# Core—Shell Coating Silicon Anode Interfaces with Coordination Complex for Stable Lithium-Ion Batteries

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**ABSTRACT:** In situ core-shell coating was used to improve the electrochemical performance of Si-based anodes with polypyrrole-Fe coordination complex. The vast functional groups in the organometallic coordination complex easily formed hydrogen bonds when in situ modifying commercial Si nanoparticles. The incorporation of polypyrrole-Fe resulted in the conformal conductive coating surrounding each Si nanoparticle, not only providing good electrical connection to the particles but also promoting the formation of a stable solid-electrolyte-interface layer on the Si electrode surface, enhancing the cycling properties. As an anode material for Li-ion batteries, modified silicon powders exhibited high reversible capacity (3567 mAh/g at 0.3 A/g), good rate property (549.12 mAh/g at 12 A/g), and excellent cycling performance (reversible capacity of 1500 mAh/g after 800 cycles at 1.2 A/g). The constructed novel concept of core-shell coating Si particles presented a promising route for facile and large-scale production of Si-based anodes for extremely durable Li-ion batteries, which provided a wide range of applications in the field of energy storage of the renewable energy derived from the solar energy, hydropower, tidal energy, and geothermal heat.

KEYWORDS: silicon, PPy-Fe, coordination complex, lithium-ion battery, cycling performance

#### ■ INTRODUCTION

Because of emerging demands for high-energy-density batteries in consumer electronics and electric vehicles, developing rechargeable lithium-ion batteries (LIBs) with high energy density and long cycle life is of critical importance.<sup>1,2</sup> Silicon is a promising candidate for negative electrodes in LIBs because of its large theoretical capacity (3579 mAh/g for  $Li_{15}Si_4$ ),<sup>3,4</sup> relatively low working potential (~0.5 V vs Li/Li<sup>+</sup>), abundant resource, low cost, low toxicity, high safety, and environmental compatibility.<sup>5,6</sup> However, for practical implementation of Si anodes in LIBs, several critical issues should be considered: (i) volume changes of more than 270% (or factor of 3.7)<sup>3</sup> with Li insertion and extraction, which induces a strong stress on the silicon particles and causes pulverization and consequently results in the fast capacity loss of the electrode and degradation of electrochemical performance, 5-7 (ii) the much lower conductivity of Si compared with the carbon anodes,<sup>6</sup> and (iii) controlling the formation of stable solid-electrolyteinterface (SEI) layers on the Si surface caused by the decomposition of liquid electrolytes.<sup>8</sup> In previous studies, silicon nanocomposites,<sup>9,10</sup> thin films,<sup>11</sup> and nanostructured silicon, including nanotubes,<sup>5</sup> nanowires,<sup>12–14</sup> nanospheres,<sup>15</sup> nanoporous structures,<sup>6,7</sup> and their composites with carbon materials<sup>6,12,16–20</sup> and conducting polymer<sup>21–25</sup> had been researched to accommodate this volume change and improve the conductivity, such as carbon–silicon core–shell nanowires,<sup>12</sup> Si/C nanospheres,<sup>16</sup> Si/C microwires grown on graphite microspheres,<sup>17</sup> and graphene/nanosized silicon composites.<sup>18–20</sup> These approaches had resulted in improvements of the electrochemical performance of Si-based anodes but only to limited extent. Moreover, synthesis of Si nanostructures usually involved high-temperature chemical vapor deposition or complex chemical reactions and/or

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templates, and their scalability and compatibility with existing battery manufacturing processes remained a challenge.

Recent studies reported that organometallic coordination complex had a special multilayer structure and that the strong and stable interlayer Fe-N coordination interaction and the high reversibility of its interlayer Fe-O-Fe interaction during cycling permitted the material to possess higher specific capacity and cycling stability compared with those of conducting polymer.<sup>26</sup> Additionally, hydrogen bonding was easy to form when commercial Si nanoparticles were coated with organometallic coordination complex that contained vast functional groups.<sup>26,27</sup> In the present study, ingenious in situ core-shell-coating commercial Si powders with polypyrrole-Fe (PPy-Fe) coordination complex (Si@PPy-Fe) was produced as an promising anode material for LIBs. This interaction can result in the conformal modifying of PPy-Fe molecules on the surface of Si particles, trapping the Si particles inside and serving as a continuous pathway for electronic conduction. Furthermore, the coating layer promoted the formation of a stable SEI layer on the Si electrode surface. The stable SEI formation on our composite electrodes during the process of charge/discharge was important for the long cycle life as well as the high Coulombic efficiency. The starting materials and the synthesis processes were both facile for large-scale production, which could be extended for manufacturing of the nextgeneration Li-ion batteries.

