Supplementary material for:

Temperature-controlled self-assembly of Ce-based tubular boron carbon nitride for enhanced tetracyclines adsorption

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S1 Characterization

FT-IR spectra were recorded on a Nicolet Nexus 470 (Thermo Electron Corporation, USA) in the range of 400-4000 cm^{-1}. A Rigaku X-ray diffraction (XRD) instrument (D/max2500 PC, Rigaku Company, Japan) with a Cu Kα radiation source (λ = 1.5418 Å) was used to record the crystalline phase. X-ray photoelectron spectroscopy (XPS) analysis was performed on a K-Alphat X-ray photoelectron spectrometer (ESCALAB 250Xi, Thermo Fischer, USA), using focused monochromatic Al-Ka radiation (hv = 1486.6 eV). Ultraviolet-visible (UV-vis) diffuse reaction spectra (DRS) were recorded on a UV-vis spectrophotometer (Solidspec-3700, Japan) in the range of 200–800 nm. The specific surface area was calculated from the nitrogen adsorption-desorption isotherms at 77 K using a TriStar II 3020 (Micromeritics, USA). The morphologies of the as-prepared BCN materials were obtained from SEM and TEM analysis using JEOL-JSM-7001F and JEOL-TEM-2010F (JEOL, Japan), respectively.

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S2 Adsorption studies

S2.1 Adsorption capacity studies

The adsorption performances of Ce_2O_2S-TBCN and samples for comparison were assessed by using tetracycline (TC) as the adsorbate. The detailed adsorption process was as follows: 10 mL of 100 mg/L TC solution was mixed with 10 mg of adsorbent in 100 mL stoppered conical flasks, followed by shaking at a speed of 130 r/min under 25℃ in a thermostatic shaker bath. The flasks were wrapped with aluminum foil to avoid photodegradation. At certain time intervals or the time of sorption equilibrium, certain amounts of supernatant were aspirated and filtered through a membrane (aperture: 0.22 μm), and then it was analyzed immediately using a ultraviolet spectrophotometer (T6, Persee Company, China). The residual concentration of TC was calculated using a linear calibration curve (absorbance versus concentration). The adsorption capacities at time t (q_t, mg/g) and equilibrium (q_e, mg/g), and the removal efficiency (%) were calculated respectively using the following equations (Eqs. (S1) and (S2)).

$$q_{t,e} = \frac{(\mathrm{C_0} - \mathrm{C_{t,e}})\mathrm{V}}{\mathrm{m}} , \tag{S1}$$

$$Removal\ Efficiency\ (\%) = \frac{(C_0 - C_e)}{C_0} * 100\% , \tag{S2}$$

Where C_o (mg/L) is the initial TC concentration. C_t and C_e (mg/L) are the residual TC concentration at time t and equilibrium, respectively. V (L) is the volume of the solution, and m (g) is the mass of adsorbents.

For isotherm studies, the initial TC concentration was varied in the range of 50-300 mg/L. The solution pH was adjusted from 3 to 11 by 0.1 mol/L HCl or NaOH in the pH effect experiment. The ion strength of the solution was maintained by 0.1 mol/L NaCl, KCl, $MgCl_2$, $CaCl_2$, $NaNO_3$, Na_2SO_4, and Na_3PO_4, respectively, to investigate the coexisting ions' effect on sorption. The antibiotics of chlortetracycline (CTC), oxytetracycline (OXY), levofloxacin (LVX), and sulfamethazine (SMZ) were used to evaluate the sorption selectivity. For the recycling study, ethanol was used as the eluent to regenerate the adsorbent. All experiments were performed in triplicate and the average data were applied.

S2.2 Adsorption kinetics studies

Pseudo-first-order and pseudo-second-order kinetics models were used to explore the adsorption mechanism, and the equations are as follows (Eqs. (S3) and (S4)):

Pseudo-first-order model:
$$\ln(q_e - q_t) = \ln q_e - K_1 t , \tag{S3}$$

Pseudo-second-order model:
$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{I}{(K_2\, q_e^2)} , \tag{S4}$$

Where q_t (mg/g) and q_e (mg/g) are the amounts of antibiotic absorbed on the adsorbent at time t (min) and equilibrium, respectively. K_1 (1/min) is the rate constant of the pseudo-first-order adsorption and K_2 (g/(mg·min)) is that of the pseudo-second-order adsorption.

