Synthesis of Hollow Flower-Like Fe₃O₄/MnO₂/Mn₃O₄ Magnetically Separable Microspheres with Valence Heterostructure for Dye Degradation

Mingliang Ma ¹, Yuying Yang ¹, Yan Chen ¹, Fei Wu ¹, Wenting Li ¹, Ping Lyu ¹,*, Yong Ma ², Weiqiang Tan ³ and Weibo Huang ¹,*

¹ School of Civil Engineering, Qingdao University of Technology, Qingdao 266033, China
² School of Material Science and Engineering, Shandong University of Science and Technology, Qingdao 266590, China
³ School of Environmental and Municipal Engineering, Qingdao University of Technology, Qingdao 266033, China
* Correspondence: lyuping_qut@sina.com (P.L.); huangweibo@qut.edu.cn (W.H.); Tel.: +86-0532-8507-1320 (P.L. & W.H.)

Received: 14 June 2019; Accepted: 1 July 2019; Published: 5 July 2019

Abstract: In this manuscript, hollow flower-like ferric oxide/manganese dioxide/trimanganese tetraoxide (Fe₃O₄/MnO₂/Mn₃O₄) magnetically separable microspheres were prepared by combining a simple hydrothermal method and reduction method. As the MnO₂ nanoflower working as precursor was partially reduced, Mn₃O₄ nanoparticles were in situ grown from the MnO₂ nanosheet. The composite microspheres were characterized in detail by employing scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Brunauer–Emmett–Teller (BET), vibration sample magnetometer (VSM) and UV–visible spectrophotometer (UV–vis). Under visible light conditions, the test for degrading rhodamine B (RhB) was used to verify the photocatalytic activity of the photocatalyst. The results showed that the efficiency of the Fe₃O₄/MnO₂/Mn₃O₄ photocatalyst in visible light for 130 min is 94.5%. The catalytic activity of photocatalyst far exceeded that of the Fe₃O₄/MnO₂ component, and after four cycles, the catalytic performance of the catalyst remained at 78.4%. The superior properties of the photocatalyst came from improved surface area, enhanced light absorption, and efficient charge separation of the MnO₂/Mn₃O₄ heterostructure. This study constructed a green and efficient valence heterostructure composite that created a promising photocatalyst for degrading organic contaminants in aqueous environments.

Keywords: Fe₃O₄/MnO₂/Mn₃O₄ photocatalyst; hollow flower-like structure; valence heterostructure; visible-light activity; recyclability

1. Introduction

In recent years, dye wastewater has attracted much attention owing to its high toxicity, strong mutagenicity, and strong carcinogenicity [1–4]. Methods for removing dyes from wastewater have been developed, including adsorption, coacervation, membrane separation, chemical catalytic oxidation, and more [5–8]. Among these methods, semiconductor-based photocatalytic technology has been widely used due to its mild reaction conditions, strong oxidizing ability, complete degradation, lack of secondary pollution, and direct use of sunlight. For this method, semiconductor photocatalysts are considered to be key materials for the degradation of organic dyes owing to their low cost, cleanliness, and sustainable use. Therefore, the development of new, high-efficiency and visible-light-responsive photocatalytic materials has become a research hotspot in the field of photocatalysis [9–14].
Manganese dioxide (MnO$_2$) has already been used as catalyst due to its abundant sources, low cost, good redox, and environmental friendliness [15–22]. The degradation of organic pollutants by active metal oxides strongly depends on the specific surface area of the catalyst. Hence, the design of a layered birnessite-type MnO$_2$ ($\delta$-MnO$_2$) into a flower-like microsphere having a high specific surface area is expected to display greater adsorption and catalytic ability. However, rapid recombination of photogenerated electron-hole pairs in photocatalysts will greatly reduce photocatalytic efficiency. Therefore, how to modify MnO$_2$ and improve its catalytic performance has become an urgent unsolved scientific challenge.

The construction of a heterojunction photocatalytic system has been demonstrated to be a promising green method to degrade organic dyes. The heterojunction can effectively separate the charge, thereby greatly improving the photocatalytic efficiency [23–26]. As a novel heterojunction, the valence heterojunction can readily realize the transfer of photogenerated carriers and energy without obvious loss, which results in significantly improving the photocatalytic activity. For this case, the presence of mixed valence states plays a decisive role in electron transport during chemical reactions [27–30]. Therefore, the induction of hausmannite trimanganese tetraoxide (Mn$_3$O$_4$) nanoparticles from pure $\delta$-MnO$_2$ nanosheets and the construction of MnO$_2$/Mn$_3$O$_4$ composites with valence heterojunctions hope to be an ideal high-efficiency photocatalyst.

Additionally, it is well known that heterogeneous catalysts have the advantage of being easier to separate and recycled than homogeneous catalysts. At the same time, the recycling of catalyst resources meets the goals of sustainable economic development and environmental protection. However, it is not convenient to separate the heterojunction catalyst from the reaction system by conventional separation methods, such as centrifugation and filtration. On the basis of our preliminary work [31–34], the hollow magnetic ferric oxide (Fe$_3$O$_4$) support was combined with the catalytically active component to prepare a hollow magnetic composite catalyst. The magnetic catalyst can be conveniently separated from the reaction medium when a suitable magnetic field is applied [35,36]. The introduction of the magnetic component greatly facilitates the recovery of the heterogeneous catalyst.

