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# Oxidation engineering triggered peroxidase-like activity of $\text{VO}_x\text{C}$ for detection of dopamine and glutathione†

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MXenes, two-dimensional nanomaterials, are gaining traction in catalysis and biomedicine. Yet, their oxidation instability poses significant functional constraints. Gaining insight into this oxidation dynamic is pivotal for designing MXenes with tailored functionalities. Herein, we crafted  $\text{VO}_x\text{C}$  nanosheets by oxidatively engineering  $\text{V}_4\text{C}_3$  MXene. Interestingly, while pristine  $\text{V}_4\text{C}_3$  displays pronounced antioxidant behavior, its derived  $\text{VO}_x\text{C}$  showcases enhanced peroxidase-like activity, suggesting the crossover between antioxidant and pro-oxidant capability. The mixed valence states and balanced composition of V in  $\text{VO}_x\text{C}$  drive the Fenton reaction through multiple pathways to continually generate hydroxyl radicals, which was proposed as the mechanism underlying the peroxidase-like activity. Furthermore, this unique activity rendered  $\text{VO}_x\text{C}$  effective in dopamine and glutathione detection. These findings underscore the potential of modulating MXenes' oxidation state to elicit varied catalytic attributes, providing an avenue for the judicious design of MXenes and derivatives for bespoke applications.

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## 1. Introduction

MXenes, two-dimensional (2D) metal carbides and nitrides, are at the forefront of research due to their potential in energy conversion, catalysis, and biomedicine.<sup>1–5</sup> Typically, MXenes are derived by selectively etching element A from the MAX phase. The MAX phase conforms to the general formula  $\text{M}_{n+1}\text{AX}_n$ , where M represents an early transition metal, A belongs to groups 13 or 14 of the periodic table, X is either C or N, and  $n$  can be 1, 2, or 3.<sup>6</sup> Monolayer or few-layered MXenes possess distinctive features: (1) foremost among them is the abundance of hydrophilic functionalities such as  $-\text{OH}$ ,  $-\text{O}$ , and  $-\text{X}$  (where X could be F or Cl). This not only grants MXenes excellent aqueous dispersibility but also facilitates facile chemical modifications, broadening their potential for tailored applications;<sup>7,8</sup> (2) MXenes host an array of transition metals with mixed valences—typically between 3 and 5. This versatile valence pattern optimizes charge-carrier transfer and

offers a broad spectrum of redox potentials, further enhancing MXenes' functional scope;<sup>9–12</sup> (3) the majority of MXenes are environmentally benign and display tunable physicochemical properties that hinge upon their elemental makeup. This adaptability accentuates their potential for diverse applications while aligning with sustainability goals.<sup>13–16</sup> Given the inherently low valence of metals in MXenes, oxidation during preparation and storage becomes inevitable. This spontaneous process can aptly be termed “auto-oxidation”.<sup>17,18</sup> Oxidation significantly alters the physical and chemical properties of MXenes, consequently impacting their functional performance in practical applications. While some studies have addressed the oxidation stability of MXenes and proposed methods to prevent it, the influence of auto-oxidation-induced transformations on MXenes' catalytic behavior remains an area warranting deeper exploration and research.<sup>19</sup>

The intrinsic susceptibility of fresh MXenes to oxidation by oxygen imparts them with remarkable antioxidant capabilities. Notably,  $\text{Ti}_3\text{C}_2$  and  $\text{V}_2\text{C}$  nanosheets have demonstrated a broad-spectrum ability to scavenge reactive oxygen and nitrogen species;<sup>20–22</sup> the activity of  $\text{Ti}_3\text{C}_2$  even surpasses that of conventional natural antioxidants by several folds. Given their commendable biocompatibility, MXenes like  $\text{V}_2\text{C}$ ,  $\text{Ti}_3\text{C}_2$ , and  $\text{Nb}_2\text{C}$ , known for their active oxygen species (ROS)-scavenging antioxidant properties, are emerging as promising therapeutics for oxidative stress-induced conditions, such as neuronal damage and acute kidney injury.<sup>22–25</sup> However, auto-oxidation significantly alters MXenes' redox potentials and valence compositions, potentially steering their chemical and biological activities in

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† Electronic supplementary information (ESI) available: Elemental atomic percentages of  $\text{V}_4\text{C}_3$  and  $\text{VO}_x\text{C}$  calculated by XPS fitted spectra (Table S1); SEM image of MAX phase  $\text{V}_4\text{AlC}_3$ , multilayered  $\text{V}_4\text{C}_3$ , few layered  $\text{V}_4\text{C}_3$  NSs and  $\text{VO}_x\text{C}$  (Fig. S1); dindar optical effect of  $\text{V}_4\text{C}_3$  nanosheets dilute solution under laser pointer irradiation (Fig. S2); XRD pattern of  $\text{V}_2\text{O}_5$  after calcination of  $\text{V}_4\text{C}_3$  nanosheets (Fig. S3). See DOI: <https://doi.org/10.1039/d3na00642e>



different directions at various oxidation phases. For instance, during  $\text{Ti}_3\text{C}_2$  oxidation, the  $\text{Ti(II)}$  fraction notably diminishes, while the  $\text{Ti(IV)}$  content escalates, leading to a marked reduction in its ability to neutralize  $\cdot\text{OH}$ ,  $\text{H}_2\text{O}_2$ , and DPPH radicals.<sup>20</sup> MXenes' uncontrollable oxidation in aqueous solutions remains a pivotal constraint for their broader application. In studying the antioxidant behavior of MXenes, we observed a gradient oxidation process, culminating in an irreversible shift from antioxidant to pro-oxidant activities. This transition can instigate unforeseen biological consequences.

In our investigation, we primarily aim to decipher the impacts of oxidation on the structural and catalytic attributes of MXenes, with  $\text{V}_4\text{C}_3$  MXene spotlighted as our model. This choice is motivated by vanadium's rich valence states (+2, +3, +4, and +5) and the inherent stability of the atomic configuration. Freshly prepared  $\text{V}_4\text{C}_3$  MXene nanosheets demonstrate an impressive capability to scavenge free radicals, underscoring their antioxidant prowess. Through controlled oxidation of a few-layered  $\text{V}_4\text{C}_3$ , we synthesized  $\text{VO}_x\text{C}$  nanosheets that adopt an intricately entangled morphology. The rise of nanozymes—nanostructures mimicking enzymatic properties—has garnered significant interest due to their exceptional merits and broad application spectrum.<sup>26–28</sup> Intriguingly, the  $\text{VO}_x\text{C}$  nanosheets we prepared manifest robust peroxidase (POD)-like activity. This is attributable to the mixed valence states within the  $\text{VO}_x\text{C}$ , which bolster the Fenton reaction cycle involving  $\text{V}^{n+}$  species and  $\text{H}_2\text{O}_2$ , perpetuating the generation of hydroxyl radicals. Leveraging the antagonistic influence of biomolecules on this POD-like behavior, we devised a proficient and sensitive colorimetric assay for the detection of dopamine and glutathione.

## 2. Experimental section

### 2.1 Chemical and materials

$\text{V}_4\text{AlC}_3$  MAX powder (400 mesh) was purchased from 11 Technology, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), horseradish peroxidase (HRP), dopamine hydrochloride, dimethyl sulfoxide (DMSO), hydrofluoric acid (HF) and 3,3',5,5'-tetramethylbenzidine (TMB) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) and 2,2'-Azinobis-(3-ethylbenzthiazoline-6-sulphonate) (ABTS) were commercially available from Aladdin Industrial Co (CA, USA). L-Glutathione (GSH) were purchased from Beijing OKA Biotechnology Co., LTD. Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) were purchased from Shanghai Maclin Biochemical Technology Co., LTD. Pure terephthalic acid (PTA) were purchased from Thermo Fisher Scientific. Tetramethyl ammonium hydroxide (TMAOH) were purchased from Sigma-Aldrich (Shanghai, China). Milli-Q water (18  $\text{M}\Omega$  cm) was used in the preparation of all solutions. All glassware and autoclave used in the following procedures were cleaned by aqua regia solution ( $\text{HNO}_3/\text{HCl} = 1 : 3 \text{ v/v}$ ).