S2.3 Adsorption isotherm studies

The adsorption equilibrium data under different initial TC concentrations were fitted by the Langmuir model, the Freundlich model, the Tempkin model and the Dubinin-Radushkevich (D-R) model to further investigate the adsorption mechanism. The isotherm equations are shown as follows (Eqs. (S5)–(S9)):

Langmuir isotherm model:
$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L\, q_m} , \tag{S5}$$

Freundlich isotherm model:
$$q_e = K_F C_e^{1/n_F} , \tag{S6}$$

Tempkin isotherm model:
$$q_e = \frac{RT}{b}(\ln K_T C_e) , \tag{S7}$$

D-R isotherm model:
$$lnq_e = lnq_m - \beta \cdot \varepsilon^3 , \tag{S8}$$

Average percentage error:
$$APE(\%) = \frac{\sum_{i=1}^{N} \left| \left(q_{e,exp} - q_{e,cal}\right) / q_{e,exp} \right|}{N} \times 100\% , \tag{S9}$$

Here, q_m (mg/g) is the maximum monolayer adsorption capacity; k_L (L/mg) is the Langmuir constant that relates to the binding energy of adsorption; K_F is the Freundlich constant; $1/n_F$ is a constant indicative of the adsorption intensity or surface heterogeneity; K_T (L/mg) is Tempkin constant related to the maximum binding energy and b is Tempkin constant reflecting adsorption heat. ε represents adsorption potential.

S2.4 Adsorption thermodynamic studies

The thermodynamics study was explored by calculating standard Gibbs free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o) by Eqs. (S10) and (S11):

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} , \tag{S10}$$

$$\Delta G^o = -RT \ln K , \tag{S11}$$

Where R is the universal gas constant (8.314 J/(mol·k)), T (K) is the temperature, and K represents the distribution coefficient—the ratio of the TC amount adsorbed on the adsorbent to the residual in solution at equilibrium.

S3 Graphs

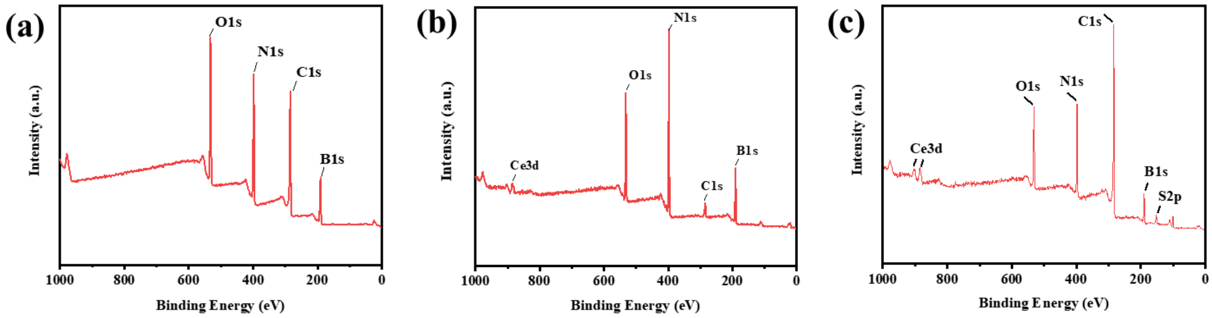

Fig. S1 XPS survey patterns of (a) BCN, (b) Ce-BN, and (c) Ce_2O_2S-TBCN.

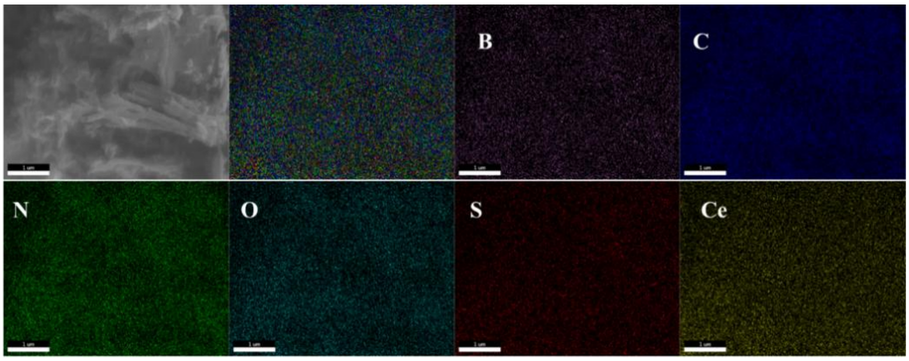

Fig. S2 EDS mapping patterns of Ce_2O_2S-TBCN.

