

Probing the Synergistic Effects of Amino Compounds in Mitigating Oxidation in 2D $Ti_3C_2T_x$ MXene nanosheets in Aqueous Environment

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1. Experimental Procedure

1.1. Materials

MAX phase was supplied from Adamas (99.5%, 400mesh), and also characterized through XRD to use further (**Fig. S1**). LiF were obtained from Aladdin (99.9% metal basis, Shanghai). A hydrochloric acid (HCl) solution was prepared by diluting concentrated HCl (37% w/w Sigma Aldrich, Shanghai) with deionized (DI) water. Amino acids: Serine (Merck, Germany), Threonine (Aladdin, Shanghai); Lysine (Merck, Germany), Glutamic acid (Merck, Germany), and Asparagine (Sigma Aldrich, Shanghai), were obtained with high purity more than 99%.

1.2 Synthesis of $Ti_3C_2T_x$ nanosheets

$Ti_3C_2T_x$ nanosheets were produced by removing aluminum from the MAX phase precursor using a selective acid etching method described in previous literature ¹. To avoid any potential hazards, caution was exercised while dissolving 3 grams of LiF into the HCl solution, as this resulted in the formation of HF. Subsequently, 3 grams of Ti_3AlC_2 (MAX) powder was gradually added to the HCl + LiF solution to prevent overheating. The mixture was stirred and maintained at a temperature of 35 °C for one day. Following the etching process, multiple washing cycles

were conducted to eliminate HF and Li⁺ cations until the pH of the mixture exceeded 6. The resulting dispersion of Ti₃C₂T_x nanosheets, with a concentration of 4.5 mg mL⁻¹, was obtained as the supernatant through vacuum filtration.

1.3 Amino functionalized MXene sample preparation

Prior to the introduction of MXene nanosheets, aqueous solutions of amino compounds were made at an equimolar concentration in a volume of 250 mL (as reference to Serine). Next, the initial mixture of MXene nanosheets was added separately and diluted down into each of the desired solutions (the concentration of Ti₃C₂T_x MXene in each system was maintained at a constant level of 0.05 mg mL⁻¹). The solutions containing Ti₃C₂T_x were stored in sealed containers for 6 weeks at room temperature. After that, the samples were washed thoroughly with deionized water to remove any unbound amino acids to further characterize.

1.4 Characterizations

Macroscopic alterations in MXene dispersions were visually detected using digital photography. The oxidation degree of the material was measured using a UV-3600 ultraviolet-visible spectrophotometer manufactured by Shimadzu Company. The light source consisted of an optical axis automated adjustment deuterium lamp and a halogen lamp. The liquid sample was tested within a range of 185 nm to 800 nm. The liquid samples were diluted to a concentration of 0.025 mg mL⁻¹ in preparation for testing. The use of Field Emission Transmission Electron Microscopy (FEI Tecnai G2 F30) allowed for the observation of temporal alterations in the microscopic properties of the sample, including its shape, crystal structure, content, and other relevant parameters. The concentration of the sample was reduced to 0.0025 mg/mL, and a small quantity of it was applied to a 200 mesh microgrid membrane (ZTE Baire Company) for testing, using multiple drops. Following the dispersion, the samples were held at room temperature and kept away from light for varying durations. The surface cross-section morphology and composition of the film were observed using a scanning electron microscope (MAIA3 XMU, Tescan) with an accelerated voltage of 5 kv. The crystal structure was analyzed using an X-ray diffractometer (Ultima IV, Rigaku). The 2θ range for the wide-angle scan ranged from 5° to 90°, with a scanning rate of 5° per minute. An X-ray photoelectron spectrometer (ESCALAB 250, THERMO VG, USA) was utilized to examine alterations in the chemical state of the surface. The Dynamic Light

Scattering (DLS) measurements were conducted using a ZS90, Malvern Instruments. The data were analyzed using the Malvern software provided by the manufacturer. We applied a cumulant method to obtain the average hydrodynamic diameter (Z-average) to assess the size distribution of the particles.

1.5 Electrochemical characterizations

The film's conductivity was assessed using a four-probe conductivity tester, while the film's thickness was determined using cross-sectional imaging via scanning electron microscopy (SEM). The sample served as the electrode for the supercapacitor, with 3M H₂SO₄ serving as the electrolyte. The counter electrode was made of activated carbon, while the reference electrode was made of Ag/AgCl. The capacitance performance of the electrode material was evaluated in a three-electrode system within the potential range of -0.6 to 0.2V. The electrochemical characteristics of MXene and serine electrode materials, stored for varying durations, were determined using an electrochemical analyzer (Shanghai Chenhua Instrument, 600E). Cyclic voltammetry (CV) involves the application of a linearly varying voltage over time to the electrode during the experiment. At each voltage, a corresponding current response is measured and recorded along with the voltage value. The Arbin charging and discharging instrument (Arbin Instrument Company, BT-G) is used to test various current densities on the multiplier performance curve. The specific capacitances (C_g) were determined through galvanostatic charge/discharge curves, using

Equation:

$$C_g = It_d / \Delta V m$$

Where I is the current (A), t_d is the discharge time (s), ΔV is the potential window (V), and m is the mass of the working electrode (g).

