Supporting Information

Synergistically enhanced oxygen reduction activity of MnO_x-CeO_2/ketjenblack composite

Jiajie Chen,[a] Nan Zhou,[b] Haiyan Wang,[a,c,*] Zhiguang Peng,[a] Huiyong Li,[b] Yougen Tang[a,*] and Kun Liu[a]

[a] *College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, P.R. China.*

E-mail: wanghy419@126.com; ygtang@csu.edu.cn. Tel.: +86 0731 8830886; fax: +86 0731 8879616.

[b] *College of Science, Hunan Agricultural University, Changsha, 410128, P.R. China.*

[c] *State Key Laboratory for Powder Metallurgy, Central South University, Changsha 410083, China*

Experimental Section

1. Synthesis of CeO_2/KB, MnO_x/KB and MnO_x-CeO_2/KB

Carbon support KB (ketjenbalck carbon, EC-300J) was treated in HNO_3 at 80 °C for 8 h to remove metal impurities and introduce oxygen containing functional groups on the carbon surface. After that, KB was washed with distilled water at least 10 times and then dried in air at 110 °C. CeO_2/KB was prepared by a simple hydrothermal method. Briefly, 1.094 g $Ce(NO_3)_3 \cdot 6H_2O$ was first dissolved into 70 ml distilled water to prepare aqueous $Ce(NO_3)_3$ solution, then 1g acid-treated KB was added into the $Ce(NO_3)_3$ solution. This suspension was stirred for at least 30 min before being transferred into a 100 mL Teflon-lined autoclave and then kept at 160 °C for 8 h. The prepared CeO_2/KB was filtered and dried in air at 110 °C. For MnO_x-CeO_2/KB, 0.1 g CeO_2/KB was added into 20 mL distilled water with continuous stirring. Then 25 mL $KMnO_4$ solution (0.2 wt%) was slowly added into the suspension prepared before. After the mixture was kept at 70°C for 1 h, the suspension was filtered, washed, and dried at 110 °C. For comparison, the MnO_x/KB catalyst was also prepared through the similar procedure as MnO_x-CeO_2/KB using 0.0854 g acid-treated KB instead of 0.1 g CeO_2/KB. All as-prepared samples were heated at 400 °C for 2 h

under flowing Ar.

2. Materials Characterization

X-ray diffraction (XRD) patterns of as-prepared samples were recorded by X-ray diffractometer (Dandong Haoyuan, DX-2700) utilizing a Cu-Kα1 source with a step of 0.02°. Scanning electron microscope (SEM) images of as-prepared MnO_x-CeO_2/KB were conducted using a Nova NanoSEM 230 SEM. Transmission electron microscope (TEM), high resolution TEM (HRTEM) images, scanning TEM (STEM) and elemental mapping of as-prepared MnO_x-CeO_2/KB were obtained using a FEI Tecnai G2 F20 S-TWIX TEM. Thermogravimetric analysis (TGA) was performed on a STA 449C with a heating rate of 10 °C/min from 25 to 800 °C. The XPS fitting was performed using XPSPEAK software. The specific surface area was calculated by using the BET equation from the N_2 adsorption isotherm.

3. Rotating disk electrode (RDE) measurements.

For the RDE measurements, 2 mg catalyst was dissolved in a 1 mL solvent mixture of 50 uL Nafion (5 wt %) and 950 uL ethanol by at least 40 min sonication to form a homogeneous ink. Then 10 uL of the catalyst ink was loaded onto on a glassy carbon rotating disk electrode of 5.61 mm in diameter (Pine Instrument Company, USA), which yielded a loading of catalyst 80.9 ug cm^{-2}. 0.1 M KOH was used as an electrolyte, pure oxygen gas (99.999%) was purged for at least 20 min before each RDE experiment to make the electrolyte saturated with oxygen. Pt wire and saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. All potentials initially measured verse the SCE were calibrated with respect to reversible hydrogen electrode (RHE).[1] The working electrode was scanned cathodically at a rate of 10 mV s^{-1} with varying rotating speed from 400 rpm to 1600 rpm. Koutecky-Levich plots were analyzed at various electrode potentials. The slopes of their linear fit lines are used to calculate the electron transfer number (n) on the basis of the Koutecky-Levich equation:[2]

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K}$$

$$B = 0.62nFC_0D_0^{2/3}\upsilon^{-1/6}$$

For the Tafel plot, the kinetic current was calculated as follows:

$$j_K = \frac{j \times j_L}{j_L - j}$$

Where j is the experimentally measured current density, j_L is the diffusion-limiting current density, j_K is the kinetic current density, ω is the electrode rotating speed in rpm, F is the Faraday constant, C_0 is the bulk concentration of O_2 , D_0 is the diffusion coefficient of O_2, and υ is the kinematic viscosity of the electrolyte. The kinetic mass activity (j_m) was calculated via the normalization of the kinetic current (j_K) with the catalyst mass loading.

