**Supplementary Material**

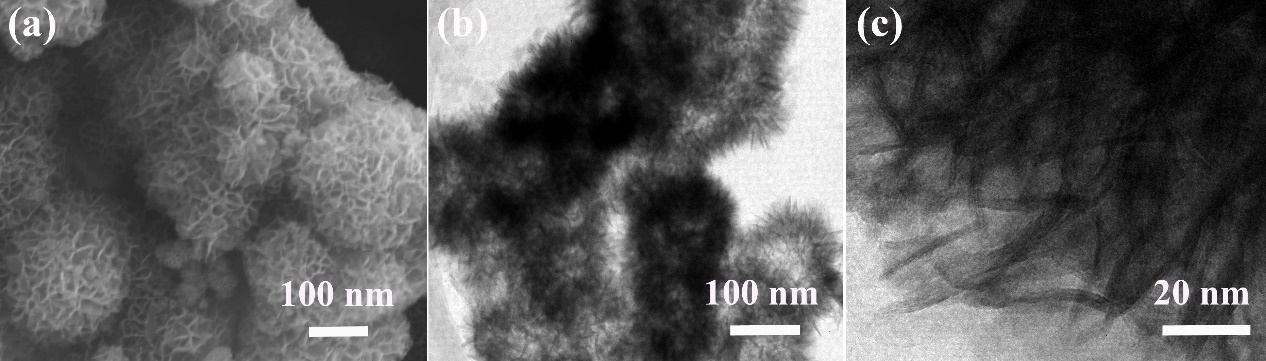
**Synergistically coupling of graphene quantum dots with Zn-intercalated MnO2 cathode for high-performance aqueous Zn-ion batteries**

