Experimental details

All reagents except for carbon fiber (Toray, Japan) are of analytical grade without further purification. The electrodes were prepared through direct reduction of permanganate ($KMnO_4$) by carbon fiber. Typically, the carbon fiber was cut into rectangular straps with length of 60 mm and width of 10 mm, and then the end of the straps, about 10 mm, was vertically immersed into an aqueous mixture of $KMnO_4$ (0.02 M) and H_3BO_3 (0.1 M) in a Teflon (PTFE)-lined stainless steel autoclave and maintained at 100 ºC for 2 hours. The carbon fiber straps loaded with MnO_2 were washed with deionized water several times to remove the residual $KMnO_4$, and dried in air for 8 h. For comparison, dopant free electrode was prepared following the same procedure except for the addition of boric acid. The morphologies of the as-prepared MnO_2 were identified by a scanning electron microscopy (Sirion 100, The Netherlands) and a transmission electron microscopy (JEOL JEM 2100, Japan). The crystallographic phases were identified by a powder X-ray diffraction system (TD-3500, China). Specific surface areas were determined with a Micromeritics ASAP 2020 instrument, using N_2 gas as adsorbate. The electrochemical performances were evaluated by using a CHI 660D electrochemical workstation (CH Instruments Inc., China) in a three-electrode setup. All electrochemical experiments were carried out in Na_2SO_4 aqueous electrolyte (0.5 mol L^{-1}) at room temperature about 20 ºC, with a saturated calomel electrode (SCE) acting as reference electrode and a large area of Pt foil using as counter electrode. Cyclic voltammetry (CV) measurements were performed at different scan rates of 2, 5, 10, 20, 50, 100, 200 and 500 mV s^{-1} across a potential range between 0 and 1.0 V (*vs.* SCE). The galvanostatic charge/discharge curves were recorded at a current density of 1 A g^{-1} with the cutoff potential of 0 and 1.0 V (*vs.* SCE). Electrochemical impedance spectra were measured using a frequency range between 100 KHz and 1 Hz with an ac perturbation of 5 mV. After electrochemical tests, the as-prepared electrode was placed into a mixed solution of H_2O_2 and H_2SO_4 at room temperature. The mass of deposited MnO_2 on the carbon fiber was determined by weight measurements before and after the dissolution process.

N_2 adsorption/desorption isotherms experiments, Fig. S2, indicate that the isotherms are type IV and exhibits a small hystheresis loop in the high-pressure region. The surface area for boron-doped electrode is about twice more than that of undoped electrode.

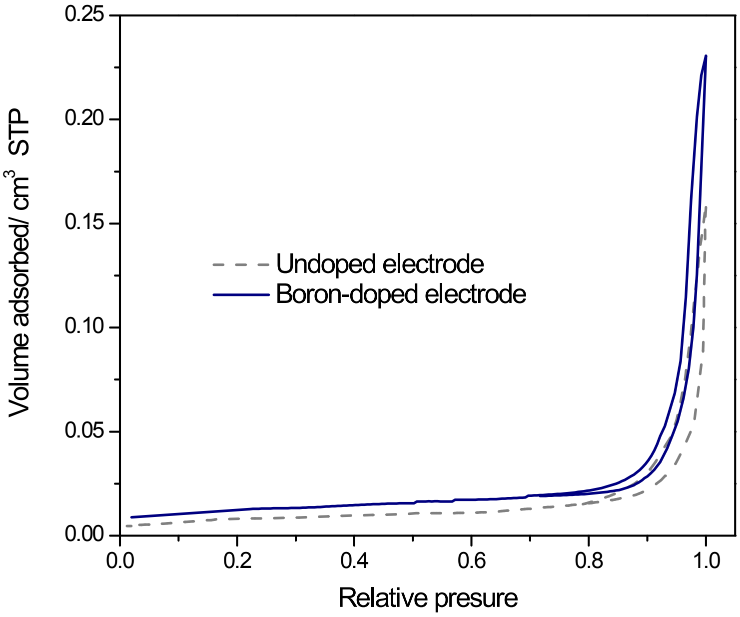
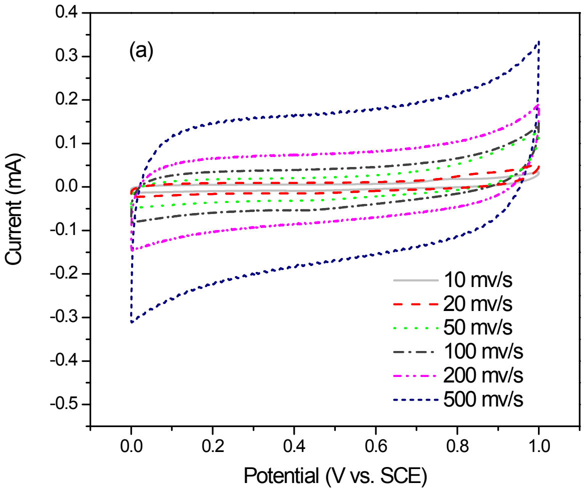


