Complete Photocatalytic Mineralization of Microplastic on TiO$_2$ Nanoparticle Film

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HIGHLIGHTS

- Efficient degradation of microplastics under UV light by TiO$_2$ film
- Triton-based TiO$_2$ film showed higher photocatalytic performance
- The role of radical species during microplastics degradation was elucidated
- Degradation mechanism and reaction intermediates were explored

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Complete Photocatalytic Mineralization of Microplastic on TiO₂ Nanoparticle Film

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SUMMARY
Recently, the environmental impacts of microplastics have received extensive attention owing to their accumulation in the environment. However, developing efficient technology for the control and purification of microplastics is still a big challenge. Herein, we investigated the photocatalytic degradation of typical microplastics such as polystyrene (PS) microspheres and polyethylene (PE) over TiO₂ nanoparticle films under UV light irradiation. TiO₂ nanoparticle film made with Triton X-100 showed complete mineralization (98.40%) of 400-nm PS in 12 h, while degradation for varying sizes of PS was also studied. PE degradation experiment presented a high photodegradation rate after 36 h. CO₂ was found as the main end product. The degradation mechanism and intermediates were studied by in situ DRIFTS and HPPI-TOFMS, showing the generation of hydroxyl, carbonyl, and carbon-hydrogen groups during the photodegradation of PS. This study provides a green and cost-efficient strategy for the control of microplastics contamination in the environment.

INTRODUCTION
Plastics are an ideal choice owing to its light weight, low cost, and high durability; nevertheless, their use still leads to the ever-widening problem of disposal. More than 8 × 10⁹ metric tons of plastic reaches the waterbodies every single year, and pollution is expected to surpass oceanic fish in the next coming years (MacArthur, 2017). Generally, the discharged plastics debased into small particles via combined effects of solar irradiation, physical degradation, and biodegradation (van Weert et al., 2019). The plastic decomposition leads to the formation of the micro (size less than 5 μm) and nano-plastics (size less than 1 μm) (Kelmans et al., 2015). Although recycling is progressively predominant, one-third of all plastics are still small or complex to recuperate economically (Garcia and Robertson, 2017). As a conventional plastic material, polystyrene (PS) and polyethylene (PE) are used in building materials (insulation and molding), foam packaging, food containers, and compact disks (Zan et al., 2004). However, their release in the water environment occurs through poor handling, wastewater treatment plants (McCormick et al., 2014), and microbial degradation (Andrady, 2011). PS and PE show adverse effects on human health and aquatic organisms owing to their recalcitrant nature (Li et al., 2018). Its contamination within the aquatic environment poses a severe threat not only to aquatic biota but also to terrestrial organisms via food webs (Barboza et al., 2018; Besseling et al., 2012; Fossi et al., 2014; Rochman et al., 2017; Watts et al., 2014). The seriousness and complication of plastics waste problems indicate that a new approach is desperately required for the decomposition of polymers.

The conventional wastewater purification technologies present difficulty in control and elimination of microplastics (Moore, 2008). Several techniques have been used for the removal of microplastics, including biodegradation (Rochman et al., 2017; Yang et al., 2013) and photodegradation (Feng et al., 2010). The biodegradation process is highly dependent on the microbial species and soil environment and requires more stringent storage conditions (Inkinen et al., 2011; Jakubowicz, 2003). Feng and his coworkers first time reported the photo-assisted Fenton degradation of polystyrene microspheres (Feng et al., 2010), whereas other studies on polystyrene degradation mainly dealt with plastic film for the development of photodegradable plastics (Kemp and McIntyre, 2006; Shang et al., 2003; Zan et al., 2006). The main limitation of Fenton-based reaction is the oxidant and iron ions loss due to the radical scavenging effect of hydrogen peroxide (H₂O₂) (Zhou et al., 2016). Recently, Kang et al. studied the degradation of cosmetic
microplastics by catalytic activation of peroxymonosulfate to generate reactive radicals using carbon hybrids (Kang et al., 2019). However, the complete mineralization of microplastics was not achieved.

Photocatalysis is considered as an advanced oxidation process for pollutants removal (Klavarioti et al., 2009). It is a well-established green technique with a primary feature that it exploits free and infinite solar energy, implying its great potential as a low-cost and environmentally friendly treatment technology (Li et al., 2019). TiO₂ is widely used as a model photocatalyst owing to its efficient oxidizing ability of organic pollutants (Yuan et al., 2017). TiO₂ has performed exceptionally well in various studies for the removal of organic pollutants under UV light, and there is a need to further study its use for microplastic degradation, although few studies have used TiO₂/plastic composite materials for the development of photodegradable plastic (Kemp and McIntyre, 2006; Shang et al., 2003; Zan et al., 2006), such as polypropylene (PP) (Kamrannejad et al., 2014), polystyrene (PS) (Shang et al., 2003), and high-density polyethylene (PE) films (Thomas et al., 2013; Thomas and Sandhyarani, 2013). TiO₂ nanotubes showed enhanced removal of low-density PE under visible light (Ali et al., 2016), whereas the activity of TiO₂ was improved using copper phthalocyanine (Zhao et al., 2008), polypyrrole (Li et al., 2010), multiwalled carbon nanotubes (An et al., 2014) for PE removal, whereas iron phthalocyanine (Fa et al., 2008) and ferric stearate (Fa et al., 2013) were applied for photodegradable PS. The photocatalytic degradation for dealing with microplastics has not been explored so far.

