Single atom dispersion of silicon as advanced versatile electrode material

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Article

Keywords: Silicon, single atom dispersion strategy, Si single atom based electrode material, volume expansion inhibition

Posted Date: July 7th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-36360/v1>

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Abstract

Silicon (Si) exhibits highest theoretical charge capacity and low discharge potential, but the associated volume expansion cannot be neglected. Here we report a single atom dispersion strategy to prepare a well distributed Si single atom based electrode material, which can effectively inhibit the volume expansion even when the storage sites are fully occupied. The dispersion of Si single atoms are achieved by bonding Si atom with acetylenic carbon atom, forming a three-dimensional diamond-like skeleton. Owing to the combination of Si and diyne in the stable diamond-like skeleton, the as-prepared material, named as silicon-diamondyne (Si-DY), exhibits extraordinary electrochemical performance. Si-DY has been predicted to exhibit ultrahigh theoretical specific capacity of 3674 mA h g^{-1} , 2810 mA h g^{-1} , and 1945 mA h g^{-1} in lithium-ion battery (LIB), sodium-ion battery (SIB) and potassium-ion battery (KIB), respectively. Especially, the as-prepared Si-DY samples also achieve very stable measured specific capacity in LIB (2350 mA h g^{-1}), SIB (812 mA h g^{-1}) and KIB (512 mA h g^{-1}), as well as ultra-long cycling stability (up to 5000 charge/discharge cycles). Those excellent results demonstrate the single atom dispersion technology of Si atoms can be an efficient way to prepare high-utilization Si based electrochemical materials.

Introduction

Since developments in electrical equipment such as vehicles are attracting the attention of the general public, high-performance rechargeable batteries, which are key power components of those electrical devices, are leading researchers to dedicate great effort in further performance enhancements. In addition to technological innovation, finding novel raw materials with high performance, large reserves, and low cost is a fundamental way to realize high-efficiency batteries¹. Silicon (Si) is regarded as one of the most promising anode materials for rechargeable batteries; the material exhibits an extremely high specific capacity of approximately 4200 mA h g^{-1} ($\text{Li}_{4.4}\text{Si}$) in lithium ion batteries (LIBs)²⁻⁴. However, as an anode, Si still has some drawbacks, such as a large volume expansion and contraction (approximately 400%), which causes extensive pulverization and rapid deterioration of the electrical contact between the active material and the conductive binder, resulting in poor cycling stability and a sharp capacity decrease^{5,6}. Moreover, the solid electrolyte interphase (SEI) layers on the Si surface are inhomogeneous and too thick, and are greatly affected by temperature and additives, also resulting in low reversible specific capacity and poor stability. Carbon (C) coating technology on the surface of Si has been reported to restrain and buffer the volume expansion, prevent the agglomeration of active nanoparticles, and improve the electrochemical performance of Si electrodes in the process of ion intercalation and deintercalation⁷⁻¹². However, the reduction in specific capacity is a decisive tradeoff if the physical carbon coating of Si is brought into play, because this approach reduces the sample density and Si volume fraction. Furthermore, expensive nanoscale materials and complex experimental procedures also represent immense obstacles to practical application¹³. Nanosizing strategy of pure Si is another emerging and promising approach to accommodating the volume expansion¹⁴⁻¹⁶. Nevertheless, in view

of the irreversible damage in the charge/discharge process, the improvement in stability is still limited and the materials' conductivity must be enhanced.

In contrast to the physical carbon coating and nanosizing methods, the chemical dispersion of Si atoms in carbon materials, which can maintain excellent electrical conductivity and offer high theoretical capacity, represents a novel and more promising approach for obtaining high-capacity anode materials. As reported by a number of theoretical studies, sp-hybridized carbon delivers higher capacity for storing ions such as lithium (Li), sodium (Na), and potassium (K) than that of sp²- and sp³-hybridized carbon atoms^{17–20}. For instance, γ -graphdiyne, which is composed of both sp- and sp²-hybridized carbon atoms, offers a theoretical storage capacity of 2719 mA h g⁻¹ (C₆Li_{7.31})¹⁷, much larger than that of graphite (C₆Li, 372 mA h g⁻¹)¹⁹, which is composed only of sp²-hybridized carbon atoms. According to this rational analysis, a stable anode material, in which the decorated Si atoms are uniformly dispersed in sp-hybridized carbon atoms, could deliver excellent electrochemical performance, including high specific capacity and cycle stability. To prepare such a material, the preferred method might be the “bottom-up” synthetic strategy, in which the skeletal structure of the material can be controlled by adjusting the precursor; this approach has been widely utilized to realize many important carbon-based materials^{21–25}.

