Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Nanocomposites of 2D-MoS_2 nanosheets with the metal-organic framework, ZIF-8

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Experimental section:

Reagents and precursors: All Chemicals and reagents used in synthesis were of high purity and are obtained from commercial sources.

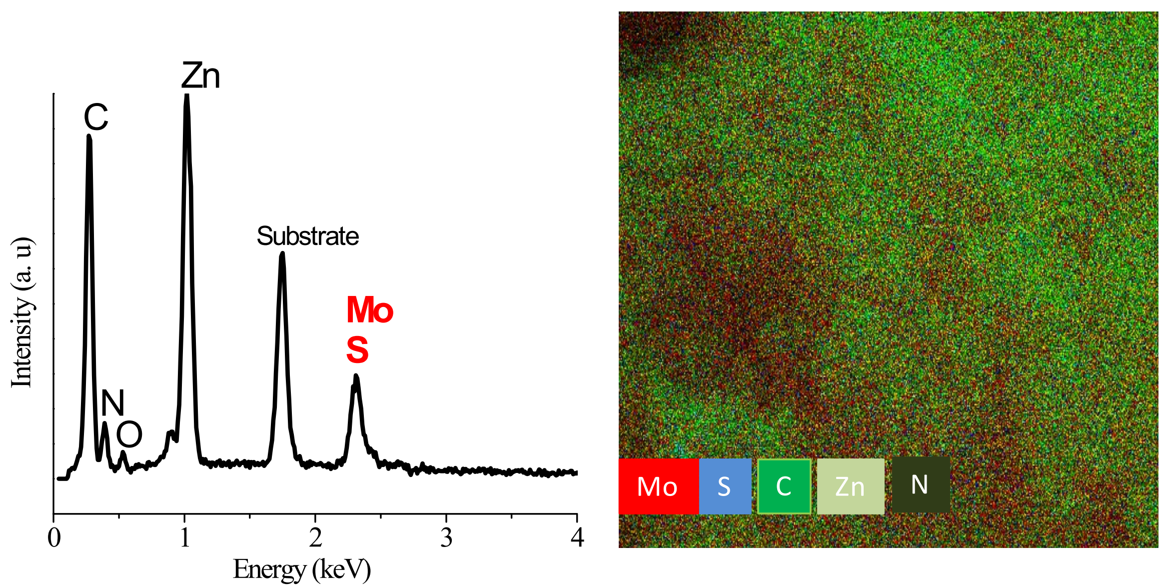

Fig. S1 Energy dispersive X-ray (EDAX) analysis of ZM-10 nanocomposite showing presence of C, N, O, Zn, Mo, S signals.

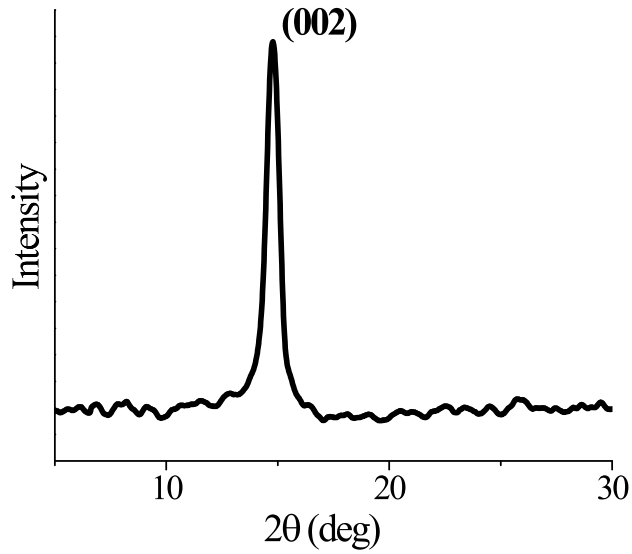

Fig. S2 (a) PXRD pattern of 1T-MoS_2.

