

## SUPPLEMENTARY INFORMATION

# Dehydrogenative lactonization of diols with platinum-loaded titanium oxide photocatalyst

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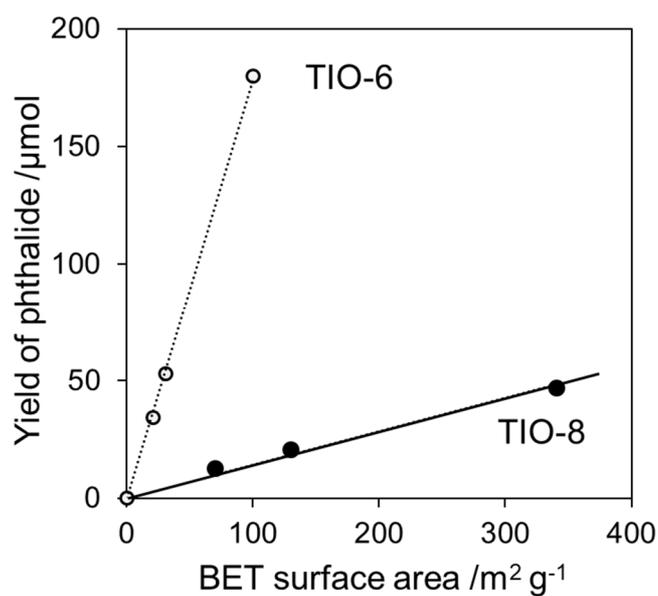
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## 1. Effect of the specific surface area of TiO<sub>2</sub> photocatalysts

The effect of the specific surface area on the photocatalytic activity was studied by using several Pt/TiO<sub>2</sub> samples prepared from TIO-6(R) and TIO-8(A) samples; TIO-6(R) was calcined at 623, 823, and 1023 K for 1 h and TIO-8(A) was calcined 623 and 823K for 1 h. The results are plotted in Fig. S1.

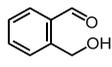
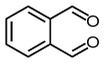


**Fig. S1** The effect of specific surface area of the photocatalysts on their photocatalytic activities of the rutile and anatase samples prepared by calcination of the Pt/TIO-6(R) and the Pt/TIO-8(A) samples. Reaction conditions were the same as those described in the caption of Fig. 1 in the main text.

## 2. Results of the reaction tests in various solvents

The solvent effect in the photocatalytic lactonization was also investigated in the presence of the Pt/TIO-8(A) sample. When the reaction was examined in water, 1,2-benzenedimethanol was slowly converted into phthalide in the presence of the Pt/TIO-8(A) sample (Table S1, entry 2). In contrast, the lactonization reaction well proceeded in acetone and THF and the yields of phthalide in these solvents were almost the same as, or higher than, that in acetonitrile (Table S3, entries 3 and 4). However, the homocoupling of acetone and THF also took place as well in these cases (Table S3, entries 3 and 4), while homocoupling of acetonitrile did not occur during the reaction in acetonitrile (Table S3, entry 1). These results can be explained by the bond dissociation energy of these compounds, *i.e.*, the C–H bond activation energy of acetonitrile ( $406 \text{ kJ mol}^{-1}$ ) is higher than that of THF ( $389 \text{ kJ mol}^{-1}$ ) and acetone ( $402 \text{ kJ mol}^{-1}$ ).<sup>S1</sup> These results indicate that the solvent affects the reaction rate and selectivity in the present photocatalytic lactonization reaction and the acetonitrile is the most suitable solvent among them due to the high C–H bond activation energy.

**Table S1.** Photocatalytic lactonization of 1,2-benzenedimethanol with the Pt/TIO-8(A) photocatalyst in various solvents <sup>a</sup>

Entry	Solvent	C–H bond dissociation energy / $\text{kJ mol}^{-1}$	Conv. (%)	Yield / $\mu\text{mol}$			Homocoupling product <sup>b</sup>	Phthalide	
								Yield (%)	Selec. (%)
1	Acetonitrile	406	>95	52	110	n.d. <sup>c</sup>	n.d.	30	30
2	Water	497	68	20	80	12	–	10	15
3	Acetone	402	90	70	120	n.d.	15	35	39
4	THF	389	>95	97	50	n.d.	47	49	49

<sup>a</sup> Reaction conditions: 200  $\mu\text{mol}$  of 1,2-benzenedimethanol dissolved in 4 mL of solvent, and the Pt/TIO-8(A) 0.1 g. The other conditions were the same as those described in the caption of Fig. 1 in the main text. <sup>b</sup> The homocoupling product from the solvents. <sup>c</sup> Not detected.

### 3. Experiments for adsorption and photocatalytic successive reaction of the product

To reveal the difference of the properties of the TiO<sub>2</sub> samples, some experiments, such as adsorption property and activity for the successive reaction of the product, were carried out and the results are shown in Table S2.

