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Supplementary Material for:

High Proton Conduction in a New Alkali Metal-Templated Open-Framework Aluminophosphate

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Synthesis

Synthesis of JU103. The reagents and solvents employed in the synthesis were commercially available and used as received without further purification. JU103 was synthesized under hydrothermal conditions in the reaction system of Na_2O-Al_2O_3-P_2O_5-H_2O. Typically, aluminum triisopropoxide was dispersed in a solution of orthophosphoric acid (85 wt%) in water under vigorous stirring at room temperature. 5M NaOH solution was added to this mixture giving the pH value of about 7. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0Al_2O_3$: $5.2P_2O_5$: $4.5Na_2O$: $780H_2O$ was formed, which was heated at 180 ºC in a 15 mL Teflon-lined stainless steel autoclave for 3 days. The crystal products were recovered by washed in distilled water and dried at room temperature overnight.

Preparation of NH_4-JU103 and Ag-JU103. The NH_4^+ exchanged JU103 was obtained by immersing 0.5g of JU103 samples in 20 mL of 1 M CH_3COONH_4 solution at 60 °C (denoted as NH_4-JU103-a) or 80°C (denoted as NH_4-JU103-b) for 5 h. The Ag^+ exchanged JU103 (denoted as Ag-JU103) were obtained by immersing 0.5 g of JU103 samples in 20 mL of 1 M $AgNO_3$ solutions at 80 °C for 5 h.

Characterization

Powder X-ray diffraction (XRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å). Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300Dv spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. The compositional analysis gave that the contents of Al, P, Na and H are 15.3%, 16.8%, 9.71%, 1.63% (calcd 15.9%, 18.2%, 10.1%, 1.61%), respectively, which are consistent with the formula given by single crystal structure analysis. Thermogravimetric analysis (TG) was carried out on a TA Q500 analyzer in air with a heating rate of 10 °C min^{-1} from room temperature to 800 °C. The IR absorption spectrum was recorded in the range of 400-4000cm^{-1} on a Nicolet 6700 FT-IR spectrometer with KBr pellets

Several tablets of JU103, NH_4-JU103 and Ag-JU103 (9.4~10.4 mm in diameter and 1.12~2.32 mm in thickness) were prepared by pressing samples on a tableting machine for the proton conductivity analyses. The measurement was carried out via impedance spectroscopy on a Solartron 1260 impedance analyzer over the frequency range from 1(or 10) Hz to 1 MHz and an applied a.c. voltage of 1000（or 2000）mV. The humidity was obtained by continuously ventilating wet nitrogen. Conductivity was calculated using the following equation : $\sigma = l / (Rs \times S)$, where l and S are the thickness (cm) and cross-sectional area (cm^2) of the pellet, respectively, and Rs that was extracted directly from the impedance plots, is the bulk resistance of the sample (Ω).

Structural Determination

Suitable single crystal of JU103 was selected for single-crystal X-ray diffraction analyses. The intensity data were collected at a temperature of 296 K on a Bruker SMART APEX2 micro-focused diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 nm) at 50 kV and 0.6 mA. Data processing was accomplished with the APEX 2 processing program. Empirical absorption corrections based on symmetry equivalents were applied. The structure of JU103 was solved in the space group $P2_1/m$ by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package. The heaviest atoms of Al, P, Na and framework O atoms could be unambiguously located. The H atoms on the framework O atoms were subsequently located. The O atoms of water molecules and associated H atoms were not located due to the high disorder. All nonhydrogen atoms were refined anisotropically. Crystal data and refinement parameters for the structure determination are presented in Table S1. The selected bond distances and bond angles are listed in the Table S2.

Table S1 Crystal data and structure refinement for JU103[a].

