

## Supporting Information

# Sodium Rivals Silver as Single-Atom Active Centers for Catalyzing the Abatement of Formaldehyde

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## 1. Catalyst Preparation

For the synthesis of HMO, an aqueous solution (400 mL) of manganese sulfate ( $\text{MnSO}_4$ ,  $0.375 \text{ mol L}^{-1}$ ), ammonium persulfate [ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ,  $0.375 \text{ mol L}^{-1}$ ] and ammonium sulfate [ $(\text{NH}_4)_2\text{SO}_4$ ,  $1.875 \text{ mol L}^{-1}$ ] was refluxed at  $100 \text{ }^\circ\text{C}$  for 12 h. After filtering and washing with deionized  $\text{H}_2\text{O}$ , the obtained black solid was dried at  $110 \text{ }^\circ\text{C}$  for 12 h, followed by being annealed at  $400 \text{ }^\circ\text{C}$  for 4 h in air to achieve HMO.

For the  $\text{Ag}_1/\text{HMO}$  synthesis,  $\text{AgNO}_3$  was initially dissolved in 20 mL deionized water to form a solution, to which ammonia (25 wt.%) was slowly added under stirring until the solution became clear to give a transparent  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$  solution. Subsequently, both the  $[\text{Ag}(\text{NH}_3)_2]\text{OH}$  solution and a  $\text{H}_2\text{O}_2$  solution (30 wt.%, 30 mL) were respectively and simultaneously added to another suspension (100 mL) containing HMO under stirring at  $20 \text{ }^\circ\text{C}$  for 1 h. The final suspension was filtered, washed with distilled water, and then dried in  $80 \text{ }^\circ\text{C}$  for 24 h to obtain the black solid.  $\text{Ag}_1/\text{HMO}$  was obtained by annealing the black solid at  $400 \text{ }^\circ\text{C}$  in air for 4 h.

## 2. Calculation of TOF

Turnover frequency (TOF) is defined as the number of HCHO molecules converted per active site per second. We calculated the TOF of each sample as follows.

### 2.1 Calculation of TOF of $\text{Ag}_1/\text{HMO}$

The TOF of  $\text{Ag}_1/\text{HMO}$  (TOF, number of converted HCHO molecules per surface Ag catalytically active site and per second) is calculated as follows:

(i) *Average density of the unit cell of  $\text{Ag}_1/\text{HMO}$ .* According to the elemental analyses, average one unit cell of  $\text{Ag}_1/\text{HMO}$  can be expressed as a formula  $\text{Ag}_{1.2}\text{Mn}_8\text{O}_{16}$ , and thus the mass ( $M_{\text{cell}}$ ) of one unit cell is calculated to be  $1.371 \times 10^{-21} \text{ g}$ . The volume ( $V_{\text{cell}}$ ) of one unit cell according to the lattice parameters ( $a = 0.9821 \text{ nm}$ ,  $c = 0.2871 \text{ nm}$ , Table S1) and the tetragonal structure feature of  $\text{Ag}_1/\text{HMO}$  (the SXRD pattern of  $\text{Ag}_1/\text{HMO}$  in Figure 1b) can be calculated:

$$V_{\text{cell}} = a^2 \times c = (0.9821 \text{ nm})^2 \times 0.2871 \text{ nm} = 0.2769 \text{ nm}^3.$$

Thus, an average density ( $\rho$ ) of the unit cell is calculated:

$$\rho = M_{\text{cell}} / V_{\text{cell}} = 4.953 \times 10^{-21} \text{ g nm}^{-3}.$$

(ii) *Number of the nanorods for 0.050 g Ag<sub>1</sub>/HMO.* The volume ( $V_{\text{rod}}$ ) and mass ( $M_{\text{rod}}$ ) of single Ag<sub>1</sub>/HMO nanorod are calculated according to the TEM/HRTEM images:

$$V_{\text{rod}} = w^2 \times l = (12 \text{ nm})^2 \times 800 \text{ nm} = 1.15 \times 10^5 \text{ nm}^3,$$

$$M_{\text{rod}} = V_{\text{rod}} \times \rho = 1.15 \times 10^5 \text{ nm}^3 \times 4.953 \times 10^{-21} \text{ g nm}^{-3} = 5.705 \times 10^{-16} \text{ g},$$

where  $w$  and  $l$  represent the average width and length of the Ag<sub>1</sub>/HMO nanorods, respectively (*Chem. Eur. J.*, **2015**, *21*, 9619). Therefore, the number ( $N_{\text{rod}}$ ) of the Ag<sub>1</sub>/HMO nanorods of 0.050 g catalyst ( $M_{\text{cat}}$ ) is:

$$N_{\text{rod}} = M_{\text{cat}} / M_{\text{rod}} = 0.050 \text{ g} \div (5.705 \times 10^{-16} \text{ g}) = 8.76 \times 10^{13}.$$

