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Dielectrics and Possible Ferroelectricity in Diol/Glycerol Covalently Grafted Kaolinites

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Contents

Details for crystal structure optimization

The geometry optimization of crystal structure was performed for K-PD, K-BD and K-GL in the density functional theory (DFT) framework. The Cambridge sequential total energy package (CASTEP) module[1] was employed in the DFT calculation. The total plane-wave pseudopotential method forms the basis of the CASTEP calculations. The exchange-correlation effects were treated within the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional.[2] The plane-wave basis set energy cut off was set at 340 eV for K-PD, K-BD and K-GL. The convergence parameters were set as follows: self-consistent field (SCF) tolerance, 1×10^{-6} eV/atom; total energy tolerance 1×10^{-5} eV/atom; maximum force tolerance, 0.03 eV/Å; maximum stress component, 0.05 GPa; and displacement of convergence tolerance, 0.001 Å. All above limits can accurately constrain the simulative process to end at the stable constructions of K-PD, K-BD and K-GL. The other calculation parameters were set at the default values in the CASTEP code. In the geometry optimization process, the unit cell parameters (*a, b, α, β* and *γ*) and the coordinates of all atoms were optimized, while the c-axis length was fixed to the value which was taken from the PXRD measurement. The initial monolayer structure of Kaolinite was taken from the single crystal structure of the raw Kaolinite.[3] Since K-PD, K-BD and K-GL can be expressed in the formula of $(K)(PD)_{0.87}$, $(K)(BD)_{0.16}$ and $(K)(GL)_{0.21}$(Table S2), the covalently grafting molecule occupancy was set to be 0.87, 0.16 and 0.21 in the geometry optimization process of K-PD, K-BD and K-GL.

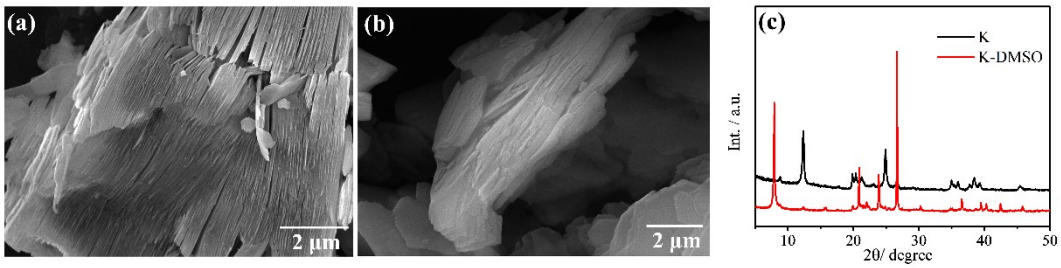

Fig. S1. SEM images of (a) K and (b) K-DMSO, respectively. (c) PXRD patterns of raw Kaolinite and K-DMSO, respectively, in the 2θ range of 5-50°.

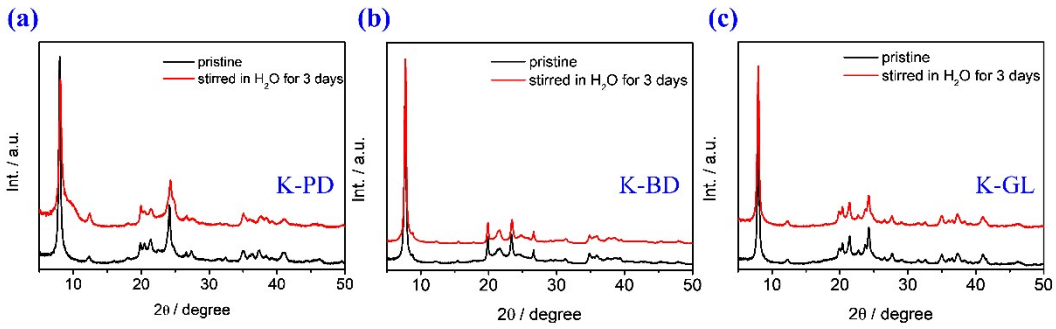

Fig. S2. PXRD patterns of (a) K-PD, (b) K-BD and (c) K-GL in 2θ ranges of 5-50°, after vigorous stirred in H_2O, respectively.

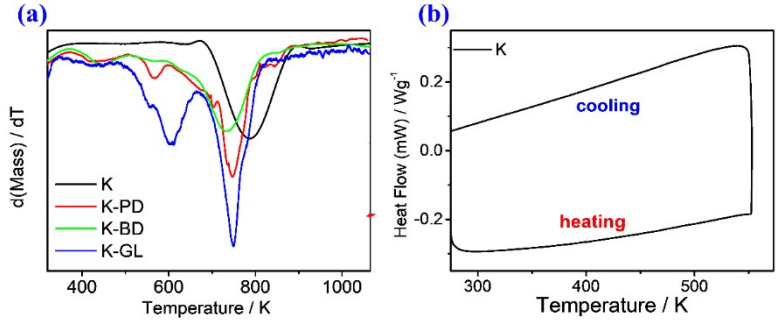

Fig. S3. (a) The first derivative TG curves of K, K-PD, K-BD and K-GL between 298 and 1073 K, respectively. (b) DSC curves of K between 273 and 553 K.

