

Vapor phase growth and oxygen vacancy engineering of ultrathin 2D Co_3O_4 nanosheets for self-rectifying memristors

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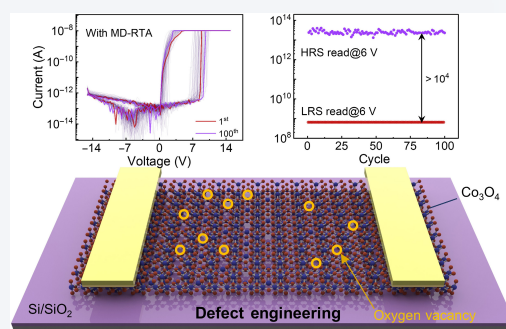
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ABSTRACT: Two-dimensional (2D) materials show great promise for building next-generation memristors. However, their application in self-rectifying memristors (SRMs)—crucial for suppressing sneak-path currents in high-density arrays—is still underexplored. In this work, we address this gap by developing ultrathin non-layered Co_3O_4 nanosheets through a vapor-phase growth strategy and precisely engineering their oxygen vacancies (O_v) for high-performance SRMs. Our synergistic approach, combining salt-assisted vapor–liquid–solid, hydrate-assisted, and spatial confinement methods, enables the controlled synthesis of high-quality Co_3O_4 nanosheets as thin as 0.46 nm with a single-atomic-layer thickness. We demonstrate that magnetically driven rapid thermal annealing (MD-RTA) effectively increases the O_v concentration from 15.15% to 33.15%, as quantitatively confirmed by X-ray photoelectron spectroscopy (XPS), Raman, and Kelvin probe force microscopy (KPFM). The resulting memristor exhibits excellent self-rectifying resistive switching behavior, with a high rectification ratio exceeding 10^4 and a large ON/OFF ratio over 10^4 . The device also achieves high switching uniformity (coefficient of variation, $C_v = 0.0979$), stable cycling endurance over 100 direction current (DC) cycles, and room-temperature operation. This study provides a reliable synthesis route for 2D non-layered materials and highlights defect engineering as an effective strategy for developing advanced in-memory computing devices with inherent crosstalk immunity.

KEYWORDS: two-dimensional (2D) materials, chemical vapor deposition, nanosheets, nonlayered metal oxides, self-rectifying memristors



1 Introduction

Memristors based on two-dimensional (2D) materials have

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garnered extensive research interest for next-generation in-memory computing and neuromorphic computing. Their atomic-scale thickness, excellent electrostatic controllability, and rich library of electronic properties make them ideal for constructing low-power and high-density devices [1, 2]. Significant progress has been made in utilizing 2D materials, such as CuSe and MoS₂ [3, 4]. However, their exploration specifically for self-rectifying memristors (SRMs), which are critical components for suppressing sneak-path currents in crossbar arrays without introducing additional selectors, remains significantly underexplored [5]. This gap limits the application of

2D materials in high-density, low-power integrated systems where crosstalk immunity is paramount.

To address this challenge, 2D transition metal oxides (2D TMOs), such as NiO [6] and MoO₃ [7], demonstrate greater potential than their layered counterparts owing to their superior chemical stability and electrical properties [8, 9]. Among various 2D TMOs, cobalt-based oxides, particularly Co₃O₄, have garnered significant attention in fields like catalysis, energy storage, sensing, and optoelectronics [10–13]. This interest stems from cobalt's multiple oxidation states, natural abundance, and the high chemical stability of its oxides [14]. Especially, for memristive applications, the resistive-switching (RS) behavior fundamentally relies on the migration and reorganization of ions or defects within the functional layer [15]. The abundance of oxygen vacancy (O_v) defects in Co₃O₄ and their migration characteristics provide inherent mechanistic advantages for developing RS devices [16–18]. This makes Co₃O₄ a highly promising candidate for realizing SRMs, as the deliberate engineering of O_v distribution can intrinsically yield current rectification. However, the controlled synthesis of high-quality, ultrathin 2D Co₃O₄ remains a formidable challenge. Its non-layered, close-packed spinel structure with isotropic covalent bonds favors the formation of three-dimensional bulk crystals, making the growth of atomically thin nanosheets highly difficult [19, 20].

In this work, we overcome the synthesis challenge by developing a novel combined vapor-phase growth strategy. This approach synergistically integrates salt-assisted vapor–liquid–solid (VLS), hydrate-assisted, and spatial confinement mechanisms on dangling-bond-free mica substrates, enabling the controllable synthesis of high-quality, ultrathin Co₃O₄ nanosheets with a thickness down to 0.46 nm with a single-atomic-layer thickness. Subsequent magnetically driven rapid thermal annealing (MD-RTA) treatment is employed as an effective oxygen-vacancy engineering strategy to tailor the concentration and distribution of oxygen vacancies. The memristor based on the resulting oxygen-vacancy-engineered Co₃O₄ nanosheets exhibits excellent self-rectifying resistive switching performance, achieving a high rectification ratio and a large ON/OFF ratio, both exceeding 10⁴ simultaneously. This exceptional performance is coupled with excellent switching uniformity and stable cycling endurance at room temperature.

