Electronic Supplementary Information (ESI)

Remarkably Enhanced Ion-Exchange Capacity of H_2O_2-Intercalated Layered Titanate

Experimental

The starting material of the layered titanate $H_{1.07}Ti_{1.73}O_4 \cdot H_2O$ (HTO) with platelike morphology was prepared using the method described in the literature[1]. 0.5g of HTO were put in 100 mL of 30 wt% H_2O_2 solution and stirred for 10 min at room temperature, and then were filtered, washed with distilled water to obtain the H_2O_2-treated HTO (named as H_2O_2-HTO). H_2O_2-HTO was treated in a 0.3 100mL $M(CH_3COO)_2$ (M=Co, Ni, Cu and Zn) solution for different stirring times at room temperature. After the treatment, the M^{2+}-ion-exchanged samples were filtered, washed with large amount of distilled water to remove the excess of ions on the surface of samples by physic adsorption, and dried at room temperature (named as M-H_2O_2-HTO). In comparison, HTO was also treated in the $M(CH_3COO)_2$ (M=Co, Ni, Cu and Zn) solution under the same conditions and obtained sample is named as M-HTO.

Rapid ion exchange experiments

0.5g of H_2O_2-HTO was treated in 0.3 mol/L 100mL $M(CH_3COO)_2$ (M=Co, Ni, Cu, Zn) solution respectively under constant stirring at ambient temperature for 40 min, and the solution was replaced after 10 min of reaction to ensure complete ion exchange. The samples were filtered, washed with large amount of distilled water to remove the excess of ions by physic adsorption and dried in air to obtain M ion-exchanged H_2O_2-HTO products.

Characterization

The crystal structure of the sample was investigated using a powder X-ray diffractometer (XRD, Rigaku D/max-2200PC) with Cu Ka (λ=0.15418 nm) radiation. The size and morphology of the samples were observed using a field-emission scanning electron microscope (Hitachi, FE-SEM, S-4800). Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) were performed on a Tecnai G2F20STWIN system at 200 kV, and the powder sample was supported on a microgrid. X-ray fluorescence (XRF, Horiba XGT-7200) was conducted to analyze the elements

distribution of samples. X-ray photoelectron spectroscopy (XPS) measurements were carried out by an Axis Ultra XPS instrument with an Al Ka X-ray source, and the spectra were calibrated to the C 1s peak at 284.6 eV. The Fourier transform infrared (FT-IR) spectra were measured in Bruker infrared spectrometer (VERTE70) with the KBr disk technique. Electron spin resonance (ESR, Bruker A300-9.5/12) spectra were tested to observe the single-electron in the samples.

