Supporting information:

Transfer hydrogenation of high concentration levulinic acid to γ-valerolactone catalyzed by glucose phosphate carbamide zirconium

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1. Dynamic light scattering of GluPC and $ZrCl_4$ aqueous solution.

The particle size distributions of GluPC and $ZrCl_4$ solutions were measured by dynamic light scattering, and the results are shown in Figure S1. As shown in Figure S1, the particle size of GluPC is mainly concentrated at 16.6 nm, and the particle size of $ZrCl_4$ solution is mainly distributed in 1.5-4.8 nm, suggesting that $ZrCl_4$ in water is hydrolyzed into a sol.

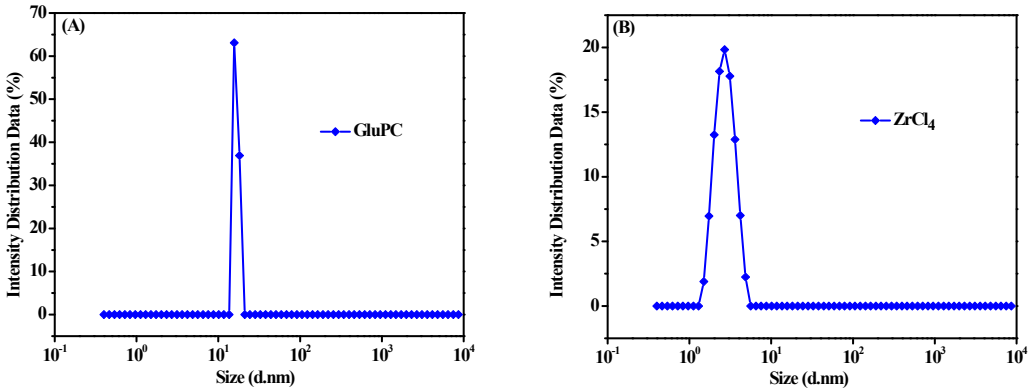

Figure S1 The particle size distributions of GluPC (A) and $ZrCl_4$ (B) aqueous solution (0.1 mg/mL) measured by dynamic light scattering.

2 Dispersion stability of GluPC-Zr in isopropanol medium

Figure S2 illuminates that the catalyst GluPC-Zr can be well dispersed in isopropanol (IPA) medium by stirring (Fig. S2A) and it doesn't sink nearly after standing for 12 h (Fig. S2B), suggesting that the catalyst has strong interaction with IPA solvent and can form a very stable brown suspension, therefore, its CHT reaction should have a pseudo homogeneous character, as supported by the following fact: Table S1 gives the comparative data of stirring and non stirring

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reactions. In that, the non stirring reaction can achieve almost the same γ-GVL yield with the stirring one, indicating that this CTH reaction can also proceed well without stirring.

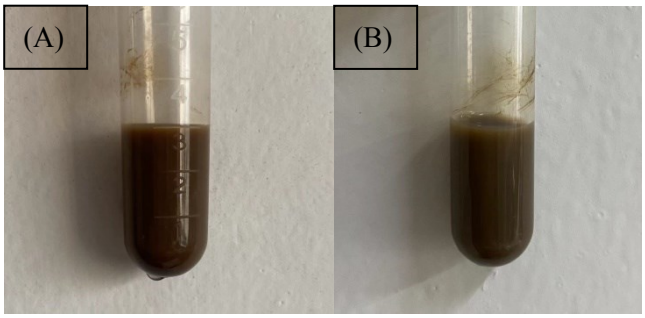

Fig S2. Initial (A) and 12 h (B) dispersion state of GluPC-Zr in IPA under standing condition

Table S1 Comparative data of stirring and non stirring for CTH reaction of LA with IPA over GluPC-Zr[a].

Entry	Operating mode	T (°C)	Time (h)	Conversion (%)	Yield of γ-GVL (%)	Yield of IPL (%)	TOF (mmol/g.h)
1	Non stirrinSg	180	12	100	95	1.99	7.9
2	Magnetic stirring	180	12	100	94.4	2.58	7.86

[a] Reaction conditions: non stirring: GluPC-Zr, 0.05 g; LA, 5 mmol; IPA, 35 mmol; 180 °C; 12 h.

