



# Interfacial redox reaction-directed synthesis of silver@cerium oxide core–shell nanocomposites as catalysts for rechargeable lithium–air batteries



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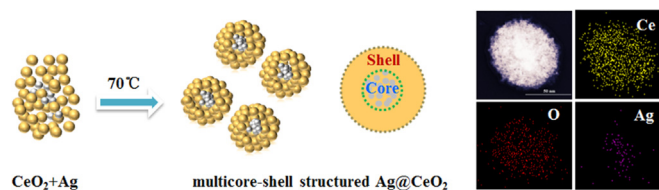
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## HIGHLIGHTS

- A novel cathode catalyst for lithium–air batteries, Ag@CeO<sub>2</sub>, has been synthesized by an interfacial redox reaction.
- Ag@CeO<sub>2</sub> nanocomposites with pomegranate-like multicore–shell structure.
- The electrode with Ag@CeO<sub>2</sub> exhibits higher catalytic activity in a simulated air environment (80%Ar: 20% O<sub>2</sub>).
- The enhanced performance is attributed to the synergy effect between the Ag core and the CeO<sub>2</sub> shell.
- It can offer plenty of active sites to promote the formation and decomposition of Li<sub>2</sub>O<sub>2</sub>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A facile oxidation–reduction reaction method has been implemented to prepare pomegranate-like Ag@CeO<sub>2</sub> multicore–shell structured nanocomposites. Under Ar atmosphere, redox reaction automatically occurs between AgNO<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> in an alkaline solution, where Ag<sup>+</sup> is reduced to Ag nanoparticles and Ce<sup>3+</sup> is simultaneously oxidized to form CeO<sub>2</sub>, followed by the self-assembly to form the pomegranate-like multicore–shell structured Ag@CeO<sub>2</sub> nanocomposites driven by thermodynamic equilibrium. No other organic amines or surfactants are utilized in the whole reaction system and only NaOH instead of organic reducing agent is used to prevent the introduction of a secondary reducing byproduct. The as-obtained pomegranate-like Ag@CeO<sub>2</sub> multicore–shell structured nanocomposites have been characterized as electro-catalysts for the air cathode of lithium–air batteries operated in a simulated air environment. Superior electrochemical performance with high discharge capacity of 3415 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup>, stable cycling and small charge/discharge polarization voltage is achieved, which is much better than that of the CeO<sub>2</sub> or simple mixture of CeO<sub>2</sub> and Ag. The enhanced properties can be

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primarily attributed to the synergy effect between the Ag core and the CeO<sub>2</sub> shell resulting from the unique pomegranate-like multicore–shell nanostructures possessing plenty of active sites to promote the facile formation and decomposition of Li<sub>2</sub>O<sub>2</sub>.

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## 1. Introduction

Growing concerns on energy crisis and environment pollution has triggered research to explore renewable and green energy sources as alternatives to fossil fuels. Lithium–oxygen batteries are generally considered as one of the most promising transformational energy storage technologies due to their extremely high energy density far exceeding that of Li-ion batteries [1–7]. Unlike the traditional Li-ion batteries, Li–oxygen batteries operate based on the formation and decomposition of Li<sub>2</sub>O<sub>2</sub> during discharge and charge, which is related to the simple electrochemical reaction between Li ions and oxygen ( $2\text{Li}^+ + \text{O}_2 + 2e \leftrightarrow \text{Li}_2\text{O}_2$ ,  $E^0 = 2.96 \text{ V vs. Li/Li}^+$ ). As a result, one of the most important advantages of Li oxygen batteries is to utilize unlimited source of oxygen from the air, providing an extremely high energy density above 1000 Wh kg<sup>-1</sup> [8–10]. However, the development of rechargeable Li–oxygen batteries is largely hindered by some critical challenges including high charging/discharging overpotential, the unacceptable low practical capacity and the requirement of high purity oxygen [4,11,12]. These limitations are mainly due to the sluggish kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in nonaqueous media [13–16]. The overpotentials mainly caused by poor ORR and OER leads to low coulombic efficiency. Moreover, Li–oxygen batteries can only survive for very limited cycles [17–20]. To overcome the drawbacks, great efforts have been devoted to exploring efficient electrocatalysts to accelerate the kinetic reactions and thus to improve the reversibility of batteries. Among the reported cathode materials, modified carbon materials [21,22], noble metal (Au, Pt) [23,24] and transition metal oxides [9,12,25,26] have been extensively studied as cathode materials to reduce the ORR and OER overpotential.