(iii) *Number of the exposed single Ag atoms of 0.050 g Ag<sub>1</sub>/HMO.* Based on the above results, the number of the exposed Ag atoms ( $N_{\text{Ag}}$ ) is equal to the number of the openings ( $N_{\text{opening}}$ ) on the {001} top-facets of the Ag<sub>1</sub>/HMO nanorods. The  $N_{\text{Ag}}$  of 0.050 g Ag<sub>1</sub>/HMO can be calculated as follows:

$$N_{\text{Ag}} = N_{\text{opening}} = (w^2 / a^2 \times 2 \times 2) \times N_{\text{rod}} = (12^2 \div 0.9821^2 \times 2 \times 2) \times 8.76 \times 10^{13} = 5.23 \times 10^{16},$$

where the expression in the parentheses is used to calculate the number of the openings of one Ag<sub>1</sub>/HMO nanorod, the first number “2” represents two ends of one Ag<sub>1</sub>/HMO nanorod, and the second one does two tunnel openings of each unit cell of Ag<sub>1</sub>/HMO.

(iv) *Calculation of the TOF.* The number of converted HCHO molecules ( $N_{\text{conv}}$ ) per one second for 0.050 g catalyst can be calculated according to the number of the fed HCHO molecules ( $N_{\text{HCHO}}$ ) per one second and the conversion rate of HCHO ( $X_{\text{HCHO}}$ ) at certain reaction temperature.

$$N_{\text{conv}} = N_{\text{HCHO}} \times X_{\text{HCHO}} = (N_{\text{A}} \times C_0 \times V_s / V_m) \times X_{\text{HCHO}} = 6.02 \times 10^{23} \text{ mol}^{-1} \times 1.40 \times 10^{-4} \times 1.67 \times 10^3 \text{ L} \div (22.4 \text{ L mol}^{-1}) \times X_{\text{HCHO}} = 6.28 \times 10^{15} \times X_{\text{HCHO}},$$

where  $N_{\text{A}}$  is the Avogadro constant ( $6.02 \times 10^{23} \text{ mol}^{-1}$ ),  $C_0$  is the concentration in volume fraction of the fed HCHO ( $1.40 \times 10^{-4}$ ),  $V_s$  is the volume of the fed total gases that pass the catalyst in one second ( $0.100 \text{ L min}^{-1} \times (1 \text{ min} / 60 \text{ s}) \times 1 \text{ s} = 1.67 \times 10^{-3} \text{ L}$ ), and  $V_m$  is the standard molar volume of gas ( $22.4 \text{ L mol}^{-1}$ ).

Then, the TOF during the time ( $t$ ) of one second can be calculated as:

$$\text{TOF} = (N_{\text{conv}} / N_{\text{Ag}}) / t = [6.28 \times 10^{15} \times X_{\text{HCHO}} \div (5.23 \times 10^{16})] \div 1 \text{ s} = 1.2 \times 10^{-1} \times X_{\text{HCHO}} \text{ s}^{-1}.$$

Therefore, the TOF at different reaction temperatures were calculated according to  $X_{\text{HCHO}}$  at the corresponding temperatures in Figure 3.

## 2.2 Calculation of the TOF of $\text{Na}_1/\text{HMO}$

The TOF of  $\text{Na}_1/\text{HMO}$  (TOF, number of converted HCHO molecules per surface Na catalytically active site and per second) is calculated as follows:

(i) *Average density of the unit cell of  $\text{Na}_1/\text{HMO}$ .* According to the elemental analyses, average one unit cell of  $\text{Na}_1/\text{HMO}$  can be expressed as a formula  $\text{Na}_{1.5}\text{Mn}_8\text{O}_{16}$ , and thus the mass ( $M_{\text{cell}}$ ) of one unit cell is calculated to be  $1.213 \times 10^{-21}$  g. The volume ( $V_{\text{cell}}$ ) of one unit cell according to the lattice parameters ( $a = 0.9808$  nm,  $c = 0.2865$  nm, Table S1) and the tetragonal structure feature of  $\text{Na}_1/\text{HMO}$  (the SXRD pattern of  $\text{Na}_1/\text{HMO}$  in Figure 1a) can be calculated:

$$V_{\text{cell}} = a^2 \times c = (0.9808 \text{ nm})^2 \times 0.2865 \text{ nm} = 0.2756 \text{ nm}^3.$$