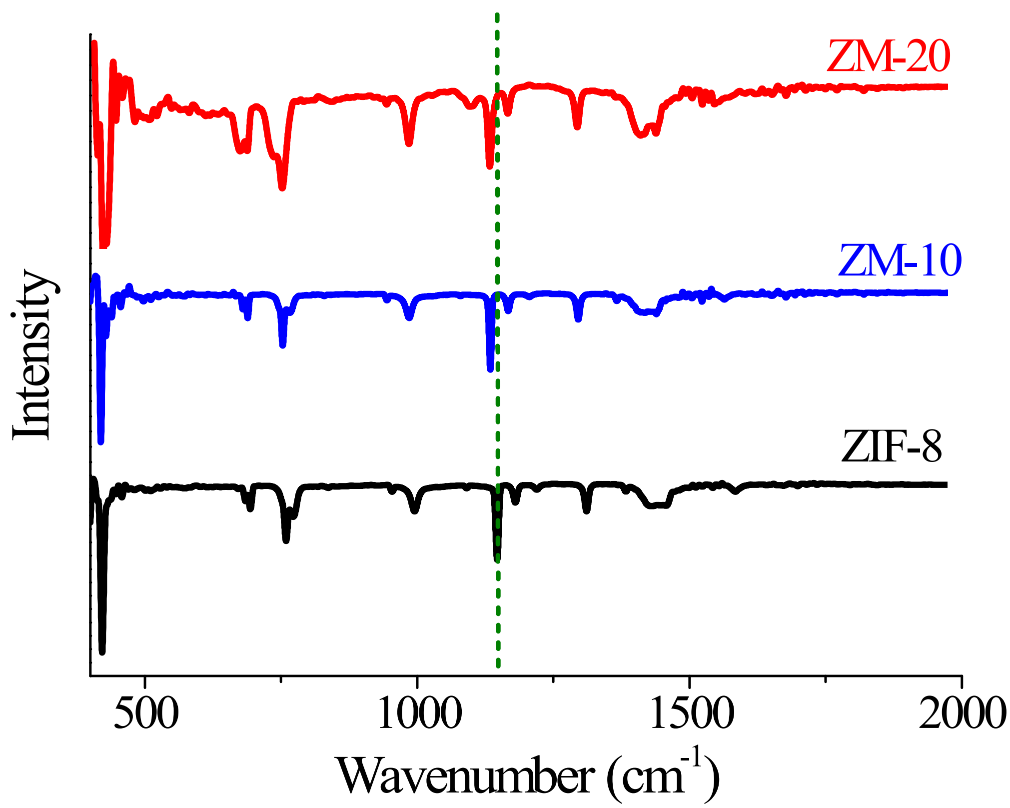

Fig. S3 Infrared spectra of ZIF-8, ZM-10 and ZM-20.