### 2.2 Characterization

UV-vis absorption spectra were obtained using a Cary 60 UV-Vis Spectrometer (Varian, USA) and a matched quartz cuvette with a path length of 1 cm. The crystal structures of the  $\text{V}_4\text{C}_3$  and  $\text{VO}_x\text{C}$

nanosheets were characterized by X-ray diffraction (XRD, D8 Advance diffractometer, Bruker, Germany) using monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) were captured on a Tecnai G2 F20 U-Twin electron microscope with an accelerating voltage of 200 kV. SEM images were obtained by FEI Field Emission Scanning Electron Microscope (FE-SEM), USA. Fourier transform infrared spectroscopy (FT-IR) were acquired by Thermo Fisher Nicolet 6700 infrared spectrometer. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo ESCALAB 250XI multifunctional imaging electron spectrometer (Thermo Fisher Scientific, USA) using 150 W Al  $\text{K}_\alpha$  radiation and a base pressure of approximately  $3 \times 10^{-9}$  mbar. The binding energies were calibrated to the C 1s line at 284.8 eV. Fluorescence spectral signals were acquired by a Hitachi F-4600 fluorescence spectrometer, Japan. The measurements were carried out at room temperature under the following conditions: microwave power 2 mW, modulation amplitude 1.0 G, attenuation 20 dB, and scan range of 100 G.

### 2.3 Synthesis of $\text{VO}_x\text{C}$ nanosheets

Preparation of multilayer  $\text{V}_4\text{C}_3$  nanosheets. 1 g of  $\text{V}_4\text{AlC}_3$  was added to a 100 mL Teflon tank and then 20 mL of hydrofluoric acid (HF, 40% $\text{v/v}$ ) was carefully added in a fume hood. After sealing the reactor, it was stirred and reacted at room temperature for 14 days to obtain a multilayer  $\text{V}_4\text{C}_3$  solution in which the Al layer was etched away. The product was washed by centrifugation several times with deionized water (3500 rpm) to  $\text{pH} > 6$ . The product was dried under vacuum at 60 °C for 12 h to obtain dried  $\text{V}_4\text{C}_3$  powder.

**Preparation of few layers  $\text{V}_4\text{C}_3$  MXene.** Firstly, 0.1 g multilayer  $\text{V}_4\text{C}_3$  powder was weighed into a 10 mL glass sample bottle, and 5 mL high concentration tetramethylammonium hydroxide solution (TMAOH, 25% aqueous solution) was added, and stirred at room temperature (25 °C) for 3 days. The TMAOH solution was then centrifuged three times at 8000 rpm. The black precipitates were re-dispersed into 20 mL deionized water, and the 2D  $\text{V}_4\text{C}_3$  solution was obtained by ultrasound under argon atmosphere for 90 min. The precipitation was then removed by centrifugation at 8000 rpm for 20 min and a 2D  $\text{V}_4\text{C}_3$  nanosheets colloidal solution was collected. The 2D  $\text{V}_4\text{C}_3$  nanosheets is dried in a vacuum freeze dryer for at least 24 h and then collected for quantification.

**Preparation of  $\text{VO}_x\text{C}$  nanosheets.**  $\text{V}_4\text{C}_3$  nanosheets is prepared into a solution of 1 mg  $\text{mL}^{-1}$  and placed in a stripped sample bottle with the solution filling not exceeding 50%. The sample bottle was placed at 40 °C for 72 h until the solution was a light dark green state.

**Preparation of  $\text{V}_2\text{O}_5$ .** The  $\text{V}_4\text{C}_3$  nanosheets was freeze-dried to obtain a black light powder, which was placed in a porcelain pot and calcined in a Muffle furnace at a heating rate of 5 °C  $\text{min}^{-1}$  and held for 3 h. After cooling, the powder was yellow.

### 2.4 Evaluation of total antioxidant activity

**The antioxidant capacity of nanosheets was assessed by ABTS assay.** Firstly, the stable free radical  $\text{ABTS}^{\cdot+}$  was freshly



made by dissolving 0.0374 g ABTS and 0.0066 g  $K_2S_2O_8$  in 30 mL deionized water for 12 h in dark, and the solution was diluted by 20 times before use. The antioxidant capacity of  $V_4C_3$  nanosheets at different oxidation stages was tested by UV-vis absorption spectroscopy. In typical, 10  $\mu\text{L}$   $V_4C_3$  or  $VO_xC$  nanosheets ( $0.5\text{ mg mL}^{-1}$ ) was added to 3 mL ABTS<sup>+</sup> solution, and the absorption spectrum was recorded with two minutes interval. The scavenging rate was calculated by plotting the absorbance at 730 nm in function of reaction time.

## 2.5 POD-like enzyme activity and enzymatic kinetics test

**The POD-like activity of  $VO_xC$  nanosheets has been tested by using TMB assay.** In typical, 20  $\mu\text{L}$  20 mM TMB and 20  $\mu\text{L}$  0.1 M  $H_2O_2$  were mixed in 3 mL  $H_2O$  or 10 mM HAc-NaAc buffer with different pH. Then, 10  $\mu\text{L}$  of  $V_4C_3$  or  $VO_xC$  ( $0.2\text{ mg mL}^{-1}$ ) was added to accelerate the oxidation of TMB. The UV-vis absorption spectra evolution was recorded using the scanning kinetics model with 1 min interval. The absorbance at 650 nm vs. reaction time was plotted to calculate the catalytic reaction kinetic parameters.

The apparent steady-state kinetic measurements were carried out. For TMB and  $H_2O_2$  as substrate, the enzymatic kinetic parameters, *Michaelis* constant ( $K_m$ ) and maximal reaction velocity ( $V_{max}$ ), were calculated according to the *Michaelis-Menten* equation:

$$1/v = K_m/V_{max} \times (1/[S]) + 1/V_{max}$$

where  $v$  is the reaction initial velocity and  $[S]$  is the concentration of the substrate.

## 2.6 Detection of dopamine and glutathione

**Detection of dopamine.** The colorimetric detection of dopamine based on the concentration-dependent inhibition of  $VO_xC$  POD-like activity was performed. Typically, dopamine is configured in a solution of 2 mM concentration. To ensure the accuracy of the experiment, the total solution of the sample to be tested was strictly controlled to be 3 mL. Therefore, during the test,  $x\ \mu\text{L}$  of dopamine solution was added to  $2940-x\ \mu\text{L}$  ( $x = 10, 20, 30, 40, 50, 60$ ) deionized water. Next, 20  $\mu\text{L}$  of 20 mM TMB solution and 20  $\mu\text{L}$  of 0.1 M  $H_2O_2$  solution were added, followed by 20  $\mu\text{L}$  of  $0.2\text{ mg mL}^{-1}$   $VO_xC$  solution, immediately mixed for timing, and UV-vis absorption spectrum data began to be recorded when the reaction lasted for two minutes, with a monitoring range of 800–400 nm. With this method, at least three repeated tests were performed to measure different amounts of dopamine.

**Detection of glutathione.** Similarly, colorimetric detection of glutathione was performed based on the concentration-dependent inhibition of POD-like activity by glutathione. Normally, glutathione is configured in a solution of 0.5 mM concentration. To ensure the accuracy of the experiment, the total solution of the sample to be tested was strictly controlled to be 3 mL. Therefore, during the test,  $x\ \mu\text{L}$  glutathione solution was added to  $2940-x\ \mu\text{L}$  ( $x = 10, 20, 30, 40, 50, 60, 70, 80, 140$ ) deionized water. Next, 20  $\mu\text{L}$  of 20 mM TMB solution and 20  $\mu\text{L}$

of 0.1 M  $H_2O_2$  solution were added, followed by 20  $\mu\text{L}$  of  $0.2\text{ mg mL}^{-1}$   $VO_xC$  solution, immediately mixed for timing, and ultraviolet-visible absorption spectrum data began to be recorded when the reaction lasted for two minutes, with a monitoring range of 800–400 nm. The method was used to perform at least three repeatable tests for different levels of glutathione.

