Supporting information

Single step conversion of cellulose to levulinic acid using temperature-responsive dodeca-aluminotungstic acid catalysts

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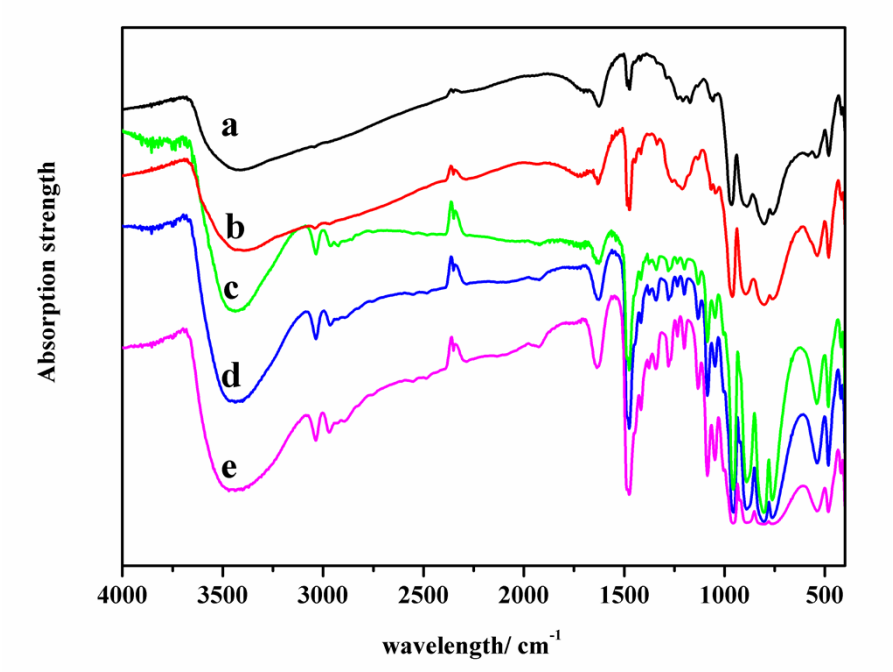


Fig. S1 The IR spectra of (a) $ChH_4AlW_{12}O_{40}$, (b) $Ch_2H_3AlW_{12}O_{40}$, (c) $Ch_3H_2AlW_{12}O_{40}$, (d) $Ch_4HAlW_{12}O_{40}$, and (e) $Ch_5AlW_{12}O_{40}$.

