Using waste to treat waste: facile synthesis of hollow carbon nanospheres from lignin for water decontamination

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1. **Materials.**

The chemicals are used without further purification. Peroxydisulfate ($K_2S_2O_8$, PDS) was bought from Rhawn Co., Ltd. oxytetracycline (OTC) from Tianjin Heowns Biochemical Co., Ltd., phenol, tetracyclines (TC) and chlortetracycline (CTC) from Shanghai Macklin Biochemical Co., 3-aminophenol and sulfamethoxazole (SMX) from Aladdin chemical reagent Co., Ltd. sodium hydroxide (NaOH, AR, 96%, Tianjin Kemiou Chemical Reagent Co., Ltd., ethyl alcohol from Tianli Chemical Reagent Co., Ltd., Tert- butylalcohol was purchased from Aladdin Reagent Co., Ltd. Sodium azide (NaN_3) from Wuhan geao Chemical Technology Co., Ltd. deionized water was utilized in all the experiments.

2. Characterization

Transmission electron microscopy (TEM) were performed by a JEOL-JEM 2100F microscope operated at 200 kV. Energy Dispersive Spectrometer (EDS) Mapping were performed with a TECNAI G2 F20 microscope operated at 200 kV. The morphologies of the catalysts were observed by scanning electron microscopy (SEM, FEI- Quanta 250 FEG). X-ray diffraction (XRD) analyses were measured on a Bruker AXS-D8 Advanced. X-ray photoelectron spectrometry (XPS) was performed on a ThermoFisher Nexsa. Electron paramagnetic resonance (EPR) spectroscopy was conducted on a Bruker A300. Fourier transform infrared spectrometer (FT-IR) were measured on ThermoFisher-IS50. Raman was performed on Horiba scientific-LabRAM HR evolution.

3. Synthesis of HCNs

First, 0.5 g of dealkali lignin was pyrolyzed at 400 ^oC, 500 ^oC resp. 600 ^oC for 4 h in a tubular furnace, with a ramp rate of 2.5 $^oC \cdot min^{-1}$. Then, the reaction system was cooled to 30 ^oC using a cooling rate of 2.5 ^oC/min. Next, the residue was obtained and washed with deionized H_2O resp. EtOH, and it was dried overnight at 60 ^oC. The final products are labeled HCN-400, HCN-500 and HCN-600, respectively.

4. Experimental Procedures.

In a typical procedure, 5 mg of PDS was added into OTC solution (20 mg/L, 50 mL) in a round-

bottom flask at 30 ℃. Then, OTC degradation was activated by adding HCN-500 (12.5 mg). During the reaction, a 2 mL of reaction solution was extracted out at determined intervals. It was filtered by 0.22 μm film, and immediately tested by UV-Vis. In the quenching experiments, TBA, EtOH, NaN_3 and BQ, respectively, was injected into the reaction medium, and the OTC degradation was carried out at the same condition. Cycle experiment: The HCN-500 was collected by the simple filtration, washed for use in the next cycle.

The degradation rate was calculated as:

Degradation rate (%) = $\frac{C_0 - C_t}{C_0} \times 100\%$

where C_0 and C_t are the initial and final pollutant concentration determined on UV absorbance value .