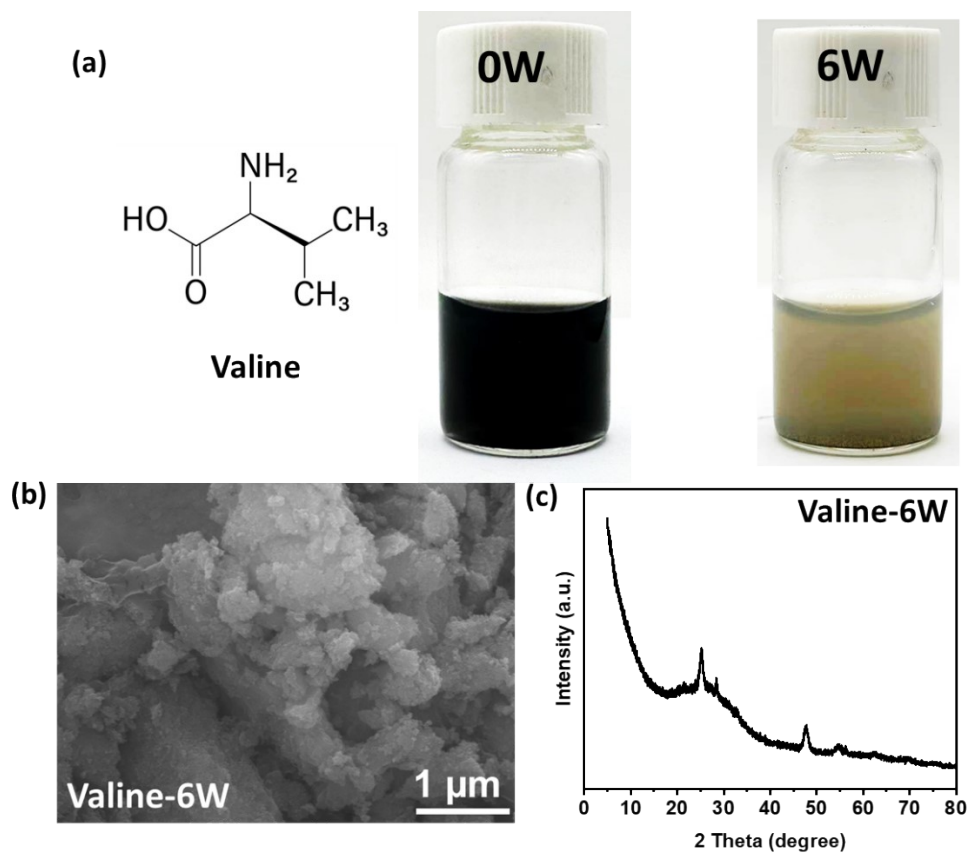


Fig. S3 Effect of valine (as lacking hydroxyl groups) on MXene stability (a) change in color after 6 weeks and their corresponding (b) SEM and (c) XRD images.

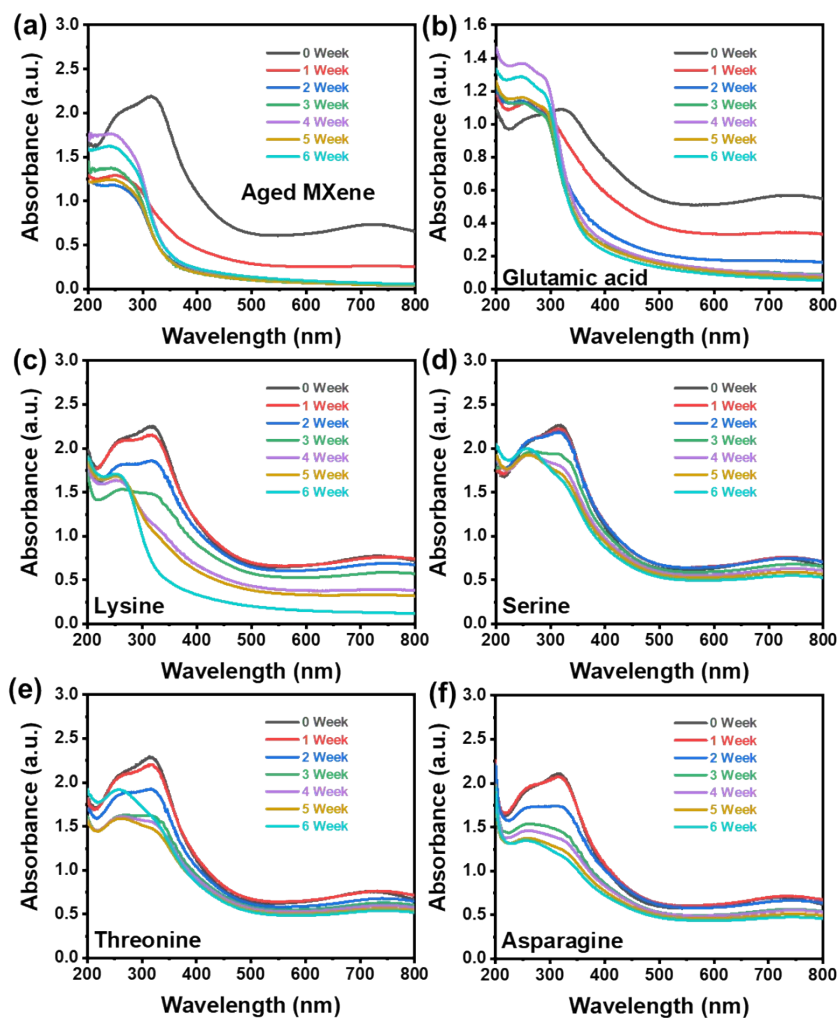


Fig. S4 UV-*vis.* analysis of (a) fresh MXene and (b-f) different amino functionalized MXene dispersion after different time intervals

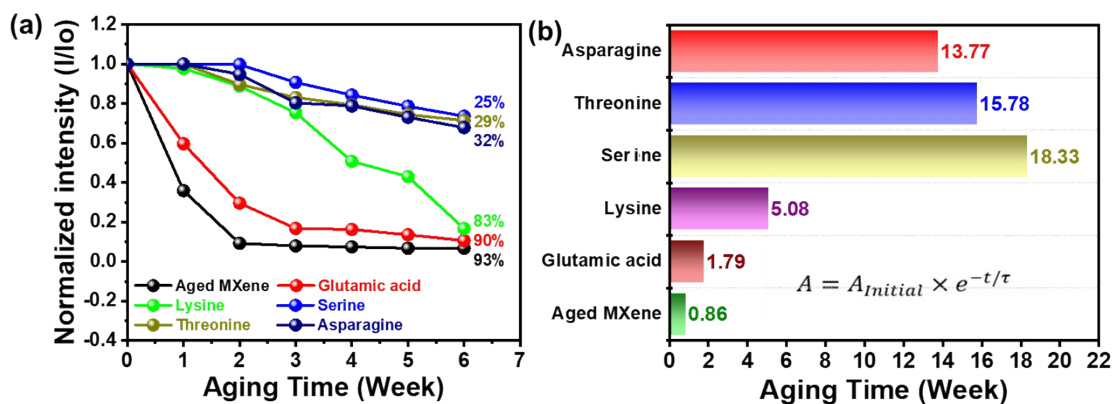


Fig. S5 (a) The normalized UV-*vis.* absorbance intensity profile and (b) time decay constant after different time intervals of fresh MXene and MXene-amino compounds