#### METHODS

**Materials Preparation.** PPy-Fe coordination complex was synthesized according to a reported method.<sup>28–32</sup> Then, solutions of 10 mg/mL PPy-Fe (10 mL) mixed with 400, 100, and 50 mg of commercial silicon powders (with an average diameter of ~100 nm) were stirred and dried at 70 °C overnight to obtain the Si@PPy-Fe materials with different contents of PPy-Fe (20 wt % for SiP-1, 50 wt % for SiP-2, and 66.7 wt % for SiP-3, respectively).

**Physical Characterization.** Elemental analysis was carried out on an X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra Dld, Japan). Fourier-transformed infrared (FT-IR) spectra were recorded on a Nicolet is50 spectrometer (ThemoFisher Scientific, America). The morphology was observed by field-emission scanning electron microscopy (FESEM, SU8010, Japan) and field-emission transmission electron microscopy (FETEM, FEI Tecnai G2 F20 S-TWIN TMP, Hongkong). An energy dispersive spectrometer (EDS) was used to do element analysis. A UV–vis–NIR spectrophotometer (SHIMADZU company, Japan) was used to carry out UV–vis–NIR spectra analysis. Thermogravimetric analysis (TGA) was carried out with a SDT 2960 (TA Instruments) up to 800 °C at a heating rate of 10 °C min<sup>-1</sup> in air.

Electrochemical Evaluation. Electrodes were prepared by mixing the as-prepared powder (70 wt %), carbon black (20 wt %), and polyvinylidene fluoride (PVDF, 10 wt %) dissolved in Nmethylpyrrolidone (NMP) to form a slurry. The slurry was cast onto a piece of titanium foil with a mass loading of  $\sim 1 \text{ mg/cm}^2$ . Electrode sheets were dried under vacuum at 70 °C for 24 h. Coin cells (CR2025) were fabricated with fresh lithium foil as the counter electrode, 1 mol  $L^{-1}$  LiPF<sub>6</sub> dissolved in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) (4:3:3 vol %) as the electrolyte, and Celgard 2400 as the separator. The assembly of the cell was conducted in an Ar-filled glovebox followed by an overnight aging treatment before the test. Electrochemical impedance spectroscopy (EIS) was also carried out on a CHI 660E (Chenhua Shanghai, China) electrochemical workstation over the frequency range from 100 kHz to 0.01 Hz. The cycle life and rate capability of the cells were tested within a voltage window of 0.01-1.5 V (vs Li<sup>+</sup>/Li) by using a battery-testing system (LAND CT 2001A, Wuhan, China). The electrode based on pure PPy-Fe coordination complex was investigated between 0.0 and 3.0 V vs Li+/Li.

## RESULTS AND DISCUSSION

Schematic illustration of Si@PPy-Fe composite was demonstrated in Figure 1 with PPy-Fe coordination complex



**Figure 1.** Schematic illustration of Si@PPy-Fe composite electrodes. (Reprinted in part with permission from ref 26. Copyright 2011 Royal Society of Chemistry.)

uniformly coated on the Si nanoparticles. FTIR spectroscopic analysis of Si, PPy-Fe, and Si@PPy-Fe recorded in the range of  $600-4000 \text{ cm}^{-1}$  in Figure 2 was carried out to recognize the



Figure 2. FTIR spectra of Si, PPy-Fe, and Si@PPy-Fe.

change of the interactions after the combination of Si nanoparticles and PPy-Fe coordination complex. Peaks at 1380 cm<sup>-1</sup> (C–N stretching vibration),<sup>26</sup> 750 cm<sup>-1</sup> (C–O stretching vibration in epoxide), and 1700 cm<sup>-1</sup> (C=O the stretching vibration)<sup>28-37</sup> appeared in the FTIR curve of PPy-Fe, and a peak of Si–O–Si  $(1160 \text{ cm}^{-1})^{38}$  in pure Si existed in the FTIR curve of Si@PPy-Fe. The vast amount of oxygencontaining functional groups was due to the overoxidation during the synthesis process of PPy-Fe.<sup>29–31</sup> The peak at 3400 and 3200 cm<sup>-1</sup> was attributed to the hydrogen-bonded O-H stretch with different degrees of bond ordering. The peak at  $3400 \text{ cm}^{-1}$  was assigned to a water structure with an intermediate level of hydrogen bonding. The peak at 3200 cm<sup>-1</sup> was generally ascribed to the symmetric OH stretching mode associated with tetrahedrally coordinated water molecules.<sup>39</sup> As a result, the enhanced peak at 3200 cm<sup>-1</sup> indicated that the functional groups in the PPy-Fe can potentially bind with the SiO<sub>2</sub> on the Si particle surfaces via hydrogen bonding.

