Supplementary Information **Open Access**

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Chromium removal from industrial wastewater using *Phyllostachys pubescens* biomass loaded Cu-S nanospheres

The pseudo-first-order adsorption kinetic model:

$$\log(q_e - q_t) = \log q_e - k_1 t$$

where k_1 (min^{-1}) is the rate constant in the pseudo-first-order adsorption process, q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of adsorbed Cr(III) or Cr(VI) on Cu-S·PPP-SH at equilibrium and at time t (min), respectively. k_1 and q_e can be calculated from the slopes and the intercepts of the plots $\log(q_e - q_t)$ versus t.

The pseudo-second-order kinetic model:

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

where k_2 (g mg^{-1} min^{-1}) is the rate constant in the pseudo-second-order adsorption process, and k_2 and q_e can be calculated from the slopes and the intercepts of the plots t / q_t versus t. This model is in agreement with chemical adsorption being the rate-controlling step.

The intra-particle diffusion model to elucidate the diffusion mechanism:

$$q_t = k_{id} t^{0.5} + I$$

where k_{id} (mg g^{-1} $min^{-0.5}$) is the intra-particle diffusion rate constant, and I (mg g^{-1}) is a constant. k_{id} and I (mg g^{-1}) can be calculated from the slopes and the intercepts of the plots q_t versus $t^{0.5}$.

The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The linear form of Langmuir isotherm equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

where C_e (mg L^{-1}) is the equilibrium concentration of chromium in solution, q_e (mg g^{-1}) is the sorption capacity at equilibrium, q_m (mg g^{-1}) is the maximum sorption capacity of the biosorbent, and b (L mg^{-1}) is the Langmuir constant termed as apparent energy of adsorption. The values of q_m and b can be determined from the slope $(1/q_m)$ and intercept $(1/q_m b)$ of the linear plots of C_e / q_e versus C_e, respectively.

The Freundlich isotherm assumes that the uptake of metal ions occur on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The Freundlich isotherm is expressed by the following empirical equation:

$$q_e = K_F C_e^{1/n}$$

and the logarithmic form of this equation is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where K_F ($mg^{(1-1/n)}$ $L^{1/n}$ g^{-1}) is the Freundlich adsorption constant representing the adsorption capacity, n is an arbitrary constant related to the adsorption intensity, and other parameters are the same as in the Langmuir isotherm. The values of K_F and n were calculated from slope $(1/n)$ and intercept $(\log K_F)$ of the plots $\log K_F$ versus $\log C_e$.

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Table S1: Constants of pseudo-first-order, pseudo-second-order and intra-particle diffusion models for Cr(III) and Cr(VI) on Cu-S·PPP-SH.

Model	Pseudo-first-order			Pseudo-second-order					
Metals	q_e	k_1	R^2	q_e	k_2	R^2			
	(mg g^{-1})	(min^{-1})		(mg g^{-1})	(g mg^{-1} min^{-1})				
Cr(III)	12.31	-0.087	0.977	16.42	0.010	0.997			
Cr(VI)	14.40	-0.042	0.964	23.05	0.007	0.999			
Model	Intra-particle diffusion								
Metals	k_{id1}	C_1	R^2	k_{id2}	C_2	R^2	k_{id3}	C_3	R^2
	(mg g min^{-1})	(mg g^{-1})		(mg g min^{-1})	(mg g^{-1})		(mg g min^{-1})	(mg g^{-1})	
Cr(III)	6.085	-2.258	0.955	0.267	14.106	0.579	—	—16.670	—0.958
Cr(VI)	2.850	1.614	0.991	4.450	-0.655	0.962	0.538		