Supporting Figures

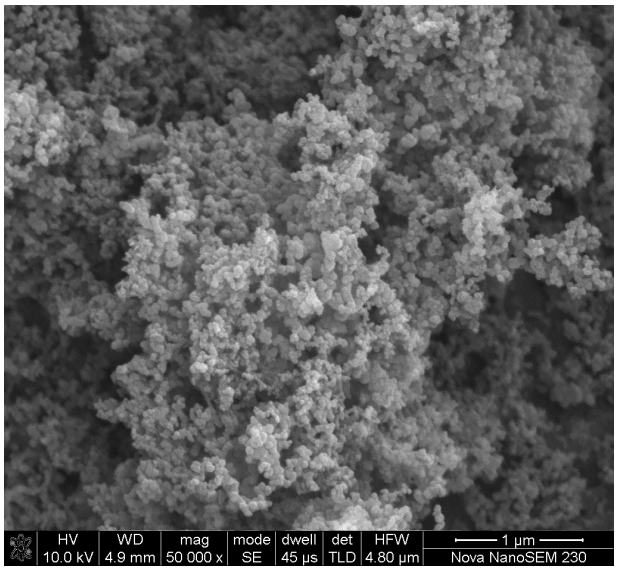

Fig. S1 Typical SEM image of MnO_x-CeO_2/KB hybrid.

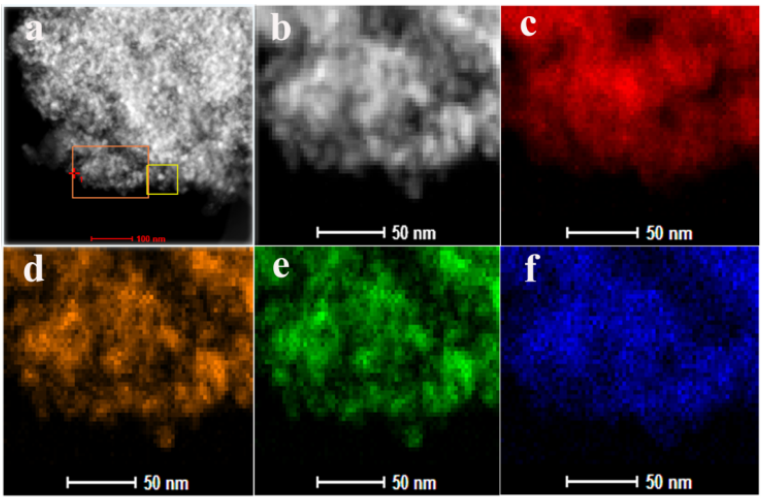

Fig. S2 STEM and elemental mapping analysis of the MnO_x-CeO_2/KB hybrid. (a) Typical STEM image. (b) STEM image taken from the left selected region marked in (a). (c-f) Corresponding elemental mapping images of (c) C, (d) O, (e) Mn, and (f) Ce.

