Electronic Supplementary Information:

Enhanced uptake of glyoxal at acidic nanoparticle interface: implications for secondary organic aerosol formation

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Methods

The choice of SA concentration

The previous studies showed that the cloud sample in the atmosphere was acidic.[1] The acidity of nanoparticles varies from 60 wt% to 80 wt% in the upper troposphere and decreases in the lower troposphere.[2, 3] Given the condition in the atmosphere, the different concentrations of SA (20 wt%, 30 wt%, 50wt% and 60 wt%) were investigated in the work. According to the density table of SA, the corresponding density of solution of SA from 20 wt% to 60 wt% is 1.136, 1.215, 1.391 and 1.494 g cm^{-3}, respectively. The concentrations of SA ([SA]) were calculated as follows:

$$c = \frac{1000\,\rho\,wt\%}{M}$$

(1)

where the ρ and M represent the density of solution of SA and molar mass of molecule, respectively.

The angular distribution

The specific property of GL at the interface is the difference of polarization relative to the bulk water because of the discrepancy of orientation of GL at the interface. Thus, a key factor in the orientation of GL at the interface is its angular distribution. The Z-axis was defined as the axis perpendicular to the nanoparticle interface and ϑ as the angle formed between the Z-axis and the C=O bond. The total energy was changed with the simulation time by the trajectory analysis at the interface. The most stable configurations were confirmed by the change of the total energy of every typical snapshot and the 100 typical snapshots from the most stable configurations were chosen to observe the angle distribution of C=O bond.

