α-MnO<sub>2</sub> nanorods decorated with Ag nanoparticles as a bifunctional catalyst for lithium air battery application Awan Zahoor<sup>a</sup>, Jeong Sook Jeon<sup>b</sup>, Maria Christy<sup>c</sup>, Yun Ju Hwang<sup>c</sup>, Ho Saeng Jang<sup>b</sup>, Kee Suk Nahm<sup>a,b,c,\*</sup>

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Rechargeable metal - air batteries that utilize aqueous alkaline electrolytes may be designed with nonprecious metals to offer high theoretical specific energy densities. For such systems, including alkaline electrolyzers and fuel cells, catalyst bifunctionality is a key requirement for rechargeable and/or reversible systems. In alkaline conditions, current state of the art OER and ORR catalysts utilize expensive precious metals such as IrO<sub>2</sub> and Pt, respectively. The expensive catalysts are major problems in commercialization of fuel cell and metal air batteries. Therefore, much of the focus has moved toward cheap and abundant catalytic materials based on transition metal oxides. Manganese oxides (MnOx) have been widely studied as an alternative to Pt-based catalysts because of their many advantages, such as abundance, low cost, environmental friendliness, and acceptable activity [1, 2]. Among various MnOx polymorphs, α-MnO<sub>2</sub> is believed to be a promising bi-functional catalyst for ORR and OER. Nevertheless, it is evident that the Bifunctional activity of  $\alpha$  -MnO2 still falls below those of Pt-based catalysts.

To further enhance the catalytic activity, MnOx may be mixed with an active transition metal; for example, MnOx has been doped with Ni. For metal – metal oxide composites, silver is a promising candidate to combine with MnOx as it is active for oxygen reduction. It is at least ~30 fold less expensive than Pd or Pt. Like Pt and Pd, it is a moderately efficient electronic conductor and can catalyzes the direct four-electron ORR.

In this work, silver nanoparticles have been deposited over the  $\alpha$ -MnO2 nanorods by different deposition techniques. The materials have been thoroughly characterized by X-ray diffraction, Brunauer-Emmett-Teller spectrometry, field-emission scanning electron microscopy. These bimetallic nanostructures are used for the electrocatalytic properties for the oxygen reduction reaction, which have been investigated by cyclic and linear sweep voltammetry. The silver deposited  $\alpha$ -MnO<sub>2</sub> nanorods have shown the better catalytic activity than  $\alpha$ -MnO<sub>2</sub> nanorods.

The enhancement in the catalytic activity is due to the ligand and ensemble effects from intimate contact between separate Ag and  $\alpha$ -MnO<sub>2</sub> nanorods.