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# Supporting Information

## Synthesis of Polyoxometalates Pillared Zn-Cr LDHs for the Photocatalytic $CO_2$ Reduction and $O_2$ Evolution

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## Catalysts preparation

### Chemicals

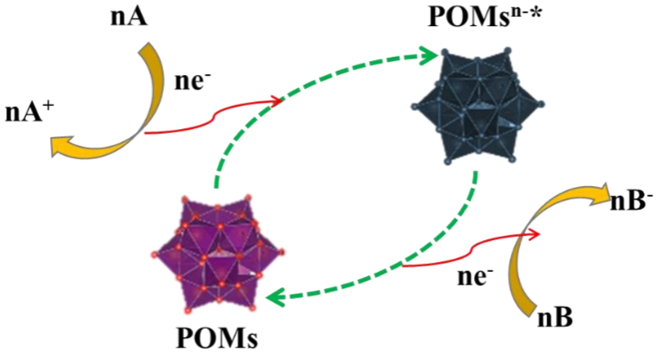
$Zn(NO_3)_2 \cdot 9H_2O$ (99.9%), $Cr(NO_3)_3 \cdot 6H_2O$ (99.9%), $NaNO_3$ (99.0%), NaOH (99.0%), $Na_2CO_3 \cdot 10H_2O$ (99.0%), $NaIO_3$ (99.5%) were purchased from Wako Pure Chemical Industries, Ltd. Ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$) was purchased from Stream Chemicals, Inc. Sodium silicotungstate hydrate ($Na_4SiW_{12}O_{40} \cdot xH_2O$) was purchased from Nippon Inorganic Colour & Chemical Co., Ltd. All the chemicals were used directly without further purification. $CO_2$ gas (99.995%) and Ar gas (G3 grade) were purchased from Taiyo Nippon Sanso Corporation. Ultrapure water was produced by Milli-Q® Advantage A10 Water Purification System.

### Preparation method

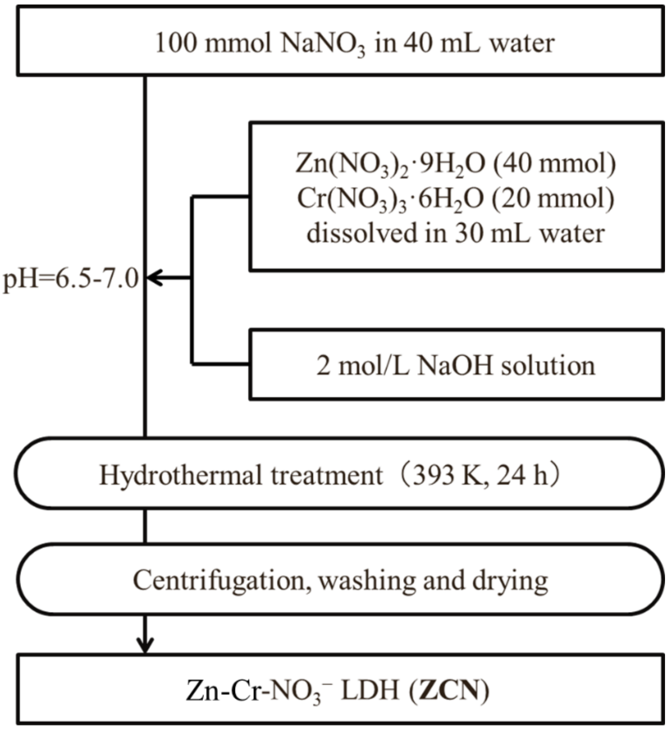
**Zn-Cr-$NO_3$ LDH (ZCN):** The ion-exchange precursor, $NO_3^-$-type Zn-Cr LDH was synthesized by the co-precipitation method (Supplementary Fig. 2). In detail, Solution A was prepared by dissolving 40 mmol of $Zn(NO_3)_2 \cdot 9H_2O$ and 20 mmol of $Cr(NO_3)_3 \cdot 6H_2O$ in 30 mL. Solution B was 2 mol/L NaOH aqueous solution and used as the precipitant. Solution C was prepared by dissolving 100 mmol $NaNO_3$ in 20 mL water. Solution A and Solution B were added dropwise into Solution C via variable-flow peristaltic pumps (Fisher Scientific) with rapid stirring to form a green slurry. The pH was maintained at 6.5-7.0 by controlling the adding speed. After co-precipitation, the slurry was transferred into 100 mL PTFE containers, sealed in an autoclave and hydrothermally treated at 393 K for 24 hours. Then the precipitate was centrifuged and washed at least 3 times. The LDH powder was obtained by grinding the precipitate after drying at 353 K in an oven overnight. The as-prepared $NO_3^-$-type LDH was described as "ZCN".

