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# Urchin-like hollow $\text{SiO}_2@ \gamma\text{-MnO}_2$ microparticles for the rapid degradation of organic dyes†

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In this paper, using hollow silica microspheres as carriers, we developed a facile one-pot method for the preparation of hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  composite microparticles. Under a certain proportion of hollow silica microspheres and manganese salt, a novel kind of hollow urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles was obtained. The structure and morphology of the composite microparticles were characterized by XRD, SEM and TEM. On this basis, using rhodamine B and methyl orange as model molecules, the oxidative degradation ability of the hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles for organic dyes in water was investigated through UV-vis analysis technology. The urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles showed excellent performance for the rapid oxidative degradation of organic dyes under acidic conditions. This study indicated that  $\gamma\text{-MnO}_2$  loaded on hollow materials can be used as an efficient tool for treating organic dye wastewater, and shows broad application prospects for solving environmental problems in the related industry.

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## 1. Introduction

Organic dyes are mostly aromatic heterocyclic compounds with stable molecule structures and chromogenic groups, which can cause great harm if leaked into the environment. In past decades, printing and dyeing wastewater has always been an important problem for industrial water treatment. According to statistics, the current discharge accounts for 35% of total industrial wastewater, and contains a large number of complex components such as dyes, pulp, surfactants, and alkali agents.<sup>1–6</sup> Generally, the removal of organic pollutants in dye wastewater can be divided into physical methods and oxidation methods. However, the physical methods do not destroy the organic pollutant molecules themselves, which needs further follow-up treatment and may cause secondary pollution. Therefore, chemical methods have become the main research hotspots for printing and dyeing wastewater treatment.<sup>7,8</sup> Among them, advanced oxidation processes (AOPs) are a very effective technology for the treatment of refractory organic compounds. Their essence is that free radicals degrade various organic pollutants in wastewater by means of electron transfer, as well as addition and dehydrogenation reactions into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other harmless substances.<sup>9</sup>

AOPs mainly include wet oxidation, photocatalytic oxidation, and electrochemical oxidation. They can convert many organic

compounds with stable structures that are also difficult to biodegrade into non-toxic, harmless and biodegradable low molecular weight substances. This characteristic endows AOPs with broad application prospects in the advanced treatment of printing and dyeing wastewater.<sup>10–12</sup> Among AOPs, the oxidative degradation of organic pollutants by transition metal oxides has attracted extensive attention due to its high efficiency and low cost.<sup>13–19</sup> In particular, manganese oxide ( $\text{MnO}_2$ ) has become a widely-used agent for treating different kinds of organic dyes because of its high stability, good environmental compatibility, and variable valence.<sup>20–23</sup> On the other hand, for oxidative degradation, the degradation efficiency of organic pollutants largely depends on the degree of the pollutants close to the surface of active metal oxides. However,  $\text{MnO}_2$  particles prepared by traditional methods such as the hydrothermal method and coprecipitation have low specific surface areas, which seriously reduces their actual efficiency in the treatment of organic pollutants in water. To solve this problem, many research efforts have been devoted to constructing various types of  $\text{MnO}_2$  microparticles with high specific surface area.<sup>24–30</sup> In fact,  $\text{MnO}_2$  microparticles have variable crystal forms and structures due to different  $[\text{MnO}_6]$  octahedral unit links, and the common crystal forms include  $\alpha\text{-MnO}_2$ ,  $\gamma\text{-MnO}_2$ ,  $\beta\text{-MnO}_2$  and  $\delta\text{-MnO}_2$ .<sup>31</sup> Among them, the octahedral units in  $\gamma\text{-MnO}_2$  form multi-chains along the *c*-axis, eventually resulting in two-dimensional infinite lamellae with large specific surface area, abundant adsorption sites, and high chemical activity. Meanwhile,  $\gamma\text{-MnO}_2$  mainly exists in the form of hydrate and has a large number of hydroxyl groups on its surface, which is beneficial for the enrichment of organic dyes on its surface. In recent years, the research on  $\gamma\text{-MnO}_2$  for AOPs has stimulated

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an extensive interest in the field of treatment of organic dyes in wastewater.<sup>32–36</sup> In addition, it is well known that materials with excellent performance depend not only on the crystalline structure and composition but also on the morphology; sometimes, even the influence of morphology plays a key role in the physicochemical performance.<sup>37,38</sup> To date,  $\text{MnO}_2$  microparticles with different morphology, including 0-D nanoparticles, 1-D nanowires, nanorods, nanotubes, 2-D nanosheets, as well as 3-D hierarchical nanostructures, have been successfully prepared. In the above-mentioned microstructures, the 3-D hierarchical nanostructures such as flower-like microparticles have attracted great attention due to their higher specific surface area, more active sites, and low densities along with better penetration.<sup>39–42</sup> However, the synthesis of 3-D hierarchical  $\text{MnO}_2$  microstructures requires complex steps, which leads to a low synthesis efficiency.<sup>36</sup> Herein, based on our previous studies,<sup>43</sup> using hollow silica microspheres as the carrier, we developed a facile method to prepare a kind of novel urchin-like hollow  $\text{SiO}_2@\gamma\text{-MnO}_2$  microparticles by the one-pot redox precipitation method, as shown in Fig. 1. Furthermore, using rhodamine B and methyl orange as the models, we studied the oxidative degradation ability of the composite microparticles for the organic dyes in water. The research results indicate that the as-prepared urchin-like hollow  $\text{SiO}_2@\gamma\text{-MnO}_2$  microparticles show excellent oxidation degradation performance for organic dyes. Under acidic conditions, organic dyes in water can be completely degraded in about 30 min. This work illustrates that  $\gamma\text{-MnO}_2$  microparticles loaded on hollow materials can be used as an efficient tool to treat organic pollutants in water, and show broad application prospects for solving some important environmental problems in the related industry.

