Spatially-resolved insulator-metal transition for rewritable optical gratings

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Optical relief gratings are usually composed of physical grooves with a constant periodicity, and typically suffer from light scattering, are mechanically fragile and are single function. Here, we develop WO₃-based gratings by using a recently reported electron-proton synergistic doping route under ambient conditions. This doping strategy is compatible with conventional ultraviolet photolithography, and we show that it induces a selective insulator-metal phase transition and coloration in WO₃, with spatial-resolution up to micron-scale. Due to the electrochromic-induced-contrast, a WO₃ volume phase grating without grooves and a WO₃ relief grating with tunable periodicity are demonstrated. Both gratings can be rewritten after a reset procedure by annealing in air. Our experiments demonstrate WO₃-based gratings and an attractive technique for rewritable oxides.

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Grating has a periodic structure that splits and diffracts light into several beams traveling in different directions. As one of the most important components in optics, gratings are commonly used in monochromators and spectrometers. The classical relief gratings can be divided into two basic categories: ruled and holographic gratings, which always consist of physical grooves. Though the fabrications of traditional gratings are mature, it is still facing great challenges. For example, the random errors and irregularities of grooves inevitably introduce stray light. Except simple lines, it is difficult to include complicated patterns into a single grating. Moreover, the traditional relief gratings usually have dense lines (>1000 per millimeter), which means they are fragile, even fingerprints or the slightest contact with any abrasive material would damage them. In addition, once a relief grating is fabricated, it has a constant period and other optical properties, which makes it difficult to undergo further modulation or reprocessing.

On the other hand, the common materials used for the production of typical relief gratings, such as glass, silicon, copper, or photore sist, do not have abundant properties to be modulated, which limits multifunction of grating devices. Currently, metal oxides have attracted tremendous interest due to their controllable properties, such as metal–insulator transition (MIT) and electrochromism, which can be effectively triggered by hydrogenation-induced electron doping. Tungsten trioxide (WO3) crystallizes in the distorted ReO3 type of structure, a perovskite-type crystal (ABO3) with vacant A sites. It is relatively easy to intercalate protons to occupy the A sites forming tungsten bronze. The protons doped WO3 accompanying pronounced MIT (more than six orders of magnitude) and coloration (from transparent to dark blue) shows broad potential in smart windows, artificial synaptic devices.

In this study, we developed rewritable WO3-based gratings by using the recently proposed doping method, i.e., electron–proton synergistic doping route. This doping technique can be conducted under ambient conditions, which proved to be compatible with conventional ultraviolet photolithography here. Thus, the spatially-resolved MIT and coloration in hydrogenated WO3 were feasible up to micrometer scale. Based on this unique doping technique, we achieved a planar grating without physical grooves, which can be taken as a kind of new volume phase grating with intrinsically low scattering. In addition, a WO3 relief grating with tunable period was also fabricated by the selective synergistic doping. More importantly, these WO3-based gratings can be reprocessed after a “reset” process by annealing in air, making the devices controllable and reusable. It is believed that the proposed WO3-based gratings here will be promising alternatives of typical gratings in the future. This advanced doping technology opens up alternative approaches for developing not only optical devices, but also rewritable ions devices and integrated circuits for various oxide electronics.

Results and discussion

Electron–proton synergistic doping in WO3 system. Figure 1a shows a schematic diagram of electron–proton synergistic doping route. When an oxide contacted with a proper metal particle are immersed into an acid solution, the free protons in the solution would be attracted into oxide, forming the H-doped oxide layer. In addition, the protons insertion into oxide would metallize the contact area and break the electrostatic screen effect, which drove continuous electron doping into the oxide. The more detailed discussion was available in Supplementary Fig. 1.

