Poly-dopamine coated graphite oxide / silicon composite as anode of lithium ion batteries

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Abstract

PDA/GO-Si composite is synthesized and tested as anode material for lithium ion batteries. Silicon nanoparticles were first cooperated with graphite oxide (GO) and then embedded into a poly-dopamine (PDA) layer. PDA provides accommodation of volume change and protection to prevent the direct contact of the Si surface with electrolyte during charge/discharge cycling. GO acts as both volume change buffer and conductive support for the electrode. An initial discharge capacity of 2903 mAh·g⁻¹ was realized. A capacity of 1300 mAh·g⁻¹ was maintained after 450 cycles. The excellent capacity reversibility and long-term cycling stability of PDA/GO-Si was attributed to the intelligent structure and composition of the synthesized material.

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1. Introduction

Lithium ion batteries have attracted extensive attention because of their high energy density[1]. However, as the most widely commercialized anode material, graphite cannot meet the fast development of the batteries market because of its limited theoretical specific capacity($372 \text{ mAh}\cdot\text{g}^{-1}$)[2]. Silicon shows a theoretical capacity of $4200 \text{ mAh}\cdot\text{g}^{-1}$ and is considered as promising high energy density anode material[3]. However, extra large volume expansion/shrinkage of Si-based materials occurs during charging and discharging processes [4, 5], resulting in electrode pulverization, disruption and structural failure of solid electrolyte interface (SEI), and the according poor cycling stability as well. Nanolization, composite with buffer material and special microstructure design of active materials is the most popular strategy to alleviate the above-mentioned problems [6-11].

Graphene is a favorable carbonaceous matrix for silicon nanoparticles (Si NPs) because of its high electronic conductivity, good mechanical flexibility, and high chemical stability [12-14]. Moreover, graphene sheets can also serve as an interfacial adhesion pathway and mechanical support to restrict Si NPs in integral electrode structure [15-17]. The interaction between Si and graphene in Si/Graphene composite is very important to maintain electrode structure integrity. To realize the strong

interaction, graphite oxide (GO) instead of graphene, was used as the precursor. Graphite oxide (GO) contains more oxygen-containing functional groups which will combine Si particles by chemical bond to improve the stability of the structure. Moreover, graphite oxide can be partially reduced to realize good performance similar to graphene [18-22].

The continuous rupturing-reformation of SEI film is the critical problem affecting the long-term cycling stability and efficiency of silicon based electrodes. To address this issue, a stable SEI film, which is not affected by the volume change of silicon electrode materials, should be constructed. Conductive polymer coating on the surface of the silicon particles has been recognized as an effective strategy [8, 23].

In this paper, a novel Si composite electrode material was designed and fabricated. Si NPs modified with graphite oxide were embedded into a poly-dopamine (PDA) layer to form a PDA/GO-Si composite, where Si NPs act as an active materials[24], GO as buffer and conductive support. Particularly, the introduced PDA provides accommodation of volume change and protection to prevent the direct contact of the Si surface with electrolyte, making electrode maintain structure integrity during long charge/discharge cycling[25]. Dopamine can be spontaneous polymerized under alkaline conditions to interact with graphite oxide tightly and stably[26-28]. Dopamine will also reduce graphite oxide to be reduced graphite oxide (RGO)[29], which in turn improves the electronic conductivity. The intimate contact between Si NPs and GO cannot only benefit the excellent conductivity of electrode,

but also favors the high volume energy density because of the obtained relatively large current density.

2. Experimental

Figure 1

Silicon was modified by aminopropyltriethoxysilane (APTES)[30] before combining with GO because both GO and silicon oxide are negatively charged[18]. APTES act as a charged bridge by reaction of silicon oxide layer and GO, respectively[31]. The synthetic route of PDA/GO-Si and its schematic structure are shown in Figure 1.

All the other chemicals mentioned were used as received without any further treatment unless otherwise specified.

