



# Reduced graphene oxide supported MnS nanotubes hybrid as a novel non-precious metal electrocatalyst for oxygen reduction reaction with high performance



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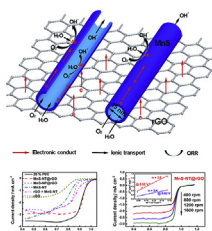
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## HIGHLIGHTS

- rGO supported MnS nanotubes (MnS-NT@rGO) hybrid was synthesized.
- Nano-tubular structure endows MnS-NT@rGO high accessible surface area for ORR.
- MnS-NT@rGO exhibits comparative catalytic activity for ORR to Pt/C.
- MnS-NT@rGO exhibits higher activity for ORR than MnO@rGO and Mn(OH)<sub>2</sub>@rGO.
- MnS-NT@rGO exhibits higher activity than rGO supported MnS nanoparticles.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electronic structure of Mn cations, electric conductivity of active materials and three dimensional structure for mass transport play vital roles in the electrocatalytic activity of Mn-based electrocatalysts for oxygen reduction reaction (ORR). To construct efficient and robust Mn-based electrocatalysts, MnS nanotubes anchored on reduced graphene oxide (MnS-NT@rGO) hybrid was synthesized and used as a novel non-precious metal electrocatalyst for ORR. The formation of nano-tubular structure, which offers more active sites and suitable channels for mass transport to enhance the electrocatalytic activity towards ORR, are carefully illustrated based on the core-dissolution/shell-recrystallization type Ostwald ripening effect. Tuned electronic structure of Mn cations, enhanced electric conductivity and suitable nano-tubular structure endow MnS-NT@rGO electrocatalyst comparative catalytic activity to commercial 20 wt % Pt/C in alkaline electrolyte. The MnS-NT@rGO electrocatalyst exhibits higher catalytic activity than rGO supported MnS nanoparticles (MnS-NP@rGO) and MnS nanotubes without rGO substrate (MnS-NT), as well as rGO supported Mn(OH)<sub>2</sub> (Mn(OH)<sub>2</sub>@rGO) and rGO supported MnO (MnO@rGO). Moreover, the MnS-NT@rGO electrocatalyst shows superior durability and methanol tolerance to commercial Pt/C.

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## 1. Introduction

Renewable energies such as solar energy and wind energy are the promising resources to solve the issues of both exhausting fossil energy and serious environmental pollution. Stable and continuous supply of these renewable energies strongly relies on the efficient conversion and storage technologies including fuel cells (FCs) and metal-air batteries (MeABs) [1–4]. However, the sluggish kinetics of oxygen reduction reaction (ORR) [3,4] in cathodes of FCs and MeABs, which must to be promoted by efficient electrocatalysts, still limit the wide applications of FCs and MeABs in the energy conversion and storage. Platinum and its alloys are considered as the best electrocatalysts for ORR with high catalytic activity and suitable stability [5–8]. Nevertheless, challenges including scarcity, poor toxicities tolerance and low stability of the Pt-based electrocatalysts still limit their large-scale commercial applications for FCs and MeABs. Therefore, the development of non-precious metal electrocatalysts for ORR with high activity and sufficient stability is urgently required for the scientific and technological importance.

In recent years, metal-free carbon based materials [9,10], transition metal oxides [11–17], transition metal chalcogenides [18–21] exhibited high electrocatalytic activity for ORR in acid or alkaline electrolytes. Among them, Mn-based oxide catalysts such as  $\text{MnO}_2$  [11],  $\text{Mn}_2\text{O}_3$  [13],  $\text{Mn}_3\text{O}_4$  [15] and Mn-Co Oxides [4,16,17] had attracted enormous interests as efficient non-precious metal electrocatalysts for ORR due to their low cost, abundant resources, low toxicity and high performance. Tuning the Mn electronic states by doping Ni or Co ions [4,17], anchoring Mn oxides on the high conductive carbon substrate [22] and constructing porous structure to enhance the mass transport [13,14] were the efficient methods to promote the electrocatalytic activity of Mn oxides electrocatalysts. Despite enormous efforts, the electrocatalytic activity and stability of Mn-based ORR electrocatalysts is still lower than that of the state-of-the-art Pt/C electrocatalysts. Therefore, further enhancement of the electrocatalytic activity for ORR of the Mn-based electrocatalysts is significant but still a challenge.

