Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Efficient Fabrication of MoS_2 Nanocomposites by Water-Assisted Exfoliation for Nonvolatile Memories

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1 Experimental

Chemicals. Molybdenum sulfide (MoS_2) powders (with flake sizes of about 2 μm, purity of 99%), N-methyl-2-pyrrolidone (NMP) (99%), isopropanol (IPA) (99%), and dimethyl sulfoxide (DMSO) (99%) were purchased from Sigma-Aldrich. Carboxylated chitosan (CC) (with sizes of about 300 μm, purity of 99%) and methanol (MeOH) were purchased from Energy Chemical. Other chemicals are of analytical grade and used without further purification.

Estimation of the amount of MoS_2 dispersion. The dispersions of CM0, CM0.05, CM0.1, CM0.2, CM0.5, CM1.0, and CM2.0 have a weight ratio of CC: MoS_2 of 0:20, 1:20, 1:10, 1:5, 1:2, 1:1, and 2:1, respectively. In order to calculate the concentration of MoS_2 nanosheets in the dispersion, after centrifugation at 1500 rpm, a known volume (10 ml) of CM1.0 dispersion in DI water was carefully filtered under high vacuum using a hydrophilic poly(vinylidene fluoride) (PVDF) membrane (pore diameter = 0.22 μm) of known mass (126.2 mg). The collected residue was thoroughly washed with DI water to remove excess of not adsorbed CC. Finally, the film containing the residue was dried in a vacuum oven at room temperature overnight until constant weight to ensure complete removal of the solvent. The mass of the membrane containing the residue material was found to be 150.3 mg, from which the final concentration of MoS_2 nanosheet was calculated to be 2.41 mg/ml. The final concentrations of dispersed CM0.2 were also obtained in similar conditions. Errors ranged from 5 to 15% in triplicates in all cases.

2 Table Part

Table S1. Summary of reported traditional liquid phase exfoliation methods in comparison to this work.

Materials	**Grinding solvent** [a]	**Sonicating solvent** [a,b]	**Sonication time**	**Layers of nanosheets**	**Reference**
MoS_2	-	formamide	12 h	5 layers	1
MoS_2	-	DI water	8 h	9-10 layers	2
MoS_2	-	DMF	10 h	1-5 layers	3
Sericin/MoS_2	-	DI water	24 h	1-12 layers	4
Silk/MoS_2	-	NMP	10 h	4-8 layers	5
MoS_2	NMP	Ethanol/water	2 h	2-14 layers	6
CC/2H-MoS_2	DI water	DI water	5 h	1-5 layers	This Work

[a] NMP is N-methyl-2-pyrrolidone.

[b] DMF is N,N-dimethyl formaldehyde.

Table S2. Summary of reported nonvolatile WORM memory device performance in comparison to this work.

Active layer [a]	ON/OFF ratio	Retention time	Reference
PEF	10^4	10^4 s	7
PCoumSi	10^3	4×10^3 s	8
AlO_x-native	10^4	10^3 s	9
MoS_2-PCBM	10^2	/	10
CC/2H-MoS_2	3×10^3	10^4 s	This Work

[a] PEF is polyethylene furanoate, PCoumSi is polycoumarinsiloxanes, PCBM is [6,6]-phenyl-C61-butyric acid methyl ester.

Table S3 Assignment of the peak positions in Fig. S5

Peak position, cm^{-1}	Assignment	Literature Source
3412	Carboxylated Chitosan: overlap –O-H on –N-H (stretching vibration)	12, 15
3280	Carboxylated Chitosan: overlap –O-H on –N-H	11, 12
3088	Carboxylated Chitosan: Symmetric N-H stretch	12
2957	Carboxylated Citosan: -CH_3 asymmetric stretching vibration	12
2924	Carboxylated: -CH_2 symmetric stretching	12
2873	Carboxylated: -CH_3 stretching	12
1650	Carboxylated Chitosan: -C=N overlap –C=O in NH=C=O	15, 16
1570	Carboxylated Chitosan: overlap -C=O on –N-H	11, 12
1414	Carboxylated Chitosan: CH_2 bending	12
1303	Carboxylated Chitosan: -N-H stretching	12
1145	Carboxylated Chitosan: C-O-C bending mode	12
1073	Carboxylated Chitosan: C-O stretch	12
1033	Carboxylated Chitosan: C-O stretching mode of polysaccharide backbone	12
888	Carboxylated Chitosan: -C-H from polysacharide's structure overlapped by S-OH of MoS_2	11, 14
607	Silicon: Overlap of Si-C an Si(LO+TA)	13
383	2H-MoS_2	14, 17