In this study, we have developed a novel and generalized approach for solid-phase photodegradation of microplastics (PS and PE) and also introduced the effect of different preparation methods on the photocatalytic performance of TiO₂. The degradation mechanism, reaction intermediates, and feasibility of mineralization were investigated. The in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), high-pressure photon ionization (HPPI)-TOFMS, and gas chromatography (GC) spectroscopy results showed that the larger fragments of PS were broken into smaller ones and finally changed into CO₂. Considering the natural availability of TiO₂ and the global environmental impact of microplastics, TiO₂-enhanced photodegradation system may be established into a promising approach to take advantage of natural material for the removal of microplastics. For real application, TiO₂-based films can be fabricated on microplastic filters, which can be directly used for the decomposition of microplastics under UV light irradiation, and it can also avoid the release of toxic intermediates into water in the technologies of liquid phase elimination of microplastics.

RESULTS AND DISCUSSION

Photocatalytic Degradation of PS and PE

The morphological changes in 400-nm PS on TiO₂ nanoparticle films fabricated with water (WT), ethanol (ET), Triton X-100 (TXT), and without catalyst (FTO) before and after UV light irradiation are shown in Figures 1 and S1. It can be seen that PS nanospheres were well dispersed on all films. Figure 1A displays the exact size and morphology of 400-nm PS on FTO (without photocatalyst) at 0 h irradiation. Almost a negligible change in PS size was observed on FTO during the whole photoirradiation reaction (Figure 1B). However, PS spheres exhibited a change in morphology and size on TiO₂-based catalysts at the initial 3 h of photoreaction (Figure S1). The light-induced coalescence of PS during degradation is because the photocatalytic degradation (hydroxyl radical oxidation) at the contact point of packed spheres is slower, which suggests that the degradation takes place on the PS-air interface. A more significant change in PS morphology and size was observed after another 3 and 6 h of irradiation (Figures S1, 1D, 1F, and 1H). TXT film exhibited an obvious change in PS morphology (Figure 1H) and size as compared with ET and WT films. Moreover, we further investigated 700 nm, 1 μm, and 5 μm sized PS spheres on TXT film, which showed significant changes in PS morphology and reduction in sphere size during the photoreaction (Figure S2). The change in PS morphology and size was further analyzed by determining the average diameter, degradation efficiency, and volume change. Based on the above observations, it is reasonable to conclude that TXT is very efficient in the photocatalytic degradation of PS.

Figure 2 displays the PS diameter, degradation efficiency, and inorganic carbon content during the photodegradation reaction. The diameter change of 400-nm PS was almost negligible on FTO, whereas this diameter became 268.18 nm on WT film after 12 h illumination. Simultaneously, the ET and TXT film shows a significant decrease in PS diameter, which was 177.78 and 100.07 nm, respectively (Figure 2A). The difference in photocatalytic performance of films can be ascribed to band energy, surface area, morphology, charge separation, light absorption, and texture (Vahl et al., 2019). Comparing the photocatalytic activity
Figure 1. FE-SEM Images of PS Spheres after Different Irradiation Time under 365 nm UV Light

(A) PS spheres on FTO (without catalyst) before irradiation.
(B) Without catalyst after 12 h irradiation.
(C) Water-based TiO$_2$ (WT) after 6 h irradiation.
(D) WT after 12 h irradiation.
(E) Ethanol-based TiO$_2$ (ET) after 6 h irradiation.
(F) ET after 12 h irradiation.
(G) Triton X-100 based TiO$_2$ (TXT) after 6 h irradiation.
(H) TXT after 12 h irradiation.
of fabricated films, TXT showed higher performance, which was attributed to its low band energy and good charge separation, which was studied in detail later. Therefore, TXT produces more electron-hole pairs under light irradiation and also extends the charge separation resulting in significant photoactivity for PS removal, whereas the mediocre performance of WT film is presumably due to its large particle size, low surface area, and a poor charge separation ability. The degradation efficiency of PS was calculated by (Equation 1):

\[
\text{PS Degradation Efficiency (\%)} = \frac{\text{Initial Volume} - \text{Final Volume}}{\text{Initial Volume}} \times 100 \quad (\text{Equation 1})
\]

It was observed that the photodegradation of PS increased with increasing irradiation time. After 12 h of UV irradiation, the degradation efficiency of 400-nm PS was 98.40%, 91.04%, and 69.25% for TXT, ET, and WT.
films, respectively (Figure 2B). Since the PS degradation efficiency was negligible on FTO (8.01%), indicating the direct photolysis of PS was insignificant. Figures 2C and 2D present the diameter change and the degradation efficiency of 700-nm and 1-μm PS, which was decreased to 251.96 and 401.28 nm, respectively, after 24 h irradiation. Meanwhile, the degradation efficiency for 1-μm and 700-nm PS was 93.49% and 95.30%, respectively, after 24 h irradiation under 365 nm UV light. However, the degradation efficiency of 5-μm PS was 99.99% after 24 h illumination under 254 nm UV and the faster degradation is attributed to the higher energy of photon and more charge carriers generated (Figure 2E).