As reported [23], the anion in the Mn-based materials, which affects the 3d electronic state structure of Mn ions due to the different electronegativity of various anionic elements (e.g.  $\text{Se} < \text{S} < \text{O}$ ), had important roles in the electrocatalytic activity of Mn-based electrocatalysts for ORR. Moreover, the better electric conductivity of metal sulfides than their oxides counterpart had been demonstrated by many researches [24,25]. Based on the tuned electronic state structure and the higher electric conductivity, manganese sulfide based electrocatalysts are expected to exhibit higher electrocatalytic activity than manganese oxide electrocatalysts. However, in recent years the metal sulfide based non-precious metal electrocatalysts for ORR mainly focus on the cobalt sulfides such as  $\text{Co}_9\text{S}_8$  nanoparticles on N/S co-doped porous carbon tube [18],  $\text{Co}_{1-x}\text{S}$ -graphene hybrid [19],  $\text{CoS}_2$  on the N/S codoped graphene oxide [20], carbon supported  $\text{Co}_3\text{S}_4$  [21],  $\text{CoS}_2$  nanocatalysts with different sizes [26] and so on. The manganese sulfide based materials are rarely reported as the electrocatalysts for ORR [27,28]. S and N co-doped three-dimensional graphene (S,N-3DG) supported MnS nanoparticles (MnS/S,N-3DG) exhibited higher electrocatalytic activity for ORR than the S,N-3DG [27], indicating the electrocatalytic activity of MnS material for ORR. Self-assembled manganese sulfide spheres on graphene layers (MnS/G) was another reported MnS-based electrocatalyst for ORR [28]. Nevertheless, the electrocatalytic activity for ORR of the reported MnS/G electrocatalyst and MnS/S,N-3DG were still lower than that of the commercial Pt/C or comparative to that of the Pt/C with low Pt content (5 wt %). Moreover, other morphological MnS nanocrystals on graphene based substrate, which can offer more accessible active sites and suitable mass transport channels for

electrocatalytic reaction, are still not reported as efficient electrocatalysts for ORR.

Herein, a reduced graphene oxide (rGO) supported MnS nanotubes hybrid (MnS-NT/rGO) as a novel non-precious metal Mn-based catalyst with comparative catalytic activity to commercial Pt/C with Pt content of 20 wt % was successfully constructed via a facile hydrothermal process without any templates or surfactants. Nanotube structure of MnS with large internal tubular diameter (much larger than the size of electrolyte ions), which was formed via the core-dissolution coupling with shell-recrystallization type Ostwald ripening effect, endows the MnS-NT@rGO hybrid high accessible surface area for electrocatalysis [29,30]. The as-prepared MnS-NT@rGO possesses much higher specific surface area ( $79.7 \text{ m}^2 \text{ g}^{-1}$ ) than rGO supported MnS nanoparticles (MnS-NP@rGO,  $33.0 \text{ m}^2 \text{ g}^{-1}$ ), although rGO was used as substrate in both of these two materials. Moreover, large internal tubular structure is suitable for the mass transportation of reactants, intermediates and products, and continuous long nanotube structure is suitable for the electronic conductivity. Based on the constructed ingenious nanotube structure, as well as the tuned electronic state of Mn cations by the sulfide with lower electronegativity, the higher electric conductivity of manganese sulfide and the further enhanced electric conductivity by the rGO substrate, the as-prepared MnS-NT@rGO electrocatalyst exhibits comparative catalytic activity to commercial Pt/C catalyst and markedly higher activity than oxides/hydroxides counterparts towards ORR, as well as superior stability and methanol tolerance to commercial Pt/C catalyst.

## 2. Results and discussion

As shown in Scheme 1, MnS-NT@rGO electrocatalyst was synthesized via a facile hydrothermal process without any templates or surfactants. Graphene oxide (GO) obtained via a modified Hummers' method was dispersed in water to form a uniform GO/water suspension. Then  $\text{Mn}^{2+}$  cations were uniformly adsorbed on the surface of GO substrates via electrostatic attraction.<sup>23</sup> With the addition of sulfide ions, MnS-NT@GO hybrid was obtained after hydrothermal reaction at  $120^\circ\text{C}$  for 12 h. The final MnS-NT@rGO hybrid was obtained after being reduced by sodium borohydride solution. For comparison, MnS nanoparticles supported on rGO hybrid (MnS-NP@rGO) was synthesized via similar process to that of MnS-NT@rGO, just using both ammonia and sulfide ions as precipitant (see Experimental details in Electronic Supplementary Information, ESI). Moreover, MnS nanotubes without substrate (MnS-NT) were obtained by the similar process to MnS-NT@rGO just without the rGO substrate (see Experimental details in ESI).

Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the MnS-NT@rGO clearly revealed that the MnS nanotubes were dispersed on the rGO substrates (Fig. 1a and b). Regular framework and macro porous structure were formed by the interwoven ultra-long MnS nanotubes (Figures S1a and S1b). The magnified TEM image (Fig. 1c) and HRTEM image (inset of Fig. 1c) confirm the nanotube structure with inner diameter of 15 nm. Continuous MnS nanotube framework and rGO substrate provided fast electronic conductive paths for charge transfer in ORR. The internal tubular structure of nanotubes with suitable size ( $\sim 15 \text{ nm}$ ), markedly larger than the  $\text{H}_2\text{O}$  ( $\sim 0.4 \text{ nm}$ ),  $\text{O}_2$  ( $\sim 0.3 \text{ nm}$ ), and  $\text{OH}^-$  ( $0.14 \text{ nm}$ ), was suitable for the mass transport of the reactants, intermediates and products in ORR process. The XRD pattern of MnS-NT@rGO electrocatalyst was given in Fig. 1d. As shown, MnS-NT@rGO is composed of MnS polycrystalline mixture with rock-salt  $\alpha$ -phase, zinc-blend  $\beta$ -phase and wurtzite  $\gamma$ -phase [25,31]. No diffraction peaks attributed to Mn oxides were observed in XRD pattern of MnS-NT@rGO. The HRTEM

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