Thus, an average density ( $\rho$ ) of the unit cell is calculated:

$$\rho = M_{\text{cell}} / V_{\text{cell}} = 4.400 \times 10^{-21} \text{ g nm}^{-3}.$$

(ii) *Number of the nanorods for 0.050 g  $\text{Na}_1/\text{HMO}$ .* The volume ( $V_{\text{rod}}$ ) and mass ( $M_{\text{rod}}$ ) of single  $\text{Na}_1/\text{HMO}$  nanorod are calculated according to the TEM/HRTEM images:

$$V_{\text{rod}} = w^2 \times l = (12 \text{ nm})^2 \times 800 \text{ nm} = 1.15 \times 10^5 \text{ nm}^3,$$

$$M_{\text{rod}} = V_{\text{rod}} \times \rho = 1.15 \times 10^5 \text{ nm}^3 \times 4.400 \times 10^{-21} \text{ g nm}^{-3} = 5.068 \times 10^{-16} \text{ g},$$

where  $w$  and  $l$  represent the average width and length of the  $\text{Na}_1/\text{HMO}$  nanorods, respectively (*Chem. Eur. J.*, **2015**, *21*, 9619). Therefore, the number ( $N_{\text{rod}}$ ) of the  $\text{Na}_1/\text{HMO}$  nanorods of 0.050 g catalyst ( $M_{\text{cat}}$ ) is:

$$N_{\text{rod}} = M_{\text{cat}} / M_{\text{rod}} = 0.050 \text{ g} \div (5.068 \times 10^{-16} \text{ g}) = 9.86 \times 10^{13}.$$

(iii) *Number of the exposed single Na ions of 0.050 g Na<sub>1</sub>/HMO.* Based on the above results, the number of the exposed Na ions ( $N_{\text{Na}}$ ) is equal to the number of the openings ( $N_{\text{opening}}$ ) on the {001} top-facets of the Na<sub>1</sub>/HMO nanorods. The  $N_{\text{Na}}$  of 0.050 g Na<sub>1</sub>/HMO can be calculated as follows:

$$N_{\text{Na}} = N_{\text{opening}} = (w^2 / a^2 \times 2 \times 2) \times N_{\text{rod}} = (12^2 \div 0.9808^2 \times 2 \times 2) \times 9.86 \times 10^{13} = 5.91 \times 10^{16},$$

where the expression in the parentheses is used to calculate the number of the openings of one Na<sub>1</sub>/HMO nanorod, the first number “2” represents two ends of one Na<sub>1</sub>/HMO nanorod, and the second one does two tunnel openings of each unit cell of Na<sub>1</sub>/HMO.

(iv) *Calculation of the TOF.* The  $N_{\text{conv}}$  of HCHO is ( $6.28 \times 10^{15} \times X_{\text{HCHO}}$ ). Then, the TOF during the time ( $t$ ) of one second can be calculated as:

$$\text{TOF} = (N_{\text{conv}} / N_{\text{Na}}) / t = [6.28 \times 10^{15} \times X_{\text{HCHO}} \div (5.91 \times 10^{16})] \div 1 \text{ s} = 1.1 \times 10^{-1} \times X_{\text{HCHO}} \text{ s}^{-1}.$$

Therefore, the TOF at different reaction temperatures were calculated according to  $X_{\text{HCHO}}$  at the corresponding temperatures in Figure 3.

### 2.3 Calculation of the TOF of HMO

The TOF of HMO (number of converted HCHO molecules per tunneled opening of HMO and per second) is calculated as follows:

(i) *Average density of the unit cell of HMO.* According to the elemental analyses, average one unit cell of HMO can be expressed as a formula  $\text{Mn}_8\text{O}_{16}$ , and thus the mass ( $M_{\text{cell}}$ ) of one unit cell is calculated to be  $1.213 \times 10^{-21}$  g. The volume ( $V_{\text{cell}}$ ) of one unit cell according to the lattice parameters ( $a = 0.9838$  nm,  $c = 0.2864$  nm) and the tetragonal structure feature of HMO (the SXRD pattern of HMO in Figure S1) can be calculated:

$$V_{\text{cell}} = a^2 \times c = (0.9838 \text{ nm})^2 \times 0.2864 \text{ nm} = 0.2772 \text{ nm}^3.$$

Thus, an average density ( $\rho$ ) of the unit cell is calculated:

$$\rho = M_{\text{cell}} / V_{\text{cell}} = 4.171 \times 10^{-21} \text{ g nm}^{-3}.$$