**Zn-Cr-$CO_3^{2-}$ LDH (ZCC):** $CO_3^{2-}$-type Zn-Cr LDH was synthesized via an ion-exchange process from the precursor ZCN (Supplementary Fig. 3). In detail, 0.5 g of $Na_2CO_3 \cdot 6H_2O$ was dissolved in 40 mL water to make a solution. 1g of ZCN was dispersed in the solution with ultrasonic treatment for 20 min. After that, the dispersion was transferred into a 50 mL PTFE container, sealed in an autoclave and hydrothermally treated at 373 K for 24 hours. Then the precipitate was filtered and washed with water repeatedly at least 3 times. The LDH powder was obtained by grinding the precipitate after drying at 353 K in an oven overnight. The as-prepared $CO_3^{2-}$-type LDH was denoted “ZCC”.

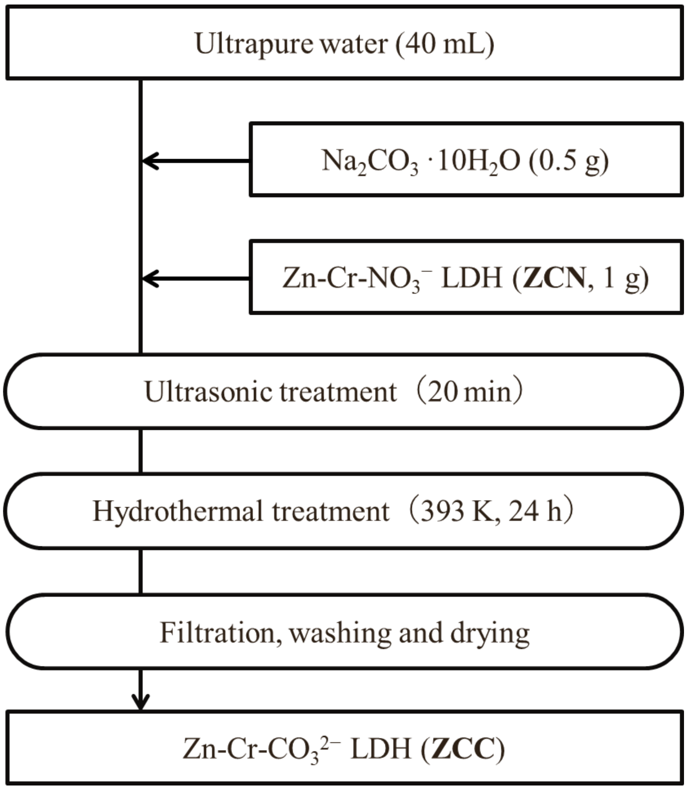
**$H_2W_{12}O_{40}^{6-}$ pillared Zn-Cr LDH (ZCHW):** $H_2W_{12}O_{40}^{6-}$ pillared Zn-Cr LDH was also synthesized via an ion-exchange process from the precursor ZCN (Supplementary Fig. 4). In detail, 1.6 g of $(NH_4)_6H_2W_{12}O_{40}$ was dissolved in 40 mL water to make a solution, and the pH was afterwards adjusted to 5.5-6.0 using 0.1 mol/L NaOH solution. 1g of ZCN was dispersed in the $H_2W_{12}O_{40}^{6-}$ solution with ultrasonic treatment for 20 min. After that, the dispersion was transferred into a 50 mL PTFE container, sealed in an autoclave and hydrothermally treated at 373 K for 24 hours. Then the precipitate was filtered and washed with water at least 3 times. The LDH powder was obtained by grinding the precipitate after drying at 353 K in an oven overnight. The as-prepared $H_2W_{12}O_{40}^{6-}$ pillared LDH was denoted “ZCHW”.



