

## Article

# Synthesis of Hollow Flower-Like $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$ Magnetically Separable Microspheres with Valence Heterostructure for Dye Degradation

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**Abstract:** In this manuscript, hollow flower-like ferric oxide/manganese dioxide/trimanganese tetraoxide ( $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$ ) magnetically separable microspheres were prepared by combining a simple hydrothermal method and reduction method. As the  $\text{MnO}_2$  nanoflower working as precursor was partially reduced,  $\text{Mn}_3\text{O}_4$  nanoparticles were in situ grown from the  $\text{MnO}_2$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst in visible light for 130 min is 94.5%. The catalytic activity of photocatalyst far exceeded that of the  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  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  $\text{MnO}_2/\text{Mn}_3\text{O}_4$  heterostructure. This study constructed a green and efficient valence heterostructure composite that created a promising photocatalyst for degrading organic contaminants in aqueous environments.

**Keywords:**  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst; hollow flower-like structure; valence heterostructure; visible-light activity; recyclability

## 1. Introduction

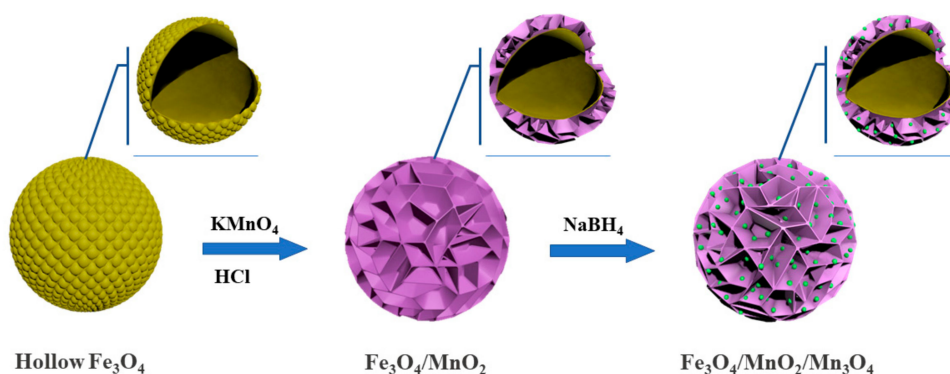
In recent years, dye wastewater has attracted much attention owing to its high toxicity, strong mutagenicity, and strong carcinogenicity [1–4]. Methods for removing dyes from wastewater have been developed, including adsorption, coacervation, membrane separation, chemical catalytic oxidation, and more [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 ( $\text{MnO}_2$ ) 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  $\text{MnO}_2$  ( $\delta\text{-MnO}_2$ ) 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  $\text{MnO}_2$  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 ( $\text{Mn}_3\text{O}_4$ ) nanoparticles from pure  $\delta\text{-MnO}_2$  nanosheets and the construction of  $\text{MnO}_2/\text{Mn}_3\text{O}_4$  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 heterogeneous 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 ( $\text{Fe}_3\text{O}_4$ ) 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  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  component allows the catalyst to be easily recycled. The synthesis steps are exhibited in Scheme 1. Firstly, the hollow  $\text{Fe}_3\text{O}_4$  magnetic core is synthesized by hydrothermal method. Then, a flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microsphere having a high specific surface area was prepared through a secondary hydrothermal method. Finally, the hausmannite  $\text{Mn}_3\text{O}_4$  nanoparticles were induced by in situ growth of flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  using a simple reduction method. The hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  magnetic catalyst was formed.  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  composite microspheres with heterojunction showed better catalytic activity than pure  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres.