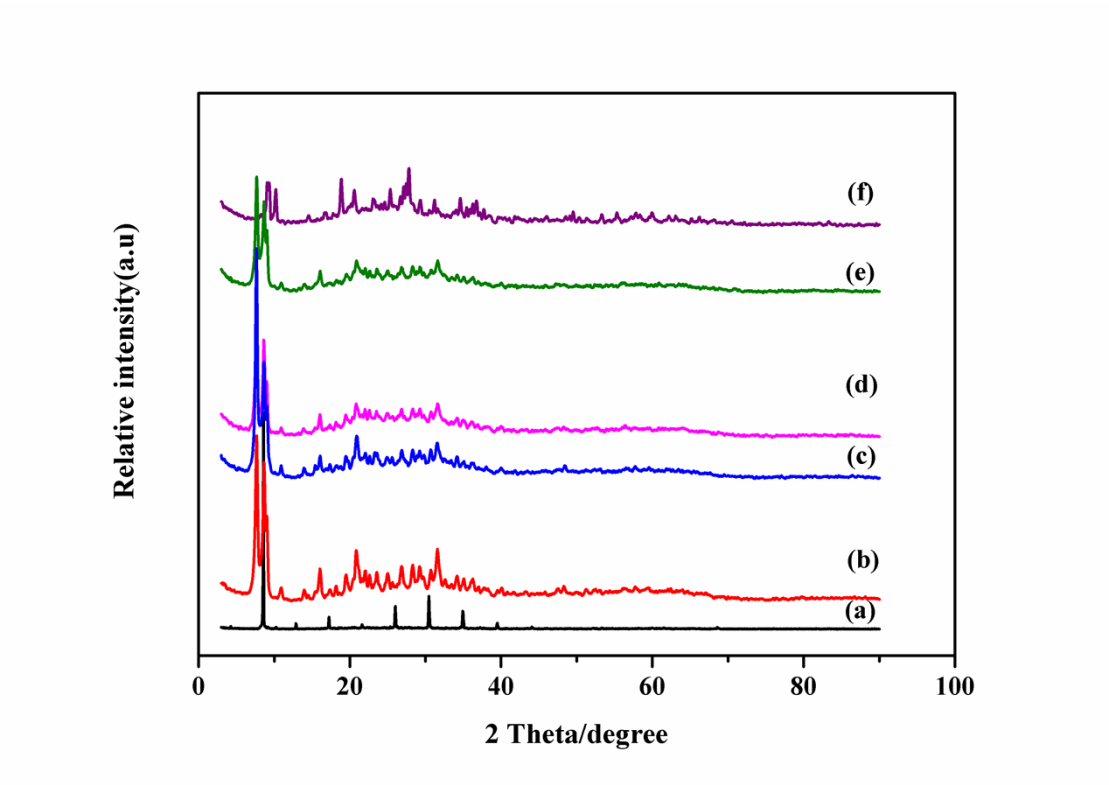


Fig. S2 XRD patterns of $Ch_nH_{5-n}AlW_{12}O_{40}$. (a) $H_5AlW_{12}O_{40}$, (b) $ChH_4AlW_{12}O_{40}$, (c) $Ch_2H_3AlW_{12}O_{40}$, (d) $Ch_3H_2AlW_{12}O_{40}$, (e) $Ch_4HAlW_{12}O_{40}$, and (f) $Ch_5AlW_{12}O_{40}$.

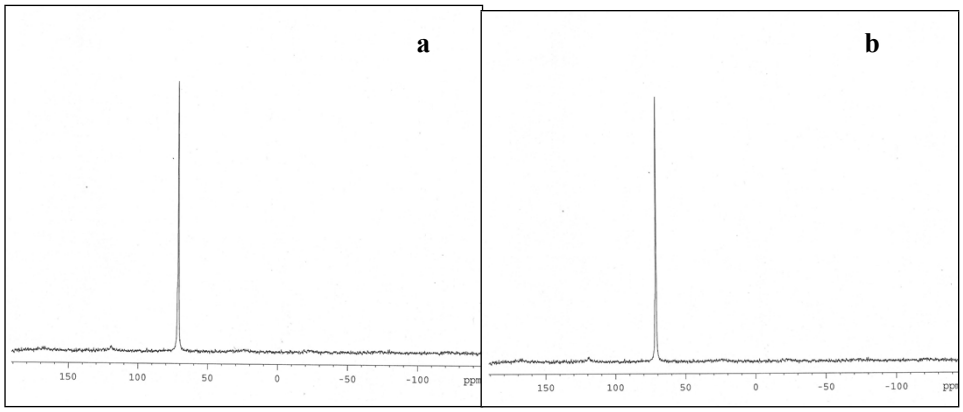


Fig. S3 ^{27}Al MAS NMR spectra of (a) $ChH_4AlW_{12}O_{40}$, and (b) $Ch_5AlW_{12}O_{40}$.