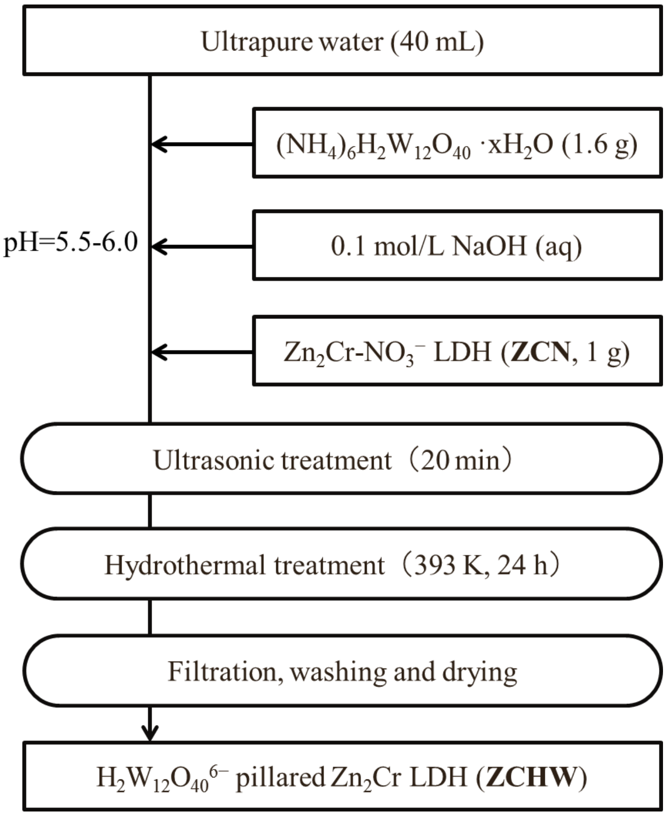
**Supplementary Fig. 1** Mechanism of redox reactions involving POMs as catalysts.



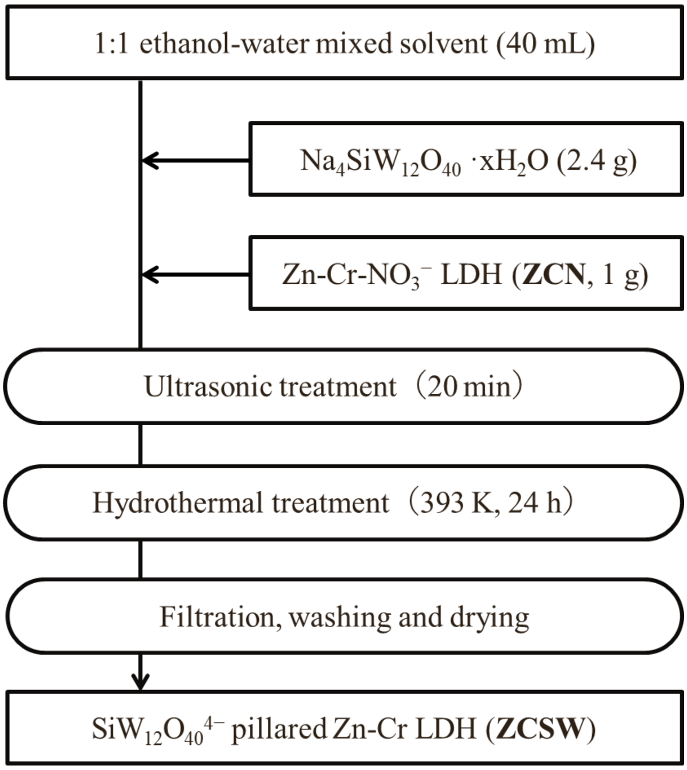
**Supplementary Fig. 2** Synthetic flowchart of Zn-Cr-NO$_3^-$ LDH by co-precipitation method.