2.1 Preparation of Graphite oxide

GO was synthesized from graphite powder using modified Hummers method[32]. 240mlsulfuric acid, 2.5gNaNO₃ and 5g graphite powder were placed into a flasks cooled by ice water bath. After cooling down to 0 °C, 15g KMnO₄was added gradually with stirring and cooling to keep the temperature below 4°C. The mixture was sequentially stirred for 2h at 4°C, for 30 min at 35°C, and for 15min at 98°C, respectively. Then H₂O₂was added to remove the unreacted KMnO₄. The mixture was finally centrifuged and washed with distilled water followed by freeze-drying process.

2.2 Ammonization of Si NPs

The pursued Si NPs (30nm Aladdin) were immersed in hydrochloride solution (37%) for 1 h at room temperature with high-speed stirring. After vacuum dried at 80 °C for 2h, 200mg as-treated Si NPs was sonicated in anhydrous toluene for 1h. Then the mixture was reacted at 90°C under nitrogen atmosphere for 12h after addition of APTES. Ammonized Si NPs (Si@NH_2) was collected after sequentially centrifugation, washing with anhydrous toluene and dried under vacuum at 60 °C overnight.

2.3 Synthesis of PDA coated graphite oxide / silicon composite

100mg GO was sonicated with 100ml deionized water for 5min. 100mg Si@NH_2 was added into 100ml deionized water for 30min ultrasonic treatment. The as-prepared Si@NH_2 and GO dispersion were mixed and stirred overnight, follows by sequential centrifugation and dried under vacuum at 60 °C.

To a continuously stirred dispersion of 100mg the above-obtained GO-Si in 100ml deionized water, 0.121g Tris (Hydroxymethyl) aminomethane and 0.1g dopamine hydrochloride were added and stirred for 24h. Dispersion of PDA coated graphite oxide / silicon was filtered and washed with deionized water until the filtrate to be colorless. After dried under vacuum at 60 °C over night and thermal treatment in tube furnace at 180°C in H_2/Ar for 12h, the PDA coated graphite oxide / silicon composite was obtained.

2.4 Physical Characterizations.

The morphology of the composites was characterized by scanning electron microscopy (SEM, JEOLJSM6700F) and transmission electron microscopy (TEM, JEOL2010F). Fourier Transform-Infrared Spectroscopy (FTIR) was conducted using Bruker R 200-L spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Kratos Axis Ultra spectrometer with focused monochromatic Al K α radiation ($h\nu = 1486.6$ eV).

2.5 Electrode fabrication and electrochemical performance Evaluation

The active material, super P, binder (PVDF) with a mass ratio of 6: 2: 2 were mixed with N-methylpyrrolidinone to form slurry. The slurry was spread on the surface of copper foil followed by vacuum drying at 80 °C for 12h and then electrode cutting. The CR2016 coin cells were assembled in an argon glove box using lithium foil as counter/reference electrode and 1M LiPF₆ in mixture of ethylene carbonate (EC), dimethyl carbonate (DEC), and ethyl methyl carbonate (EMC)(1:1:1, v/v) as electrolyte. The charge/discharge performance test was performed on a CT2001A9 battery test system (Land). The voltage range was set between 0.005V and 3V. The Electrochemical impedance spectrums (EIS) and cyclic voltammetry testing were carried out on the CHI660A station (CH Instruments, Shanghai, China). The frequency range of EIS was 0.1-100000 Hz. The potential range of CV was 0.005-3.0V, and the scanning speed was 0.01mV/s.

3. Results and discussion

Figure 2

Figure 2 shows TEM images of GO-Si and PDA/GO-Si with different magnification. Layered structure of RGO is clearly observed. It can be also seen that spherical Si NPs with diameter ranging from 30 to 60nm are uniformly dispersed and sandwiched between GO layers. From high resolution TEM image of PDA/GO-Si particle (Figure 2f), it is apparent that Si NPs were covered by a homogenous phase with a thickness of about 8 nm which is not observed for GO-Si composite (Figure 2c). In addition, the huge difference in transparency for PDA/GO-Si (Figure 2a and 2b) and GO-Si (Figure 2d and 2e) also suggests the successful modification of silicon by coating with PDA. The clear and smooth surface of silicon particle before and after PDA treatment indicates great coating architecture which can effectively inhibit the direct contact of silicon and electrolyte, and benefit low irreversible capacity and high cycling stability.