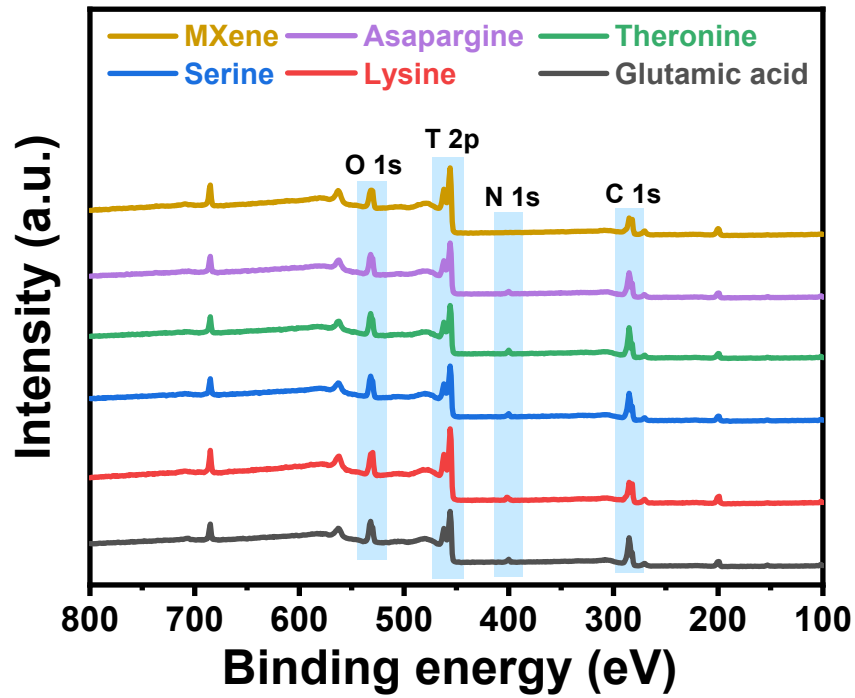


Fig. S6 The XPS survey of fresh MXene and MXene-amino compounds

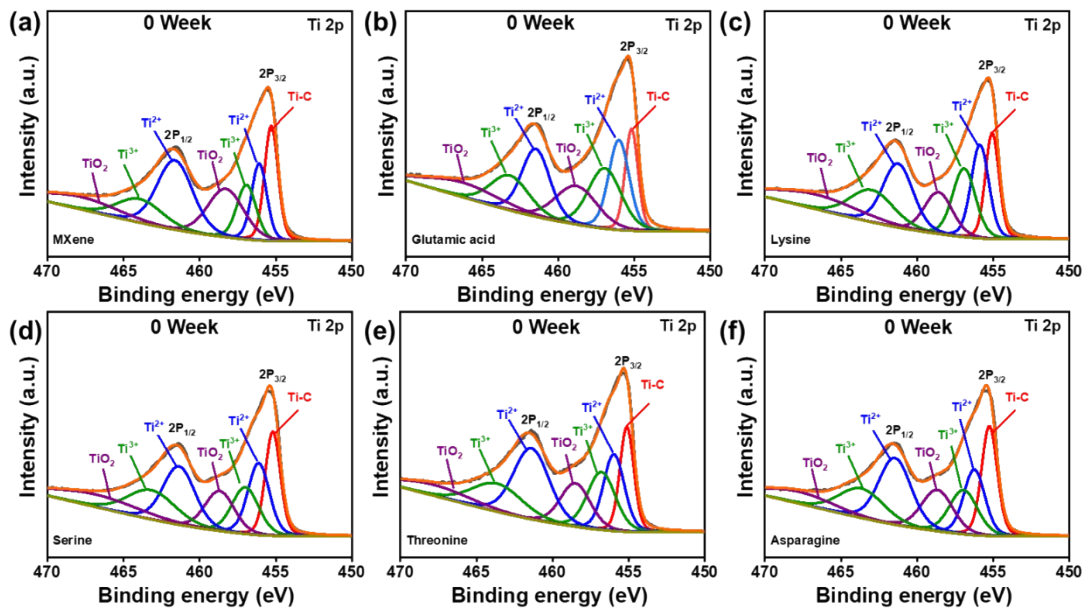


Fig. S7 The deconvoluted XPS spectra of Ti 2p (a) MXene, (b) glutamic acid, (c) lysine, (d) serine, (e) threonine and (f) asparagine functionalized MXene films after 0 weeks of aging

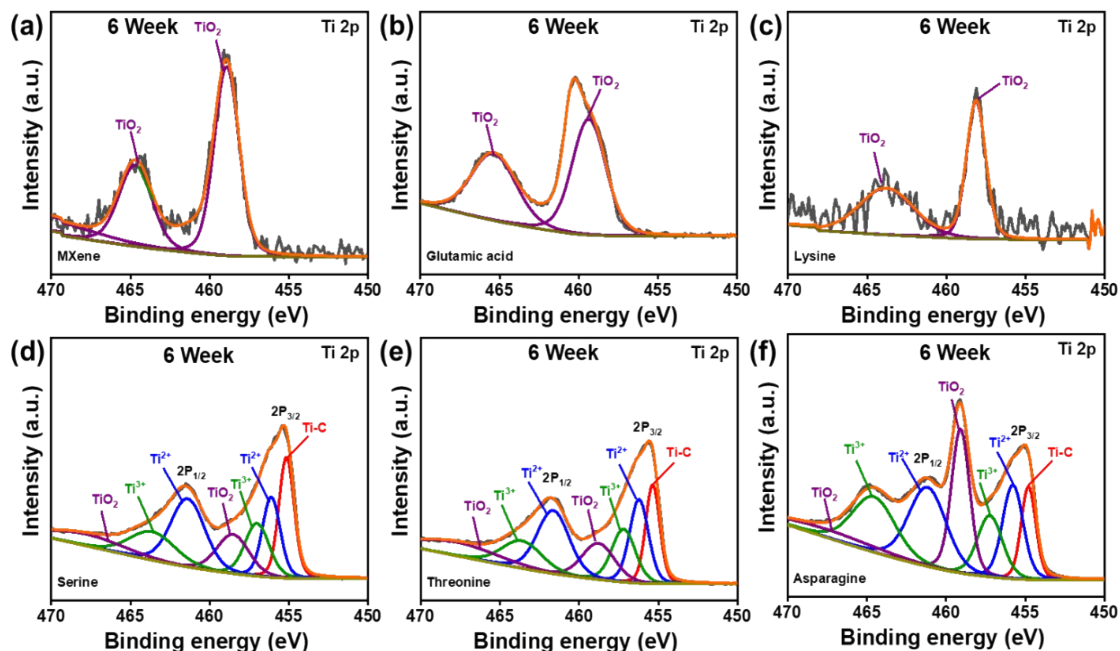


Fig. S8 The deconvoluted XPS spectra of Ti 2p (a) MXene, (b) glutamic acid, (c) lysine, (d) serine, (e) threonine and (f) asparagine functionalized MXene films after 6 weeks of aging

