Supporting Information

Synthesis of a Porous C_3N-Derived-Framework with High Yield by Gallic Acid Cross-Linking using Salt Melts

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Experimental Section

Reagents and materials

Gallic acid (97.5 %-102.5 %), 2,3-diaminophenazine (90 %), and 17310 Paraffin wax were obtained from Sigma-Aldrich. Anhydrous Zinc chloride ($ZnCl_2$, > 97 %) and Aspirin (99 %) were purchased from Acros Organics. 1 M hydrochloric acid (HCl) and acetic acid (98 %) were obtained from Merck KGaA. Ammonium formate (99 %) and Naphtalene (99 %) were purchased from Aldrich. Coenzym Q10 (> 98 %) was obtained from Carl Roth GmbH. All the chemicals were used without any further purification.

Materials Synthesis

5 mmol gallic acid, 5 mmol 2,3-diaminophenazine, and $ZnCl_2$ (in a weight ratio of precursor: salt of 1:10) were mixed in a 100 mL flask in the inert N_2 atmosphere. Subsequently, the mixture was continuously heated to different temperatures (300, 350, 400, 450, 500, and 550 ^oC) for 3 h (the 850 ^oC sample was prepared in an oven in the inert N_2 atmosphere). After cooling down to room temperature, the resulting black carbon/salt product was stirred in deionized water for 15 h and 1 M HCl for 15 h. Then the product was filtered, washed with water and ethanol, and dried in vacuum at 80 ^oC for 24 h.

All samples are referred to as GD-X, X is the preparation temperature.

The D-500 was made by the same method as GD-500 without the precursor gallic acid.

Materials characterization

Fourier transformed infrared (FTIR) spectra were recorded by a Varian 600 FTIR spectrometer. Thermogravimetric analysis (TGA) was obtained using a NETZSCHTG 209 F1 device, in an air flow with a heating rate of 5 $^oC\ min^{-1}$. Scanning electron microscopy (SEM) was performed using a LEO 1550-Gemini microscope. Prior investigation, a thin (~15 nm) layer of platinum was applied on top of the sample to increase conductivity. Energy-dispersive X-ray (EDX) investigations were conducted by a Link ISIS-300 system (Oxford Microanalysis Group). X-ray diffraction patterns (XRD) were investigated on a Bruker D8

Advance instrument with Cu-Kα radiation. High-resolution transmission electron microscopy (HRTEM) was observed on a double-Cs-corrected JEOL ARM 200F instrument operated at 200 kV. Elemental analysis was measured on a Vario Micro device. X-ray photoelectron spectroscopy (XPS) was recorded with a Thermo Scientific K-Alpha$^+$ X-ray Photoelectron Spectrometer.

Pore structure properties of the materials were measured via nitrogen adsorption and desorption at 77 K using a volumetric technique on a Quantachrome Quadrasorb SI porosimeter. Prior to analysis, the samples were degassed under vacuum at 150 ^{o}C for 20 h. Brunauer-Emmett-Teller (BET) surface area was calculated in the relative pressure $P/P_0 < 0.2$. Total pore volume (V_t) was determined from the amount of nitrogen adsorbed at $P/P_0 = 0.995$. The pore size distributions of the samples were obtained by quenched solid Density Functional Theory (QSDFT) model with slit/cylindrical pore shape using nitrogen adsorption branch kernel. Ar physisorption was measured at 87 K. The pore size distribution was calculated using QSDFT method (adsorption branch kernel) for Ar adsorbed on carbon with cylindrical/sphere pore shape at 87 K.

DSC test

Before the fabrication process for the composites, GD-500 was degassed under vacuum at 250 ^{o}C for 20 h.

Acetic acid/carbon composites: 0.03 g acetic acid was dropped into 0.05 g GD-500 powder, then the residual gas in the pore of the carbon was removed by pulling a vacuum for 1 h.

Naphtalene, $HCOONH_4$, Aspirin/carbon composites: 0.03 g Naphtalene, $HCOONH_4$, and aspirin were first dissolved in ethanol (0.15 ml), respectively. Then, 0.05 g GD-500 was added into the solution. After the ultrasonic for 3 h, the mixed ink was dried at 80 ^{o}C for 24 h in an oven to remove the ethanol.