Figure 3

To further ascertain the successful coating of PDA thin films, FT-IR spectra were recorded as shown in Figure 3. Clear absorption band at 3409cm^{-1} in the spectrum of Si@NH_2 is attributed to the $-\text{NH}_2$ anti-scaling. Absorption bands at 2928cm^{-1} and 876cm^{-1} are assigned to the NH_2 stretching and twisted vibration, respectively[33]. The absorption bands at 1715 cm^{-1} and 1050 cm^{-1} in the spectrum of GO-Si is the result of stretching vibration of C=O and the $-\text{COOH}$ on the GO. Compared to the spectrum of Si@NH_2 , the significant reduction of absorption bands at 1600 cm^{-1} to 1400 cm^{-1} and disappearance of absorption band of 876 cm^{-1} indicate that GO and silicon are

chemically bonded after heat treatment. After addition and polymerization of dopamine, the decreased intensity of absorption bands at 1715 cm^{-1} and 1050 cm^{-1} is attributed to the reduction of GO. The increase in peak intensity from 1600 cm^{-1} to 1400 cm^{-1} , especially the sharp peak strengthen at 1557 cm^{-1} , is caused by the cross-link reaction of PDA on the secondary amino group[28, 34, 35], suggesting the formation of PDA on the surface of GO-Si. The re-appearance of the broad absorption band at 3409 cm^{-1} after PDA treatment is attributed to the existed amino groups of PDA, further confirming the successful coating of PDA.

Figure 4

X ray photoelectron spectroscopy (XPS) surveys for Si@NH₂, GO-S and PDA/GO-Si are shown in Figure 4. After modification of APTES, N_{1s} core peaks for hydrogen-bonded NH₂ (400.65 eV) and free NH₂ (399.5 eV) are observed (Figure 4c), indicating the successful attachment of amino group on Si NPs. After incorporation with GO, the appearance of peak at 401.8 eV suggests the C-N bond formation. Accordingly, positive shift of Si-Si peak and negatively shift of Si-O peak are observed. With PDA treatment, the disappearance of Si-O at 103.55eV is caused by the PDA layer formation since XPS probes cannot penetrate the PDA layer. Similar to FTIR observation, the re-appearance of peak at 399.5 eV for free amino groups confirms the successful coating of PDA on GO-Si.

Figure 5

To evaluate electrochemical performance of the as-synthesized PDA/GO-Si composite material, the initial three CV curves of PDA/GO-Si with a potential window of open circuit voltage to 0.005 V at scanning rate of $0.1\text{mV}\cdot\text{s}^{-1}$ were tested. As depicted in Figure 5, a reduction peak at about 0.7 V is observed in the first cycle and disappeared in the subsequent cycles, which can be attributed to the irreversible formation of solid electrolyte interface (SEI) layer on the surface of the PDA/GO-Si. The similar redox peak area of 1st cycle to that of 2nd cycle suggests that the PDA/GO-Si electrode tends to be stable after the formation of SEI during first discharge.

Figure 6

The charge/discharge performance of GO-Si and PDA/GO-Si were investigated for long galvanostatic cycling. As shown in Figure 6a, the capacity of GO-Si decays sharply in the first 10 cycles, and then a capacity of $568\text{mAh}\cdot\text{g}^{-1}$ is obtained after 450 cycles. Compared to the poor cycling stability of element silicon electrode[36], it can be seen that the bonded GO in GO-Si benefits the cycling stability of silicon electrode. However, the initial discharge/charge of PDA/GO-Si deliver a capacity of 2903/1974 $\text{mAh}\cdot\text{g}^{-1}$ with capacity retention of 68%. The capacity decreases slightly in the first 20 cycles and then gradually stabilized with a coulombic efficiency of around 99.5%. After 450 cycles, a capacity of $1300.6\text{mAh}\cdot\text{g}^{-1}$ still remains. The significant cycling performance improvement of PDA/GO-Si compared to GO-Si demonstrates that PDA coating is excellent effective to help cycling stability maintaining. The slightly

