Supplementary Information

Boosting the photocatalytic activity of mesoporous $SrTiO_3$ for nitrogen fixation through multiple defect and strain engineering

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Experimental

Materials

Titanium butoxide (TBOT, ≧ 99.0%), hexadecyl trimethyl ammonium bromide (CTAB, 99%), strontium chloride hexahydrate ($SrCl_2 \cdot 6H_2O$, 99.5%), N,O-Bis(trimethylsilyl)acetamide (BSA, 95%), sodium nitroferricyanide dihydrate ($Na_2[Fe(CN)_5NO] \cdot 2H_2O$,99.0%), sodium salicylate ($NaC_7H_5O_3$,≧ 99.5%) and sodium hydroxide (NaOH,97%), sodium hypochlorite (NaClO, ρCl≧ 5.0%), ammonium chloride ($^{14}NH_4Cl$, 99.5%) were purchased from Aladdin. Concentrated hydrochloric acid (HCl) was purchased from Damao chemical reagent factory. Anhydrous ethanol was supplied by Macklin. Ammonium chloride ($^{15}NH_4Cl$,99.0%) was purchased from CIL. Dimethyl sulfoxide-d_6 (d_6-DMSO) was supplied by Sigma. All reagents were analytical grade and without further purification. The water used here was ultrapure (18.2 $M\Omega \cdot cm^{-1}$).

Preparation of STO

In a typical synthesis of polycrystalline mesoporous STO nanoparticles, a 15 mL solution containing 3 mmol of TBOT, 3 mmol of $SrCl_2 \cdot 6H_2O$, certain amount of CTAB and BSA were loaded into a Teflon autoclave after 30 minutes of magnetic stirring. Then NaOH was added to ensure the concentration of NaOH was 2 $mol \cdot L^{-1}$ in the solution. The autoclave was sealed and maintained at 200°C for 12 hours and then allowed to cool to room temperature naturally. After being washed with distilled water until the solution pH is 7, the white color products were obtained. Then, STO nanoparticles with mesoporous surface were treated in a H_2 (15 vol%)-Ar atmosphere at 1000 °C for 1 h followed by quenching in liquid nitrogen. The strained mesoporous STO nanoparticles (MSTO-s) was obtained. Except that no BSA was added, the synthesis procedure of cube-shaped STO nanoparticles as same as the mesoporous STO. The steps are shown in Fig.S1.

Characterization

The structures of the as-prepared samples were monitored using XRD (Rigaku Corporation, SmartLab) analysis at a scan rate of 8° min^{-1} with Cu Kα radiation (V = 40 KV, I = 30 mA). The specific surface area and pore size distribution of the material was tested by Brunauer-Emmett-Teller analysis at 77 K (BET, MICROMERITICS□INSTRUMENT CORP, ASAP 2460). Transmission electron microscope (TEM, FEI Company, Tian ETEM G^2 80-300) was used to characterize the morphology of the prepared material. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 spectrometer with monochromatic Al Kα radiation (150 W, 1486.6 eV). Fluorescent spectrophotometry was recorded on a FluoroMax 4 (Horiba Jobin Yvon) spectrophotometer, while UV-vis spectra were performed on a spectrophotometer in the range between 300 and 800 nm (UV-vis, Perkin Elmer Lambda 650). Raman spectra were obtained by a LabRAM HR Raman spectrometer with a He/Ne laser in the range from 70 to 1200 cm^{-1}. The N_2 isotope labelling experiment was tested on ^{1}H-nuclear magnetic resonance (NMR) spectroscopy (Bruker AVANCE III HD500, Germany).