5. Physical characterization of the nanocatalysts (Fig. S1-S10 and Table S1)

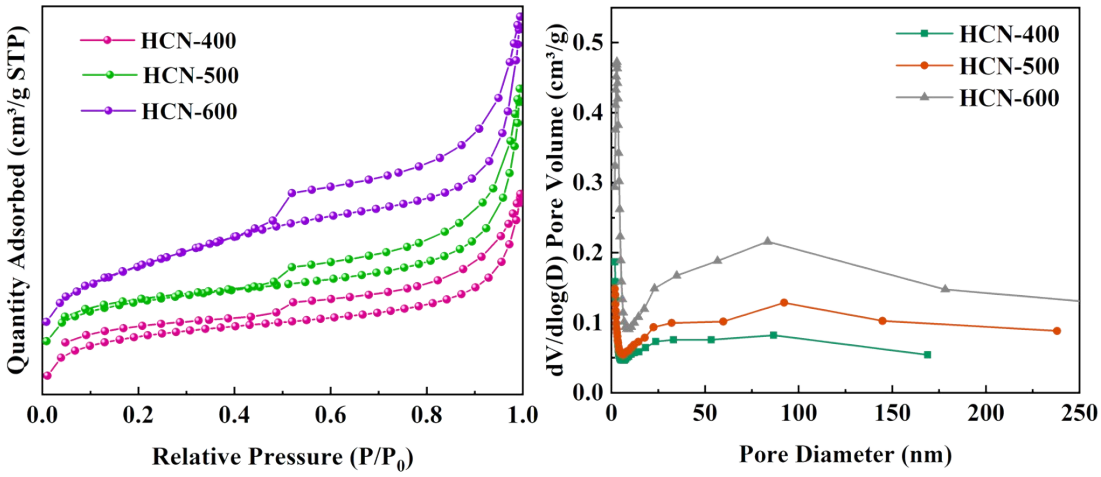

Figure S1. BET of HCNs.