Figures S3 and S4 present volume and surface area changes in varying sizes of PS, and effectual changes were observed with the increase in irradiation time. Figures 2F and S3D show the concentration of CO₂ with TiO₂ and PS with TiO₂/PS. At the initial phase, the concentration of CO₂ increases linearly owing to the fast photodegradation of PS (direct contact of PS with TiO₂ nanoparticles) and then slowly decelerates in the subsequent phase because of slow desorption process. CO₂ plot of TiO₂ with PS was 10 times higher than the control experiment signifying that CO₂ was produced from the PS decomposition, whereas in control experiment, a slight quantity of CO₂ might be due to the presence of organic impurities. Moreover, a small amount of carbon monoxide (CO) appeared owing to the stretching of C-H bond in the TiO₂/PS system (Cho and Choi, 2001).

Furthermore, we conducted an experiment to check PS decomposition in the liquid phase to evaluate if it would make the same contribution as the solid phase. The comparison results are illustrated in Figure S5. Interestingly, the mineralization efficiency of microplastic that occurred on the solid (microplastic)-solid (TiO₂) interface was much higher than that in the liquid phase. This is because there is less chance of hydroxyl radicals and holes to react with microplastic particles in the liquid phase (suspended, close contact between TiO₂ and microplastic particle becomes difficult), whereas on the solid-solid interface the key structural feature is that it facilitates charge separation to hinder recombination and enhances the photocatalytic degradation efficiency (Li and Gray, 2007). Moreover, the exposed surface of PS in the solid phase is higher owing to the direct contact with TiO₂ film, which leads to the direct attack of reactive species without any hindrance, whereas in the liquid phase the slower degradation is due to the hydrophilicity of PS particles in water solution, which makes the attack of reactive species slower.

Figure 3. Photocatalytic Degradation of PE on TXT Film under 254-nm UV Light
(A) PE at 0 h; (B) PE after 6 h; (C) PE after 12 h; (D) PE after 24 h; (E) PE after 36 h; (F) Raman spectrum of PE with different time profiles. (Highlighted parts present PE, and the same point was used for Raman imaging and detection throughout the experiment.)
We further investigated the activity of TXT film for the degradation of PE, and analysis was carried out through Raman spectroscopy. Figure 3A presents the actual PE morphology before UV light irradiation, and the plus (+) symbol presents the selected point for Raman detection and spectrum. Interestingly, PE shows changes in morphology and size with the increase in irradiation time (Figures 3B–3D) and finally, tens of micrometers-sized PE particles totally disappeared after 36 h of UV irradiation, signifying the complete degradation of PE (Figure 3E), although an insignificant degradation was observed on FTO (Figure S6). Figure 3F shows the Raman band of PE at 1,064, 1,133, 1,296, and 1,442 cm\(^{-1}\), which corresponds to C-C stretching, CH\(_2\) twisting, and CH\(_2\) bending (Wright et al., 2019). Raman spectra of PE exhibited a decline in PE peak with irradiation time, but no peak of PE was detectable after 36 h of photo-reaction, which was consistent with Raman imaging. In summary, TXT film also showed efficient photocatalytic activity for PE degradation under UV light. The oxidation state of TiO\(_2\) film remained the same before and after the degradation reaction, and results are shown in Figure S7. Figure S8 shows the actual morphology of the TXT film before and after the degradation reaction. It can be seen that there was no prominent change in catalyst morphology after 12 h of PS degradation reaction, which suggests that the prepared film is highly stable. We investigated the effect of light energy, wavelength, and degradation rate under different light sources (254 nm, 365 nm, and visible light), and the results are shown in Figure S9.

Structure, Morphology, and Optical Properties of Prepared Catalysts

The crystalline structure of the prepared TiO\(_2\) films on FTO substrate was examined by X-ray diffraction (XRD) as shown in Figure 4A. All diffraction peaks of the synthesized films correspond well to a reference pattern of tetragonal anatase and rutile phases with the joint committee on powder diffraction standards (JCPDS) file Nos. 21-1,272 and 21-1,276. The diffractogram consists of peaks at (2 Theta) 25.28°, 48.04°, and 55.06° along with Miller indices values (101), (200), and (211) of anatase TiO\(_2\), respectively. The peaks at (2 Theta) 27.45° and 36.08° match very well with the diffraction (110) and (101) crystal planes of rutile phase TiO\(_2\). It is notable that the width of (101) planes in TXT was stronger at (2 Theta) 25.28° as compared with the FTO substrate.
with ET and WT representing the higher nano crystallinity of film. The diffraction peaks from FTO glass was also observed, which can be attributed to the thinness and high porosity of TiO2 films.

Raman spectroscopy is beneficial for local structure analysis of the catalysts. Raman spectrum was recorded at wavenumber 100 to 1,100 cm$^{-1}$, and the FTO glass spectrum was used as a control experiment. The Raman spectrum of the TiO2 show peaks at 142.64 (Eg), 195 (Eg), 394.65 (B1g), 514.04 (A1g), and 637.46 cm$^{-1}$ (Eg), which are assigned to the anatase phase of TiO2, whereas a minor peak that appears at 445 (Eg) is attributed to the rutile phase of TiO2 (Figure 4B) (Wang et al., 2016). All samples show analogs peak, and no other peak was observed.

