

Supplementary Information

Engineering bimetallic capture sites on hierarchically porous carbon electrode for efficient phosphate electrosorption: Multiple active centers and excellent electrochemical properties

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Text S1 Materials

Tetrabutyl titanate (TBOT), Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), terephthalic acid (H_2BDC), and N,N-dimethylformamide (DMF) were purchased from Shanghai Macklin Biochemical Co., Ltd (China). Graphite papers were purchased from Hebei King Carbon Technology Co., Ltd (China). Polytetrafluorethylene (PTFE, 60wt%) was purchased from Shanghai Hesun Electric Co., Ltd (China). Carbon black was purchased from Cabot Corporation (United States of America). All the aqueous solution used in experiments were distilled water and all chemical reagents were analytical grade.

Text S2 Fabrication of AC-COOH

The carboxylated activated carbon (AC-COOH), as a cationic capturer, was fabricated via adding a certain pretreated activated carbon powder to the nitric acid solution (1:1). When the white smoke has disappeared, stirred the mixture in a 60 °C water bath for 2 h. After cooled down to room temperature, the obtained slurry was washed several times with deionized water until the pH of the supernatant was 7. Finally, the resultant was transferred to an oven at 110 °C for 2 h, the completely dried solid was ground into powder and named as AC-COOH.

Text S3 Structural and elemental characterization

The crystallinities of samples were investigated by powder X-ray diffraction (XRD) measurements (D/Max-2400, Rigaku) with 100 mA and 40 kV operation conditions. X-ray photoelectron spectroscopy (XPS) was carried out on an Escalab 210 system (Energy spectrum instrument with Al $\text{K}\alpha$ source). Nitrogen (N_2) adsorption-desorption tests were carried out via the adsorption apparatus (ASAP 2460,

MICROMERITICS), and the specific surface area, pore volume, and pore size distribution were obtained by the Brunauer-Emmett-Teller (BET) calculation model. Scanning electron microscope (SEM, Hitachi S-3500N) and transmission electron microscope (TEM, JEM-ARM200F) were utilized to observe the morphologies and microstructure. Fourier transform infrared (FTIR, Bruker TENSOR 37) spectroscopy was investigated in the wavenumber range of 4000-500 cm^{-1} . Thermogravimetric analysis (TG, Rigaku TG-DTA8122) was performed from 30 to 1000 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. Electron paramagnetic resonance analysis was conducted by Bruker EMXplus.

Text S4 Evaluation of fabricated electrodes for phosphate removal

Both electrosorption systems used asymmetric electrodes, in which as-prepared TLMOF, TLPCs, and LPC composites worked as phosphate capturing electrode and AC-COOH composite worked as cations capturing electrode. During the electrosorption procedure, 60 mL of specific phosphate solution was added into the electrosorption reactor with varied potential differences. All the experiments taken at a certain time were evaluated according to the molybdenum blue method.

Generally, the electrosorption experiments were conducted in 100 mg/L PO_4^{3-} solution prepared from KH_2PO_4 by applying a direct voltage of 1.0 V to measure adsorption kinetics. All the conditional experiments were investigated using LaPC composite as anode and AC-COOH as the cathode. The adsorption isotherms were studied with various initial phosphate concentrations from 50 to 1000 mg/L PO_4^{3-} . The effect of reaction temperature was studied via 25, 45, and 65 $^{\circ}\text{C}$. The influence of reaction pH on PO_4^{3-} removal was investigated using the same process, the initial pH value was adjusted by HCl/NaOH solution to 3, 5, 7, 9, and 11. For the effect of

coexisting substances on PO_4^{3-} removal, 100 mg/L of NO_3^- , Cl^- , HCO_3^- , SO_4^{2-} and humic acid (HA) was dissolved into 100 mg/L PO_4^{3-} solution, respectively. The ionic strength experiments were conducted with various NO_3^- concentrations from 0.001 to 1 M in 100 mg/L PO_4^{3-} solution. Moreover, direct voltages from 1 to 7 V were applied between the pair of parallel electrodes to investigate the phosphate removal performance under different voltages. For the desorption procedure, reacted phosphate solution was substituted by 0.05 M NaOH solution with the voltage revised to -2 V.