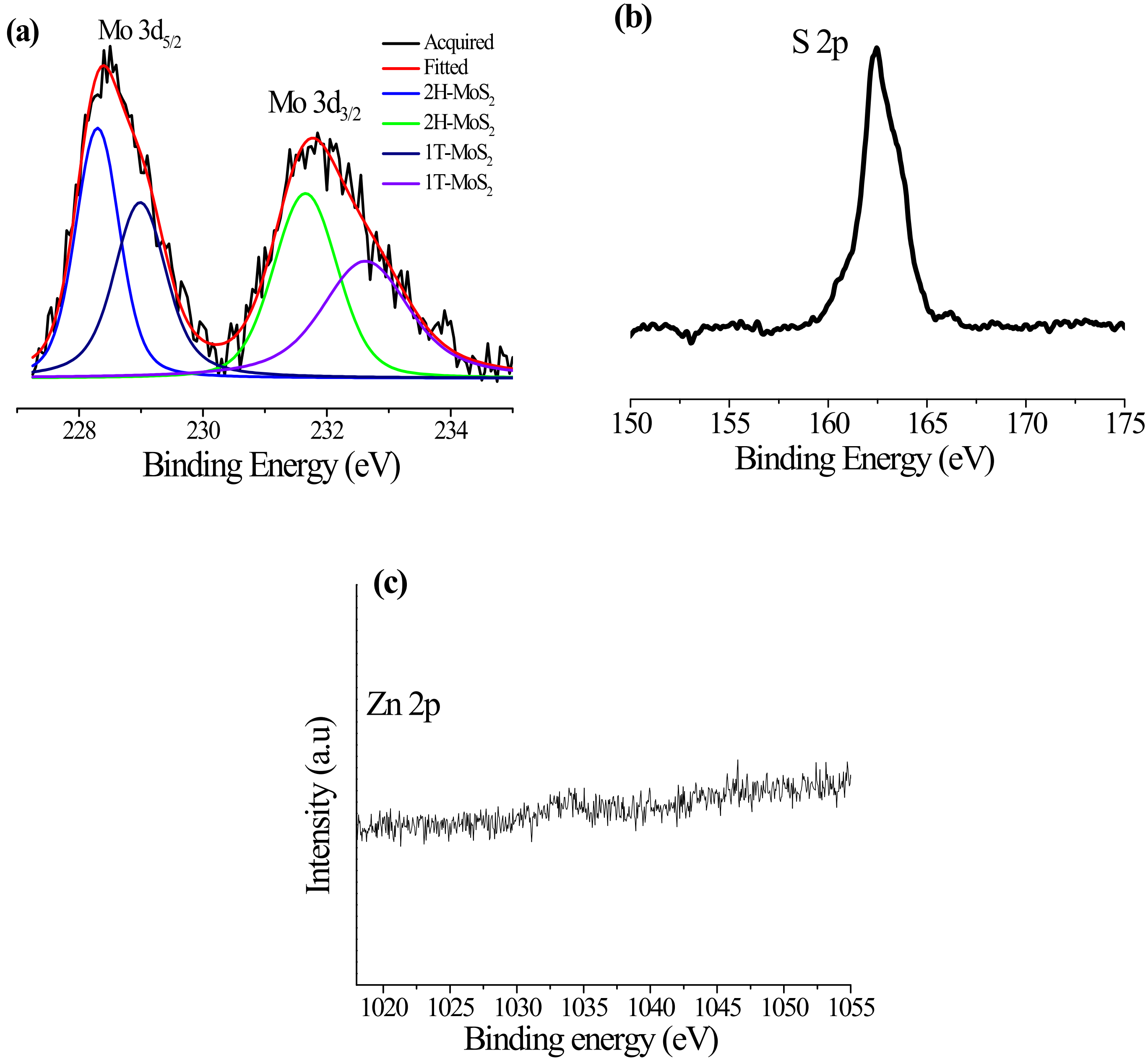

Fig. S4 High resolution (a) Mo (3d), (b) S (2p) and (c) Zn (2p) X-ray photoelectron spectrum of 1T-MoS_2. (Mo (3d) peaks are deconvoluted to show 1T and 2H components).

