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Shape-memory V_3O_7 ·H₂O Electrocatalyst for Foldable N₂ Fixation

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Shape-memory materials can retain their functionalities during mechanical deformation, thus hold great promise for utilizations in versatile wearable and portable systems. Here we report a shape-memory $V_3O_7 \cdot H_2O$ monolith to works as a new emerging foldable electrocatalyst for nitrogen reduction reaction (NRR). Remarkably, the electrocatalyst has been designed according to our unexpected observation that metal oxides, commonly considered as a class of tough and brittle materials, can show shape-memory properties after anisotropic alignment of their microstructures by using an ice-templated freeze-casting method. We demonstrate the $V_3O_7 \cdot H_2O$ electrocatalyst for promoting NRR characteristic of excellent performances, including an ammonia yield rate of $36.42 \ \mu g \ h^{-1} \ mg^{-1}$, Faradic efficiency of 14.20% at -0.55 V (*vs.* RHE), and operation for seven cycles without activity or structural degradation. Remarkably, the NRR Faradic efficiencies do not change during electrode deformations, while ammonia yield rates only show a slight decline even after significant foldings. We further elucidate through density function theory that NRR proceeds at vanadium active sites of $V_3O_7 \cdot H_2O$ *via* associative distal pathway with $*N_2 + H^+ \rightarrow *N_2H$ as the rate-limiting step.

Introduction

Known as one of the most critical industrial chemicals, ammonia (NH₃) has attracted increasing attention as a viable energy carrier with intensive energy densities and high hydrogen percentages.¹⁻² Generally, ammonia has been produced by the hydrogenation of nitrogen gas (N₂) from atmosphere, which is extremely difficult because of the inherently tough N=N triple bondings.³⁻⁴ In industry, this energy barrier has been overcome by Haber-Bosch process under harsh reaction conditions of high-temperature (350-550 °C) and pressure (150-350 atm), which has consumed more than 1% of annual energy supply in the world.^{2, 4} Moreover, the Haber-Bosch process has belched out millions of tonnes of carbon dioxide into atmosphere every year. Consequently, to alleviate these problems, it is of great importance to develop alternative pathways for N₂ fixation under mild and eco-friendly conditions.

Electrochemical N_2 fixation is a viable technique to produce ammonia, as it can work under ambient temperature and pressure without involving fossil fuels.⁵⁻⁷ The primary process of nitrogen electrofixation is cathodic nitrogen reduction reaction (NRR, N₂ + $6H_2O + 6e \rightarrow 2NH_3 + 6OH^{-}$), which takes place at complex N₂/electrolyte/electrode interfaces involving a six-electron coupled with proton transferring process.⁸ Consequently, various NRR electrocatalysts, both molecular and heterogeneous, have been designed to enhance the reaction efficiency. Molecular catalysts possess the advantage of highly exposed active sites,⁹ but tend to de-activate during electrochemical cycling. In contrast, heterogeneous catalysts (such as metals¹⁰ and their oxides¹¹⁻¹³ and heteroatom-doped carbons¹⁴) are more structurally stable, and can easily interface with electrode systems. Among heterogeneous catalysts, metal oxides (like vanadium oxide⁸) are promising candidates for NRR because of their suitable N₂ protonation and ammonia desorption capability.¹¹⁻¹² Several strategies have been reported to enhance their properties like morphology control,12 downsizing,¹¹ and hybridization with secondary elements.¹³

Recently, flexible energy systems have received enormous interest because of their remarkable features such as lightweight, small-size unit, and shape conformability,¹⁵⁻¹⁸ which constitute promising candidates for the utilizations in versatile foldable, portable and wearable devices. However, the currently reported nitrogen fixation systems are generally present in the form of bulky and heavy architectures, indicating that they are far behind the requirement of flexibility.^{1, 19} Traditional NRR electrodes are prepared by the deposition of powder- or thin film-form electrocatalysts, such as metal oxides¹¹⁻¹³ and others,¹⁴onto rigid substrates (like glassy carbon¹⁹ and silicon wafer¹), resulting in bulk

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and fragile electrochemical devices. Lately, several soft current collectors (such as carbon-fiber paper²⁰⁻²¹ and metal foams²²⁻²³) have been employed to make NRR catalyst electrodes by taking advantages of their excellent properties of interconnected porous networks, high electrical conductivity, and mechanical stability. Integrating these soft substrates with catalytic active species has been achieved by the synthetic strategies of solution-casting or direct growth.¹²⁻¹⁵ However, owning to the intrinsically fragile nature of powders¹⁹ or thin-films,¹ the flexible behaviors of asresultant NRR electrodes are still compromised, leading to considerable activity decay in the process of electrode deformations.