Text S5 Electrochemical measurements

Cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were performed by an electrochemical workstation (Versa STAT 3, Princeton Applied Research, USA) in a three-electrode system, in which active electrode, platinum gauze electrode, and Ag/AgCl electrode served as working electrode, counter electrode, and reference electrode, respectively. These measurements were investigated in phosphate solution (1 M KH_2PO_4) at a neutral pH. The scanning potential of CV ranged from -0.2 to 1.2 V with the sweep rates included 5, 10, 20, 50 and 100 mV/s. The frequency of EIS ranged from 0.1 to 100,000 Hz. The EIS data were analyzed via Nyquist plots and equivalent circuits fitted by ZSimpWin software.

Cyclic voltammetry (CV) measurement was employed to assess the electrochemical properties of fabricated electrodes in phosphate solution. The specific capacitances of as-prepared samples were calculated using the following Equation S1:

$$C_s = \frac{\int I dV}{2mv\Delta V} \quad \text{Equation S1}$$

Where C_s (F/g) is the mass specific capacitance, I (A/g) is the response current density, m (g) is the weight of active material, v (V/s) is the scan rate, and ΔV (V) is the potential window.

The contributions of capacitive charge and diffusion-controlled charge were calculated as the following Equation S2 and Equation S3:

$$i(v) = av^k \quad \text{Equation S2}$$

$$i(v) = k_1v + k_2v^{0.5} \quad \text{Equation S3}$$

Where i represents the current (A), v is the scanning rate (A/s), a is the adjustable parameter, k_1v and k_2v stand for the current density related to capacitive current and diffusion-controlled current, respectively.

The charge efficiency (η , %) and inverse specific energy consumption (SEC^{-1} , mg/J) were calculated as the following Equation S4 and Equation S5, respectively:

$$\eta = \frac{Q_n F}{\Sigma} \quad \text{Equation S4}$$

$$SEC^{-1} = \frac{((C_0 - C_t)V)}{V_d \int_0^t (iV)dt} \quad \text{Equation S5}$$

Where F is the constant of Faraday (96485 C/mol), Q_n (mol/g) is electrosorption capacity, and Σ (C/g) is passing charge by integrating corresponding current. C_0 (mg/L) and C_t (mg/L) represents the phosphate concentrations at initial time and time t , respectively, V (mL) represents then volume of solution, V_d (V) refers to the applied voltage.

Text S6 Phosphate electrosorption performances

The phosphate electrosorption of fabricated electrodes were calculated according to Equation S6:

$$q_t = \frac{C_0 - C_t}{m} \times V \quad \text{Equation S6}$$

Where q_t (mg/g) refers to the phosphate electrosorption capability at certain time, C_0 (mg/L) and C_t (mg/L) represents the phosphate concentrations at initial time and time t , respectively, m (g) is the weight of the active material, and V (mL) represents then volume of solution.

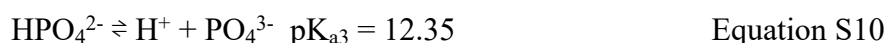
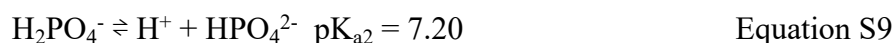
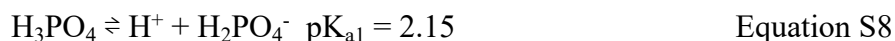
The phosphate electrosorption rate was calculated according to Equation S7:

$$PER = \frac{q_t}{t} \quad \text{Equation S7}$$

Where PER (mg/g/min) refers to phosphate electrosorption rate, and t (min) is the reaction time.

Text S7 The formation of phosphate acids in the solution according to the change in pH value

Phosphate acid can yield different species at different pH values as follows:



Text S6 Isotherm models of electrosorption process

The equilibrium data were fitted to the Langmuir and Freundlich isotherm model. The Langmuir isotherm model showed as Equation S11, demonstrated that adsorption procedure occurred at specific sites of the adsorbent.

$$q_e = q_m K_l \frac{C_e}{1 + K_l C_e} \quad \text{Equation S11}$$

The Freundlich isotherm model showed as Equation S12, demonstrated that adsorption procedure occurred at heterogenous adsorbent surface.

$$q_e = K_f C_e^{1/n} \quad \text{Equation S12}$$

Where K_l and K_f are constants related to the Langmuir adsorption and Freundlich affinity, respectively. q_m (mg/g) represents the Langmuir maximal adsorption capacity, and $1/n$ are Freundlich constants related to adsorption capacity direction invariable, and C_e (mg/L) is the solution concentration at equilibrium.

