Photoconverting polyethylene terephthalate into exclusive carbon dioxide by heterostructured NiO/Fe₂O₃ nanosheets under mild conditions

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ABSTRACT Degradation of polyethylene terephthalate (PET) plastics by the traditional technologies usually requires high energy consumption and encounters poor product selectivity. Herein, we report the photoconversion of PET into carbon dioxide with 100% selectivity by in-plane heterostructured NiO/Fe₂O₃ nanosheets in pure water under normal temperature and pressure. High-resolution transmission electron microscopy, X-ray absorption near-edge spectroscopy and X-ray photoelectron spectra demonstrate the construction of the Z-scheme heterojunction, which can help to accelerate the separation of electron-hole pairs for enhanced PET conversion property. Various *in-situ* characterization techniques and experiments unveil that PET is photodegraded into carbon dioxide by the photogenerated holes, while oxygen is photoreduced into water by the photoexcited electrons. This work will open new avenues toward resolving the white pollution crisis.

Keywords: photocatalysis, PET, normal temperature and pressure, selectivity

INTRODUCTION

Plastic products are indispensable for our lives thanks to their desirable properties of lightness, durability and low price. It is estimated that the annual production of plastics would reach approximately 1.12 billion tons worldwide by 2050 [1]. As a typical plastic, polyethylene terephthalate (PET), a semicrystalline thermoplastic polyester, has been widely used in packaging, textile and electronics industry since it was first synthesized in 1941 [2,3]. Nowadays, the global production of PET has exceeded 50 million tons every year [4], while the spontaneous decomposition of discarded PET plastics in the nature normally requires hundreds of years [5]. That is mainly because PET molecules contain the extremely stable benzene rings, which account for the resistance to their dissociation. To date, in addition to the traditional incineration and landfills, pyrolysis of PET has been largely reported and even applied in practice [6]. However, this process is often proceeded under high temperature and pressure, and the obtained products always encounter poor selectivity [7–9]. Also, the eco-friendly biodegradation of PET is deemed to be a potential strategy for converting PET into

dimethyl terephthalate and ethylene glycol [10], whereas the bio-enzymes are usually expensive. Compared with these methods, photodegradation of PET may possess distinct advantages in some respects since solar energy is clean and inexhaustible, and it does not demand rigorous reaction conditions [11]. Recently, Uekert *et al.* [12] have successfully photoconverted PET into organic chemicals with the conversion efficiency of ca. 16.6% in strong alkaline aqueous conditions, whereas there has been no report concerning the solar-driven PET degradation in pure water without adding any sacrificial agent under mild conditions.

Until now, photocatalytic plastics conversion suffers from low conversion efficiency, which is primarily attributed to the small number of active sites and the fast carrier recombination for the single-component photocatalyst during the catalytic process [13,14]. Given this aspect, two-dimensional (2D) in-plane heterojunction catalysts may be utilized to boost the photocatalytic performance [15]. On the one hand, 2D materials with large fraction of uncoordinated dangling bonds can provide abundant active sites. On the other hand, the construction of in-plane heterojunction confined in the 2D materials would produce the built-in electric fields on the heterointerfaces, which can guide the directional transfer of carriers and hence effectually promote the carrier separation. In particular, the establishment of Z-scheme heterojunction is more favorable relative to the conventional heterojunction (e.g., type-II) because the Z-scheme heterojunction retains the electrons and holes with higher redox potentials, thus contributing to the high catalytic efficiency [16–18]. From the above analysis, it is appealing to design and establish 2D catalysts with in-plane Z-scheme heterojunction to enhance the property of PET photoconversion under mild conditions.

EXPERIMENTAL SECTION

Synthesis of the NiO/Fe₂O₃ nanosheets

In a modified synthetic procedure from a previous study [19], 30 mL of deionized water was mixed with 1.35 mmol of Ni(CH₃COO)₂·4H₂O, 0.15 mmol of Fe(NO₃)₃·9H₂O and 6 mmol of urea, and then stirred for a period of time at room temperature. Subsequently, the solution was added into a Teflon-lined autoclave and heated at 180°C for 6 h. After the products

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were washed for several times, the dry oven was employed to desiccate the obtained products overnight. Ultimately, the obtained products after drying were calcined at 400°C for half an hour at air atmosphere.