Photocatalytic nitrogen reduction

All photocatalytic N_2 reduction experiments were performed on a designed photo-reduction cell at ambient temperature and pressure. A 300 W Xe lamp was used as an artificial solar light source, while the illumination intensity was 2 suns. Typically, 10 mg of photocatalyst was dispersed into 100 mL of 10 vol% aqueous ethanol solution and sonicated for 30 min in darkness to ensure homogeneity. The solution was bubbled with pure nitrogen for 60 min to remove the dissolved oxygen prior to each test. During the photoreduction, the reaction solution was under magnetic stirring and N_2 gas flow rate was 30 mL·min^{-1}. A aliquot of reaction solution was collected every 1 h, and the photocatalyst was centrifuged by centrifugation.

Determination of ammonia

Ammonia product was quantitatively determined by the indophenol blue method. [1-2] Briefly, 2 mL reaction solution was added into 500 μL oxidizing solution containing NaOH (0.125 mol·L^{-1}) and NaClO (ρCl ≧ 5.0%). And then further adding 500 μL coloring solution and catalyst solution containing 0.125 mol·L^{-1} NaOH, 0.625 mol·L^{-1} $NaC_7H_5O_3$ and 0.2 mg $Na_2[Fe(CN)_5NO]\cdot 2H_2O$. The mixed solution was kept in darkness for 3 h before UV-vis measurement. The adsorption peak of indophenol at around 660 nm was recorded and used for the amount of produced ammonia calculation. When tested in 10 vol% ethanol aqueous solution, the concentration-absorbance curve was calibrated using $^{14}NH_4Cl$ solution with $^{14}NH_4^+$ concentrations of 0.0, 17.9, 35.8, 53.7, 71.6, 89.5, 107.4 μmol·L^{-1} and the amount of ethanol was added to the standard curve as same as the amount of ethanol tested. The calibration curve (Fig.S2) ($y = 0.0053x + 0.00598$, $R^2 = 0.9993$) showed good linear relation of absorbance value with $^{14}NH_4^+$ concentration by three times independent calibrations.

N_2 isotope labelling experiment

To verify the origin of generated ammonia, we perform the catalytic N_2 reduction using isotopic $^{15}N_2$ as a nitrogen source. The $^{15}N_2$ gas purchased from Sigma (Sigma-Aldrich, SKU No: 364584-10 L). The ammonia produced was tested by ^{1}H-NMR measurement on a Bruker AVANCE III HD500. The ^{1}H-NMR signal of $^{15}NH_4^+$ is split by the nuclear spin of ^{15}N into a well-known doublet (~73 Hz) in the region near 6.9~7.2 ppm, while ^{14}N produces a triplet (~52 Hz) in the same region.[3-6]

To increase the utilization of $^{15}N_2$ gas and remove the contaminants in the $^{15}N_2$ gas, a gas circulation system was designed to perform the isotopic labelling experiment. Schematic diagram of this system is shown in Fig. S5. A water container was used for gas collection through water displacement; the volume of $^{15}N_2$ can be precisely adjusted between 0-140 mL. Some impurities such as NO_x can be adsorbed and trapped in water before the photocatalysis, and the volume of $^{15}N_2$ gas can be monitored and controlled as per required. The $^{15}N_2$ gas was circled in the sealed system and gas flow rate was controlled by adjusting the applied voltage of the peristaltic pump. The photocatalytic $^{15}N_2$ reduction experiments were performed on a designed photo-reduction cell (10 mL) at ambient temperature and pressure. The gas flow rate was 20 mL.min^{-1}. The illumination intensity was 2 suns. Typically, 1.0 mg of photocatalyst was dispersed into 10 mL of 10 vol% aqueous ethanol solution and sonicated for 30 min in darkness to ensure homogeneity. The aqueous solution was bubbled with pure Ar for 30 min to remove the dissolved oxygen prior to each test. The reaction time was kept for 4 hours. The product was qualitatively monitored using ^{1}H-NMR with d_6-DMSO as a reference. The sample spectra were obtained by using the NOESY method with the following parameters: TD = 65536, NS= 2048, P1 = 32.25 μs, SW = 19.99 ppm, D1 = 1 s, D8 = 0 s, AQ = 1.36 s, O1P = 6.175 ppm. The sample volume in the NMR experiment was 0.8 mL containing 20 vol% d_6-DMSO solutions. A mixture of $^{15}N_2$ and $^{14}N_2$ were also used as the nitrogen source to perform the photocatalytic reactions. The experimental procedure was the same as the pure $^{15}N_2$ isotope labelling experiments.