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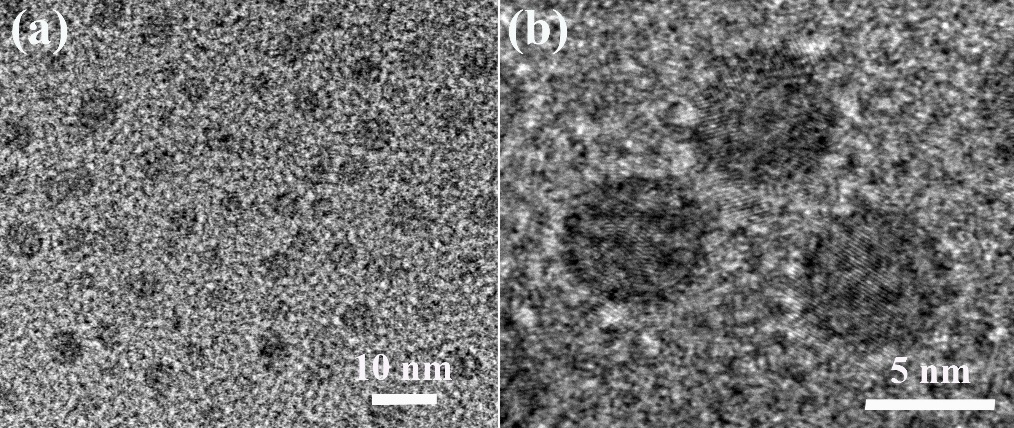
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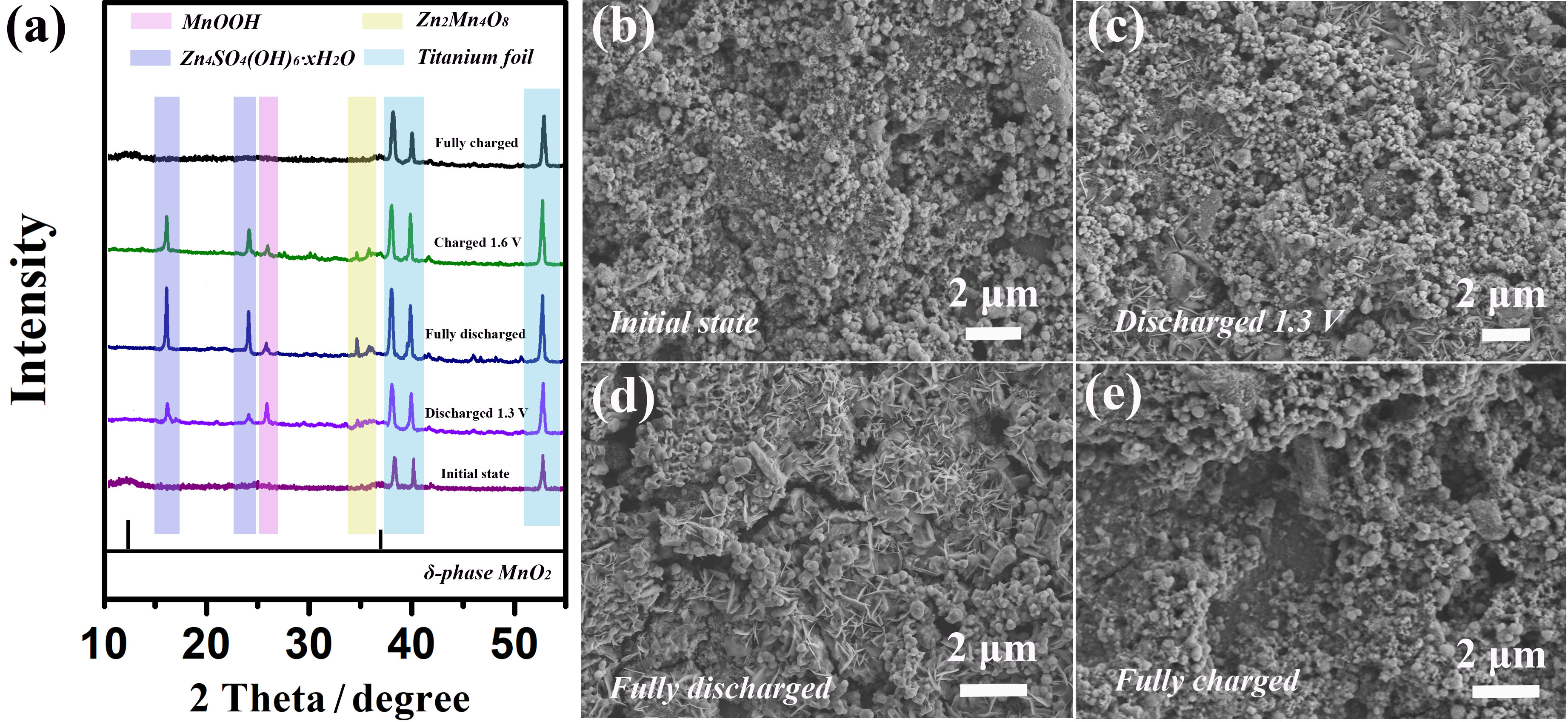
**Fig. S1.** (a) SEM image, (b) low-resolution and (c) high-resolution TEM images of pristine MnO2.

As shown in Fig. S1a and S1b, the pristine MnO2 consists of many monodispersed and uniform nanoflowers with the size of 200 nm, wherein the surface of MnO2 nanosheets is smooth and no GQDs can be observed on the surface of MnO2 nanosheets (Fig. S1c).



**Fig. S2.** (a) Low-resolution and (b) high-resolution TEM images of GQDs.

As shown in Fig. S2, the GQDs are effectively synthesized from GO via a facile solvothermal approach. The resultant GQDs are nanometer-sized graphene sheets with excellent electron mobility.



**Fig. S3.** (a) Ex-situ XRD pattern and (b-e) SEM images of the cathode collected at various charging and discharging states.