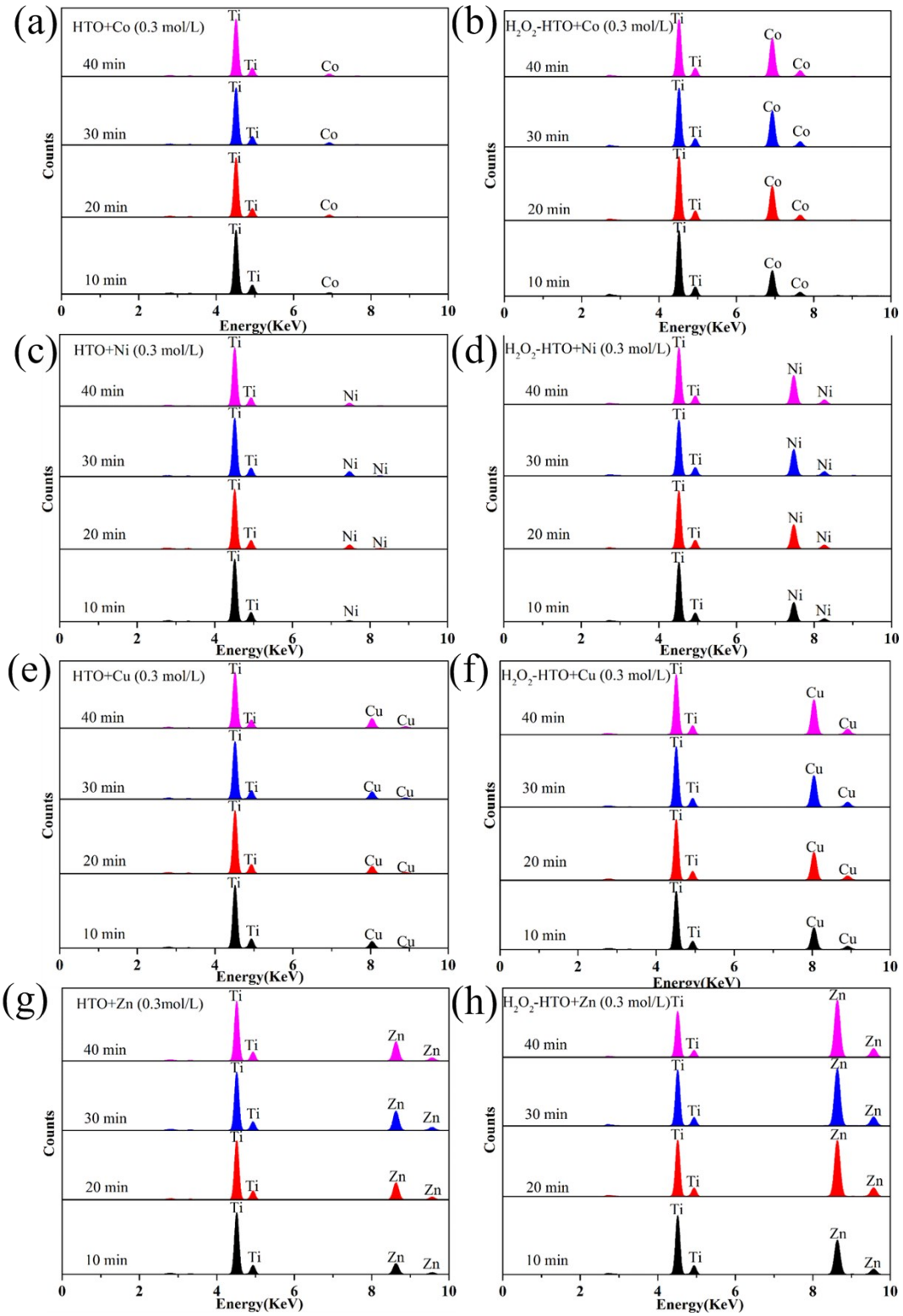

Fig. S1 XRF spectra of products obtained by ion-exchange treatments of (a, c, e, g) HTO and (b, d, f, h) H_2O_2-HTO with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} (0.3mol/L) within 40 min.

Table S1 The change of pH and M^{2+} content (M/Ti) before and after ion exchange treatment within 40 min.

Ions	Exchange time	HTO pH		HTO M/Ti(At%)	H_2O_2-HTO pH		H_2O_2-HTO M/Ti(At%)
		Before	After		Before	After	
Co^{2+}	10min	7.87	7.34	0.033:1.73	7.87	6.38	0.55:1.73
	20min	7.87	7.51	0.053:1.73	7.87	6.85	0.74:1.73
	30min	7.87	7.57	0.064:1.73	7.87	7.15	0.83:1.73
	40min	7.87	7.65	0.068:1.73	7.87	7.44	0.91:1.73
Ni^{2+}	10min	7.73	7.51	0.022:1.73	7.73	6.77	0.39:1.73
	20min	7.73	7.59	0.088:1.73	7.73	7.47	0.49:1.73
	30min	7.73	7.62	0.104:1.73	7.73	7.47	0.56:1.73
	40min	7.73	7.56	0.064:1.73	7.73	7.58	0.59:1.73
Cu^{2+}	10min	5.80	5.78	0.105:1.73	5.80	5.72	0.36:1.73
	20min	5.80	5.80	0.114:1.73	5.80	5.81	0.42:1.73
	30min	5.80	5.83	0.122:1.73	5.80	5.00	0.48:1.73
	40min	5.80	5.76	0.168:1.73	5.80	5.83	0.53:1.73
Zn^{2+}	10min	6.97	6.86	0.145:1.73	6.97	6.48	0.46:1.73
	20min	6.97	6.95	0.235:1.73	6.97	5.79	0.75:1.73
	30min	6.97	6.96	0.268:1.73	6.97	6.89	0.78:1.73
	40min	6.97	7.01	0.257:1.73	6.97	6.99	0.93:1.73

Table S2 The change of pH and M^{2+} content (M/Ti) before and after ion exchange treatment for 48h.

Ions	**HTO**			**H_2O_2-HTO**		
	pH		M/Ti(At%)	pH		M/Ti(At%)
	Before	After		Before	After	
Co^{2+}	7.87	7.50	0.18:1.73	7.87	5.67	1.07:1.73

