Supporting information

Growth characteristics of Ti-based fumaric acid hybrid thin films by molecular layer deposition

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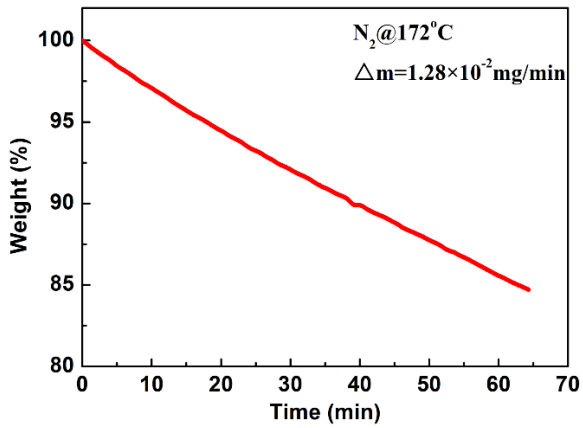

Figure S1. Volatilization curve of fumaric acid at constant temperature of 172 °C in N_2.

Figure S2 shows the XPS spectra of hybrid films stored 20 months after Ar-ion sputtering in XPS chamber. For the C1s spectrum, besides the C-C and C=O peaks, there is one peak at 282.2 eV appearing. This signal maybe comes from the carbide. Correspondingly, there are also two peaks at 457.0 and 462.0 eV, likely representing the Ti-C bonds. It can be concluded that the structure of the hybrid films would be

destroyed, decomposing into titanium carbide possibly. So the XPS measurement of the hybrid films were conducted without surface sputtering.

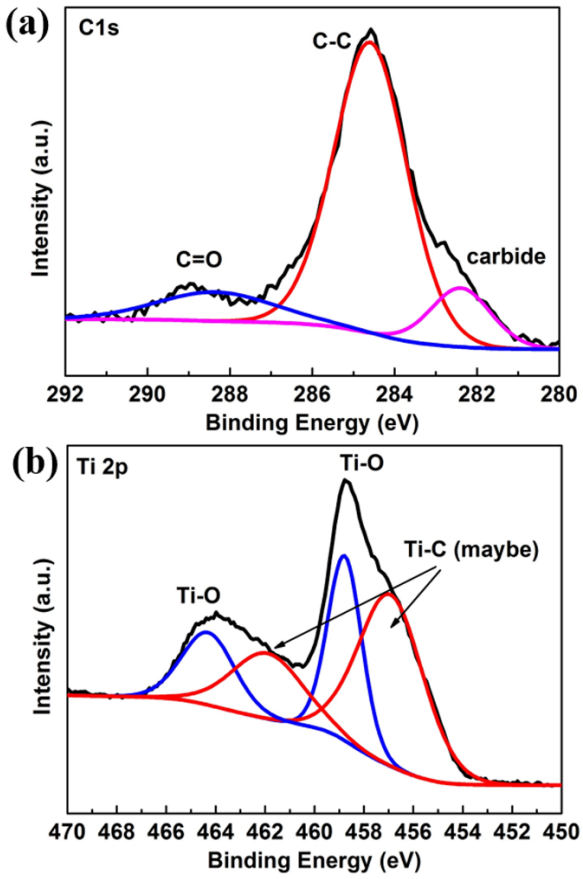

Figure S2. XPS spectra of (a) C 1*s* and (b) Ti 2*p* of hybrid films after Ar-ion sputtering.

After subtracting the C from oil vapor surface contaminant by using control sample of 850 ^{o}C RTA sample, the XPS compositional ratio of hybrid films deposited at various temperatures were illustrated in the Table S1. The C signal of the sample with 850 ^{o}C RTA treatment is totally come from the oil vapor or surface contaminant. Supposing the C signal from the oil vapor and surface contaminant is almost same for all the samples, it can be found the contaminant percentage of C is about 6.3%-10.9% for the hybrid films deposited at various T. It can be seen that there is no obvious and

substantial change for all the hybrid film compositions between Table 1 and Table S1.

