

# **Partial exfoliation of layered double hydroxides in DMSO: a route to transparent polymer nanocomposites**

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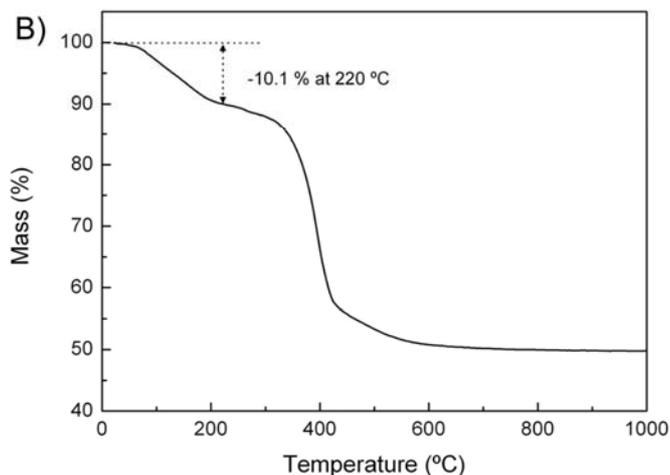
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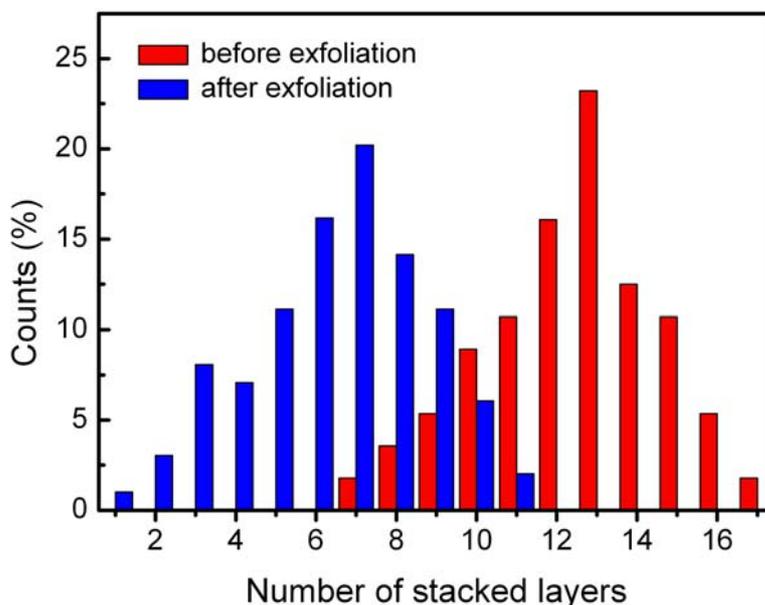
## **Electronic Supplementary Information**

A) ICP-AES elemental analysis:

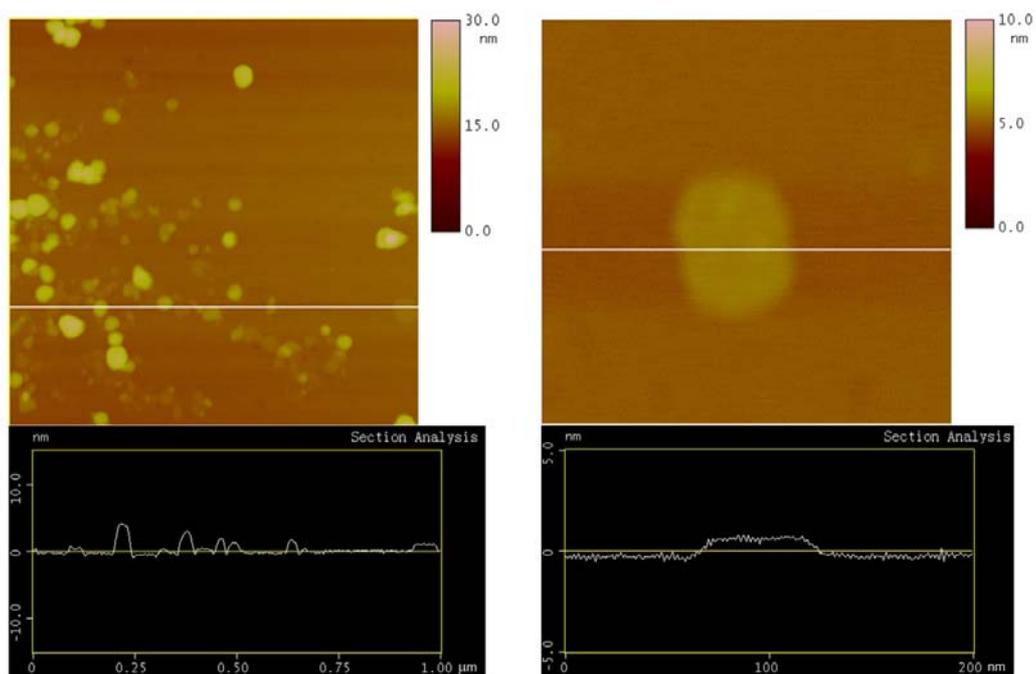
Element	Conc	S.D.	Unit
Al	146	1	mg/L
Mg	266	1	mg/L



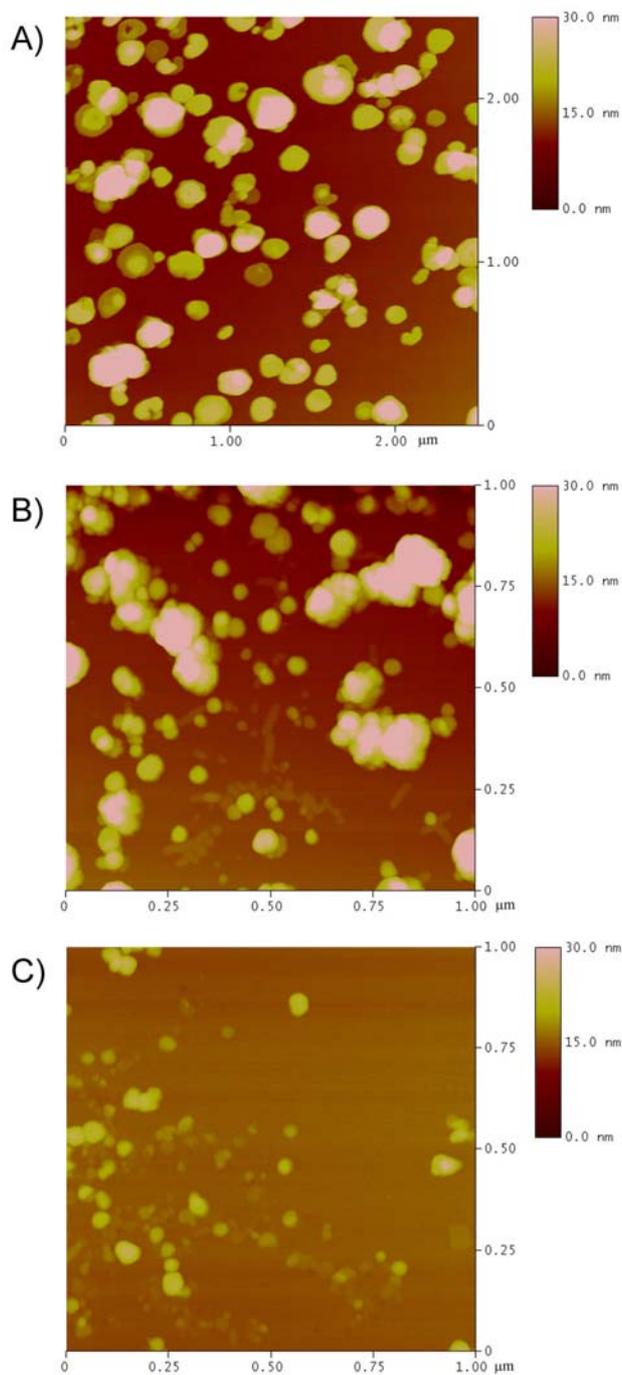
**Fig. S1** A) ICP-AES elemental analysis and B) TG curve of  $\text{Mg}_2\text{Al-NO}_3$  LDH sample. In panel B, the first stage of weight loss (10.1%) below 220 °C is due to the removal of interlayer water molecules. The second stage of weight loss derives from the dehydroxylation and decomposition of the interlayer nitrate anions.



