Supporting Information

Determining the TiO_2-Photocatalytic Aryl-Ring-Opening Mechanism in Aqueous Solution Using Oxygen-18 Labeled O_2 and H_2O

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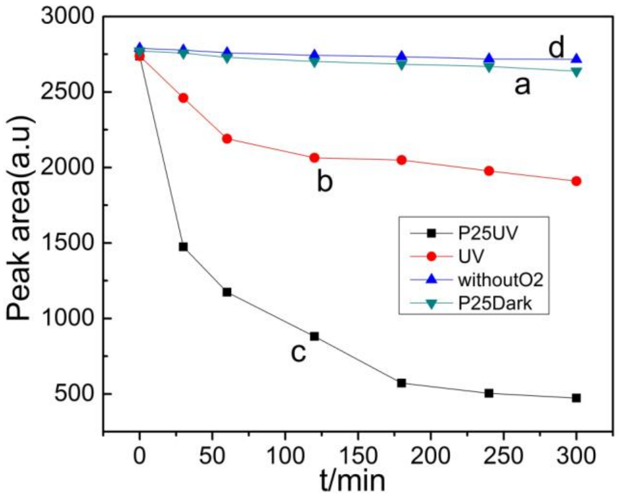

Figure S1. Degradation of DTBC under different conditions. (**a**):P25 and dark (**b**) UV and without P25 (**c**) P25 and UV light (d) Ar-sparging.

Figure S1 shows the time-course of the substrate under different conditions (a):P25 and without UV light; (b) UV and without P25; (c) P25 and UV Light; (d) just like c but without O_2. The substrate was analyzed at regular time intervals by HPLC. We should notice that the curve b demonstrates the DTBC can sensitize under UV irradiation, however, there was no initial ring-opening products in the final reaction products which were discussed in this study. Moreover, it can be ignored by comparing to cure c (photo catalyze reaction) which is the main reaction path. The cure d suggests that O_2 plays very important roles in the degradation of DTBC. The observed cleavage of DTBC requires the presence of O_2: deoxygenated solutions irradiated in parallel fashion do not give evidence of oxidation. Thus, either oxygen gas or a species derived from it must function as the effective source of oxygen atoms.

Table S1. The main intermediates MS and ^{1}H NMR data

peak	compounds	^{1}H NMR(300MHz,CDCl3)	MS m/e(ref.int.)
2	**3,5-di-tert-butyl-1-oxacyclohepta-3,5-diene-2,7-dione**	δ1.16(s,9H), 1.28(s,9H), 6.14(d,1H), 6.45 (d,1H)	236(M,3),221(3),208(4),193(5),177(11) 178(18),166(19),149(100)
3	**3,5-di-tert-butyl-5-(carboxymethyl)-2-furanone**	δ0.98(s,9H), 1.23(s,9H), 2.81(d,1H),2.95 (d,1H), 6.94 (s,1H)	199(13),198(95),183(100),153(26), 184(15),137(11)
4	**4,6-di-tert-butyl-2-pyrone**	δ1.19(s,9H),1.26(s,9H), 6.00(d,1H), 6.01(d,1H)	208(M,45),194(13),193(94),166(65), 165(100),151(21),137(33)
5	**3,5-di-tert-butyl-2-pyrone**	δ1.20(s,9H),1.32(s,9H), 7.04(d,1H),7.14(d,1H)	208(M,26),193(3),180(11),166(15), 165(100),151(92),109(7),95(18)
6	**3,5-di-tert-butyl-2-hydroxy-1,4-benzoquinone**	δ1.28(s,9H), 1.37(s,9H), 6.50(s,1H),7.18 (s,1H).	221(100),236(77),203(18),193(63), 165 (61),179(30)
7	**3,4-Epoxy-3,4-dihydro-4,6-di-tert-butyl-1,2-benzoquinone**	δ1.10(s,9H), 1.21(s,9H), 3.84(s,1H), 7.09 (s,1H)	221(1),207(4),208(1),194(11),193(84) 180(100),179(35),165(48),151(41)