In this work, a hollow flower-like magnetic manganese-based photocatalyst is synthesized. To the best of our knowledge, this is the first time that a flower-like MnO$_2$ and Mn$_3$O$_4$ nanoparticles are combined to form a heterogeneous photocatalyst for dye degradation. The increased specific surface area and the presence of the valence heterojunction increase the active sites and achieve efficient charge separation, which greatly improves the catalytic performance of the catalyst. In addition, the magnetic hollow Fe$_3$O$_4$ component allows the catalyst to be easily recycled. The synthesis steps are exhibited in Scheme 1. Firstly, the hollow Fe$_3$O$_4$ magnetic core is synthesized by hydrothermal method. Then, a flower-like Fe$_3$O$_4$/MnO$_2$ microsphere having a high specific surface area was prepared through a secondary hydrothermal method. Finally, the hausmannite Mn$_3$O$_4$ nanoparticles were induced by in situ growth of flower-like Fe$_3$O$_4$/MnO$_2$ using a simple reduction method. The hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ magnetic catalyst was formed. Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ composite microspheres with heterojunction showed better catalytic activity than pure Fe$_3$O$_4$/MnO$_2$ microspheres.

Scheme 1. The synthesis steps of hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ magnetic photocatalyst.
2. Results and Discussion

2.1. Characterization of the Photocatalyst

The morphologies of hollow Fe₃O₄ microspheres, hollow flower-like Fe₃O₄/MnO₂ microspheres, and hollow flower-like Fe₃O₄/MnO₂/Mn₃O₄ photocatalyst were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). From the SEM image of Figure 1a, it could be found that as-synthesized Fe₃O₄ microspheres were spherical in shape and well-monodispersed. Meanwhile, it was clear that their diameters were mainly about 200 nm. Figure 2a shows the TEM image of Fe₃O₄ microspheres, in which a distinct gray/dark interface inside each microsphere indicated the existence of hollow structure. When the Fe₃O₄ microspheres were coated with MnO₂, their surface morphology was changed into flower-like hierarchical structure. Figure 1b,c show the SEM images of hollow flower-like Fe₃O₄/MnO₂ microspheres at distant and close view, respectively. One could easily observe that MnO₂ shells were assembled by numerous nanosheets. Figure 2b,c shows the TEM images of Fe₃O₄/MnO₂ microspheres, powerfully certifying the core–shell structure and demonstrating the shell thickness of 180 nm. In the SEM image of Figure 1d, hollow flower-like Fe₃O₄/MnO₂/Mn₃O₄ photocatalysts were displayed with rough edges of MnO₂ nanosheets. The subtle morphological change was believed to result from the formation of Mn₃O₄ nanoparticles. The detailed morphology and composition of Fe₃O₄/MnO₂/Mn₃O₄ photocatalyst are shown in TEM images in Figure 2d,e. It could be seen that the Mn₃O₄ nanoparticles with diameters of about 4 nm were evenly distributed on the periphery and inside of the folded MnO₂ nanosheets. Figure 2f shows the high-resolution transmission electron microscopy (HRTEM) image of Fe₃O₄/MnO₂/Mn₃O₄ photocatalyst. The interplanar spacing of 0.352 nm was assigned to the (002) plane of MnO₂, and the interplanar spacings of 0.245 and 0.164 nm were attributed to the (202) and (303) planes of Mn₃O₄. The results presented herein strongly confirmed the successful synthesis of Fe₃O₄/MnO₂/Mn₃O₄ photocatalyst.

![Figure 1](image-url)
Figure 2. TEM images of hollow Fe$_3$O$_4$ microspheres (a), hollow flower-like Fe$_3$O$_4$/MnO$_2$ microspheres (b,c), and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst (d-f).

Phase structures of hollow Fe$_3$O$_4$ microspheres, hollow flower-like Fe$_3$O$_4$/MnO$_2$ microspheres and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst were analyzed by X-ray diffraction (XRD). Figure 3a showed that the diffraction peaks located at 30.1°, 35.4°, 43.1°, 53.4°, 57.1°, and 62.5° were successively attributed to (220), (311), (400), (422), (511), and (440) crystal planes. The XRD pattern showed good consistency with that of pure Fe$_3$O$_4$ (JCDPS 85-1436) [37]. Moreover, no other diffraction peaks were observed, which indicated that the preparation of hollow Fe$_3$O$_4$ microspheres was high in purity. As for Fe$_3$O$_4$/MnO$_2$ microspheres, in the XRD pattern of Figure 3b, except for the diffraction peaks of pristine Fe$_3$O$_4$, three new peaks at 12.54°, 25.24°, and 58.32° could be clearly viewed, corresponding to (001), (002), and (203) crystal planes of MnO$_2$ (PDF NO. 80-1098) [38]. With respect to Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst, the XRD pattern of Figure 3c displayed another four new peaks at 18.00°, 36.45°, 56.01°, and 65.40°, which were assigned to (101), (202), (303), and (323) crystal planes of Mn$_3$O$_4$ (PDF NO. 24-0734) [39]. The XRD patterns powerfully demonstrated the successful synthesis of MnO$_2$ and Mn$_3$O$_4$ phases.