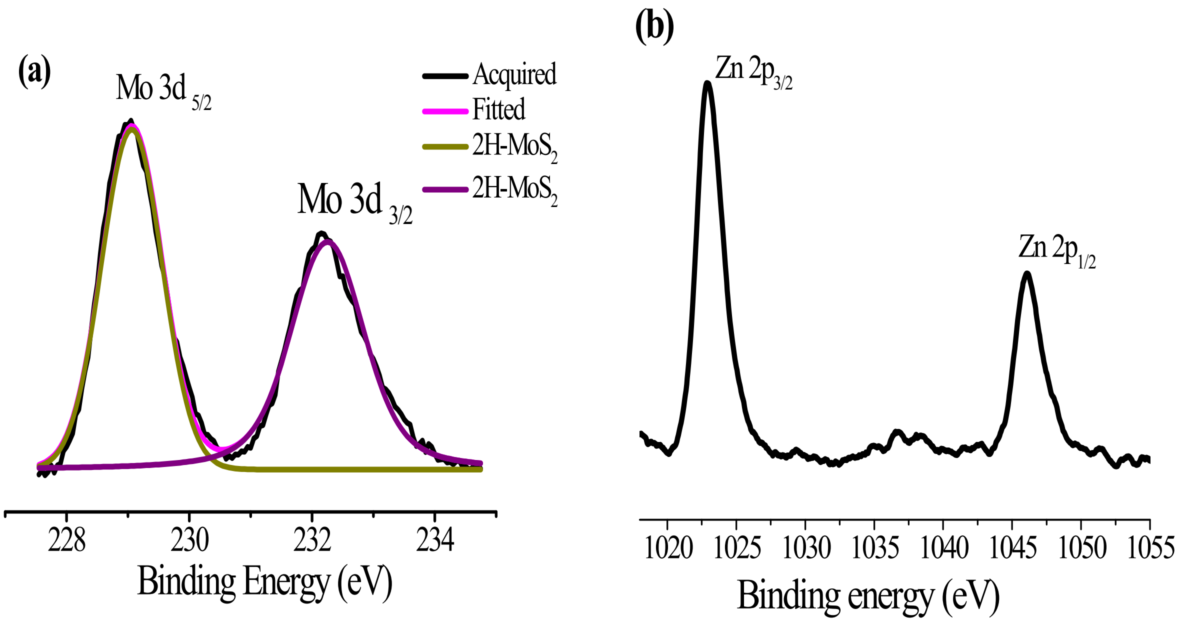

Fig. S5 High resolution (a) Mo (3d) and (c) Zn (2p) X-ray photoelectron spectrum of ZM-10.

On exfoliating bulk MoS_2 which is in 2H-form by nature partially converts to metallic 1T-polytype, quantification of different polytypes through XPS is difficult since some of transformed 1T-MoS_2 reverts back to 2H-phase while drying process; unavoidable during preparation of sample. Even though we obtained 1T/2H ratio of ~ 48 % in case of exfoliated MoS_2 as revealed by the convoluted Mo (3d) core level signals (Fig. S4) while MoS_2-ZIF-8 exhibits peaks only due to 2H-phase (Fig. S5). Since core level Mo (3d) signals of 1T-MoS_2 are broader, and it is a combination of different components (1T and 2H-phase) difficult to correlate these core level signals.

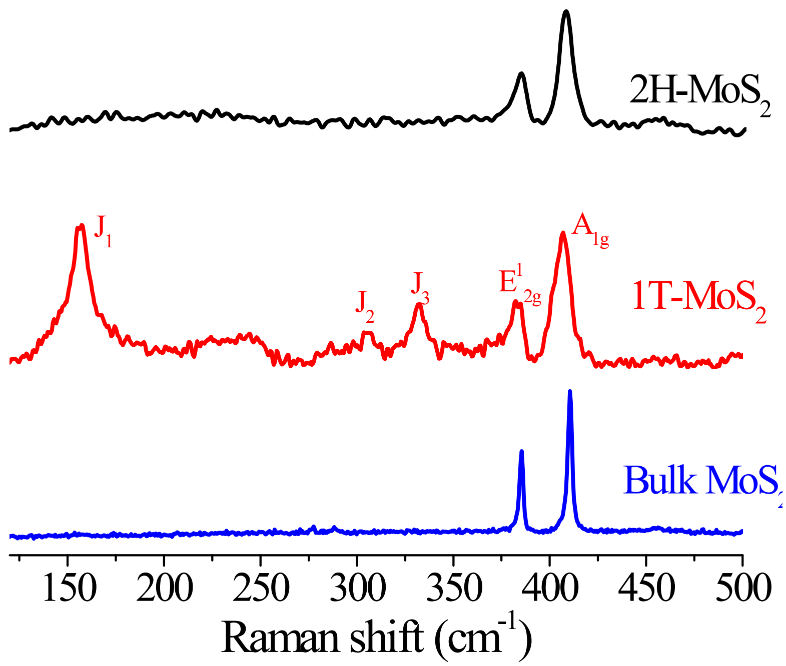

Fig. S6 Raman spectra of bulk, 1T and 2H MoS_2.

