

# Anisotropic Volume Expansion and Ultrafast Lithiation of Si Nanowires Revealed by In-Situ Transmission Electron Microscopy

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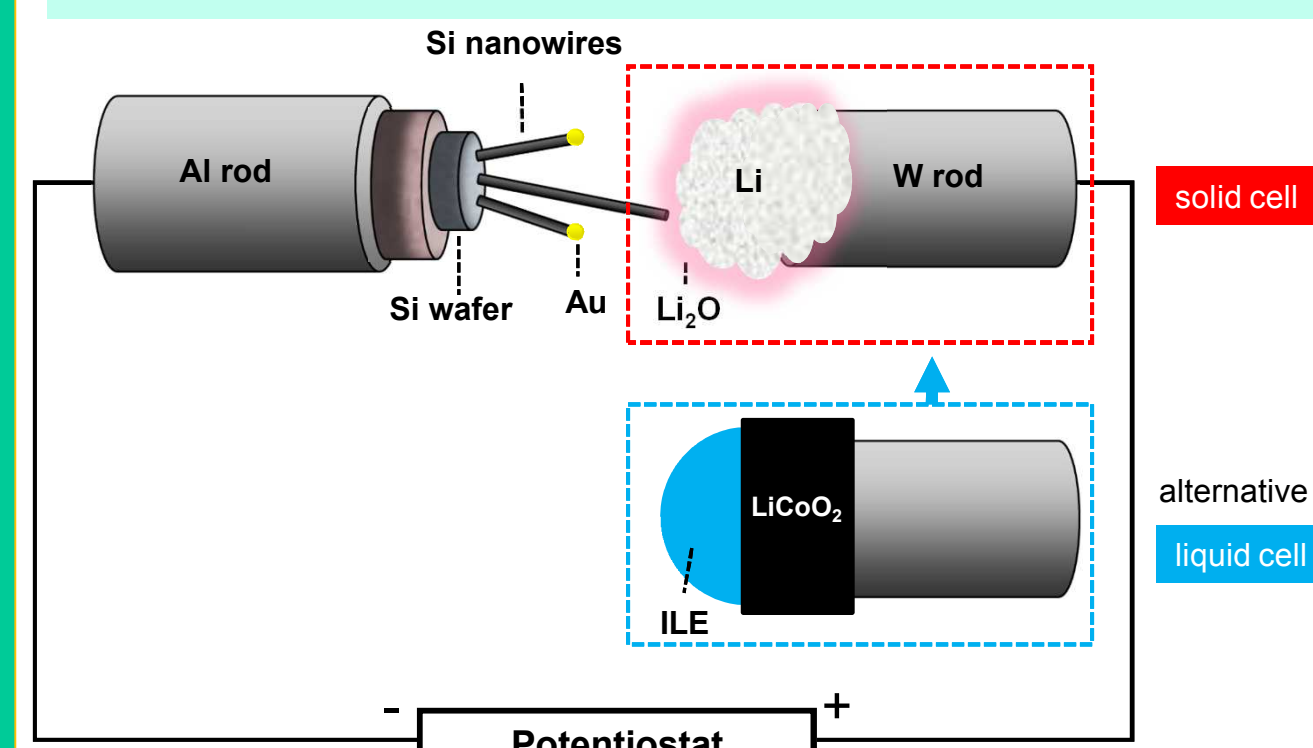
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## I. Introduction & Method

Si has attracted much attention as a promising anode material for lithium ion batteries (LIBs) for its high capacity (3579 mAh/g for  $\text{Li}_{15}\text{Si}_4$ , compared to 372 mAh/g for  $\text{LiC}_6$  of graphite used in today's commercial LIBs). However, Si undergoes huge volume expansion (281%) when alloying with lithium to form the  $\text{Li}_{15}\text{Si}_4$  phase, causing pulverization of Si and loss of electrical contact. As a result, Si-based electrodes exhibit rapid capacity fading during cycling. Understanding the atomic scale mechanism of the lithiation behavior will help to develop strategies to mitigate these adverse effects.