## 2. Experimental section

### 2.1 Materials and instruments

Styrene (St),  $\alpha$ -methacrylic acid (MAA), potassium permanganate ( $\text{KMnO}_4$ ), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Manganese nitrate tetrahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) and tetraethyl orthosilicate (TEOS) were purchased from Aladdin Industrial Corporation (Shanghai, China). Anhydrous ethanol (EtOH) was purchased from Wuxi City Yasheng

Chemical Reagent Co., Ltd. Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), ammonia ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ), and rhodamine B (RhB,  $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ ) and methylene blue ( $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ ) were purchased from Sino-pharm Chemical Reagent Co., Ltd. Polyvinylpyrrolidone ( $(\text{C}_6\text{H}_9\text{NO})_n$ ) and methyl orange ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{Na}$ ) were purchased from Shanghai Yuanye Bio-Technology Co., Ltd. All chemical reagents were of analytical grade and used without any further purification. Deionized water was obtained from Wahaha Group Co., Ltd and used in all experiments.

The UV-vis spectra were recorded on a UV-3600 spectrophotometer (Shimadzu, Japan). Scanning electron microscopy (SEM) images were obtained by a Jeiss Ultra Plus SEM microscope (Carl Zeiss, Germany). The TEM observations in this paper were performed on a JEM-2100 transmission electron microscope (JEOL Japan). X-ray diffraction (XRD) patterns were recorded on a D8 ADVANCE X-ray diffractometer (Bruker, Germany) with Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV, 40 mA). The high temperature calcination of the as-prepared materials was carried out in a GSL-1100X tubular furnace (HF Kejing, China). In this paper, all tests of the same type were performed under the same conditions.

### 2.2 Synthesis of hollow $\text{SiO}_2$ microspheres by the template method

Firstly, 250 mL ultrapure water, 8 mL (0.069 mol) styrene, 0.16 g (0.6 mmol) potassium persulfate, and 0.32 mL (3.2 mmol)  $\alpha$ -methacrylic acid were successively added into a 500 mL three-neck flask equipped with a condensation tube, followed by heating to 75 °C under the protection of argon. After stirring uniformly for 12 h, carboxylated polystyrene microspheres (PS) were obtained by centrifugation and washing with water several times. Secondly, 0.26 g ( $7.2 \times 10^{-4}$  mmol) polyvinylpyrrolidone (PVP) and 40 mL ultrapure water were added into a 250 mL single-neck flask. After ultrasonic treatment for 1 h, the mixture completely formed a colorless solution. Subsequently, 1 g of the as-prepared PS microspheres and 40 mL anhydrous ethanol were added into the solution. After stirring at a constant speed for 24 h, PVP-modified carboxylated PS microspheres were obtained, which acted as the template for the synthesis of hollow  $\text{SiO}_2$  microspheres.

The hollow  $\text{SiO}_2$  microspheres were synthesized by the template method described as follows. The as-prepared PVP-modified PS microspheres were mixed with 73.5 mL

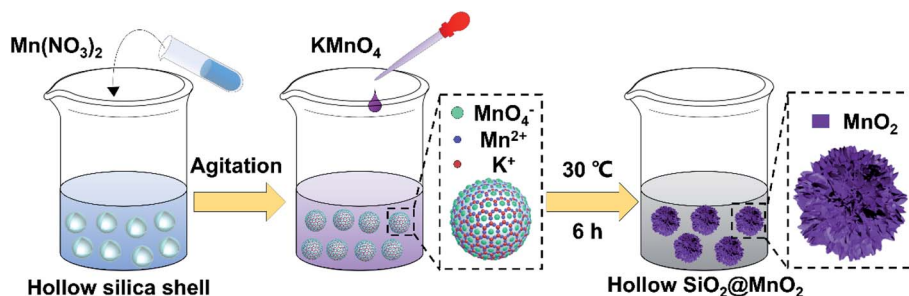


Fig. 1 The synthetic route of the urchin-like hollow  $\text{MnO}_2$  microparticles.

anhydrous ethanol and 3.87 mL ammonia (25 wt%) in a 250 mL single-neck flask under stirring. Then, 0.08 mL, 0.08 mL, 0.16 mL, and 0.32 mL of tetraethyl orthosilicate (10 vol% in absolute ethanol) were successively dropped into the solution at the rate of 0.04 mL min<sup>-1</sup> with an interval of two h. After stirring for 12 h at room temperature, the core-shell PS@SiO<sub>2</sub> microparticles were obtained by centrifugation. Finally, the hollow silica shells were prepared by calcining the PS@SiO<sub>2</sub> microparticles at 700 °C for 6 h in air atmosphere.