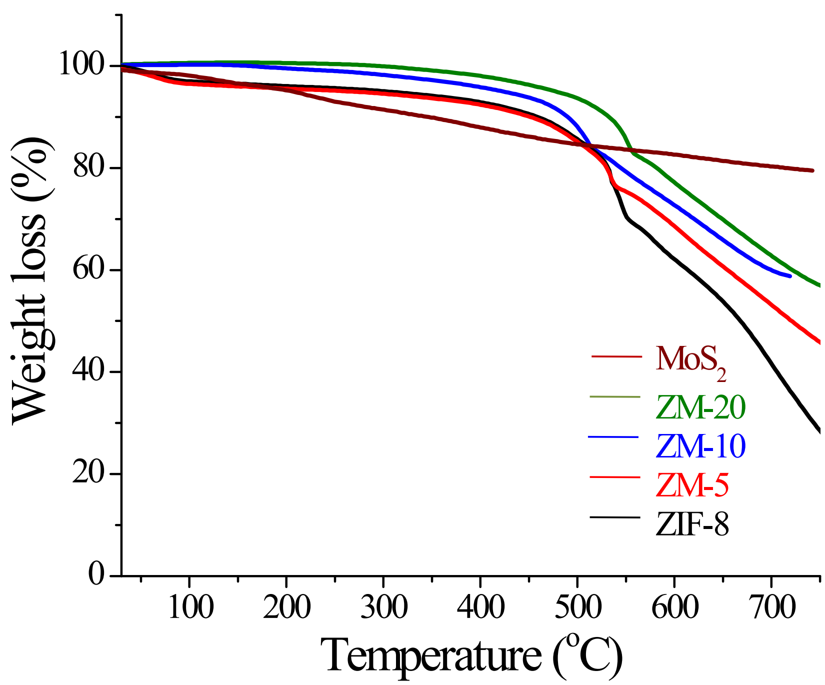

Fig. S7 Thermo gravimetric profile of ZIF-8, ZM-5, ZM-10, ZM-20 and MoS_2 in a nitrogen atmosphere.

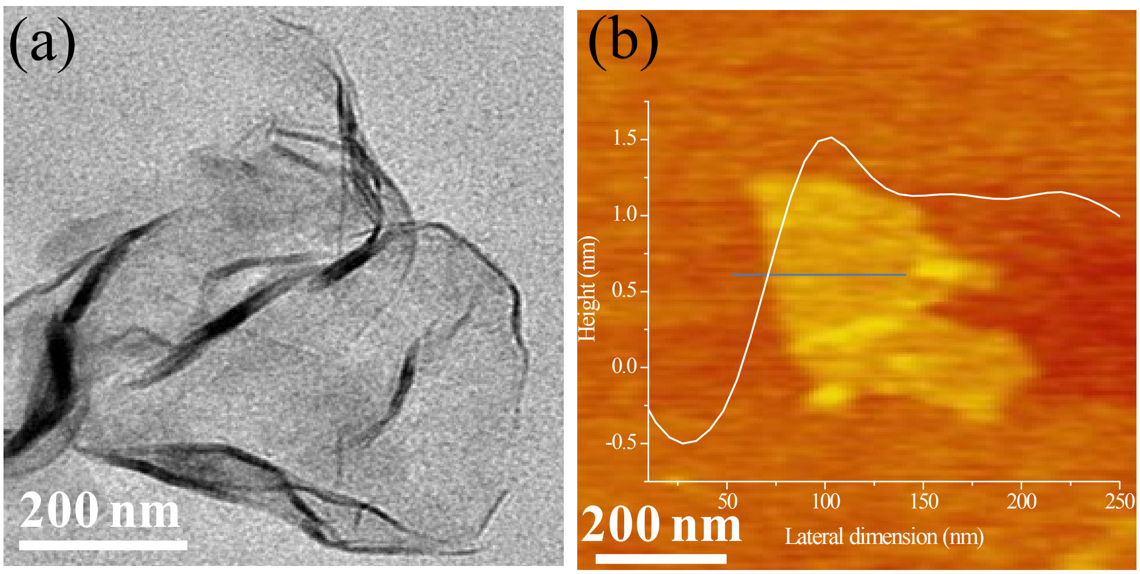

Fig. S8 (a) TEM and (b) AFM image of exfoliated MoS_2.