increase in capacity during later cycles mainly comes from the activation of PDA for lithiation, the detailed mechanism should be further investigated. In order to understand the electrochemical performance of PDA/GO-Si anode materials in detail, the rate capability of PDA/GO-Si electrodes were further evaluated by changing the discharged/charge current density from 100 mA•g⁻¹ to 1000mA•g⁻¹ with 70 cycles. After 70 cycles, the discharge capacity retention is similar to that in galvanostatic cycling at a current density of 500mA•g⁻¹, indicating the excellent rate and capacity recovery. The great capacity retention performance of PDA/GO-Si electrode is attributed to the effective PDA coating which helps the electrode maintains structure integrity and inhabit the continuous destruction and reconstruction of SEI on the surface of Si NPs.

Figure7

In order to further clarify the potential reason of the excellent cycling properties of PDA/GO-Si electrode, electrochemical impedance spectra (EIS) were recorded. The EIS spectra are present in the form of Nyquist plots composed of a semicircle at the high and medium frequency attributed to the charge transfer reaction at the interface between electrode and electrolyte, and the inclined line in the low frequency corresponding to the lithium-ion diffusion in the solid electrode[37, 38]. The internal resistance of the cell was related to the junction point of the semi-circle and the real axis in high frequency. As shown in Figure 7, PDA/GO-Si electrode exhibit lower internal and charge transfer resistance than that of GO-Si, indicating the effective

action of PDA to boost the electron transfer and electrochemical lithiation/delithiation. The lower internal resistance of the PDA/GO-Si electrode may come from the realization of tight connection between silicon and GO with the help of PDA.

Figure 8

Figure 8 shows the SEM images of pristine silicon (top) and PDA/GO-Si (below) electrode before and after cycling, respectively. Fig. 8a to 8c reveals that initial integrity structure of pristine silicon electrodes collapses after 100 cycles and shows big cracks, which is the main reason of the poor cycling stability of pristine silicon electrode materials. However, there is no obvious crack is observed in PDA/GO-Si electrode after 100 cycles. And more interestingly, a much perfect structure integrity is shown after 450 cycles for PDA/GO-Si electrode, suggesting that the evolved cracks are effectively alleviated and even shows self-healing effect. The gradually increasing of PDA/GO-Si electrode specific capacity with longer cycling time may be come from the progressively recovering of the electrode integrity. The detail mechanisms should be further investigated in our future work.

4. Conclusion

PDA/GO-Si composites were synthesized and applied as electrode material for lithium ion batteries. In the PDA/GO-Si composites, silicon particles dispersed uniformly between GO layers. The introduced GO layers act as a buffer and electrode structure integrity support. The PDA coating inhabits the direct contact of silicon to electrolyte and helps the stable SEI maintaining. The introduced PDA layer can also

improve the conductance because it helps the realization of tight connection between silicon and GO. The battery assembled from the synthesized materials shows excellent capacity reversibility and long-term cycling stability. An initial discharge capacity of $2903 \text{ mAh}\cdot\text{g}^{-1}$ was realized. After 20 charge/discharge cycles, the capacity gradually stabilized with a coulombic efficiency of around 99.5%. A capacity of $1300 \text{ mAh}\cdot\text{g}^{-1}$ remained after 450 cycles. The excellent capacity reversibility and long-term cycling stability of PDA/GO-Si was attributed to the intelligent structure and composition of the synthesized material.