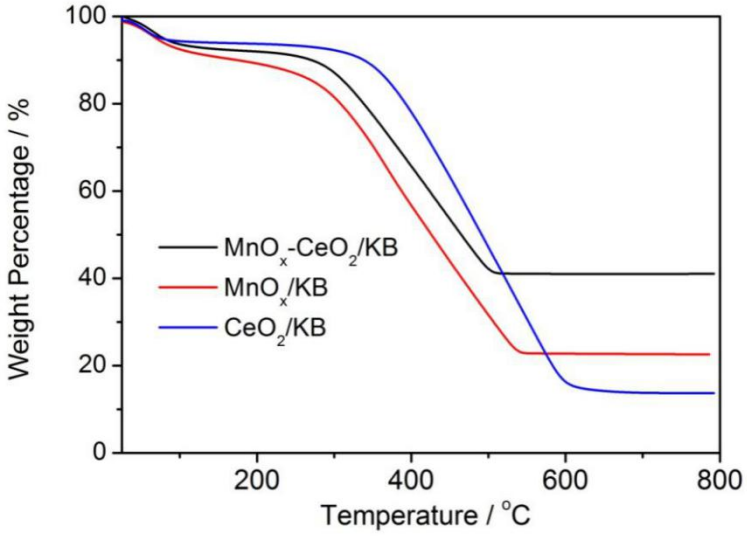

Fig. S3 TGA curves of MnO_x-CeO_2/KB, MnO_x/KB and CeO_2/KB in air.

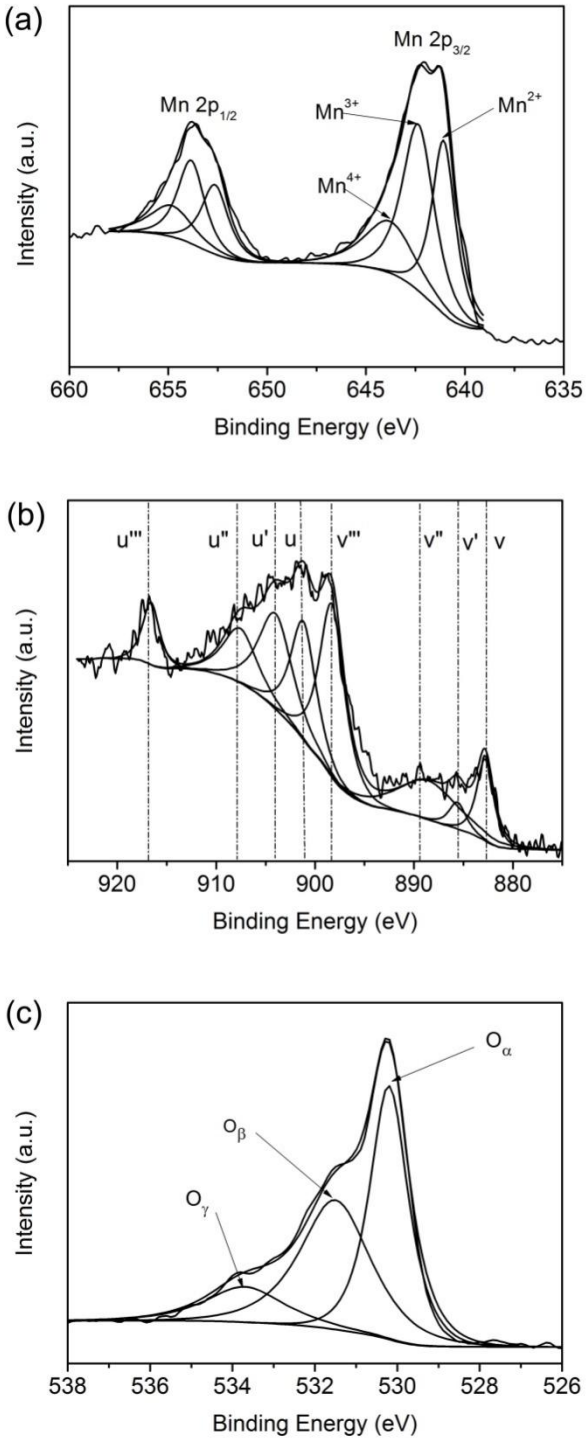

Fig. S4 XPS spectra of Mn 2p (a), Ce 3d (b) and O 1s (c) in the MnO_x-CeO_2/KB hybrid.

