Supplementary Information for:

Engineering New Layered Solids from Exfoliated Inorganics: a Periodically Alternating Hydrotalcite – Montmorillonite Layered Hybrid

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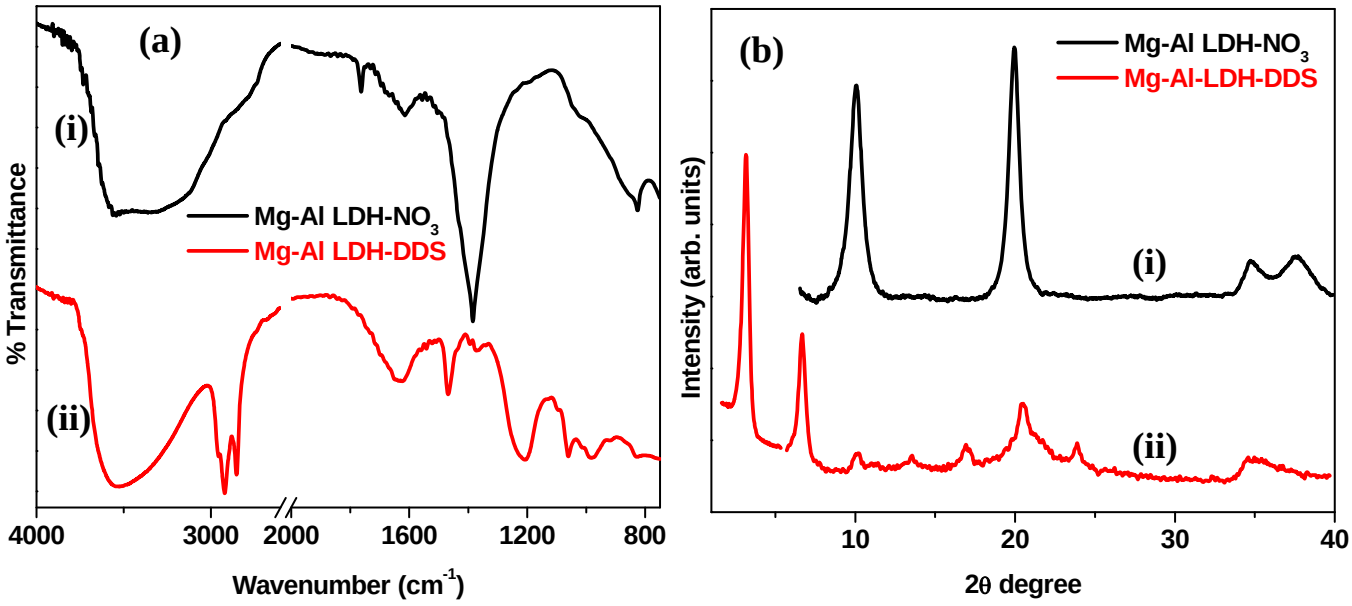
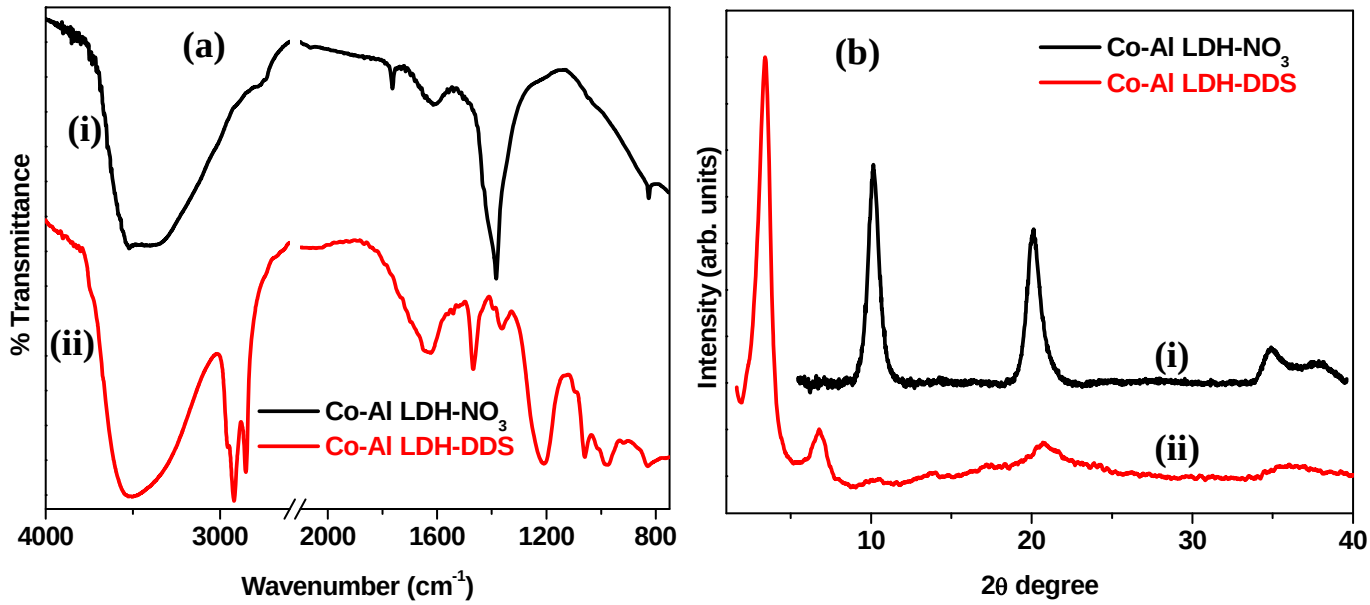