The essential parameter of the Langmuir model can be evaluated in terms of a dimensionless separation factor or equilibrium parameter, R_L , as defined as follows:

$$R_L = \frac{1}{1 + K_l C_0} \quad \text{Equation S13}$$

Where K_l represents the Langmuir equilibrium constant, and the C_0 is the initial phosphate concentration (mg/L). The R_L value demonstrates the favorability of the adsorption process: linear ($R_L = 1$), irreversible ($R_L = 0$), unfavorable ($R_L > 1$), or favorable ($0 < R_L < 1$).

Text S8 Kinetic model of electrosorption process

The process of phosphate electrosorption can be fitted by kinetic models including pseudo-first-order and pseudo-second-order. The pseudo-first-order kinetic model equation presented as Equation S14, illustrated that adsorption procedure mainly occurred via surficial active sites and affinity.

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad \text{Equation S14}$$

The pseudo-second-order kinetic model equation presented as Equation S15, demonstrated that adsorption process mainly occurred owing to valency forces via exchanging or sharing electrons between adsorbent and adsorbate.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Equation S15}$$

Where q_t (mg/g) and q_e (mg/g) are the phosphate electrosorption capacities at time t and at equilibrium, respectively; t (min) is the reaction time, k_1 and k_2 are denoted as the rate constants for pseudo-first-order and pseudo-second-order models, respectively.