Ni^{2+}	7.73	7.66	0.08:1.73	7.73	6.77	0.61:1.73
Cu^{2+}	5.80	5.98	0.24:1.73	5.80	6.13	0.64:1.73
Zn^{2+}	6.97	6.75	0.51:1.73	6.97	5.92	1.07:1.73
Mn^{2+}	6.80	5.88	0.31:1.73	6.80	5.28	0.97:1.73
Ca^{2+}	6.35	5.74	0.17:1.73	6.35	5.43	0.21:1.73
Mg^{2+}	8.49	6.58	0.26:1.73	8.49	6.40	0.48:1.73
Ba^{2+}	7.50	5.98	0.03:1.73	7.50	6.13	0.04:1.73
Sr^{2+}	8.06	6.55	0.124:1.73	8.06	6.93	0.305:1.73
Cd^{2+}	6.23	5.54	0.25:1.73	6.23	5.45	0.12:1.73
Cr^{3+}	3.90	3.38	0.01:1.73	3.90	3.68	0.04:1.73

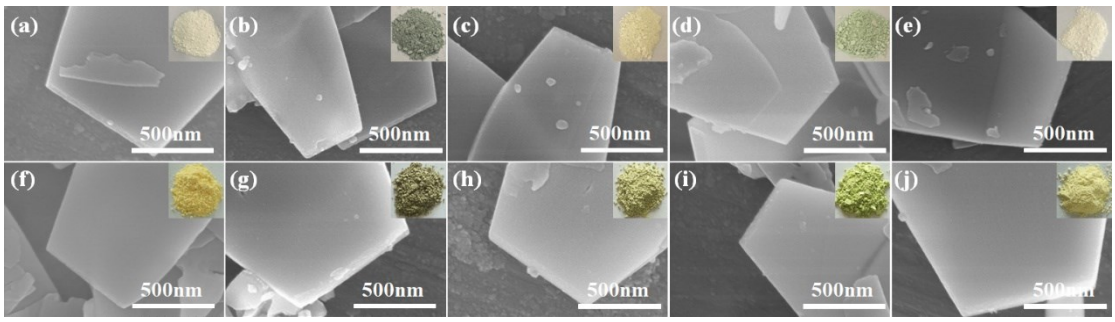

Fig. S2 SEM images and optical photos of (a) HTO, (b) Co-HTO, (c) Ni-HTO, (d) Cu-HTO, (e) Zn-HTO, (f) H_2O_2-HTO, (g) Co-H_2O_2-HTO, (h) Ni-H_2O_2-HTO, (i) Cu-H_2O_2-HTO and (j) Zn-H_2O_2-HTO.

Table S3 Zeta potential of HTO before and after the H_2O_2 treatment.

Sample	Zeta potential (mV)
HTO	-581 mV (ethanol system)
	-26.3 mV (water system)
H_2O_2-HTO	$-3.31X10^4$ mV (ethanol system)
	-41.9 (water system)