Q_{10}, Wax/carbon composites: 0.03 g Q10 or wax were mixed with 0.05 g GD-500. Then, the Q_{10}, Wax/carbon mixture was heated to 53 ^{o}C and 70 ^{o}C under vacuum for 2 h.

The calorimetric experiments were conducted using a NETZSCH TG 209 F1 instrument.

Aspirin release study

The aqueous release of pure aspirin and aspirin loaded GD-500 sample was determined in purified water at a temperature of 25 ^{o}C. Briefly, 30 mg aspirin or 80 mg of aspirin loaded GD-500 (equivalent to 30 mg aspirin) were put into dialysis bags. After adding 1 mL of water to the bags, they were clamped with a clip and put into 40 mL water baths. 0.5 mL samples were collected from the bath solution at defined time intervals (5, 10, 15, 20, 30, 45 and 60 min). The samples were analysed in a Cary 50 UV-visible spectrophotometer at an absorption wavelength of 276 nm.

Supplementary Figures

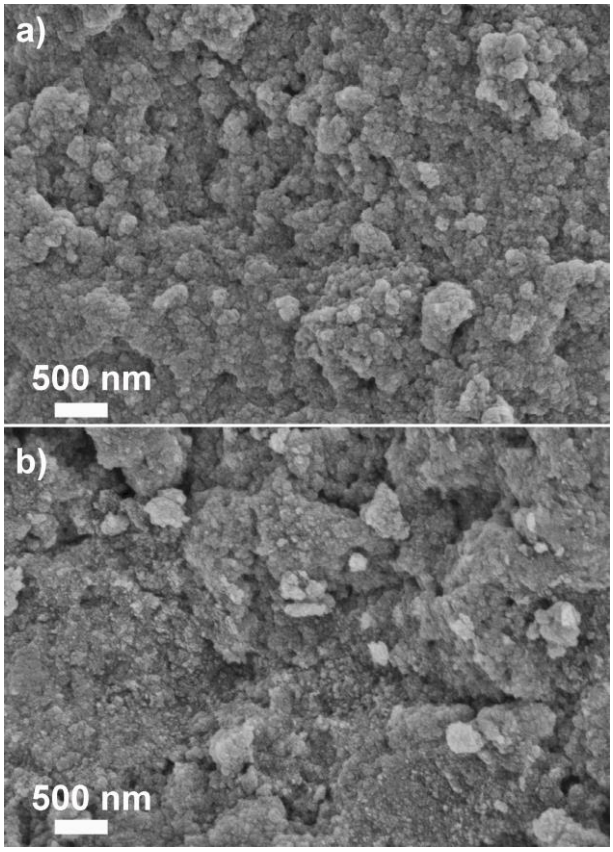

Figure S1. SEM images of a) GD-300, b) GD-500.

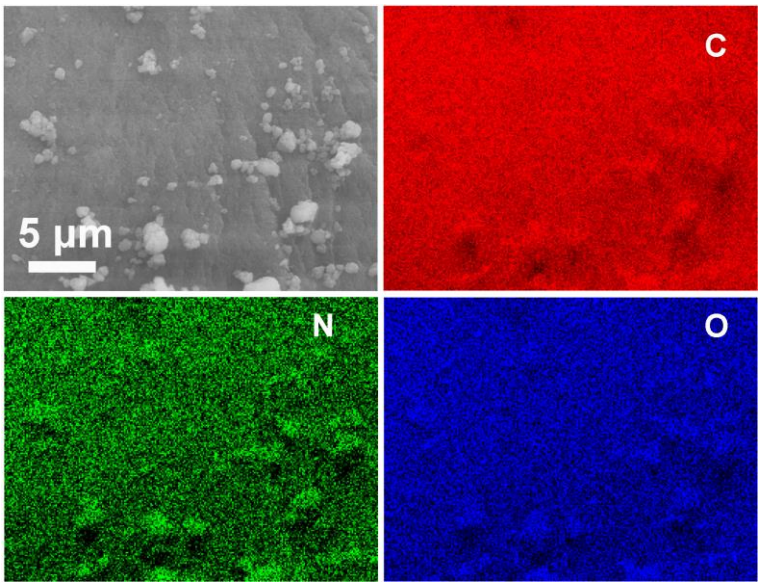

Figure S2. EDX mappings of carbon, nitrogen, and oxygen for GD-500.