**Scheme 1.** The synthesis steps of hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  magnetic photocatalyst.

## 2. Results and Discussion

### 2.1. Characterization of the Photocatalyst

The morphologies of hollow  $\text{Fe}_3\text{O}_4$  microspheres, hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres, and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  microspheres, in which a distinct gray/dark interface inside each microsphere indicated the existence of hollow structure. When the  $\text{Fe}_3\text{O}_4$  microspheres were coated with  $\text{MnO}_2$ , their surface morphology was changed into flower-like hierarchical structure. Figure 1b,c show the SEM images of hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres at distant and close view, respectively. One could easily observe that  $\text{MnO}_2$  shells were assembled by numerous nanosheets. Figure 2b,c shows the TEM images of  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalysts were displayed with rough edges of  $\text{MnO}_2$  nanosheets. The subtle morphological change was believed to result from the formation of  $\text{Mn}_3\text{O}_4$  nanoparticles. The detailed morphology and composition of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst are shown in TEM images in Figure 2d,e. It could be seen that the  $\text{Mn}_3\text{O}_4$  nanoparticles with diameters of about 4 nm were evenly distributed on the periphery and inside of the folded  $\text{MnO}_2$  nanosheets. Figure 2f shows the high-resolution transmission electron microscopy (HRTEM) image of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst. The interplanar spacing of 0.352 nm was assigned to the (002) plane of  $\text{MnO}_2$ , and the interplanar spacings of 0.245 and 0.164 nm were attributed to the (202) and (303) planes of  $\text{Mn}_3\text{O}_4$ . The results presented herein strongly confirmed the successful synthesis of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst.

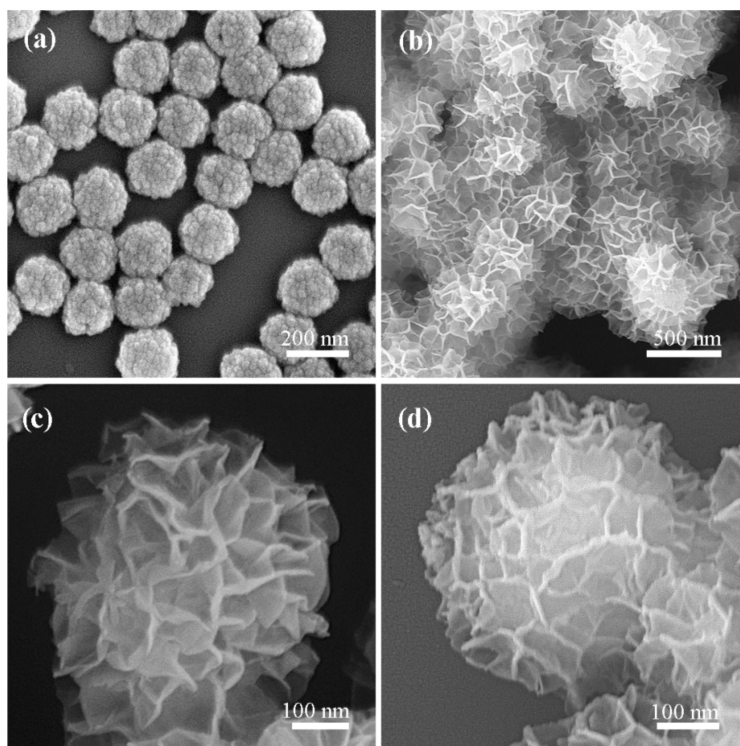


**Figure 1.** SEM images of hollow  $\text{Fe}_3\text{O}_4$  microspheres (a), hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (b,c), and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (d).

