Single-Nanowire Electrochemical Probe Detection for Internally Optimized Mechanism of Porous Graphene in Electrochemical Devices

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Experimental

1. Synthesis of MnO$_2$, MnO$_2$/rGO, and MnO$_2$/pGO nanowires

The MnO$_2$/rGO nanowires were produced by the hydrothermal method. In a typical synthesis, 2 mmol KMnO$_4$, 2 mmol NH$_4$F and 2 ml of rGO suspension (~2 mg/ml) were added to 80 ml of distilled water and magnetically stirred at room temperature for 20 min. The sample was then placed into a 100 ml autoclave and heated at 180°C for 24 h. After the sample was washed and dried, a brownish-black powder was obtained. The pure MnO$_2$ nanowires were prepared using the same method described above without the addition of rGO. Then, we dealt MnO$_2$/rGO with 10 mmol/L hydrazine hydrate for different times, including 1, 2, 3, 6, 12, and 24 hours. For improved structure and capacity over the different hydrazine hydrate MnO$_2$/rGO nanowires, we chose to hydrate for 3 hours to produce the MnO$_2$/pGO nanowires.

2. Structure Characterization

X-ray diffraction (XRD) measurements were performed to investigate crystallographic information using a D8 Discover X-ray diffractometer with a non-monochromated Cu Kα X-ray source. Field-emission scanning electron microscopic (FESEM) images were collected using a JSM-7001F microscope at an acceleration voltage of 10 kV. Transmission electron microscopic (TEM) and high-resolution TEM images were recorded with a JSM-2100F STEM/EDS microscope. The X-ray photoelectron (XPS) spectra were recorded on a Shimadzu Axis Ultra
spectrometer with an Mg Kα = 1253.6 eV excitation source. An Autolab 302N Probe Station (Lake Shore, TTPX) and Semiconductor Characterization System (Agilent, B1500A) were used to test the electrochemical performances of the single-nanowire devices.

3. Fabrication of Single-Nanowire Electrochemical Devices

Our manganese dioxide single-nanowire electrochemical device is configured with one single nanowire as a cathode, one flake of Au as an anode, and KOH (6 mol/L) as an electrolyte. The single-nanowire devices were fabricated by the following steps. EBL patterning of contact pads was performed on a highly doped silicon wafer with 300 nm SiO₂, followed by developing, rinsing, Cr/Au (5/50 nm) deposition by thermal evaporation, and then lift-off. The prepared MnO₂ NWs were then deposited on the substrate by contacting the MnO₂ nanowires and contact pad with Cr/Au electrode through EBL patterning, developing, rinsing, Cr/Au (5/150 nm) deposition by thermal evaporation, and then lift-off. A probe station was used for air characterization to check the I-V cyclic voltammetry performances of the MnO₂ NWs. EBL patterning and developing of SU-8 2002 was used to create the isolation layer of the gold electrode to avoid leakage current. A drop of KOH (6 mol/L) electrolyte was used to coat the nanowire and the counter electrode (Au). The performance of the device was then tested. Furthermore, two other single-nanowire devices were fabricated by the same processes.
4. **Electrochemical Characterization**

For electrochemical characterization, the electrochemical performances of these single-nanowire electrochemical devices were measured by Autolab. The different single-nanowire electrochemical devices were fabricated using a mechanical shaping process modified from a previous method adopted to fabricate graphene-based, single-nanowire electrochemical devices. Electrochemical performances of the single-nanowire electrochemical devices were investigated in a two-electrode system using a cyclic voltammetry station and I-V properties. The scan rate of the CV response varied from 20 to 500 mV/s with a potential range from 0 to 0.8 V.
**Figure S1.** The construction processes of MnO$_2$/pGO wire-in-scroll NWs. The brown dots represent the precursor of nanowire template, which forms the nanowires after hydrothermal processes. The gray sheets and scroll represent reduced graphene oxide.

**Figure S2.** SEM images of different MnO$_2$/rGO NWs produced by different hydrothermal times: (a) 3 h, (b) 6 h, (c) 12 h, (d) 18 h.
Figure S3. (a,b) SEM and TEM images of MnO$_2$. (c) SEM image of MnO$_2$/rGO. (d-f) SEM images of MnO$_2$/rGO dealt with 10 mmol/L of hydrazine hydrate for different times: (d) 6h (MnO$_2$-rGO-6h), (e) 12h (MnO$_2$-rGO-12h), (f) 24 h (MnO$_2$-rGO-24h).
Figure S4. (a) SEM image of MnO$_2$-rGO-12h. (b) TEM image of MnO$_2$-rGO-12h.

Figure S5. The XRD patterns of MnO$_2$, MnO$_2$/rGO, MnO$_2$-rGO-3h (MnO$_2$/pGO), MnO$_2$-rGO-6h, MnO$_2$-rGO-12h and MnO$_2$-rGO-24h.
Figure S6. The TG curves of MnO₂, MnO₂/rGO and MnO₂/pGO NWs.

