Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Where Oxygen Goes on Graphene-Catalyst in Water Splitting

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1. Characterizations

The X-ray diffraction (XRD) measurements were carried out on a German Bruker D8-ADVANCE diffractometer with Cu Kα radiation; the scanning range was 10–70° with a 5° min^{-1} scanning speed. The morphologies of obtained products were analyzed by using a JSM-6390LV scanning electron microscopy (SEM). The morphologies of the samples were observed on transmission electron microscopy (TEM, JEOLJEM-2100). A high-resolution transmission electron microscope (HRTEM, JEM-2100) was used to observe the morphology of the prepared samples at 200 kV. Fourier transform infrared (FT-IR) spectra were recorded using an FTIR Analyzer (Perkin-Elmer, Spectrum 400), and the KBr was served as a reference sample. Raman measurement was carried out using a Renishaw in Via Raman spectroscopy, the power of the laser was 1%, and the laser excitation was 532 nm, wavenumber range (100–800 cm^{-1}), and the exposure time was 1s. The Brunauer–Emmett–Teller (BET) method was used to measure the specific surface area of the samples using nitrogen adsorption-desorption isotherms at 77 K. The ultraviolet-visible diffuse reflectance spectra (DRS) of the photocatalysts were recorded in the 200–800 nm regions with a UV-2600 ultraviolet-visible spectrophotometer against $BaSO_4$.The photoluminescence (PL) spectra were measured on a fluorescence spectrometer (JY HORIBA FluoroLog-3) equipped with an excitation wavelength of 300 nm. X-ray photoelectron spectroscopy (XPS, AXISULTRA) was employed to identify the chemical states of the surface compositions in a Kratos-Axis-Ultra system equipped with monochromatic Al Kα X-rays (1486.6 eV). TGA measurements were conducted over a temperature range of 25–800 ºC at a heating rate of 10 ºC min^{-1} Under the N_2 atmosphere. The electron spin resonance (EPR) spectra of the samples were recorded on a Bruker E500 spectrometer in the air at room temperature. The fluorescence lifetimes of the photocatalytic materials were obtained by using a

FLUOROMAX-4 spectrophotometer at room temperature. The photocurrent–time curve was obtained using a three-electrode photoelectrochemical cell and a workstation (CHI600E China) with a 100 W xenon lamp with a 100 mL 0.1 M Na_2SO_4 solution as the electrolyte. The In situ Raman spectroscopic detection measurements were performed at room temperature using a HORIBA LabRam spectrometer with a 785 nm excitation wavelength at 0.5mW between 200 and 2500cm^{-1}. To avoid laser-induced deintercalation and photochemistry, the laser power was kept below 0.5 mW, the laser spot size of B1mm (Olympus LMPlanFl 50*, NA 0.50). A charge-coupled device is used to detect the signal after analyzing the signal via a monochromator. The spectrometer was calibrated in frequency using a HOPG crystal.

2. Evaluation of photocatalytic water splitting

Photocatalytic overall water splitting reactions were carried out in a side-irradiation vessel connected to a glass gas-circulation system. It was performed in the CEL-PAEM-D6 online system (China Education AU-light Company Limited, Beijing) under different light irradiation, respectively. A 300 W Xe lamp (CEL-HXF100) was used as an incident light source, and the intensity was 100 mW cm^{-2}. In a typical photocatalytic overall water splitting reaction, 50 mg as-prepared samples were dispersed in deionized water (50 mL) under constant magnetic stirring and top-irradiation. After completely removing air from the reaction slurry by evacuation, the reaction system was irradiated for one hour. During irradiation, the collected gas was analyzed by A GC-7920 gas chromatograph equipped with a thermal conductivity detector and a 5A molecular sieve column, and N_2 as the carrier gas.