For better understanding the reaction mechanism, ex-situ XRD (Fig. S3a) and SEM measurements (Fig. S3b-e) have been carried out to analyze the phase and structural evolutions upon charging and discharging. As seen from Fig. S3a, a new phase with obvious diffraction peaks at around 16.1° and 24.2° appear during the discharging process, which could be assigned to the zinc sulfate hydroxide hydrate (Zn4SO4(OH)6·xH2O,JPCDS #39-0688). The Zn4SO4(OH)6·xH2O phase exhibits a two-dimensional layered architecture (Fig. S3c), which is constructed by the stacking of Zn(OH)2 layers with ZnSO4 and filling of water molecules in the interlayer tunnels. After fully discharge, the peak intensity of Zn4SO4(OH)6·xH2O increases obviously, suggesting the growth of Zn4SO4(OH)6·xH2O phase with the large-size sheets (Fig. S3d). In the reverse charging process, both the diffraction peaks of the Zn4SO4(OH)6·xH2O phase and the large-size sheets disappear (Fig. S3e), revealing the reversible dissolution/precipitation of the Zn4SO4(OH)6·xH2O phase. Apart from the Zn4SO4(OH)6·xH2O phase in the discharged cathode, the diffraction peak at 26° corresponds to MnOOH (JPCDS#41-1379), while those in the range of 34°–36° are attributed to Zn2Mn4O8 (JPCDS #09-0459). These characteristic peaks cannot be observed in the fully charged cathode, indicating that the energy storage mechanism is related to the co-insertion/extraction process of H+ and Zn2+ accompanied by the dissolution/precipitation of the Zn4SO4(OH)6·xH2O phase. The electrochemical reaction process can be listed as follows:

The cathode reaction:

MnO2 + H+ + e- → MnOOH

4MnO2 + 2Zn2+ + 4e- + H2O → Zn2Mn4O8·H2O

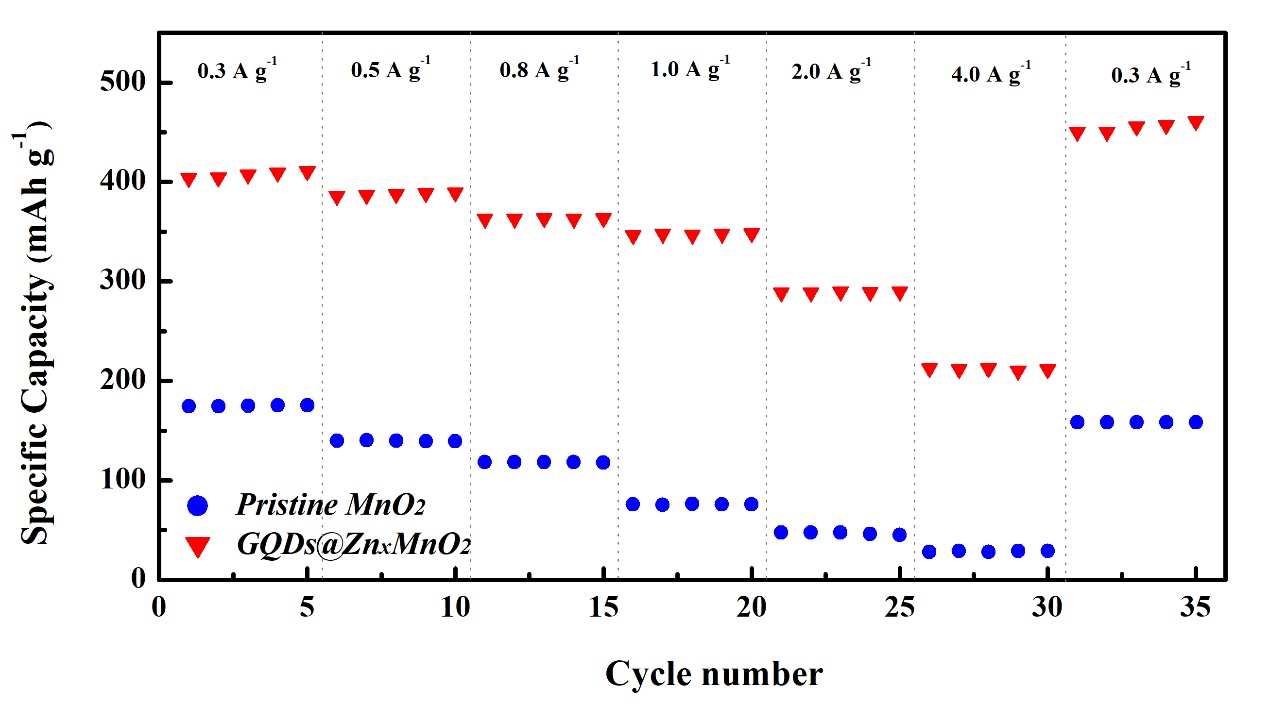
2MnOOH + SO42- + 4Zn2+ + 7H2O + 2e- → Zn4SO4(OH)6·5H2O + 2Mn2+