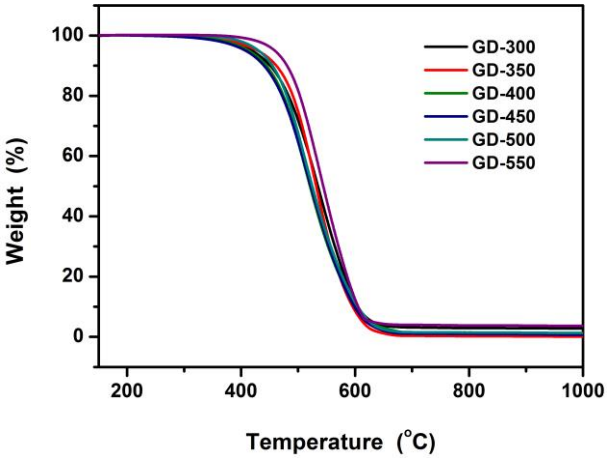

Figure S3. Thermal analysis of GD-300, 350, 400, 450, 500, and 550 measured under air with a heating rate of 5 K min^{-1}.

Table S1. Textural properties of the samples.

Sample	S_{BET} (m^2 g^{-1})	S_{mic} (m^2 g^{-1})	V_t (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	$D_{average}$ (nm)
GD-300	0.7	0	0.004	0	24.37
GD-350	78	35	0.06	0.02	2.90
GD-400	299	154	0.18	0.08	2.44
GD-450	679	461	0.37	0.19	2.17
GD-500	833	562	0.49	0.23	2.36
GD-550	946	522	0.71	0.23	3.00
GD-850	921	266	1.003	0.12	4.35

S_{BET} calculated from nitrogen adsorption isotherms (77 K) by the Brunauer-Emmett Teller method. V_t: total pore volume at $P/P_0 = 0.995$. V_{mic}: Cumulative DFT pore volume (< 2 nm).

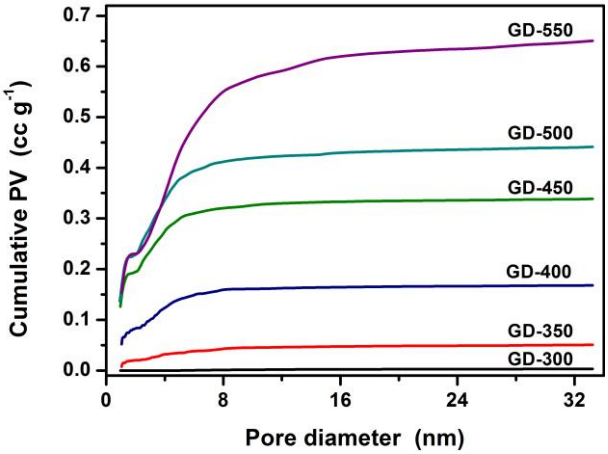

Figure S4. Cumulative QSDFT pore size distribution curves for the GD-300, 350, 400, 450, 500, and 550.