Figure 3. XRD patterns of hollow Fe$_3$O$_4$ microspheres (a), hollow flower-like Fe$_3$O$_4$/MnO$_2$ microspheres (b), and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst (c).
For further determining the chemical compositions of Fe$_3$O$_4$/MnO$_2$ microspheres and Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst, X-ray photoelectron spectroscopy (XPS) measurement was carried out. Figure 4a displayed the characteristic peaks of manganese (Mn), oxygen (O), and adventitious carbon (C). The high-resolution Mn 2p spectra of Fe$_3$O$_4$/MnO$_2$ microspheres were presented in Figure 4b, in which Mn 2p$_{3/2}$ was at 654.3 eV and Mn 2p$_{3/2}$ peaks was at 642.5 eV, respectively [40]. The shape and binding energy of Mn 2p$_{3/2}$ peak was in line with that of δ-MnO$_2$. No other peaks were observed at this binding energy, implying the inexistence of Mn(III) and Mn(II). Hence, the oxidation state of Mn was +4. With regard to Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst, as shown in Figure 4c, there were two characteristic peaks of Mn(III) and Mn(II) located at 641.4 and 640.3 eV for the Mn 2p$_{3/2}$ peak. This case demonstrated that the photocatalyst contained multivalent state manganese (Mn(II), Mn(III), and Mn(IV)) of Mn$_3$O$_4$ and MnO$_2$ [41,42]. Such a conclusion was verified by the XPS spectrum of O 1s. By contrast, the high-resolution O 1s spectra of Fe$_3$O$_4$/MnO$_2$ microspheres and Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst were exhibited in Figure 4d,e. For the former, the binding energies of approximately 529.7, 531.1, and 531.7 eV was separately caused by the bulk oxygen of MnO$_2$, surface hydroxyl bonded to Mn, and absorbed oxygen. Nevertheless, for the latter, another extraordinary peak at 530.2 eV was detected in addition to the three binding energies above, which originated from the existence of lattice oxygen of Mn$_3$O$_4$ [43]. This also demonstrated that the photocatalyst consisted of Mn$_3$O$_4$ and MnO$_2$. The Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst was rich in oxygen, which played a key role in the next photocatalytic reaction.

Figure 4. XPS spectrum of hollow flower-like Fe$_3$O$_4$/MnO$_2$ microspheres and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst (a); Mn 2p spectra of hollow Fe$_3$O$_4$/MnO$_2$ spheres (b) and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ microspheres (c); O 1s spectra of hollow Fe$_3$O$_4$/MnO$_2$ microspheres (d) and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ microspheres (e).
The specific surface area and the porosity of samples were obtained through the N\textsubscript{2} adsorption–desorption isotherms [44]. As shown in Figure 5a, the pore width of Fe\textsubscript{3}O\textsubscript{4} microspheres was mainly ca. 4.0 nm. In Figure 5b,c, a typical IV isotherm of Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2} microspheres and Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} photocatalyst was observed, indicating the formation of pore structures resulting from the accumulation of MnO\textsubscript{2} nanosheets. In Table 1, the specific surface area of Fe\textsubscript{3}O\textsubscript{4} microspheres, Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2} microspheres, and Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} photocatalyst were respectively calculated to be 71.8, 117.3, and 143.03 m\textsuperscript{2}/g. At the same time, their pore volume was calculated to be 0.17, 0.27, and 0.34 cm\textsuperscript{3}/g, respectively. Therefore, the introduction of MnO\textsubscript{2} nanosheets to form a flower-like structure is advantageous for increasing the porosity and specific surface area of the composite microspheres, and thus is expected to enhance the catalytic properties. In addition, it could be observed that the formation of Mn\textsubscript{3}O\textsubscript{4} nanoparticles on the flower-like Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2} microspheres further increased the specific surface area of the photocatalyst. Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} photocatalyst possessing noticeably high specific surface area and porosity could effectively provide more active sites, accelerating the photocatalytic process.

![Figure 5. N\textsubscript{2} adsorption–desorption isotherms of hollow Fe\textsubscript{3}O\textsubscript{4} microspheres (a), hollow flower-like Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2} microspheres (b), and hollow flower-like Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} photocatalyst (c). Insets in (a–c) are the corresponding pore width distribution plots.](image)

**Table 1.** Physical parameters of the prepared samples.

| Sample                     | Surface Area (m\textsuperscript{2}/g) | Pore Volume (cm\textsuperscript{3}/g) |
|----------------------------|---------------------------------------|---------------------------------------|
| Fe\textsubscript{3}O\textsubscript{4} | 38.47                                 | 0.17                                  |
| Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2} | 117.66 | 0.27 |
| Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} | 143.03 | 0.34 |

The magnetic properties of hollow Fe\textsubscript{3}O\textsubscript{4} microspheres, hollow flower-like Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2} microspheres and hollow flower-like Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} photocatalyst were exhibited by vibrating sample magnetometer (VSM) curves tested at room temperature. From Figure 6, the saturated magnetization values of them were 73.68, 36.61, and 35.34 emu/g, respectively. There was no doubt that the saturated magnetization value decreased considerably along with the formation of MnO\textsubscript{2} nanosheets and Mn\textsubscript{3}O\textsubscript{4} nanoparticles, in turn. Such a decrease was a result of a reduction in proportion of the magnetite component. It should be pointed out that Fe\textsubscript{3}O\textsubscript{4}/MnO\textsubscript{2}/Mn\textsubscript{3}O\textsubscript{4} photocatalyst still possessed excellent magnetic responsivity. In
the inset image, the separation–redispersion behavior of Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst, displayed in water, testified that this photocatalyst has remarkable magnetic manipulation ability.

Figure 6. Hysteresis loops of hollow Fe$_3$O$_4$ microspheres (a), hollow flower-like Fe$_3$O$_4$/MnO$_2$ microspheres (b), and hollow flower-like Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst (c).

