Enhanced Photocatalytic Degradation of Perfluorooctanoic Acid by Mesoporous Sb$_2$O$_3$/TiO$_2$ Heterojunctions

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Perfluorooctanoic acid (PFOA), a typical perfluorinated carboxylic acid, is an emerging type of permanent organic pollutants that are regulated by the Stockholm Convention. The degradation of PFOA, however, is quite challenging largely due to the ultra-high stability of C-F bonds. Compared with other techniques, photocatalytic degradation offers the potential advantages of simple operation under mild conditions as well as exceptional decomposition and defluorination efficiency. Titanium dioxide (TiO$_2$) is one of the most frequently used photocatalysts, but so far, the pristine nanosized TiO$_2$ (e.g., the commercial P25) has been considered inefficient for PFOA degradation, since the photo-generated hydroxyl radicals from TiO$_2$ are not able to directly attack C-F bonds. Mesoporous Sb$_2$O$_3$/TiO$_2$ heterojunctions were therefore rationally designed in this work, of which the confined Sb$_2$O$_3$ nanoparticles in mesoporous TiO$_2$ framework could not only tune the band structure and also increase the number of active sites for PFOA degradation. It was found that, after loading Sb$_2$O$_3$, the absorption of UV light was enhanced, indicating a higher efficiency of light utilization; while the band gap was reduced, which accelerated the separation of photo-generated charge carriers; and most importantly, the valence band edge of the Sb$_2$O$_3$/TiO$_2$ heterojunction was significantly lifted so as to prevent the occurrence of hydroxyl radical pathway. Under the optimal ratio of Sb$_2$O$_3$–TiO$_2$, the resulting catalysts managed to remove 81.7% PFOA in 2 h, with a degradation kinetics 4.2 times faster than the commercial P25. Scavenger tests and electron spin resonance spectra further revealed that such improvement was mainly attributed to the formation of superoxide radicals and photo-generated holes, in which the former drove the decarboxylation from C$_7$F$_{15}$COOH–C$_7$F$_{15}$$^+^*$, and the latter promoted the direct electron transfer for the conversion of C$_7$F$_{15}$COO$^-$–C$_7$F$_{15}$COO$^*$. The Sb$_2$O$_3$/TiO$_2$ photocatalysts were highly recyclable, with nearly 90% of the initial activity being retained after five consecutive cycles, guaranteeing the feasibility of long-term operation.

Keywords: perfluorooctanoic acid, photocatalysis, TiO$_2$, heterojunction, mesoporous
INTRODUCTION

Perfluorooctanoic acid (PFOA) is an important industrial surfactant that used to be widely adopted in many applications (Wang Z. et al., 2017). As a typical perfluorinated carboxylic acid, the high stability of PFOA makes it extremely difficult to decompose (Wang S. et al., 2017), and its broad distribution in a variety of environments have been confirmed by a large number of studies (Giesy and Kannan, 2002; Post et al., 2012; Zareitalabad et al., 2012; Houtz et al., 2013; Ghisi et al., 2019), causing significant concerns on human health (Sunderland et al., 2018). Therefore, it has been listed in the Stockholm Convention as a persistent organic pollutant to be eliminated (UNEP, 2019). However, such a photo-generated OH radicals for the subsequent pollutant oxidation (Nakata and Fujishima, 2012; Pelaez et al., 2012; Schneider et al., 2014; Nasr et al., 2018). However, such a photo-generated OH* strategy has been found not feasible for the degradation of PFOA (Li et al., 2012), as the oxidation potential value of hydroxyl radicals (276 kJ/mol) is not enough to break either the C-F bond (ca. 460–540 kJ/mol) or C-C bond (347 kJ/mol), and is even inefficient to turn C7F15COO− into C7F15COO* radicals for the subsequent pollutant oxidation (Nakata and Fujishima, 2012). Since the photocatalytic degradation of PFOA, early studies were conducted in an acidic (HClO4) solution, at a pH below the pKa of PFOA (2.8), which enhanced the PFOA ionization to form C7F15COO− radicals (Dillert et al., 2007; Panchangam et al., 2009). On the other hand, it was also reported that the addition of oxalic acid as a hole-scavenger for photo-excited TiO2 led to the formation of a strong reductant, carboxyl anion radical (CO2−*), which could directly convert the molecular C2F3COOH into C2F3COO* radicals (Wang and Zhang, 2011). Apart from the above, another versatile approach was to modify TiO2 with noble metals, non-noble metals, or metal-free carbon supports (Estrellan et al., 2010; Song et al., 2012; Chen et al., 2015; Chen et al., 2016; Li et al., 2016; Gomez-Ruiz et al., 2018), through which the photogenerated electrons were trapped, reducing the electron-hole recombination and prolonging the lifetime of holes.

