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Supporting Information

In-situ Formation of Highly Controllable and Stable Na_3PS_4 as Protective Layer for Na Metal Anode

Yang Zhao[1+], Jianwen Liang[1+], Qian Sun[1], Lyudmila V. Goncharova[2], Jiwei Wang[1], Changhong Wang[1], Keegan R Adair[1], Xiaona Li[1], Feipeng Zhao[1], Yipeng Sun[1], Ruying Li[1], Xueliang Sun[1]*

[1] Department of Mechanical and Materials Engineering
University of Western Ontario, London, Ontario, N6A 5B9, Canada
**E-mail: xsun@eng.uwo.ca (X.L. Sun)*
[2]Department of Physics and Astronomy
University of Western Ontario, London, Ontario, N6A 3K7, Canada
[+]Dual Contributors

Experimental section

Preparation of Na@NaPS: The typical P_4S_{16} was synthesized by using the previous report [1]. The Na_3PS_4 protective layers were fabricated by the in-situ solution-based method. All the experiment were performed in the Ar-filled glove box (H_2O and O_2 < 0.1 ppm) to prevent the effects from the moisture and oxygen. Typically, the P_4S_{16} powders with controllable amount (10 mg, 20 mg, and 30 mg) were dissolved in 20 mL solvent of diethylene glycol dimethyl ether (DEGDME) with the calculated concentration of 0.5, 1 and 1.5 mg mL^{-1}. The prepared P_4S_{16}-DEGDME solutions were kept in glove box for more than 3 day to obtain the clear liquid with complete dissolution. A fresh Na foil with the diameter of 3/8 inch was prepared with the aid of a homemade press machine by pressing a piece of sodium metal stick (from Aldrich) as a starting sodium metal. Then, a piece of Na foil and 1 mL of P_4S_{16}-DEGDME solutions (with different concentrations) were added into a reactor with the controlled reaction times (15 min, 60 min and 90 min). After reaction, the coated Na foil was taken out from the solution and transferred into the heating chamber connected with glove box. The coated Na foil was dried at 80 ^oC for 2 h to remove the residual solvent of DEGDME. The experiment design of different P_4S_{16} concentration and reaction time are shown in **Table. S1**.

Electrochemical measurements: The electrochemical analysis was performance in CR2032 coin-type cells. The coin cells were assembled in an ultra-pure argon filled glove box by symmetrical Na/Electrolyte-Separator/Na configuration using polypropylene separators (Celgard 3501). The electrolyte used in this study is 1 M sodium hexafluorophosphate ($NaPF_6$ 98%, Aldrich) dissolved in ethylene carbonate (EC) and propylene carbonate (PC) with volume ratio of 1:1. The Na stripping/plating studies were carried out in a Land Battery Test System at room temperature. Constant current densities were applied to the electrodes during repeated stripping/plating while the potential was recorded over time.

To investigate the full cell performances, the carbon coated $NaCrO_2$ ($NaCrO_2$/C) was synthesized by solid-state reaction as described previously [2-3]. The $NaCrO_2$/C electrodes were prepared by casting a dimethylformamide (DMF) slurry containing $NaCrO_2$/C, Super P and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 onto carbon-coated Al foil. The cathodes were cut into discs with a diameter of 10 mm and dried at 80 ^{o}C prior to use. The areal loading of $NaCrO_2$/C is about 6-8 mg. The full batteries were tested also via CR2032 cells using Na@NaPS-3 as anode and $NaCrO_2$/C as cathode in a Land Battery Test System at room temperature. The electrolyte used in full cells was 1 M sodium perchlorate ($NaClO_4$, Aldrich) dissolved in propylene carbonate (PC) with 2 % of fluoroethylene carbonate as additive.

Characterization: The cells were disassembled after stripping/plating process in the Ar-filled glove box and then the cycled Na foil was put into the solvent of dimethyl carbonate (DMC) to remove the electrolyte components from the surface of Na foil. After that, the Na foils were cut using scissor for the cross-section view SEM measurement. The prepared samples of Na foil were sealed with the Ar-filled tubes before characterization and then transferred to the SEM chamber with minimize air-exposure. SEM images were taken using a Hitachi 3400N Environmental Scanning Electron Microscopy at an acceleration voltage of 5 kV. The Na foil and Na@NaPS-3 (after plating/stripping) are transferred from our ALD glove box directly to an Ar glovebox connected XPS (Kratos AXIS Ultra Spectrometer) system for XPS analysis in the Surface Science Western. Rutherford Backscattering Spectrometry measurements were conducted using 2.5 MeV

He^+ beam (Western Tandetron Facility) at several locations on the surface to confirm the uniformity of the thicknesses and composition. All samples were transferred in Ar-filled glove bag with minimum exposure to air. A Sb-implanted amorphous Si sample with a known 4.82×10^{15} atoms /cm^2 Sb content used for calibration. The ToF-SIMS measurements were conducted using an ION-TOF (GmbH, Germany) ToF-SIMS IV with a bismuth liquid metal ion source. The base pressure of the analysis chamber was $\sim 10^{-8}$ mbar. The action of the primary ion beam bombardment on the sample surface induces the emission of negative secondary ions. The analysis area was 334×334 μm^2. Sputtering with a Cs^+ ion beam (3 keV) was used for depth profiling analysis with the sputtering areas of 100×100 μm^2.