Shape-memory materials represent a category of functional materials renowned for their excellent mechanical flexibility, which can maintain the original functionalities after being quasi-plastically distorted.²⁴⁻²⁵ The corresponding phenomenon is known to be shape-memory effect, which is originated from different mechanisms with respect to the recently reported two subclass of members, *i.e.*, superelasticity for shape memory alloys and visco-elasticity for shape memory polymers.²⁴ Remarkably, shape-memory materials have also exhibited excellent structural features such as rich meso/macropores and hierarchically arranged architectures, thus could become potential candidates for flexible and foldable electrocatalysts. Currently, no shape-memory materials have been explored for electrocatalytic reactions (such as NRR) yet.

In this work, the initial plan is to manipulate V₃O₇·H₂O, commonly considered as a tough material, into an ordered 3D architecture; but we unexpectedly see the resultant 3D monolith characteristic of typical shape memory behaviour, *i.e.*, it can quickly restore the original shape after significant mechanical deformation. To our best knowledge, this is the first observation of shape-memory effect in oxide materials. Consequently, we make use of this new emerging property of V₃O₇·H₂O to fabricate a foldable NRR electrocatalyst, which has delivered excellent performances both with and without electrode deformations. We further elucidate the NRR mechanisms for V₃O₇·H₂O electrocatalyst by theoretical simulations.

RESULTS AND DISCUSSIONS

Synthesis and morphology characterizations of V₃O₇·H₂O monolith. Different from traditional methods, 26-27 we propose a two-step procedure for preparing shape-memory V_3O_7 ·H₂O monolith that involves the crystal growth of V_3O_7 ·H₂O nanobelts followed by an ice-templated assembly assisted by freeze casting (Figs. 1a,S1-S3). In the first step, vanadium acetylacetonate (VO(acac)₂) has been used as the feeding source to hydrolyze in aqueous solution under hydrothermal treatment. The corresponding reaction intermediates have been taken out and examined by Fourier Translation Infrared Spectroscopy (FT-IR, Fig. S4) and Raman spectroscopy (Fig. S5), which illustrate a typical "nuclei and crystal growth" mechanism.

In the second step, V₃O₇·H₂O aqueous solution was prepared in a tube (Figs. S6,S7), and freezed and thawed under different conditions. When liquid nitrogen (-35 °C) is slowly poured into the bottom of the tube, water is frozen into ice at a suitable temperature gradient from bottom to up (~0.5 °C min⁻¹ mL⁻¹).²⁸⁻²⁹

Consequently, V_3O_7 ·H₂O was forced to align along the direction of ice solidification movement, resulting in 2O highly 30 refered 540 anisotropic 3D structure (Fig. S8c). During this process, we find two important synthetic parameters to influence the morphology, including dispersion concentrations and freezing methods. Beyond the concentration range of 0.75-4.8 mg mL⁻¹, V₃O₇·H₂O cannot form a 3D monolithic architecture (Fig. S3). On the other hand, only disordered V₃O₇·H₂O monoliths or powders were obtained if the freezing method was changed into quick liquid nitrogen freezing (rate: 5 °C min⁻¹ mL⁻¹), freezing by a refrigerator (rate: 0.014 °C min⁻¹ mL⁻¹), or directly dry in air (Figs. S8a,b).

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Fig. 1 Synthesis and morphology of V₃O₇·H₂O monolith. a) Schematic illustration of two-step synthetic procedure (scale bar: 100μ m). b-d) SEM images of V₃O₇·H₂O monolith (scale bars are 200 μ m, 1 μ m, and 200 nm for b, c and d. The inset of (b) is an optical image. e, f) SEM element mapping of O and V (scale bar, 200 nm). g) AFM image and corresponding height profile. h-j) TEM images (scale bars are 200, 100, and 5 nm for h, i, and j).