Synthesis of the NiO nanosheets

Deionized water (30 mL) was mixed with 1.35 mmol of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 6 mmol of urea, and then stirred for a period of time at room temperature. Subsequently, the solution was added into a Teflon-lined autoclave and heated at 180°C for 6 h. After the products were washed several times, the dry oven was employed to desiccate the obtained products overnight. Ultimately, the obtained products after drying were calcined at 400°C for half an hour at air atmosphere.

Synthesis of the Fe_2O_3 nanoparticles

Deionized water (30 mL) was mixed with 0.15 mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 6 mmol of urea, and then stirred for a period of time at room temperature. Subsequently, the solution was added into a Teflon-lined autoclave and heated at 180°C for 6 h. After the products were washed for several times, the dry oven was employed to desiccate the obtained products overnight. Ultimately, the obtained products after drying were calcined at 400°C for half an hour at air atmosphere.

Characterizations

Transmission electron microscopy (TEM) images were performed with a JEOL-2010 TEM with an acceleration voltage of 200 kV. High-resolution TEM (HRTEM) images were carried out on a JEOL JEM-ARM200F TEM/scanning TEM with a spherical aberration corrector. Veeco DI Nano-scope Multi-Mode V system was employed to acquire atomic force microscopy (AFM) images. The NiO/ Fe_2O_3 nanosheet and the NiO nanosheet powders were initially dispersed in water. After being placed still for several seconds, the suspension was dripped into the carbon-coated TEM support grid and the silicon substrate for TEM test and AFM measurement, respectively. X-ray diffraction (XRD) patterns were obtained from a Philips X'Pert Pro Super diffractometer with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Ultraviolet-visible (UV-vis) diffuse reflectance spectra were measured on a Perkin Elmer Lambda 950 UV-vis-near-infrared (NIR) spectrophotometer. X-ray photoelectron spectroscopy (XPS) survey spectra were recorded by using an ESCALab MKII X-ray photoelectron spectrometer with an X-ray source (Mg K α $h\nu = 1253.6 \text{ eV}$), in which every XPS signal was referenced to C 1s. Fe and Ni contents were measured by inductively coupled plasma mass spectroscopy (ICP-OES) (PerkinElmer Optima 7300 DV). Room-temperature photoluminescence (PL) spectra and Raman spectra were detected on a RenishawRM3000 Micro-Raman system. *In-situ* electron spin resonance (ESR) spectra were measured on an ESR spectrometer (JEOL JES-FA200) at room temperature. *In-situ* Fourier transform infrared spectroscopy (FTIR) spectra were obtained by using a Thermo Scientific Nicolet iS50. PET plastics were crushed into powders by a pulverizer (BENCHEN SCIENCE AND TECHNOLOGY, BC3-1) for further photocatalytic conversion. Synchrotron-radiation photoemission spectroscopy (SRPES) and synchrotron-radiation vacuum UV photoionization mass spectrometry (SVUV-PIMS) spectra were executed under Station BL11U and BL04B at the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

Photoconversion of pure PET and mineral water bottles into CO_2 under normal temperature and pressure