Compound	JU103	
Empirical formula	$H_3 Al_4 Na_3 O_{19} P_4$	
Formula weight	607.79	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$	
Unit cell dimensions	a = 7.5370(18) Å	α= 90°
	b = 12.525(3) Å	β= 98.510(4)°
	c = 9.700(2) Å	γ= 90°
Volume	905.6(4) $Å^3$	
Z	2	
Density (calculated)	2.229 g/cm^3	
Absorption coefficient	0.778 mm^{-1}	
F(000)	600	
Theta range for data collection	2.12 to 26.44°.	
Index ranges	$-9\leq h\leq 7$, $-15\leq k\leq 15$, $-10\leq l\leq 12$	
Reflections collected	5077	
Independent reflections	1944 [R(int) = 0.0301]	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8726 and 0.8536	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1944 / 0 / 167	
Goodness-of-fit on F^2	1.119	
Final R indices [I>2sigma(I)]	R_1 = 0.1169 wR_2 = 0.3265	
R indices (all data)	R_1 = 0.1212, wR_2 = 0.3291	

$w=1/[\sigma^2(F_o^2)+(0.1724P)^2+28.4650P]$ $P=(F_o^2+2F_c^2)/3$

Table S2 Selected bond lengths [Å] and angles [°] for JU103

Al(1)-O(5)	1.834(7)	Al(1)-O(2)	1.864(6)
Al(1)-O(1)	1.865(7)	Al(1)-O(4)	1.881(7)
Al(1)-O(3)	1.955(7)	Al(1)-O(9)	1.995(7)
Al(2)-O(6)#2	1.881(6)	Al(2)-O(6)	1.881(6)
Al(2)-O(1)	1.882(6)	Al(2)-O(1)#2	1.882(6)
Al(2)-O(7)#2	1.937(7)	Al(2)-O(7)	1.937(7)
Al(3)-O(8)	1.763(10)	Al(3)-O(10)	1.777(7)
Al(3)-O(10)#4	1.777(7)	Al(3)-O(11)	1.857(10)
Al(3)-O(12)	1.976(10)	P(1)-O(6)	1.520(7)
P(1)-O(5)#6	1.525(7)	P(1)-O(4)	1.528(7)
P(1)-O(10)	1.556(7)	P(2)-O(8)	1.517(10)
P(2)-O(7)	1.526(7)	P(2)-O(7)#4	1.526(7)
P(2)-O(9)	1.566(9)	P(3)-O(3)#4	1.523(7)
P(3)-O(3)	1.523(7)	P(3)-O(11)#3	1.548(9)
P(3)-O(12)#3	1.562(11)	O(1)-H(1O)	0.9628
O(2)-H(2O)	0.9582		

O(5)-Al(1)-O(2)	93.8(3)	O(5)-Al(1)-O(1)	95.7(3)
O(2)-Al(1)-O(1)	169.7(3)	O(5)-Al(1)-O(4)	94.6(3)
O(2)-Al(1)-O(4)	90.1(4)	O(1)-Al(1)-O(4)	93.0(3)
O(5)-Al(1)-O(3)	87.3(3)	O(2)-Al(1)-O(3)	90.6(4)
O(1)-Al(1)-O(3)	86.0(3)	O(4)-Al(1)-O(3)	178.0(3)
O(5)-Al(1)-O(9)	168.9(3)	O(2)-Al(1)-O(9)	76.5(3)
O(1)-Al(1)-O(9)	93.6(3)	O(4)-Al(1)-O(9)	90.9(3)
O(3)-Al(1)-O(9)	87.4(3)	O(6)#2-Al(2)-O(6)	180.000(2)
O(6)#2-Al(2)-O(1)	89.7(3)	O(6)-Al(2)-O(1)	90.3(3)
O(6)#2-Al(2)-O(1)#2	90.3(3)	O(6)-Al(2)-O(1)#2	89.7(3)
O(1)-Al(2)-O(1)#2	179.999(2)	O(6)#2-Al(2)-O(7)#2	92.8(3)
O(6)-Al(2)-O(7)#2	87.2(3)	O(1)-Al(2)-O(7)#2	90.1(3)
O(1)#2-Al(2)-O(7)#2	89.9(3)	O(6)#2-Al(2)-O(7)	87.2(3)
O(6)-Al(2)-O(7)	92.8(3)	O(1)-Al(2)-O(7)	89.9(3)
O(1)#2-Al(2)-O(7)	90.1(3)	O(7)#2-Al(2)-O(7)	179.999(2)
O(8)-Al(3)-O(10)	96.6(3)	O(8)-Al(3)-O(10)#4	96.6(3)
O(10)-Al(3)-O(10)#4	115.8(5)	O(8)-Al(3)-O(11)	94.4(5)
O(10)-Al(3)-O(11)	120.6(3)	O(10)#4-Al(3)-O(11)	120.6(3)

