Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

SUPPLEMENTARY INFORMATION

The Role of Electronic Interaction in the Hybrid of Ag and Mn_3O_4 Nanocrystals Covalently Coupled with Carbon as Advanced Oxygen Reduction Electrocatalysts

Jingjun Liu, Juzhe Liu, Weiwei Song, Feng Wang*, Ye Song

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, China

The Ag and Mn_3O_4 particle sizes calculated by Scherrer's formula

The calculated particle sizes for Ag and Mn_3O_4 nanoparticles in this synthesized composite are about 20 nm and 14 nm respectively, by using Scherrer's formula based on XRD patterns data. The obtained results are shown in Table S1.

Table S1. The Ag and Mn_3O_4 particle size in different catalysts calculated by Scherrer's formula

Catalyst	Ag particle size (nm)	Mn3O4 particle size (nm)
Ag/C	18	--
Mn3O4-Ag /C	20	14
Mn3O4/C	--	17
Blend	22	18

TG and DSC curves for $Mn(NO_3)_2$ and $AgNO_3$ precursors during thermal decomposition

For $Mn(NO_3)_2$ sample, there is a dramatic mass loss at the range of 100-200 °C accompanied by exothermic DSC peaks, which can be attributed to the decomposition of manganous nitrate, as shown in Figure S1(A). Different from $Mn(NO_3)_2$, $AgNO_3$ is stable before about 400°C shown in Figure S1 (B), showing superior thermostability over $Mn(NO_3)_2$. Therefore, Mn_3O_4 was preferentially deposited on the carbon by thermal decomposition due to the much lower thermal stability of $Mn(NO_3)_2$ than that of $AgNO_3$ precursor.

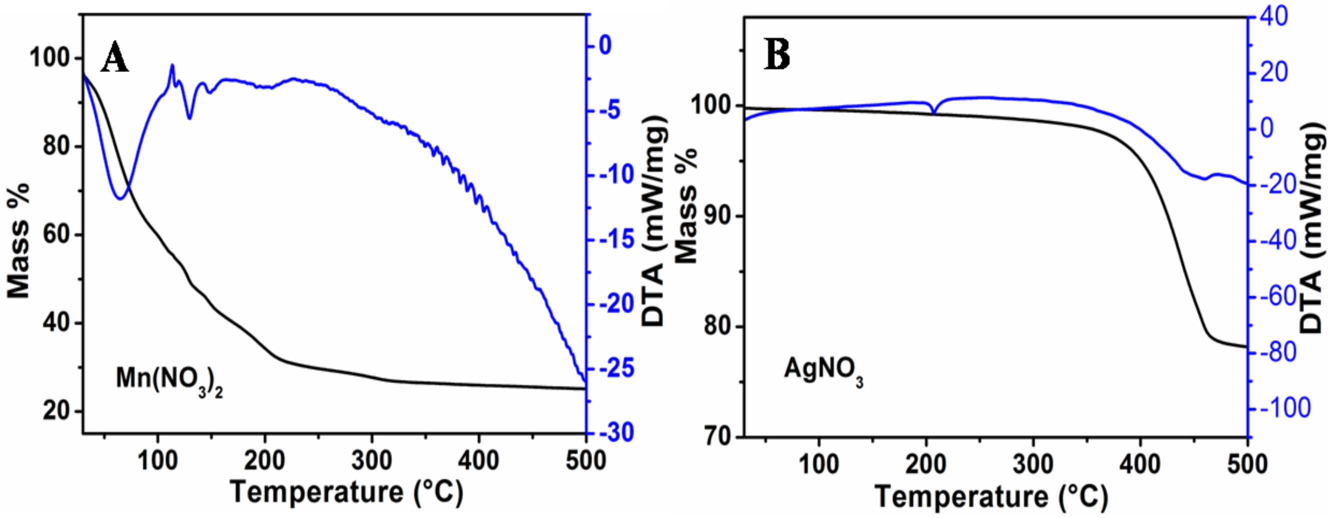

Figure S1. TG and DSC curves for (A) $Mn(NO_3)_2$ and (B)$AgNO_3$ from 30 °C to 800 °C with the heating rate of 5°C min^{-1} in air condition.