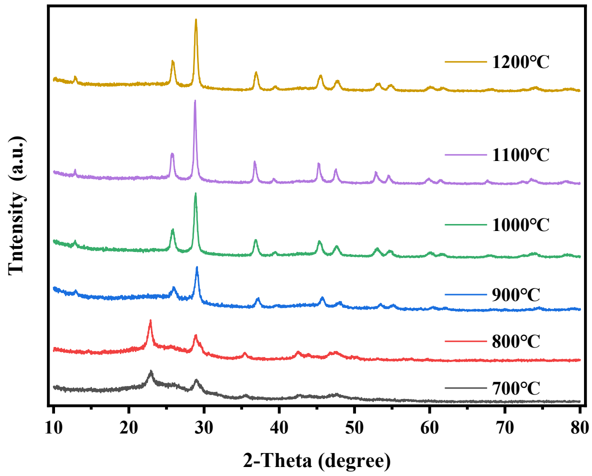

Fig. S3 The XRD patterns of Ce-doped BCN in different calcination temperatures.

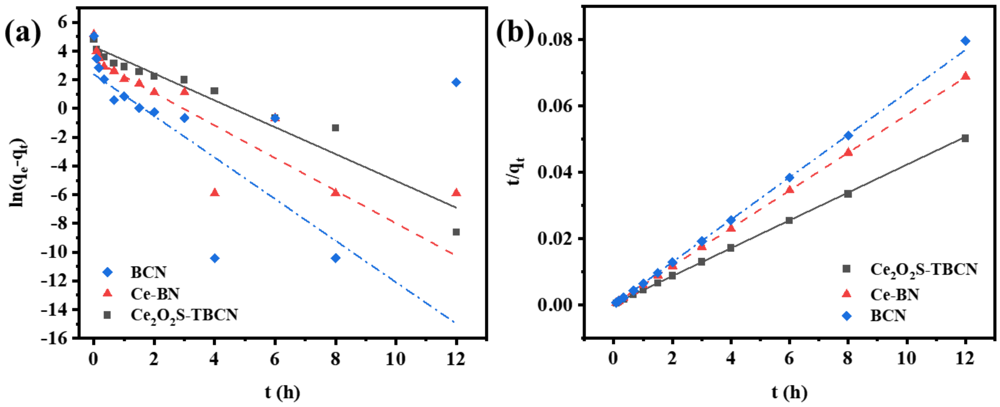

Fig. S4 (a) Fitting results of the pseudo-first-order model, and (b) the pseudo-second-order model related to BCN, Ce-BN, and Ce_2O_2S-TBCN.