Fig. S1 Absorption/desorption isotherms for undoped and boron-doped electrodes.

The CV curves of the carbon fiber electrode at different scan rates were given for comparison (Fig. S2). According to its area (Fig. S2b), the contribution of the substrate to the capacitance of the as-prepared electrodes is negligible.



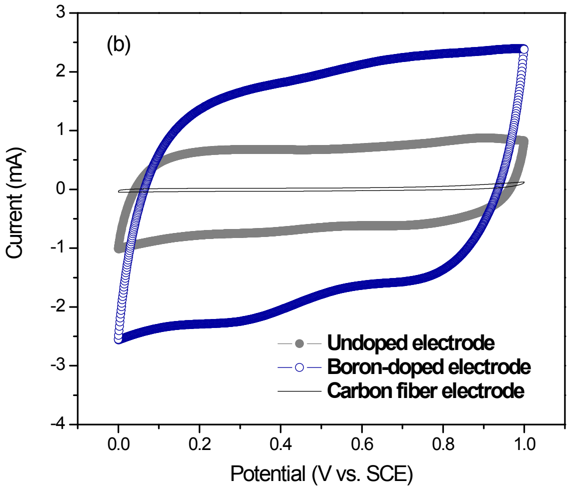
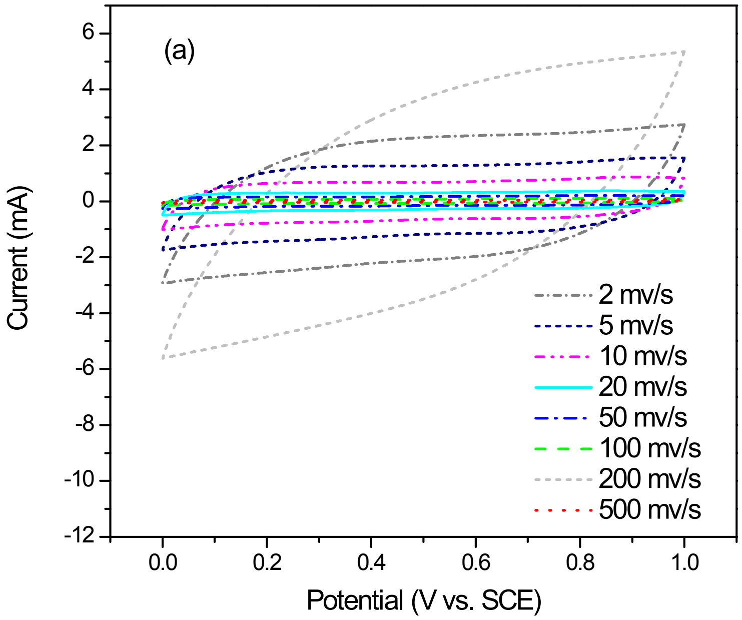


Fig. S2. (a) CV curves for carbon fiber electrode at scan rates of 10, 20, 50, 100, 200 and 500 mV s^{-1} and (b) CV curves at 50 mV s^{-1} for undoped, boron-doped and carbon fiber electrode in a 0.5M Na_2SO_4 aqueous electrolyte.