Here, in this study, mesoporous Sb2O3/TiO2 heterojunctions were rationally designed to improve the photocatalytic degradation of PFOA. Incorporation of porous structures has been long regarded as an effective strategy to promote the performance of TiO2 photocatalysts (Du et al., 2011; Zhou et al., 2014), but surprisingly, it has not been applied for the removal of PFOA yet, as far as the authors are aware. Compared with pristine TiO2, the mesoporous one features a higher surface area/more active sites, as well as faster mass transfer. Nanosized Sb2O3 were further embedded into the mesoporous TiO2 framework via a facile hydrothermal method. Antimony trioxide is a novel semiconductor with a broad band gap over 3 eV, but the photocatalytic activity of pure Sb2O3 nanoparticles is fairly low (Karanakaran et al., 2010). Coupling Sb2O3 with another semiconductor, mainly the TiO2, has been explored previously (Li et al., 2001; Liu et al., 2012; Wang et al., 2018; Wang et al., 2019), but none of them has attempted to investigate the photocatalytic activity on PFOA degradation. In this regard, it is hypothesized that the combination of a mesoporous structure and the integration of Sb2O3/TiO2 heterojunctions may enhance the PFOA removal kinetics.

EXPERIMENTAL

Materials

All materials were of analytical grade and used as received. Antimony chloride (SbCl3) was purchased from Aladdin Industrial Corporation. Perfluorooctanoic acid (C7F15COOH, 96% purity), tetrabutyl titanate (C16H36O4Ti), and ethanol were obtained from Sigma-Aldrich. Deionized water (DI water) was used in all experiments.

Synthesis of Photocatalysts

20 ml tetra-n-butyl titanate (TBOT) were added dropwise to 200 ml DI water, and afterward, the mixture was left for 36 h at room temperature. The samples were then filtered, washed with DI water and ethanol for 3 times, and dried in vacuum oven at 60°C for 12 h to obtain the mesoporous TiO2.

To synthesize Sb2O3/TiO2 composites, 0.028 g of SbCl3 was dissolved in 20 ml ethanol and 0.5 g mesoporous TiO2 were added into 20 ml DI water. Both of these two solutions were stirred for 20 min, then mixed together, and further stirred for 30 more min. The pH of the mixture was adjusted to neutral with ammonia. After that, the suspension was transferred to a 200 ml Teflon-lined autoclave and heated at 180°C for 10 h. After the autoclave was naturally cooled to room temperature, the resulting light blue sample was separated by centrifugation, washed with DI water and ethanol for 3 times, and dried in vacuum oven at 60°C for 12 h to obtain the mesoporous TiO2.