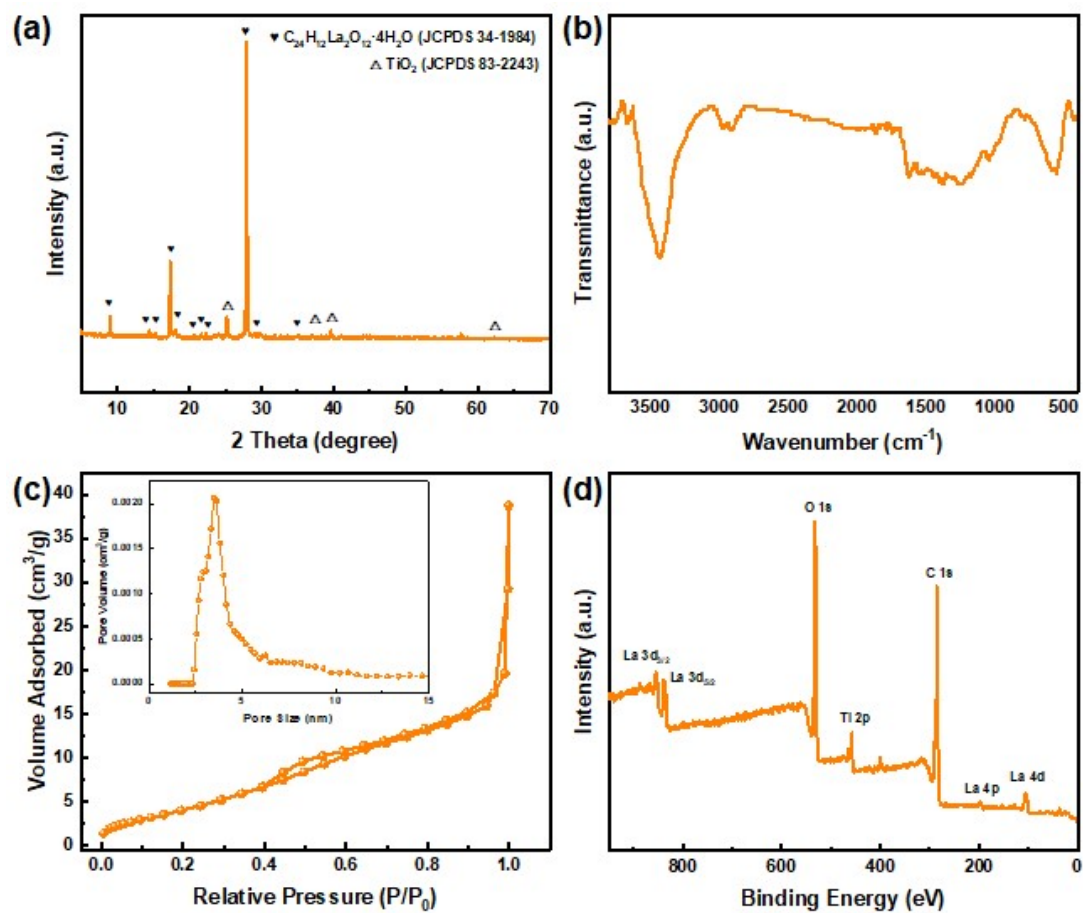


Fig. S1. (a) XRD pattern, (b) FTIR spectra, (c) N_2 adsorption/desorption profiles with pore size distributions, and (d) XPS survey spectra of TLMOF.

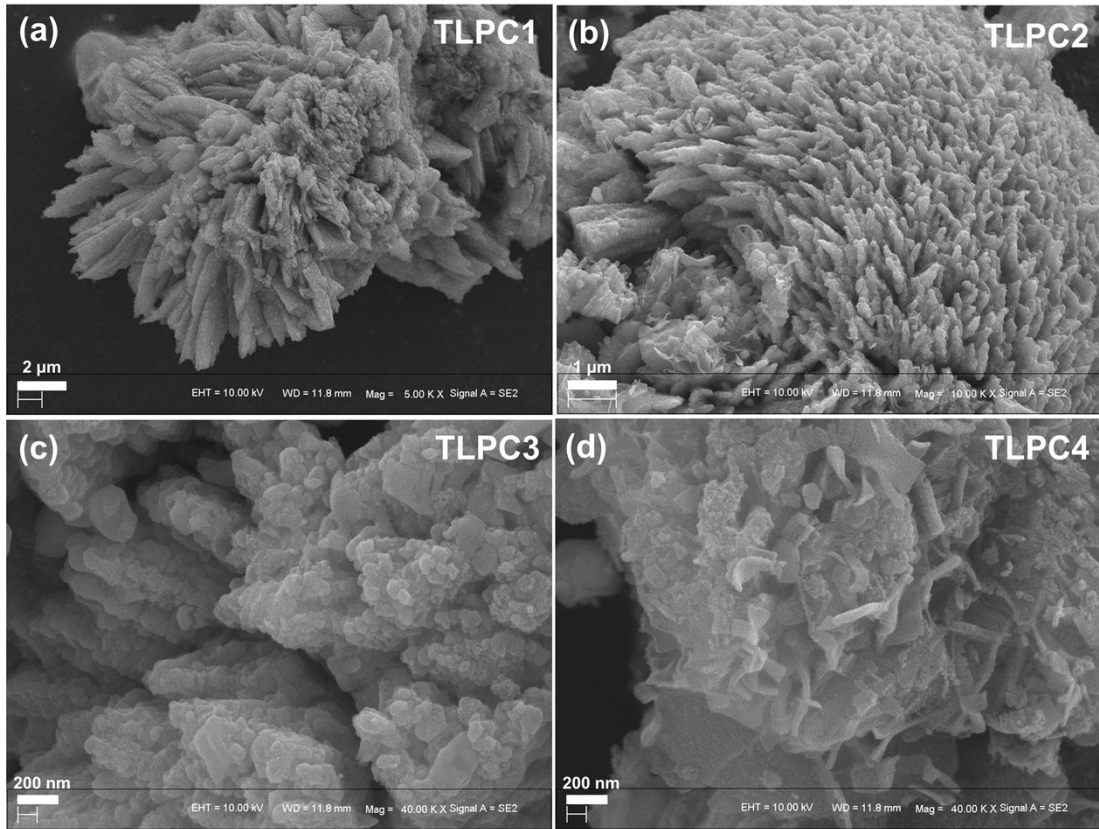


Fig. S2. SEM images of prepared TLPCs composites: (a) TLPC1, (b) TLPC2, (c) TLPC3, and (d) TLPC4.

