Kirkendall Effect Modulated Hollow Red Phosphorus Nanospheres for High Performance Sodium-Ion Batteries Anodes

Linqin Zhu,† Zixuan Zhu,† Jianbin Zhou,* and Yitai Qian

Department of Chemistry and Hefei National Laboratory for Physical Science at Microscale, University of Science & Technology of China, Hefei, Anhui 230026, P.R. China

Experimental procedures

Synthesis of hollow red phosphorus nanosphere (HRPN)

PCl_5 was purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Mg powder was purchased from Shanghai Maoguo Nanotechnology Co. LTD with two average sizes of Mg powder (~80 nm and ~400 nm). The other chemical reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. All materials are carefully ground in the glove box before being loaded into the Teflon-lined stainless steel autoclave. The Mg powder (0.105 g) was mixed with $AlCl_3$ (3.12g), NaCl (0.43 g) and KCl (0.45 g), and then transferred into a 20 mL Teflon-lined stainless steel autoclave. Subsequently, PCl_5 powder (0.6 g) was added into the autoclave. The above procedure was conducted in a glove-box filled with Ar. The sealed autoclave was heated at 220 ^oC for 60 h. After cooling to room temperature naturally, the as-prepared sample was washed with deionized water and then ethanol for several times to remove impurities. Finally, the product was dried in a vacuum at 80 ºC for 6 h. The contrast experiments were conducted at 220 °C for 12 h, 36 h in the autoclave, respectively.

Characterization

The phase of the as-prepared samples was firstly measured by X-ray diffraction (XRD, Philips, X'pert X-ray diffractometer with Cu Kα, λ=1.54182 Å). The surface chemical content of sample was detected by Raman spectroscopy (Lab-RAM HR UV/VIS/NIR) at 532 nm and X-ray photoelectron spectroscopy (XPS) data were recorded on an ESCA-Lab MKII X-ray photoelectron spectrometer. The morphologies of sample were characterized on scanning electron microscopy (SEM, JEOL-JSM-6700F) and transmission electron microscopy (TEM, Hitachi H7650). High-resolution transmission electron microscopy (HRTEM) images were acquired on a JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. The Brunauer– Emmett–Teller (BET) surface area and pore distribution plots were measured with an ASAP 2020 Accelerated Surface Area and Porosimetry instrument.

Electrochemical characterization

The electrochemical properties of the samples were evaluated through 2016 coin-type half-cells with a separator of glass fiber (GF/D) from Whatman and electrolyte consisting of 1 M $NaClO_4$ in a mixture of ethylene carbonate (EC), diethylcarbonate (DEC) (1:1 by volume) and 5 wt% fluoroethylene carbonate (FEC), the Na metal is utilized as the counter electrode. The cells were assembled in an argon-filled glove box (H_2O, O_2 < 1 ppm). For preparing working electrode, the slurry mixed with the active materials (70 wt%), carbon black (20 wt%) and sodium alginate (SA) binder (10 wt%) in water solvent was coated on a copper foil and dried at 70 °C for 10 h in a vacuum oven. The mass loading of HRPN was 1.26–1.4 mg/cm^2. All the galvanostatic charge/discharge tests were conducted on a battery tester (LANDCT2001A) at different current densities in the voltage window of 0.01-2.0 V and the cyclic voltammograms tests were

using a CHI660D electrochemical workstation at room temperature in the voltage windows of 0.01-2.5 V at a scan rate of 0.1 mV/s.

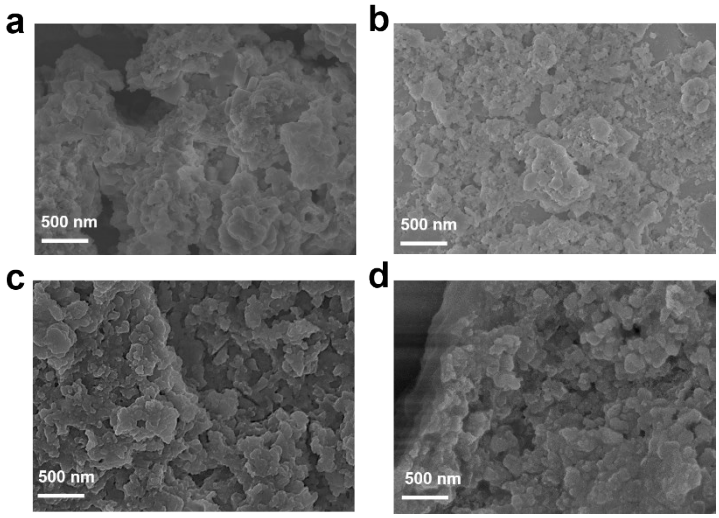

Fig.S1 SEM images of the HRPN synthesized by molten salts process with different reaction times of 0 hours (a), 12 hours (b), 36 hours (c) and 60 hours (d) after water washing.

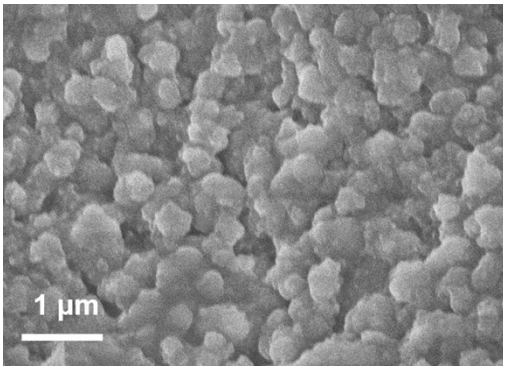

Fig.S2 The SEM of phosphorus synthesized by larger size magnesium powders (~400 nm).

Table S1. The yield of HRPN

Experiment number	theoretical product quantity(mg)	Actual product quantity(mg)	Yield
1	89.24	50.31	56.37%
2	89.24	49.73	55.69%
3	89.24	50.11	56.14%