Acknowledgements

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References

- [1] B. Jang, M. Park, O.B. Chae, S. Park, Y. Kim, S.M. Oh, Y. Piao, T. Hyeon, Direct synthesis of self-assembled ferrite/carbon hybrid nanosheets for high performance lithium-ion battery anodes, *Journal of the American Chemical Society*, 134 (2012) 15010-15015.
- [2] T. Cassagneau, J.H. Fendler, High Density Rechargeable Lithium-Ion Batteries Self-Assembled from Graphite Oxide Nanoplatelets and Polyelectrolytes, *Advanced Materials*, 10 (1998) 877-881.
- [3] S. Bourderau, T. Brousse, D.M. Schleich, Amorphous silicon as a possible anode material for Li-ion batteries, *Journal of Power Sources*, s 81–82 (1999) 233-236.
- [4] Y.N. Jo, Y. Kim, J.S. Kim, J.H. Song, K.J. Kim, C.Y. Kwag, D.J. Lee, C.W. Park, Y.J. Kim, Si-graphite composites as anode materials for lithium secondary batteries, *Journal of Power Sources*, 195 (2010) 6031-6036.
- [5] X. Feng, H. Cui, R. Miao, N. Yan, T. Ding, Z. Xiao, Nano/micro-structured silicon@carbon composite with buffer void as anode material for lithium ion battery, *Ceramics International*, 42 (2016) 589-597.

- [6] J. Zhang, C. Zhang, S. Wu, X. Zhang, C. Li, C. Xue, B. Cheng, High-Coulombic-Efficiency Lithium Battery Based on Silicon Particle Materials, *Nanoscale research letters*, 10 (2015) 395.
- [7] B. Wang, X. Li, T. Qiu, B. Luo, J. Ning, J. Li, X. Zhang, M. Liang, L. Zhi, High volumetric capacity silicon-based lithium battery anodes by nanoscale system engineering, *Nano Lett*, 13 (2013) 5578-5584.
- [8] Z. Lu, J. Zhu, D. Sim, W. Shi, Y.Y. Tay, J. Ma, H.H. Hng, Q. Yan, In situ growth of Si nanowires on graphene sheets for Li-ion storage, *Electrochimica Acta*, 74 (2012) 176-181.
- [9] C. Li-Feng, R. Riccardo, C.K. Chan, P. Hailin, C. Yi, Crystalline-amorphous core-shell silicon nanowires for high capacity and high current battery electrodes, *Nano Letters*, 9 (2009) 491-495.
- [10] X. Wang, G.-S. Gai, Y.-F. Yang, W.-C. Shen, Preparation of natural microcrystalline graphite with high sphericity and narrow size distribution, *Powder Technology*, 181 (2008) 51-56.
- [11] M. Su, Z. Wang, H. Guo, X. Li, S. Huang, L. Gan, W. Xiao, Enhanced cycling performance of Si/C composite prepared by spray-drying as anode for Li-ion batteries, *Powder Technology*, 249 (2013) 105-109.
- [12] M. Zhou, F. Pu, Z. Wang, T. Cai, H. Chen, H. Zhang, S. Guan, Facile synthesis of novel Si nanoparticles-graphene composites as high-performance anode materials for Li-ion batteries, *Physical chemistry chemical physics : PCCP*, 15 (2013) 11394-11401.
- [13] Y. Zhu, W. Liu, X. Zhang, J. He, J. Chen, Y. Wang, T. Cao, Directing Silicon–Graphene Self-Assembly as a Core/Shell Anode for High-Performance Lithium-Ion Batteries, *Langmuir the Acs Journal of Surfaces & Colloids*, 29 (2013) 744-749.
- [14] K.S. Kim, Y. Zhao, H. Jang, Y.L. Sang, J.M. Kim, K.S. Kim, J.H. Ahn, P. Kim, J.Y. Choi, B.H. Hong, Large-scale pattern growth of graphene films for stretchable transparent electrodes, *Nature*, 457 (2009) 706-710.
- [15] X. Zhou, A.-M. Cao, L.-J. Wan, Y.-G. Guo, Spin-coated silicon nanoparticle/graphene electrode as a binder-free anode for high-performance lithium-ion batteries, *Nano Research*, 5 (2012) 845-853.
- [16] X. Zhao, C.M. Hayner, M.C. Kung, H.H. Kung, In-Plane Vacancy-Enabled High-Power Si-Graphene Composite Electrode for Lithium-Ion Batteries, *Advanced Energy Materials*, 1 (2011) 1079-1084.
- [17] M. Gu, S. Ko, S. Yoo, E. Lee, S.H. Min, S. Park, B.-S. Kim, Double locked silver-coated silicon nanoparticle/graphene core/shell fiber for high-performance lithium-ion battery anodes, *Journal of Power Sources*, 300 (2015) 351-357.
- [18] H. Tang, J. Zhang, Y.J. Zhang, Q.Q. Xiong, Y.Y. Tong, Y. Li, X.L. Wang, C.D. Gu, J.P. Tu, Porous reduced graphene oxide sheet wrapped silicon composite fabricated by steam etching for lithium-ion battery application, *Journal of Power Sources*, 286 (2015) 431-437.