3Zn2Mn4O8·H2O + 8SO42- + 61H2O + 26Zn2+ + 12e- → 8Zn4SO4(OH)6·5H2O + 12Mn2+

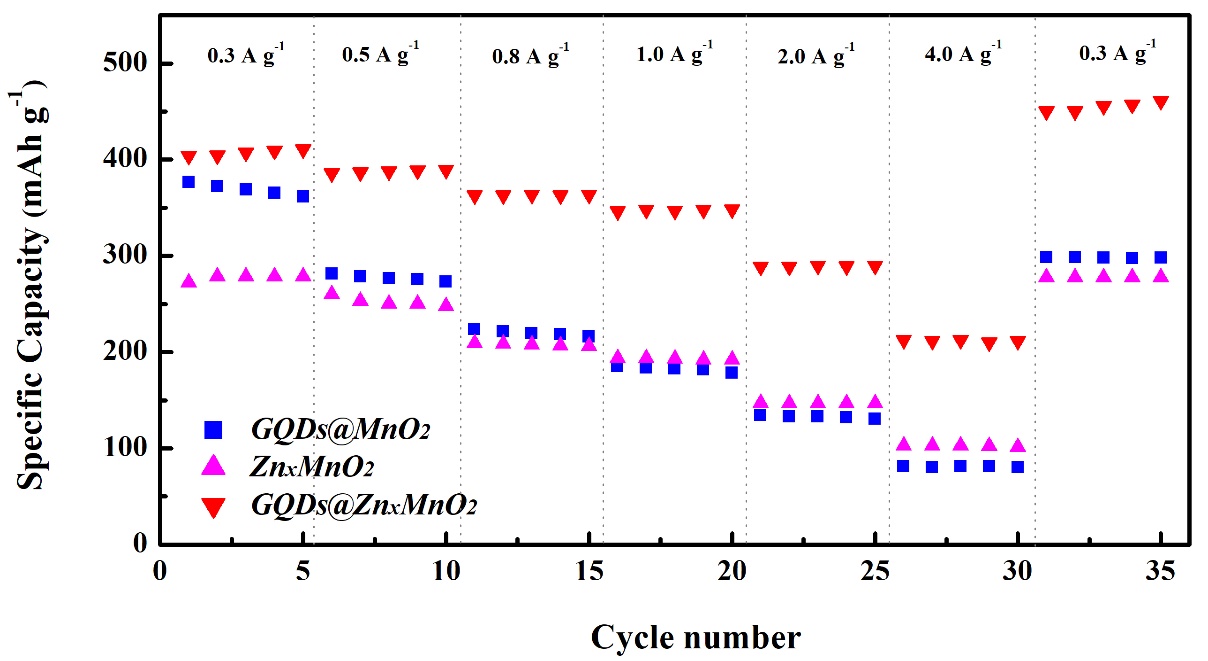
The anode reaction: Zn - 2e- → Zn2+

Different from the one-electron redox process of Mn4+/Mn3+ limited by its theoretical capacity of 308 mAh g−1 and voltage of 1.2–1.4 V [S1, S2], the two-electron Mn4+/Mn2+ reaction shows a high theoretical capacity of ∼616 mAh g−1 and high voltage [S2]. Based on the Mn4+/Mn2+ two-electron energy storage mechanism, the GQDs@ZnxMnO2 cathode can deliver a large discharge capacity of 403.6 mAh g−1 in aqueous ZIBs.