O(8)-Al(3)-O(12)	169.3(5)	O(10)-Al(3)-O(12)	89.1(3)
O(10)#4-Al(3)-O(12)	89.1(3)	O(11)-Al(3)-O(12)	74.8(4)
O(6)-P(1)-O(5)#6	111.5(4)	O(6)-P(1)-O(4)	112.1(4)
O(5)#6-P(1)-O(4)	110.8(4)	O(6)-P(1)-O(10)	109.2(4)
O(5)#6-P(1)-O(10)	103.8(4)	O(4)-P(1)-O(10)	109.2(4)
O(8)-P(2)-O(7)	109.78(17)	O(8)-P(2)-O(7)#4	109.8(3)
O(7)-P(2)-O(7)#4	110.7(5)	O(8)-P(2)-O(9)	111.1(5)
O(7)-P(2)-O(9)	107.7(3)	O(7)#4-P(2)-O(9)	107.7(3)
O(3)#4-P(3)-O(3)	110.0(5)	O(3)#4-P(3)-O(11)#3	112.5(3)
O(3)-P(3)-O(11)#3	112.5(3)	O(3)#4-P(3)-O(12)#3	112.2(4)
O(3)-P(3)-O(12)#3	112.2(3)	O(11)#3-P(3)-O(12)#3	97.1(5)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z;	#2 -x+1,-y+2,-z+2;	#3 x,y,z+1;
#4 x,-y+3/2,z;	#5 x,y,z-1	#6 -x,-y+2,-z+2
#7 -x,-y+2,-z+1	#8 x,-y+3/2,z+1	#9 -x+1,y-1/2,-z+2
#10 x+1,y,z	#11 x+1,-y+3/2,z	#12 x,-y+5/2,z
#13 -x,y+1/2,-z+1		

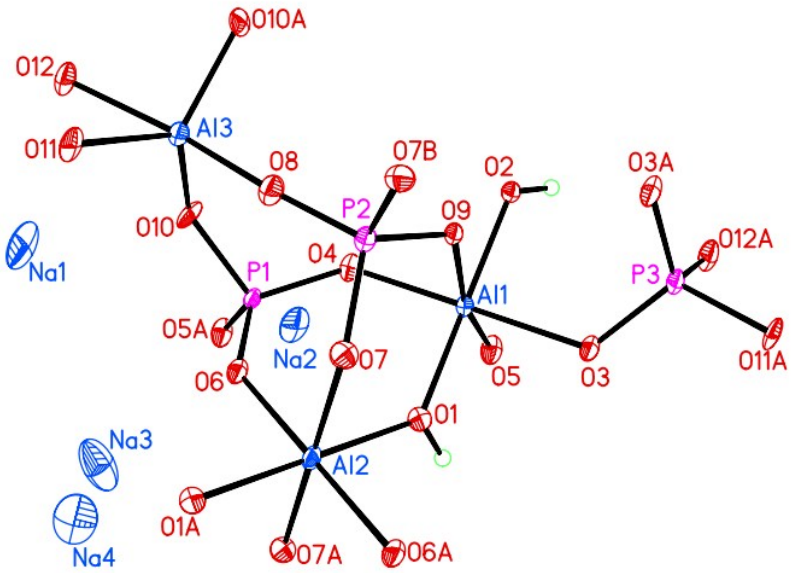

Fig. S1 Thermal ellipsoid of JU103 given at 50% probability, showing the atomic labeling scheme

