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Carbon coated bimetallic sulfide hollow nanocubes as advanced sodium ion battery anode

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Abstract

Sodium ion battery (SIB) as next-generation battery has been drawing much attention due to the abundance and even distribution of sodium source. Metal sulfides with high theoretical capacity and good electrical conductivity are promising anode candidates for SIB, however, the structural collapse caused by severe volume change during the de/sodiation process typically resulted in a fast capacity decay, limited rate capability and cycling stability. In our work, by careful composition and structure design, poly-dopamine coated Prussian blue analogues derived carbon coated bimetallic sulfide hollow nanocubes (PBCS) were prepared with distinguished morphology, higher surface area, smaller charge transfer resistance and higher sodium diffusion coefficient than the uncoated bimetallic sulfides (PBS). An optimum carbon coated bimetallic sulfide hollow nanocube anode delivers a specific capacity of ~ 500 mAh/g at 50 mA/g with EC/DMC (ethylene carbonate/dimethyl carbonate 1:1 vol%) electrolyte in the presence of fluoroethylene carbonate additives. A capacity of 122.3 mAh/g can be realized at 5000 mA/g, showing good rate performance. In addition the carbon coated bimetallic sulfide hollow nanocubes can maintain capacity of 87 mAh/g after being cycled at 500 mA/g for 150 times,, indicating its good cycling stability. The structure integrity, high

specific capacity, good rate performance and cycling stability of PBCS render it a promising anode material for advanced SIB.

1. Introduction

Lithium ion batteries (LIB) have been dominating the energy storage market owing to the high energy density with extended cycle life.^[1] However, the demand for Li source is ever increasing, with Lithium reserve of only 20 ppm in earth crust, thus the price of Li carbonates has tripled since 2000s.^[2, 3] It is even predicted that the lithium source may deplete in the near future.^[2, 4] Hence, it is of importance to unleash alternatives beyond Li ion batteries. Sodium as an alkaline metal, shows similar electrochemical behavior with Li, despite that the energy density of Sodium ion batteries (SIB) is compromised due to the higher standard potential ($E^0_{\text{Na/Na}^+} = -2.71 \text{ V}$, $E^0_{\text{Li/Li}^+} = -3.04 \text{ V}$ versus standard hydrogen electrode) and the heavier and larger Na ions.^[2, 5, 6] The price of sodium carbonates is only around one twentieth of the lithium carbonates, with 100 times higher abundance on earth crust, as a result the specific cost /Ah of SIB is estimated to be 10 times lower than that of LIB counterparts, thus sodium ion batteries are highly attractive for stationary applications, where energy density is not critical.^[2, 3, 5-7] In SIB, many developments have been made at the cathode, including sodium layered oxides,^[8] phosphates,^[9, 10] Prussian blue analogues,^[11, 12] etc. It was reported that carbon coated $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode can realize a power density that outperforms the carbon coated LiFePO_4 based LIB.^[13] However, the anode still needs to be further developed as the typical graphitic carbons anode in LIB cannot intercalate Na^+ ions.^[5, 14]

Instead of typical graphite, hard carbon and expanded graphite have been developed to be applied as anode materials for SIB with enhanced specific capacity.^{[15] [16]} However, the achievable capacity is limited to lower than 300 mAh/g even at a low current density. Metal sulfides as anode materials have high theoretical capacity and good electronic conductivity,

delivering capacity higher than the carbon (hard carbon or expanded graphite) anode.^[17, 18] Nonetheless, the main issue of metal sulfides as anode is the severe volume expansion or shrinkage caused by sodiation/desodiation during electrochemical tests, leading to limited capacity, rate performance and cycle life.^[19] One way to overcome this problem is to introduce carbon-based materials, which can improve the electronic conductivity as well as to buffer the stress caused by volume changes, thus enhancing both the cycling stability and rate performance.^[20-22] For example poly-dopamine (PDA) coating has been shown to be effective in providing a carbon layer to protect the electrodes.^[23, 24] The second way is to design hierarchical nanostructures with hollow interiors, which can provide internal space for the volume expansion, thus enhancing the cycling stability.^[25] The other way is to employ bimetallic sulfides which exhibit richer redox/conversion reactions compared with monometallic sulfides, the formation of separated nanoscopic structures of metal sulfides has a buffering effect in the first cycle, leading to enhanced capacity and cycling stability.^[26]

Prussian blue analogues with divalent and trivalent metal ions bridged by the linear $\text{-C}\equiv\text{N-}$ anions have a three dimensional open framework with large interstitial sites, providing pathways for Na^+ conduction, thus it has been applied as cathode materials for SIB.^[11, 27, 28] Moreover, Prussian blue analogues can easily form a nanocube morphology in the preparation process, thus it is also widely applied as a precursor for the preparation of other functional materials.^[11] NiS nano-frames derived from NiCo Prussian blue analogues can deliver high specific capacitance of $\sim 1400 \text{ F/g}$ at 4 A/g and gave good cycling stability when applied as supercapacitor material.^[29] $\text{Co}_{0.59}\text{Fe}_{0.41}\text{P}$ nanocubes prepared by the phosphidation of CoFe Prussian blue analogues were reported to deliver good performance in both acid and alkaline solutions when applied as hydrogen evolution catalysts.^[30]