The radial distribution function and coordination number

The radial distribution function (RDF) can be used to estimate the strength of the hydrogen-bonding (HB) between special atoms. The HB between GL and water at the interface in the neutral and acidic systems occurs. The number of water around the GL molecule was obtained by calculating the coordination number (N). Considering the density at the interface is equal to 50% of the nanoparticle interior,[4] the N parameter is obtained as the integrations of g(r) within r=2.5 Å.
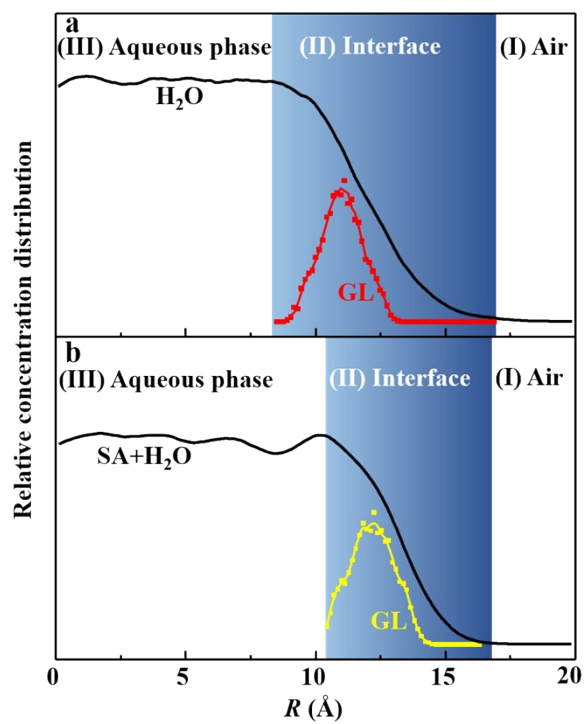
Fig. S1 Relative concentration distribution of GL and the corresponding solvent at (a) the A-N interface and (b) the A-A intefaces.
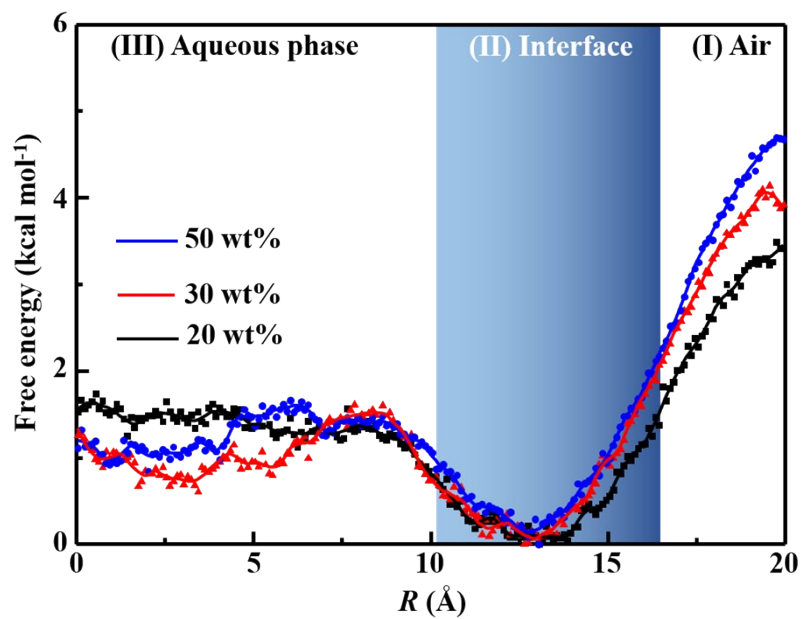
Fig. S2 The free energy profile of gaseous GL approaching into acidic nanoparticles with the different concentrations of SA (20 wt% (black), 30 wt% (red), and 50 wt% (blue)).