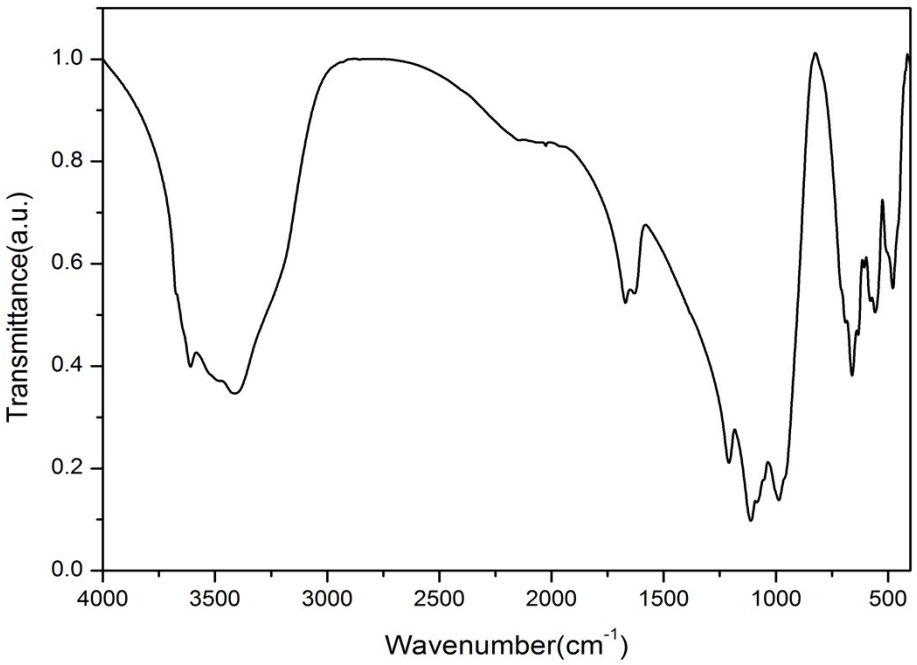

Fig. S2 IR curve of JU103

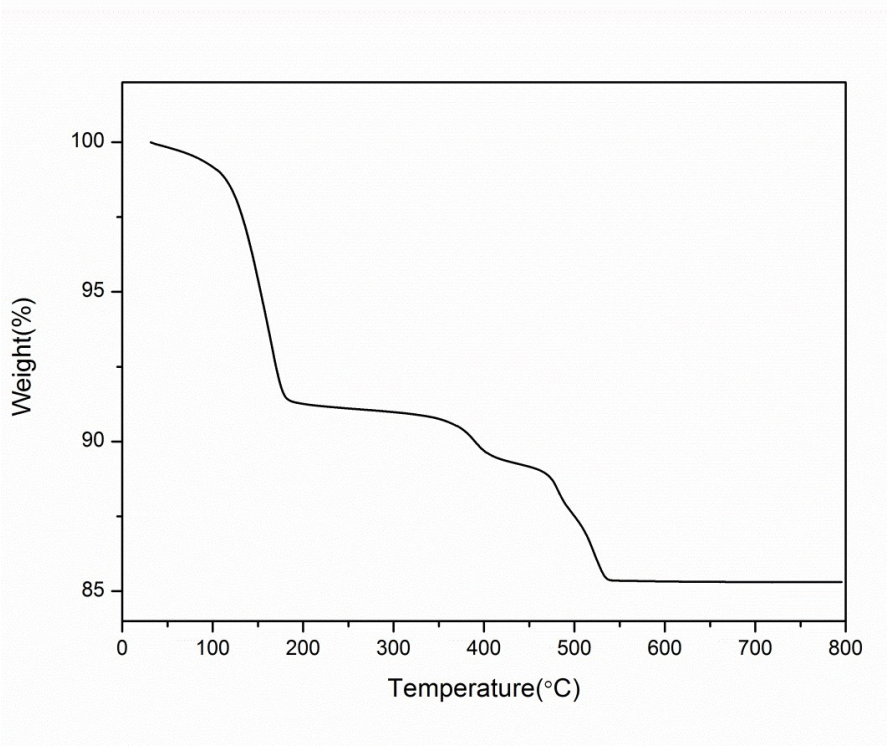

Fig. S3 TG curve of JU103

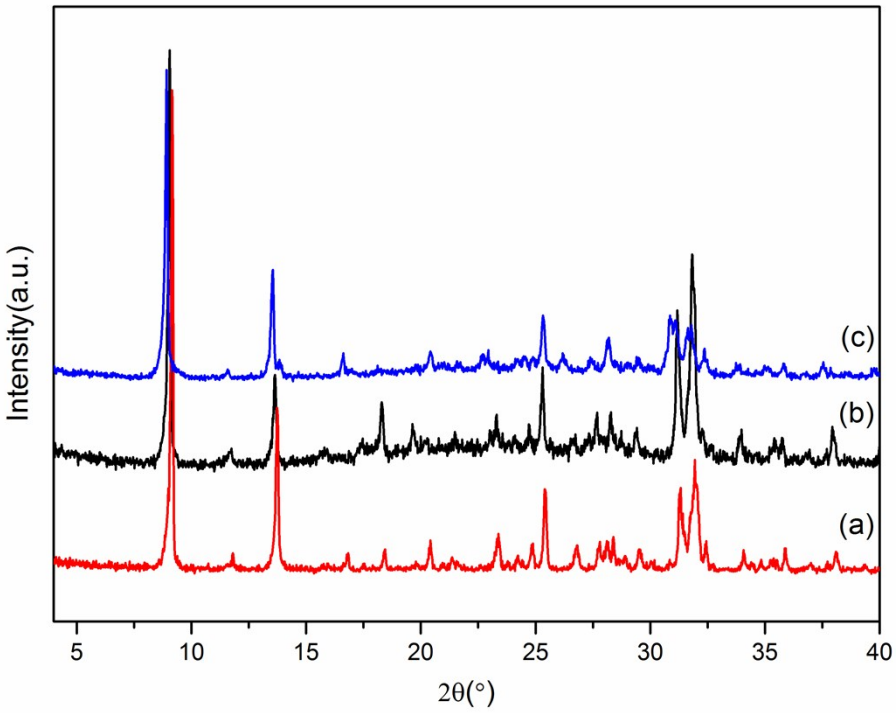

Fig. S4 Powder X-ray diffraction patterns of (a) JU103, (b) Ag-JU103, (c) NH4-JU103-b

