Supporting Information

Dual-templates imprinted capsule with remarkably enhanced catalytic activity for pesticides degradation and elimination simultaneously

Yong Guo and Tianying Guo *

Key Laboratory of Functional Polymer Materials, Ministry of Education, Institute of Polymer Chemistry, College of Chemistry, Nankai University Weijin Road, No. 94, Tianjin, 300071, China.

* To whom correspondence should be addressed: E-mail: tyguo@nankai.edu.cn.

Materials.

Azodiisobutyronitrile (AIBN), vinyltriethoxysilane, ammonium hydroxide (24%), *p*-nitrophenol, HF solution (35%) were all purchased from Tianjin Chem-reagent Institute (China). Zinc dimethacrylate was purchased from Aldrich. Paraoxon (purity>98%) was purchased from Shanghai Quandao Co. (China), DVB were distilled under vacuum before used. AIBN were recrystallized in ethanol before used. Other chemicals were analytical grade used as received.

Methods.

Typical synthesis of v-SiO$_2$ seed: 360 ml water was mixed with 40 ml ethanol, then added 10 ml vinyltriethoxysilane in it, and the solution was stirred at room temperature for 2 h. Then 24 ml $NH_3.H_2O$ (24%) was added slowly, kept it reacted 0.5 h. The silica microsphere was separated by centrifugation, washed five times with ethanol and then dried in vacuum at room temperature for 24 h. Before used, the v-SiO$_2$ seed were treated with toluene at room temperature for 24 h.

Typical synthesis of silica/polymer core/shell$_1$ microsphere (MIP-N): 0.0713 g p-nitrophenol was dissolved in 200 ml acetonitrile, then 0.2412 g MAA-Zn was added slowly. After stirring gently for 2 h, 0.9348 g DVB, 0.1347 g AIBN and 0.168 g v-SiO$_2$ seed were added. This mixing solution was purged with nitrogen for 30 min while cooled in ice bath with stirring; then dispersed in an ultrasonic bath for 1 min. The polymerization was done at 80ºC for 21 h. The result silica/polymer core/shell$_1$ microsphere was separated from the mixed solution by centrifugation, and then washed with acetonitrile for 3 times and ethanol for 3 times and dried in vacuum overnight at 30ºC. Then, the resulted microsphere was treated with 5/1(V/V) ethanol/ water containing 1.0 M of NaOH (totally 30 ml) for 15 h to remove the template. The microsphere was cleaned by ethanol/water mixture (5/1 V/V). After removal the template, Zn^{2+} was also disappeared. To upload Zn^{2+}, the resulted microsphere was treated with 4/1(V/V) ethanol/ water containing 0.2 M of $ZnCl_2$ (totally 25 ml) for 15 h and then dried in vacuum overnight at 30ºC. In the same way, the MIP-P was prepared using paraoxon as template and the mole ratio of template to functional monomer was 1:4, and NIP was also prepared but without template.

Typical synthesis of silica/polymer core/shell$_1$/shell$_2$ microsphere (MIP-N/P): 0.05 g paraoxon was dissolved in 143 ml acetonitrile, then 0.172 g MAA-Zn was added slowly. After stirring gently for 2 h, 0.668 g DVB, 0.0962 g AIBN and 0.12 g MIP-N (without removing template) were added. This mixing solution was purged with nitrogen for 30 min while cooled in ice bath with stirring; then dispersed in an ultrasonic bath for 1 min. The polymerization was done at 80ºC for 21 h. The result microsphere was separated from the mixed solution by centrifugation, and then washed with acetonitrile for 3 times and ethanol for 3 times and dried in vacuum overnight at 30ºC. Then the removal of template and upload of Zn^{2+} was the same as MIP-N.

Typical preparation of hollow microsphere (H-MIP-N/P): 0.1 g of MIP-N/P (without removing template) was dispersed in 25 ml ethanol, then 5 ml HF solution (totally 2 wt%) was added, after stirring gently for 7 h, the product was separated from the solution by centrifugation, and then washed with ethanol/water mixture (5/1 V/V) for 3 times. Then the removal of template and upload of Zn^{2+} was the same as MIP-N.

Characterization methods.

Fourier transform infrared (FT-IR) spectra were recorder on a FTS135 (BIORED, USA) spectrometer. The samples were dried and mixed with KBr to be compressed to a plate for measurement. The scan range is 4000-400cm^{-1}.

Ultraviolet-visible (UV-Vis) absorption spectra were performed on a UV-2550 (Shimadzu, Japan) ultraviolet-visible spectrophotometer.

