting reduced to alcohol as NO_3^- becomes NO_2 in the reaction with $AgNO_3$. However, due to reduced partial pressure and low quantity, it could not be detected with a residual gas analyser.

To understand whether the reaction between MoS₂ and Ag⁺ is thermodynamically favourable or not, isothermal calorimetric titration experiments were performed (Fig. 6). The reaction cell was filled with 7.8 µM MoS₂ which was titrated against 0.62 mM AgNO3 at 30 °C. Under optimized conditions, 2 μ L of AgNO₃ was added to the MoS₂ cell at a regular interval of 180 s and the reaction was continued until saturation. The final data were fitted using one site model assuming only one type of binding/reaction site. The number of binding sites, which is often considered as the reaction stoichiometry, was found to be 1.8. This is quite expected as the formed reaction product is Ag₂S. The binding constant which is also taken as the rate constant was found to be 9.03 \times 10³ mol⁻¹. The reaction is highly exothermic with a negative enthalpy change $(\Delta H \text{ is } -7.57 \times 10^4 \text{ cal mol}^{-1})$. As the reaction involves association of the reactants to form products, the entropy change is expected to be negative (experimental value is -227 cal mol⁻¹ deg⁻¹).

After understanding the thermodynamic feasibility of the reaction, the effect of the AgNO₃ concentration was checked keeping all other parameters constant. The concentration of AgNO₃ was varied from 200 μ L to 400 μ L and to 1.6 mL (5.8 mM). For a lower concentration (200 μ L AgNO₃ solution), unreacted MoS₂ remained in solution which was seen in TEM (Fig. S11B†) and the feature due to MoS₂ NS remained in the UV/Vis spectra (Fig. S12†). The reacted part of the MoS₂ converted to porous sheets. For 400 μ L of AgNO₃ solution, the



Fig. 6 (A) Real time ITC thermograph of the reaction between MoS_2 and $AgNO_3$ and (B) corresponding heat change showing the exothermic reaction. The resulting thermodynamic parameters are listed in (B).

MoS₂ sheets converted to porous materials and Ag₂S particles were formed but at a high concentration of AgNO₃ (1.6 mL), small Ag–Ag₂S particles were formed along with the porous sheets. The HRTEM image of Ag–Ag₂S particles is shown in the inset of Fig. S11I.[†] The reaction was carried out in the absence of light to see the effect of light in the reaction. In the absence of light also the same products were obtained which proves that light has no effect in the reaction.

It was presumed that the second step of the reaction is governed by metal-sulphur interactions. Reactions with other metal ions, such as Au³⁺ from the same group of silver and Hg²⁺ from the adjacent group, were tried to firmly establish this point. Not so surprisingly, mercuric ions also reacted with MoS₂ NSs and formed flower like structures composed of HgS particles (Fig. 7A). The formation of HgS particles was confirmed from HRTEM images and EDS data (Fig. 7B). The lattice spacing of (200) plane of HgS at 0.21 nm was seen.⁴⁷ But in the cases of Au³⁺ ions, only gold nanoparticles were seen⁴⁸ (Fig. 7C and D) and the reaction did not proceed further which is attributed to the low stability of gold sulphide and the oxidation of Au(0) to Au^{3+} or Au^{+} being not electrochemically favorable.⁴⁹ The formation of Au NPs in this reaction also proves that metal NP formation is the first step in these metal-MoS₂ NS reactions.



Fig. 7 Reaction with other metal ions. (A) TEM image of flower like HgS particles formed in the reaction of Hg^{2+} with MoS₂ NSs. (B) HRTEM image of the same. The EDS spectrum shown in the inset confirms the presence of both Hg and S. (C) TEM image of gold NPs formed on the MoS₂ sheet. (D) HRTEM image of a single Au NP on MoS₂ NS. The EDS spectrum taken from the same region is shown in the inset.

Conclusions

This study highlights the unique nanoscale reactivity of MoS_2 NSs towards Ag^+ ions in solution leading to chemical disintegration of NSs accompanied by complete changes in the morphology of the sheets. While the overall reaction was found to be energetically favorable, it does go to completion through a series of distinguishable steps. The products from each of these steps were observed and characterized with the help of high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy. The reaction of these NSs with other metal ions leads to the formation of products depending on the metal–sulphur bond energies. This study provides not only a deep insight into the stability and reactivity of inorganic graphene equivalents, but also points towards the direct synthesis of useful NS-heterostructures from solution.

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