Computational details

In this work, DFT calculations were carried out using the CASTEP package. Generalized gradient approximation with the Perdew-Burke-Ernzerhof functional was used to describe the exchange-correlation interaction. The so-called DFT+U method was used to enhance the description of the strongly correlation of d electrons, $U = 3.5$ eV for Ti 3d electrons. A 3 × 3 five-layer periodic slab supercell with a 15 Å vacuum layer (a=11.71 Å, b=11.71 Å, c=22.81 Å) was used to model the $SrTiO_3$ (001) surface. The lattice stress of 0.0%, 2.5%, 5.0%, 10%, 15% are achieved by changing the lattice constant a to be11.71 Å, 11.42 Å, 11.12 Å, 10.54 Å, 9.95 Å respectively. The energy cut-off for the plane-wave basis set was set to 600 eV for all relaxation, energy and electronic properties calculations. The Brillouin zone was sampled with Monkhorst-Pack 2×2×1 k-points generated manually. A Gaussian smearing with a width of 0.01 eV was used in all calculations. The convergence tolerance of energy was set to 2.0×10^{-6} eV/atoms. The maximal displacement and force is 2.0×10^{-3} Å and 0.03 eV/Å, respectively.

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Fig. S1 Synthesis procedures for STO, MSTO and MSTO-s materials.

Fig. S2 The SEM image of nonporous $SrTiO_3$ nanoparticles.

Fig. S3 The HRTEM image of MSTO-s sample with disordered surface structure.

Fig. S4 The concentration-absorbance curve for the $^{14}NH_4Cl$ calibration solutions in addition 10 vol% ethanol. These error bars in every concentration are the standard deviation of at least three replicates of independent measurement.

Fig. S5 Yield of ammonia obtained under different conditions: (Ⅰ) Ar atmosphere; (Ⅱ) N_2 atmosphere without illumination.

Fig. S6 The time-dependence of ammonia yield.

Fig. S7 Schematic diagram of the N_2 isotope gas circulation system.

Fig. S8 (a) The PDOS of d orbitals of $SrTiO_3$ with different concentration of oxygen. (b) The total PDOS of $SrTiO_3$ with different concentration of oxygen.

Fig. S9 The PDOS of $SrTiO_3$ with strain.