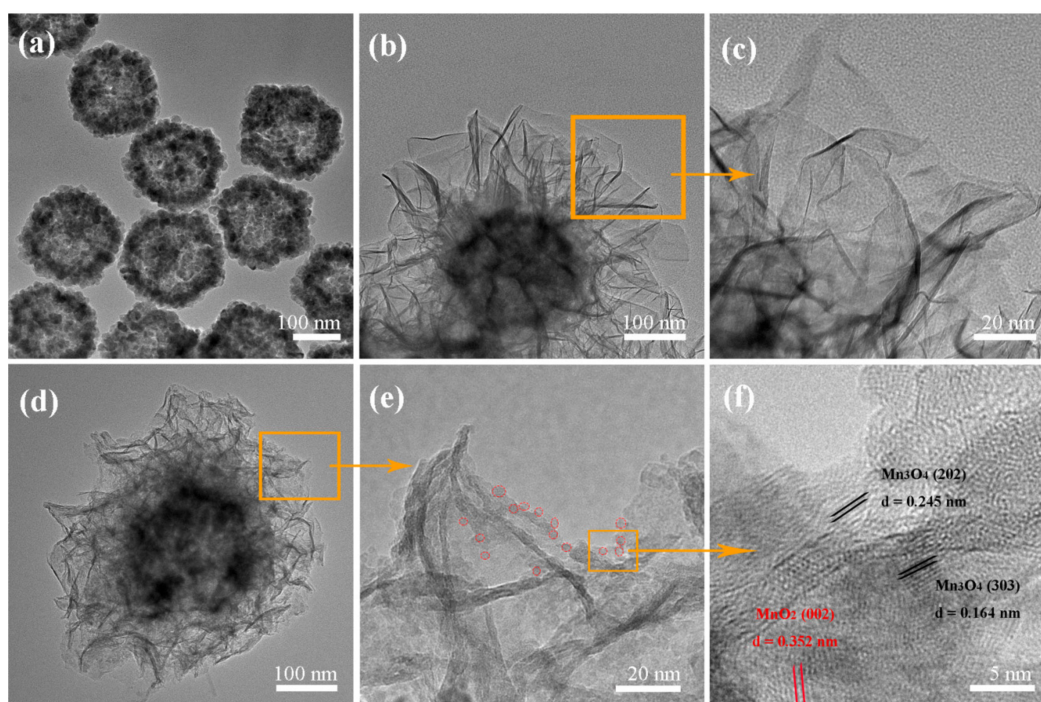


**Figure 2.** TEM images of hollow  $\text{Fe}_3\text{O}_4$  microspheres (a), hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (b,c), and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (d–f).

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

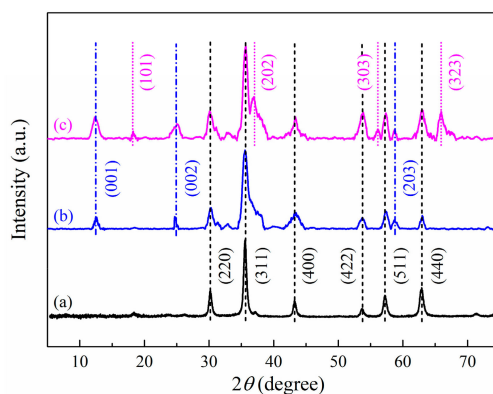


**Figure 3.** XRD patterns of hollow  $\text{Fe}_3\text{O}_4$  microspheres (a), hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (b), and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (c).

For further determining the chemical compositions of  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres and  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres were presented in Figure 4b, in which Mn 2p<sub>1/2</sub> was at 654.3 eV and Mn 2p<sub>3/2</sub> peaks was at 642.5 eV, respectively [40]. The shape and binding energy of Mn 2p<sub>3/2</sub> peak was in line with that of  $\delta\text{-MnO}_2$ . 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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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<sub>3/2</sub> peak. This case demonstrated that the photocatalyst contained multivalent state manganese (Mn(II), Mn(III), and Mn(IV)) of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  [41,42]. Such a conclusion was verified by the XPS spectrum of O 1s. By contrast, the high-resolution O 1s spectra of  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres and  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{MnO}_2$ , 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  $\text{Mn}_3\text{O}_4$  [43]. This also demonstrated that the photocatalyst consisted of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$ . The  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst was rich in oxygen, which played a key role in the next photocatalytic reaction.