Based on above model, we predicted that WO3 could be a good sample due to its high work function and 6.59 eV, as shown in the histogram of Fig. 1c. Indeed, when a WO3 film was touched by a zinc particle (~2 mm size) with the work function of 4.33 eV and put into a diluted H2SO4 solution, a dark blue region was formed and spread quickly to the whole film in Fig. 1d. An animated process is in Supplementary Video 1. Because the spreading speed is limited, the doping region can be controlled and selected easily as shown in the scheme of Fig. 1e, a zinc pen was used for writing the characters of “WO3” in a piece of WO3 film (Fig. 1f), see more details in Supplementary Fig. 2 and Supplementary Video 2. The thick/thin lines in Fig. 1f should be attributed to slow/quick handwriting speed due to the prominent diffusion. More importantly, the color in WO3 film was reversible. The “WO3” characters were erased by 300 °C annealing in air as shown in Fig. 1g. The animated process is in Supplementary Video 3.

Experimental and calculated results for WO3 system. The H atoms existed in the samples were examined by secondary-ion mass spectrum (SIMS) in Fig. 2a. The results showed that after the synergistic doping, the WO3 film was hydrogenated into H2WO4 effectively, which had the highest H concentration (red curve) compared with the pristine WO3 (hyacinth curve) and restored WO3 (green curve). In contrast, O element was pretty constant for these three samples in Supplementary Fig. 3, thus the possible oxygen vacancies were excluded as same as the synergistic effect happened in VO2 system. To estimate the value of x in HxWO3 film, the carrier density was 2.1 x 1021 cm−3 derived from the Hall measurement corresponding to x = ~0.1 (Supplementary Fig. 4). Any Zn element cannot be traced no matter at surface or in volume of H2WO3 (Supplementary Table 1). It was reported that for many H-doped insulators, their pristine characteristic peaks in Raman spectrum were usually changed even disappeared because of hydrogenation. In Fig. 2b, it was observed that the 802 cm−1 peak belonged to pristine WO3 film was really disappeared in H2WO3 film. Even the peaks of the sapphire substrate cannot be distinguished in Fig. 2b, which may be due to that the applied 633 nm excitation laser cannot go through the H2WO3 film. To verify this hint, we conducted UV–Vis–infrared transmission tests. Indeed, the great difference of the transmission for these three samples were observed in Fig. 2c. The pristine WO3 film showed very high visible and near-infrared transmission, while the transmission of the hydrogenated H2WO3 film was near zero, except the low transmission in the range from 350 to 530 nm. This transmission property was quite consistent with the observation in Fig. 1d, which showed that the H2WO3 film was heavily dark blue by eyesight.

As we know, infrared is usually reflected by metal, which implies a MIT between pristine WO3 and H2WO3. A more convinced electric characterization was conducted. Figure 2d showed the resistance–temperature (R–T) measurement for the pristine WO3 film and the hydrogenated one. The resistance of pristine WO3 film (~108 Ω) was decreased up to six orders of magnitude if hydrogenated to H2WO3 (~102 Ω), indicating a pronounced MIT. It also pointed out that the metallic H2WO3 was quite stable at ambient according to the R–T cycle tests in the
**Fig. 1 The electron-proton synergistic doping for WO₃ film.**

a. The schematic diagram of electron-proton synergistic doping route. The whole system is immersed into an acid solution. The purple bubbles are free protons and the yellow column is a low-work function metal particle.

b. The mechanism of electron-proton synergistic doping effect: electrons flowing from metal with a higher Fermi level (i.e., lower work function $W_m$) to oxide with a lower Fermi level (i.e., higher work function $W_s$) at the interface.

c. The work function values for Zn and WO₃.

d. Experiments prove that Zn and WO₃ can realize the synergistic effect, which can be observed by eyesight due to the electrochromic effect.

e. Schematic depiction: this synergistic effect has a good spatial selection.

f. Sharp zinc pen was used to write “WO₃” in WO₃ film in acid solution.

g. This synergistic effect is reversible by 300 °C annealing in air.