Characterization

The crystallite structures of Sb2O3/TiO2 and TiO2 were characterized using X-ray powder diffraction (XRD). Spectra were collected on a D8 Advance diffractometer (Bruker D8 Discover, United States) using Cu-Kα radiation. Infrared absorption spectra were conducted on a NICOLET 380 Fourier transform infrared (FT-IR) spectrometer (NICOLET, United States) using KBr pellets. The infrared absorption spectra were recorded in the range of 4000–400 cm−1 with a resolution of 4 cm−1. Fourier transform infrared (FT-IR) spectra were obtained using KBr pellets.
The morphologies and structures of the samples were characterized by transmission electron microscopy (TEM, FEI Teanci G2 F20, United States) and scanning electron microscopy (SEM, Hitachi SU8220, Japan) operating at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data was obtained using an Escalab 250Xi spectrometer (Thermo Fisher Scientific, China) with monochromatic Al KR radiation. DR-UV of the powders was obtained by diluting with 60 wt% BaSO₄, pressing into a wafer, and measured using a Shimadzu UV-2450 spectrometer. Pore volume and Brunauer-Emmet-Teller (BET) surface area measurements of the synthesized Sb₂O₃/TiO₂ were analyzed through N₂ adsorption/desorption isotherms with a Micromeritics Surface Area and Porosity Analyzer (Micromeritics ASAP 2020, United States). Photoluminescence (PL) emission spectra were measured with Picoquant Fluo Time 300 equipped with a Xenon lamp (λ = 250–800 nm). Time-resolved emission spectra (TRES) were collected after excitation with 280 and 375 nm lasers.

**Photocatalytic Procedure and Perfluorooctanoic Acid Analysis**

The photocatalytic reactor was equipped with one 4W UVC UShio G4T5 low pressure mercury germicidal lamps and a stir plate. In a typical photocatalytic PFOA degradation experiment, 5 mg of the photocatalyst (2.5 g/L Sb₂O₃/TiO₂ or TiO₂) was first dispersed into a 50 ml quartz round bottom flask containing 20 ml of DI water dissolved with 10 ppm PFOA. Initial pH for most experiments was without adjustment. At defined time interval, aliquots were extracted, and filtered with 0.22 µm syringe filters. The concentration of the remaining PFOA, during the photocatalytic activity test, was measured by V-630 UV-vis spectrometer (Jasco International Co., Japan) and ultra-high performance liquid chromatography-mass spectrometry system (UPLC-MS, Thermo Fisher ScientificT Quantum). A C-18 column (ZORBAX eclipse XDB, 2.1, 100, and 3.5 mm, Agilent Technologies, United States) was used for chromatographic separation. The column temperature and the flow rate were set at 20°C and 150 µL/min, respectively. The mobile phase of eluent A (2.5 mmol/L ammonium acetate water solution) and eluent B (acetonitrile). The gradient of eluent B was started with 30%, increased to 70% at 4 min, then decreased to 30% at 7 min, and maintained for another 3 min to keep stabilization. The samples were analyzed by multiple reaction monitoring in negative ion mode. Calibration curves of PFOA was in the linear range from 0.1–20 ppm. The limit of detection was 1 ppb at the signal to noise ratio of 3.

Electron paramagnetic resonance (EPR) spectroscopy measurement was conducted by a spectrometer (JES FA300, Japan). The photocatalyst (2.0 mg) was dispersed in water/methanol solution (10 ml) by ultrasonication. Then, 50 µL DMPO (5,5-dimethyl-L-pyrroline N-oxide, 50 mM) was added in the suspension (200 µL) for DMPO-OH* and DMPO-O₂* measurements. The photocatalyst was added in the quartz tube and irradiated by UV light.