2.2. Photocatalytic Tests

The test of degrading rhodamine B (RhB) under simulated visible light was employed to verify the photocatalytic activity of the photocatalyst, as seen in Figure 7. To examine the catalytic effect of Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst, in Figure 7a–c, the control experiments on pure RhB, RhB+Fe$_3$O$_4$/MnO$_2$ microspheres and RhB + Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst were conducted under the same experimental conditions. What was noteworthy was that RhB was degraded completely in the presence of Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst after 130 min, while neither of the other two groups was completely degraded. Figure 7d showed the variation of RhB concentration ratio $C_t/C_0$ with increasing visible light irradiation time, in which $C_0$ was the initial concentration of RhB and $C_t$ was the concentration of RhB during the reaction. After 130 min illumination, it could be seen intuitively that pure RhB only had 2.3% self-decomposition through the dye sensitization pathway [45], RhB solution with adding Fe$_3$O$_4$/MnO$_2$ microspheres reached 63.5% decomposition, but the RhB solution with the addition of Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst microspheres amazingly reached 94.5%.

Figure 7. Cont.
The photocatalytic reaction belonged to a pseudo first-order reaction and could be fitted by the Langmuir–Hinshelwood model of $\ln(C_0/C) = -kt$, where $k$ was the apparent first-order rate constant [46–49]. In Figure 7e, compared with the rate constant $k = 0.009$ min$^{-1}$ of Fe$_3$O$_4$/MnO$_2$ microspheres, Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst exhibited the rate constant $k = 0.025$ min$^{-1}$, confirming that the elaborately fabricated photocatalyst had excellent photocatalytic activity. It was very important that for the photocatalyst, on the one hand, the quality and the chemical properties remained unchanged and, on the other hand, extraordinary reusability was maintained. Herein, the introduced magnetic Fe$_3$O$_4$ microspheres could readily favor the recycling of the catalyst through magnetic separation. Figure 7f displayed the results of the photocatalyst being subjected to recycling experiments. There was no doubt that the conversion rate was reduced after the photocatalyst had been recycled. However, even after four cycles, the Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst still 78.4% decomposition. This fact strongly demonstrates that the prepared photocatalyst had outstanding recyclability.

Minimizing the amount of catalyst was the key to reducing the cost of the catalytic reaction, which was also important for guiding the practical application of the catalyst. Hence, the effect of the dosage of Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst on RhB degradation was investigated. In Figure 8a, it can be seen that the degradation efficiency of RhB was greatly improved by increasing the dosage of photocatalyst from 1 to 10 mg. This was because as the dosage increased, the total active surface increased correspondingly, thereby enhancing catalytic performance. Once the dosage exceeded 10 mg, the degradation efficiency was almost constant. This situation meant that after the maximum dosage was applied, the increase of the dosage had no effect on promoting degradation efficiency, which might be ascribed to an agglomeration of photocatalyst under high concentrations. As a result, for RhB degradation (65 mL of 10 mg/L), the dosage of Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst was fixed at 10 mg for subsequent studies.

The effect of the pH on RhB degradation was investigated to determine the optimal pH range for the Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst. In Figure 8b, it was seen that RhB degradation was obviously influenced by the pH of the reaction system. It was measured that the isoelectric point of the prepared catalyst in water was about pH = 3. When the pH was below 3, the periphery of the photocatalyst was positively charged, resulting in a repulsion between the photocatalyst and RhB cations. When the pH was beyond 3, the surface of the photocatalyst was negatively charged, giving rise to an increased electrostatic interaction between the photocatalyst and RhB cations. In this case, the favorable adsorption process accelerated RhB degradation. As the pH was in the range from 7 to 9, the degradation decreased. Due to the high pH, the MnO$_2$ component of the photocatalyst could interact with hydroxyl ions to form hydrated manganese oxides, thereby deteriorating the degradation efficiency. As a conclusion, the relatively acidic environment was more advantageous for the degradation of cationic dyes in the case of using Fe$_3$O$_4$/MnO$_2$/Mn$_3$O$_4$ photocatalyst.
The possible photocatalytic mechanism for $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$ photocatalyst was proposed and diagrammatized in Scheme 2. The flower-like morphology of the photocatalyst effectively increased the scattering and reflection of incident light, and the light could reach all the particles thanks to reflection and scattering phenomena in the media, which greatly improved light utilization. In addition, MnO$_2$ and Mn$_3$O$_4$ could constitute a heterojunction structure. Photogenerated carriers could be effectively separated in heterojunctions, which enhanced photocatalytic performance [43].

For the photocatalytic test, $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$ microspheres had better catalytic performance than $\text{Fe}_3\text{O}_4/\text{MnO}_2$ microspheres, which indicated that the composite of MnO$_2$ and Mn$_3$O$_4$ could significantly enhance the photocatalytic performance. Theoretically, the conduction band and valence band of MnO$_2$ were more positive than those of Mn$_3$O$_4$, which favored the transfer of photogenerated charge in thermodynamic theory. Under visible light irradiation, the electrons ($e^-$) excited into the conduction band in Mn$_3$O$_4$ would be transferred to the conduction band of MnO$_2$. The holes ($h^+$) were left in the valence band of Mn$_3$O$_4$. This effectively avoided the recombination of $e^-$ and $h^+$ and prolonged the lifetime of the carriers. Both $e^-$ and $h^+$ dominated the active centers to the photocatalysis. In the photocatalytic process, $h^+$ could combine with hydroxyl ions, resulting in the formation of hydroxyl radicals in the valence band of MnO$_2$. In the meantime, the superoxide radical anions appeared in the conduction band of Mn$_3$O$_4$ by interacting with the $e^-$ and the dissolved O. Hydroxyl radicals and superoxide radicals could effectively degrade organic pollutants in wastewater. In addition, the RhB could also be directly degraded by $h^+$ in the valence band of Mn$_3$O$_4$ [40,41].
3. Materials and Methods

