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# **Electronic Supplementary Information**

# Decoupled alkaline water electrolysis by $K_{0.5}MnO_2$ -Ti mediator via K-ion insertion/extraction

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# **Experimental section**

#### Synthesis and characterization of KMO-Ti

KMO-Ti was prepared via a simple gel-sol process using potassium carbonate and manganese acetate as the potassium and manganese sources, respectively. Typically, 2.25 g of manganese acetate, 0.97 g of potassium carbonate, and 1.92 g of citric acid were dispersed in deionized water, followed by adding different amounts of tetrabutyl titanate. After stirring for 60 min, the transparent solution was stirred at 80 °C to obtain dried gel. The resulting precursor was preheated at 450 °C for 5 h and then calcined at 900 °C for 12 h with the heating rate of 5 °C min<sup>-1</sup>. After heat treatment, the oven was switched off and the sample was cooled down naturally. The whole process was performed in air. For comparison, according to the mass fractions of Ti in the KMO-Ti, samples were marked as KMO-1%Ti, KMO-3%Ti and KMO-5%Ti (the KMO-Ti mentioned in the main text had a Ti concentration of 3 wt%). At the same time, the sample without Ti doping (KMO) was prepared under the same conditions as above without adding tetrabutyl titanate.

Crystal structures and phase composition of the samples were determined using a powder X-ray diffractometer (X'Pert PRO MPD, PANalytical, the Netherlands) with  $(\theta/2\theta)$  Bragg–Brentano geometry. The element concentrations of the samples were measured by an X-ray fluorescence spectrometer (S4PIONEER, the Germany). X-ray photoelectron spectroscopy (XPS) data could be measured by a Kratos Axis-Ultra DLD instrument with a monochromatized Al K $\alpha$  line source (150 W). The binding energies were calibrated to the adventitious C 1s peak at 284.8 eV. The scanning electron

microscope (SEM) and elemental mapping analysis were performed by a JEOL JSM-7800F miscroscope attached with an OXFORD INCA EDS detector.

## Preparation and electrochemical test of the electrode

The KMO-Ti electrode was prepared according to the following steps: a mixture of 85 wt% KMO-Ti, 7.5 wt% acetylene black, and 7.5 wt% polytetrafluoroethylene was thoroughly mixed to form a film, which was pressed onto a titanium mesh that served as a current collector surface. Among them, acetylene black can enhance the conductivity of the mediator electrode, and polytetrafluoroethylene as a binder can avoid the KMO-Ti catalysts fall off from the titanium mesh during electrochemical measurements. The KMO-Ti electrode was characterized by CV and galvanostatic charge-discharge tests. The electrolyte was 1 M KOH solution. The aforementioned experiments were performed with a typical three-electrode method, in which a Pt plate and a Hg/HgO electrode were used as the counter and reference electrodes, respectively.

# Fabrication of the electrolytic cell

The cell was constructed with a commercial Pt coated Ti mesh electrode for the HER, a commercial RuO<sub>2</sub>/IrO<sub>2</sub> coated Ti mesh electrode for the OER, and a KMO-Ti electrode as the redox mediator. The KMO-Ti electrode  $(1.5 \times 2 \text{ cm}^2)$  was located between the HER electrode  $(1.5 \times 2 \text{ cm}^2)$  and the OER electrode  $(1.5 \times 2 \text{ cm}^2)$ . In Step 1, the KMO-Ti electrode and HER electrode were employed as the anode and cathode, respectively. Subsequently, In Step 2, the KMO-Ti electrode and OER electrode were employed as the cathode and anode, respectively. The voltages (versus time) of Step 1 and 2 were recorded to characterize the electrolysis profile. With an additional reference electrode (Hg/HgO electrode), the chronopotentiometry data (potential versus time) of a single electrode were also recorded during Step 1 and 2.



Fig. S1 CV curve of the KMO-Ti electrode at different scan rates in 1 M KOH.



Fig. S2 Relationship of anodic peak current versus scan rate (red line) and cathodic peak current versus scan rate (black line).



**Fig. S3** Rate performances of (a) KMO, (b) KMO-1%Ti, (c) KMO-3%Ti, and (d) KMO-5%Ti for selected current densities in 1 M KOH aqueous solution.



Fig. S4 Photograph of the decoupled water electrolysis cell.



**Fig. S5** Chronopotentiometry curve of the direct water electrolysis at a current of 5 mA with a step time of 600 s.



**Fig. S6** Cell voltages for the decoupled HER and OER of KMO-Ti at different currents. The mass loading of KMO-Ti is 30 mg cm<sup>-2</sup>.



**Fig. S7** Cell voltages for the decoupled HER and OER of KMO-Ti at (a) 10 mA, (b) 20 mA, (c) 50 mA, and (d) 100 mA. The mass loading of KMO-Ti is 30 mg cm<sup>-2</sup>.



**Fig. S8** (a) Cell voltages for the decoupled HER and OER using KMO-Ti mediator (the mass loading of KMO-Ti is 60 mg cm<sup>-2</sup>) at 200 mA. (b) Chronopotentiometry curve of the one-step water electrolysis at a current of 200 mA with a step time of 100 s.



Fig. S9 Stability performance of the separate  $H_2/O_2$  generation at a current of 100 mA with a step time of 100 s. The mass loading of KMO-Ti is 30 mg cm<sup>-2</sup>.



Fig. S10 Gas chromatography data for (a) HER and (b) OER.

Redox mediator	Electrolyte	Redox Mechanism	Specific capacity	Gas	Step voltage at 10 mA	Ref.
K <sub>0.5</sub> MnO <sub>2</sub> -Ti	1 M KOH	K <sup>+</sup> intercalation/de-	100 mAh $g^{-1}$	$H_2/O_2$	1.08 V for HER;	This
Ni(OH) <sub>2</sub> /NiOOH	1 М КОН	Proton insertion	at 0.1 A $g^{-1}$ 210 mAh $g^{-1}$ at 0.2 A $g^{-1}$	$H_2/O_2$	1.6 V for OER; 0.4 V for HER	1
NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	1 M NaOH	Na <sup>+</sup> intercalation/de- intercalation	103 mAh g <sup>-1</sup> at 0.5 C	$H_2/O_2$	(200 mA) 1.23 V for OER; 0.34 V for HER	2
Na <sub>0.44</sub> MnO <sub>2</sub>	1 M NaOH and saturated NaCl	Na <sup>+</sup> intercalation/de- intercalation	48 mAh g <sup>-1</sup> at 0.1 A g <sup>-1</sup>	H <sub>2</sub> /Cl <sub>2</sub>	1.3 V for HER; 1.07 V for	3
Active carbon	1 M NaOH	double layer	1.1 F cm <sup>-2</sup> at 1 mA cm <sup>-2</sup>	$H_2/O_2$	2.54 V for HER; 2.43 V for OER	4
Co <sub>2</sub> P/CoP NAs	1 М КОН	$\mathrm{Co}^{2+} \rightarrow \mathrm{Co}^{3+}$	12.95 F cm <sup>-1</sup> at 5 mA cm <sup>-2</sup>	$H_2/O_2$	(1 A) 1.45 V for HER; 0.25 V for OER	5
Mn doped Ni <sub>2</sub> P	1 М КОН	$Ni^{2+}  ightarrow Ni^{3+}$	5.95 F cm <sup>-1</sup> at 5 A g <sup>-1</sup>	$H_2/O_2$	1.6 V for HER; 0.17 V for OER	6

 Table S1 Performance comparison of recently reported redox mediators for decoupled

 alkaline water electrolysis.

\* represents the chlorine evolution reaction (CER).

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