Supporting Information

Topochemical transformation of low energy crystal facets to high energy facets: A case from $Bi_2O_2CO_3$ {001} facets to β-Bi_2O_3 {001} facets with improved photocatalytic oxidation of NO

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Experimental details

Synthesis: $Bi_2O_2CO_3$ (BOC) particles were synthesized by modifying a reported method.[1] In a typical synthesis, 4.85 g of $Bi(NO_3)_3 \cdot 5H_2O$ 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 $Na_2CO_3 \cdot 10H_2O$ 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_2O_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 ^oC /min from 50 to 800 ^oC in nitrogen atmosphere. The Brunauer-Emmett-Teller (BET) surface area measurements were performed on a Quadrasorb SI in N_2-adsoeption 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 pesudopotentials. Monkhorst-Pack scheme with a *k*-points grid of 3×3×1 and 1×1×2 was employed for $Bi_2O_2CO_3$ and *β*-Bi_2O_3, respectively. $Bi_2O_2CO_3$ crystallizes in a body-centered orthorhombic *I*mm2 space group with lattice parameters of a= 3.865 Å, b=3.862 Å and c= 13.675 Å. *β*-Bi_2O_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 $Bi_2O_2CO_3$ and *β*-Bi_2O_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 $Bi_2O_2CO_3$ and β-Bi_2O_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 (η) of NO was calculated as η (%) = (1-c/c_0) ×100%, where C and C_0 are concentrations of NO in the outlet stream and the feeding stream, respectively.

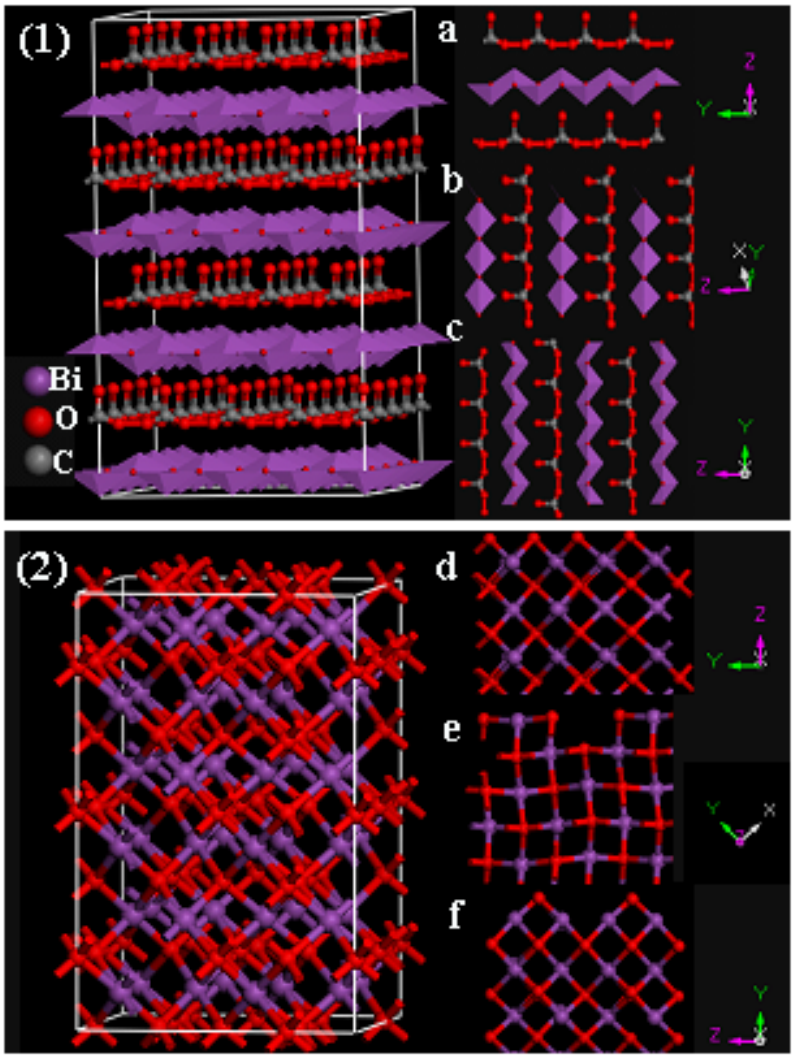

Figure S1. Schematic bulk structure of $Bi_2O_2CO_3$ using Imm2 space group (1) with side view of (001) (a), (110) (b) and (010) (c) facet; β-Bi_2O_3 crystal using P-4b2 space group (2) with side view of (001) (d), (110) (e) and (010) (f) facet, respectively.