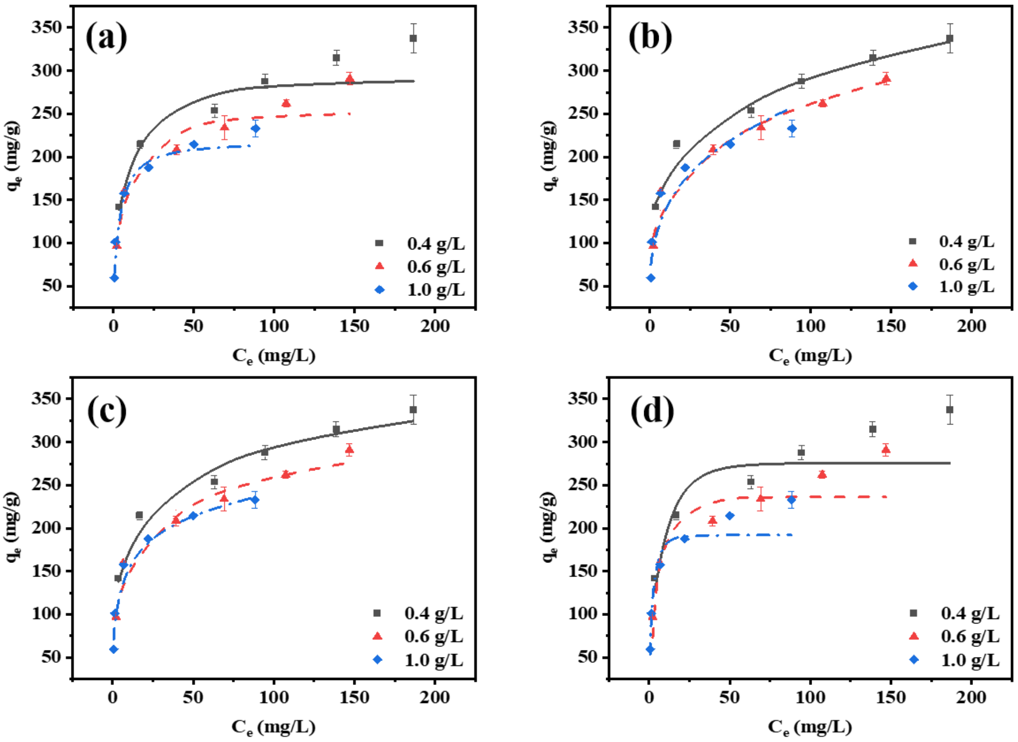

Fig. S5 The adsorption isotherms for the uptake of TC on Ce_2O_2S-TBCN: (a) the Langmuir model, (b) the Freundlich model, (c) the Tempkin model, and (d) the Dubinin-Radushkevich model.

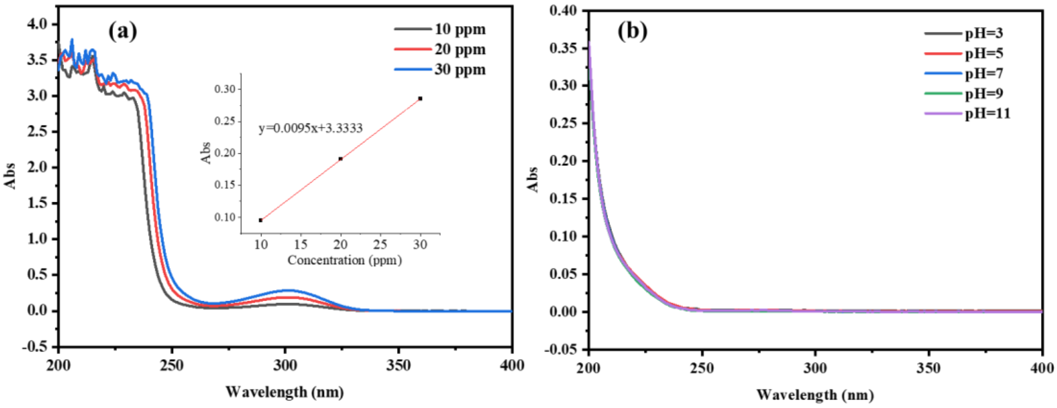

Fig. S6 The UV-vis spectra of (a) Ce standard solution and (b) Ce_2O_2S-BCN leachate in different pH environments.

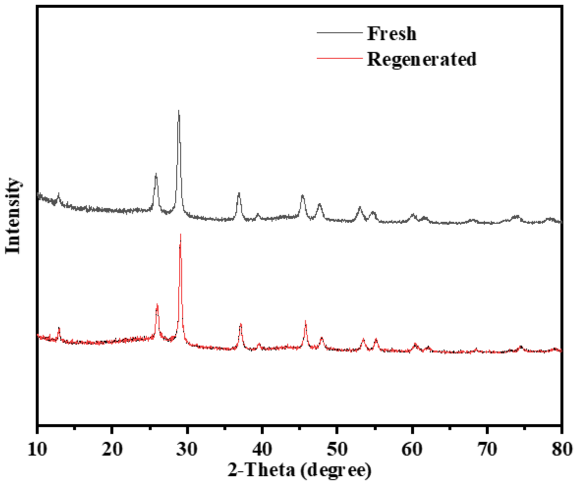

Fig. S7 XRD patterns of fresh and regenerated Ce_2O_2S-TBCN.

S4. Tables

Table S1 The specific surface area and pore size parameters of Ce_2O_2S-TBCN.

Calcination temperature (℃)	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
700	360.95	6.66	0.60
800	386.62	5.71	0.55
900	758.08	3.72	0.71
1000	1339.02	4.21	1.41
1100	1224.65	4.59	1.40
1200	1075.05	4.64	1.25

[a] The data are obtained by Ar adsorption-desorption isotherms.

Table S2 ICP-determined Ce leaching from Ce_2O_2S-TBCN under vrying pH Conditions.

pH values	Concentration of Ce (mg/L)
3	−0.106
5	−0.107
7	−0.108
9	−0.106
11	−0.106