**Table S2.** Results of adsorption tests of 1,2-benzenedimethanol and phthalide, and reaction test for the photocatalytic successive reaction of phthalide.

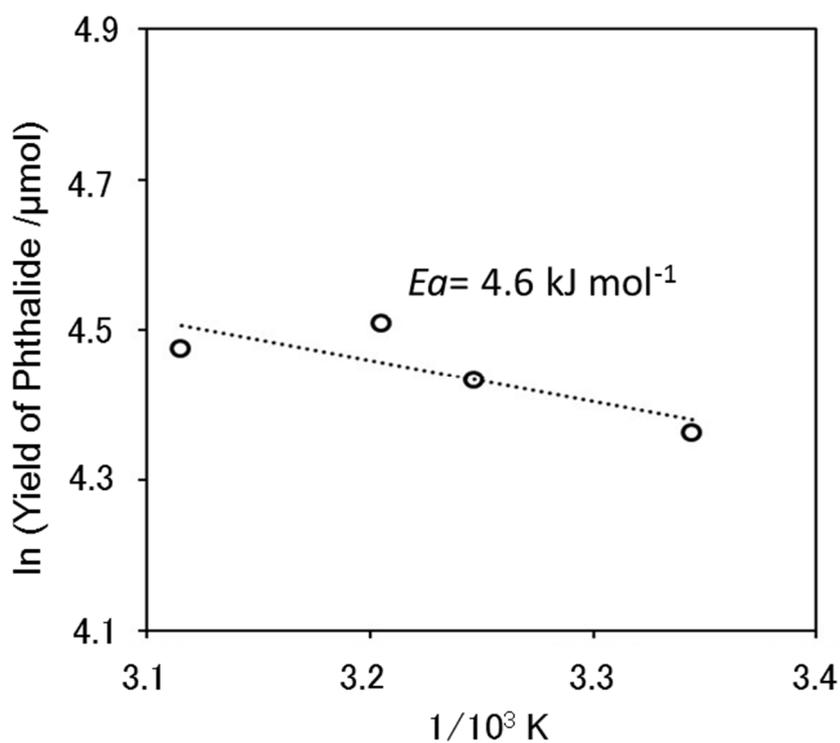
Entry	Sample	Crystal phase	Adsorbed amount of diol <sup>a</sup> (μmol)	Adsorbed amount of phthalide <sup>a</sup> (μmol)	Amount of phthalide after light irradiation <sup>b</sup> (μmol)
1	Pt/TIO-6	(R)	10	7	187
2	Pt/TIO-8	(A)	12	10	97
3	Pt/TIO-4	(A, R)	Trace	trace	77

<sup>a</sup> 20 μmol of benzenedimethanol or phthalide was dissolved in acetonitrile of 4 mL in the presence of 0.1 g of photocatalyst. After stirring in the dark for 10 min, the concentration of the compound was measured to calculate the adsorption amount. <sup>b</sup> Reaction conditions were the same as those described in the caption of Fig. 1 except for the use of 200 μmol of phthalide instead of 1,2-benzenedimethanol. Blank tests confirmed that phthalide and benzenedimethanol were not adsorbed by the reactor and phthalide did not decrease under the photoirradiation in the absence of the photocatalyst sample.

After 1 h light irradiation in the presence of phthalide with the Pt loaded TiO<sub>2</sub> photocatalyst, no compounds except phthalide were detected in the liquid phase by GC-MS and small amount of CO was detected in the gas phase by GC-TCD. These results show that phthalide was decomposed to other compounds to some extent although the products from phthalide were not detected except for CO. The Pt/TIO-8(A) sample decomposed phthalide more than the Pt/TIO-6(R) sample, suggesting that the high photocatalytic activity of anatase TiO<sub>2</sub> promoted the successive oxidation of phthalide. The rutile TiO<sub>2</sub> would have moderate photocatalytic activity to obtain phthalide without promoting the further reaction.

#### 4. Pseudo Arrhenius plot for the phthalide formation in the photocatalytic lactonization

The effect of the reaction temperature in the photocatalytic reaction was examined and the results are summarized in the pseudo Arrhenius plot as shown in Fig. S2.



**Fig. S2.** Pseudo Arrhenius plot for the phthalide formation from 1,2-benzenedimethanol with the Pt/TiO<sub>2</sub>-6(R) sample. A 70 mL of test tube was employed as a reactor. The other conditions were the same as those described in the caption of Fig. 1 except for the reaction temperature.

## 5. The coexistence effect of acid catalysts

The coexistence effect of heterogeneous acid catalysts was examined and the results are listed in Table S3.