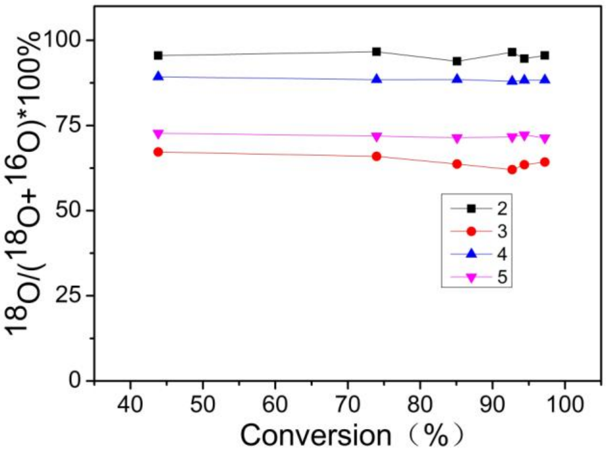

Figure S2. The isotope abundance of products **2**, **3**, **4** and **5** at different conversion yields under $^{18}O_2$ and $H_2{}^{16}O$ condition.

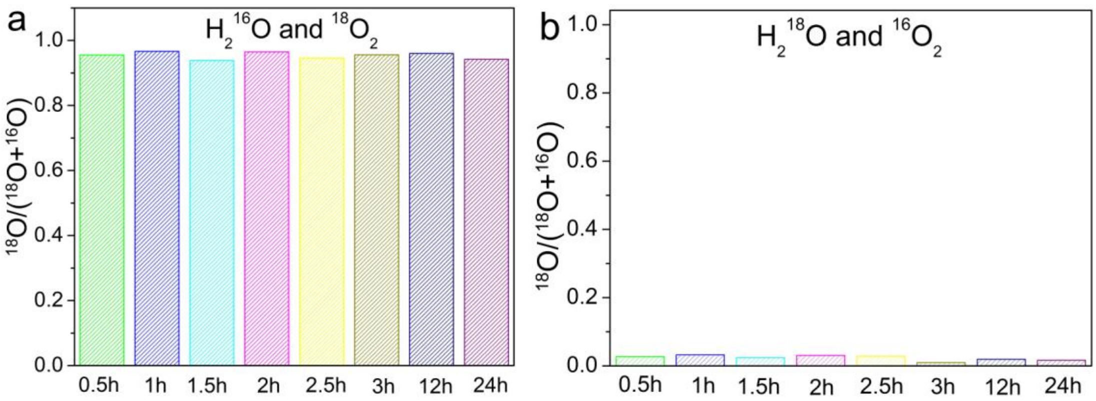

Figure S3. The ^{18}O isotope exchange experiments of product **2** in dark reaction at different time (a) 97% ^{18}O labeled **2** at $^{16}O_2$ and $H_2{}^{16}O$ condition, (b) no ^{18}O labeled **2** at $^{16}O_2$ and $H_2{}^{18}O$ condition.