Through comprehensive characterization, including X-ray photoelectron spectroscopy (XPS), Raman, and Kelvin probe force microscopy (KPFM), we elucidate the critical role of O_v migration in governing the resistive switching and self-rectifying behavior. This study not only provides a reliable pathway for synthesizing 2D non-layered materials but also demonstrates their great potential for advancing high-density, low-power in-memory computing systems.

2 Results and discussion

The ultrathin nonlayered Co₃O₄ nanosheets were synthesized on a mica substrate through spatial confinement, hydrate-assisted, and salt-assisted chemical vapor deposition (CVD) method [21–25]. As illustrated in Fig. 1(a), an alumina boat containing a measured amount of calcium sulfate dihydrate (CaSO₄·2H₂O) was placed in the upstream region to maintain a stable water vapor supply. Cautious control of the water partial pressure is essential, as too high a partial pressure would lead to poor crystallization quality of the nanosheets [26]. Therefore, all reaction gases were pre-dried using a commercial dehydration process. Importantly, the hydrate-derived H₂O plays an anisotropic thermodynamic regulation role during 2D growth: It can lower the Gibbs free-energy barrier for lateral growth while increasing the free-energy barrier for vertical growth, thereby promoting lateral expansion and suppressing vertical growth, as summarized in Fig. S1 in the Electronic Supplementary Material (ESM). In the central heating zone, a mixture of the precursor and metal salt was confined between two mica sheets, forming a spatially restricted reaction microenvironment. The incorporation of metal salt, such as KI, serves to reduce the melting temperature of the reaction system [21]; without KI, nanosheet growth is effectively suppressed. The entire thermal process was conducted under high-purity air to provide an oxidizing atmosphere and facilitate crystallization. Based on differing reaction pathways, two growth modes exist: solvent-free crystallization and solvent-assisted crystallization [23]. The growth of Co₃O₄ nanosheets follows the solvent-assisted mode [27], which occurs through three stages: eutectic melting, nucleation, and growth as illustrated in Fig. 1(b). In Stage I, CoCl₂·6H₂O undergoes dehydration under rapid heating to form CoCl₂, which then reacts

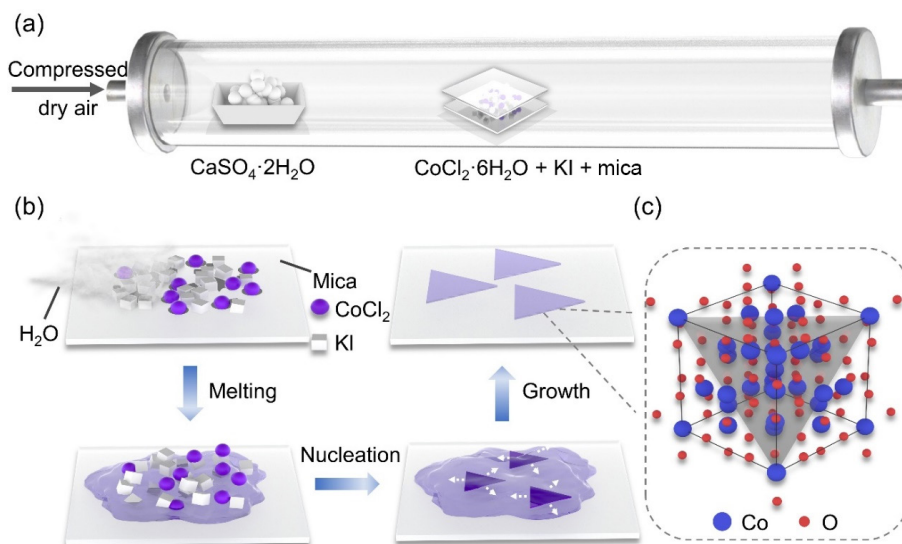


Figure 1 Synthesis of 2D ultrathin Co₃O₄ nanosheets. (a) Schematic illustration of the CVD. (b) Schematic illustration of the salt-assisted vapor–liquid–solid growth process of 2D Co₃O₄ nanosheets on mica. (c) The atomic model of the spinel structure.

