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二氧化硅包覆的杂多酸在双氧水存在条件下催化氧化甘油

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Selective Oxidation of Glycerol with Hydrogen Peroxide Using Silica-Encapsulated Heteropolyacid Catalyst

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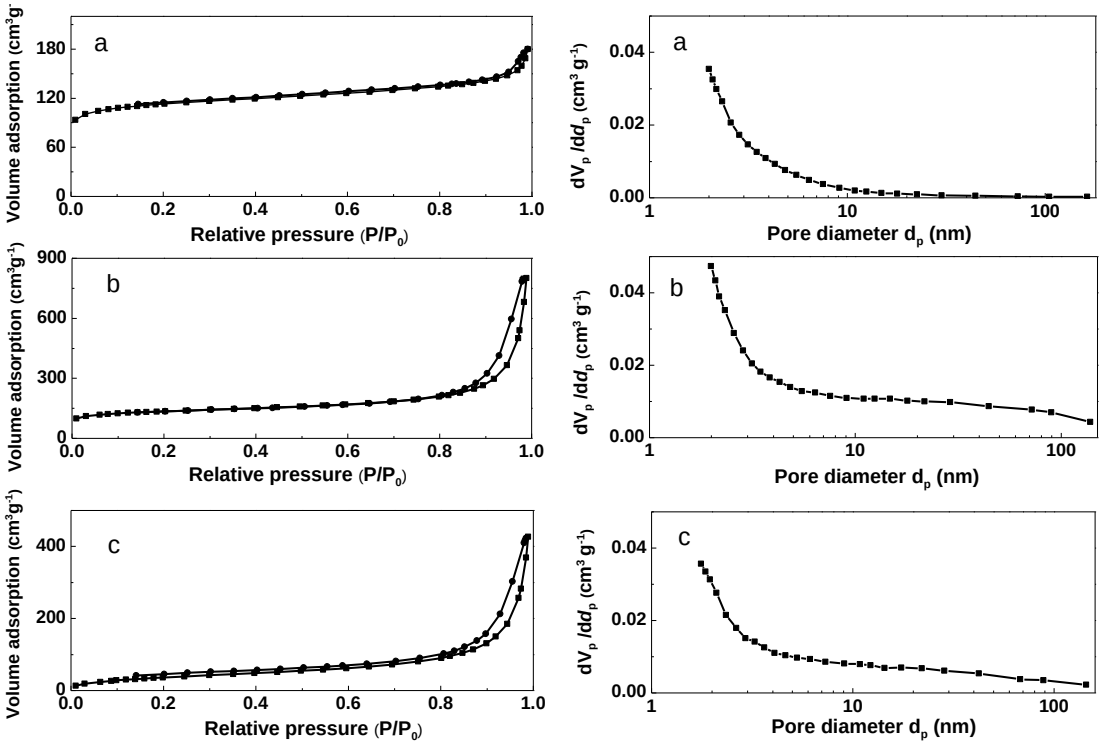

Fig. S1 Nitrogen absorption desorption curves and pore distribution curves of (a) SiO_2; (b) HPA@SiO_2 catalyst; (c) HPA@SiO_2-S-N_2 catalyst.

Table S1 The physical and chemical properties of SiO_2, HPA@SiO_2 and HPA@SiO_2-S-N_2.

Entries	Catalysts	Pore size/nm	Pore volume/($cm^3 \cdot g^{-1}$)
1	SiO_2	7.1	10.2
2	HPA@SiO_2	20.8	11.1
3	HPA@SiO_2-S-N_2	16.3	10.7

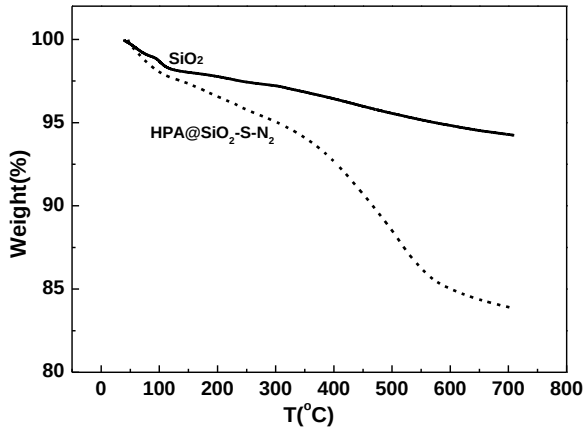

Fig. S2 The thermal gravity analysis of (a) SiO_2 and (b) HPA@SiO_2-S-N_2 catalysts.

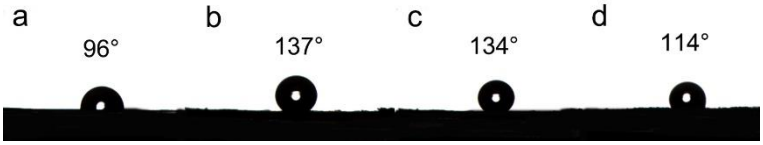

Fig. S3 Water contact angle over (a) HPA@SiO_2; (b) HPA@SiO_2-S; (c) HPA@SiO_2-S-N_2; (d) The HPA@SiO_2-S-N_2 catalyst after reused for 5 times.

Table S2 Oxidation of glycerol reaction with different acid additives in the absence of catalyst [a].

Entry	Additives	Conversion/%	Selectivity/%			
			FA	GCA	AA	others
1	$AlCl_3$	0	0	0	0	-
2	$ZnCl_2$	0	0	0	0	-
3	$InCl_3$	0.8	0	0	53	47
4	HCl	13	39	0	18	43
5	*p*-$CH_3(C_6H_4)SO_3H$	14	59	0	2	39
6	H_2SO_4	9	41	0	8	51
7	$(CF_3SO_2)_2NH$	28	43	0	5	52
8	CF_3SO_3H	30	43	0	9	48

[a] Reaction conditions: 1.25 mmol of glycerol, 6.25 mmol of 30% aqueous H_2O_2, 0.88 mL CH_3CN, acid = 0.5 mmol. *T* = 70 ℃, *t* = 12 h. FA = formic acid; GCA = glycolic acid. The carbon mass balance for the glycerol oxidation was about 75%.

Table S3 The selective oxidation of different substrate molecules with CF_3SO_3H[a].

Entry	Substrates	Conversion/%	Selectivity/%							C%
			FA	GCA	IS	LA	AA	GA	others	
1	Ethylene glycol	25	68	0	–	0	0	0	32	98
2	Glucose	65	45	4	–	12	6	0	33	51
3	Sorbitol	60	52	11	0	0	0	21	16	69
4	Fructose	85	45	22	–	28	0	0	5	77
5	1,2-Propanediol	36	46	0	–	0	18	0	36	85
6	Xylitol	46	43	5	–	0	24	3	25	79

[a] Reaction conditions: 1.25 mmol of glycerol, 6.25 mmol of 30% aqueous H_2O_2, 0.88 mL CH_3CN, CF_3SO_3H: 0.5 mmol. *T* = 70 °C, *t* = 12 h. FA = formic acid; GCA = glycolic acid; IS = isosorbide; LA = lactic acid; AA = acetic acid; GA = glyoxylic acid.