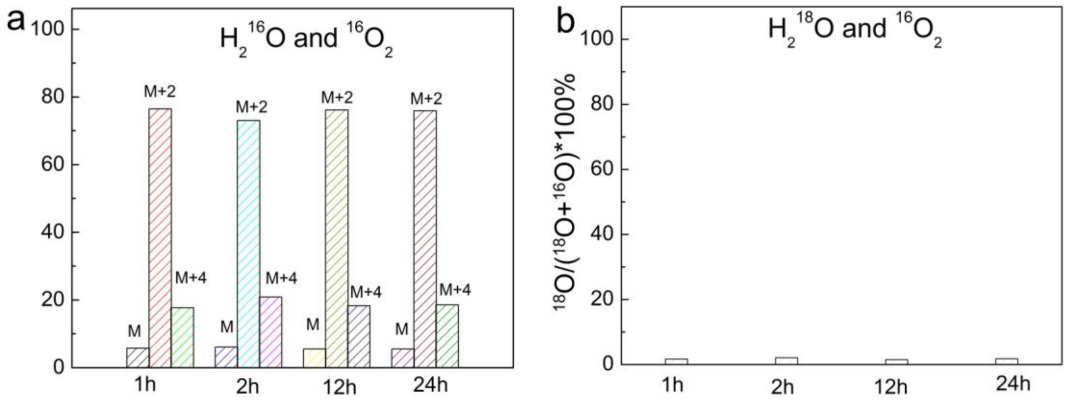

Figure S4. The ^{18}O isotope exchange experiments of product **3** in dark reaction at different time (a) 78% M+2 ^{18}O labeled **3** at $^{16}O_2$ and $H_2{}^{16}O$ condition, (b) no ^{18}O labeled **3** at $^{16}O_2$ and $H_2{}^{18}O$ condition.

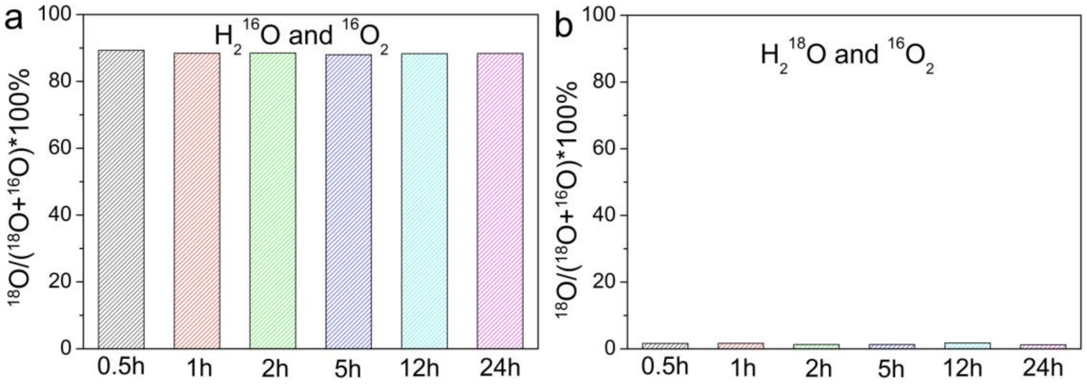

Figure S5. The ^{18}O isotope exchange experiments of product **4** in dark reaction at different time (a) 89% ^{18}O labeled **4** at $^{16}O_2$ and $H_2{}^{16}O$ condition, (b) no ^{18}O labeled **4** at $^{16}O_2$ and $H_2{}^{18}O$ condition.

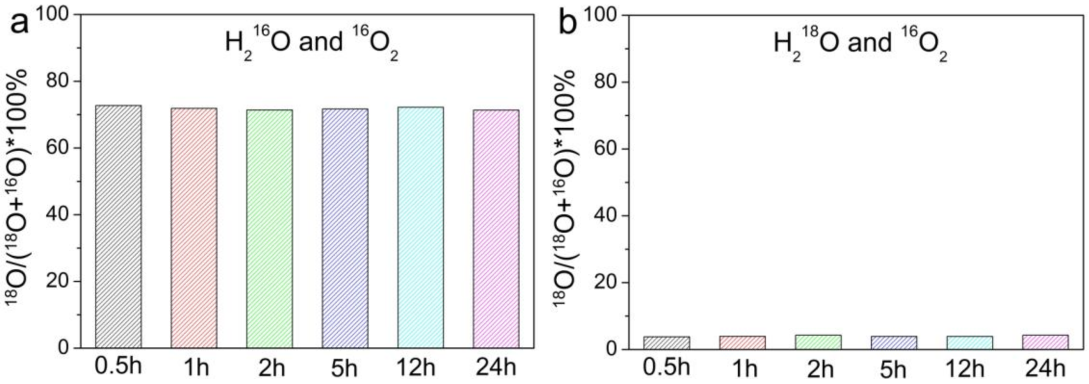

Figure S6. The ^{18}O isotope exchange experiments of product **5** in dark reaction at different time (a) 74% ^{18}O labeled **5** at $^{16}O_2$ and $H_2{}^{16}O$ condition, (b) no ^{18}O labeled **5** at $^{16}O_2$ and $H_2{}^{18}O$ condition.