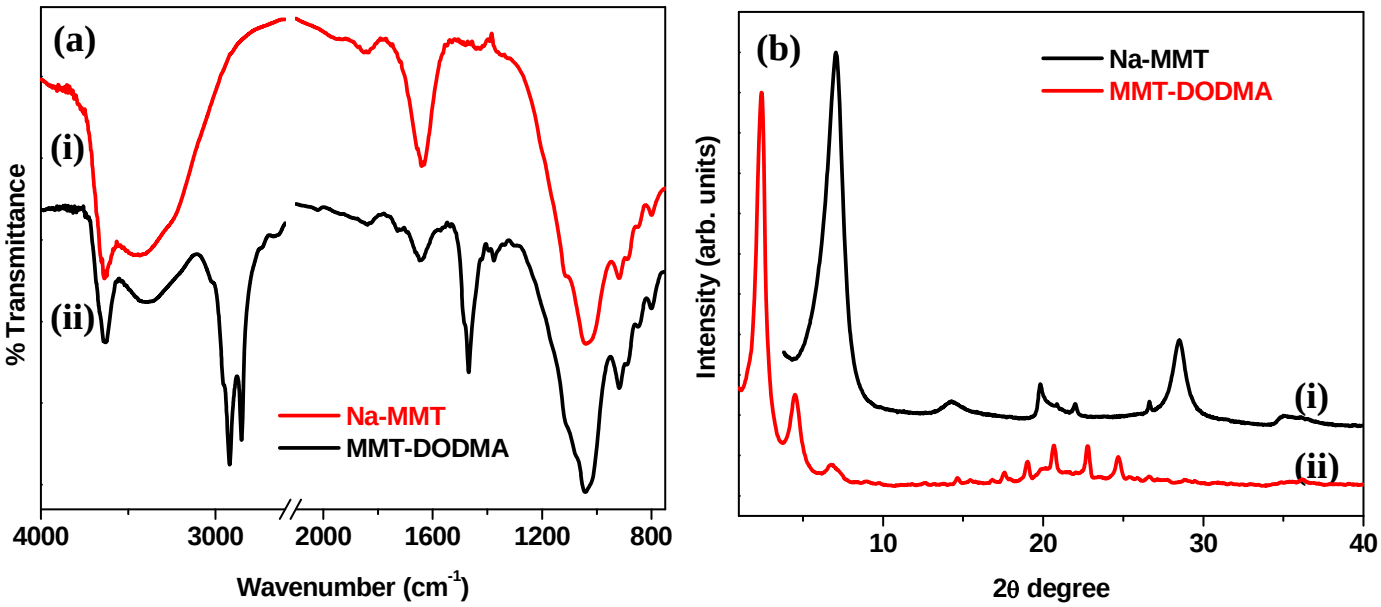
Supplementary Figure S1: Characterization of Mg-Al LDH-NO_3 and Mg-Al LDH-DDS. (a) FTIR spectra of (i) Mg-Al LDH-NO_3 and (ii) Mg-Al LDH-DDS. (b) X-ray diffraction patterns of (i) Mg-Al LDH-NO_3 and (ii) Mg-Al LDH-DDS.