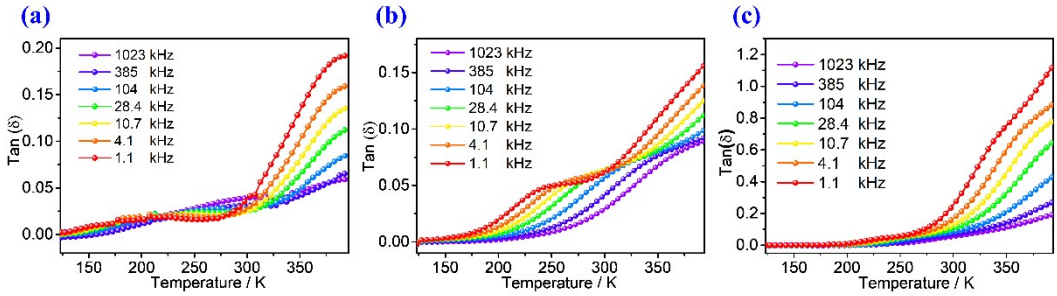

Fig. S4. Plots of Tan(δ)-T at the selected frequency for (a) K-PD, (b) K-BD and (c) K-GL.

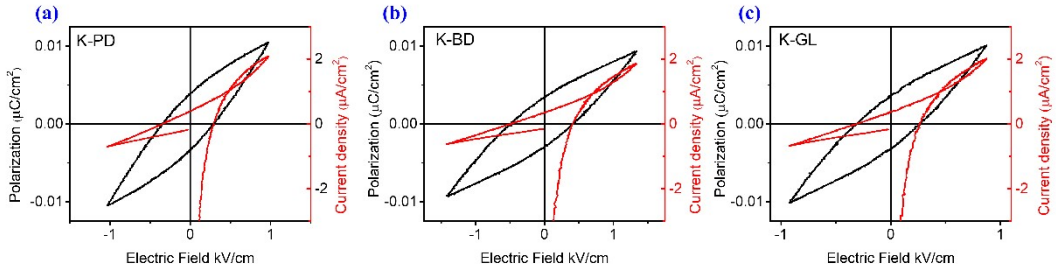

Fig. S5. Plots of polarization (left) and current density (right) versus electric field of (a) K-PD, (b) K-BD and (c) K-GL after evaporated Au electrode.

Table S1: basal plane distance (d_{001}) of K-PD, K-BD, K-GL vs. reported literature

Guest molecular	Intercalated compound	d_{001}(Å)	d_{001}(Å) (Ref)
1,3-Propanediol	K-PD	11.08	11.13[4]
1,4-Butanediol	K-BD	11.54	11.61[5]
Glycerol	K-GL	11.05	11.10[6]

Table S2: Mass percentage and theoretical formula of K-PD, K-BD and K-GL

	C (mass%) [a]	H (mass%) [a]	N (mass%) [a]	Theoretical formula [b]
K-PD	15.45	4.56	/	(K) $(PD)_{0.87}$
K-BD	2.78	2.2	/	(K) $(BD)_{0.16}$
K-GL	3.59	2.8	/	(K) $(GL)_{0.21}$

[a]Mass percentage tested by Element Analyses, [b] Kaolinite represent $Al_2Si_2O_5(OH)_4$ abbreviated as K, 1,3-Propanediol, 1,4-Butanediol and Glycerol abbreviated as PD, BD and GL.

Table S3: Characteristic IR vibration bands and assignments (cm^{-1}) in K, K-PD, K-BD and K-GL

K	K-PD	K-BD	K-GL	Assignation
3696, 3650, 3621	3697, 3658, 3622	3698, 3656, 3622	3696, 3659, 3621	$\nu(OH)_{\text{inner \& inner surface}}$
1116, 1066, 1033	1117, 1065, 1030	1114, 1065, 1029	1116, 1065, 1031	ν_{as}(Si-O)
696, 468, 428	693, 472, 431	695, 471, 432	698, 472, 430	δ(Si-O)
914	909	911	912	β(Al-OH)
/	3449	3450	3448	ν_{as}(O-H) of H_2O
/	1632	1632	1635	β(O-H) of H_2O
/	2974	2973	2975	$\nu_{as}(CH_2)$
/	2896	2897	2899	$\nu_s(CH_2)$

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Graphical Abstracts