### 2.3 Preparation of urchin-like hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles

The urchin-like hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles were prepared by the one-pot redox precipitation method, which is described as follows. Firstly, 0.02 g hollow silica microspheres, 0.173 g (0.689 mmol) manganese nitrate tetrahydrate and 20 mL ultrapure water were added into a 50 mL single-neck flask, followed by ultrasonication for 1 h. Then, 0.073 g (0.462 mmol) KMnO<sub>4</sub> was added into 10 mL ultrapure water to form a homogeneous solution, which was subsequently dropped into the above mixture solution at the rate of 0.5 mL min<sup>-1</sup> under stirring. Subsequently, the color of the mixture solution changed from white to light brown, and finally to purple brown. The resulting solution was then stood at 30 °C for 6 h until the solution color turned black. Finally, after centrifuging and washing with water several times, the black urchin-like hollow SiO<sub>2</sub>@MnO<sub>2</sub> microparticles were obtained by drying at 80 °C overnight. On this basis, parallel experiments were carried out with different amounts of hollow silica microspheres to study the effect of the reaction materials' ratio on the morphology of the products.

### 2.4 Degradation of organic dyes by the hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles

In the oxidative degradation process, rhodamine B (RhB) was first selected as the dye model molecule. The specific operation steps are shown as follows. First, 5 mL rhodamine B (RhB) aqueous solution (0.05 mmol L<sup>-1</sup>) was added to 25 mL ultrapure water, and 0.1 M HCl or NaOH solution was used to adjust the pH value of the initial solution. Then, the quantitative as-prepared SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles were added into the above solution under magnetic stirring. At a given time interval, the oxidative degradation process was monitored by UV-Vis spectrophotometry. The oxidation degradation rate of RhB was investigated by the following formula.

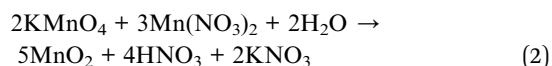
$$\bar{\sigma} = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

where  $A_0$  is the initial concentration of RhB and  $A_t$  is the concentration of RhB at a certain time interval. The concentration of RhB is determined by its peak intensity at the maximum absorption. In order to optimize the experimental conditions, the effects of oxidants with different morphologies and pH values (2, 3.5, 5, 7, 10.5) on the degradation efficiency were investigated.

## 3. Results and discussion

### 3.1 Characterization of the hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles

In this paper, using hollow silica microspheres as the framework, the hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles were synthesized by a controlled redox precipitation method under low temperature, as shown in the following formula (2).



In the reaction, the MnO<sub>2</sub> layer is formed on the surface of SiO<sub>2</sub> by the reactive deposition of the manganese precursor. There is no doubt that the ratio of hollow SiO<sub>2</sub> microspheres to manganese salt has a great influence on the morphology of the final product. Therefore, we conducted a series of parallel synthetic experiments with different amount ratio of hollow SiO<sub>2</sub> microspheres to the manganese precursor. Table 1 shows the raw material parameters of the parallel experiments.

Fig. 2 shows the corresponding SEM and TEM images of the products prepared under different conditions. The experimental results indicate that, with the change in the amount ratio of the raw materials, the morphologies of the synthesized products changed greatly. When the amount of hollow SiO<sub>2</sub> microspheres was relatively large, the deposited MnO<sub>2</sub> cannot completely cover the surface of the hollow SiO<sub>2</sub> microspheres, forming an uneven and discontinuous microsphere appearance. With the decrease in the amount of the SiO<sub>2</sub> microspheres, the surface of hollow SiO<sub>2</sub> microspheres was gradually coated by MnO<sub>2</sub>. Under a certain proportion, a kind of urchin-like hollow MnO<sub>2</sub> microparticles with radial spinous surface were obtained, as shown in Fig. 2(C and H). When the amount of hollow SiO<sub>2</sub> microspheres is too small, it will cause the collapse of the sheet structure of MnO<sub>2</sub> and form the black MnO<sub>2</sub> particles.

Fig. 3 shows the EDS-mapping of the urchin-like hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles and the control sample. It is observed that the element ration of Mn/Si on the surface of the urchin-like hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles is much higher than that of the reference sample, *i.e.*, on the surface of the urchin-like hollow SiO<sub>2</sub>@γ-MnO<sub>2</sub> microparticles, MnO<sub>2</sub> is more evenly distributed on the surface of the SiO<sub>2</sub> carrier, which is also consistent with the observation by the electron microscope. Based on the acidic state in the preparation process, we speculate that under the condition of a certain amount of carrier, more uniform protonation sites can be formed on the

Table 1 Raw material parameters of the parallel experiments

| Hollow-SiO <sub>2</sub> | MnN <sub>2</sub> O <sub>6</sub> ·4H <sub>2</sub> O | KMnO <sub>4</sub> |
|-------------------------|--|-------------------|
| 0.08 g                  | 0.173 g  | 0.073 g           |
| 0.04 g                  | 0.173 g  | 0.073 g           |
| 0.02 g                  | 0.173 g  | 0.073 g           |
| 0.005 g                 | 0.173 g  | 0.073 g           |
| 0                       | 0.173 g  | 0.073 g           |