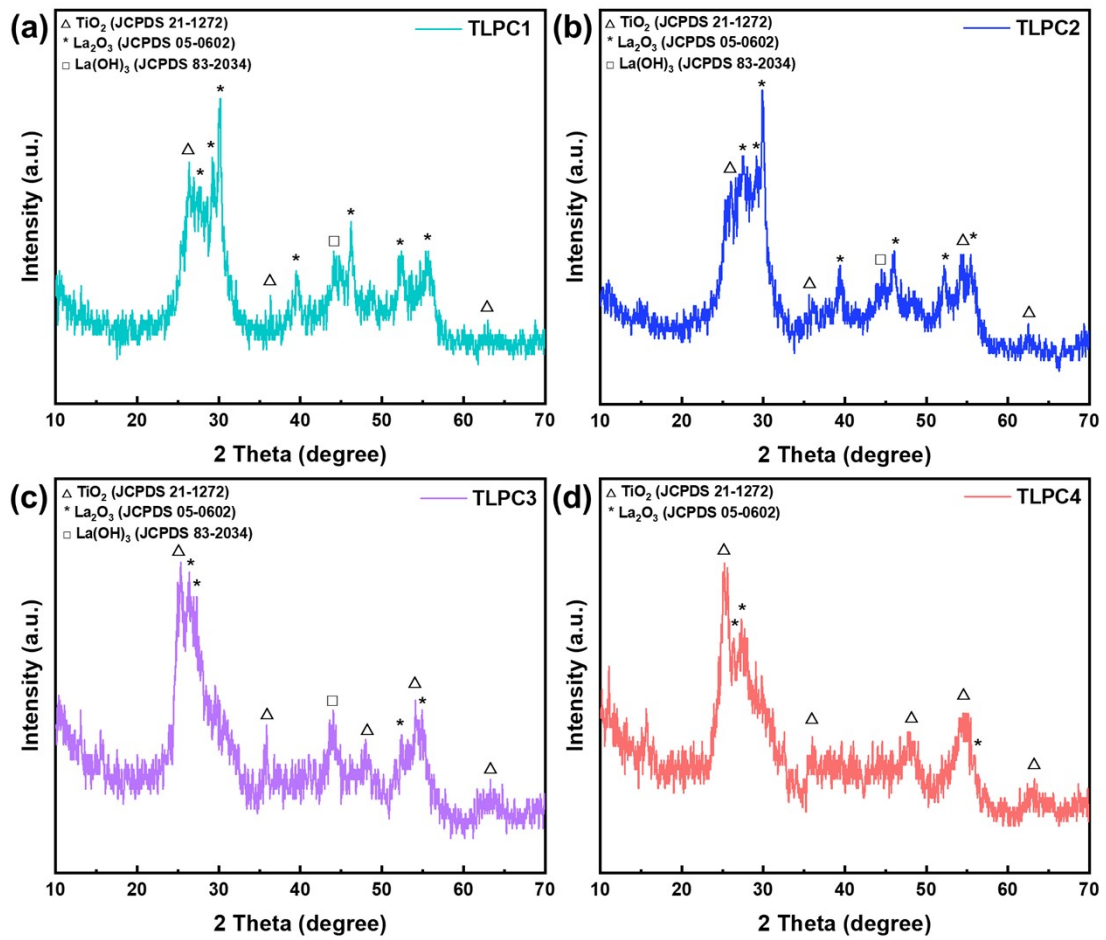


Fig. S3. XRD patterns of prepared TLPCs composites: (a) TLPC1, (b) TLPC2, (c) TLPC3, and (d) TLPC4.