Based on the above discussions, we design the carbon coated bimetallic sulfide hollow nanocubes resembling the morphology of the Prussian blue precursors in which the Prussian

blue analogue precursors were coated by PDA for sulfidation. The higher electronic conductivity of metal sulfides compared with metal oxides was harnessed in this work,^[18] the hollow nanocubes can provide a rigid structure with internal space for the de/sodiation induced volume changes and high surface area for electrolyte uptake, which is beneficial to realizing better electrochemical performance than one-dimensional nanostructures.^[31] and Compared to the non-carbon coated bimetallic sulfides, the carbon coated bimetallic sulfide hollow nanocubes possess higher surface area, smaller charge transfer resistance and higher diffusion coefficient, allowing it to endure the volume change and facilitate charge transfer/storage process during the electrochemical testing. As a result, the optimum carbon coated bimetallic sulfide hollow nanocubes delivers a high capacity of ~500 mAh/g at a current density of 50 mA/g; even at a high current density of 5 A/g, a capacity of more than 100 mAh/g can be retained. Furthermore, a capacity of 87 mAh/g can be obtained after being cycled for 150 times at 500 mA/g, showing superior electrochemical performance than the non-carbon coated bimetallic sulfides.

2. Result and Discussion

PB precursors with different Co: Fe feeding ratios were prepared and characterized by XRD and SEM. As seen from Figure S1, PB precursors with cubic crystal structure were successfully prepared with nanocube morphology. After sulfidation process, PB precursors were transformed into sulfides. As shown in **Figure 1a**, the XRD diffraction patterns of PB3-1S can be ascribed to a mixture of sulfides including bimetallic sulfides Co_8FeS_8 (cubic #029-0484) and monometallic sulfides Co_4S_3 (hexagonal, #002-1458); Co_3S_4 (cubic, #042-1448) and Fe_9S_{10} (hexagonal, #035-1043). Based on the relative intensity of the diffraction peaks, it is evident that the bimetallic sulfide Co_8FeS_8 is the major component in the product. By introducing a layer of PDA, after the same sulfidation process the PDA coated PB3-1 precursor was transformed into PBC1-1S, of which the XRD patterns resemble that of PB3-

1S, indicating that carbon coating does not affect the composition of the sulfidized products. The morphology of PB3-1S and PBC1-1S was revealed by SEM, as seen in Figure. 1b-c, the PB3-1 nanocubes without PDA coating decomposed into randomly distributed particles. On the other hand, with a layer of PDA coating the nanocube morphology can be retained after the sulfidation process. PBC1-1S was also characterized by TEM, as shown in Figure 1d. It is clearly seen that the nanocube morphology can be retained with size of ~ 100 nm, the higher transmittance at the interior of the nanocubes is indicative of the porous and hollow nature, which is expected to exhibit higher porosity. From the high resolution TEM image, the lattice d-spacings were measured to be ~ 0.57 nm, which is predominantly observed and is associated with the preferred orientation of (111) crystal planes of Co_8FeS_8 . This observation of predominantly Co_8FeS_8 crystals also reflect the majority phase is Co_8FeS_8 in the product. The presence of amorphous carbon coatings can also be confirmed from the HRTEM image, the amorphous carbon is coated on the surface of nanocubes with the thickness of more than 4 nm. The hollow nature of the nanocubes can also be confirmed from the high resolution TEM images in the insets of Fig. S3b-c. The multiphases of sulfides are randomly distributed as can be confirmed from Fig. S3a, with lattice fringes of various d-spacing values correspond to the different crystal planes of the sulfides.

N_2 -sorption isotherms of PB3-1S and PBC1-1S were measured to quantify the specific surface area and porosity of the samples. As seen in **Figure 2a**, only limited amount of N_2 can be ad/desorbed by PB3-1S even at high pressure, while for PBC1-1S the quantity of N_2 ad/desorbed is larger, exhibiting a typical IV type isotherms.^[32] The surface area and total pore volume of PBC1-1S calculated by Brunauer–Emmett–Teller (BET) method were $25.45 \text{ m}^2/\text{g}$ and $0.0665 \text{ cm}^3/\text{g}$ respectively, which is much higher than those of PB3-1S ($1.79 \text{ m}^2/\text{g}$ and $0.0023 \text{ cm}^3/\text{g}$). The pore size distribution of PB3-1S and PBC1-1S can be seen from the inset in Figure 2a, it is found that PB3-1S hardly exhibits any porous structure, in line with

