Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information
Nontraditional Template Synthesis of Microjagged Bismuth Oxide: A Highly Efficient Visible Light Responsive Photocatalyst

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[1] Experimental section:

Synthesis of free-standing Bi_2O_3 with 3D jagged morphology and relative H_2O_2-treated samples:

In a typical process, $Bi(NO_3)_3{\cdot}5H_2O$ (0.97 g, 2 mmol) and WO_3 (0.187 g, 1 mmol) powders were dissolved into 40 ml distilled water. After the mixture was ultrasonicated for about 30 min, the mixed solution was transferred to a Teflon-lined stainless steel autoclave with a capacity of 100 mL and put into a pre-heated oven and kept at 180 ^oC for 24h. After reaction, the obtained precipitates were filtered and washed with distilled water several times and dried in air at room temperature. After drying, the WO_3 template was removed by selective dissolution in a 5 M NaOH solution at 95 ^oC for 24h to yield free-standing Bi_2O_3 photocatalysts. The as-prepared Bi_2O_3 samples were subsequently immersed into 30 % H_2O_2 solution and washed sufficiently to ensure no residual H_2O_2 in samples, and the final H_2O_2-treated Bi_2O_3 with different surface Bi_2O_{4-x} content can be obtained at different immersion time.

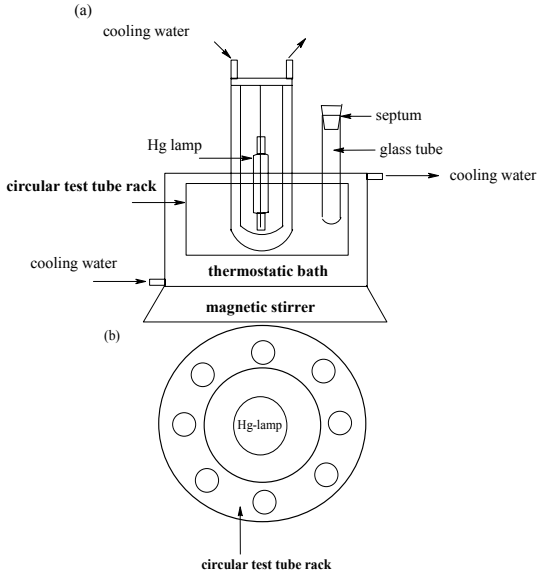
Characterization: A Hitachi S-4800 field emission scanning electron microscope (FESEM, Hitachi CO. Ltd. S-4800) was utilized to the morphology investigation. TEM images were collected by using a JEOL JEM 2010F microscope working at 200 kV. X-ray diffraction (XRD, Rigaku D/Max-2550pc) measurements were carried out using filtered Cu *Kα* radiation. Energy dispersive X-ray analysis (EDXA, Inca Energy-200) is used to investigate the sample composition. A Shimadzu UV-1601PC spectrophotometer was used to record the UV-vis spectra of the sample. The chemical state transition of surface element was determined by X-ray Photoelectron Spectroscopy (XPS, JEOL, JPS-9010MCY)

Photocatalytic activity measurement: The overall photocatalytic activity was tested as the amounts of CO_2 gas that generated from the oxidation decomposition of aqueous acetaldehyde solution (0.25 vol%, ca.85 μmol) containing a suspension of the photocatalyst powder (40 mg) under the irradiation of UV lamp with the cutoff filters ($\lambda > 400$ nm and $\lambda > 320$ nm) at 25^oC. The irradiation intensity measured by radiometer between 320 to 380 nm was about 8% in the total spectrum of UV lamp. For photocatalysis experiments, the rate of agitation was set at 700 rpm. The reaction stoichiometry of acetaldehyde solution has been ascertained to be following:

$$CH_3CHO + 5/2\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

The CO_2 concentrations were measured using a gas chromatography (Align model GC-6890N) equipped with a 2 m Porapak-Q column, a methanizer, and a flame ionization detector, using N_2 as the carrier gas.

Photocatalytic reactor: A photocatalytic reactor was used in this study and the schematic details are depicted in Scheme S1. An ultrahigh-pressure Hg lamp (500 W) was located in the center of the reactor along the axis and protected by a water-cooled quartz jacket. At the bottom of the reactor a magnetic stirrer was used to achieve effective dispersion agitating mechanically. A circular test tube rack was inserted on the thermostatic bath to hold up the Pyrex glass tubes. Thus the UV light was collected into the glass tube and ensured the photocatalytic reaction performed uniformly and completely. The reactor was fitted with a magnetic stirrer for stirring at 700 rpm to keep the catalyst in suspension.



Scheme S1. The schematic illustration of the cylindrical photocatalytic reactor: (a) cross-sectional view, (b) top view.

[2] EDXA analysis

Composition of the 3D superstructure in different parts was checked using an X-ray energy spectrometer (EDS). The body of the peak part is composed of Bi and O with the ratio of Bi to O approximately equal to 2:3 (EDS1), conforming to the chemical formula of Bi_2O_3. The coronal part, however, shows the presence of W and O with the ratio of 1:3 in EDS2. That is to say, the whole component unit is made up of WO_3 in the coronal and Bi_2O_3 in the peak part.