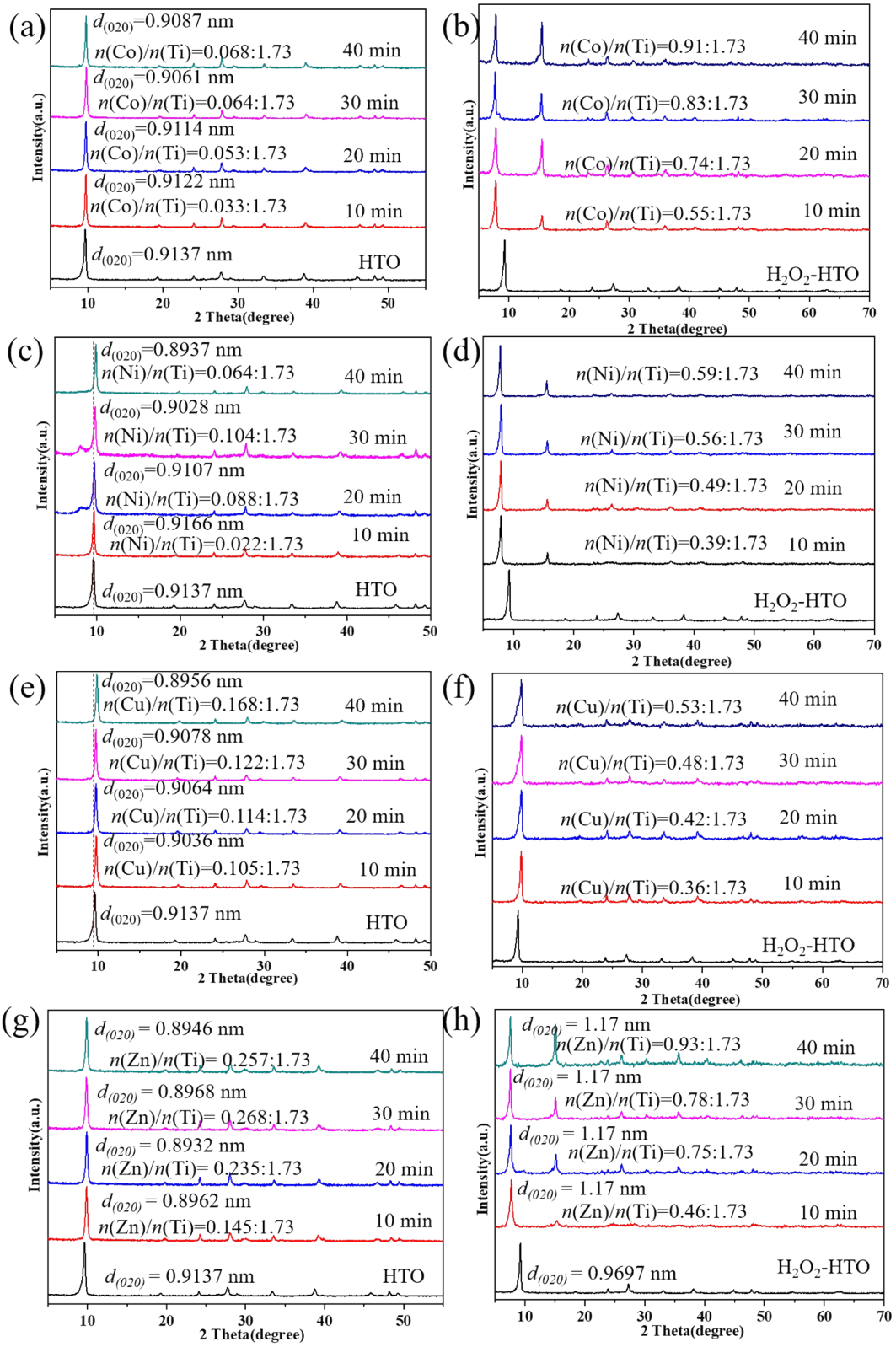

Fig. S3 XRD patterns of products obtained by ion-exchange treatments of (a, c, e, g) HTO and (b, d, f, h) H_2O_2-HTO with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} within 40 min.

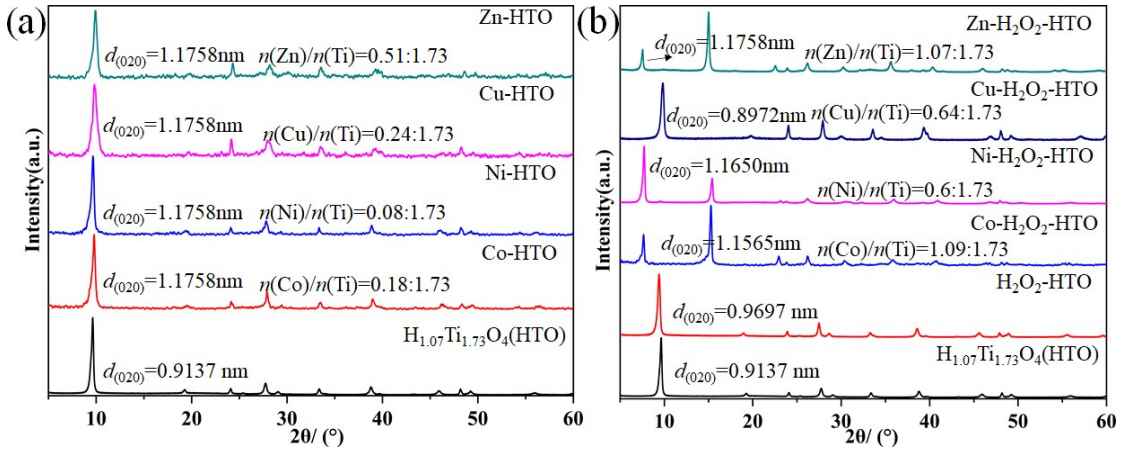

Fig. S4 XRD patterns of products obtained by ion-exchange treatments of (a) HTO and (b) H_2O_2-HTO with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} for 48h.

