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# A Facile 3D Binding Approach for High Si Loading Anodes

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ABSTRACT

Silicon is regarded as one of the most promising anode materials for Li-ion batteries owing to its high theoretical capacity (4200 mA h g$^{-1}$, $Li_{22}Si_5$), but the short cycle life mainly caused by the dramatic volume effect has hindered its practical application. To address this major issue, we report here an effective and scalable approach to fabricate a novel Si electrode via the addition of silane coupling agent, which not only connects silicon and polyacrylic acid (PAA) covalently but also crosslinks PAA, thus forming an entire 3D binding network. The dual functions of 3-amino-propyltriethoxysilane (APTES) in an electrode with 80% Si nanoparticles greatly improves the structural stability during the charge/discharge process, leading to excellent electrochemical performances, such as 1000 mA h g$^{-1}$ over 1200 cycles and high silicon loading of ca. 4.2 mA h cm$^{-2}$. Moreover, this binder system is also effective for the thick silicon/graphite electrodes towards practical application.



## 1. Introduction

With the rapid development of the modern communication, energy storage and traffic technologies, demands for next generation lithium ion batteries with higher energy density become urgent. Due to its high theoretical capacity (4200 mA h g$^{-1}$, $Li_{22}Si_5$) and moderate delithiation potential (0.4 V vs Li/Li$^+$), silicon has attracted enormous attentions as a promising anode material [1]. However, silicon undergoes a tremendous expansion and contraction during the lithiation/delithiation process [2], which leads to a series of problems, such as pulverization of silicon, cracking of the electrode, electronic disconnection and the instability of the solid-electrolyte interphase (SEI) [3,4]. To minimize the volume effects, many strategies have been proposed including use of porous silicon structure [5,6], nanosize silicon [7–9] and Si/C composites [10–14]. In addition to active materials, binder is also a key factor which directly affects the electrochemical performance of silicon-based electrodes [15].

At present, the frequently applied binders for silicon-based anodes are sodium carboxymethyl cellulose (CMC) [16], sodium alginate (SA) [15] and polyacrylic acid (PAA) [17], with which the adhering action mainly arises from hydrogen bonds between silicon oxide layers on the Si surfaces and the polar functional groups of the binders. This weak interaction cannot ensure the long-term cycle performance and high areal capacity. To address this issue, various new binders have been investigated, such as polymerized β-cyclodextrin (β-CDp) [18], synthetic self-healing polymers [19,20], gum Arabic [21], xanthan gum (XG) [22], guar gum(GG) [23,24] and some conductive binders [25–27]. Besides these synthetic or natural binders, significant advancements have also been made on ameliorating the existing binders. Crosslinking can enhance the mechanical properties of binders and has been proven to be effective in the binder design [28–32]. It was reported that in-situ crosslinking of PAA with polyvinyl alcohol (PVA) [30] or CMC [29] significantly enhanced the cycle performance of the Si-based anodes. Moreover, in view of that the electrode is an integrated system, binder design from the components interaction and 3-dimensional configuration is important [33].

Here we introduce a coupling agent 3-amino-propyltriethoxysilane (APTES) to Si electrodes, which not only connects Si and PAA covalently but also crosslinks PAA as illustrated in Fig. 1. This 3-dimensional integration strategy enables a high areal capacity (ca. 4.2 mA h cm$^{-2}$) for silicon electrode with only 10% PAA. Moreover, when applied in thick silicon/graphite electrode for practical consideration, the proposed electrode has exhibited relatively stable cycling behavior over 150 cycles, in comparison with a rapid degradation after the initial several cycles for the conventional Si + PAA electrode.