(ii) *Number of the nanorods for 0.050 g HMO.* The volume ( $V_{\text{rod}}$ ) and mass ( $M_{\text{rod}}$ ) of single HMO nanorod are calculated according to the TEM/HRTEM images:

$$V_{\text{rod}} = w^2 \times l = (12 \text{ nm})^2 \times 800 \text{ nm} = 1.15 \times 10^5 \text{ nm}^3,$$

$$M_{\text{rod}} = V_{\text{rod}} \times \rho = 1.15 \times 10^5 \text{ nm}^3 \times 4.171 \times 10^{-21} \text{ g nm}^{-3} = 4.805 \times 10^{-16} \text{ g},$$

where  $w$  and  $l$  represent the average width and length of the HMO nanorods, respectively (*Chem. Eur. J.*, **2015**, *21*, 9619). Therefore, the number ( $N_{\text{rod}}$ ) of the HMO nanorods that 0.050 g catalyst ( $M_{\text{cat}}$ ) contains:

$$N_{\text{rod}} = M_{\text{cat}} / M_{\text{rod}} = 0.050 \text{ g} \div (4.805 \times 10^{-16} \text{ g}) = 1.04 \times 10^{14}.$$

(iii) *Number of the tunnel openings of 0.050 g HMO.* The  $N_{\text{opening}}$  on the {001} top facets of the HMO nanorod can be calculated as follows:

$$N_{\text{opening}} = (w^2 / a^2 \times 2 \times 2) \times N_{\text{rod}} = (12^2 \div 0.9838^2 \times 2 \times 2) \times 1.04 \times 10^{14} = 6.19 \times 10^{16},$$

where the expression in the parentheses is used to calculate the number of the openings of one HMO nanorod, the first number “2” represents two ends of one HMO nanorod, and the second one does two tunnel openings of each unit cell of HMO.

(iv) *Calculation of the TOF.* The  $N_{\text{conv}}$  of HCHO is ( $6.28 \times 10^{15} \times X_{\text{HCHO}}$ ). Then, the TOF during the time ( $t$ ) of one second can be calculated as:

$$\text{TOF} = (N_{\text{conv}} / N_{\text{opening}}) / t = [6.28 \times 10^{15} \times X_{\text{HCHO}} \div (6.19 \times 10^{16})] \div 1 \text{ s} = 1.0 \times 10^{-1} \times X_{\text{HCHO}} \text{ s}^{-1}.$$

Therefore, the TOF at different reaction temperatures were calculated according to  $X_{\text{HCHO}}$  at the corresponding temperatures in Figure 3.

## Tables and Figures

**Table S1.** Crystallographic data and details of HMO, Na<sub>1</sub>/HMO and Ag<sub>1</sub>/HMO in the SXRD data collections and the Rietveld refinements.

Samples	HMO	Na <sub>1</sub> /HMO	Ag <sub>1</sub> /HMO
Chemical formula	MnO <sub>2</sub>	Na <sub>0.18</sub> MnO <sub>2</sub>	Ag <sub>0.15</sub> MnO <sub>2</sub>
Crystal system	tetragonal	tetragonal	tetragonal
Space group	<i>I4/m</i>	<i>I4/m</i>	<i>I4/m</i>
<i>Z</i> <sup>[a]</sup>	8	8	8
<i>a</i> / Å	9.838(2)	9.808(4)	9.821(4)
<i>c</i> / Å	2.864(4)	2.865(9)	2.871(6)
<i>V</i> / Å <sup>3</sup>	277.2(4)	275.6(0)	276.9(9)
<i>R</i> <sub>p</sub> <sup>[b]</sup> / %	6.63	6.89	5.70
<i>R</i> <sub>wp</sub> <sup>[c]</sup> / %	8.61	9.09	7.63
<i>R</i> <sub>exp</sub> <sup>[d]</sup> / %	4.07	3.51	4.09
$\chi^2$ <sup>[e]</sup>	4.47	6.72	3.47
Wavelength / Å	0.6887	0.6887	0.6887
$2\theta$ range / °	3-55	3-55	3-55
$2\theta$ step width / °	0.02	0.02	0.02

<sup>[a]</sup> *Z*, the number of MnO<sub>2</sub>, Na<sub>0.18</sub>MnO<sub>2</sub> and Ag<sub>0.15</sub>MnO<sub>2</sub> formula units per unit cell;

<sup>[b]</sup> *R*<sub>p</sub>, the unweighted profile factor;

<sup>[c]</sup> *R*<sub>wp</sub>, the weighted profile factor;

<sup>[d]</sup> *R*<sub>exp</sub>, the expected *R* parameter;

<sup>[e]</sup>  $\chi^2$ , the goodness of fitting, defined as the square of the ratio of *R*<sub>wp</sub>/*R*<sub>exp</sub>.



**Table S2.** Structure parameters of HMO, Na<sub>1</sub>/HMO and Ag<sub>1</sub>/HMO determined by the Rietveld refinement of the corresponding SXRD data.