Further composition analysis of the Si@PPy-Fe was carried out using XPS. In the survey region from 0 to 800 eV (Figure 3a), it was evident that Si, C, O, N, and Fe elements all existed in the sample, indicating that PPy-Fe molecules were in situ modified on the surface of Si particles. The high-resolution C 1s (Figure 3b) was clearly divided into four components at 284.5, 285.3, 286.5, and 288.5 eV corresponding to C–C, C–N, C== N, and C==O.<sup>40</sup> N 1s (400.4 eV) and  $-NH^+-$  (401.5 eV)<sup>39</sup> peaks further justified the existence of PPy-Fe coordination complex (Figure 3c). The high-resolution spectrum of O 1s in

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Figure 3. (a) Full XPS spectrum and the high-resolution (b) C 1s, (c) N 1s, (d) O 1s, (e) Fe 2p, and (f) Si 2p XPS spectrum of Si@PPy-Fe.

Figure 3d showed a curve that can be fit to two peaks with binding energies at 532.2 and 533.2 eV. The peak at 532.3 was attributed to hydroxide and/or oxy-hydroxide,<sup>40</sup> and the peak at 531.0 eV was assigned to the C–O bond.<sup>41</sup> Two characteristic peaks of Fe  $2p_{1/2}$  at 710.6 eV and Fe  $2p_{3/2}$  at 723.7 eV were observed from signals of the Fe 2p regions<sup>42</sup> (Figure 3e). Figure 3f showed that the Si 2p spectra was divided into two peaks at the binding energies of around 98.9 eV corresponding to the overlapped Si  $2p_{3/2}$  and Si  $2p_{1/2}$  of Si–Si bonds in silicon<sup>43</sup> and 102.5 eV corresponding to the surface SiO<sub>x</sub> component.<sup>44,45</sup>

To characterize the electrochemical properties of Si@PPy-Fe composite electrodes, the voltage profiles of the Si@PPy-Fe electrode based on a 300 mA/g current density was shown in Figure 4a. The first cycle lithiation potential showed a plateau profile at 0.1–0.01 V, consistent with the behavior of crystalline Si,<sup>34</sup> and it delivered a very high lithium storage capacity of 4000 mAh/g (on the basis of the weight of Si).<sup>3,46</sup> The following cycles exhibited characteristic voltage plateaus at 0.2 and 0.43 V, respectively, for lithiation and delithiation.<sup>47</sup> Additionally, the Coulombic efficiency in the initial cycle was ordinarily 62% because SEI formation of Si@PPy-Fe consumed a certain large percentage of the lithium and increased to nearly

100% during the subsequent cycles in large part due to the formation of a stable SEI on the composite electrode.<sup>22</sup> It should be emphasized that no obvious change in both charge and discharge profiles was observed even after 50 cycles, indicating the extraordinarily stable performance of the Si@ PPy-Fe electrodes. For comparison, the cycling performances of the electrodes based on pure Si and Si@PPy-Fe with different contents of PPy-Fe (20 wt % for SiP-1, 50 wt % for SiP-2, and 66.7 wt % for SiP-3, respectively) were examined on a 300 mA/ g current density and exhibited in Figure 4b. It can be observed that the pure Si electrode showed very fast capacity fading and bore a negligible capacity value ( $\sim$ 240 mAh/g) after 20 cycles because of the large volume changes with Li insertion and extraction. Comparatively speaking, with the increase of the content of PPy-Fe complex, the electrodes showed better durability. Noticeably, SiP-3 electrode showed good capacity retention (about 100%) with ~2000 mAh/g. The capacity of SiP-1and SiP-2 was significantly improved but with inferior cycling stability. After first cycle, EIS was conducted (Figure 4c). The inset showed an equivalent circuit model according to the simulation. In this circuit, R<sub>s</sub> represented the Ohmic resistance of the electrode system, including the electrolyte and the cell components.  $R_{CT}$  represented the interfacial charge

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Figure 4. (a) Voltage profiles plotted for the 1st, 2nd, 10th, 20th, and 50th cycles of the SiP-2 electrode at a current density of 300 mA/g. (b) Charge/discharge capacities of pure Si SiP-1, SiP-2, and SiP-3 at a current density of 300 mA/g for 50 cycles. (c) Nyquist plots of coin cells based on SiP-1, SiP-2, SiP-3, and pure Si over the frequency range from 100 kHz to 0.01 Hz. The inset shows an equivalent circuit model. (d) Cycling performance of SiP-2 for 100 cycles at 1200 mA/g. (e) Charge/discharge capacity of the SiP-2 electrode at various rates for 75 cycles. All the specific capacities and current density were reported on the basis of the weight of Si.