## 3. Results and discussion

### 3.1 Formation of $VO_xC$ via oxidation engineering of $V_4C_3$

As delineated in Fig. 1, we introduce a meticulously designed protocol to fabricate  $VO_xC$  nanosheets. The genesis of these nanosheets stems from a systematic oxidation engineering of few-layered (FL)  $V_4C_3$  MXene nanosheets under controlled conditions at 40 °C. For this endeavor,  $V_4AlC_3$  MAX phase, characterized by its dense 3D layered architecture, was judiciously selected as the foundational precursor. To realize the FL- $V_4C_3$  nanosheets, we employed the well-established HF etching technique, followed by a 25% TMAOH intercalation process (Fig. S1a–c†).<sup>29</sup> As inferred from the TEM imaging (Fig. 2a), the newly synthesized  $V_4C_3$  nanosheets display dimensions ranging from 300 to 500 nm. These nascent nanosheets bear a multitude of hydrophilic moieties (–OH, –F, –O) on their surface, thereby facilitating an excellent dispersion in aqueous solutions and manifesting the quintessential Tyndall phenomena, as depicted in Fig. S2.† Recognizing the inherent propensity of the FL- $V_4C_3$  nanosheets, especially in their fresh state, towards oxidation in aqueous environments—predominantly due to the extensive presence of low-valence vanadium—we embarked on a systematic study of their oxidation dynamics.<sup>12</sup> Consequently, we deliberately undertook the oxidation process of  $V_4C_3$  under a carefully controlled condition at 40 °C. Upon exposure to a heat treatment at 40 °C for a span of 72 h, the  $V_4C_3$  MXene nanosheets undergo a transformation to form their oxidation derivatives,  $VO_xC$  nanosheets, as vividly depicted in Fig. 2b and S1d.† Intriguingly, these  $VO_xC$  nanosheets exhibit a characteristic belt-like morphology, reminiscent of thin, delicately curled sheets, and boast an impressive span, extending beyond the 2  $\mu\text{m}$  mark.

The HRTEM revealed the intricate lattice fringe of  $VO_xC$ . An adjacent planar separation was meticulously calculated to be 0.205 nm, corresponding to the (002) plane of  $VO_xC$ , as showcased in Fig. 2c. XRD served as an instrumental technique in deciphering the crystalline structures of both  $V_4C_3$  and  $VO_xC$ . A noteworthy observation is the vanishing of the (004), (006), and (008) diffraction peaks of  $V_4C_3$ . Concurrently, the (002) diffraction peaks of  $V_4C_3$  migrate to an elevated angle with a pronounced diminution in intensity as oxidation time escalates, as highlighted in Fig. 2d and e. Most strikingly, the diffraction peak of  $V_4C_3$  nanosheets exhibits a steady decline and vanishes post 20 h, underscoring the hypothesis that oxidation precipitates the degradation and ensuing amorphization of  $V_4C_3$  nanosheets. As oxidation ensues, the (002) diffraction peak makes a re-emergence post the 60 h mark, signifying the orchestrated re-organization and re-crystallization of  $VO_xC$ . This underpins a transformative pathway for  $VO_xC$ , reminiscent of a “breakage-followed-by-



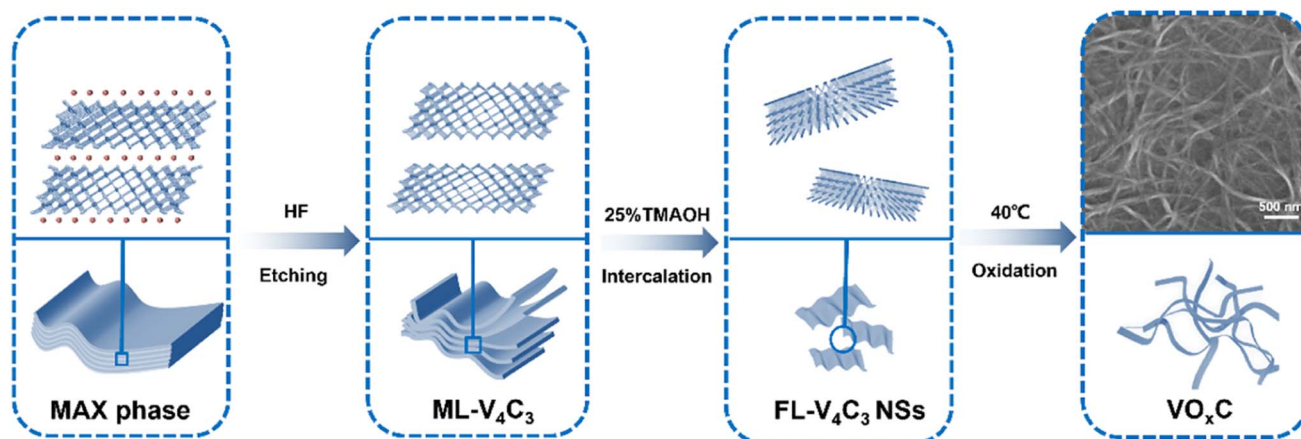


Fig. 1 Schematic illustration for the synthesis and structure diagram of  $\text{VO}_x\text{C}$  nanosheets.

reconstruction” paradigm, while ensuring the resultant  $\text{VO}_x\text{C}$  retains its quintessential layered MXene crystalline structure.

The dynamism of the UV-vis spectra of the  $\text{V}_4\text{C}_3$  suspension, mapped across the span of oxidation at 40 °C, delineates the shifting optical properties inherent to the metamorphosis from  $\text{V}_4\text{C}_3$  to  $\text{VO}_x\text{C}$ . Of particular note are the emergent peaks at wavelengths 280 and 400 nm, serving as hallmarks of the  $\text{VO}^{2+}$  absorption band. This further corroborates the reconstruction narrative of  $\text{VO}_x\text{C}$ , mirroring findings from the XRD analysis (Fig. 2f).

Furthermore, the oxidative journey begets a palpable expansion in the DLS diameter, evolving from  $\sim 250$  nm in  $\text{V}_4\text{C}_3$  to  $\sim 350$  nm in  $\text{VO}_x\text{C}$  (Fig. 2g). Concurrently, we witness a declination in zeta potential values, transitioning from  $-44.8$  mV to a more subdued  $-29.6$  mV (Fig. 2h). FT-IR was instrumental in corroborating shifts in the surface functional group composition and bond structuring pre- and post-oxidation (Fig. 2i). The spectra for  $\text{VO}_x\text{C}$  are indicative of a discernible attenuation in the  $-\text{OH}$  signal juxtaposed against an escalation in the  $\text{C}=\text{O}$  signal intensity, a trend that resonates with the increased tethering of oxygen during oxidation.

Cumulatively, these revelations shed light on profound transformations in morphology, dimensions, crystallinity, surface characteristics, and optical nuances associated with  $\text{V}_4\text{C}_3$  and its oxidized counterpart,  $\text{VO}_x\text{C}$ . This underscores the pivotal role auto-oxidation plays in sculpting the MXene framework. Providentially, this lends an intuitive avenue to fathom the structure–activity nexus, thereby facilitating the nuanced tailoring of MXene functionalities.

Beyond the notable metamorphosis in atomic structure,  $\text{V}_4\text{C}_3$ 's oxidation journey substantially reconfigures both its elemental composition and bond disposition. The XPS survey spectra vouch for the concurrent presence of V, C, and O across both the  $\text{V}_4\text{C}_3$  and  $\text{VO}_x\text{C}$  spectra, as illuminated in Fig. 3a. Intriguingly, while elemental consistency persists, a remarkable oxygen upsurge is discerned. Spectrum analysis reveals an escalation in the oxygen fraction, notably surging from 25.23% in  $\text{V}_4\text{C}_3$  to 43.10% in  $\text{VO}_x\text{C}$ . A deeper dive into the bonds

suggests that this newly incorporated oxygen predominantly pairs with V in a V–O arrangement, as detailed in Table S1.†

In the meticulous V 2p high-resolution XPS spectra of  $\text{V}_4\text{C}_3$  nanosheets, four distinct deconvolutional peaks emerge. These correspond to the diverse states: V–C ( $\text{V}^{2+}$ ),  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ , and  $\text{V}^{5+}$ . The manifestation of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  signals might owe their presence to incidental oxidation of  $\text{V}_4\text{C}_3$  during storage and subsequent measurements. On the other hand, the discerned doublet peaks in  $\text{VO}_x\text{C}$  echo the signatures of  $\text{V}^{3+}$ ,  $\text{V}^{4+}$ , and  $\text{V}^{5+}$ .<sup>30,31</sup> Astoundingly, post-oxidative treatment, the V–C bond in  $\text{VO}_x\text{C}$  ceases to exist, highlighting the formation of  $\text{VO}_x\text{C}$  as a nuanced tapestry of mixed valence vanadium oxide, as exemplified in Fig. 3b. Diving deeper into the valence intricacies, a coexistence of multiple vanadium valences is evident in both  $\text{V}_4\text{C}_3$  and  $\text{VO}_x\text{C}$ .  $\text{V}_4\text{C}_3$  is predominantly colored by lower valences, with  $\text{V}^{2+}$  and  $\text{V}^{3+}$  jointly accounting for approximately 60% and cumulatively reaching near 90% with  $\text{V}^{4+}$ . In stark contrast,  $\text{VO}_x\text{C}$  showcases  $\text{V}^{4+}$  as the dominant player at about 50%, flanked by roughly equal contributions from  $\text{V}^{3+}$  and  $\text{V}^{5+}$ .