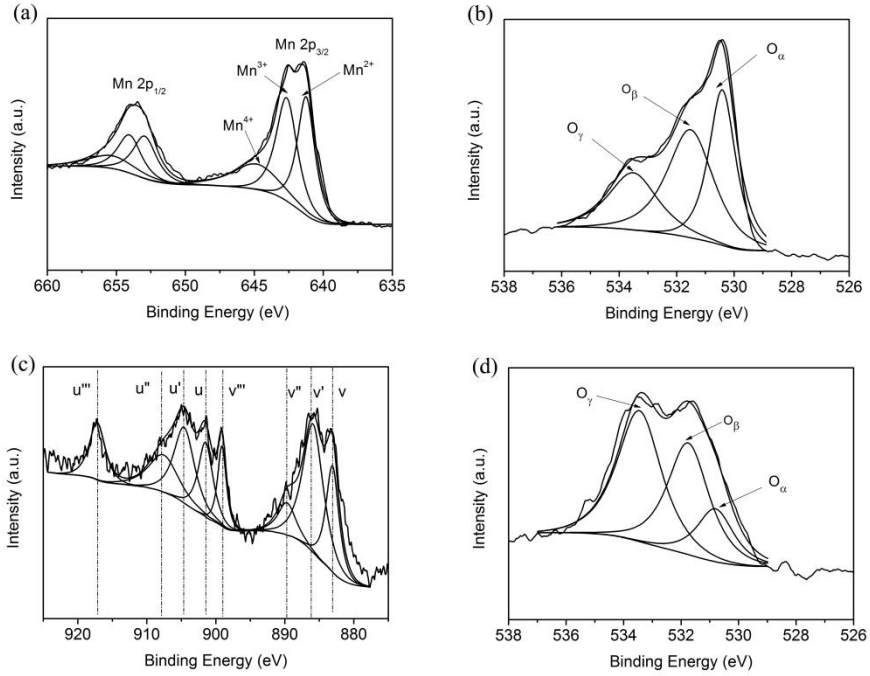

Fig. S5 XPS spectra of Mn 2p (a), O 1s (b) in MnO_x/KB and Ce 3d (c), O 1s (d) in CeO_2/KB.

The Mn 2p and O 1s spectra in MnO_x/KB are similar to those of the MnO_x-CeO_2/KB hybrid. The Ce 3d (c), O 1s (d) in CeO_2/KB are a little different with those of MnO_x-CeO_2/KB hybrid. The peak marked as v' in CeO_2/KB is much stronger than that in MnO_x-CeO_2/KB, indicating that the proportion of Ce^{3+} species in CeO_2/KB is larger than that of MnO_x-CeO_2/KB, which is associated with a larger proportion of defect oxygen ($O_\beta/O_\alpha+O_\beta$). The decrease of Ce^{3+} species and defect oxygen in MnO_x-CeO_2/KB compared with CeO_2/KB may be due to the fact that the MnO_x nanoparticles are located in the vicinity of CeO_2. We can also conclude that the oxygen-containing functional groups decrease when MnO_x deposited on the carbon surface of CeO_2/KB since the peak denoted as O_γ in MnO_x-CeO_2/KB is much weaker than that in CeO_2/KB.