Recently CeO<sub>2</sub> has been shown to exhibit good catalytic activities [27–29]. Besides, hybrid nanomaterials have been proposed to further promote the catalytic activities of CeO<sub>2</sub>, such as doping CeO<sub>2</sub> with other metals to make substituted cerium or growing CeO<sub>2</sub>@Cu<sub>2</sub>O nanocubes and CeO<sub>2</sub>@MnO<sub>2</sub> nanorods [30,31]. It is reported that gold-nanoparticles-decorated Gd<sub>0.3</sub>Ce<sub>0.7</sub>O<sub>1.9</sub> nanotubes exhibit the excellent catalytic activity for oxygen reduction reaction (ORR), which is much better than that of gold bulk electrode and as-reported gold/rGO hybrid catalysts and close to the behavior of a commercial Pt/C catalysts [32]. The combination of two different materials into core–shell structured nanoparticles allows remarkable improvement in catalytic behavior as compared with single-component nanoparticles due to the so-called “synergistic effect” between the core and shell [33]. The structural details can be selected to design in such a way that they positively interact with each other in order to significantly enhance their properties and obtain unique properties that cannot be achieved with simple nanoparticles. Core–shell structured CNT@RuO<sub>2</sub> composite was studied to be cathode for Li–oxygen batteries and showed superior catalytic activity for ORR and OER with a round-trip efficiency of 79% at a current of 100 mA g<sub>total</sub><sup>-1</sup> [34]. The RuO<sub>2</sub> coating layer on the CNTs can effectively prevent direct contact between the CNTs and the discharge product Li<sub>2</sub>O<sub>2</sub> and thus to reduce the formation of Li<sub>2</sub>CO<sub>3</sub>, which can induce large polarization and may lead to charge

failure. However, it is still a big challenge to prepare high quality core–shell nanoparticles with well-defined structure, especially when the core and shell are largely distinctive in their chemical and physical characteristics (e. g., elemental metal core and transition metal oxide compound shell), so that core–shell nanoparticles are highly desirable for using as catalysts for Li–oxygen batteries.

Interfacial oxidation–reduction reaction has been successfully employed to synthesize hollow structure nanotube and binary composites [29,35]. For example, hollow Ce–Mn binary oxide nanotubes were prepared by the interfacial reaction between the Ce(OH)CO<sub>3</sub> template and KMnO<sub>4</sub>, followed by selective wash with HNO<sub>3</sub> to remove unreacted templates, where MnO<sub>4</sub><sup>-</sup> is reduced to manganese oxide and the Ce<sup>3+</sup> in Ce(OH)CO<sub>3</sub> is simultaneously oxidized to form cerium oxide [30]. One-dimensional tubular Ag/MnO<sub>x</sub> nanocomposites were also prepared by treating Ag nanowire with KMnO<sub>4</sub> aqueous solution under the solvent condition, and pH level has a vital role in the morphology and the electrochemical performance of the nanocomposites [36]. In both examples introduced above, the approach involves multi step reaction that templates must be firstly synthesized, which was then reduced by the KMnO<sub>4</sub>. Moreover, poor interfacial kinetics between the Ce(OH)CO<sub>3</sub> template and the KMnO<sub>4</sub> necessitates very long reaction time of over 6 days to obtain the Ce–Mn binary oxides. Thus, it is highly desirable to explore an effective way to realize the simple, facile, and clean synthesis of highly active Ce-based core–shell structure in a large scale.

In this study, a facile interfacial redox reaction method was developed to synthesize monodisperse multicore–shell structured Ag@CeO<sub>2</sub> nanocomposites. The reaction occurred under oxygen-free conditions which promoted the effective oxidation of Ce<sup>3+</sup> ions by Ag precursor rather than by O<sub>2</sub>. The less-expensive precious metal Ag was chosen as the core material because of its superior ORR and OER activities. The as-obtained multicore–shell structured Ag@CeO<sub>2</sub> nanocomposites have been considered as ORR and OER catalyst and assembled into the air electrode of Li–air batteries. Electrochemical characterizations have showed that much superior ORR and OER activities have been achieved as compared with a mixture of CeO<sub>2</sub> and Ag nanocrystals or CeO<sub>2</sub> nanocrystals alone, which is ascribed to the strong synergistic effect between the Ag core and the CeO<sub>2</sub> shell, ensuring high availability of the catalytic sites and very homogeneous dispersing of the core/shell nanoparticles, providing high specific surface area for efficient catalytic oxygen reduction reaction and oxygen evolution reaction.

## 2. Experimental section

### 2.1. Synthesis of multicore–shell structured Ag@CeO<sub>2</sub> nanocomposites

The whole synthetic process was carried out under Ar protection. 2 mmol Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was added to 100 mL of H<sub>2</sub>O, and then Ar was bubbled into the solution for 30 min. Then, 2 mL of 2 M NaOH aqueous solution was rapidly added, followed immediately by the quick addition of 2 mL of 0.1 M AgNO<sub>3</sub>. The as-obtained solution was stirred at 70 °C for 1 h. After being cooled to room temperature, the sample was centrifuged and washed with distilled

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