

Supporting Information for

Polypyrrole hollow nanospheres: Stable cathode materials for sodium-ion batteries

Dawei Su,^{*,a} Jinqiang Zhang,^a Shixue Dou^b and Guoxiu Wang^{*,a,c}

^a Centre for Clean Energy Technology, Faculty of Science, University of Technology, Sydney, NSW 2007, Australia. Fax: +61-2-9514-1460; Tel: +61-2-9514-1741; E-mail: Dawei.Su@uts.edu.au, Guoxiu.Wang@uts.edu.au

^b Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia. Fax: +61-2-4221-5731; Tel: +61-2-4221-4558;

^c College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016 P.R. China

Experimental Section

Synthesis of PMMA nanosphere templates

The PMMA nanospheres were synthesized through emulsion polymerization of methyl methacrylate (MMA) ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$, Aldrich, $\geq 99\%$) based on a technique described in the literature.^[17] Typically, the phenolic inhibitors of MMA were first removed by filtration through aluminium oxide (Al_2O_3 , Sigma-Aldrich, $\geq 99\%$). Then, 15 mL MMA was distilled in 175 mL water in the presence of 12 mg sodium dodecyl sulphate (SDS, $(\text{CH}_3(\text{CH}_2)_{10}\text{-CH}_2\text{OSO}_3\text{Na}$, Sigma-Aldrich, $\geq 98.5\%$) surfactant and 116.9 mg potassium peroxydisulphate (KPS, $\text{K}_2\text{S}_2\text{O}_8$, Sigma-Aldrich, $\geq 99\%$) initiator. The MMA was polymerized at $70\text{ }^\circ\text{C}$ for 4 h under nitrogen. The resultant PMMA solution began to turn opaque as it started to polymerize and finally formed a milky white colloidal solution. After being washed with distilled water several times and dried at $70\text{ }^\circ\text{C}$ in a vacuum oven overnight, the PMMA nanospheres were obtained.

Synthesis of PPy hollow nanospheres

First, the PMMA nanospheres (200 mg) were dispersed in the 50 mL distilled water. Then, the pyrrole solution was added into the PMMA solution. Using iron chloride (Sigma-Aldrich, $\geq 99\%$) addition, the pyrrole was polymerized in an ice bath. After stirring for 3 h, the color of the solution changed to black, indicating the completion of the reaction. After washing with distilled water several times, the PMMA nanosphere templates were simply washed away with acetone. Finally, the products were dried at $70\text{ }^\circ\text{C}$ in a vacuum oven overnight,

Structural and physical characterization

The morphology was analysed by field emission scanning electron microscopy (FESEM, Zeiss Supra 55VP). The structural details were further characterized by transmission electron

microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2011). Raman spectra were collected via a Renishaw inVia Raman spectrometer system (Gloucestershire, UK) equipped with a Leica DMLB microscope (Wetzlar, Germany) and a Renishaw helium neon laser source with a power of 17 mW at 633 nm. Fourier transform infrared (FTIR) spectra of the samples were collected on a Nicolet Magna 6700 FTIR spectrometer with 0.9 cm⁻¹ standard optical resolution using a KBr beam splitter. N₂ adsorption–desorption isotherms were collected on a Micromeritics 3Flex analyser at the testing temperature of 77 K. Brunauer-Emmett-Teller (BET) analysis was used to determine the surface area and was calculated using the isothermal points at a relative pressure of $P/P_0 = 0.05-0.25$.

Computational methods.