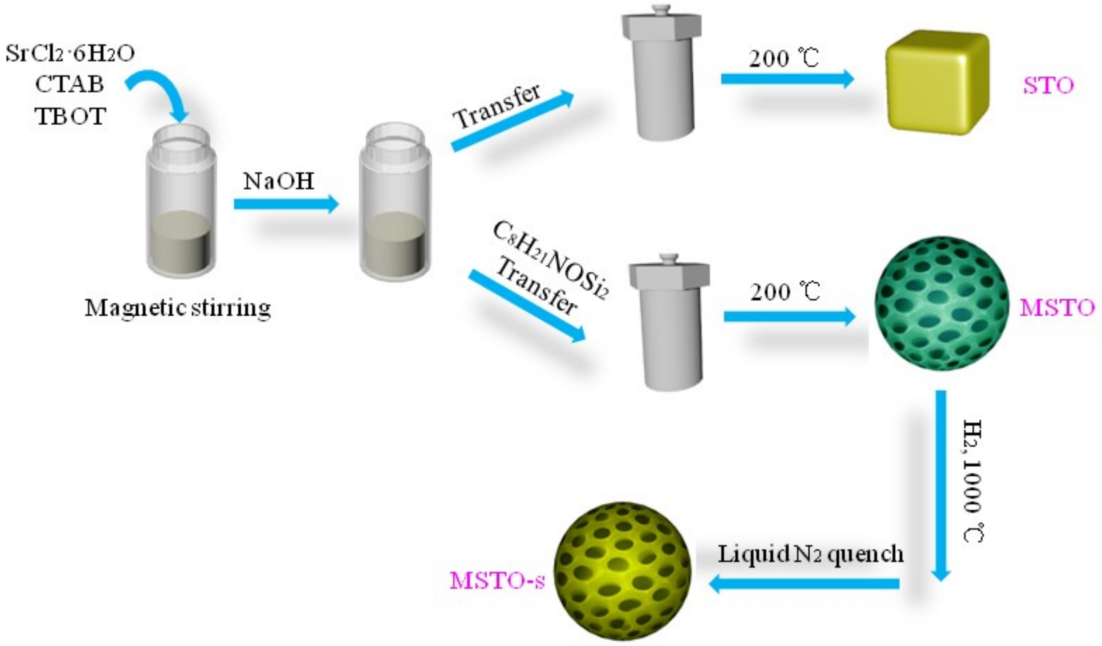


Fig.S1 Synthesis procedures for STO,MSTO and MSTO-s materials.

Table S1. Lattice parameters of (110) and (111) facets of MSTO-s, MSTO and STO nanoparticles

Method	XRD (nm)		TEM (nm)	
Facet	(110)	(111)	(110)	(111)
STO	0.2768	0.2260	0.277	0.226
MSTO	0.2767	0.2259	0.277	0.226
MSTO-s	0.2752	0.2250	0.275	0.224

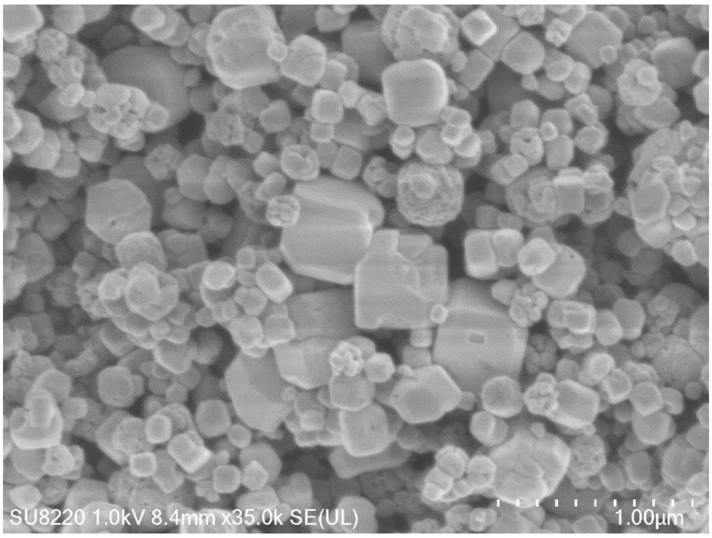


Fig.S2 The SEM image of conventional cubic $SrTiO_3$ nanoparticles, exhibiting a flat nonporous surface.