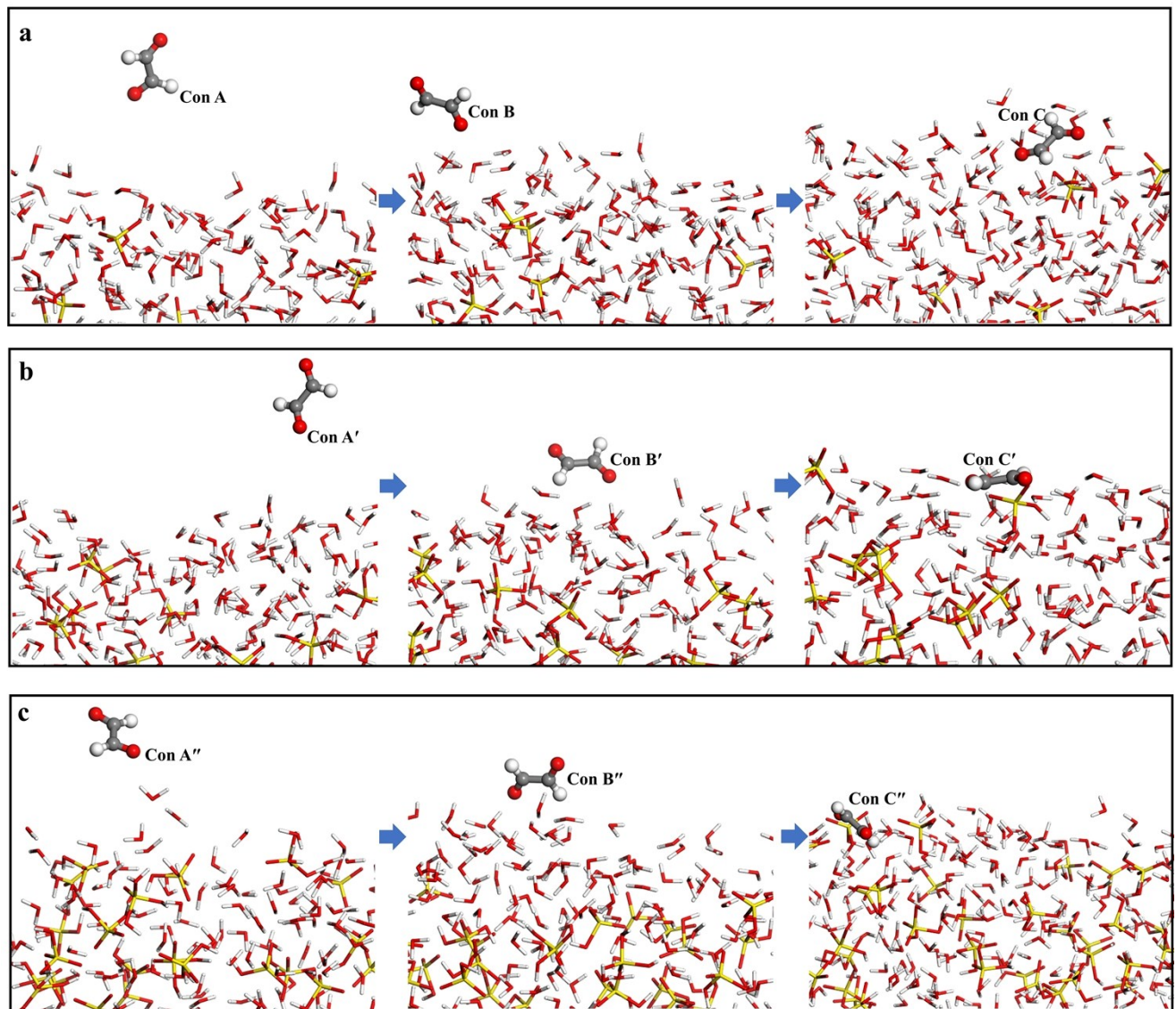
Fig. S3 Typical snapshots along with the trajectories of gaseous GL to the acidic nanoparticles with the concentrations of SA (a) 20 wt%, (b) 30 wt% and (c) 50 wt%, respectively. The Con A, Con A' and Con A" is snapshots at the point of the maximum free energy in acidic system; the Con B, Con B' and Con B" correspond to the snapshots at the A-A surface which are the bounds between gas phase and interface, and the Con C, Con C' and Con C" represent the most stable structures at the acidic nanoparticle interface.
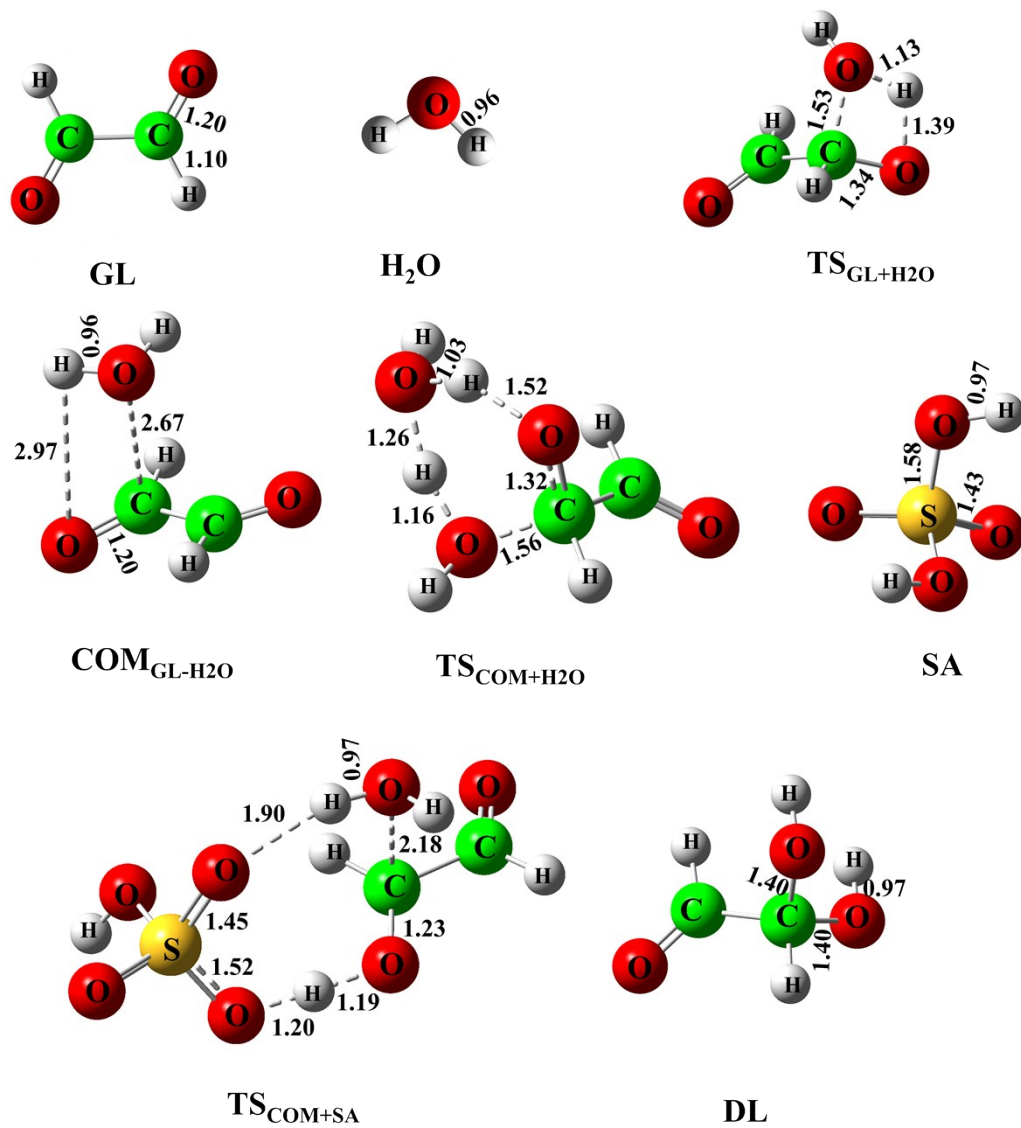
Fig. S4 The optimized geometries of the reactants, complex, transition states and products at the M06-2X/6-311G(d,p) level. The unit of the bond length is Å.