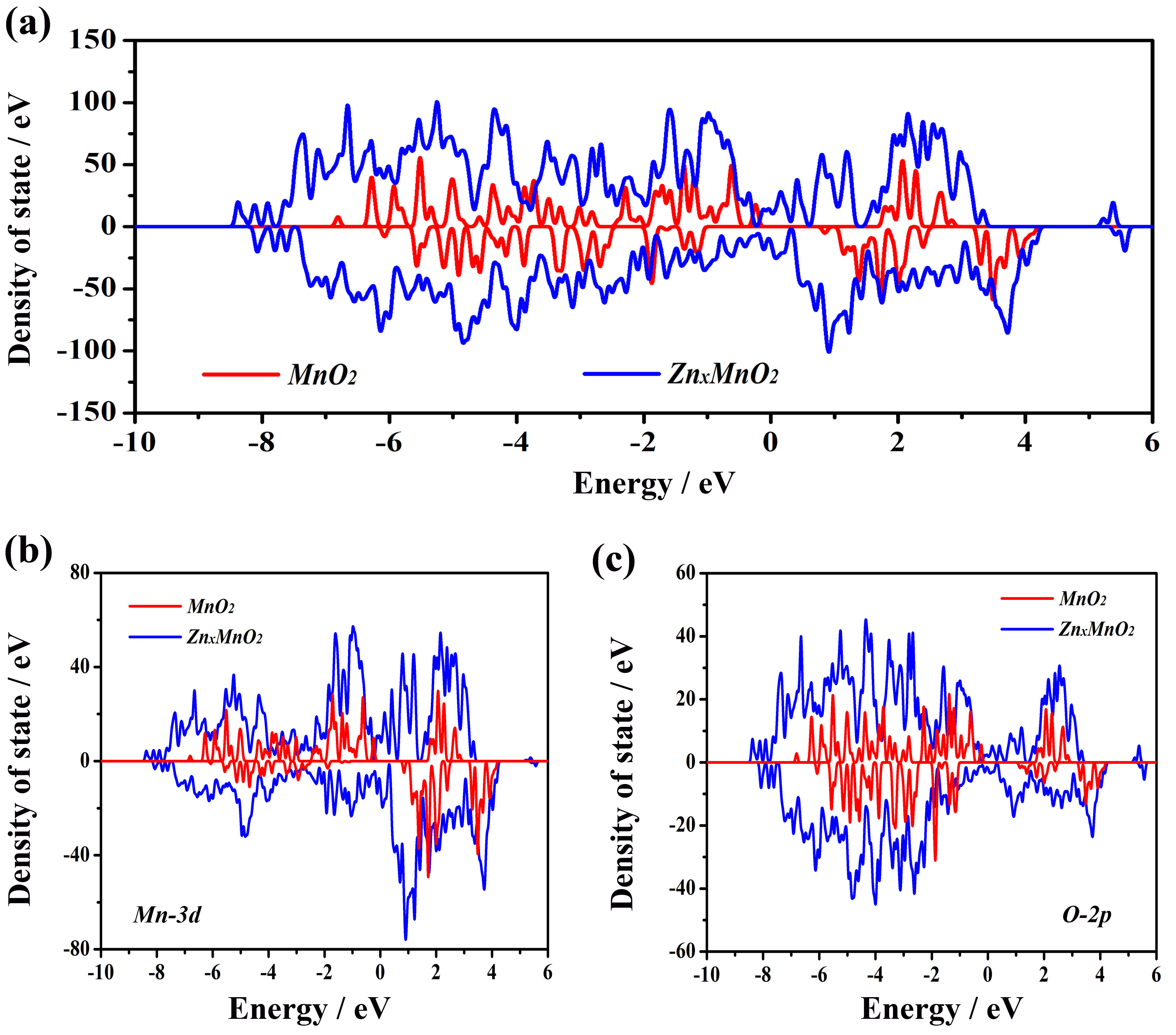
The reason why two-electron reaction is easy to occur could be attributed to the layered δ-phase MnO2 with Zn-intercalation in the electrode material.Compared to α-, β-, γ-, and λ-MnO2, the layered δ-MnO2 with lower crystallinity contains higher energy and possesses the ability to carry out a deeper reaction via the Mn4+/Mn2+ two-electron reaction pathway [S3]. For instance, Xia et al. [S4] demonstrated the two-electron reaction mechanism of layered δ-MnO2 cathode with the H+/Zn2+ co-insertion/extraction, accompanied by the formation and disappearance of zinc sulfate hydroxide hydrate on the surface of the δ-MnO2 cathode. Apart from the intrinsical characteristics of δ-MnO2 structure, the Zn-intercalation is also beneficial for the occurrence of two-electron reaction. The Zn-intercalation could not only decrease the electrostatic repulsion between carrier ions and host framework of δ-MnO2, but also enlarge the interlayer spacing of δ-MnO2 to accommodate with water molecules and carrier ions [S5, S6], thereby allowing for the abundant co-insertion/extraction of H+ and Zn2+ ions accompanied with efficient two-electron reaction during the charging-dicharging process.