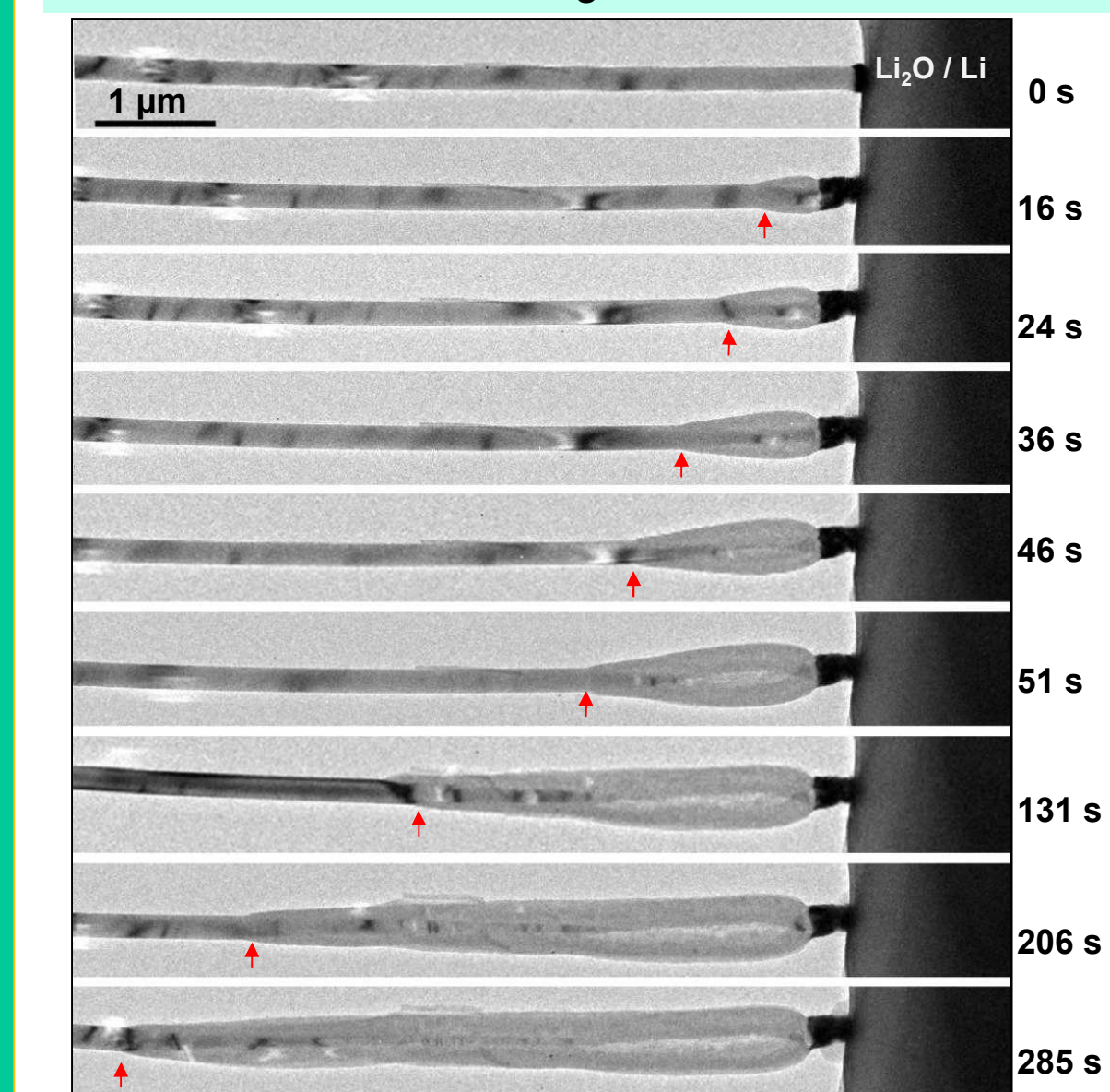
*In situ* transmission electron microscopy (TEM) enables real-time observations of microstructural evolution of the electrode materials during battery operation, providing important insight about the electrochemical reactions [Huang, *et al.*, *Science*, 330, 1515 (2010); Chiang, *Science*, 330, 1485 (2010)]. We have constructed two types of nano-batteries inside a TEM to lithiate individual Si nanowires, *i.e.* a solid cell and a liquid cell (Fig. 1).



**Fig. 1. Experimental setup.** The solid cell consisted of a Si nanowire electrode, a solid-state  $\text{Li}_2\text{O}$  electrolyte, and a Li metal electrode, while the liquid cell used an ionic liquid electrolyte (ILE) and a bulk  $\text{LiCoO}_2$  cathode. The growth substrate for the Si nanowires, *i.e.*, the Si wafer, was cleaved and glued to an Al rod with conducting epoxy, which insured good electrical contact between individual Si nanowires and the bulk Al rod. The  $\text{Li}_2\text{O}$  layer formed on the Li metal was due to brief air exposure during the sample transfer process.

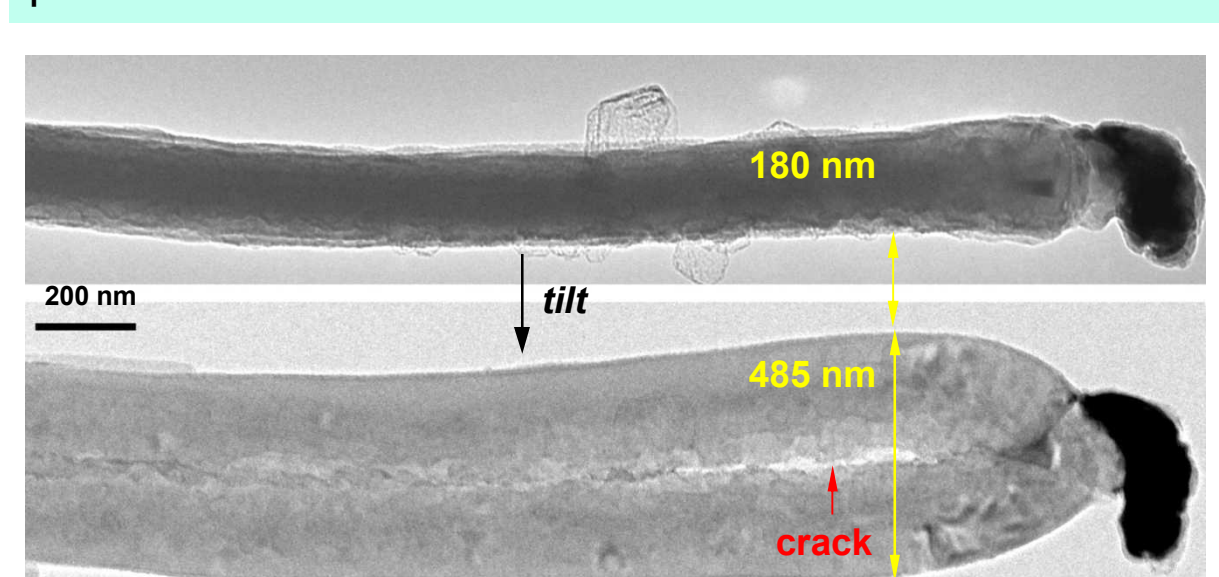
## II. Anisotropic Swelling of Si Nanowires during Lithiation

When lithiated, instant volume expansion was seen (Fig. 2). When tilted, a lithiated Si nanowire showed different thicknesses at different angles, often with a crack in the center (Fig. 3), indicating anisotropic radial swelling.

