Supporting Information

Catalysts Characterizations

X-ray powder diffraction (XRD) patterns of samples were determined with an X-ray diffractometer (Bruker D8 ADVANCE, Germany), using Cu Kα radiation (λ = 0.15406 Å). The scan range was taken over from 5° to 80° with a step size of 8°/min. The monolithic catalyst samples were analyzed by a Smartlab X-ray diffractometer for material characterization and quantitative analysis using a Johansson Kα1 high-resolution optical path, a fine-focusing 9 KW rotary-target X-ray generator with a scanning range of 5-80° in 8°/min steps.

The surface morphology of the samples was measured using a field emission scanning electron microscope (ZEISS Gemini 300, Germany). For the powdered samples, the samples were dispersed in anhydrous ethanol and the dispersed samples were dripped onto the smooth surface of a clean wafer, which was allowed to dry naturally, and then the other side of the wafer was attached to a conductive tape on the sample stage and placed in the sample chamber for testing. For block samples, the samples were cut into 1 cm × 1 cm squares for testing. The distribution of the elements in the samples was obtained using an accompanying energy spectrometer (EDS).

X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo-ESCALAB 250XI (Thermo Fisher Scientific, USA). The binding energy was calibrated using the C1s peak at 284.8 eV. For block samples, they were cut into 2 cm × 2 cm squares for testing.

The samples were analyzed by infrared spectroscopy using an infrared spectrometer (FTIR, Thermo Fisher, USA) in the range of 500-4000 cm^{-1}, and the spectra were collected after several scans in a room temperature environment.

H_2 temperature-programmed reduction (H_2-TPR) and O_2 temperature-programmed desorption (O_2-TPD) were carried out using an AutoChem 2920 (Micromeritics, USA). The sample used was 100 mg of 40-60 mesh catalyst. In a typical H_2-TPR analysis, The catalyst was pretreated in a flow of He (30 mL/min) for 60 min at 200 °C. After cooling to 40 °C, the reduction process was carried out under a flow of a 5 vol% H_2/Ar gas mixture (30 mL/min) between 100 and 800 °C at a heating rate of 10 °C/min. For O_2-TPD analysis, each sample (100 mg) was pretreated at 200°C in a flow of He (30 mL/min) for 60 min. After cooling to room temperature, the gas was transformed to O_2/Ar (30 mL/min), heating from 100 to 800 °C.As for H_2O-TPD exploration, each catalyst was pretreated at 200 °C in a flow of N_2 (30 mL/min) for 60 mins, ensure that the physical adsorbed water was removed. The sample was then treated under humid gas (30 mL/min) for 60 mins, then transferred to N_2 (30 mL/min) atmosphere, heating from 100 to 800 °C at a rate of 10 °C/min.

Table S1 Surface chemical compositions and the S 2p XPS results for pH=1, 4 and 7 catalysts

Catalysts	Mn^{3+}/Mn^{4+}	O_{ads}/H_2O_{ads}	XPS S/%At
pH=1	2.05	2.44	3.63
pH=4	2.94	3.35	1.98
pH=7	4.07	6.31	0.62

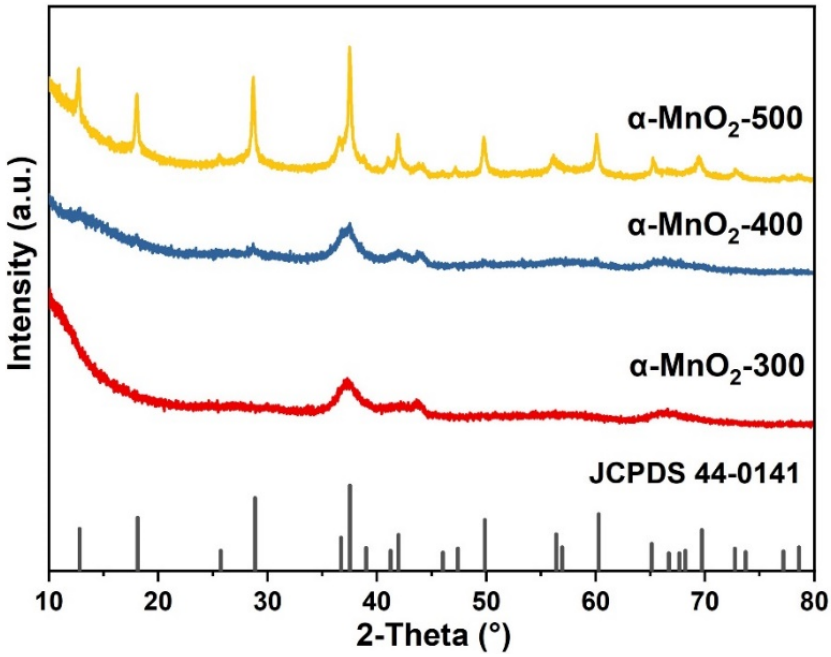

Fig S1 XRD patterns of α-MnO_2 powder catalysts at different calcination temperatures