**Fig. S4.** The comparison of rate capabilities of pristine MnO2 and GQDs@ZnxMnO2 cathodes in aqueous ZIBs.

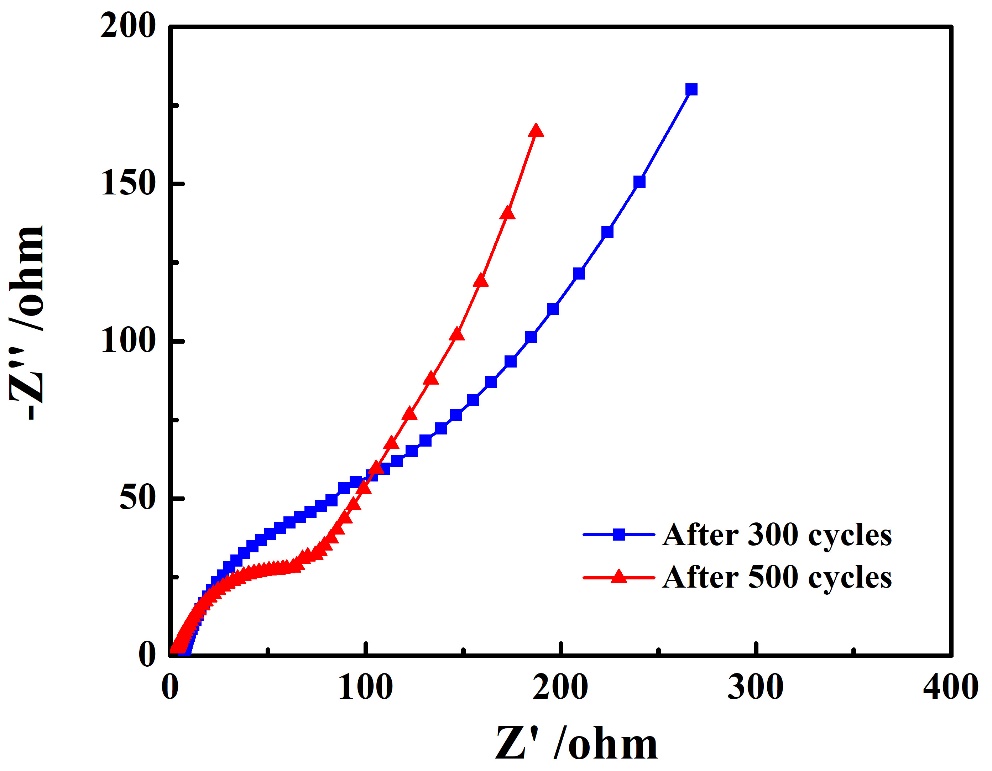


**Fig. S5.** The comparison of rate capabilities of GQDs@MnO2, ZnxMnO2 and GQDs@ZnxMnO2 cathodes in aqueous ZIBs.



**Fig. S6.** DFT calculations about the (a) TDOS patterns for pristine MnO2 and ZnxMnO2. The corresponding (b) Mn 3d and (c) O 2p PDOS patterns of pristine MnO2 and ZnxMnO2.

DFT calculations have been performed to explore the density of states and electronic properties of pristine MnO2 and ZnxMnO2. According to the total density of state (TDOS) as shown in Fig. S6a, the pristine MnO2 possesses a distinct separation between the conduction and valence bands at the Fermi level with a bandgap of ~1.59 eV. By contrast, the bandgap of ZnxMnO2 is drastically narrowed because of the increased TDOS in the vicinity of Fermi level, suggesting that more charge carriers could be introduced into the ZnxMnO2 owing to the Zn intercalation, thereby providing the higher carrier and enhanced electronic conductivity for the ZnxMnO2. Fig. S6b and S6c illustrate the partial density of state (PDOS) for pristine MnO2 and ZnxMnO2, respectively. Stronger Mn 3d and O 2p electron states can be observed in the ZnxMnO2, further indicating the enhanced Mn and O electrochemical activities in the ZnxMnO2 after the Zn intercalation [S7, S8].



**Fig. S7.** EIS plots of the aqueous ZIBs based on GQDs@ZnxMnO2 cathode after 300 and 500 cycles.

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