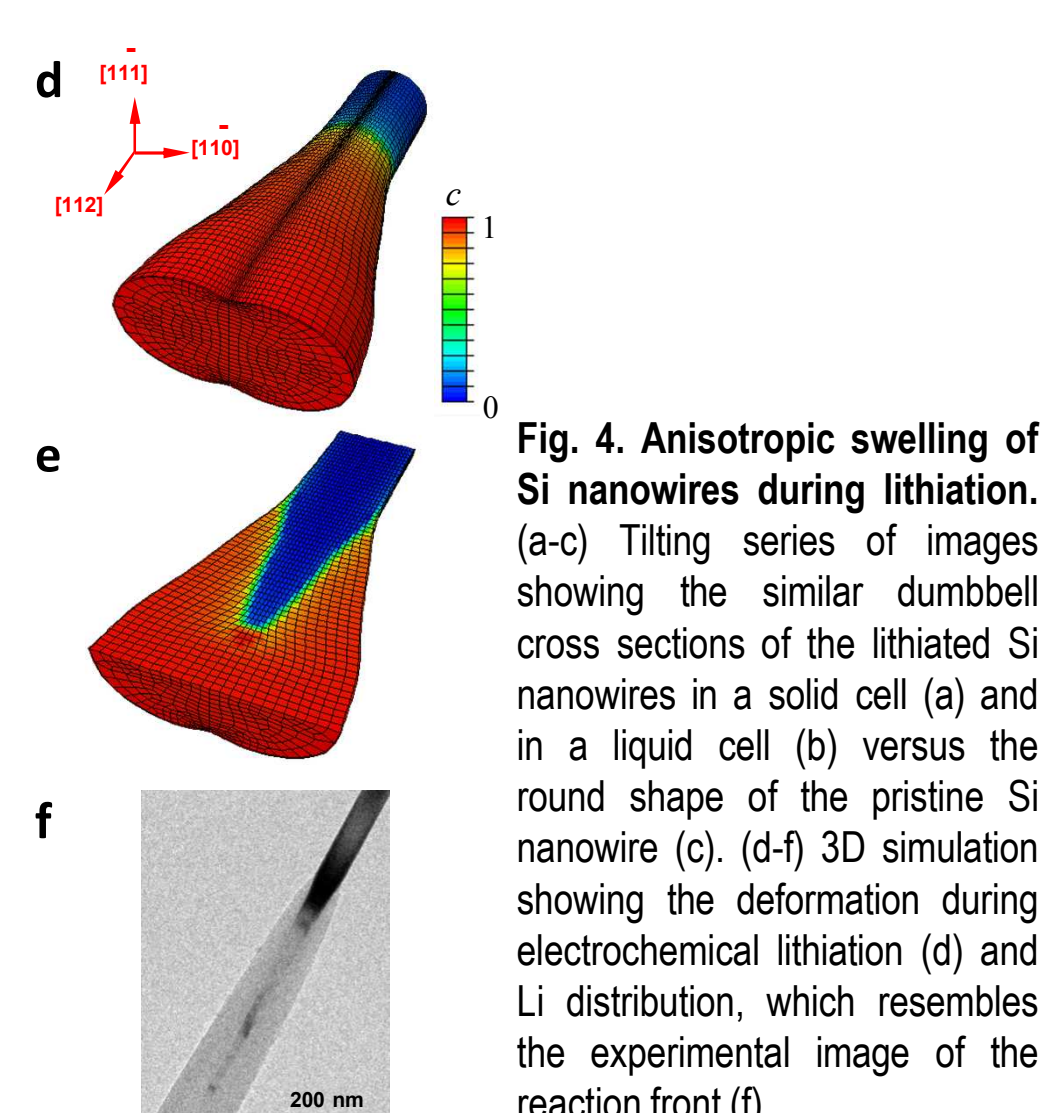
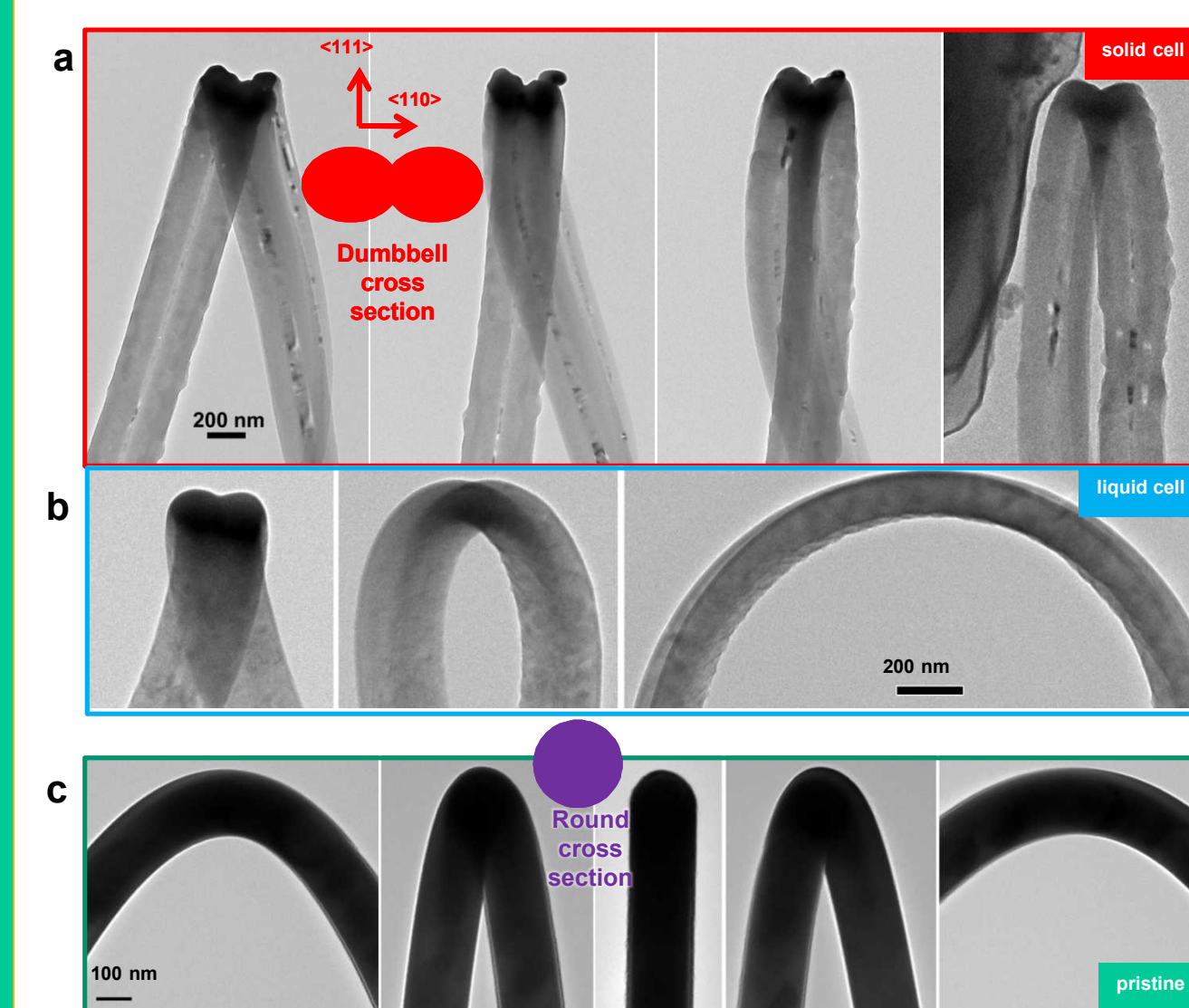