the random isolated particles observed by FESEM (Figure 1b). With carbon coating, PBC1-1S possesses large amount of mesopores with size of less than 50 nm, which is due to the hollow nature of the carbon coated nanocubes. The higher surface area and pore volume of PBC1-1S is beneficial for electrolyte penetration, which is expected to deliver better electrochemical performance.^[10, 33] The Raman spectrum of PBC1-1S was also measured and collected as in Figure 2b. It can be seen that two main peaks located at wavenumber of around 1360 cm^{-1} and 1572 cm^{-1} respectively, corresponding to the D (disorder) band and G (graphitic) band, confirming the presence of carbon coating on the bimetallic sulfide hollow nanocubes.^[18, 34] The intensity ratio between the D band and G band is indicative of defect ratio. The higher intensity of D band indicates large amount of defects in the carbon coating, in line with the C-N bond detected as seen in Figure S4c. X-ray photoelectron spectroscopy technique was applied to reveal the chemical bonds in PB3-1S, as displayed in Figure 2c-d. In the Co 2p spectrum, the extensive broadening is caused by multiple splitting and the two doublets can be deconvoluted with shakeup satellites. The peaks located at 780.5 eV, 797 eV are characteristic of Co $2p_{3/2}$ and Co $2p_{1/2}$ of Co^{2+} (typical of Co-S bond).^[35, 36] The peaks located at 778.5 eV, 794 eV can be associated with the Co $2p_{3/2}$ and Co $2p_{1/2}$ of Co^{3+} . The peak separation between Co $2p_{3/2}$ and Co $2p_{1/2}$ is about 14.5 eV, and presence of a pair of satellite peaks in the high binding energy side (marked as sat in figure) indicates that few Co^{2+} cations occupy octahedral coordination and majority are likely Co^{3+} in the octahedral sites.^[37] Likewise, the Fe 2p spectrum can also be deconvoluted into two doublets with shakeup satellite peaks. The peaks located at binding energy of 708.8 eV and 722.5 eV suggest the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of Fe^{2+} (typical of Fe-S bond), the other two peaks located at 710.5 eV, 724.2 eV correlate with the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ of Fe^{3+} .^[21] The intense satellite structure (marked as sat in figure) is assumed to be a direct consequence of the band structure associated with octahedral Fe^{2+} in the sulfide lattice, which allows for admixture of sulfur 2p character.^[37]

The S 2p spectrum of PB3-1S can be found in Figure S4d, which can be splitted into two peaks located at 162.6 and 163.5 eV, corresponding to S 2p_{1/2} and S 2p_{3/2}.^[18, 36] The exact identification of the chemical environment of S in the bimetallic sulfide is extremely difficult due to the close electronegativity of Co (1.88 eV) and Fe (1.83 eV). In comparison to other bimetallic sulfide (CoxMoyS),^[38] in which splitting in the XPS spectrum of S2p can be seen due to the large electronegativity difference (Mo-S and Co-S), there is no peak splitting of S2p in the sample PB3-1S due to the negligible electronegativity differences between Co-S and Fe-S, possibly forming polar covalent bond. The Co 2p, Fe 2p and S 2p spectra of PBC1-1S resemble those of PB3-1S, indicating similar chemical environment for the elements.

The selection of samples was based on the optimization of electrochemical performance, which are PB3-1S and PBC1-1S, respectively. The electrochemical performance optimization can be found in Figure S5 and Figure S8. Due to the higher diffusion coefficient, PB3-1S delivers the best rate performance than the other bimetallic sulfides with different Co : Fe feeding ratios. After carbon coating, PBC1-1S shows the better rate performance with the smallest charge transfer resistance. It should be noted that the electrochemical performance evaluation of PBC1-1S was based on the total weight of active materials including the carbon layer, which is ~ 24 wt. % according to the thermal gravimetric analysis in Figure S6. CV curves were tested to investigate the electrochemical behavior of the sulfidized products PB3-1S and PBC1-1S as anodes for SIB, as shown in **Figure 3a-b**. These two samples show similar electrochemical behaviors. In the first cycle, the two cathodic peaks at ~0.5 and ~0.8 V can be ascribed to the multistep sodiation mechanism, including the sodium insertion that forms sodiated metal sulfides and the conversion mechanism forming metal and Na₂S.^[20, 21] In the sodium insertion mechanism, Na⁺ ions will be inserted into the crystal sites in the sulfides without changing the crystal structure. In the conversion mechanism, Na⁺ ions will reduce metal sulfides, forming pure metal and Na₂S. The anodic peaks at ~ 1.7 V can be ascribed to

