Breaking the Barrier: $MnWO_4$ Photocatalyst Enables Solar Chlorine Production from Seawater without Noble Metals

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1. Experiment section

1.1 Materials

$Na_2WO_4 \cdot 2H_2O$, $MnCl_2$, NaCl, $C_4H_4Na_2O_6$, N,N-diethyl-p-phenylenediamine (DPD), $KMnO_4$, Na_2SO_4, anhydrous ethanol, 5,5-dimethyl-1-pyrroline N-oxide (DMPO), 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO), methylpyrrolidone, and polyvinylidene fluoride (PVDF) were of analytical grade and directly used without further purification. Fluorine tin oxide (FTO) was obtained directly commercially. Milli-Q water (Millipore, USA) was used in the experiment.

1.2 Preparation of $MnWO_4$

In this experiment, a simple one-step hydrothermal method has been reported[1] to synthesize pure $MnWO_4$. Firstly, 6 mmol of $C_4H_4Na_2O_6$, 6 mmol of $MnCl_2$, and 6 mmol of Na_2WO_4 are dissolved in 20 ml of distilled water, respectively. Then add $MnCl_2$ to $C_4H_4Na_2O_6$ solution to form solution A after mixing evenly, and blend Na_2WO_4 with solution A to form solution B. Stirring magnetically at room temperature for 15 minutes, and add an appropriate amount of NaOH solution during stirring. Subsequently, solution B is transferred to a 100 ml Teflon-lined stainless-steel autoclave and heated for 3 hours in a 200 ℃ oven. After naturally cooling to room temperature, centrifugal washing is performed for multiple times, and samples are obtained after drying.

1.3 Characterization

The X-ray diffraction (XRD) information of samples was obtained by a Rigaku Ultima IV X-ray diffractometer (Japan) with Cu Kα radiation (λ=0.15418 nm, 40 kV, and 40 mA) under the 2θ ranging from 10 to 80°. The structures and morphologies of the samples were obtained by scanning electron microscopy (SEM, Regulus 8100, Japan) and transmission electron microscopy (TEM, JEM-2100F, Japan) with energy-dispersive X-ray (EDX, Oxford INCA x-act). The surface composition information of the samples was measured by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA) at room temperature. The UV-visible diffuse reflectance spectroscopy (UV-vis DRS) was measured by a Hitachi U4100 UV-Vis spectrometer (Japan). $BaSO_4$ was used as the reflectance standard sample. Electron paramagnetic

resonance (EPR) signals were recorded with a BRUKER EMXplus EPR spectrometer at room temperature with or without visible light irradiation using DMPO for the detection of superoxide ($\cdot O_2^-$) active species, and TEMPO for the detection of the hole (h^+). The photoluminescence spectroscopy was measured by fluorescence spectrometer (Edinburgh FLS1000).

1.4 Photocatalytic production of HClO

In this experiment, 0.5 M NaCl solution was used to simulate seawater, The photocatalytic HClO production performance of $MnWO_4$ was studied by using 0.5 M NaCl solution and natural seawater from Huiquan Bay (Qingdao). For convenience, Cl_2 and HClO in this experiment are unified as HClO. Above all, add 50 mL of NaCl solution (natural seawater) and 150 mg of photocatalyst to a quartz bottle. Then introduce air into the quartz bottle at a flow rate of 50 mL/min with no light, and continue stirring for 30 minutes to stabilize the concentration of dissolved oxygen in the solution to achieve equilibrium. Subsequently, it was irradiated with a 5 W white LED lamp (380-780 nm, PCX50C Discover, China Limited). After 1 hour of illumination, take 2 mL of the upper layer solution and measure the HClO concentration (C_{HClO}) using the DPD method[2]. Due to the conversion of the DPD reagent (China Limited) to the oxidized form of HClO, the concentration of HClO was measured using a Hitachi U2900 UV-Vis spectrophotometer (Japan) at a maximum absorption wavelength of 552 nm, and C_{HClO} was calculated according to Eq. 1.

$$C_{HClO} = Abs_{552} \div \left(2.1 \times 10^4\right) \times 10^6 \ \mu M \quad (1)$$

where Abs_{552} is the absorbance at 552 nm. Obtain the effective chlorine concentration (C_{Cl}) in the solution from the calibration curve which has reported on previous work[2].

The recycling experiment involves pouring out the supernatant after centrifugation and adding 0.5 M NaCl (natural seawater) again to repeat the above experimental steps.

1.5 Photoelectrochemical measurement

Photoelectrochemical (PEC) tests were performed on a CHI760C electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). All PEC performance tests were carried out in a three-electrode system. The electrolyte is Na_2SO_4 aqueous

solution (0.2 M), and the light source is a 300 W Xe lamp. The three-electrode system includes a reference electrode (Ag/AgCl electrode), a platinum electrode and a working electrode ($MnWO_4$/FTO photoelectrode). $MnWO_4$/FTO photoelectrode was prepared by drop coating method. Photocatalyst solution was prepared with polyvinylidene fluoride as electrode binder, methyl pyrrolidone as dispersant and $MnWO_4$ as photocatalyst. Before coating $MnWO_4$ photocatalyst, FTO glass was repeatedly treated in ultrapure water, ethanol, and acetone, respectively. Subsequently, take 200 μL solution coated on FTO (1 cm × 1 cm). Then dry at 80 ℃ for 1 hour. Repeat four times to increase the thickness of the FTO surface coated $MnWO_4$.