3. UV-vis and PL spectra of GluPC aqueous solution.

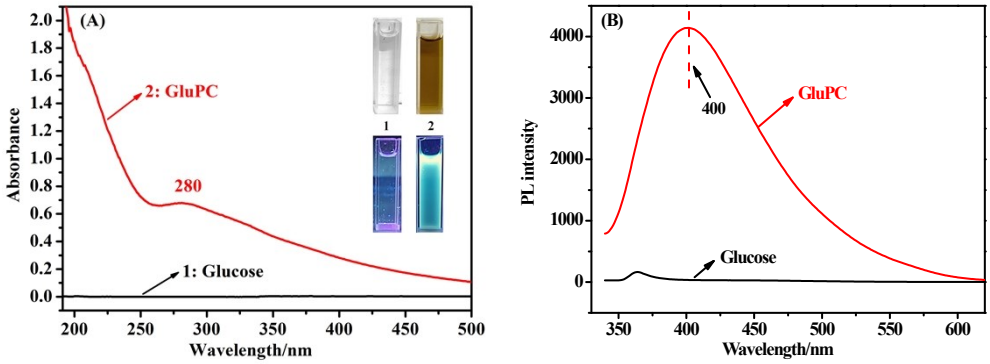

Figure S3 The UV-vis (A) and PL spectra (B) of glucose and GluPC aqueous solutions (0.1 mg/mL).

Figure S3(A) shows that the UV-vis signals of glucose is silent in 200-500 nm, but its ligand GluPC aqueous solution exhibits two typical absorption bands at near 200 and 280 nm, which are respectively assigned to π-π* transition of an aromatic C=C system and n-π* transition of the $–NH_2$ or other related groups in carbon quantum dots (CQDs) [1-3]. Inset in Figure S3(A) illuminates that GluPC solution is yellow color under visible light and can become blue under light illumination of

365 nm. Figure S3(B) reveals that glucose aqueous solution is also silent under 320 nm light excitation but its ligand solution can emit a strong PL signal at a central wavelength of 400 nm. These phenomena are clearly indicative of the CQD characters of GluPC [4-7].

4. XPS

Figure S4(A) gives the survey XPS spectra for GluPC and GluPC-Zr samples. In that, the XPS signals of C1s, N1s, O1s and P2p can be clearly found in the survey XPS spectrum of GluPC, and the survey XPS spectrum of GluPC-Zr also exhibits a Zr3d XPS signal except the above XPS signals. Figure S4B is the high resolution XPS spectrum for the surface C atoms of these two samples. In that, two C1s energy peaks in GluPC are shifted to slightly higher energy levels after introducing the Zr species. Figure S4C-F illuminate that the deconvoluted high resolution XPS spectra for the surface C, O, P and N atoms of GluPC by Gaussian simulation further support the existence of various hydrophilic groups described in FT-IR spectrum of GluPC. Notably, as shown in Table S2, the surface Zr content of GluPC-Zr obtained from XPS analysis was lower than the actual Zr content measured by ICP analysis, and the two contents of P measured by these two methods are almost equal to each other, which indicates that most of Zr^{4+} sol particles could be coated by GluPC ligand.

Table S2 Chemical compositions By ICP analysis and the contents of various surface elements of GluPC and GluPC-Zr by XPS analysis.

Element	**Chemical composition (wt%)[a]**		**Content of various elements on the surface (Atomic%)[b]**	
	GluPC	**GluPC-Zr**	**GluPC**	**GluPC-Zr**
Zr	-	13.6	0.05	6.46
C	-	-	52.6	32.01
O	-	-	27.57	48.93
P	17.6	7.2	4.45	8.18
N	-	-	15.33	4.42

[a] The content of Zr and P was determined by ICP analysis method. [b] The contents on surface were determined by XPS methods.