Reagent-grade PET (CAS: 25038-59-9) with the size of ca. five millimeters was purchased from Kuer Chemical Technology (Beijing) Co., Ltd. without any further purification. The reagent-grade PET and mineral water bottles were further pulverized into powders to ensure the close contact with photocatalysts. Then 20 mg of NiO/ Fe_2O_3 nanosheets or NiO nanosheets and 100 mg PET were initially mixed, the solid mixtures and 10 mL water were added into the glass reactor. During the photoconversion processes, the reaction system was under continuous magnetic stirring, while the temperatures of the reaction cell were controlled at $298 \pm 0.2 \text{ K}$ by the recirculating cooling water system. The light source for the photocatalysis was a 300-W Xe lamp (CEL-HXF300, Beijing Ceaulight Technology Co., Ltd., China) with a standard AM 1.5G filter. The liquid products were quantified by nuclear magnetic resonance (NMR) spectroscopy. After 3-h illumination, the gas and liquid products were quantified by the gas chromatograph and NMR spectroscopy, respectively. In addition, the mixture of photocatalysts and PET powders was collected by filtration and drying. Approximately 100 mg of solid mixture was residual, and hence 20 mg of PET was further added into the mixture for the next cycle test. The 1D ^1H spectrum was measured with water suppression using a pre-saturation method. The gas products were qualitatively analyzed by Techcomp GC7900 gas chromatograph (FID detector, TDX-01 column) by identifying the chromatographic peaks. To analyze the content of CO_2 dissolved in the solution, 2.0 mL supernate was taken immediately after the photocatalysis; after adding excess $\text{Ba}(\text{OH})_2$ powders to the solution, the white precipitate could be obtained; after the following centrifugation and the gravimetric analysis for the white precipitate, the produced CO_2 dissolved in the solution during the photoconversion of PET could be calculated. Apparent quantum efficiency is calculated *via* the following equation:

$$\text{AQE}(\%) = 100 \times \frac{4n_{\text{CO}_2}N_Ahc}{t_{\text{irr}}\lambda IA},$$

where n_{CO_2} is the amount of formed CO_2 (mol), N_A is the Avogadro's constant (mol^{-1}), h is the Planck's constant (J s), c is the speed of light (m s^{-1}), t_{irr} is the irradiation time (s), λ is the wavelength (m), I is the light intensity (W m^{-2}), and A is the irradiated area (m^2).

RESULTS AND DISCUSSION

Bearing the above in mind, earth-abundant and chemically stable metal oxides can act as the promising candidate. Taking NiO and Fe_2O_3 as examples, their staggered conduction band (CB) and valence band (VB) furnish the prerequisite for the formation of Z-scheme heterojunction [20]. Under illumination, the photogenerated electrons can transfer from the CB of Fe_2O_3 to the VB of NiO, which is beneficial for the separation of electron-hole pairs. Herein, the in-plane heterostructured NiO/ Fe_2O_3 nanosheets were successfully fabricated by calcining the Ni-Fe precursors that were synthesized *via* a straightforward hydrothermal process. As shown in Fig. S1, the XRD pattern of the synthetic sample could be indexed to cubic NiO (JCPDS No. 47-1049) [21]. In addition, the TEM image in Fig. 1a depicted their sheet-like morphology, and the AFM image in Fig. 1b elaborated that their average thickness of about 1.66 nm. Interestingly, Fe K-edge X-ray absorption near-edge (XANES) spec-

Figure 1 (a) TEM and (b) AFM images and the corresponding height profiles of the NiO/Fe₂O₃ nanosheets. (c) Fe K-edge XANES spectra of the NiO/Fe₂O₃ nanosheets and the commercial Fe₂O₃. (d) HRTEM and (e, f) the enlarged HRTEM images of the NiO/Fe₂O₃ nanosheets, in which (e) and (f) correspond to those of areas 1 and 2 in (d), respectively. The related schematic atomic models of (g) cubic NiO and (h) hexagonal Fe₂O₃.

trum of the synthetic sample was strictly consistent with that of the commercial Fe₂O₃ (Fig. 1c), strongly demonstrating the Fe₂O₃ domains confined in the NiO nanosheets. Moreover, HRTEM images in Fig. 1d–f also manifested the coexistence of two different structural domains. Of note, Fig. 1e, g revealed that the 0.209-nm interplanar distances and the dihedral angle of 90° could be assigned to the (200) and (020) planes of cubic NiO. Meanwhile, Fig. 1f, h disclosed that the 0.218-nm interplanar distances and the dihedral angle of 60° could be attributed to the (200) and (020) planes of hexagonal Fe₂O₃ (JCPDS No. 72-0469). As displayed by the elemental mapping images in Fig. S2, Fe, Ni and O elements were dispersed on the NiO/Fe₂O₃ nanosheets. Furthermore, the ICP-OES uncovered that the contents of Ni and Fe elements in the nanosheets were ca. 49 and 8 wt%, respectively (Table S1). For comparison, the NiO nanosheets with nearly the same thickness were further prepared (Fig. S3). As unveiled by the Raman spectra in Fig. S4, there was an obvious shift of Raman peak for the NiO nanosheets after the introduction of Fe₂O₃ domains, which implied the crystal lattice distortion of NiO nanosheets owing to the intrusion of Fe elements [22]. Consequently, all the above results powerfully certified the successful preparation of the 2D in-plane heterostructure (NiO/Fe₂O₃ nanosheets) and the NiO nanosheets.