The morphology of the prepared TiO2 films was characterized by using field-emission scanning electron microscopy (FE-SEM) (Figures 4C–4E). Figure 4E revealed that the presence of Triton X-100 significantly affected the morphology of TiO2 (Suwanchawalit et al., 2017), such as the formation of nanoparticles, induced a particle size reduction, and fine pore formation (Godinez and Darnault, 2011). Particle size can influence the surface area and the recombination rate of photogenerated electron-hole pairs. Organic solvents act as a morphology-directing agent and effect on the texture of film during the annealing process, which leads to change in its optical and electrical properties and pore content. The particle size of the prepared films was calculated by using the nano measurer 1.2 software (inserted in Figures 4C–4E). The average particle size in TiO2 could be varied between 27.3 and 31.1 nm. However, the average particle size in ET and WT was ranging from 47.2 to 62.3 nm and 104.1 to 123.8 nm, respectively. It could be seen that the distribution curves fit well the Gaussian function with R$^2$ values of 0.921, 0.974, and 0.968 for WT, ET, and TXT, respectively, indicating that the size distribution of the samples was consistent with a normal distribution. Water contact angle and optical properties measurements of the nanoporous TiO2 films are shown in Figures S10 and S11, respectively. TEM images of the synthesized film showed that TiO2 film exhibited cuboid and spherical-shaped particles, whereas ET and WT have only a spherical-shaped particle and a dark color in TEM images was observed owing to a high electron density of Ti element (Figure S12). The cross-sectional SEM images show that TiO2 film has a thickness of about 1.21 μm (Figure S13). TXT film has a high surface area as compared with ET and WT films, as shown in Figure S14 and Table S1.

The charge carrier generation and separation in the synthesized photocatalysts were investigated by using the amperometric i-t technique and electrochemical impedance spectroscopy (EIS) (Figures 4F and 4G). The transient photocurrent response of the films (WT, ET, and TXT) was studied at an applied potential of 0.8 V under simulated solar light illumination. The rise and drop of the photocurrent respond well to chopped light. The photocurrent drops when the light was off and increases instantly when the light was on, specifying that the current was completely due to the light response of the catalyst, and the rate of charge transfer was very speedy. Figure 4F illustrates that the TXT produces the transient photocurrent density of 0.058 mA cm$^{-2}$, which was higher than the ET (0.053 mA cm$^{-2}$) and WT (0.046 mA cm$^{-2}$). This i-t result indicates that the TXT has a better efficiency in the generation, separation, and transport of electron-hole pairs, which was in good agreement with the following EIS result. The smaller arc radius suggests a more effective separation of photogenerated electron-hole pairs and faster interfacial charge transfer. As can be seen from Figure 4G, the arc radius of TXT catalyst was smaller than the ET and WT, signifying that TXT could facilitate the effective separation and transfer of photogenerated electron-hole pairs that occur on the TXT surface. These electric characteristics showed that Triton X-100 played an effective role in improving the photocatalytic efficiency of the film.

**Mass Spectrum and Degradation Mechanism**

Nature of the chemical substances formed during the degradation process of PS was characterized through high-pressure photon ionization (HPP)-TOFMS. Mass spectra were obtained before and after 120 min of UV irradiation, and no dominant peak was observed at 0 min. Numerous characteristic ion fragments were formed during the photodegradation of PS such as m/z = 27 (C2H3$^+$), 39 (C2H5$^+$), 41 (C3H5$^+$), 51 (C6H5$^+$), 63 (C6H7$^+$), 77 (C9H11$^+$), 91 (C8H9$^+$), and 105 (C6H10$^+$) (Ng et al., 2018). These fragments were originated from the cleavage of PS spheres. The O-containing intermediates were observed with peak m/z values 43.01 (C2H4O$^-$), 44.94 (C2H5O$^-$), 57.03 (C2H6O$^-$), 59.04 (C2H4O$^-$), and 87.04 (C2H4O$^-$), but the intensities of these peaks are very weak. Therefore, these peaks were not considered in reaction intermediates. Figure 5A shows the m/z spectra of these commonly observed ions. Among the various degradation
intermediates, the m/z 105 belongs to the styrene (Bruns et al., 2017), whereas the m/z 77 and 91 correspond to the benzene and toluene. The other small fragments with m/z 27, 39, 41, and 51 were derived from the breakdown of bigger m/z fragments. As the photodegradation reaction proceeds, the PS fragments were further broken and finally changed into CO2 according to the GC result.

For further consolidation, an in situ DRIFTS study was done to understand the chemical functionality of organic species during the photodegradation reaction of PS (Figures 5B and S15). The IR spectra of TiO2/PS at about 3,600–3,200 cm−1 were attributed to the hydroxyl group formation (Kaczmarek et al., 2008), and the band that appears at 1,650–1700 cm−1 was due to a carbonyl group (C=O) (Subramani and Sepperumal, 2016; Zan et al., 2004). These two bands were assigned to the formation of aromatic and aliphatic ketones of the acetophenone and OH group in the PS chain. The reason for these two bands formation may be the chain scission or a competitive cross-linking or the oxidation of the benzene ring. A minor peak at 2,314 cm−1 was observed, which was due to CO2 formation during the reaction. The band at 1,527 cm−1 was associated with stretching of the C=C bonds (Gipson et al., 2015) from the aromatic ring, and the intensity of these bands increases continuously with increasing the illumination time of TiO2/PS composite. The band that appears at 1,425 cm−1 was due to C−H bend (Truc et al., 2017), whereas the band at 873 cm−1 corresponds to C−H stretching vibration of the aromatic ring and deformation vibration in cyclic carbonyl compounds (Al-Kadhemy et al., 2016). The bond smashing provides evidence that the TiO2 and UV irradiation accelerate the bond cleavage of PS. Figure S16 presents the thermogravimetric analysis (TGA) curve of PS, which signifies the complete mineralization after 24 h irradiation.