HRTEM images for both Ag/C and Ag−Mn_3O_4/C from thermal decomposition

Figure S2 presents the HRTEM image of the synthesized Ag/C by thermal decomposition of $AgNO_3$ precursors mixed with the carbon black. There are few Ag particles anchoring on the carbon surface as shown in Figure S2. It is evident that Ag particles alone can hardly deposit on the carbon support without Mn_3O_4 through this method. This suggests that the resulting Ag particles produced by pyrolysis of only $AgNO_3$ were unable to form the intimate contact with carbon support. On the contrary, as $Mn(NO_3)_2$ is presented, Ag and Mn_3O_4 can be attached firmly on the surface of the carbon surface via the thermal decomposition of $Mn(NO_3)_2$ and $AgNO_3$ at elevated temperatures, even though undergone vigorous sonication, indicating an intimate contact between carbon and Ag as well as Mn_3O_4 phases, as shown in Figure S3. It strongly imply that the introduction of $Mn(NO_3)_2$ into the synthesis system not only provides the origin of Mn_3O_4 but also plays an important part in coinstantaneous deposition of Ag on the carbon.

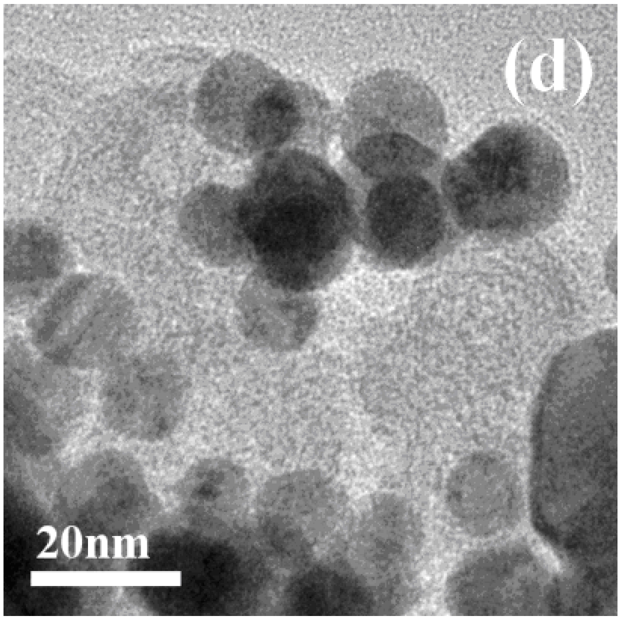

Figure S2. HRTEM image for the synthesized Ag/C by the thermal decomposition of $AgNO_3$ precursor

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) for Ag−Mn3O4/C

Figure S3 depicts the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) for the synthesized Ag−Mn_3O_4/C composite respectively, which provide an additional evidence for the formation of the intimate contact between two nanoparticles and their carbon support. Neeft et al. [1] confirmed that a metal or a metal oxide can effectively promote the oxidation of carbon in tight contact mode but perform hardly any activity in loose contact. Insight into the pure carbon support, there is a dramatic mass loss at the range of 500-650°C, accompanied by an exothermic DSC peak at 600°C, which can be attributed to the oxidation of carbon and emission of CO_2/CO gas. Oxidation temperature for the blend sample (mixing of commercial Ag particles and a commercial Mn_3O_4 particles and carbon) is just a little lower than that of the pure carbon, and DSC peak is at 500 °C. However, the oxidation temperature for the hybrid catalytic decreases largely to only 330 °C, which can be attributed to the accelerated oxidation of carbon caused by the anchored metal and metal oxidation nanoparticles. As a result, it provides supporting evidence of the formation of the tight contact mode in the Mn_3O_4−Ag/C hybrid catalyst. This crucial intimate contact between two nanoparticles and carbon support can substantially change the electronic structure of the hybrid material through the covalent electron transfer across the interfacial interaction between them.