3.1. Materials

Ferric chloride hexahydrate (FeCl₃·6H₂O), sodium polyacrylate, urea, sodium citrate, potassium permanganate (KMnO₄), ethanol, hydrochloric acid (HCl), RhB, and sodium borohydride (NaBH₄) were bought from Shanghai Ebi Chemical Reagent Co., Ltd. All reagents were of analytical grade and applied without further purification. Distilled water was utilized throughout all the preparation procedures.

3.2. Synthesis of Flower-Like Fe₃O₄/MnO₂ Microspheres

Hollow Fe₃O₄ microspheres were fabricated by solvothermal method [50]. The prepared Fe₃O₄ hollow microspheres (0.3 g) were added to a KMnO₄ aqueous solution (0.055 M, 80 mL), followed by the ultrasonication for 30 min. Then, HCl (37%, 1.0 mL) was dropwise added to the above solution. Thereafter, the homogeneous solution was transferred to a Teflon-lined stainless-steel autoclave and reacted at 100 °C for 6 h. The product was isolated by an external magnet after cooling to room temperature. The product was then separately washed 3 times with deionized water and ethanol and lyophilized to obtain flower-like Fe₃O₄/MnO₂ microspheres.

3.3. Synthesis of Flower-Like Fe₃O₄/MnO₂/Mn₃O₄ Microspheres

The prepared Fe₃O₄/MnO₂ microspheres (0.2 g) were fully dispersed in a deionized water (50 mL). Then, an aqueous solution of NaBH₄ (0.75 M, 20 mL) was poured into the suspension. The suspension was stirred for half an hour at room temperature. The product was washed with deionized water several times and lyophilized to obtain Fe₃O₄/MnO₂/Mn₃O₄ microspheres.

3.4. Photocatalytic Tests

Photocatalyst (10.0 mg) was dispersed into a RhB solution (10.0 mg/L, 65 mL). The solution was stirred for 60 min under dark conditions to achieve an equilibrium of adsorption and desorption. Then, the visible light was simulated with a 400 W metal halide lamp to carry out a photocatalytic reaction. The absorbance change of the solution was tested by UV–vis at intervals, the degradation curves of RhB solution with time were recorded, and the rate of photocatalytic degradation was calculated.

3.5. Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were conducted on a JEM-3010 instrument (Hitachi Co., Tokyo, Japan). Scanning electron microscopy (SEM) images were conducted on a JSM-6700F instrument (JEOL Ltd., Tokyo, Japan). X-ray diffraction (XRD) patterns were obtained by a Shimadzu XRD-7000 X-ray diffraction meter (Shimadzu Co., Kyoto, Japan). X-ray photoelectron spectroscopy (XPS) characterization was measured on a JPS-9010 MC spectrometer (JEOL Ltd., Tokyo, Japan). The specific surface area and the average pore diameter of the catalysts were tested by Brunauer–Emmett–Teller (BET) method respectively with an ASAP 2020 system (Quantachrome, Boynton Beach, FL, USA). Vibrating sample magnetometer (VSM) curves were conducted on a Lake Shore 7307 instrument (Lake Shore Ltd., Columbus, OH, USA). Visible light irradiation was simulated on a BL-GHX-V photochemical reactor (Shanghai Bilang Instruments Co., Ltd., Shanghai, China). UV–vis absorption spectra were measured on a UV-5200PC UV–vis spectrophotometer (YuanXi, Shanghai, China).

4. Conclusions

In summary, the flower-like microspheres composite consisting of Fe₃O₄ core and MnO₂ and Mn₃O₄ shells were successfully synthesized. First, monodisperse hollow Fe₃O₄ microspheres were obtained, where after grading MnO₂ nanosheets was grown around the Fe₃O₄ microspheres in a simple hydrothermal system, and then Mn₃O₄ nanoparticles were in situ fabricated on the MnO₂
nanosheets using a simple reduction method. The prepared Fe3O4/MnO2/Mn3O4 photocatalyst exhibited impressive photocatalytic activity under visible light. Specifically, with the aid of this photocatalyst, the degradation rate of RhB could be as high as 94.5% under visible light irradiation for 130 min. Moreover, after four cycles of testing, the catalytic performance of the catalyst remained at 78.4%. The presentation of excellent photocatalytic performance was attributed to the flower-like morphology of MnO2 and heterojunction between MnO2 and Mn3O4. The former greatly improved the light utilization efficiency, and the latter effectively achieved spatial separation of photoinduced carriers. This strategy established an efficient and green binary heterojunction which enriches the way for the preparation of valence isomeric photocatalysts.

Author Contributions: Conceptualization, M.M. and Y.Y.; investigation, Y.Y., Y.C., F.W. and W.L.; writing—original draft preparation, Y.Y.; writing—review and editing, M.M., Y.M. and Y.Y.; resources, M.M. and Y.M.; supervision, P.L., W.H. and W.T.

Funding: This research was funded by the National Natural Science Foundation of China (51503116 and 51578298) and the Shandong Provincial Natural Science Foundation (ZR2019BB063).

