## Supporting Information

# Visible-light Photocatalytic Mechanism of Bisphenol-A on Nano-$Bi_2O_3$: A combined DFT calculation and Experimental Study

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**1. Modeling of catalyst $Bi_2O_3$**

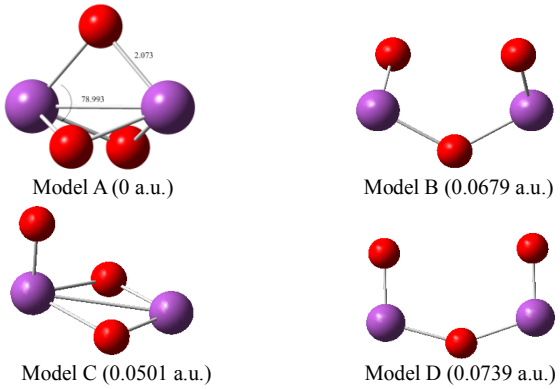


**Fig. S1.** Optimized structures of $Bi_2O_3$ catalyst. Data in parentheses are the relative energies referencing to Model A. (B3LYP/C H O 6-31G* Bi LanL2DZ .Red for oxygen and purple for bismuth).

**2. Preparation and Characterization of $Bi_2O_3$**

β-$Bi_2O_3$ nanosheets were prepared by a facile solvothermal calcining process similar to our previously reported method,[1] with just the replacement of D-fructose by glucose. Specifically, $Bi(NO_3)_3$•$5H_2O$ and glucose were first dissolved completely in ethylene glycol. Then the mixture was poured into a Teflonlined stainless-steel autoclave and incubated in an oven at 160 °C for 15 hours. After completion of the reaction, the precipitates were collected by centrifugation, washed several times with distilled water and ethanol to remove any ionic residue, and dried in an oven at 60 °C. Finally, the product obtained was calcined in the air at 300 °C for 1 hour in a muffle furnace.

The phase composition of the synthesized catalyst was characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advance (Bruker AXS, Germany) X-ray diffractometer with Cu K α. The morphology and structure were examined by transmission electron microscope (TEM, JEM-2100HR, Japan). It can be observed from Fig.S2a, that all diffraction peaks of the sample before and after calcination can be unambiguously assigned to the rhombohedral bismuth (JCPDS No. 85-1329) and tetragonal $Bi_2O_3$ (JCPDS No. 78-1793), respectively. The formation mechanism of β-$Bi_2O_3$ may be explained by both the "in situ reduction" and the "in situ oxidation" processes.[1] Then, the morphology of the as-synthesized β-$Bi_2O_3$ was characterized by the TEM technique, as show in Fig.S2b. , which clearly reveals its nanosheet structure.

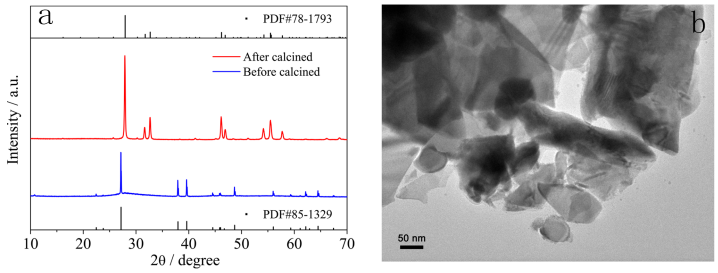


**Fig. S2** (a) XRD patterns of the sample before and after calcination at 300 °C; (b) TEM images of the sample after calcination.

**3. Materials and Reagents**

BPA, used as a target compound, was purchased from Sinopharm Group Chemical Reagent Co. Ltd. Stock solution was prepared by dissolving BPA in Milli-Q water to about 20mg $L^{-1}$. The chemicals used for the mobile phase of HPLC and HPLC-MS detections included HPLC-grade methanol and acetonitrile from Kermel Chemical (China) and Mill-Q ultrapure water.

**4. Degradation Experiments**

The photocatalytic degradation experiments were performed in a photochemical reactor (XPA-VII, Xujiang, China) equipped with a 1000 W Xe lamp combined with a 420 nm cutoff filter as the light source, and the system was cooled by a circulating water bath maintained at room temperature. All photocatalysis reactions were performed using the same initial conditions: 50 ml BPA solution (20 $mgL^{-1}$) was mixed with 50 mg catalyst under constant magnetic stirring. Before the irradiation, the mixture was stirred for 1 hour in the dark to allow the system to reach adsorption equilibrium. All of the samples, each 4ml in volume, were taken intermittently for analyses, and the solid was subsequently removed from the solution using a 0.45 μm nitrocellulose filter.