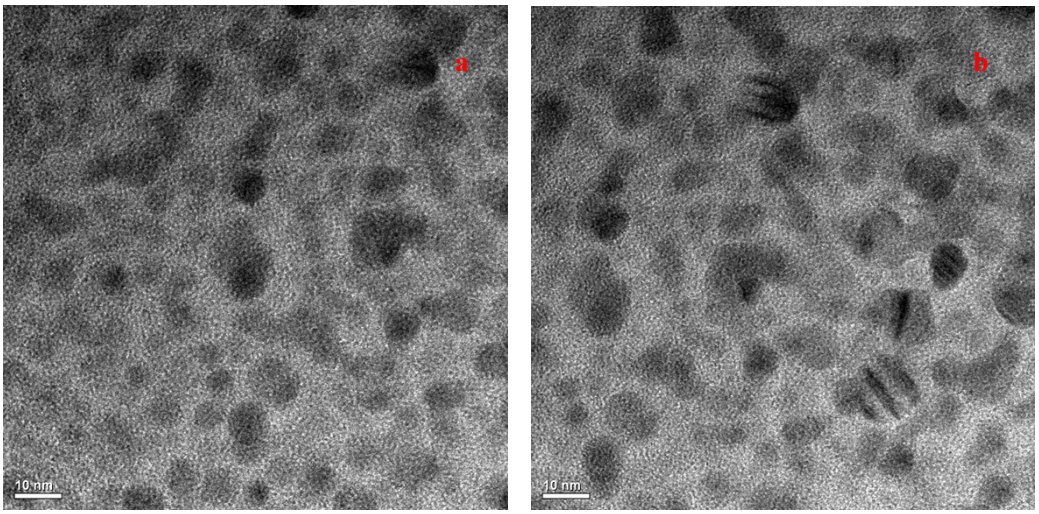


Fig. S4 The TEM images of $ChH_4AlW_{12}O_{40}$ (a) fresh, and (b) after reaction.

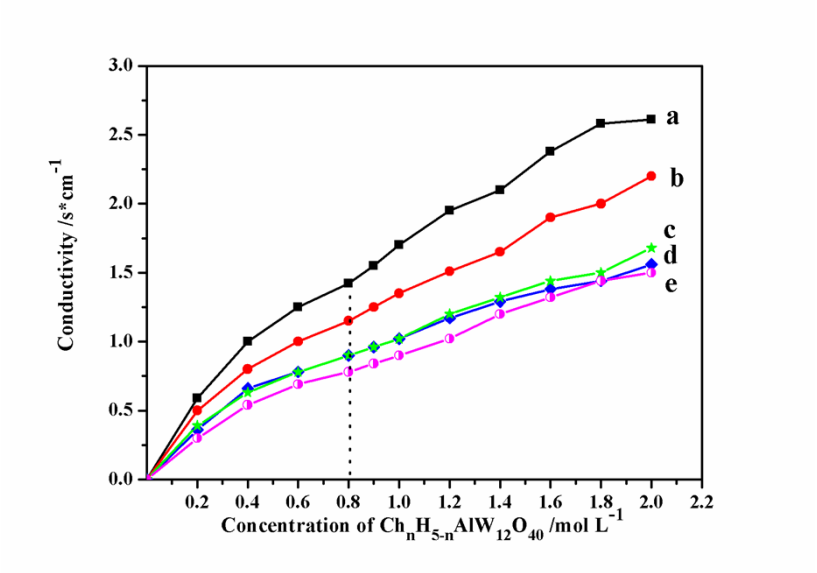


Fig. S5 The conductivity of $Ch_nH_{5-n}AlW_{12}O_{40}$ at the room temperature. (a) $ChH_4AlW_{12}O_{40}$, (b) $Ch_2H_3AlW_{12}O_{40}$, (c) $Ch_3H_2AlW_{12}O_{40}$, (d)$Ch_4HAlW_{12}O_{40}$, and (e) $Ch_5AlW_{12}O_{40}$.