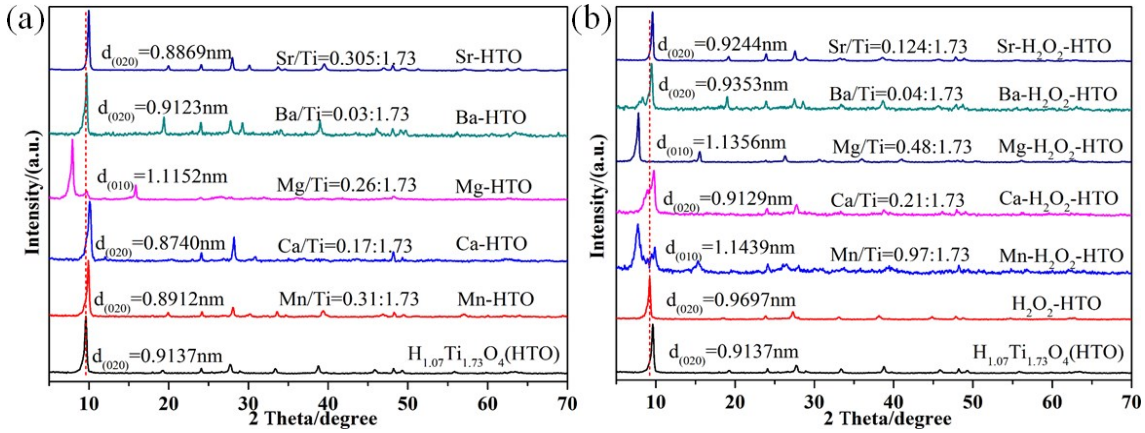

Fig. S5 XRD patterns of products obtained by ion-exchange treatments of HTO (a) and H_2O_2-HTO (b) with Mn^{2+}, Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+} for 48h

Table S4 Refined structural parameters of HTO and H_2O_2-HTO before and after ion-exchanged-treatments.

Sample	Crystal system	a (Å)	b (Å)	c (Å)	Space group	Rp (%)	Rwp (%)
HTO	orthorhombic	3.78335	18.3246	3.00172	Ima2	8.76	8.72
H_2O_2-HTO	orthorhombic	3.79939	18.6295	2.98932	Ima2	6.00	5.97
Zn-HTO	orthorhombic	3.75781	17.9772	7.11390	Ima2	8.29	8.32
Zn-H_2O_2-HTO	orthorhombic	3.77615	23.7187	2.97914	Ima2	5.45	6.08

Co-H_2O_2-HTO	orthorhombic	3.78593	23.2067	2.98551	Ima2	9.58	9.80
Ni-H_2O_2-HTO	orthorhombic	3.80627	23.1777	2.98154	Ima2	7.62	7.53
Cu-H_2O_2-HTO	orthorhombic	3.78562	17.8442	2.98609	Ima2	9.77	6.54

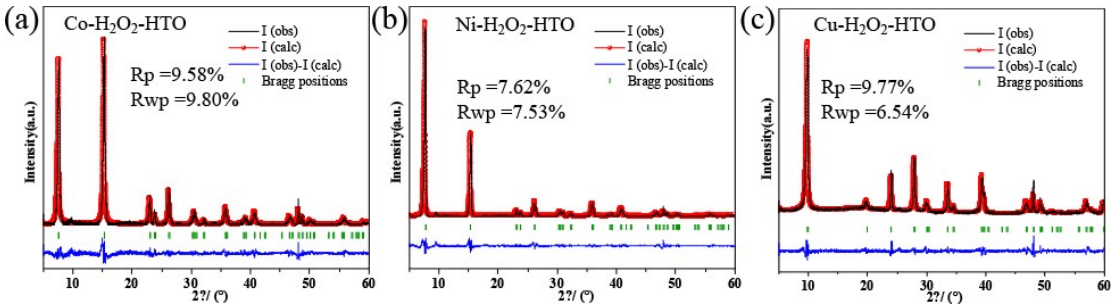

Fig. S6 Experimental XRD patterns (solid lines) and refinement fitting patterns (red line) of (a) Co-H_2O_2-HTO, Ni-(b) H_2O_2-HTO and (c) Cu-H_2O_2-HTO.

Measurement of H_2O_2 content in H_2O_2-HTO by XPS

XPS was employed to further confirm the existence of O-O bond before and after ion exchange, as shown in Fig. S7, where the binding energies were calibrated for specimens charging by referencing the C 1s to 284.60 eV. It is found that no peaks of other elements except C, O, Zn along with Ti were observed in the survey spectra (Fig. S7(A-a)). HTO shows two peaks in the O1s spectrum (Fig. S7(B-a)). The peak at 529.91 eV is assigned to the O1s of Ti-O bond in TiO_6 octahedral layer and the peak located at 530.93 eV to the O1s of interlayer H_2O. After H_2O_2 treatment, the XPS spectrum shows three peaks in the O1s spectrum (Fig. S7(B-b)). Except peaks of Ti-O bond and interlayer H_2O, a O1s peak of -O-O- bond located at 531.90 eV was observed in H_2O_2-HTO.[2] The results suggest H_2O_2 was intercalated into HTO after H_2O_2 treatment.