Figure 5. Mass Spectrum and Degradation Mechanism
(A) Mass spectra obtained by high-pressure photon ionization (HPPI)-TOFMS during the photodegradation of PS. (B) DRIFTS study of PS at different time intervals.
In order to understand the photodegradation mechanism of PS, including the role, and possible pathway for the formation of active species, corresponding effective scavengers were added in the reaction system. Figure S17 shows the change in PS diameter over TXT film after 6 h irradiation under different reaction conditions. TBA was employed to scavenge the \( \cdot \text{OH} \) (hydroxyl radical), EDTA to trap \( h^+ \) (holes), and the anaerobic experiment was conducted to check the role of oxygen. The addition of EDTA completely inhibited the PS degradation, whereas TBA and anaerobic experiments induced the depression effect. A slight degradation in anaerobic condition was observed owing to the attack of electron on PS particles yielding the PS cation radical, which further leads to its degradation (Lu et al., 2011; Szabó-Bárdos et al., 2011). Along this, holes and hydroxyl radicals were also formed by TiO\(_2\) and became dominant oxidants to attack plastic particles that cause degradation (Lee et al., 2014). Therefore, we conclude that \( h^+ \), \( \cdot \text{OH} \), and oxygen play an important role in the photodegradation of PS, whereas the \( h^+ \) was the dominant active species in our reaction. The possible reaction of \( h^+ \) with other species produces more active species causing the highly favorable generation of \( \cdot \text{OH} \). Moreover, the degradation performance of microplastics as compared with the literature and details are presented in Table S2.

The photodegradation reaction of PS on a solid state was initiated by holes and reactive oxidative species such as \( \cdot \text{OH} \) and \( \text{O}_2^-\). UV light stimulates the TiO\(_2\) to produce an electron in the conduction (e\(_{\text{CB}}\)) and formation of a positive hole in the valence band (h\(_{\text{VB}}\)) (Equation 2). There are two possibilities for reaction initiation. In the first pathway, the oxidation reaction takes place at the valence band. h\(_{\text{VB}}\) is a powerful oxidizing agent and capable of oxidizing organic compounds resulting in CO\(_2\) and H\(_2\)O (Equation 3), as well as it can also oxidize the compounds by generating hydroxyl radicals (Equation 4) (Kesselman et al., 1997). \( \cdot \text{OH} \) radicals have an electrophilic nature; they can non-selectively oxidize all electron-rich organic compounds and eventually result in their mineralization (Equation 5) (Shang et al., 2003).

\[
\begin{align*}
\text{TiO}_2 & \rightarrow h^+ + e_{\text{CB}} \quad \text{(Equation 2)} \\
h^+_{\text{VB}} + \text{microplastic} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(Equation 3)} \\
h^+_{\text{VB}} + \text{H}_2\text{O} & \rightarrow \cdot \text{OH} + \text{H}^+ \quad \text{(Equation 4)} \\
\cdot \text{OH} + \text{microplastic} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(Equation 5)}
\end{align*}
\]

In the second pathway, the degradation reaction takes place at the conduction band. The e\(_{\text{CB}}\) reacts with oxygen, forming a superoxide radical (Equation 6). This superoxide radical reaction with water produces \( \cdot \text{OOH} \) (Equation 7) that generates hydrogen peroxide (Equation 8). The hydrogen peroxide finally changed into \( \cdot \text{OH} \) (Equation 9), which reacts with microplastic and leads to its degradation (Cho and Choi, 2001).

\[
\begin{align*}
\text{O}_2 + e_{\text{CB}} & \rightarrow \text{O}_2^- \quad \text{(Equation 6)} \\
\text{O}_2^- + \text{H}_2\text{O} & \rightarrow \cdot \text{OOH} + \text{OH}^- \quad \text{(Equation 7)} \\
2 \cdot \text{OOH} & \rightarrow \text{O}_2 + \text{H}_2\text{O}_2 \quad \text{(Equation 8)} \\
\text{H}_2\text{O}_2 & \rightarrow 2 \cdot \text{OH} \quad \text{(Equation 9)}
\end{align*}
\]

**Conclusion**

This work proposed the efficient degradation and complete mineralization of microplastics by TiO\(_2\) nanoparticles film under UV light irradiation. Among synthesized films, TXT exhibits high performance as compared with ET and WT. A significant photocatalytic degradation and mineralization for varying sizes of PS such as 5 \( \mu \text{m} \), 1 \( \mu \text{m} \), and 700 \( \text{nm} \) and polyethylene (PE) were observed by TXT. The superior activity of TXT film is due to surface hydrophilicity and film texture. Surface hydrophilicity can enhance the interaction between semiconductors and plastic, particles that improved the film texture leading to charge transfer and separation that results in the fast degradation of microplastics. The degradation mechanism was studied by in situ DRIFTS and mass spectrometer, showing the generation of hydroxyl, carbonyl, and carbon-hydrogen groups, which is evidence for the photodegradation of PS. The film fabrication process does not include any costly, toxic, and hazardous chemicals, which makes this method highly efficient, beneficial, and economically important. Moreover, the solid phase photodegradation of microplastics also avoids the release of possible toxic intermediates into water in the liquid phase technology. Overall, the present study put forward a green and sustainable method for microplastic waste degradation from the environment.
Limitations of the Study
The main limitation of this study is that, initially, microplastics should be separated from water bodies, which can be done by using microplastic filters. Second, the complete mineralization of microplastics was observed under UV light. So, there is need for promising applications for microplastic mineralization under visible light.