Supplementary Method S1: Preparation and characterization of Co-Al LDH-DDS.

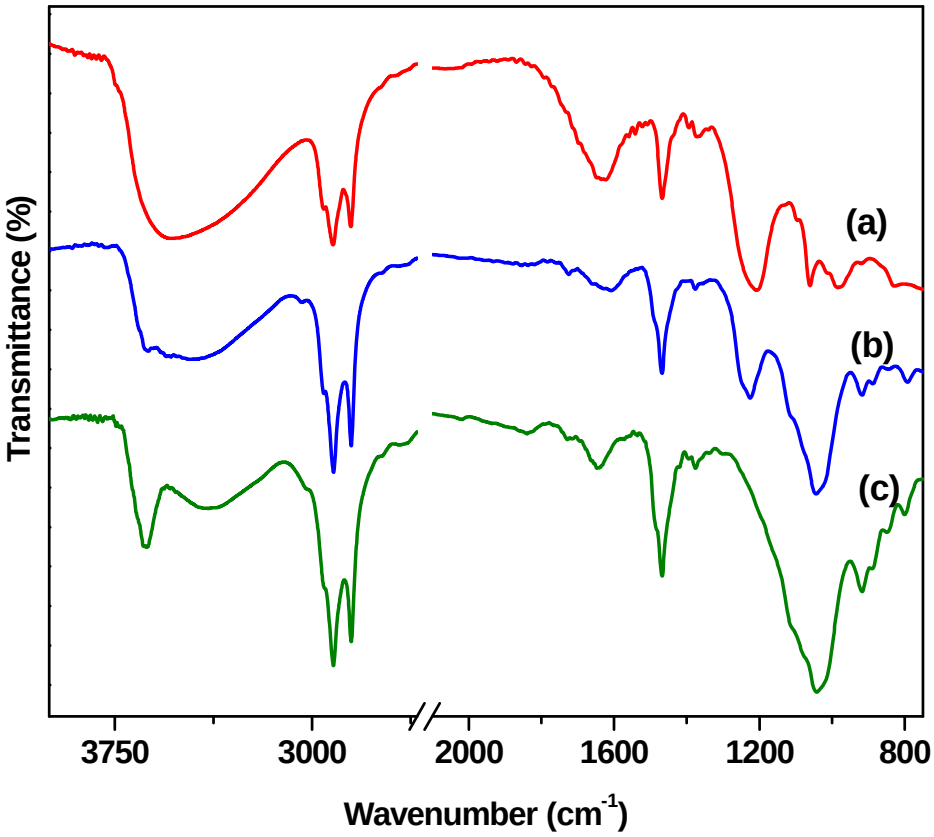
The dodecyl sulfate (DDS) intercalated Co-Al LDH, Co-Al LDH-DDS, was prepared by a similar procedure similar to that used for the preparation of Mg-Al LDH-DDS. The anionic surfactant dodecyl sulfate (DDS) was introduced within the galleries of Co-Al LDH by ion-exchanging the NO_3^- ions in Co-Al LDH-NO_3 with dodecyl sulfate anions. Co-Al LDH-NO_3 was prepared by the coprecipitation method by drop wise addition of 100 mL of aqueous $Co(NO_3)_2$ and $Al(NO_3)_3$ (mole ratio of Co/Al = 2) into aqueous ammonia solution at a constant pH of 8, under N_2 atmosphere. The ion exchange reaction was carried out by stirring one equivalent of Co-Al LDH-NO_3 with 3 equiv of sodium dodecyl sulfate in water for 48 h at 70^oC. The ion exchanged Co-Al LDH-DDS, was filtered and washed with hot water to remove excess DDS. The formation of Co-Al LDH-DDS was confirmed by X-ray diffraction and FTIR spectroscopy. FTIR spectra showed absence of the characteristic NO_3^- band at 1384 cm^{-1} in the ion exchanged sample and the presence of new bands due to intercalated DDS ions (Supplementary Fig. S2a). The XRD patterns showed the complete absence of *00l* reflections corresponding to Co-Al LDH-NO_3 and the presence of new *00l* reflections of Co-Al LDH-DDS with a lattice spacing expansion from 0.875 nm to 2.62 nm (Supplementary Fig. S2b). The actual composition of the Co-Al LDH-DDS, $Co_{0.67}Al_{0.33}(OH)_2(DDS)_{0.33} \cdot 0.89H_2O$, was established by combining the results of ICP-OES, TGA and elemental (C H N) analysis.