DFT calculations were performed based on DMol³ code, employing Local Density Approximation (LDA)-PWC formalism for the exchange-correlation energy function with the convergence tolerance of 5×10^{-4} eV.^[18] The maximum self-consistent field convergent tolerance was less than 1×10^{-5} eV atom⁻¹. The energy barriers for adsorption of Na⁺ and Li⁺ were calculated from the difference between the energy of the bulk PPy, E_{PPy} , the energy of Na or Li, $E_{\text{Na/Li}}$, and the energy of sodiated/lithiated PPy, $E_{\text{sodiated/lithiated PPy}}$:

$$E_{\text{energy barriers}} = E_{\text{sodiated/lithiated PPy}} - (E_{\text{PPy}} + E_{\text{Na/Li}}) \quad (1)$$

Electrochemical testing

The electrodes were prepared by dispersing the as-prepared PPy hollow nanospheres (80 wt %), acetylene carbon black (10 wt %), and poly (vinylidene fluoride) binder (PVDF, 10 wt %) in N-methyl-2-pyrrolidone (NMP) to form a slurry. The resultant slurry was pasted onto aluminium foil using a doctor blade and dried in a vacuum oven for 12 h, followed by

pressing at 200 kg cm⁻². The loading of each electrode was approximately 1.2 mg. Electrochemical measurements were carried out using two-electrode coin cells (CR2032-type) with Na metal as reference and counter electrode and glass microfiber (Whatman) as the separator. The CR2032-type coin cells were assembled in an argon-filled glove box (UniLab, Mbraun, Germany). The electrolyte solution was 1 M NaClO₄ dissolved in a mixture of ethylene carbonate (EC) and propylene carbonate (PC), with a volume ratio of 1:1. Cyclic voltammetry (CV) was carried out on a CHI 660C electrochemistry workstation with a scan rate of 0.1 mV s⁻¹ from 1.5 to 3.5 V. The charge-discharge measurements were performed at ambient temperature at different current densities in the voltage range from 1.5 to 3.8 V. The A.C. impedance spectra were measured in frequency range from 0.01 Hz to 100 kHz. In order to investigate the sodium-driven structural and morphological changes in the as-prepared PPy hollow nanospheres, Swagelok-type cells were assembled. After cycling, the active materials were removed from the electrodes and washed with propylene carbonate (PC) before being used for *ex-situ* SEM, TEM, FTIR, and Raman analyses.