Pivoting to the C 1s spectrum of  $\text{V}_4\text{C}_3$  nanosheets, the analysis discerns four Gaussian peaks, symbolizing V–C, C–C, C–H, and C–O. Herein, the V–C peak is conspicuously absent post-oxidation, accompanied by a diminution in the C–H peaks, while the C–C and C–O peaks see a significant surge in intensity, as captured in Fig. 3c. The orchestrated O 1s peaks, signifying varied oxygen bonds in V–C(OH)<sub>x</sub>, C=O, V–O, and V–O<sub>x</sub>, buttress the assertion of a marked augmentation in bound V oxygen, a narrative articulated in Fig. 3d.

Collectively, through mentioned above analytical techniques (TEM, XRD, XPS, *etc.*), the oxidation proceeding mechanism have been uncovered. With the oxidation proceeding, the morphology, size distribution, crystal structure, chemical element, and valence compositions have changed dramatically, underscoring the  $\text{V}_4\text{C}_3$  nanosheets go through destruction, disintegration, and reconstruction to form  $\text{VO}_x\text{C}$  nanosheets. These insights paint a compelling picture of the oxidation's transformative potential, underscoring its finesse in masterfully orchestrating the chemical and valence tapestry of MXenes.



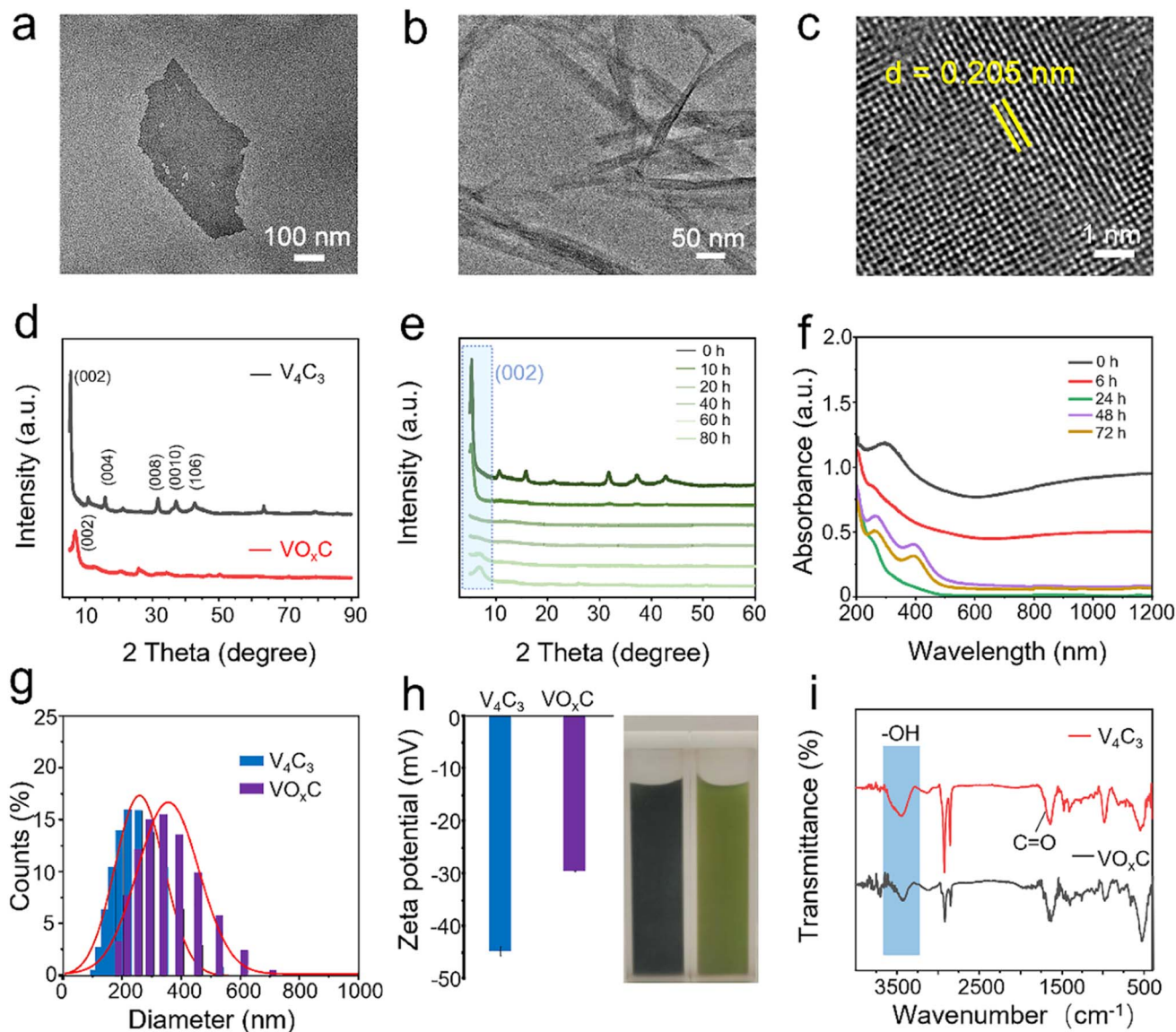


Fig. 2 Characterization of  $V_4C_3$  and  $VO_xC$  nanosheets. (a) TEM image of fresh  $V_4C_3$  nanosheets; (b) TEM and (c) HRTEM images of  $VO_xC$  nanosheets after auto-oxidation treatment for 72 h at 40 °C; (d) XRD patterns of fresh  $V_4C_3$  and  $VO_xC$  nanosheets; (e) XRD patterns of  $V_4C_3$  at different oxidation times; (f) UV-vis absorption spectra of  $V_4C_3$  at different oxidation times; (g) kinetic dimension comparison of fresh  $V_4C_3$  and  $VO_xC$  nanosheets; (h) zeta potential comparison and optical image of fresh  $V_4C_3$  and  $VO_xC$  nanosheets; (i) FT-IR comparison before and after oxidation of fresh  $V_4C_3$  and  $VO_xC$  nanosheets.

### 3.2 Oxidation engineering triggered the POD-like activity of $VO_xC$ nanosheets

The auto-oxidative process introduces profound shifts in the redox potential of  $V_4C_3$  nanosheets, catalyzing unanticipated biological activities. Predominantly, the antioxidant prowess emerges as a central narrative. The evolution of the antioxidant disposition of  $V_4C_3$  nanosheets through the oxidation arc holds paramount significance in biological contexts. Our meticulous exploration unveiled that nascent  $V_4C_3$  nanosheets exhibit a flair for ROS scavenging, underscoring their remarkable antioxidant fortitude. To distill the core of this study, we gauged antioxidant efficacy through the lens of the total antioxidant capacity (TAC), facilitated by the reduction of  $ABTS^{+}$ . This

entity, borne from the oxidation of  $ABTS$  via  $K_2S_2O_8$ , is a staple in TAC assays. Parallely, the pro-oxidant mettle was mapped via its prowess in orchestrating TMB oxidation, a chromogenic substrate emblematic of POD-like activity assays. This oxidation typically manifests as a distinctive blue hue, characterized by its unique absorption spectrum. In their pristine state,  $V_4C_3$  nanosheets can deftly quench  $ABTS^{+}$ , resonating with their antioxidant acumen, yet remain inert to catalyzing TMB oxidation in an  $H_2O_2$  milieu.