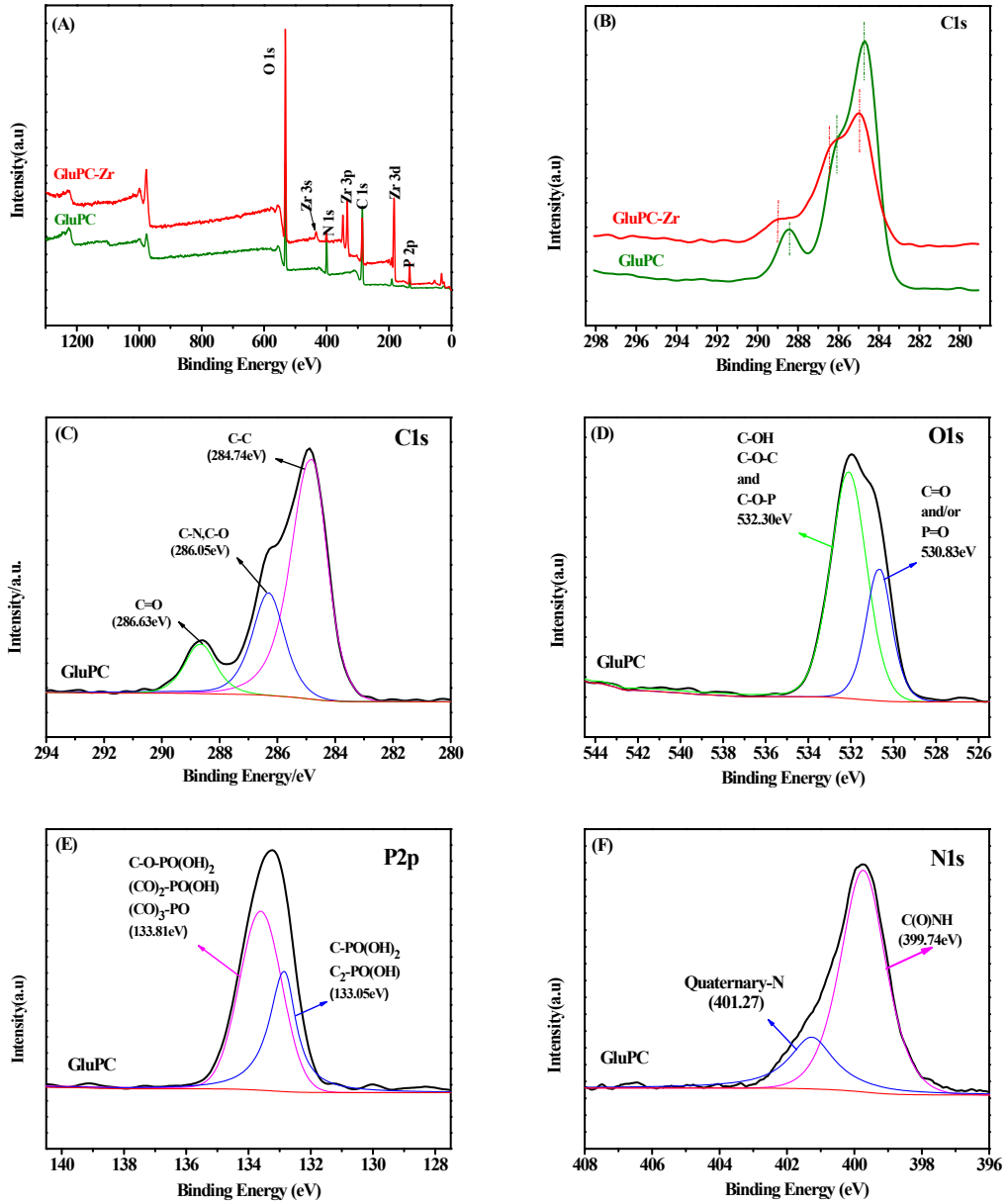

Figure S4 XPS survey scan (A), and high resolution XPS spectra for C1s (B), as well as the deconvoluted high resolution XPS spectra for the surface C, O, P and N atoms of GluPC (C-F).

5. Quantitative analysis of pyridine-adsorbed FT-IR

Table S3 The quantitative analysis the amount of Brønsted acid and Lewis acid sites.

Catalyst	Temperature (°C)	Brønsted acid (mmol/g)	Lewis acid (mmol/g)	B/L
GluPC-Zr	40	0.059	0.309	0.19
	100	0.053	0.198	0.27

6. Porous parameters

Table S4 Porous parameters of the fresh and used GluPC-Zr catalysts.

Sample	S_{BET} (m^2/g)	$S_{t\text{-}plot}$(m^2/g)	V_p (cm^3/g)	D (nm)
GluPC-Zr (fresh)	224	175	0.40	10.9
GluPC-Zr (recovered)	277	248	0.67	12.7

7. Recycling experiments of ML

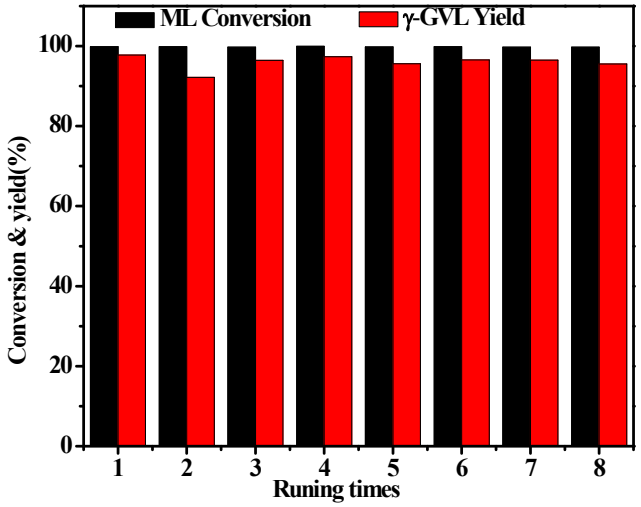

Figure S5 Reusability of GluPC-Zr in CTH reactions of ML with IPA.

Figure S5 demonstrates that GluPC-Zr has an excellent reusability in the CTH reaction of ML with IPA and can still provide ca. 97% γ-GVL yield after the seventh cycle run.

References

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