3 Figure Part

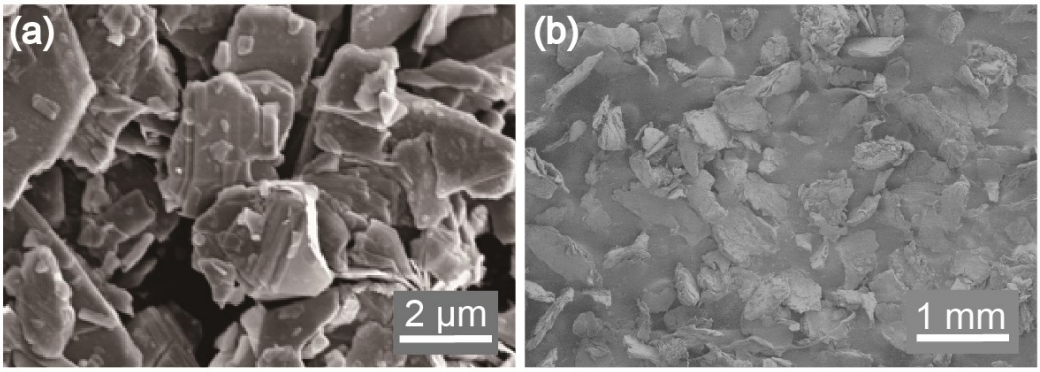

Fig. S1 SEM image of bulk MoS_2 powder (a) and CC powder (b).

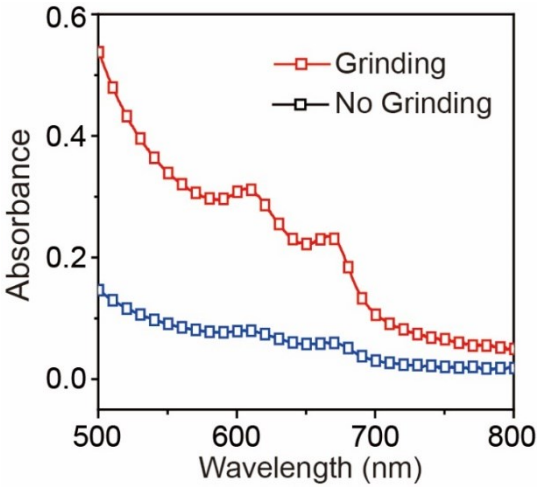

Fig. S2. UV-vis absorption spectra of the ground and ungrounded CC/2H-MoS_2 nanocomposites.