**RESULTS AND DISCUSSION**

**Compositional and Structural Characteristics of Mesoporous Sb₂O₃/TiO₂ Heterojunctions**

As shown in Figure 1A, the XRD patterns of the as-prepared TiO₂ and 1–10%-Sb₂O₃/TiO₂ composite displayed a distinct diffraction peak at 2θ = 25.33°, which was indexed to the (101) plane of anatase TiO₂ (JCPDS No. 83-2243). After loading Sb₂O₃, the two new peaks at 43.08 and 43.67° were assigned to the (220) and (240) planes of TiO (JCPDS No. 72-0020), which was probably attributed to the partial replacement of Ti-O by Sb-O. As the ratio of Sb₂O₃ to TiO₂ increased, the intensity of the above two peaks first increased, then became most prominent in the pattern of 3%-Sb₂O₃/TiO₂, and finally decayed. In the meantime, it was also noted that, the diffraction peaks of the (111) plane of Sb₂O₃ (JCPDS No. 71-0383) was only observed in 10%-Sb₂O₃/TiO₂. Since the peak position for the (111) plane of
Sb$_2$O$_3$ overlapped with the (121) plane of TiO$_2$, the above phenomena suggested that, at a low loading content, the Sb$_2$O$_3$ nanoparticles were embedded in the mesoporous TiO$_2$; and when the loading was high, the excess amount of Sb$_2$O$_3$ grow outside of the TiO$_2$ framework, ending up as the higher energy crystal facets found in the 10%-Sb$_2$O$_3$/TiO$_2$. The findings from XRD patterns were further supported by the FT-IR spectra of TiO$_2$ and Sb$_2$O$_3$/TiO$_2$ composites (Figure 1B). The wide finger band under 1,000 cm$^{-1}$ was assigned to the grid structure of Ti-O-Ti. Hence, the narrowed the range of Ti-O-Ti peak, as the Sb$_2$O$_3$ content increased, also indicated the successful incorporation of Sb into TiO$_2$ structure. Besides, the other two bands located at 1,636 and 3,438 cm$^{-1}$ were normally ascribed to the bending and stretching of $\text{OH}$. Morphologies of the as-synthesized 3%-Sb$_2$O$_3$/TiO$_2$ were further characterized by their SEM and TEM images (Figure 2). As seen in Figures 2A,B, the coarse bowl-like Sb$_2$O$_3$/TiO$_2$ particles were composed of nanoparticles with a mean particle size of ca. 10 nm and interconnected pores in the similar range. The HRTEM image (Figure 2C) revealed that those nanoparticles were mainly of anatase TiO$_2$ with a d-spacing of 0.356 nm for the (101) plane, surrounded by the Sb$_2$O$_3$ nanocrystals with a d-spacing of 0.348 nm for the (111) plane, which was in good accordance with the XRD results. In addition, the elemental mapping of Sb$_2$O$_3$/TiO$_2$ (Figure 2D) also confirmed the uniform distribution of Sb (blue) and Ti (red) in the composites.

As shown in the Ti 2p and Sb 3d XPS spectra of 3%-Sb$_2$O$_3$/TiO$_2$ (Figure 3A), the two peaks at 464.33 and 458.63 eV were assigned to the Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ peaks of anatase TiO$_2$, respectively, with a characteristic splitting of 5.7 eV; and similarly, the other two at 539.96 and 530.26 eV were ascribed to the Sb 3d$_{3/2}$ and Sb 3d$_{5/2}$ peaks of Sb$_2$O$_3$. These observations were consistent with the aforementioned XRD and TEM measurements, affirming once again the formation of Sb$_2$O$_3$/TiO$_2$ heterojunctions. The XPS valence band of TiO$_2$ and 3%-Sb$_2$O$_3$/TiO$_2$ was estimated to be at 2.90 and 1.58 eV (Figure 3B), respectively, proving that the integration of Sb$_2$O$_3$ was capable of raising the valence band to prevent the indirect OH$^\bullet$ pathway (the redox potential for H$_2$O/OH$^\bullet$ was 2.27 eV). The light absorption characteristics of mesoporous TiO$_2$ and mesoporous Sb$_2$O$_3$/TiO$_2$ heterojunctions exhibited a red shift in the absorption edge, which became ever more significant as the loading of Sb$_2$O$_3$ increased. The band gap
energies of the mesoporous TiO$_2$ and the Sb$_2$O$_3$/TiO$_2$ composites were estimated based on the intercept of the Tauc plot of $(\alpha h\nu)^2$ vs. the photon energy ($h\nu$), which decreased from 3.30–2.91 eV as the content of Sb$_2$O$_3$ increased from 0–10% (Figure 3D). Hence, lower excitation energy was required to initiate the electron transition in Sb$_2$O$_3$/TiO$_2$. Meanwhile, the broader range of light adsorption and higher intensity by the heterojunctions allowed the utilization of more irradiation.