Samples	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
HMO	Mn	0.3530(4)	0.1701(1)	0	1.0
	O <sub>sp3</sub>	0.1376(6)	0.1899(4)	0	1.0
	O <sub>sp2</sub>	0.5287(3)	0.1861(7)	0	1.0
Na <sub>1</sub> /HMO	Na	0	0	0	0.18
	Mn	0.1517(4)	0.3334(8)	0.5	1.0
	O <sub>sp3</sub>	0.1600(4)	0.2078(5)	0	1.0
	O <sub>sp2</sub>	0.1646(9)	0.4529(7)	0	1.0
Ag <sub>1</sub> /HMO	Ag	0	0	0	0.15
	Mn	0.1492(2)	0.3319(6)	0.5	1.0
	O <sub>sp3</sub>	0.1582(3)	0.2054(7)	0	1.0
	O <sub>sp2</sub>	0.1680(0)	0.4553(7)	0	1.0

**Table S3.** EXAFS parameters Ag<sub>1</sub>/HMO, Ag foil and Ag<sub>2</sub>O at the Ag *K*-edge.

Samples	Shell	$CN$ <sup>[a]</sup>	$R$ <sup>[b]</sup> / Å	$\sigma^2$ <sup>[c]</sup> / Å <sup>2</sup>	$\Delta E_0$ <sup>[d]</sup> / eV
Ag <sub>1</sub> /HMO	Ag-O	4	2.33(1)	0.018(4)	- 3.7
	Ag-Ag	2	2.83(1)	0.027(7)	- 2.2
Ag foil	Ag-Ag	12	2.89(1)	0.016(7)	+2.8
Ag <sub>2</sub> O	Ag-O	2	2.03(7)	0.00(4)	+ 4.9
	Ag-Ag	12	3.31(1)	0.046(0)	- 4.1

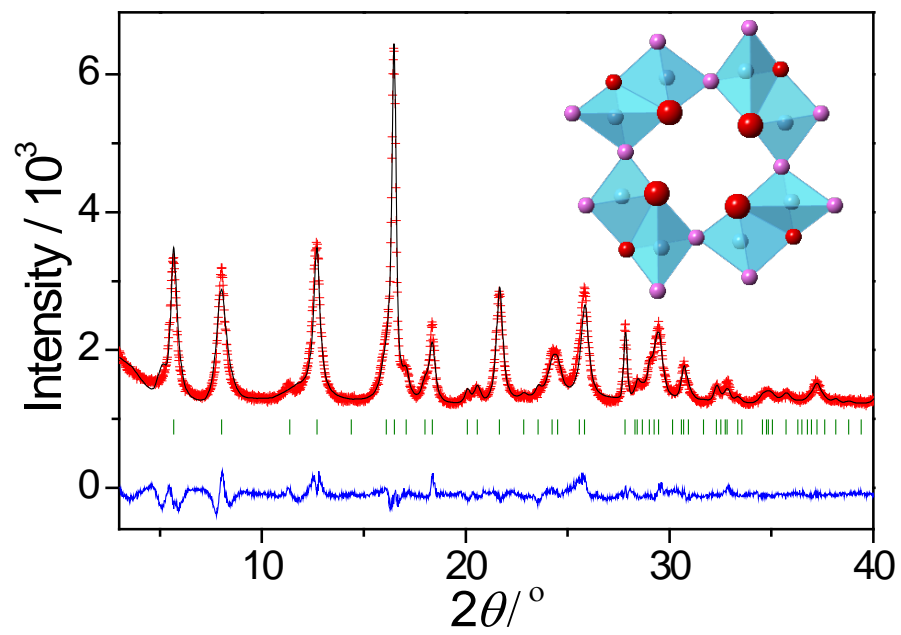
$R$ -space fit,  $\Delta k = 2.1$ - $9.5 \text{ \AA}^{-1}$ ,  $\Delta r = 1.2$ - $3.9 \text{ \AA}$ ;

<sup>[a]</sup>  $CN$ , coordination number;

