Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Polymer grafted on carbon nanotubes as a flexible cathode for aqueous zinc ion batteries

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Experimental methods

Materials: 3-Hydroxytyramine hydrochloride (dopamine, 99%) was purchased from ACROS Organics. Tris(hydroxymethyl)aminomethane (Tris, 99.8%), hydrochloric acid (HCl, 36.5-38%) and zinc sulfate heptahydrate ($ZnSO_4 \bullet 6H_2O$, 99-103%) were purchased from Fisher Scientific. Carbon nanotube, multi-walled (MWCNT, >98% carbon basis) was purchased from Sigma-Aldrich. Zinc foil (0.25mm, 99.98% metals basis) was purchased from Alfar Aesar.

Sample preparation: 1 mg/ml dopamine was added into the tris-HCl aqueous solution (pH 8.5) dispersed with 0.5 mg/ml CNT. After stirring for 16 hours, the solution was vacuum filtered by a hydrophilic separator (Dreamweaver Silver 20). The free standing film can be peeled off from the separator when dried under vacuum at 70 °C overnight. The loading amount of polydopamine was 38.1% which was calculated by comparing with the pristine CNT film prepared with similar method. The loading density in the film was 0.9-1.3 mg/cm^2. Polydopamine particles were prepared with similar methods without adding CNT.

Sample characterization: The morphology of polydopamine electrode was characterized using transmission electron microscopy (TEM, FEI Tecnai G2 Sphera at 200 KV) and scanning electron microscopy (SEM, FEI Quanta 250) with atomic composition and elemental mapping analysis by an integrated energy-dispersive X-ray (EDX) spectrometer. The chemical structure of the membrane was characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum Two) and X-ray photoelectron spectroscopy

(XPS, Kratos Analytical, Kratos AXIS Supra). The UV-vis spectroscopy was conducted on Hitachi UH-4150. Reduced or oxidized state samples for FTIR and XPS were cycled at 200 mA/g for 20 cycles then discharged or charged to 0.3 V or 1.4 V respectively.

Electrochemical test: 2032-type coin cells were used for all the electrochemical tests. Zinc foil was used as the anode and filter paper (Whatman grade 2) was used as the separator. Argon purged 3.3 M $ZnSO_4$ aqueous solution (pH 4.5) was used as the electrolyte without pH adjustment. Cyclic voltammetry was performed on a potentiostat (Biologic VSP-300). Galvanostatic cycling was tested on a battery tester (Landt CT2001A). The pre-cycled sample was cycled for 50 cycles at 200 mA/g first. Then, after carefully washing and drying, the electrode was re-assembled into a new battery to test.