the reverse oxidation process of the metal into metal sulfides. In the subsequent cycles, the cathodic peaks overlapped and shifted to a higher potential at ~ 0.9 V, due to the structure and volume change during the first conversion reactions. In addition, we analyze the electrochemical mechanism based on the TEM images as shown in Figure 3d. From the high resolution TEM images d-spacings of 0.22, 0.28 and 0.43 nm can be observed, corresponding to the diffraction rings in the selected area electron diffraction patterns as shown in the inset. D-spacings of 0.22 nm can be ascribed to (100) planes of pure Co (JCPDF # 005-0727) or Fe (JCPDF # 034-0529) metal. However, d-spacings of 0.28 and 0.43 nm indicates the presence of Co_3S_4 (JCPDF # 047-1738) and Co_4S_3 (JCPDF # 019-0363). The absence of Na_2S was due to its amorphous nature. Based on these findings, the electrochemical mechanism was a conversion-based mechanism. The current density of the cathodic and anodic peaks of PB3-1S was significantly decreased along with cycles, indicating a poor capacity retention. After 4 cycles, the current density of PB3-1S cathodic peak was reduced to around 0.1 A/g, while the cathodic peak of PBC1-1S remains distinguishable with higher current density of ~ 0.17 A/g. The better current density retention of PBC1-1S indicates a better capacity retention during electrochemical tests. In addition, from the TEM images of PBC1-1S discharged to 0.01V were shown in Figure S9. It can be seen that d-spacing values and diffraction patterns confirmed the presence of pure metal, proving the conversion-based mechanism. The first 4 galvanostatic charge/discharge profiles of PB3-1S and PBC1-1S were also measured as displayed in Figure 3c. The first discharge/charge capacity of PB3-1S and PBC1-1S were 744.53/522.41 mAh/g and 867.12/539.53 mAh/g. It is worth noting that the calculation of capacity is based on the total weight of electrode materials, including the low capacity amorphous carbon coating layers (~ 24 wt%). The actual increase in capacity of the PBC1-1S is much higher after subtracting the weight of carbon (due to the negligible contribution in sodium storage), giving a value of 1140.9/709.9 mAh/g. The low efficiency in the first cycle can be ascribed to the formation of

solid electrolyte interface (SEI).^[17] The discharge and charge plateaus are in correspondence with the cathodic and anodic peaks as seen in Fig. 3a-b.

Galvanostatic charge/discharge tests were also conducted under different current densities to reveal the rate capability of PB3-1S and PBC1-1S, as shown in **Figure 4a**. At low current density of < 200 mA/g, PB3-1S and PBC1-1S shows similar capacity and rate performance. Considering the weight percentage of low capacity amorphous carbon coating, an increase in capacity of PBC1-1S at low current densities is realized. As the current density was increased, the capacity of PBC1-1S was notably higher than that of PB3-1S. After the current density was brought back to 50 mA/g, the capacity of PB3-1S is significantly reduced to less than 350 mAh/g while PBC1-1S can restore a capacity of ~ 480 mAh/g, indicating the better rate performance of PBC1-1S. The EIS spectrum of PB3-1S and PBC1-1S were plotted in Figure 4b. It can be seen that PBC1-1S delivers a smaller charge transfer resistance, demonstrating the good electrical contact between the carbon layer shell and inner bimetallic sulfides, facilitating the charge transfer process. The diffusion coefficient of Na⁺ in PB3-1S and PBC1-1S were also evaluated using GITT techniques (see details from experimental section) and plotted in Figure 4c. The variation of diffusion coefficient at different sodiation degree can be ascribed to the multi-step sodiation process including intercalation and conversion, which is consistent with literature.^[24, 39] It can be seen that with a carbon layer coating, the Na⁺ diffusion coefficient in PBC1-1S is much higher than that in PB3-1S at different sodiation degree, as listed in Table S1. The smaller charge transfer resistance and faster Na⁺ diffusion in PBC1-1S than PB3-1S is in agreement with the better rate performance of PBC1-1S.

As ionic conductor, electrolyte in the battery plays a crucial role in the performance of battery. It has been found that with addition of fluoroethylene carbonate (FEC) in the electrolyte, the specific capacity and cycling stability of anode materials can be notably enhanced, which can be ascribed to the thinner and more stable passivation layer on metal counter/reference

electrode, mitigated electrolyte decomposition and a faster charge transfer process.^[40] In our work, FEC was added in the electrolyte to further improve the performance of carbon coated bimetallic sulfide hollow nanocubes as shown in **Figure 5**. It can be seen from Figure 5a that with presence of FEC in electrolyte, the specific capacity of PBC1-1S can reach 122.3 mAh/g at high current density of 5000 mA/g, which is almost 6 times than that of PBC1-1S without FEC (20.84 mAh/g at 5000 mA/g). With current density decreased to 50 mA/g, capacity of ~380 mAh/g can be restored, higher than that of PBC1-1S in absence of FEC additives. The cycling stability of PB3-1S and PBC1-1S were evaluated in the electrolyte with FEC additives, it is found that after 150 cycles at 500 mA/g, the specific capacity of PB3-1S was drastically decayed from 201 to 25 mAh/g even with the presence of FEC additives. On the contrary, PBC1-1S can still remain a capacity of 87 mAh/g out of 361.3 mAh/g after 150 cycles at 500 mA/g, revealing the better cycling stability for the carbon coated bimetallic sulfide hollow nanocubes. The SEM images of PB3-1S and PBC1-1S after cycling can be found in Fig. S9. As shown in the images, after 150 cycles for PB3-1S the random particles agglomerated and merged together due to the repeated de/sodiation. On the other hand, the nanocube morphology of PBC1-1S remains distinguishable after 150 cycles, albeit noticeable agglomeration that also explains the capacity decay upon cycling.