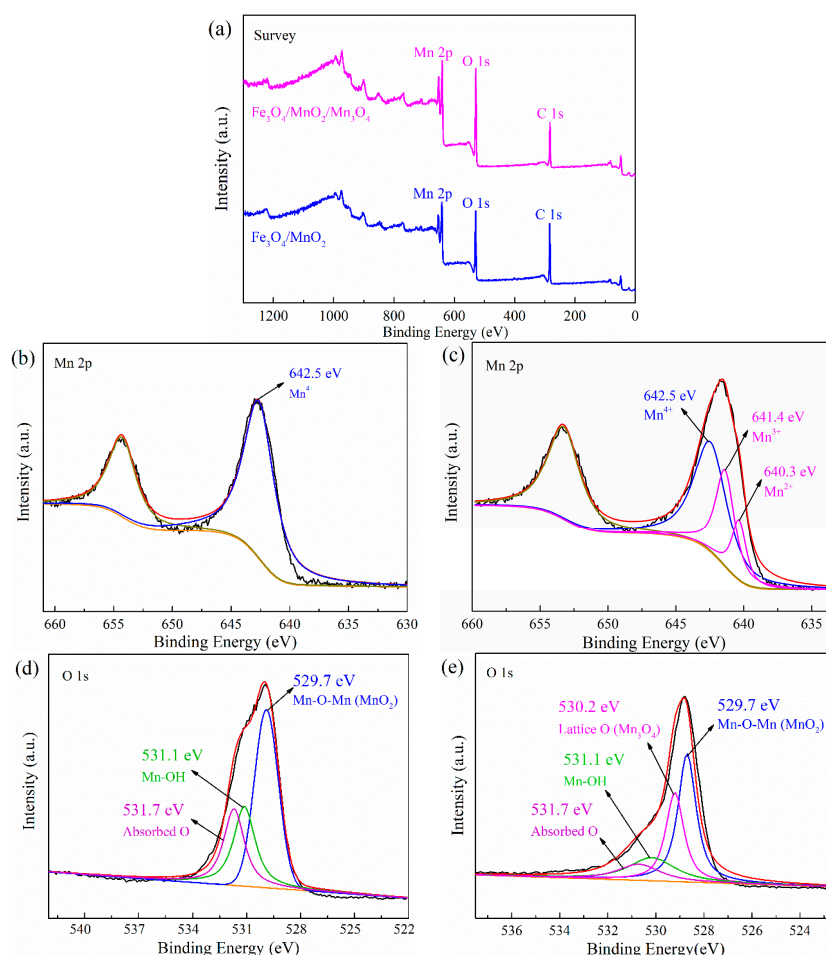


**Figure 4.** XPS spectrum of hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (a); Mn 2p spectra of hollow  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  spheres (b) and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  microspheres (c); O 1s spectra of hollow  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (d) and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  microspheres (e).

The specific surface area and the porosity of samples were obtained through the  $N_2$  adsorption–desorption isotherms [44]. As shown in Figure 5a, the pore width of  $Fe_3O_4$  microspheres was mainly ca. 4.0 nm. In Figure 5b,c, a typical IV isotherm of  $Fe_3O_4/MnO_2$  microspheres and  $Fe_3O_4/MnO_2/Mn_3O_4$  photocatalyst was observed, indicating the formation of pore structures resulting from the accumulation of  $MnO_2$  nanosheets. In Table 1, the specific surface area of  $Fe_3O_4$  microspheres,  $Fe_3O_4/MnO_2$  microspheres, and  $Fe_3O_4/MnO_2/Mn_3O_4$  photocatalyst were respectively calculated to be 71.8, 117.3, and 143.03  $m^2/g$ . At the same time, their pore volume was calculated to be 0.17, 0.27, and 0.34  $cm^3/g$ , respectively. Therefore, the introduction of  $MnO_2$  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  $Mn_3O_4$  nanoparticles on the flower-like  $Fe_3O_4/MnO_2$  microspheres further increased the specific surface area of the photocatalyst.  $Fe_3O_4/MnO_2/Mn_3O_4$  photocatalyst possessing noticeably high specific surface area and porosity could effectively provide more active sites, accelerating the photocatalytic process.