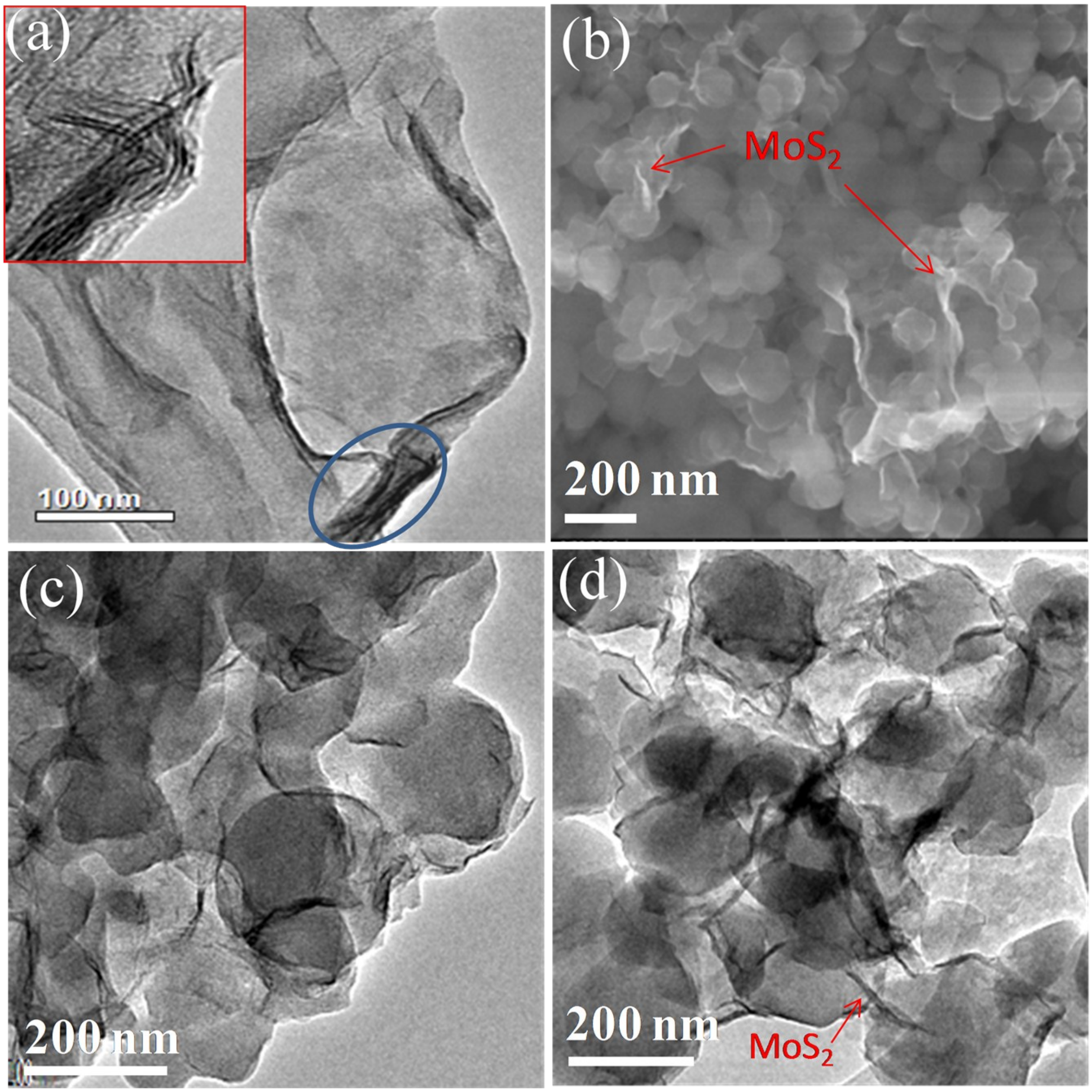

Fig. S9 (a) TEM image of exfoliated MoS_2, (b) FESEM images of ZM-5 and (c, d) TEM images of ZM-10 and ZM-20.