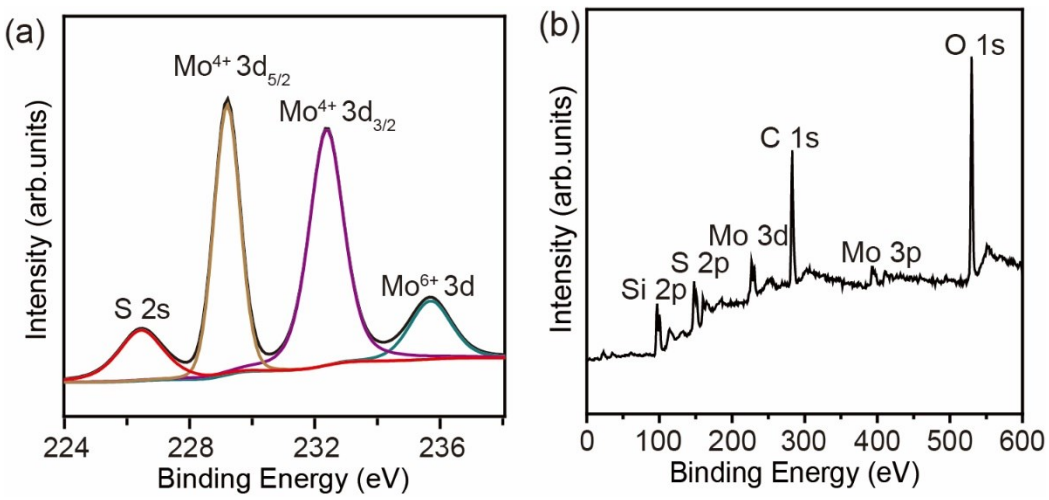

Fig. S3. S-2s and Mo-3d XPS spectrum (a) and XPS survey spectrum (b) of CM0.2 deposited on Si wafer.