Herein, we report a single atom dispersion strategy of Si atoms, with which a hierarchical porous material called silicon-diamondyne (Si-DY) has been prepared. The as-prepared Si-DY, which is composed of Si atoms linked by sp-hybridized acetylenic bonds, is a well-defined three-dimensional (3D) porous network compound. The diamond-like skeleton structure ensures the stability of this material, while the abundant acetylenic bonds provide excellent conductivity and a large number of active sites, as well as transport passageways in the uniform cavities for ion storage and diffusion. Those benefits endow Si-DY with great potential in the application of energy storage devices such as rechargeable batteries. Since the porous Si-DY was obtained by a cross-coupling reaction of tetraethynylsilane on the copper (Cu) surface, the as-prepared Si-DY films can be well controlled and utilized directly as electrode without further treating. Notably, theoretical predictions display that this porous Si-DY is particularly suitable for the storage of ions such as Li, Na, and K with ultra-high theoretical capacities of 3674, 2810, and 1945 mA h g⁻¹, respectively. Additionally, the Si-DY electrodes for LIBs, sodium-ion batteries (SIBs), potassium-ion batteries (KIBs), and even pouch cells exhibit excellent electrochemical performance, such as high reversible capacity (2350 mA h g⁻¹, 812 mA h g⁻¹ and 512 mA h g⁻¹ at 50 mA g⁻¹ for LIB, SIB and KIB, respectively), outstanding rate capability (980 mA h g⁻¹ at 5000 mA g⁻¹), and ultra-long cycling stability (stable for 5000 cycles), implying that Si-DY possesses great potential for application in the high performance batteries.

Results

Preparation and characterization

Although the strategies of C coating technology on the surface of Si and nanosizing of pure Si have been widely reported, it is still the challenge to explore the way of atomic-level Si dispersion and application (Fig. 1a). To achieve the atomic-level Si dispersion, it is required us to find both a better technology for well-dispersion and a suitable supporter for Si atoms. A possible method to address the issue might be the “bottom-up” predesign route. So we proposed a chemical reaction synthesis strategy to realize this target. As shown in Fig. 1b, Si-DY was synthesized by a modified Glaser coupling of tetraethynylsilane on a Cu surface, so Si atoms were directly “covered” by acetylenic carbon atoms, which is completely different from the C coating and nanosizing strategies (Fig. 1a). Each Si atom was previously bonded with four acetylenic carbon atoms in the precursor, ensuring that all the Si was in a well-dispersed state in the as-prepared Si-DY. Theoretical calculations showed that, the cross-dehydrogenation coupled product is delivered with stable energy of -11.82 and -43.03 eV, indicating that the cross-coupling of the monomers to generate Si-DY is a thermodynamically favorable reaction. In addition, since Si atoms are bonded with sp-C atoms, the abundant conductive acetylenic bonds effectively improve the conductivity of Si-DY, which is conducive for the application of Si-DY as electrode. The reaction mechanism (Supplementary Fig. 1) and corresponding calculated energies (Supplementary Table 1) have been summarized in the Supplementary information.