with KI vapor, leading to the formation of molten droplets on the mica surface. These droplets capture water vapor and oxygen from the environment, entering Stage II where Co_3O_4 nuclei form. With the continuous supply of reactants, the process enters Stage III. Here, the synergistic effect of water vapor and spatial confinement promotes the lateral growth of the Co_3O_4 nuclei while suppressing vertical growth. Finally, most of the solvent is volatilized, and the ultrathin nanosheets are left on the substrates. Figure 1(c) shows the non-layered spinel crystal structure of Co_3O_4 , featuring a cubic close-packed arrangement of O^{2-} ions, where Co^{3+} and Co^{2+} ions occupy octahedral and tetrahedral interstices, respectively [23]. The growth regulation on mica is illustrated in Fig. S2 in the ESM. Mica was selected as the growth substrate owing to its atomically flat, dangling-bond-free surface and low surface diffusion barrier, which together favor the controlled formation of high-quality two-dimensional ultrathin nanosheets [5, 24]. Notably, Co_3O_4 nanosheets can also be grown on sapphire and Si substrates; however, the resulting nanosheets are consistently thicker than those obtained on mica, highlighting the critical role of the mica surface in enabling ultrathin 2D growth, as shown in Fig. S3 in the ESM.

After investigating the synthesis mechanism of Co_3O_4 nanosheets, we performed fundamental characterization of the Co_3O_4 nanosheets. Figure 2(a) presents the optical microscopy (OM) image of the ultrathin Co_3O_4 nanosheets. Atomic force microscopy (AFM) reveals that the flakes have sub-nanometer

thicknesses, with measurements as thin as 0.46 nm, which is equivalent to a single atomic layer, as illustrated in Fig. 2(b). The material surface exhibits excellent flatness at the micrometer scale, with minimal height variation and highly uniform characteristics (Fig. S4 in the ESM). To verify the uniformity and phase purity of the synthesized Co_3O_4 nanosheets, Fig. 2(c) presents the Raman spectrum acquired under 532 nm laser excitation. Five characteristic Raman peaks are clearly observed at 197, 483, 523, 621, and 692 cm^{-1} , confirming the structural integrity of the Co_3O_4 nanosheets. Specifically, the peaks at 197, 523, and 621 cm^{-1} are assigned to the F_{2g} mode, the peak at 483 cm^{-1} to the E_{2g} mode, and the peak at 692 cm^{-1} to the A_{1g} mode. Notably, the A_{1g} peak originates from the symmetric stretching vibration of the $\text{Co}^{3+}\text{-O}$ bond at the octahedral sites [28, 29]. It is the most intense and sensitive peak among all characteristic peaks. Furthermore, the typical OM image of a Co_3O_4 nanosheet and the Raman mapping image at three vibrational modes exhibit uniform contrast, indicating the high phase homogeneity and uniform structure across the entire Co_3O_4 nanosheet (Fig. S5 in the ESM). Atomic-resolution transmission electron microscopy (TEM) further demonstrates that the grown ultrathin Co_3O_4 nanosheets possess high-quality single-crystal structures. Using a poly(methyl methacrylate) (PMMA)-assisted transfer method, the nanosheets were transferred onto copper grids for TEM measurements [30, 31]. Atomic-resolution TEM images (Figs. 2(d) and 2(e)) approximately reveal an interplanar spacing of 0.284 nm for the