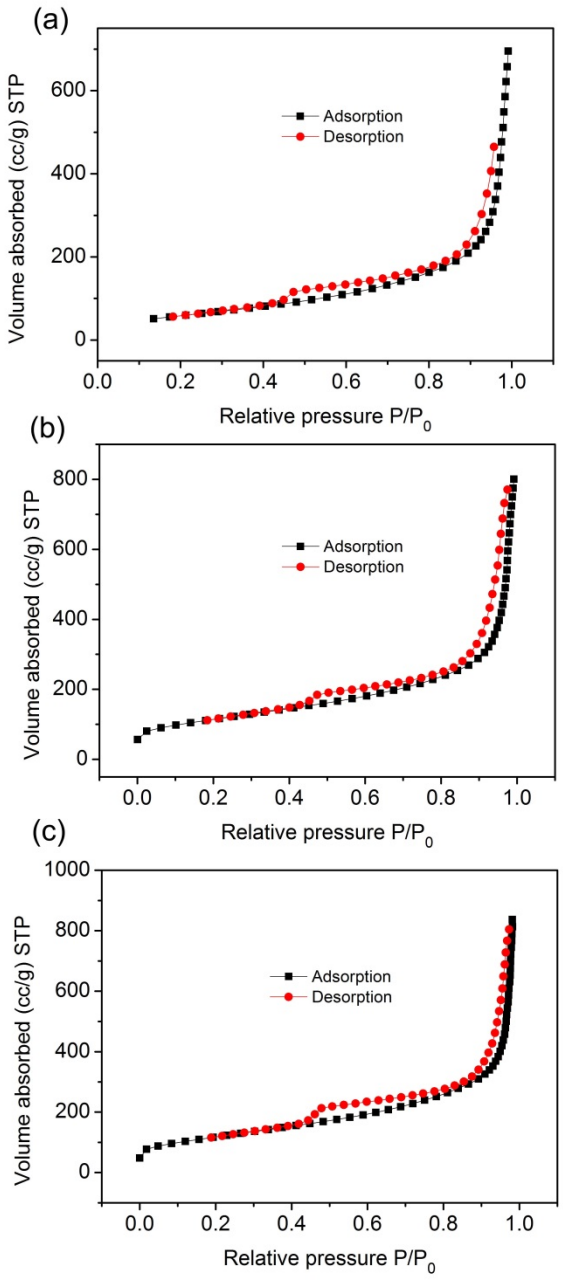

Fig. S6 N_2 adsorption-desorption isotherms of MnO_x-CeO_2/KB (a), MnO_x/KB (b) and CeO_2/KB (c).

