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Formation of Fe_3O_4@MnO_2 ball-in-ball hollow spheres as a high performance catalyst for enhanced catalytic performances

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Preparation of hierarchical MnO_2 hollow/solid spheres

MnO_2 hollow spheres[1]*:* SiO_2 spheres (200 mg) into 0.01 M $KMnO_4$ (70 mL) solution under stirring. Subsequently, the mixture was transferred to a 100 mL autoclave and kept at 160 ^oC for 12 h. After the autoclave was cooled to room temperature, the product was etched by 2 M NaOH to remove the SiO_2 core. The final products, the hierarchical MnO_2 hollow spheres were obtained after centrifugation and washed by deionized water.

MnO2 solid spheres: The MnO_2 solid sphere was prepared using similar methods without the presence of SiO_2 spheres.

Preparation of Fe_3O_4 hollow/solid spheres

Fe_3O_4 hollow spheres[2]*:* In a typical synthesis of hierarchical Fe-glycerate hollow spheres, $Fe(NO_3)_3{\cdot}6H_2O$ (0.202 g) and glycerol (7.5 mL) were added into isopropanol (52.5 mL). After stirring for 5 min, 1 mL of deionized water was added into the above solution. After stirring for another 10 min, the container was then transferred to a stainless steel autoclave and kept in an electrical oven at 190 ^oC for 12 h. After cooling to room temperature naturally, the precipitate was separated by centrifugation, washed with several times with ethanol and dried in an oven at 70 ^oC overnight, and then annealed at 350 ^oC for 3 h in N_2.

Fe_3O_4 solid spheres[3]*:* $FeCl_3{\cdot}6H_2O$ (1.35 g) was dissolved in ethylene glycol (40 mL) to form a clear solution, followed by the addition of NaAc (3.6 g) and polyethylene glycol (1.0 g). The mixture was stirred vigorously for 30 min and then sealed in 50 mL autoclave. The autoclave was heated to and maintained at 200 ^oC for 24 h, and allowed to cool to room temperature. The black products were washed several times with ethanol and dried at 60 ^oC for 6 h.

Catalytic degradation procedure

Methylene blue (MB) degradation was performed in a 250 mL conical flask with MB (30 mg/L) solution and dipped in a constant-temperature water bath (298 K). The catalysts (300 mg/L) was first added to the solution and stirred for 120 min and then PMS (20 mM) was added to the solution to start the degradation.

Solution pH was adjusted by 0.01 M H_2SO_4 or NaOH. At defined time intervals, an aliquot of 3 mL solution was withdrawn by a syringe, which was immediately quenched by ethanol (3 mL). The catalysts were separated using magnet, and the concentration of MB (λ=664 nm) was determined using a UV-vis spectrometer. The effects of foreign ions (Cl^-, NO_3^-, SO_4^{2-}, ClO_4^-, Na^+, K^+, Ca^{2+}) at 0.1 M on the degradation reaction were studied. The experiments were carried out under the same reaction conditions with MB (30 mg/L), PMS (20 mM), pH~7.98 and the used catalysts (300 mg/L) at 298 K. Various model pollutants (victoria blue B (VB), rhodamine B (RhB), methyl orange (MO), phenol and methyl violet (MV)) at 30 mg/L on the degradation reaction were studied. The experiments were carried out under the same reaction conditions with PMS (20 mM), pH~7.98 and the used catalysts (300 mg/L) at 298 K. In addition, two sets of quenching tests were carried out to determine the radical species formed in the catalytic system by using *tert*-butyl alcohol (TBA) and ethanol as the radical scavengers.

For the kinetic rates of dye degradation, the pseudo-first order kinetic was employed,[4]

$$-\frac{d[MB]}{dt} = k_{obs}[MB]$$

where $[MB]_0$ (mg/L) and [MB] (mg/L) are the MB concentrations at time 0 and at any specific time t, respectively; and k_{obs} is the pseudo-first-order degradation rate constant (min^{-1}).