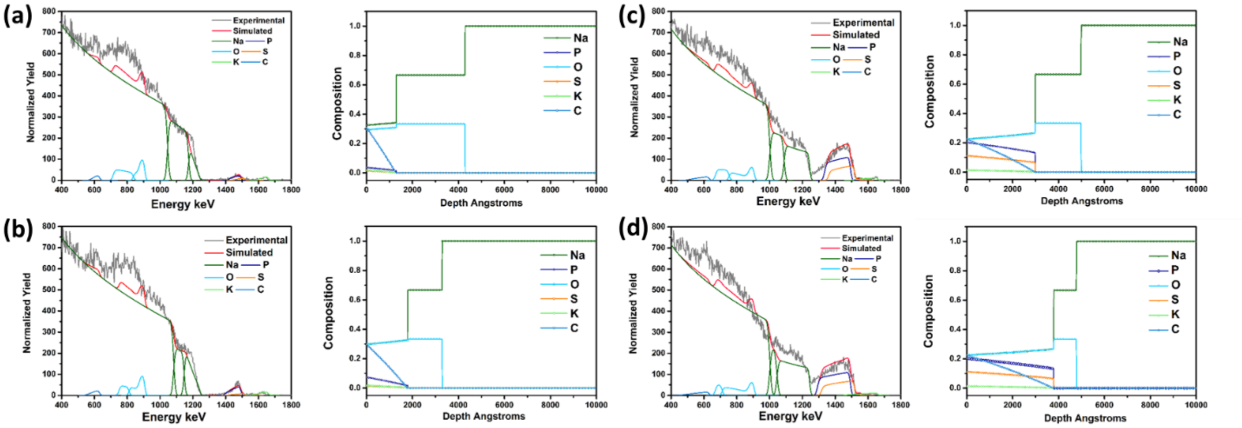

Figure S1 RBS spectra and calculated depth profiles of Na@NaPS-1 (a), Na@NaPS-2 (b), Na@NaPS-4 (c) and Na@NaPS-5 (d).

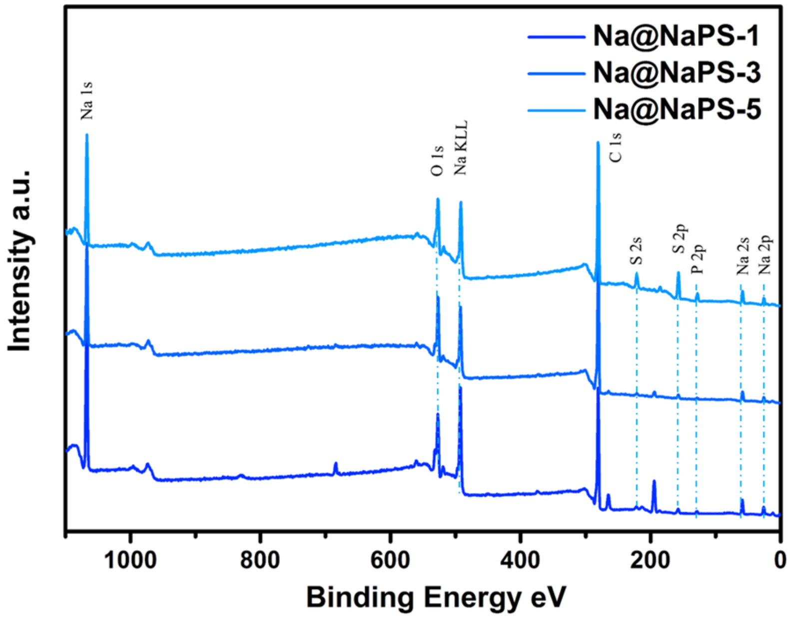

Figure S2 XPS spectra of Na@NaPS-1, Na@NaPS-3 and Na@NaPS-5.