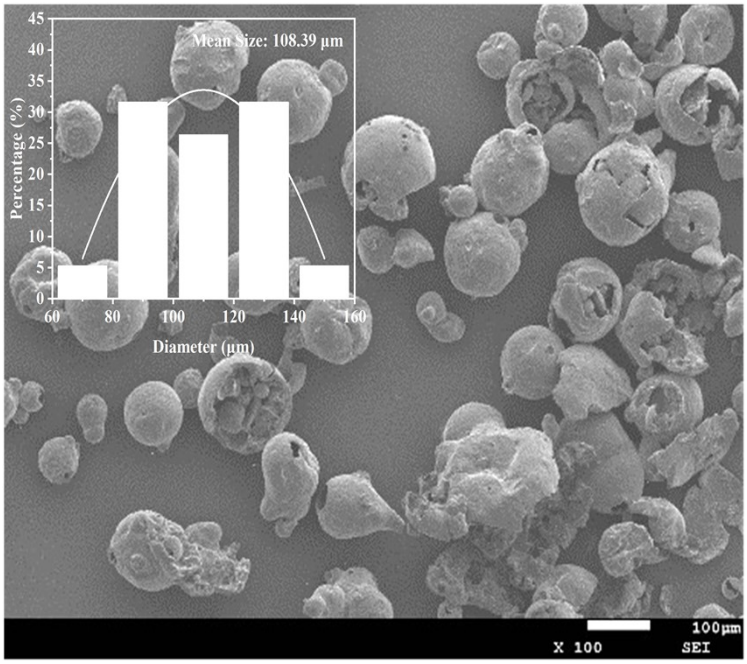

Figure S2. SEM of dealkali lignin

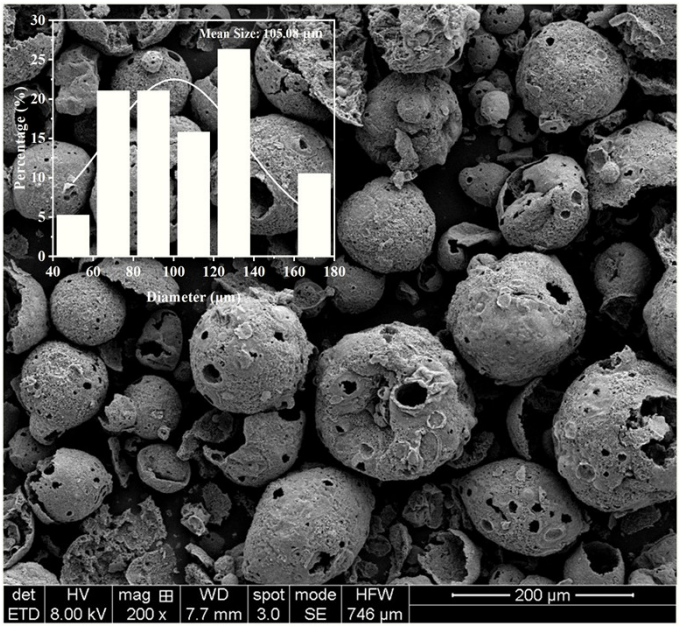

Figure S3. SEM of HCN-400

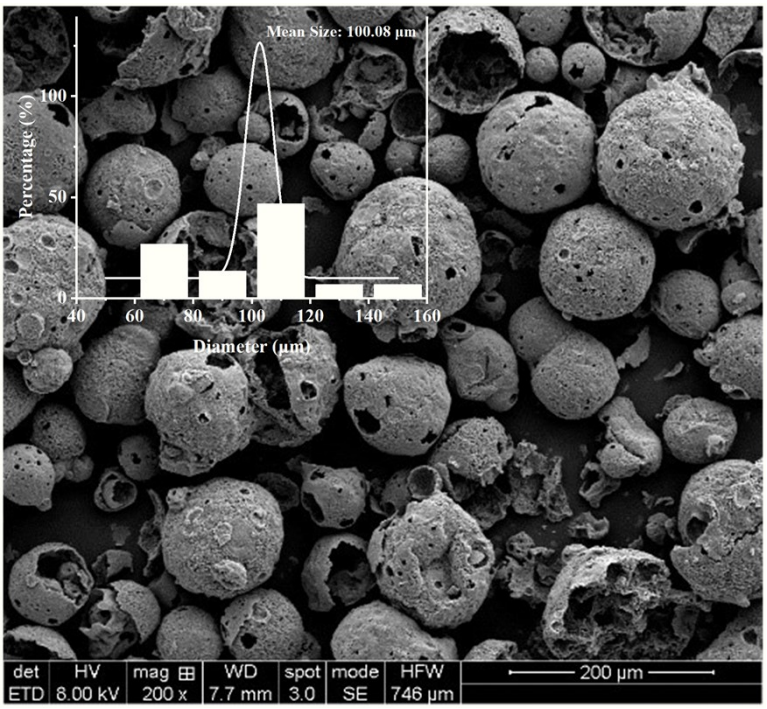

Figure S4. SEM of HCN-500

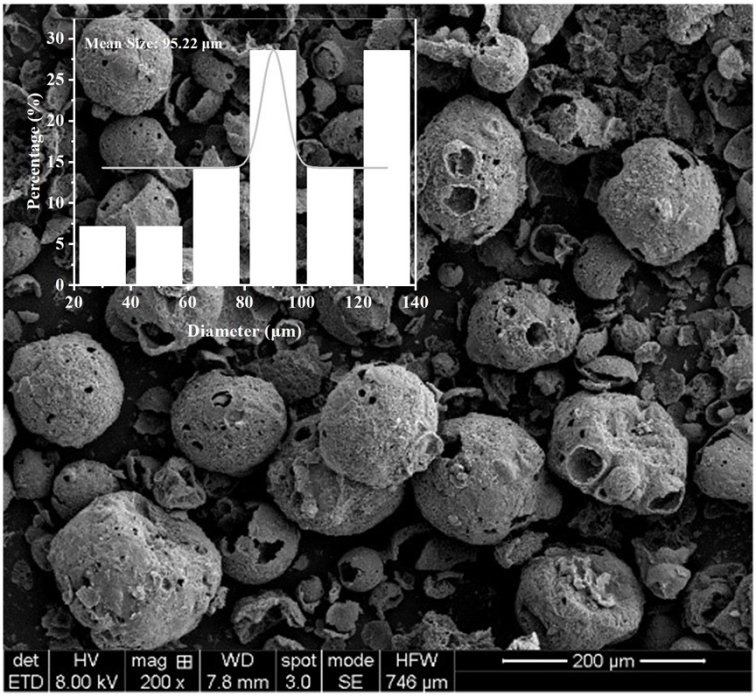

Figure S5. SEM of HCN-600

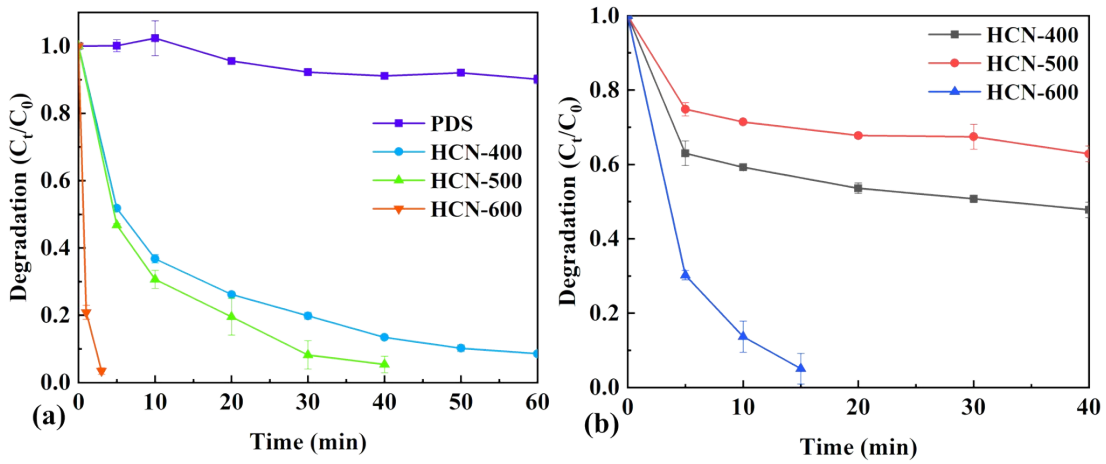

Figure S6. (a) Comparison of OTC degradation catalyzed by HCN-400, HCN-500 and