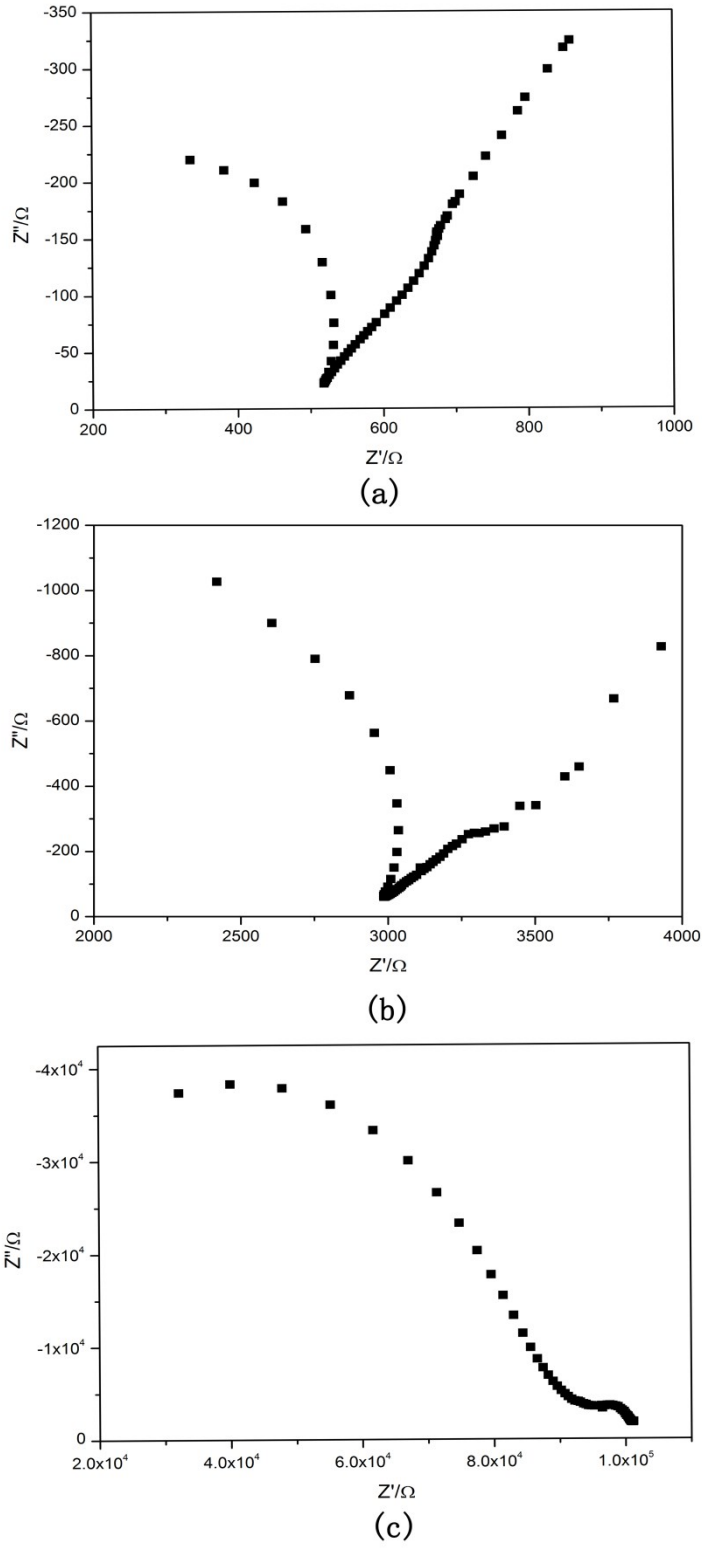

Fig. S5 a.c. impedance plots of (a) NH_4-JU103-a, (b) NH_4-JU103-b and (c) Ag-JU103 with ion-exchange degree of 5%, 40% and 65%, respectively, at 293K and 98% RH

