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# Silicon lithium-ion battery anode with enhanced performance: Multiple effects of silver nanoparticles

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ABSTRACT

Silicon has been regarded as one of the most promising next generation lithium-ion battery anode. However, the poor cyclic stability of the Si based anode has severely limited its practical applications, which is even worse with high mass loading density (>1 mg $cm^{-2}$). A new concept has been developed to enhance the electrochemical performance of the Si nanoparticle anode. Silver nanoparticles are composited with the silicon nanoparticles in a facile way for the first time. It is found that the mechanical properties of the Si electrode have been significantly improved by the incorporation of the silver nanoparticles, leading to enhanced cyclic performance. With the Si/Ag mass ratio of 4:1, the reversible specific discharge capacity is retained as 1156 mA h $g^{-1}$ after 100 cycles at 200 mA $g^{-1}$, which is more than three times higher than that of the bare silicon (318 mA h $g^{-1}$). The rate performance has been effectively improved as well due to excellent electron conductivity of the silver nanoparticles.



## 1. Introduction

Lithium-ion batteries (LIBs) have been widely utilized in portable electronic devices and automotive vehicles due to their exceptional performance including high energy density and long cycling life [1–7]. Silicon is considered as one of the most promising anode candidates to replace commercial graphite owing to its appropriate lithiation potential, and high theoretical capacity (4200 mA h $g^{-1}$ vs. 372 mA h $g^{-1}$) [8]. Nevertheless, drastic volume change (ca. 360%) is accompanied with the repeated Li alloying/dealloying processes [9,10]. It causes crack of the silicon particles and pulverization of the whole electrode as well, which results in fast capacity fading and very poor cyclic stability [11,12]. Reducing particle size and constructing hierarchical structures have been applied to accommodate the volume change of the silicon during cycling [13,14]. In addition, the intrinsic poor electronic conductivity of the elemental Si greatly impedes electrochemical kinetics of the lithiation/delithiation processes, leading to moderate rate performance [15,16]. Compositing with secondary medium such as Cu [17,18], Ag [19,20], Ni [21], $B_4C$ [22], carbon [23–26] and graphene [27–30] have been intensively investigated to absorb the mechanical stress generated by volume change and enhance the electron conductivity of the silicon based electrode as well.

Compared to the extensively applied carbonaceous medium, metals possess particular advantages including superior electron conductivity and excellent mechanical property [31]. Among the different metals, silver exhibits great chemical stability and outstanding electron conductivity. In addition, it is reported that the silver nanoparticles can promote the formation of the solid electrolyte interphase (SEI) film on the surface of the Si, which is favorable to maintain the integrity of the whole electrode [32]. So it could be regarded as an excellent candidate to composite with silicon. The frequently exploited synthetic methods for the

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Si/Ag composites are mainly mechanical alloying [33,34], electroless deposition (ED) [20,31,34–37], high-energy mechanical milling process [20], templated-assisted (T-A) [31], thermal treatment (TT) process [38], magnesiothermic reduction (MR) [31,34,38], and wet chemical methods [39]. These methods are either time consuming or require delicate control over experimental conditions. Additionally, porous silicon has been employed as anodes to composite with silver to improve the electrochemical performance. However, the fabrication of porous silicon is complicated, tricky to scale up, and require corrosive chemicals to etch away templates (such as hydrofluoric acid).

Furthermore, by analyzing the studies summarized above, it is found that the issue of the mass loading density of the electrode has been largely ignored. However, for practical applications, the mass loading density of the Si electrode needs to reach the level of around 1 mg $cm^{-2}$. It is several times higher than many of the reported values [40,41]. It has been well recognized that it is of great importance to develop new strategies to improve the cyclic stability of the Si electrode with reasonable mass loading density.

Besides mass loading density, the issue of electrode mechanical property has seldom been seen addressed [42,43]. Considering that the fast capacity fading is accelerated by the collapse of the electrode, it is essential to understand the correlation between the electrode mechanical property and the electrochemical performance.

Here in this work, a facile method is proposed to improve the performance of the Si nanoparticle electrode. Silver nanoparticles are used as a reinforcing agent to enhance the mechanical properties of the electrode. Si/Ag nanocomposites are prepared by directly mixing the easily accessible silicon and silver nanoparticles through simple ultrasonication in ethanol, followed by drying process. The Si/Ag mass ratios are tuned to investigate the influence of the silver nanoparticles on the mechanical properties and electrochemical performance of the electrodes. Particularly, it is worth pointing out that the mass loading density of the Si/Ag nanocomposites are controlled to be more than 1 mg $cm^{-2}$ on the copper current collector.