transfer resistance, which was connected to the semicircle in the high frequency region. CPE was the double layer capacitance. Z<sub>w</sub> represented Warburg impedance, which was described as a diffusive resistance of the Li ion within the electrode pores.<sup>48–51</sup> The related values for resistance of  $R_{\rm S}$ ,  $R_{\rm CT}$  and Z<sub>w</sub> were depicted in Table S1 and corresponded well to the capacity demonstrated in Figure 4b for pure Si, SiP-1, SiP-2, and SiP-3, respectively. Figure 4d, e showed the cycling stability at 1200 mA/g and rate performance at various charge/ discharge current ranging from 300 to 18 000 mA/g of SiP-2. Notably, the reversible capacity reached 2000 mAh/g after 100 cycles, and when the current rate was finally returned to its initial current density of 600 and 300 mA/g after a total of 65 cycles, a capacity of 2950 and 3200 mAh/g, respectively, was still recoverable and sustainable with a little decrease. This was due to the PPy-Fe coating layers not only promoting the formation of a stable SEI layer on the Si electrode surface, enhancing the cycling properties but also increasing electronic conductivity to enhance rate capability.

To highlight the superior cycling stability of the SiP-3, we tested the cycle performance of the electrode at a higher current density of 1200 mA/g (Figure 5a). Apparently, the discharge capacity was 1575 mAh/g at the 1st cycle and increased to the maximum value of 2636 mAh/g at the 14th cycle because of electrochemical activation and side reaction from electrolyte. After 800 cycles, a capacity of 1500 mAh/g was retained, consistent with the fundamental insight that high amounts of inert material improved the cycling stability of Si powder electrodes provided by Beattie et al.<sup>3</sup> The average columbic efficiency was 99.9% over all cycles. The capacity rise over the early cycles had been reported to be related with that combining the cycling kinetics improvement from electrochemical activation and side reaction from electrolyte. Indeed, similar phenomena had been observed in many previous studies of Si-based anodes.<sup>52-55</sup> Figure 5b,c showed the lowmagnification SEM images of morphological changes of pure Si and Si@PPy-Fe electrodes after 10 cycles. It can be obviously observed that the repeated lithium reactions over dozens of cycles led to catastrophic particle pulverization and electrode



**Figure 5.** (a) Charge/discharge capacities and the efficiency of the SiP-3 electrode at current density of 1200 mA/g for 800 cycles. The specific capacities and current density were reported on the basis of the weight of Si. Low-magnification SEM images of (b) pure Si electrode and (c) Si@ PPy-Fe electrode after 10 cycles. (The white arrows in b indicate cracks due to electrode expansion.) (d) High-magnification SEM image of Si@PPy-Fe electrode after 10 cycles. (e) TEM image showing that the Si nanoparticles (red arrow) were coated with a uniform PPy-Fe layer (green arrow).

expansion as shown in Figure 5b. However, the electrode composed of Si@PPy-Fe after 10 cycles exhibited no fractured structure because of the conformal modifying of PPy-Fe molecules on Si nanoparticles surface (Figure 5c). The highmagnification SEM image (Figure 5d) showed that the Si nanoparticles appeared to be encapsulated by a conformal PPy-Fe coating, which was further justified in the TEM images (Figure 5e). The superior electrochemical performance of the Si@PPy-Fe composite electrodes can be attributed to the advantageous features offered by the unique hierarchical microstructure. To explain further the superiority of the Si@ PPy-Fe for lithium storage material, the electrochemical performance of the electrode based on pure PPy-Fe coordination complex was investigated. The discharge/charge voltage profiles (Figure 6a) after 100 cycles and the cycling performance in Figure 6b both demonstrated excellent stability of PPy-Fe coordination complex. However, the initial Coulombic efficiency of PPy-Fe electrode was only ~20%. To justify the great contribution of the material for improving the property of silicon-based materials, the performance of Si@ PPy-Fe was compared with some recent publications as shown in Table 1, further indicating that after in situ core-shellcoating commercial Si nanoparticles with PPy-Fe, the special structure of PPy-Fe as organometallic coordination complex helped improve the electron conductivity and cycling performance of Si material.

#### CONCLUSIONS

A novel and facile approach was developed to fabricate a promising silicon-based anode material by in situ core-shellcoating commercial Si powders with PPy-Fe coordination complex for LIBs. The incorporation of polypyrrole-Fe molecules resulted in the conformal conductive coating surrounding each Si nanoparticle (i) buffering the tension produced by volume expansion, (ii) providing good electrical connection to the particles, and (iii) promoting the formation of a stable SEI layer on the Si electrode surface, enhancing the cycling properties. The modified silicon powders exhibited high reversible specific capacity (3567 mAh/g at 0.3 A/g), good rate property (549.12 mAh/g at 12 A/g), and extremely excellent cycling stability (reversible capacity of 1500 mAh/g after 800 cycles at 1.2 A/g). Our results showed that this highperformance Si@PPy-Fe composite electrode was feasible to be scaled up for manufacturing the next generation of highenergy Li-ion batteries. Furthermore, this novel in situ and high-yield strategy through synthesizing organic coordination complex can also be extended to build a variety of other interesting materials for important applications in highperformance LIBs, supercapacitors, adsorbents, catalysts, and sensors in many scientific disciplines.