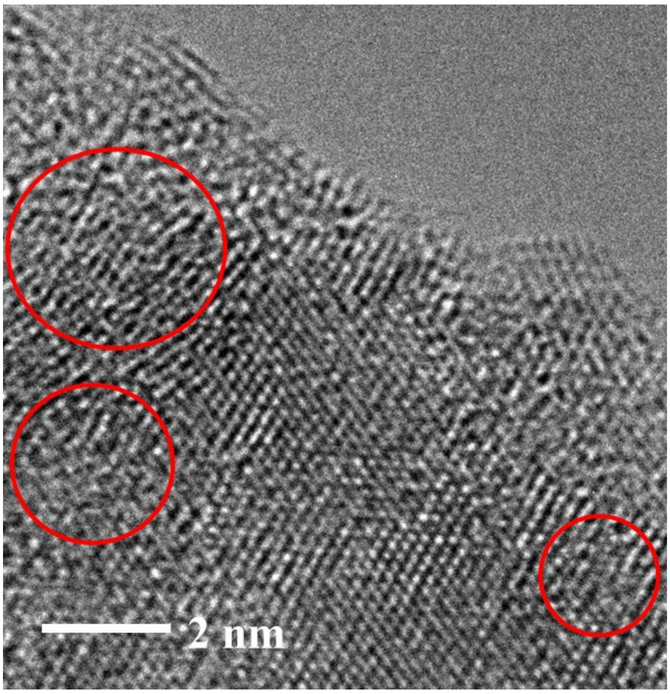


Fig.S3 The HRTEM image of MSTO-s sample with disordered surface structure.

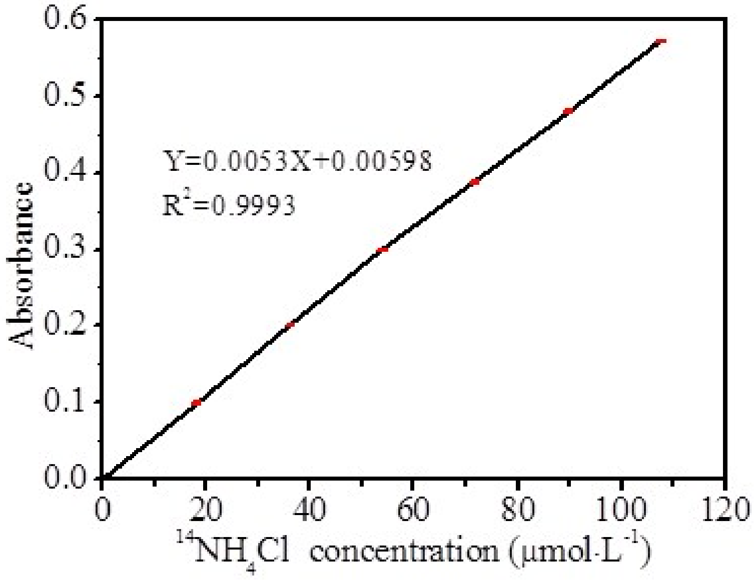


Fig.S4 The concentration-absorbance curve for the $^{14}NH_4Cl$ calibration solutions in addition 10 vol% ethanol. These error bars in every concentration are the standard deviation of at least three replicates of independent measurement.