- [19] B. Rajagopalan, J.S. Chung, Reduced chemically modified graphene oxide for supercapacitor electrode, *Nanoscale research letters*, 9 (2014) 1-10.
- [20] U. Saha, R. Jaiswal, J.P. Singh, T.H. Goswami, Diisocyanate modified graphene oxide network structure: steric effect of diisocyanates on bimolecular cross-linking degree, *Journal of Nanoparticle Research*, 16 (2014).
- [21] F. Tu, S. Liu, T. Wu, G. Jin, C. Pan, Porous graphene as cathode material for lithium ion capacitor with high electrochemical performance, *Powder Technology*, 253 (2014) 580-583.
- [22] F. Tu, S. Liu, G. Jin, G. Yan, C. Pan, Fabrication of graphene from graphene oxide by ultrasonication with high Li storage capability, *Powder Technology*, 249 (2013) 146-150.
- [23] Y. Chen, S. Zeng, J. Qian, Y. Wang, Y. Cao, H. Yang, X. Ai, Li(+)-conductive polymer-embedded nano-Si particles as anode material for advanced Li-ion batteries, *ACS applied materials & interfaces*, 6 (2014) 3508-3512.
- [24] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, *Science*, 318 (2007) 426-430.
- [25] C. Fang, Y. Deng, Y. Xie, J. Su, G. Chen, Improving the Electrochemical Performance of Si Nanoparticle Anode Material by Synergistic Strategies of Polydopamine and Graphene Oxide Coatings, *The Journal of Physical Chemistry C*, 119 (2015) 1720-1728.
- [26] M.J. Sever, J.T. Weisser, J. Monahan, S. Srinivasan, J.J. Wilker, Metal-mediated cross-linking in the generation of a marine-mussel adhesive, *Angewandte Chemie*, 43 (2004) 448-450.
- [27] J.J. Wilker, Positive charges and underwater adhesion, *Science*, 349 (2015) 582-583.
- [28] S.H. Hwang, D. Kang, R.S. Ruoff, H.S. Shin, Y.B. Park, Poly(vinyl alcohol) Reinforced and Toughened with Poly(dopamine)-Treated Graphene Oxide, and Its Use for Humidity Sensing, *Acs Nano*, 8 (2014) 6739-6747.
- [29] W. Li, T. Shang, W. Yang, H. Yang, S. Lin, X. Jia, Q. Cai, X. Yang, Effectively Exerting the Reinforcement of Dopamine Reduced Graphene Oxide on Epoxy-Based Composites via Strengthened Interfacial Bonding, *ACS applied materials & interfaces*, 8 (2016) 13037-13050.
- [30] D.B. Knorr, Jr., N.T. Tran, K.J. Gaskell, J.A. Orlicki, J.C. Woicik, C. Jaye, D.A. Fischer, J.L. Lenhart, Synthesis and Characterization of Aminopropyltriethoxysilane-Polydopamine Coatings, *Langmuir : the ACS journal of surfaces and colloids*, 32 (2016) 4370-4381.
- [31] Y. Wen, Y. Zhu, A. Langrock, A. Manivannan, S.H. Ehrman, C. Wang, Graphene-bonded and -encapsulated si nanoparticles for lithium ion battery anodes, *Small*, 9 (2013) 2810-2816.
- [32] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *Journal of the American Chemical Society*, 80 (1958) 1339.

