# Supporting Information

## Synchronously Enhanced Storage Stability and Adsorption Ability of MXene Achieved by Grafting Polyethylenimine†

Liang Li[1,2], Xian-ying Shi[1,2], Ting Huang[1,2*], Nan Zhang[1,2], Yong Wang[1,2*]

1. School of Chemistry, Southwest Jiaotong University, Chengdu, 610031, China
2. Key Laboratory of Advanced Technologies of Materials (Ministry of Education), Southwest Jiaotong University, Chengdu, 610031, China.

## S-I. Adsorption experiments

### 1.1 Adsorption kinetics

Adsorption kinetics were carried out at the initial concentrations of MO and Cr(VI) of 110 and 165 mg $L^{-1}$, respectively. The classical pseudo-first-order (equation (1)) and pseudo-second-order (equation (2)) kinetics models were selected to evaluate the adsorption performance. [1,2]

**Pseudo first-order model:**

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{1}$$

**Pseudo second-order model:**

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

Where $t$ (min) represents any time in the adsorption process and $q_t$ (mg $g^{-1}$) denotes the corresponding adsorption capacity, $q_e$ (mg $g^{-1}$) is the equilibrium adsorption capacity. $K_1$ ($min^{-1}$) and $K_1$ (g mg·$min^{-1}$) refer to the adsorption rate constants for the pseudo-first-order model and pseudo-second-order model, respectively.

### 1.2 Adsorption isotherms

The isothermal adsorption experiments were carried out at different initial concentrations of MO (120~300 mg $L^{-1}$, pH=3) and Cr(VI) (100~200 mg $L^{-1}$, pH=2) adsorption solutions. The

* Corresponding author:
E-mail: yongwang1976@swjtu.edu.cn (Y. Wang); huangting@home.swjtu.edu.cn (T. Huang)

classical Langmuir and Freundlich isotherm adsorption models were selected to simulate the adsorption isotherms,[3] as follows:

**Langmuir isothermal model:**

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

The assumptions of the Langmuir isothermal model include the same adsorption energy of the adsorption sites, generating a homogeneous monolayer of target molecule and no interaction with others, and forming a dynamic equilibrium between adsorption and desorption. Where $q_e$ and $q_m$ represent the equilibrium adsorption capacity (mg $g^{-1}$) and the maximum adsorption capacity (mg $g^{-1}$). The $K_L$ is Langmuir constant and represents the adsorption free energy, and the value is inversely proportional to the capacity of the adsorbate tendency to attach to the adsorbent. $C_e$ represents the equilibrium concentration (mg $L^{-1}$).

**Freundlich isothermal model:**

$$\ln q_e = \ln K_F + (\frac{1}{n}) \ln C_e \tag{4}$$

The Freundlich isothermal model assumes that the form of adsorption is multilayer adsorption and suitable for the heterogeneous adsorption. The $K_F$ is the Freundlich constant and represents the adsorption free energy between the adsorbate and the adsorbent. At the same time, $n$ also is constant which is the measure of the intensity of adsorption.

**1.3 Adsorption thermodynamics**

To identify the adsorption capacity of MPEI600 at different temperatures, the temperature of the adsorption solution was varied from 25 to 40 ℃ for MO adsorption measurements and from 25 to 55 ℃ for Cr(VI) adsorption measurements. The initial MO and Cr(VI) concentrations were 120 and 110 mg $L^{-1}$, and the volume of adsorption solution is 100 mL. The Van't Hoff equation was selected to fit the adsorption capacity of MO and Cr(VI) on MPEI600.[1,4]

**Van't Hoff equation:**

$$\Delta G^0 = -RT \ln K_L \tag{5}$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{6}$$

$$K_L = \frac{q_e}{C_e} \tag{7}$$

Where $\Delta G^0$ (kJ mol$^{-1}$), $\Delta S^0$ (kJ mol·K$^{-1}$) and $\Delta H^0$ (kJ mol$^{-1}$) are Gibbs free energy change, entropy change and enthalpy change, respectively. $K_L$ and $R$ respectively represent thermodynamic equilibrium constant and perfect gas constant, and $T$ (K) denotes absolute temperature.