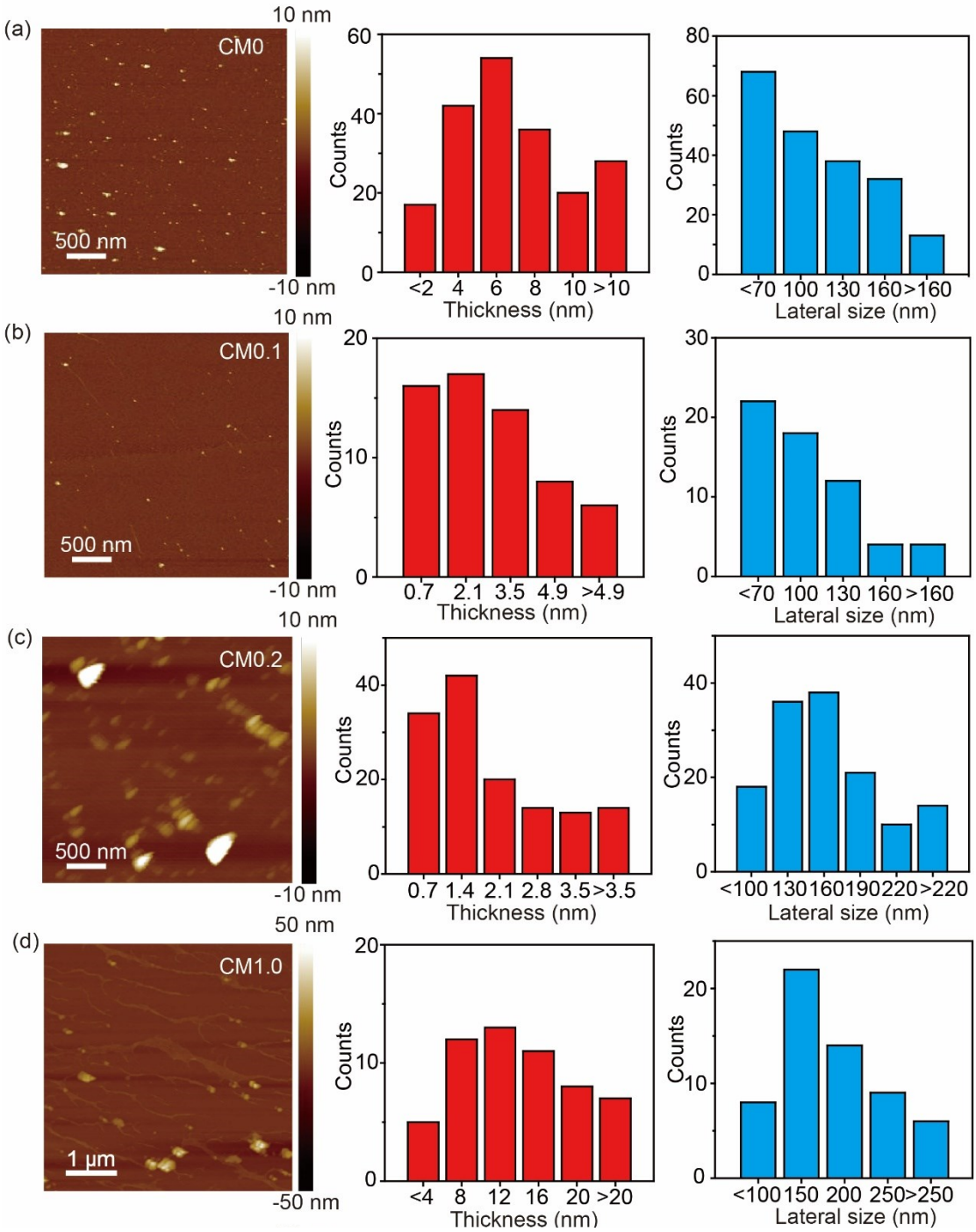

Fig. S4. AFM images of CM0 (a), CM0.1 (b), CM0.2 (c), and CM1.0 (b) with the corresponding thickness and lateral size distributions of the nanosheets.

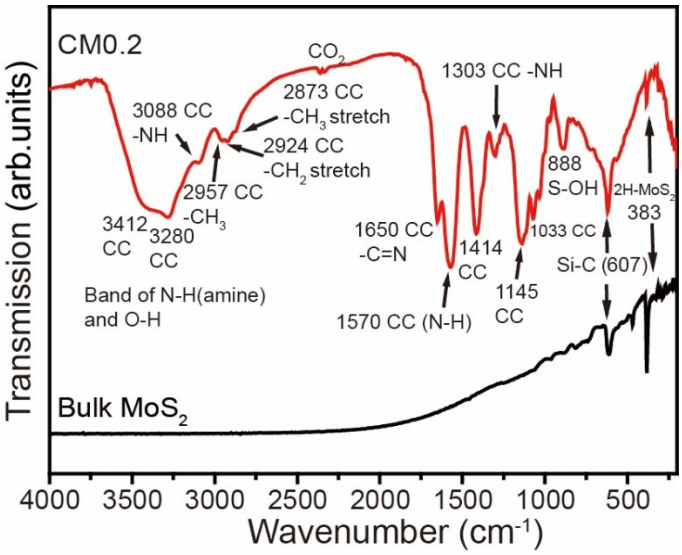

Fig. S5. FTIR spectra of CM0.2 and bulk MoS_2.

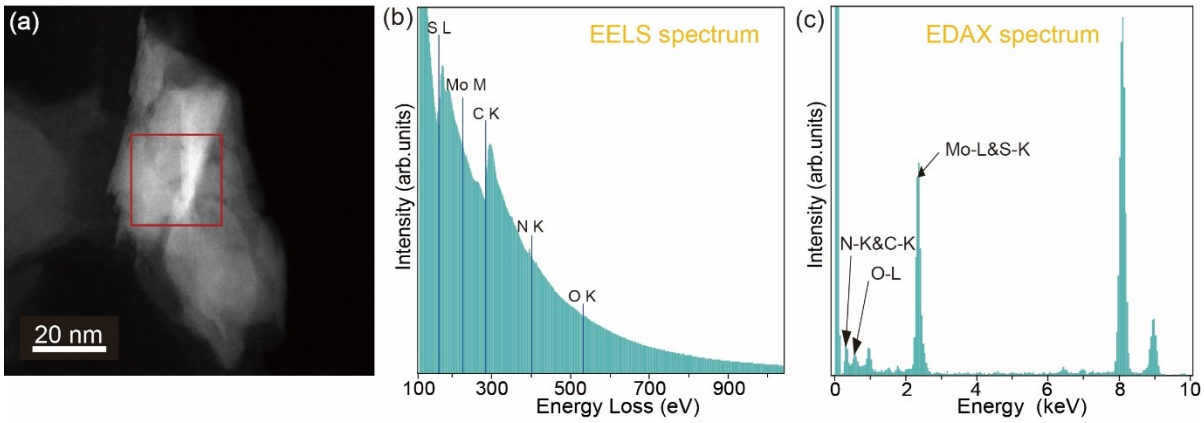

Fig. S6. (a) HAADF-STEM image of CM0.2 and the corresponding (b) EELS spectrum and (c) EDX spectrum.