The N$_2$ adsorption-desorption isotherms were adopted to characterize the porous structures of TiO$_2$ and Sb$_2$O$_3$/TiO$_2$ composites. It was seen in Supplementary Figure S1 that all these samples exhibited a typical type IV curves with H2 hysteresis loops, which corresponded to a well-defined mesoporous structure. The narrow pore size distributions (derived from the adsorption branches using BJH model) indicated that the resulting mesopores were quite uniform in each sample. It was also noted that the specific surface area of Sb$_2$O$_3$/TiO$_2$ was slightly smaller than that of pristine TiO$_2$, and kept decreasing as the Sb$_2$O$_3$ loading increased, which was probably attributed to the partial pore blocking by nanoconfined Sb$_2$O$_3$. The corresponding pore characterization data were summarized in Supplementary Table S1.

Photocatalytic PFOA Degradation Activities and Mechanisms of Sb$_2$O$_3$/TiO$_2$ Heterojunctions

Figure 4A presented the performance of photocatalytic degradation of PFOA by TiO$_2$ embedded with various amount of Sb$_2$O$_3$. When the initial PFOA concentration was 10 ppm and catalyst dosage was 0.25 g/L, the as-synthesized mesoporous TiO$_2$ exhibited a 73% higher removal rate (55.9%) than the commercial P25 (32.3%) after 120 min of operation. The nanoconfinement of Sb$_2$O$_3$ into mesoporous TiO$_2$ framework further enhanced the PFOA degradation efficiency, and a maximal removal rate of 81.83% was realized by 3%-Sb$_2$O$_3$/TiO$_2$. Contribution of the PFOA adsorption by catalysts should be negligible—before light was turned on, the solution had already been stirred in the dark for 30 min and no apparent decrease of PFOA concentration was observed. The PFOA removal rates between 20 and 120 min were used to calculate the degradation kinetics. According to the Langmuir-Hinshelwood model, a pseudo-first-order kinetics was applied to fit the photo-induced rate constant. Based on that, the degradation kinetics of mesoporous TiO$_2$ (6.3 $\times$ 10$^{-3}$ min$^{-1}$) and 3%-Sb$_2$O$_3$/TiO$_2$ (12.6 $\times$ 10$^{-3}$ min$^{-1}$) were found to be 1.6- or 4.2-times higher than that of the commercial P25 (6.3 $\times$ 10$^{-3}$ min$^{-1}$). More importantly, a volcano-type relationship.
TiO₂ and Sb₂O₃/TiO₂, both the PFOA and the photocatalysts were predominantly negatively charged. Such a repelling effect became more significant as the pH value increased, which explained the lower degradation activity at a higher pH. This finding was in stark contrast to most of the previous studies on TiO₂ based photocatalysts, but was highly consistent with the other characterization results in this work, e.g., the XPS valence band position and the band gap estimated from UV-vis spectra. The electron spin resonance (ESR) measurements were further conducted to resolve the aforementioned radicals, using DMPO as the spin-trap reagent (Figure 7B). The signal of DMPO-OH⁻ adduct was strong in the measurement with pristine TiO₂, then gradually decayed in 1- and 3%-Sb₂O₃/TiO₂, and became completely invisible when the Sb₂O₃ content reached 7% or higher. By contrast, only four peaks of DMPO-OH⁻ were seen between the Sb₂O₃ loading content and the photocatalytic PFOA degradation efficiency (Figure 4B).