**1.4 Stability and recyclability tests**

To study the adsorption stability of pure MXene and MPEI600 composite, the samples had been stored for 2 months at room temperature without deliberately avoiding the sunlight and air, and then the adsorption behaviors of MXene and MPEI600 were tested. Adsorbents after adsorbing MO and Cr(VI) were collected, and eluted using 0.5 M NaOH solution (100 mL) under $N_2$ atmosphere for 2 h. Subsequently, the adsorbent was washed with DI water until the pH value of the cleaning solution reached neutral, and then the adsorbent was reused for next adsorption experiments.

## S-II. Results and discussion

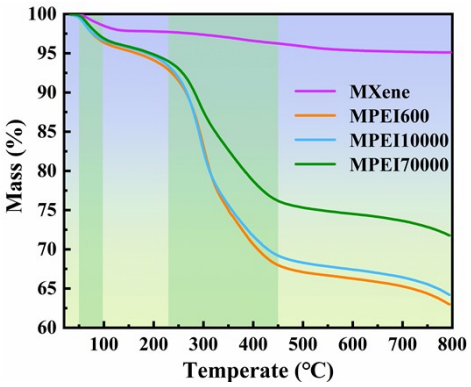


**Fig. S1** TGA curves of MXene, MPEI600, MPEI10000 and MPEI70000.

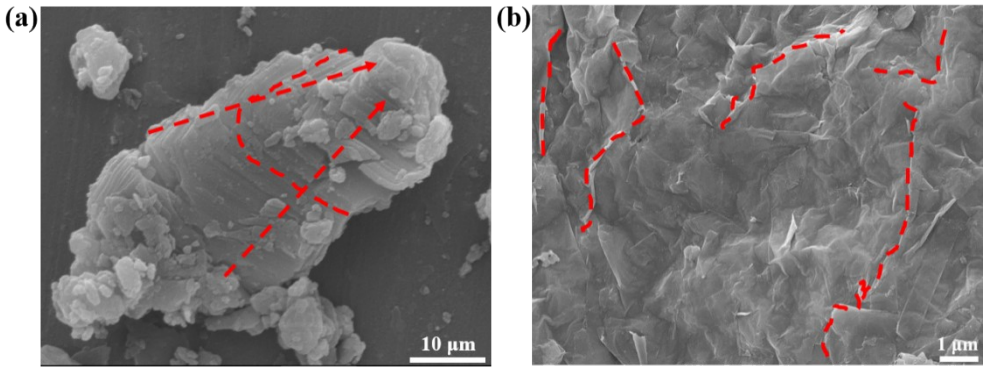


**Fig. S2** SEM images of (a) MAX and (b) MXene.

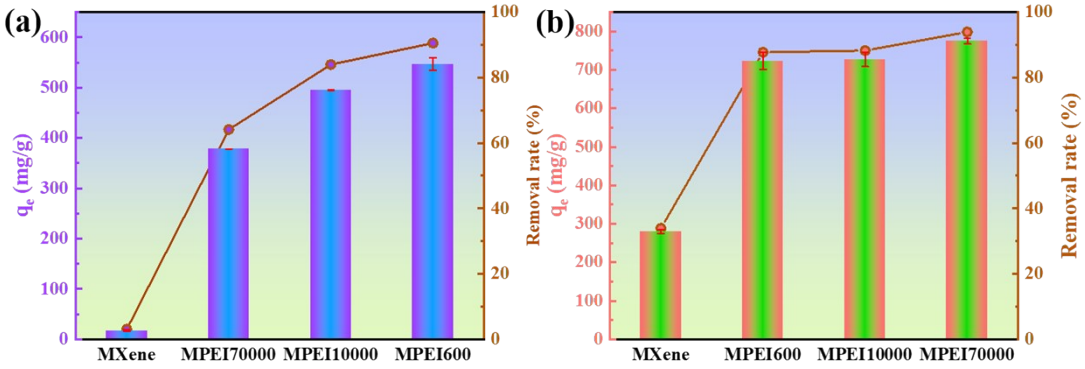


**Fig. S3** (a) Removal rate and adsorption capacity of (a) MO and (b) Cr(VI) adsorbed by different samples as indicated.