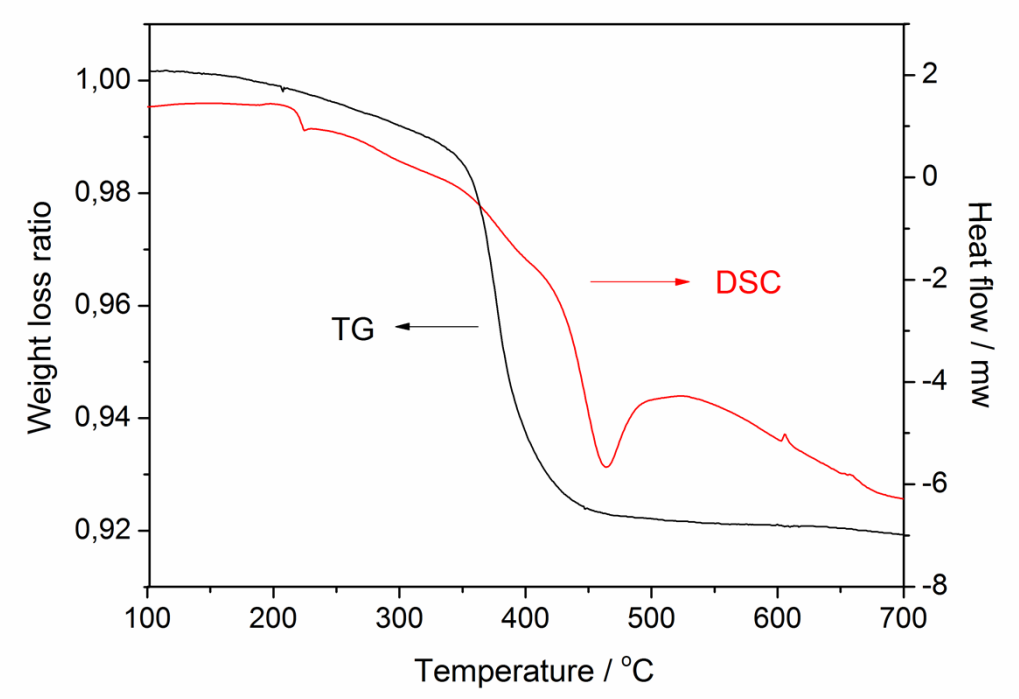

Figure S2. TG-DSC curves of the prepared $Bi_2O_2CO_3$ particles

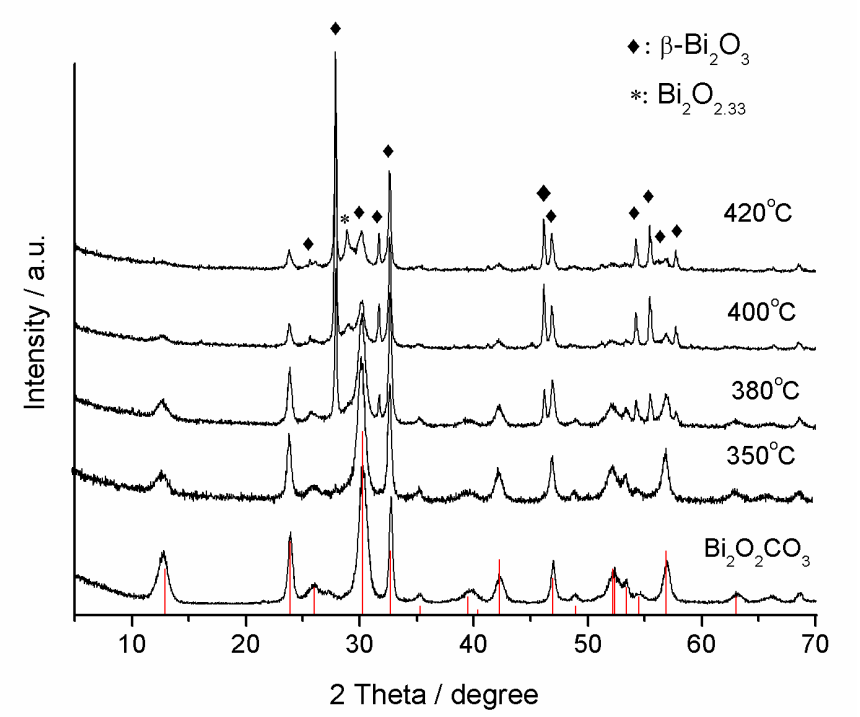

Figure S3. PXRD patterns of the prepared $Bi_2O_2CO_3$ and the samples after annealing at different temperatures. The reference pattern of tetragonal Bi2O2CO3 (JCPDS No. 41-1488) is shown at the bottom.