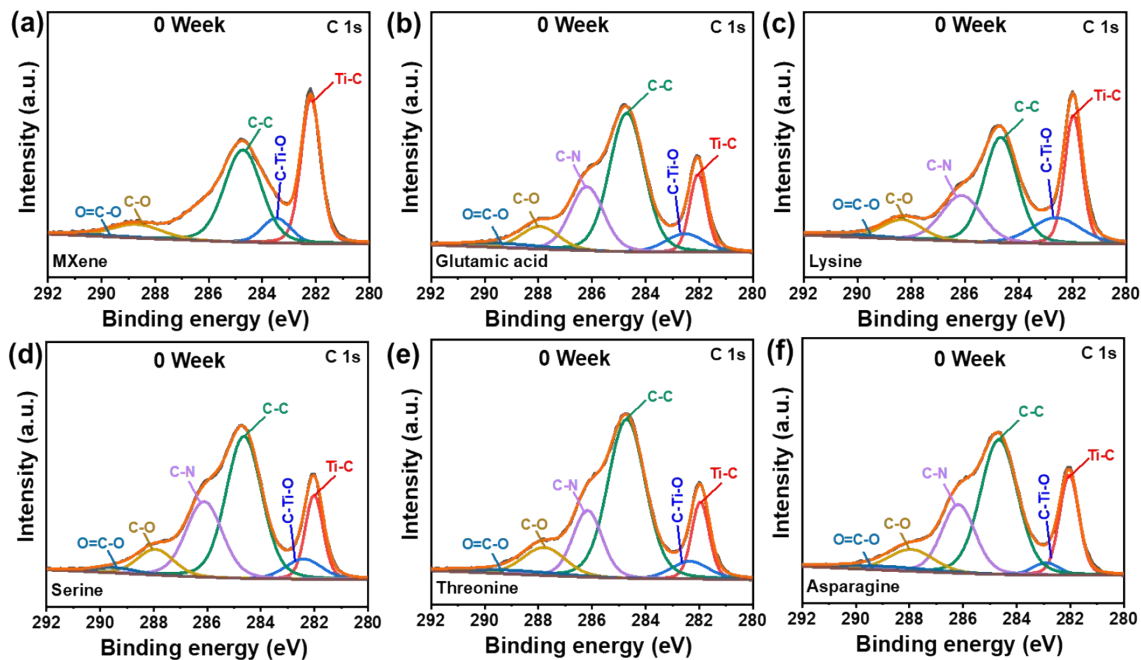


Fig. S9 The deconvoluted XPS spectra of C 1s (a) MXene, (b) glutamic acid, (c) lysine, (d) serine, (e) threonine and (f) asparagine functionalized MXene films after 0 weeks of aging

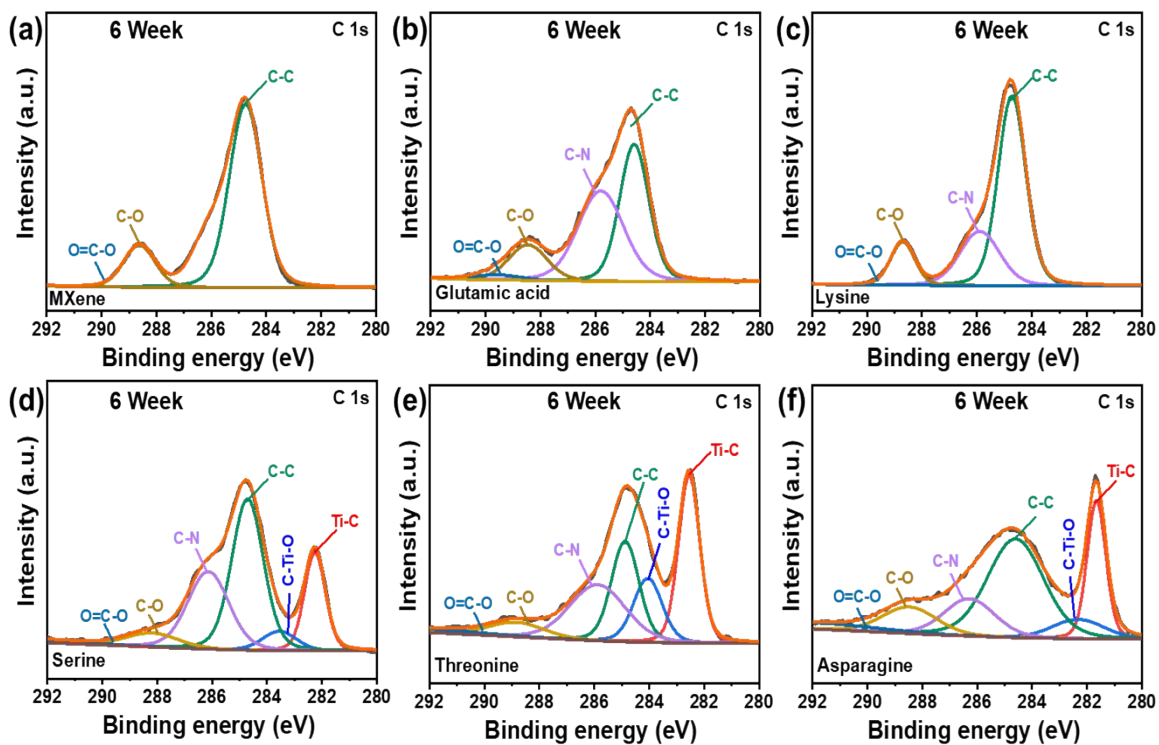


Fig. S10 The deconvoluted XPS spectra of C 1s (a) MXene, (b) glutamic acid, (c) lysine, (d) serine, (e) threonine and (f) asparagine functionalized MXene films after 6 weeks of aging