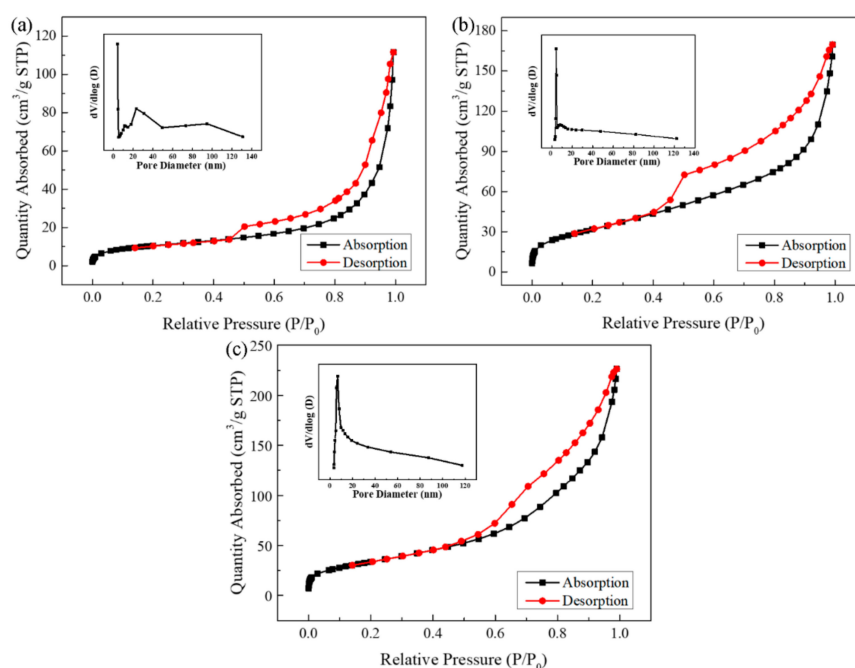


**Figure 5.**  $N_2$  adsorption–desorption isotherms of hollow  $Fe_3O_4$  microspheres (a), hollow flower-like  $Fe_3O_4/MnO_2$  microspheres (b), and hollow flower-like  $Fe_3O_4/MnO_2/Mn_3O_4$  photocatalyst (c). Insets in (a–c) are the corresponding pore width distribution plots.

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

| Sample                  | Surface Area ( $m^2/g$ ) | Pore Volume ( $cm^3/g$ ) |
|-------------------------|--------------------------|--------------------------|
| $Fe_3O_4$               | 38.47                    | 0.17                     |
| $Fe_3O_4/MnO_2$         | 117.66                   | 0.27                     |
| $Fe_3O_4/MnO_2/Mn_3O_4$ | 143.03                   | 0.34                     |

The magnetic properties of hollow  $Fe_3O_4$  microspheres, hollow flower-like  $Fe_3O_4/MnO_2$  microspheres and hollow flower-like  $Fe_3O_4/MnO_2/Mn_3O_4$  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  $MnO_2$  nanosheets and  $Mn_3O_4$  nanoparticles, in turn. Such a decrease was a result of a reduction in proportion of the magnetite component. It should be pointed out that  $Fe_3O_4/MnO_2/Mn_3O_4$  photocatalyst still possessed excellent magnetic responsivity. In

the inset image, the separation–redispersion behavior of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst, displayed in water, testified that this photocatalyst has remarkable magnetic manipulation ability.

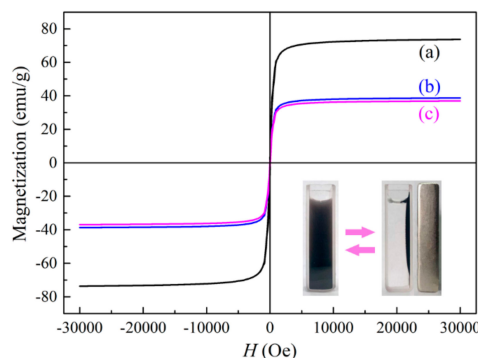


**Figure 6.** Hysteresis loops of hollow  $\text{Fe}_3\text{O}_4$  microspheres (a), hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (b), and hollow flower-like  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (c).

## 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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst, in Figure 7a–c, the control experiments on pure RhB, RhB+ $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres and RhB +  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst were conducted under the same experimental conditions. What was noteworthy was that RhB was degraded completely in the presence of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres reached 63.5% decomposition, but the RhB solution with the addition of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst microspheres amazingly reached 94.5%.