However, as oxidation progresses, a captivating narrative unfolds: the once dominant antioxidant efficacy, as gauged by  $ABTS^{+}$  reduction, wanes progressively until it vanishes (Fig. 4a). Intriguingly, after an incubation of 40 h, the once dormant



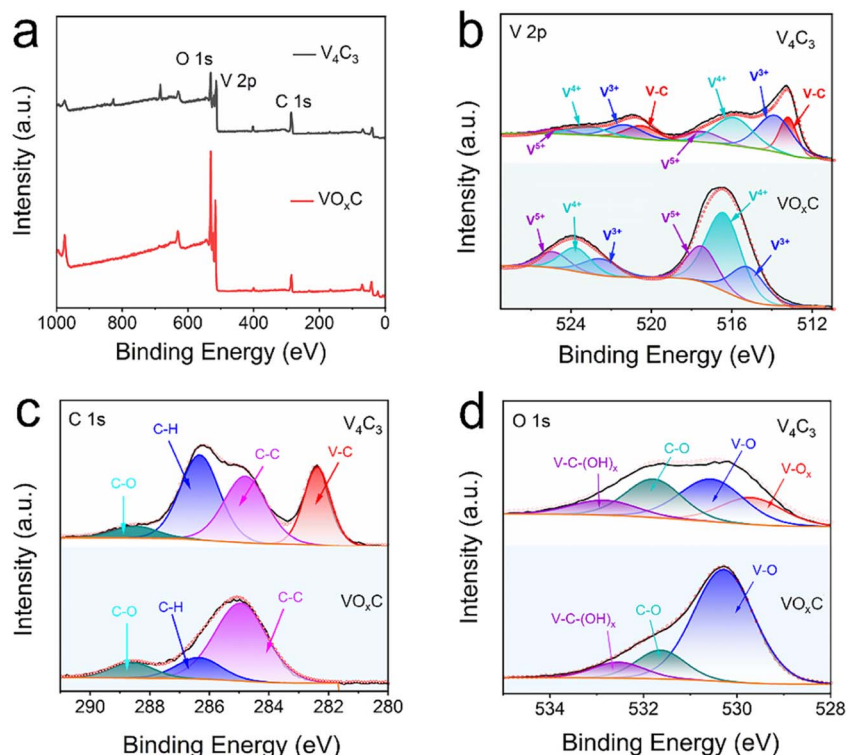


Fig. 3 XPS spectra of  $\text{VO}_x/\text{C}$  nanosheets. (a) Survey spectra; (b–d) high-resolution fitted spectra of V 2p, O 1s, and C 1s.

POD-like dynamism to drive TMB oxidation stirs to life, amplifying subsequently (Fig. 4a). These crescendo peaks post a 60 h oxidation interval, where the POD zeal reaches its zenith and the ABTS<sup>+</sup> quenching capability plunges to its nadir. Fig. 4b and c vouch for the capability of  $\text{VO}_x/\text{C}$  in spearheading TMB oxidation in an  $\text{H}_2\text{O}_2$  backdrop and a time-centric paradigm, devoid of any oxidase (OXD)-like undertones. Fig. 4a encapsulates this transformational journey, portraying the poignant intersection between antioxidant and pro-oxidant trajectories around the 40 h mark during the  $\text{V}_4\text{C}_3$  nanosheet oxidation. This empirical revelation underscores the crux of our findings:  $\text{V}_4\text{C}_3$  oxidation is the linchpin that pivots the sheets from their inherent antioxidant stature to a newfound pro-oxidant persona, replete with intrinsic POD-like activity.

Temperature is pivotal in governing the oxidation kinetics of  $\text{V}_4\text{C}_3$  and subsequently sculpting the emergence of  $\text{VO}_x/\text{C}$ . Indeed, it's conceivable that such variations could inflect the nuances of POD activity. To unravel this thermodynamic interplay, we embarked on a systematic investigation spanning four distinct oxidation temperatures: 40 °C, 50 °C, 60 °C, and 70 °C. Our objective was to chart the interplay between POD-like activity and the temperature trajectory.

As illustrated in Fig. 4d,  $\text{VO}_x/\text{C}$ , when nurtured at 40 °C, reaches the zenith of POD-like activity. However, a captivating trend emerges with escalating temperatures. Each incremental rise attenuates the POD prowess of the resulting  $\text{VO}_x/\text{C}$  nanosheets. To present a stark contrast,  $\text{V}_4\text{C}_3$  nanosheets underwent rigorous oxidation through calcination at 500 °C in an air milieu, culminating in the formation of  $\text{V}_2\text{O}_5$  nanocrystals

(Fig. S3†). When juxtaposed, the POD-like dynamism of  $\text{VO}_x/\text{C}$  (birthed at 40 °C) conspicuously outshines, being an astounding 5.5-fold more potent than its  $\text{V}_2\text{O}_5$  counterpart (Fig. 4e).

Further exploration into the catalytic nuances of  $\text{VO}_x/\text{C}$  led to a systematic assessment of its responses to variations in pH, as well as  $\text{H}_2\text{O}_2$  and TMB concentrations, as depicted in Fig. 4f–h. Intriguingly,  $\text{VO}_x/\text{C}$ 's optimal catalytic activity manifested at a pH of 5.0. This pH mark stands marginally elevated compared to canonical nano-peroxidases, suggesting a unique response profile for  $\text{VO}_x/\text{C}$  in the nano-peroxidase family.<sup>32</sup> The concentration of  $\text{H}_2\text{O}_2$  shares the same trends on affecting the catalytic rate, which is positively proportional to  $\text{H}_2\text{O}_2$  and TMB concentration in the detection range. By fitting the typical double reciprocal plots ( $1/\nu$  vs.  $1/[S]$ ) to the *Michaelis-Menten* equation, we calculated the enzyme kinetic parameters of  $\text{VO}_x/\text{C}$  as peroxidase using  $\text{H}_2\text{O}_2$  and TMB as substrate, respectively (Fig. 4e and g). When TMB is the substrate, the *Michaelis* constant ( $K_m$ ) and maximum reaction velocity ( $V_{\text{max}}$ ) was calculated to be 0.01912 mM and  $9.745 \times 10^{-6} \text{ M s}^{-1}$ , respectively. When  $\text{H}_2\text{O}_2$  is substrate, the  $K_m$  and  $V_{\text{max}}$  of  $\text{VO}_x/\text{C}$  were calculated to be 1.54 mM and  $33.45 \times 10^{-6} \text{ M s}^{-1}$ , respectively. This test results suggest that  $\text{VO}_x/\text{C}$  exhibited superior POD-like activity. To reveal the POD-like catalytic mechanism, the production of hydroxyl radicals in the presence of  $\text{VO}_x/\text{C}$  and hydrogen peroxide was determined by fluorescence spectroscopy. TA is selected as the fluorescent probe to  $\cdot\text{OH}$ . The results showed a stronger fluorescence signal after the mixture of TA,