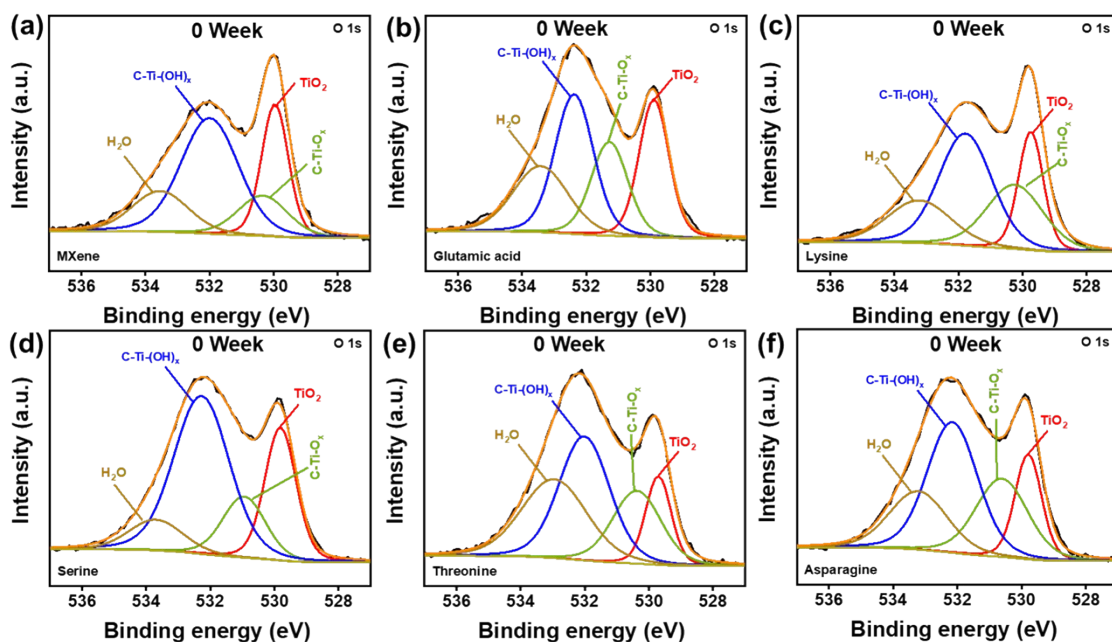


Fig. S11 The deconvoluted XPS spectra of O 1s (a) MXene, (b) glutamic acid, (c) lysine, (d) serine, (e) threonine and (f) asparagine functionalized MXene films after 0 weeks of aging

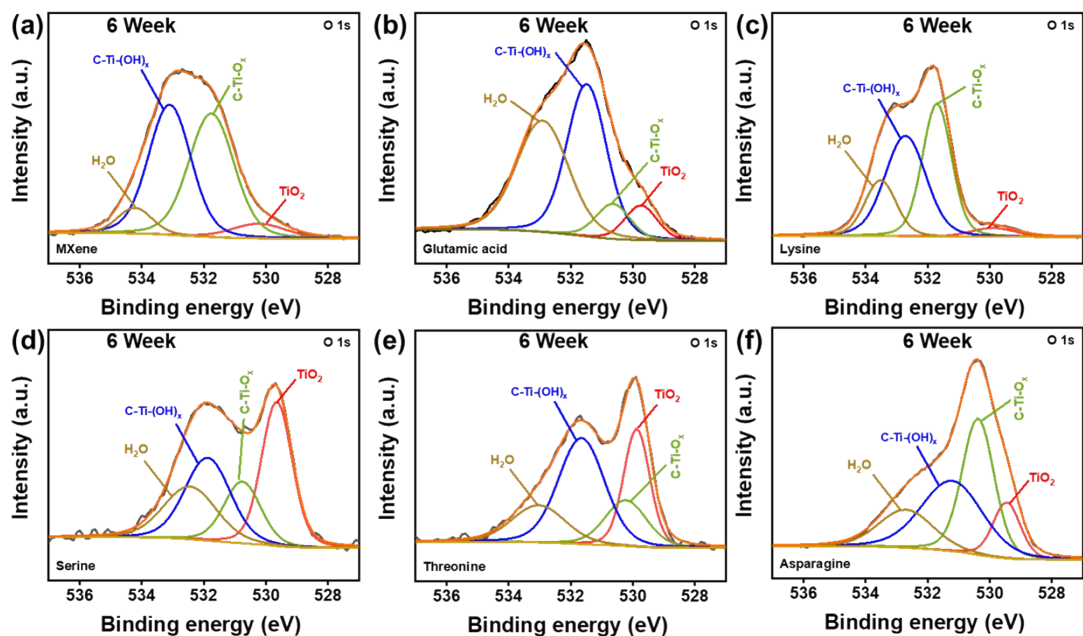


Fig. S12 The deconvoluted XPS spectra of O 1s (a) MXene, (b) glutamic acid, (c) lysine, (d) serine, (e) threonine and (f) asparagine functionalized MXene films after 6 weeks of aging

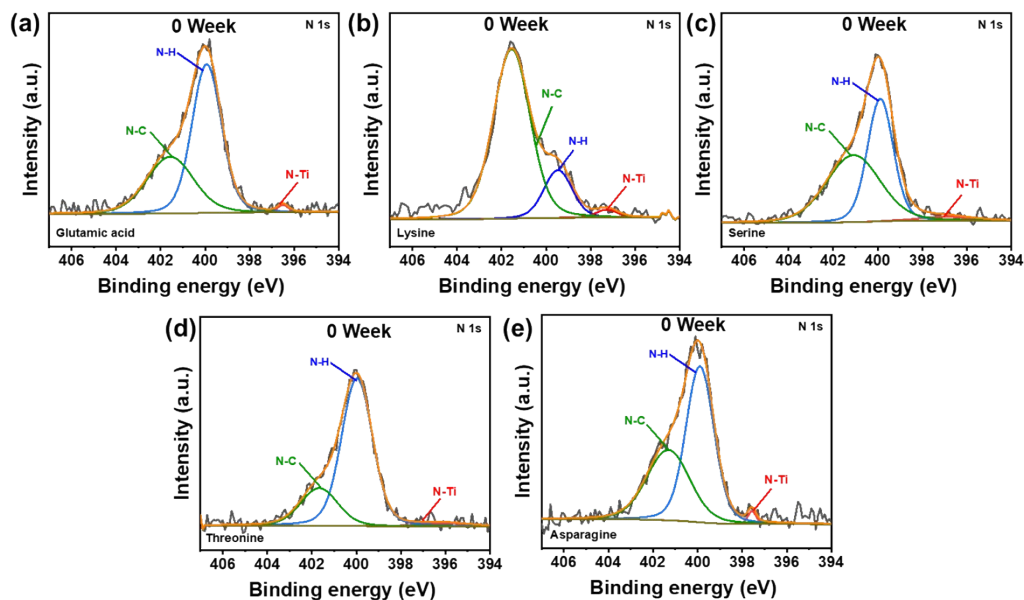


Fig. S13 The deconvoluted XPS spectra of N 1s (a) glutamic acid, (b) lysine, (c) serine, (d) threonine and (e) asparagine functionalized MXene films after 0 weeks of aging