3. CO_2 evaluation measurement

The gas–solid phase CO_2 experiment was conducted in a home-made evaluation system. It was performed in the CEL-PAEM-D6 online system (China Education AU-light Company Limited, Beijing) under UV light irradiation, respectively. A 300 W Xe lamp (CEL-HXF100) was used as an incident light source, and the intensity was 100 mW cm^{-2}. In a typical CO_2 evaluation measurement reaction, 50 mg as prepared samples were dispersed in deionized water (50mL) under constant magnetic stirring and top-irradiation. After completely removing air from the reaction slurry by evacuation, the reaction system was irradiated for one hour. Under the light irradiation (a 300 W Xeon lamp coupled with an AM 1.5 filter was used as the light source), the gaseous mixture were analyzed by a gas chromatograph (GC-7920) every 1 h, carbon involved products,such as hydrogen, oxygen, nitrogen, carbon dioxide, etc., were detected by the thermal conductivity detector. The qualitative and quantitative analyses of the gaseous products were based on the external method taking the concentrated standard gases as reference. The data reproducibility was checked by performing the same reaction in duplicate.

4. Apparent quantum efficiency (AQE) determination

The apparent quantum efficiency under 365nm light irradiation was measured using the photocatalytic reactor setup according to the following equations:

$$Apparent\ quantum\ efficiency\ (\%) = \frac{Mols\ of\ reacted\ electrons\ per\ unit\ time}{Mols\ of\ incident\ photons\ per\ unit\ time} \times 100$$

$$Mols\ incident\ photons\ per\ unit\ time\ (N_{Einstein}) = \frac{Number\ incident\ photons\ per\ unit\ time}{N_A}$$

$Number\ of\ incident\ photons\ N_p\ per\ unit\ time\ can\ be\ calculated\ by$:

$$N_P = \frac{Intensity\ (E)}{Photon\ energy\ (E_P)}$$

$$photon\ energy\ (E_P) = \frac{hc}{\lambda}$$

$$E = Irradiance \times reactor\ area\ illuminiated\ =\ 0.04\,J \cdot s^{-1} \cdot cm^{-2} \times 50.24\,cm^2 = 2.01\,J \cdot s^{-1}$$

$$E_P = \frac{(6.625 \times 10^{-34}\,J \cdot s) \times (3 \times 10^{17}\,nm \cdot s^{-1})}{365\,nm} = 5.45 \times 10^{-19}\,J$$

$$N_P = \frac{E}{E_P} = \frac{2.01\,J \cdot s^{-1}}{5.45 \times 10^{-19}\,J} = 3.69 \times 10^{18} s^{-1}$$

$$N_{Einstein} = \frac{N_P}{N_A} = \frac{3.69 \times 10^{18} s^{-1}}{6.02 \times 10^{23} mol^{-1}} = 6.13 \times 10^{-6} mol \cdot s^{-1}$$

$$AQE\ (\%) = \frac{2 \times H_2\,production\,rate}{N_{Einstein}} \times 100 = \frac{2 \times 5.28 \times 10^{-10} mol \cdot s^{-1}}{6.13 \times 10^{-6} mol \cdot s^{-1}} \times 100 = 0.02\%$$

Supplemental Figs.

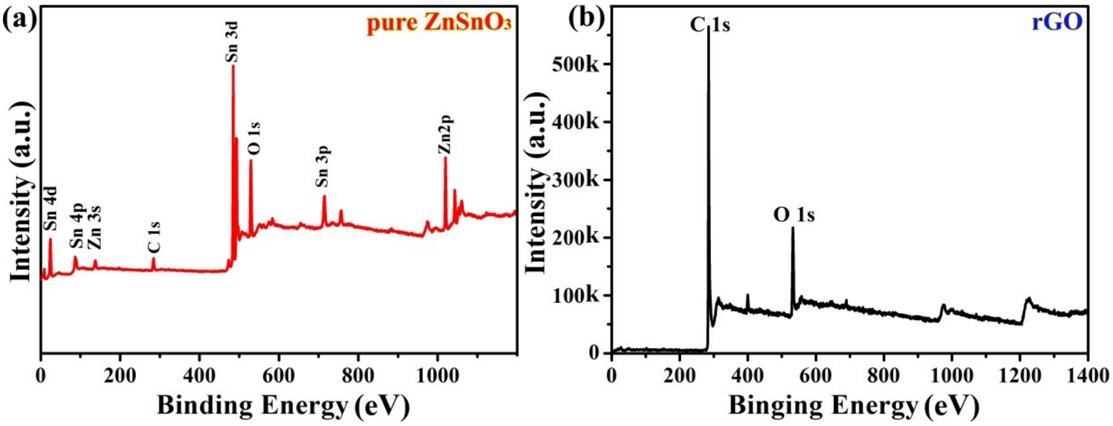


Fig. S1 The full ranged XPS spectra of (a) $ZnSnO_3$-rGO and (b) rGO.