HCN-600. Conditions: 20 mg/L of OTC, 0.1 g/L of PDS and 0.5 g/L of catalyst at 30 °C; (b) Comparison of OTC adsorption by HCN-400, HCN-500 and HCN-600. Conditions: 20 mg/L of OTC and 0.5 g/L of catalyst at 30 °C;

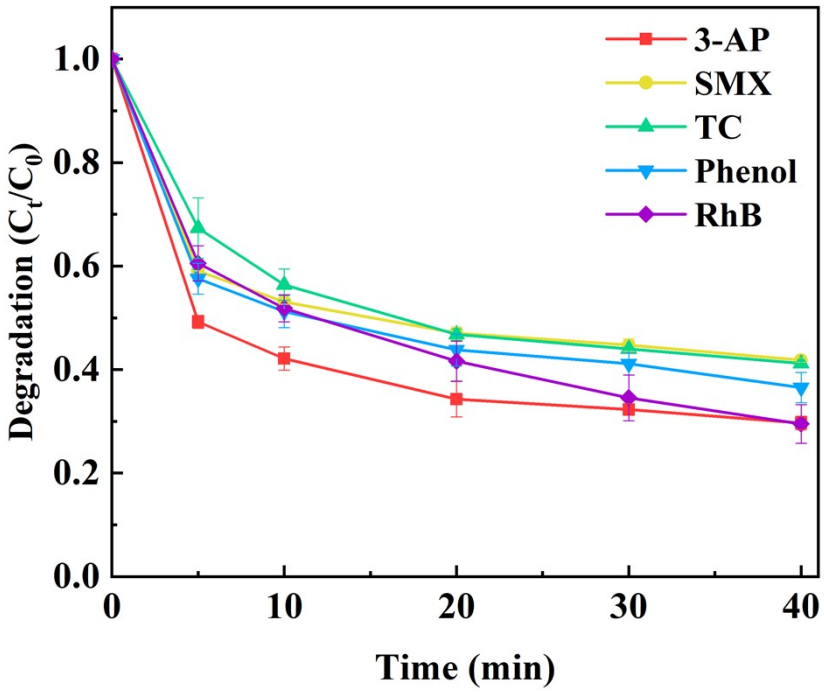

Figure S7. The removal of 3-aminophenol (3-AP), sulfamethoxazole (SMX), tetracycline (TC), phenol and Rhodamine B (RhB) over HCN-500/PDS system.