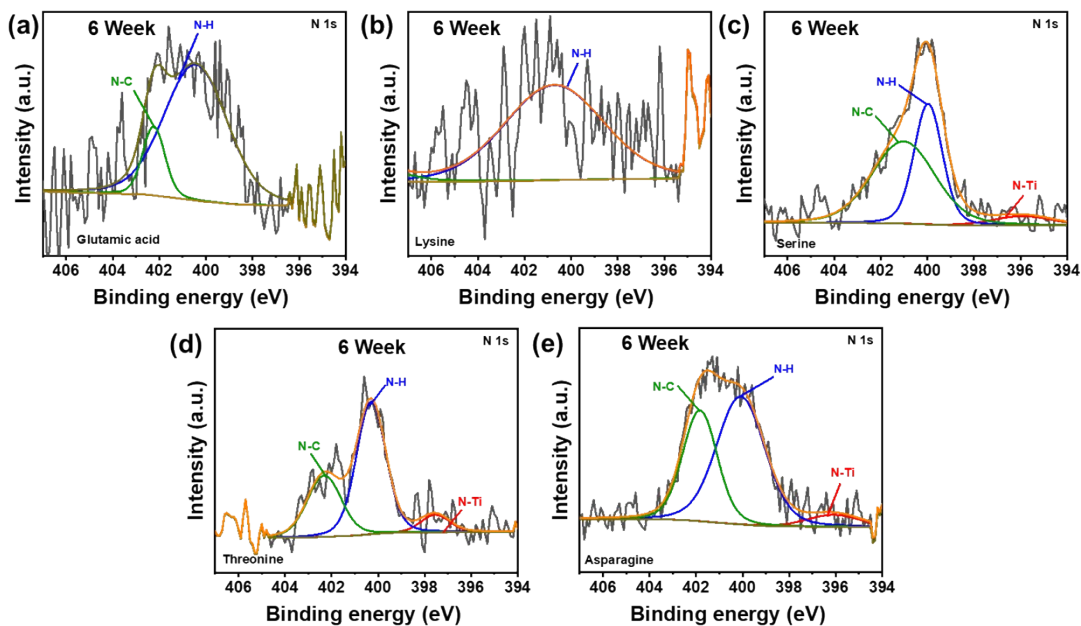


Fig. S14 The deconvoluted XPS spectra of N 1s (a) glutamic acid, (b) lysine, (c) serine, (d) threonine and (e) asparagine functionalized MXene films after 6 weeks of aging

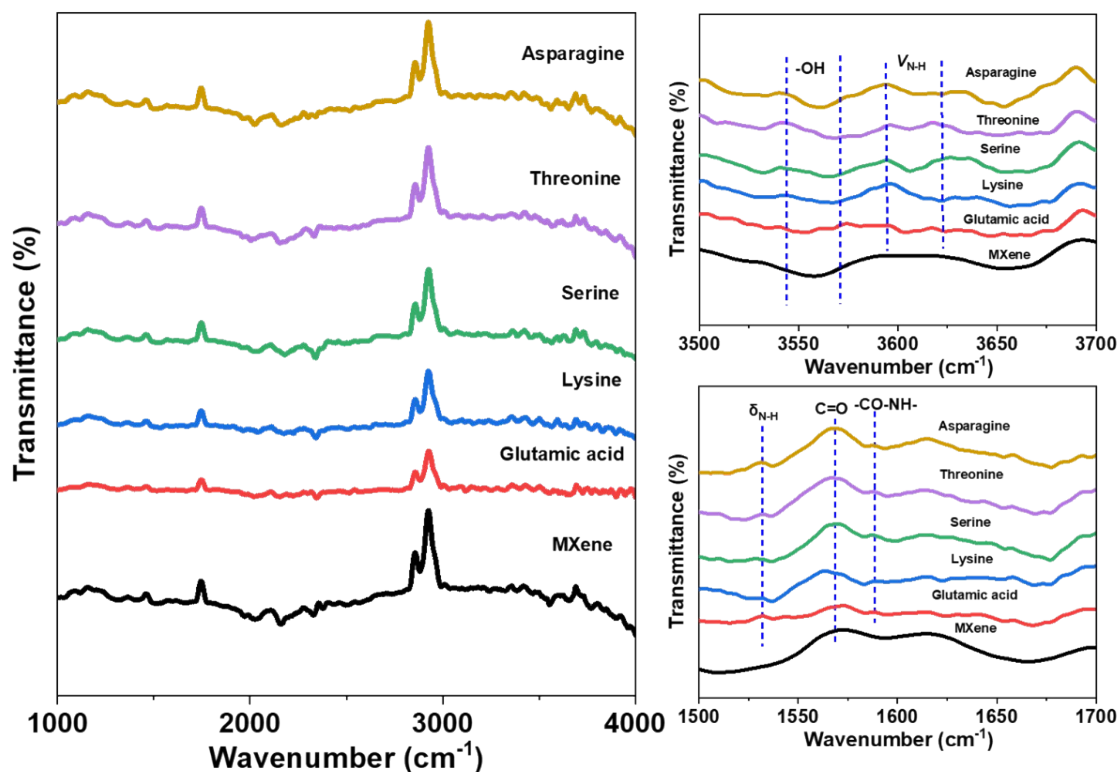


Fig. S15 The FTIR profile of fresh MXene and glutamic acid, lysine, serine, threonine and asparagine functionalized MXenes.

