Designing of advanced nano-assemblies for lithium-sulfur battery electrode

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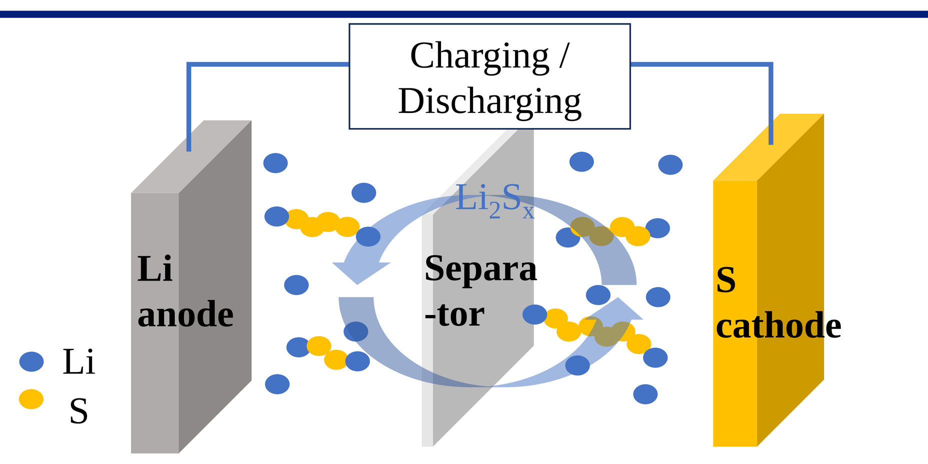
Introduction

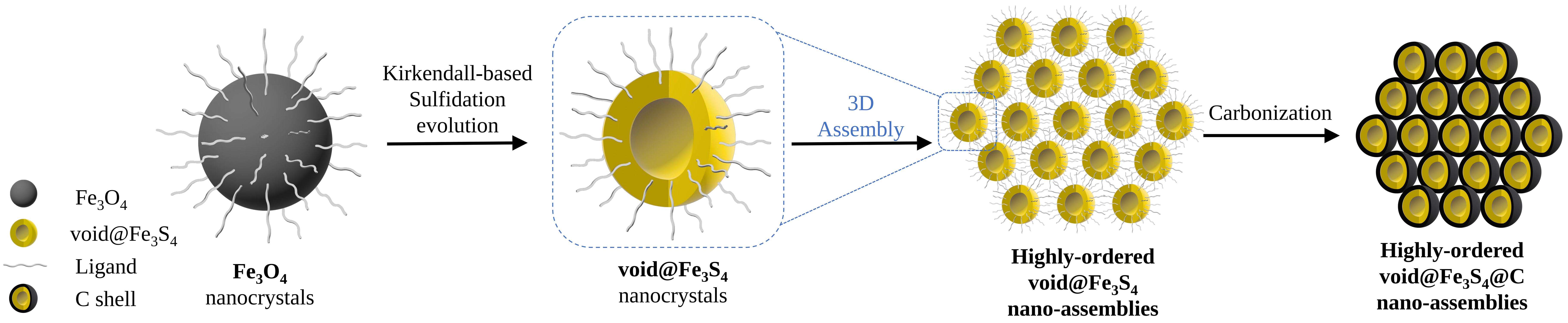
Lithium-Sulfur batteries have attractive attention because of low cost and high theoretical specific capacities. However, the performance of lithium-sulfur batteries was hindered by several issues during charge-discharge process. (i) Diffusion into the lithium anode, (ii) high-volume expansion changing, (iii) low electrical conductivity, and (iv) too fast redox kinetics of lithium polysulfide species (Li_2S_x, $4 \le x \le 8$). It leads to severe structural degradation with lithium dendrites on anode.

Here, I will discuss the several problem-solving approaches to address these issues. The advanced nano-assemblies, void@Fe_3S_4@C nanoarchitecture provide high-volume expansion, high electrical conductivity, and strong chemical interaction with lithium polysulfide species by polar nature.