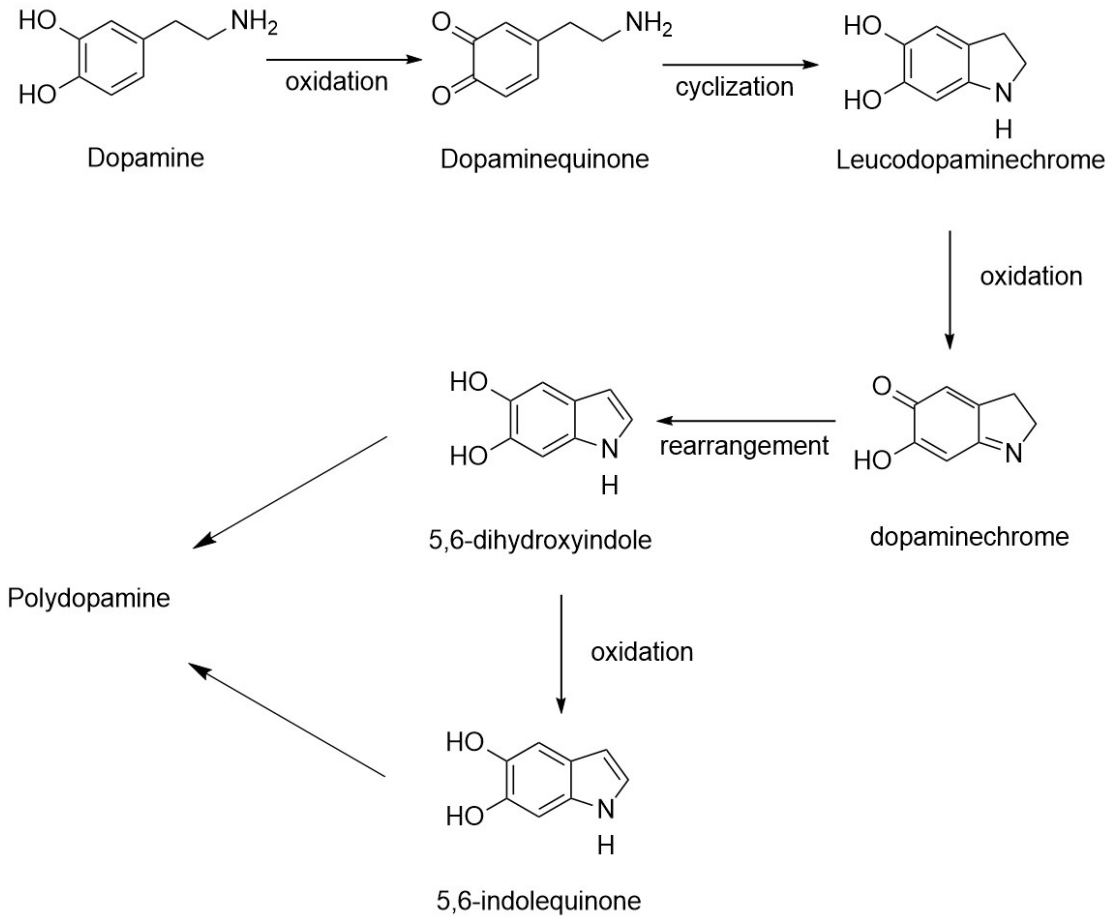

Figure S1. Possible reaction mechanism of PDA.

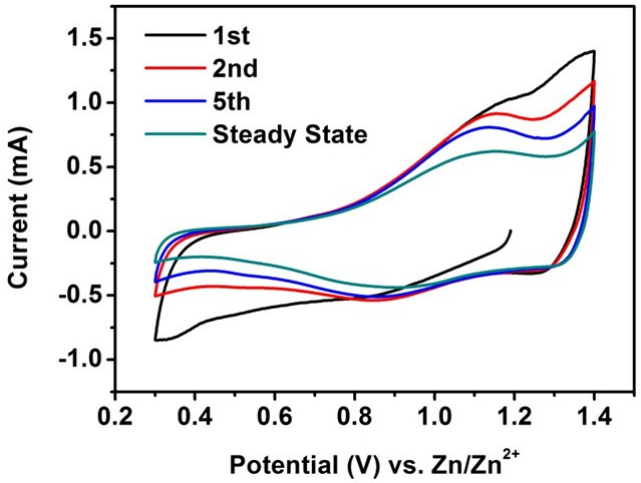

Figure S2. Cyclic voltammetry profiles of initial cycles and steady state scan at 1 mV/s.