Due to structure reinforcing effect, the electrode incorporated with silver nanoparticles tends to keep structure integrity and good cyclic stability, while the electrode without silver nanoparticles is easily deteriorated, leading to poor cyclic performance. It has been well established that nanoparticles can be used as additives to enhance the mechanical properties such as modulus and/or strength of plastics. However, the impact of incorporating nanoparticle additive on the mechanical property and electrochemical performance of the LIB electrode has been rarely investigated. Furthermore, besides acting as a mechanical reinforcing agent, the silver nanoparticles make additional contributions to improve the electrochemical performance. They function as buffer medium to absorb mechanical stress and as electron conductive paths to enhance electrochemical kinetics.

## 2. Experimental

All chemicals were used as received without further purification. Silicon nanoparticles (Nps, 30 nm, 99.9% in purity) were purchased from HT-NANO Shanghai, China. Silver nanoparticles (80–90 nm, 99.9% in purity) were obtained from Nanjing XFNANO Materials Tech Co., Ltd. Absolute ethanol was bought from Sinopharm. Corp., China. Sodium alginate was purchased from Aladdin Reagent Co., Ltd., China. Conductive carbon Super P was bought from SCM Chem. Shanghai, China. Electrolyte was purchased from Dongguan Shanshan Battery Material Co., Ltd.

### 2.1. Si/Ag nanocomposites preparation

The sample preparation approach is described as follows: silicon and silver nanoparticles (0.3 g in total) were added together in ethanol (4 g), followed by ultrasonication for 1 h to homogenize the dispersion of silicon and silver nanoparticles in solvent. Thereafter, the Si/Ag mixture was dried at 60 °C overnight. The Si/Ag mass ratios were systematically varied as 1:0, 4:1, 2:1, 1:1, 1:2, and 1:4 (Fig. 1).

### 2.2. Sample characterization

X-ray diffraction (XRD) characterization was performed on a diffractometer (Bruker AXS D8 Advance, 0.1541 nm, 2.2 kW) with a two-theta range of 5°–90°. The scanning electron microscopy (SEM) images of the bare silicon nanoparticles and Si/Ag nanocomposite were obtained with Hitachi S4800 scanning electron microscope (Tokyo, Japan) at an accelerating voltage of 4 kV. The morphologies of the electrodes and the energy dispersive spectrum (EDS) elemental mapping were carried out with FEI QUANTA 250 FEG (America FEI) at an accelerating voltage of 15 kV. The cycled electrodes were extracted from the coin cells and rinsed with dimethyl carbonate (DMC) repeatedly in the glove box. After drying under vacuum in a mini chamber of the glove box, the electrodes were carefully transferred into the chamber of the field emission SEM (FESEM). The mechanical properties of the pristine electrodes were investigated with a MTS G200 nano indentation system at room temperature. The Oliver-Pharr method was employed with a continuous stiffness measurement option (Berkovich tip). Twelve indentation experiments were performed on different spots of each individual sample.

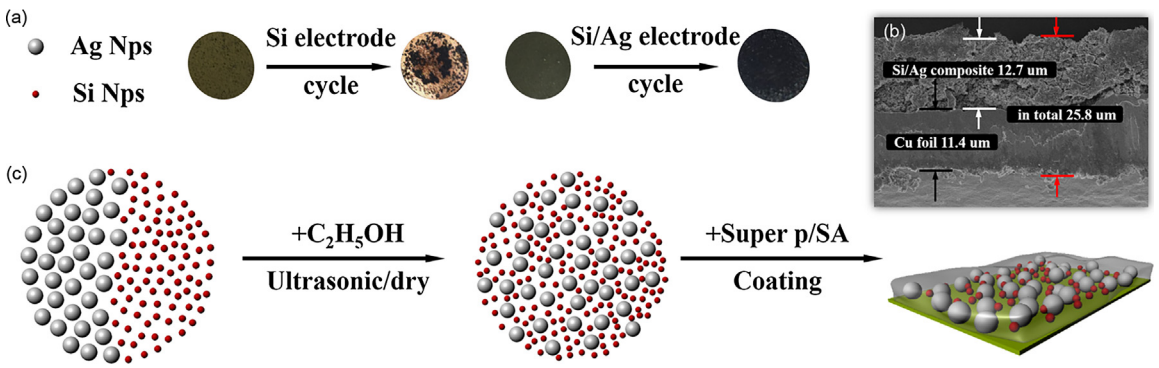


**Fig. 1.** Schematic of macroscopic visual change of electrodes after cycling test (a), cross-sectional view of newly prepared Si/Ag electrode with Si/Ag ratio of 1:1 (b) and fabrication process of Si/Ag electrode (c).

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