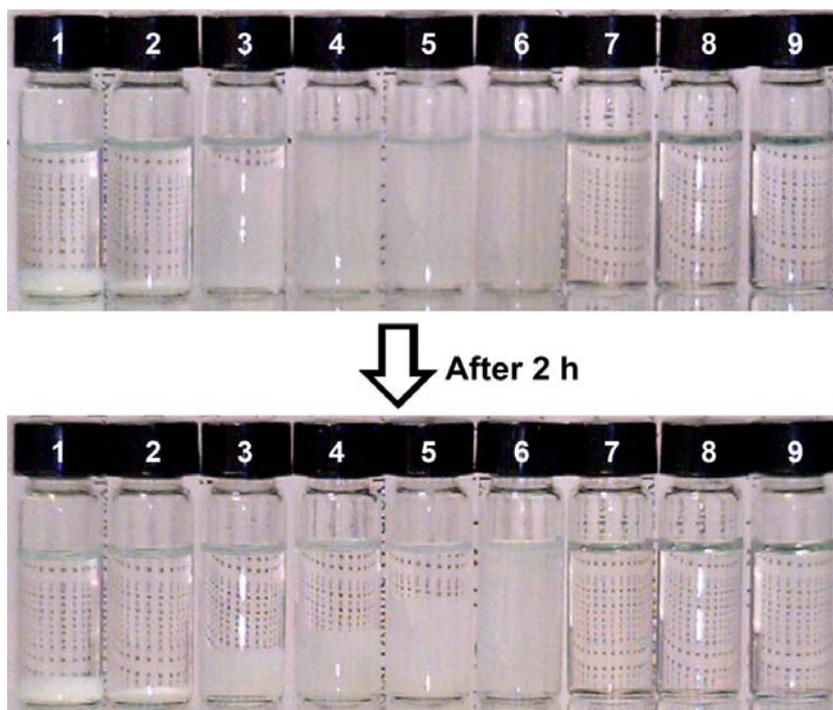
**Fig. S2** The distribution histogram of LDH layer number before and after DMSO exfoliation.



**Fig. S3** Tapping-mode AFM images of the LDH nanosheets deposited on mica substrate from formamide suspension, with height profiles along the marked white lines.



**Fig. S4** Tapping-mode AFM images of the LDH nanoplatelets deposited on mica substrate from A) water, B) DMSO, and C) formamide suspensions. The average lateral size calculated based on the AFM images are  $109.8 \pm 33.3$  nm,  $37.7 \pm 13.2$  nm, and  $24.4 \pm 9.1$  nm, respectively.