The electrochemical performance of PBC1-1S was also compared with other PB-based materials applied as battery electrodes, as shown in Table S2. Normally PB-based materials are applied as cathode materials, with capacity less than 200 mAh/g at low current density and less than 100 mAh/g at high current density, while delivering good cycling performance.^[11, 27, 41] When applied as anode materials, PB-based materials deliver high capacity at low current densities, while suffering from fast capacity decay upon increasing current densities with limited cycling performance.^[42] By applying PB as precursor, our PBC1-1S is able to deliver high capacity with high rate performance, while the cycling stability still needs to be enhanced.

3. Conclusion

In a summary, by coating poly-dopamine on Prussian blue precursors prior to sulfidation process, carbon coated bimetallic sulfide hollow nanocubes PBC1-1S were prepared. The nanocube morphology of Prussian blue precursors were well-retained by PBC1-1S, with higher surface area, smaller charge transfer resistance and higher diffusion coefficient. As a result with fluoroethylene carbonate additives in the electrolyte, PBC1-1S anodes can deliver a specific capacity of ~ 500 mAh/g at 50 mA/g while maintaining capacity of 122.3 mAh/g at 5000 mA/g, showing good rate performance. In addition the carbon coated bimetallic sulfide hollow nanocubes can maintain capacity of 87 mAh/g after being subjected to 150 cycles at 500 mA/g. The overall good electrochemical performance of PBC1-1S represents the merits of composition tuning and structural design, which serves to inspire advances in sodium ion battery anodes based on bimetallic sulfides.

4. Experimental Section

Materials Preparation: CoFe Prussian blue (PB) analogues were prepared by wet chemical bath method. Generally, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and sodium citrate dihydrate were used as purchased without further purification. Firstly, 30 mM $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 4.5 mM sodium citrate dihydrate were dissolved in 100 mL DI water under magnetic stirring for 10 minutes to form solution A. Secondly, 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$ was dissolved in 100 mL DI water under magnetic stirring for 10 minutes to form solution B. Subsequently, solution A was slowly added into solution B under magnetic stirring, then the solution was aged for 10 hours at room temperature. After centrifugation at 10000 rpms for 5 minutes and washing with DI water and ethanol for 3 times, the precipitates were dried in oven at 60 °C overnight and collected. The product was denoted as PB3-2. By changing the molar ratio between $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_3\text{Fe}(\text{CN})_6$ to 4:1, 3:1 and 3:4, the products were denoted as PB4-1, PB3-1, and PB3-4

respectively. The PB with different Co : Fe ratio was sulfidized by thiourea at elevated temperature. In a typical synthesis, PB3-1 and thiourea with mass ratio of 1:2 were put in a ceramic crucible with thiourea at the upstream in the furnace. And the temperature of the furnace was increased to 500 °C at a rate of 1 °C/min and maintained for 3 hours, with argon as the flow gas. After that the furnace was cooled down to room temperature with a rate of 15 °C/min. The sulfidized product of PB3-1 was labeled as PB3-1S. In separate experiments, Fe PB was also prepared by replacing $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

Buffer solution with pH ~8.5 was prepared and the pH was tuned using dilute HCl and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions. After obtaining the Prussian blue analogues, 80 mg PB3-1 was dispersed in 100 mL alkaline buffer by ultrasonication for 10 minutes. 80 mg dopamine was dissolved in 10 mL DI water by magnetic stirring for 10 minutes. Then the dopamine solution was added into the PB3-1 dispersed buffer solution dropwise under magnetic stirring. After 4 hours stirring, the black solution was centrifuged at 10000 rpms for 5 minutes and washed by DI water for 3 times, then the black precipitates were collected by drying in oven at 60 °C overnight. And the products were denoted as PBPDA1-1. By changing the weight of dopamine added in DI water to 40, 120 and 160 mg, the products were denoted as PBPDA2-1, PBPDA2-3 and PBPDA1-2. Lastly, PBPDA1-1 was sulfidized by a similar procedure as mentioned above. The sulfidized products of PBPDA1-1 were collected and denoted as PBC1-1S.

Materials Characterization and Performance Measurement: The X-ray diffraction (XRD) (Shimadzu powder diffractometer; Cu $K\alpha$ -radiation ($\lambda = 1.5406 \text{ \AA}$)) technique was applied to detect the crystal structure of the samples. Scanning electron microscopy (SEM, JEOL 7600F) was used to observe the structure and morphology of the samples. Transmission electron microscope (TEM, JEOL 2010) was applied to reveal the fine structure at high magnification of the samples. Raman spectroscopy was employed to characterize the chemical states of the samples with a monochromatic laser with a wavelength of 633 nm. X-ray photoelectron

spectroscopy (XPS) analysis was performed using the VG ESCA Lab XPS system with monochromatic Al K α X-ray ($h\nu$ =1486.7 eV), to investigate the chemical bonds of samples. Thermal gravimetric analysis (TGA, TA Instruments 2950) was also applied to estimate the carbon content in the samples, with a heating rate of 10 °C/min from room temperature to 600 °C in air atmosphere.