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Guo, R.; Jiao, T.; Li, R.; Chen, Y.; Guo, W.; Zhang, L.; Zhou, J.; Zhang, Q.; Peng, Q. Sandwiched Fe3O4/carboxylate graphene oxide nanostucture s constructed by layer-by-layer assembly for highly efficient and magnetically recyclable dye removal. ACS Sustain. Chem. Eng. 2018, 6, 1279–1288. [CrossRef]
2. Kaviyarasu, K.; Kotseki, L.; Simo, A.; Fuku, X.; Mola, G.T.; Kennedy, J.; Maaza, M. Photocatalytic activity of ZrO2 doped lead dioxide nanocomposites: Investigation of structural and optical microscopy of RhB organic dye. Appl. Surf. Sci. 2017, 421, 234–239. [CrossRef]
3. Dong, W.-H.; Wu, D.-D.; Luo, J.-M.; Xing, Q.-J.; Liu, H.; Zou, J.-P.; Luo, X.-B.; Min, X.-B.; Liu, H.-L.; Luo, S.-L.; et al. Coupling of photodegradation of RhB with photoreduction of CO2 over rGO/SrTi0.95Fe0.05O3-delta catalyst: A strategy for one-pot conversion of organic pollutants to methanol and ethanol. J. Catal. 2017, 349, 218–225. [CrossRef]
4. Chitiphon, C.; Radheshyam, P.; Keiko, S. Dye-sensitized photocatalyst of sepiolite for organic dye degradation. Catalysts 2019, 3, 235.
5. Oveis, M.; Asli, M.A.; Mahmoodi, N.M. MIL-Ti metal-organic frameworks (MOFs) nanomaterials as superior adsorbents: Synthesis and ultrasound-aided dye adsorption from multicomponent wastewater systems. J. Hazard. Mater. 2018, 347, 123–140. [CrossRef] [PubMed]
6. Zhang, B.; Chen, J.; Wang, J.; Huyan, Y.; Zhang, H.; Zhang, Q. Flowerlike BSA/Zn3(PO4)2/Fe3O4 magnetic hybrid particles: preparation and application to adsorption of copper ions. J. Chem. Eng. Data 2018, 63, 3913–3922. [CrossRef]
7. Zhang, B.; Huyan, Y.; Wang, J.; Chen, X.; Zhang, H.; Zhang, Q. Fe 3 O 4 @SiO 2 @CCS porous magnetic microspheres as adsorbent for removal of organic dyes in aqueous phase. J. Alloy. Compd. 2018, 735, 1986–1996. [CrossRef]
8. Zhang, J.; Yi, J.; Jiao, Y. Preparation and application of water-soluble TiO2-ionic liquids hybrid nanomaterials. J. Inorg. Mater. 2018, 33, 577–581. [CrossRef]
9. Cheng, L.; Xiang, Q.; Liao, Y.; Zhang, H. CdS-based photocatalysts. Energy Environ. Sci. 2018, 11, 1362–1391. [CrossRef]
10. Li, X.; Yu, J.; Jaroniec, M. Hierarchical photocatalysts. Chem. Soc. Rev. 2016, 45, 2603–2636. [CrossRef] [PubMed]
11. Xia, Y.; Li, Q.; Lv, K.; Li, M. Heterojunction construction between TiO2 hollowsrsce and ZnIn2S4 flower for photocatalysis application. Appl. Surf. Sci. 2017, 398, 81–88. [CrossRef]
12. Samuel Osei-Bonsu, O.; Francis, O.; Govender, P.P. Tuning the electronic and structural properties of Gd-TiO2-GO nanocomposites for enhancing photodegradation of IC dye: The role of Gd3+ ion. Appl. Catal. B: Environ. 2019, 243, 106–120.
13. Xu, Y.; Li, A.; Yao, T.; Ma, C.; Zhang, X.; Shah, J.H.; Han, H. Strategies for Efficient Charge Separation and Transfer in Artificial Photosynthesis of Solar Fuels. ChemSusChem 2017, 10, 4277–4305. [CrossRef] [PubMed]
14. Ma, Y.; Hou, C.; Zhang, H.; Qiao, M.; Chen, Y.; Zhang, H.; Zhang, Q.; Guo, Z. Morphology-dependent electrochemical supercapacitors in multi-dimensional polyaniline nanostructures. J. Mater. Chem. A 2017, 5, 14041–14052. [CrossRef]

15. Xiong, X.; Ji, Y.; Xie, M.; You, C.; Yang, L.; Liu, Z.; Asiri, A.M.; Sun, X. MnO2-CoP3 nanowires array: An efficient electrocatalyst for alkaline oxygen evolution reaction with enhanced activity. Electrochim. Commun. 2018, 86, 161–165. [CrossRef]

16. Miao, L.; Wang, J.; Zhang, P. Review on manganese dioxide for catalytic oxidation of airborne formaldehyde. Appl. Surf. Sci. 2019, 466, 441–453. [CrossRef]

17. Gao, F.; Tang, X.; Yi, H.; Chu, C.; Li, N.; Li, J.; Zhao, S. In-situ DRIFTS for the mechanistic studies of NO oxidation over alpha-MnO2, beta-MnO2 and gamma-MnO2 catalysts. Chem. Eng. J. 2017, 322, 525–537. [CrossRef]