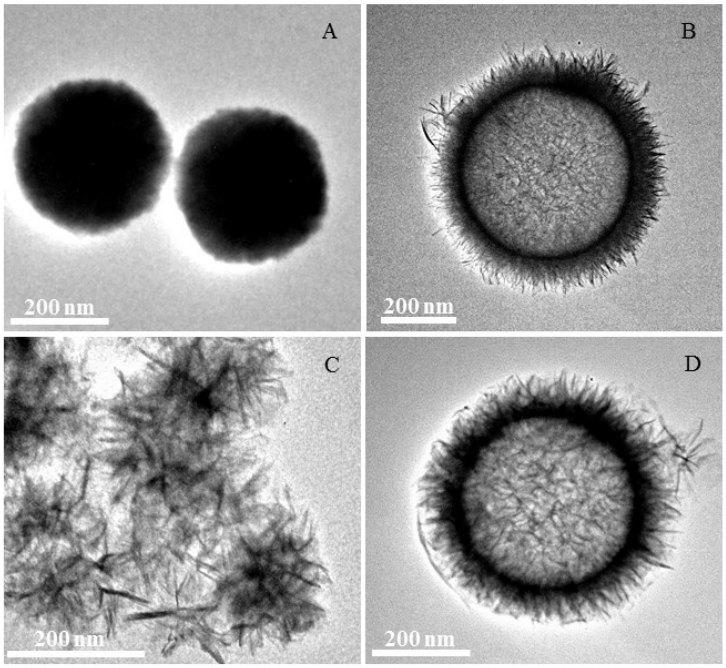

Figure S1. The TEM images of Fe_3O_4 solid/hollow spheres (A and B) and hierarchical MnO_2 hollow/solid spheres (C and D)

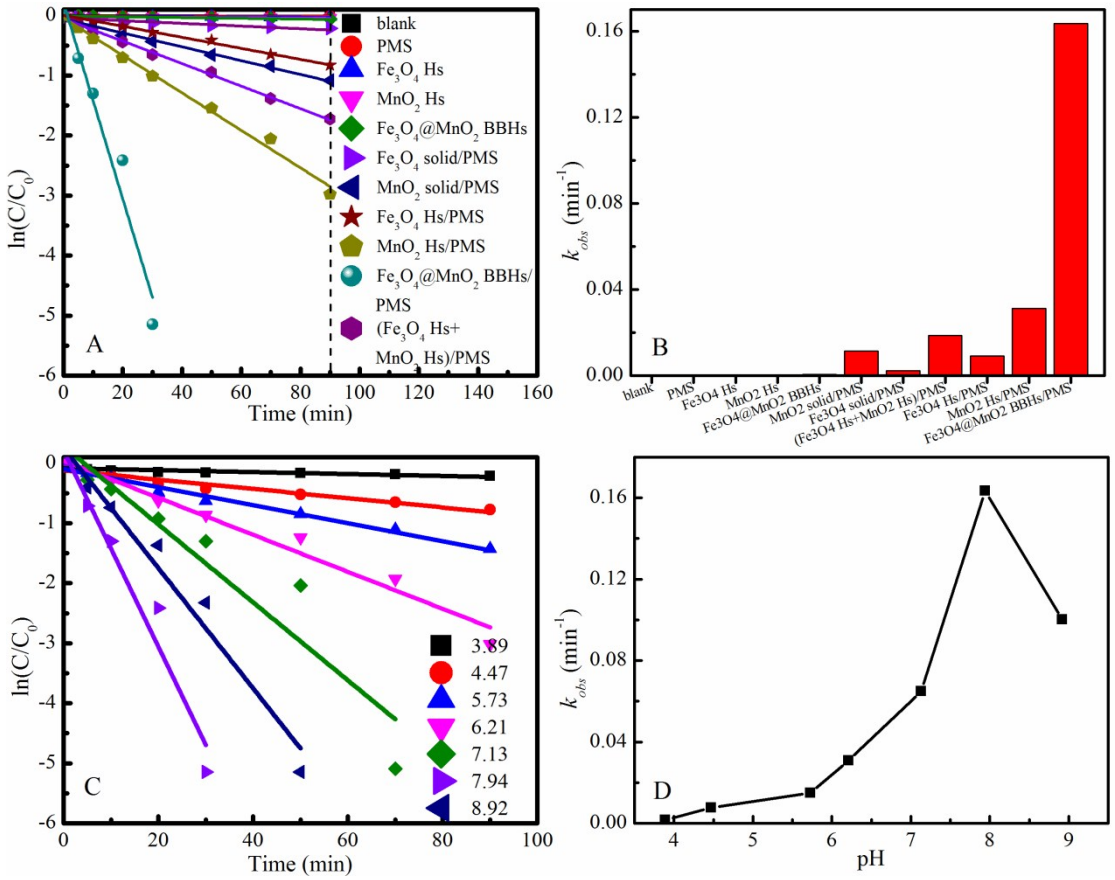

Figure S2. The pseudo-first order kinetic of MB degradation onto the different catalysts (A and B) and pH (B and C).