Electrochemical Testing and Analysis: The electrochemical tests were conducted in a CR2032 half-cell configuration, with the Na plate as both reference and counter electrode. The working electrode was prepared by mixing active materials, carbon black and polyvinylidene fluoride (PVDF) (80:10:10) in NMP. The slurry was then loaded onto a copper foil and dried at 70 °C in vacuum overnight. The mass loading of the active materials was 1.0 ~1.5 mg. The assembly of the half-cell was conducted in the Argon filled glove box with O₂ and H₂O level < 0.1 ppm, and the assembled cells were aged overnight to allow the penetration of electrolyte as well as to stabilize the cell. The electrolyte employed is 1M NaClO₄ in EC (ethylene carbonate) : DMC (dimethyl carbonate) (v/v 1:1). 5wt % FEC was added to prevent electrolyte decomposition. Cyclic voltammetry (CV) measurements were conducted by Autolab with a scan rate of 0.1 mV/s, in a voltage range of 0.01 ~ 3.0 V versus Na/Na⁺. Electrochemical impedance spectroscopy (EIS) was also measured by Autolab with AC voltage of 5 mV amplitude in a frequency range of 0.01~100 KHz at open circuit potential. The galvanostatic charge/discharge (GCD) and cycling tests were conducted by the Neware battery-testing instrument, to reveal the rate capability and stability of the electrode materials. Galvanostatic intermittence titration techniques (GITT) were applied and measured by Autolab based on the following equation^[24]:

$$D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

In which t is the duration of the current pulse (s), τ is the relaxation time (s), and ΔE_s is the steady-state potential change by the current pulse. ΔE_t is the potential change during the constant current pulse after eliminating the IR drop. L is sodium ion diffusion length (cm); for compact electrode, it is equal to thickness of electrode. In our case, constant current pulse of 100 mA/g was applied with duration of 1200s while the relaxation time is 1800s.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) XRD patterns of the sulfidized products PB3-1S and PBC1-1S; SEM images of (b) PB3-1S; (c) PBC1-1S; and (d) TEM images of PBC1-1S, inset is the HRTEM image.

Figure 2. (a) N₂-sorption isotherms of PB3-1S and PBC1-1S, inset is the pore size distribution; (b) Raman spectrum of PBC1-1S; (c-d) Co 2p and Fe 2p spectrum of PB3-1S.

Figure 3. CV curves of (a) PB3-1S; (b) PBC1-1S measured in a potential range of 0.01~3.0V vs. Na/Na⁺ at a scan rate of 0.1 mV/s; (c) the first 4 galvanostatic/charge discharge cycles of PB3-1S and PBC1-1S at a current density of 50 mA/g; d) the high resolution TEM images of PBC1-1S discharged to 0.01 V, inset is the selected area electron diffraction pattern.

Figure 4. (a) Specific capacity of PB3-1S and PBC1-1S at different current densities; (b) EIS measurements of PB3-1S and PBC1-1S measured at open circuit potential after four cycles of

CV test; and (c) the diffusion coefficient of PB3-1S and PBC1-1S at different sodiation degree.

Figure 5. (a) the specific capacity of PBC1-1S with and without the presence of FEC at various current densities and (b) the cycling stability of PB3-1s and PB3-1PDA1-1s with the presence of FEC.

Carbon coated bimetallic sulfide hollow nanocubes can be obtained by poly-dopamine coating on Prussian Blue analogue precursors prior to the sulfidation process. The optimum carbon coated bimetallic sulfide nanocubes as sodium ion battery anode can deliver improved specific capacity, rate performance and cycling stability, due to the higher surface area, smaller charge transfer resistance and higher diffusion coefficient.

Keyword: Prussian blue analogues; sulfidation; bimetallic sulfides; sodium ion battery.

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Carbon coated bimetallic sulfide hollow nanocubes as advanced sodium ion battery anode

ToC figure

Supporting Information

Carbon coated bimetallic sulfide hollow nanocubes as advanced sodium ion battery anode*Jingwei Chen, Li Shaohui, Vipin Kumar, and Pooi See Lee**

Figure S1. (a) XRD diffraction patterns of Prussian blue precursors with different Co: Fe feeding ratios; SEM images of (b) Fe PB; (c) PB4-1; (d) PB3-1; (e) PB3-2; (f) PB3-4.

As can be seen from Fig. S1a, PB precursors with different Co: Fe feeding ratios show similar diffraction peaks, which can be indexed to a series of crystal planes of cubic Prussian blue analogues (JCPDS # 73-0687), in accordance with literatures.^[1] The morphology of PB precursors with different Co: Fe feeding ratios were revealed by SEM as seen from Fig. S1b-e. All PB analogues show nanocube structures, forming isolate nanocubes with size of ~ 100 nm. Fe PB exhibits an overlapping nanocube morphology, with nanocubes interconnecting with each other, while the size of nanocubes is tens of nanometers.

Figure S2. (a) XRD diffraction patterns of sulfidized Prussian blue precursors; SEM images of (b) Fe PBS; (c) PB4-1S; (d) PB3-1S; (e) PB3-2S; (f) PB3-4S.

