Supporting Information for:

Laccase-carrying Electrospun Fibrous Membranes for Adsorption and Degradation of PAHs in Shoal Soils

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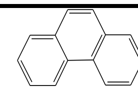
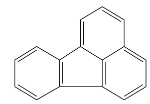
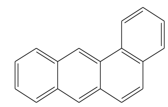
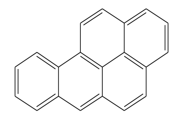
This Supporting Information contains the detailed information on "**Selected physicochemical properties of four PAHs**", "**The physical and chemical characteristics of the selected shoal soil**", "**Selected properties of three LCEFMs**", "**Schematic diagram of electrospinning device**", "**Scanning electron microscopy (SEM) images of LCEFMs and fibrous size distribution**", and "**Control experiments**".

In total, there are three tables, three figures, and the document length is five pages.

Table S1 Selected physicochemical properties of four PAHs.

PAHs	Mol. Formula[a]	M_W[b] (g·mol^{-1})	LogK_{ow}[c]	S_w[d] (mg·L^{-1})	V_s[e] (cm^3·mol^{-1})	Mol. Structure[f]
Phenanthrene	$C_{14}H_{10}$	178.2	4.46	1.15	199	
Fluoranthene	$C_{16}H_{10}$	202.3	5.16	0.26	217	
Benz[a]anthracene	$C_{18}H_{12}$	228.3	5.76	0.0094	248	
Benzo[a]pyrene	$C_{20}H_{12}$	252.3	6.13	0.0016	263	

a Molecular formula.
b Molecular weight.
c Octanol-water partition coefficient.
d Water solubility.
e Molar volume.
f Molecular structure.
a, b, c and d Taken from SRC physprop database.
e and f Taken from the website: http://chrom.tutms.tut.ac.jp/JINNO/DATABASE.

Table S2 The physical and chemical characteristics of the selected shoal soil.

Sample site	pH	TOC (%)	Average aperture (nm)	Surface area (m^2/g)	Distribution of particle size (%)		
					<10 µm	10~50 µm	50~250 µm
Baisha shoal	7.64	0.16	12.97	9.25	13.2	14.1	72.7

Table S3 Selected properties of three laccase-carrying electrospun fibrous membranes.

LCEFMs	Retained activity[a] (%)	A_{surf}[b] ($m^2 \cdot g^{-1}$)	V_{total}[c] ($cm^3 \cdot g^{-1}$)	Contact angle[d] (°)
PDLLA	75.6	4.73	0.0152	95.1
PDLGA	79.8	5.96	0.0169	70.3
MPEG-PLGA	83.7	7.81	0.0118	57.0

a The activity of laccase-carrying electrospun fibrous membranes relative to that of free laccase.
b Surface area, calculated from the adsorption-desorption isotherm of N_2 at 77K by multi-point BET.
c Single point adsorption total pore volume.
d Contact angle of polymer.

PAHs extracted from water samples. Firstly, add 1 mg $Na_2S_2O_3$ to 10 mL water sample and adjust the pH value to pH 2 with HCl. Then 4×0.1 mL methylene chloride, 4×0.1 mL methanol, and 4×0.1 mL ultra pure water was added into the sample. Next, the combined fraction was dried over the Na_2SO_4 column (Flush 2×5 mL methylene chloride slowly through the column). Then the sample was concentrated to 1 mL in a rotary evaporator. For further analysis, add 3 mL methanol and concentrate to 0.5 mL again.

Schematic diagram of electrospinning device (shown in Fig. S1). The device consists of three major components: a high-voltage power supply, a spinning system (spinning nozzles), and a grounded conductor (collecting barrel). In our experiments, the emulsion was fed into the spinning nozzles using a peristaltic pump. The spinning nozzles were connected to a high voltage DC (direct current) supply, which injects charge of a certain polarity into the emulsion. If the electrostatic force is sufficient to overcome the surface tension of the emulsion, the Taylor cone is formed and a liquid jet (fiber jet) is emitted from the apex of nozzles. The fiber jet then undergoes a stretching and whipping process, and it is ultimately deposited on the collector barrel randomly.