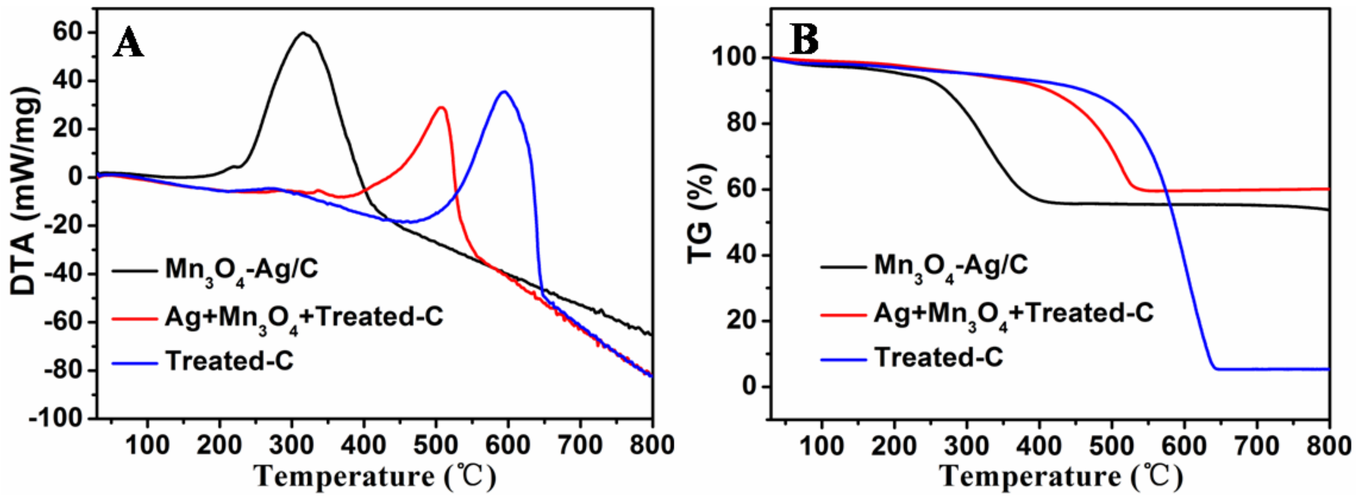

Figure S3. (A) Differential Thermal Analysis (DTA) and (B) Thermogravimetric analysis (TGA) of Mn_3O_4−Ag/C composite, the blend (a mixture of commercial Ag, Mn_3O_4 particles and carbon support) and carbon support (Treated-C) from 30 °C to 800 °C with the rate of 5 °C min^{-1} in air condition.

XPS spectrum for Ag−Mn3O4/C and carbon support

Figure S4 shows the as-synthesized Ag–Mn_3O_4/C hybrid catalyst is composed of C, O, N, Ag and Mn elements, while the HNO_3-treated the Mn_3O_4-Ag/C (Treated-C) is composed of C and O elements. The content of the oxygen element is up to 23.1 at%, while the content of the nitrogen is only 1.2 at%. Compared with that of the predominated oxygen atoms, the content of nitrogen is neglected. Moreover, after HNO_3-treatment for Ag–Mn_3O_4/C hybrid in order to completely removing both Ag and Mn3O4 nanoparticles from carbon support, we found that the peak of the residual nitrogen disappeared, as shown in Figure S4. It implies the possible formation of interfacial C–N–metal bonds at the interfaces between the nanoparticles and carbon support in the Ag–Mn_3O_4/C hybrid, through the pyrolysis of NO_3^- ions. Similar to the predominated C–O–metal bonds, the formation of the covalent C–N–metal bonds may also facilitate the electro-catalytic activity for the ORR on the hybrid, as evidenced from results in the literature report [2]. However, since the content of the nitrogen atoms is too low in this hybrid, relative to that of the covalent oxygen atoms, the effect of the covalent nitrogen atoms on the ORR activity was negligible in this paper.

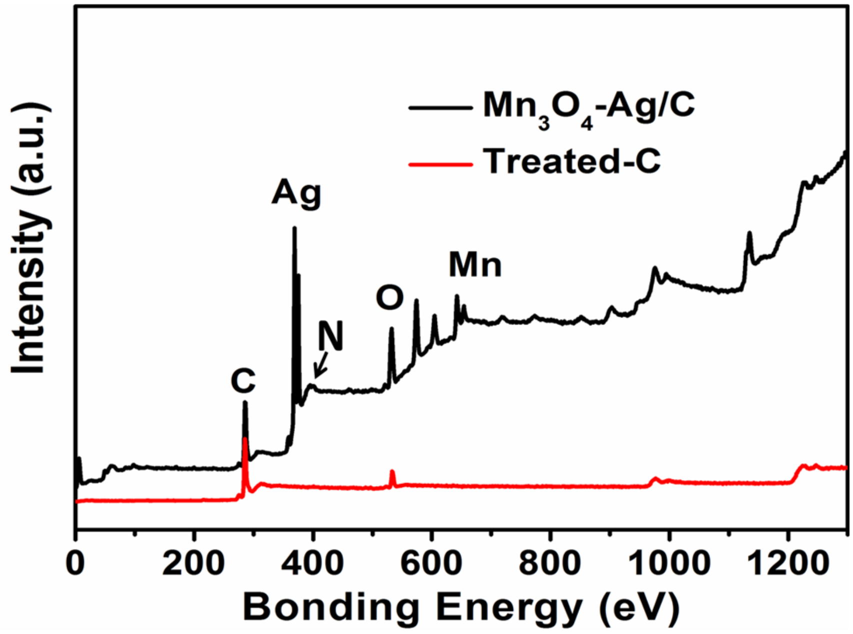

Figure S4. XPS spectra of the synthesized Mn_3O_4-Ag/C and HNO_3-treated the Mn_3O_4-Ag/C in HNO_3 to completely removing both Ag and Mn_3O_4 from carbon support (Treated-C)

References

(1) Neeft, J. P. A.; Makkee, M.; Moulijin, J. A. *Chem. Eng. J.,* **1996**, 64, 295.

(2) Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. *Nat. Mater.,* 2011, 10, 780-786