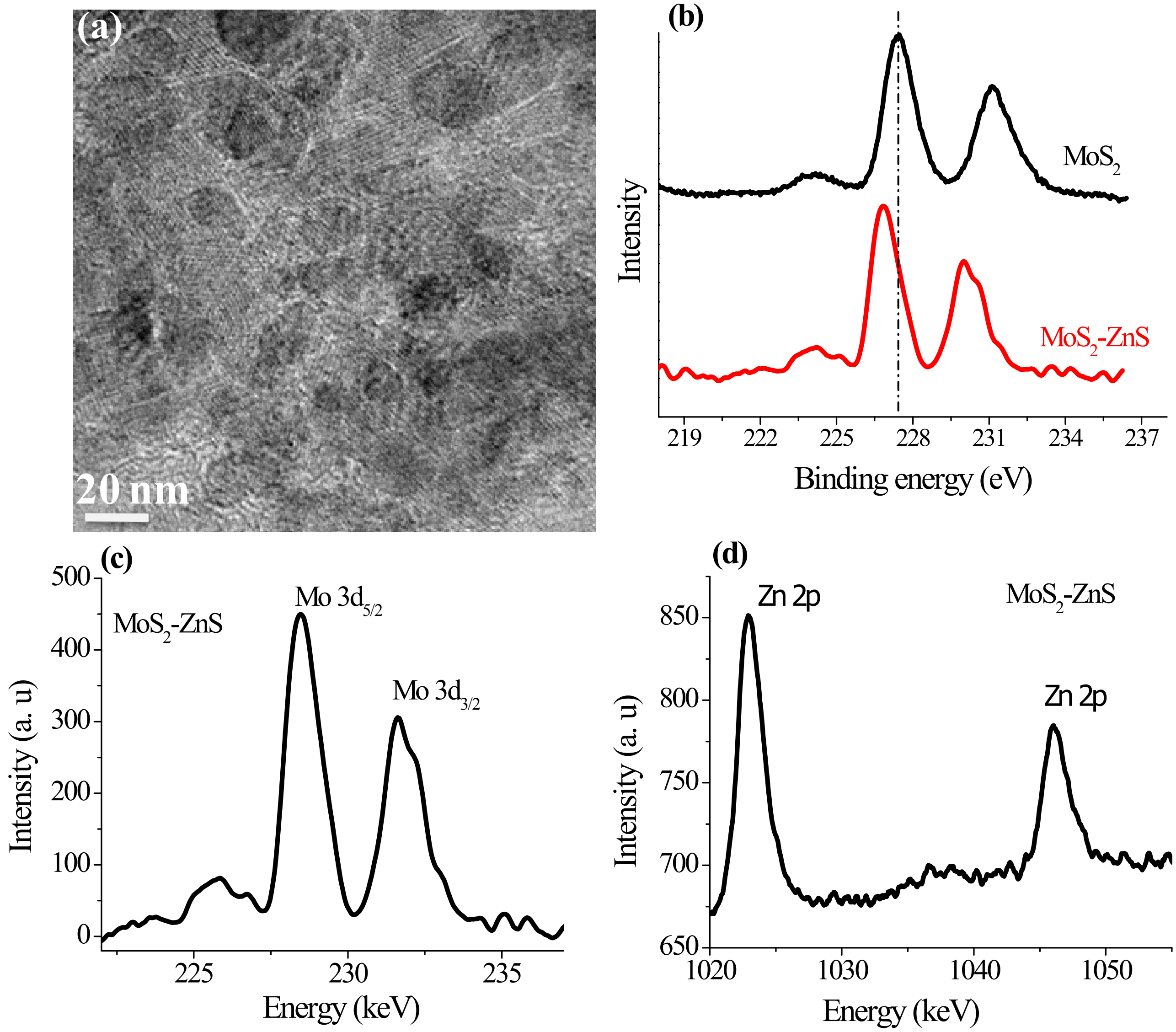

Fig. S10 (a) HRTEM image of MoS_2-ZnS; (b) High resolution Mo (3d) X-ray photoelectron spectra of MoS_2 and MoS_2-ZnS obtained from ZM-20; (c, d) High resolution Mo (3d) and Zn (2p) X-ray photoelectron spectrum of MoS_2-ZnS.