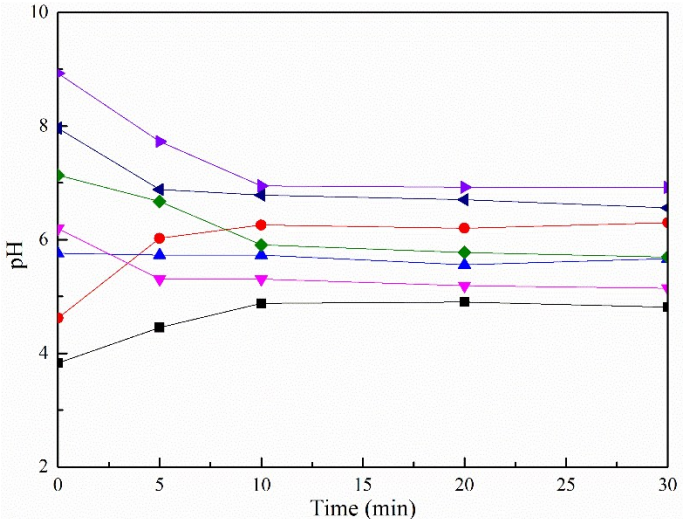

Figure S3. pH variation during the reaction in the $Fe_3O4@MnO_2$ BBHs system.

Figure 1 shows that the final pH values remain ~4.8-~6.9 after ~30 min probably due to the buffering ability of the catalyst. Moreover, for low initial pH, the rise of initial pH is also beneficial for the formation of surface hydroxyl groups on the catalyst, which can behave as an active site for electron transfer and thus improve the performance of the catalyst.

The pH was set at initial. The surface charge of metal oxides is highly dependent on the relation between solution pH and pHpzc of metal oxides. At pH < pHpzc, the surface charge of metal oxides is positive while negative at pH > pHpzc. On the other hands, the existed form of PMS was HSO_5^- at acid and neutral condition and SO_5^{2-} at pH 9.5. The pHpzc of $Fe_3O_4@MnO_2$ BBHs was determined as ~8.1. Thus, at pH 9.5, the interaction between negative charged surface and SO_5^{2-} is reduced due to the formation of repulsive force. Additionally, PMS is unstable at basic pH and can be self-decomposed mainly through non-radical route with a maximum decomposition rate at the pH value equal to its second pKa (~9.4). Both of the reasons lead to the decline of the MB degradation efficiency while enhancement of the MB degradation at pH < 8.1. In the $Fe_3O_4@MnO_2$ BBHs/PMS system, the MB degradation efficiency was declined as the pH increased from ~7.94 to ~8.92, revealing the electrostatic factors and self-decomposition of HSO_5^- through non-radical route controlled the generation of the sulfate radicals. However, the MB degradation efficiency was declined as the pH decreased from ~7.94 to ~3.89 rather than enhanced. The lower rate of MB degradation at this pH might be attributed to the relatively higher

stability of the oxidant at acidic pH values that could reduce the generation of radicals. Besides, in acidic condition, the formation of H-bond between H^+ and the O-O group of HSO_5^- would be more significant that decrease the positive charge of HSO_5^-, thus hindering the interaction between HSO_5^- and the catalyst surface.