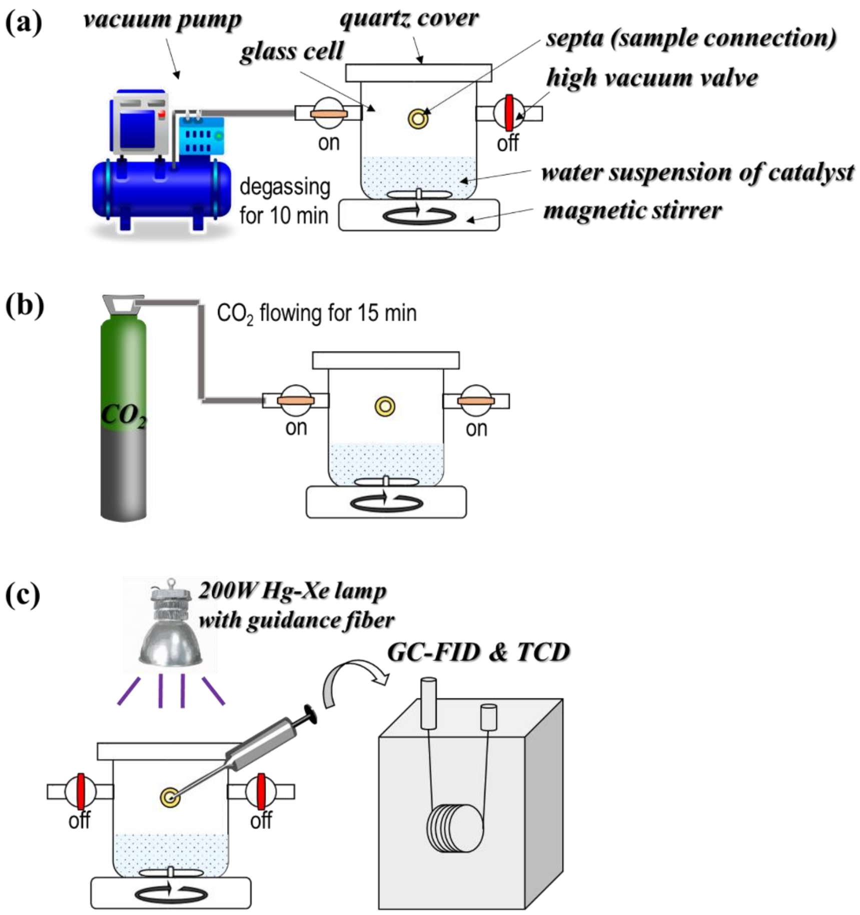
**Supplementary Fig. 3** Synthetic flowchart of Zn-Cr-$CO_3^{2-}$ LDH by ion-exchange method.



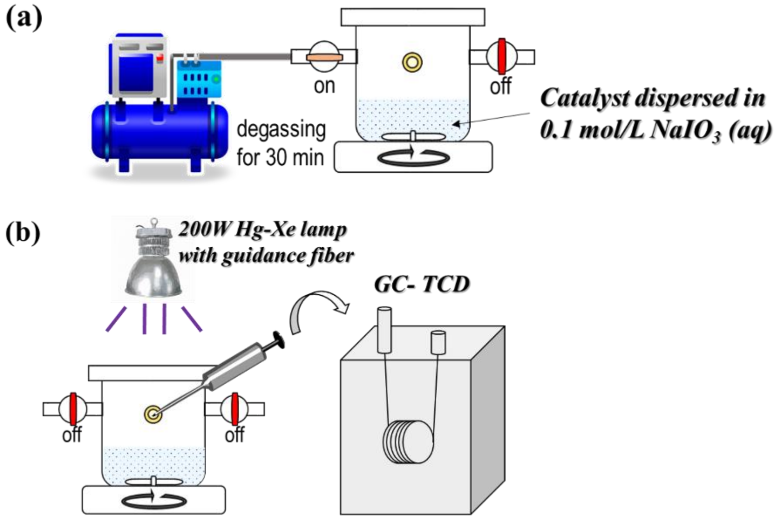
**Supplementary Fig. 4** Synthetic flowchart of $H_2W_{12}O_{40}^{6-}$-pillared Zn-Cr LDH by ion-exchange method.



