Formation of Bi$_2$WO$_6$ Bipyramids with Vacancy Pairs for Enhanced Solar-Driven Photoactivity

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In order to improve the photoactivity, many attempts have focused on increasing the exposure of highly reactive surfaces on crystals. However, the connection between the reactive surfaces and enhancement is still elusive. Herein, Bi$_2$WO$_6$ nanostructured bipyramids with a large fraction of {100} facets are fabricated by the solvothermal method. The formation of “Bi–O” dimer vacancy pairs on the {100} high-energy facets is responsible for the reduction in band gap and the decrease in the recombination of photo-excited charge carriers, which is unambiguously confirmed by the positron annihilation spectra (PAS), X-ray photoelectron spectrum (XPS), and theoretical calculations. The effective separation of electron–hole pairs and the narrowing bandgap significantly improve the photocatalytic activity of Bi$_2$WO$_6$ nanobipyramids, especially under solar light irradiation. These findings can be applied broadly to the design and fabrication of energy efficient and robust catalysts.

1. Introduction

Both energy and the environment are vital topics for human survival. Heterogeneous photocatalysts offer great potential for converting solar energy into chemical energy and for the environmental remediation.[1–5] Typical examples are TiO$_2$-based photocatalytic decomposition of organic contaminants and environmental remediation. Therefore, modifying the physical morphology, to achieve more high energy surfaces in Bi$_2$WO$_6$, becomes an important alternative strategy for enhancing its photoactivity.[25] By exposing high-energy surfaces can enhance the photovoltaic and photocatalytic properties of a catalyst.[26–29] Specifically, by increasingly exposing the high-energy facets in Bi$_2$WO$_6$ can improve the effective separation of electron–hole pairs, thereby arriving at the fabrication of more efficient catalysts. Moreover, to deduce the relationship between the ratio of high energy surface and the enhanced effect, the overwhelming majority of researchers have only fixed their attention on the strength of the interaction of the reactive surfaces with reactant molecules.[30] However, this explanation does not fully explain the enhancement. Recently, there are reports that these reactive facets are accompanied always by various types of surface defects.[31–33] Furthermore, with recent advances in scanning tunneling microscopy (STM), electron paramagnetic resonance spectroscopy (EPR), and positron annihilation spectroscopy (PAS),[34–36] the role of defects in photocatalysis now can be thoroughly studied. In contrast to bulk defects, which only act as trap sites for charge carriers, surface defects can be adsorption sites where charge carriers can be transferred more easily to the adsorbed species, thereby impeding their recombination and enhancing the photocatalytic efficiency. Therefore, it is hypothesized that surface defects on the reactive surfaces of a crystal can play an important role in controlling the photocatalytic efficiency.
Herein, a facile procedure was used to fabricate Bi$_2$WO$_6$ nanobipyramids that have high density of high-energy facets. The photoelectric and photocatalytic characteristics of this Bi$_2$WO$_6$ nanobipyramids will be more photosensitive than those Bi$_2$WO$_6$ plates. In addition, the defects in the bipyramid-structured Bi$_2$WO$_6$ were characterized thoroughly by various surface and crystal chemistry techniques and verified by theoretical computations such as density of states and density function theory, as well as experimental techniques such as electrochemical impedance spectroscopy (EIS) and UV–vis light spectrophotometry as to gain insights into the effect of defects on photocatalytic properties.

2. Result and Discussion

The X-ray powder diffraction (XRD) patterns of the Bi$_2$WO$_6$ samples are shown in Figure 1. The peaks can clearly identify the orthorhombic phase of Bi$_2$WO$_6$ (JCPDS 39-0256). However, it is worth noting that obvious changes in the intensity ratios for various peaks can be observed. More specifically, in the case of plate-structured Bi$_2$WO$_6$ (P-Bi$_2$WO$_6$), the intensity ratio of the {200} to {113} facet was 0.3, which was remarkably smaller than 0.6 of bipyramid-structured Bi$_2$WO$_6$ (B-Bi$_2$WO$_6$). This indicated that B-Bi$_2$WO$_6$ with a larger fraction of {100} crystalline planes was fabricated successfully.