The cross-coupling of the terminal alkynes performs well in an organic alkaline solution at $60\text{ }^{\circ}\text{C}$. Detailed NMR results are outlined in Supplementary Figs. 2–5. As shown in Supplementary Fig. 6, the liquids in the reaction system can be kept clear during the preparation process of Si-DY, which means the cross-coupling reaction can be carried out efficiently and selectively on the surface of Cu sheets. In order to obtain more intuitive evidence, we selected the part of the solution after reaction for NMR detection. Supplementary Fig. 7 is the ^{13}C NMR results of the residues in solvent after reaction. According to the ^{13}C NMR result, there is no unreacted tetraethynylsilane in the reaction solution, which proves the high yield of the reaction. Meanwhile, that also proves that the reaction did not occur in solvent and demonstrates the high selectivity of the reaction on Cu sheets. The 3D molecular skeleton of Si-DY, which is composed only of sp-C and $\text{sp}^3\text{-Si}$ atoms, is similar to the structure of diamond that is formed by $\text{sp}^3\text{-C}$ atoms. The butadiyne units, each linked to two $\text{sp}^3\text{-Si}$ atoms, enlarge the diameter of the cavity in Si-DY to 1.43 nm (Fig. 1b). Viewed from different perspectives, with its 3D network structure, Si-DY exhibited various inner channels extending in all directions with different specific sizes, as shown in Fig. 1b and Supplementary Fig. 8. Those channels not only supply feasible paths for the transport and diffusion of ions, but also provide sufficient space and attachment sites for metal ion (such as Li, Na, K) storage.

The as-prepared Si-DY films are continuous, uniform, self-supported, and bendable (see Fig. 2a). Scanning electron microscopy (SEM) images in Figs. 2b–d clearly shows the porous morphologies of Si-DY film composed by thin nanosheets, which not only reduce the barrier heights of ion diffusion to enhance the power density, but also enlarge the specific surface area. Cross-sectional SEM images show that the thickness of the as-prepared porous Si-DY film was approximately $3\text{ }\mu\text{m}$ (Fig. 2d). More detailed SEM images and photographs can be found in Supplementary Figs. 9 and 10. Nitrogen adsorption-desorption study was performed to further understand the porous structure of the as-prepared Si-DY. As

shown in Supplementary Fig. 11a, the as-prepared Si-DY delivers a adsorption isotherm of type IV with a H3-type hysteresis loop, indicating the hierarchical porous structure is mainly composed by mesopores²⁶. Meanwhile, at the very low P/P_0 region, the adsorption quantity of nitrogen also increases obviously, suggesting there are also lots of micropores in Si-DY. The Brunauer-Emmett-Teller (BET) surface area of Si-DY is $598 \text{ m}^2 \text{ g}^{-1}$, and the pore size distribution is mainly in the range of $0 \sim 10 \text{ nm}$ (Supplementary Fig. 11b), further certifying that the sample is mainly composed by mesopores and micropores, which is a critical factor for ion transport and diffusion. Interestingly, four typical configurations delivered the pore size of 0.45, 0.61, 1.2 and 1.4 nm (as displayed in Supplementary Fig. 8), are consistent with the experimental value, which further proves that Si-DY is a 3D structured porous nanomaterial. Macropores at 216 nm can also be observed, implying these pores in Si-DY are hierarchical, which can be guaranteed for the ion intercalation and diffusion to obtain excellent electrochemical performance for rechargeable batteries.

Corresponding transmission electron microscopy (TEM) images (Figs. 2e,i) clearly show the peeled Si-DY nanosheet, and agree well with the SEM images. High-resolution TEM (HRTEM) images (Figs. 2f,j) and corresponding selected area electron diffraction (SAED) patterns (Figs. 2g,k) show the high crystallinity of Si-DY in specific areas and reveal the Si-DY lattice structure. Different images of the HRTEM together with SAED patterns were acquired from different observation perspectives, confirming the structure of the 3D diamond-like Si-DY. As shown in Figs. 2f,g, the lattice fringe of the hexagon pattern agrees well with the theoretical model, corresponding to the (1, 2, 2) spacing of 0.429 nm (Fig. 2h). The moiré structure^{27,28} was also obtained with a lattice fringe of 0.304 nm (Figs. 2j,k), which closely matches the density functional theory (DFT) results of the (1, 0, 3) spacing (Fig. 2l). Many more HRTEM images of the fabricated Si-DY nanosheets are shown in Supplementary Figs. 12 and 13.