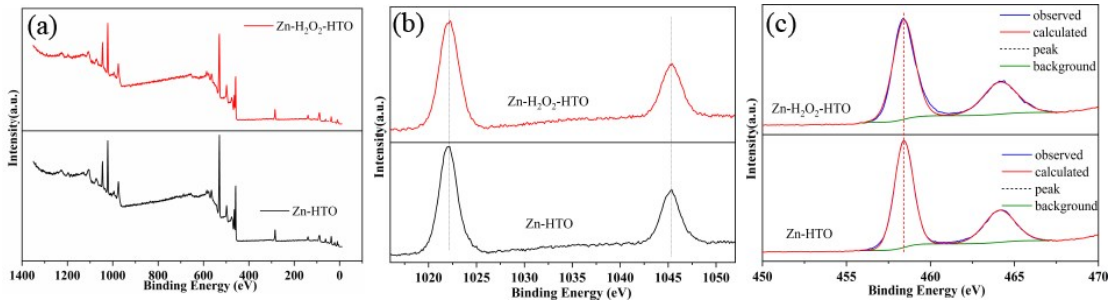

Fig. S7(A) (a) XPS survey spectra, (b) Zn2p, and (c) Ti2p XPS spectra of Zn-HTO and Zn-H_2O_2-HTO

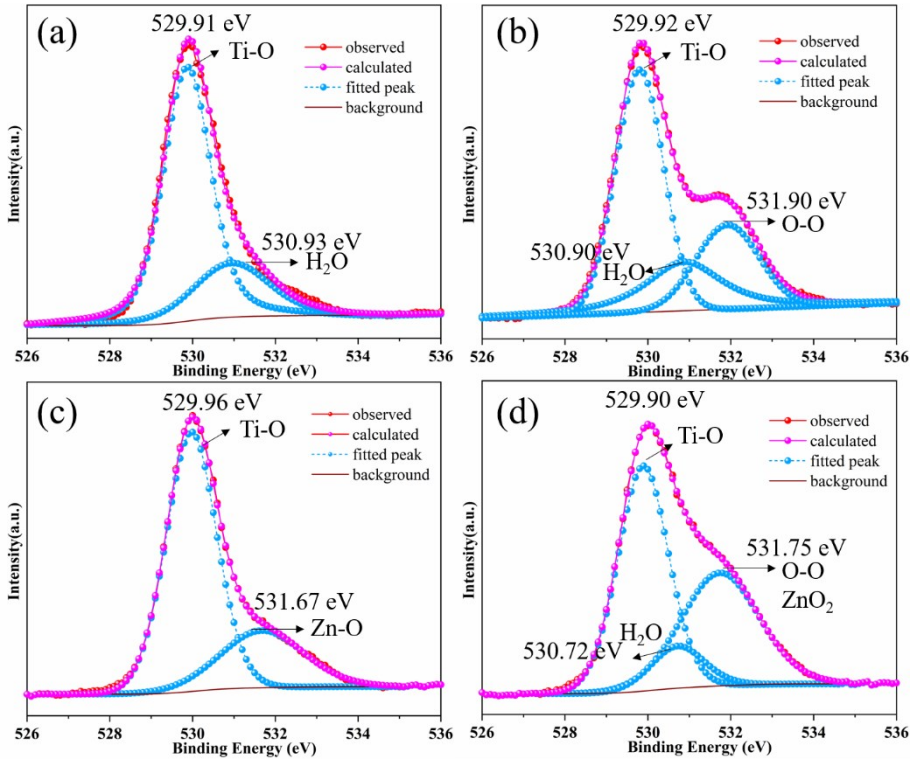

Fig. S7(B) The resolution binding energy spectra of O1s of (a) HTO, (b) H_2O_2-HTO, (c) Zn-HTO and (d) Zn-H_2O_2-HTO.

The O1s spectrum of Zn-HTO can be fitted to two peaks located at 529.96 and 531.67 eV (Fig. 7(B-c)), which correspond to the Ti-O bond in TiO_6 octahedral layer, and Zn-O formed by ion-exchange, respectively. No peak of H_2O is found in Zn-HTO, indicating that the loss of H_2O during H^+/Zn^{2+} ion exchange in HTO. The O1s spectrum of Zn-H_2O_2-HTO can be fitted to three peaks (Fig. 7(B-d)), and the peak at 529.90 eV is attributed to Ti-O bond in TiO_6 octahedral layer while the peak at 531.75 eV corresponds to O-O bond in the interlayer of Zn-H_2O_2-HTO. Besides, a clear peak is observed at 530.72 eV, attributing to the existence of interlayer H_2O. It shows that H_2O molecules

within interlayer still exist before and after H_2O_2-HTO ion exchanging with Zn^{2+}, which differs with Zn-HTO. Zn2p spectra of Zn-HTO and Zn-H_2O_2-HTO are almost the same, and the binding energy appeared at 1022.00 eV indicates the presence of Zn(II) (Fig. S7(A-b)). [3] The peaks located at 458.41 eV and 464.19 eV are assigned to Ti2p 2/3 and Ti2p 1/2, respectively, showing the existence of Ti(IV) (Fig. S7(A-c)). The XPS analysis further confirmed the existence of O-O bond before and after ion exchange treatment, and also suggest that the valence of exchanged cation and Ti in TiO_6 octahedron layer has no change before and after ion exchange.