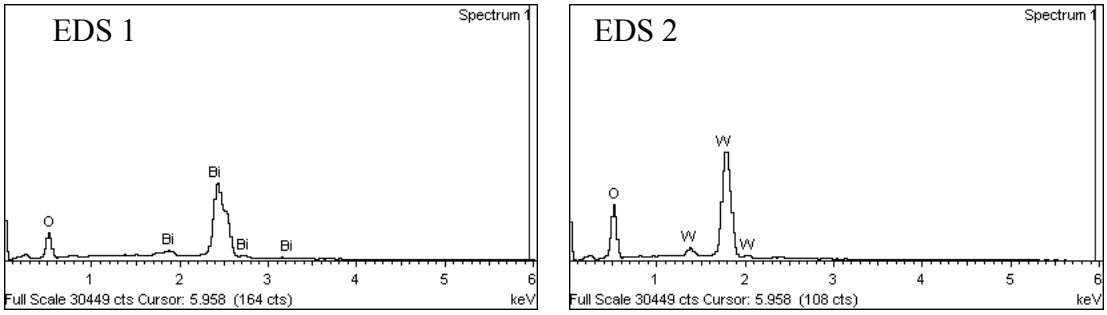


Fig. S1. EDS1 and EDS2 are EDS profiles of the nanocomposite shown in figure 1(b), in the two areas marked by frames.

[3]SEM analysis

Fig. S2a-c show the SEM images of 3D mircrojagged Bi_2O_3 nanocomposites prepared at 150 ^oC, 180 ^oC and 210 ^oC. It can be observed that only the reaction at 180 ^oC gave the optimal 3D mircrojagged Bi_2O_3 nanocomposites. The assembly of tooth units showed the disorder and obscure under the preparation condition of 150 ^oC and 210 ^oC. This may be attributed that the temperature effect has great influence on the hydrolysis rate of bismuth salt and finally affects the formation of microjagged morphology.

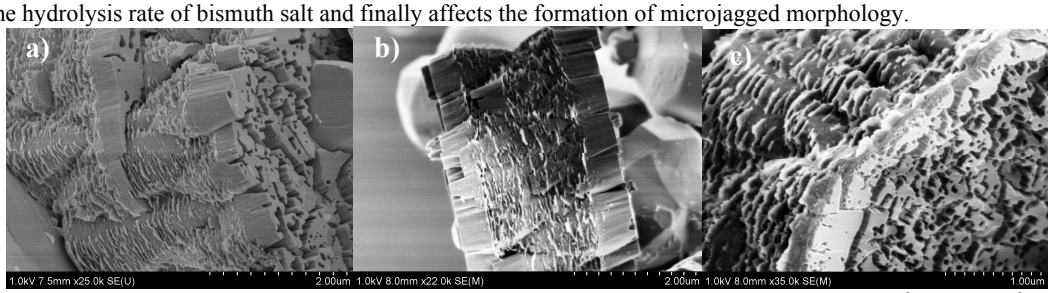


Fig. S2. SEM images of 3D microjagged Bi_2O_3 nanocomposites prepared at different temperatures. (a) 150 ^oC, (b) 180 ^oC and (c) 210 ^oC

[4] XRD analysis

The X-ray diffraction (XRD) profile of the H_2O_2-treated Bi_2O_3 shows the presence of a main phase, monoclinic Bi_2O_3 (α-Bi_2O_3), with a minor phase exhibiting two characteristic reflections at 2θ= 27.9° and 32.3°. The two characteristic reflections can be clearly indexed with the formation of the oxidized Bi_2O_{4-x} species [1] on the surface of α-Bi_2O_3. With extending the immersion time, the surface Bi_2O_3 phase can be gradually covered by surface Bi_2O_{4-x} phase.

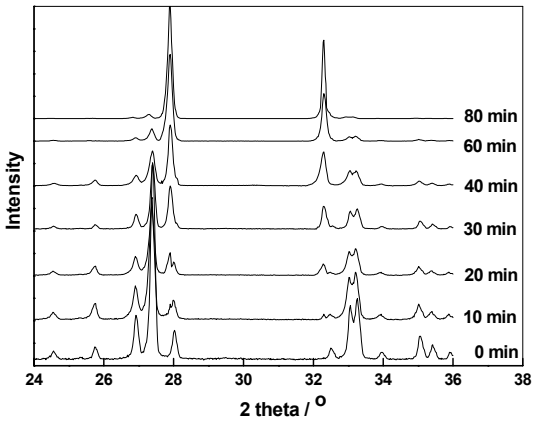


Fig. S3. The XRD patterns of the samples treated at different immersion time in H_2O_2 solution.