The morphologies of Bi$_2$WO$_6$ samples were characterized by FESEM. The products from the hydrothermal synthesis appear as 2D plates, and their morphologies were significantly affected by the pH conditions. When the pH was 1.0, the Bi$_2$WO$_6$ appeared of peony-like aggregations convoluted by lots of 2D nanoplates, which are denoted as P-Bi$_2$WO$_6$ (Figure 2a). As pH increased, the flower structure was disaggregated due to the anisotropic growth of the Bi$_2$WO$_6$ nanoplates (Figure S1b–d, Supporting Information). In the process of solvothermal synthesis, the polyvinylpyrrolidone (PVP) was utilized for modifying the morphology. Bipyramid-structured Bi$_2$WO$_6$ could be obtained in the presence of PVP (Figure 2c), while irregular Bi$_2$WO$_6$ nanoparticles were formed without PVP (Figure S2, Supporting Information). This is ascribed to the selective interactions between the PVP molecules and the specific planes of the Bi$_2$WO$_6$, which could significantly inhibit the anisotropic growth of {113} facets. During the nucleation process, the “–C=O” in the PVP unit prefers to interact with the unsaturated atoms in order to reduce surface energy. Therefore, the unsaturated “W” atoms on the Bi$_2$WO$_6$ surface are more active for bonding with PVP. Thus, with the shrinkage...

Figure 1. XRD spectra of plate-structure Bi$_2$WO$_6$ (P-Bi$_2$WO$_6$) (hydrothermal synthesis, pH = 1) and bipyramid-structured Bi$_2$WO$_6$ (B-Bi$_2$WO$_6$) (solvothermal synthesis, with PVP).

Figure 2. a) SEM and b) HRTEM images of the P-Bi$_2$WO$_6$ (hydrothermal synthesis, pH = 1); c) SEM and d) HRTEM images of the B-Bi$_2$WO$_6$ (solvothermal synthesis, with PVP) (inset showing their fast-Fourier transform patterns and the corresponding schematic drawings).
of the restricted planes and continuous enlargement of the other planes, a bipyramid structure evolved. Furthermore, the HRTEM image revealed also the crystalline details of Bi$_2$WO$_6$. In the P-Bi$_2$WO$_6$ crystal, the spacing at the lattice fringes was found to be 3.15 Å, which was corresponding to the {113} plane (Figure 2b) and was the most stable facet in Bi$_2$WO$_6$.\[14\] In addition, a truncated bipyramid of a B-Bi$_2$WO$_6$ nanocrystal was carefully analyzed by the HRTEM. The fringe spacing of 3.15 Å corresponds to {113} planes, while the spacing of 2.73 Å corresponds to {200} planes (Figure 2d). The above fringe spacing and the angle in the fast-Fourier transform (FFT) image (Figure 2d, inset) implied that the top/bottom surfaces of the truncation are bound by a (100) facet. The inset in Figure 2b,d shows sketched crystal structures of the P-Bi$_2$WO$_6$ and B-Bi$_2$WO$_6$, respectively.

Furthermore, the photoelectrochemical properties of the two types of Bi$_2$WO$_6$ were investigated. First, the conversion activity of photons to current was measured via photocurrent action spectra. Generally, higher photocurrent corresponds to higher separation efficiency for the photogenerated electron–hole pairs, and thus represents higher photoactivity.\[42,43\] Figure 3a shows the photoactivity of different Bi$_2$WO$_6$ photocatalysts including P25 TiO$_2$ for the purpose of comparison. Results clearly show that the plated-structured Bi$_2$WO$_6$ has a lower photocurrent property in the region from 300 to 360 nm in contrast to P25 TiO$_2$. However, as the morphology converted to bipyramid, the B-Bi$_2$WO$_6$ with an extensive number of {100} facet achieved much higher photocurrent efficiency than that of P-Bi$_2$WO$_6$. The maximum photocurrent of B-Bi$_2$WO$_6$ approximated to that of P25 TiO$_2$ in the region from 335 to 345 nm. Furthermore, in the region from 345 to 420 nm, even in visible light region (>420 nm), higher photocurrent was achieved in B-Bi$_2$WO$_6$, which could be benefit to the efficient utilization of the solar-light resource.

In addition, the effect of morphology on the photoresponse of Bi$_2$WO$_6$ was evaluated using chronoampermetric technique at +0.3 V. Upon power excitation, both types of Bi$_2$WO$_6$ displayed instantaneous photocurrent, which was then promptly returned to a steady state when the light was turned off. Notably, the bipyramid-structured B-Bi$_2$WO$_6$ showed a photocurrent density of 24 µA cm$^{-2}$, almost ten times that of the plate-structured P-Bi$_2$WO$_6$ (Figure 3b) under solar light irradiation. A similar trend was also observed under visible-light irradiation, except that the peak photocurrent was much smaller than that under solar light for both Bi$_2$WO$_6$ samples (Figure 3c).