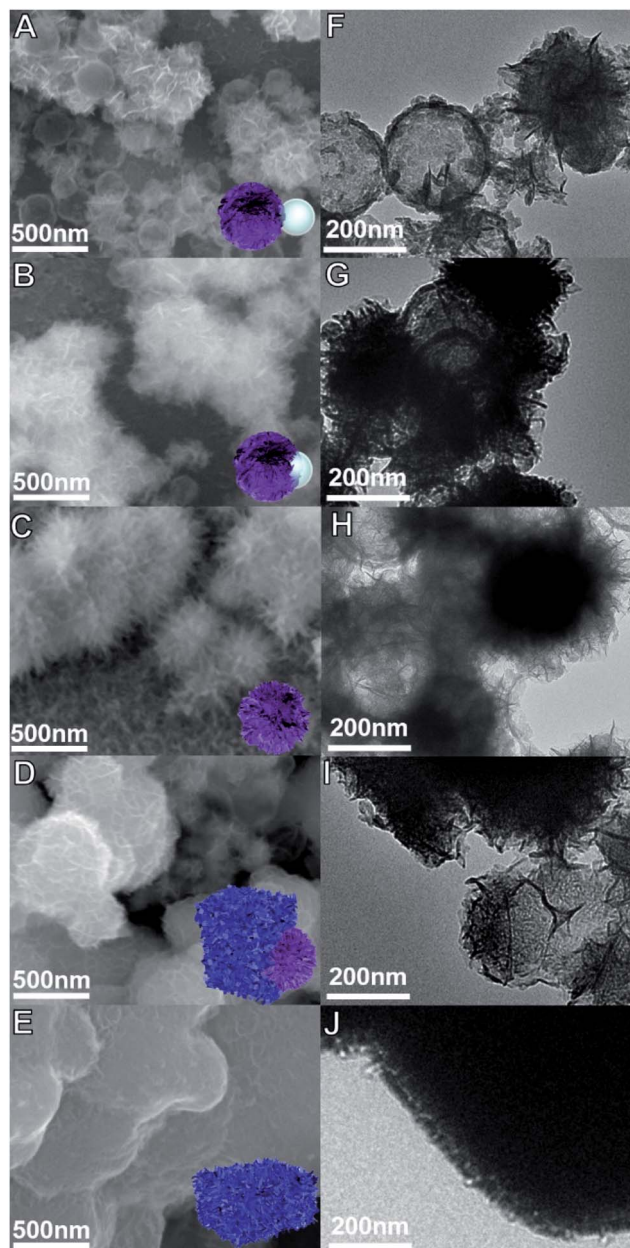


Fig. 2 The SEM and corresponding TEM images of  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles prepared under different conditions. (Amount of hollow  $\text{SiO}_2$  microspheres: A, F: 0.08 g, B, G: 0.04 g, C, H: 0.02 g, D, I: 0.005 g, E, J: 0).

surface of hollow  $\text{SiO}_2$  microspheres, which is conducive for the aggregation of manganese nitrate and the formation of a uniform reaction center. After the addition of potassium permanganate, the crystal grows longitudinally due to the electrical exclusion of the  $\text{MnO}_2$  nanocrystal surface, and finally forms the urchin-like structure. According to the above reasoning, the increase or decrease of hollow  $\text{SiO}_2$  microspheres is not conducive for the formation of the urchin-like structure.

The crystal structure of the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles was determined by X-ray diffraction, as shown in Fig. 4. The peaks at  $23.4^\circ$ ,  $37.2^\circ$ ,  $42.5^\circ$ ,  $57^\circ$ , and  $65.7^\circ$  can be

assigned to the lattice planes of (1 2 0), (1 3 1), (3 0 0), (1 6 0), and (4 2 1) in hexagonal type  $\text{MnO}_2$ , respectively ( $\gamma\text{-MnO}_2$ , JCPDS 14-0644 crystal system: orthorhombic, lattice parameters:  $6.36 \times 10.15 \times 4.09 \text{ \AA}$ ). The wide peak near  $22^\circ$  proves the existence of the silica shell skeleton. Generally, a higher concentration of manganese ion is beneficial for the formation of the  $\gamma\text{-MnO}_2$  phase at low temperature.<sup>44,45</sup> This theory is consistent with our synthetic strategy that potassium permanganate was added to the suspension containing divalent manganese ions. Though the  $\gamma\text{-MnO}_2$  phase is metastable and can be transformed into the  $\alpha\text{-MnO}_2$  phase. However, the previous reports shows that the  $\gamma\text{-MnO}_2$  phase can be stabilized at a lower reaction temperature ( $\leq 60^\circ \text{C}$ ) and shorter reaction time of the  $\text{MnO}_4^-/\text{Mn}^{2+}$  system. At the same time, our work shows that the tunnel structures of  $\gamma\text{-MnO}_2$  can be easily obtained by simple control in the process of precursor addition.<sup>46</sup>

### 3.2 Degradation activity of the hollow urchin-like $\text{SiO}_2@ \gamma\text{-MnO}_2$ microparticles for dyes

The degradation of dye in water by  $\text{MnO}_2$  is realized by the oxidative reaction. The redox reaction can be expressed as  $\text{MnO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$ . Therefore, a low pH value can improve the reducing potential of  $\text{MnO}_2/\text{Mn}^{2+}$  as well as the oxidizing power of the system, which means that low pH is in favor of the oxidative degradation of the dyes.<sup>47</sup> Fig. 5 shows the UV-Vis spectra of rhodamine B solution at different pH values (2, 3.5, 5, 7, 10.5) in the presence of urchin-like hollow  $\gamma\text{-MnO}_2$  microparticles ( $1.5 \text{ mg mL}^{-1}$ ) and in the absence of the catalyst. The experimental results indicated that the characteristic peak of rhodamine B decreased significantly, and the maximum peak blue shifted under acidic conditions, *i.e.*, the degradation rate of RhB under acidic conditions was higher than that under alkaline conditions. In this process, the color of the solution began to gradually change from pink to colorless and transparent. When the pH value of solution  $> 7$ , the UV-Vis spectra of the rhodamine B solution hardly changed within 24 h. The parallel blank experiment showed that the RhB solution had only slight natural degradation in the absence of  $\text{MnO}_2$  under acidic conditions. Moreover, there is no doubt that the attenuation of characteristic peaks of RhB is not caused by adsorption because adsorption rarely leads to a blue shift of the absorption peak. On the other hand, under acidic conditions, the surface of  $\text{MnO}_2$  is prone to protonation and subsequent positive charge, which is not conducive to the adsorption of RhB. If the fading of the dyes originates from the pure adsorption of RhB on the  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles, it would be enhanced with the increase in the solution pH, which is contrary to our experimental results. Therefore, the degradation of RhB is not caused by adsorption.