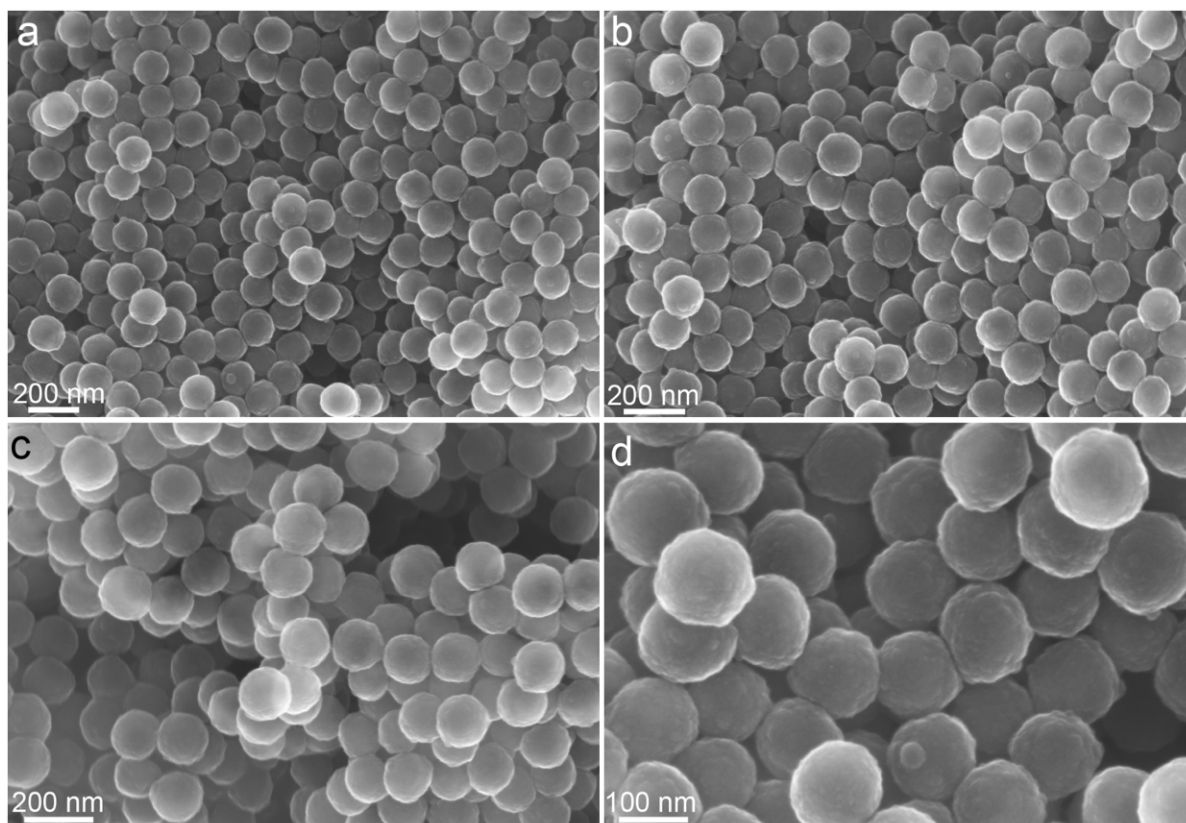


Figure S1. FESEM images of PMMA nanospheres at different magnifications.

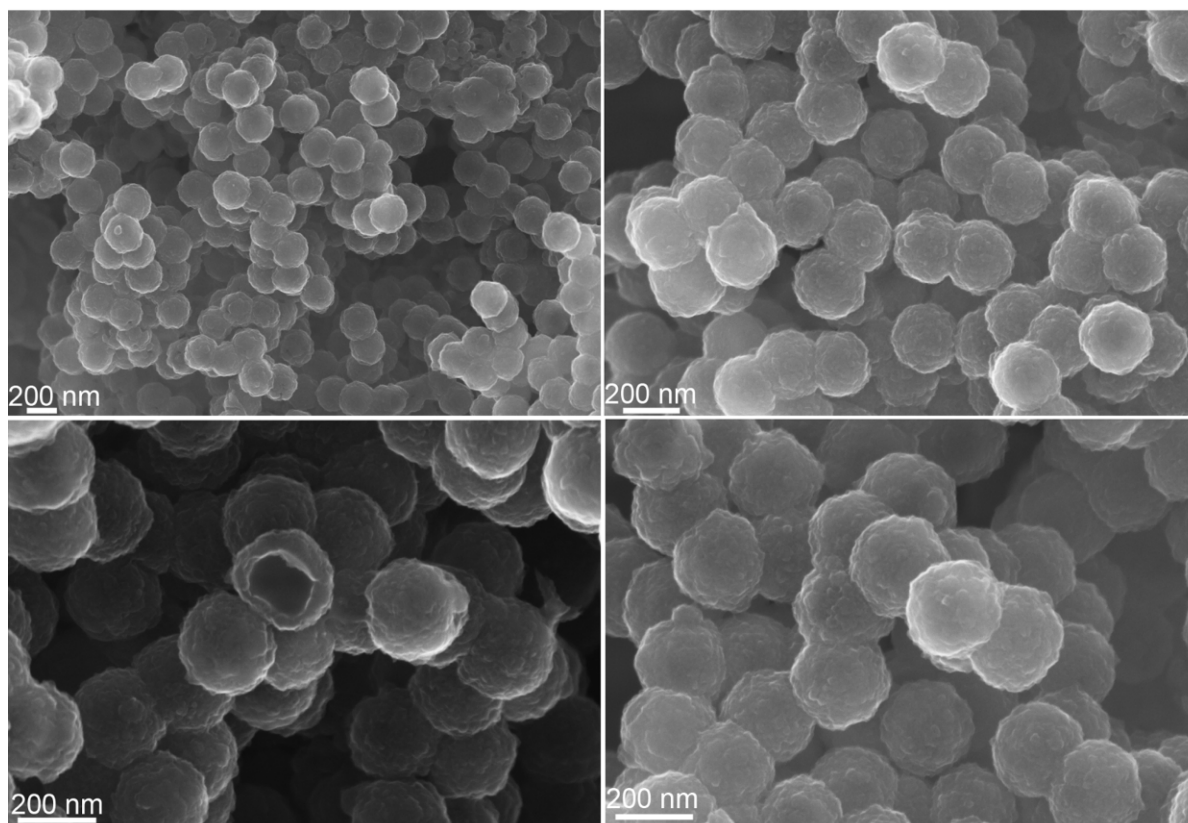


Figure S2. FESEM images of PPy nanospheres at different magnifications.