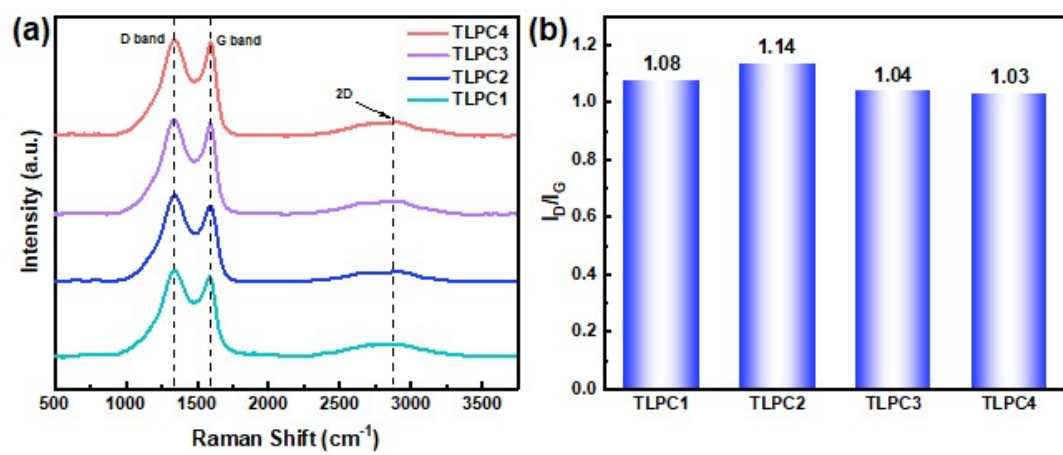


Fig. S4. (a) Raman patterns of prepared TLPCs composites and (b) results of I_D/I_G .

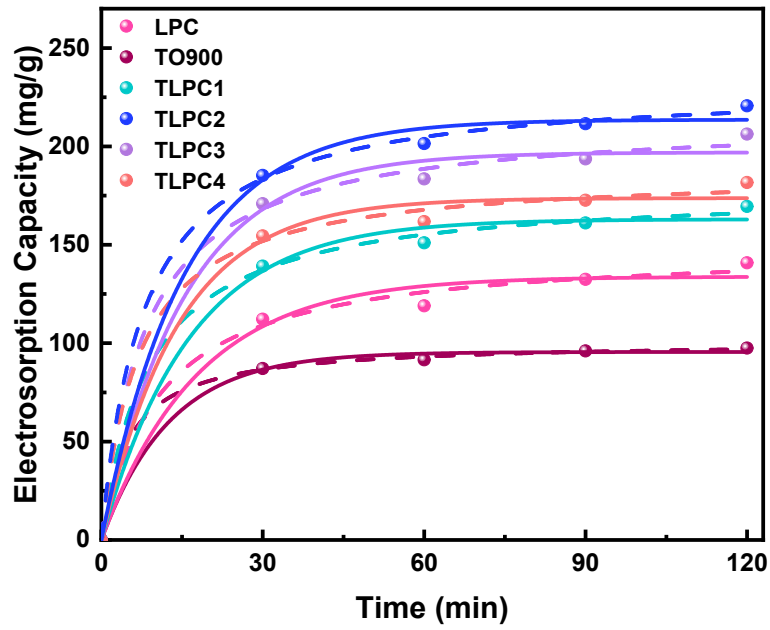


Fig. S5. Pseudo-first-order (full line) and pseudo-second-order (dotted line) electro sorption kinetics of phosphate with different electrode materials.