It is proposed that when the Bi$_2$WO$_6$ crystal containing more {100} facets will benefit the separation of photogenerated charge carriers. Figure 3d shows the Nyquist plot of results of electrochemical impedance spectroscopy (EIS) for both Bi$_2$WO$_6$ electrodes in dark and under light illumination. Results showed that the electrical resistance of both photocatalysts was smaller under light irradiation than that in dark as indicated by the
smaller semicircle of the Nyquist plot. Furthermore, in contrast to the P-Bi$_2$WO$_6$, the bipyramid-structured B-Bi$_2$WO$_6$ exhibited much smaller electrical resistance both in dark and under light irradiation, indicating that the structure facilitated charge transfer.

To clarify the underlying mechanism of the higher photoactivity for the Bi$_2$WO$_6$ bipyramids relative to plates, a density function theory (DFT) was performed to calculate the surface energy of the {100} and {113} facets of Bi$_2$WO$_6$. The calculation results show that the surface energy of the {100} facet (1.21 J m$^{-2}$) is higher than that of the {113} facet (1.02 J m$^{-2}$), implying that {100} facets should be more reactive than {113} facets. Generally, during the nucleation process of the catalysts, in order to maintain these surfaces with the high energy as much as possible, there occurs large-scale atom reconstruction on those facets, which leads to the formation of defects, accordingly.$^{[44,45]}$ Therefore, it is speculated that the Bi$_2$WO$_6$ with a...
greater proportion of {100} facets would possess more surface defects, which serve as the major sites that increase the transfer of photoexcited charge carriers.

The presence of defects was further verified by the positron annihilation measurements. Table 1 shows the three positron lifetime components, \( \tau_1 \), \( \tau_2 \), and \( \tau_3 \), with intensities \( I_1 \), \( I_2 \), and \( I_3 \). \( \tau_3 \) is due to the annihilation of orthopositronium atoms formed in the large voids present in the material.\(^{46,47}\) \( \tau_1 \) generally results from the small-size defects that exist in the bulk.\(^{48,49}\) \( \tau_2 \) derives from the positrons trapped by the larger size defects, which are mainly located on the surface of the materials.\(^{50}\) The relative intensity \( (I) \) reflects the concentrations of the corresponding defects.\(^{51}\) Results showed that the \( I_1/I_2 \) ratio was 0.6 and 1.22 for B-Bi\(_2\)WO\(_6\) and P-Bi\(_2\)WO\(_6\) respectively, indicating a higher concentration of surface defects in the B-Bi\(_2\)WO\(_6\). In order to further identify the species making up the surface defects in B-Bi\(_2\)WO\(_6\), the XPS measurements were performed to reveal the electronic structure of the two types of Bi\(_2\)WO\(_6\). As depicted in Figure 4, the two Bi\(_2\)WO\(_6\) samples are composed of four elements, Bi, O, W, and adventitious carbon. Besides, based on quantitative results areas, the atomic ratio of Bi and W in P-Bi\(_2\)WO\(_6\) surface is calculated to be 2 ± 0.021, while the value is 1.9 ± 0.01:1 in B-Bi\(_2\)WO\(_6\). In comparison with P-Bi\(_2\)WO\(_6\), the peak of W 4f\(^{7/2}\) in B-Bi\(_2\)WO\(_6\) shifted from 35.83 to 35.42 eV, indicating the variation of the electron density close to the W atoms due to the deficiency of Bi on the surface.\(^{52-54}\) Meanwhile, according to the results of DFT calculations, the similar electronic environment appeared upon the introduction of “Bi–O” vacancy pairs on the {100} facet. Therefore, we speculated that the “Bi–O” dimer vacancy should be the most likely defect on the {100} facet in B-Bi\(_2\)WO\(_6\).