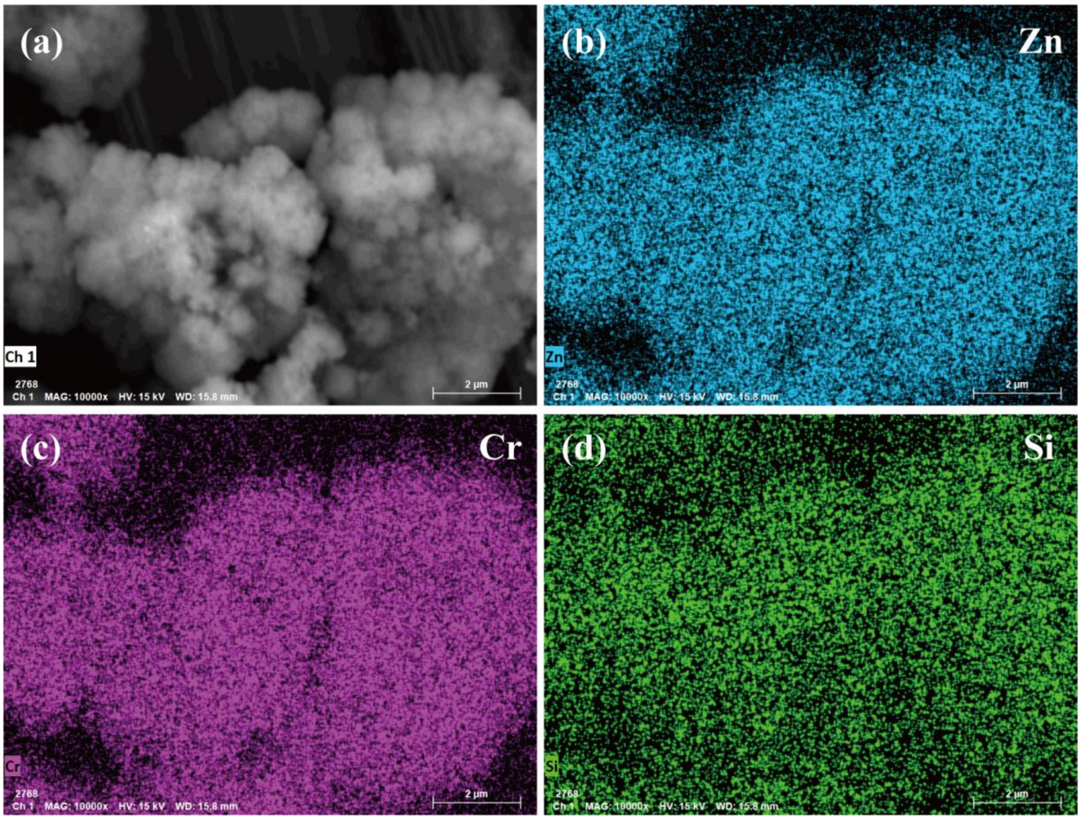
**Supplementary Fig. 5** Synthetic flowchart of $SiW_{12}O_{40}^{4-}$-pillared Zn-Cr LDH by ion-exchange method.



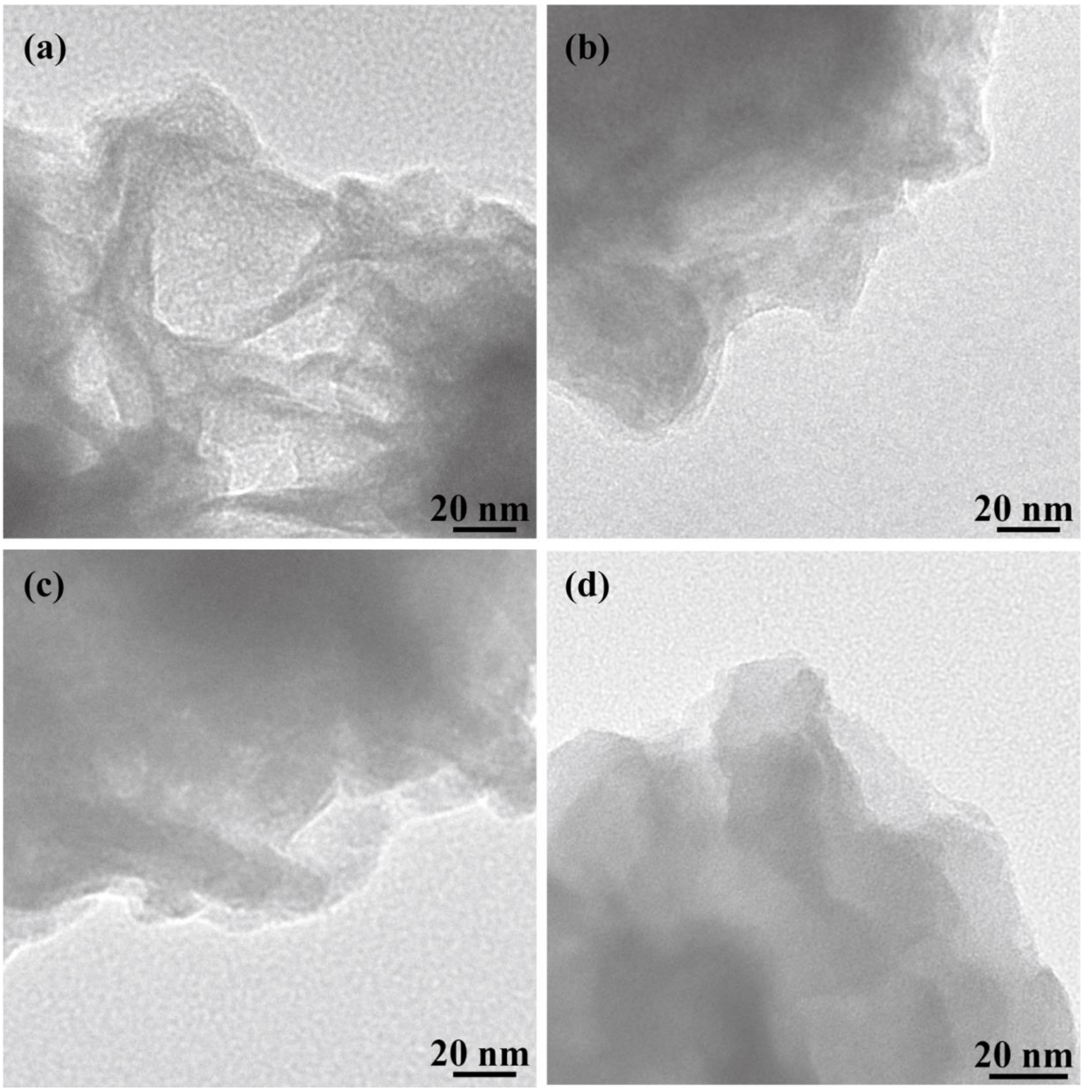
**Supplementary Fig. 6** Schematic diagram of the apparatus for the photo-reduction of $CO_2$: (a) degassing, (b) $CO_2$ flowing, (c) UV irradiation, sampling, and quantification.



