Supporting Information

**Topochemical transformation of low energy crystal facets to high energy facets: A case from Bi$_2$O$_2$CO$_3$ {001} facets to β-Bi$_2$O$_3$ {001} facets with improved photocatalytic oxidation of NO**

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Experimental details

Synthesis: Bi$_2$O$_2$CO$_3$ (BOC) particles were synthesized by modifying a reported method.$^1$ In a typical synthesis, 4.85 g of Bi(NO$_3$)$_3$·5H$_2$O were dissolved in 10 mL of 1 M HNO$_3$ aqueous solution and stirred for 30 min at room temperature to form a clear solution (denoted as solution A). In addition, 1.0 g of cetyltrimethylammonium bromide (CTAB) and 8.45 g of Na$_2$CO$_3$·10H$_2$O were added to 90 mL distilled water (denoted as solution B). Then, solution A was dropped into solution B with constant stirring. After 10 min of stirring, the resulting white precipitate was filtered, washed with distilled water and ethanol for three times and dried at 60 °C for 4 h to obtain BOC samples with no further treatment. The thermal treatment of BOC samples for preparing β-Bi$_2$O$_3$ were performed in a oven with temperature from 350 to 420 °C for 5 h under atmosphere and the obtained samples were denoted as BOC-350, BOC-380, BOC-400 and BOC-420 corresponding to the temperature at 350, 380, 400 and 420 °C, respectively.

Characterization: Powder X-ray diffraction (PXRD) analysis was conducted on a PANalytical X’pert diffractometer operated at 40 kV and 40 mA using Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 microscope. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo ESCALAB 250Xi with Al Kα emission at 1486.6 eV. All binding energies were referenced to the C 1s peak at 284.8 eV. Diffuse reflectance spectra (DRS) data were recorded on a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere using BaSO$_4$ as the reflectance standard sample. Absorbance values were transformed by the Kubelka-Munk method. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis were performed with DSC823 and TGA/SDTA85/e systems at a heating rate of 10 °C /min from 50 to 800 °C in nitrogen atmosphere. The Brunauer-Emmett-Teller (BET) surface area measurements were performed on a Quadrasorb SI in N$_2$-adsorption mode.

Theoretical calculations: All the first-principle calculations were performed with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional implemented in the CASTEP code. The electron wave function was expanded in a plane wave cutoff energy of 400 eV with Vanderbilt-type ultrasoft pseudopotentials. Monkhorst-Pack scheme with a k-points grid of 3×3×1 and 1×1×2 was employed for Bi$_2$O$_2$CO$_3$ and β-Bi$_2$O$_3$, respectively. Bi$_2$O$_2$CO$_3$ crystallizes in a body-centered orthorhombic Imm2 space group with lattice parameters of a= 3.865 Å, b=3.862 Å and c= 13.675 Å. β-Bi$_2$O$_3$ crystallizes in a tetragonal space group P-4b2 with cell constants of a=b=10.95 Å and c=5.63 Å. Both the atomic positions and lattice constants were relaxed for Bi$_2$O$_2$CO$_3$ and β-Bi$_2$O$_3$ with the SCF tolerance of 1.0×10$^{-6}$ eV/atom. Based on the optimized geometries, stoichiometric low miller index surfaces (001), (110) and (010) were cleaved by using the slab mode (Figure S1). A vacuum gap of 10 Å was used to separate the interactions between the periodic images perpendicular to the surface. The periodically repeated slab contained 96 and 80-atom
supercells for the planes of Bi$_2$O$_2$CO$_3$ and $\beta$-Bi$_2$O$_3$, respectively. Only the atomic positions were allowed to relax for the slab models.

**Photoelectrochemical and photocatalytic measurements:** All photoelectrochemical (PEC) measurements were conducted in a three electrode system on a CH 660D electrochemical work station, using the FTO glass with or without the prepared samples as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and Pt wire as the counter electrode, and potentials are quoted with respect to SCE. For photoelectrochemical tests, the working electrode was irradiated from the prepared films side under a 300 W Xe lamp. Incident visible-light was obtained by utilizing a 420 nm cutoff filter. Photocatalytic activity was investigated by removal of NO at ppb levels in a continuous flow reactor at ambient temperature. A 100 W tungsten halogen lamp was vertically placed outside the reactor. Required pieces of Bi films (2 × 2 cm) were placed on a dish accordingly. The NO gas was acquired from a compressed gas cylinder at a concentration of 100 ppm of NO (N$_2$ balance). The initial concentration of NO was diluted to about 550 ppb by the air stream. The desired relative humidity (RH) level of the NO flow was controlled at 50% by passing the zero air streams through a humidification chamber. The gas streams were premixed completely by a gas blender, and the flow rate was controlled at 2.4 L/min by a mass flow controller. After the adsorption-desorption equilibrium was achieved, the lamp was turned on. The concentration of NO was continuously monitored by a chemiluminescence NO analyzer (Thermo Environmental Instruments Inc., 42i-TL). The removal ratio (\(\eta\)) of NO was calculated as \(\eta \,(\%) = (1-c/c_0) \times 100\%\), where \(C\) and \(C_0\) are concentrations of NO in the outlet stream and the feeding stream, respectively.
Figure S1. Schematic bulk structure of Bi$_2$O$_2$CO$_3$ using Imm2 space group (1) with side view of (001) (a), (110) (b) and (010) (c) facet; β-Bi$_2$O$_3$ crystal using P-4b2 space group (2) with side view of (001) (d), (110) (e) and (010) (f) facet, respectively.
Figure S2. TG-DSC curves of the prepared Bi$_2$O$_2$CO$_3$ particles

Figure S3. PXRD patterns of the prepared Bi$_2$O$_2$CO$_3$ and the samples after annealing at different temperatures. The reference pattern of tetragonal Bi2O2CO3 (JCPDS No. 41-1488) is shown at the bottom.
Figure S4. UV-vis absorption spectra of the prepared Bi$_2$O$_2$CO$_3$ and the samples after annealing at different temperatures.

Figure S5. XRD pattern and SEM image of the commercial β-Bi$_2$O$_3$ particles.