Supplementary Figure S2: Characterization of Co-Al LDH-NO_3 and Co-Al LDH-DDS. (a) FTIR spectra of (i) Co-Al LDH-NO_3 and (ii) Co-Al LDH-DDS. (b) X-ray diffraction patterns of (i) Co-Al LDH-NO_3 and (ii) Co-Al LDH-DDS.



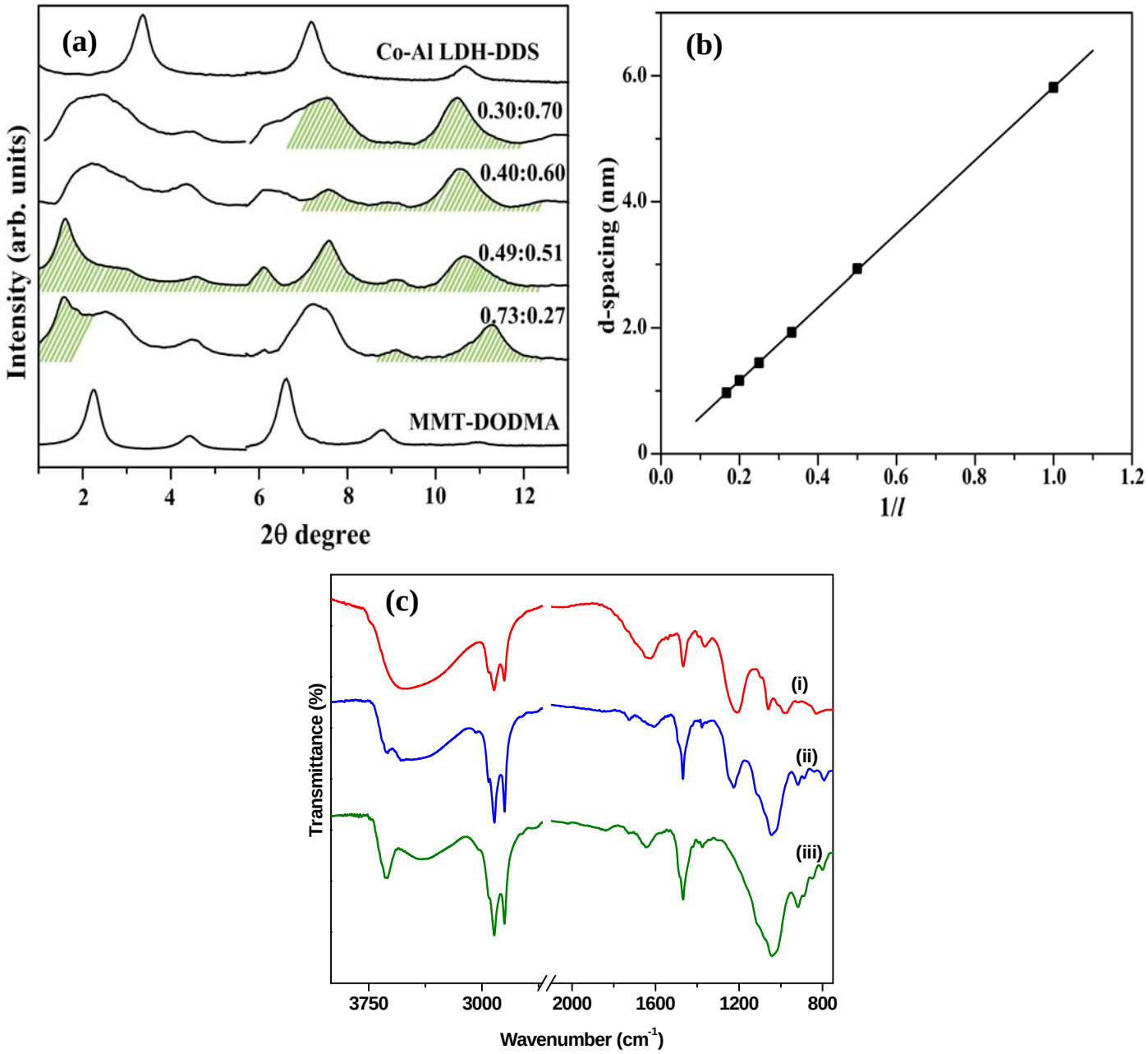
Supplementary Figure S3: Characterization of Na-MMT and MMT-DODMA. (a) FTIR spectra of (i) Na-MMT and (ii) MMT-DODMA. (b) X-ray diffraction patterns of (i) Na-MMT and (ii) MMT-DODMA.