18. Jiang, C.; Ge, Y.; Chen, W.; Hua, L.; Li, H.; Zhang, Y.; Cao, S. Hierarchically-structured TiO2/MnO2 hollow spheres exhibiting the complete mineralization of phenol. Catalysts 2019, 9, 13. [CrossRef]

19. Zhu, G.; Zhu, J.; Jiang, W.; Zhang, W.J.; Zhu, Y.; Zhang, Q. Surface oxygen vacancy induced alpha-MnO2 nanofiber for highly efficient ozone elimination. Appl. Catal. B Environ. 2017, 209, 729–737. [CrossRef]

20. Tan, X.; Wan, Y.; Huang, Y.; He, C.; Zhang, Z.; He, Z.; Hu, L.; Zeng, J.; Shu, D. Three-dimensional MnO2 porous hollow microspheres for enhanced activity as ozonation catalysts in degradation of bisphenol A. J. Hazard. Mater. 2017, 321, 162–172. [CrossRef]

21. Zhu, S.; Li, X.; Kang, J.; Duan, X.; Wang, S. Persulfate activation on crystallographic manganese oxides: Mechanism of singlet oxygen evolution for nonradical selective degradation of aqueous contaminants. Environ. Sci. Technol. 2019, 53, 307–315. [CrossRef] [PubMed]

22. Gong, W.; Meng, X.; Tang, X.; Ji, P. Core-Shell MnO2-SiO2 Nanorods for Catalyzing the Removal of Dyes from Water. Catalysts 2017, 7, 19. [CrossRef] [PubMed]

23. Low, J.; Yu, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A.A. Heterojunction photocatalysts. Adv. Mater. 2017, 29, 20. [CrossRef] [PubMed]

24. Marschall, R. Semiconductor composites: strategies for enhancing charge carrier separation to improve photocatalytic activity. Adv. Funct. Mater. 2014, 24, 2421–2440. [CrossRef]

25. Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X. Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. Chem. Soc. Rev. 2014, 43, 5234. [CrossRef] [PubMed]

26. Zheng, L.; Zheng, Y.; Chen, C.; Zhan, Y.; Lin, X.; Zheng, Q.; Wei, K.; Zhu, J. Network Structured SnO2/ZnO Heterojunction Nanocatalyst with High Photocatalytic Activity. Inorg. Chem. 2009, 48, 1819–1825. [CrossRef] [PubMed]

27. Chiu, M.-H.; Zhang, C.; Shiu, H.-W.; Chuu, C.-P.; Chen, C.-H.; Chang, C.-Y.S.; Chen, C.-H.; Chou, M.-Y.; Shih, C.-K.; Li, L.-J. Determination of band alignment in the single-layer MoS2/WSe2 heterojunction. Nat. Commun. 2015, 6, 7666. [CrossRef] [PubMed]

28. Dong, F.; Zhao, Z.; Xiong, T.; Ni, Z.; Zhang, W.; Sun, Y.; Ho, W.-K. In Situ Construction of g-C3N4 5 Metal-Free Heterojunction for Enhanced Visible-Light Photocatalysis. ACS Appl. Mater. Interfaces 2013, 5, 11392–11401. [CrossRef]

29. He, Z.; Shi, Y.; Gao, C.; Wen, L.; Chen, J.; Song, S. BiOCl/BiVO4 p-n heterojunction with enhanced photocatalytic activity under visible-light irradiation. J. Phys. Chem. C 2014, 118, 389–398. [CrossRef]

30. Ma, Y.; Hou, C.; Zhang, H.; Zhang, Q.; Liu, H.; Wu, S.; Guo, Z. Three-dimensional core-shell Fe3O4/Polyaniline coaxial heterogeneous nanonets: Preparation and high performance supercapacitor electrodes. Electrochimica Acta 2019, 315, 114–123. [CrossRef]

31. Ma, Y.M.; Yang, R.; Feng, L.; Jia, G.; Chen, W.; Li, P.L. Preparation and characterization of magnetic hollow Fe3O4/P(GMA-EGDMA)-SO3H/Au-PPy recyclable catalyst for catalytic reduction of 4-nitrophenol. Appl. Organomet. Chem. 2018, 32, e4534.

32. Ma, M.; Yang, Y.; Li, W.; Feng, R.; Li, Z.; Lyu, P.; Ma, Y. Gold nanoparticles supported by amino groups on the surface of magnetite microspheres for the catalytic reduction of 4-nitrophenol. J. Mater. Sci. 2019, 54, 323–334. [CrossRef]