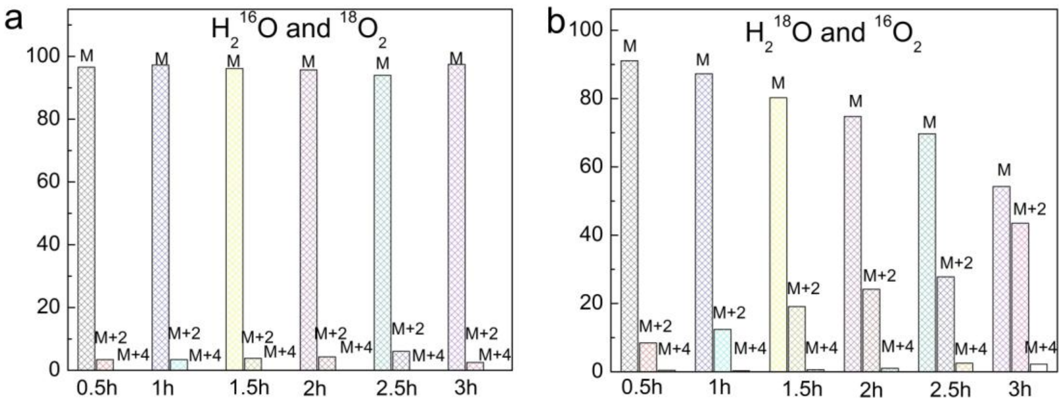

Figure S7. The ^{18}O isotope exchange experiments of no ^{18}O labeled product **8** in dark reaction at different time. (a) $^{18}O_2$ and $H_2{}^{16}O$ condition. (b) $^{16}O_2$ and $H_2{}^{18}O$ condition.

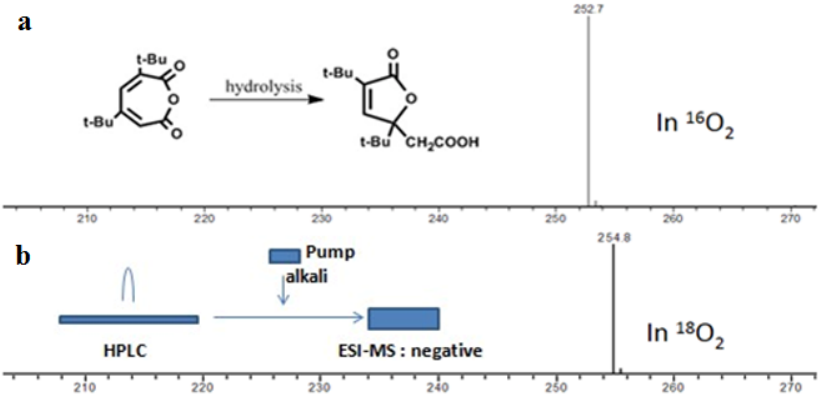

Figure S8. The ESI-MS spectra of the product 2 obtained from the photocatalytic oxidation of DTBC at different isotope label conditions, the inset shows the analysis process by the HPLC-MS (ESI). (a) $^{16}O_2$ and $H_2{}^{18}O$ condition. (b) $^{18}O_2$ and $H_2{}^{16}O$ condition.