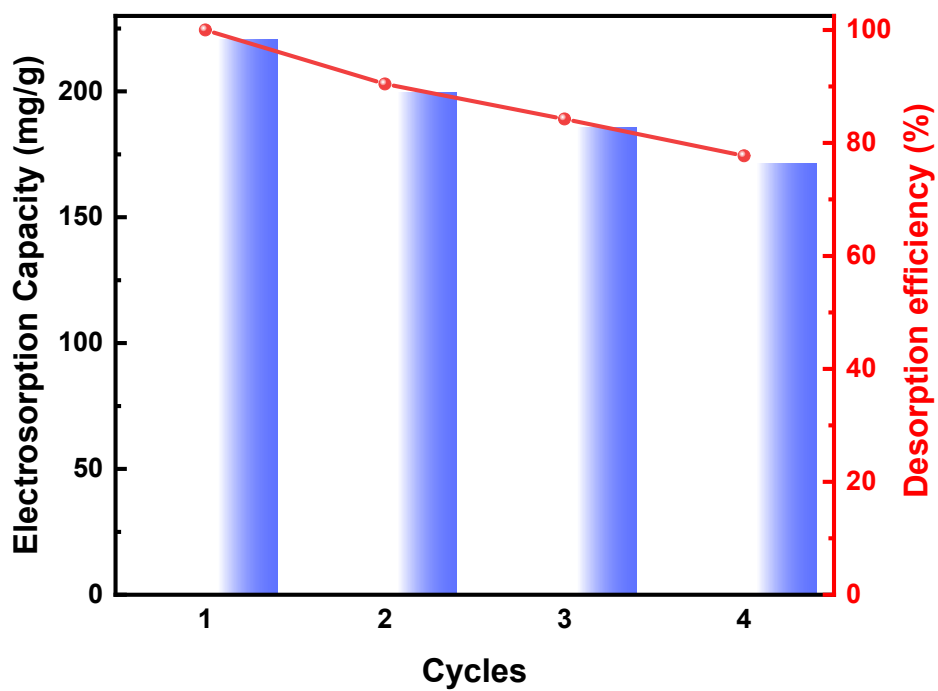


Fig. S6. Recyclability tests in phosphate electro sorption on TLPC2 electrode at different regeneration cycles.

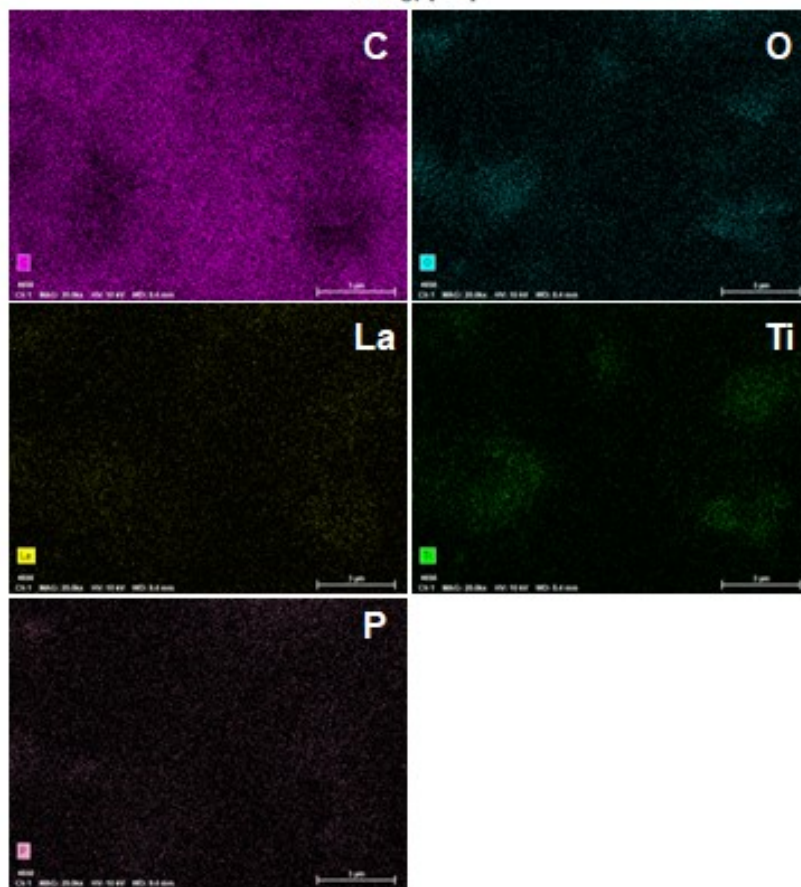
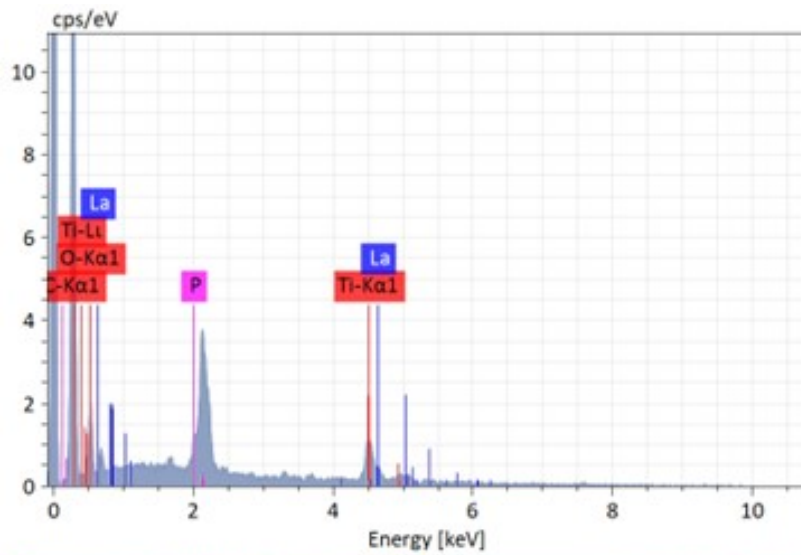