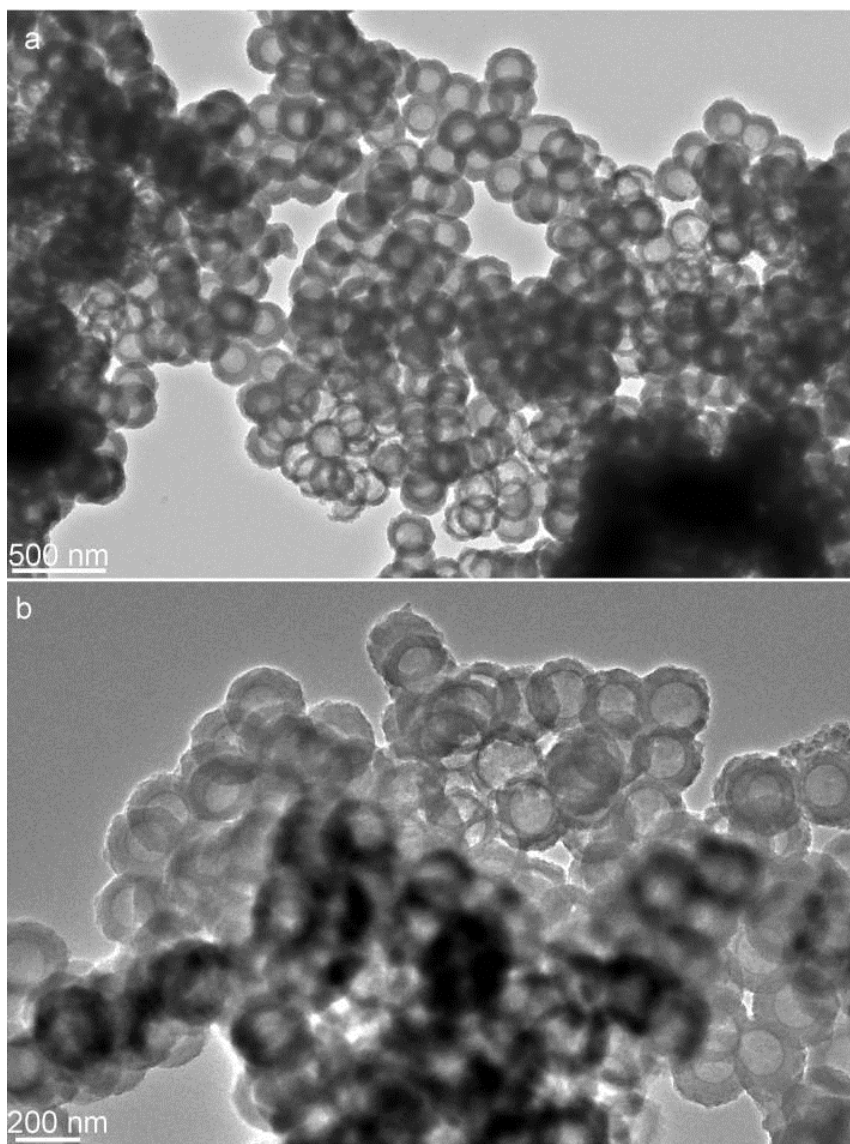


Figure S3. Low magnification TEM images of PPy hollow nanospheres.

