

Electronic Supplementary Material

Decoration of ZnIn₂S₄ on cellulose/chitosan composite sponges for efficient tetracycline removal under sunlight

Lei Xia¹, Liyuan Shi^{1,2}, Jiaqi Zhao¹, Chang Liu¹, Youbo Di (✉)³, Xupin Zhuang (✉)^{1,2}

1 State Key Laboratory of Separation Membranes and Membrane Processes, Tiangong University, Tianjin 300387, China

2 School of Textile Science and Engineering, Tiangong University, Tianjin 300387, China

3 School of Textile Engineering, Taiyuan University of Technology, Taiyuan 030024, China

E-mails: diyoubu@163.com (Di Y); zhxupin@tiangong.edu.cn (Zhuang X)

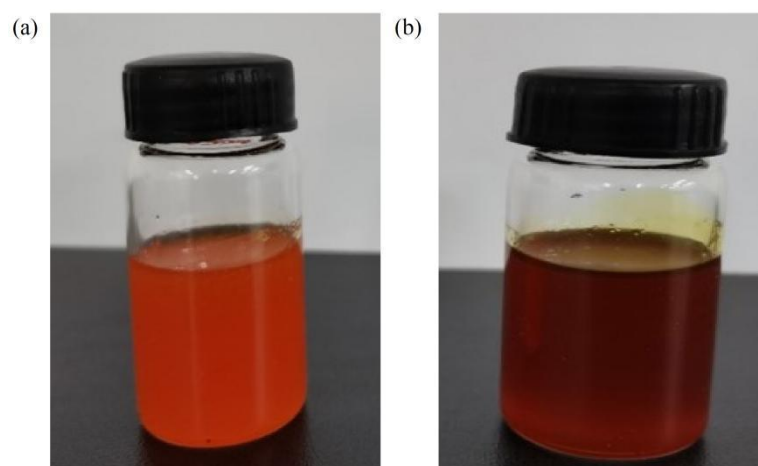


Fig. S1. (a) Cellulose xanthate; (b) Chitosan xanthate

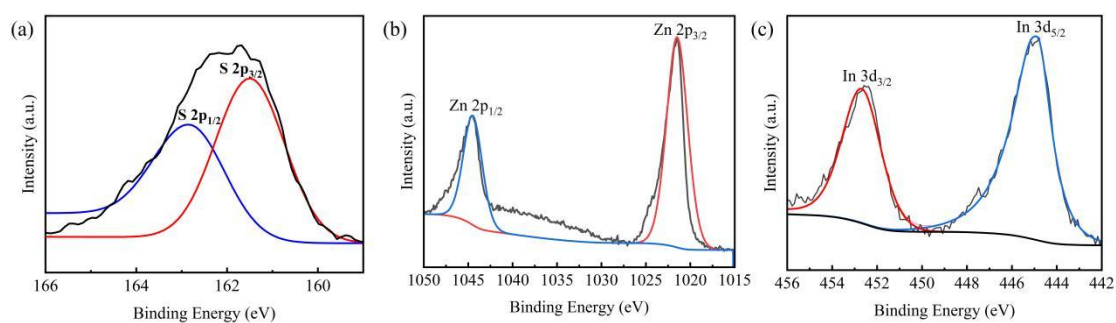


Fig. S2. (a) The XPS spectra of S 2p deconvolution; (b) Zn 2p deconvolution and (c) In 3d.

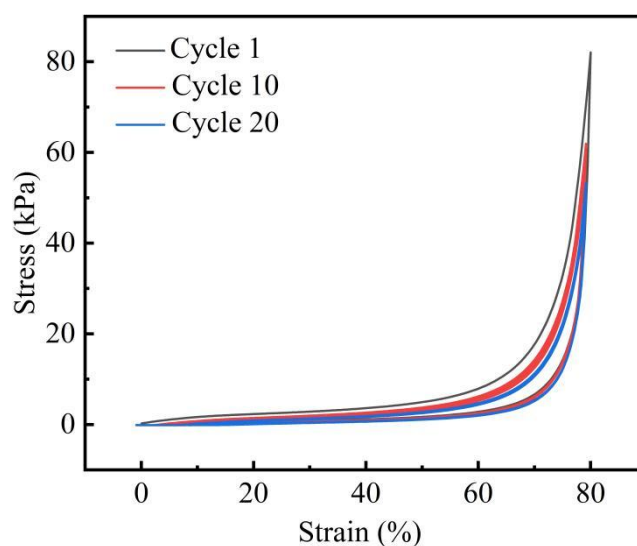


Fig. S3. Compression and recovery property of ZnInCCS.