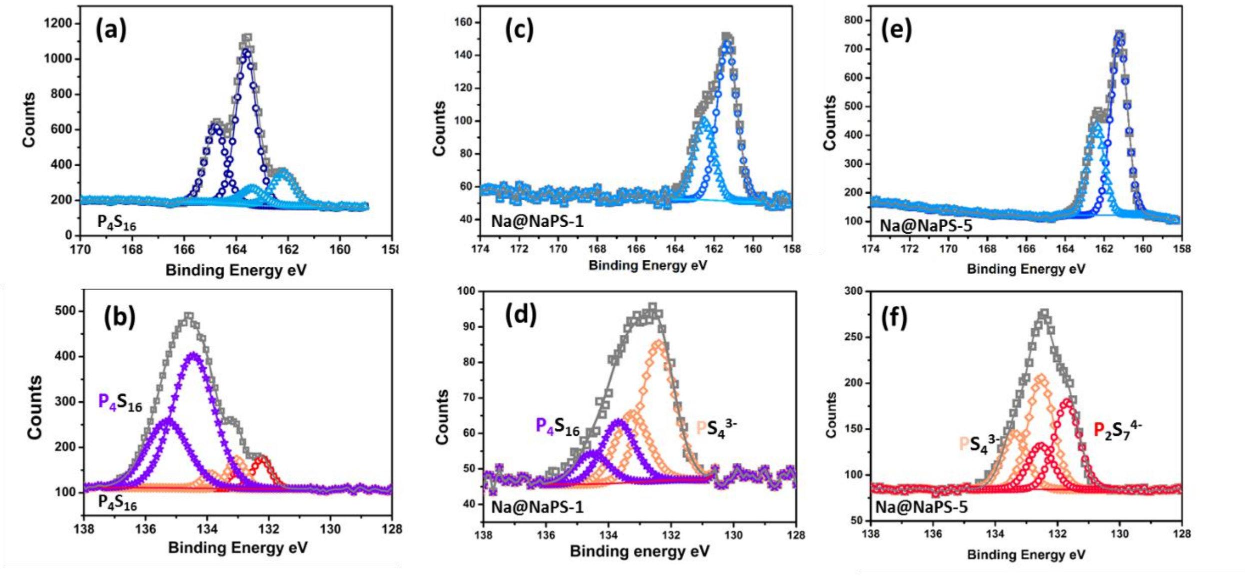

Figure S3 XPS S 2p spectrum of P_4S_{16} (a), Na@NaPS-1 (c) and Na@NaPS-5 (e); XPS P 2p spectrum of P4S16 (b), Na@NaPS-1 (d) and Na@NaPS-5 (f).

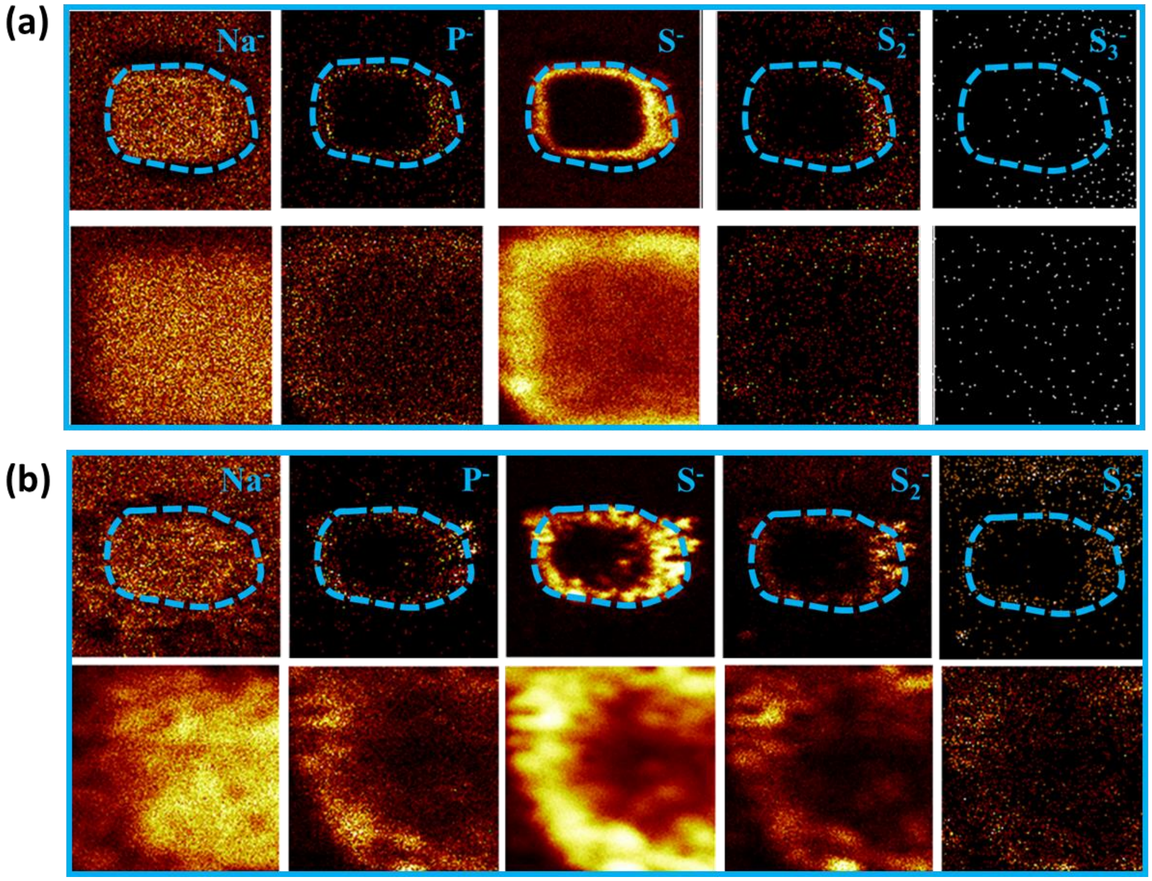

Figure S4 TOF-SIMS chemical ion images of the Na^-, P^-, S^-, S_2^-, S_3^- species for Na@NaPS-1 (a) and Na@NaPS-5 (b). The analysis area was 334 × 334 μm^2 and the sputtering areas of 100 × 100 μm^2.