Fig. 6(A) shows the corresponding degradation curve of RhB under different pH conditions. Within 10 min, the degradation rates of RhB at pH = 2, 3.5, and 5 were 90.6%, 87.1%, and 71.6%, respectively. However, in the case of pH = 7, the degradation rate of RhB was only 54.4% within 10 min and there was almost no change after 24 h. This phenomenon may be due to that the small molecular amines produced in the



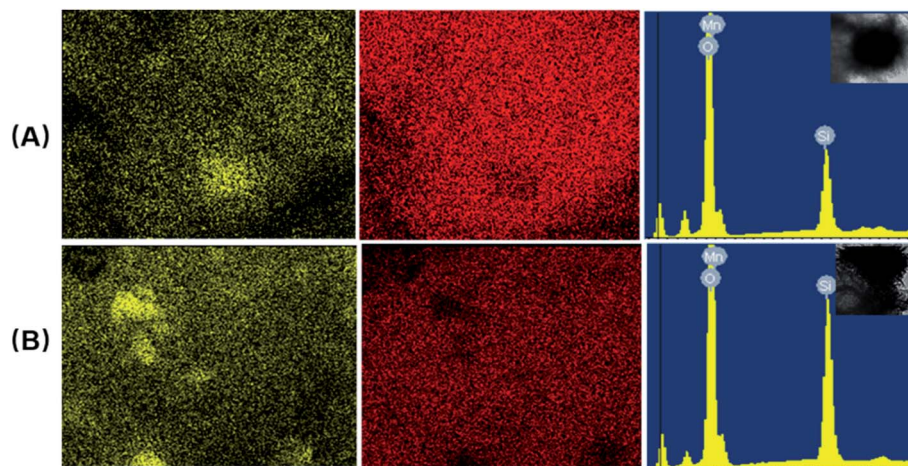


Fig. 3 EDS-mapping of the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles ((A): 0.02 g hollow  $\text{SiO}_2$  microspheres) and the control sample ((B): 0.04 g hollow  $\text{SiO}_2$  microspheres).

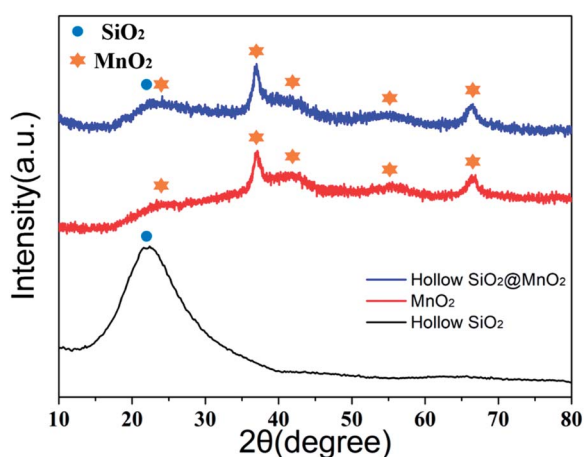


Fig. 4 XRD patterns of the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles, hollow- $\text{SiO}_2$  shell and pure  $\text{MnO}_2$  particles.

degradation process, which decreased the oxidation ability of  $\text{MnO}_2$ . However, the degradation rate of rhodamine was almost zero in 24 h at pH = 10.5. According to the experimental results, the degradation kinetics curve was drawn with  $\ln(A_0/A_t)$  as the ordinate and time  $t$  as the abscissa, as shown in Fig. 6(B). It can be seen from the results that there is a good linear relationship between  $\ln(A_0/A_t)$  and  $T$  at different pH, which indicates that the oxidative degradation of RhB by the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles under different pH conditions conforms to the characteristics of quasi first-order kinetics. Therefore, the degradation of the organic dye by the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles can be described by the L-H kinetic model, and the migration of the dye to the microparticle surface follows the state of monolayer adsorption.

In order to investigate the effect of material morphology on the oxidative degradation ability, rhodamine B was further degraded by the different as-prepared  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles under acidic conditions (pH = 3.5). The experimental results indicated that the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$

microparticles show better degradation ability, as shown in Fig. 7. Under the catalysis of the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles, RhB was basically degraded completely within 30 min, whereas the absorption peak of the RhB solution decreased only about 50% under the catalysis of the other three kinds of materials. As for catalysis by pure  $\text{MnO}_2$  particles, the absorption peak of the RhB solution decreased about 61%, as shown in Fig. S1.† In addition, pure hollow silica microspheres have no catalytic effect. It is exciting that compared with other materials, the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles show ultra-high activity in the degradation of rhodamine B. Except the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles, it takes 4–24 h for other materials to reach a high degradation rate of RhB. This phenomenon may be attributed to the fact that the urchin-like structure has better active sites and specific surface area.