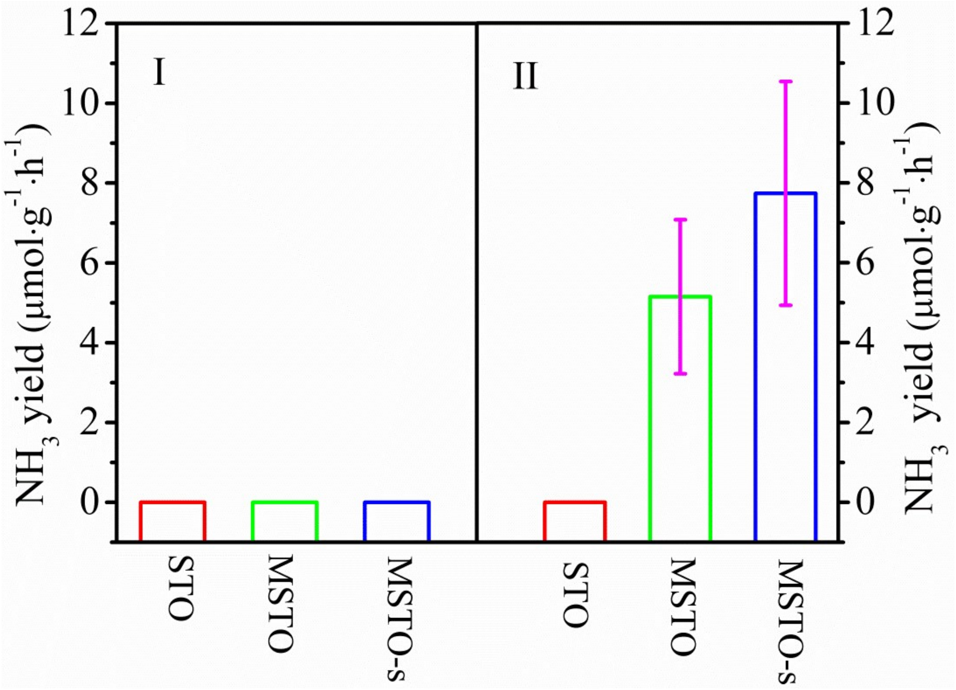


Fig.S5 Yield of ammonia obtained under different conditions: (Ⅰ) Ar atmosphere; (Ⅱ) N_2 atmosphere without illumination.

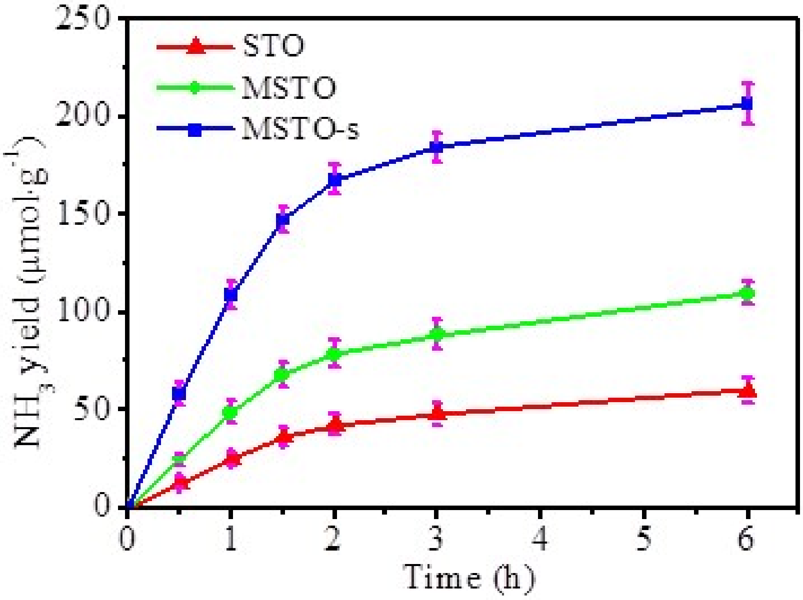


Fig.S6 The time-dependence of ammonia yield.