Question arises, how the “Bi–O” vacancies affect the photocatalytic activity of Bi\(_2\)WO\(_6\)? Figure 5a depicts the structure of a perfect Bi\(_2\)WO\(_6\) {100} facet, which is constructed of perovskite-like (WO\(_4\))\(^{2-}\) and alternating (Bi\(_2\)O\(_2\))^\(^+\) units. Interestingly, after the introduction of dimer “Bi–O” vacancy pairs, the structure of the optimized model of the defect Bi\(_2\)WO\(_6\) appears seriously distorted (Figure 5b), which can provide a larger space for polarizing the related atoms and orbitals, improving the separation efficiency of the electron–hole pairs.\(^{55,56}\) To further verify the hypothesis, the transient infrared absorption for the two Bi\(_2\)WO\(_6\) samples was subsequently measured. The transient infrared technique has been extensively used to study photocatalysts for understanding the optical transition of the photoelectron pairs in the conduction band. And the absorbance intensity at 2000 cm\(^{-1}\) of the time-resolved infrared

| Sample  | \( \tau_1 \) | \( \tau_2 \) | \( \tau_3 \) | \( I_1 \) | \( I_2 \) | \( I_3 \) | \( I_1/I_2 \) |
|---------|------------|------------|------------|--------|--------|--------|-----------|
| P-Bi\(_2\)WO\(_6\) | 190.4 | 463 | 2,486 | 54.21 | 44.53 | 1.26 | 1.22 |
| B-Bi\(_2\)WO\(_6\) | 184.1 | 402 | 2,426 | 37.05 | 61.41 | 1.54 | 0.60 |

Figure 6. Transient IR absorption spectra of a) B-Bi\(_2\)WO\(_6\) (solothermal synthesis, with PVP) and c) P-Bi\(_2\)WO\(_6\) (hydrothermal synthesis, pH = 1); time profiles of absorbance at 2000 cm\(^{-1}\) of b) B-Bi\(_2\)WO\(_6\) and d) P-Bi\(_2\)WO\(_6\) irradiated by 355 nm pulses in vacuum.
absorption spectroscopy (TAS) reflects the quantity of photoexcited electrons, while the decay is due to their recombination with holes.\textsuperscript{12,57} As shown in Figure 6a,c, at the onset of a laser pulse, there were rapid rises of the absorption peaks observed in both B-Bi\textsubscript{2}WO\textsubscript{6} and P-Bi\textsubscript{2}WO\textsubscript{6}. It was also noted that there was much stronger intensity of the IR absorption or higher concentration of photoexcited electrons generated on B-Bi\textsubscript{2}WO\textsubscript{6} surface.\textsuperscript{58} The absorbance was barely measurable at 80 µs in P-Bi\textsubscript{2}WO\textsubscript{6}, whereas there was still considerable absorbance intensity observed at 350 µs in B-Bi\textsubscript{2}WO\textsubscript{6}, which signifies a lower recombination of the electron–hole pairs (Figure 6b,d). Results clearly indicated that both the quantity (concentration) and the quality (lifetime) of photoelectrons on B-Bi\textsubscript{2}WO\textsubscript{6} were significantly greater than on P-Bi\textsubscript{2}WO\textsubscript{6}, which is in close agreement with results of DFT calculations.

In addition, the density of states (DOS) of Bi\textsubscript{2}WO\textsubscript{6} was studied. For perfect Bi\textsubscript{2}WO\textsubscript{6} crystal, the valence band is composed of O 2p\textsuperscript{+}Bi 6s6p, and the conduction band is contributed mainly from the O 2p\textsuperscript{+}W 5d orbitals and to a lesser from the Bi 6p orbital (Figure 7a). According to the electron density contour maps for the bottom of the conduction band (LUMO), the existence of the “Bi–O” vacancy pairs causes the electron density to shift to W atoms (Figure 5b), and thereby changes the electronic structure of Bi\textsubscript{2}WO\textsubscript{6}. The change of the electronic structure results in a downshift of O 2p and W 5d orbitals to the VBM, and an upshift of Bi 6s6p orbitals to the CBM, which decrease the band gap energy of Bi\textsubscript{2}WO\textsubscript{6} accordingly (Figure 7b,c). The above conclusion agrees with the results of diffuse reflection spectra (DRS) (Figure 7d). Results in Figure 7d showed that P-Bi\textsubscript{2}WO\textsubscript{6} and B-Bi\textsubscript{2}WO\textsubscript{6} had a band gap of or 2.65 and 2.50 eV, respectively. Therefore, it is believed that the maximum utilization of sunlight can be achieved in B-Bi\textsubscript{2}WO\textsubscript{6}.