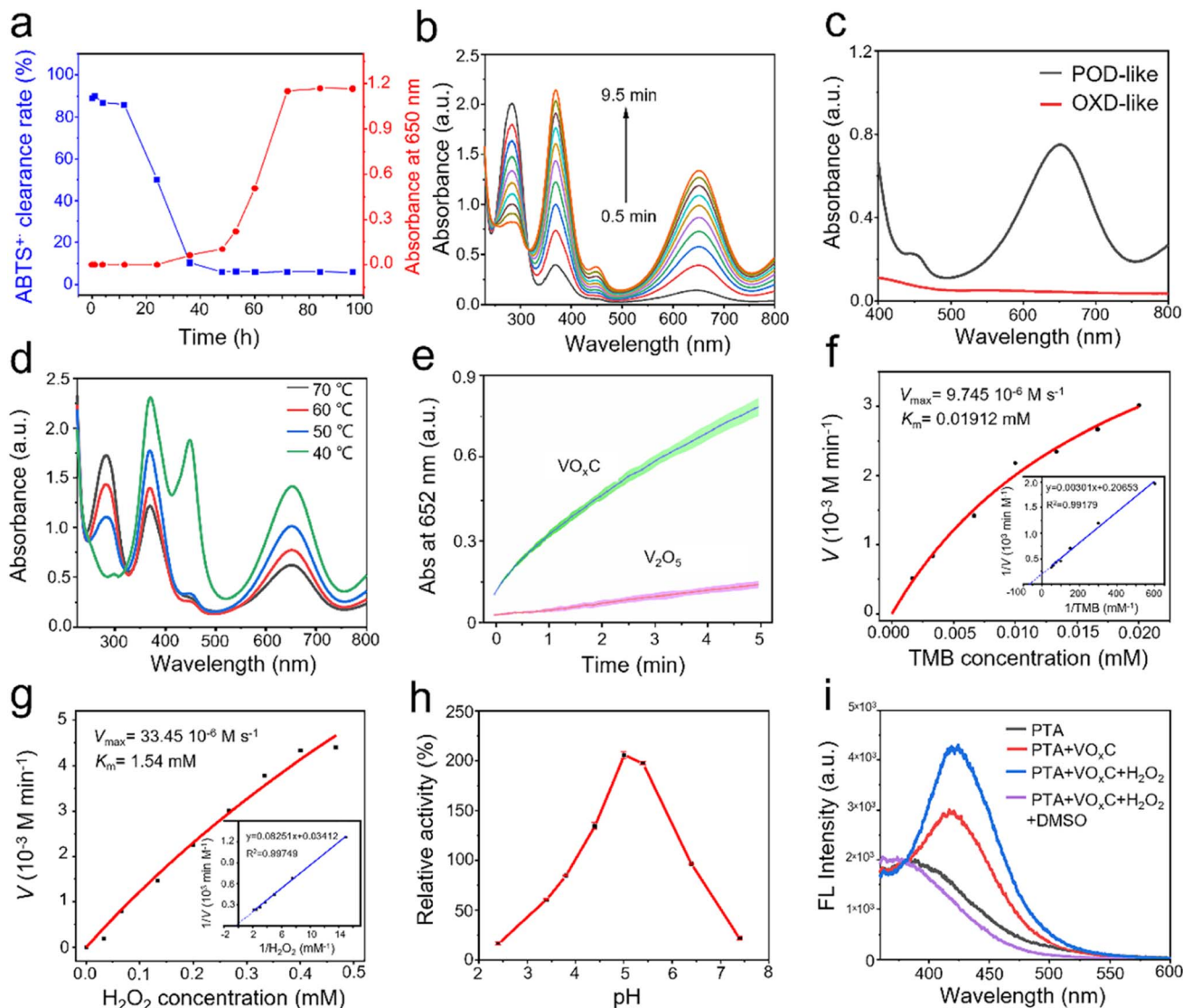


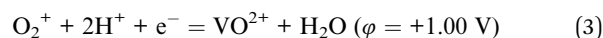
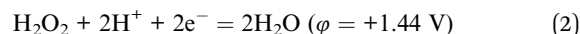
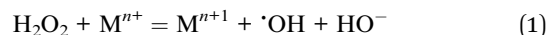
Fig. 4 POD-like activity of  $\text{VO}_x\text{C}$ . (a) The transformation of antioxidant and POD-like activity during the oxidation process; (b) kinetic absorption spectra of  $\text{H}_2\text{O}_2$  oxidation of TMB catalyzed by  $\text{VO}_x\text{C}$ ; (c) comparison of TMB absorption spectra of  $\text{VO}_x\text{C}$  catalytic oxidation with and without  $\text{H}_2\text{O}_2$ ; (d) the comparison of  $\text{VO}_x\text{C}$  prooxidation activities at different oxidation temperatures; (e) comparison the POD-like activity of  $\text{VO}_x\text{C}$  and  $\text{V}_2\text{O}_5$ ; (f–g) effect of TMB and  $\text{H}_2\text{O}_2$  concentration on the rate of  $\text{VO}_x\text{C}$  catalytic oxidation of TMB; the illustration shows the corresponding double reciprocal plots; (h) relative POD activity at different pH values; (i) fluorescence spectra of hydroxyl captured by PTA.

$\text{VO}_x\text{C}$  and  $\text{H}_2\text{O}_2$ , and the signal could be removed by typical  $\cdot\text{OH}$  scavenger DMSO, demonstrating the generation of  $\cdot\text{OH}$ .

### 3.3 Possible mechanism for POD-like activity

Drawing from our comprehensive analysis, a conceptual trajectory detailing the metamorphosis from  $\text{V}_4\text{C}_3$  to  $\text{VO}_x\text{C}$  emerges (Fig. 5a). Initiated by oxidative interactions, the resilient V–C bonds are compromised, leading to a substantial alteration in the initial structural framework. As the oxidation journey continues, there's a subsequent structural renaissance marked by the reorganization and re-crystallization of the  $\text{VO}_x\text{C}$  nanocrystals. This transformative sequence culminates in pronounced shifts in both morphology and chemical composition (Fig. 5b).

Pivoting to the underlying mechanics of POD-like activity, we venture into the domain of valence engineering. The canonical Fenton or Fenton-like processes, underpinned by the interaction between  $\text{H}_2\text{O}_2$  and specific transition metal ions (notably  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$ ), have been acclaimed for their prowess in spawning hydroxyl radicals through reaction (1). Many studies are reporting the POD-like activity of nanomaterials is attributed to hydroxyl radicals' production based on Fenton reactions.<sup>33</sup>



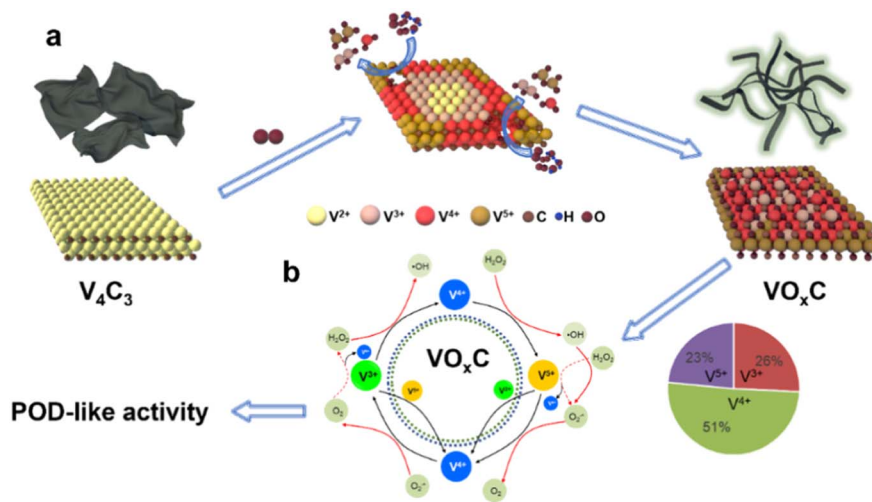
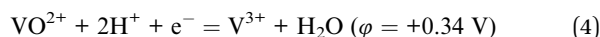
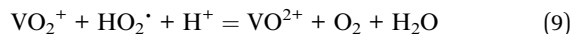
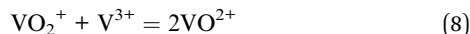
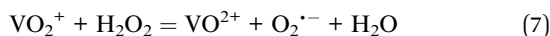
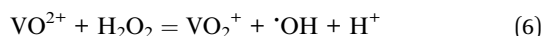
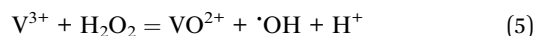


Fig. 5 The schematic diagram for the (a) formation mechanism of VO<sub>x</sub>C and (b) the valence engineering driven catalytic mechanism for POD-like activity of VO<sub>x</sub>C.



Vanadium complexes represent an important kind of catalysts in chemical and biological applications because of their unique electronic property.<sup>34</sup> In our VO<sub>x</sub>C, the chemistry of vanadium is accessible with 3 adjacently mixed valence states +3 to +5 in an aqueous solution. As we calculated above, oxidation can balance the V valence compositions. The proportional composition of V<sup>3+</sup>, V<sup>4+</sup> and V<sup>5+</sup> in VO<sub>x</sub>C is 26%, 51% and 23%, respectively. Such mixed valence state with V<sup>4+</sup> dominating possesses abundant electron transport behaviors. The standard redox half-reactions for H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O, VO<sub>2</sub><sup>+</sup>/VO<sup>2+</sup> and VO<sup>2+</sup>/V<sup>3+</sup> are shown above.<sup>35</sup> Theoretically, either V<sup>3+</sup> and V<sup>4+</sup> can react with hydrogen peroxide to generate hydroxyl radicals based on Fenton mechanisms (eqn (5) and 6).<sup>36</sup>



Strikingly, the VO<sub>2</sub><sup>+</sup> species can be reduced back to VO<sup>2+</sup> through three pathways, as depicted in eqn (7)–(9). These routes allow for the completion of the cycle. Owing to the presence of mixed valences, it is hypothesized that there are multiple pathways to produce hydroxyl radicals, as well as four pathways for the regeneration of VO<sup>2+</sup> and V<sup>3+</sup>. This maintains the cycle (Fig. 5b). As a result, VO<sub>x</sub>C exhibits a highly efficient and persistent ability to generate hydroxyl radicals, demonstrating robust and sustained POD-like activity.

Notably, it is important to understand why the freshly prepared V<sub>4</sub>C<sub>3</sub> does not exhibit POD-like activity or generate hydroxyl radicals. The freshly prepared V<sub>4</sub>C<sub>3</sub>, which has

undergone minimal oxidation, mainly comprises vanadium in lower valence states. The V<sup>2+</sup>, V<sup>3+</sup> and V<sup>4+</sup> not only have the potential to produce hydroxyl radicals based on the Fenton mechanism, but they also act as potent reducing agents capable of reducing ·OH and H<sub>2</sub>O. This results in complex reaction dynamics.