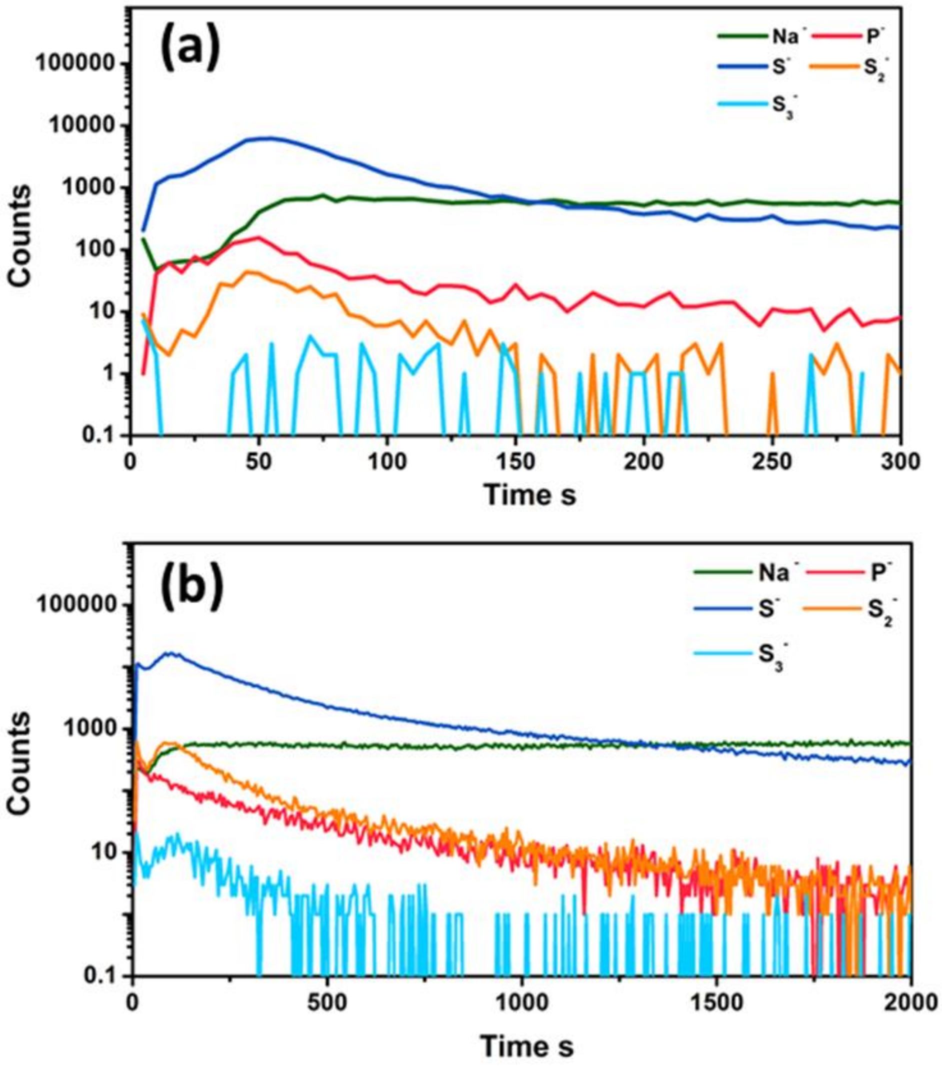

Figure S5 TOF-SIMS depth profiles of Na^-, P^-, S^-, S_2^-, S_3^- species for Na@NaPS-1 (a) and Na@NaPS-5 (b).

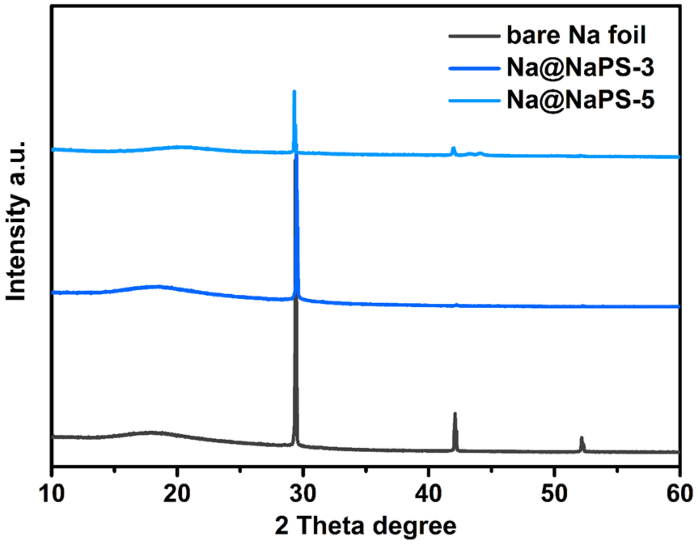

Figure S6 XRD patterns of bare Na, Na@NaPS-3 and Na@NaPS-5.