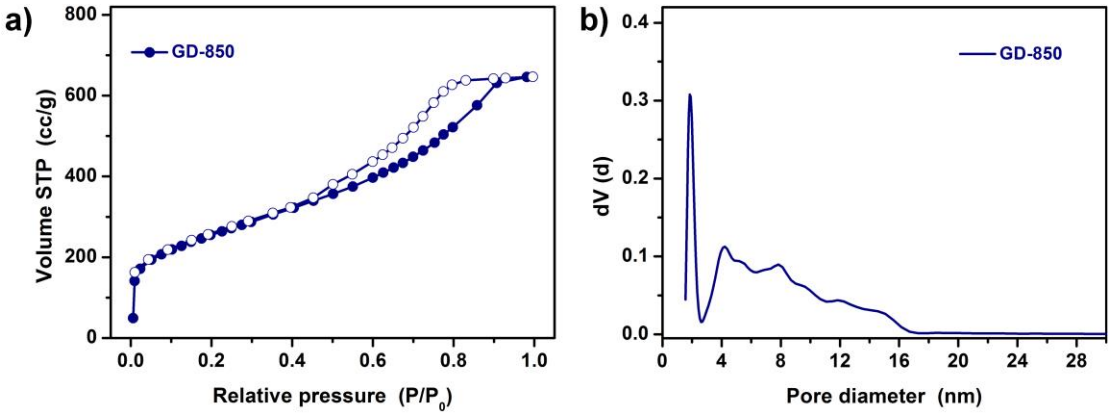

Figure S5. a) N_2 adsorption and desorption isotherms at 77 K for GD-850. b) Pore size distribution curve calculated by QSDFT for GD-850.

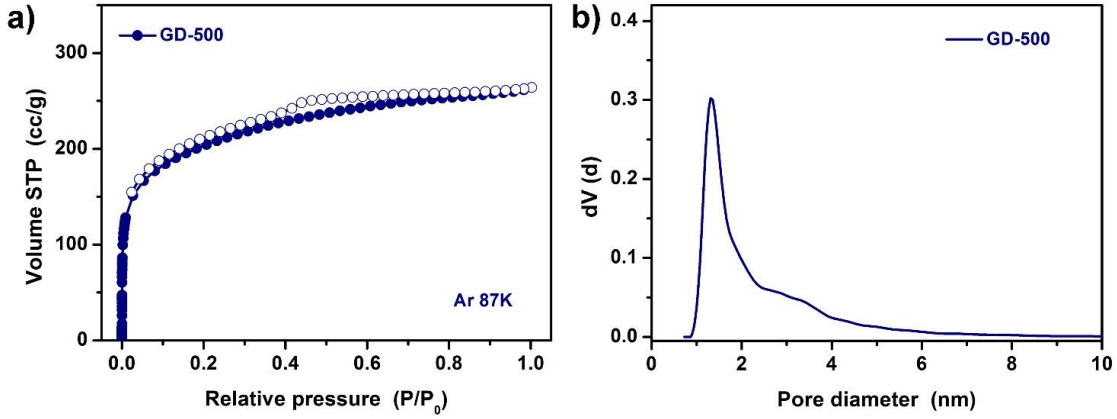

Figure S6. Ar adsorption and desorption isotherms at 87 K for GD-500. b) Pore size distribution curve calculated by QSDFT for GD-500.

Table S2. Elemental analysis of the samples.

Sample	N [wt %]	C [wt %]	H [wt %]	C/N	Other (O) [wt %]
GD-300	12.09	75.05	3.17	6.21	9.69
GD-350	12.71	74.51	3.11	5.86	9.67
GD-400	12.53	72.09	3.06	5.75	12.32
GD-450	12.30	73.17	2.96	5.95	11.57
GD-500	11.41	76.62	3.18	6.71	8.79
GD-550	10.67	76.09	2.69	7.14	10.55
D-500	19.66	73.3	3.12	3.73	3.92