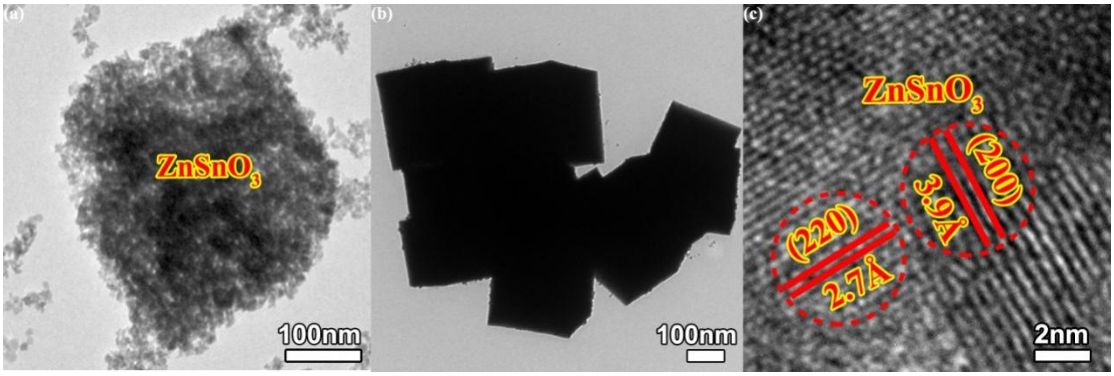


Fig. S2 (a) TEM image of a typical $ZnSnO_3$ sample. (b) TEM image of a typical $ZnSnO_3$-rGO sample. (c) HRTEM image of a typical $ZnSnO_3$ sample.

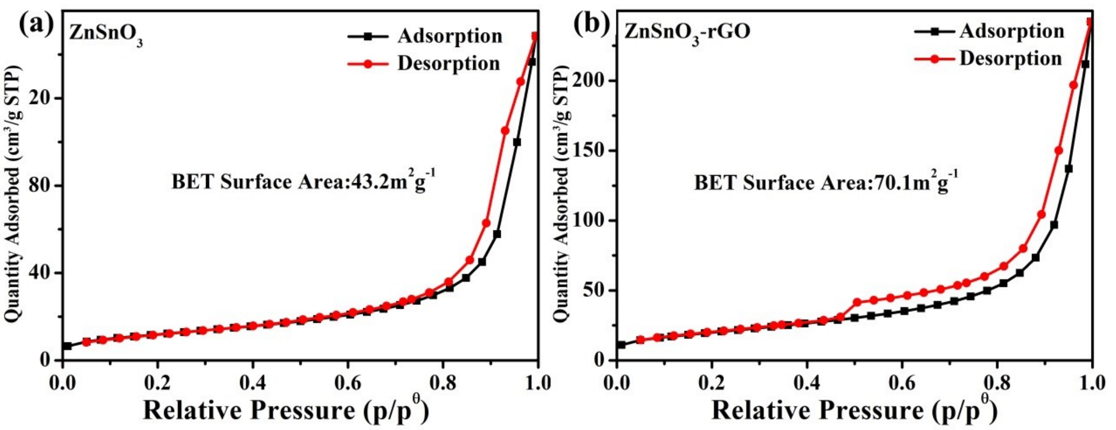


Fig. S3 Nitrogen adsorption-desorption isotherms of (a) $ZnSnO_3$ and (b)$ZnSnO_3$-rGO.