Table S1 Numbers of SA (N_1) and water (N_2) molecules under the acidic nanoparticles with the different concentrations of SA ([SA]) between 20 wt% to 60 wt%. The length of the box is 26 Å.

wt%	N_1	N_2	[SA][a]	Density[b]
20	25	535	2.319	1.136
30	39	501	3.719	1.215
50	75	409	7.097	1.391
60	97	352	9.147	1.494
[a]The unit is mol L^{-1}.				
[b]The value is the density of the corresponding solution of SA and the unit is g cm^{-3}.				

Table S2 Coordination numbers (N) of water molecules in the first solvation shell for $O_{GL}-H_{water}$ at the interface and in the nanoparticle interior region in the neutral and acidic systems.

System	Phase	N
neutral	interface	2.9
acidic	interface	2.2
neutral	nanoparticle interior	6.0
acidic	nanoparticle interior	6.3

Table S3 Cartesian coordinates, vibrational frequencies (in cm^{-1}), absolute energies (in hartrees), and thermal corrections (in hartrees) of stationary points in the reactions of GL and H$_2$O and SA at the M06-2X/6-311G(d,p) level.

Species	Cartesian coordination			Absolute energies	Thermal corrections	Frequencies
GL	C 0.95816500	-0.57721300	-0.00012400	-227.7966871	0.011649	136, 333, 571, 842, 1097, 1103, 1354, 1402, 1822, 1854, 3067, 3073
	H 1.17429600	-1.65771000	-0.00003700			
	C -0.51528800	-0.20165000	0.00008800			
	O 1.80656400	0.27429600	0.00008200			
	O -1.36402900	-1.05294600	0.00003600			
	H -0.73085400	0.87886100	0.00021000			
H$_2$O	O 2.26394800	0.30023000	0.00000000	-76.4257234	0.003105	1602, 3859, 3936
	H 3.22450700	0.35184600	0.00000000			
	H 1.99188700	1.22300900	0.00000000			
TS$_{GL+H2O}$	C 0.98946300	-0.09102100	-0.36642000	-304.1777444	0.032456	-1412, 79, 300, 339, 424, 472, 725, 839, 961, 1037, 1160, 1191, 1277, 1318, 1356, 1428, 1837, 2193, 3046, 3117, 3718
	H 0.86275300	-0.22369100	-1.45619300			
	C -0.29924500	0.16337300	0.39256400			
	O 2.06809800	-0.06047100	0.16619600			
	O -1.02066500	1.16173800	-0.14913800			
	O -1.30790700	-0.94836800	0.08144000			
	H -1.75153500	-0.00559500	-0.36044300			
	H -1.01671800	-1.57654100	-0.60415600			
	H -0.15202300	0.14852100	1.47595000			
COM$_{GL-H2O}$	C 0.33204600	-0.80846700	0.39379100	-304.2316561	0.031483	112, 144, 154, 177, 179, 337, 364, 396, 565, 866, 1096, 1106, 1344, 1392, 1601, 1811, 1851, 3062, 3068, 3841, 3919
	H 0.27547700	-0.66571900	1.48538200			
	C -0.84842700	-0.26634400	-0.39442200			
	O 1.23375300	-1.38453300	-0.15677000			
	O -1.85897900	0.07103300	0.16471800			
	O 0.78939000	1.79101800	-0.10529600			