**Fig. 2. Instant volume expansion during lithiation of a Si nanowire.** The red arrows mark the reaction fronts.

The growth direction of the pristine Si nanowires was  $\langle 112 \rangle$  of the cubic diamond structure. Crystallographic analyses based on electron diffraction showed that larger swelling occurred along the  $\langle 110 \rangle$  directions than along  $\langle 111 \rangle$ . This anisotropic swelling was constantly observed in various samples (*e.g.*, nanowire or nanoparticle) and under various conditions (*e.g.*, in a solid cell or liquid cell, Fig. 4) believed to be intrinsic to the Li-Si alloying process.



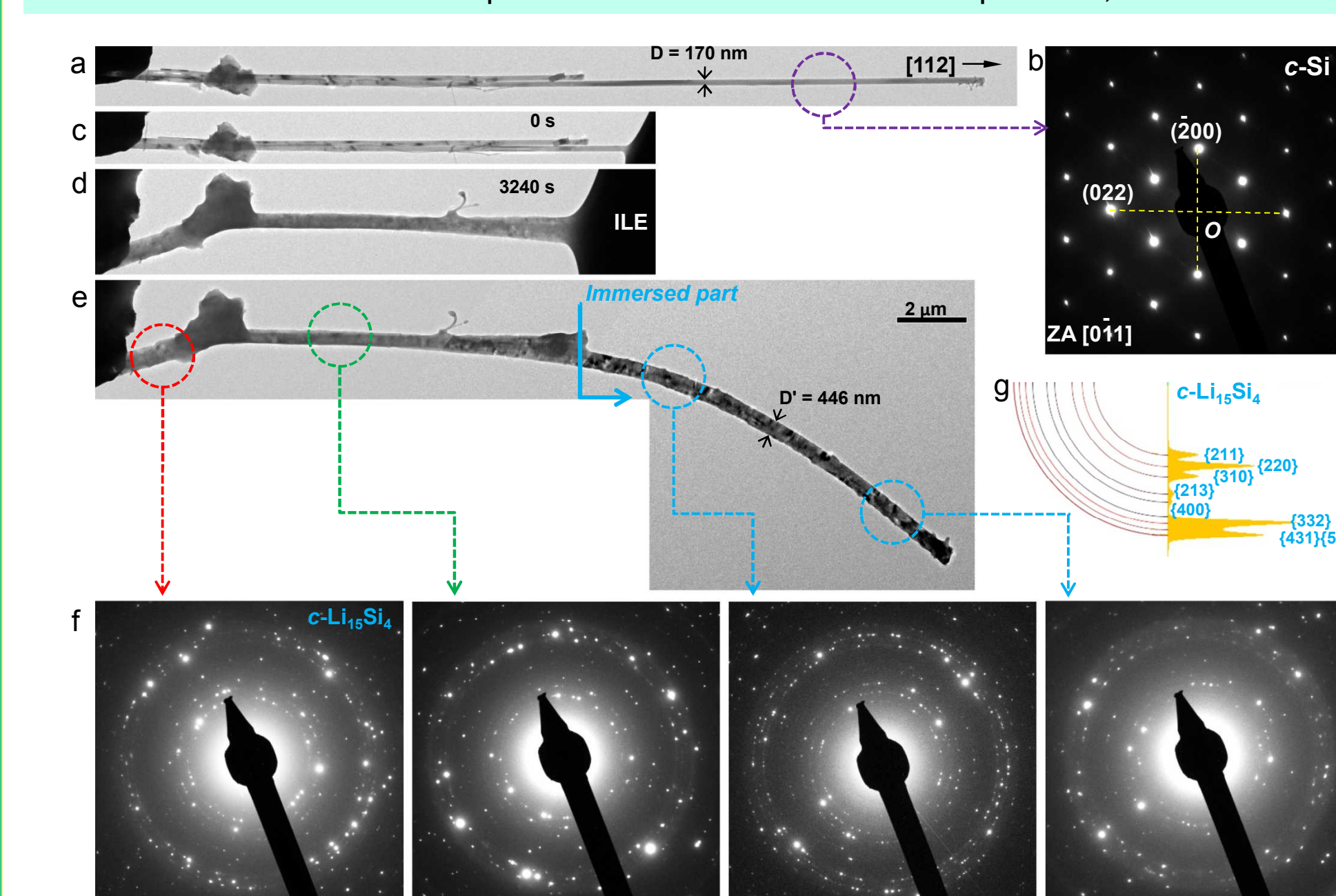
**Fig. 3. Tilted images showing different thicknesses viewed at different angles.** The radial swelling was anisotropic and there as a crack in the center.