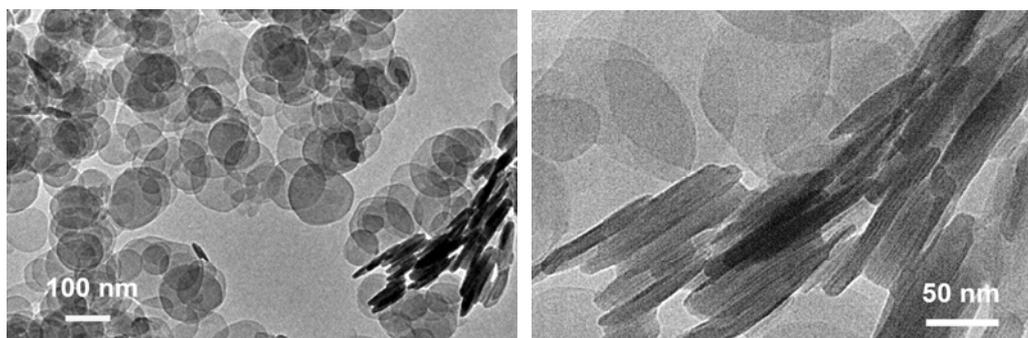


**Fig. S5** Photographs of the colloidal suspensions of LDHs in 1) acetone, 2) acetonitrile, 3) THF (tetrahydrofuran), 4) DMF (dimethyl formamide), 5) ethanol, 6) water, 7) NMP (N-methylpyrrolidone), 8) DMSO (dimethyl sulfoxide), and 9) formamide. Among these solvents, 7) NMP, 8) DMSO and 9) formamide led to the formation of transparent LDH suspensions. When 1) acetone, 2) acetonitrile, and 3) THF were used, sedimentation occurred just after shaking. For 4) DMF and 5) ethanol, the LDHs flocculated after standing 2 hours. The LDH suspension in 6) water was translucent, and no sediment was observed after standing over months.

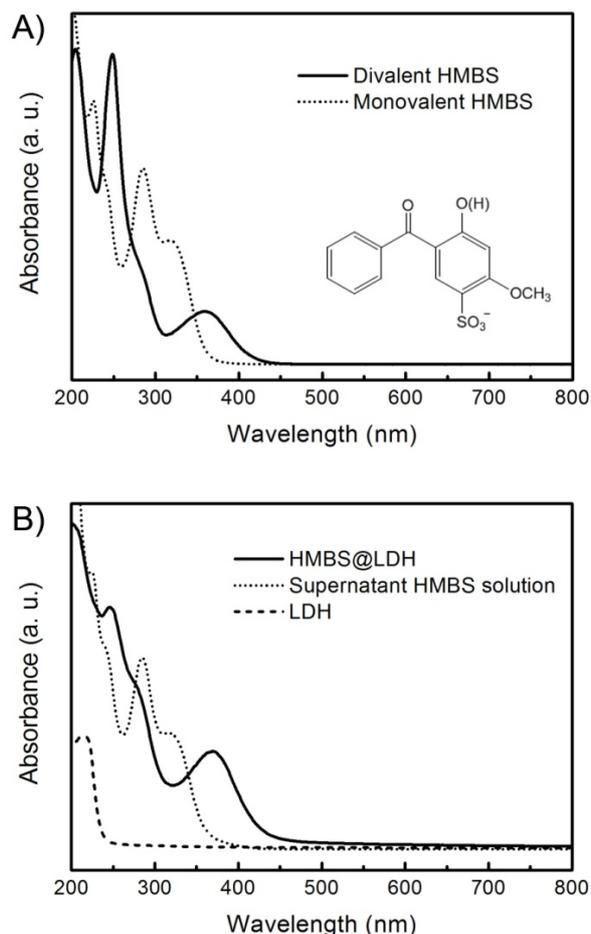
**Table S1** ICP-MS elemental analyses of the LDH and HMBS@LDH supernatant solutions after exfoliation in formamide and DMSO (the suspensions were centrifuged at 16 000 rpm for 60 min).

	Formamide			DMSO		
	Content in supernatant (%)		Al:Mg	Content in supernatant (%)		Al:Mg
	Al	Mg		Al	Mg	
LDH	0.81	25.40	1:31.4	0.087	0.90	1:10.5
HMBS@LDH	0.027	5.07	1:186	≤0.0041	0.75	1:183.8

The elemental analysis result shows that the dissolution degree of LDHs in DMSO is much lower than that in formamide. It also shows that after being intercalated with HMBS, the dissolution degree of LDHs, especially for the Al content, was greatly decreased.

