Supporting Information

Incorporation of Keplerate type Mo-O based macroanions into layered double hydrotalcite resulting in formation of all-inorganic composite films with remarkable third-order optical nonlinearities

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Preparation of $(NH_4)_{42}[\{(Mo^{VI})Mo_5^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2^{V}O_4(CH_3COO)\}_{30}] \cdot \approx 300H_2O \cdot 10CH_3COONH_4$

The compound was prepared according to the literature method (Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Peters, F., Organizational Forms of Matter: An Inorganic Super Fullerene and Keplerate Based on Molybdenum Oxide. *Angewandte Chemie International Edition* **1998**, *37*, 3359-3363.). In a typical preparation, 5.6 g $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ and 12.5 g CH_3COONH_4 was dissolved in 250 mL of water. The solution of 0.8 g $N_2H_4\cdot H_2SO_4$ in water was added to the above solution, stirred for ten minutes and the colour of the solution changed to blue-green, followed by addition of 83 mL 50% (V/V) glacial acetic acid. After the reaction, the mixture was placed in an open conical flask at room temperature in a fume hood (the colour slowly turns to brown). Red-brown crystals were filtered off and the precipitate was washed with ethanol, finally dried and kept at room temperature for 4 days. Yield: 52% (based on ammonium molybdate).

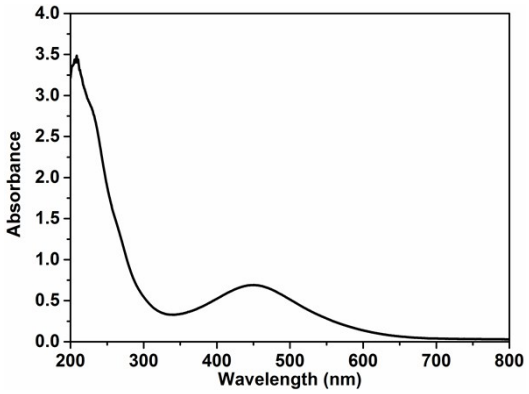

Fig. S1 UV-vis spectrum of the aqueous solution of $(NH_4)_{42}[\{(Mo^{VI})Mo_5{}^{VI}O_{21}(H_2O)_6\}_{12}\{Mo_2{}^{V}O_4(CH_3COO)\}_{30}]\cdot\approx 300H_2O\cdot 10CH_3COONH_4$

Zn_2Al-LDH preparation

The ZnAl-CO_3 and ZnAl-NO_3 LDH compounds were prepared according to the literature method (Zhao, J.; Kong, X.; Shi, W.; Shao, M.; Han, J.; Wei, M.; Evans, D. G.; Duan, X., Self-Assembly of Layered Double Hydroxide Nanosheets/Au Nanoparticles Ultrathin Films for Enzyme-Free Electrocatalysis of Glucose. *Journal of Materials Chemistry* **2011**, *21*, 13926-13933.). In a typical preparation, $Zn(NO_3)_2\cdot 6H_2O$ (2 mmol), $Al(NO_3)_3\cdot 9H_2O$ (1 mmol) and urea (12 mmol) were dissolved in 200 mL of water. The solution was heated and stirring for 24 hours at 100 °C. The obtained carbonate type LDH (Zn_2Al-CO_3) was washed with water and dried at 60 °C. The 0.1 g obtained Zn_2Al-CO_3 containing 0.15 mmol $NaNO_3$ is dispersed in 100 mL of aqueous solution containing 0.15 mmol $NaNO_3$ and CO_2 is removed, 31 uL concentrated HNO_3 was added and stirred under N_2 atmosphere for 24h, the ion exchange transformed to NO_3^- form. The precipitated (Zn_2Al-NO_3) was isolated by centrifugation, washed with deionized water and dried at room temperature. The XRD patterns and SEM images of the resulting Zn_2Al-LDH were shown in Figs. S2 and S3, respectively, which are matching with the reported ones.

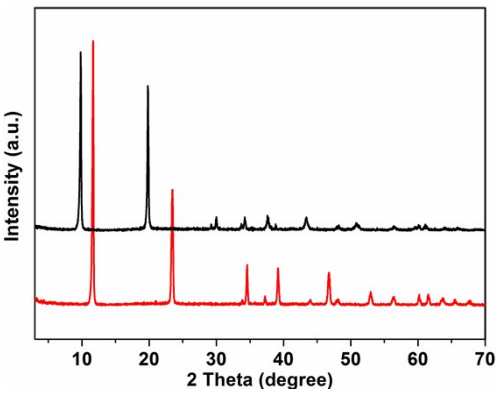

Fig. S2 XRD patterns of Zn_2Al-CO_3 (red line) and ZnAl-NO_3 LDH (black line).

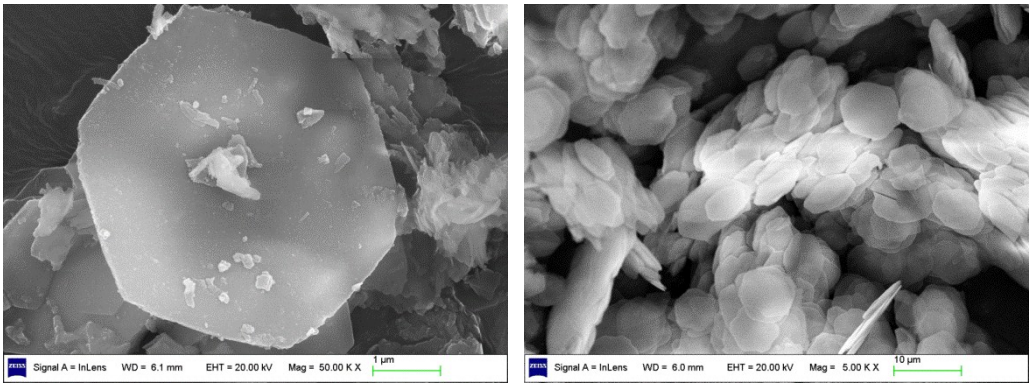

Fig. S3 SEM images of Zn_2Al-LDH with different magnifications. Both the ZnAl-CO_3 LDH and ZnAl-NO_3 LDH show the same morphology.