Table S2. Mass analysis of the product **3** formed under different isotope label conditions

peak	React under $H_2{}^{16}O$ and $^{16}O_2$			$H_2{}^{16}O$ and $^{18}O_2$			$H_2{}^{18}O$ and $^{16}O_2$		
	m/z	PC	assignment	m/z	PC	assignment	m/z	PC	assignment
P^+-C_4H_7	199	13	$C_{10}H_{15}O_4$	202	19	$C_{10}H_{15}O_2{}^{18}O_2$	202	12	$C_{10}H_{15}O_2{}^{18}O_2$
				200	83	$C_{10}H_{15}O_3{}^{18}O$	200	82	$C_{10}H_{15}O_3{}^{18}O$
P^+-C_4H_8	198	95	$C_{10}H_{14}O_4$	198	6	$C_{10}H_{14}O_4$	198	30	$C_{10}H_{14}O_4$
				187	22	$C_9H_{11}O_2{}^{18}O_2$	187	13	$C_9H_{11}O_2{}^{18}O_2$
P^+-C_5H_{10}	184	15	$C_9H_{12}O_4$	185	100	$C_9H_{11}O_3{}^{18}O$	185	100	$C_9H_{11}O_3{}^{18}O$
P^+-C_5H_{11}	183	100	$C_9H_{11}O_4$	183	6	$C_9H_{11}O_4$	183	38	$C_9H_{11}O_4$
				157	0	$C_9H_{13}{}^{18}O_2$	157	0	$C_9H_{13}{}^{18}O_2$
				155	18	$C_9H_{13}O^{18}O$	155	5	$C_9H_{13}O^{18}O$
P^+-$C_5H_9O_2$	153	26	$C_9H_{13}O_2$	153	5	$C_9H_{13}O_2$	153	24	$C_9H_{13}O_2$
				139	7	$C_8H_9O^{18}O$	139	3	$C_8H_9O^{18}O$
P^+-$C_6H_{13}O_2$	137	11	$C_8H_9O_2$	137	3	$C_8H_9O_2$	137	9	$C_8H_9O_2$

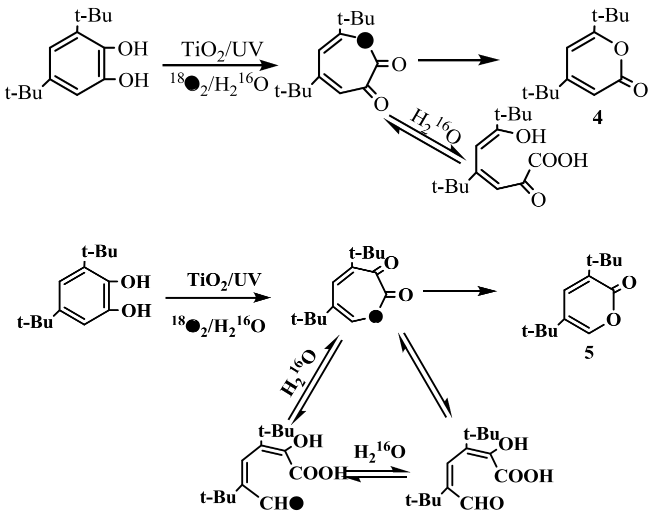

Figure S9. The formation process of extradiol product **4**, **5** and their O isotope exchange steps[1,2].