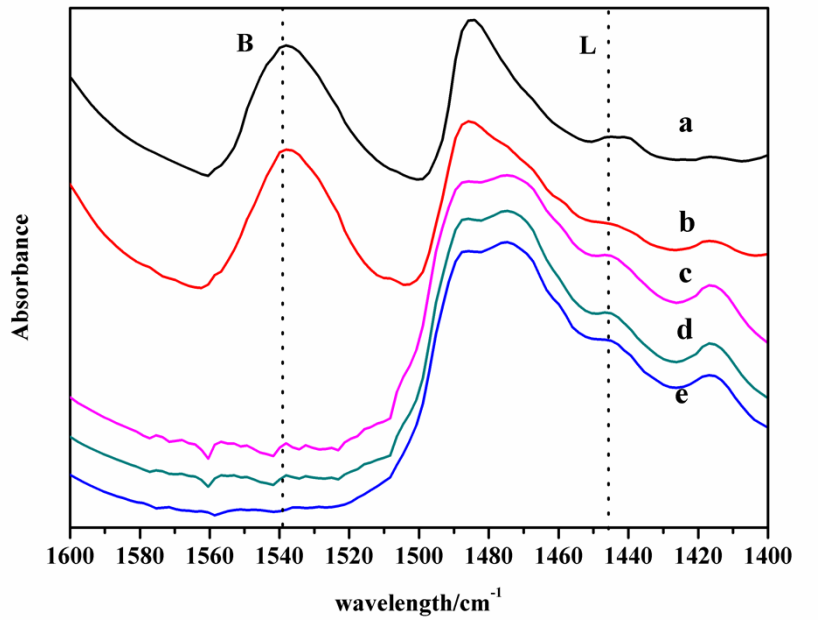


Fig. S6 The IR spectra of $Ch_nH_{5-n}AlW_{12}O_{40}$ adsorbed pyridine. (a) $ChH_4AlW_{12}O_{40}$, (b) $Ch_2H_3AlW_{12}O_{40}$, (c) $Ch_3H_2AlW_{12}O_{40}$, (d) $Ch_4HAlW_{12}O_{40}$, and (e) $Ch_5AlW_{12}O_{40}$.

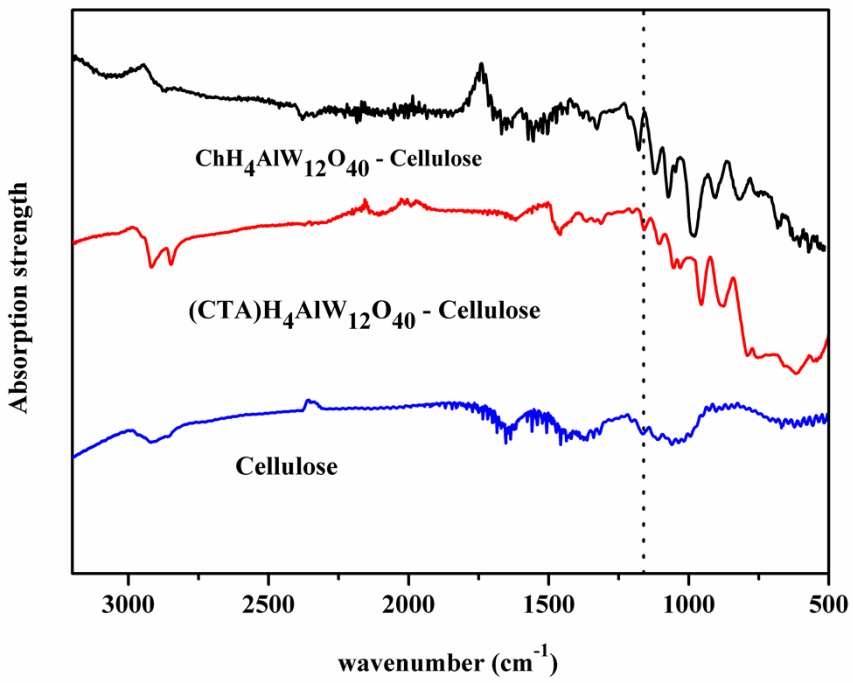


Fig. S7 The IR spectra of catalyst adsorbing cellulose. (a) Cellulose - $ChH_4AlW_{12}O_{40}$, and (b) cellulose – (CTA) $H_4AlW_{12}O_{40}$.