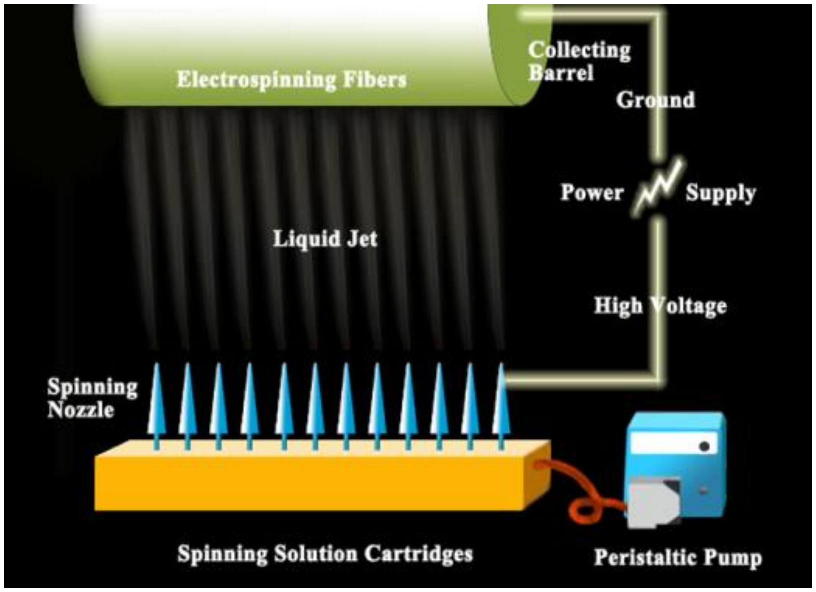


Fig. S1 Schematic of multi-head electrospinning device for preparation of LCEFM.