Zn_2Al-LDH exfoliation

The exfoliation of ZnAl-NO_3 LDH was carried out according to the literature method (Li, L.; Ma, R.; Ebina, Y.; Iyi, N.; Sasaki, T., Positively Charged Nanosheets Derived Via Total Delamination of Layered Double Hydroxides. *Chemistry of materials* **2005**, *17*, 4386-4391.). In detail, the Zn_2Al-NO_3 (0.1 g) and 100 mL of formamide was added to the Erlenmeyer flask, stirred with a mechanical stirrer at 160 rpm under N_2 for two days. The resulting mixture was centrifuged at 3000 rpm for further 10 minutes to obtain a transparent and stable well-dispersed colloidal suspension.

The following formulas are used to calculate the third order nonlinear refractive index n_2 (esu), the nonlinear absorption coefficient β (esu) and the third-order optical nonlinear

susceptibility $\chi^{(3)}$ (esu) (Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Stryland WV. IEEE J Quantum Electron 1990; 26: 760).

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}\left|\Delta\phi_0\right| \qquad (1)$$

$$\Delta\phi_0 = kL_{eff}\gamma I_0 \qquad (2)$$

$$L_{eff} = (1-e^{-\alpha_0 L})/\alpha_0 \qquad (3)$$

$$n_2(esu) = \frac{cn_0}{40\pi}\gamma(m^2/W) \qquad (4)$$

where, $\Delta T_{P\text{-}V}$ is the normalized peak-valley difference, $\Delta\varphi_0$ is the phase shift of the beam at the focus, $K = 2\pi/\lambda$ is the wave vector, I_0 (unit: W/m^2) is the intensity of the light at focus, L_{eff} is the effective length of the sample defined in terms of the linear-absorption coefficient α_0 and the true optical path length through the sample, n_0 is the linear refractive index, and γ is optical Kerr constant. The conversion can be realized between n_2 (esu) and γ (m^2/W) by equations (4).

When the sample is measured under open aperture, the normalized transmittance T (z, s = 1) can be expressed as

$$T(z, s=1) = \sum_{m=0}^{\infty}\frac{[-q_0(z)]^m}{(m+1)^{3/2}} \qquad (5)$$

where $q_0(z) = \beta I_0 L_{eff} \Big/ (1+z^2/z_0^2)$, β is nonlinear absorption coefficient. From equation (5) we can get β. From equation (6), we can get the third-order optical nonlinear susceptibility $\chi^{(3)}$.

$$\chi^{(3)} = \sqrt{(\frac{cn_0}{160\pi^2}\gamma)^2 + (c\beta n_0^3\lambda/64\pi^3)^2} \qquad (6)$$

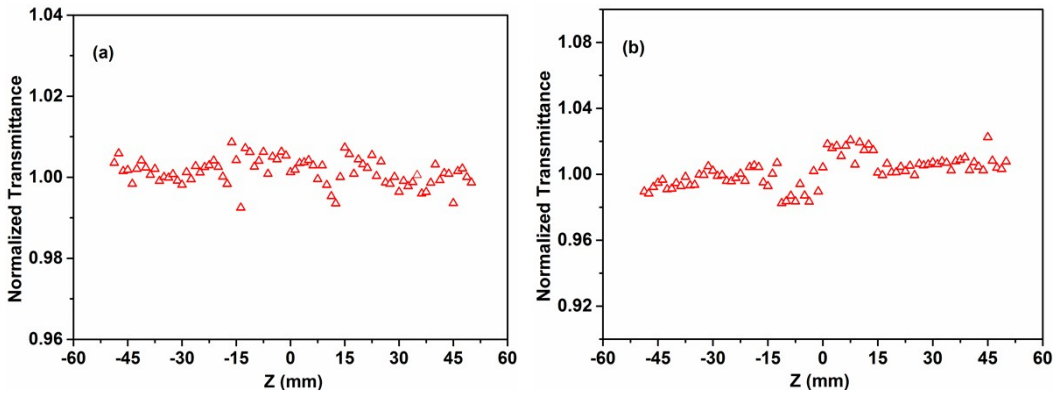

Fig. S4 Z-scan curves of the Zn_2Al-NO_3 LDH suspension under open-aperture (a) and closed-aperture (b).

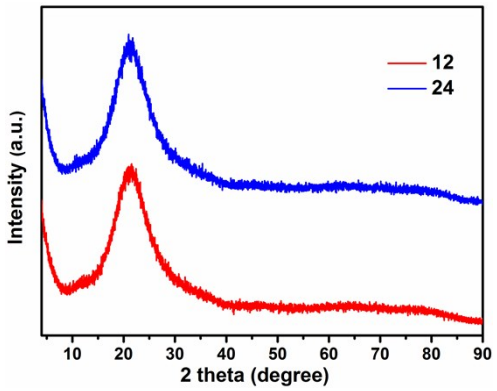

Fig. S5 The XRD patterns of the composite films (Zn_2Al-LDH/{Mo_{132}-Ac})$_n$ with number of layers; n = 12 (red line) and n = 24 (blue line), showing only wide peaks because of the fact that the materials deposited on the films are not thick enough..