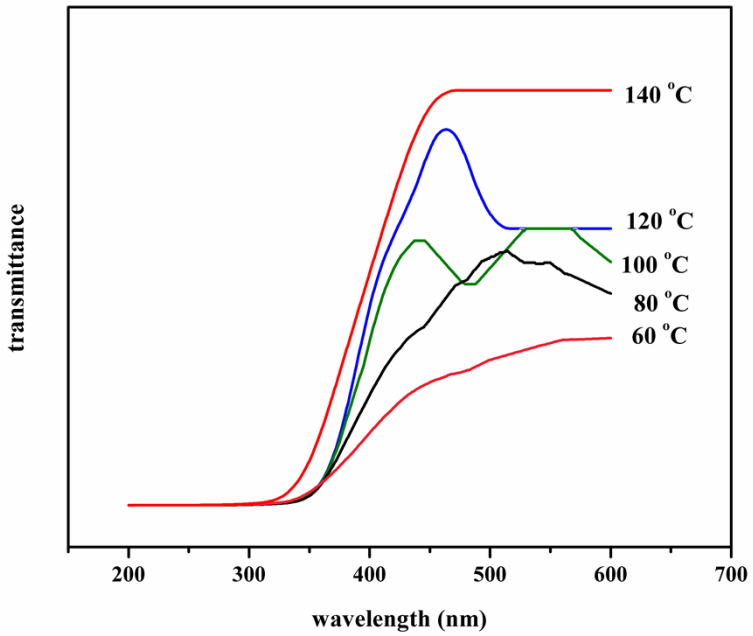


Fig. S8 The visible spectra of $ChH_4AlW_{12}O_{40}$ in different temperature

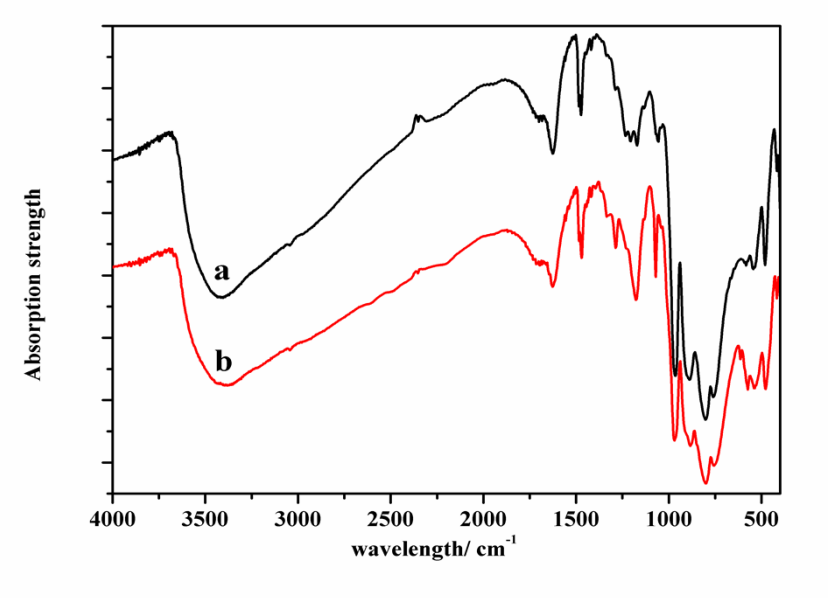


Fig. S9 The IR spectra of the $ChH_4AlW_{12}O_{40}$ (a) before (b) after the reaction

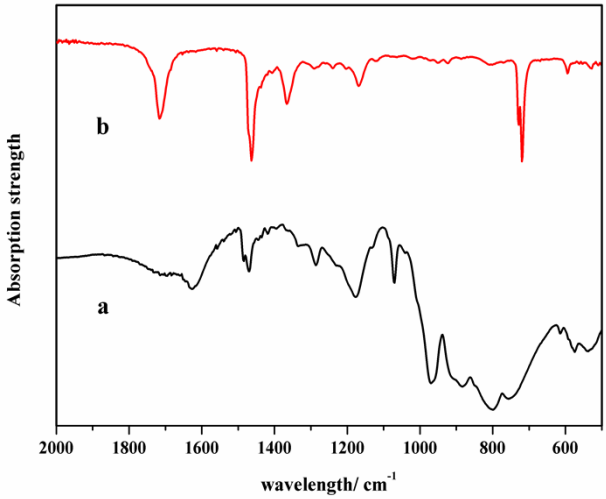
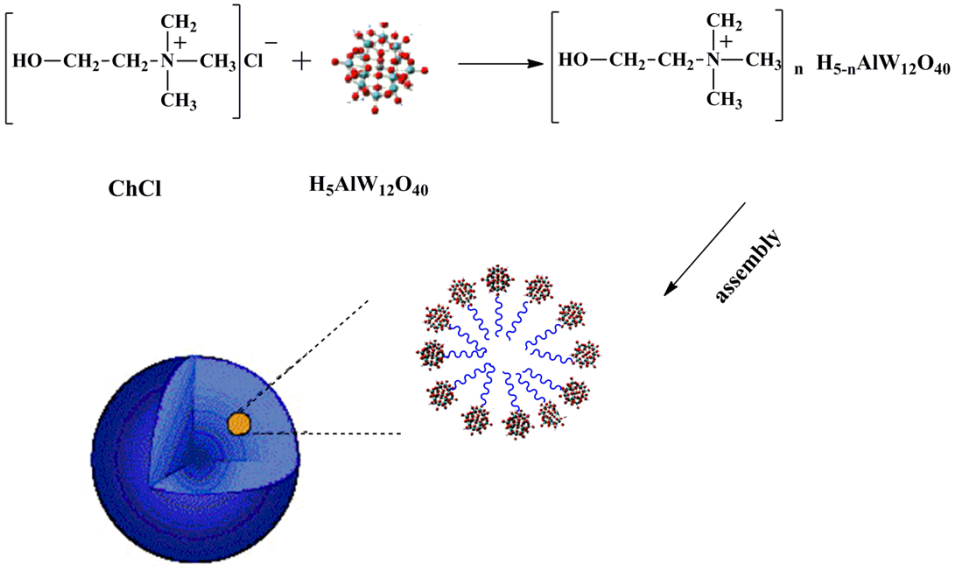