Moreover, the photocatalytic performances of as-prepared Bi\textsubscript{2}WO\textsubscript{6} samples have been estimated using DIC as the probe molecule. The DIC was chosen for two main reasons: (i) it exhibits no visible light absorption, excluding the effect of photosensitization during the photocatalytic process; (ii) the DIC has been detected in wastewater and drinking water,\textsuperscript{59} which has toxicity to the liver, kidney, and gill cells, as well as causing renal lesions.\textsuperscript{59–61} Therefore, it is of great significance to remove DIC from aqueous systems. In the presence of B-Bi\textsubscript{2}WO\textsubscript{6}, nearly 30 ± 5% of DIC is adsorbed in dark. Under solar light irradiation, the degradation of DIC followed a pseudo-first-order kinetics with an apparent rate constant (k) of 3.127 min\textsuperscript{-1} by B-Bi\textsubscript{2}WO\textsubscript{6}, which was almost ten and three times higher than that by P-Bi\textsubscript{2}WO\textsubscript{6} and P25 TiO\textsubscript{2}, respectively (Figure 8a). With exposure to visible light (>420 nm), in contrast to the negligence effect with P25 TiO\textsubscript{2} (Figure S4, Supporting Information), the photocatalytic degradation of DIC by B-Bi\textsubscript{2}WO\textsubscript{6} was completed in 30 min (Figure 8c). The outstanding photocatalytic performances essentially in agreement with the results of the above photoelectrochemical measurements, and this confirmed the B-Bi\textsubscript{2}WO\textsubscript{6} had unlimited potential in the application of the solar light. Furthermore, it is worthy of notice that the quadruple time-of-flight mass spectrometry (Q-TOF-MS) signal of B-Bi\textsubscript{2}WO\textsubscript{6} treated DIC...
containing solution became identical to that of ultrapure water, whereas the TiO$_2$-treated DIC solution still showed the presence of numeral intermediates (Figure 8b).

ESR spectra and radical-trapping experiments were carried out for B-Bi$_2$WO$_6$. A fourfold characteristic peak with an intensity ratio of 1:2:2:1 was observed for DMPO-$\cdot$OH adduct, as shown in Figure 8d. Under visible light, the sextet peak of DMPO-O$_2^-$/HO$_2^-$ adduct was observed. Therefore, it is reasonable to suggest that the reactive oxygen species (ROS) generated in the aqueous solution contributes to the high efficient photocatalytic performance. Additionally, the stability of the photocatalysts was studied by multicycle degradation experiments. The photoactivity of B-Bi$_2$WO$_6$ remained high and constant over ten consecutive cycles (Figure S7, Supporting Information), which indicates the stability of the photocatalyst. For practical application of photocatalysis to environmental remediation, it is especially important that the photocatalysts have high degree of stability.

3. Conclusion

Bi$_2$WO$_6$ nanobipyramid was fabricated via a facile strategy successfully. Results of theoretical calculations and experimental observations clearly showed that the presence of a high density of the high energy surface {100} in Bi$_2$WO$_6$ was important to the formation of defects, i.e., “Bi–O” vacancy pairs, which were keys to the increase in solar-light photoactivity. Accordingly, the presence of vacancy pairs changed the chemical and electronic structure of Bi$_2$WO$_6$, which, in turn, promoted the degree of the separation of the photogenerated electron–hole pairs, narrowed the band gap energy, and ultimately increased the utilization efficiency of the solar light. The nature of a nanobipyramid structure in Bi$_2$WO$_6$ can enhance the photoactivity significantly. The findings provided insights into the mechanisms on photoactivity by elucidating the connection between reactive surfaces and enhanced photochemical reactivity; an information useful to the design and fabrication sensitive catalysts.

4. Experimental Section

Materials: All chemical reagents were purchased and used without further purification including bismuth nitrate (Aldrich), sodium tungstate (Alfa), polyvinylpyrrolidone (PVP) (M$_w$ = 30 000, Aldrich), nitric acid (HNO$_3$) (guaranteed reagent), ethylene glycol (EG) (guaranteed reagent, 100%), diclofenac sodium (Sigma). TiO$_2$ particles (P25, Degussa) were purchased from Degussa Co.
Fabrication of Bismuth Tungstate: Bipyramid-structured Bi$_2$WO$_6$ (B-Bi$_2$WO$_6$). 1.2 g PVP was dissolved in 40 mL boiling ethylene glycol to gain a transparent mixture; then, 2 mmol Bi(NO$_3$)$_3$·5H$_2$O was dissolved in the solution within 2 min. Finally, 1.0 mmol of Na$_2$WO$_4$·2H$_2$O was added. After reaction 60 min under ultrasound, the mixture was transferred to a Teflon-lined autoclave (filled up to 80% of its total volume). The autoclave was sealed and maintained in an electro-oven at 180 ºC for 24 h. After the autoclave was air-cooled to room temperature, the mixture was filtered, washed with distilled water and absolute alcohol several times to collect Bi$_2$WO$_6$ which was named B-Bi$_2$WO$_6$.