Fig. S7. EDS spectra of used TLPC2 electrode and mapping spectra of C, O, La, Ti, P elements.

Table S1 Surface and pore parameters of prepared samples.

Composite	BET specific surface area (m ² /g)	Pore diameter (nm)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
TLMOF	17.48	13.72	0.060	0.006
LPC	216.17	4.22	0.228	0.093
TLPC1	120.03	4.54	0.138	0.054
TLPC2	138.77	4.40	0.152	0.061
TLPC3	142.98	4.88	0.174	0.062
TLPC4	154.78	4.54	0.175	0.067
TO900	26.93	14.00	0.094	0.011

Table S2 Surface chemical atomic concentration, binding energy and full-width half-maximum of samples based on XPS characterization.

	Element	TLMOF	TLPC1	TLPC2	TLPC3	TLPC4	LPC
Atomic (%)	C 1s	64.33	76.04	77.43	63.64	71.57	75.36
	O 1s	32.06	17.43	16.50	26.90	18.92	19.27
	Ti 2p	2.62	2.50	3.25	6.90	7.28	-
	La 3d	0.98	4.02	2.83	2.56	2.23	5.16
Full-width half- maximum (eV)	C 1s	1.64	1.26	1.28	1.50	1.25	1.19
	O 1s	3.21	2.85	3.16	2.27	1.71	2.79
	Ti 2p	1.50	1.50	1.50	1.60	1.58	-
	La 3d	5.83	3.46	3.52	3.61	3.31	4.23
Binding energy (eV)	C 1s	284.80	284.80	284.80	284.80	284.80	284.80
	O 1s	532.43	530.87	530.64	530.64	530.48	531.66
	Ti 2p	458.45	458.75	458.78	459.07	459.00	-
	La 3d	838.01	834.90	835.20	835.27	835.28	836.11

Table S3 Specific capacitance results of fabricated electrodes from CV curves.

Electrode/ Scan rate	5 (mV/s)	10 (mV/s)	20 (mV/s)	50 (mV/s)	100 (mV/s)
LPC (F/g)	60.54	40.58	23.79	10.82	3.90
TLPC1 (F/g)	44.13	31.97	20.92	10.72	4.98
TLPC2 (F/g)	88.27	58.54	37.42	18.71	9.31
TLPC3 (F/g)	62.00	48.84	32.54	15.88	7.72
TLPC4 (F/g)	68.06	50.84	32.75	16.88	6.95
TO900 (F/g)	62.96	45.02	29.81	15.41	7.41

Table S4 Phosphate electrosorption kinetic constants with various fabricated electrodes.

Electrode	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	$k_2 \times 10^{-3}$ (g/mg/min)	R^2
LPC	133.82	0.056	0.987	149.12	0.393	0.994
TO900	95.54	0.079	0.997	100.92	1.090	0.999
TLPC1	162.98	0.061	0.994	178.61	0.482	0.998
TLPC2	213.59	0.065	0.997	231.56	0.551	0.999
TLPC3	196.96	0.064	0.994	214.56	0.524	0.998
TLPC4	173.73	0.070	0.993	187.32	0.564	0.997

Table S5 Parameters of water sample from Yueya River in Tianjin, China

Index	Value	Index	Value
pH	8.56	Dissolved oxygen	14.23 mg/L
PO ₄ ³⁻ -P	3.0 mg/L (adjusted)	Permanganate Index	5.38 mg/L
NH ₄ ⁺ -N	0.116 mg/L	Turbidity	5.7 NTU
NO ₃ ⁻ -N	3.82 mg/L	Conductivity	2955.2 μs/cm

The above data comes from the monitoring data of the local government.