Resource Availability

Lead Contact
Further information and requests for resources and reagents should be directed to and will be fulfilled by the Lead Contact, Zhang Liwu (zhanglw@fudan.edu.cn).

Materials Availability
This study did not generate new materials. Detailed information on experiments can be found in the accompanying Transparent Methods.

Data and Code Availability
This study did not generate a new code. All relevant data are available from the Lead Contact upon reasonable request.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.101326.

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AUTHOR CONTRIBUTIONS
L.Z. was the originator of the concept and planned and supervised the experiments. I.N. synthesized the photocatalysts, analyzed data, carried out photodegradation experiments, and wrote the manuscript. A.-U.-R.B., K.L., and H.C. performed the PEC experiments. T.W. and Y.L. did the in situ DRIFTS and HPPI-TOFMS measurements. S.A. and Y.Y. carried out the GC analysis. Y.F. assisted in Raman experiments. All authors reviewed the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing financial interests.

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Supplemental Information

Complete Photocatalytic Mineralization of Microplastic on TiO₂ Nanoparticle Film

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Supplemental Information for

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**Figure S11. Optical Measurements. Related to Figure 4.** (A) UV–vis absorption spectrum of TXT, ET, and WT (B) The Tauc plot of the TXT, ET, and WT nanoporous film. (UV–vis diffraction reflection spectroscopy (UV–vis DRS shows the absorption edges at about 390 nm representing the strong UV absorption region of WT and ET, while in TXT, a noticeable shift in the absorption edge towards the visible region at wavelength > 400 nm was observed (Figure S11A). The shift in the visible region has been claimed as a consequence of exciton confinement with a decrease in particle size indicative of the quantum size effect (Satoh et al., 2008). The bandgap of a semiconductor photocatalyst is linked with its absorption wavelength, and the bandgap decreases with an increasing absorption edge (Karthiga et al., 2015). The bandgap value of TXT, ET, and WT catalysts are 3.18, 3.32, and 3.43 eV, respectively (Figure S11B). The result confirms that triton X-100 based TiO₂ can efficiently improve the light absorption.)
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(A) TXT film at 4 μm scale bars. (B) TXT film at 2 μm scale bars.
Table S1. BET surface area, pore-volume, and pore size of the prepared catalysts. Related to Figure 4, S14.

| Sample | BET surface area (m²/g) | Pore volume (cm³/g) | Pore size (nm) |
|--------|-------------------------|---------------------|----------------|
| WT     | 50.65                   | 0.329               | 21.50          |
| ET     | 53.13                   | 0.357               | 21.19          |
| TXT    | 55.74                   | 0.390               | 34.69          |

Figure S14. Nitrogen isotherm and pore diameter distribution of TiO₂ films. Related to Figure 4. (A) Nitrogen isotherm of TXT, ET, and WT (B) Pore diameter distribution curve of TXT, ET, and WT. (Specific surface area and pore-size distribution analysis of prepared TiO₂ films were measured through Brunauer-Emmett-Teller (BET). Table S1 shows the BET results of TXT, ET, and WT films which were calculated by using the multipoint BET method. It was interesting to observe that TXT film has a high surface area, pore-volume, and pore size as compared to ET and WT films. It can be seen in Figure S14A, all TiO₂ films show the type H3 accordance with BDDT classification presenting the existence of mesopores. Figure S14B shows that the pore diameter of TXT film was higher as compared to the ET and WT films).
Figure S15. *In-situ* DRIFTs spectrum of PS with a time interval. Related to Figure 5.
Figure S16. Mineralization of PS. Related to Figure 2. Thermogravimetric analysis of polystyrene loaded TiO₂ film before and after UV irradiation. (The complete mineralization was examined through thermogravimetric analysis (TGA), and the curves are presented in Figure S16. TGA of polystyrene (PS) loaded TiO₂ film showed different weight loss percentages at different temperatures before and after UV irradiation. Before reaction, thermal decomposition of polystyrene began at 263 °C, and a sudden decrease in weight was noticed at a narrow temperature range from 234-274 °C accompanied with a shoulder peak at about 280 °C. The complete decomposition of PS was taken place at 490 °C and then directly changed to gaseous species. Interestingly, negligible change in the TGA curve was observed after the degradation reaction, signifying the complete mineralization of PS and stability of the TiO₂ sample).
Figure S17. Detection of active species. Related to Figure 5. Hole Scavenging experiment result after 6 h of photoirradiation (Blank test was conducted without a photocatalyst (PS was dropped on cleaned FTO) control experiment was done on TXT film, 10 mM EDTA and 1000 mM TBA was added in 2 mL PS solution and 30 µL PS was dropped on TXT film for active species detection).
| Catalysts         | Morphology | Microplastics Type | Degradation System | Degradation Efficiency | Light Source                                  | Reference                                |
|------------------|------------|--------------------|--------------------|------------------------|-----------------------------------------------|------------------------------------------|
| PE/N-TiO₂        | Powder     | HDPE               | Liquid             | 6.40% after 20 h       | Fluorescent visible light                     | (Ariza-Tarazona et al., 2019)            |
| C, N-TiO₂        | Powder     | HDPE               | Liquid             | 71.77% after 50 h      | LED lamp with visible spectrum                | (Ariza-Tarazona et al., 2020)            |
| Mn@NCN Ts        | Powder     | PE                 | Liquid             | 54% after 8 h          | 0.2 g/L; PMS at 160°C                         | (Kang et al., 2019)                      |
| Photooxidation   | -          | 14C-PS             | Liquid             | 28.1% after 48 h       | 254 nm UV light                              | (Tian et al., 2019)                      |
| TiO₂             | Film       | PS                 | Solid              | 99.99% after 24 h      | 254 nm UV light                              | This study                               |
| TiO₂             | Powder     | PS                 | Liquid             | 44.66% after 12 h      | 254 nm UV light                              | This study                               |