$S_8 \leftrightarrow Li_2S_8 \leftrightarrow Li_2S_6 \leftrightarrow Li_2S_5 \leftrightarrow Li_2S_4 \leftrightarrow Li_2S_2 \leftrightarrow Li_2S$

Schematic illustration of this study



Results

1. Synthesis of homogeneous iron oxide nanocrystals

(i)

$$Fe(acac)_3 \xrightarrow[\text{OA, OAm, Solvent, } \Delta]{} Fe_3O_4 : OA / OAm$$

acac: acetylacetonate
OA: oleic acid
OAm: oleylamine

Molar ratio
[**$Fe(acac)_3$: Oleylamine** : Oleic acid (fixed)]

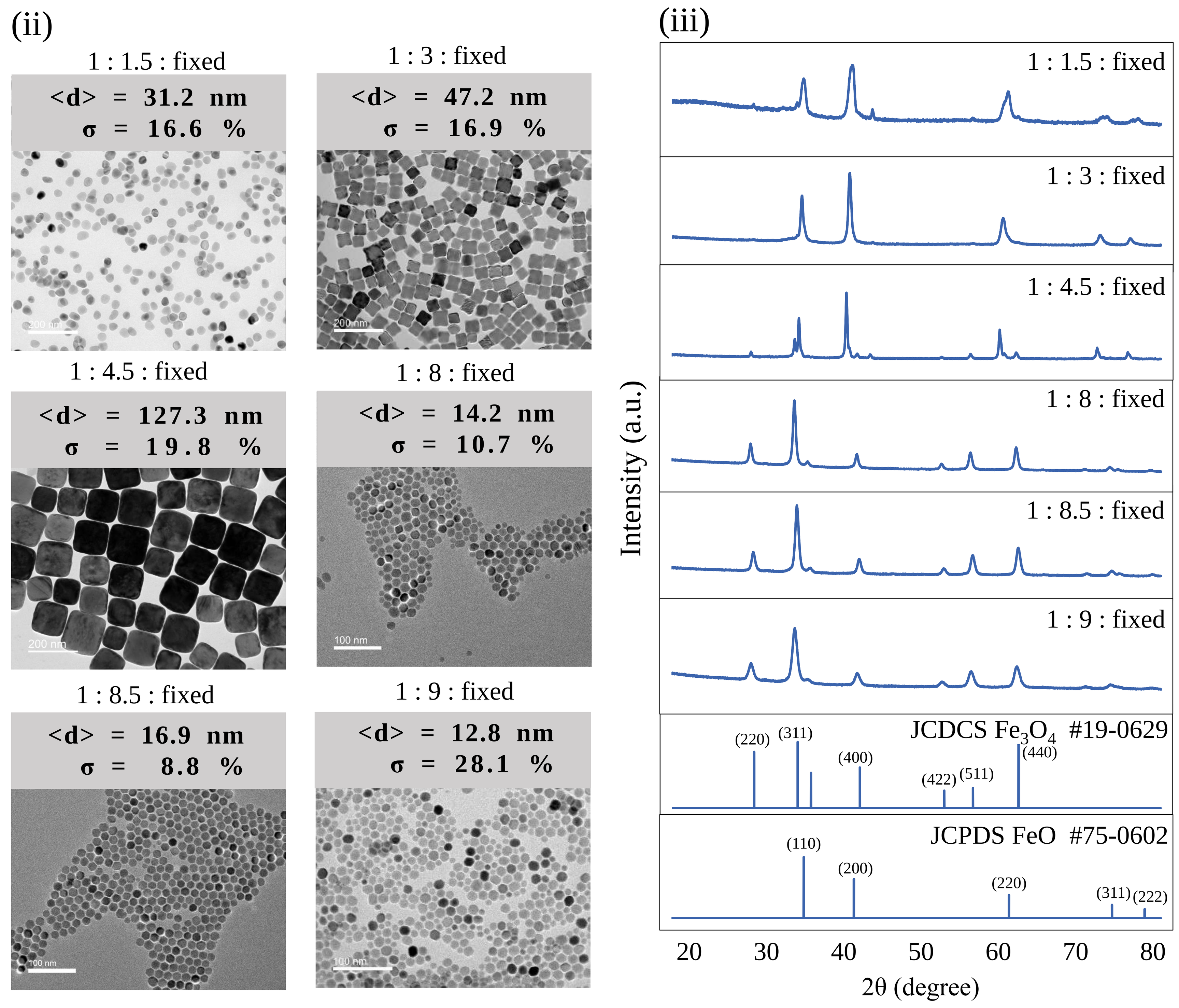


Figure 1. Synthesis of iron oxide nanocrystals controlling the molar ratio of iron precursor and oleylamine. (i) chemical reaction, (ii) morphological, and (iii) structural properties of iron oxide nanocrystal.