Figure S7. The Raman spectra of MnO₂, MnO₂/rGO, MnO₂/pGO NWs and rGO, showing no obvious shifts among the MnO₂, MnO₂/rGO and MnO₂/pGO NWs. Due to the small content of graphene (3.38 wt%), the D and G shifts between MnO₂/rGO and MnO₂/pGO NWs are not obvious.
**Figure S8.** The O 1s XPS spectrum of MnO₂. The O 1s core level spectrum is used to confirm the presence of oxygen vacancies in MnO₂. The spectra can be fit with two components, which are related to the Mn-O-Mn bond (529.7 eV) of tetravalent oxide and the Mn-OH bond (531.43 eV) of hydrated trivalent oxide. Quantitative analysis shows that oxygen vacancies exist in MnO₂ because of the proportion of Mn³⁺ in MnO₂ (13.84%).

**Figure S9.** The fabrication processes of dropping electrolyte coating on a single-nanowire electrochemical device. The processes involve four steps. Step 1. EBL patterning of contact pads on a highly doped silicon wafer with 300 nm of SiO₂, followed by developing, rinsing, Cr/Au (5/50 nm) deposition by thermal evaporation, and lift-off. The prepared MnO₂, MnO₂/rGO and MnO₂/pGO NWs are deposited on the substrate. Step 2. Contacting the nanowires and contact pad with Cr/Au electrode through EBL patterning, developing, rinsing, Cr/Au (5/150 nm) deposition by thermal evaporation, and lift-off. Step 3. Using a probe station for air characterization to check the I-V cyclic voltammetry performance of the MnO₂, MnO₂/rGO and MnO₂/pGO NWs. EBL patterning and developing of SU-8 2002 as an isolation layer of the gold
electrode to avoid leakage current. Step 4. Drop coating the KOH (6 mol/L) electrolyte on the nanowire and the counter electrode (Au), and test the performance of device.

**Figure S10.** The CV curves at scan rates of 20, 30, 40, 50, and 100 mV/s for the as-prepared MnO₂ and MnO₂/rGO single-nanowire electrochemical devices in 6 mol/L KOH.

**Figure S11.** The single-nanowire transport properties of the MnO₂, MnO₂/rGO and MnO₂/pGO NWs.
**Figure S12.** Nyquist plots of MnO$_2$, MnO$_2$/rGO and MnO$_2$/pGO in a frequency regime from 1 to 100 kHz with a three-electrode system. The EIS measurements are performed in an aqueous solution of 6 mol/L KOH.

The ion diffusion coefficient can also be calculated using the following equation:

$$D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2}$$

where $R$ represents the gas constant, $T$ represents the absolute temperature, $A$ represents the surface area of the anode (cm$^2$), $n$ represents the number of electrons transferred in the half-reaction for the redox couple (2), $F$ represents the Faraday constant, $C$ represents the concentration of ions in the solid, $D$ represents the diffusion coefficient (cm$^2$/s), and $\sigma$ represents the Warburg factor relative to $Z_{re}$. From the slope of the lines in the inset, $\sigma$ can be obtained.

$$Z_{re} = R_D + R_L + \sigma \omega^{-1/2}$$

According to the linear fit, the slope of the real part of the complex impedance is versus $\omega^{-1/2}$ (The response of AC impedance changes noisily when the frequency is below $10^3$ Hz. Only impedance data in the frequency range of $10^3$~$10^6$ Hz is stable in the single-nanowire system.) at the potential of 0.3 V (vs HgCl/Hg) for MnO$_2$, MnO$_2$/rGO and MnO$_2$/pGO NWs are 4.08×$10^6$, 4.39×$10^7$ and 7.06×$10^6$, respectively. The ions diffusion coefficients at room temperature are calculated to be 5.55×$10^{-8}$, 5.21×$10^{-9}$ and 2.31×$10^{-8}$ cm$^2$/s for the MnO$_2$, MnO$_2$/rGO and MnO$_2$/pGO NW, respectively.

In general, the EIS contains $R_{con}$, $R_{ct}$, and $R_w$. In this single-nanowire device system, the nanowire is surrounded by electrolyte, so ions are very easily transported to the interface of the active material. According to our understanding, the frequency of $10^6$ Hz corresponds to $R_{ct}$,
which may be due to the fast ion diffusion in our system. $R_{\text{con}}$ and $R_{\text{ct}}$ cannot be tested with Autolab 302N because of the upper frequency limitation. Only $R_w$ can be calculated. In this way, the ion diffusion coefficients, which are calculated from the EIS, support our assertions in the manuscript.

**Figure S13.** The plots of $\mu^{0.5}$ vs $i/\mu^{0.5}$ used for calculating constants $k_1$ and $k_2$ at different potentials from a variety of cathodic voltammetric sweeps. According to a power law relationship, $I = k\mu$ for non-diffusion limited processes and $i = k\mu^{0.5}$ for diffusion limited processes. Thus, total current $i(V) = k_1\mu + k_2\mu^{0.5}$ and $i(V)/\mu^{0.5} = k_1\mu^{0.5} + k_2$ at different potentials are calculated from cyclic voltammograms at different scan rates ranging from 20 to 500 mV/s. Plots of $i/\mu^{0.5}$ vs $\mu^{0.5}$ have been drawn at a variety of potentials. The $k_1$ (slope) and $k_2$ (intercept) are calculated from the straight line.

**Figure S14.** The CV curves at scan rates of 20, 30, 40, 50, and 100 mV/s for the as-prepared MnO$_2$ and MnO$_2$/rGO symmetric single-nanowire electrochemical devices in 6 mol/L KOH.
Figure S15. The CV curves at a scan rate of 100 mV/s for the MnO\(_2\)/pGO symmetric single-nanowire electrochemical devices and background device in 6 mol/L KOH.