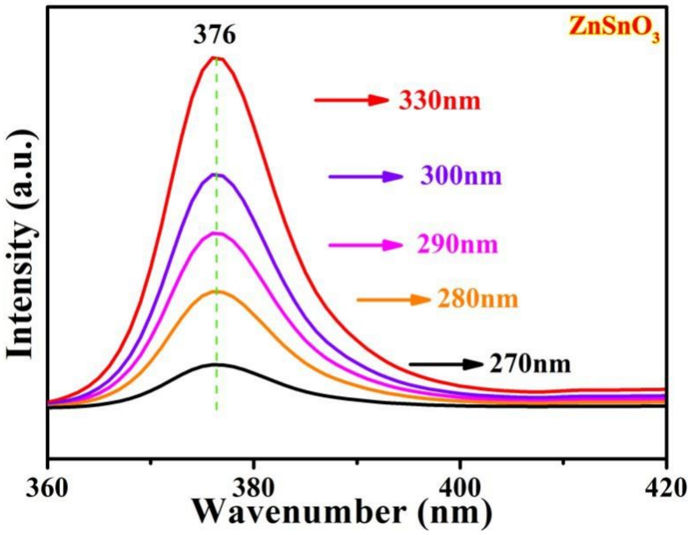
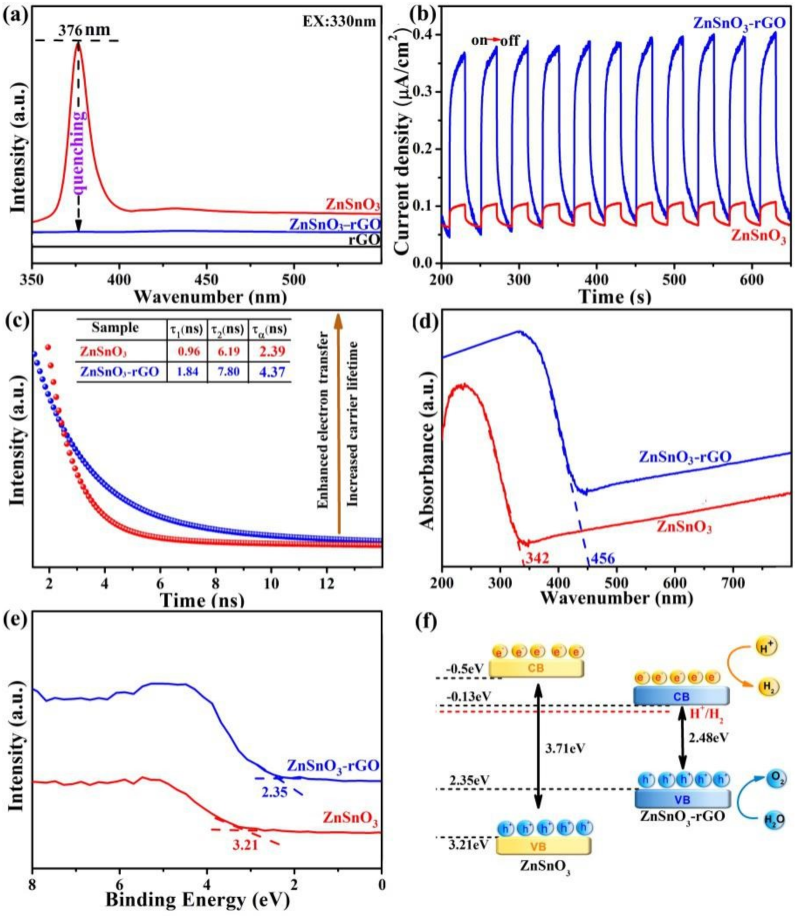


Fig. S4 PL spectra of $ZnSnO_3$ with different wavelength excited light.



Sample	τ_1(ns)	τ_2(ns)	τ_α(ns)
ZnSnO$_3$	0.96	6.19	2.39
ZnSnO$_3$-rGO	1.84	7.80	4.37

Fig. S5 (a) PL spectra of rGO, ZnSnO$_3$ and ZnSnO$_3$-rGO at EX=330. (b) Photocurrent density of ZnSnO$_3$ and ZnSnO$_3$-rGO. (c) Fluorescence lifetime of ZnSnO$_3$ and ZnSnO$_3$-rGO. (d) UV–vis DRS of ZnSnO$_3$ and ZnSnO$_3$-rGO samples. (e) Valence-band spectra measured by XPS. (f) The band structures of the ZnSnO$_3$ and ZnSnO$_3$-rGO samples.