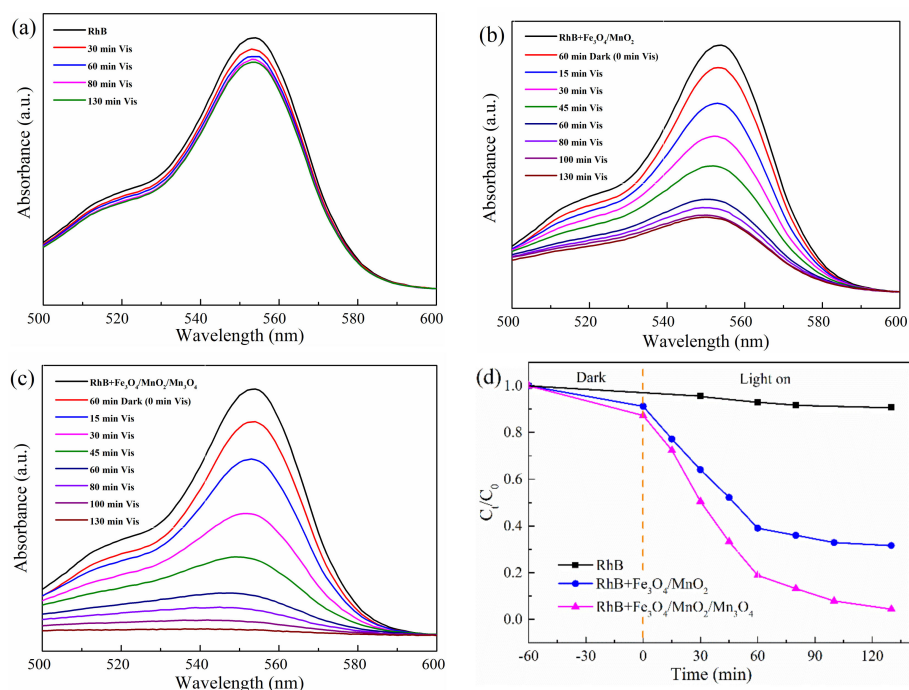


**Figure 7.** Cont.

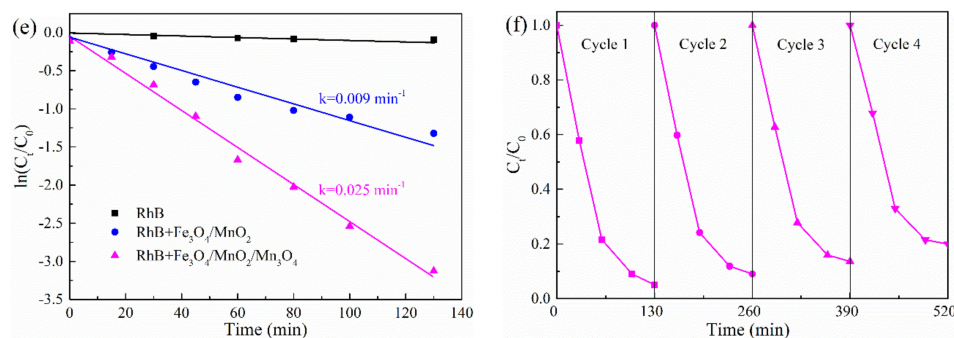


**Figure 7.** UV-vis spectra of RhB solutions in different performing times in the presence of pure RhB (a),  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (b), and  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (c). Conversion of  $C_t/C_0$  for the degradation of RhB (d). Linear fit of experimental data by first-order kinetic model (e). Consecutive degradation of RhB with  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst for four cycles (f). Reaction conditions: RhB = 65 mL of 10 mg/L; Catalyst = 10 mg; initial natural pH =  $5.0 \pm 0.1$ ; Illuminant = 400 W metal halide lamp;  $T = 25^\circ\text{C}$ ; Time = 130 min.

The photocatalytic reaction belonged to a pseudo first-order reaction and could be fitted by the Langmuir–Hinshelwood model of  $\ln(C_t/C_0) = -kt$ , where  $k$  was the apparent first-order rate constant [46–49]. In Figure 7e, compared with the rate constant  $k = 0.009 \text{ min}^{-1}$  of  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres,  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst exhibited the rate constant  $k = 0.025 \text{ min}^{-1}$ , 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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{pH} = 3$ . 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  $\text{MnO}_2$  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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst.

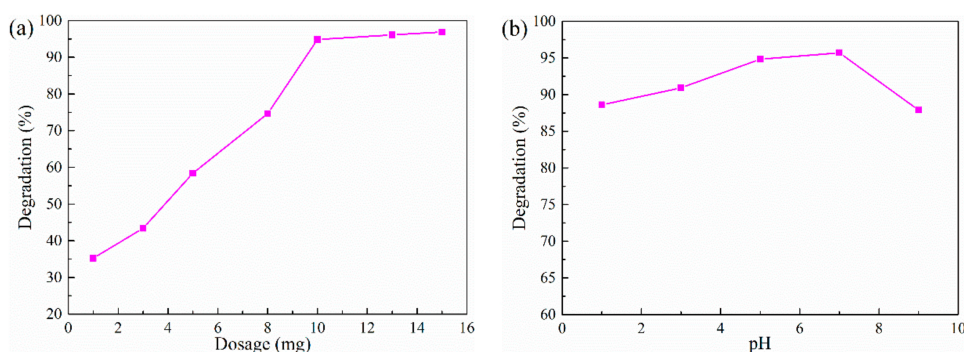
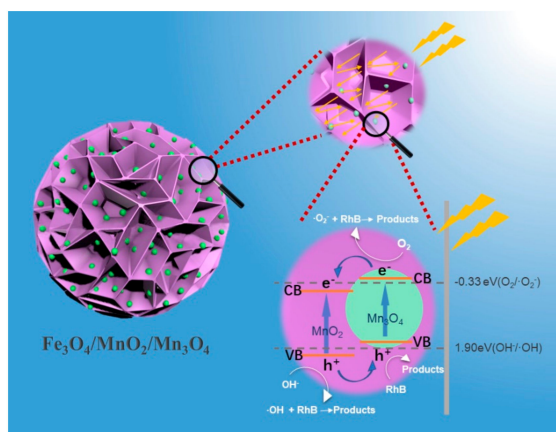