Here, HDPE = High-density polyethylene; PE = Polyethylene; 14C-PS = Adioactively polystyrene, PS = Polystyrene.
Figure S18. Schematic illustration of photocatalyst fabrication. Related to Figure 4. (At the initial stage, the TiO$_2$ powder was ground, after getting fine powder ethanol, and Triton X-100 was added to make a precursor solution. This precursor solution was dropped on FTO following the calcination process. A number of the coating can be increased to attain the desired film thickness).
**Transparent Methods**

**Material Growth**

Precursor solution of TiO$_2$ was prepared by grinding the TiO$_2$ (P25) powder (80 % anatase, and 20 % rutile from Degussa, Germany) in a mortar. The stuck TiO$_2$ powder inside mortar was removed with a spatula in order to grind aggregates. After getting the fine powder, 1 mL of DI water and 300 μL of Triton X-100 (Sinopharm Chemical Reagent Co., Ltd. China) were added dropwise and ground to make a paste. Triton X-100 was used as a non-ionic surfactant. Furthermore, 15 mL of ethanol (China General Reagent Co., Ltd.) was added dropwise into TiO$_2$ paste. The obtained precursor solution was sonicated 30 min, stirred for 40 min, and then named as TXT based TiO$_2$. Ethanol-based TiO$_2$ (ET) photocatalyst was synthesized by the same method except Triton X-100. Water-based TiO$_2$ (WT) was prepared by adding only DI water in TiO$_2$ powder.

Microplastics PS and PE were studied as a model pollutant. They were chosen based on their morphology, environmental abundance, and global production. PS spheres had a smooth surface and a definite size. Different sizes of PS spheres were studied due to their specific size while polyethylene had a rough texture and irregular shaped different sized particles. Microplastics solutions of PS and PE were prepared by the following method. 20 μL of standard concentrated solution of PS spheres (Standard polystyrene microspheres from Huge) were added in 20 mL of DI water and sonicated for 30 min. PE solution was prepared by adding 0.005 g of commercial PE powder (PE-50200 from Shanghai Youngling Electromechanical Technology Co., Ltd. China) in 5 mL of DI water and sonicated for 30 min.

**Film Fabrication**

The nanoporous WT, ET, and TXT based TiO$_2$ structures were fabricated on piranha [H$_2$SO$_4$:H$_2$O$_2$ = 3:1] cleaned FTO glasses (Wuhan Jinge-Solar Energy Technology Co., Ltd. China). The precursor solution of TiO$_2$ (25 μL) was dropped on conduction side of FTO (covered area 1.25 × 1 cm$^2$) dried in airflow oven at 70 °C and calcined at 450 °C for 30 min with a ramping rate of 5 °C min$^{-1}$. The schematic illustration is given in Figure S18.
**Characterization**

To study the crystal structure of synthesized TXT, ET, and WT based TiO$_2$ photocatalysts, X-ray diffraction (XRD) analysis was done. XRD spectra were collected by Bruker D8 Advance (XRD) with a Cu Kα radiation value ($\lambda=1.54$ Å) ranging from 10° to 70° (2θ) with a scanning speed of 2° min$^{-1}$. Raman spectrum and imaging were recorded by using the Raman xploRA plus spectrometer (HORIBA), with a green laser ($\lambda = 532$ nm) as an excitation source and Raman microscope objective 50x. The morphological characteristics of synthesized catalyst (TXT, ET, WT) and PS spheres were analyzed through field emission scanning electron microscopy (FE-SEM), transmission electron microscope (TEM), and phenom Prox. Each sample was sputtered with gold before SEM analysis. The size of PS spheres was calculated using ImageJ software. To examine the light absorption and optical band gap of fabricated photocatalyst films, the UV–vis absorption spectra were acquired by using a UV–vis diffraction reflection spectroscopy (SHIMADZU UV–2600). Specific surface area and pore-size distribution analysis of prepared TiO$_2$ films were measured through Brunauer-Emmett-Teller (BET). Amperometric $i$-$t$ curve measurement was performed on an electrochemical station (CHI 660E, Shanghai Chenhua Co., Ltd. China) with a 300 W Xe lamp as a light source (100 mW cm$^{-2}$). The reactor cell consisted of three electrodes, a working electrode (fabricated film), a counter electrode (Pt wire), and a reference electrode (Ag/AgCl) in 0.1 M solution of Na$_2$SO$_4$ electrolyte. The electrochemical impedance spectroscopy (EIS) was also obtained by using the same electrodes and electrolyte solution. The hydrophilicity of films was measured by the contact angle system (POWER EACH, model JC2000DM), and the droplet images were taken through a CCD camera. The chemical state of TiO$_2$ film was measured via X-ray photoelectron spectroscopy (XPS).