As shown in Fig. 3a of the Raman spectrum, a weak peak appears at 2130 cm^{-1} can be well assigned to the butadiyne bonds, proving the existence of the $\text{-C}\equiv\text{C-}$ triple bonds in Si-DY. Although each three butadiyne linkages connected on the same Si atom are not in the same plane, two butadiyne linkages connected on the same Si are on the same plane, and this coplanar specialty causes the overlap of electron clouds in spatial. Therefore, each butadiyne linker is partially conjugated in different planes with the other six butadiyne bonds, which connected to the two Si at both ends, thereby, the electron cloud on the diacetylene bond is dispersed to a greater extent in the 3D space, resulting in a red shift in Raman spectra. More importantly, the strong single peak appears at 1720 cm^{-1} , which is attributed to the diacetylene bond, proving that the synthesized Si-DY is a 3D structured material rich in diacetylene bonds. Presence of diacetylene bonds with a peak appears around 2130 cm^{-1} , which is belong to the typical acetylenic bond ($\text{-C}\equiv\text{C-}$) stretching vibration, is further proved via Fourier transform infrared (FT-IR) spectrum in Supplementary Fig. 14. A peak appears at 450 cm^{-1} can be well ascribed to the Si-C single bonds, suggesting large amount of Si atoms in Si-DY. Furthermore, theoretically calculations are in good agreement with the experimental Raman results, which further reveals the accuracy of the material composition (Fig. 3a and Supplementary Fig. 15). Additionally, different positions yield the same Raman peaks, indicating the as-prepared Si-DY films are uniform and continuous (Supplementary Fig. 16). Even

after exposure to air for 180 days, Raman detection again gave the same signal as the initial, demonstrating that the Si-DY films are very stable in air (Supplementary Fig. 16).

As direct evidence of the Si-DY carbon skeleton, typical acetylenic peaks were observed near 79–95 ppm in ^{13}C NMR (Fig. 3b), which can be attributed to the sp-C atoms linked between two acetylenic carbon atoms. The peaks found from 61–63 ppm can be assigned to the sp-C atoms bonded to Si atoms. Meanwhile, the solid-state ^{29}Si NMR spectrum exhibits a single peak at –93 ppm (Fig. 3c), representing the existence of the solely sp³ Si atoms in Si-DY. In the X-ray photoelectron spectroscopy (XPS) image, the C1s peak, which appears at 284.8 eV (in Supplementary Fig. 17), can be mainly attributed to sp-C atoms (Fig. 3d). Furthermore, the single peak of Si 2p appearing at 102.2 eV (Fig. 3e) can be well ascribed to the sp³-Si atoms, which agrees closely with the solid state ^{29}Si NMR image. Moreover, XPS analysis shows that the atomic ratio of C to Si is 0.87: 0.11, which agrees well with the molecular composition of Si-DY. Additionally, the atomic ratio of C/Si in Si-DY was further confirmed by elemental analysis and energy-dispersive X-ray (EDX) analysis in Supplementary Fig. 18 and 19, the value of these results is 8: 1 and 8.3: 1, respectively.

As established by the Si-DY structure, the conjugation feature of the large number of introduced diacetylene bonds is beneficial to the conductivity. Si-DY films exhibit excellent conductivity, which was measured to be $2.0 \times 10^{-2} \text{ S m}^{-1}$ on average, as shown in Fig. 3f. Additionally, the self-supported continuous Si-DY film exhibits an optical band gap of 1.93 eV (Fig. 3g), which compares well with the value of 1.8 eV predicted by the DFT calculations (Supplementary Fig. 20). The low carrier barrier and excellent conductivity prove that the atomic C coating can effectively improve the conductivity of Si, forming a conductive 3D porous network.

Theoretical prediction and electrochemical evaluation of Si-DY anode

According to the previous reports on ion storage in graphdiyne-based anodes^{20,21,29}, five main storage sites are proposed as shown in Fig. 4a and Supplementary Figs. 21–23. The K, Na, and Li atoms can be absorbed on both the π (py) and π (pz) of the triple bonds. The binding energies (Eb) of those configurations are 1.55 and 1.37 eV for K, 1.12 and 1.21 eV for Na, and 1.64 and 1.77 eV for Li. The K, Na, and Li can also be adsorbed near the single bond between two sp-C atoms, with Eb in the range of 1.06 to 1.83 eV. It can be seen from the calculated results that the strongest adsorption sites for these three metal atoms are near Si atoms, which indicates the favorable influence of the Si element on the metal ion storage. At each adsorption site, the Eb of Li ions is the strongest, which can be well explained by the size of the ionic radius. The relative size of all the atoms and diffusion tunnel are showed in Figs. 4b–d and Supplementary Fig. 8. It can be clearly found that, the stable diamond-like molecular skeleton and the large number of nanopores in Si-DY are both beneficial factors for ion diffusion, playing a vital role in improving the electrochemical performance.