In order to investigate the general adaptation of the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles for dye degradation applications, we further studied the degradation of methylene blue and methyl orange by the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$ , as shown in Fig. 8. The experimental results show that the as-prepared urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  still have good degradation performance for the two dyes, and the degradation rate of methylene blue and methyl orange can reach 83.6% and 87.5% in 10 min, respectively. Our studies indicate that the as-prepared urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles have strong oxidative degradation ability for organic dyes with different charge characteristics.

In practice, printing and dyeing wastewater may contain a variety of dyes. In order to study the effect of a mixed system on the degradation performance of the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles, we next studied the degradation performance of the materials for simulated mixed dye wastewater. Fig. 9 shows the UV-Vis spectra of the mixed solution containing two dyes with different charge characteristics in the presence of urchin-like hollow  $\gamma\text{-MnO}_2$  microparticles. The experimental results show that the synthesized urchin-like hollow  $\gamma\text{-MnO}_2$  microparticles still show good degradation





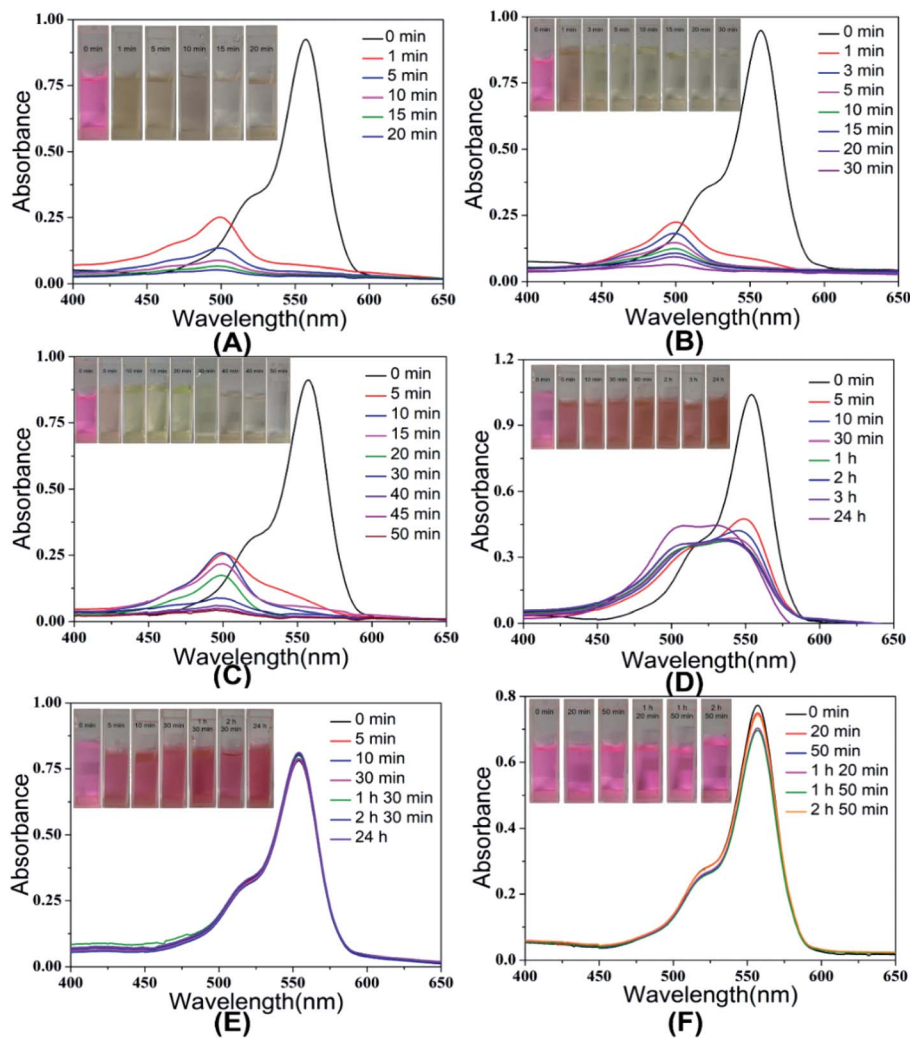


Fig. 5 UV-Vis spectra of RhB degradation by the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles at different pH ((A): pH = 2, (B): pH = 3.5, (C): pH = 5, (D): pH = 7, (E): pH = 10.5, (F): pH = 3.5 without catalyst).

performance for the mixed dye system. However, it shows better degradation behavior for mixed dyes with different charge characteristics. For the mixed solution of the anionic dye of

methyl orange and the cationic dye of methylene blue, it basically fades after 20 min, whereas for the mixed solution of the