**Figure 6.** (a) Voltage profiles plotted for the 1st, 2nd, 10th, 20th, 50th, and 100th cycles of the pure PPy-Fe electrode at a current density of 100 mA/g. (b) Cycle performance of pure PPy-Fe coordination complex at a current density of 100 mA/g for 200 cycles. CV curves of an electrodes based on (c) pure PPy-Fe and (d) Si@PPy-Fe obtained at a potential scan rate of 0.1 mV/s.

Table 1. Overview of Different Types	of Silicon Materia	als As Anode	es for LIBs
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silcon-based materia	ls	voltage range (V)	current densities (mA/g)	capacity (mAh/g)	capacity retention	citation
porous silicon/carbon com	posites	0-2	50	1877	55% for 100 cycles	6
silicon-based multicompon	ent	0.01-1.2	420	1450	85% for 100 cycles	8
carbon-silicon core-shell	nanowires	0.01-1	500	2000	75% for 50 cycles	12
graphene/nanosized silicor composites	1	0.005-1.2	300	3000	83% for 30 cycles	18
composite of graphene and encapsulated silicon	1	0.01-1	500	1600	70% for 1000 cycles	20
SiNP-PANi hydrogel comp	oosite	0.01-1	1000	1600	88% for 1000 cycles	22
Si@PPy-Fe composite	SiP-2	0.01-1.5	300	3567	84% for 50 cycles	this work
	SiP-3		1200	1600	94% for 800 cycles	uns work

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b12392.

SEM images of silicon and Si@PPy-Fe powders, the content of different elements of cycled pure Si and Si@ PPy-Fe electrodes, element mapping of the cycled Si@ PPy-Fe electrode, XPS spectra, FT-IR spectra, and UV-vis spectra of pure PPy and PPy-Fe coordination complex, the color changes after polymerization and coordination, TG profiles of SiP-1, SiP-2, and SiP-3. (PDF)

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#### Notes

The authors declare no competing financial interest.

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## REFERENCES

(1) Armand, M.; Tarascon, J. M. Building Better Batteries. *Nature* 2008, 451, 652–657.

(2) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. *Nature* **2001**, *414*, 359–367.

(3) Beattie, S. D.; Larcher, D.; Morcrette, M.; Simon, B.; Tarascon, J. M. Si Electrodes for Li-Ion Batteries – A New Way to Look at an Old Problem. *J. Electrochem. Soc.* **2008**, *155*, A158–A163.

(4) Obrovac, M. N.; Christensen, L. Structural Changes in Silicon Anodes During Lithium Insertion/Extraction. *Electrochem. Solid-State Lett.* **2004**, *7*, A93–A96.

#### **ACS Applied Materials & Interfaces**

(5) Song, T.; Xia, J. L.; Lee, J. H.; Lee, D. H.; Kwon, M. S.; Choi, J. M.; Wu, J.; Doo, S. K.; Chang, H.; Park, W. I.; Zang, D. S.; Kim, H.; Huang, Y. G.; Hwang, K. C.; Rogers, J. A.; Paik, U. Arrays of Sealed Silicon Nanotubes as Anodes for Lithium Ion Batteries. *Nano Lett.* **2010**, *10*, 1710–1716.

(6) Zhang, Z. L.; Wang, Y. H.; Ren, W. F.; Tan, Q. Q.; Chen, Y. F.; Li, H.; Zhong, Z. Y.; Su, F. B. Scalable Synthesis of Interconnected Porous Silicon/Carbon Composites by the Rochow Reaction as High-Performance Anodes of Lithium Ion Batteries. *Angew. Chem., Int. Ed.* **2014**, 53, 5165–5169.

(7) Wada, T.; Ichitsubo, T.; Yubuta, K.; Segawa, H.; Yoshida, H.; Kato, H. Bulk-Nanoporous-Silicon Negative Electrode with Extremely High Cyclability for Lithium-Ion Batteries Prepared Using a Top-Down Process. *Nano Lett.* **2014**, *14*, 4505–4510.

(8) Lee, J. I.; Ko, Y.; Shin, M.; Song, H. K.; Choi, N. S.; Kim, M. G.; Park, S. High-Performance Silicon-based Multicomponent Battery Anodes Produced via Synergistic Coupling of Multifunctional Coating Layers. *Energy Environ. Sci.* **2015**, *8*, 2075–2084.

(9) Kasavajjula, U.; Wang, C.; Appleby, A. J. Nano- and Bulk-Siliconbased Insertion Anodes for Lithium-ion Secondary Cells. *J. Power Sources* **2007**, *163*, 1003–1039.