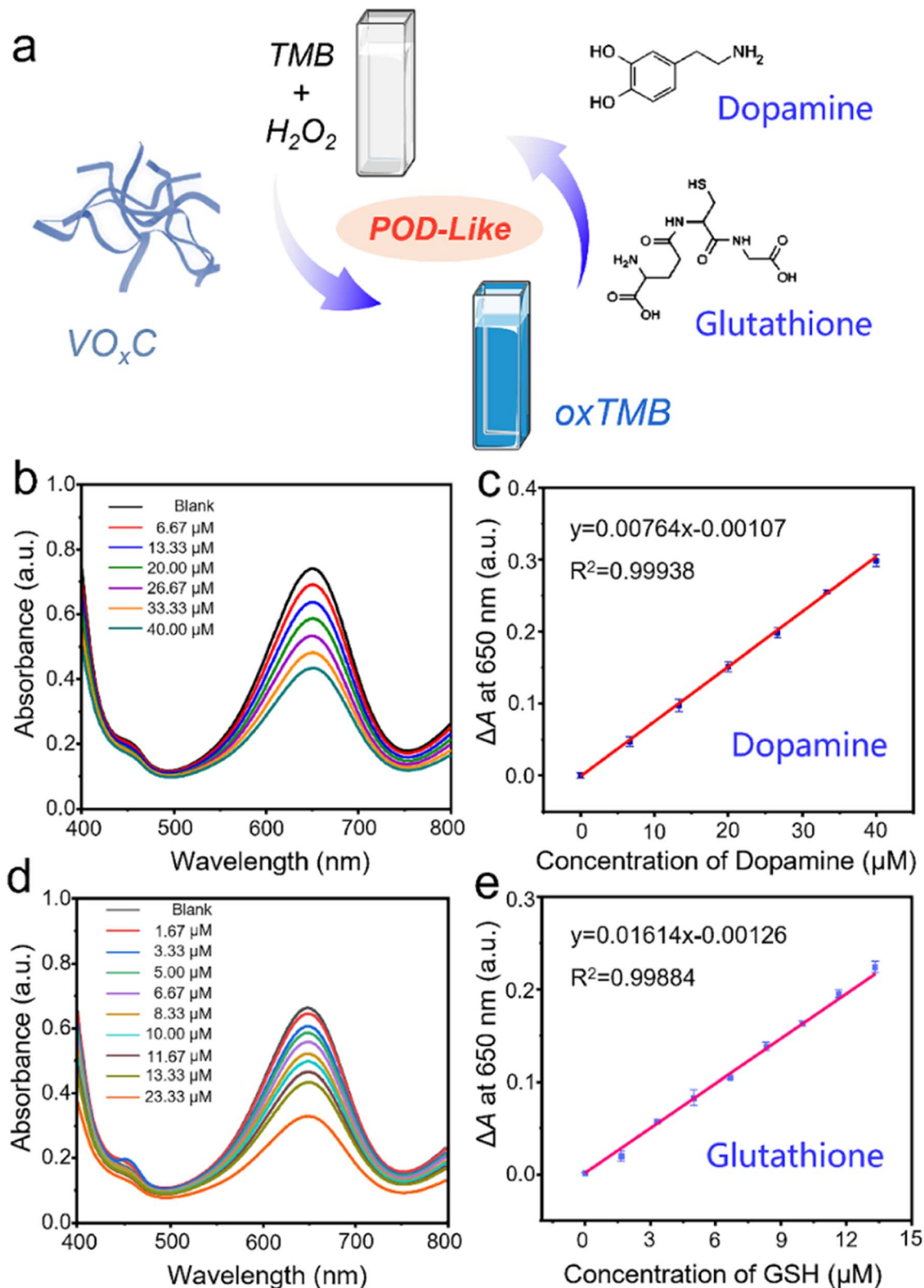
The rich presence of low-valence states with strong electron-donating capabilities can effectively and quickly reduce highly active ·OH, explaining the observed phenomena. These findings highlight that the valence composition of mixed-valence vanadium is critical in regulating biological activities, such as anti-oxidant and pro-oxidant behaviors. In this study, we demonstrated that controlling auto-oxidation provides a potential strategy for regulating valence composition.

#### 3.4 Detection of dopamine and glutathione

The inherent POD-like functionality of VO<sub>x</sub>C has remarkable implications not just in the realm of catalysis, but also in the domain of biological detection. Dopamine, a pivotal neurotransmitter and hormone, assumes significant interest due to its potential dysregulation, leading to a multitude of health disorders. An overexpression can trigger conditions like mania, obesity, and addictive behaviors, whereas a deficiency is often linked to Parkinson's disease and attention deficit hyperactivity disorder. Thus, the importance of accurate detection of dopamine for managing health conditions can't be overstated.

In our investigations, we discovered that the POD-like activity of VO<sub>x</sub>C could be suppressed by dopamine, consequently slowing down the oxidation of TMB. Interestingly, this inhibition was found to be dependent on the concentration of dopamine, which sets the foundation for the colorimetric detection of this neurotransmitter. We designed experiments in which the concentrations of VO<sub>x</sub>C, H<sub>2</sub>O<sub>2</sub>, and TMB were kept constant while varying the dopamine concentrations. As dopamine was introduced, we observed a decrease in absorbance at 650 nm, indicating a reduction in TMB oxidation (Fig. 6b).





**Fig. 6** Detection of dopamine and glutathione by using the POD-like activity of  $\text{VO}_x\text{C}$ . (a) Scheme of the inhibitory mechanism for biomolecular detection. (b) The UV-vis absorption spectrum evolution in the absence and presence of dopamine with different concentrations. (c) The dependence of  $\Delta A$  at 650 nm on the concentration of dopamine. (d) The UV-vis absorption spectrum evolution in the absence and presence of glutathione with different concentrations. (e) The dependence of  $\Delta A$  at 650 nm on the concentration of glutathione.



Following this, we plotted a response curve of  $A_0 - A$  ( $\Delta A$ ), where  $A_0$  denotes the absorbance of the control group and  $A$  represents the absorbance in the presence of varied dopamine concentrations. The plot displayed a robust linear relationship ( $R^2 = 0.999$ ) within the dopamine concentration range of 6.67–40  $\mu\text{M}$ , with the limit of detection (LOD) for dopamine determined to be 2.5  $\mu\text{M}$  ( $S/N = 3$ ) (Fig. 6c). Interestingly, dopamine molecules, with their amino and phenolic hydroxyl groups, have the potential to act as electron donors, reducing  $\text{H}_2\text{O}_2$  and leading to the formation of dopamine-*o*-quinone. This involvement of dopamine competes with TMB for  $\text{H}_2\text{O}_2$  consumption, thereby reducing the amount of  $\text{H}_2\text{O}_2$  involved in TMB oxidation and subsequently leading to a decrease in absorbance at 650 nm. This intriguing discovery underscores the potential utility of  $\text{VO}_x\text{C}$  in dopamine detection.

Often hailed as “The Mother of All Antioxidants,” glutathione occupies a pivotal position in biological systems, instrumental in governing immune responses and determining longevity. A scarcity of this antioxidant in the body frequently correlates with numerous chronic ailments and diseases. In a manner mirroring dopamine, glutathione's potent antioxidant properties can also stifle the POD-like activity of  $\text{VO}_x\text{C}$ . Seizing upon this inhibitory paradigm, we engineered a colorimetric assay for glutathione detection. Maintaining consistent concentrations of  $\text{VO}_x\text{C}$ ,  $\text{H}_2\text{O}_2$ , and TMB, we varied glutathione levels within controlled bounds. Our observations conclusively revealed that the oxidation rate of TMB is markedly suppressed by glutathione, and this suppression is strikingly concentration-dependent (Fig. 6d).

Further analysis provided a lucid view: plotting the response  $\Delta A$  at 650 nm against glutathione concentrations spanning from 1.67 to 23.33  $\mu\text{M}$  unveiled a tight linear correlation, as evident from an  $R^2$  value of 0.9988. This assay demonstrated an impressive LOD for glutathione, pegging it at 0.36  $\mu\text{M}$ . Therefore, leveraging the unique POD-like properties of  $\text{VO}_x\text{C}$  nanosheets presents an elegant and efficient route to detect crucial bio-analytes like dopamine and glutathione, further enriching the palette of analytical tools in biomedicine.

## 4. Conclusion

In conclusion, the POD-like activity of  $\text{VO}_x\text{C}$  nanosheets triggered by oxidatively engineering  $\text{V}_4\text{C}_3$  MXene was presented in this work. With the oxidation proceeding, the  $\text{V}_4\text{C}_3$  nanosheets go through destruction, disintegration, and reconstruction to form  $\text{VO}_x\text{C}$  nanosheets and the morphology, size distribution, crystal structure, chemical element, and valence compositions have changed dramatically. Especially,  $\text{V}_4\text{C}_3$  is a non-enzymatic antioxidant that can scavenge free radicals, while the  $\text{VO}_x\text{C}$  shows superior POD-like activity to generate hydroxyl radicals. The valence engineering-driven mechanism underlying the POD-like activity was proposed, the oxidation balanced the valence composition of V in  $\text{VO}_x\text{C}$  that can facilitate the Fenton reaction through multiple pathways to persistently produce hydroxyl radicals. Based on the inhibitory effect on the POD-like activity of  $\text{VO}_x\text{C}$ , a facile method has been developed for the detection of dopamine and glutathione. Although oxidation

instability has been considered as the bottleneck challenge in MXenes development, it, fortunately, provides a facile way to delicately treat MXenes and produce various derivatives with versatility. Our study may suggest a reference for exploring MXenes' oxidation chemistry and catalytic function and a full understanding of their chemical and biological activities.