To gain an insight into the adsorption reaction efficiency, the adsorption kinetics of ZnInCCS for TC were studied using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models.

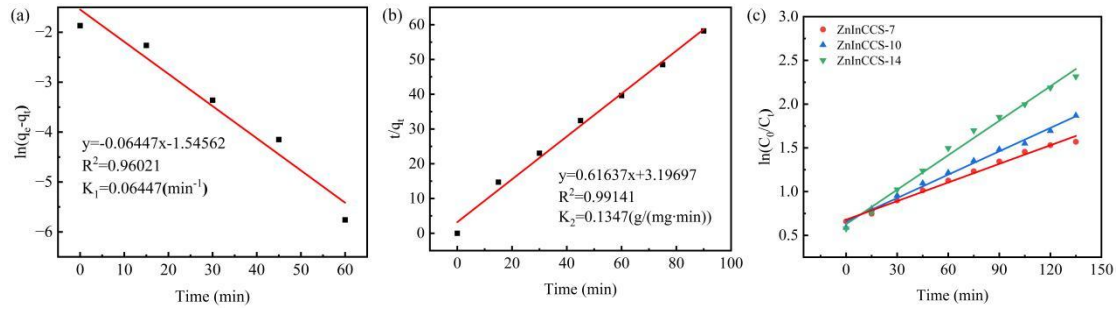


Fig. S4. (a) PFO model of adsorption TC; (b) PSO model of adsorption TC; (c) Relationship between $\ln(C_0/C_t)$ and irradiation time of the ZnInCCS.

The PFO model can be formulated as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

The PSO model can be formulated as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

In the equations, q_e (mg/g) is the adsorption capacity of ZnInCCS at equilibrium; q_t (mg/g) represents the adsorption capacity at t time (min); k_1 (min^{-1}) is the rate constant of the PFO model; and k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) is the adsorption rate constant of the PSO model.

The linear fitting images of the PFO and PSO models for ZnInCCS are shown in Fig. S4 (a) and (b). It could be seen from the figures that the correlation coefficient R^2 of the PSO model was higher than that of the PFO model, indicating that the PSO kinetic equation better predicted the kinetic process. According to the assumptions of the PSO model, the adsorption process might involve chemisorption. This suggested

that the amino and hydroxyl groups of ZnInCCS might play important roles in the adsorption of TC, indicating that the adsorption system involved a chemical process related to electron sharing or electron transfer.

The photocatalytic activity of ZnInCCS was evaluated using the PFO model. Based on the reaction rate constant (k), the photocatalytic degradation rates for different ZnIn₂S₄ loadings were calculated using equation (3):

$$\ln\left(\frac{C_0}{C_t}\right) = kt + b \quad (3)$$

Where C_0 is the initial concentration of the TC solution, C_t is the concentration of the TC solution after a reaction time (t), and k is the relative degradation rate constant, which can be calculated based on the slope and intercept of the linear plot. As shown in Fig. S4(c), the linear plot of the PFO kinetic model indicated that the k values were in the order of ZnInCCS-14 > ZnInCCS-10 > ZnInCCS-7. The related parameters are shown in Table.S1, with all samples having a correlation coefficient (R^2) greater than 0.99, indicating that the photocatalytic degradation process of TC conformed to the PFO kinetic model. As the loading of ZnIn₂S₄ increased, the degradation rate of TC by ZnInCCS also increased, with the maximum value reaching $13.15 \times 10^{-3} \text{min}^{-1}$, demonstrating that ZnInCCS was an excellent photocatalyst.

Table.S1 Photodegradation parameters of different samples.