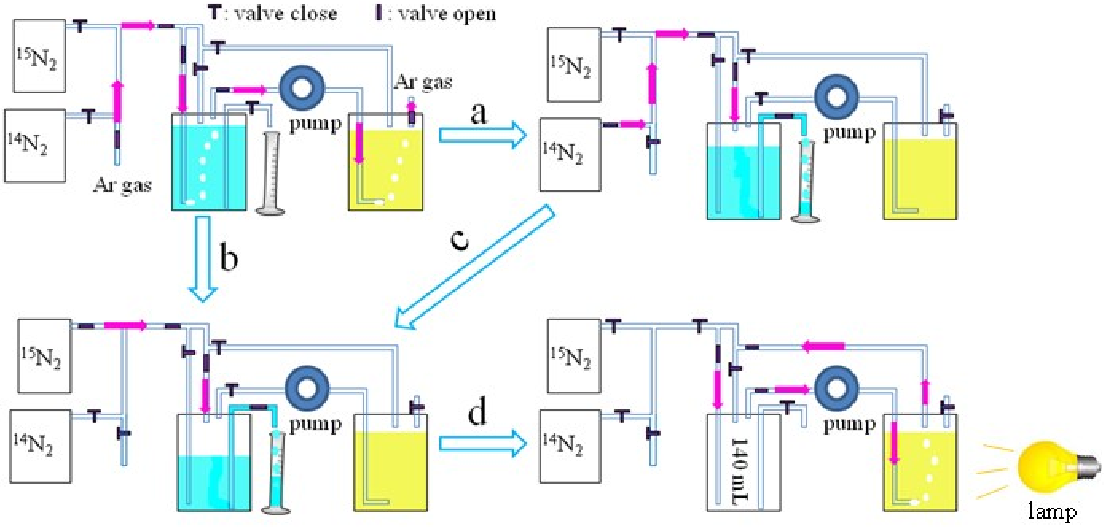
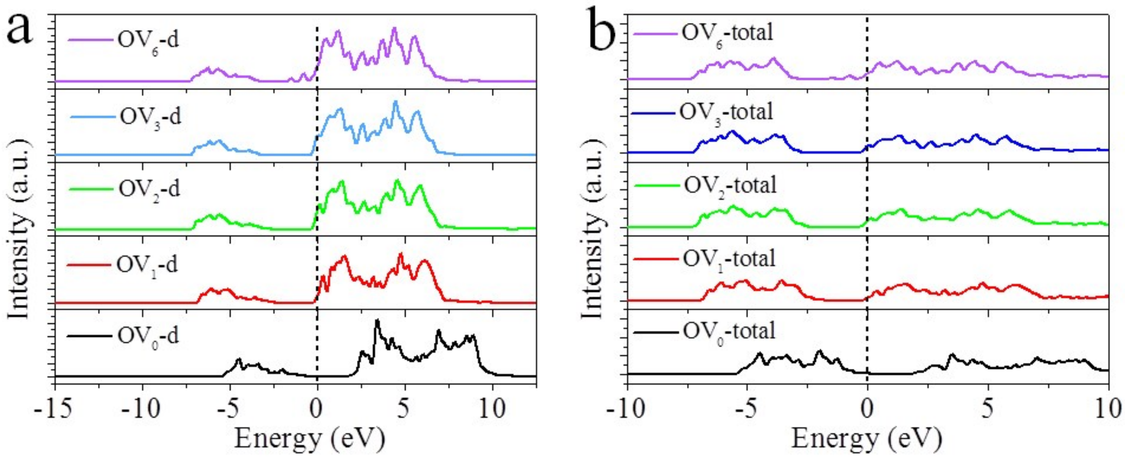


Fig.S7 Schematic diagram of the N_2 isotope gas circulation system.



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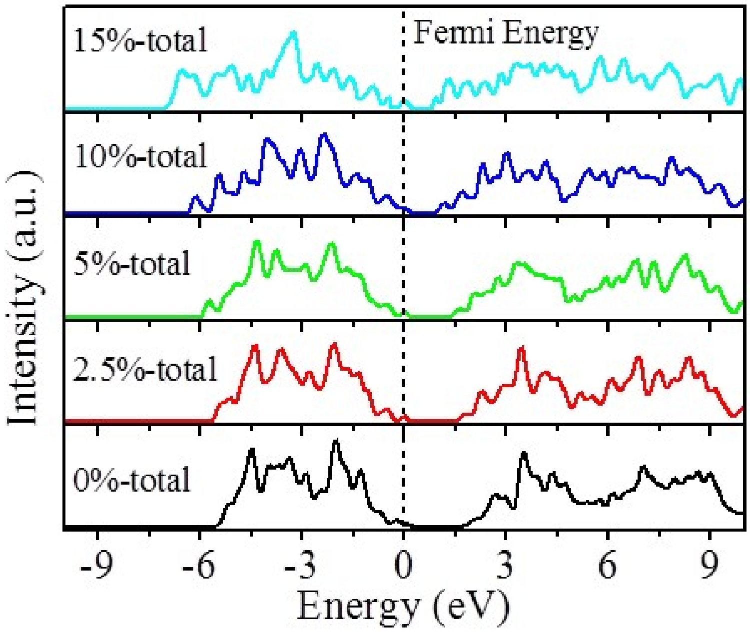

Fig.S9 The PDOS of $SrTiO_3$ with strain.