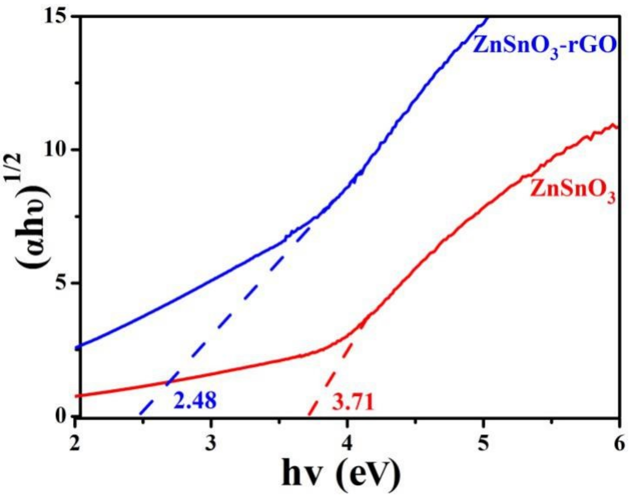


Fig. S6 Optical band gaps determined by the UV–vis DRS.

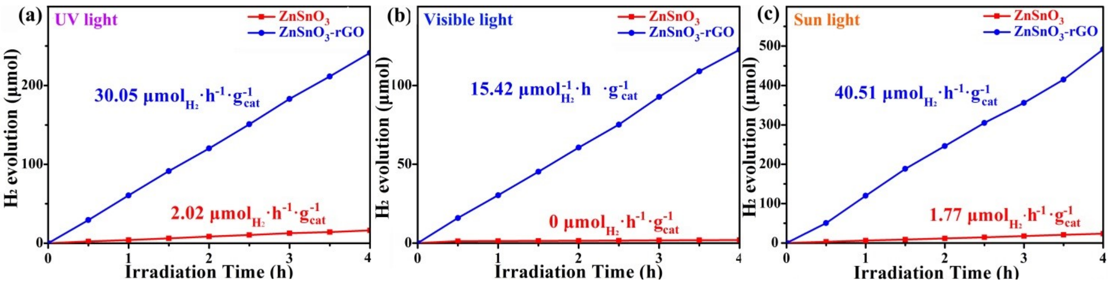


Fig. S7 Typical time course of hydrogen evolution for $ZnSnO_3$ and $ZnSnO_3$-rGO samples under (a) UV light (b) Visible light and (c) Simulated sunlight.

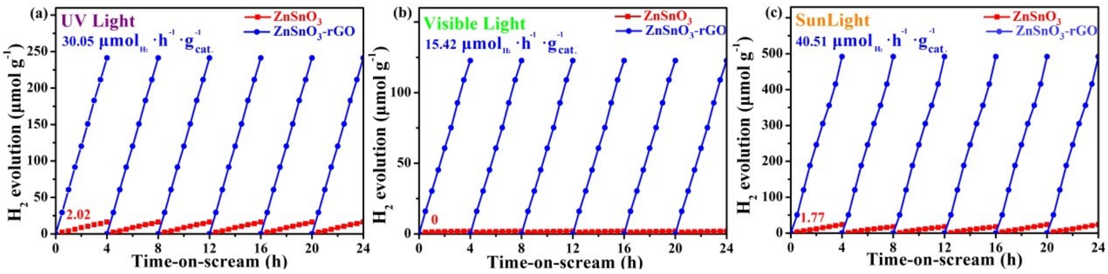


Fig. S8 Photocatalytic water splitting for H_2 generation in 6 repeated cycles (4 h/cycle) under (a) UV Light (b) Visible Light (c) Simulated sun Light.

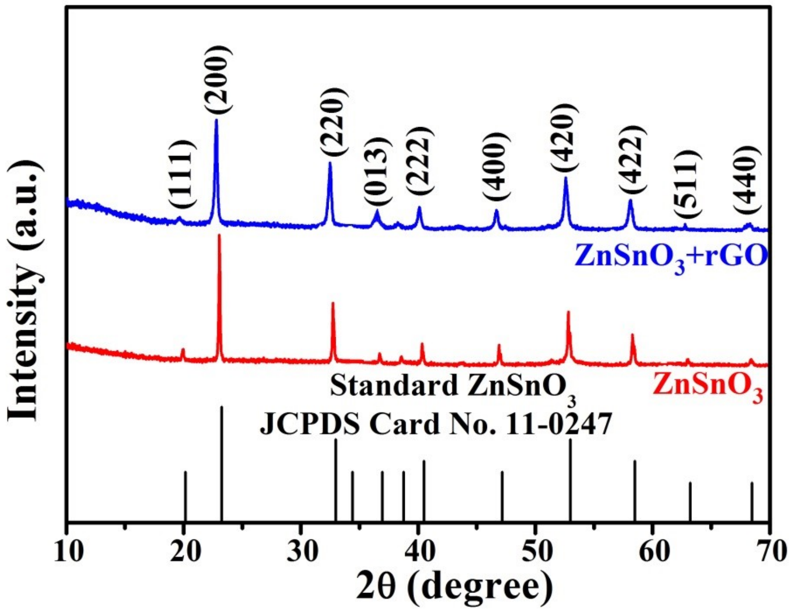


Fig. S9 XRD patterns of $ZnSnO_3$ and $ZnSnO_3$-rGO samples after photocatalytic reaction.