**Fig. 4. Anisotropic swelling of Si nanowires during lithiation.** (a-c) Tilted series of images showing the similar dumbbell cross sections of the lithiated Si nanowires in a solid cell (a) and in a liquid cell (b) versus the round shape of the pristine Si nanowire (c). (d-f) 3D simulation showing the deformation during electrochemical lithiation (d) and Li distribution, which resembles the experimental image of the reaction front (f).

## III. Phase Transformation from Si to $\text{Li}_{15}\text{Si}_4$ during Lithiation

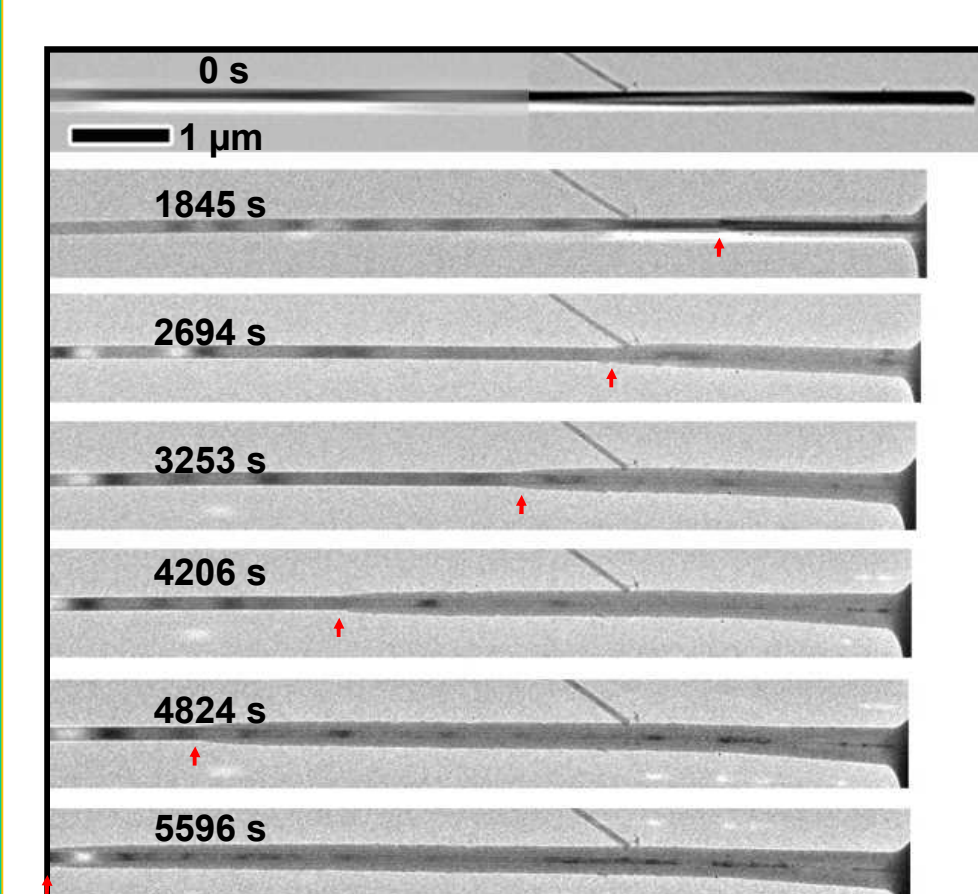
The fully lithiated phase of Si in an electrochemical cell is still controversial. Although  $\text{Li}_{22}\text{Si}_5$  (or  $\text{Li}_{27}\text{Si}_6$ ) was identified as the most Li-rich alloy phase in the Li-Si phase diagram, some *in situ* X-ray diffraction (XRD) studies indicated that  $\text{Li}_{15}\text{Si}_4$ , rather than the widely believed  $\text{Li}_{22}\text{Si}_5$ , is the fully lithiated phase [e.g., Obravac, *et al.*, *Electrochem. Solid-State Lett.* 7, A93 (2004)]. In our tests,  $\text{Li}_{15}\text{Si}_4$  was the *only* crystalline phase identified as the final product, which crystallized out of the intermediate amorphous  $\text{Li}_x\text{Si}$  phase. So the phase transformations during lithiation can be describes as:  $\text{Si} \rightarrow \text{a-Li}_x\text{Si} \rightarrow \text{c-Li}_{15}\text{Si}_4$ . This was consistent in our *in situ* experiments conducted at room temperature, for various samples and conditions (Fig. 5).



**Fig. 5. Phase transformation from Si to  $\text{Li}_{15}\text{Si}_4$ .** (a-b) Pristine single-crystalline Si nanowire. (c) Half of the nanowire immersed in the ionic liquid electrolyte. (d-e) Fully lithiated nanowire before (c) and after being pulled out (d). (f) Electron diffraction patterns (EDPs) from different sites showing the same crystalline  $\text{Li}_{15}\text{Si}_4$  ( $\text{c-Li}_{15}\text{Si}_4$ ) phase. (g) Simulated EDP of  $\text{c-Li}_{15}\text{Si}_4$ .