Next, the morphology of V₃O₇·H₂O monolith is characterized by optical image (inset of Figs. 1b,S3), which show a dark green macroscopic cylinder architecture with a mass density of 4.8 mg cm⁻ ³. The 3D monolith is composed of fluffy and ordered arrays composed of interwoven nanobelts according to scanning electron microscope images (SEM, Figs. 1b-d,2f-h). These nanobelts have a typical size of ~100 nm, thickness of ~15 nm, and length over several micrometers with very smooth surface and good structural flexibility (Figs. 1g-i). These features are different from the powder counterpart obtained from dry in air (Figs. 1a,S1,S2). Highresolution TEM (HRTEM) image shows well-resolved lattice fringes with a regular spacing of 0.467 nm, corresponding to the space between adjacent (020) crystal lines (Fig. 1j). The elements of V, O are uniformly distributed throughout the nanobelts as revealed by element mapping and energy dispersive spectroscopy (EDS, Figs. 1e,f,S9).

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Structure and mechanical property characterizations of V₃O₇·H₂O **monolith.** The structure of $V_3O_7 H_2O$ monolith is firstly characterized by X-ray diffraction (XRD), showing all the characteristic peaks corresponding to orthorhombic crystal phases of V₃O₇·H₂O (PDF# 85-2401, space group: *Pnam*, a = 16.9298 Å, b = 9.3598 Å, c = 3.6443 Å, Fig. 2a).^{26, 30-31} This result is consistent to other analytic methods including FT-IR (Fig. 2b), Raman spectra (Fig. S10), and X-ray photoemission spectroscopy (XPS, Fig. S11), all of which indicate the material contains V and O components without impurities. In addition, XPS V2p is deconvoluted into V2p_{3/2} at 515.6 and 516.8 eV, and $V2p_{1/2}$ at 522.6 and 523.9 eV, which correspond to V^{4+} and V^{5+} of $V_3O_7 \cdot H_2O$ phase (Fig. 2c). The XPS O1s spectrum at 529.6, 530.9 and 532 eV are attributed to $O-V^{5+}$, HO-V and $O-V^{4+}$ of V₃O₇·H₂O, respectively (Fig. 2d). Further, a remarkable structural advantage of V_3O_7 ·H₂O monolith is its high BET surface area of 22.3 m^2 g⁻¹ and a pore volume of 0.077 cm³ g⁻¹ (Fig. S12), which outperforms its powder counterpart (14.3 m² g⁻¹ and 0.035 cm³ g⁻¹). The result is consistent with the phenomenon shown by SEM (Figs. 1a,b,2f-h,S1).



Fig. 2 Structure and mechanical property characterizations of $V_3O_7 \cdot H_2O$ monolith. *a-e*) Structural characterizations: *a*) XRD patterns, showing a similar cystal structure to $V_3O_7 \cdot H_2O$ powder counterpart. *b*) FT-IR spectra. *c*, *d*) XPS spectra of V2p and O1s. *e-v*) mechanical properties: *e-t*) Real-time optical and SEM images for a typical compression cycle from 0 to 3 s (The scale bars are 500 μ m for *f*, *j*, *n*, *r*; 300 μ m for *g*, *k*, *o*, *s*; 100 μ m for *h*, *l*, *p*, *t*). *u*) Repeated compression cycles up to 50% strain. *v*) SEM image of $V_3O_7 \cdot H_2O$ monolith electrode after bending (scale bar, 300 μ m).