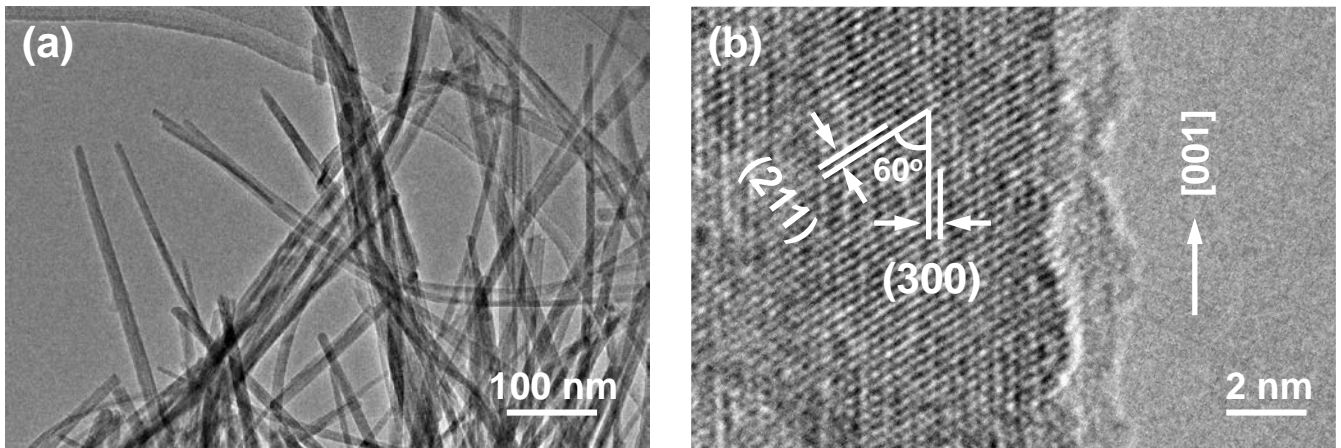
<sup>[b]</sup>  $R$ , distance between absorber and backscatter atoms;

<sup>[c]</sup>  $\sigma^2$ , Debye-Waller factor;

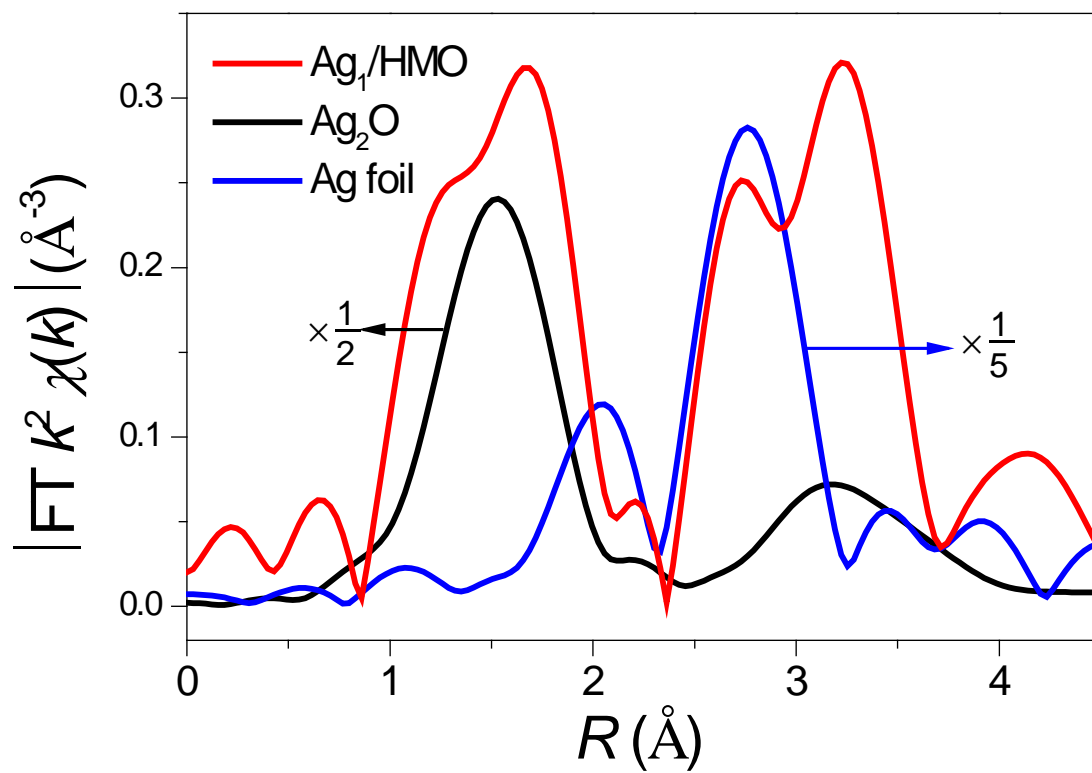
<sup>[d]</sup>  $\Delta E_0$ , energy shift.