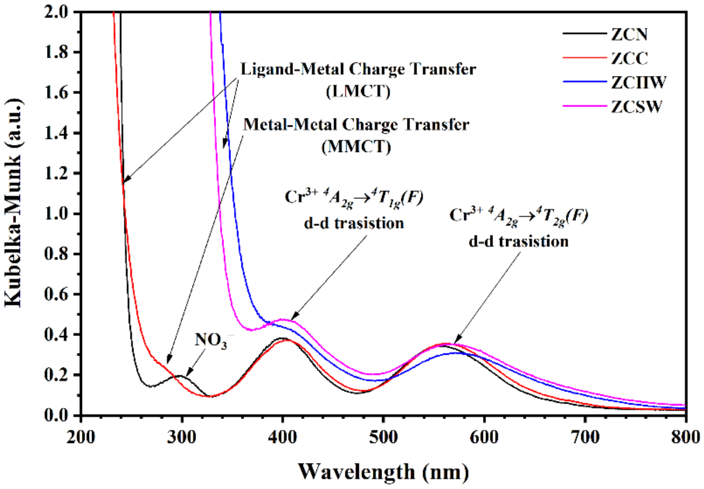
**Supplementary Fig. 7** Schematic diagram of the apparatus for the photo-oxidation of water in NaIO$_3$ aqueous solution: (a) degassing, (c) UV irradiation, sampling, and quantification.



**Supplementary Fig. 8** EDS mapping images of ZCSW.



**Supplementary Fig. 9** TEM images of (a) ZCN, (b) ZCC, (c) ZCHW and (d) ZCSW.



**Supplementary Fig. 10** UV-Vis DRS spectra Zn-Cr LDHs intercalated with different inorganic anions.

**Supplementary Table 1** FT-IR data of the fingerprint peaks observed in the pristine POMs and as-prepared POMs pillared LDHs

| Material | $W=O_d$ (cm$^{-1}$) $O_d$: corner oxygen | $W\text{-}O_b\text{-}O$ (cm$^{-1}$) $O_b$: bridge oxygen (different $W_3O_{10}$) | $W\text{-}O_c\text{-}O$ (cm$^{-1}$) $O_c$: bridge oxygen (same $W_3O_{10}$) | Si-O (cm$^{-1}$) |
|---|---|---|---|---|
| $Na_4SiW_{12}O_{40}$ | 979 | 925 | 782 | 1020 |
| ZCSW | 955 | 905 | 791 | 1005 |
| $(NH_4)_6H_2W_{12}O_{40}$ | 937 | 881 | 772 | N/A |
| ZCHW | 937 | 881 | 758 | N/A |