The PB precursors were sulfidized by thiourea at elevated temperature and characterized by XRD and SEM techniques. As seen in Fig. S2a, after sulfidation the Prussian blue analogues were transformed into a mixture of sulfides. Monometallic sulfides can be obtained by applying monometallic Fe PB as precursor. It is noted that with high Co: Fe ratio in PB precursor (PB4-1), no bimetallic sulfides can be obtained after sulfidation (PB4-1S). By further increasing the Co: Fe ratio in the PB precursor, bimetallic sulfide Co_8FeS_8 (cubic; JCPDF #029-0484) can be obtained, with the presence of monometallic sulfides Co_4S_3 (hexagonal; JCPDF #002-1458) and Fe_7S_8 (hexagonal; JCPDF #024-0220). As seen from Fig. S2b-f, after the sulfidation process, the PB precursor nanocubes were transformed into random particles, with different degree of agglomeration. It is noted that Fe PBS and PB4-1S are less agglomerated than the other 3 sulfide products, which might be associated with the components in the solid solution to form bimetallic sulfides (PB3-1S, PB3-2S, PB3-4S).

Figure S3. TEM images of PBC1-1S (a) high resolution images; (b) low magnification observation of two nanocubes, inset is the high resolution TEM images of the dashed circle area; (c) low magnification observation of the hollow interior of a nanocube, inset is the high resolution TEM images of the dashed circle area.

The high resolution TEM image of PBC1-1S can be found in Fig. S3a, lattice fringes with different d-spacings can be observed, which were measured to be 0.24, 0.29, 0.26, 0.24 and 0.59 nm. D-spacing values of 0.29 and 0.59 nm corresponds to the (311) and (111) crystal planes of Co_8FeS_8 , 0.24 nm corresponds to (400) crystal plane of Co_3S_4 , while 0.26 nm corresponds to (101) crystal plane of Co_4S_3 , which confirms the presence of multiphase sulfides and the random distribution of these sulfides. In Fig. S3b, two nanocubes were clearly observed, while the high resolution (the dashed circle area) analyses evidently show the hollow interior of the nanocubes. Also, the hollow interior of the nanocubes can be seen from Fig. S3c (from the dashed circle area), it is found that no lattice fringes can be observed in the “voided” area, confirming the hollow nature of the PBC1-1S nanocubes.

Figure S4. X-ray photoelectron analysis of (a) Co 2p, (b) Fe 2p and (c) C 1s spectrum in PBC1-1S. (d) S 2p spectrum in both PB3-1S and PBC1-1S.

The Co 2p and Fe 2p spectra of PBC1-1S resembles those of PB3-1S, indicating the presence of Co^{2+} , Co^{3+} , Fe^{2+} and Fe^{3+} . The C 1s spectrum of PBC1-1S can be deconvoluted into two peaks located at 284.6 eV and 285.9 eV respectively, representing the graphitic carbon and the C=N bonds derived from the pyrolysis of PDA.^[2] The S 2p spectra of PB3-1S and PBC1-1S are quite similar, both of which can be ascribed to the S^{2-} .

Figure S5. (a) Specific capacities of different sulfide products at various current densities; (b) the diffusion coefficient of sulfide products at different sodiation degree. The measurement of diffusion coefficient was realized by applying GITT (galvanostatic intermittent titration technique), details can be found in experimental section.

In order to measure the specific capacity of the sulfidized products, galvanostatic charge discharge method was applied under different current densities, as shown in Figure S5a. In the first several cycles, degradation of capacities can be observed from all samples, which is related to the SEI formation and side reactions, commonly observed in conversion mechanism based anode materials.^[3, 4] After the first 4 charge/discharge cycles, the discharge capacity of PB3-1s can retain 530.78 mA/g, while that of Fe PBS, PB4-1S, PB3-2s and PB3-4s are 439.24 and 315.14 mAh/g respectively, indicating a better capacity retention of PB3-1s at low current density. Upon increasing the current densities, PB3-1s can still retain higher capacity than the other 4 samples, demonstrating the better rate performance of PB3-1S. In addition, the discharge capacity of PB3-1s can be restored to ~470 mAh/g when the current density is decreased to 50 mA/g. The better rate performance of PB3-1S can be ascribed to the higher diffusion coefficient than that of other sulfide products at different sodiation degree, the values can be found in Table S1. The variation of diffusion coefficient at different sodiation degree can be ascribed to the multi-step mechanism during the discharge process, in accordance to what has been reported.^[5]

Figure S6. Thermal gravimetric analysis of PB3-1S and PBC1-1S.