Table S1. XPS compositional ratio of hybrid films deposited at various temperatures

Deposition T (°C)	Atomic ratio			
	C	O	Ti	Cl
180	7.82	7.49	1.00	0.08
200	7.56	7.25	1.00	0.08
220	7.27	7.10	1.00	0.08
250	6.58	6.50	1.00	0.07
275	5.62	5.66	1.00	0.07
300	4.29	4.80	1.00	0.06
350	1.76	2.76	1.00	0.03

The GC-MS measurement of fumaric acid dissolved in ethanol was performed at 200 and 300 °C, respectively. The GC-MS results in Figure S3 show that there is only fumaric acid at 200 °C, however some maleic anhydride (cis-butenedioic anhydride) is detected besides fumaric acid at 300 °C. It indicates that some fumaric acid molecules (~10%) form maleic anhydride by splitting off H_2O at 300 °C.

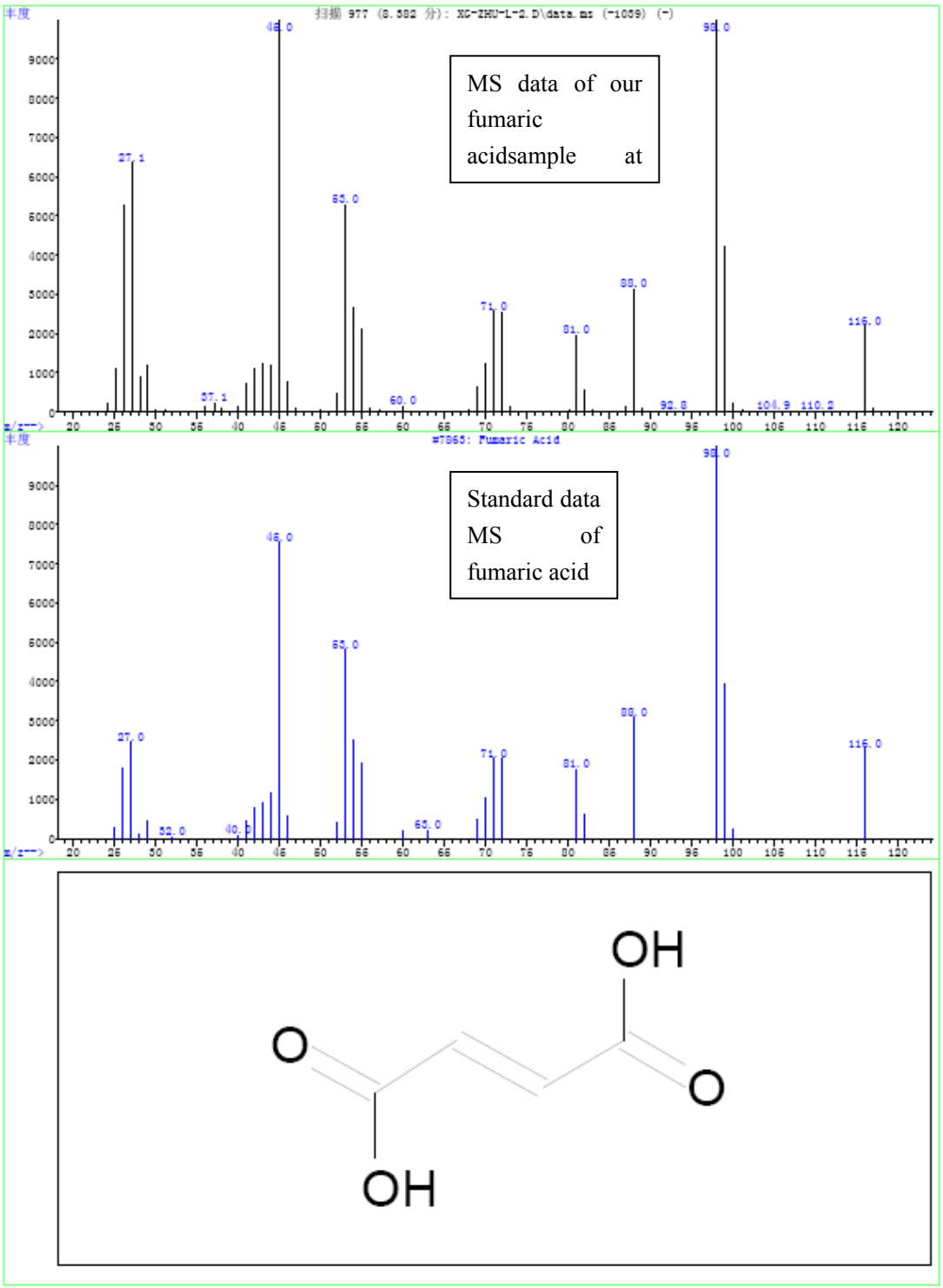

Figure S3. (a) MS data of fumaric acid at 200 ºC from GC-MS

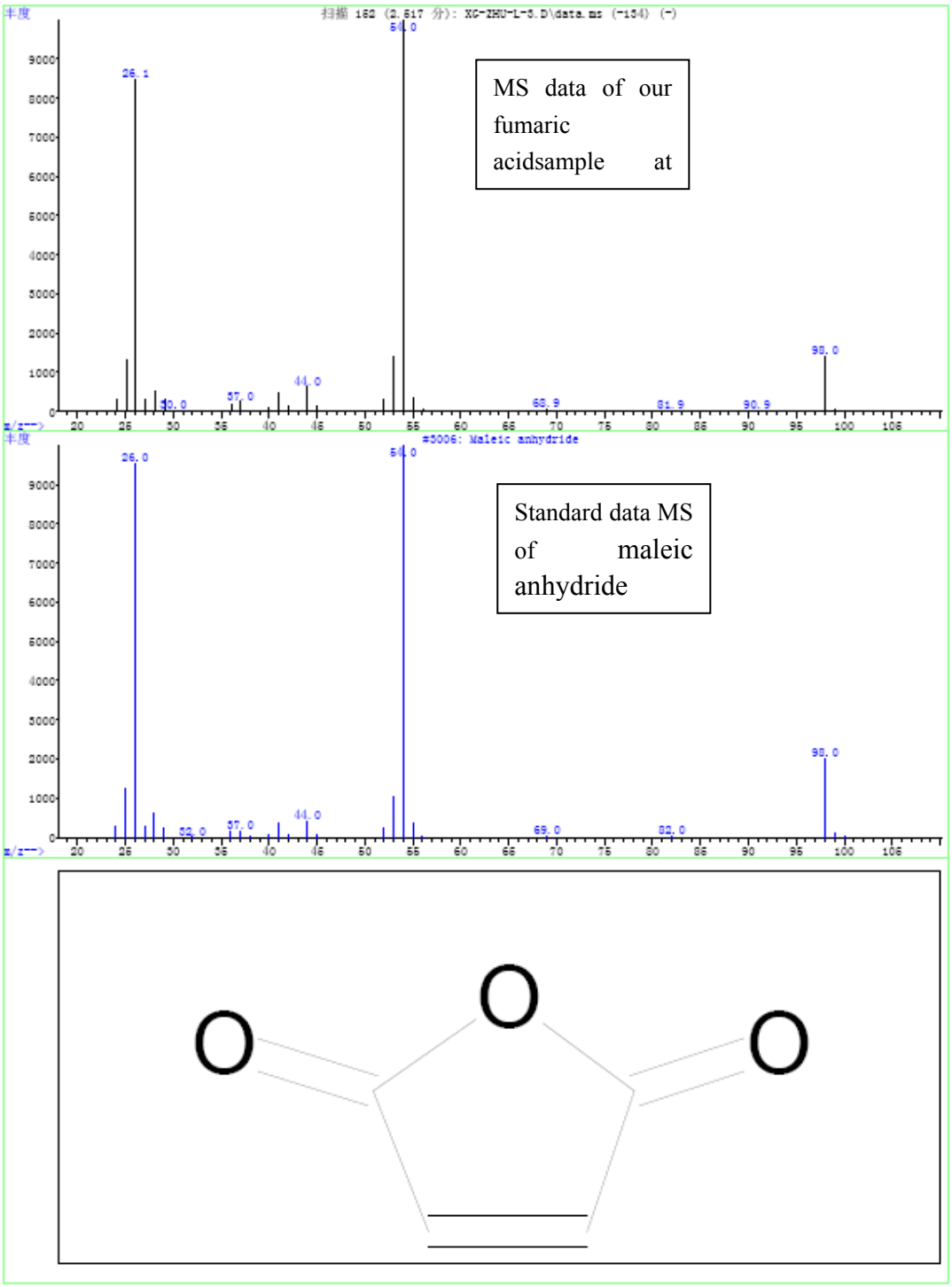

Figure S3. (b1) MS data of fumaric acid at 300 °C from GC-MS