**Fig. 2 The characterizations and theoretical calculations for the electron doping WO₃ film.**

a. The secondary-ion mass spectrum (SIMS) tests for the WO₃ film after treated by electron-proton synergistic doping route, labeled by HₓWO₃. Then the HₓWO₃ annealed at 300 °C in air leads to the restored WO₃ sample.

b. The Raman peak at 802 cm⁻¹ for pristine WO₃ film is disappeared in HₓWO₃. While it can be restored after annealing the HₓWO₃ sample.

c. The UV-Vis-infrared transmission curves for the pristine WO₃, the HₓWO₃ and the restored WO₃ samples.

d. Resistance-temperature ($R$-$T$) results show the resistance of pristine WO₃ film is quite stable within the temperature from 40 to 100 degrees, while it will decrease with six orders of magnitude after the film was hydrogenated to HₓWO₃, indicating a pronounced metal-insulator transition (MIT). The inset is the R-T cycle test in air, showing the metallic HₓWO₃ is quite stable at ambient.

e. Computed differential charge distribution at Zn/WO₃ interface. Isosurface is 0.005 electrons per Å³.

f. Energy diagram along the reaction pathways of H migrating from WO₃ surface (initial state: IS) to subsurface (final state: FS) via the transition state (TS). Energy of IS is set as zero.

g. h. Density of states (DOS) of WO₃ (g) and H-doped WO₃ (h), together with inset photographs for the atomic models.
for the Zn/WO₃ interface, electrons would be transferred from Zn to WO₃. Considering the Fermi level difference between Zn and WO₃, electrons would be attracted to the WO₃ phase, while the other areas were all hydrogenated. The calculated results are consistent with previous reports. The mechanism of the quick insertion of H atom into WO₃ film by the zinc-acid treatment was also investigated by theoretical calculations. Considering the Fermi level difference for the Zn/WO₃ interface, electrons would flow from Zn to WO₃. The computed differential charge distributions of Zn/WO₃ interface confirmed the charge transfer behavior (Fig. 2e) as the model predicted in Fig. 1b, c. Bader charge analysis found ~0.07 electrons being transferred from each Zn atom to WO₃, leaving negative charges in the WO₃ part. The extra negative charges in WO₃ could attract the surrounding protons in acid solution to penetrate into the lattice. By simulating the reaction pathways of a hydrogen atom migrating from WO₃ surface to subsurface (Supplementary Fig. 8), we demonstrated that the H-migration barrier (ΔEₕ) is substantially lowered by increasing the number of negative charges (Fig. 2f). With charge conditions of 1 hole, neutral, and 0.5 electron, the ΔEₕ value is 2.46, 1.32, and 1.20 eV, respectively. One can thus infer that electrons accumulated in the WO₃ can help proton diffusion into the lattice, and the encounter of protons and electrons inside the lattice completes the hydrogenation of WO₃, which was confirmed by the SIMS results in Fig. 2a. Thus, the same mechanism happened in WO₃ system is suitable for WO₃ system. Importantly, H-doping induces significant changes to the electronic structures of WO₃. The calculated density of states in Fig. 2g, h show that the hydrogenation effective shifts up the Eₕ, closing the original bandgap in WO₃ and consequently bestowed metallic features to the doped system of H₂WO₃, which are responsible for the MIT (Fig. 2c) and low transmissivity of visible light and infrared (Fig. 2d) in our experiments. These calculated results are consistent with previous reports.

Production of WO₃-based gratings. Because the observed synergistic doping effect in WO₃ film was quite fast and the doping area was selective at ambient, some interesting patterns could be fabricated by combining with UV lithography. Fortunately, photoresist usually made by photopolymer materials are often stable in acid. In addition, the pristine WO₃ film and H₂WO₃ film showed pronounced transmission variation in visible and near-infrared range (Fig. 2c), so optical gratings are possibly produced. Thus, at first, we prepared a macroscopic pattern on a WO₃ film as shape of “USTC” by a photoresist layer. It was found that the covered parts (the four characters) kept the original WO₃ phase, while the other areas were all hydrogenated, showing the fact that the photoresist layer can hinder the synergistic effect (Fig. 3a). A demonstration in Supplementary Video 4 recorded the diffusion around the covered photoresist. Furthermore, a set of microscopic bars of photoresist were fabricated by UV lithography in Fig. 3b. Then the bare microchannels of WO₃ film can be “dyed” freely by moving and touching a Zn probe in acid, for example, the two microchannels were selected to be colored (Fig. 3b). A demonstration is in Supplementary Video 5, where the colorations spread very fast along the selected channels.

