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Electronic Supplementary Information

Facile synthesis of 3D hierarchical MnO₂ microspheres and its ultrahigh removal capacity of organic pollutant

Syed Khalid and Chuanbao Cao^{*}

Research Center of Materials Science, Beijing Key Laboratory of Construction Tailorable

Advanced Functional Materials and Green Applications, Beijing Institute of Technology,

Beijing 100081, P. R. China.

Table S1. Dye concentration (D.C) , catalyst concentration (C.C), dye to catalyst weight ratio (W.R), degradation time (D.T) and rate constant (K) comparison with few reported catalysts for various organic pollutants.

Catalyst	D.C	C.C	W.R	D.T	К	Ref.
	(mg/L)	(mg/L)	(mg/mg)	(min.)	(min.) ⁻¹	
3D hierarchical MnO ₂	400	10	40/1	25	0.12008	This
microspheres						work
Tublar g-C ₃ N ₄	10	2500	1/250	75	0.02116	1
g-C ₃ N ₄ micro strings	10	2500	1/250	60	0.03336	2
WO ₃ /CdWO ₄ composite	10	1000	1/100	50	0.07982	3
CuS flowers	12	200	3/50	55	0.049247	4
3D WO ₃ Octahedra	20	500	1/25	60	0.03254	5
CuS microspheres	12	2000	3/500	48	0.02418	6
Hierarchical CuS	12	2000	3/500	50	0.0403	7
AgBr @WO₃ rods	10	1000	1/100	240	0.00588	8
MCM-41-Fe/Al	10	100	1/10	200		9
TiO ₂ -C composite	200	500	2/5	180		10
$H_2Ti_2O_4(OH)_2$ flowers	100	100	1/1	11		11
Si/SiC@C@TiO ₂ composite	120	200	3/5	35	0.0703	12
β -MnO ₂ nanorods	25	1000	1/40	60		13
MnO ₂ various microstructures	10	2000	1/200	120		14
β -MnO ₂ microrod	40	535	8/107	40		15
β -MnO ₂ nanopincers	20	135	4/27	120		16
MnO ₂ nanoballoons	15.38	2	7.69	100		17



Figure S1. FTIR spectrum of 3D hierarchical MnO₂ microspheres



Figure S2. Time profiles of MB degradation under different conditions in the presence of TBA and BQ

we have also investigated the applicability of 3D H MnO₂ microsphere to degrade the pesticide. Parathion methyl (PM; C₈H₁₀NO₅PS) was selected as the target pesticide. It is an organophosphate pesticide and insecticide.¹⁸ The testing procedure was derived from that already used to degrade organophosphate pesticide.¹⁸ High performance liquid chromatography (HPLC) was used to measure PM concentration at specific interval of time

during degradation process. PM solution (100mL) was prepared with the concentration of (100 mg/L). MnO₂ solution (100 mL) was prepared with the concentration of (5000 mg/L). The above solutions were prepared in non-polar organic sorbent (n-heptane). The degradation performance was determined by mixing specific volumes of PM and reactive sorbent in a glass vial (4 ml). The degradation process was carried out in dark to avoid the exposure of sunlight. 250 µL each of the reactive sorbent and PM solutions were mixed together in a glass vial. After specific interval of time (5, 10, 20, 30, 40, 50, 60, 90 and 100 minutes), the reaction was terminated by adding methanol in each vial. The solutions were centrifuged at 8000 rpm for 4 min (three times) to remove sorbent particles. All measurements were carried out by using HPLC (Perkin Elmer 410 Bio). HPLC measurements were used to determine the concentration of PM and 4-nitrophenol (4-NP) at specific interval of time. The main degradation product of PM in non-polar media is 4-nitrophenol, its concentration will be increased as a result of PM decomposition.¹⁸ The control experiments were also carried out prior to degradation process, firstly initial concentration (C₀) of PM was determined by repeating the above procedure without the addition of the reactive sorbent. Secondly we also analyzed commercially obtained 4-NP from Sigma-Aldrich without the addition of sorbent and PM, as chromatographic standard for our measurements.

During degradation process the concentration of PM and 4-NP solutions (C_t) were measured at different interval of time using HPLC. The degradation efficiency R (%) was calculated by

$$R = \left(\frac{C_0 - C_t}{C_0}\right) \times 100$$

Where C_0 and C_t were the initial and residual concentrations of PM respectively.

The concentration of PM decreases with the increase of time (Fig. S3). Initially PM concentration decreases very rapidly and about 54 % degraded in just 30 minutes (Fig.S3). As the reaction time progressed, the PM concentration continued to drop but at a slower rate(Fig.S3). At the end of degradation process the relative concentration of PM became very low which is an indicative of its maximum decomposition. MnO₂ microspheres take 100 minutes to degrade around 90 % of PM (Fig. S3). Whereas the relative concentration of 4-NP

increases continuously with the increase of degradation time (Fig. S3). HPLC measurements indicate only the formation of 4-NP as the main degradation product of PM which is in accordance to the previous report.¹⁸



Figure S3. Kinetics of Parathion methyl (PM) degradation and 4-NP formation in the presence of 3D hierarchical MnO₂ microspheres

The PM degradation mechanism can be described as follows; firstly the PM molecules are adsorbed through sulphur on the surface of the sorbent at an acidic site (metal cation Mn^{4+}), followed by S_N^2 -type nucleophilic substitution.¹⁸⁻²⁰ FTIR study of MnO_2 microspheres (Fig. S1) also confirms the strong absorption sites are available for organic compounds at its metallic vibration band and surface hydroxyl group.^{19, 20} The hydroxyl group attach with the reactive sorbent (Fig.S1) is responsible for effective degradation process due to its strong nucleophilic behavior towards phosphorus (P) atoms attached with PM.²¹ As a result of strong nucleophilic attack, PM molecules are decomposed into 4-NP.²¹ The ultrathin nanosheets building blocks (2 nm), mesoporous porosity, higher surface reactivity and high specific surface area (184.32 m² g⁻¹) are responsible for effective degradation of PM.²² The higher surface reactivity is due to its nanocrystalline nature (8.8 nm) as evidenced by XRD measurement.²³ The higher specific surface area provides large number of exposed active sites of [MnO₆] to the surrounding PM molecules which results in much higher adsorption.

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