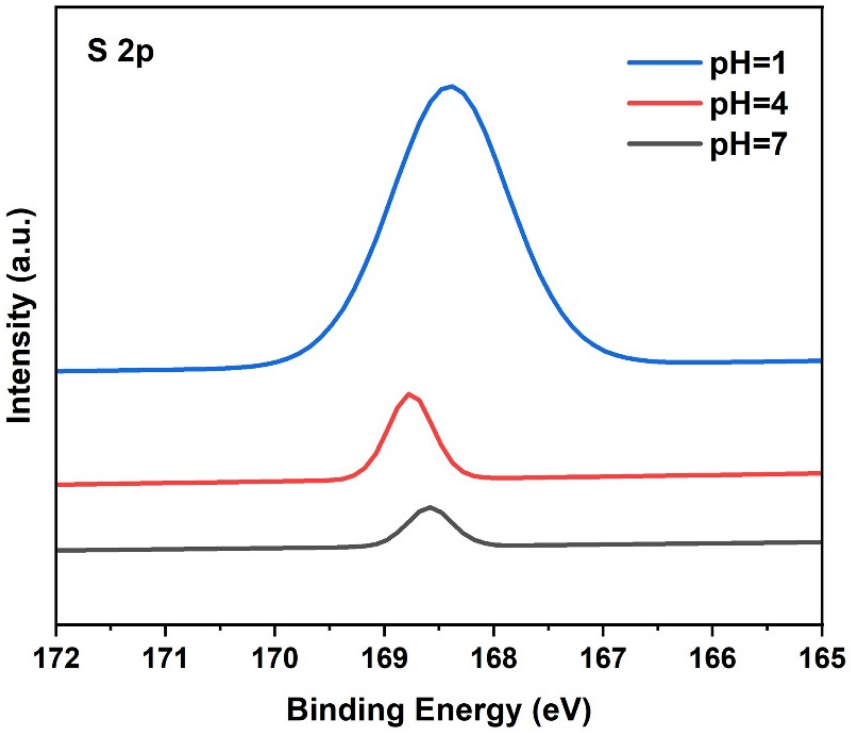

Fig S2 S 2p XPS spectra of pH=1,4 and 7 catalysts

Fig S3 EDS element mapping image of selected region of α-MnO_2 monolithic catalyst

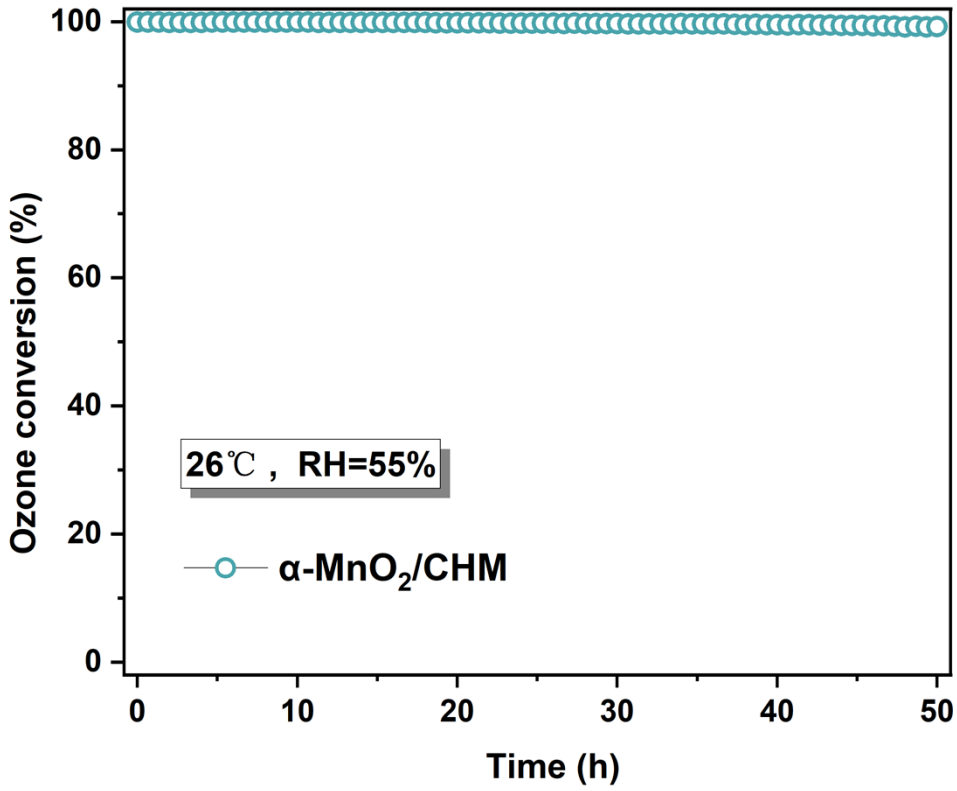

Fig S4 Stability test of α-MnO_2 monolithic catalyst