Based on the above results, it was suggested that the controllable optical grating devices could be produced in this way. The specific procedures were described in Supplementary Fig. 11. After lift-off, the pattern of bars and squares were made in WO₃ films as shown in Fig. 3c, d, respectively (extended results in Supplementary Fig. 12). The contrast of the patterns should originate from the difference of metal and insulator areas. The diffraction spots patterns were recorded in Fig. 3m, n, and quite consistent with the results in Fig. 3k, l from the gratings covered photoresist layer. These results indicated our synergistic effect was an alternative technology for grating fabrication. In addition, we should emphasize that this kind of grating is different from the common relief gratings with physical grooves, such as shown in Fig. 3c, d, because these gratings are composed by the periodic metal and insulator WO₃ area with smooth surface (Fig. 3i, j). Because of this, we named it “planar grating”. More importantly, this planar grating can be restored and reprocessed, since these periodic patterns could be removed by annealing in air. Indeed, the diffraction spots were disappeared as shown in Supplementary Fig. 13.

Traditional relief gratings usually have a fixed period. Here, we developed a kind of relief grating with reversibly tunable periods. By combining UV lithography and reactive ion etching (RIE), a WO₃ relief grating of 16 μm period was made in Fig. 3o, the surface morphology in Fig. 3p and the related diffraction spots (period: ~13.3 mm) in Fig. 3t. We immersed this grating in dilute H₂SO₄ solution. Then the original period could be easily doubled to be 32 μm by a Zn probe contacting the bars alternatively, since the touched WO₃ bars were hydrogenated and dyed quickly. Resultantly, the period of diffraction spots was half of the original period as shown in Fig. 3u. While if only a quarter of WO₃ bars were dyed (Fig. 3r), which means a new period of 64 μm, the period of diffraction spots was 1/4 of the original one (Fig. 3v). These results are consistent with the reciprocal law of grating diffraction. To further verify the observation, another way to realize 64 μm period, dyeing three quarters of WO₃ bars, was also conducted in Fig. 3s. Indeed, the diffraction spots in Fig. 3w showed the same period as that in Fig. 3v. The extended photos of the colored gratings in different periods were exhibited in Supplementary Fig. 14, indicating the flexible period selection in WO₃ relief grating by the synergistic doping. More importantly, it should be emphasized again that all the processed gratings can be restored by annealing as shown in Supplementary Fig. 15, making this technique suitable for rewritable grating device fabrication in the future.

Low scattering performance of the planar grating. For typical relief gratings, scattering originates from random errors and irregularities of surfaces and sides, which cannot be avoided due to the physical grooves. In contrast, our planar grating with...
smooth surface can basically survive in these scattering. Figure 4a, b showed the derived diffraction intensity of relief grating coated photoresist and planar grating corresponding to Fig. 3l, n, respectively. It was observed that the background scattering in Fig. 4a was unambiguously stronger than that of Fig. 4b. The intensity along the dashed lines in Fig. 4a, b was plotted in Fig. 4c correspondingly, the red curve showing better quality not only lower scattering (blue dots), but also narrower width of peaks (inverted triangles). The calculated result indicated 21.3% scattering was suppressed in the planar grating compared with that of relief grating. Similar results also appeared in Fig. 4d, e, 11.3% suppression of scattering in Fig. 4f. In fact, the proposed planar grating can be considered as a kind of new volume phase grating without physical grooves. The low scattering is also reported in volume phase holography diffraction gratings (VPH diffraction gratings)\textsuperscript{18,19}. Possibly serious scattering in doping gratings caused by inhomogeneity of doping is far away from our planar grating because the synergistic doping is homogenous, since it happens quickly and has outstanding diffusion. It should be noticed the low scattering in our planar gratings is intrinsic rather than accidental results caused by different technics. After preparation of the photoresist arrays, subsequent steps were conducted to fabricate the planar gratings (Supplementary Fig. 9). However, the deservedly stronger scattering originating from accumulative errors did not be observed in experiments. Finally, thanks to the smooth surface, the planar gratings should have