(10) Wang, X. F.; Chen, Y.; Schmidt, O. G.; Yan, C. L. Engineered Nanomembranes for Smart Energy Storage Devices. *Chem. Soc. Rev.* **2016**, DOI: 10.1039/C5CS00708A.

(11) Graetz, J.; Ahn, C. C.; Yazami, R.; Fultz, B. Highly Reversible Lithium Storage in Nanostructured Silicon. *Electrochem. Solid-State Lett.* **2003**, *6*, A194–A197.

(12) Cui, L. F.; Yang, Y.; Hsu, C. M.; Cui, Y. Carbon-Silicon Core-Shell Nanowires as High Capacity Electrode for Lithium Ion Batteries. *Nano Lett.* **2009**, *9*, 3370–3374.

(13) Ge, M. Y.; Rong, J. P.; Fang, X.; Zhou, C. W. Porous Doped Silicon Nanowires for Lithium Ion Battery Anode with Long Cycle Life. *Nano Lett.* **2012**, *12*, 2318–2323.

(14) Chen, Y.; Liu, L. F.; Xiong, J.; Yang, T. Z.; Qin, Y.; Yan, C. L. Porous Si Nanowires from Cheap Metallurgical Silicon Stabilized by a Surface Oxide Layer for Lithium Ion Batteries. *Adv. Funct. Mater.* **2015**, *25*, 6701–6709.

(15) Yao, Y.; McDowell, M. T.; Ryu, I.; Wu, H.; Liu, N.; Hu, L. B.; Nix, W. D.; Cui, Y. Interconnected Silicon Hollow Nanospheres for Lithium-Ion Battery Anodes with Long Cycle Life. *Nano Lett.* **2011**, *11*, 2949–2954.

(16) Zhang, Z. L.; Zhang, M. J.; Wang, Y. H.; Tan, Q. Q.; Lv, X.; Zhong, Z. Y.; Li, H.; Su, F. B. Amorphous Silicon-Carbon Nanospheres Synthesized Bychemical Vapor Deposition using Cheap Methyltrichlorosilane as Improved Anode Materials for Li-ion Batteries. *Nanoscale* **2013**, *5*, 5384–5389.

(17) Zhu, X. Y.; Chen, H.; Wang, Y. H.; Xia, L. H.; Tan, Q. Q.; Li, H.; Zhong, Z. Y.; Su, F. B.; Zhao, X. S. Growth of Silicon/Carbon Microrods on Graphite Microspheres as Improved Anodes for Lithium-ion Batteries. *J. Mater. Chem. A* **2013**, *1*, 4483–4489.

(18) Xiang, H. F.; Zhang, K.; Ji, G.; Lee, J. Y.; Zou, C. J.; Chen, X. D.; Wu, J. S. Graphene/Nanosized Silicon Composites for Lithium Battery Anodes with Improved Cycling Stability. *Carbon* **2011**, *49*, 1787– 1796.

(19) Luo, J. Y.; Zhao, X.; Wu, J. S.; Jang, H. D.; Kung, H. H.; Huang, J. X. Crumpled Graphene-Encapsulated Si Nanoparticles for Lithium Ion Battery Anodes. *J. Phys. Chem. Lett.* **2012**, *3*, 1824–1829.

(20) Zhao, X.; Li, M. J.; Chang, K. H.; Lin, Y. M. Composites of Graphene and Encapsulated Silicon for Practically Viable High-Performance Lithium-Ion Batteries. *Nano Res.* **2014**, *7*, 1429–1438.

(21) Shao, D.; Zhong, H. X.; Zhang, L. Z. Water-Soluble Conductive Composite Binder Containing PEDOT: PSS as Conduction Promoting Agent for Si Anode of Lithium-Ion Batteries. *ChemElectroChem* **2014**, *1*, 1679–1687.

(22) Wu, H.; Yu, G. H.; Pan, L. J.; Liu, N.; McDowell, M. T.; Bao, Z. N.; Cui, Y. Stable Li-ion Battery Anodes by In-Situ Polymerization of Conducting Hydrogel to Conformally Coat. Silicon Nanoparticles. *Nat. Commun.* **2013**, *4*, 1943.

(23) Guo, Z. P.; Wang, J. Z.; Liu, H. K.; Dou, S. X. Study of Silicon/ Polypyrrole Composite as Anode Materials for Li-ion Batteries. *J. Power Sources* **2005**, *146*, 448–451.

(24) La, H. S.; Park, K. S.; Nahm, K. S.; Jeong, K. K.; Lee, Y. S. Preparation of Polypyrrole-Coated Silicon Nanoparticles. *Colloids Surf.*, A **2006**, 272, 22–26.