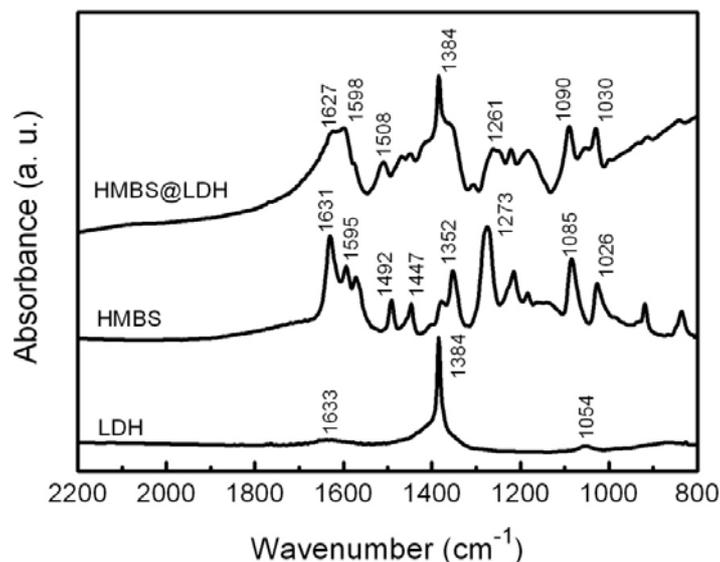


**Fig. S6** Typical TEM images of HMBS@LDH nanocrystals.

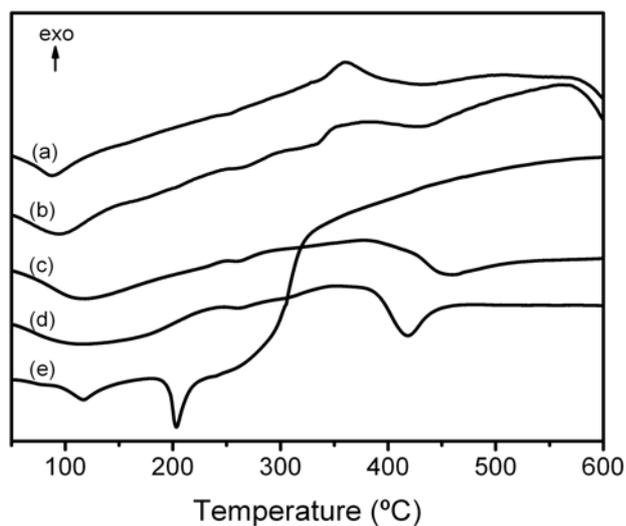


**Fig. S7** A) UV-Vis spectra of divalent and monovalent HMBS sodium salts. The inset is the chemical structure of HMBS molecule. B) UV-Vis spectra of LDHs, supernatant HMBS solution after intercalation, and HMBS@LDHs. HMBS is a dibasic acid containing a strong sulfonic group ( $pK_a \approx 1.6$ ) and a weaker phenolic group ( $pK_a \approx 8$ ).<sup>1</sup> As shown in panel A, its monovalent and divalent sodium salts exhibited very different UV-Vis absorption. In our case, monovalent HMBS anions were used to exchange the nitrate ions of LDHs, yielding a light-yellow HMBS@LDH intercalation product. The UV-Vis spectrum shown in panel B indicated that the intercalated HMBS within the LDH was a mixture of the monovalent and the divalent anions. However, the HMBS molecules in the supernatant solution still maintained in the monovalent form (panel B). The presence of the divalent HMBS anions within the LDH interlayers can be ascribed to a conversion from the monovalent to the divalent anions through the following reaction:<sup>1</sup>