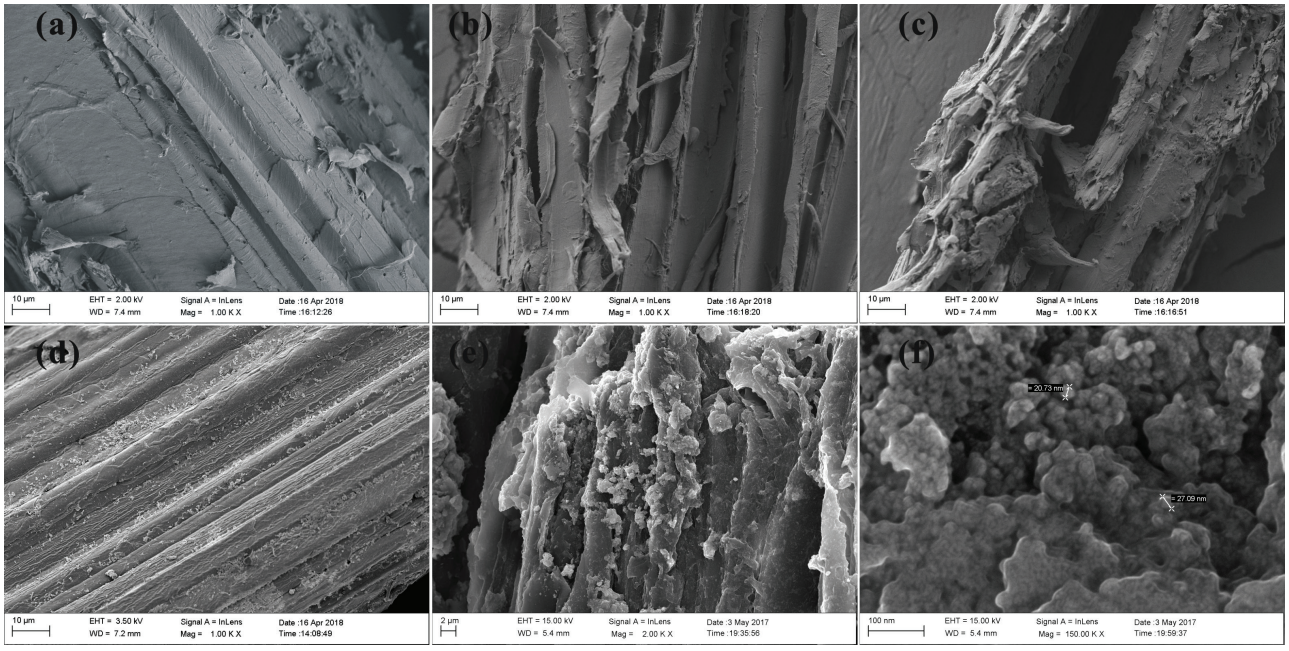


Figure S1: SEM images of (a) PPP, (b) PPP-OH, (c) PPP-SH and (d-f) Cu-S·PPP-SH.

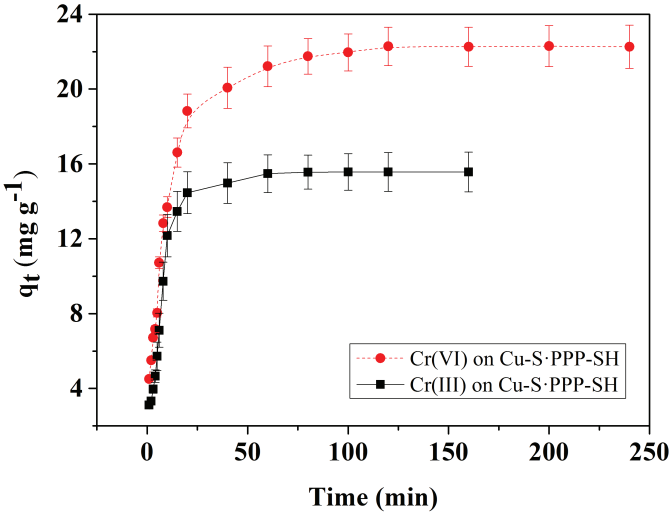


Figure S2: Effect of contact time on adsorption of Cr(III) and Cr(VI) by Cu-S·PPP-SH. Conditions: pH 6.1 and 1.9 for Cr(III) and Cr(VI), initial metal ion concentrations 50 mg L^{-1}, adsorbent concentrations 2.0 g L^{-1}, temperature 25 °C.