**Table S3.** The lactonization of 1,2-benzenedimethanol by the physical mixture of the Pt/TiO-6(R) photocatalyst and acid catalyst <sup>a</sup>

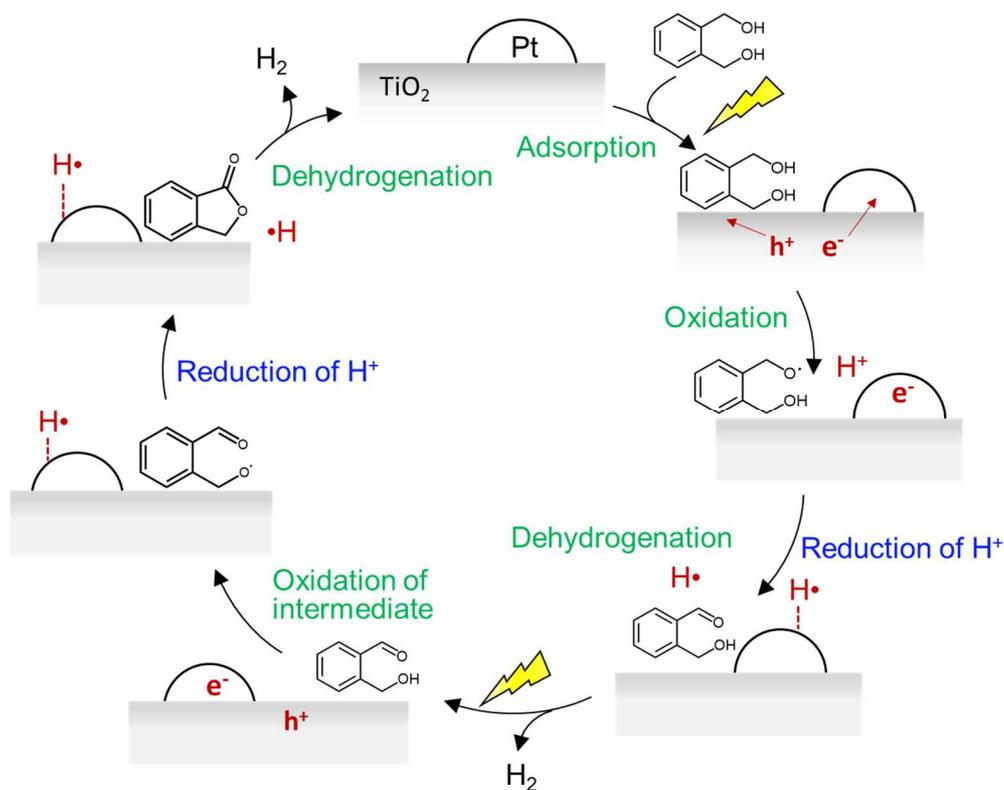
Entry	Additional acid catalyst (0.1 g)	Conversion (%)	Product / $\mu\text{mol}$		
			Phthalide (selec. % )	2-(hydroxymethyl) benzaldehyde	H <sub>2</sub>
1	-	90	110 (31)	240	250
2	TiO-6	81	100 (33)	210	200
3	Al <sub>2</sub> O <sub>3</sub>	98	200 (50)	172	320
4	TiNT <sup>b</sup>	98	230 (59)	72	310

<sup>a</sup> Reaction conditions: 400  $\mu\text{mol}$  of 1,2-benzenedimethanol, 4 mL of acetonitrile, 0.1 g of the Pt/ST-01 sample and 0.1 g of the additional acid catalyst. The other conditions were the same as those described in the caption of Fig. 1.

<sup>b</sup> Protonated titanate nanotube.

When TiNT (Protonated titanate nanotube)<sup>S2</sup> was used as an additional catalyst for the lactonization, the other reaction proceeded as well as lactonization. Analysis by using GC-MS showed that the product was an aromatic compound having CHO and/or OH group. Although this compound was not assigned yet, it would be formed via dehydration of starting compound or intermediate compound because TiNT has strong Brønsted acid sites.

## 6. Reaction mechanism of the photocatalytic lactonization



**Fig. S3.** Proposed reaction mechanism for two-step oxidation in the photocatalytic lactonization.

## Reference

- [S1] Y-R. Luo, *Handbook of bond dissociation energies in organic compounds*, CRS press, 2007.
- [S2] M. Kitano, K. Nakajima, J. N. Kondo and M. Hara, *J. Am. Chem. Soc.*, 2010, **132**, 6622; M. Kitano, E. Wada, K. Nakajima, S. Hayashi, S. Miyazaki, H. Kobayashi and M. Hara, *Chem. Mater.*, 2013, **25**, 385; E. Wada, M. Kitano, K. Nakajima and M. Hara, *J. Mater. Chem. A*, 2013, **1**, 12768.