To uncover how the in-plane heterostructure affects the electronic properties, XPS spectra were examined on the NiO/Fe₂O₃ nanosheets and the NiO nanosheets. As revealed by the Fe 2p XPS spectra in Fig. 2a, only Fe³⁺ was detected on the NiO/Fe₂O₃ nanosheets [23], which further confirmed the existence of

Fe₂O₃ domains, matching well with the results of XANES spectra in Fig. 1c. Interestingly, the Ni 2p XPS spectra in Fig. 2b disclosed that the NiO/Fe₂O₃ nanosheets showed a higher binding energy shift of XPS spectra (ca. 0.75 eV) with respect to the NiO nanosheets, hinting the steady electron transfer from NiO to Fe₂O₃ domains. That was to say, there was an internal electric field that pointed from the NiO to Fe₂O₃ in the NiO/Fe₂O₃ nanosheets. To further unveil the electronic band structures of the in-plane heterostructured NiO/Fe₂O₃ nanosheets, SRPES was carried out over the NiO nanosheets and the Fe₂O₃ nanoparticles which were prepared by the same strategy without adding the nickel acetate (Fig. S5) [24]. As exhibited in Fig. S6, the VB edge of the NiO nanosheets and the Fe₂O₃ nanoparticles located at 1.22 and 2.31 V *versus* normal hydrogen electrode (NHE) at pH 7. On the basis of the UV-vis diffuse reflectance spectra and the corresponding band gap, their electronic band structures *versus* NHE at pH 7 could be acquired in Fig. 2c. Of note, the above-mentioned electron transfer could induce an internal electric field that pointed from the NiO to Fe₂O₃. In this case, the built-in electric field would drive the transfer of photoexcited electrons from the CB band of Fe₂O₃ domains to the VB band of NiO domains under illumination, thus establishing a band structure of typical Z-scheme heterojunction rather than the Type II heterojunction [25]. As a result, the construction of Z-scheme in-plane heterostructured NiO/Fe₂O₃ nanosheets could favor the separation of photogenerated electron-hole pairs for enhanced photocatalytic property (Fig. 2c), affirmed by the PL spectra in Fig. 2d.

To unravel how the in-plane heterojunction in NiO nano-

Figure 2 (a) Fe 2p XPS spectra for the NiO/Fe₂O₃ nanosheets; (b) Ni 2p XPS spectra for the NiO/Fe₂O₃ nanosheets and the NiO nanosheets; (c) schematic illustrating the electronic band structures of the NiO nanosheets and the Fe₂O₃ nanoparticles; (d) PL spectra for the NiO/Fe₂O₃ nanosheets and the NiO nanosheets.