On the basis of the predicted storage sites and the rigidity of the molecular skeleton, theoretical configurations that can guarantee both the stability and the maximum number of adatoms are proposed

as shown in Figs. 4e–h. The repeating unit of SiC_8 was selected as the optimized model for maximum storage in Si-DY-based electrodes. As shown in Fig. 4f, the calculated capacity for the optimized $\text{Li}_{17}\text{SiC}_8$ is 3674 mA h g^{-1} . Although the calculated capacity for $\text{Li}_{17}\text{SiC}_8$ is already high, this is still not the maximum limit for Li storage, because there are still many other sites (such as defects and cavities) that can enhance the storage. Furthermore, we also calculated capacities for Na and K ion storage, corresponding to $\text{Na}_{13}\text{SiC}_8$ (Fig. 4g) and K_9SiC_8 (Fig. 4h) with values of 2810 and 1945 mA h g^{-1} , respectively. See Supplementary Figs. 24–26 for the corresponding storage sites for Li, Na, and K. Notably, after the maximum storage of Li, Na, or K, the volume of those optimized configurations are not changed while compared with the theoretical model (SiC_8 in Fig. 4e), which further proves the excellent stability of Si-DY.

As we all known, most LIB bulk electrode materials do not have sufficient interstitial space to accommodate and transport Na or K ions because of the larger ion sizes of Na (diameter $\Phi = 2.04 \text{ \AA}$) and K (diameter $\Phi = 2.76 \text{ \AA}$)³⁰. In our case, the 3D diamond-like structure of Si-DY can also offer numerous sites and channels to satisfy the storage and diffusion of larger ions such as Na and K (Fig. 4i). Importantly and intriguingly, this Si-DY material can be successfully applied as the anode for LIBs, SIBs, and KIBs, delivering excellent electrochemical performance. As exhibited in Figs. 4j–l, the assembled LIBs, SIBs, and KIBs incorporating Si-DY electrodes all exhibited similar specific capacities during twice successive rate cyclability, demonstrating excellent rate and reproducibility performance. The fabricated LIBs, SIBs, and KIBs based on Si-DY delivered high capacities of $2350, 812, \text{ and } 512 \text{ mA h g}^{-1}$ under the current density of 50 mA g^{-1} , exhibiting that Si-DY is a promising anode that can be utilized in high-power energy devices. Capacity values of 2007, 1840, 1615, 1414, and 1225 mA h g^{-1} were obtained at 100, 200, 500, 1000, and 2000 mA g^{-1} for assembled LIBs, respectively. Even at a higher current density of 5000 mA g^{-1} , the reversible capacity was up to 980 mA h g^{-1} . Under 100, 200, 500, 1000, and 2000 mA g^{-1} , the prepared SIBs deliver the capacity values of 782, 617, 505, 353, and 258 mA h g^{-1} , and the fabricated KIBs obtain the capacity values of 387, 270, 151, 92, and 52 mA h g^{-1} , accordingly. Even after several charge/discharge cycles under different current densities, the specific capacities of the Si-DY electrodes were recovered to the original level, demonstrating that Si-DY is highly tolerant of the fast ion insertion/extraction process, which can be attributed to the high content of sp-C atoms, large specific surface area, and the unique nanostructured morphology.

To further study the cyclic performance of Si-DY electrodes, long-term cycling was investigated. The fabricated LIBs, SIBs, and KIBs based on Si-DY delivered high capacities of 2303, 790, and 496 mA h g^{-1} under the current density of 50 mA g^{-1} for 100 cycles (Figs. 5a,d,g), further demonstrating that Si-DY can be used as a promising stable anode in energy storage devices. As shown in Figs. 5c,f,i and Supplementary Figs. 27–29, Si-DY electrodes were also measured at different current densities from 100 to 5000 mA g^{-1} . All these cyclic performances at different rates further displayed the excellent stability of the Si-DY electrodes. Specifically, even under high current density of 5000 mA g^{-1} , the as-prepared LIBs also offer a stable capacity of approximately 944 mA h g^{-1} for 5000 cycles, with an excellent Coulombic