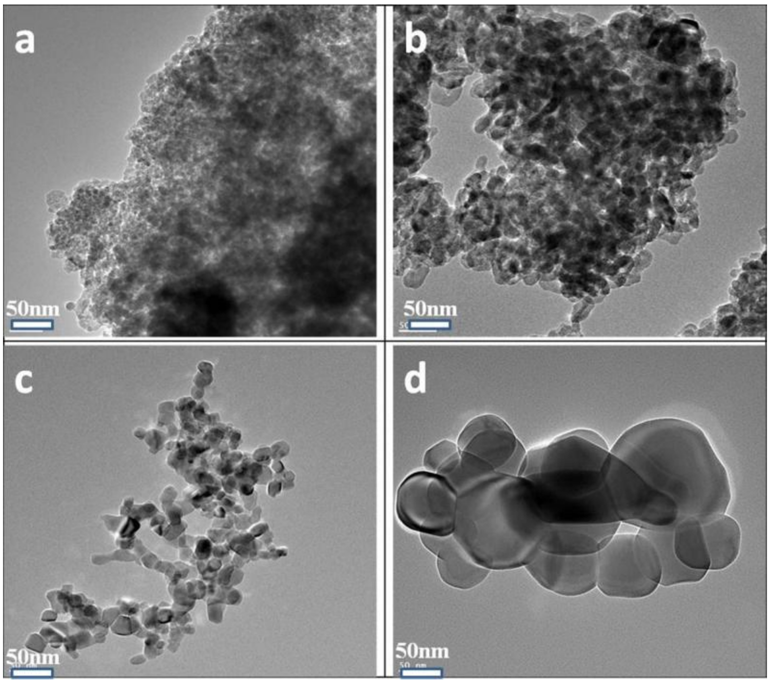

Figure S10. TEM images of the different particle sizes of the four TiO_2 samples. (a) TiO_2-a, (b) TiO_2-b, (c) TiO_2-c, and (d) TiO_2-d.

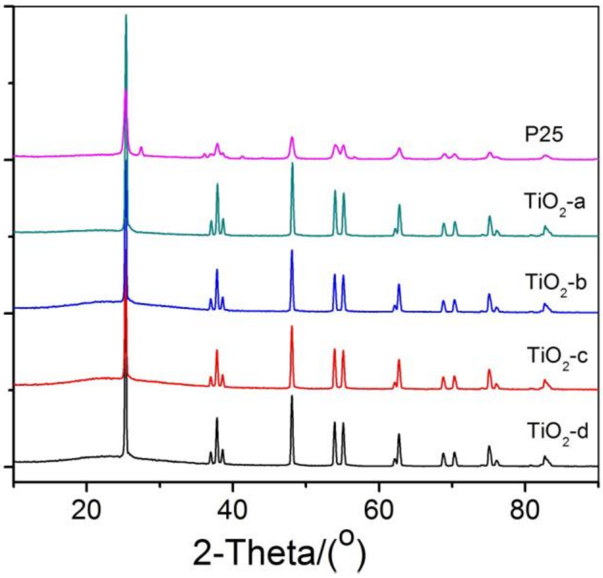

Figure S11. XRD patterns of the TiO_2 samples.

Table S3. Characteristics of the TiO_2 samples and relative positron lifetime and intensities.

Sample	size/nm	specific surface area(m^2/g)	Crystalline phase	τ_1(ns)	τ_2(ns)	τ_3(ns)	I_1(%)	I_2(%)	I_3(%)	I_1/I_2	κ
TiO_2-a	9.7	99.31	anatase	0.1938	0.3719	2.461	41.8	57	1.223	0.7333	140.85
TiO_2-b	16.5	75.04	anatase	0.1879	0.3615	2.436	38.6	60.2	1.205	0.6412	153.85
TiO_2-c	30	53.73	anatase	0.1905	0.3833	2.567	36.4	62.2	1.323	0.5852	164.23
TiO_2-d	120	11.42	anatase	0.1882	0.3615	2.465	41.9	57.1	1.03	0.7338	145.45

τ_1, τ_2, and τ_3 mean the three positron lifetime components for the TiO_2 samples, I_1, I_2, and I_3 are their relative intensities. τ_1 is generally attributed to the free annihilation of positrons in defect-free crystal. τ_2 arises from positrons trapped larger size defects such as oxygen vacancy clusters. τ_3 means the annihilation of orthopositronium atoms formed in the large voids[3] .κ is the positron trapping rate which is proportional to the defect concentration[4].

$$\kappa \approx I_2\left(\frac{1}{\tau_1}-\frac{1}{\tau_2}\right)\propto \mathrm{C}_{\mathrm{defects}}$$

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