The shape-memory property for $V_3O_7 \cdot H_2O$ monolith has been examined by optical and SEM images in a typical compression and unloading cycle (mass density is 4.80 mg cm⁻³, Figs. 2e-t). As indicted by direction arrows: $V_3O_7 \cdot H_2O$ monolith is in fully relaxed initial state (0 s), applied external forces to 50% strain (1 s), restore its structure after release external forces (2 s), and complete relax process (3 s). The corresponding microstructures of shape change have been further examined by SEM (Figs. 2f-h,j-l,n-p,r-t), which clearly displays the anisotropic layered structure of $V_3O_7 \cdot H_2O$ nanobelts monolith. The adjacent layer spacing change from 125 to 32 µm after applying 50% strain to the architecture, which restore to 88 and 125 µm after the external force release within 2 and 3 s. The above phenomenon confirms the full recovery of ordered and anisotropic architecture of V_3O_7 ·H₂O nanobelt during compression cycles. Further, V_3O_7 ·H₂O monolith could exhibit excellent cycling performance with little structural degradation after ten cycles (Fig. 2u). Even if it has been deposited onto a carbon fiber substrate to making electrode (mass loading: 0.2 mg cm⁻²), it still maintains the structural integrity after applying external forces during electrode deformation (Fig. 2v). All of these results indicate V₃O₇·H₂O monolith is a favorable candidate for making flexible electrodes to promote electrocatalytic reactions.



Fig. 3 Electrocatalytic NRR performance tested by H-cell of V_3O_7 -H₂O monolith. a) Linear sweep voltammetry curves recorded at the scan rate of 5 mV s⁻¹ in N₂and Ar-saturated 0.1 M Na₂SO₄ electrolytes. The inset of (a) shows Faradaic efficiency (FE) and NH₃ yield rates as comparison to powder counterpart at -0.55 V (vs. RHE) in N₂ atmosphere. b) Chronoamperometry curves at different applied potentials (vs. RHE). c) FE and NH₃ yield rates at different applied potentials. d) 500 MHz ¹H NMR spectra analyses at -0.55 V (vs. RHE for 20 hrs) by using ¹⁴N₂ or ¹⁵N₂ as N₂ feeding sources. e) FE and NH₃ yields for recycling test at -0.55 V (vs. RHE). f) stability test for 20 hrs at -0.55 V (vs. RHE). The inset of (f) shows the LSV plots before and after stability test.

Electrocatalytic nitrogen reduction performances tested by H-cell. Electrocatalytic NRR was performed by using V₃O₇·H₂O monolith decorated on carbon paper substrate as working electrode in 0.1 M Na₂SO₄ aqueous electrolyte by H-cell. The electrolytic resistance of overall system is only 6.5 Ω , so all data are presented without iR compensation. Firstly, linear sweep voltammetry (LSV) is tested in N₂-saturated electrolytes (Fig. 3a), which shows a different current density as comparison to Ar-saturated counterpart, thus indicating the occurrence of NRR in electrochemical system.²⁰⁻²¹ To quantify NRR activities, N₂ electrolysis was carried out for 2 hrs from -0.35 to -0.75 V (*vs.* RHE, Fig. 2b), with their products determined by indophenol blue and Watt-Chrisp methods (Figs. S13-S21). Consequently, the maximal NH₃ yield rate and Faradic efficiency of V₃O₇·H₂O monolith are 12.96±0.3 µg h⁻¹ mg⁻¹ and 6.03±0.6% at -0.55

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V (vs. RHE, Figs. 3b,c,S22). The activities of V₃O₇·H₂O monolith are 4.05 and 1.37 times higher than its powder counterpart (3.82 µg h⁻¹ mg⁻¹ and 4.39%, the inset of Figs. 3a,S23,S24). In addition, the charge transfer resistances (R_{ct}) of V₃O₇·H₂O monolith and powder electrodes have been evaluated by electrochemical impedance spectroscopy (EIS). As shown in Fig. S25, V₃O₇·H₂O monolith shows a semicircle comparable to V₃O₇·H₂O powder in the Nyquist diagram, indicating the similar R_{ct} for these electrodes (3.1 vs. 2.5 Ω). However, the electrochemical specific surface area (ECSA) of V₃O₇·H₂O monolith is 87.14 cm⁻², which is twice of V₃O₇·H₂O powder (42.57 cm⁻², Fig. S26). The above results indicate the remarkable structural advantages of 3D monolithic architecture.