The morphology of microspheres were observed by transmission electron microscopy (TEM, Tecnai G2 F20)

To further confirm the composition of the microspheres, samples of v-SiO_2, MIP-N/P, and H-MIP-N/P were characterized by FTIR spectroscopy. As seen in **Figure S1**, for the spectrum of v-SiO_2, the band at 3062 cm^{-1} is due to the C-H stretching vibrations of vinyl groups, the band at 1277 cm^{-1} is assigned to the in-of-plane symmetric vibrations of Si-C, whereas the peak at 968cm^{-1} is attributed to the vibrations of Si-OH. After MAA-Zn and DVB copolymerization on the surface of the silica seed, it can be found in the spectrum of MIP-N/P that all the bands mentioned above exist but the intensity are relative weak. In addition, the expanded band between 1530 cm^{-1} to 1600 cm^{-1} is assigned to the asymmetric vibrations of carboxylate groups. After removing the silica seed, comparing H-MIP-N/P with MIP-N/P, the peaks at 3062 cm^{-1}, 968 cm^{-1} and 1277 cm^{-1} disappear, which means that the silica seed was completely removed. All these results indicate that the v-SiO_2 surface was coated with the polymer and H-MIP-N/P was obtained.

It is known that polymer shell was the effective component for catalysis hydrolytic degradation of paraoxon. To compare the catalytic activity of these microspheres more rationally, the concept of activity sites were considered. According to the data of microspheres yield, to maintain the activity sites as identical as possible, the amount of MIP-N, MIP-P, NIP, MIP-N/P and H-MIP-N/P were used as follows 0.01g, 0.01g, 0.01g, 0.015g and 0.01g respectively.

The UV-Vis spectra of paraoxon and *p*-nitrophenol were detected and shown in Figure S2. At 275nm, which is the maximum absorption peak of paraoxon, the absorbance of *p*-nitrophenol has little influence on the absorbance of paraoxon. So 275nm was chosen as detect peak during paraoxon catalytic hydrolysis test.

Evaluation of hydrolytic activity of microsphere: The activity of microsphere was assayed using 1 mM of paraoxon as substrate. The hydrolysis activity of microsphere was measured spectrophotometrically by monitoring the decrease of paraoxon. A certain amount of microsphere was dispersed in 363μL ethanol with the help of ultrasound, after that 4.5ml (20 mM) Tris-HCl buffer (pH 9.0) were added. The dispersion system under a constant temperature 30ºC for 10 min and 137μL paraoxon in ethanol was added. Then, the activity of the microsphere was determined in batch mode using magnetic agitation at 30ºC. An amount of 100 μL of the reaction solution was sampled, diluted with 20 mM Tris-HCl buffer (pH 9.0) and the absorbance at 275 nm was determined using UV spectrophotometry

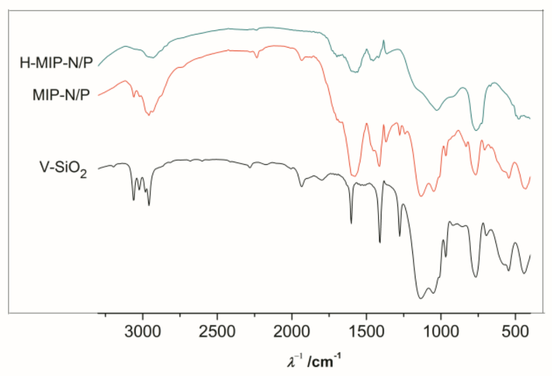

Figure S1. The FTIR spectra of v-SiO$_2$, MIP-N/P, H-MIP-N/P.

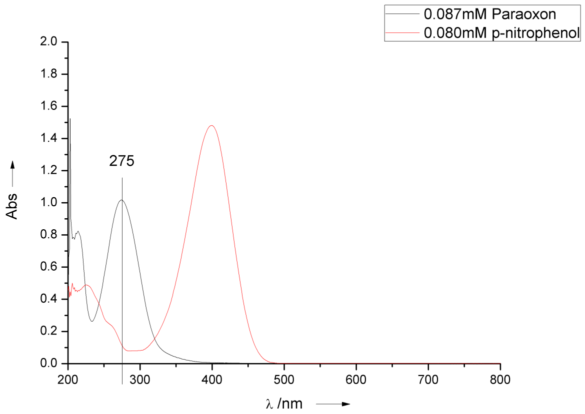

Figure S2. The UV-Vis spectra of 0.087mmol/L paraoxon and 0.08mmol/L *p*-nitrophenol.

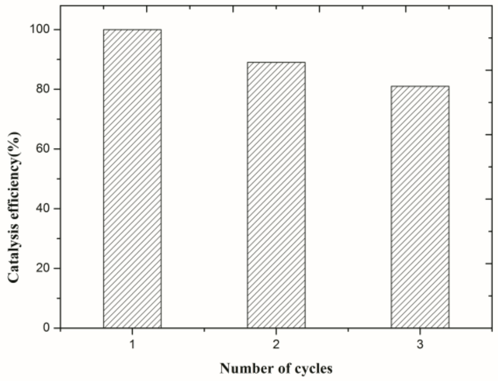

Figure S3. The reusability of H-MIP-N/P.