

## Microstructure of boron and phosphorus co-doped colloidal silicon nanocrystals

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Colloidal silicon (Si) nanocrystals (NCs) have great advantage as non-toxic materials for biomedical and optoelectronic applications [1,2]. Similar to other semiconductor NCs, the physical size of Si NCs can be controlled, typically from 2–10 nm in diameter; accordingly, the luminescent range can be tuned by exploiting quantum confinement effects. In addition, co-doping with boron (B) and phosphorus (P) enables us to control the luminescent flexibly (i.e. optical energy bandgap below 1.12 eV of bulk Si).

Our group has developed methodologies to fabricate colloidal Si NCs by B and P co-doping technique [3]. Disperse Si NCs in solution can be produced through simple steps such as co-sputtering, annealing, and hydrofluoric acid (HF) etching, without any surface treatment by ligands. A variety of fluorescent range has been achieved from visible to near-infrared light. Despite the interesting optical properties, little is known about the atomic structure of the B and P co-doped colloidal Si NCs. Studying the detailed microstructure of the colloidal Si NCs, especially in 3D, is an important step as it changes material properties and its behavior in solution.

In this study, atom probe tomography (APT) and first principles density functional theory (DFT) simulation are employed to reveal the accurate atomic scale structure of the B and P co-doped colloidal Si NCs (Figure 1 and 2). The sample in this study is selected from disperse Si NCs in aqueous solution at the final stage of the fabrication procedure. The result of the atomic scale distribution of elements between the initial (Si NCs in solid before HF etching) and the final (colloid Si NCs after HF etching) stages of the co-doped Si NCs is compared. Both APT and DFT results show that the B atoms are favourably located at the outside of the Si NCs near the interface of Si NCs and SiO<sub>2</sub> matrix, while the P atoms are more likely to be located at the inside of the Si NCs. More specifically, B and P atoms prefer to form B-P pairs around the interface region. In addition, the APT results show that more B-enrichment has been detected at the interface of the Si NCs in the colloidal sample, strongly suggesting that the B-rich layers surround the Si NCs act as a resistance to the HF etching. These results reveal the detailed understanding of the atomic scale structure of the co-doped colloidal Si NCs in 3D and pave the way towards improving the performance of applications.

### References

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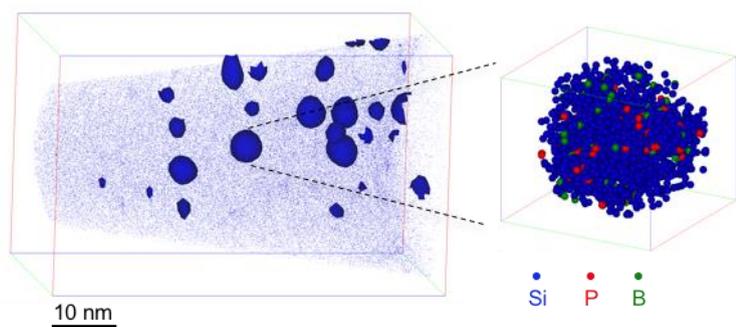


Figure 1. APT 3D reconstruction of B and P co-doped colloidal Si NCs.

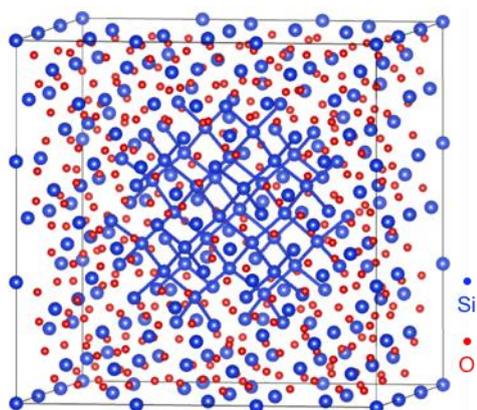


Figure 2. DFT relaxed 680-atom supercell where a Si NC embedded in SiO<sub>2</sub> matrix.