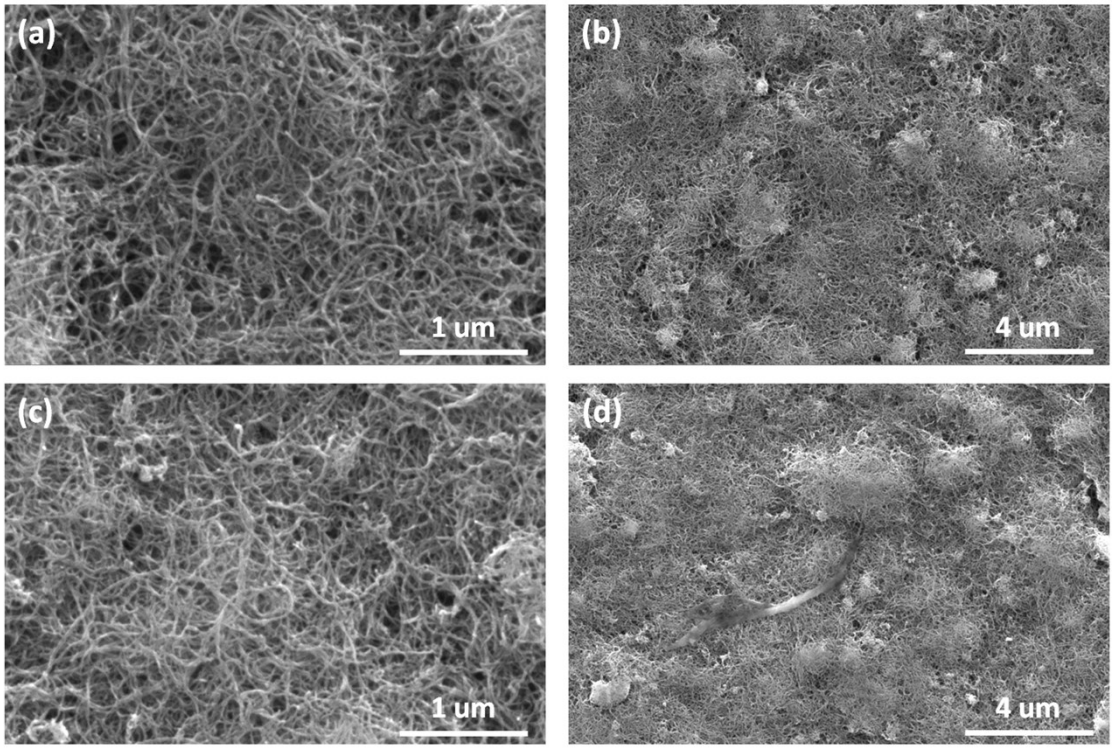

Figure S3. SEM images of PDA electrode. (a)(b) Before cycling. (c)(d) After 400 cycles at 200 mA/g

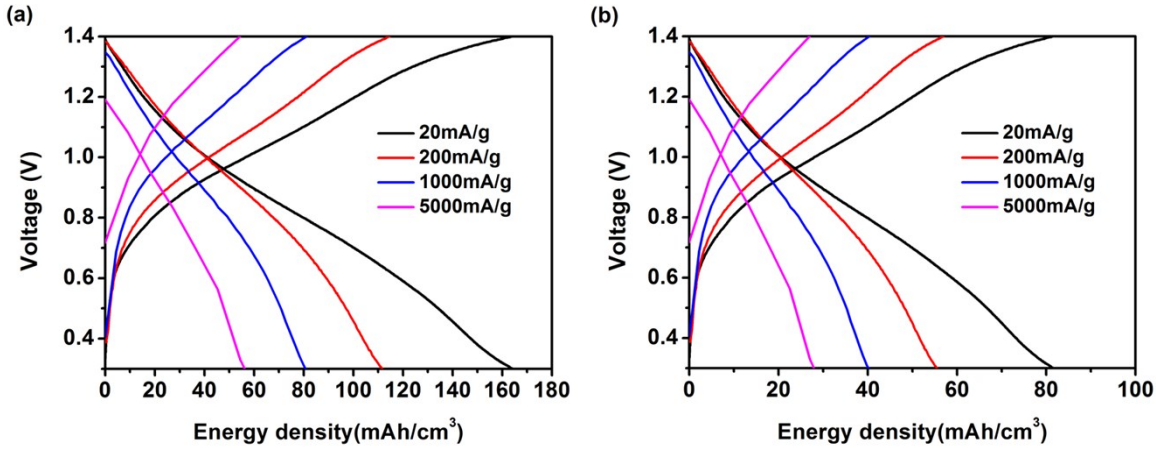

Figure S4. Volumetric specific capacity at different current densities: (a) polydopamine (b) polydopamine electrode. Converted from Figure 2(c).

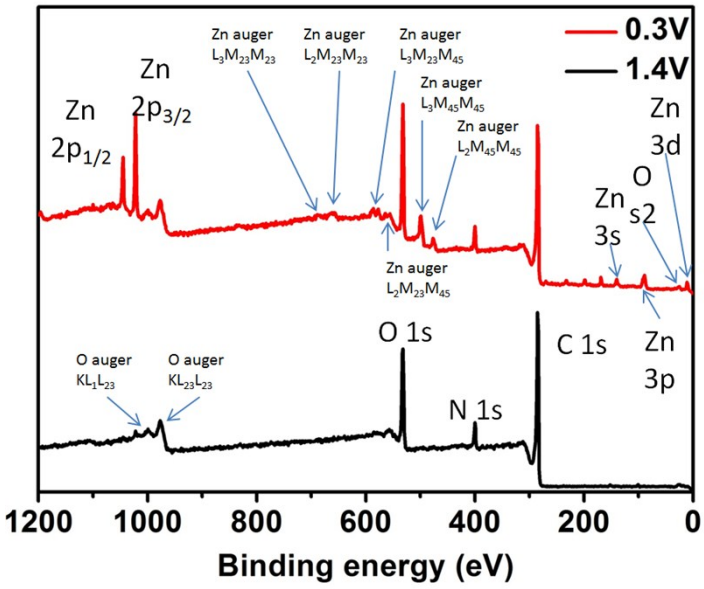

Figure S5. *Ex-situ* low resolution XPS analysis of PDA electrodes at charged (1.4 V) and discharged (0.3 V) states.