33. Ma, M.; Yang, Y.; Liao, D.; Lyu, P.; Zhang, J.; Liang, J.; Zhang, L. Synthesis, characterization and catalytic performance of core-shell structure magnetic Fe3O4/P(GMA-EGDMA)-NH2/HPG-COOH-Pd catalyst. Appl. Organometall. Chem. 2019, 33, e4708. [CrossRef]
34. Ma, M.; Yang, Y.; Liu, Y.; Li, W.; Chen, G.; Ma, Y.; Lyu, P.; Li, S.; Wang, Y.; Wu, G. Preparation of magnetic Fe3O4@P(GMA-DVB)-PEI/Pd highly efficient catalyst with core-shell structure. *Appl. Organomet. Chem.* 2019, 33, e4850. [CrossRef]
35. Shokouhimehr, M.; Hong, K.; Lee, T.H.; Moon, C.W.; Hong, S.-P.; Zhang, K.; Suh, J.M.; Choi, K.S.; Varma, R.S.; Jang, H.W. Magnetically retrievable nanocomposite adorned with Pd nanocatalysts: Efficient reduction of nitroaromatics in aqueous media. *Green Chem.* 2018, 20, 3809–3817. [CrossRef]
36. Ahadi, A.; Rostamnia, S.; Panahi, P.; Wilson, L.D.; Kong, Q.; An, Z.; Shokouhimehr, M. Palladium Comprising Dicationic Bipyridinium Supported Periodic Mesoporous Organosilica (PMO): Pd@Bipy–PMO as an Efficient Hybrid Catalyst for Suzuki–Miyaura Cross-Coupling Reaction in Water. *Catalysts* 2019, 9, 140. [CrossRef]
37. Ma, M.; Zhang, Q.; Dou, J.; Zhang, H.; Geng, W.; Yin, D.; Chen, S. Fabrication of 1D Fe3O4/P(NIPAM-MBA) thermosensitive nanochains by magnetic-field-induced precipitation polymerization. *Colloid Polym. Sci.* 2012, 290, 1207–1213. [CrossRef]
38. Qiao, M.; Lei, X.; Ma, Y.; Tian, L.; Wang, W.; Su, K.; Zhang, Q. Facile synthesis and enhanced electromagnetic microwave absorption performance for porous core-shell Fe3O4@MnO2 composite microspheres with lightweight feature. *J. Alloy. Compd.* 2017, 693, 432–439. [CrossRef]
39. Geng, Z.; Wang, Y.; Liu, J.; Li, G.; Li, L.; Huang, K.; Yuan, L.; Feng, S. Delta-MnO2-Mn3O4 nanocomposite for photocatalytic degradation of ciprofloxacin by a ternary Mn2O3/Mn3O4/MnO2 valence state heterojunction. *Chem. Eng. J.* 2018, 353, 805–813. [CrossRef]
40. Zhao, J.; Zhao, Z.; Li, N.; Nan, J.; Yu, R.; Du, J. Visible-light-driven photocatalytic degradation of ciprofloxacin by MnO2/Mn3O4-MnO2 heterojunction. *ACS Appl. Mater. Interfaces* 2016, 8, 27825–27831. [CrossRef]
41. Xiong, M.; Chen, L.; Yuan, Q.; He, J.; Luo, S.-L.; Au, C.-T.; Yin, S.-F. Controlled synthesis of graphitic carbon nitride/beta bismuth oxide composite and its high visible-light photocatalytic activity. *Carbon* 2015, 86, 217–224. [CrossRef]
42. Ramírez, A.; Hillebrand, P.; Stellmach, D.; May, M.; Bogdanoff, P.; Fiechter, S. Evaluation of MnOx, Mn2O3, and MnO4 electrodedeposited films for the oxygen evolution reaction of water. *J. Phys. Chem. C* 2014, 118, 14073–14081. [CrossRef]
43. Zhao, J.; Nan, J.; Zhao, Z.; Li, N.; Liu, J.; Cui, F. Energy-efficient fabrication of a novel multivalence Mn3O4-MnO2 heterojunction for dye degradation under visible light irradiation. *Appl. Catal. B: Environ.* 2017, 202, 509–517. [CrossRef]
44. Ma, Y.; Ma, M.; Yin, X.; Shao, Q.; Lu, N.; Feng, Y.; Lu, Y.; Wujcik, E.K.; Mai, X.; Wang, C.; et al. Tuning polyaniion nanostructures via end group substitutions and their morphology dependent electrochemical performances. *Polyim.* 2018, 156, 128–135. [CrossRef]
45. Sun, H.; He, Q.; She, P.; Zeng, S.; Xu, K.; Li, J.; Liang, S.; Liu, Z. One-pot synthesis of Au@TiO2 yolk-shell nanoparticles with enhanced photocatalytic activity under visible light. *J. Colloid Interface Sci.* 2017, 505, 884–891. [CrossRef] [PubMed]
46. Xia, P.; Zhu, B.; Cheng, B.; Yu, J.; Xu, J. 2D/2D g-C3N4/MnO2 nanocomposite as a direct Z-scheme photocatalyst for enhanced photocatalytic activity. *ACS Sustain. Chem. Eng.* 2018, 6, 965–973. [CrossRef]
47. Zheng, X.Z.; Han, W.; Yang, F.; Qu, B.; Liu, X.W. 3D Co3O4@MnO2 heterostructures grown on a flexible substrate and their applications in super-capacitor electrodes and photocatalysts. *Dalton Trans.* 2016, 45, 16850–16858. [CrossRef]
48. Zhou, J.; Wang, Y.; Ma, Y.; Zhang, B.; Zhang, Q. Surface molecularly imprinted thermo-sensitive polymers based on light-weight hollow magnetic microspheres for specific recognition of BSA. *Appl. Surf. Sci.* 2019, 486, 265–273. [CrossRef]
49. Zhang, L.; Lian, J.; Wu, L.; Duan, Z.; Jiang, J.; Zhao, L. Synthesis of a Thin-Layer MnO2 Nanosheet-Coated Fe3O4 Nanocomposite as a Magnetically Separable Photocatalyst. *Langmuir* 2014, 30, 7006–7013. [CrossRef]
50. Liu, Y.; Li, C.; Zhang, H.; Fan, X.; Liu, Y.; Zhang, Q. One-pot hydrothermal synthesis of highly monodisperse water-dispersible hollow magnetic microspheres and construction of photonic crystals. *Chem. Eng. J.* 2015, 259, 779–786. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).