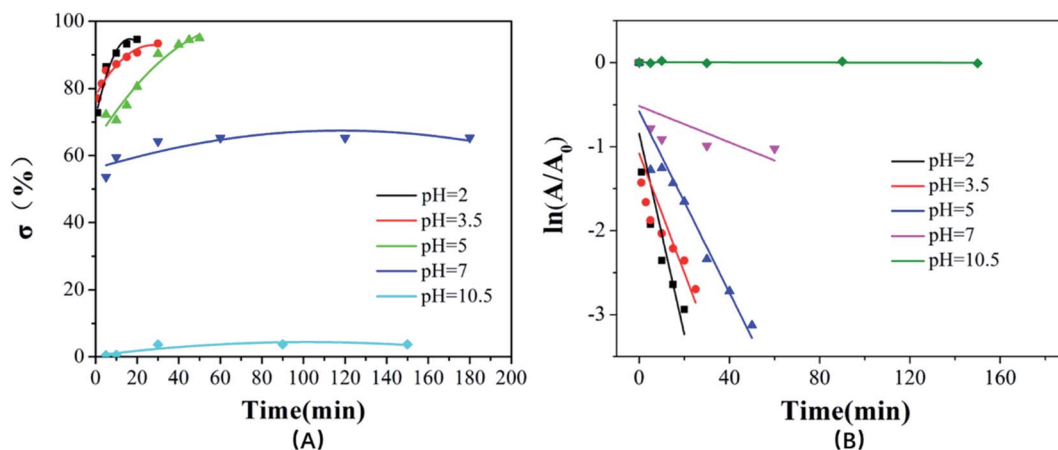


Fig. 6 The degradation curve (A) and kinetic curves (B) of RhB by the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles at different pH.

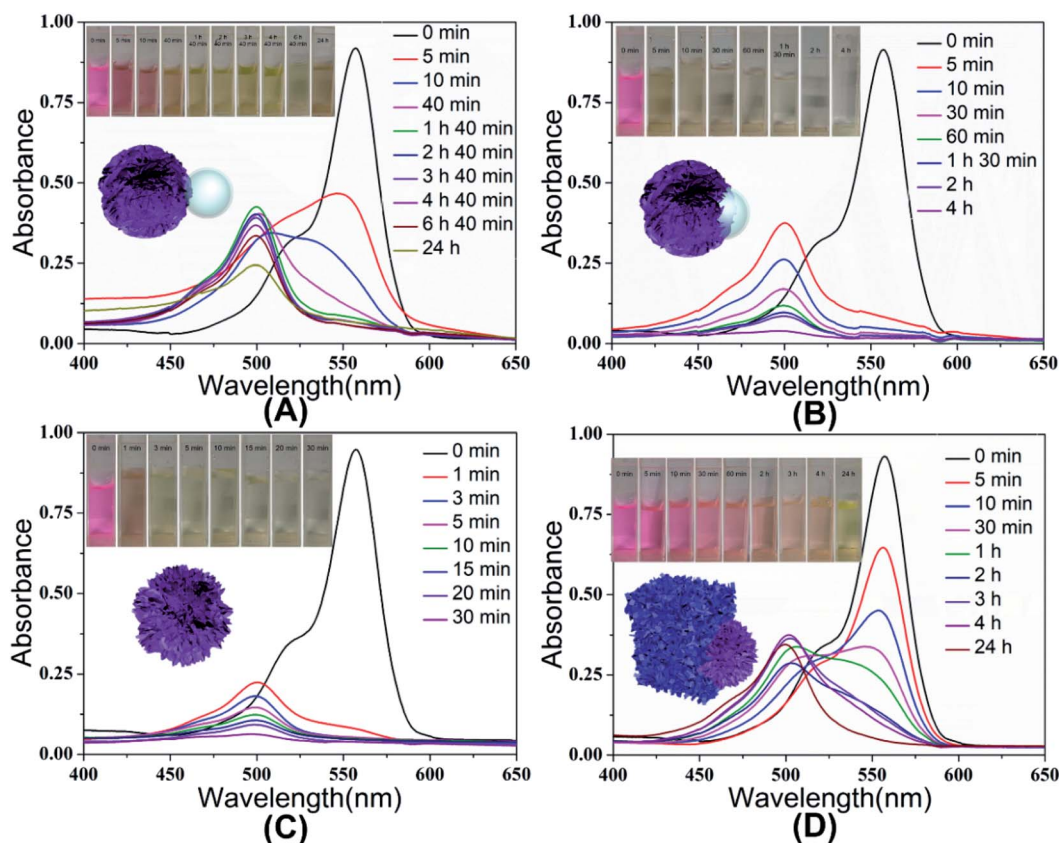


Fig. 7 UV-Vis spectra of RhB solution with the existence of different as-prepared  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles at pH = 3.5.

cationic dye of rhodamine B and methylene blue, the degradation rate is about 80% after 35 min.

Fig. 10 shows the oxidation degradation mechanism of the urchin-like  $\text{SiO}_2@ \text{MnO}_2$  particles to RhB. Initially, due to the special urchin-like structure, which provides strong capillary force and more oxidation active sites, RhB molecules are fast adsorbed and enriched in the pores of the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$

$\text{MnO}_2$  microparticles, and subsequently degraded by  $\text{MnO}_2$ . In the degradation process, the color of the dye solution changed from pink to light yellow green, and finally to colorless. In the corresponding UV spectra, the blue shift of the absorption peak to about 493 nm can be attributed to the *n*-deethylation of RhB.<sup>48</sup> The further decolorization of the solution indicates the destruction of the conjugated xanthene structure

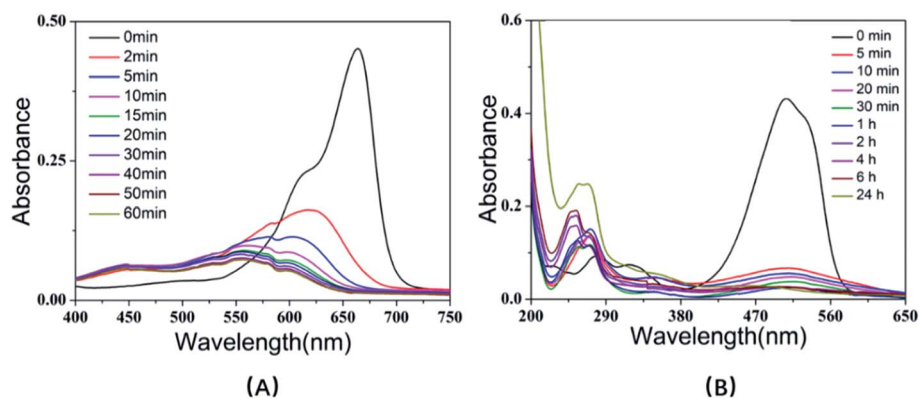


Fig. 8 UV-Vis spectra of methylene blue (A) and methyl orange (B) solution with urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles at pH = 3.5.