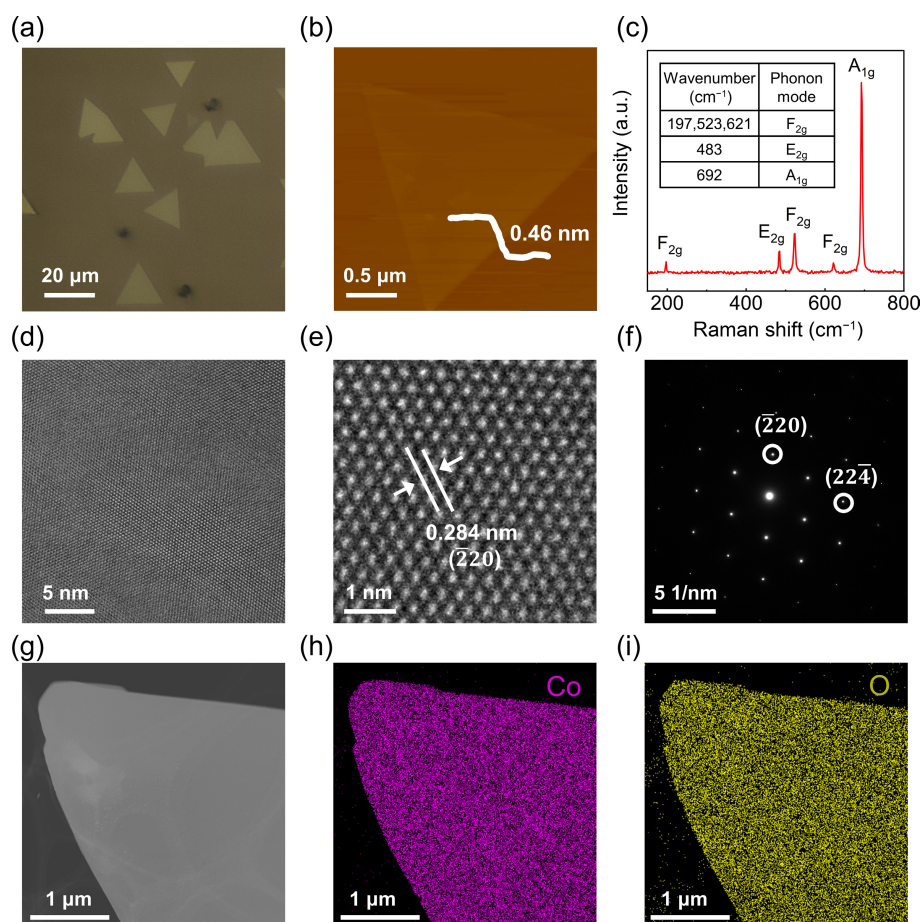


Figure 2 Characterization of ultrathin Co_3O_4 nanosheets. (a) OM image of typical as-grown Co_3O_4 nanosheets on mica. (b) AFM image of the Co_3O_4 nanosheets with a thickness of 0.46 nm. (c) Typical Raman spectrum of Co_3O_4 nanosheets. ((d) and (e)) Atomic-resolution TEM images of Co_3O_4 nanosheets. (f) SAED pattern of the Co_3O_4 . (g) TEM image of the selected area. ((h) and (i)) Energy dispersive X-ray spectroscopy (EDS) mapping images of Co and O.

($\bar{2}20$) planes, consistent with the standard X-ray diffraction data (PDF #65-3103). The selected-area electron diffraction (SAED) pattern (Fig. 2(f)) exhibits distinct hexagonal diffraction spots, confirming the single-crystal structure. Elemental mapping analysis of a representative nanosheet (Fig. 2(g)) reveals a uniform distribution of Co and O elements (Figs. 2(h) and 2(i)). It should be noted that the Co_3O_4 nanosheets used for the fabrication of the gold (Au)/ Co_3O_4 /Au memristors are not identical to the thinnest nanosheet (~ 0.46 nm) shown in Fig. 2(b).

To elucidate the mechanism by which MD-RTA modulates the performance of Co_3O_4 nanosheet memristors, we systematically characterized the key physicochemical properties of the nanosheets before and after MD-RTA. The procedure of MD-RTA is illustrated in Fig. 3(a). Briefly, the nanosheets are placed in a ceramic boat positioned outside the tube furnace, and a pair of magnets is used to translate the boat rapidly. After the furnace reaches the preset temperature, the boat is swiftly pushed into the central isothermal zone for annealing; upon completion, it is immediately pulled back to the room-temperature region to enable rapid cooling. Compared to conventional RTA systems, MD-RTA offers distinct technical advantages and promising application potential. Firstly, MD-RTA can be achieved simply by moving the sample through a standard tube furnace, offering lower cost and easy operation. Secondly, a faster and more controlled thermal treatment process is achieved by rapidly moving the samples between high-temperature and ambient-temperature zones, which helps prevent the formation of undesired defects and the degradation of the crystal structure in ultra-thin nanosheets, which

usually results from slow thermal treatment. Finally, MD-RTA facilitates the efficient induction and kinetic entrapment of non-equilibrium oxygen vacancies under tailored atmospheres. The Co 2p XPS spectrum (Fig. 3(b)) exhibits typical spin-orbit split double peaks (Co 2p_{3/2} and Co 2p_{1/2}). The binding energies and satellite peak features confirm the coexistence of Co^{3+} and Co^{2+} , confirming the synthesis of the spinel Co_3O_4 phase [32–35]. The oxygen vacancy concentration ($C_{\text{defect}}(\%)$) was calculated according to $C_{\text{defect}} = \frac{A_{\text{O}_V}}{A_{\text{O}_L} + A_{\text{O}_V}} \times 100\%$, where A_{O_V} and A_{O_L} are the integrated areas of lattice oxygen (O_L) and defect-related oxygen components, respectively. Peak fitting of the O 1s spectrum for pristine Co_3O_4 nanosheets (Fig. 3(c)) revealed O_L (84.85%) at 529.9 eV and O_V -related peaks (O_V , 15.15%) at 531.4 eV. The low initial O_V concentration indicates high crystallinity of the CVD-grown Co_3O_4 nanosheets, consistent with reports that ultra-low O_V concentrations typically suppress resistance fluctuations and thus narrow the RS window in memristors [13, 36–38]. After MD-RTA, which was applied to modulate the O_V concentration, the O_V fraction increases markedly to 33.15% (Fig. 3(d)), accompanied by slight shifts of O_L and O_V to 529.6 and 531.3 eV, respectively. Nanoscale surface-potential mapping by KPFM (Figs. 3(e)–3(g)) shows that the surface potential difference of MD-RTA-treated nanosheets (~ 20 mV) is substantially lower than that of untreated samples (~ 80 mV). This decrease is consistent with the electron-donating nature of oxygen vacancies, providing direct evidence for their increased concentration [39]. Raman spectroscopy (Fig. S6 in the ESM) further shows that the characteristic Co–O vibrational peak near 670 cm^{-1} weakens and red-shifts after MD-RTA,

