## Perovskite Manganese Oxide with Tunable Metal-Oxygen Covalency for Efficient Bisphenol A Degradation

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Text S1. X-ray diffraction (XRD) measurements were performed with a Rigaku Ultima IV (Cu Ka radiation,  $\lambda = 1.5406$  Å) in the range of 20°–90° and at a scanning rate of 1°/min to evaluate phase purity and analyze crystal structure. The corresponding XRD patterns were analyzed by using FullPROF program based on the Rietveld refinement method. X-ray photoelectron spectroscopy (XPS) was used to obtain the surface composition and electronic structure, which were recorded with an ESCALAB 250Xi electron energy spectrometer, using Al Ka (1486.6 eV) as the Xray excitation source. The obtained spectra were corrected by a C 1s line with a binding energy of 284.6 eV and fitted by Avantage software. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was used to observe the micro morphology of materials. The specific surface areas of the catalysts were obtained with a Brunauer-Emmett-Teller (BET) analysis system with a N2 adsorptive medium. The metal ion concentration was analyzed by an inductively coupled plasma emission spectrometer (ICP-OES). The concentration of pollutants is determined by high performance liquid chromatography (HPLC, Agilent 1200) with a C18 reversed phase column (4.6 mm × 150 mm). X-ray absorption spectra (XAS) of O K-edge was performed at the Beamlines MCD-A and MCD-B (Soochow Beamline for Energy Materials) in the NSRL (National Synchrotron Radiation Laboratory), Hefei, China.

**Text S2.** All calculations were performed using the Vienna ab initio simulation package (VASP)[1]. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was utilized to express electron exchange correlation[2], and the projector augmented wave (PAW) method was applied to describe the pseudo-potentials[3]. Dispersion-corrected DFT-D3 schemes were employed to describe possible van der Waals (vdW) interactions[4]. The energy cut-off for the plane-wave basis was set to 450 eV. The Brillouin zone in reciprocal space was sampled using the Monkhorst-Pack scheme with  $1 \times 2 \times 3$  k-point grids for geometry optimization. All structures were fully relaxed until the forces were smaller than 0.02 eV Å<sup>-1</sup>, and the convergence threshold in electronic relaxation was set to

10–5 eV using the conjugate gradient algorithm. The values of the adsorption energies  $(E_{ads})$  were obtained using the following Eq. 2.

## $E_{ads} = E_{BPA-perovskite} - E_{perovskite} - E_{BPA} \qquad (2)$

where  $E_{BPA-perovskite}$  refers to the energy of the system that BPA adsorbed by perovskite substrate,  $E_{perovskite}$  refers to the energy of perovskite substrate, and  $E_{BPA}$  refers to the energy of BPA.



Fig. S1 SEM images of (a) LMO; (b) L0.9MO; (c)LCMO; (d) LSMO; (e) LCKMO.



Fig. S2 TEM(a) and HRTEM(b) images of L0.9MO; TEM(c) and HRTEM(d) images of LSMO.



Fig. S3 HAADF-STEM images and corresponding element analysis of (a) LMO, (b) L0.9MO, (c) LSMO, (d) LCKMO.



**Fig. S4** Specific surface areas of different samples, (a) LMO; (b) L0.9MO; (c) LCMO; (d) LSMO; (e) LCKMO.



Fig. S5 The relationship between peak area and BPA concentration.



Fig. S6 The kinetic fitting results in various systems.



Fig. S7 The XRD profiles of LCMO before and after testing.



Fig. S8 TEM(a), HRTEM(b), HAADF-STEM images and corresponding element analysis (c) of LCMO after testing.



Fig. S9 Mn 2p XPS spectrum of different catalysts.



**Fig. S10** Normalized intensity in pre-edge region of different perovskite manganese oxides.



Fig. S11 Optimized structures of different samples; (a) LMO, (b) L0.9MO, (c) LCMO, (d) LSMO, (e) LCKMO.



Fig. S12 Computed charge deviation of O of different manganese oxides.



**Fig. S13** The adsorption energy of BPA at different sites on the (010) crystal planes of LMO, LCMO, and LCKMO



Fig. S14 Charge differential density of BPA adsorbed on LCMO.



**Fig. S15** BPA removal efficiencies in LCMO systems with the presence of (a) anions; (b) cations; The corresponding kinetic fitting results in (c) LCMO/anions systems; (d) LCMO/cations.



**Fig. S16** BPA removal efficiencies (a) and corresponding kinetic fitting results (b) in different reaction systems at pH=3.61; BPA removal efficiencies (c) and corresponding kinetic fitting results (d) in different reaction systems at pH=4.55; BPA removal efficiencies (e) and corresponding kinetic fitting results (f) in different reaction systems at pH=5.02

	La(NO <sub>3</sub> ) <sub>3</sub> c36H <sub>2</sub> O (g)	Ca(NO <sub>3</sub> ) <sub>2</sub> C34H <sub>2</sub> O (g)	$Sr(NO_3)_2(g)$	KNO <sub>3</sub> (g)	$Mn(NO_3)_2(g)$
LMO	2.165	0	0	0	1.165
L0.9MO	1.949	0	0	0	1.165
LCMO	1.624	0.295	0	0	1.165
LSMO	1.624	0	0.265	0	1.165
LCKMO	1.624	0.236	0	0.025	1.165

Table S1. Detailed dosing amount of precursors for perovskite manganese oxides.

	LMO	L0.9MO	LCMO	LSMO	LCKMO
Space group	Pbnm	Pbnm	Pbnm	Pbnm	Pbnm
Lattice parameters	a= 5.519 Å	a= 5.513 Å	a= 5.474 Å	a= 5.524 Å	a= 5.499 Å
	b= 5.469 Å	b= 5.471 Å	b= 5.459 Å	b= 5.481 Å	b= 5.462 Å
	c= 7.769 Å	c= 7.755 Å	c= 7.730 Å	c= 7.766 Å	c= 7.726 Å
	α=β=γ=90°	α=β=γ=90°	α=β=γ=90°	α=β=γ=90°	α=β=γ=90°
Cell volume	234.49 Å <sup>3</sup>	233.90 Å <sup>3</sup>	230.99 Å <sup>3</sup>	235.13 Å <sup>3</sup>	232.05 Å <sup>3</sup>
Mn-O1(O2)	1.960	1.970	2.013	1.993	1.970
Mn-O3(O4)	1.713	1.747	1.813	1.977	1.920
Mn-O5(O6)	2.203	2.142	2.060	1.929	1.997
Average Mn-O length	1.959	1.953	1.962	1.966	1.962

Table S2. Lattice parameters and structural information of perovskite manganese oxides.

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