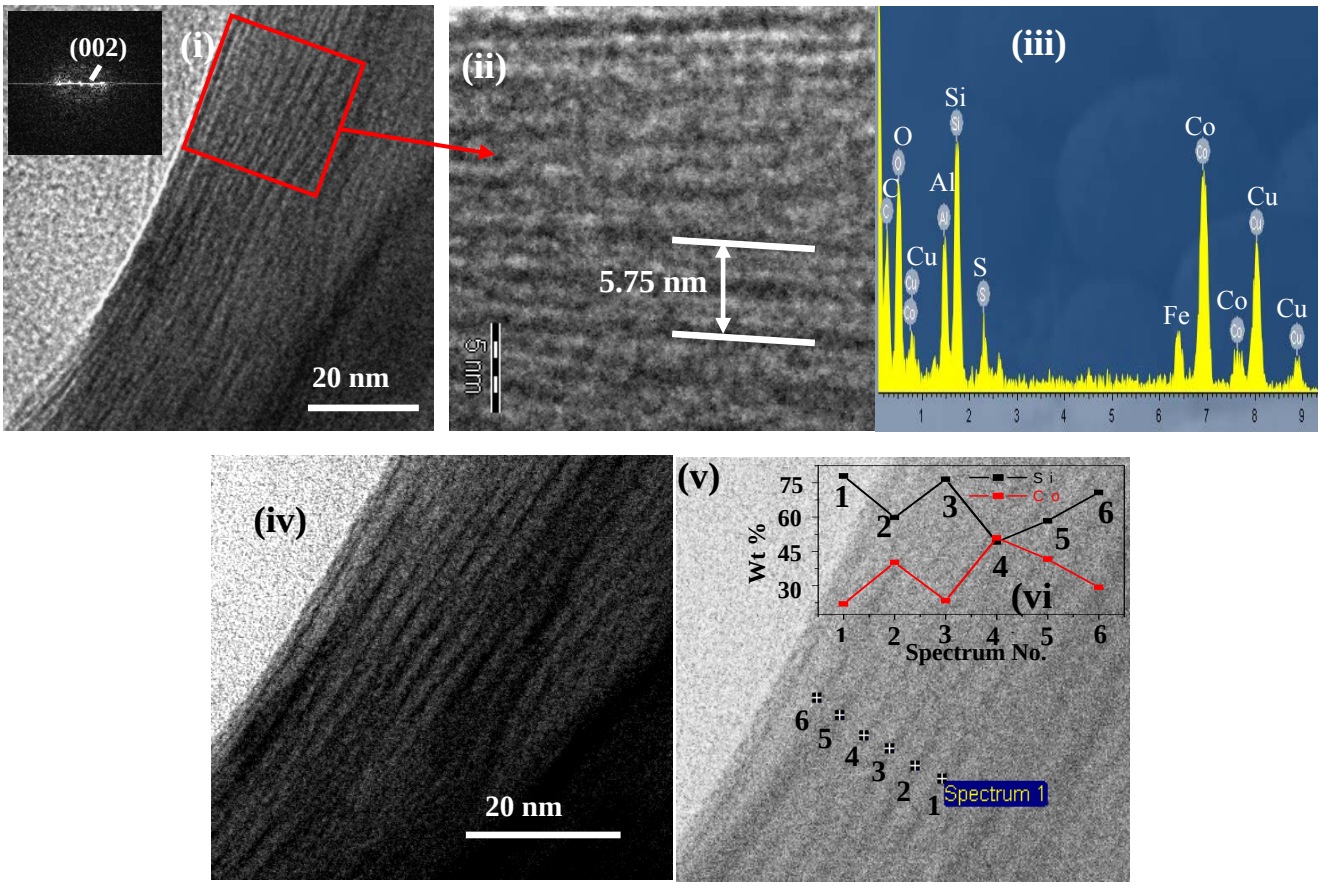
Supplementary Figure S4: FTIR spectra of (a) Mg-Al LDH-DDS (b) 1:1 Mg-Al LDH-DDS-MMT-DODMA hybrid (c) MMT-DODMA.

Supplementary Method S2: Preparation of Co-Al LDH-MMT hybrid:

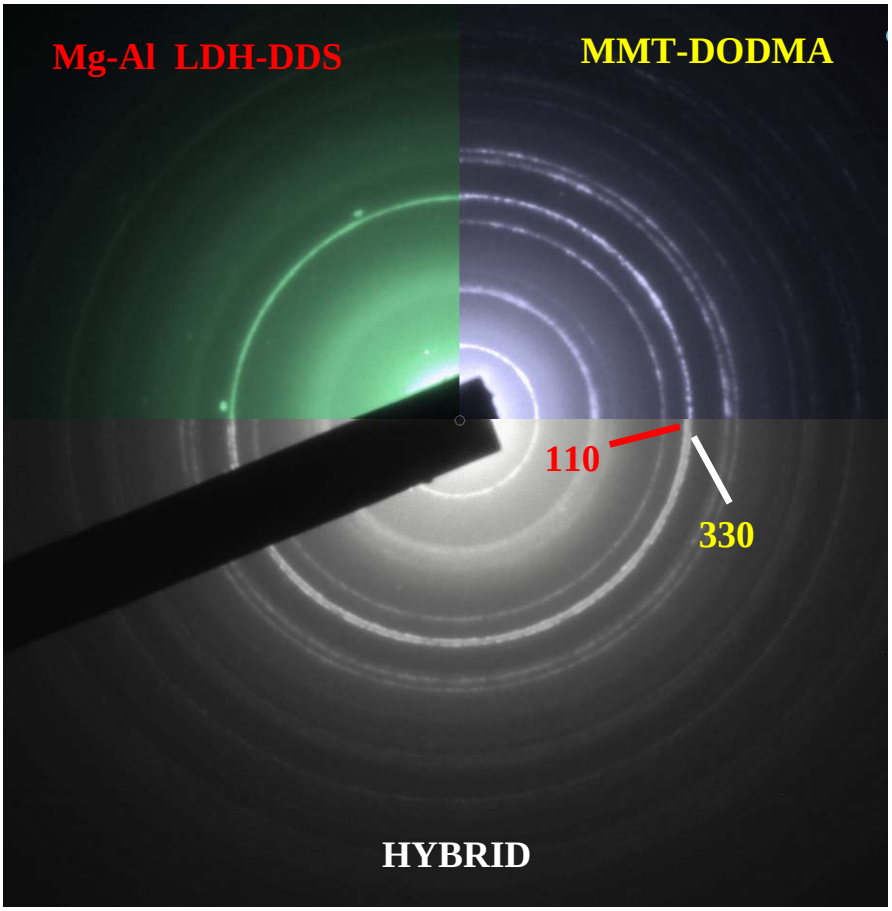
Co-Al LDH-DDS and MMT-DODMA were sonicated in chloroform separately for 15 minutes. The concentration of hydrotalcite or montmorillonite in dispersion is 2mg/ml. The dispersions of Co-Al LDH-DDS and MMT-DODMA were mixed and sonicated for 20 minutes. This dispersion was drop coated on a glass substrate and chloroform allowed to evaporate slowly and the X-ray diffraction pattern recorded. The composition of the resultant solid was determined by ICP-OES, TGA and elemental analysis. The composition of the hybrid that gave a unique XRD pattern is $Co_{0.34}Al_{0.53}Mg_{0.06}Fe_{0.066}Si_{0.98}O_{2.43}(OH)_{1.51}(DDS)_{0.17}(DODMA)_{0.11}\cdot 0.52H_2O$. This indicates that the hybrid is formed when the mole ratio of Co-Al LDH-DDS to montmorillonite is 1:1.



Supplementary Figure S5. (a) X-ray diffraction patterns of the solid obtained on solvent evaporation from different molar ratio mixtures of dispersions of Co-Al LDH-DDS and MMT-DODMA in chloroform. The shaded features are the Bragg reflections not observed in either Co-Al LDH-DDS or MMT-DODMA. (b) The linear variation of the d-spacing versus 1/*l* for the 1:1 hybrid. The interlayer spacing of the 1:1 hybrid is 5.81 nm and that of the Co-Al LDH-DDS is 2.62 nm and MMT-DODMA 3.91 nm. (c) FTIR spectra of (a) Co-Al LDH-DDS (b) 1:1 Co-Al LDH-DDS-MMT-DODMA hybrid (c) MMT-DODMA.