The resulting 3%-Sb₂O₃/TiO₂ with an optimal activity were selected for the following examination of operating conditions. It was displayed in Figure 5A that, as the dosage of 3%-Sb₂O₃/TiO₂ catalysts increased, the initial removal kinetics within the first 20 min was greatly enhanced, probably due to the larger total amount of active sites for PFOA degradation. On the other hand, despite the fact that the final degradation rate at 120 min was higher in the 0.25 g/L test than in the 0.1 g/L one, further addition of 3%-Sb₂O₃/TiO₂ improved little the overall performance, because the excess catalysts may interfere the light transmission or cause agglomeration of the catalysts, resulting in the scattering of the irradiated light and reduction of photon utilization. The impact of initial PFOA concentration was examined as well (Figure 5B). When 1 or 5 ppm PFOA was added, the two degradation curves were almost identical; and if the concentration of PFOA went even higher, the overall removal rate would drop a little, but a nearly 70% degradation at 120 min was still achievable for 20 ppm PFOA. The pH value of the solution also played a crucial role in the photocatalytic PFOA degradation performance. Note that the initial pH of the solution was ca. 4.4, a negative correlation was identified between the PFOA degradation activity and the pH value (Figure 5C). One possible reason for this phenomenon should be attributed to the relationship between the acid dissociation constant (pKₐ) of PFOA and the point of zero charge (PZC) of photocatalysts. The pKₐ value of PFOA was reported to be 2.8 (Goss, 2008), and it was shown in Figure 5D that the PZC of TiO₂ and 3%-Sb₂O₃/TiO₂ were 5.30 and 3.57, respectively. Therefore, when the pH of solution was higher than the pKₐ of PFOA and the PZC of TiO₂ and Sb₂O₃/TiO₂, both the PFOA and the photocatalysts were predominantly negatively charged. Such a repelling effect became even more significant as the pH value increased, which explained the lower degradation activity at a higher pH.

Photoluminescence spectroscopy (PL) and time-resolved photoluminescence spectroscopy (TR-PL) were then adopted to examine the behavior of electron-hole recombination. As seen in Figure 6A, all the samples exhibited an emission band from 350 to 500 nm in the PL spectra measured at an excitation wavelength of 325 nm. The lower emission intensity generally corresponded to a slower recombination rate, and it was found that the emission intensity of TiO₂, 1 and 3%-Sb₂O₃/TiO₂ was close to each other, while those of 7 and 10%-Sb₂O₃/TiO₂ were higher. The average lifetime of the emission decay, calculated from the TR-PL spectra (Figure 6B), was 27.09, 33.28, 26.26, 14.98, and 9.54 ns, for the pristine TiO₂ and 1, 3, 7 and 10% Sb₂O₃/TiO₂ heterojunctions, in accordance with the finding in PL intensity. In short, compared with the pristine TiO₂, the electron-hole recombination of 1%-Sb₂O₃/TiO₂ was slightly slower, the 3%- one was comparable, and the 7 and 10%-ones were faster.

To elucidate the origin of the enhanced photocatalytic PFOA degradation activity by Sb₂O₃/TiO₂, a series of scavengers, including t-butanol to quench OH⁻, p-benzoquinone (BQ) to quench O₂•⁻, and EDTA as the scavenger for the h⁺, were employed to determine the specific role of each reactive species. As shown in Figure 7A, the degradation of PFOA was most significantly suppressed by BQ, then by EDTA, and almost negligible with TBA, suggesting that the photo-induced generation of O₂•⁻ and h⁺, rather than OH⁻, made the main contribution to the degradation of PFOA. Besides, the sum of the individual loss of photocatalytic activity by BQ and EDTA scavengers was almost equal to the total activity of 3%-Sb₂O₃/TiO₂. This finding was in stark contrast to most of the previous studies on TiO₂ based photocatalysts, but was highly consistent with the other characterization results in this work, e.g., the XPS valence band position and the band gap estimated from UV-vis spectra. The electron spin resonance (ESR) measurements were further conducted to resolve the aforementioned radicals, using DMPO as the spin-trap reagent (Figure 7B). The signal of DMPO-OH⁻ adduct was strong in the measurement with pristine TiO₂, then gradually decayed in 1- and 3%-Sb₂O₃/TiO₂, and became completely invisible when the Sb₂O₃ content reached 7% or higher. By contrast, only four peaks