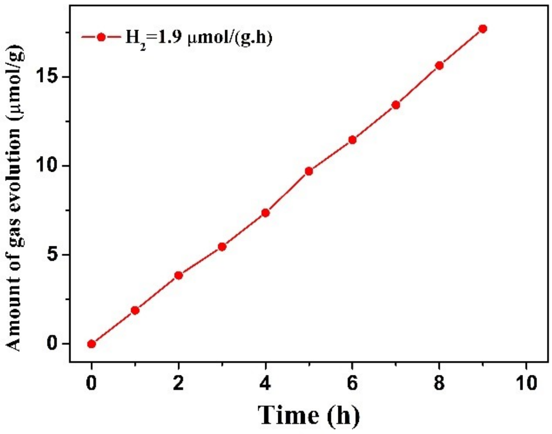


Fig. S10 Typical time course of hydrogen evolution for $ZnSnO_3$-rGO samples under 365nm UV light.

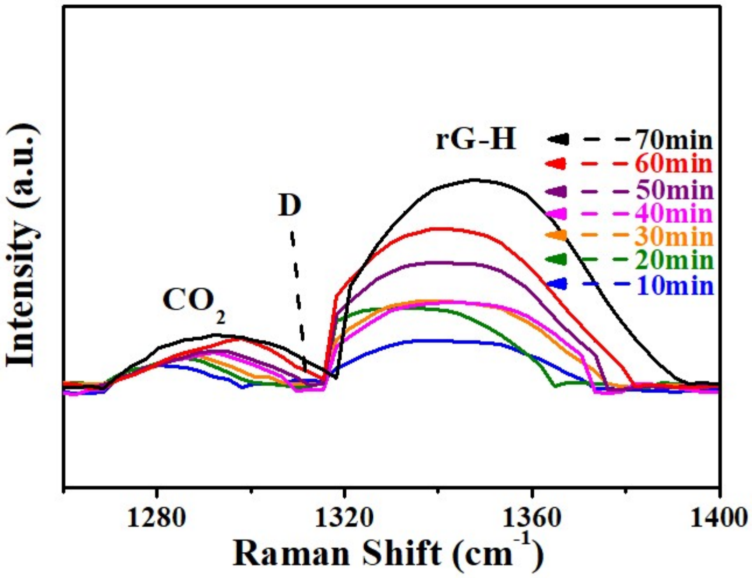


Fig. S11 In-situ Raman (regional amplification) of $ZnSnO_3$-rGO samples.

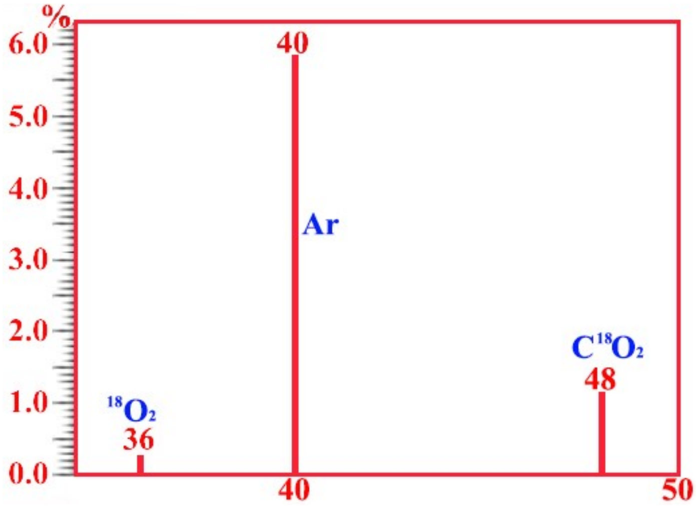


Fig. S12 MS spectrum of generated $C^{18}O_2$.