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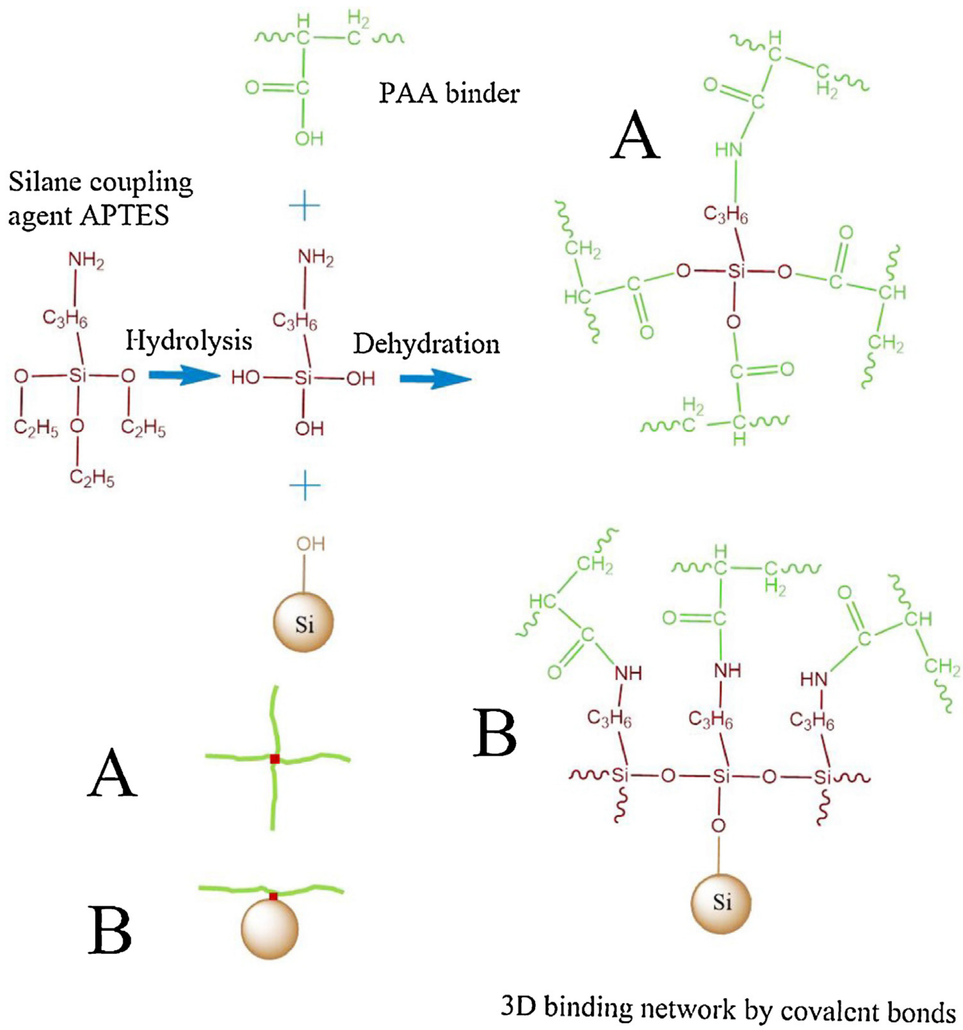


**Fig. 1.** Design and structure of the electrode with APTES.

## 2. Experimental

### 2.1. Electrode preparation

Silicon nanoparticles (50–200 nm, Alfa-Aesar) were mixed with Super P (40 nm, Timical) and PAA (Mv ~ 450 000, Aldrich) in an 8:1:1 weight ratio in water. After stirred for 1 h, a certain amount of APTES (Sinopharm Chemical Reagent Co.) was added and the slurry was stirred for another 4 h. The obtained slurry was coated on a Cu foil current collector and then dried at 70 °C under vacuum for 6 h. Finally, the coated foil was cut to Φ12 mm sheets for assembling cells. Conventional Si + PAA electrode was prepared in the same route just without APTES.

For the thick Si/graphite electrode towards practical application, silicon nanoparticles, nanosized graphite (Timical), KS–6 L (Timical), Super P and PAA were blended in the weight ratio of 40:25:15:5:15 in water. The slurry was stirred for 1 h and then 0.3 wt. % APTES (based on all the electrode materials) was added. The rest routes are the same as the mentioned above.

### 2.2. Cells assembling and electrochemical tests

The electrochemical performance of the as-prepared anodes was tested via CR2016 coin cells using ENTEK ET20-26 as separator, 1 M $LiPF_6$/EC + DMC (1:1 by volume, ethylene carbonate (EC), dimethyl carbonate (DMC)) as electrolyte, plus 10% fluoroethylene carbonate (FEC), and pure lithium foil as counter electrode. The cells were assembled in an argon-filled glove box (MB-10 compact, MBraun) containing less than 5 ppm water or oxygen. The cycling performance was evaluated on a LAND battery test system (Wuhan Kingnuo Electronics Co., Ltd., China) with constant current densities and the cut-off voltage of 0.01/1.2 V vs $Li/Li^+$ at 25 °C. The specific capacities were calculated on the basis of the Si weight for silicon anodes and the total weight of all the electrode materials for Si/graphite anodes.

### 2.3. Morphology and structure characterization

The morphologies and microstructures of the electrodes were observed by a FEI Nova SEM 230 ultra-high resolution FESEM. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a FTIR spectrometer (Bruker VECTOR22), where PAA and APTES were mixed in weight ratio of 1:3 in water, and then dried at 70 °C in vacuum for 6 h while PAA and APTES were directly used for a comparison. For X-ray photoelectron spectroscopy (XPS) tests, 0.5 g silicon nanoparticles and 0.015 g APTES were dispersed in 25 ml water and then stirred for 5 h. Then silicon particles coated by APTES were collected by centrifugation and washed by water. The particles were dried at 70 °C in vacuum for 6 h and designated as Si@APTES. Silicon particles and electrode with 1% APTES were