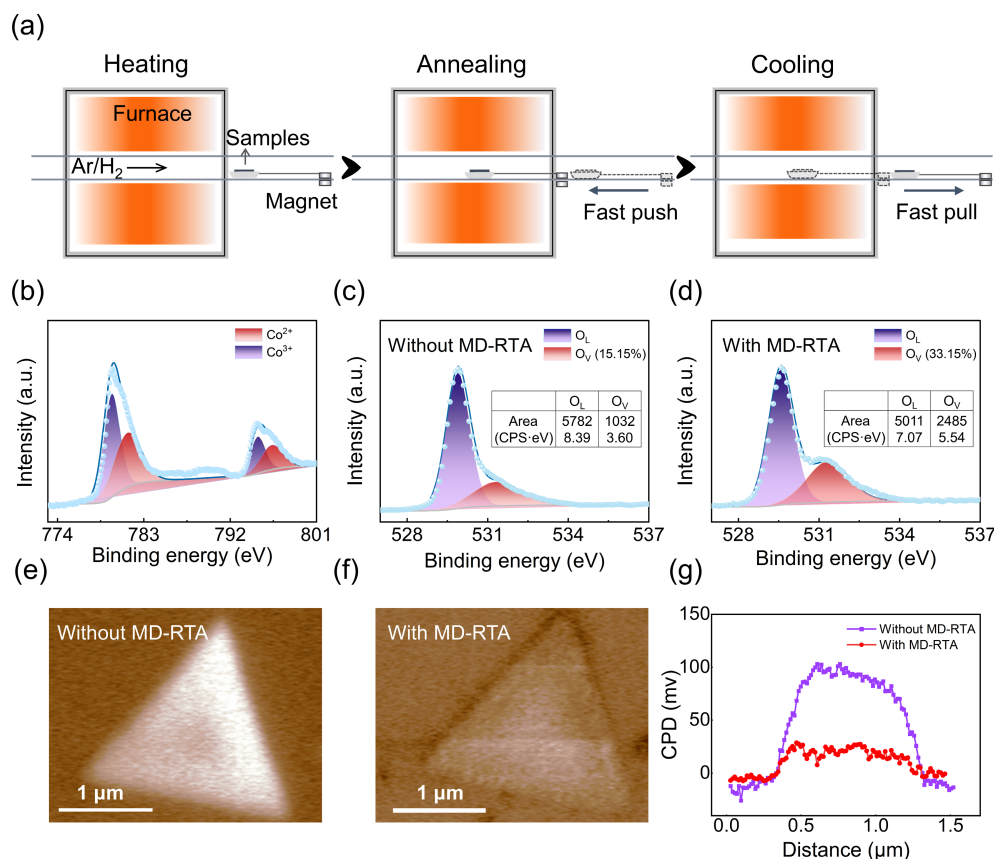


Figure 3 Comparative characterization of the physicochemical properties of Co_3O_4 nanosheets before and after MD-RTA for elucidating the RS mechanism of the self-rectifying behavior. (a) Schematic illustration of MD-RTA. ((b)–(d)) The XPS spectra of Co, O without MD-RTA, and O with MD-RTA. ((e)–(g)) Surface potential of Co_3O_4 nanosheets before and after MD-RTA.

corroborating an increase in O_v concentration from the perspective of lattice dynamics and supporting the above conclusions. Together, these results establish the physicochemical basis by which MD-RTA regulates oxygen-vacancy concentration to modulate the RS characteristics of the devices [40, 41]. To establish a direct correlation between O_v and the modulation of self-rectifying characteristics, we performed a systematic comparative analysis of Co_3O_4 nanosheets with varying defect concentrations. As quantified by the deconvolution of O 1s XPS spectra (Figs. S7(a)–S7(d) in the ESM), the O_v densities were precisely controlled at 23.68%, 33.15%, 38.57%, and 45.48%, respectively. The corresponding current–voltage (I – V) characteristics (Figs. S7(e)–S7(h) in the ESM) reveal a sensitive dependence of the switching kinetics on the O_v concentration. Our results indicate that while intermediate O_v levels facilitate synergistic modulation of the interfacial barrier and conductive filament evolution, excessive defects induce unstable switching behavior. Specifically, at the low O_v density (23.68%), the device exhibits small resistive switching window, suggesting that a sub-threshold defect density is insufficient to effectively modulate the Au/Co_3O_4 barrier or sustain stable filament formation. The device with 33.15% O_v density demonstrates the most robust self-rectifying switching behavior, suggesting that a moderate vacancy concentration provides an optimal balance among interfacial barrier modulation, field-driven vacancy migration, and defect-assisted transport. As the O_v concentration further increases to 38.57%, the memristor loses its self-rectifying characteristics, accompanied by intensified current fluctuations under reverse bias. This degradation is attributed to the high density of O_v , which promotes a more homogeneous defect distribution. Such a configuration facilitates the formation of robust conductive filaments under external electrical stimuli, which are resistant to spontaneous rupture. Consequently, when the O_v concentration reaches 45.48%, the device undergoes a functional transition, exhibiting typical non-volatile resistive switching behavior. The findings demonstrate that optimal concentrations of O_v are imperative for attaining high rectification ratios and reliable resistive switching in $Au/Co_3O_4/Au$ memristors.