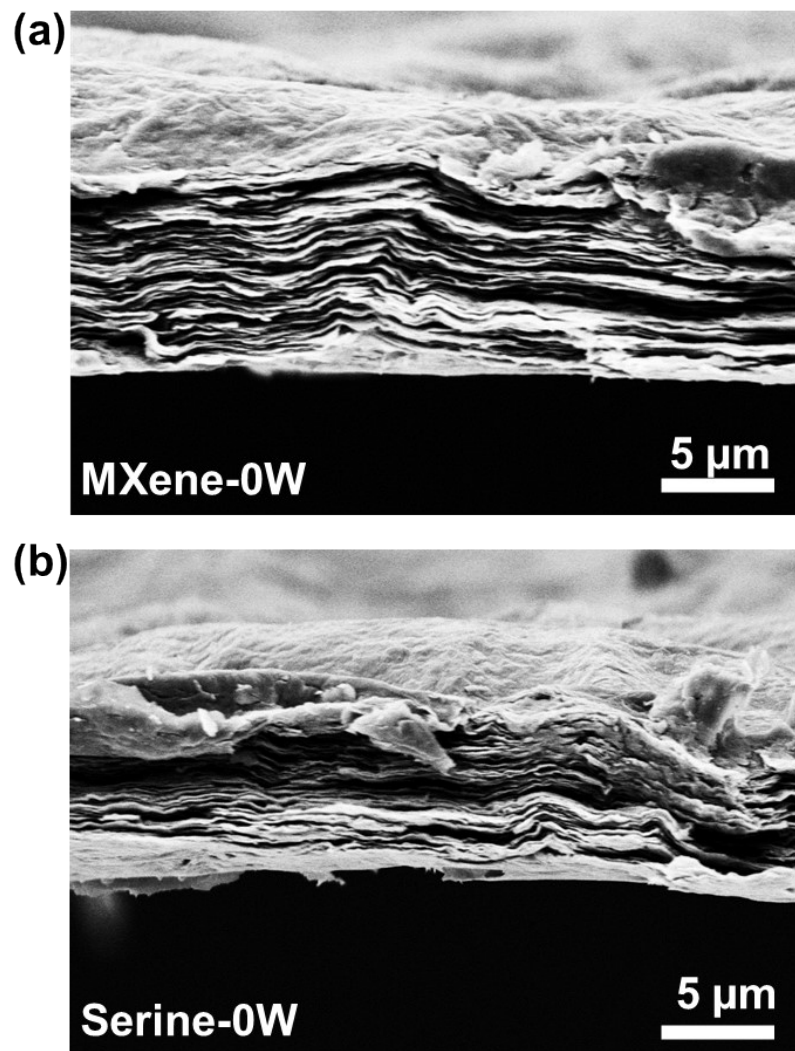


Fig. S16 The cross-sectional SEM images of (a) fresh MXene and (b) serine functionalized MXene after 0 weeks of aging

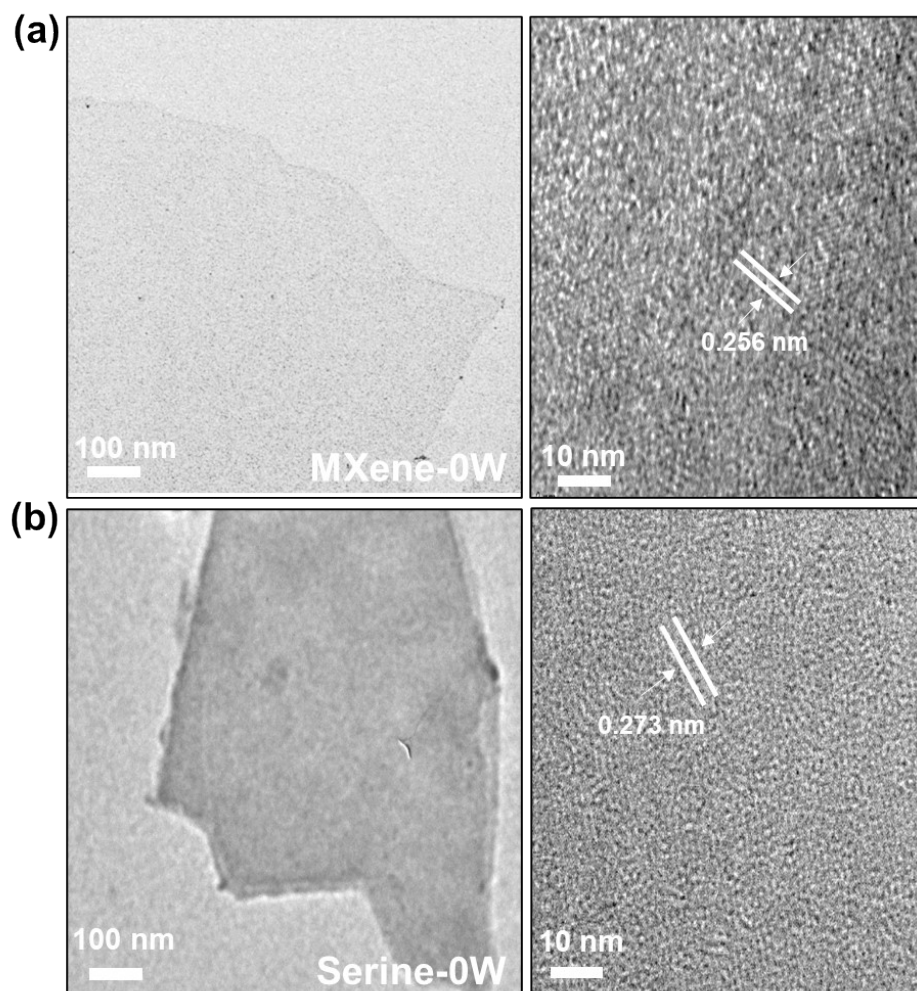


Fig. S17 HR-TEM images of (a) fresh MXene and (b) serine functionalized MXene after 0 week of aging