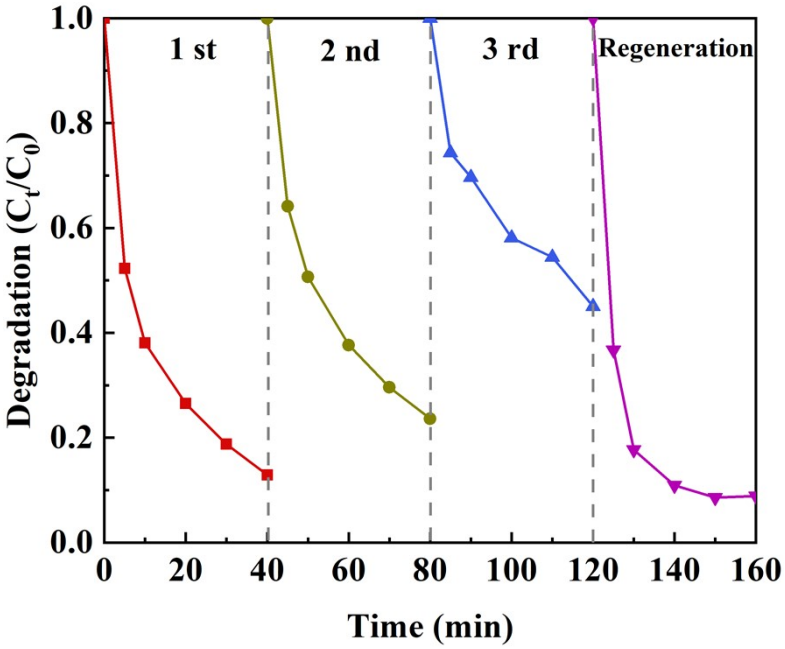

Figure S8. Stability of HCN-500 in OTC degradation.