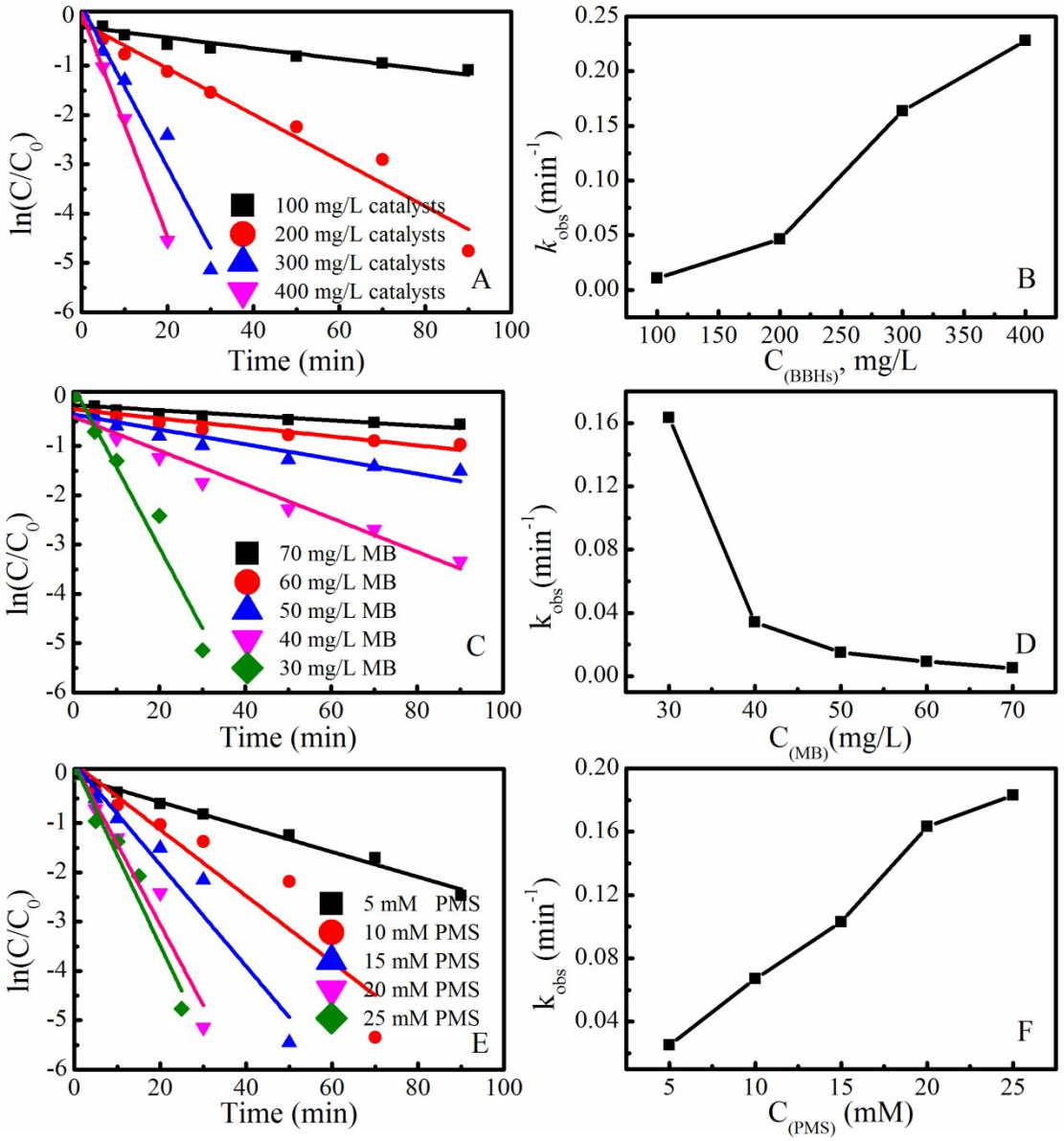

Figure S4. The pseudo-first order kinetic of MB degradation onto the Fe_3O_4@MnO_2 BBHs under different condition: catalyst loading (A and B), MB concentration (C and D) and PMS concentration (E and F).

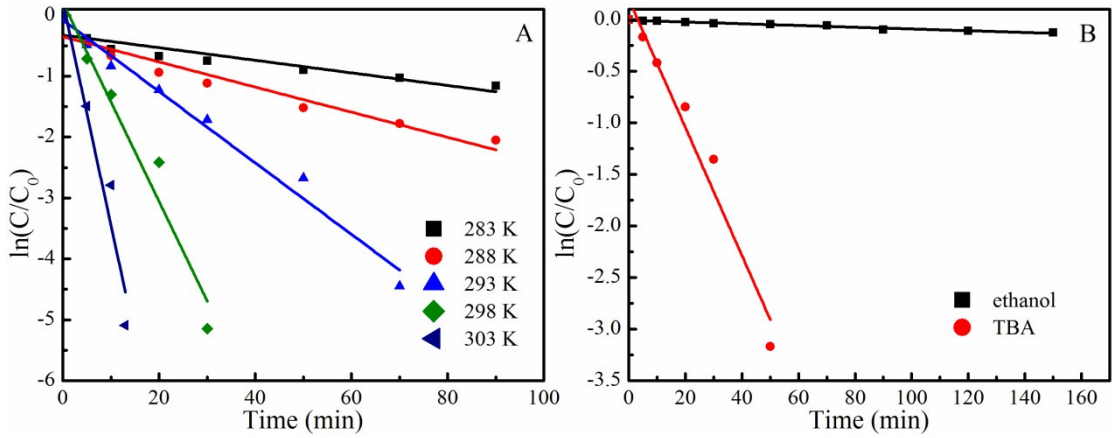

Figure S5. The pseudo-first order kinetic of MB degradation onto the Fe_3O_4@MnO_2 BBHs under different temperature (A) and radical scavengers (B).