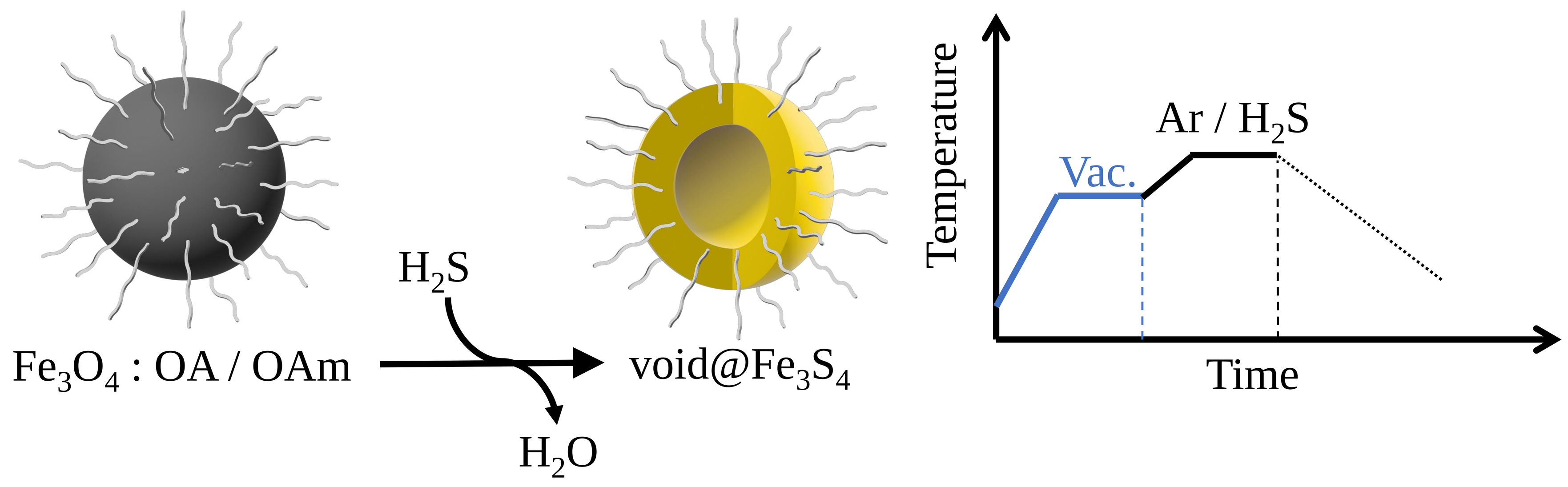
Conclusion

In this study, we tried to synthesize spherical shaped iron oxide nanocrystals by controlling the molar ratio of surfactant.

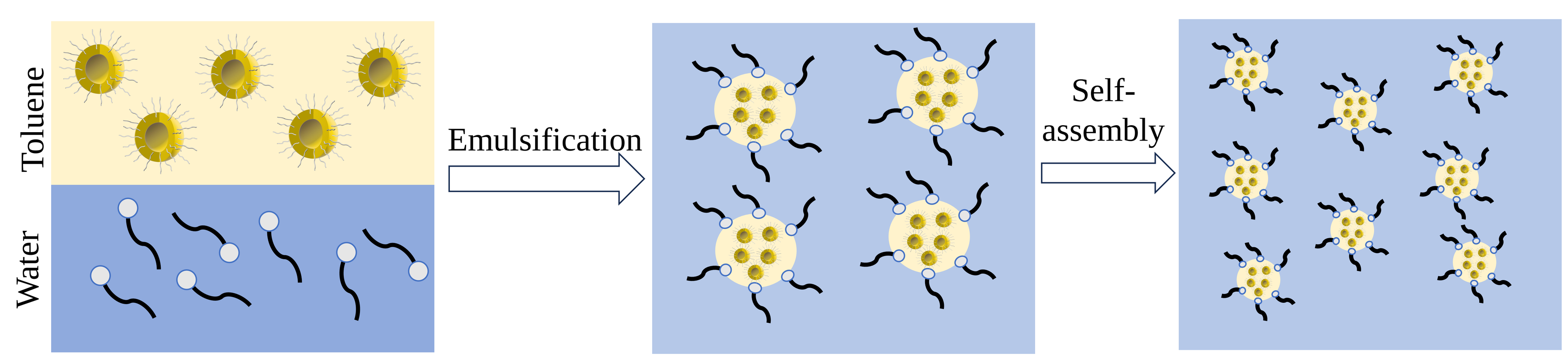
When oleylamine was used as a ligand at a molar ratio more than 8 times that of $Fe(acac)_3$, we achieved truncated and spherical-shaped Fe_3O_4 nanocrystals. Oleic acid and oleylamine mainly coordinate to the {111} and {110} surfaces of Fe_3O_4. When the ratio of oleylamine to oleic acid exceeds 1.5, the ligand capping density is lower, leading to anisotropic crystal growth and resulting in truncated and spherical Fe_3O_4.