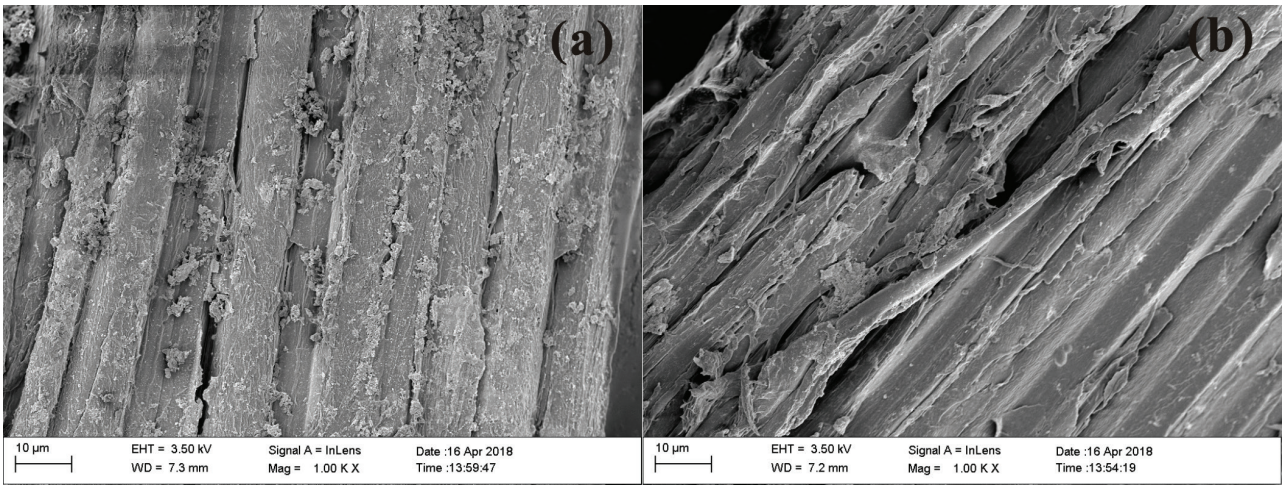
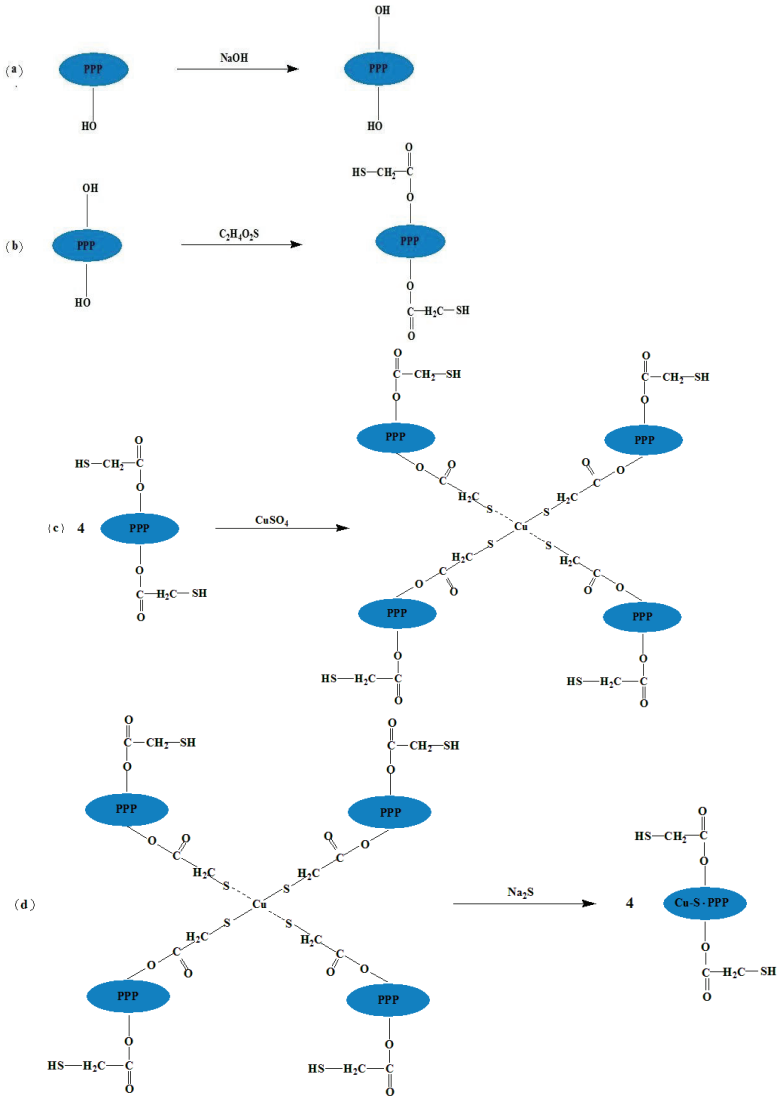