Sample	Apparent rate constant, k (min ⁻¹)	Correlation coefficient, R ²
ZnInCCS-7	7.09×10^{-3}	0.9901
ZnInCCS-10	8.91×10^{-3}	0.9910
ZnInCCS-14	13.15×10^{-3}	0.9907

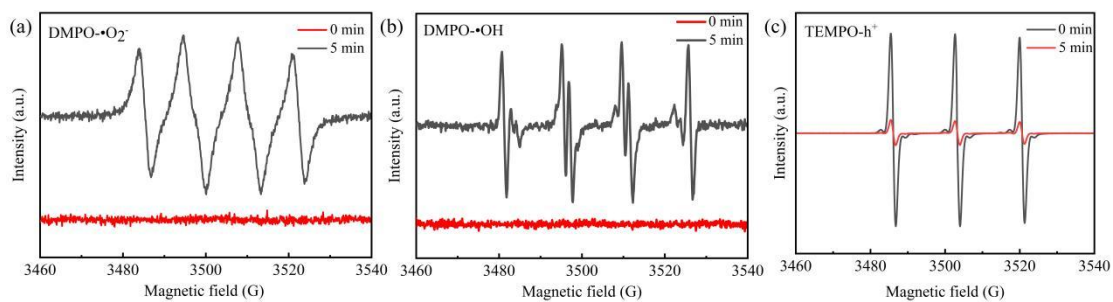


Fig. S5. The ESR spectra of ZnInCCS in the dark and under 5 min of irradiation.

(a) DMPO- $\text{O}_2^{\bullet-}$; (b) DMPO- OH ; (c) TEMPO- h^+ .

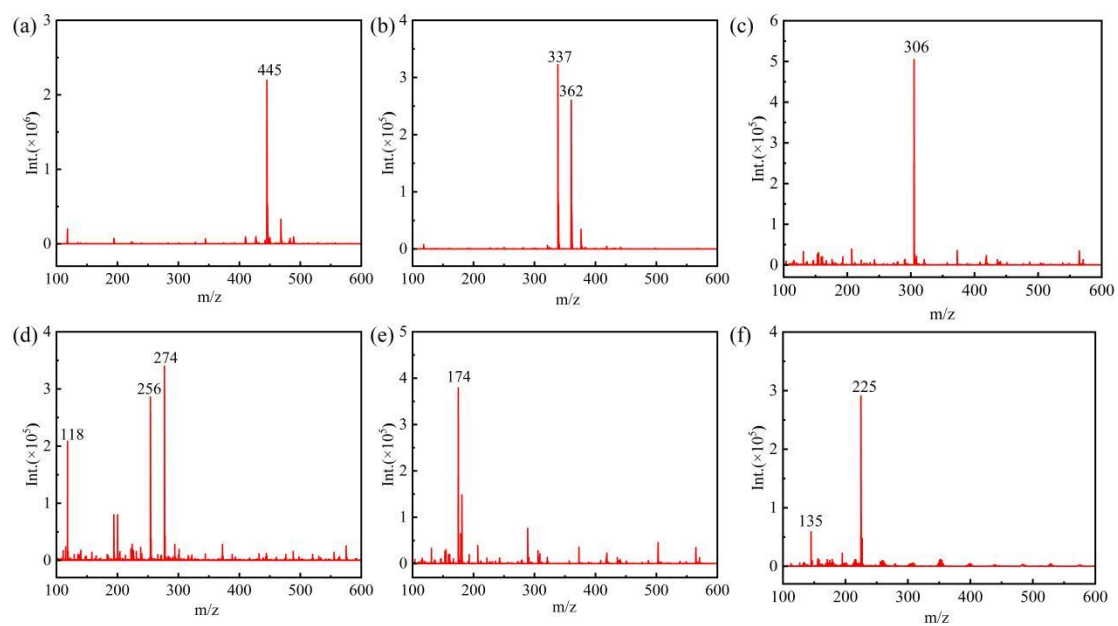


Fig. S6. (a-f) Mass spectrometry of degradation intermediates detected at 0 min and 60 min of TC solution degradation.