Further Study

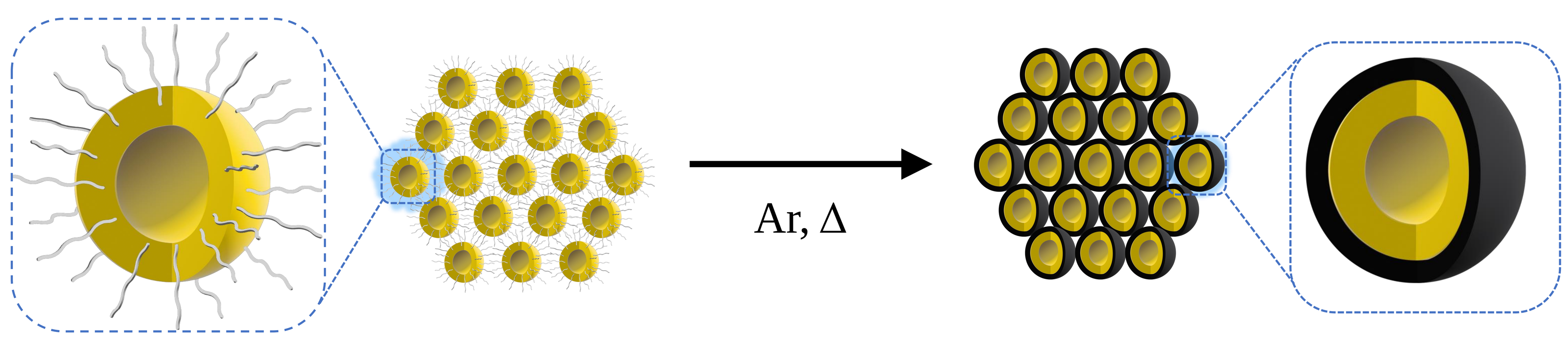
1. We successfully achieved **Fe_3O_4** nanocrystals with sized of 17 nm on the reaction condition ($Fe(acac)_3$: OA : OAm = 1 : fixed : 8.5, molar ratio)
2. We will refer the "J. Cheon et al., J. Am. Chem. Soc. 2020, 142, 9130−9134", will synthesize **void@Fe_3S_4** nanocrystals
 (i) Kirkendall-based Sulfidation evolution



3. We will refer the "Angang Dong et al., Nano Energy. 2019, 63, 103851", will synthesize **Highly-ordered void@Fe_3S_4 nano-assemblies**
 (ii) Emulsion-based assembly



4. We will refer the "Angang Dong et al., Nano Energy. 2019, 63, 103851", will synthesize **Highly-ordered void@Fe_3S_4@C nano-assemblies**
 (iii) Carbonization



Advanced Highly-ordered void@Fe_3S_4@C nano-assemblies are one of the promising approaches for addressing the issues on lithium-sulfur battery (*i.e.* diffusion, high-volume expansion changing, low electrical conductivity, fast redox kinetic..)

Reference

[1] J. Cheon et al., J. Am. Chem. Soc. 2020, 142, 9130−9134 [2] J. Cheon et al., J. Am. Chem. Soc. 2014, 136, 14670−14673 [3] J. Cheon et al., Nano Today. 2017, 13, 61-76 [4] Angang Dong et al., Nano Energy. 2019, 63, 103851 [5] Sun, S. et al., J. Am. Chem. Soc. 2004, 126(1), 273-279 [6] Park, J., et al., *Nature Materials*, 2005, 4(10), 741-746