Figure S3: SEM images of Cu-S·PPP-SH for the adsorption of (a) Cr(III) and (b) Cr(VI) after repeated use for three times.



Scheme S1: The possible modification mechanism of (a) PPP-OH, (b) PPP-SH, (c) $(PPP\text{-}S)_2Cu$ and (d) Cu-S·PPP-SH.

(a)

$$3\text{Cu-S}\cdot\text{PPP-SH}+2\text{H}_2\text{CrO}_4+12\text{H}_3\text{O}^+ \rightarrow 3\text{Cu}^{2+}+3\text{S}+3\text{PPP-SH}+2\text{Cr}^{3+}+20\text{H}_2\text{O}$$

$$3\text{Cu-S}\cdot\text{PPP-SH}+2\text{HCrO}_4^-+14\text{H}_3\text{O}^+ \rightarrow 3\text{Cu}^{2+}+3\text{S}+3\text{PPP-SH}+2\text{Cr}^{3+}+22\text{H}_2\text{O}$$

$$3\text{Cu-S}\cdot\text{PPP-SH}+2\text{CrO}_4^{2-}+16\text{H}_3\text{O}^+ \rightarrow 3\text{Cu}^{2+}+3\text{S}+3\text{PPP-SH}+2\text{Cr}^{3+}+24\text{H}_2\text{O}$$

$$3\text{Cu-S}\cdot\text{PPP-SH}+\text{Cr}_2\text{O}_7^{2-}+14\text{H}_3\text{O}^+ \rightarrow 3\text{Cu}^{2+}+3\text{S}+3\text{PPP-SH}+2\text{Cr}^{3+}+21\text{H}_2\text{O}$$

$$3\text{PPP-SH}+\text{Cr}^{3+} \rightarrow (\text{PPP-S})_3\text{Cr}+3\text{H}^+$$

$$2\text{PPP-SH}+\text{Cu}^{2+} \rightarrow (\text{PPP-S})_2\text{Cu}+2\text{H}^+$$

(b)

$$3\text{Cu-S}\cdot\text{PPP-SH}+\text{Cr}^{3+} \rightarrow (\text{Cu-S}\cdot\text{PPP-S})_3\text{Cr}+3\text{H}^+$$

$$3\text{Cu-S}\cdot\text{PPP-SH}+\text{Cu}^{2+} \rightarrow (\text{Cu-S}\cdot\text{PPP-S})_2\text{Cu}+2\text{H}^+$$

Scheme S2: The possible adsorption mechanisms of Cu-S·PPP-SH: (a) Cr(VI) adsorption; (b) Cr(III) adsorption.