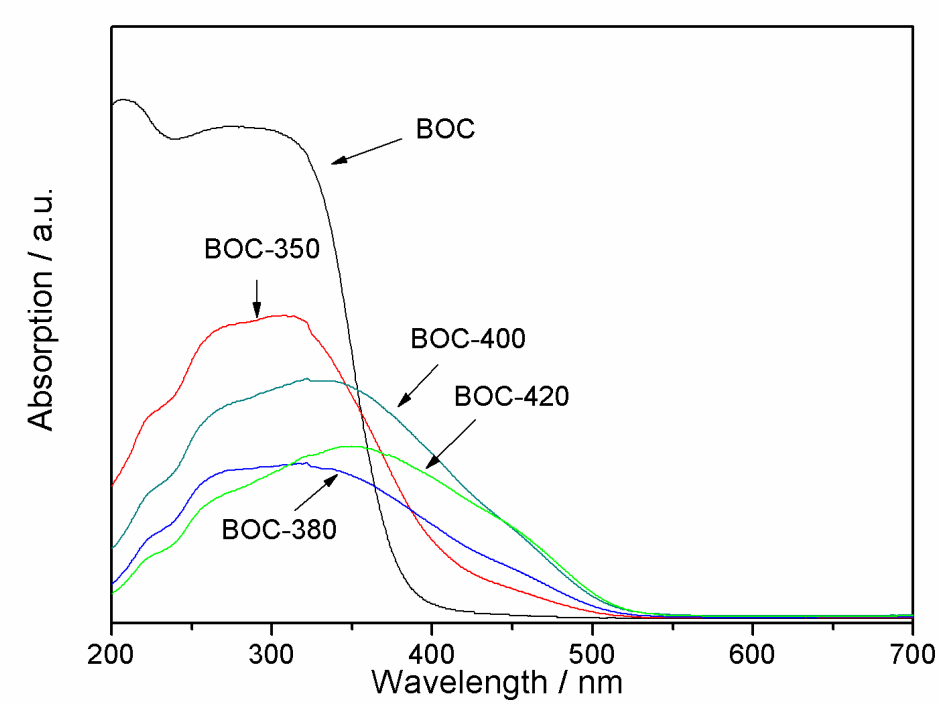

Figure S4. UV-vis absorption spectra of the prepared $Bi_2O_2CO_3$ and the samples after annealing at different temperatures.

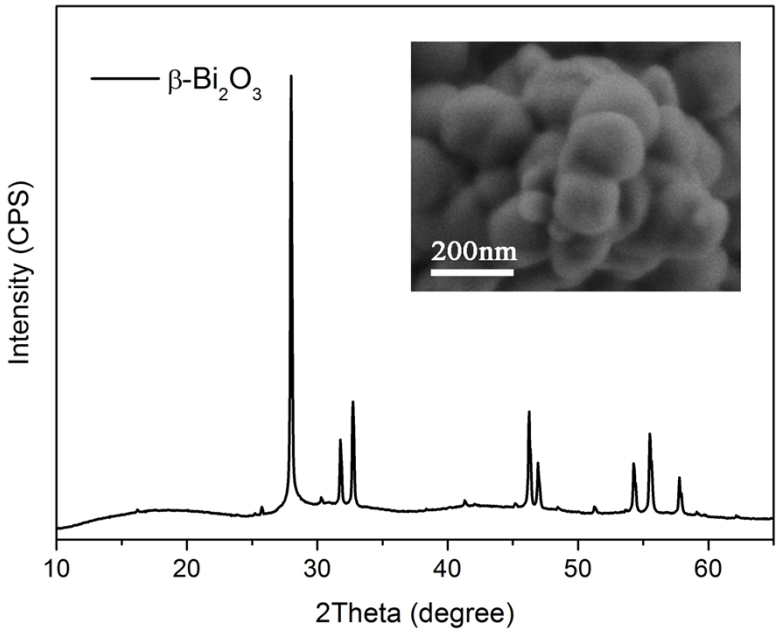

Figure S5. XRD pattern and SEM image of the commercial β-Bi_2O_3 particles.