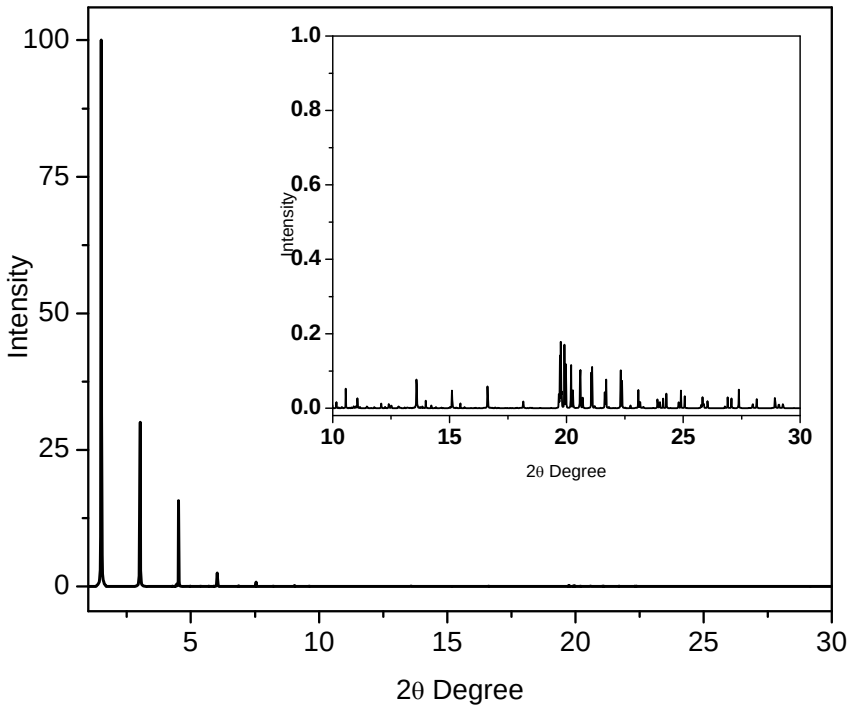


Supplementary Figure S6: (i) Cross-sectional HRTEM of 1:1 Co-Al LDH-DDS MMT-DODMA hybrid. (ii) The FFT generated diffraction pattern and an enlarged view of the Fourier filtered image obtained by an inverse FFT of the diffraction pattern. (iii) STEM and (iv) EDAX images corresponding to HRTEM image. (V) EDS spectrum of entire region (vi) Point scan EDS analysis.



Supplementary Figure S7. The SAED ring patterns of Mg-Al LDH-DDS, MMT-DODMA and hybrid of 1:1 Mg-Al LDH-DDS : MMT-DODMA.

Comparison of the selected area Electron Diffraction (SAED) patterns of Mg-Al LDH-DDS, MMT-DODMA and the 1:1 Mg-Al LDH-DDS:MMT-DODMA hybrid. The SAED patterns of the 1:1 hybrid show diffraction rings that belong to either Mg-Al LDH-DDS or MMT-DODMA. The broad ring at the higher angles corresponds to both the 110 plane of LDH (indicated in red color) and 330 plane of MMT (indicated in yellow color). The SAED pattern of the hybrid contains reflections of the Mg-Al LDH-DDS and MMT-DODMA sheets.



Reflection	2θ	Intensity
001	1.52	100
002	3.04	30
003	4.56	16
004	6.08	2.5
005	7.60	0.9
006	9.12	0.18
007	10.64	0.05

Supplementary Figure S8. Calculated XRD pattern for MgAl LDH-MMT hybrid in the Bragg-Brentano geometry. Reflection positions and intensities are shown in the accompanying Table.

Supplementary Table S1. Compositions from ICP, TGA and CHN analysis.

S. No	Sample Name	Actual Composition
1	Mg-Al LDH-DDS	$Mg_{0.66}Al_{0.33}(OH)_2(DDS)_{0.34}\cdot 0.89H_2O$
2	Co-Al LDH-DDS	$Co_{0.67}Al_{0.33}(OH)_2(DDS)_{0.331}\cdot 0.66H_2O$
3	MMT-DODMA	$Al_{1.49}Mg_{0.24}Fe_{0.27}Si_4O_{10}(OH)_2(DODMA)_{0.52}\cdot 0.35H_2O.$
4	Mg-Al LDH- MMT Hybrid	$Mg_{0.39}Al_{0.54}Fe_{0.07}$ $Si_{1.02}O_{2.50}(OH)_{1.50}(DDS)_{0.17}(DODMA)_{0.12}\cdot 0.75H_2O$
5	Co-Al LDH- MMT Hybrid	$Co_{0.34}Al_{0.53}Mg_{0.06}Fe_{0.066}$ $Si_{0.98}O_{2.43}(OH)_{1.51}(DDS)_{0.17}(DODMA)_{0.11}\cdot 0.52H_2O$