## IV. Ultrafast Lithiation of Phosphorous-Doped and Carbon-Coated Si Nanowires

Intrinsic Si is a semiconductor with low electrical conductivity. In real batteries, conducting agents are usually added to improve the rate and overall performance. We compared the lithiation speeds of four different types of Si nanowires, *i.e.*, (1) intrinsic (Fig. 6); (2) phosphorous-doped (P-doped, Fig. 5); (3) carbon-coated (C-coated, Fig. 8); and (4) P-doped and C-coated (Fig. 7).



**Fig. 6. Slow lithiation of an intrinsic Si nanowire.** The average migration speed of the reaction front (marked by the red arrows) was 1.7 nm/s.

**Fig. 7. Ultrafast lithiation of an intrinsic Si nanowire.** The average migration speed of the reaction front (marked by the red arrows) was 213 nm/s.

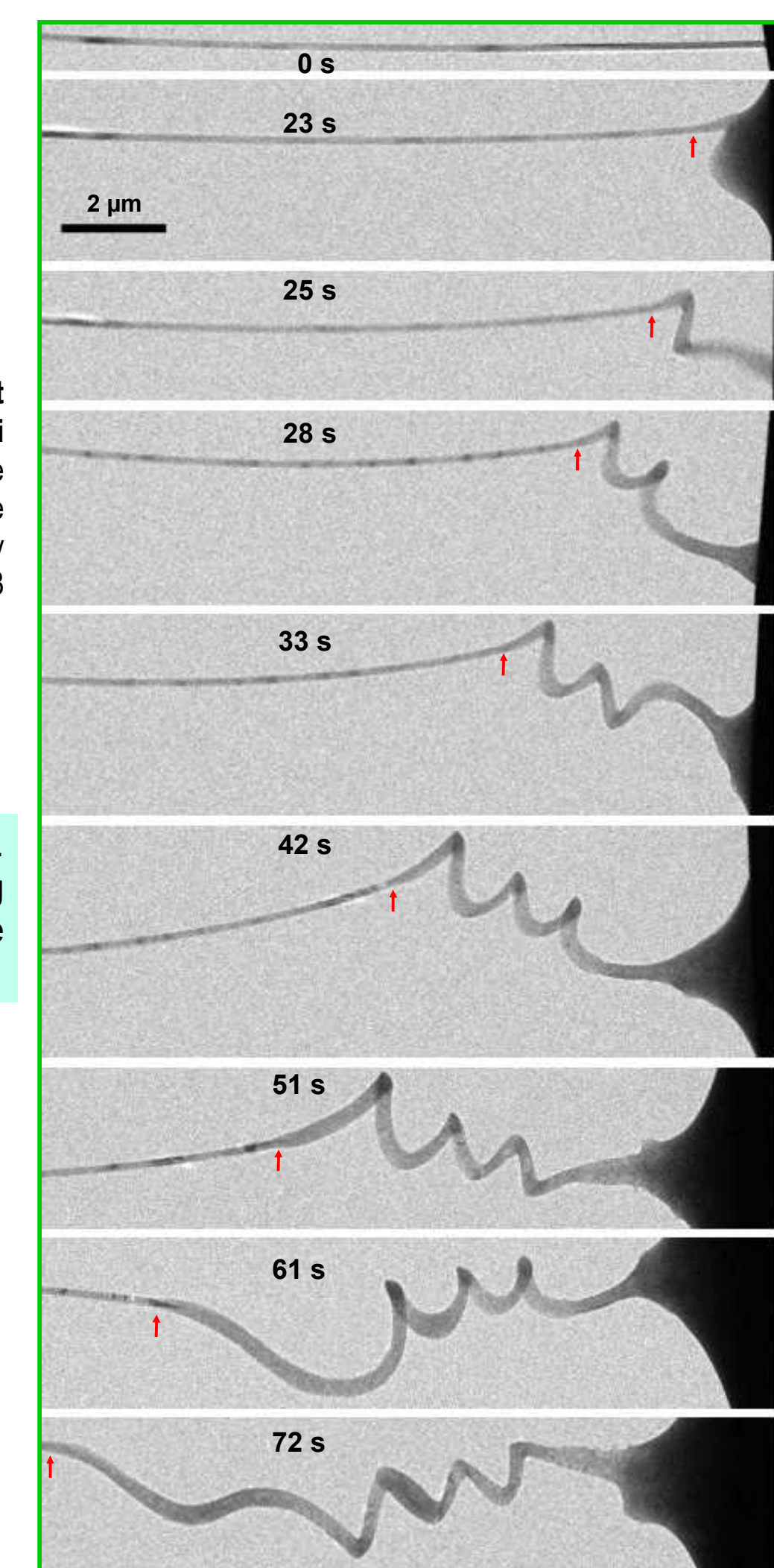
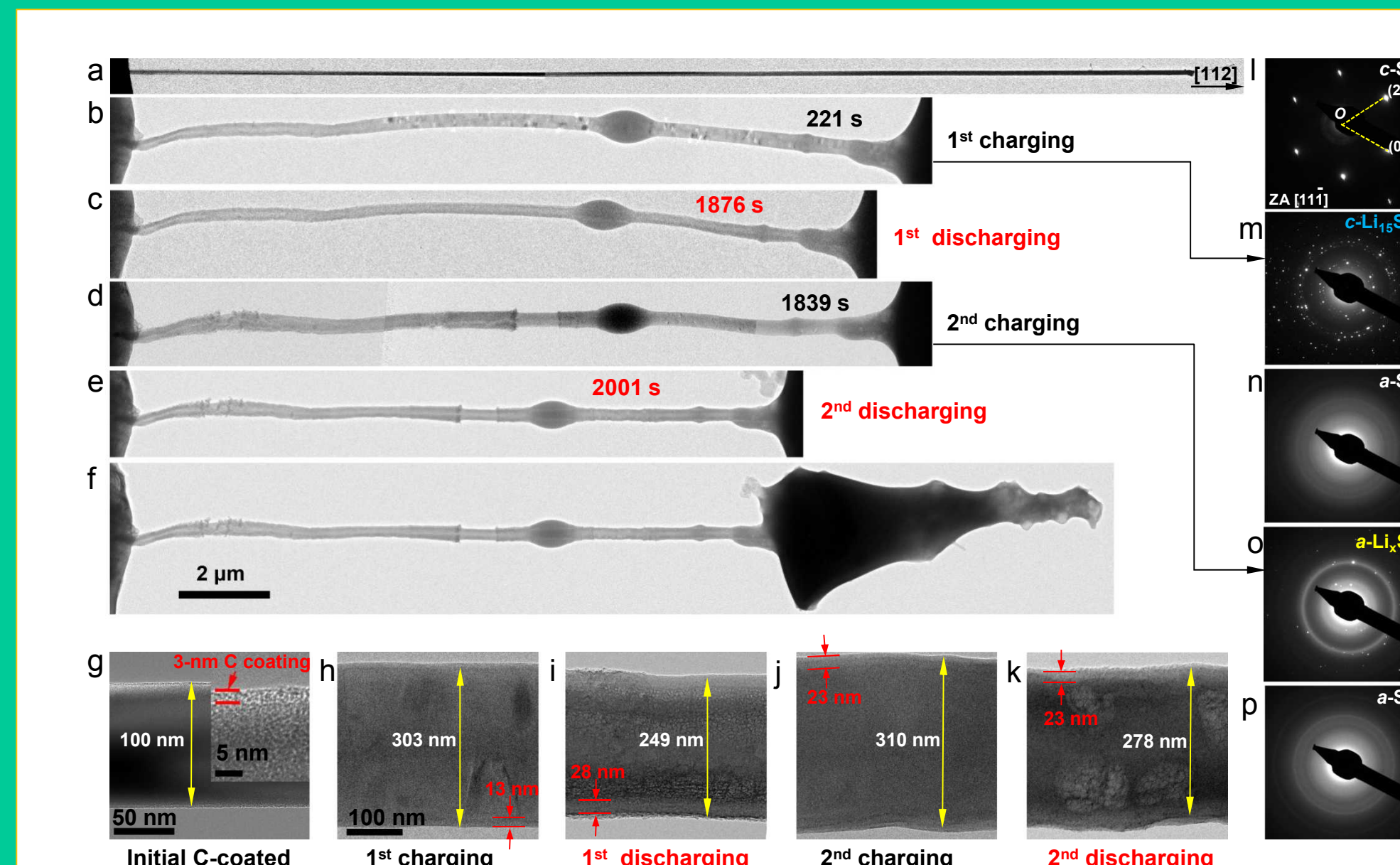