(25) Chew, S. Y.; Guo, Z. P.; Wang, J. Z.; Chen, J.; Munroe, P.; Ng, S. H.; Zhao, L.; Liu, H. K. Novel Nano-Silicon/Polypyrrole Composites for Lithium Storage. *Electrochem. Commun.* 2007, *9*, 941–946.

(26) Mao, Y.; Kong, Q. Y.; Guo, B. K.; Fang, X. P.; Guo, X. W.; Shen, L.; Armand, M.; Wang, Z. X.; Chen, L. Q. Polypyrrole-Iron-Oxygen Coordination Complex as High Performance Lithium Storage Material. *Energy Environ. Sci.* **2011**, *4*, 3442–3447.

(27) Mao, Y.; Kong, Q. Y.; Shen, L.; Wang, Z. X.; Chen, L. Q. Polythiophene Coordination Complexes as High Performance Lithium Storage Materials. *J. Power Sources* **2014**, *248*, 343–347.

(28) Qian, T.; Wu, S. S.; Shen, J. Facilely Prepared Polypyrrole-Reduced Graphite Oxide Core-Shell Microspheres with High Dispersibility for Electrochemical Detection of Dopamine. *Chem. Commun.* **2013**, *49*, 4610–4612.

(29) Zhou, J. Q.; Qian, T.; Yang, T. Z.; Wang, M. F.; Guo, J.; Yan, C. L. Nanomeshes of Highly Crystalline Nitrogen-Doped Carbon Encapsulated Fe/Fe<sub>3</sub>C Electrodes as Ultrafast and Stable Anodes for Li-ion Batteries. *J. Mater. Chem. A* **2015**, *3*, 15008–15014.

(30) Liu, X. J.; Qian, T.; Xu, N.; Zhou, J. Q.; Guo, J.; Yan, C. L. Preparation of On Chip, Flexible Supercapacitor with High Performance Based on Electrophoretic Deposition of Reduced Graphene Oxide/Polypyrrole Composites. *Carbon* **2015**, *92*, 348–353.

(31) Qian, T.; Yu, C. F.; Zhou, X.; Ma, P. P.; Wu, S. S.; Xu, L. N.; Shen, J. Ultrasensitive Dopamine Sensor Based on Novel Molecularly Imprinted Polypyrrole Coated Carbon Nanotubes. *Biosens. Bioelectron.* **2014**, 58, 237–241.

(32) Qian, T.; Xu, N.; Zhou, J. Q.; Yang, T. Z.; Liu, X. J.; Shen, X. W.; Liang, J. Q.; Yan, C. L. Interconnected Three-Dimensional V2O5/ Polypyrrole Network Nanostructures for High Performance Solid-State Supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 488–493.

(33) Li, Y. F.; Qian, R. Y. Electrochemical Overoxidation of Conducting Polypyrrole Nitrate Film in Aqueous Solution. *Electrochim. Acta* 2000, 45, 1727–1731.

(34) Song, J. X.; Zhou, M. J.; Yi, R.; Xu, T.; Gordin, M. L.; Tang, D. H.; Yu, Z. X.; Regula, M.; Wang, D. H. Interpenetrated Gel Polymer Binder for High-Performance Silicon Anodes in Lithium-ion Batteries. *Adv. Funct. Mater.* **2014**, *24*, 5904–5910.

(35) Beck, F.; Braun, P.; Oberst, M.; Bunsenges, B. Organic Electrochemistry in the Solid State-Overoxidation of Polypyrrole. *Ber. Bunsen-Ges.* **1987**, *91*, 967–974.

(36) Wernet, W.; Wegner, G. Electrochemistry of Thin Polypyrrole Films. *Makromol. Chem.* **1987**, *188*, 1465–1475.

(37) Ge, H.; Qi, G.; Kang, E.; Neoh, K. G. Study of Overoxidized Polypyrrole Using X-ray Photoelectron Spectroscopy. *Polymer* **1994**, 35, 504–508.

(38) Mawhinney, D. B.; Glass, J. A.; Yates, J. T. FTIR Study of the Oxidation of Porous Silicon. J. Phys. Chem. B 1997, 101, 1202–1206.
(39) Yalamanchili, M. R.; Atia, A. A.; Miller, J. D. Analysis of Interfacial Water at a Hydrophilic Silicon Surface by in-Situ FTIR/ Internal Reflection Spectroscopy. Langmuir 1996, 12, 4176–4184.

(40) Nam, D. H.; Lim, S. J.; Kim, M. J.; Kwon, H. S. Facile Synthesis of  $SnO_2$ -Polypyrrole Hybrid Nanowires by Cathodic Electrodeposition and their Application to Li-ion Battery Anodes. *RSC Adv.* **2013**, *3*, 16102–16108.