![Figure 4](https://example.com/figure4.png) | (A) PFOA degradation performance and (B) rate constants of P25, TiO₂, 1%-Sb₂O₃/TiO₂, 3%-Sb₂O₃/TiO₂, 7%-Sb₂O₃/TiO₂, and 10%-Sb₂O₃/TiO₂.
FIGURE 5 | The influence of (A) catalyst dosage, (B) initial PFOA concentration, and (C) solution pH on the photocatalytic degradation of PFOA by 3%-Sb$_2$O$_3$/TiO$_2$, and (D) the point of zero charge of TiO$_2$ and 3%-Sb$_2$O$_3$/TiO$_2$.

FIGURE 6 | (A) PL emission spectra, and (B) TR-PL spectra of TiO$_2$, 1%-Sb$_2$O$_3$/TiO$_2$, 3%-Sb$_2$O$_3$/TiO$_2$, 7%-Sb$_2$O$_3$/TiO$_2$, and 10%-Sb$_2$O$_3$/TiO$_2$. 
were observed in the $\text{O}_2^{\cdot -}$ measurements with pristine TiO$_2$ and 1%-Sb$_2$O$_3$/TiO$_2$, but they were then splitted into eight when the Sb$_2$O$_3$ went up to 3% or higher, which was probably due to the lower PZC of the catalysts than the pH of the solution. The highest intensity of DMPO-$\text{O}_2^{\cdot -}$-adduct in 3%-Sb$_2$O$_3$/TiO$_2$ is a strong evidence to support the $\text{O}_2^{\cdot -}$-dominant pathway proposed in this work for the photocatalytic degradation of PFOA.

Finally, the reusability of the synthesized 3%-Sb$_2$O$_3$/TiO$_2$ photocatalysts was investigated. After each cycle, the photocatalysts were recovered through the following steps: the suspension was first left for a while to allow the precipitation of the photocatalysts, the supernatant was then extracted and removed, the remaining photocatalysts were washed with DI water and ethanol for three times, and finally kept in the oven at 60°C for drying. The exact same reactor and photocatalysts were applied in the next cycle of measurement. The result of the recycling test was given in Figure 8. After five consecutive cycles of operation, ca. 88% of the initial photocatalytic degradation efficiency was retained, which clearly demonstrated the potential feasibility of using this high-performance photocatalyst in the long-term PFOA removal applications.

**CONCLUSION**

In this study, a highly efficient mesoporous Sb$_2$O$_3$/TiO$_2$ heterojunction was designed to enhance the photocatalytic activity of PFOA degradation. The embedding of Sb$_2$O$_3$ nanocrystals into mesoporous TiO$_2$ framework was realized via a facile hydrothermal method. The crystal structures, morphology, chemical composition, and optical properties of the proposed Sb$_2$O$_3$/TiO$_2$ catalysts were carefully examined. Most importantly, it was found that the valence band edge was raised, the band gap was reduced, and the light adsorption was enhanced. The resulting 3%-Sb$_2$O$_3$/TiO$_2$ managed to remove 81.7% of the initial PFOA in 120 min, with a degradation rate 4.2 times faster than the commercial P25. Detailed mechanistic analysis revealed that the photo-
generated superoxide radicals and holes were the two main contributors to the improved performance (Figure 9), while the photo-induced formation of hydroxyl radicals was prohibited, and the recombination of electron and hole remained the same. In addition, it was also noted that nearly 90% of the catalytic activity was successfully retained after five cycling tests, indicating the promise of this photocatalyst in practical applications.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

KQ conceived the study and wrote the paper. XY and JZ performed the experiments. XY, JZ, and KQ analyzed the data. Y-JW, N-NS, and H-HL helped prepare Figures. H-HL also helped polish the paper.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2021.690520/full#supplementary-material

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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