Based on the XPS analyses, various atom contents (atom %) in H_2O_2-HTO can be evaluated from the peak areas of the XPS spectrum, as shown in Table S5. The chemical formula of H_2O_2-HTO can be expressed as $H_{1.07}Ti_{1.73}O_{3.6}(\text{-O-O-H})_{0.8}\cdot 1.5H_2O$, in which ion-exchangeable H^+ content can be estimated to be about H/Ti=1.87:1.73 by assuming that all H^+ ions in $H_{1.07}Ti_{1.73}O_{3.6}(\text{-O-O-H})_{0.8}$ are ion-exchangeable. Therefore, the theoretical ion-exchange capacity for M^{2+} is about M/Ti=0.94:1.73 that is close to Zn content in Zn-H_2O_2-HTO. Therefore, the theoretical ion-exchange capacity of H2O2-HTO for divalent ions (M/Ti= 0.94:1.73) is much larger than that of HTO (M/Ti=0.54:1.73).

Table S5 The contents of C1s, Ti2p and O1s calculated from XPS spectra of H_2O_2-HTO

Name	Peak BE	FWHM eV	Area (P)	Atomic %
C1s	284.49	1.94	20545.61	19.31
Ti2p	458.47	1.36	99987.27	15.37
O1s of Ti-O	529.92	1.36	102311.1	36.31
O1s of H_2O	531.90	1.64	44099.63	15.66
O1s of -O-O-	530.90	1.16	13042.29	13.34

Table S6 The molar ratios of Zn/Ti in different layered tianates obtained by ion-exchanging treatments with Zn^{2+} for 48 h and theoretical exchange capacities

Sample	Measured exchange capacity (Zn/Ti) for Zn^{2+}	Theoretical exchange capacity (Zn/Ti) for Zn^{2+}
H_2O_2-treated $H_{1.07}Ti_{1.73}O_4$ (H_2O_2-HTO)	0.62	0.62
$H_{1.07}Ti_{1.73}O_4$ (HTO)	0.29	0.31
$H_2Ti_2O_5$	0.27	0.5
$H_2Ti_3O_7$	0.0067	0.33
$H_2Ti_4O_9$	0.16	0.25
$H_2Ti_5O_{11}$	0.19	0.2

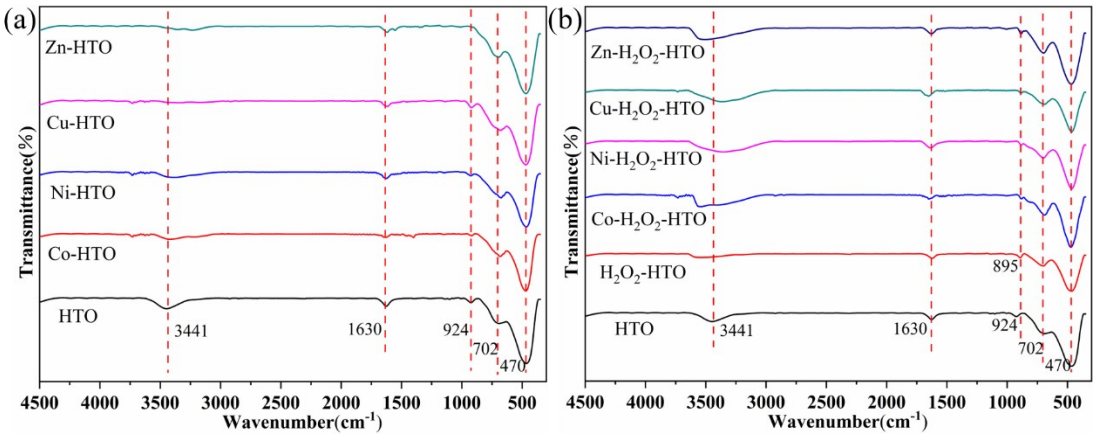

Fig. S8 FT-IR spectra of HTO, H_2O_2-HTO, M-HTO and M-H_2O_2-HTO.