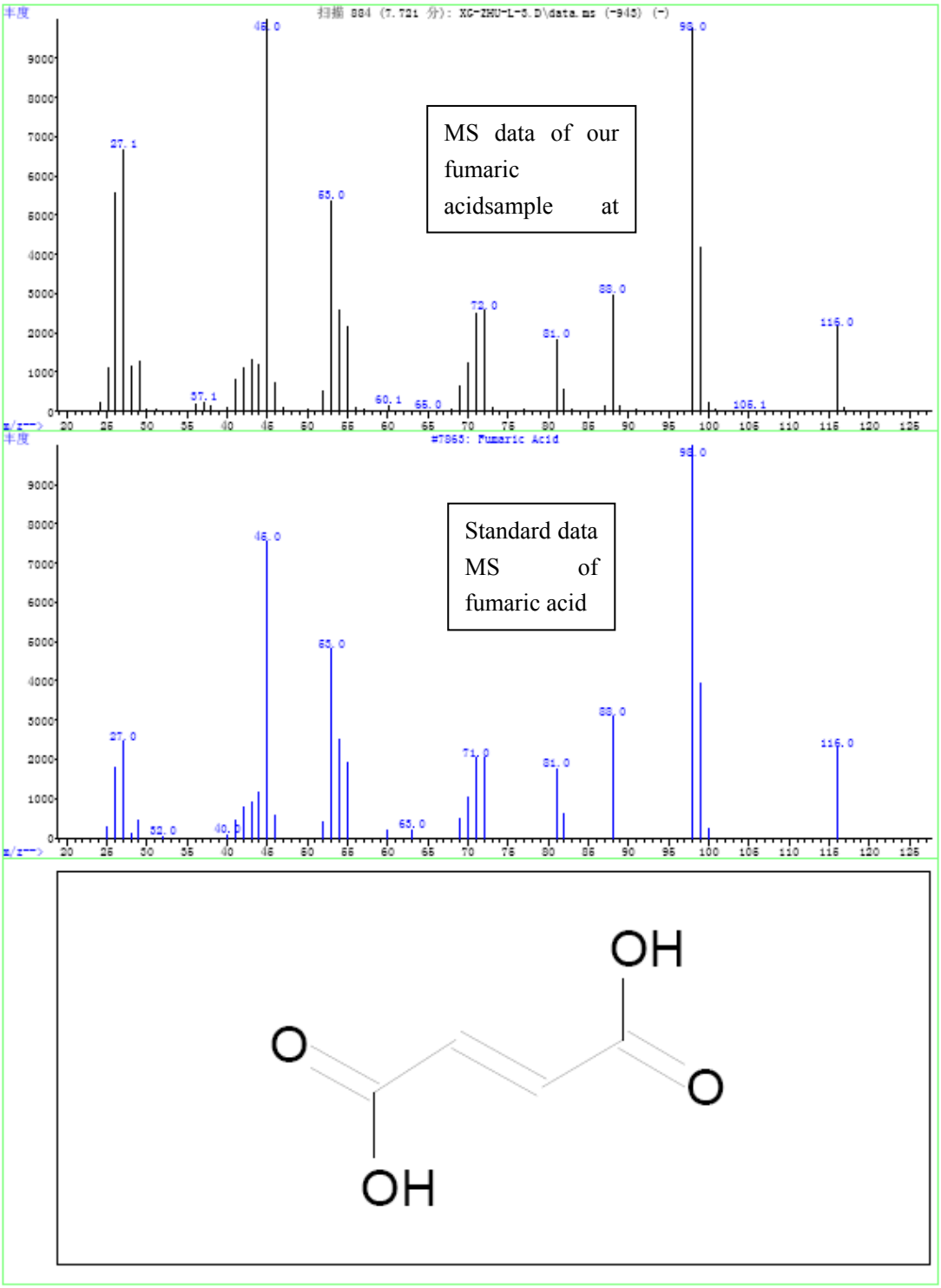

Figure S3. (b2) MS data of fumaric acid at 300 °C from GC-MS

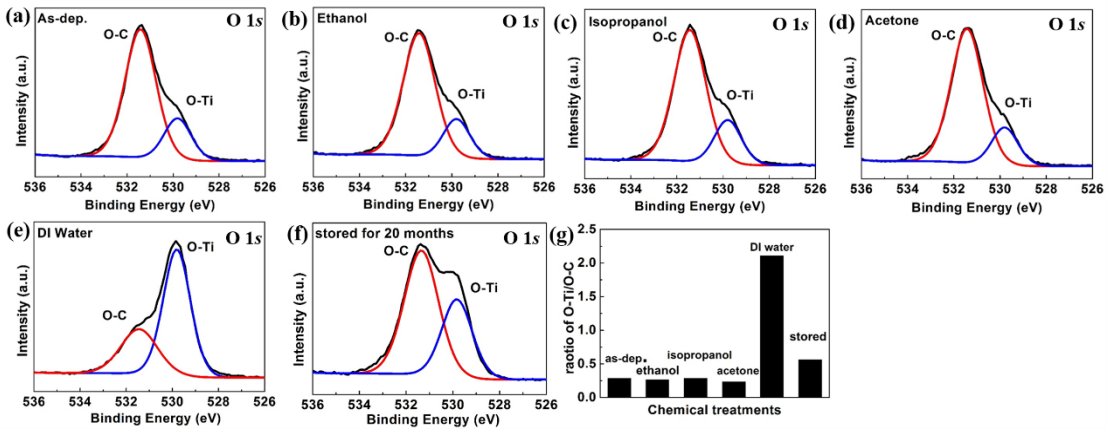

Figure S4. O 1s spectra of (a) the as-deposited hybrid films and the samples immerged in (b) ethanol, (c) isopropanol, (d) acetone, (e) DI water and (f) stored for 20 months. (g) The ratio of O-Ti to O-C for the hybrid films with different chemical treatment.

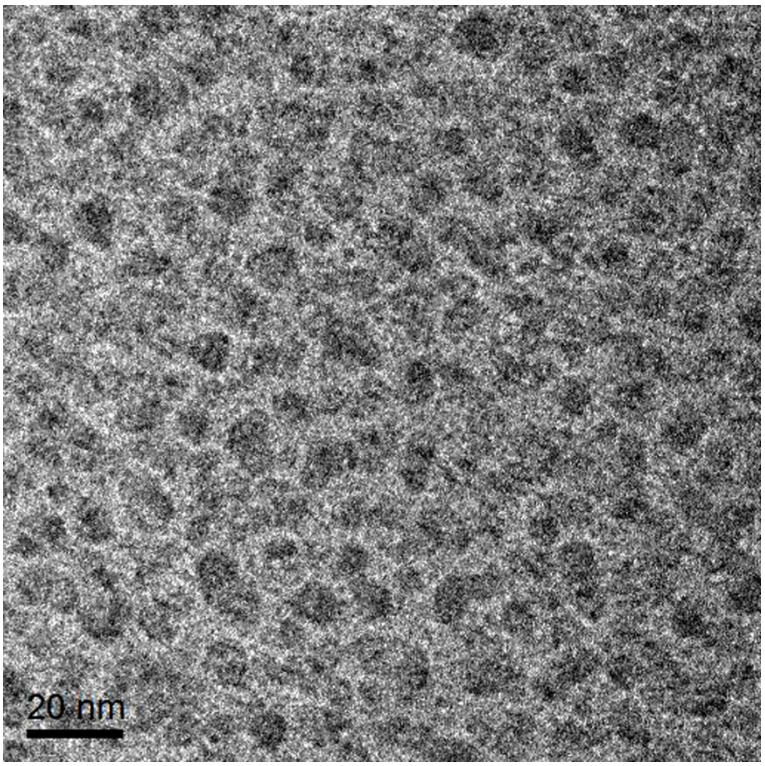

Figure S5. TEM image of hybrid films after 10s 850 ^{o}C RTA process.

TEM was conducted for the RTA treated sample of 200 cycles, shown as Figure S5. It can be found that the hybrid film was indeed transformed into nanoparticles with the diameter of ~10 nm, not porous TiO_2 films.The corresponding HRTEM image

shows the (101) and (111) lattice planes can be well recognized with lattice spacing of 2.49 Å and 2.19 Å, which can be assigned to rutile phase of TiO_2.