Following the physicochemical characterization, we further evaluated the electrical performance of memristors based on two-dimensional Co_3O_4 nanosheets. Figure 4(a) shows an OM image of the planar device circuit connection, in which a bias voltage was applied to the upper electrode while the lower electrode was grounded. O_v are the key defects modulating the RS behavior. After MD-RTA, a higher O_v concentration is generated in regions of the Co_3O_4 nanosheets that are not in contact with the Au electrodes. Under a negative bias (Fig. 4(b)), O_v drifts along the electric field and accumulates near the Au/Co_3O_4 interface, leading to an inhomogeneous O_v distribution and an increased interface barrier height (Φ). The elevated barrier suppresses electron transport via Schottky emission, resulting in a small negative current. Conversely, under a positive bias (Fig. 4(c)), O_v migrates toward the Co_3O_4/Au interface, facilitating a more uniform distribution and the formation of a continuous electron conduction path. The resulting decrease in the interface barrier allows electrons to be transported through both Schottky emission and Poole–Frenkel emission, yielding a significantly enhanced current response [42]. The high-resistance state (HRS) corresponds to sparse and inhomogeneous O_v clusters forming discontinuous percolation paths before the SET process (switching from the HRS to the low-resistance state (LRS)), whereas the LRS emerges after SET, when field-driven O_v

migration produces a dense, uniform, and continuous conductive pathway [43–46]. Figures 4(d) and 4(e) present typical logarithmic I – V curves of the $Au/Co_3O_4/Au$ device obtained from 100 consecutive direction current (DC) voltage sweeps before and after MD-RTA; the red and purple curves correspond to the 1st and 100th sweeps, respectively, and the remaining sweeps are shown in gray. Figure 4(f) presents representative linear-scale I – V curves from a single sweep, where the red and purple curves denote the pre-annealing and post-annealing states, respectively. Measurements employed bidirectional voltage scanning ($-15 \rightarrow 15 \rightarrow -15$ V) with a 10 nA current compliance to prevent permanent damage to the nanosheets. The as-fabricated device (without MD-RTA) exhibits negligible RS over 100 cycles, with low current levels and no characteristic transitions. After annealing, the device exhibited an ultralow current ($\sim 10^{-12}$ A) during the negative bias sweep. During the positive bias sweep, abrupt current changes occur at threshold voltages of 8.4 V (SET) and 3.3 V (RESET: switching from the LRS to the HRS), demonstrating stable self-rectifying resistive switching with reproducible HRS/LRS switching over 100 cycles. The statistical distribution of voltage required to switch the device from HRS to LRS (V_{SET}) for the MD-RTA device (Fig. 4(g)) fits a normal distribution with a mean (μ) of 8.98 V and a standard deviation (σ) of 0.88 V. The coefficient of variation ($C_v = \sigma/\mu$) of the rectification ratio is 0.0979, indicating excellent switching uniformity. As a core parameter for synergistic optimization of low power consumption and high performance in memristors, the post-annealing device exhibits a subthreshold swing (SS) of 43.57 mV·dec⁻¹ (Fig. 4(h)), highlighting its potential for neuromorphic computing applications, such as leaky integrate-and-fire (LIF) neuron emulation [47]. The cumulative resistance distributions of HRS and LRS over all 100 cycles (Fig. 4(i)) show a high resistance ratio (R_{ON}/R_{OFF} : the resistance ratio between HRS and LRS) exceeding 10^4 , meeting essential requirements for memory and advanced neuromorphic computing systems. In addition, the device exhibits stable retention characteristics for over 10^4 s, where the ON state current measured at +10 V and the OFF state current measured at -5 V remain clearly distinguishable, preserving a current window exceeding 10^4 without obvious degradation (Fig. S8 in the ESM).