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Next, the source of N₂ during NRR was elucidated by ¹⁵N₂ isotope experiments at the applied potential of -0.55 V (*vs.* RHE). As shown in Fig. 2d, 500 MHz nuclear magnetic resonance (NMR) analysis shows a distinct double peak signal from ¹⁵NH₃ rather than a triplet from ¹⁴NH₃, thus indicate ammonia produced from nitrogen rather than external contamination. In addition, the electrolytic system has shown excellent selectivity and durability, which produce little N₂H₄ by-product as determined by Watt-Chrisp methods (Fig. S27). The NH₃ yield rate and FE of V₃O₇·H₂O monolith-based electrode did not change significantly for five electrochemical cycling tests at -0.55V (*vs.* RHE, Figs. 2e,S28) and the electrode can work continuously for at least 20 hrs without performance degradation (Figs. 2f).



Fig. 4 Electrocatalytic NRR performance tested in flow-cells for V_3O_7 ·H₂O monolith. a) Schematic illustration of a flow cell system. b) the optimal NH₃ yield rates and FEs of V_3O_7 ·H₂O monolith and powder in flow-cells as comparison to H-cells at -0.55 V (vs. RHE) in N₂ atmosphere. c) Chronoamperometry curves of V_3O_7 ·H₂O monolith in flow-cells at -0.55 V (vs. RHE) for seven cycles; inset of (c) are NH₃ yield rates, FEs for cycling test at -0.55 V (vs. RHE) and ¹H NMR spectra analyses at -0.55 V (vs. RHE) by using ¹⁵N₂ as gas feeding source.

Electrocatalytic nitrogen reduction performances in flow-cells. To further improve the NRR performances, we adopted a newly designed flow-cell (Figs. 4a,S29). We use a gas-diffusion layer with smart components that can promote the reaction kinetics at three-phase boundary. Also, the novel compact cell design can decrease the transport resistance. Further, electrolytes have been cycled by using an external pump, which can bring large quantities of N₂ feedstock and take away the NH₃ products. According to the theory from physical chemistry, the reaction equilibrium can be shifted right $(2N_2 + 6H_2O \rightarrow 4NH_3 + 3O_2)$; that is, more ammonia can be produced.

Consequently, as shown in Fig. 4b,S30, the maximal NH₂ yield rate and Faradic efficiency for V₃O₇·H₂O moholith from the vield 36.42 µg h⁻¹ mg⁻¹ and 14.20% at -0.55 V (vs. RHE). These values are significantly exceed corresponding performances obtained from Htype electrochemical cell with ammonia yield of 12.96 µg h⁻¹ mg⁻¹ and Faradaic efficiency of 6.03% (Fig. 3c). In addition, V₃O₇·H₂O powder in flow-cells are also characteristic of increased NH₃ yield rate of 16.52 µg h⁻¹ mg⁻¹ and Faradic efficiency of 8.11% at -0.55 V (vs. RHE, Figs. 4b,S31). As comparison to recently reported NRR catalysts, our V₃O₇·H₂O monolith is one of the most active electrocatalysts in the literature (Table S2).

Importantly, the electrochemical testing in flow-cell has maintained excellent stability with little activity degradation in NH_3 yield rates and Faradaic efficiencies after seven cycles (Fig. 4c). This result is consistent to the analyses of SEM, element mapping, XRD, FT-IR and XPS that shows negligible changes of morphology, structure and chemical state for the electrode after cycling test (Fig. S32-36). Further, the isotope labelling experiment with $^{15}N_2$ feeding gas show obvious characteristic doublet signals for $^{15}NH_4^+$ (the inset of Fig. 4c), which thus verified NRR process sourced from N_2 gas precursor rather than external pollutions.



Fig. 5 NRR performance of V_3O_7 -H₂O monolith and powder during electrode deformations. a-e) V_3O_7 -H₂O monolith: a) Chronoamperometry curves for different electrode foldings at -0.55 V (vs. RHE). The inset of (a) shows the optical images of electrode foldings. b-e) The corresponding utraviolet (UV) absorption spectra, total charge analyses, NH₃ yield rates and FEs at -0.55 V (vs. RHE), respectively. *f*,*g*) V_3O_7 -H₂O powder: total charge analyses and NH₃ yield rates at -0.55 V (vs. RHE) for different electrode foldings. h) Comparison total Charge analyses and NH₃ yield rates for different electrode foldings.