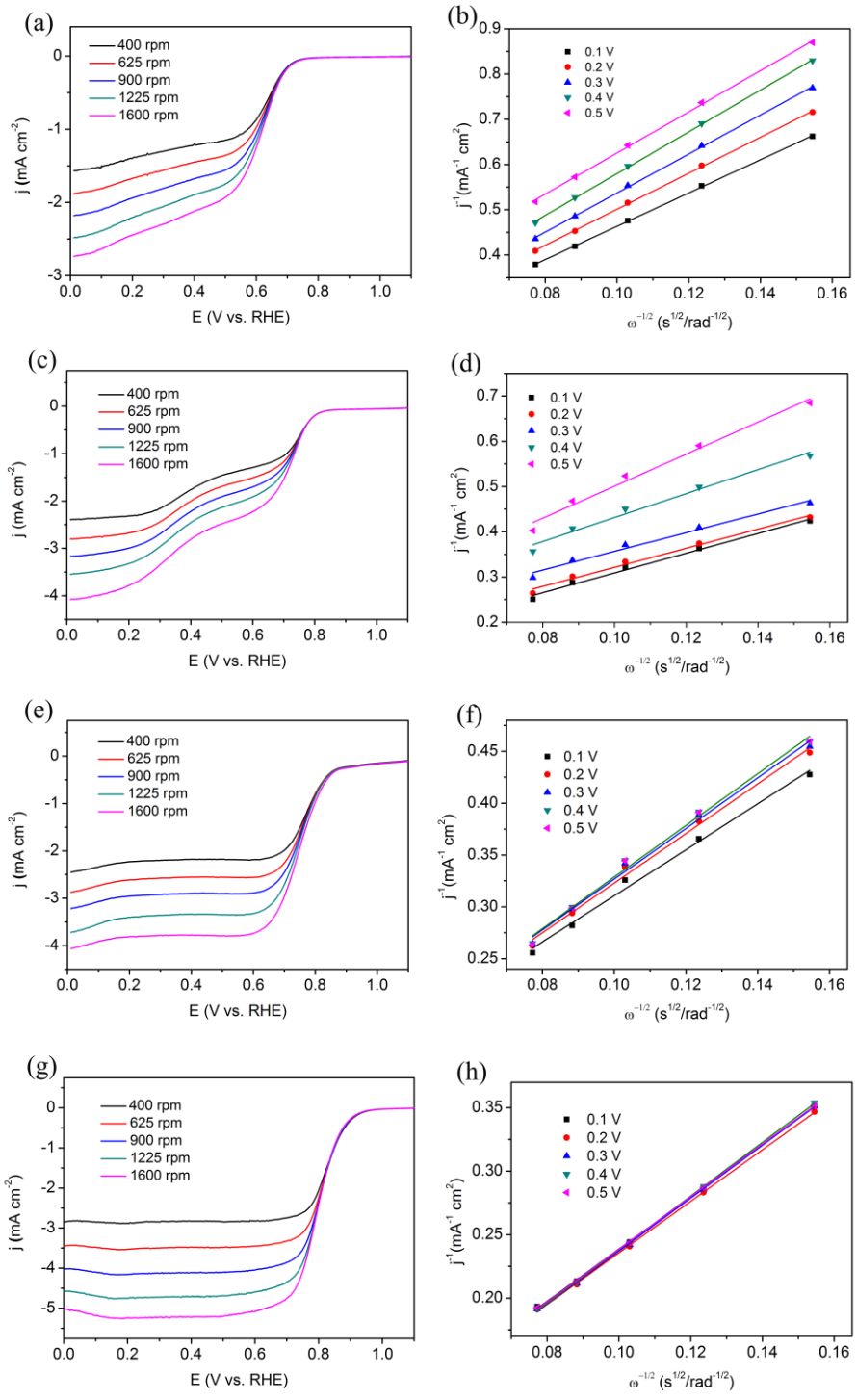

Fig. S7 (a, c, e and g) Detailed LSV curves of KB, CeO_2/KB, MnO_x/KB and Pt/C at different rotating speeds using RDE in O_2 saturated 0.1 M KOH solution with a sweep rate of 10 mV s^{-1}. Catalyst loading was 80.9 ug cm^{-2} for all samples; (b, d, f and h) the calculated Koutecky-Levich plots for KB, CeO_2/KB, MnO_x/KB and Pt/C at different potentials.

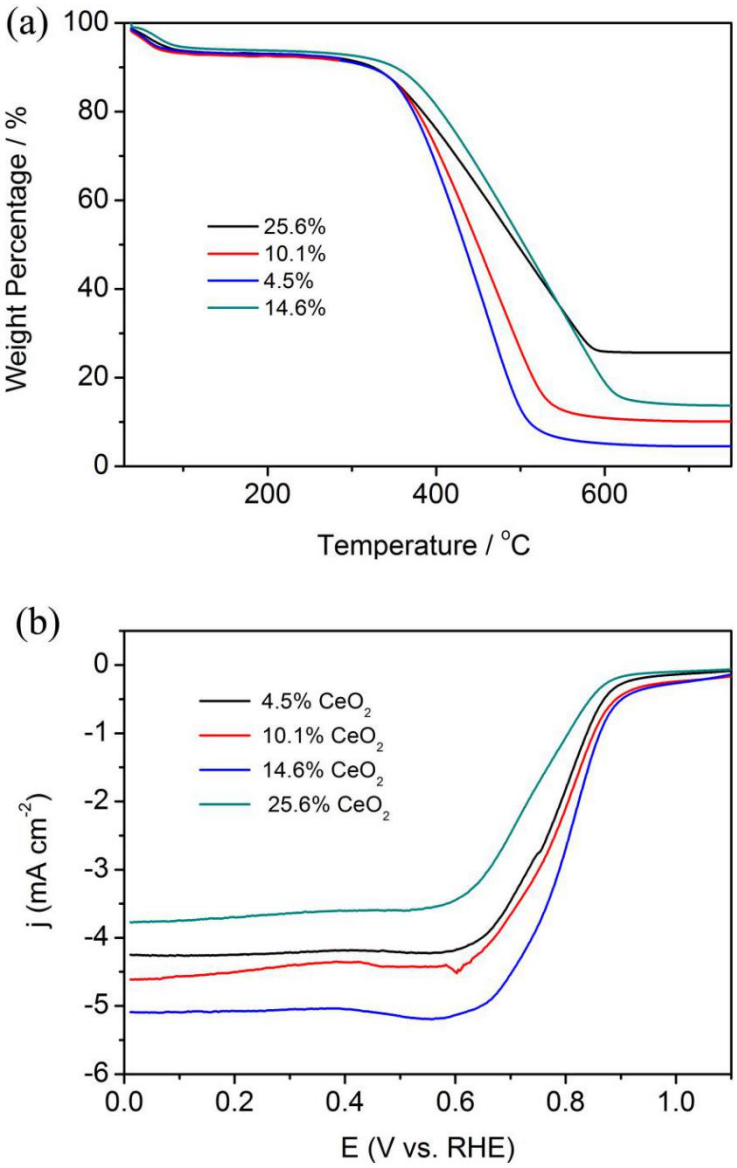

Fig. S8 (a) TGA curves of different mass loading of CeO_2/KB. (b) LSV curves of different mass loading of CeO_2 of MnO_x-CeO_2/KB using RDE in O_2 saturated 0.1 M KOH solution with a sweep rate of 10 mV s^{-1}.

References:

1. Y. Meng, W. Song, H. Huang, Z. Ren, S.-Y. Chen and S. L. Suib, *Journal of the American Chemical Society*, 2014, **136**, 11452-11464.

2. H. Zhang, H. Li, H. Wang, K. He, S. Wang, Y. Tang and J. Chen, *Journal of Power Sources*, 2015, **280**, 640-648.