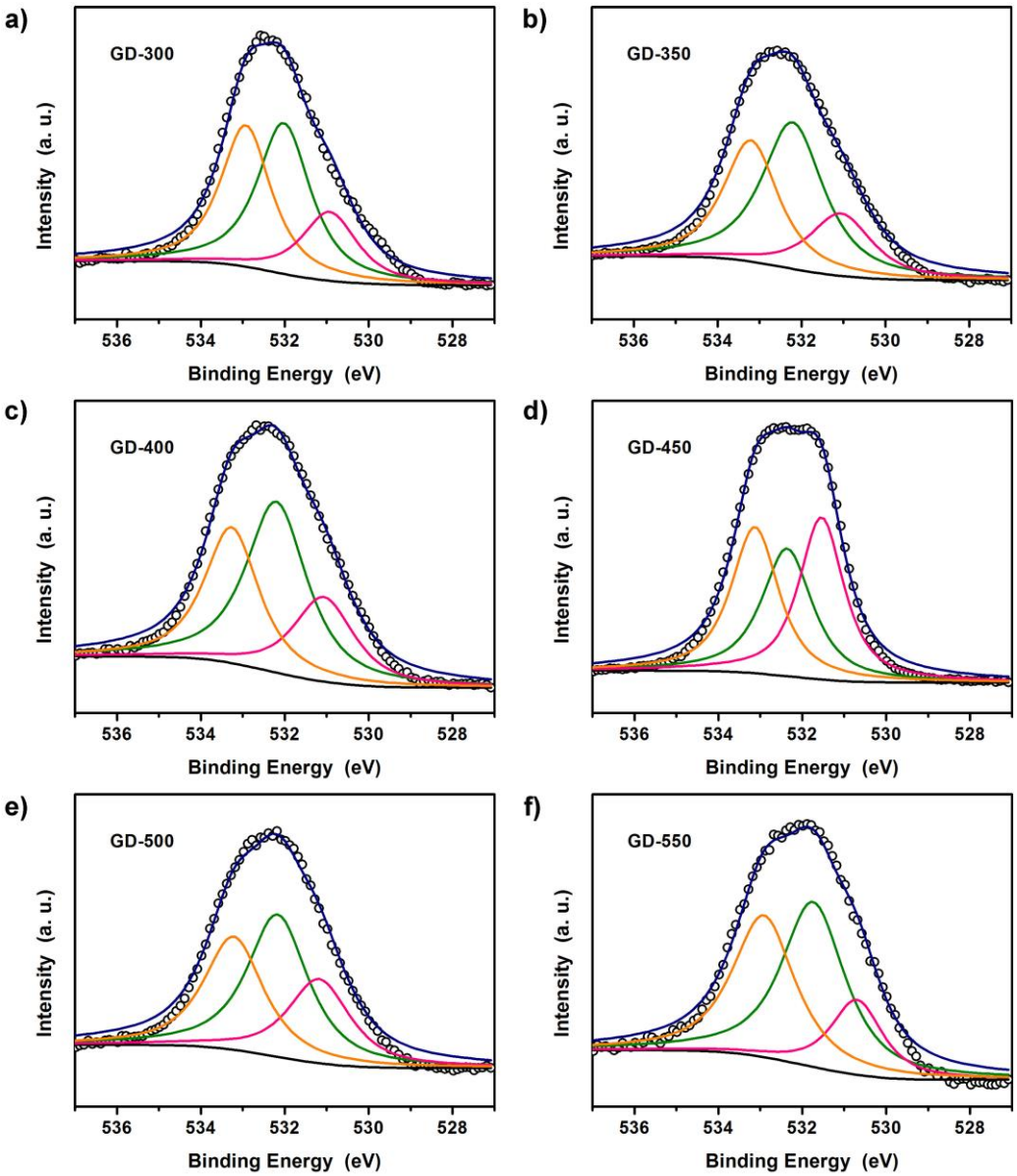

Figure S7. XPS O 1s spectra of the GD-300, 350, 400, 450, 500, and 550.

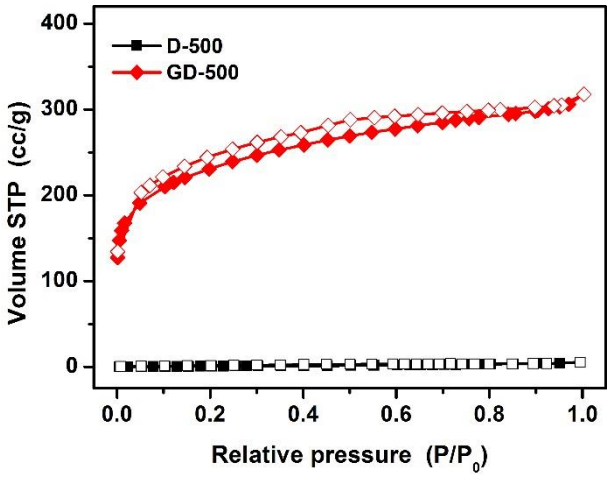

Figure S8. N_2 adsorption and desorption isotherms at 77 K for the GD-500 and D-500.

