

## Case Examination on Volume Expansion of Crystalline Si Nanoparticles under Sodiation: *In Situ* TEM Study Using Graphene Liquid Cells

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Silicon nanoparticles are very famous as the best anode material for batteries because of its high theoretical capacity [1]. This material has been proved to have effective performance in lithium ion batteries. Due to some limitations in lithium ion batteries such as scarcity of lithium and high cost, the need has been made to search the alternative candidate to lithium [2,3]. Sodium ion batteries have been extensively considered to be among the promising alternative candidates to lithium ion battery as they are accompanied with desirable properties such as abundant of sodium resources, low cost and low toxicity. Moreover, Sodium and lithium show most similar chemical characteristics. Although sodium has higher ionic radius (0.98Å) than lithium (0.68Å), this leads to scientific challenges in optimizing and discovering anode material for sodium ion batteries. However, significant problem arises when silicon is used in the sodium ion batteries, because most previous *ex situ* studies reported that crystalline silicon is inactive when used as anode material in sodium ion battery [4-6]. Nevertheless, recent *ex situ* study proved the possibility of sodiation of silicon nanoparticles for both amorphous and crystalline phases with a volume expansion of 28.4% and initial sodiation/desodiation 1027 mAh g<sup>-1</sup> and 270 mAh g<sup>-1</sup> at a current density of 20 mA g<sup>-1</sup> [7]. This study is contrary to the previous studies, and it is currently controversial as to whether sodium actually reacts with Si and whether volume expansion does occur. Understanding whether volume expansion truly occurs in Si is crucially important as it is the indication that sodiation process truly takes place, and opens up new opportunities to use Si as the viable anode material for sodium ion batteries.

To confirm whether the volume expansion truly occurs in the crystalline structure of Si, we have utilized *in situ* TEM investigation using graphene liquid cell (GLC) on the reaction mechanism between crystalline silicon and sodium. The experiment have been attempted through incorporation of several steps such as (i) synthesis of monolayer graphene on Cu substrate using plasma chemical vapor deposition (CVD), (ii) monolayer Graphene transferred on the TEM grid (200 mesh Au grid), (iii) solution preparation; 1mg of Si nanoparticles dissolved in 1M of NaPF<sub>6</sub> liquid electrolyte consisting the solvent mixture of Ethylene carbonate, followed by entrapment of a liquid solution between layers of graphene.

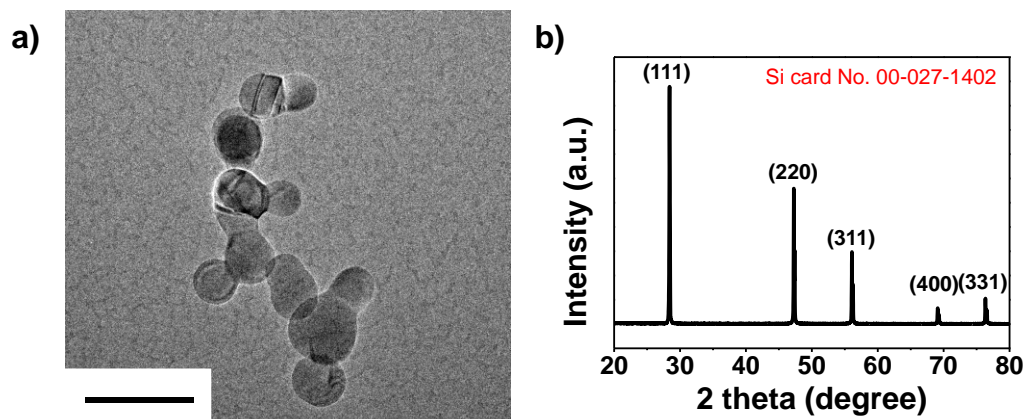
TEM image and x-ray diffraction (XRD) pattern of Si nanoparticles are shown in Figure 1, where the crystal structure of Si nanoparticle is diamond cubic. During the *in situ* observations (Figure 2), the sodium ions were found to dissociate from NaPF<sub>6</sub> and randomly moved around in the electrolyte while hitting the surrounding silicon nanoparticles but no significant reaction between Na and Si has not occurred, However, coalescence phenomenon of silicon nanoparticles has been observed, whereby the

Si nanoparticles seem to be freely circulating within the electrolyte then undergo aggregations to form larger nanoparticles.

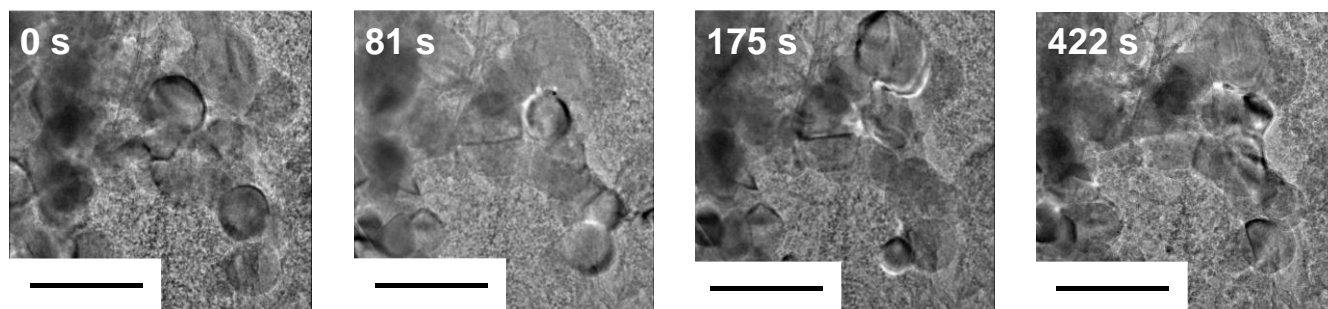
In conclusion, it is demonstrated through this study that crystalline Si remains inactive in reacting with Na to undergo alloying process and that the coalescence of Si nanoparticles occurs. Delving more into the exact driving force for the coalescence of Si nanoparticles is crucial to aid in understanding for designing more suitable architecture of Si that best prevents such issues. [8]

References:

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**Figure 1.** (a) TEM image of Si nanoparticle and (b) XRD pattern of Si nanoparticle confirming its diamond cubic structure. (Scale bar=200 nm)



**Figure 2.** Time-series TEM observation images of the morphological changes of Si nanoparticles under sodiation. Although coalescence of Si nanoparticles occurs, the appearance of volume expansion has not been observed. (Scale bar=200 nm)