Shape memory V_3O_7 · H_2O monolith for foldable NRR. To see if V_3O_7 · H_2O electrode can satisfy the flexibility demands, its NRR performance was measured with different electrode foldings and compared with V_3O_7 · H_2O powder sample. Fig. 5a shows the 2 hr-chronometric response plots of the electrodes with one to three folding, which demonstrated current decrease of only 5.7%, 16.1%, and 32.9%, respectively. Correspondingly, the ammonia yield rate

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declines slightly from 12.96 (no folded) to 12.06 (one fold), 11.21 (two folds) and 8.51 μ g h⁻¹ mg⁻¹ (three folds, Figs. 5b-d). In great contrast, the powder V₃O₇·H₂O-based electrodes can only maintain 25% of NH₃ yield rate after three folding, which shows a much worse activities as comparison to shape-memory V₃O₇·H₂O monolith (Figs. 5f-h,S37,S38). In addition, the FEs of V₃O₇·H₂O monolith and powder did not change with the number of electrode foldings (Fig. 5e,S39), which indicate that the intrinsic activity of the electrode material was not reduced. This result is consistent to SEM image of V₃O₇·H₂O monolith-based electrode that can still maintain structural integrity after applying external forces during deformation (Fig. 2w). The afore-mentioned results suggest that V₃O₇·H₂O monolith possesses excellent physical flexibility, durability, and mechanical integrity towards folding treatments during electrocatalytic processes.



Fig. 6 NRR Mechanism study for V_3O_7·H₂O monolith. *a, b)* Optimized structures for hydrogen atom at V_3O_7 ·H₂O monolith and corresponding Gibbs free energy change. c) Optimized structures for associative alternative pathway for V_3O_7 ·H₂O monolith. d) Gibbs free energy changes for three possible NRR pathways.

Mechanism study. To elucidate the active sites for NRR at V₃O₇·H₂O electrode, computation calculations were performed by using DFT.³²⁻³⁷ According to XRD and XPS analyses (Figs. 2a,c,d), a structural model is built by cleaving $V_3O_7{\cdot}H_2O$ surface across (200) crystal direction that form a slab with (2×2) unit cell based on Pnam space group. Generally, NRR takes place via associative-alternate, associative-distal, or dissociative pathways,4, 38-39 while our calculations suggest that V₃O₇·H₂O promote NRR favorably through associative-alternate pathway with the lowest energy barrier of 2.28 eV than other pathways (Figs. 6d,S40-S43). Further, the reaction active sites have been identified to be vanadium atoms characteristic of a smaller Gibbs free energy as comparison to oxygen atoms inside V₃O₇·H₂O (2.28 vs. 3.86 eV, Fig. S43). This result is further confirmed by the calculated Gibbs free energy of hydrogen adsorption (Figs. 6a,b), which reveals the vanadium active sites have a favorable hydrogen adsorption capability than oxygen active sites (-3.26 vs. -4.46 eV) thus can access to more hydrogen from water to promote NRR (N₂ + 6H₂O + 6e \rightarrow 2NH₃ + 6OH⁻).

Next, each intermediate step of associative-alternate pathway at $V_3O_7\cdot H_2O$ electrode has been discussed (Fig. 6d). The NRR process

begins with moderate physisorption of N₂ gas molecules onto electrode surface with a small Gibbs free energy of 0.22 eV,1 which enables N₂ activation for subsequent hydrogenation steps. Secondly, the Gibbs free energy for the first hydrogenation step of NRR (*i.e.*, *NN + $H^+ \rightarrow$ *NNH) is 2.28 eV, followed by the second proton-electron pair transfer proceeding on an un-hydrogenated nitrogen atom, which leads to the formation of *NHNH intermediate with a Gibbs free energy of 0.29 eV. Next, the relative Gibbs free energies for the third and fourth proton-electron pair transfer gains to produce *NH and *NH₂ with the Gibbs free energy of 0.97 and 0.08 eV, respectively. Consequently, the first ammonia (NH₃) molecule has formed after the fifth proton-electron pair transfer step with another hydrogenation on *NNH₂ moiety with a Gibbs free energy of 1.57 eV. The electrocatalytic reaction is finally closed by the release of second NH₃ molecule with an energy input of -0.81 eV.