3 Conclusions

In summary, we report an innovative synthesis of high-quality ultrathin 2D non-layered Co_3O_4 nanosheets with a thickness of merely 0.46 nm on a dangling-bond-free mica substrate, achieved by strategically integrating salt-assisted VLS growth, a hydrate-assisted approach, and a spatial confinement strategy. Comprehensive characterization employing AFM, Raman spectroscopy, and atomic-resolution TEM systematically confirmed the excellent crystallinity and phase purity of the nanosheets. Subsequent MD-RTA treatment, as revealed by XPS, Raman analysis, and KPFM, significantly enhanced the O_v concentration from an initial 15.15% to 33.15%, providing a crucial physicochemical basis for the RS behavior. Based on these findings, the constructed $Au/Co_3O_4/Au$ van der Waals (vdW) memristor exhibits outstanding self-rectifying resistive switching characteristics: Its ON/OFF ratio and rectification ratio all exceed 10^4 , coupled with high uniformity (standard deviation of threshold voltage distribution of 0.88 V), and excellent room-temperature durability. This work not only overcomes the bottleneck in the controlled synthesis of two-dimensional non-layered materials but

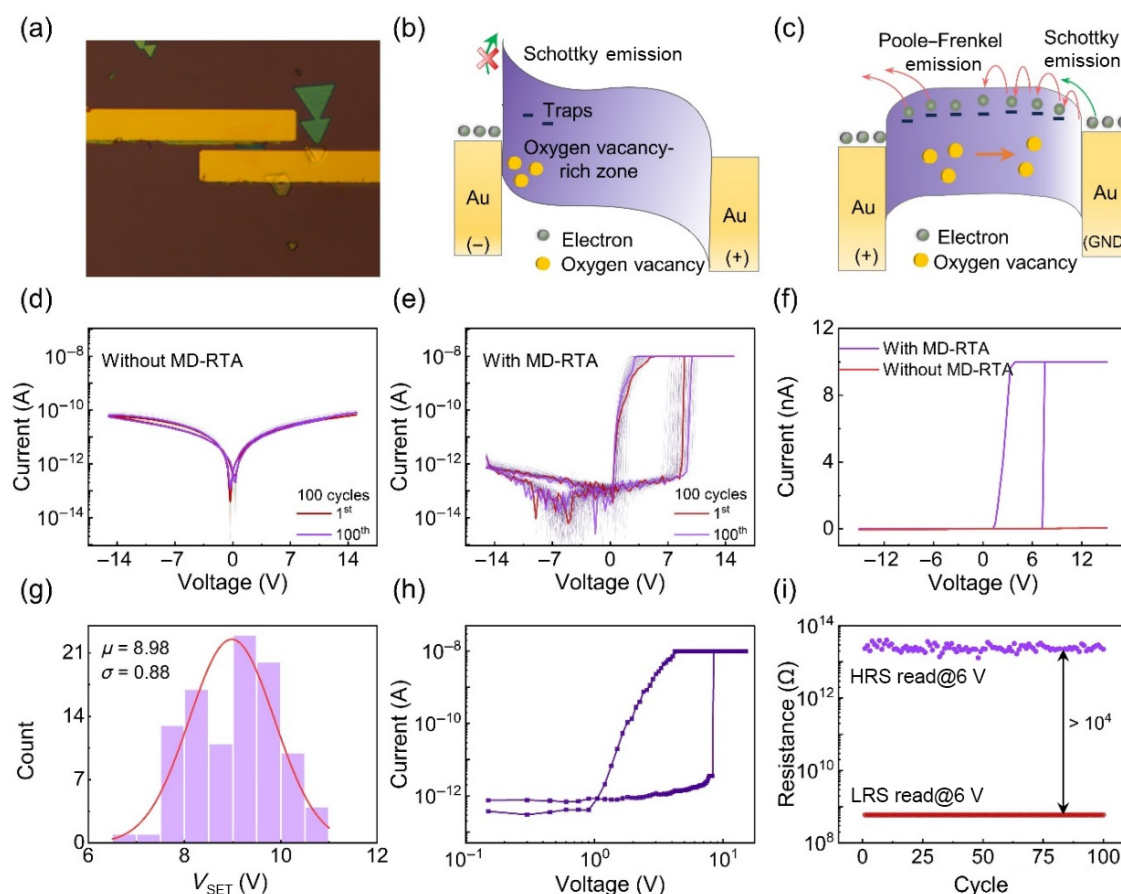


Figure 4 Characterization of planar Au/Co₃O₄/Au memristor. (a) OM image of fabricated Au/Co₃O₄/Au memristor. The conducting mechanisms of the self-rectifying memristors are shown when (b) negative bias and (c) positive bias are added. ((d) and (e)) *I*-*V* curves of Au/Co₃O₄/Au memristors before and after MD-RTA during 100 consecutive DC voltage scan cycles. (f) *I*-*V* curves of Au/Co₃O₄/Au memristors before and after MD-RTA under linear coordinates. (g) Statistical distributions of threshold voltages for the Au/Co₃O₄/Au memristor from consecutive 100 *I*-*V* scan curves. (h) subthreshold swing of the Au/Co₃O₄/Au memristor. (i) HRS and LRS distributions in consecutive 100 *I*-*V* scan curves.

also achieves high-performance self-rectifying memristors through O_v regulation. It provides a promising solution for the development of next-generation in-memory computing and non-volatile memory devices.