Fig. S10 The IR spectra of (a) $ChH_4AlW_{12}O_{40}$ and (b) after reaction in double solvent system



Scheme S1 The formation of $Ch_{4x}H_{5-x}AlW_{12}O_{40}$

Table S1 The elemental analysis of $Ch_nH_{5-n}AlW_{12}O_{40}$

Catalysts	Elementary results (calculated values in parenthesis)/%				
	H	**C**	**N**	**Al**	**W**
$[(CH_3)_3NCH_2CH_2OH]H_4AlW_{12}O_{40}$	0.61(0.52)	2.01(2.08)	0.47(0.32)	0.91(1.81)	74.02(76.45)
$[(CH_3)_3NCH_2CH_2OH]_2H_3AlW_{12}O_{40}$	1.01(1.64)	3.89(3.43)	0.9(1.5)	0.87(1.22)	71.52(73.97)
$[(CH_3)_3NCH_2CH_2OH]_3H_2AlW_{12}O_{40}$	1.39(1.52)	5.65(5.56)	1.32(1.76)	0.85(1.13)	69.21(70.60)
$[(CH_3)_3NCH_2CH_2OH]_4HAlW_{12}O_{40}$	1.75(1.80)	7.30(9.44)	1.7(1.83)	0.81 (1.01)	67.04(65.93)
$[(CH_3)_3NCH_2CH_2OH]_5AlW_{12}O_{40}$	2.08(2.53)	8.85 (10.26)	2.06(2.42)	0.80(0.75)	65(64.80)

Table S2 Different performances of solid acid catalysts in the hydrolysis of cellulose

catalyst	Solution	Temperature (°C)	Time (h)	Conversion (%)	Yields (%)		Ref.
					Glucose	LA	
Sulfonated Sugar Derived Carbon	H_2O/[BMIM]Cl	120	4	-	57	-	1
$InCl_3$	IL/ DMSO	160	5	84.6	-	-	2
Fe_3O_4@C-SO_3H	H_2O	140	12	48.6	25.3	-	3
Functional polymeric ionic liquids	[BMIM]Cl/DMSO	160	5	24.6	-	-	4
cellulose-derived carbonaceous catalyst (CCC)	[BMIM]Cl	140	0.5	60.7	-	-	5
Al-$NbOPO_4$	H_2O	180	24	90	-	52.9	6
zirconium dioxide	H_2O	180	3	100	-	53.9	7
CP-SO_3H-1.69	H_2O	170	10	-	-	33.1	8
	H_2O/GLV	170	10	100	ND	65.5	8
$H_3PW_{12}O_{40}$	H_2O	180	2	54.7	50.5	-	9
$H_5BW_{12}O_{40}$	H_2O	60	48	-	77	-	10
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	H_2O	160	6	-	8.2	-	11
(CTA)$H_2PW_{12}O_{40}$	H_2O	170	8	44.1	39.3	-	12
[MIMPS]H_2PW	H_2O /MIBK	140	12	-	-	63.1	13
willow-derived sulfonated carbon	H_2O	160	8	78.0	65.0	-	14
HCl	H_2O	180	20 min	100		44	15

H_2SO_4	H_2O	150	2	100		43	16
$AlCl_3$	[BMIM]Cl/DMSO	150	9	-		43	17
$ChH_4AlW_{12}O_{40}$	H_2O	140	3	94.6	75.9	-	This work
$ChH_4AlW_{12}O_{40}$	H_2O /MIBK	120	10	98.9	-	74.8	This work

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