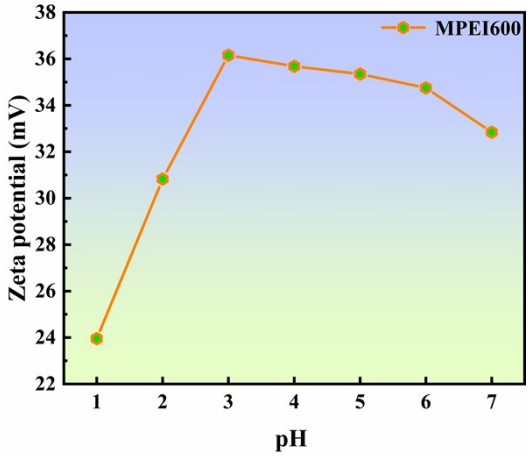


**Fig. S4** Zeta potential of MPEP600 solution at different pH values.

**Table. S1** Kinetic parameters for adsorption of MO and Cr(VI) by MPEI600.

| | Pseudo-first-order model | | | Pseudo-second-order model | | |
|---|---|---|---|---|---|---|
| | $q_e$ (mg g$^{-1)}$ | $K_1$ (min$^{-1}$) | $R^2$ | $q_e$ (mg g$^{-1}$) | $K_2$ (g mg·min$^{-1}$) | $R^2$ |
| MO | 131.8 | 0.00844 | 0.956 | 467.3 | 0.000292 | 0.999 |
| Cr(VI) | 154.9 | 0.00636 | 0.750 | 719.4 | 0.000280 | 0.999 |

**Table. S2** Parameters associated with the Langmuir and Freundlich isotherms for adsorption of MO and Cr(VI) by MPEI600.

| | Langmuir model | | | Freundlich model | | |
|---|---|---|---|---|---|---|
| | $q_m$ (mg g$^{-1}$) | $K_L$ (L mg$^{-1}$) | $R^2$ | $K_F$ (L mg$^{-1}$) | $n$ | $R^2$ |
| MO | 909.1 | 0.106 | 0.995 | 373.2 | 5.86 | 0.968 |
| Cr(VI) | 1239.5 | 0.038 | 0.985 | 122.9 | 2.05 | 0.995 |

**Table. S3** Thermodynamic parameters for the adsorption of MO and Cr(VI) by MPEI600.

| | $T$ (K) | $\Delta H^0$ (kJ mol$^{-1}$) | $\Delta S^0$ (kJ mol·K$^{-1}$) | $\Delta G^0$ (kJ mol$^{-1}$) |
|---|---|---|---|---|
| MO | 298.15 | 13.1 | 0.0637 | -5.82 |
| | 303.15 | | | -6.34 |
| | 308.15 | | | -6.51 |
| | 313.15 | | | -6.81 |
| Cr(VI) | 298.15 | 12.8 | 0.0520 | -2.69 |
| | 308.15 | | | -3.21 |
| | 318.15 | | | -3.42 |
| | 328.15 | | | -3.71 |