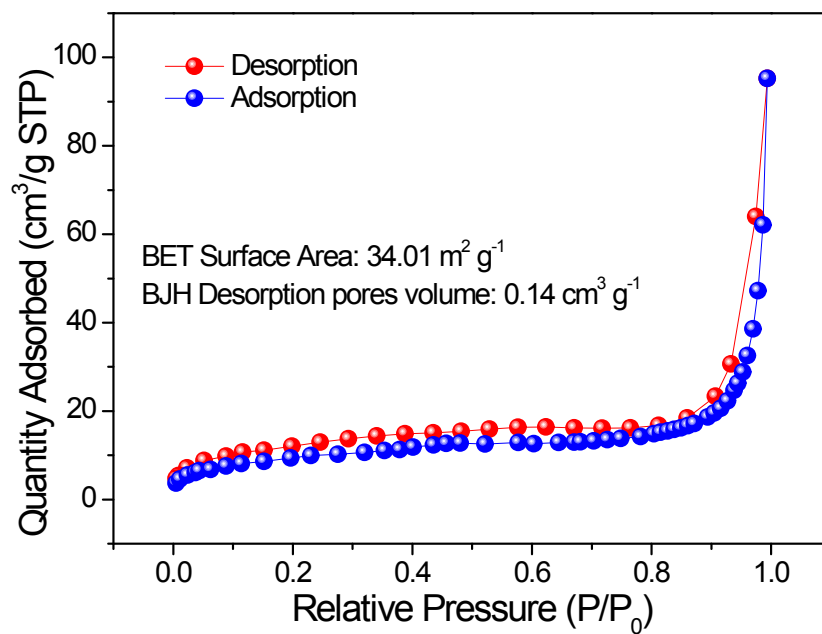


Figure S4. Nitrogen sorption isotherm of PPy hollow nanospheres. The BET surface area and BJH desorption pore volume are listed on the Figure.

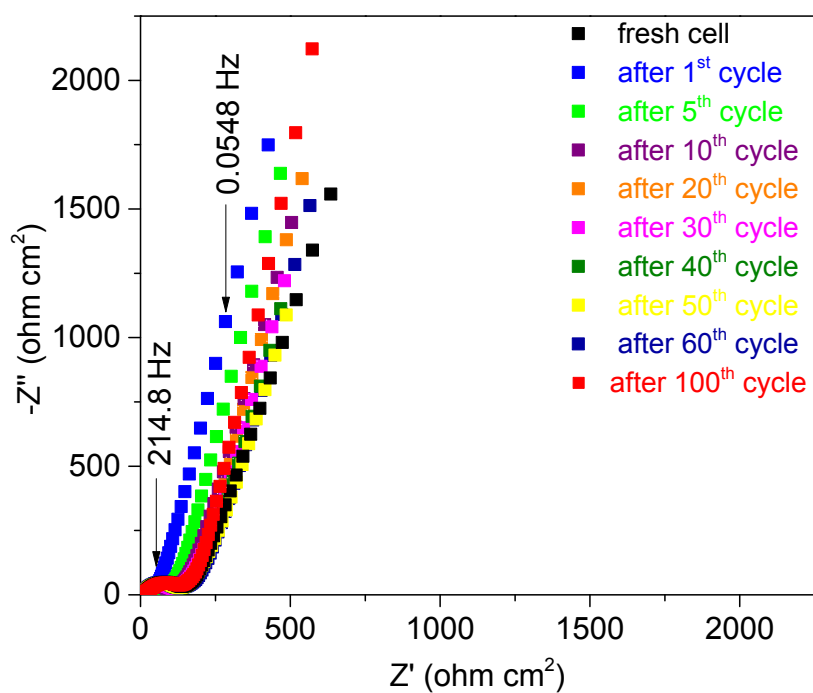


Figure S5. Nyquist diagram of the PPy hollow nanospheres electrode before and after different charge and discharge cycles at 100 mA g⁻¹ current density.