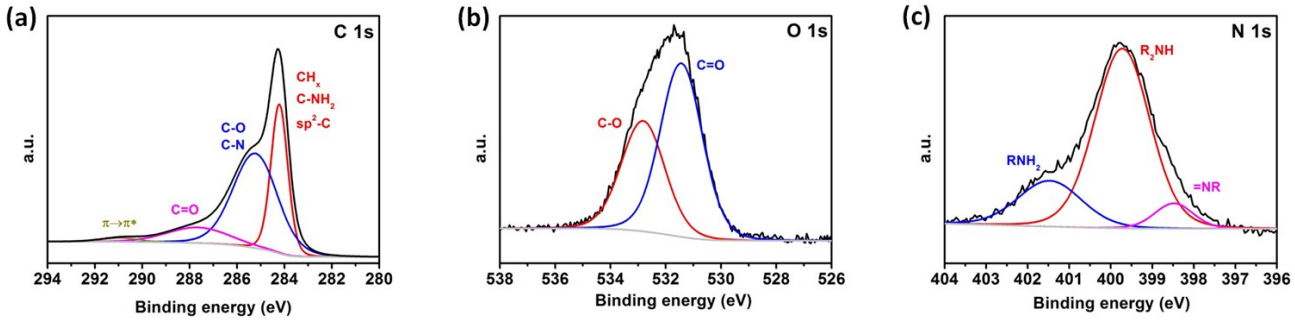

Figure S6: High resolution X-ray photoelectron spectroscopy (XPS) spectra of pristine PDA electrode. (a) C 1s, (b) O 1s, (c) N 1s.

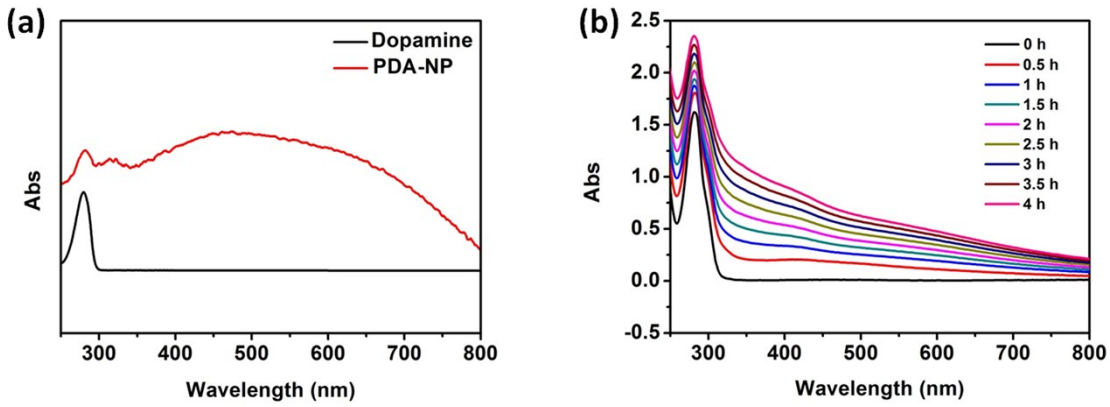

Figure S7. UV-vis analysis (a) Dopamine monomer and washed PDA nanoparticles in water.

(b) *In-situ* characterization of the polymerization of dopamine.

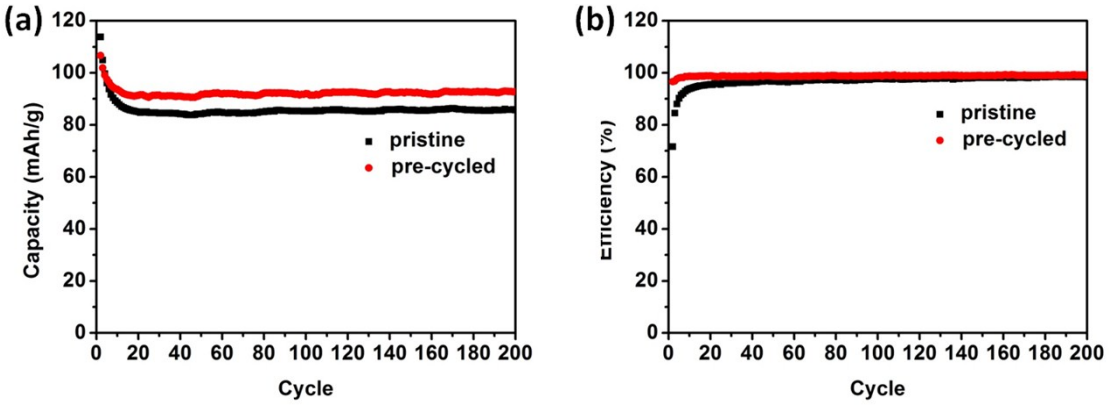

Figure S8. Cyclic performance of pristine and pre-cycled PDA electrode.