**Figure 8.** Effects of the dosage of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst on RhB degradation (a). Reaction conditions: RhB = 65 mL of 10 mg/L; Catalyst = variable; initial natural pH =  $5.0 \pm 0.1$ ; Illuminant = 400 W metal halide lamp;  $T = 25^\circ\text{C}$ ; Time = 130 min. Effects of the pH on RhB degradation in the presence of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst (b). Reaction conditions: RhB = 65 mL of 10 mg/L; Catalyst = 10 mg; pH = variable; Illuminant = 400 W metal halide lamp;  $T = 25^\circ\text{C}$ ; Time = 130 min.

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,  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$  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  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$  could significantly enhance the photocatalytic performance. Theoretically, the conduction band and valence band of  $\text{MnO}_2$  were more positive than those of  $\text{Mn}_3\text{O}_4$ , which favored the transfer of photogenerated charge in thermodynamic theory. Under visible light irradiation, the electrons ( $e^-$ ) excited into the conduction band in  $\text{Mn}_3\text{O}_4$  would be transferred to the conduction band of  $\text{MnO}_2$ . The holes ( $h^+$ ) were left in the valence band of  $\text{Mn}_3\text{O}_4$ . 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  $\text{MnO}_2$ . In the meantime, the superoxide radical anions appeared in the conduction band of  $\text{Mn}_3\text{O}_4$  by interacting with the  $e^-$  and the dissolved  $\text{O}_2$ . 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  $\text{Mn}_3\text{O}_4$  [40,41].



**Scheme 2.** Possible mechanism of  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  photocatalyst for the improved photocatalytic performance under visible light.

### 3. Materials and Methods

#### 3.1. Materials

Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium polyacrylate, urea, sodium citrate, potassium permanganate ( $\text{KMnO}_4$ ), ethanol, hydrochloric acid ( $\text{HCl}$ ), RhB, and sodium borohydride ( $\text{NaBH}_4$ ) 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 $\text{Fe}_3\text{O}_4/\text{MnO}_2$ Microspheres

Hollow  $\text{Fe}_3\text{O}_4$  microspheres were fabricated by solvothermal method [50]. The prepared  $\text{Fe}_3\text{O}_4$  hollow microspheres (0.3 g) were added to a  $\text{KMnO}_4$  aqueous solution (0.055 M, 80 mL), followed by the ultrasonication for 30 min. Then,  $\text{HCl}$  (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  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres.

#### 3.3. Synthesis of Flower-Like $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$ Microspheres

The prepared  $\text{Fe}_3\text{O}_4/\text{MnO}_2$  microspheres (0.2 g) were fully dispersed in a deionized water (50 mL). Then, an aqueous solution of  $\text{NaBH}_4$  (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  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  core and  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$  shells were successfully synthesized. First, monodisperse hollow  $\text{Fe}_3\text{O}_4$  microspheres were obtained, where after grading  $\text{MnO}_2$  nanosheets was grown around the  $\text{Fe}_3\text{O}_4$  microspheres in a simple hydrothermal system, and then  $\text{Mn}_3\text{O}_4$  nanoparticles were in situ fabricated on the  $\text{MnO}_2$

nanosheets using a simple reduction method. The prepared  $\text{Fe}_3\text{O}_4/\text{MnO}_2/\text{Mn}_3\text{O}_4$  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  $\text{MnO}_2$  and heterojunction between  $\text{MnO}_2$  and  $\text{Mn}_3\text{O}_4$ . 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.

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