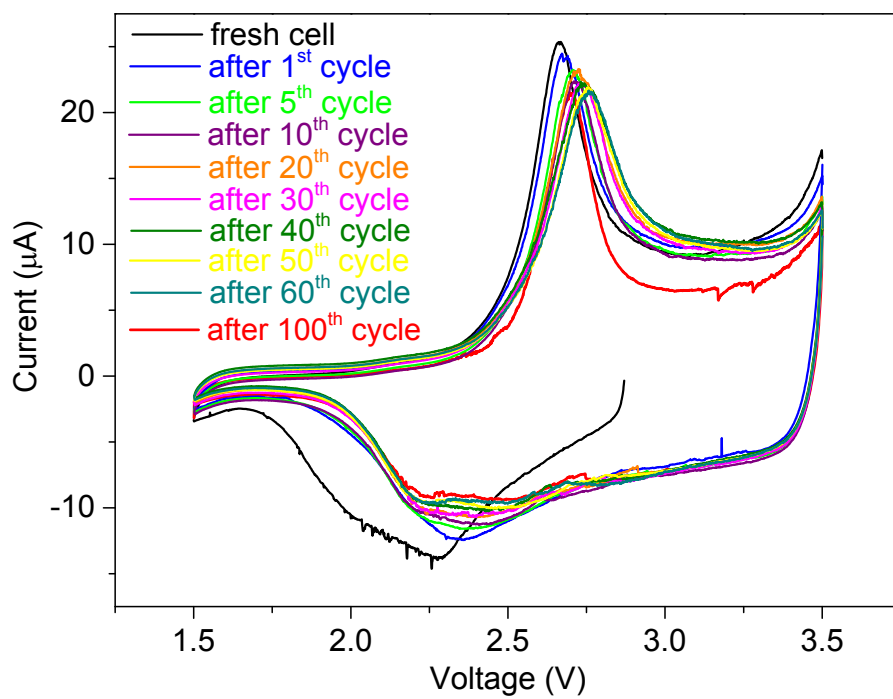


Figure S6. CV curves of the PPy hollow nanospheres electrode before and after different charge and discharge cycles.