efficiency of 99.9 % (Figs. 5c). Si-DY electrodes also deliver excellent stability in both SIBs and KIBs, operating stably for 3800 cycles in SIBs and 500 cycles in KIBs (Figs. 5f,i). Such excellent electrochemical performance with high capacities and ultralong cycling stability for all three kinds of rechargeable batteries has rarely been reported previously, implying that Si-DY can be applied well in a variety of energy storage devices. The high specific capacities in LIBs (Fig. 5b), SIBs (Fig. 5e), and KIBs (Fig. 5h) are highly prominent, and better than that of numerous other materials such as graphite³¹, hard carbon^{32, 33}, graphene,³⁴ heteroatom-doped graphene,^{35–37} phosphorus-based alloy materials³⁸, and many other C/Si-based materials^{10–13, 39–42}. For a comprehensive comparison, the related references and materials are summarized in Supplementary Tables 2–4.

The initial Coulombic efficiency of the LIBs calculated from the charge-discharge profile (Supplementary Fig. 30) was 58 %, comparable to many other C-based materials, and attributed to the large specific surface area and the formation of an SEI layer⁴³. Almost all the discharge capacities were acquired below 1.5 V, indicating that Si-DY is an anode with great potential for Li ion storage^{38, 43, 44}. The charge-discharge profiles of SIBs and KIBs can also be found in Supplementary Fig. 31. As shown in Supplementary Fig. 32, the Si-DY electrode delivers an irreversible cyclic voltammogram (CV) band during the first cathodic scan near 0–1.3 V, which can be attributed to the formation process of SEI film and the insertion or extraction reaction of Li ions into or from the porous Si-DY. This phenomenon is perfectly consistent with the charge-discharge profiles. In-situ Raman spectroscopy was also performed to study the Li and Na storage mechanism of the Si-DY using in-situ LIBs and SIBs in an electrolyte solution. As shown in Fig. 5j and Supplementary Fig. 33, the signals of the peak at 450 and 1720 cm⁻¹ gradually weaken during the discharge process, demonstrating that both -Si-C- and -C≡C- bonds can play the role of storage sites for Li and Na ions.

The physical morphology and chemical composition were also studied after charge and discharge cycles to investigate the stability of the Si-DY electrodes. As shown in Supplementary Fig. 34, after 50, 100, 200, and 500 charge/discharge cycles, stable SEI layers were grown on the Si-DY surface. The SEI layer, which is insoluble in organic electrolyte and existed stably, can effectively prevent the co-embedding of solvent molecules and the resulting damage to electrode materials, greatly improving the cycle performance and service life of the electrode⁴⁵. Furthermore, ex-situ Raman spectroscopy demonstrated that the Si-DY electrodes exhibit the same signals after different numbers of charge/discharge cycles (Fig. 5k), indicating that Si-DY has outstanding stability for ultralong cycling performance.

The continuous uniform Si-DY films deliver a good flexibility, and it can be restored to the original shape even after several times of bending test (see Fig. 6a), implying that Si-DY can be well utilized in the development of soft pack batteries. As shown in Fig. 6b, a large pouch cell with an area of 9×9 cm² was fabricated, and this charged cell can continuously illumine the LED screen. In the first charge/discharge profile, the assembled pouch cell delivers a high reversible specific capacity of approximately 900 mA h g⁻¹ under 200 mA g⁻¹. The galvanostatic charge/discharge profiles of the Si-DY pouch cell obtained after bending at different angles are almost identical (Supplementary Fig. 35), and before bending, bending at

90°, and after bending, the measured voltage values are exactly the same (Fig. 6c), further proving that the flexible pouch cell can continue working normally even under folding conditions. Furthermore, the LED lamps remained lit even after the pouch cell was folded at different angles, including 180°, 145°, 90°, 45°, 0°, and 180° (Fig. 6d), demonstrating the outstanding flexibility of the Si-DY pouch cell. More intuitive Supplementary Video 1 exhibits more directly that the assembled pouch cell can keep the LED lamp on continuously. Meanwhile, Supplementary Videos 2 and 3 also vividly prove that the assembled pouch cell can keep working well and be easily bent during the working process, indicating that Si-DY is also a promising anode for application in flexible energy storage devices.