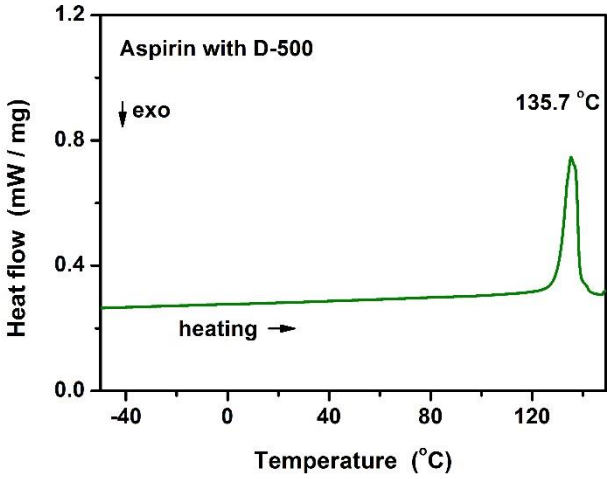

Figure S9. DSC record of the sample Aspirin with D-500.

Table S3. Elemental analysis of the samples.

Sample	N [wt %]	C [wt %]	H [wt %]	C/N	O [wt %]
Aspirin		60	4.44		35.56
GD-500	11.41	76.62	3.18	6.71	8.79
Aspirin in GD-500 (theoretical)	7.13	70.39	3.65	9.87	18.8
Aspirin in GD-500	8.06	69.52	3.42	8.63	19