sheets influence the property of PET photoconversion, the experiments of solar-driven PET conversion over these two samples were carried out in pure water without any sacrificial agent or alkali. A 300-W Xe lamp with a standard AM 1.5G filter was used as the light source, and the photodegradation experiments were performed under normal temperature and pressure. During the photocatalytic process, no organic liquid product was detected by the NMR spectra (Fig. S7) and ignorable CO₂ gas was detected by the gas chromatography over neither the NiO/Fe₂O₃ nanosheets nor the NiO nanosheets. It is worth noting that plentiful of CO₂ dissolved in the solution could be detected by the coprecipitation method (see the EXPERIMENTAL SECTION), in which the mole number of the generated CO₂ was equal to that of the BaCO₃ precipitate. In other words, both the two samples could realize the photoconversion of PET plastics into CO₂ with 100% selectivity in pure water under normal temperature and pressure. As displayed in Fig. 3a, the NiO/Fe₂O₃ nanosheets showed the CO₂ evolution rate of 3.7 mmol g⁻¹ h⁻¹, roughly 3.3 times that for the NiO nanosheets. In other words, the PET conversion for the NiO/Fe₂O₃ nanosheets could come up to ca. 15.6%. Note that the apparent quantum yield for the NiO/Fe₂O₃ nanosheets was calculated to be ca. 1.89% at 350 nm. One of the main reasons was that the establishment of Z-scheme heterojunction could accelerate the carrier separation, and hence the NiO/Fe₂O₃ nanosheets displayed higher activity for PET photoconversion into CO₂.

Control experiments demonstrated that there was no detectable CO₂ in the absence of either light illumination, or photocatalyst, or PET, verifying that the CO₂ was originated from the photodegradation of PET by the photocatalysts. Moreover, Fig. 3b uncovered that nearly the same amount of CO₂ could be obtained when the reaction atmosphere was changed from air to O₂ atmosphere for the two samples, whereas there was no detectable CO₂ when the experiment was executed under the Ar atmosphere, insinuating that O₂ participated in the PET photoconversion process. More notably, the CO₂ formation rate and selectivity for both the NiO/Fe₂O₃ nanosheets and the NiO nanosheets were not passivated after five consecutive cycles of photocatalysis (Fig. 3c, d). Moreover, the XRD patterns and TEM images in Figs S8–S11 attested that the phases and the morphologies of these two samples showed negligible variation after the photodegradation test, testifying their favorable photostability. It was worth noting that both the NiO/Fe₂O₃ nanosheets and the NiO nanosheets could also realize the photoconversion of mineral water bottles, mainly composed of PET, into CO₂ with the formation rates of ca. 4.16 and 1.28 mmol g⁻¹ h⁻¹ under normal temperature and pressure (Fig. S12).

To dive deep into the mechanism of PET photoconversion into CO₂, *in-situ* characterization techniques were utilized to monitor the surface reaction intermediates during the process. Taking the *in-situ* FTIR measurements over the NiO/Fe₂O₃

Figure 3 The evolution rates of CO₂ during the photoconversion of PET at (a) air atmosphere; (b) O₂ and Ar atmosphere; (c) CO₂ yields and (d) CO₂ selectivities during the measurement for the photoconversion of pure PET at air atmosphere over the NiO/Fe₂O₃ nanosheets and the NiO nanosheets in water under normal temperature and pressure. The error bars in (a) and (b) represent the standard deviations of three independent measurements of the same sample.

nanosheets as an example, several bands were generated with the increase of irradiation time during the PET photoconversion process. As exhibited in Fig. 4a, b, the peaks at ca. 2320 and 2360 cm⁻¹ could be assigned to the CO₂ molecules, demonstrating the production of CO₂ [26]. In addition, the peaks at roughly 1540 and 1590 cm⁻¹ could belong to the COOH* groups, while the peaks at approximately 1180 and 1220 cm⁻¹ could be attributed to the CH₃O* group. Also, the peaks at about 1080 cm⁻¹ could be ascribed to the CHO* group [27–30]. That was to say, the *in-situ* FTIR spectra manifested the formation of COOH*, CH₃O* and CHO* intermediates during the PET photoconversion process. Moreover, as shown in the *in-situ* ESR spectra, the ESR signals of 1:2:2:1 quartet pattern, attributed to the DMPO-O₂^{•-} spin adducts [31,32], could affirm the generation of O₂^{•-} radicals during the PET photoconversion procedure (Fig. 4c). These results further attested the conjecture for the electronic band structures of Z-scheme heterojunction in Fig. 2c. That was to say, if the electrons migrated from the CB of NiO to that of Fe₂O₃ domains (Type II heterojunction), O₂^{•-} radicals could not be produced during the PET photoconversion procedure [33]. To reveal the origin of CO₂, isotope-labeling experiments and SVUV-PIMS were employed to discern the reaction products during the PET photoconversion under normal temperature and pressure at air atmosphere with a small amount of ¹⁸O₂. The SVUV-PIMS signal at *m/z* = 46 (C¹⁶O¹⁸O) in Fig. 4d elucidated that O₂ involved in the PET photo-