	H	0.51209700	2.00229200	0.79350000			
	H	1.71542200	1.54182200	-0.00837200			
	H	-0.71803100	-0.24967500	-1.48794100			
TS$_{COM+H2O}$	C	0.32777800	0.31873300	-0.61484500	-380.6462366	0.054379	-868, 42, 79, 297, 339, 364, 405, 444, 506, 531, 648, 754, 789, 985, 1003, 1053, 1168, 1250, 1337, 1357, 1421, 1532, 1610, 1735, 1831, 2562, 3023, 3048, 3788, 3849
	H	0.87766000	1.03123300	-1.24130800			
	C	1.24142200	-0.32114600	0.41723200			
	O	-0.40719900	-0.58552700	-1.22840600			
	O	2.44345300	-0.22780800	0.38696000			
	H	0.72077100	-0.95515500	1.15988200			
	O	-2.13638400	-0.50810900	0.53615400			
	H	-1.95913700	-1.07063900	1.30149100			
	H	-1.53465200	-0.83956200	-0.23887800			
	O	-0.54910300	1.24215900	0.29048500			
	H	-0.90674000	1.96021000	-0.25343200			
	H	-1.41924200	0.52267000	0.57637600			
SA	O	0.34271300	-0.83513700	1.21135500	-700.211748	0.010715	266, 335, 388, 443, 491, 527, 551, 864, 903, 1122, 1142, 1213, 1400, 3711, 3722
	S	-0.00005600	-0.14498600	0.00156800			
	O	-0.34333500	-0.86212700	-1.19224100			
	O	1.16968600	0.82708300	-0.42095700			
	O	-1.16908900	0.83709700	0.40229300			
	H	1.55806000	1.29539100	0.34063500			
	H	-1.55696500	1.28905000	-0.36932500			
TS$_{COM+SA}$	C	-1.74116900	-0.46015500	-0.04347400	-1004.4584404	0.062562	-583, 46, 61, 93, 106, 122, 160, 211, 219, 280, 300, 311, 346, 420, 430, 473, 551, 567, 586, 612, 718, 748, 865, 953, 1051, 1088, 1130, 1151, 1247, 1272, 1329, 1365, 1400, 1552, 1611,
	O	-1.66331000	1.71046000	-0.21596500			
	O	-1.16465400	-0.91681300	-1.03587600			
	H	-1.24542000	-0.35510600	0.92541000			
	H	0.01240400	-1.03691800	-0.86901900			
	O	1.13161300	1.26833500	-0.15679700			

	H	-0.69632800	1.77776400	-0.13879400			1707, 1859, 3099, 3168, 3712, 3754, 3853
	O	1.19072500	-1.12710100	-0.67500300			
	S	1.88027500	0.03557200	0.01433200			
	O	1.73077500	-0.27207500	1.57339300			
	O	3.28525500	0.04577500	-0.32072300			
	H	-1.84451100	1.89734800	-1.14724800			
	H	2.20806600	-1.08032900	1.82871300			
	C	-3.24754700	-0.32508600	-0.07361500			
	H	-3.69640400	-0.27202000	-1.07659300			
	O	-3.87164300	-0.30713600	0.94981400			
DL	C	0.93879800	0.00188800	0.37583400	-304.2499671	0.039282	88, 328, 381, 386, 411, 462, 635, 1026, 1049, 1218, 1226, 1303, 1328, 1438, 1454, 1457, 1846, 3004, 3169, 3811, 3813
	H	0.85603100	0.00452800	1.48016800			
	C	-0.39162100	0.00004700	-0.35765900			
	O	2.00534800	0.00001900	-0.18286600			
	O	-1.09603300	-1.17025800	-0.03367400			
	O	-1.09925800	1.16841200	-0.03467400			
	H	-1.19500400	-1.21360800	0.92729000			
	H	-1.19698400	1.21224600	0.92651500			
	H	-0.22756200	-0.00015300	-1.43330500			

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