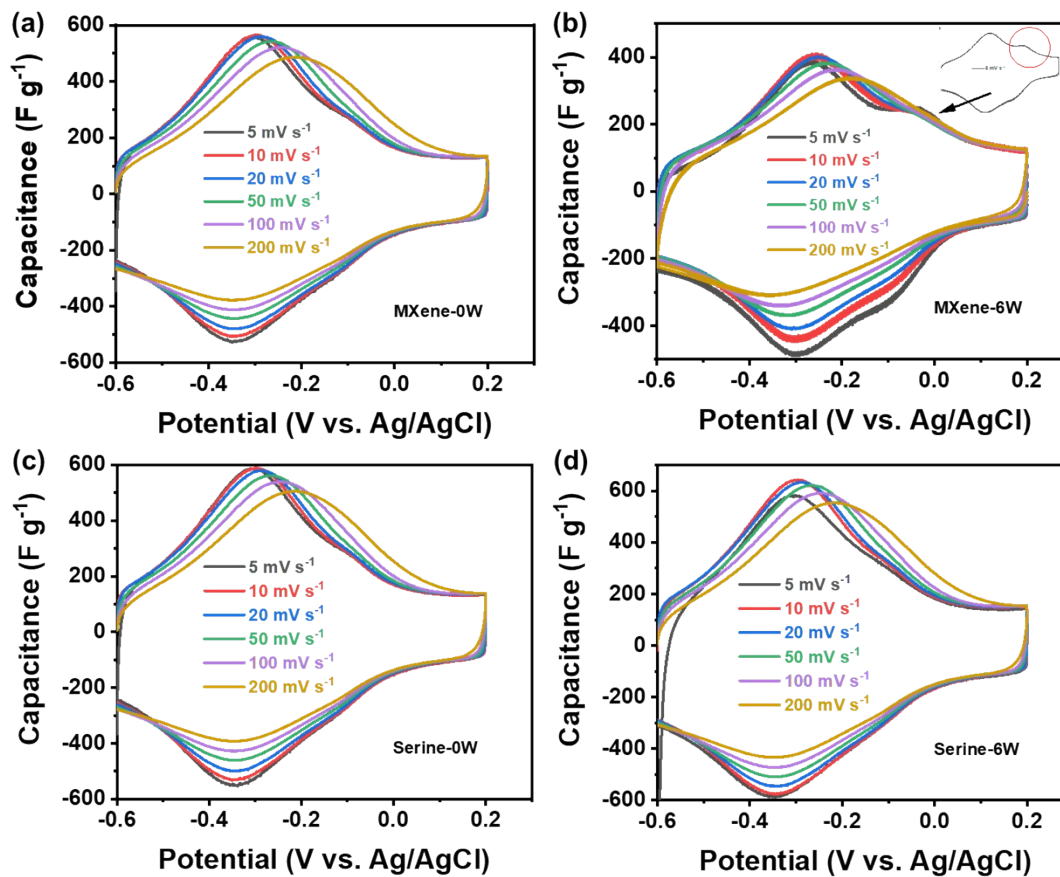


Fig. S18 CV profile of (a, b) fresh MXene and (c, d) serine functionalized MXene after 0 and 6 weeks of aging time at different scan rates

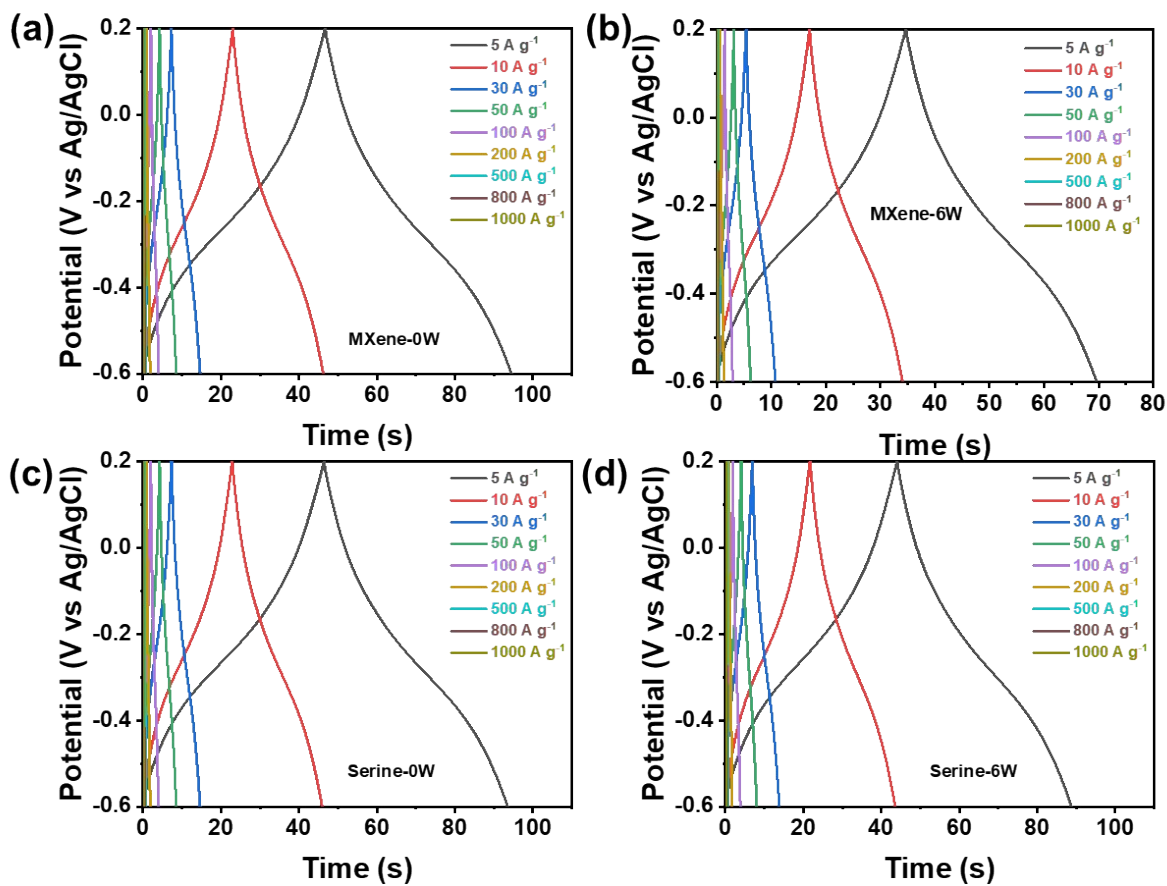


Fig. S19 Charge discharge curve of (a, b) MXene and (c, d) serine functionalized MXene after 0 and 6 weeks of aging time at different current densities

Table S1. Comparison of succinic acid as antioxidant with recent reported antioxidants

Antioxidant	Concentration (mg L ⁻¹)	MXene stable time (day)	Ref
Sodium L-ascorbate	0.2	80	2
Sodium citrate	0.2	80	2
Polyphosphate	15.0	21	3
Sodium polyphosphate	2.5	15	4
Sodium citrate	0.3	150	5
Asparagine	0.05	96	This work
Threonine	0.05	110	This work
Serine	0.05	128	This work

Reference

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