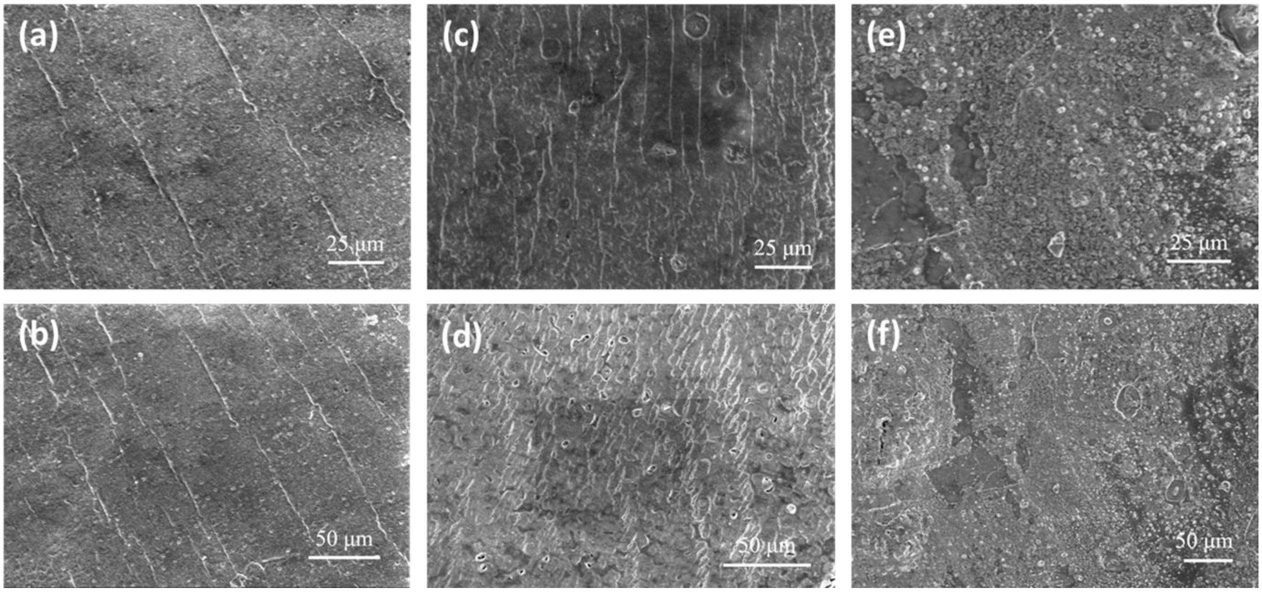

Figure S7 Top-view SEM images of Na@NaPS-1 (a, b), Na@NaPS-3 (c, d) and Na@NaPS-5 (e, f).

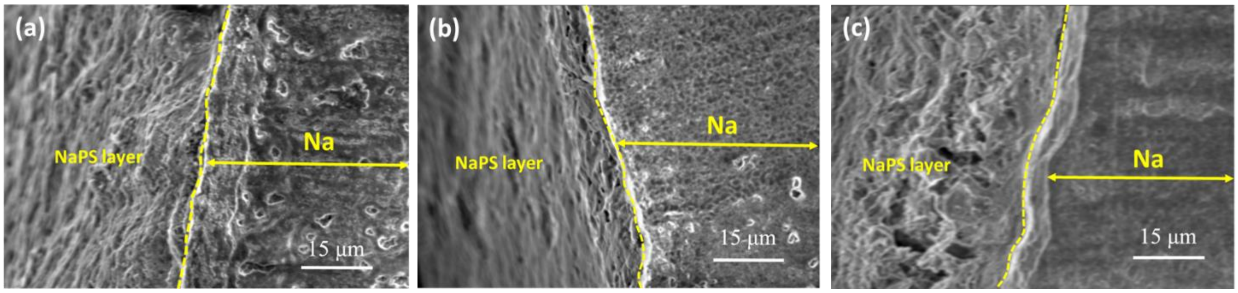

Figure S8 Cross-section view SEM images of Na@NaPS-1 (a), Na@NaPS-3 (b) and Na@NaPS-5 (c).

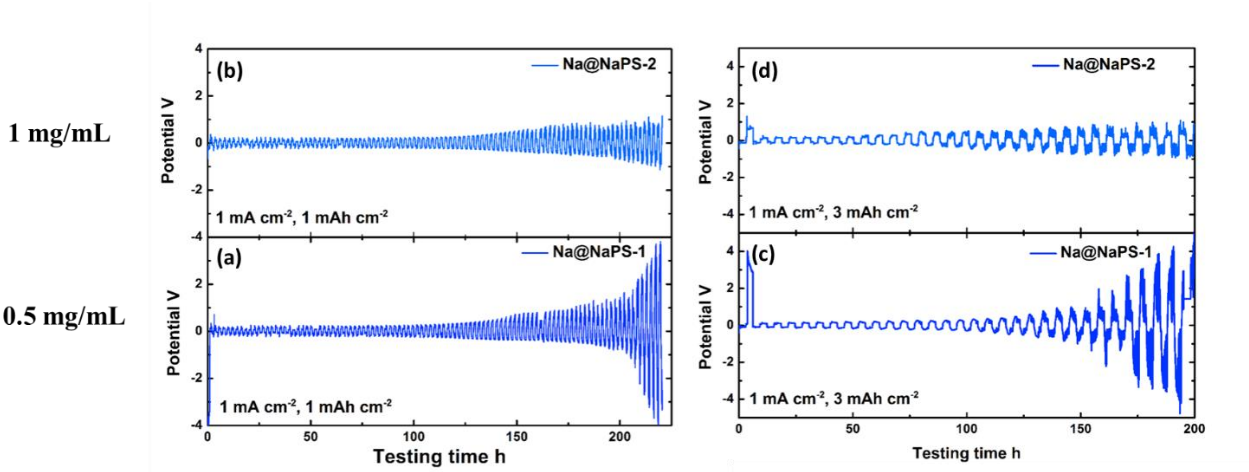

Figure S9 Comparison of the cycling stability of Na@NaPS-1 (a) and Na@NaPS-2 (b) at the current density of 1 mA cm^{-2} with the capacity 1 mAh cm^{-2}; Comparison of the cycling stability of Na@NaPS-1 (c) and Na@NaPS-2 (d) at the current density of 1 mA cm^{-2} with the capacity 3mAh cm^{-2}.