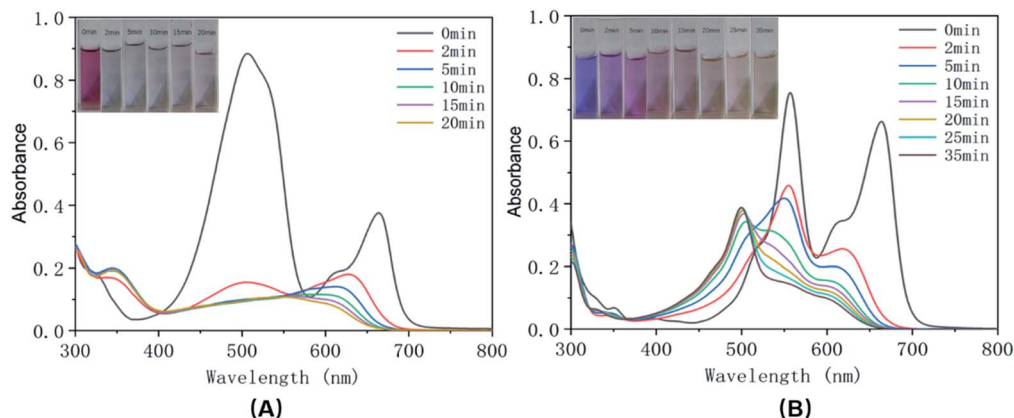


Fig. 9 UV-Vis spectra of the mixed solution of methyl orange and methylene blue (A) and the mixed solution of RhB and methylene blue (B) with the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles at pH = 3.5.

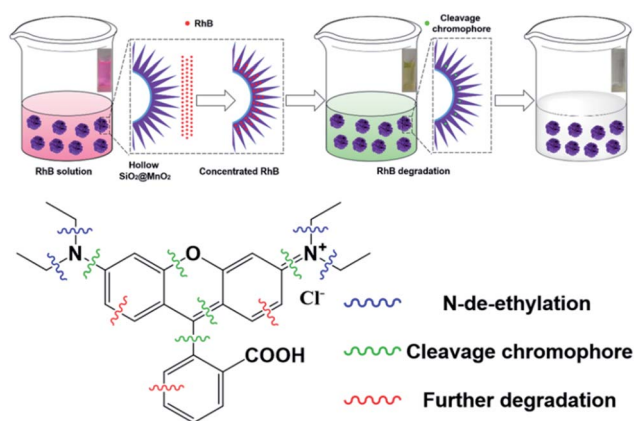


Fig. 10 The oxidative degradation of RhB by the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles.

(chromophore).<sup>49,50</sup> On the other hand. Because of the continuous degradation of RhB by  $\text{MnO}_2$ , the concentration of RhB in the micropores of the urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles is low, and the continuous diffusion and transfer of RhB to

surface of the  $\text{MnO}_2$  microparticles is driven by the concentration difference of RhB.

Fig. 11 show that after five cycles of continuous use of the sea urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles, the degradation rate of RhB still reached 82%, which indicates that the urchin-like hollow  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles have good reuse efficiency.

## 4. Conclusion

In this paper, using hollow  $\text{SiO}_2$  microspheres as the template, urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles were synthesized by facile oxidation-reduction precipitation method at room temperature. This method overcomes some shortcomings of traditional hydrothermal method such as high temperature requirement and low coating amount. Furthermore, in acidic solution, the as-prepared microparticles showed high oxidative degradation efficiency for organic dyes in a short time (RhB 87.1% and methyl orange 87.5% in 10 min). In addition, it still showed good degradation performance for the mixed dye solution. This research shows broad application prospects for solving some important environmental problems in the related industry.

## Conflicts of interest

There are no conflicts to declare.

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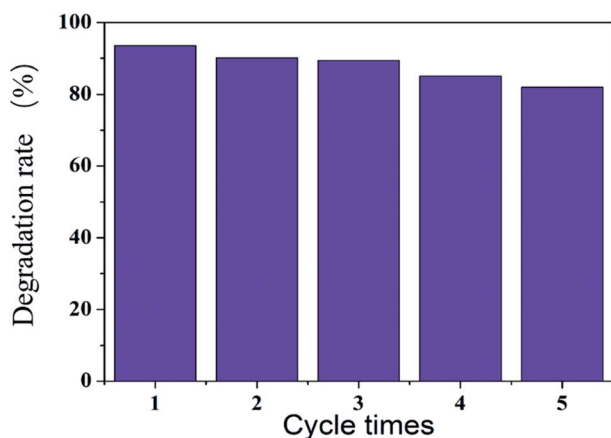


Fig. 11 Degradation rate of rhodamine B by the continuous use of urchin-like  $\text{SiO}_2@ \gamma\text{-MnO}_2$  microparticles.



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