The thermal gravimetric analysis of PB3-1S and PBC1-1S were measured to estimate the carbon content in PBC1-1S. As can be seen from the TGA curves of PB3-1S, from room temperature to ~ 250 °C gradual weight loss can be observed, which can be ascribed to the evaporation of water molecules absorbed at the surface of particles.^[6] The slow weight increase upon temperature increase can be ascribed to the oxidation of the sulfides into sulfates and also oxidation state change of the metal ions.^[6, 7] After decomposition at ~ 500 °C the weight percentage of PB3-1S was finally stabilized at 82.9 wt%. On the other hand, the weight increase caused by the sulfide oxidation was compromised by the decomposition of carbon coating layer in PBC1-1S, leading to a total weight decrease at high temperature. Based on these analysis, the sulfide content in PBC1-1S was ~ 76 wt% ($63.1\%/82.9\%$), thus the carbon content in PBC1-1S was estimated to be 24 wt%.

Figure S7. (a) XRD patterns of PBC2-1S, PBC1-1S, PBC2-3S, PBC1-2S; and SEM images of (b) PBC2-1S; (c) PBC1-1S; (d) PBC2-3S; (e) PBC1-2S.

PB3-1 was selected as the precursor and coated by different amount of PDA for further sulfidation. The amount of dopamine chloride to be added are 40, 80, 120 and 160 mg for the preparation of PBC2-1S, PBC1-1S, PBC2-3S, and PBC1-2S. The carbon coated sulfide nanocubes were characterized by XRD and SEM as displayed in Figure S7. After the sulfidation process, the PDA coated PB3-1 was transformed in a mixture of sulfides including bimetallic sulfide Co_8FeS_8 (cubic; JCPDF #029-0484), and monometallic sulfides Co_4S_3 (hexagonal; JCPDF #002-1458), Co_3S_4 (hexagonal; JCPDF #042-1448) and Co_{1-x}S (hexagonal JCPDA # 042-0826). The morphology of the carbon coated bimetallic sulfide nanocubes were revealed by SEM as shown in Fig. S7b-e. With different amount of carbon coating, the nanocube morphology of PB3-1 can be well retained after the sulfidation process, forming carbon coated bimetallic sulfide nanocubes.

Figure S8. (a) Specific capacity at different current densities and (b) EIS spectrum of carbon coated bimetallic sulfide hollow nanocubes with different amount of PDA coating before sulfidation.

The rate performance of the bimetallic sulfide nanocubes coated with different amount of carbon was revealed in Fig. S8a. It can be seen that PBC1-1S exhibits best capacity retention upon increasing current density, and capacity approaching 400 mAh/g can be restored after decreasing the current density to 50 mA/g. Carbon coating can mitigate the stress caused by volume change during de/sodiation process, with small amount of carbon coating this buffer effect is not obvious while the capacity will be compromised with excess amount of carbon coating, as the carbon species is considered to have little contribution to the total capacity of the electrode.^[8] As a result, with appropriate amount of carbon coating PBC1-1S exhibits the best rate performance, which is also in association with the smallest charge transfer resistance of PBC1-1S than the other carbon coated sulfides.

Figure S9. SEM images of (a) PB3-1S and (b) PBC1-1S after 150 cycling tests.

As can be seen from the SEM images, after 150 cycles for PB3-1S the random particles agglomerated and merged together due to the repeated de/sodiation. On the other hand, the nanocube morphology of PBC1-1S remains distinguishable after 150 cycles albeit noticeable agglomeration that also explains the capacity decay upon cycling.

Table S1. Diffusion coefficient values (cm²/s) of different samples

Sodiation level	Fe PBS	PB4-1S	PB3-1S	PB3-2S	PB3-4S	PBC1-1S
25%	1.89E-11	6.82E-12	5.00E-11	3.01E-12	1.17E-11	8.28E-11
50%	1.32E-11	5.78E-12	8.35E-12	1.56E-12	5.25E-12	3.58E-11
75%	1.85E-11	1.28E-11	3.04E-11	3.67E-12	9.14E-12	1.33E-10
100%	2.58E-11	2.13E-11	8.74E-11	5.94E-12	1.61E-11	1.44E-10

Table S2. Performance comparison

Material System	Specific capacity (mAh/g)	Rate performance (mAh/g)	Cycling performance	Reference
Na _{1.72} MnFe(CN) ₆	~120 @ 12 mA/g	45 @ 4.8 A/g	93% @ 30 cycles	[9]
Na _{0.61} Fe[Fe(CN) ₆] _{0.94}	~ 165 @ 25 mA/g	80 @ 0.6 A/g	100% @ 150 cycles	[10]
Na _{1.70} FeFe(CN) ₆	120 @ 200 mA/g	73.6 @ 1.2 A/g	~ 80% @ 100 cycles	[2]
K _{0.88} Fe _{2.04} (CN) ₆ • yH ₂ O	400 @ 8.75 mA/g	150 @ 1.75 A/g	~ 60% @ 100 cycles	[11]
Mn[Fe(CN) ₆] _{0.6667} • nH ₂ O	565.6 @ 100 mA/g	132 @ 1 A/g	~ 54% @ 100 cycles	[12]
Co ₃ [Co(CN) ₆] ₂	299.1 @ 20 mA/g	132.5 @ 2A/g	N.A.	[13]
PBC1-1S	497 @ 50 mA/g	122 @ 5 A/g	45% @ 100 cycles	Our work

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