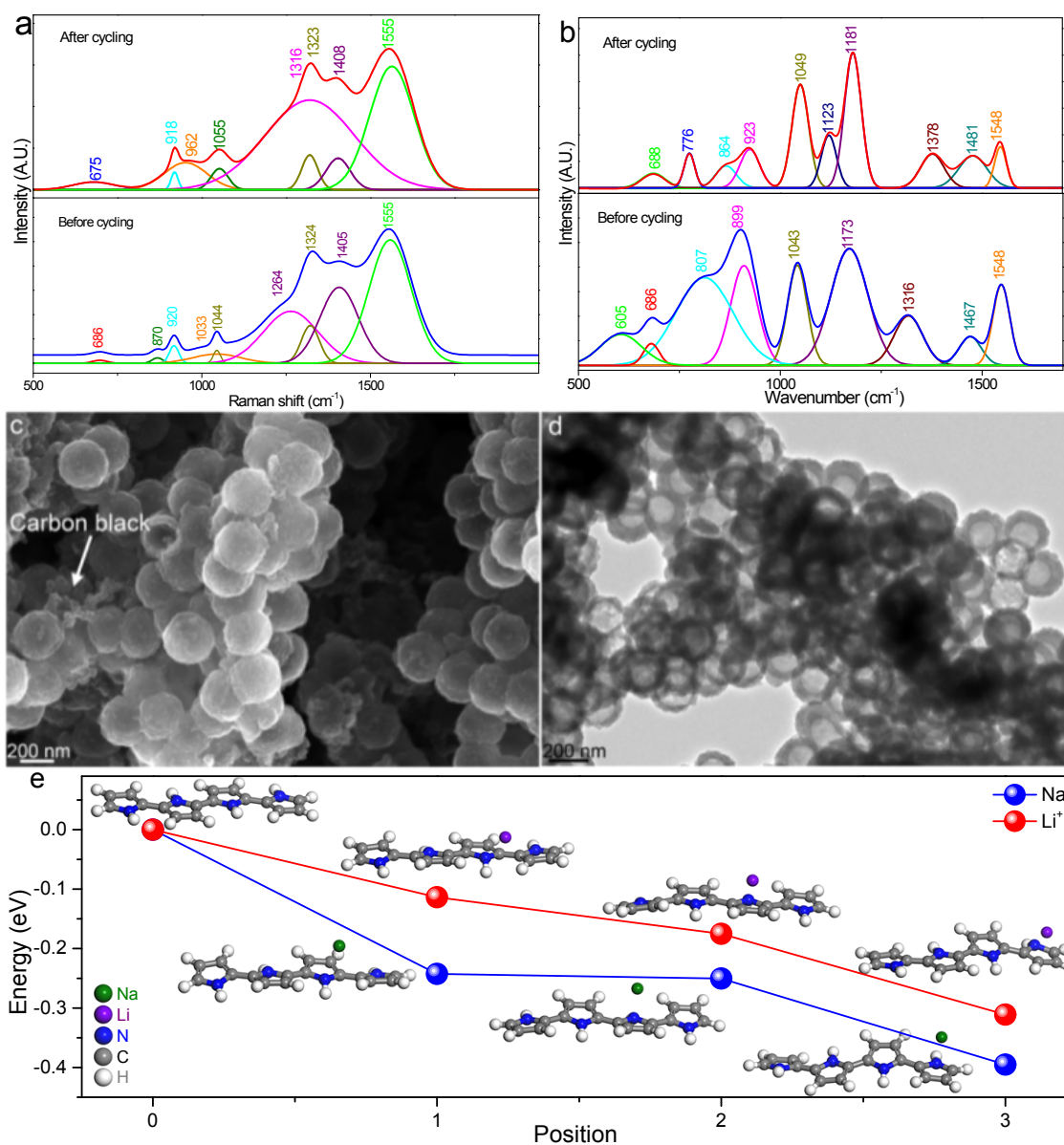


Figure S7. (a) Raman scattering spectra of PPY hollow nanosphere electrodes before cycling and after 100 cycles (charged state). (b) FTIR spectra of PPY hollow nanosphere electrodes before cycling and after 100 cycles (charged state). (c) FESEM image and (d) TEM image of PPY hollow nanosphere electrode after 100 cycles. (e) Energy barriers of sodiated/lithiated PPY with Na/Li ion on different positions.

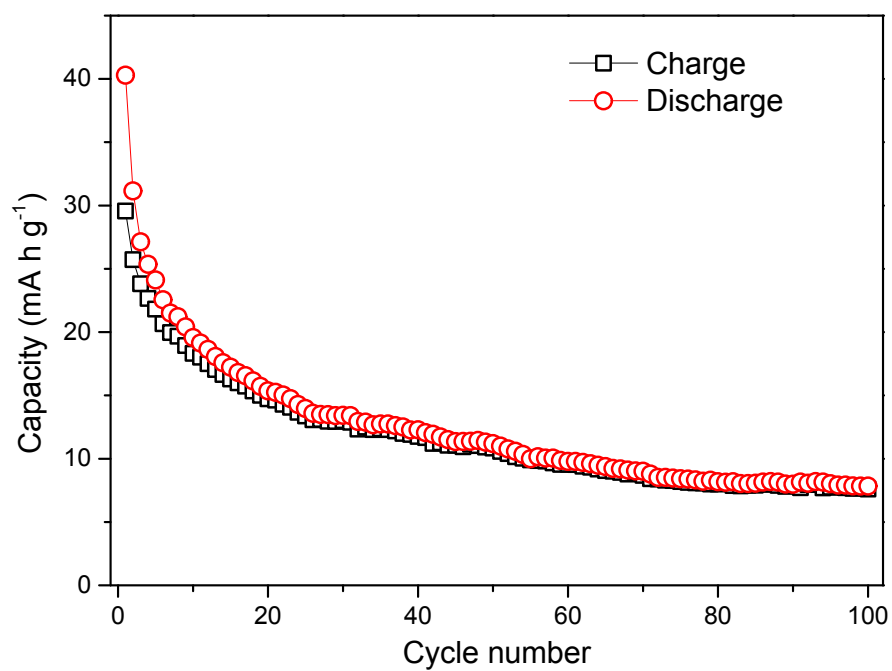


Figure S8. Cycling performance of PPy hollow nanospheres as cathode material for Li-ion battery. Current density: 20 mA g⁻¹