Conclusions

In summary, we demonstrated a single atom dispersion technology to prepare a transformative electrochemical energy material that has a very clear composition, theory, structure, nature, and excellent performance. The as-prepared porous Si-DY, which is composed of Si connected by diacetylenic linkers, is a well-defined 3D diamond-like material, and has been observed excellent electrochemical performance as the versatile anode in rechargeable batteries. The ultrahigh reversible capacity, superior rate capability, and ultralong cycling stability applied in LIBs, SIBs and KIBs, indicate that Si-DY is a promising anode material with great potential for practical energy devices. Additionally, our results may lead to new ideas in the field of designing electrochemical energy materials and devices, which can bring new understanding to scientists in the energy field and promote progress in electrochemistry.

Methods

Synthesis of Si-DY.

All reactions were performed under argon (Ar) condition unless otherwise noted. Pyridine was pretreated under reflux with KOH. Tetrahydrofuran (THF) was dried by distillation over sodium/benzophenone. Tetrachlorosilane and other common reagents were purchased from J&K Scientific Ltd. and used without further purification. Copper foil was purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC) and treated by sonicating in 1M HCl, water, ethanol and acetone, sequentially, for 10 minutes, dried under a flow of nitrogen and used immediately. Tetrakis(trimethylsilyl)ethynylsilane and tetraethynylsilane can be successfully prepared following the reported process⁴⁶, and the reaction is depicted in Figure S1. Sixteen pieces of treated copper foils (1.0 cm × 10.0 cm) were placed into a three-necked flask under Ar, then tetrahydrofuran (110 mL) and pyridine (10 mL) were added, after that, tetraethynylsilane (128 mg, 1 mmol) in tetrahydrofuran (50 mL) was dropped within 3 hours. The mixture was stayed in dark without stirring for three days at 60 °C, and the black Si-DY films were generated on the Cu surface. Other sizes of Si-DY films can be prepared by adjusting the monomer concentration and the area of Cu foil.

Characterization.

^1H NMR, ^{13}C NMR were recorded on a Bruker AVANCE-III 600 (600 MHz for ^1H , 150 MHz for ^{13}C) instrument in CDCl_3 with tetramethylsilane as an internal standard. Morphology details were examined using field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscopy (TEM, HITACHI H-7650). The chemical structure of the products was characterized by UV-vis adsorption spectroscopy (HITACHI U-4100), Fourier transform infrared spectroscopy (FT-IR, Thermo-Fisher Nicolet iN10) and Raman spectroscopy (Thermo Scientific DXRxi, 532 nm). The X-Ray photoelectron spectrometer (XPS) was collected on VG Scientific ESCALab 220i-XL X-Ray photoelectron spectrometer, using Al K radiation as the excitation sources. All first-principles calculations were performed based on the DFT as we reported previously^{20, 23}. The density of states (DOS) were further calculated with the Perdew, Burke, and Ernzerhof (PBE) functional using VASP software.

Electrochemical measurement.

2032 Coin-type cells were fabricated to evaluate the electrochemical Li/Na storage capacity of the Si-DY based electrode with pure Li/Na/K foils as the counter electrode^{21, 47-49}. The Si-DY films grown on the copper foil were cut into pieces (1.0 cm $\times$ 1.0 cm), dried in vacuum at 80 °C for 12 h, after that used as working electrodes without adding any binders. The polypropylene separator (Celgard 2500), and the liquid electrolyte (ethylene carbonate, dimethyl carbonate, 1:1 by volume) with 1.0 M LiPF_6 were used for LIBs. Glass fiber, (ethylene carbonate, dimethyl carbonate, 1:1 by volume) with 1.0 M NaClO_4 and 5 wt % fluoroethylene carbonate (FEC) additive were used for SIBs. The pouch Li-ion cells comprised of Lithium cobaltate (LiCoO_2) as positive and Si-DY as negative electrode material. The separator of the pouch cell is poly (vinylidene fluoride) film. The electrolyte we adopted is the solution of LiPF_6 . The geometry of the cell is common, with a dimension of 1 mm thick, a width of 92 mm, and a height of 90 mm. All these cells were assembled in Ar atmosphere glove box and the electrochemical performance were evaluated between 0.005 and 3 V using a LAND battery testing system.