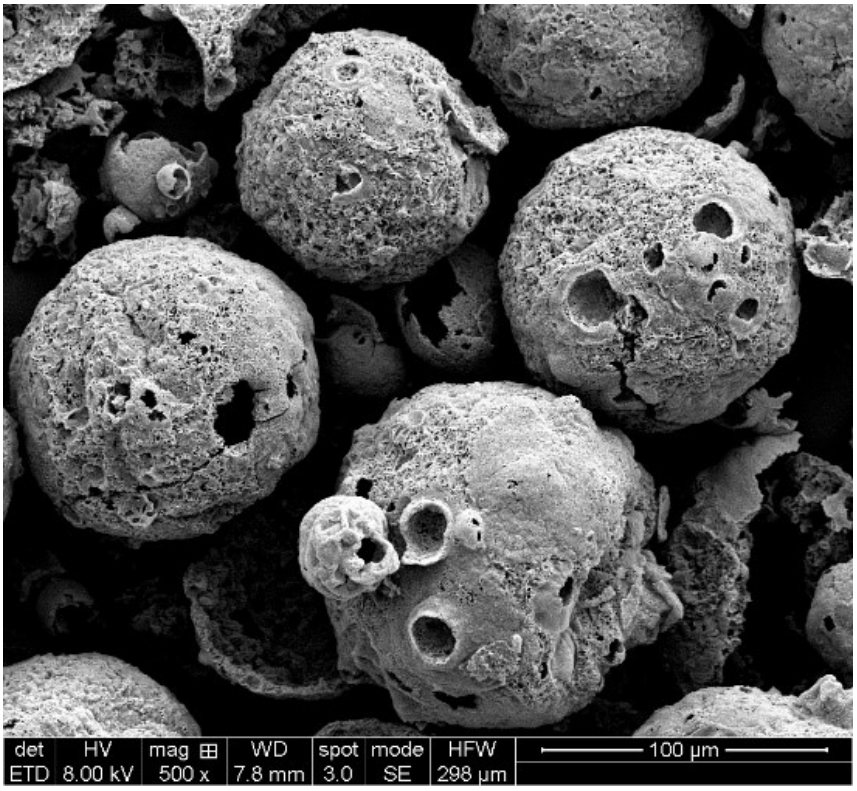

Figure S9. SEM of reactivated HCN-500

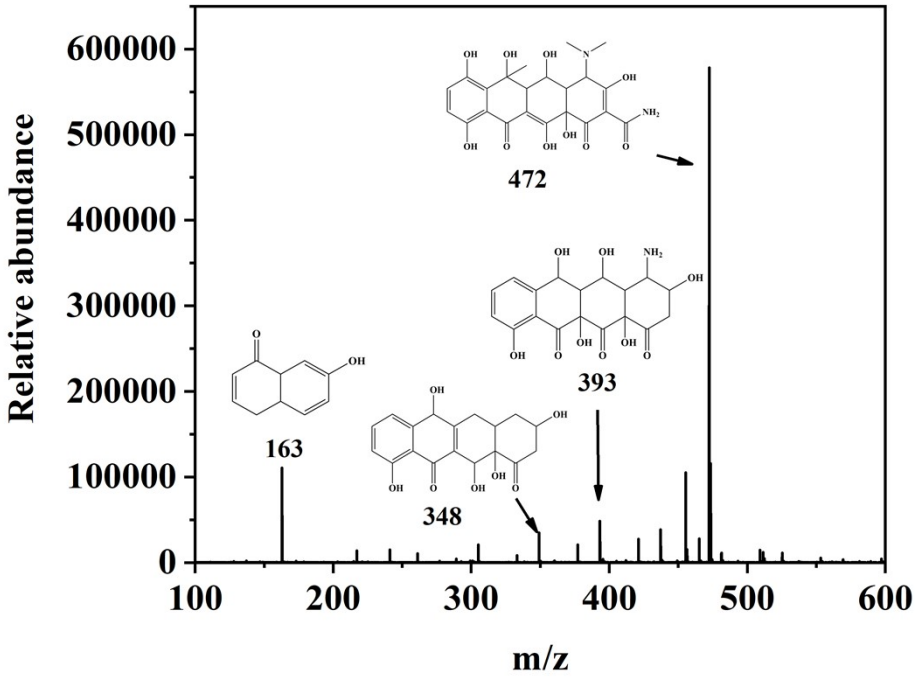

Figure S10. HR-MS of the totally degraded OTC solution

Table S1 Comparison of HCN-500/PDS with other reported catalytic systems for OTC degradation.

Entry	OTC	Catalyst	Oxidant	Other additive	Degradation efficiency	Time	Ref
1	**20 mg/L**	**HCN-500 (0.5 g/L)**	**PDS (0. 1 g/L)**	**-**	**95%**	**40 min**	**This work**
2	20 mg/L	BBC_3 (0.3 g/L)	PDS (2 mM)	-	94%	120 min	[31a]
3	5 mg/L	O-Gcn (0.1 g/L)	PMS (1 mM)	-	63.7%	60 min	[31b]
4	20 mg/L	ACN-10 (0.3 g/L)	-	300 W XL ($\lambda > 420$ nm)	79.3%	60 min	[31c]
5	15 mg/L	N,S-CSs900-10%-OH (0.5 g/L)	PMS (3 mM)	PH=4	95.9%	60 min	[31d]
6	20 mg/L	TCN-5 (0.5 g/L)	-	300 W XL ($\lambda > 420$ nm)	93%	60 min	[31e]
7	50 mg/L	CB (0.05 g/L)	PDS (1 g/L)	PH=5	60%	40 min	[31f]
8	30 mg/L	g-C_3N_4 (0.5 g/L)	-	300 W XL ($\lambda > 420$ nm)	64.8%	120 min	[31g]
9	50 mg/L	14Fe_3O_4-Cs (0.5 g/L)	H_2O_2 (10 Mm)	-	90%	120 min	[31h]
10	600 mg/L	nZVI-BC_{1000} (0.1 g/L)	PDS (0.5 mM)	-	98.3%	300 min	[31i]
11	20 mg/L	1-B@TBC-600 (0.1 g/L)	PMS (0.5 mM)	-	90%	20 min	[31j]
12	30 mg/L	Co@NC-800 (0.2 g/L)	PMS (0.2 g/L)		91.3%	30 min	[31k]
13	30 mg/L	CN (300 mg/L)	PMS (0.1 g/L)	PH=4.34	69.1%	45 min	[31l]
14	20 mg/L	2-EC (0.5 g/L)	H_2O_2 (10.0 mM)	PH=5	97.1%	120 min	[31m]