4 Methods

4.1 Synthesis of 2D ultrathin Co₃O₄ nanosheets

2D Co₃O₄ nanosheets were synthesized on mica substrates via a hydrate-assisted CVD method. Weighed hexahydrate cobaltous chloride (CoCl₂·6H₂O, 99.99% Macklin) and potassium iodide (KI, 99% Aladdin), in a mass ratio of 5:1, were ground and mixed thoroughly in an agate mortar. The reaction was conducted in a slender quartz tube (inner diameter 20 mm, length 80 cm) heated by a one-zone furnace. ~ 800 mg CaSO₄·2H₂O powder (99%, Macklin) is positioned upstream at a controlled distance from the center as the water source. The distance from the center was typically 18 cm to achieve a temperature of 120 °C at the water precursor boat for the non-volatile decomposition of hydrated sulfates, a process generating water vapor. Freshly cleaved Fluor phlogopite mica (Taiyuan Fluor Phlogopite Mica Company, 20 mm × 10 mm × 0.2 mm) is used as the substrate. ~ 3 mg metal precursor mixture was sandwiched between two pieces of mica in an alumina boat at the center of the tube furnace. Before growth, flush the tube with Ar gas at a flow rate of 400 sccm for 15 min to

remove residual air and moisture. Then, 100–150 sccm high-purity compressed dry air is used as the carrier gas. The temperature was ramped up to 630 °C at a rate of 25 °C·min⁻¹ and maintained for 15 min to allow for the growth of the nanosheet. After the heating and growing step, the system cools naturally to room temperature, resulting in high-quality Co₃O₄ nanosheets on the substrate.

4.2 Transfer and MD-RTA of Co₃O₄ nanosheets

PMMA-assisted transfer of Co₃O₄ onto a target substrate. First, 1.5 g of PMMA powder was dissolved in 10 mL of anisole. Next, photoresist (BP212) was spin-coated onto the mica bearing the nanosheets. Then, the PMMA solution was spin-coated onto the photoresist and cured. The mica sheet was immersed in hot water for 8 min and subsequently in room-temperature water for 5 min as shown in Fig. S9 in the ESM. Then peel off the PMMA/BP212 film containing the nanosheets from the mica and transfer it onto the target substrate. Finally, the sample was immersed in acetone to completely remove the PMMA/BP212 layers, leaving the nanosheets on the substrate. The Co₃O₄ nanosheets underwent MD-RTA under an Ar/H₂ atmosphere (10% H₂). Specifically, the tube furnace was preheated to 500 °C and stabilized under a mixed Ar/H₂ flow. The Co₃O₄ nanosheets were then rapidly pushed into the central hot zone using a magnet, maintained at the target temperature for 180 s, and subsequently pulled back to the room-temperature zone to achieve rapid cooling.

4.3 Fabrication of vdW Au/Co₃O₄/Au memristor

First, patterned Au electrodes were deposited on a Si/SiO₂ sacrificial substrate using standard photolithography, e-beam evaporation, and a lift-off process. The substrate was then exposed to hexamethyldisilazane (HMDS) vapor in a sealed chamber at 80 °C for 15–20 min to weaken the adhesion between the PMMA layer and the sacrificial substrate. Next, the PMMA layer carrying the Au electrodes was picked up using thermal-release tape. Finally, the Au electrodes were transferred and released onto a Co₃O₄ nanosheet using a transfer platform. After MD-RTA, Au electrodes were peeled off using thermal-release tape and subsequently transferred again onto the same nanosheet surface using a transfer platform.

Electronic Supplementary Material: Supplementary material (additional discussion on the hydrate-assisted growth mechanism of ultrathin Co₃O₄ nanosheets, regulation of Co₃O₄ nanosheet growth on mica, AFM images of ultrathin Co₃O₄ nanosheets with varying thicknesses, Raman mapping of a Co₃O₄ nanosheet, Raman spectra of Co₃O₄ nanosheets before and after MD-RTA, the transfer procedure and optical images of the nanosheet samples, and the schematic illustration of the annealing method) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908794>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. J. B., Y. H. K., H. F. M., and X. D. Y. conceived the project. Y. H. K. and H. F. M. carried out the sample Co₃O₄ fabrication by CVD. Y. J. B., Y. D., S. L. L., M. Y. L., and S. Y. C. performed the Raman and TEM characterizations. Y. H. K. performed the fabrication of devices. Y. J. B. and Y. H. K. performed the performance measurements of devices. Y. H. K., J. H. Z., C. Y. Z., Z. G. M., L. H. Z., J. H. Y., H. F. M., and X. D. Y. contributed to manuscript editing. All the authors have approved the final manuscript.

Use of AI statement

None.

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