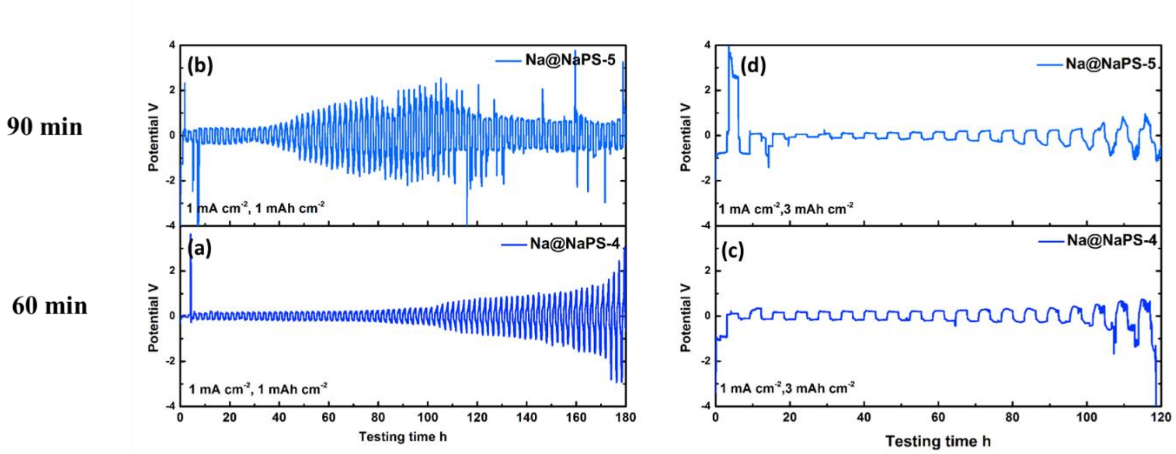

Figure S10 Comparison of the cycling stability of Na@NaPS-4 (a) and Na@NaPS-5 (b) at the current density of 1 mA cm^{-2} with the capacity 1 mAh cm^{-2}; Comparison of the cycling stability of Na@NaPS-4 (c) and Na@NaPS-5 (d) at the current density of 1 mA cm^{-2} with the capacity 3mAh cm^{-2}.

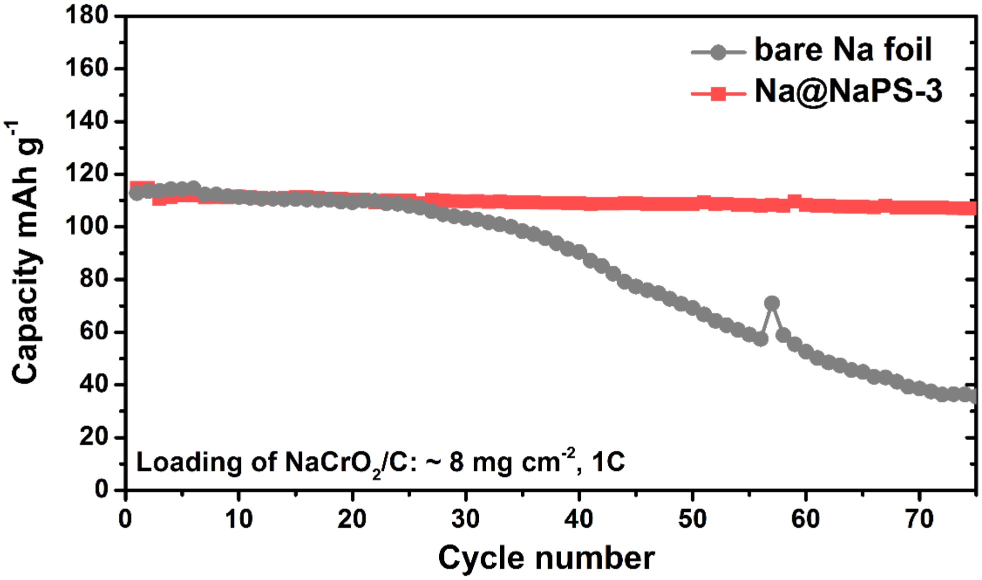

Figure S11 Cycling performance of full cells ($NaCrO_2$/C as cathode) using bare Na foil and Na@NaPS-3 at 1 C. The loading of $NaCrO_2$/C is about ~8 mg cm^{-2}, corresponding to the areal capacity of ~1.1 mAh cm^{-2}.