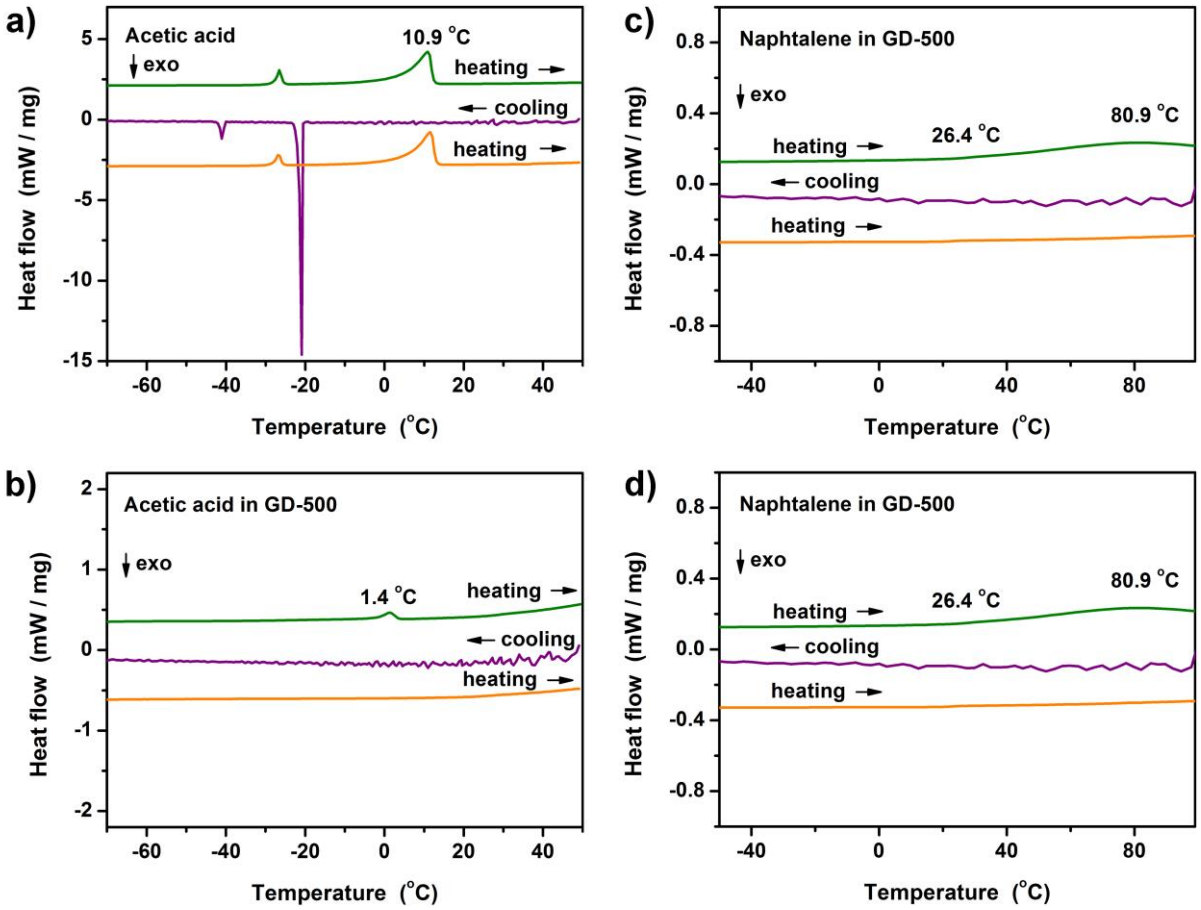

Figure S10. DSC records of the samples a) Acetic acid, b) Acetic acid with GD-500, c) Naphthalene, and d) Naphthalene with GD-500.

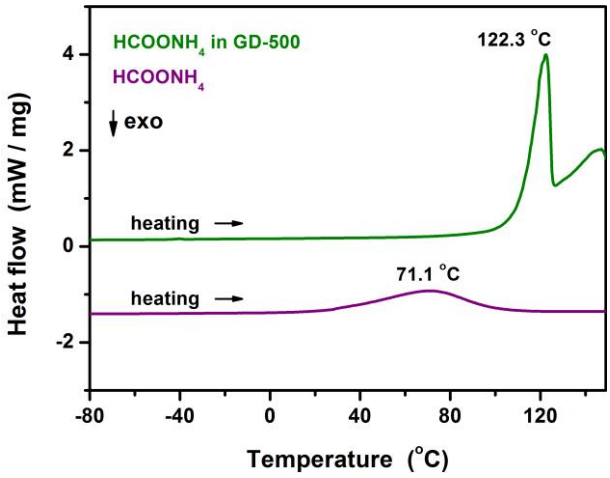

Figure S11. DSC records of the samples a) $HCOONH_4$, b) $HCOONH_4$ with GD-500.

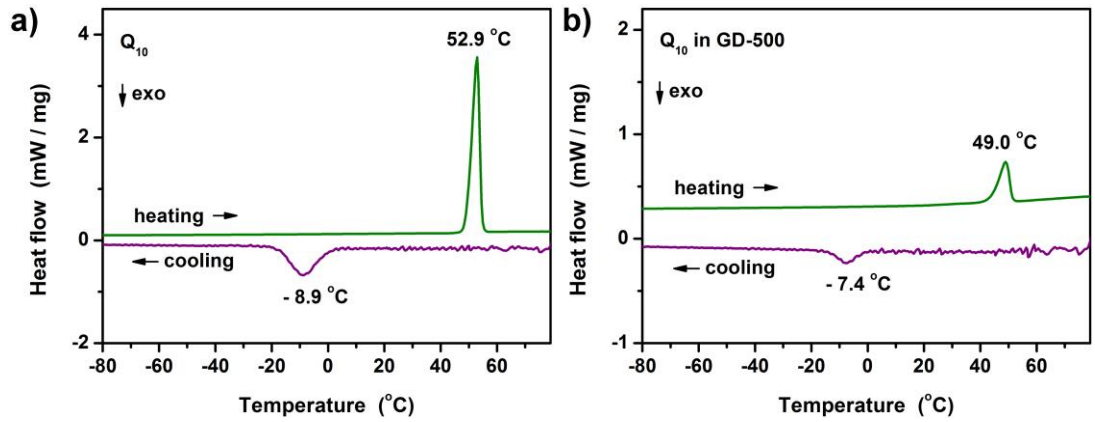

Figure S12. DSC records of the samples a) Q_{10}, b) Q_{10} with GD-500.