**5. Frontier orbital analysis**

According to the frontier orbital theory,[2-5] electrophilic, nucleophilic, and radical reactions occur respectively at the following sites: (1) For an electrophilic reaction, the site is where the electron density $f_e = 2\sum_i (C_{ri}^{HOMO})^2$ is the highest when the two electrons are in the highest occupied molecular orbital (HOMO) at ground state; (2) for a nucleophilic reaction, the site is where the electron density $f_n = 2\sum_i (C_{ri}^{LUMO})^2$ is the highest when the two electrons are in the lowest unoccupied molecular orbital (LUMO) at ground state; and (3) for a radical reaction, the site is where the density of the sum of each electron $f_r = \sum_i (C_{ri}^{HOMO})^2 + \sum_i (C_{ri}^{LUMO})^2$ is the highest when the two electrons are respectively in the HOMO and LUMO, where *r* is the index of atomic orbitals.

Table S1 Frontier electron densities on atoms of BPA calculated at the B3LYP/6-31G* level

| Atom | $f_e$ | $f_n$ | $f_r$ |
|---|---|---|---|
| $C_1$ | 0.00988 | 0.0772 | 0.0435 |
| $C_2$ | 0.0327 | 0.0277 | 0.0302 |
| $C_3$ | 0.0326 | 0.0277 | 0.0302 |
| $C_4$ | 0.165 | 0.0358 | 0.100 |
| $C_5$ | 0.0614 | 0.2873 | 0.174 |
| $C_6$ | 0.0253 | 0.2815 | 0.153 |
| $C_7$ | 0.0346 | 0.2916 | 0.163 |
| $C_8$ | 0.0908 | 0.2814 | 0.186 |
| $C_9$ | 0.114 | 0.0009 | 0.0573 |
| $C_{10}$ | 0.165 | 0.0358 | 0.100 |
| $C_{11}$ | 0.0253 | 0.2814 | 0.153 |
| $C_{12}$ | 0.0614 | 0.2872 | 0.174 |
| $C_{13}$ | 0.0908 | 0.2812 | 0.186 |
| $C_{14}$ | 0.0346 | 0.2915 | 0.163 |
| $C_{15}$ | 0.114 | 0.0010 | 0.0573 |
| $O_{16}$ | 0.162 | 0.0001 | 0.0811 |
| $O_{17}$ | 0.162 | 0.0001 | 0.0811 |

**6. Table S2 Total energy (a.u.) in gaseous phase and aqueous phase.**

| Gaseous phase | Sum of electronic and thermal Free Energies | Aqueous phase | Sum of electronic and thermal Free Energies | △E (Aqueous-Gaseous) |
|---|---|---|---|---|
| R1 | -967.742242 | R1 | -967.839565 | -0.097 |
| TS1 | -967.730243 | TS1 | -967.820792 | -0.091 |
| IM1 | -967.742182 | IM1 | -967.82694 | -0.085 |
| TS2 | -967.741875 | TS2 | -967.825167 | -0.083 |
| IM2 | -967.785585 | IM2 | -967.864088 | -0.079 |
| R2 | -619.792068 | R2 | -619.813863 | -0.022 |
| TS3-1 | -619.768886 | TS3-1 | -619.796484 | -0.028 |
| TS3-2 | -619.765423 | TS3-2 | -619.789343 | -0.024 |
| P1 | -619.787136 | P1 | -619.81526 | -0.028 |
| R3 | -653.628146 | R3 | -653.704132 | -0.076 |
| TS4 | -653.619956 | TS4 | -653.692816 | -0.073 |
| P2 | -653.624833 | P2 | -653.702302 | -0.077 |
| R4 | -650.812201 | R4 | -650.904411 | -0.092 |
| TS5 | -650.788518 | TS5 | -650.869877 | -0.081 |
| IM3 | -650.792784 | IM3 | -650.88459 | -0.092 |
| TS6 | -650.758196 | TS6 | -650.841401 | -0.083 |
| P3 | -650.905712 | IM4 | -650.937741 | |
| | | P3 | -650.985674 | -0.080 |
| R5 | -611.267250 | R5 | -611.336095 | -0.069 |
| TS7 | -611.230381 | TS7 | -611.309052 | -0.079 |
| IM5 | -611.237418 | IM5 | -611.317597 | -0.080 |
| TS8 | -611.206139 | TS8 | -611.280133 | -0.074 |
| P4 | -611.342889 | P4 | -611.420291 | -0.077 |
| R6 | -764.779260 | R6 | -764.852958 | -0.074 |
| TS9 | -764.761213 | TS9 | -764.8404 | -0.079 |
| P5 | -764.825701 | P5 | -764.894584 | -0.069 |

**Reference**

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