Plate-Structured Bi$_2$WO$_6$ (P-Bi$_2$WO$_6$): First, 2 mmol Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 15 mL 10% HNO$_3$ solution (Solution I). After stirring for 60 min, 15 mL of the aqueous solution containing 1.0 mmol of Na$_2$WO$_4$·2H$_2$O was added to solution I under continuous stirring. Then, the pH value of the resulting white suspension was adjusted to 1.0 with NaOH (4 mol·L$^{-1}$). The obtained colloidal precipitate was transferred into a 40 mL Teflon lined autoclave. The colloidal precipitate was transferred to a 40 mL Teflon lined autoclave tube and autoclaved at 180 ºC for 24 h, the Bi$_2$WO$_6$ so collected was denoted as P-Bi$_2$WO$_6$.

Characterizations: The crystal structure of samples was characterized by powder X-ray diffraction (XRD) (X’Pert Pro PW 3040-Pro, PANalytical, Inc.) using Cu Kα irradiation operating at 40 kV and 40 mA with a fixed slit. The morphologies of the samples were observed with a scanning electron microscope (SEM). The lattice and fringe spacings were obtained with a JOEL high-resolution transmission electron microscope (HRTEM). Specific surface area was measured by a volumetric method on an automatic adsorption instrument. XPS experiments were performed on Bi$_2$WO$_6$ with a PHI5000 Versa Probe system (Physical Electronics, MN), and the binding energies of XPS spectra were calibrated with the reference to the C1s peak at 284.80 eV. To investigate the light absorption and emission behavior, UV–vis absorption spectra were utilized in diffuse reflection mode using an integrating sphere (UV2401/2, Shimadzu). The characteristics of the photogenerated electrons were studied with time-resolved infrared absorption spectroscopy, and the light source for the photoexcitation was the third harmonic of a Q-switched Nd:YAG laser. The samples were fixed on a calcium fluoride (CaF$_2$) plate with a density of 1.5 mg cm$^{-2}$. The infrared (IR) light emitted from a MoSi$_2$ source was focused on the Bi$_2$WO$_6$ samples in vacu. The IR output was transformed to an electric signal in an MCT detector.

Photoelectrochemical Measurements: The photocurrent action spectra were measured in a home-built two-electrode configuration experimental system,[25] where the photocatalysts coated on ITO-coated glass by the doctor-blade method served as the working electrode, with an active area of 1.0 cm$^2$, and a platinum wire was used as the counter electrode in the 0.2 mol KCl electrolyte. A 500 W Xenon lamp with a monochromator was used as the light source. The cell was illuminated from the ITO side of the Bi$_2$WO$_6$ electrode by the incident light. The photocurrent signal was collected using a lock-in amplifier (Stanford Instruments SR830 DSP). The light intensity was 15 µW cm$^{-2}$, and the illumination area of the light was restricted to 25 mm$^2$. Before measurements, an experiment using a P25 TiO$_2$-coated electrode was performed as a reference. The photoelectrochemical properties in this study were measured using a Princeton Versa STAT 3 in a standard three-electrode configuration with Bi$_2$WO$_6$ electrodes used as photoanodes, Pt foil as the counter electrode, and an Ag/AgCl electrode as the reference electrode. 0.2 mL KCl purged with N$_2$ was used as an electrolyte. An AM 1.5 solar power system was used as the light irradiation source.

Photocatalytic Test: A 300 W Xenon lamp was used as solar light, and wavelengths below 420 nm were cut off by an optical filter for visible light. The photocatalytic performance was evaluated by the degradation of Diclofenac (DIC) with initial concentration of 20 mg L$^{-1}$. More specifically, 50 mg catalyst samples were added to 100 mL of contaminant-containing solution. Before irradiation, to achieve adsorptive equilibrium, suspensions were mixed under vigorous stirring in the dark. After desired intervals, samples were taken and centrifuged to separate the supernatant liquid from catalysts. In addition, degradation test of the contaminant with P25 TiO$_2$ was used as control.

Positron Annihilation Measurement: Positron annihilation lifetime spectra (PALS) were measured using a conventional fast-slow coincident system. The coincidence spectrometer used had a prompt time resolution of 208 ps (FWHM) for the γ-rays from a 60Co source selected under the experimental conditions. The sample powders were pressed into a disk (diameter: 10.0 mm, thickness: 1.0 mm). A 30 μCi 22Na positron source was sandwiched between two identical sample disks.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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