**Fig. 3** The performance of rewritiable WO\textsubscript{3}-based gratings. a Photoresist is covered on a WO\textsubscript{3} film as the shape of "USTC", which proves that photoresist would hinder the electron–proton synergistic doping. b The synergistic effect is compatible with UV lithography, which can be conducted in microchannels by coating photoresist. c–f The photos recorded by optical microscope: a photoresist array in bar shape (c) and a photoresist array in square shape (d). After being processed by synergistic doping and lift-off, the corresponding pattern of bars (e) and squares (f) were obtained. Panels c–f have the same scale bar. The period is 16 μm. g–j The corresponding surface morphology of samples in panels c–f. k–n The corresponding diffraction spots of samples in panels c–f. For panels k–n, scale bar is the same. o The WO\textsubscript{3} relief grating in the period of 16 μm, p surface morphology, q–s Adjusting the period of the relief grating by the synergistic doping, 32 μm for panel q, 64 μm for panel r, 64 μm for panel s. u–w The corresponding diffraction spots of samples in panels q–s. For panels o and q–s, scale bar is the same. For panels t–w, scale bar is the same.
better accidental resistant than typical relief gratings, whose grooves are easily damaged by fingerprints, aerosols, moisture, or the slightest contact with any abrasive material.

Conclusion

To conclude, we applied electron–proton synergistic doping to WO₃ film successfully and realized a direct visualization of insulator–metal transition in WO₃ film due to its pronounced electrochromic effect. This phase transition originated from the H₂O₃ film due to its pronounced electrochromic effect. The period of the WO₃ relief grating can also be tuned by selective hydrogenation. More importantly, all the prepared gratings can be restored via an annealing procedure then repro- cessed. Our experiment not only demonstrate a facile electron–proton synergistic doping strategy for oxide materials, but also supply a technique for tunable and rewratable grating fabrication in the future.

Methods

WO₃ film deposition. WO₃ thin films were prepared on c-Al₂O₃ single-crystal substrates by reactive magnetron sputtering in an argon–oxygen atmosphere at 200 °C with a stoichiometry WO₃ target. Before loading the Al₂O₃ substrates into the chamber, they were cleaned with acetone and ethanol in an ultrasonic bath, and then rinsed several times with deionized water. The chamber, they were cleaned with acetone and ethanol in an ultrasonic bath, and then rinsed several times with deionized water. The average rate of heating up is 0.15 K s⁻¹ and cool down by nature. Highly sensitive SIMS measurements (Quad PHIL600) were conducted to directly examine the hydrogen, oxygen, and alumi- num concentration in each sample. H⁺ signals were normalized by the background signal in the substrate. The inductively coupled plasma optical emission spectrometer (ICAP 7400) was used to trace zinc concentration after the prepared H₂WO₃ was dissolved in hot H₂SO₄ solution. Encapsulating films in vacuum sealer bags by Deli 14886 (Vacuum Power: –85 kPa). To examine the crystal structure, XRD tests were carried out by Philips X'pert Pro, radiation source Cu Kα, λ = 0.15418 nm. The SEM images were recorded by XL-30 ESEM. Raman spectroscopy tests were recorded at room temperature by LabRAM HR Evolution. A 633 nm laser was used as the excitation source. The optical transmission was measured at room tem- perature by using a UV–Vis–IR spectroscopy (SolidSpec 3700). A home-made device was used for measuring the diffraction of the grating (Supplementary Fig. 10). The wavelength of the laser is 532 ± 10 nm. The max output power is <3000 mW. A three-dimensional profilometer (ContourGT-K 3D Optical Micro- scope) was used to measure surface morphology. An optical microscope (Leica DM1000) was used to record microimages. Photosresist arrays were made by standard UV photolithography. RIE was conducted by Oxford, Plasma Pro NGP 80. Hall measurement was carried on PPMS (DynaCool-14T). The Hall bar of H₂WO₃ was prepared by RIE through a silicon stencil. MATLAB R2019b was used to analyze the defraction intensity. In order to evaluate the scattering performance, we calculated each integration (I) of the two curves in Fig. 4c (Fig. 4d), respectively, marked Sᵢ for gray curve, S_r for red curve. The suppression of scattering (Δ) expressed as Δ = (Sᵢ – S_r)/Sᵢ.