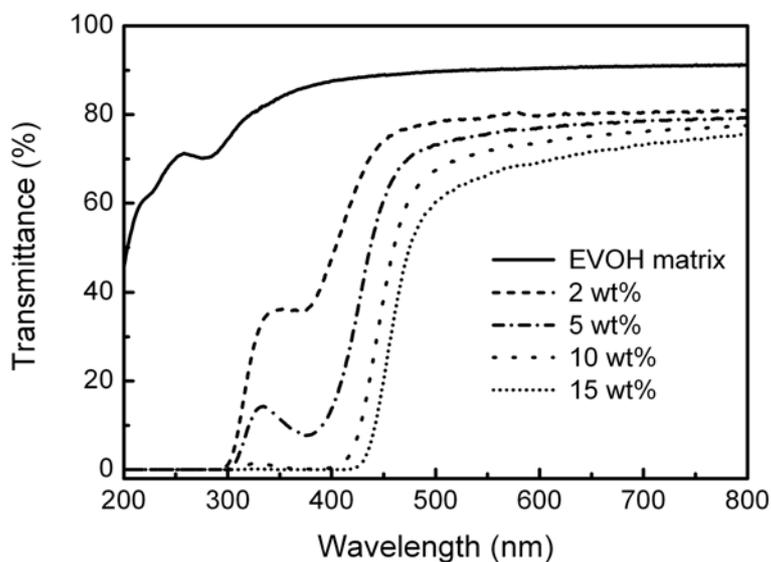




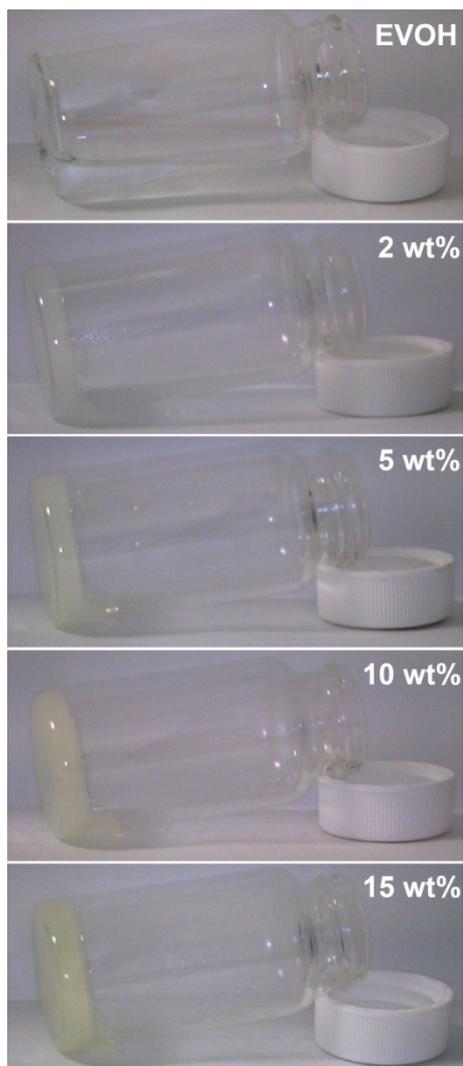
**Fig. S8** FTIR spectra of LDHs, HMBS and HMBS@LDHs. In the spectrum of LDHs, the intense absorption peak at  $1384\text{ cm}^{-1}$  is attributed to N–O stretching vibrations of  $\text{NO}_3^-$  ions. HMBS is characterized by absorption bands at  $1085$  and  $1026\text{ cm}^{-1}$  (sulphonate  $\nu\text{SO}_3^-$ );  $1352\text{ cm}^{-1}$  ( $\nu\text{R-SO}_2\text{-OH}$ );  $1273\text{ cm}^{-1}$  ( $\nu\text{Ar-O-CH}_3$ );  $1595$ ,  $1492$ , and  $1447\text{ cm}^{-1}$  (aromatic ring  $\nu\text{C=C}$ ); and  $1631\text{ cm}^{-1}$  (carbonyl  $\nu\text{C=O}$ ). After the intercalation of HMBS into LDHs, the characteristic absorption bands of HMBS appeared in the spectrum of HMBS@LDH, indicating the successful intercalation of HMBS anions into the interlayer galleries of the LDHs. Compared to those of free HMBS, the variation in the band positions and intensities is ascribed to the interaction between the intercalated HMBS molecules and the host LDH layers.<sup>2</sup>