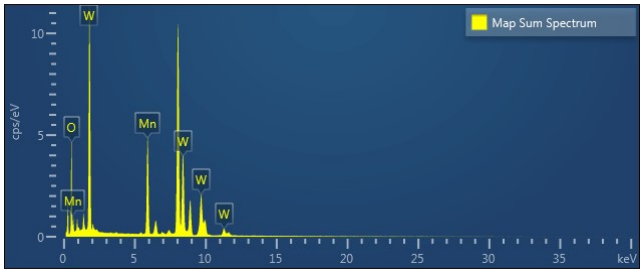

Fig. S1. The EDS spectrum of $MnWO_4$

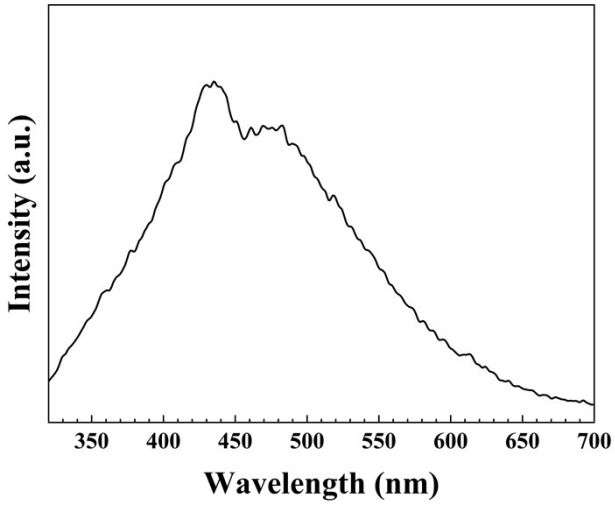

Fig. S2 Photoluminescence spectrum of $MnWO_4$

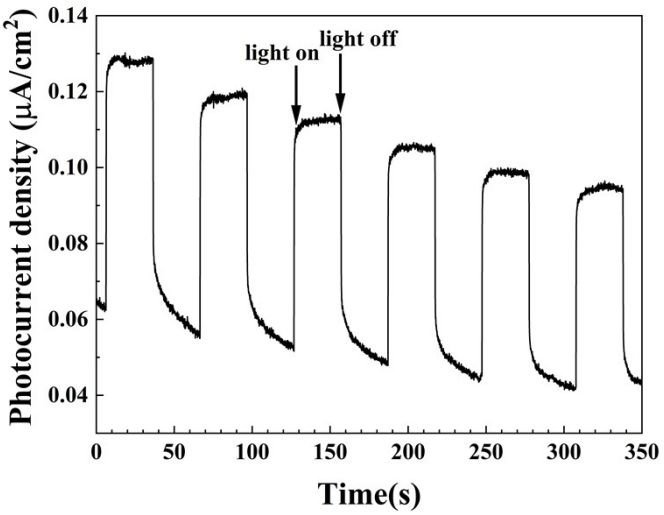

Fig. S3 Transient photocurrent response of $MnWO_4$

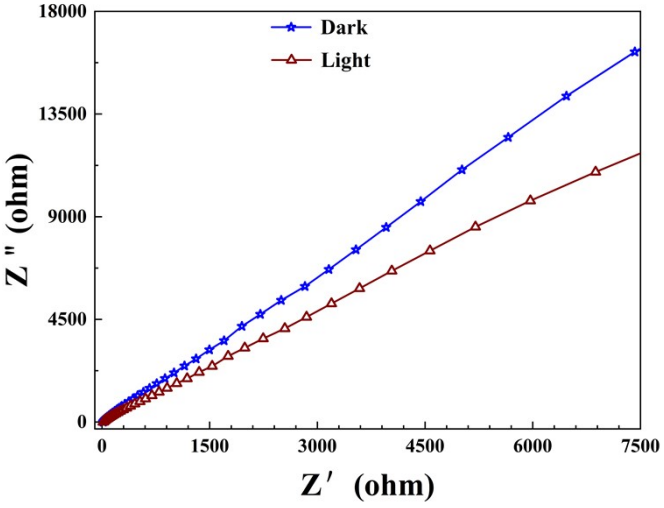

Fig. S4 EIS Nyquist plots of $MnWO_4$

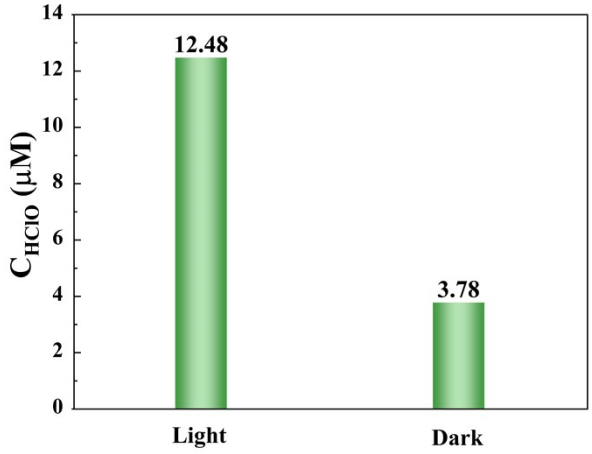

Fig. S5 HClO production of 3 mg/mL $MnWO_4$ under dark and light

References

1. Y. Wang, L. Yang, Y. Wang, X. Wang and G. Han, *Ceramics International*, 2014, **40**, 5085-5090.
2. Q. Lu, Y. Wang, D. Zhang and H. Cong, *Research on Chemical Intermediates*, 2022, **48**, 29-47.