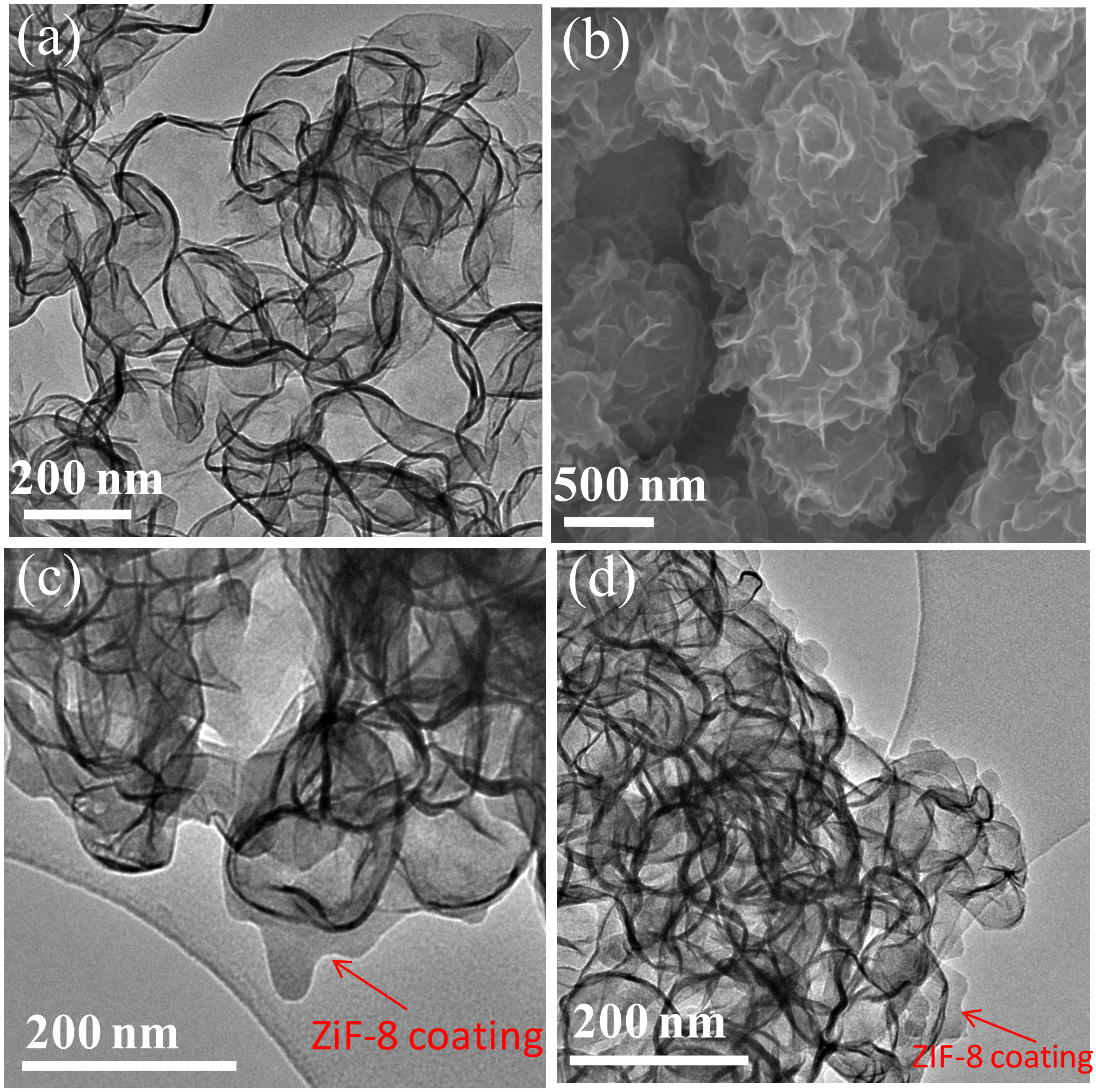

Fig. S11 (a, b) TEM and FESEM images of 2H-MoS_2 and (c, d) TEM images of and MoS_2-ZIF-8 (Arrows indicates ZIF-8 coating over nanosheets) obtained from 2H-MoS_2.

To confirm the coordination modulation effect of negatively charged sulfur, we have prepared MoS_2-ZIF-8 composite starting from 2H-MoS_2 instead of 1T-polytype with the similar procedure. Unlike the situation of 1T-MoS_2, semiconducting 2H-MoS_2 does not have negative charges on sulfur atoms of basal-plane. 2H-MoS_2 nanosheets required for these experiments are obtained from hydrothermal method.[1] On in-situ composite formation (similar procedure like 1T-MoS_2) we observed coating of ZIF-8 at the 2H-MoS_2 nanosheet edges as revealed by TEM images (Figures S11a, b), in contrast to ZM nanocomposites. The ZIF-8 coating is attributed to the dangling bonds of 2H-MoS_2 at the edges which are the only nucleation sites for available for ZIF-8 precursor's results in the growth at the edge sites in the absence of basal-plane negative charges.

Reference

1. K. Pramoda, K. Moses, U. Maitra and C. N. R. Rao, *Electroanalysis*, 2015, **27**,1892.