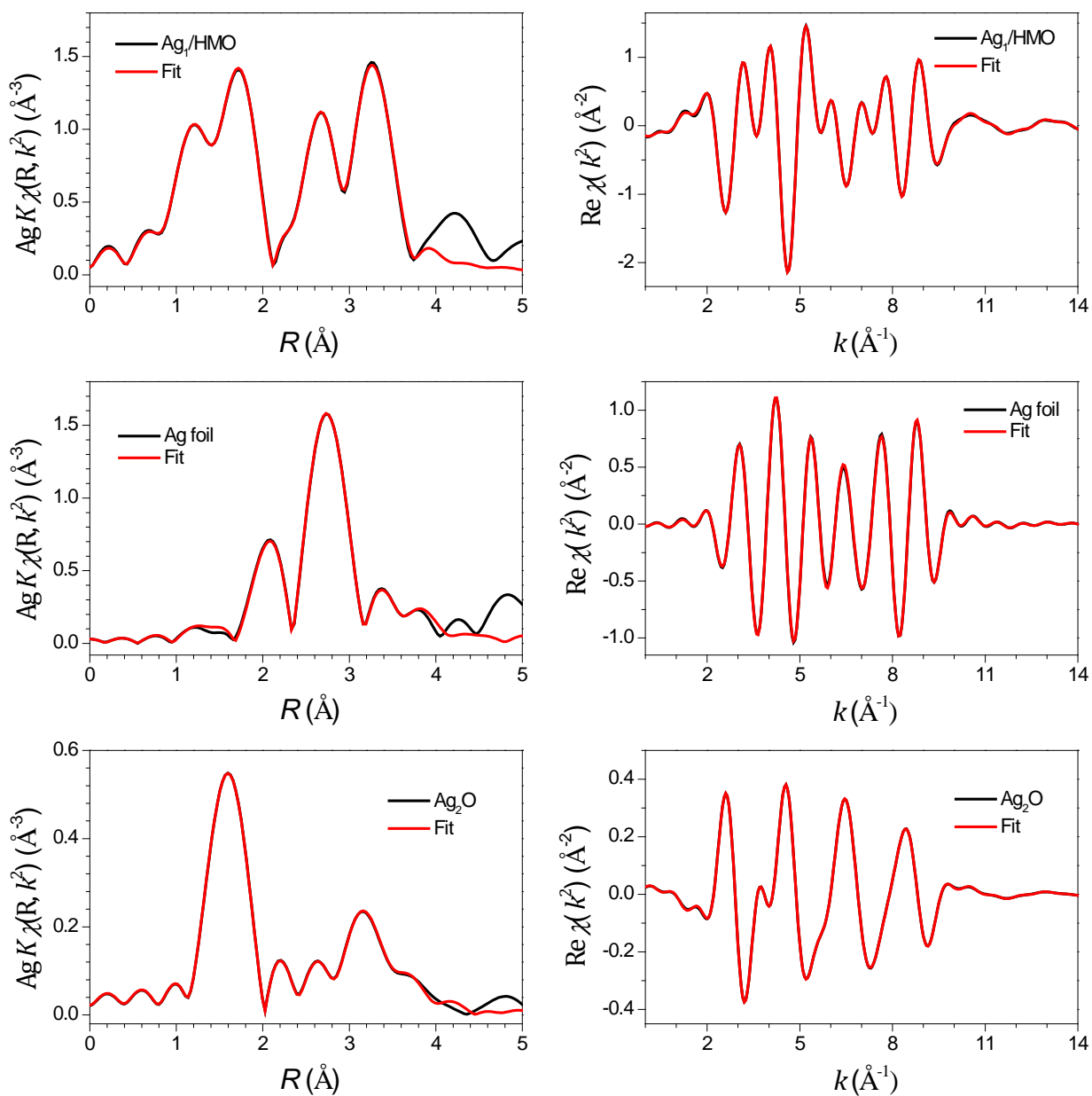
**Figure S1.** SXR D pattern and the Rietveld refinement of HMO.



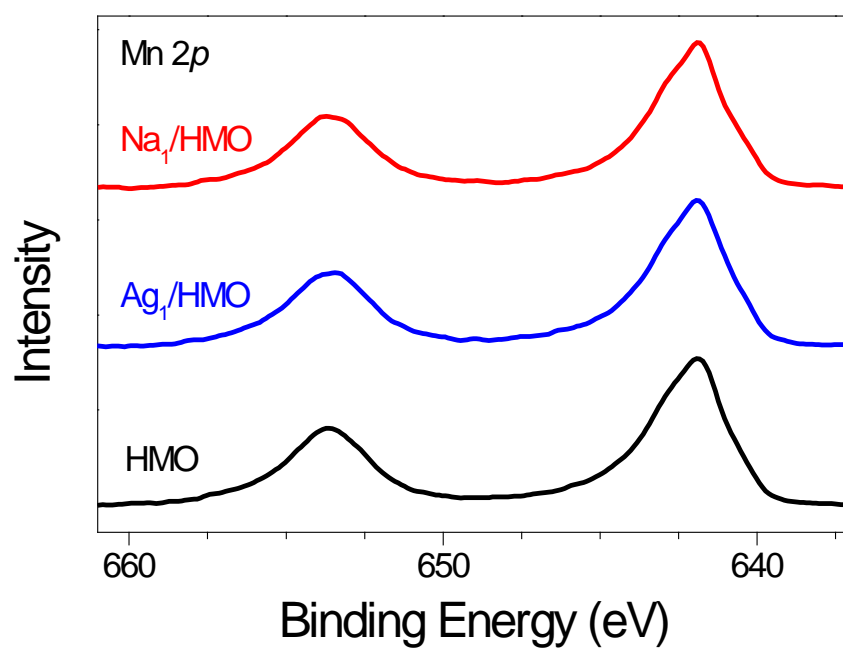
**Figure S2.** (a) TEM image and (b) HRTEM image of HMO.