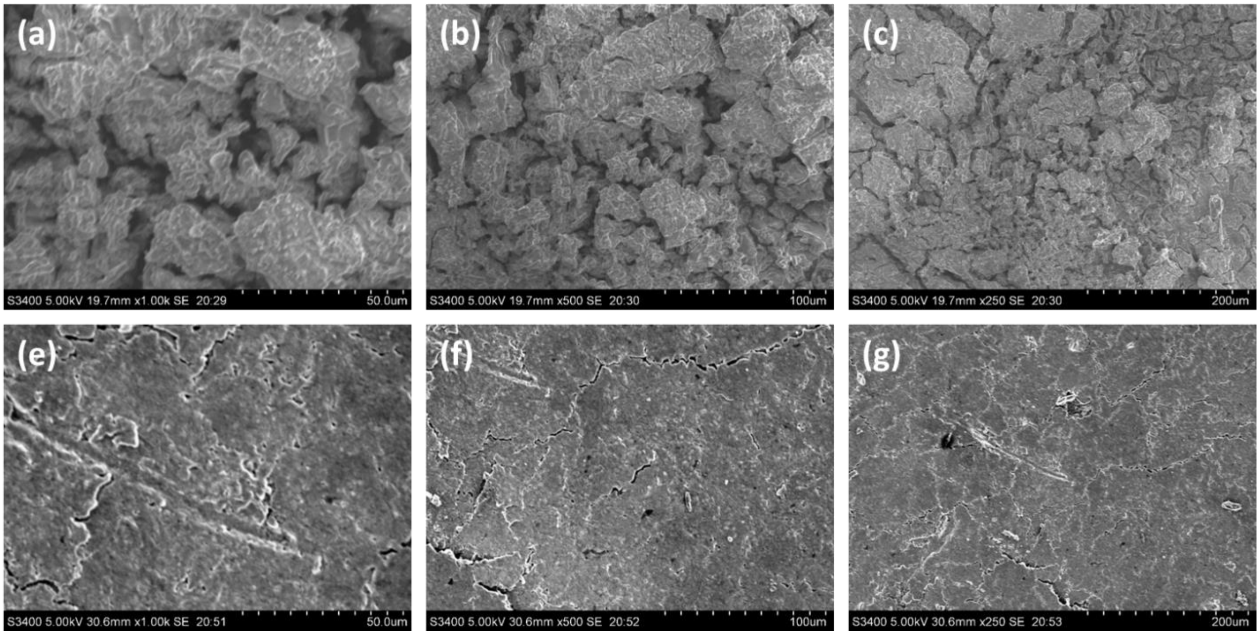

Figure S12 Top-view SEM images of the bare Na foil (a-c) and Na@NaPS-3 (e-g) after 10 cycles of stripping/plating at a current density of 1 mA cm^{-2} with the capacity of 1 mAh cm^{-2}.

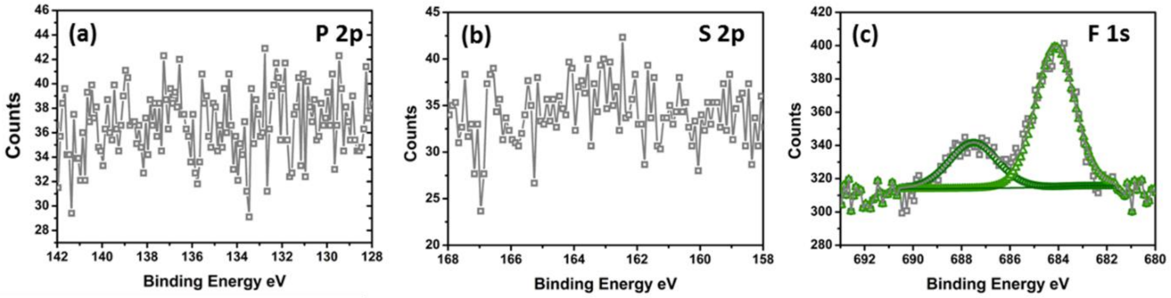

Figure S13 XPS spectra and P 2p (a), S 2p (b) and F 1s (c) spectrum of bare Na foil after cycling.