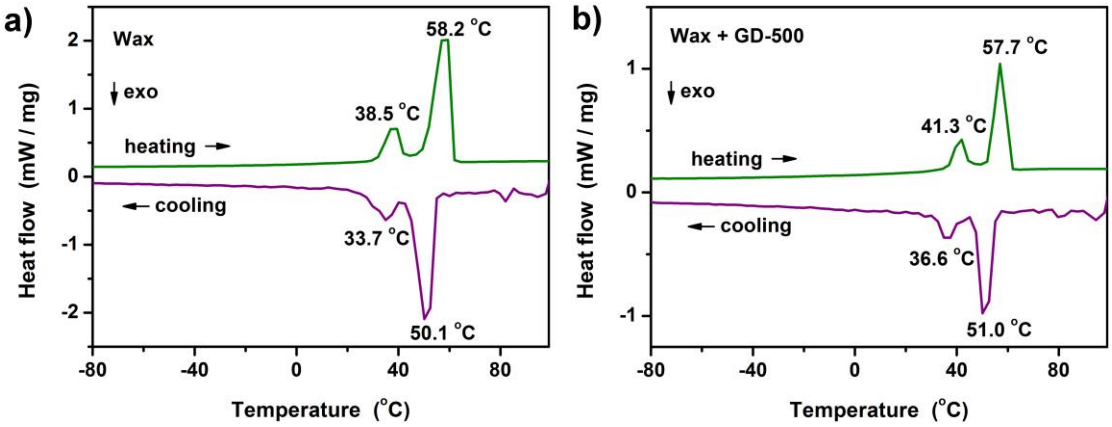

Figure S13. DSC records of the samples a) Wax, b) Wax with GD-500.

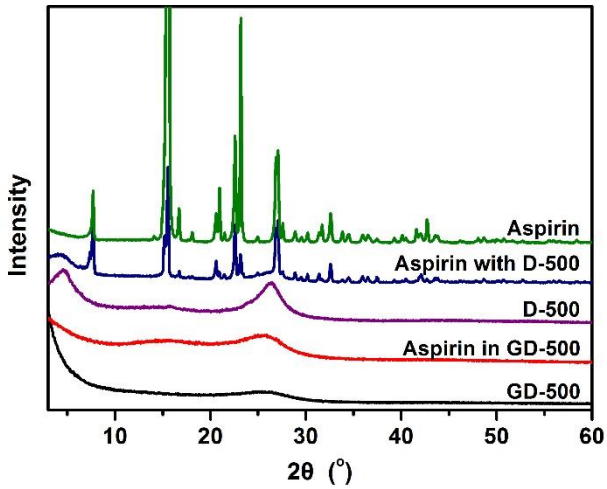

Figure S14. XRD patterns of bulk Aspirin, Aspirin with D-500, D-500, Aspirin in GD-500 and GD-500.

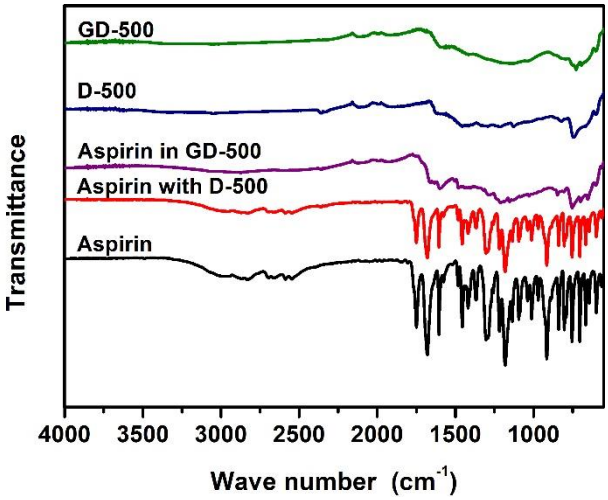

Figure S15. FT-IR spectra of bulk Aspirin, Aspirin with D-500, Aspirin in GD-500, D-500 and GD-500.