**Photodegradation Experiment**

For solid-phase degradation, PS spheres solution (20 μL) was dropped on the catalyst films as well as on bare FTO (without catalyst) and dried at room temperature. Two UV lights (each UV light consists of four lamps with 32 W) were used as an artificial light source with a wavelength of 365 nm (3.05 mW cm$^{-2}$) and 254 nm (4.95 mW cm$^{-2}$) for the degradation of microplastics. 254 nm
UV light is deeper into the UV spectrum and typically generated about 90% of the energy as compared to 365 nm. The photodegradation experiment was done in a lamp housing box (35 cm × 25 cm × 15 cm) under the ambient air condition, and the outside temperature was maintained by using a small air fan. The distance between the light source and the samples was 10 cm. All photodegradation experiments were carried out at room temperature without the addition of any oxidant, and each experiment was repeated three times, and average data is presented here.

The liquid phase degradation experiment was carried out by adding 0.05 g of TXT powder in 100 mL of PS solution (100 μL of PS (5 μm size) in 100 mL DI water). The solution was kept for stirring continuously during degradation reaction under 254 nm UV light irradiation, and samples were taken with the time interval.

**Detection of Active Species**

For the identification of relevant active species formed on the solid (microplastic)-solid (TiO₂) interface under UV light, different scavengers were added, e.g., ethylenediaminetetraacetic acid (EDTA) was used to scavenge the holes (h⁺), tert-butyl alcohol (TBA) was used as a hydroxyl radical (·OH) scavenger, and the anaerobic experiment was conducted to check the role of oxygen. Briefly, the solutions of 10 mM EDTA and 1000 mM TBA were prepared in 2 mL of PS. 30 μL of PS solution with scavengers (EDTA and TBA) was dropped on TXT film for the detection of active species. Anaerobic hole scavenging experiment was conducted by placing the PS loaded TiO₂ film in an airtight reaction chamber (upper half part made of quartz and button half part made of Teflon, equipped with helical spin structure) under irradiation. Before irradiation, the air was removed from the chamber through the groove, and a vacuum environment was built through injection. The blank test was conducted without a photocatalyst (PS was dropped on cleaned FTO). All films were kept under UV light irradiation for 6 h, and analysis was done through SEM. The photodegradation of PS was observed to check the inhibition effect of these scavengers.

**In-situ DRIFTS Experiment**

*In-situ* DRIFTS analysis was done on a Shimadzu FT-IR spectrometer (Tracer-100) armed with
a highly sensitive mercury cadmium telluride detector (MCTD) cooled through liquid nitrogen, and a temperature controller was fixed to the DRIFTS chamber to confirm the constant reaction temperature (Praying Mantis Kit, Harrick). For the in-situ DRIFT experiment, TiO\textsubscript{2} nanoparticles were prepared by the following method: TiO\textsubscript{2} precursor solution was dried for 6 h at 120 °C and then calcined at 450 °C with a ramping rate 5 °C min\textsuperscript{-1} for 30 min. The PS/TiO\textsubscript{2} composite was prepared by mixing 20 mL of PS solution (40 μL in 20 mL DI water) in prepared TiO\textsubscript{2} powder and dried at 70 °C. A small proportion of PS/TiO\textsubscript{2} composite powder was used for DRIFTS experiment. The employed condition was: RH = 85 %, air (100 mL/min), and 365 nm UV light.

**Intermediates Detection**

The reaction intermediates during the PS degradation were detected by high-pressure photon ionization-time of flight mass spectrometry (HPPI-TOFMS) ion mass analyzer (Wang et al., 2016). The sample was prepared by dropping 40 μL solution of PS on TXT film which was dried at room temperature. For intermediates analysis, the prepared PS loaded TXT film was kept in a reaction chamber (upper half part made up of quartz and button part made up of Teflon, equipped with helical spin structure and the shallow groove) supplied with a continuous airflow under 365 nm UV light for 120 min. Employed relative humidity was 100 % at 25 °C, and the HPPI-mass spectrum was recorded automatically.

**End Product Analysis**

Final products of microplastics degradation were analyzed by gas chromatography (SHIMADZU GC-2014). The concentration of end product was expressed in ppm. Sample for GC analysis was prepared by making the composite of 1 g of TiO\textsubscript{2} powder with 700 μL solution of PS and dried at 70 °C. The obtained powder was put in a designed airtight quartz chamber under 365 nm UV light. Before reaction, the airtight chamber was vacumed, and pure air was injected in it. Moreover, complete mineralization was examined through thermogravimetric analysis (TGA).
**RAMAN Analysis of PE**

The degradation of PE was investigated by using Raman xploRA plus spectrometer (HORIBA) following the RAMAN imaging technique, while the RAMAN spectrum was recorded with green laser ($\lambda = 532$ nm) as an excitation source. A visual search was done via Raman microscope objective 50x to take the image and spectrum of the selected area of PE with time intervals. Throughout the whole experiment, the same point was selected (all influencing parameters were kept the same) for the analysis of PE degradation.
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