Table 1 compares the lithiation behavior of the four types of Si nanowires. At fast lithiation speeds, nanowires were twisting during the charging process (Fig. 7), but neither cracks were seen nor the integrity of the nanowires was degraded.

Table 1. Comparison of lithiation behavior of four types of Si nanowires.

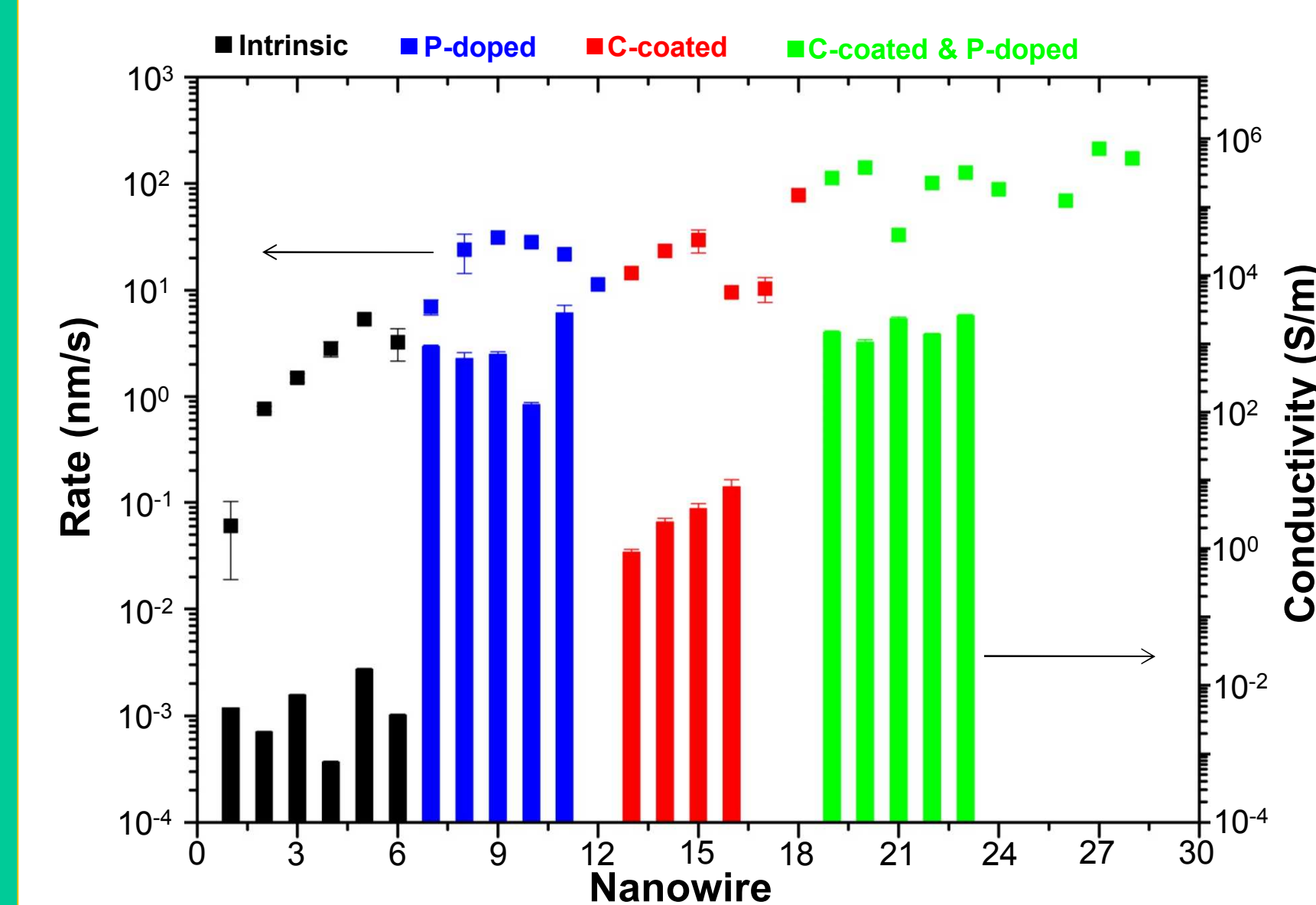
	Intrinsic	P-Doped	C-Coated	P-Doped & C-Coated
Lithiation Speed	1X	~ 10X	~ 10X	~ 100X
Final Phase	a- $\text{Li}_x\text{Si}$	c- $\text{Li}_{15}\text{Si}_4$	c- $\text{Li}_{15}\text{Si}_4$	c- $\text{Li}_{15}\text{Si}_4$
Twisting	N	N	N	Y
Cracking	N	N	N	N