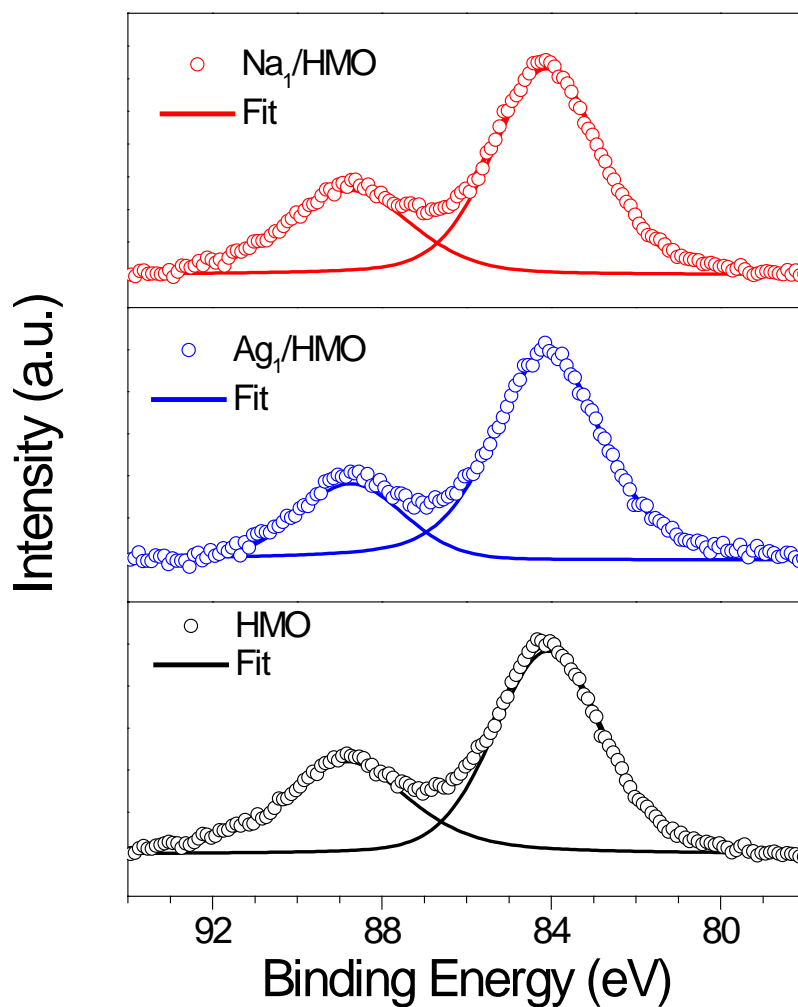
**Figure S3.** Ag  $K$ -edge  $\chi(R)$   $k^2$ -weighted FT EXAFS spectra of  $\text{Ag}_1/\text{HMO}$ , Ag foil and  $\text{Ag}_2\text{O}$ .



**Figure S4.**  $R$ -space ( $\Delta k = 2.1\text{-}9.5 \text{ \AA}^{-1}$ ) and inverse FT spectra ( $\Delta r = 1.2\text{-}3.9 \text{ \AA}$ ) at the Ag  $K$ -edge of the Ag<sub>1</sub>/HMO, Ag foil and Ag<sub>2</sub>O.



**Figure S5.** Mn 2p XPS of Na<sub>1</sub>/HMO, Ag<sub>1</sub>/HMO and HMO.



**Figure S6.** Mn 3s XPS of Na<sub>1</sub>/HMO, Ag<sub>1</sub>/HMO and HMO. Curve fitting was performed using a mixed Gaussian-Lorentzian function after a Shirley background subtraction. There are no any special constraints between the two peaks in Mn 3s XPS.