Further, the significantly enhanced NRR performance of V₃O₇·H₂O electrode is attributable to its remarkable structural characteristics. Firstly, V₃O₇·H₂O has one-dimensional nanobelt structure with a typical thickness of only ~15 nm and length up to several micrometers, which has ordered aligned into a 3D anisotropic architecture driven by ice-templated method. Therefore, the aggregation of 1D nanobelts can be effective prevented, and the 3D monolith can exhibit a high specific surface area of 22.3 m² g⁻¹ as comparison to its powder counterpart (14.3 m² g⁻¹, Fig. S12). This result is consistent to intrinsic activities of V_3O_7 ·H₂O monolith and powder normalized according to ECSA as shown in Supplementary Figs. S26. The intrinsic NH₃ yield rate of V₃O₇·H₂O monolith is 190.63 μg $h^{\text{-1}}$ $m^{\text{-2}},$ which is roughly 1.5 times of that for $V_3O_7 \cdot H_2O$ powder (125.46 μ g h⁻¹ m⁻², Fig. S44). Therefore, V₃O₇·H₂O monolith can provide a large number of accessible active sites as catalytic centers for promoting NRR. Secondly, the ordered assembly of 1D V_3O_7 ·H₂O nanobelts has generated hierarchical porosity that can increase the transport of electrolyte and gas diffusion within the electrode. We can see from the SEM images (Figs. 1,2) that $V_3O_7 \cdot H_2O$ nanobelts have formed ultra-large pore over tens of micrometers between the ordered nanobelts array, in addition to a wide range of pores around tens to hundreds of nanometers between adjacent nanobelts. Also, N₂ isotherm displays the formation of mesoporous in the range of 5-50 nm and centered at 28 nm (Fig. S12), which shows a porous volume of 0.077 m² g⁻¹ for V_3O_7 ·H₂O monolith as comparison to 0.033 m² g⁻¹ for the powder counterpart. Consequently, V₃O₇·H₂O monolith has delivered a much larger NH₃ yield rate (36.42 vs. 16.52 μ g h⁻¹ mg⁻¹) and FE (14.20% vs. 8.11%) than the powder counterpart.

Importantly, the distinguished hierarchical structure of $V_3O_7 \cdot H_2O$ monolith gives rise to high shape-memory properties. According to the literature,²⁶ metal oxides are conventionally considered as a class of tough materials that are prone to fail in a brittle manner when subjected to macroscopic deformation. When metal oxide monoliths are severely compressed, the inter-sheet van der Waals adhesion would overwhelm the elastic energy stored, preventing elastic recovery. Indeed, shape memory has not been observed in randomly structured $V_3O_7 \cdot H_2O$ architecture or powders. In great contrast, our proposed ice-templated method can enable the capability of ordered and anisotropic alignment of metal oxide nanostructures, and introduce a new emerging property of 3D

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metal oxide monoliths. This behavior is similar to shape memory alloys owning to "superelasticity" mechanism.¹⁸ Consequently, metal oxides-based electrodes can become long-term compressible and foldable, and thus can be more conveniently applied to actual electrocatalytic nitrogen fixation and other energy conversion processes. Therefore, this work has opened up enormously opportunities for applying versatile metal oxides in the form of shape-memory monoliths for a broad range of technical applications.

Conclusions

In conclusion, we have demonstrated a shape-memory V_3O_7 ·H₂O monolith characteristic of ordered and anisotropic microstructure through an ice-templated freeze-casting method. With low mass density, superelasticity, high specific surface, and hierarchical porosity all combined together, our V_3O_7 ·H₂O material has been demonstrated as a new class of foldable electrode, which has delivered good NRR performances with high NH₃ yield rates and FE, and flexibility for electrocatalytic reactions. We would expect that such exceptional metal oxides-based materials open up enormous opportunities for a broad range of technological applications. In particular, our work allows for exploring the emerging properties and applications of metal oxides in structurally adaptive and 3D macroscopic architecture. This work will thus pave the way for new categories of metal oxide-based flexible devices. Further, many other functional metal oxide materials could be readily filled into the open void space, which offers plenty of room to fabricate many new metal oxide-based hybrid materials.

Conflicts of interest

The authors declare no competing financial interests.

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