Declarations

Acknowledgements

This study was supported by the National Natural Science Foundation of China (21790050, 21790051, 21701182, 51822208, 21771187, 11704024, 51802324), the Frontier Science Research Project (QYZDB-SSW-JSC052) of the Chinese Academy of Sciences, and the National Key Research and Development Project of China (2018YFA0703501).

Author contributions

C.H., Y.L. and Z.Y. designed the experiments. C.H. and Y.L. conceived and supervised the research. Z.Y. and Y.S. performed the analysis and carried out most of the experiments. C.Z., X.L. and X.W. performed

the DFT simulations. Z.Y., Y.S., J.H., N.W., Y.L. and C.H. performed the analysis. Z.Y. and C.H. wrote the manuscript with help from all co-authors.

Competing financial interests

The authors declare no competing financial interests.

Data availability

The authors declare that the data supporting the findings of this study are available within the article and its Supplementary information files.

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Figures

Figure 1

Strategies of effectively using Si anode. a, C coating, Si nanosizing and the possible single atom dispersion technology for Si anode. b, Schematic illustrations of the single atom dispersion of Si using sp²-C atoms and the synthetic process for Si-DY. Light blue represents the bulk Si anode, grey represents C materials, light blue spheres represent Si atoms and grey spheres represent C atoms.

Figure 2

Structural characterization of Si-DY. a, Photograph, b-d, SEM (b, c), and (d) cross-sectional SEM images of as-prepared Si-DY films. e-l, HRTEM images (e, f, i, j), experimental SAED patterns (g, k), and corresponding simulated SAED patterns (h, l).

Figure 3

Chemical composition characterization of Si-DY. a, Raman spectrum and the predicted vibrational modes of the as-prepared Si-DY film, in which the red arrows show the atomic motion directions of the main contributors. b-c, Solid-state ¹³C (b), ²⁹Si (c) NMR; inset of b is the repeating unit. d-e, XPS of C 1s (d) and Si 2p (e) of the bulk Si-DY powders. f, I-V curves of as-prepared Si-DY films; insets are the repeating skeleton and a schematic illustration of the device comprising silver electrode (gray), Si-DY film (blue), and Cu foil (yellow). g, UV-vis diffuse reflection of the as-prepared Si-DY film.

Figure 4

Theoretical calculation and experimental measurement of Si-DY anode. a, Calculated binding energies and corresponding storage sites. b-d, Proposed diffusion paths of Li (b), Na (c), and K (d) ions in Si-DY (the relative size of all the atoms and diffusion tunnel are showed as the pictures). e-h, The geometries of the optimized configuration (e) and fully occupied modes for Li (f), Na (g), and K (h). i, Schematic diagram of the Si-DY based half-cell; inset is the assembled half-cell. j-l, Rate and reproducibility performance of the Si-DY-based electrodes for LIBs (j), SIBs (k), and KIBs (l).

Figure 5

Electrochemical performance of Si-DY anode. a,c, Cycle performance of the Si-DY-based electrodes for LIBs at 50 (a) and 5000 (c) mA g⁻¹. d,f, Cycle performance of the Si-DY-based electrodes for SIBs at 50 (d) and 2000 (f) mA g⁻¹. g,i, Cycle performance of the Si-DY-based electrodes for KIBs at 50 (d) and 1000 (f) mA g⁻¹. b,e,h, Comparison with some C and Si based anode materials in LIBs (b), SIBs (e), and KIBs (h). j, In-situ Raman spectra; inset is the assembled in-situ LIB. k, Ex-situ Raman spectra after 50, 100, 200 and 500 charge/discharge cycles under 2000 mA g⁻¹.

Figure 6

Application of Si-DY anode in flexible energy storage devices. a, Photographs of bending test of the flexible Si-DY film. b, Photograph of an assembled pouch cell applied for lighting an LED screen; inset is the first charge/discharge profile of the assembled pouch cell under 200 mA g⁻¹ between 0.005 and 3 V. c, Voltage measurement of Si-DY based pouch cell before bending, bending 90° and after bending. d, Photographs of the flexible pouch cell applied for lighting LED lamps, bent at different angles.

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