[5] XPS analysis for the samples

The chemical state transition of surface element was determined by X-ray Photoelectron Spectroscopy (XPS). For bare Bi_2O_3, the peaks located at 161.754 eV and 166.983 eV are assigned to Bi 4f 7/2 and Bi 4f 5/2 region (Fig. S4a). However, it is clear that the corresponding binding energy assigned to Bi 4f 7/2 and Bi 4f 5/2 region shifts to 161.031 eV and 166.428 eV (Fig.S4b) after H_2O_2 treatment, suggesting that the surface was highly oxidized and formed Bi_2O_{4-x} species.

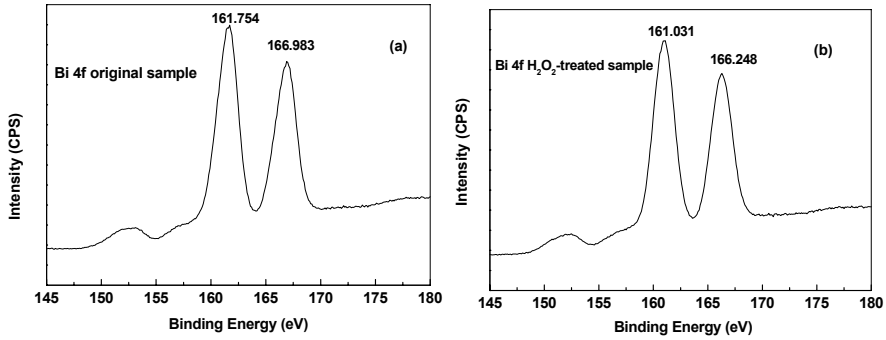


Fig. S4. The high-resolution XPS spectra of (a) Bi 4f region of pure Bi_2O_3 and (b) Bi 4f region of H_2O_2-treated Bi_2O_3 samples.

[6] UV-vis spectra of the samples

Fig. S5 presents the UV/Vis spectra of pure Bi_2O_3 and H_2O_2-treated Bi_2O_3 samples. The microjagged Bi_2O_3 samples are light-yellow in color and the final H_2O_2-treated Bi_2O_3 samples appear brown. It is known that the optical absorption coefficient near the band edge follows the equation $(\alpha h\nu)^2=A(h\nu-Eg)$ for a direct-bandgap material in which α, h, ν, Eg, and A are the absorption coefficient, Planck constant, light frequency, band gap, and a constant, respectively [2]. This relationship gives the band gap (Eg) by extrapolating the straight portion of $(\alpha h\nu)^2$ against hν plot to the point α= 0, which are about 2.3 eV and 2.8 eV for H_2O_2-treated Bi_2O_3 samples and pure Bi_2O_3. The high band gap value of the mixed material can be explained as originating from bulk O(2p)-Bi^{3+}($6p^o$) and surface O(2p)-Bi^{5+}($6s^o$) transitions made available by H_2O_2 treatment.

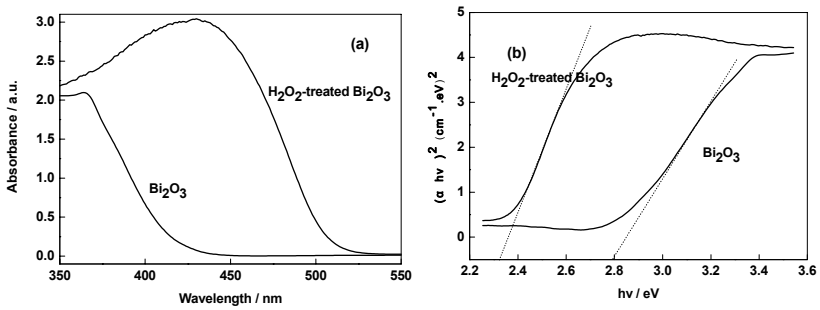


Fig. S5. (a) UV-vis spectrum for the as-prepared Bi_2O_3 samples analyzed by the diffuse reflectance method. Adsorption coefficient (α) was obtained by the Kubelka-Munk method; (b) the square of adsorption coefficient α vs. photon energy.

[7] HRTEM image of the H_2O_2-treated Bi_2O_3 sample

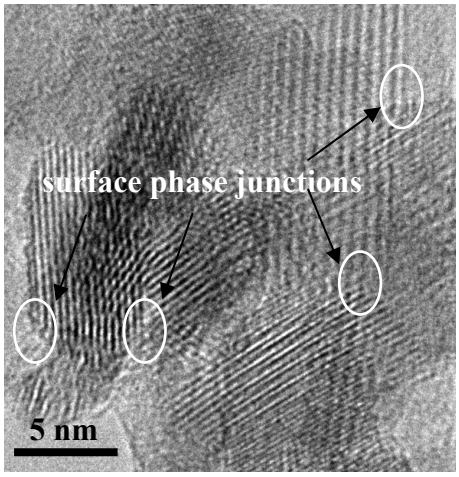


Fig. S6. TEM image obtained from a H_2O_2-treated Bi_2O_3 sample

Reference

[1] A. Hameed, T. Montini, V. Gombac, P. Fornasiero. *J. Am. Chem. Soc.* **2008,** *130*, 9658–9659.

[2] M. A. Butler. *J. Appl. Phys.* **1977**, *8*, 1914-1920.