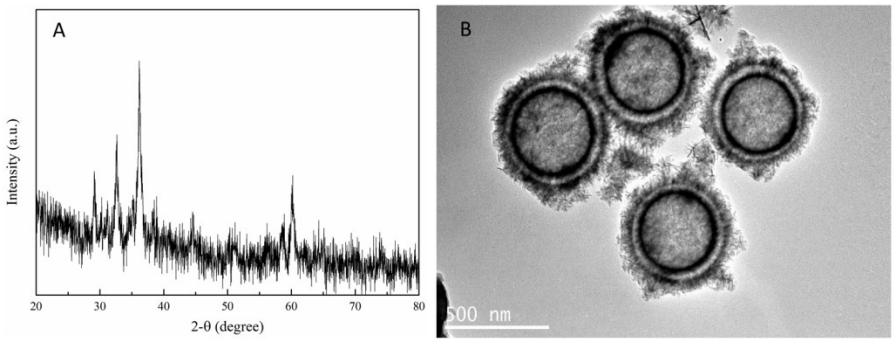

Figure S6. The XRD and TEM results revealed that the hierarchical ball in ball hollow structures and crystalline of the recovered catalyst was scarcely changed.

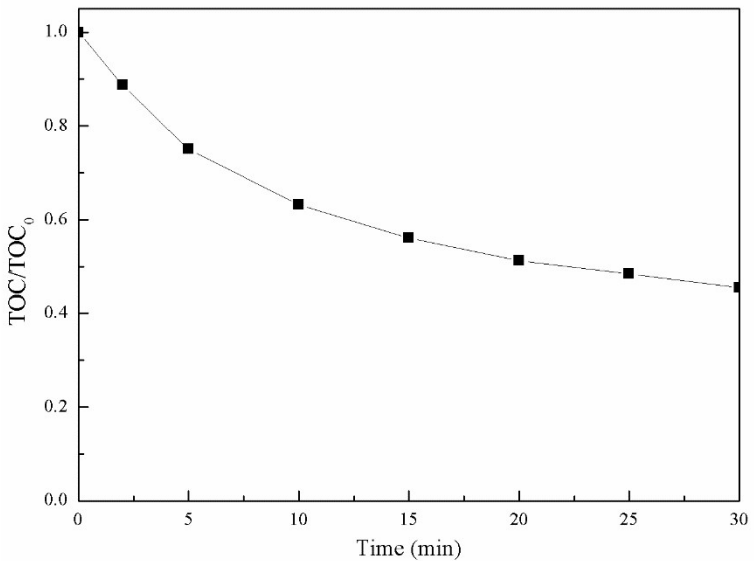

Figure S7. TOC removal during the degradation of MB.

Table S1. The pseudo first-order rate constant (k_{obs}) of the degradation of MB under different pH using PMS activated by different catalysts

Catalysts (30 mg/L)	MB (mg/L)	PMS (mM)	T (K)	pH	k_{obs} (min^{-1})	R^2
blank	30	0	298	7.94	0.00002	0.939
PMS		20			0.00008	0.986
Fe_3O_4 Hs		0			0.0002	0.941
MnO_2 Hs					0.0003	0.955
Fe_3O_4@MnO_2 BBHs					0.0006	0.953
Fe_3O_4 solid sphere		20			0.0022	0.912
MnO_2 solid sphere					0.0115	0.989
Fe_3O_4 Hs+ MnO_2 Hs					0.0187	0.976
Fe_3O_4 Hs					0.0092	0.996
MnO_2 Hs					0.0312	0.995
Fe_3O_4@MnO_2 BBHs					0.1634	0.943
Fe_3O_4@MnO_2 BBHs	30	20	298	3.89	0.0016	0.929
				4.47	0.0077	0.932
				5.73	0.0149	0.982
				6.21	0.0308	0.968
				7.13	0.0649	0.921
				7.94	0.1634	0.943
				8.92	0.1001	0.961

Table S2. The pseudo first-order rate constant (k_{obs}) of the degradation of MB under different conditions using PMS activated by Fe_3O_4@MnO_2 BBHs.

Fe_3O_4@MnO_2 BHHs (mg/L)	MB (mg/L)	PMS (mM)	T (K)	Inhibitor	pH	k_{obs} (min^{-1})	R^2
100	30	20	298	-	7.94	0.0108	0.922
200						0.0466	0.963
300						0.1634	0.943
400						0.2279	0.996
300	70	20	298			0.0052	0.866
	60					0.0091	0.921
	50					0.0151	0.942
	40					0.0342	0.954
	30					0.1634	0.963
300	30	5	298			0.0253	0.998
		10				0.0671	0.928
		15				0.1032	0.935
		20				0.1634	0.943
		25				0.1832	0.944
300	30	20	283			0.0103	0.896
			288			0.0207	0.922
			293			0.0587	0.978
			298			0.1634	0.943
			303			0.3666	0.986
300	30	20	298	ethanol		0.0008	0.969
				TBA		0.0624	0.955

References

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