**Fig. 8. Microstructure evolution of a C-coated Si nanowire in the first two cycles.** (a-e) Low magnification images showing the overall morphology changes. (f) Morphology of the nanowire after being pulled out of the electrolyte. (g-k) High magnification images showing the diameter changes. (l-p) Electron diffraction patterns showing the phase transformations.

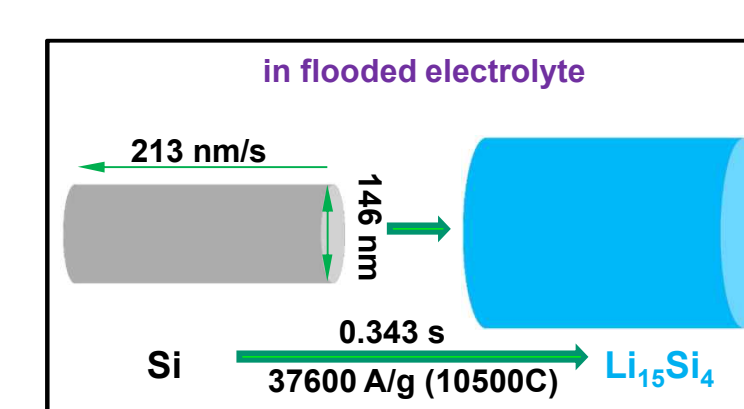
Statistics of many nanowires showed a clear link between the conductivity and the lithiation speed (Fig. 9). The carbon coating and phosphorus doping each resulted in a 2 to 3 orders of magnitude increase in electrical conductivity of the nanowires that, in turn, resulted in a 1 order of magnitude increase in charging rate.

It is worth noting that the existence of the carbon coating may also influence the lithiation kinetics, solid-electrolyte-interface (SEI) formation, *etc.*, as evidenced by the big chunk materials formed (Fig. 8f) in contrast to the clean surface of the P-doped nanowire (Fig. 5e). These observed effects guarantee further mechanistic studies for a deeper understanding of the electrochemical reactions on the atomic scale.



**Fig. 9. Statistics of the lithiation speed and conductivity of the four types of Si nanowires.**

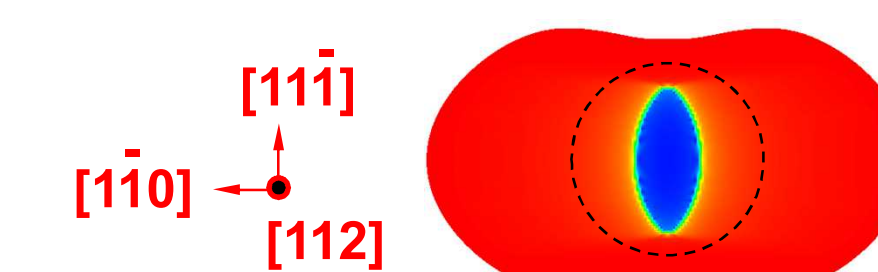
In a real battery, the electrode material is immersed in the electrolyte and the lithium insertion route is short. Consider the P-doped and C-coated Si nanowire in Fig. 7, if immersed in electrolyte and with the same high lithiation speed of 213 nm/s, it takes only 0.343 s to fully lithiate the nanowire, corresponding to the record high C rate (Fig. 10).



**Fig. 10. Record-high charging rate could be achieved in a flooding geometry for Si nanowires.**

## V. Conclusions

- In summary, we conducted *in situ* electrochemical lithiation tests of Si nanowires and got the following results:
- (1) The swelling of Si crystals during lithiation is highly anisotropic and the preferential swelling directions are  $\langle 110 \rangle$ ;
  - (2) A crack may form in the center of a  $\langle 112 \rangle$ -oriented Si nanowire after lithiation due to the anisotropic swelling;
  - (3) Carbon-coating and phosphorous-doping can enhance the charging rate of Si nanowires by one order of magnitude in the first cycle; A record-high charging rate was achieved by combining carbon-coating and P-doping.
  - (4)  $\text{Li}_{15}\text{Si}_4$  is the fully lithiated phase for Si at room temperature, corresponding to a capacity of 3579 mAh/g.



Liu, *et al.* "Anisotropic swelling and fracture of silicon nanowires during lithiation", submitted (2011).  
Liu, *et al.* "Ultrafast Electrochemical Lithiation of Individual Si Nanowire Anodes", *Nano Lett.* ASAP, doi: 10.1021/nl200412p (2011).

## VI. Acknowledgement

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