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Supplementary Materials for

Hollow nanoporous red phosphorus as advanced anode for sodium-ion battery

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1 Experimental section

1.1 Material preparation

Phosphorus triiodide (PI_3, 99%, Sigma Aldrich), cetyltrimethylammonium bromide (CTAB, 99%, Aladdin), anhydrous ethylene glycol (99%, Aladdin), ethanol (99.7%, Sinopharm), iodobenzene (98%, Alfa Aesar), commercial red phosphorus powder (98.5%, Aladdin) were used in sample preparation. The HNPRP was prepared with a typical reaction. PI_3 solution in iodobenzene (1.6 M) was injected into CTAB solution in ethlylene glycol (0.018 M) under intense magnetic stirring for 10 min. After the reaction (the solution color did not change any more), the prepared red phosphorus with residual solution was obtained by centrifugation (4000 rpm). And then it was heated in vacuum drying chamber (Jinghong, China) at 200 ℃ for 6 h.

1.2 Materials characterization

The microstructure of the prepared sample was characterized by scanning emission microscope (SEM, HITACHI SU-70), high resolution transmission electron microscope (HRTEM, JEOL JEM-2100). The structure and composition were characterized using X-ray diffraction (XRD, Rigaku Dmax-rc diffractometer), LabRAM HR800 spectrometer for Raman spectra. Emmett–Teller (BET) surface area and pore distribution plots were measured by Micromeritics ASAP 2020.

1.3 Electrochemical characterization

As-prepared active material (HNPRP, RP) was mixed with super P (buy from lzy battery sales department in China) and a carboxymethyl cellulose (CMC) binder (Aladdin) (70 : 15 : 15 in weight) in deionized water to form a homogenous slurry. Then it was painted on a copper foil (lzy battery sales department in China) and then dried at 80 °C under vacuum drying chamber for 10 h to form the electrodes. The total loading mass of the electrode is about 0.786 mg/cm^2, while loading mass of the hollow nanoporous red phosphorus is about 0.55 mg/cm^2. The tap density of the hollow nanoporous red phosphorous is about 0.63 g/cm^3. Na sheet (home-made) was used as the counter electrode, while Celgard 2400 was used as the separator. A mixture of 1 M $NaClO_4$ in propylene carbonate with 5% fluoroethylene carbonate (FEC) additive was used as the electrolyte. All the cells (CR2016 coin-type) (lzy battery sales department in China) were assembled in a glove box with oxygen/water content lower than 1 ppm and tested at room temperature. Cyclic voltammetric (CV) measurements were carried out with the coin cells at a scan rate of 0.1 mV s^{-1} between 0.05 and 2.5 V (vs. Na^+/Na) using a CHI 660E electrochemical workstation (Shanghai, China). Galvanostatic discharge/charge cycles were conducted between 0.01 and 2.0 V (vs. Na^+/Na) on a Neware-CT-3008 test system (Shenzhen, China). Electrochemical impedance spectroscopy (EIS) was also performed on a CHI 660E electrochemical workstation with a frequency of 100 kHz to 0.01 Hz

Supplementary Figure

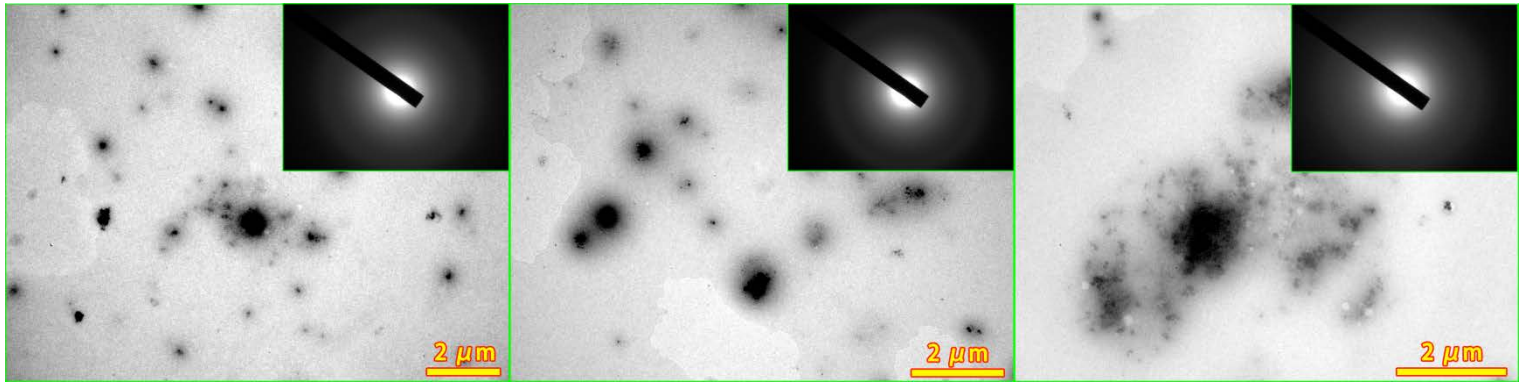

Figure S1 TEM and corresponding SAED images of the iodine-doped RP immersed in the residual solution after centrifugation.