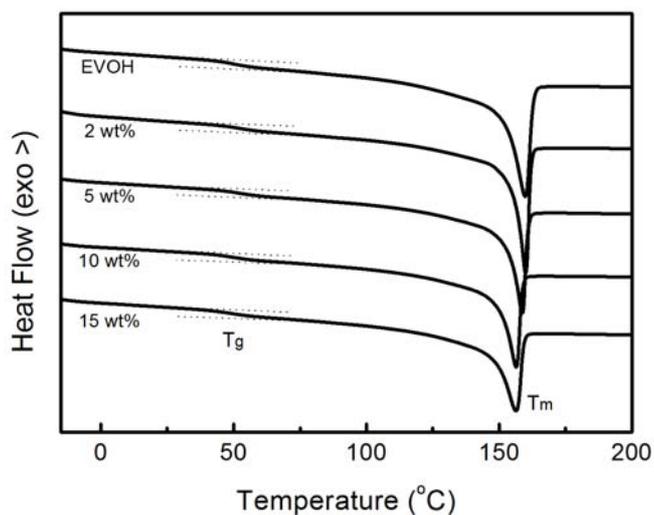
**Fig. S9** DSC curves of (a) HMBS@LDH-DMSO (dried from DMSO suspension), (b) HMBS@LDH-Formamide (dried from formamide suspension), (c) HMBS@LDH (dried from water suspension), (d) LDHs and (e) HMBS.



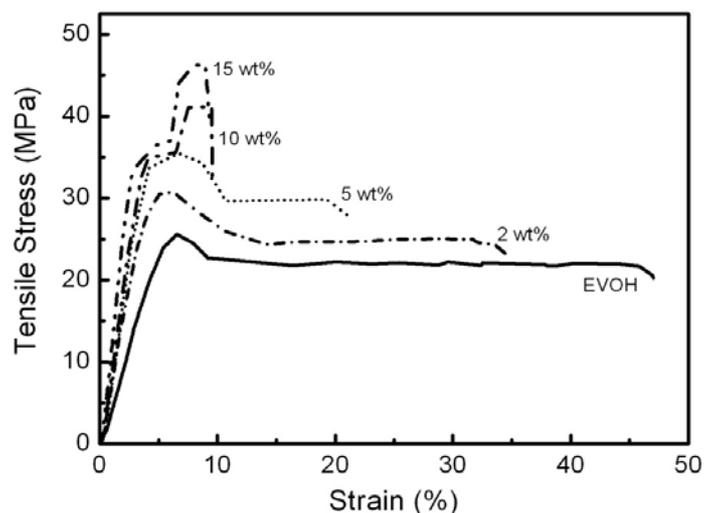
**Fig. S10** UV-Vis transmission spectra of EVOH and HMBS@LDH/EVOH composite films with different HMBS@LDH compositions using N, N-dimethylacetamide (DMAc) as the processing solvent, in which the HMBS@LDHs were not exfoliated.



**Fig. S11** EVOH solution in DMSO (EVOH, 5 wt%) and viscous gels formed from the EVOH solution in DMSO containing HMBS@LDHs with solid concentrations of 2, 5, 10, and 15 wt%, respectively.



**Fig. S12** Second-heating-scan DSC curves of EVOH films with different loadings of HMBS@LDHs.



**Fig. S13** Representative stress-strain curves of EVOH films with different loadings of HMBS@LDHs.

- 1 K. R. Franklin, E. Lee and C. C. Nunn *J. Mater. Chem.*, 1995, **5**, 565.
- 2 Y. J. Feng, D. Q. Li, Y. Wang, D. G. Evans and X. Duan *Polymer Degradation and Stability*, 2006, **91**, 789.