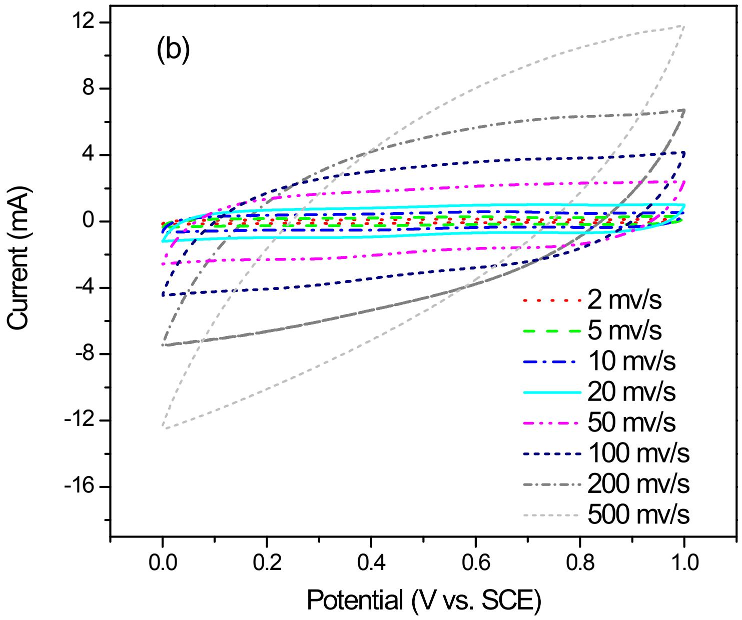


Fig. S3 CV curves for (a) undoped and (b) boron-doped electrodes in a 0.5M Na_2SO_4 aqueous electrolyte at scan rates of 2, 5, 10, 20, 50, 100, 200 and 500 mV s^{-1}.

To further understanding the charge-transfer resistance of the as-prepared electrodes, electrochemical impedance measurements were conducted. The initial non-zero intercept at the real impedance axis corresponds to the ohmic resistance (R_i), including the ionic resistance of the electrolyte, the intrinsic resistance of MnO_2, the resistance of carbon fibers and the contact resistance at the interface between active material, electrolyte and current collector. The R_i for the boron-doped electrode is smaller than that of undoped electrode, being consistent with the analysis of the hydrophilic properties of electrode surface. The inclined line in the low frequency region is attributed to the Warburg impedance, which is associated with proton diffusion in MnO_2 film. The lines with their slope gradually changing represent the finite length diffusion and the slope exhibits an enhancement of electronic conductivity.

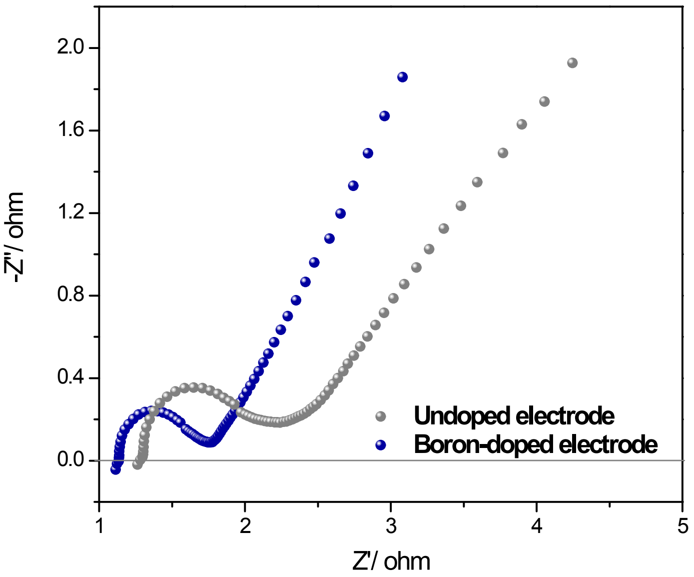


Fig. S4. Nyquist plots for undoped and boron-doped electrodes in a 0.5 M Na_2SO_4 aqueous electrolyte.