degradation to produce CO₂. Additionally, an SVUV-PIMS signal at *m/z* = 20 (H₂¹⁸O) was detected during this procedure, which illustrated that O₂ participated in the photoreduction process to form H₂O. Similar to those of the NiO/Fe₂O₃ nanosheets, the *in-situ* FTIR spectra and *in-situ* ESR spectra over the NiO nanosheets in Figs S13 and S14 suggested the same pathway for PET photoconversion into CO₂. Based on the above analyses, it could be concluded that PET plastics were photo-degraded into CO₂ through the stepwise oxidation of CH₃O*, CHO* and COOH* intermediates by the photogenerated holes; and meanwhile, O₂ was photoreduced into H₂O via the protonation of O₂^{•-} by the photoexcited electrons (Fig. 4e).

CONCLUSIONS

We designed and constructed a novel 2D in-plane heterostructure to accelerate the carrier dynamics for achieving improved PET photoconversion efficiency. As an example, in-plane heterostructured NiO/Fe₂O₃ nanosheets were synthesized through calcining the Ni-Fe precursors, certified by the HRTEM image, XPS spectra and XANES spectra. PL spectra elaborated that the NiO/Fe₂O₃ nanosheets possessed the promoted carrier separation and migration efficiency relative to the NiO nanosheets. More importantly, *in-situ* FTIR spectra, *in-situ* ESR spectra, SVUV-PIMS spectra and ¹⁸O₂ isotope-labeling experiments confirmed that O₂ not only took part in the PET photo-degradation process to produce CO₂ through the stepwise oxi-

Figure 4 (a) 3D colormap surface and (b) 2D contour color fill of *in-situ* FTIR spectra; (c) *in-situ* ESR spectra using methanol as the solvent for detecting the reaction intermediates during the PET photoconversion over the NiO/Fe₂O₃ nanosheets under normal temperature and pressure. (d) SVUV-PIMS spectra during the PET photoconversion over the NiO/Fe₂O₃ nanosheets under normal temperature and pressure at air atmosphere with a small amount of ¹⁸O₂. (e) Schematic representations for the mechanism of PET photoconversion into CO₂.

dation of various intermediates, but also involved in the photoreduction process to generate H₂O *via* the protonation of O₂^{•-}. Therefore, the CO₂ evolution rate of the NiO/Fe₂O₃ nanosheets was approximately 3.3 times that of the NiO nanosheets. In brief, this work provided a promising lead for the design of high-efficiency catalysts to photodegrade the PET plastics, with effort to alleviate the white pollution problem.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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异质结NiO/Fe₂O₃纳米片在温和条件下实现PET高选择性光降解

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摘要 通过传统技术降解聚对苯二甲酸乙二醇酯(PET)塑料的过程往往需要消耗大量能量且所得到的产物种类复杂。鉴于此, 我们报道了一种新颖的PET降解策略, 即在温和条件下、纯水溶液中利用面内异质结NiO/Fe₂O₃纳米片实现了PET塑料的100%选择性光降解。其中, 我们通过高分辨透射电子显微镜、X射线近边吸收谱和X射线光电子能谱证实了所制备的NiO/Fe₂O₃纳米片为Z-scheme异质结; 通过光致发光光谱证实了此Z-scheme异质结的构建有利于促进反应过程中光生电子-空穴对的分离, 从而提高了PET塑料的光降解效率。此外, 我们通过多种原位表征技术和标记实验证实了PET塑料被光生空穴降解成二氧化碳, 同时氧气被光生电子还原为水的反应机理。总之, 该工作为解决白色污染危机提供了一种有前景的解决方案。