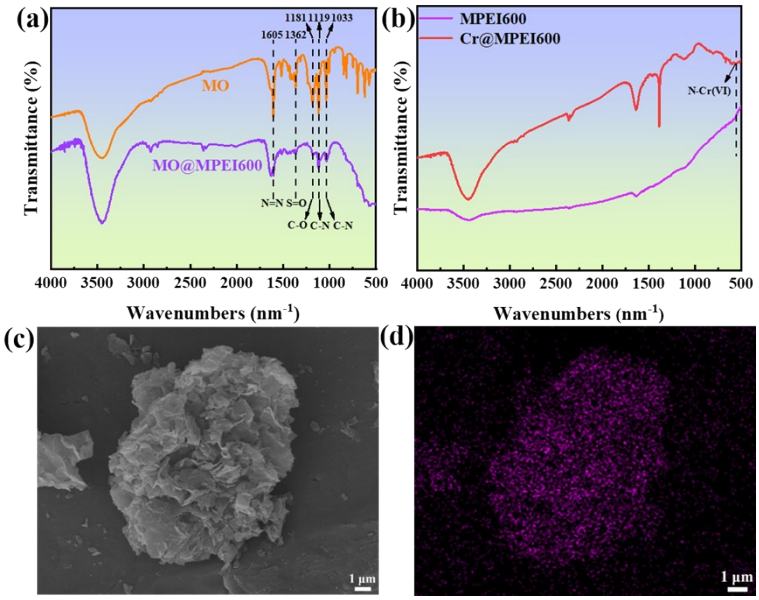


**Fig. S5** FTIR spectra of (a) MO and MO@MPEI600 and (b) MPEI600 and Cr@MPEI600. (c) SEM image and (d) Cr elemental distribution of MPEI600 after adsorbing Cr(VI).

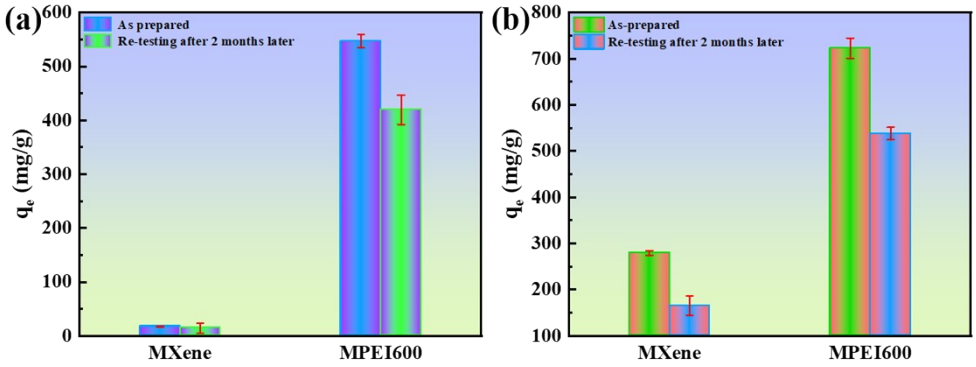


**Fig. S6** Comparison of the adsorption performance by MXene and MPEI600 as indicated before and after being stored for two months. (a) MO, and (b) Cr(VI).

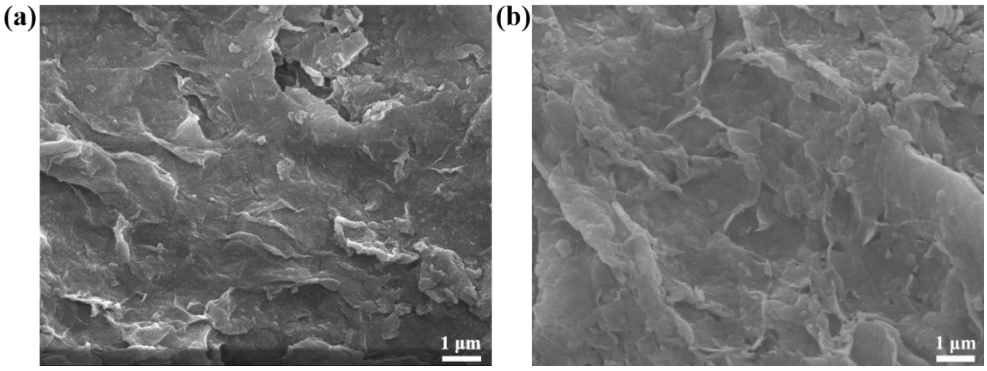


**Fig. S7** SEM images of MO@MPEI600 (a) and Cr@MPEI600 (b) after four adsorption cycles.

## References

1. X. Shi, M. Gao, W. Hu, D. Luo, S. Hu, T. Huang, N. Zhang, Y. Wang. *Sep. Purif. Technol.*, 2022, **287**, 120596.
2. C. Cai, R. Wang, S. Liu, X. Yan, L Zhang, M. Wang, Q. Tong, T Jiao. *Colloid. Surface. A*, 2020, **589**, 124468.
3. A.A.A. Darwish, M. Rashad, H.A. AL-Aoh. *Dyes. Pigm.*, 2019, **160**, 563-571.
4. H. Xu, X. Li, Y. Hao, X. Xu, Y. Zhang, J. Zhang. *J. Mol. Liq.*, 2022, **347**, 118253.