(41) Schroeder, A.; Francz, G.; Bruinink, A.; Hauert, R.; Mayer, J.; Wintermantel, E. Titanium Containing Amorphous Hydrogenated Carbon "lms(a-C: H/Ti): Surface Analysis and Evaluation of Cellular Reactions using Bone Marrow Cell Cultures in Vitro. *Biomaterials* **2000**, *21*, 449–456.

(42) Gao, G.; Wu, H. X.; Zhang, Y. X.; Wang, K.; Huang, P.; Zhang, X. Q.; Guo, S. W.; Cui, D. X. One-step Synthesis of Fe<sub>3</sub>O<sub>4</sub>@C

#### **ACS Applied Materials & Interfaces**

Nanotubes for the Immobilization of Adriamycin. J. Mater. Chem. 2011, 21, 12224–12227.

(43) Zhao, Y.; Peng, L. L.; Ding, Y.; Yu, G. H. Amorphous Silicon Honeycombs as a Binder/Carbon-Free, Thin-Film Li-ion Battery Anode. *Chem. Commun.* **2014**, *50*, 12959–12962.

(44) Barr, T. L. An ESCA Study of the Termination of the Passivation of Elemental Metals. J. Phys. Chem. 1978, 82, 1801–1811.

(45) Sahota, M. S.; Short, E. L.; Beynon, J. An Analysis of Silicon Oxide Thin Films by Computer Simulation of Si2p XPS Spectra using the Sanderson Technique. J. Non-Cryst. Solids **1996**, 195, 83–88.

(46) Jiang, X.; Yang, X. L.; Zhu, Y. H.; Yao, Y. F.; Zhao, P.; Li, C. Z. Graphene/Carbon-Coated Fe<sub>3</sub>O<sub>4</sub> Nanoparticle Hybrids for Enhanced Lithium Storage. *J. Mater. Chem. A* **2015**, *3*, 2361–2369.

(47) Kwon, T.; Jeong, Y. K.; Lee, I.; Kim, T. S.; Choi, J. W.; Coskun, A. Systematic Molecular-Level Design of Binders Incorporating Meldrum's Acid for Silicon Anodes in Lithium Rechargeable Batteries. *Adv. Mater.* **2014**, *26*, 7979–7985.

(48) Mai, L. Q.; Dong, F.; Xu, X.; Luo, Y. Z.; An, Q. Y.; Zhao, Y. L.; Pan, J.; Yang, J. N. Cucumber-Like  $V_2O_5$ /Poly(3,4-ethylenedioxythiophene) & MnO<sub>2</sub> Nanowires with Enhanced Electrochemical Cyclability. *Nano Lett.* **2013**, *13*, 740–745.

(49) Chen, H. W.; Wang, C. H.; Dong, W. L.; Lu, W.; Du, Z. L.; Chen, L. W. Monodispersed Sulfur Nanoparticles for Lithium-Sulfur Batteries with Theoretical Performance. *Nano Lett.* **2015**, *15*, 798– 802.

(50) Han, J. B.; Dou, Y. B.; Zhao, J. W.; Wei, M.; Evans, D. G.; Duan, X. Flexible CoAl LDH@PEDOT Core/Shell Nanoplatelet Array for High-Performance Energy Storage. *Small* **2013**, *9*, 98–106.

(51) Shen, X. W.; Qian, T.; Zhou, J. Q.; Xu, N.; Yang, T. Z.; Yan, C. L. Highly Flexible Full Lithium Batteries with Self-Knitted  $\alpha$ -MnO<sub>2</sub> Fabric Foam. ACS Appl. Mater. Interfaces **2015**, 7, 25298–25305.

(52) Ko, M.; Chae, S.; Jeong, S.; Oh, P.; Cho, J. Elastic a-Silicon Nanoparticle Backboned Graphene Hybrid as a Self-Compacting Anode for High-Rate Lithium Ion Batteries. *ACS Nano* **2014**, *8*, 8591–8599.

(53) Evanoff, K.; Magasinski, A.; Yang, J. B.; Yushin, G. Nanosilicon-Coated Graphene Granules as Anodes for Li-Ion Batteries. *Adv. Energy Mater.* **2011**, *1*, 495–498.

(54) Liu, N.; Lu, Z. D.; Zhao, J.; McDowell, M. T.; Lee, H. W.; Zhao, W. T.; Cui, Y. A Pomegranate-Inspired Nanoscale Design for Large-Volume-Change Lithium Battery Anodes. *Nat. Nanotechnol.* **2014**, *9*, 187–192.

(55) Chang, J.; Huang, X.; Zhou, G.; Cui, S.; Hallac, P. B.; Jiang, J.; Hurley, P. T.; Chen, J. Multilayered Si Nanoparticle/Reduced Graphene Oxide Hybrid as a High-Performance Lithium-Ion Battery Anode. *Adv. Mater.* **2014**, *26*, 758–764.