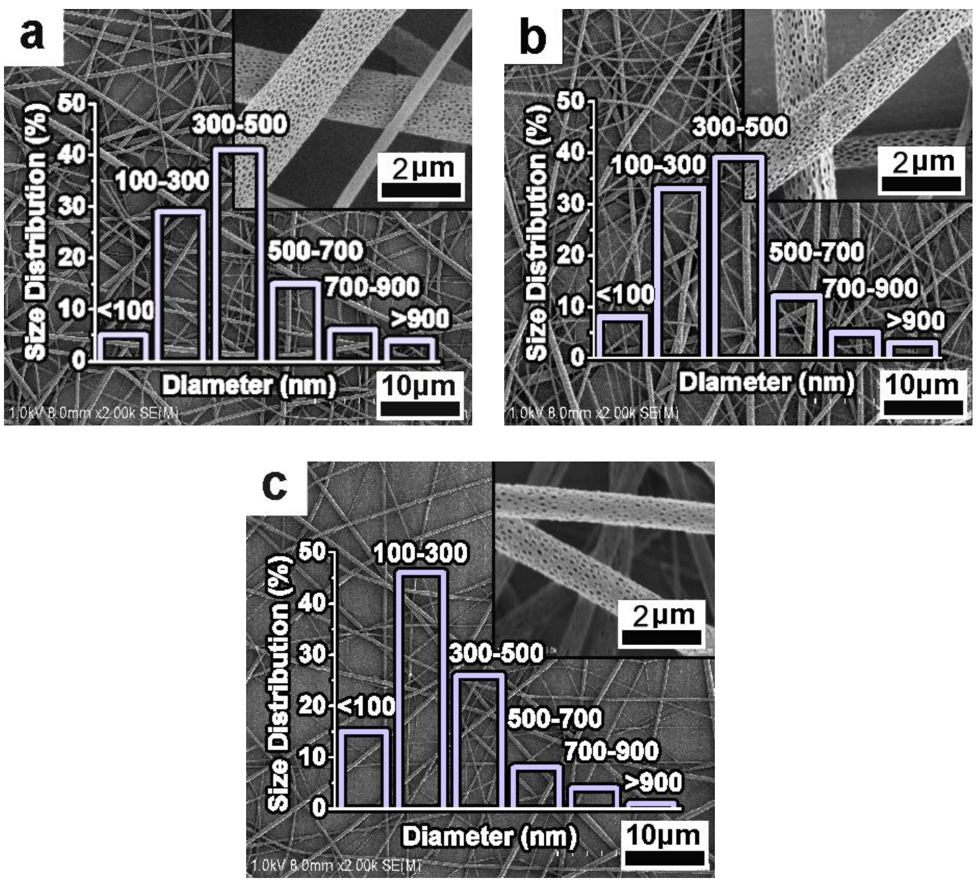


Fig. S2. Scanning electron microscopy (SEM) images of PDLLA (a), PDLGA (b) and MPEG-PLGA (c) laccase-carrying electrospun fibrous membranes and corresponding fiber size distribution.

Control experiments. The control experiments have been carried out for treatment of PAHs under six different conditions. In the constant reaction solution, free laccase, PDLLA PEFM~~s~~ (without laccase), PDLLA LCEFM, deactivated LCEFM, and pure PDLLA EFM~~s~~ with free laccase were added to investigate the kinetics of different reaction between laccase, PAHs, and membrane. Taking benz(a)anthracene for example (see Figure S3), it is clear shown that benz(a)anthracene was stable in the aqueous solution. Free laccase was unable to degrade benz(a)anthracene efficiently. Less than 30% of benz(a)anthracene could be removed in 24 h treatment. PDLLA PEFM~~s~~ adsorbed benz(a)anthracene from aqueous solution intensively. When PEFM~~s~~ or deactivated LCEFM was added into the reaction system, the similar removal kinetics was obtained, no matter with ~~and~~ or without laccase. However, the removal efficiency was dramatically enhanced when the laccase was immobilized in the membrane. Obviously, the enhanced removal efficiency was largely attributed to the assistance of laccase-degradation rather than the adsorption on the membrane. By analyzing the benz(a)anthracene concentration on the membrane, the degradation by laccase accounts for a large part of the removal efficiency.

Similarly, the kinetic rules of phenanthrene, fluoranthene, and benzo(*a*)pyrene were regressed following 1st, 2nd, and 3rd order kinetic equation based on the removal results. The removal kinetics by LCEFM was determined as 3rd order reaction. The pre-concentration of PAH around the fibers was the key impact on the enhanced removal efficiency.

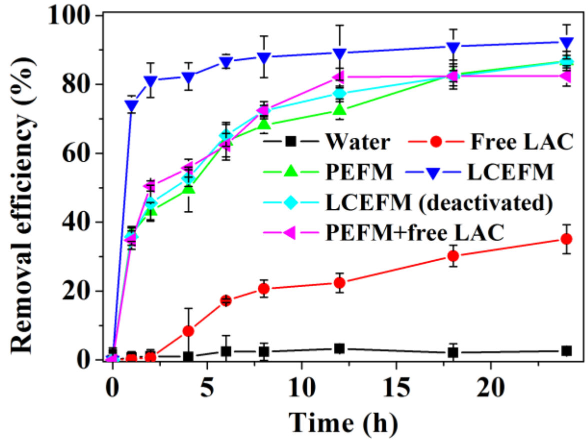


Fig. S3 The removal efficiency of benz(a)anthracene under 6 conditions, including 1) water; 2) free laccase; 3) PDLLA pure electrospun fibrous membrane~~s~~ (PDLLA PEFM~~s~~); 4) PDLLA laccase-carrying electrospun fibrous membrane~~s~~ (PDLLA LCEFM~~s~~); 5) deactivated PDLLA LCEFM~~s~~; and 6) PDLLA PEFM~~s~~ + free laccase.