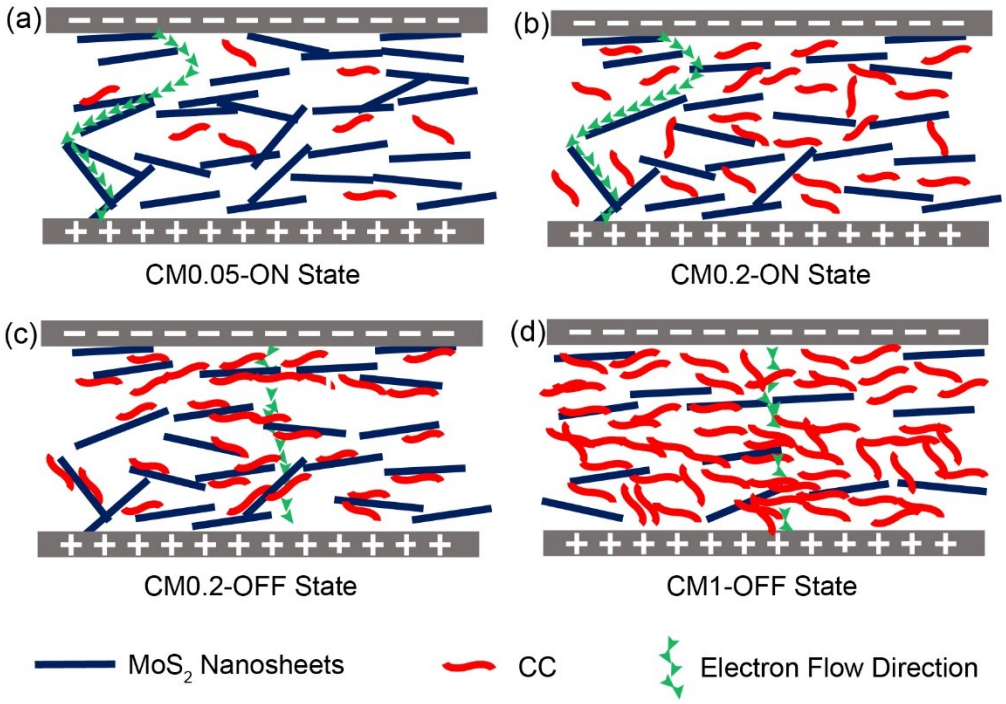

Fig. S7. The memory behavior and mechanisms in CMx-based (x=0.05, 0.2 and 1.0) memory devices.

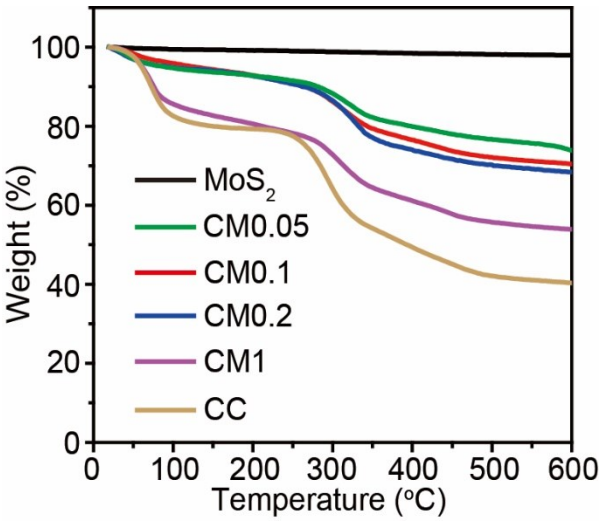

Fig. S8. TGA curves of the bulk MoS_2, CM0.05, CM0.1, CM0.2, CM1 and CC.

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