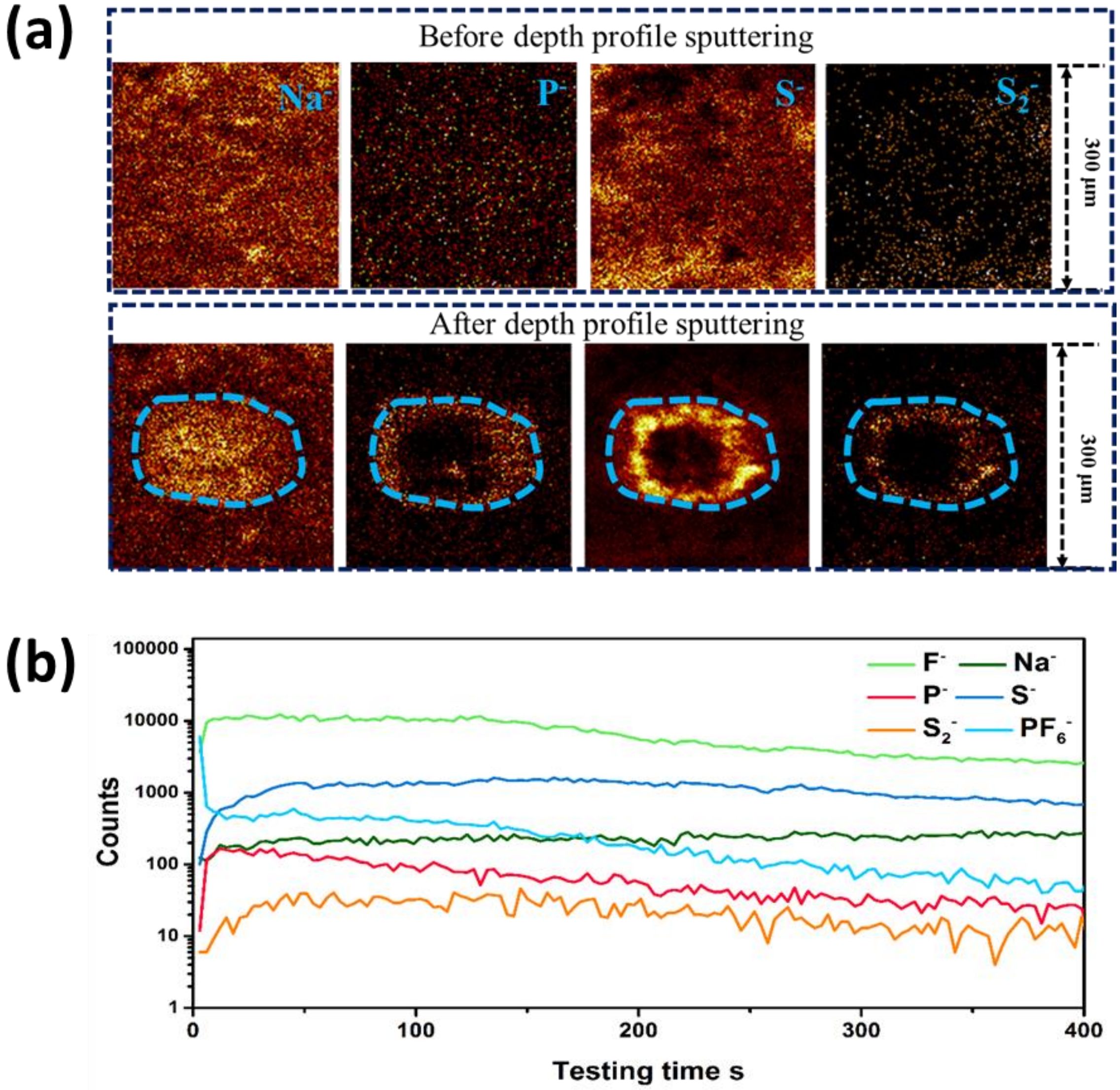

Figure S14 (a) TOF-SIMS chemical ion images of the Na^-, P^-, S^-, and S^{2-} species for Na@NaPS-3 after cycling (Blue circles correspond to the sputtering areas); The analysis area was 300 × 300 μm2 with a sputtering area of 100 × 100 μm^2; (b) TOF-SIMS depth profiles of F^-, Na^-, P^-, S^-, S^{2-} and PF^{6-} species for Na@NaPS-3 after cycling. All the cells are tested at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2}.

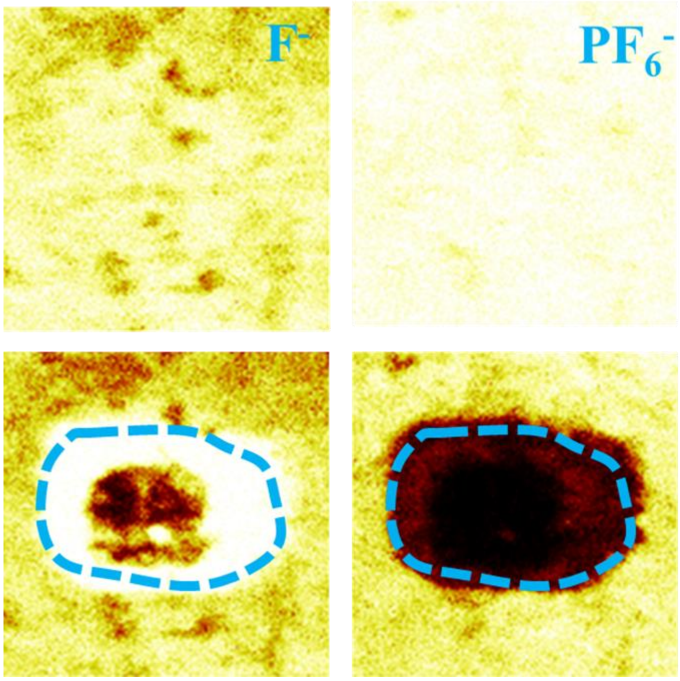

Figure S15 TOF-SIMS chemical ion images of the F^- and PF_6^- species for Na@NaPS-3 after cycling. The analysis area was 300 × 300 μm^2 and the sputtering areas of 100 × 100 μm^2.

Table S1 Experimental design to control the factors of precursor concentration and reaction time

	P_4S_{16} concentration	Reaction time
Na@NaPS-1	0.5 mg/ml	15 min
Na@NaPS-2	1 mg/ml	15 min
Na@NaPS-3	1.5 mg/ml	15 min
Na@NaPS-4	1.5 mg/ml	60 min
Na@NaPS-5	1.5 mg/ml	90 min

Table S2 Compositions of P and S in different samples based on XPS results

	P At% (XPS)	S At% (XPS)
Na@NaPS-1	0.9 %	1.2 %
Na@NaPS-3	0.5 %	1.4 %
Na@NaPS-5	6.0 %	2.4 %

References

[1] Angew. Chem. Int. Ed., 2017, 56, 2937 –2941

[2] Electrochemistry Communications, 2012, 22, 85–88

[3] Energy Environ. Sci., 2015, 8, 2019