- [33] R. Peña-Alonso, F. Rubio, J. Rubio, J.L. Oteo, Study of the hydrolysis and condensation of γ -Aminopropyltriethoxysilane by FT-IR spectroscopy, *Journal of Materials Science*, 42 (2006) 595-603.
- [34] S. Georgios, P. Dimitrios, B. Durairaj, ChemInform Abstract: Surface - Initiated Polymerization from Carbon Nanotubes: Strategies and Perspectives, *ChemInform*, 42 (2013) 677-704.
- [35] Z.F. Li, H. Zhang, Q. Liu, Y. Liu, L. Stanciu, J. Xie, Novel Pyrolyzed Polyaniline-Grafted Silicon Nanoparticles Encapsulated in Graphene Sheets As Li-Ion Battery Anodes, *ACS applied materials & interfaces*, 6 (2014) 5996-6002.
- [36] J.H. Ryu, J.W. Kim, Y.-E. Sung, S.M. Oh, Failure Modes of Silicon Powder Negative Electrode in Lithium Secondary Batteries, *Electrochemical and Solid-State Letters*, 7 (2004) A306.
- [37] S.-L. Chou, J.-Z. Wang, M. Choucair, H.-K. Liu, J.A. Stride, S.-X. Dou, Enhanced reversible lithium storage in a nanosize silicon/graphene composite, *Electrochemistry Communications*, 12 (2010) 303-306.
- [38] Q. Lv, Y. Liu, T. Ma, W. Zhu, X. Qiu, Hollow Structured Silicon Anodes with Stabilized Solid Electrolyte Interphase Film for Lithium-Ion Batteries, *ACS applied materials & interfaces*, 7 (2015) 23501-23506.
- [39] J. Zhang, T. He, W. Zhang, J. Sheng, I.S. Amiinu, Z. Kou, J. Yang, L. Mai, S. Mu, Na-Mn-O Nanocrystals as a High Capacity and Long Life Anode Material for Li-Ion Batteries, *Advanced Energy Materials*, (2016) 1602092.
- [40] J. Jamnik, J. Maier, Nanocrystallinity effects in lithium battery materials, *Physical Chemistry Chemical Physics*, 5 (2003) 5215.

Figure Captions

Figure 1. Schematic of the procedure for the fabrication of PDA/GO-Si

Figure 2. Transmission Electron Microscope (TEM) images of GO-Si composite (a, b, c) and PDA/GO-Si composite (d, e, f), respectively.

Figure 3.FT-IR spectra of the Si@NH₂, GO-Si and PDA/GO-Si, respectively.

Figure 4.Figure 4. XPS spectra of Si@NH₂, GO-Si and PDA/GO-Si. (a) survey spectra; (b) and (c) Si and N core peaks of Si@NH₂; (d)-(f)C, Si and N core peaks of GO-Si; (g)-(i) C, Si and N core peaks of PDA/GO-Si

Figure 5.CV curves of PDA/GO-Si electrode at a voltage of 0.005-3 V and scan rate of 0.1 mV•s⁻¹.

Figure 6.Charge/discharge cycling performance of GO-Si and PDA/GO-Si at a current density of 500mA•g⁻¹(a) and rate performance (b) of GO-Si and PDA/GO-Si composite electrode.

Figure 7. Nyquist plots of GO-Si, PDA/GO-Si anodes before charge/discharge cycling .

Figure 8. The SEM images of: Si electrode before (a) and after cycles (b、 c) and PDA/GO-Si electrode before (d) and after cycles (e、 f)

Graphical abstract

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