Characterizations. The purity of zinc particle and needle is >99.99%. The %wt H₂SO₄ solution was adopted in all experiments. The square resistance as a function of temperature was examined by an electric measurement system (ZI2810B) with a variable temperature stage (Eurotherm 3504). The average rate of heating up is 0.15 K s⁻¹ and cool down by nature. Highly sensitive SIMS measurements (Quad PHIL600) were conducted to directly examine the hydrogen, oxygen, and alumi- num concentration in each sample. H⁺ signals were normalized by the background signal in the substrate. The inductively coupled plasma optical emission spectrometer (ICAP 7400) was used to trace zinc concentration after the prepared H₂WO₃ was dissolved in hot H₂SO₄ solution. Encapsulating films in vacuum sealer bags by Deli 14886 (Vacuum Power: –85 kPa). To examine the crystal structure, XRD tests were carried out by Philips X'pert Pro, radiation source Cu Kα, λ = 0.15418 nm. The SEM images were recorded by XL-30 ESEM. Raman spectroscopy tests were recorded at room temperature by LabRAM HR Evolution. A 633 nm laser was used as the excitation source. The optical transmission was measured at room tem- perature by using a UV–Vis–IR spectroscopy (SolidSpec 3700). A home-made device was used for measuring the diffraction of the grating (Supplementary Fig. 10). The wavelength of the laser is 532 ± 10 nm. The max output power is <3000 mW. A three-dimensional profilometer (ContourGT-K 3D Optical Micro- scope) was used to measure surface morphology. An optical microscope (Leica DM1000) was used to record microimages. Photosresist arrays were made by standard UV photolithography. RIE was conducted by Oxford, Plasma Pro NGP 80. Hall measurement was carried on PPMS (DynaCool-14T). The Hall bar of H₂WO₃ was prepared by RIE through a silicon stencil. MATLAB R2019b was used to analyze the diffraction intensity. In order to evaluate the scattering performance, we calculated each integration (I) of the two curves in Fig. 4c (Fig. 4d), respectively, marked Sᵢ for gray curve, S_r for red curve. The suppression of scattering (Δ) expressed as Δ = (Sᵢ – S_r)/Sᵢ.

Computational details. All the calculations of the present work were performed by the Vienna Ab Initio Simulation Package with the density functional theory[35]. We chose the frozen-core all-electron projected augmented wave[36] model for core states and the Perdew–Burke–Ernzerhof[37] for exchange and correlation functional. We set the kinetic energy cutoff of 400 eV for the plane-wave expansion of the electronic wave function. We set the force and energy convergence criterion to be 0.02 eV Å⁻¹ and 10⁻⁵ eV, respectively. The length of vacuum space was 20 Å to avoid interactions between periodic images. The solid–solid interfaces are built by attaching the ZnO and WO₃ surface with mismatch <5%. The energy barrier was calculated as ΔE_b = ETS – EIS, where ETS and EIS represent the energies of the initial structures (IS) and the transition states (TS).
Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
Y.C. and C.Z. conceived the project. Y.C. fabricated the devices, performed the measurements, and analyzed the data. C.H., X.Z., and B.L. grew the WO3 films. C.H. performed the SEM, XRD, and Raman characterizations. H.R. performed the SIMS experiments. G.Z. contributed many valuable comments and ideas in revised manuscript. Y.C. and L.L. analyzed scanning performance of the planar grating. L.X. and J.J. conducted the theoretical calculations. Y.C., J.J., and C.Z. wrote the paper, and all authors commented on it.

Competing interests
The authors declare no competing interests.

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