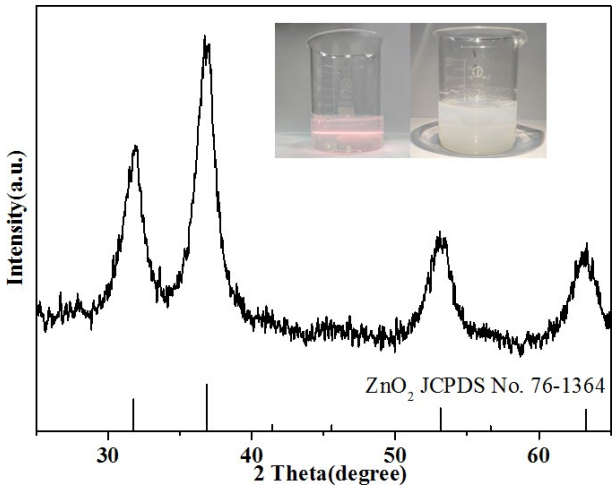

Fig. S9 XRD pattern of product obtained by reaction of H_2O_2 reacting and $Zn(CH_3COO)_2$ solutions and optical photos of solution change before and reaction.

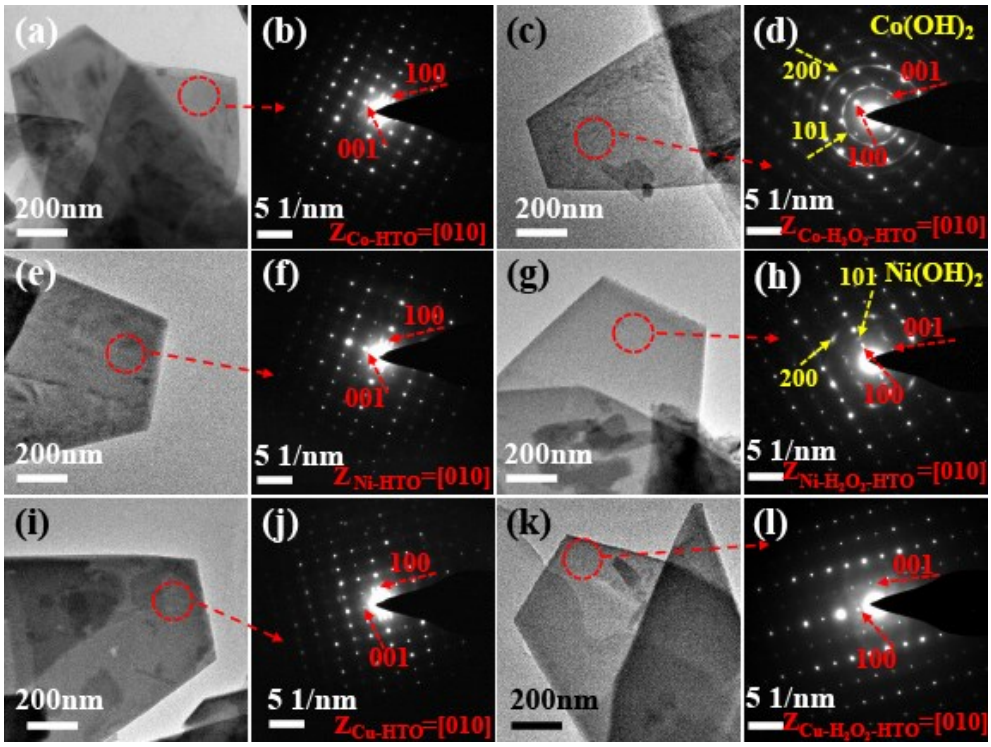

Fig. S10 TEM images and SAED patterns of (a)(b) Co-HTO(c)(d) Ni-HTO (e)(f) Cu-HTO (g)(h) Zn-HO

TEM images show that Co-HTO, Ni-HTO and Cu-HTO possess plate-like morphology with the surface smooth. And they display similar SAED patterns to HTO with [010]-crystal-axis vertical to the basal plane of them. It is surprised that Co-H_2O_2-HTO and Ni-H_2O_2-HTO show one set of diffraction rings with *d*-values of 0.281 and 0.243 nm except for one set of diffraction spots with similar *d*-values to H_2O_2-HTO. The diffraction rings of Co-H_2O_2-HTO and Ni-H_2O_2-HTO can be attributed to $Co(OH)_2$

and $Ni(OH)_2$, respectively. On the contrary, the diffraction rings are not observed in Cu-H_2O_2-HTO, which may be due to without formation of $Cu(OH)_2$.

Notes and references

1. Q. Feng, M. Hirasawa, K. Kajiyoshi and K. Yanagisawa, *Journal of the American Ceramic Society*, 2005, **88**, 1415-1420.

2. X. Kong, C. Zeng, X. Wang, J. Huang, C. Li, J. Fei, J. Li and Q. Feng, *Scientific reports*, 2016, **6**, 1-8.

3. H. Li, C. J. Firby and A. Y. Elezzabi, *Joule*, 2019, **3**, 2268-2278.