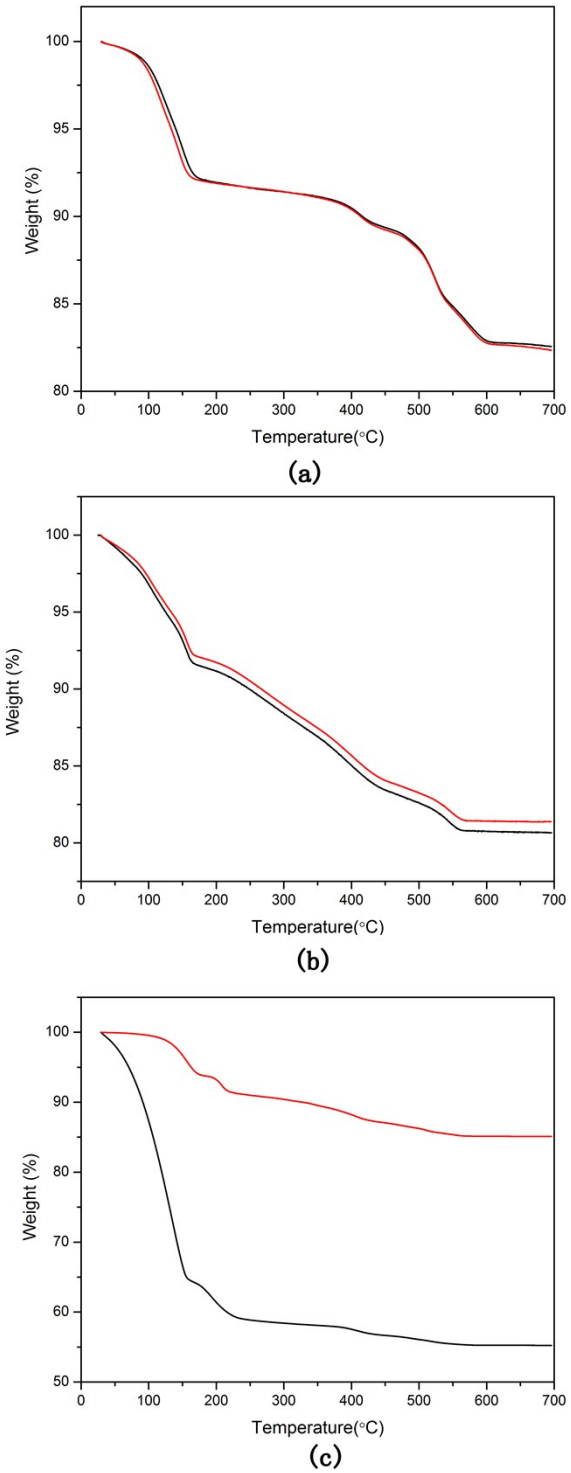

Fig. S6 TG curves of (a)Ag-JU103, (b)NH_4-JU103-b and (c)Na-JU103 at dry atmosphere (red) and RH98% gas (black)