## Author contributions

He WW developed the concept and conceived the experiments. Jia HM and Liu Quan carried out the main experiments and wrote the manuscript. Chen YY and Zhou G performed partial experiments. Si JJ, Lan HH and He WW revised the manuscript. All the authors contributed to the data analysis and scientific discussion.

## Conflicts of interest

The authors declare no conflict of interest.

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## References

- 1 Á. Morales-García, F. Calle-Vallejo and F. Illas, *ACS Catal.*, 2020, **10**, 13487–13503.
- 2 L. Chen, X. Y. Dai, W. Feng and Y. Chen, *Acc. Chem. Res.*, 2022, **3**, 785–798.
- 3 Z. M. Qiu, Y. Bai, Y. D. Gao, C. L. Liu, Y. Ru, Y. C. Pi, Y. Z. Zhang, Y. S. Luo and H. Pang, *Rare Met.*, 2022, **41**, 1101–1128.
- 4 Y. Cheng, L. Li, Z. Liu, S. Yan, F. Cheng, Y. Yue, S. Jia, J. Wang, Y. Gao and L. Li, *Research*, 2022, **2022**, 9843268.
- 5 Y. Cheng, Y. Xie, H. Cao, L. Li, Z. Liu, S. Yan, Y. Ma, W. Liu, Y. Yue, J. Wang, Y. Gao and L. Li, *Chem. Eng. J.*, 2023, **453**, 139823.
- 6 M. Naguib, V. N. Mochalin, M. W. Barsoum and Y. J. A. m. Gogotsi, *Adv. Mater.*, 2014, **26**, 992–1005.
- 7 R. M. S. Yoo and A. Djire, *ACS Catal.*, 2023, **13**, 6823–6836.
- 8 X. S. Lv, L. Z. Kou and T. Frauenheim, *ACS Appl. Mater. Interfaces*, 2021, **13**, 14283–14290.
- 9 X. S. Sun, X. J. He, Y. Zhu, E. Obeng, B. R. Zeng, H. Deng, J. I. Shen and R. D. Hu, *Chem. Eng. J.*, 2023, **451**, 138985.
- 10 Z. L. Tan, J. X. Wei, Y. Liu, F. u. Zaman, W. Rehman, L. R. Hou and C. Z. Yuan, *Rare Met.*, 2022, **41**, 775–797.
- 11 Y. Cheng, Y. Xie, Z. Liu, S. Yan, Y. Ma, Y. Yue, J. Wang, Y. Gao and L. Li, *ACS Nano*, 2023, **17**, 1393–1402.
- 12 Y. Cheng, Y. Xie, Y. Ma, M. Wang, Y. Zhang, Z. Liu, S. Yan, N. Ma, M. Liu, Y. Yue, J. Wang and L. Li, *Nano Energy*, 2023, **107**, 108131.
- 13 H. Huang, C. h. Dong, W. Feng, Y. Wang, B. c. Huang and Y. Chen, *Adv. Drug Delivery Rev.*, 2022, **184**, 114178.



- 14 J. L. Wu, Y. Y. Yu and G. X. Su, *Nanomaterials*, 2022, **12**, 828.
- 15 Y. Cheng, Y. Xie, S. Yan, Z. Liu, Y. Ma, Y. Yue, J. Wang, Y. Gao and L. Li, *Sci. Bull.*, 2022, **67**, 2216–2224.
- 16 L. Li, Y. Cheng, H. Cao, Z. Liang, Z. Liu, S. Yan, L. Li, S. Jia, J. Wang and Y. Gao, *Nano Energy*, 2022, **95**, 106986.
- 17 R. A. Soomro, P. Zhang, B. M. Fan, Y. Wei and B. Xu, *Nano-Micro Lett.*, 2023, **15**, 108.
- 18 F. C. Cao, Y. Zhang, H. Q. Wang, K. Khan, A. K. Tareen, W. Qian, H. Zhang and H. Ågren, *Adv. Mater.*, 2022, **34**, 2107554.
- 19 X. F. Zhao, A. Vashisth, E. Prehn, W. M. Sun, S. A. Shah, T. Habib, Y. Chen, Z. Tan, J. L. Lutkenhaus and M. Radovic, *Green Matter.*, 2019, **1**, 513–526.
- 20 H. Q. Geng, Y. P. Ren, G. Qin, T. Wen, Q. Liu, H. Y. Xu and W. W. He, *RSC Adv.*, 2022, **12**, 11128–11138.
- 21 Y. Li, R. Z. Fu, Z. G. Duan, C. H. Zhu and D. D. Fan, *ACS Nano*, 2022, **16**, 7486–7502.
- 22 W. Feng, X. G. Han, H. Hu, M. Q. Chang, L. Ding, H. J. Xiang, Y. Chen and Y. H. Li, *Nat. Commun.*, 2021, **12**, 2203.
- 23 X. Zhao, L. Y. Wang, J. M. Li, L. M. Peng, C. Y. Tang, X. J. Zha, K. Ke, M. B. Yang, B. H. Su and W. Yang, *Adv. Sci.*, 2021, **8**, 2101498.
- 24 C. J. Du, W. Feng, X. Y. Dai, J. H. Wang, D. Y. Geng, X. D. Li, Y. Chen and J. Zhang, *Small*, 2022, **18**, 2203031.
- 25 X. Y. Ren, M. F. Huo, M. M. Wang, H. Lin, X. X. Zhang, J. Yin, Y. Chen and H. H. Chen, *ACS Nano*, 2019, **13**, 6438–6454.
- 26 R. F. Zhang, X. Y. Yan and K. L. Fan, *Acc. Chem. Res.*, 2021, **2**, 534–547.
- 27 H. Wei, L. Z. Gao, K. L. Fan, J. W. Liu, J. Y. He, X. G. Qu, S. J. Dong, E. K. Wang and X. Y. Yan, *Nano Today*, 2021, **40**, 101269.
- 28 Q. Yang, Y. Y. Mao, Q. Liu and W. W. He, *Rare Met.*, 2023, **42**, 2928–2948.
- 29 Y. Wei, P. Zhang, R. A. Soomro, Q. Z. Zhu and B. Xu, *Adv. Mater.*, 2021, **33**, 2103148.
- 30 X. Wang, S. Lin, H. Y. Tong, Y. N. Huang, P. Tong, B. C. Zhao, J. M. Dai, C. H. Liang, H. Wang, X. B. Zhu, Y. P. Sun and S. X. Dou, *Electrochim. Acta*, 2019, **307**, 414–421.
- 31 Y. Liu, Y. Jiang, Z. Hu, J. Peng, W. H. Lai, D. L. Wu, S. W. Zuo, J. Zhang, B. Chen, Z. W. Dai, Y. G. Yang, Y. Huang, W. Zhang, W. Zhao, W. Zhang, L. Wang and S. L. Chou, *Adv. Funct. Mater.*, 2020, **31**, 2008033.
- 32 L. Z. Gao, J. Zhuang, L. Nie, J. B. Zhang, Y. Zhang, N. Gu, T. H. Wang, J. Feng, D. L. Yang, S. Perrett and X. Yan, *Nat. Nanotechnol.*, 2007, **2**, 577–583.
- 33 H. J. Dong, W. Du, J. Dong, R. C. Che, F. Kong, W. L. Cheng, M. Ma, N. Gu and Y. Zhang, *Nat. Commun.*, 2022, **13**, 5365.
- 34 R. R. Langeslay, D. M. Kaphan, C. L. Marshall, P. C. Stair, A. P. Sattelberger and M. Delferro, *Chem. Rev.*, 2019, **119**, 2128–2191.
- 35 F. A. Cotton, G. Wilkinson, C. A. Murillo and M. Bochmann, *Adv. Inorg. Chem.*, John Wiley and Sons, Inc., 1999.
- 36 G. D. Du and J. H. Espenson, *Inorg. Chem.*, 2005, **44**, 5514–5522.

